Class XII

CBSE

Competitive Exams

IIT-JEE Mains
IIT-JEE Advanced
BITSAT

Chemistry

Physical, Organic and Inorganic

Notes

Akshansh Chaudhary

classmate
Date 14.4.10
Page

Ch: Chemical Kinetics

Chemical kinetics is the study of rate of a chemical rxn.

Rate → Avg. Rate = $\frac{\Delta C \to \text{conc.}}{\Delta t} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$ (A: reactant, P: product)

→ Inst. Rate = $\lim_{\Delta t \to 0}\left[-\frac{\Delta[A]}{\Delta t}\right] = \lim_{\Delta t \to 0}\left[\frac{\Delta[P]}{\Delta t}\right]$.

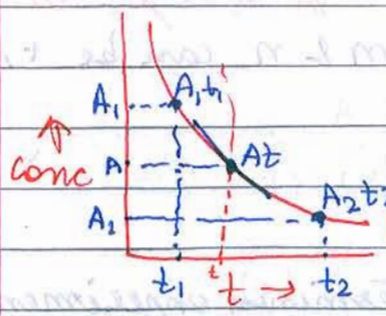
$A \longrightarrow P$

t_1 A_1 P_1

t_2 A_2 P_2

Avg Rate : Its change in conc over time interval in which the change is measured.

Inst. Rate : Its the rate at a given instant of time.

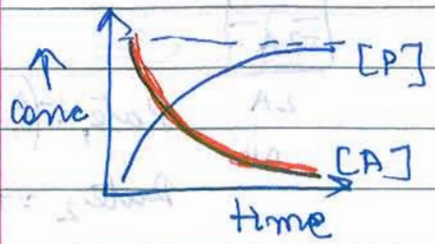


Avg rate is slope of st. line connecting A_1t_1 & A_2t_2.

Inst. rate = slope of 'At'.

$= -\frac{dC}{dt} = -\frac{d[A]}{dt} = \frac{d[P]}{dt}$

It is slope of tangent at any pt. on the conc. vs time curve.



$A \longrightarrow 2B$.

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$$

General $aA + bB \longrightarrow pP + qQ$.

$$\Rightarrow \text{Rate of rxn} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{p}\frac{d[P]}{dt} = \frac{1}{q}\frac{d[Q]}{dt}$$

★ RATE LAW : It is an expⁿ which relate rate of a chemical rxn with amt of reacting species (reactant). [not with amt. of product]

$aA + bB \longrightarrow pP + qQ$

$\text{Rate} \propto [A]^m [B]^n$; m & n are some consts. → order

$\text{Rate} = k[A]^m [B]^n$ → const. of proportionality | k : Rate const (or specific rxn rate)

- For a particular rxn, k is a specific const.
- Rate const is characteristic of chemical rxn & it depends only on T & catalyst.
- m is partial order w.r.t A & n is partial ord. with respect to B ; m & n can be +, −, 0

(m+n) = order of rxn.

★ • ORDER OF RXN

$A \longrightarrow P$

$\text{Rate} = k[A]^m$ | m = (i) determined experimentally

	$[A]$	$[2A]$	
$t = 0$	A	2A	$\text{Rate}_1 = -\left(\frac{A' - A}{t}\right)$
$t = t$	A'	A''	$\text{Rate}_2 = -\left(\frac{A'' - 2A}{t}\right)$

Way in which Rate_1 & Rate_2 are related gives m.

Ord. of rxn is the power (exponent) raised to the conc. term in an experimentally derived rate law.

✱ Properties of Ord. of rxn

P1 Ord. of a rxn is characteristic of a rxn, independent of any physical / chemical parameter.

P2 Ord. of a rxn is an experimental qty, can take any real value (0, -ve, +ve, 2, fraction)

✱ ORDER = 1

$$t=0 \quad A \longrightarrow P$$
$$a \qquad\qquad 0$$
$$t=t \quad a-x \qquad x$$

$A \longrightarrow P$

$$-\frac{d[A]}{dt} = k[A]$$

$$\Rightarrow \frac{d[A]}{[A]} = -k\,dt$$

$[A]_0$ = conc. of [A] remaining unreacted at $t=t$

$$\Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = \int_{t=0}^{t=t} -k\,dt$$

$$\Rightarrow [\ln[A]]_{[A]_0}^{[A]} = -kt$$

$$\Rightarrow \ln[A] - \ln[A_0] = -kt$$

$$\Rightarrow \ln[A] = -kt + \ln[A_0]$$

$$y = mx + c$$

$$\Rightarrow kt = \ln\frac{[A_0]}{[A]}$$

$$\Rightarrow kt = \ln\frac{[A]_0}{[A]} \quad \text{(1st ord. integral rate law)} \qquad \Rightarrow \frac{[A]_0}{[A]} = e^{kt}$$

$$\Rightarrow [A] = [A]_0\, e^{-kt}$$

- For IST ORD. RXN, half-life is independent of conc. of reactant/product.
- Half life of Ist ord. rxn depends on T & catalyst (∵ k depends on them)

CONCEPT

$A \xrightarrow{t_{1/2} = 5\ hr} B$; So in 5 hrs, conc. of A becomes 1 M.

2M & in 10 hrs, conc. of A becomes 0.5 M ($\frac{1}{2}$)

15 hrs → $\frac{0.5}{2} = 0.25$.

Q. A Ist ord. chem. rxn, $A \rightarrow P$ is 20% complete in 1 hr. Determine time reqd for 90% completion.

$$kt = \ln \frac{[A]_0}{[A]}$$

$$\Rightarrow k(2) = \ln \frac{[100]}{[80]}$$

$$\Rightarrow k = \frac{2.303}{2}(0.7 - 0.6)$$

$$= 1.151\ (0.1)$$

$$\Rightarrow k = 0.115$$

2303 01 121

Now, k ($k'(1) = \ln \frac{5}{4}$)

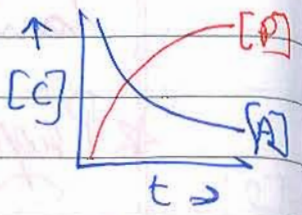
& $k(t) = \ln 10$.

$$\Rightarrow \frac{1}{t} = \frac{\ln 5/4}{\ln 10} = \frac{\log 5 - \log 4}{\log 10}$$

$$\Rightarrow t^{-1} = 0.1 \Rightarrow t = 10\ hrs$$

$[A] = [A]_0 e^{-kt}$

↳ If we increase t linearly, conc. of reactant decreases exponentially -



If $t = \infty$

$[A] = 0$,

So, the first ord. rxn completes in infinite time -

Now,

Also, $a - x = a e^{-kt}$

$\Rightarrow \boxed{x = a(1 - e^{-kt})}$

↳ As t increases, x increases. Hence, conc. of product inc. with time.

HALF - LIFE ($t_{1/2}$)

Half life is the time in which ½ of reactant is consumed/reacted.

Now, $kt = \ln \frac{[A_0]}{[A]}$

At $t = t_{1/2}$, $[A] = \frac{[A_0]}{2}$

$\Rightarrow kt_{1/2} = \ln \frac{[A_0]}{[A_0]/2}$

$= \ln 2$

$= 2.303 \times (0.3)$

$\Rightarrow t_{1/2} = \frac{2.303 \times (0.3)}{k}$

$\Rightarrow \boxed{t_{1/2} = \frac{0.693}{k}} \approx \frac{0.7}{k}$

For 1st ord. rxn, half life is independent of initial conc. of reactant

2303
.6909

Q. 1st ord rxn $A \rightarrow P$

~~20%~~ 25 %. complete ($A = 75\%$) $t = 5$ hrs

Determine % age completion in 20 hrs.

$$k(5) = 2.303(0.6 - 0.48)$$

$$k(20) = 2.303(2 - \log x)$$

$$\Rightarrow \frac{1}{4} = \frac{0.12}{2 - \log x}$$

$$\Rightarrow 2 - \log x = 0.48$$

$$\Rightarrow 1.6 = \log x$$

$$\Rightarrow x = 4$$

Or $\frac{1}{4} = \frac{\ln 1/3}{\ln 100/x}$

$$\Rightarrow \ln \frac{100}{x} = \ln \left(\frac{1}{3}\right)^4$$

$$\Rightarrow \frac{100}{x} = \left(\frac{1}{3}\right)^4$$

$$\Rightarrow x = \frac{81 \times 100}{256} = \frac{64 \times 4}{25}$$

$$\Rightarrow x = 32\%.$$

So, % age completion = 68% (100 − 32 %)

Q. 1st ord. rxn $A \rightarrow P$

conc. of reactant remaining (A) after 2 hr & 4 hr from beginning are 2×10^{-3} M & 4×10^{-4} M, resp at same T determine ½ life & conc. of A remaining after 8 hrs.

$$k(t_1) = 2.303 \log \frac{A_0}{2 \times 10^{-3}[A_1]} \rightarrow (1)$$

$$k(t_2) = 2.303 \log \frac{A_0}{4 \times 10^{-4}[A_2]} \rightarrow (2)$$

$$\Rightarrow 2 = \frac{\log \frac{A_0}{4\times10^{-4}}}{\log \frac{A_0}{2\times10^{-3}}}$$

$$\Rightarrow \log\left(\frac{A_0}{2\times10^{-3}}\right)^2 = \log\left(\frac{A_0}{4\times10^{-4}}\right)$$

$$\Rightarrow \frac{A_0}{4\times10^{-6}} = \frac{1}{4\times10^{-4}}$$

$$\Rightarrow A_0 = \frac{4\times10^{-6}}{4\times10^{-4}}$$

$$\Rightarrow A_0 = 0.01$$

$$\log \frac{9\times10^{-4}}{2\times10^{-3}} = \log 2\times10^{-1} = \log 2 - \log 1 = 0.7$$

$$\begin{array}{r} 1151 \\ \times 35 \\ \hline 5755 \\ 3453\times \\ \hline 40285 \end{array}$$

Now,

$$k(2) = 2.303 \log \frac{0.01}{2\times10^{-3}}$$

$$\Rightarrow k = 1.151(0.7)$$

$$\Rightarrow k = 0.4\,0285$$

Now,

$$t_{1/2} = \frac{0.693}{8.057} = \frac{693}{8057} = \frac{0.7}{0.84} = \frac{7}{8}$$

$$= \frac{7}{4}\ \text{hrs}.$$

$$(0.4)(8) =$$

Subtracting (1) & (2)

$$\Rightarrow k(t_2 - t_1) = \ln\frac{[A_0]}{[A_2]} - \ln\frac{[A_0]}{[A_1]}$$

$$= \ln\frac{[A_1]}{[A_2]}$$

$$k = \frac{1}{2}\ln\frac{2\times10^{-3}}{4\times10^{-4}}$$

$$= \frac{\ln 5}{2} = \frac{\ln 2}{t_{1/2}} \Rightarrow t_{1/2} = \frac{2\times 0.3}{0.7}$$

$\Rightarrow t_{1/2} = \frac{6}{7}$

$k t_3 = \ln \frac{[A_0]}{[A_3]} \longrightarrow (1)$

(3) → (2)

$\Rightarrow k(t_3 - t_2) = \ln \frac{[A_2]}{[A_3]}$

$\Rightarrow 4k = \ln \frac{[A_2]}{[A_3]} = 2.4 \times \frac{\ln 5}{2}$

~~$\Rightarrow 4k = \ln 5^2$~~

$\Rightarrow \frac{[A_2]}{[A_3]} = 5^2$

$\Rightarrow [A_3] = \frac{[A_2]}{25} = \frac{4 \times 10^{-4}}{25}$

$= \frac{4 \times 100}{25 \times 100} \times 10^{-4}$

$\Rightarrow [A_3] = 0.16 \times 10^{-4}$ mol/L.

Q Rate of following 1st ord. rxn measured after 10 min & 20 min from beginning are found to be 0.5 mol/L/min & 0.4 mol/L/min.

(a) $t_{1/2} = ?$

(b) Rate at (70 min)

$-\frac{d[x]}{dt} = k[x]$

$k(10) = \ln \left[\frac{1}{0.5}\right]$

$= \frac{2.303 (0.3)}{10}$

$\Rightarrow k = 0.6909$

$t_{1/2} = \frac{0.69}{0.69} \approx 1 \text{ min}$

$k(70) = 2.303 \cdot \log \frac{1}{}$

$k(t_1) = \ln \left[\frac{A_0}{A_1}\right] \Rightarrow k(t_2 - t_1) = \ln \left[\frac{A_1}{A_2}\right]$

$k(t_2) = \ln \left[\frac{A_0}{A_2}\right]$

or

$R = k[A]$

$\Rightarrow \frac{R_1}{R_2} = \frac{[A_1]}{[A_2]}$

$\Rightarrow k(10) = \ln \frac{0.5}{0.4}$

$\Rightarrow \frac{\ln 2}{t_{1/2}}(10) = \ln \frac{5}{4}$

$\Rightarrow t_{1/2} = \frac{10 \log 2}{\log 5 - \log 4}$

$\Rightarrow t_{1/2} = 30 \text{ min}.$

$k(t_3 - t_1) = \ln \frac{[A_3]}{[A_1]}$

$\Rightarrow \frac{\ln 2}{30}(20-10) = \ln \frac{[A_1]}{[A_3]} = \ln \left[\frac{R_1}{R_3}\right]$

$\Rightarrow 2 \ln 2 = \ln \frac{[A_3]}{[A_1]}$

$\Rightarrow \ln 4 = \ln \frac{[A_3]}{[A_1]}$

$\Rightarrow 4 = \frac{[A_3]}{[A_1]} \Rightarrow [A_3] = 4[A_1]$

$\Rightarrow 2\ln 2 = \ln\left(\frac{R_1}{R_3}\right)$

$\Rightarrow R_3 = \frac{R_1}{4} = \frac{0.4}{4} = 0.125$

$\Rightarrow R_1 = 0.1$

☆ $A \longrightarrow P$

i a_0

$t_{1/2}$ $\frac{a_0}{2} \xrightarrow{t_{1/2}} \frac{a_0}{4} = \left(\frac{1}{2}\right)^2 a_0 \xrightarrow{t_{1/2}} \left(\frac{1}{2}\right)^3 a_0 \longrightarrow$

$\longrightarrow - \xrightarrow{n\, t_{1/2}} \left(\frac{1}{2}\right)^n a_0$

☆☆ a amt of reactant remaining $= \left(\frac{1}{2}\right)^n a_0$. → amt of reactant left after nth power of $t_{1/2}$ ☆☆

~~If b time 1/2 after~~

Q. Action of a drug follow 1st ord. kinetics with $t_{1/2} = 6$ hrs. A patient takes a doze of 16 mg of this drug at a regular interval of 6 hr. Determine amt of drug remaining in his body just after 4th doze. JEE

O O O O $\left(\frac{1}{2}\right)^4 (16)$

$\xleftrightarrow{t_{1/2}}$ $\xleftrightarrow{}$ $\xleftrightarrow{}$ $\xrightarrow{}$

1/8 1/4 1/2 1 $2+4+8+16 = 30$.

~~$= 16+16$~~

~~$(1)\left(\frac{1}{2}\right)$~~

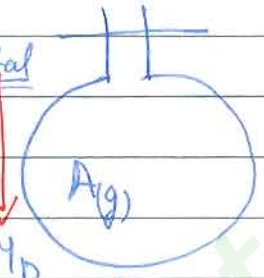
~~1/2~~

☆ KINETICS OF Gaseous Rxns.

$$A_{(g)} \xrightarrow{\text{ord}=1} 2B_{(g)} + 3C_{(g)}$$

	$A_{(g)}$	$2B_{(g)}$	$3C_{(g)}$
i	n_0, P_0	~~2n~~ 0	0
t=t	n_0-n, P_0-p	$2n, 2p$	$3n, 3p$

Total P_0+4p



V, T → constt.

$n_0 \propto P_0$

$n \propto p$

$$Kt = \ln \frac{n_0}{n_0 - n}$$

$$= \ln \frac{P_0}{P_0 - p}$$

$$\frac{n_0}{n_0 - n} = \frac{P_0}{P_0 - p}$$

Q The following rxn

$A_{(g)} \longrightarrow 2B_{(g)} + C_{(g)}$ → 1st ord.

$P_0 + 2p$.

Rxn is carried out in a sealed flask with initially only $A_{(g)}$ present at 800 mm Hg (P_0) & after 4 hrs, $P_0 + 2p = 1600$ mm Hg, determine, $t_{1/2}$ & p in flask at t = 12 hrs.

~~$P_0 = P_0$~~ $P_0 = 800$ mm Hg, $p = 400$ mm Hg

$$K(4) = \ln \frac{800}{400} 2.$$

$$\Rightarrow \boxed{k = \frac{0.693}{4}}$$

$$\boxed{t_{1/2} = \frac{0.693}{k} \; 4 \text{ hrs}}$$

800 400

$$\frac{0.693}{4}\left(\frac{4}{t_{1/2}}\right) = \ln \frac{800}{800 - p'}$$

$$= 2.079 = \ln \frac{800}{800 - p'}$$

$\Rightarrow 3\ln 2 = \ln \frac{800}{800-p'}$

$\Rightarrow 8 = \frac{800}{800-p'}$

$\Rightarrow p' = 700$

$\Rightarrow P = 800 + 1400$

$= 2200$ ~~atm~~ mm Hg

Or

$t_{1/2} = 4$ hrs , after $t = 12$ hrs $= 3(4$ hrs $= 3(t_{1/2})$

$\Rightarrow P_A = \left(\frac{1}{2}\right)^3 800 = 100$ mm left.

So, $800 - 100$ mm $= 700$ mm C form

Q gaseous dimethyl ether →

$$CH_3OCH_3(g) \rightarrow CH_4(g) + CO(g) + H_2(g)$$

follow 1st order kinetics.

Some dimethyl ether is taken in a flask, sealed & heated to a constt T & the P inside flask after 5 hrs, & after very long time was found to be 250 & 450 mm Hg

Determine $t_{1/2}$, P after $t = 10$ hrs ; T + constt.

	$CH_3OCH_3(g)$	→	$CH_4(g)$	+	$CO_{(g)}$	+	$H_2(g)$	P_T
$t=0$	P_0							
$t=t$	$P_0 - P$		P		P		P	$P_0 + 2P$
$t=\infty$	0		P_0		P_0		P_0	$3P_0$

$5k = \ln \frac{P_0}{P_0 - P}$ After very long time.

Now

$3P_0 = 450$ mm Hg $\Rightarrow P_0 = 150$ mm Hg.

At 5 hrs, $P_0 + 2p = 250$

$\Rightarrow p = 50$ mm Hg

$\Rightarrow 5k = \ln \frac{150}{100} = \ln 3 - \ln 2$

$\Rightarrow 5 \frac{\ln 2}{t_{1/2}} = \ln 3 - \ln 2$

$\Rightarrow 5 \frac{\log 2}{t_{1/2}} = \log 3 - \log 2$

$= 0.18$

$\Rightarrow \frac{1.5}{0.18} = t_{1/2} = \frac{15}{18} \left(\frac{5}{6}\right)$ hrs

At $t = 10$ hrs.

$10k = \frac{1}{5} \ln \frac{P_0}{P_0 - P'}$

$\Rightarrow 10\left(\frac{1}{5} \ln \frac{3}{2}\right) = \ln \frac{150}{150 - p'}$

$\Rightarrow \frac{150}{150 - p'} = \frac{9}{4}$

$\Rightarrow 600 = 2250 - 9p'$

$\Rightarrow 9p' = 1650$

$\Rightarrow p' = \frac{1650}{9} = 183.$

$\Rightarrow P_{Total} = P_0 + 2P'$ Ans

✡ KINETICS of NUCLEAR RXNS.

$$_{6}C^{14} \longrightarrow {}_{7}N^{14} + {}_{-1}e^{0}$$

✡✡ the superscripts & subscripts must balance.

$$-\frac{d}{dt} n_{C^{14}} = k\, n(C^{14})$$

$\frac{d}{dt}$: rate of decrease of no. of moles of C_{14}.

$n(C^{14})$: no. of moles of C^{14} produced.

rate of decay / disintegration / rate of nuclear rxn.

$$\left\{ -\frac{dN}{dt} = \lambda N \right.$$

λ: decay constt (same as k → rate constt)

N: no. of atoms of C^{14} / any other isotope remaining undecayed.

$$\Rightarrow \int_{N_0}^{N} -\frac{dN}{N} = \int_{t=0}^{t=t} \lambda\, dt .$$

$$= -\left[\ln(N) \right]_{N_0}^{N} = \lambda t$$

$$= \ln \frac{N}{N_0} = -\lambda t .$$

$$\Rightarrow \lambda t = \ln \frac{N_0}{N} .$$

$$\Rightarrow \boxed{N = N_0 e^{-\lambda t}} \quad ✡✡$$

$$t_{1/2} = \frac{\ln 2}{\lambda}$$

$$-\frac{dN}{dt} = \lambda N_t = A$$ ★★★ V. Imp.

$-\frac{dN}{dt}$ → called as Activity (Inst. rate)

At $t=0$; $-\frac{dN_0}{dt} = \lambda N_0 = A_0$ (Initial Activity)

$$\Rightarrow \frac{A_0}{A} = \frac{N_0}{N}$$

So, now, $\lambda t = \ln \frac{A_0}{A}$

& $A = A_0 e^{-\lambda t}$

- all the above work is same as done before
  - K replaced by λ.
  - Rate " " Activity (A)

1st ord
N x N

★ U^{238} $t_{1/2} = 4.5 \times 10^9$ yrs.

Q. U^{238} $t_{1/2} = 4.5 \times 10^9$ yrs. Determine the no. of U^{238} atoms disintegrating per minute from a sample of 10 mg.

$-\frac{dN}{dt}$ 4.5×10^9 yrs $= \frac{0.693}{\lambda}$

$\Rightarrow \lambda = \frac{0.693}{4.5 \times 10^9 \times 365 \times 24 \times 60}$

$-\frac{dN}{dt} = ? \Rightarrow \lambda = \left(\frac{7 \times 10^{-10}}{45 \times 365 \times 24 \times 60}\right)\left(\frac{10}{100 \times 238}\right)$

$N = \frac{10 \times 10^{-3}}{238} \times 6 \times 10^{23} = \frac{6 \times 10^{21}}{238}$

Chemistry Notes Akshansh

$$\Rightarrow -\frac{dN}{dt} = \lambda N = A = \left(\frac{0.7}{4.5\times10^{9}\times365\times24\times\frac{60}{10}}\right)\left(\frac{6\times10^{23}}{238}\right)$$

$$= \frac{7\times10^{-10}\times10^{21}}{45\times365\times24\times238}$$

$$= \frac{70}{938196\times100} = 7000 \text{ decay min}^{-1}$$

$= 0.000$

Q. $t_{1/2}$ of I^{131} = 12 hrs. It takes 8 hr in transport^{n} from reactor to laboratory by shortest possible route. Determine the min amt which must be supplied by reactor so that lab receives 5 kg of KI^{131}

$$k = \frac{0.7}{12}$$

$$\lambda k(8) = \ln\frac{A_0}{5000}$$

$$\Rightarrow \frac{0.7\left(\frac{7}{4}\right)}{63}(8) = \ln\frac{A_0}{5000}$$

$$\Rightarrow \frac{\ln 2}{12}(8) = \ln\frac{A_0}{5000}$$

$$\Rightarrow 2\ln 2 = 3\ln\frac{A_0}{5}$$

$$\Rightarrow 4 = \frac{(A_0)^3}{125}$$

$$\Rightarrow \sqrt[3]{500} = A_0, \text{ kg} \Rightarrow 8 \text{ kg}.$$

≈ 7.8 kg.

Chemistry Notes Akshay

☆ APPLIC^{n} of RADIOACTIVITY

C-14 - DATING

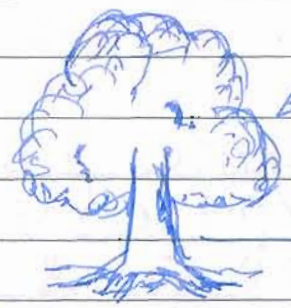
$^{14}CO_2$

atmosphere

$^{12}CO_2$ + some $^{14}CO_2$ formed.

photosynthesis.

some is going inside plant.



$C^{14} \rightarrow {}_{7}N^{14} + {}_{-1}e^{0}$

At equi

rate of entry of $^{14}CO_2$ inside plants (for photosynthesis) = rate of exist of ^{14}C. So, some amt of ^{14}C is there inside the plant

☆ In a living plant, there is 1.4×10^{-12} C^{14}/g Carbon

☆ When plant dies, ~~dece~~ that time is called zero time. The decay of ^{14}C goes on inside the dead plant.

After 10,000 yrs, say,
If 1g of C is extracted from plant, its value will be less than initial.

Now,

$$\lambda t = \ln \frac{N_0}{N}$$

N_0 → activity of initial

N → activity of ~~fresh~~ dpm

t → age of ~~sample~~ plant can be calculated.

Q. Activity of a sample of fossil is 214 dph. A fresh wooden sample contain 1.4×10^{-12} g of C^{14} per g of C. $t_{1/2}$ of C^{14} is 5600 yr. Determine age of fossil.

mass $A_0 = 1.4 \times 10^{-12}$

$A_0 = 214$ dph

$t_{1/2} = 5600$ yrs

$t = ?$

$\frac{N_0}{N} = \frac{A_0}{A}$

$-\frac{dN}{dt} = \lambda N$

$\lambda = \frac{0.7}{t_{1/2}}$

$\Rightarrow \lambda = \frac{0.7}{5600 \times 365 \times 24}$

$A_0 = \frac{A \times N_0}{N}$ $\quad \lambda N = 214$ dph

$\Rightarrow N = \frac{214 \times 5600 \times 365 \times 24}{0.7}$

$N_0 = \frac{0.1}{14} \times 1.4 \times 10^{-12} \times 6 \times 10^{23}$

$= 6 \times 10^{10}$

$A_0 = \lambda N_0$

$= \frac{0.7 \times 6 \times 10^{10}}{5600 \times 365 \times 24}$

$= \frac{7 \times 10^7}{56 \times 365 \times 4}$

$= \frac{7}{81766} \times 10^7$

$= 0.0000856 \times 10^7$

$\Rightarrow A_0 = 856$

$\lambda t = \ln \frac{856}{214}$

$\Rightarrow \frac{\ln 2 \times t}{5600 \times 365 \times 24} = \ln 4$

$= \frac{0.693 \times t}{5600 \times 365 \times 24} = 2 \ln 2 \times 5600 \times 365 \times 24$

$\Rightarrow t = 11200$ yrs

2 Chemistry Notes Akram

$A = \lambda N \quad A_0 = \lambda N_0$

Q. (A) 10 yr C^{14} $t_{1/2}$ = 5600 yrs.
(B) 100 yr
(C) 6000 yrs Amt. by which C^{14} changes, can be accurately calculated by which option?
(D) 10^9 yrs.

Ans (c) ✓ ∵ $t_{1/2}$ ≈ 5600 yr & 6000 yrs is closest to $t_{1/2}$. In 100 yrs, very less C^{14} would decay & in 10^9 yrs almost all C^{14} would decay. Hence, its value would be approx. Hence in 6000 yrs, value would be suitable for age determinⁿ.

Q. Age of which sample will be closest to age of civilisⁿ :-
(A) wooden box (B) Stone axe (C) Utensil
(D) Bones.

Ans Bones : they would be of that civilisⁿ. They contain a lot of elements so, its detection would be difficult. A wooden box only has C-14 isotope. Hence, its value & age can be determined.

ZERO ORDER RXN

$A \longrightarrow P$

$-\frac{d[A]}{dt} = k[A]^0 = k.$

$\Rightarrow k$ = conc sec^{-1}.

$k = M\,sec^{-1} = mol\,L^{-1}\,s^{-1}$.

* rxn occurs at constt rate are necessarily of ord = 0,

$k = \frac{1}{(conc)^{n-1}\, t}$

[A]	1	0.75	0.40	0.1	Molar
t	0	0.05	0.12	0.18	min

Rate $= 0.5 = -\left(\frac{1-0.75}{0-0.05}\right)$

$= -\left(\frac{0.75-0.40}{0.05-0.12}\right)$

Since rate is same. So, its independent of conc. So, ord = 0.

$-\frac{d[A]}{dt} = k \cdot x$

$k = \frac{[A]}{t} \times x$

$k = \frac{1}{t} \ln \frac{[A]}{[A_0]}$ y

1st

$-\frac{d[A]}{dt} = k$

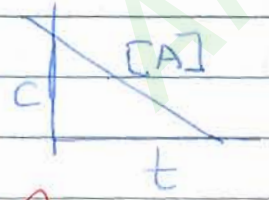
$\Rightarrow \int_{[A_0]}^{[A]} -d[A] = k \int_0^t dt$

$\Rightarrow [A_0] - [A] = kt$

$\Rightarrow [A] = -kt + [A_0]$

$y = m x + C$

zero ord.



In zero ord. rxn inst. rate = avg. rate.
∴ graph is st. line.

HALF LIFE

$\frac{[A_0]}{2} = -kt_{1/2} + [A_0]$

$\Rightarrow t_{1/2} = \frac{[A_0]}{2k}$ → zero ord.

Q.59 $_1H^3$, $t_{1/2} = 12.3$ yrs.

$_1H^3 : {}_1H^1 = 8 \times 10^{-18} : 1$

10 g water sample, how much $_1H^3$ at $t = 40$ yrs?

$\lambda t = \ln \frac{N_0}{N}$

$10\,g\ H_2O = \frac{10}{18} \times 2 \times 6 \times 10^{23}$ } total no. of atoms of H_2

$= {}_1H^3 + {}_1H^1$

÷ by $_1H^3$

$\Rightarrow \frac{20 \times 10^{23}}{3 \times {}_1H^3} = \frac{1018}{8}$ (ignore)

$\Rightarrow N_0 ({}_1H^3) = \frac{8 \times 20 \times 10^{23}}{3}$

$= \frac{16 \times 10^{24}}{3} = 5.3 \times 10^{24}$

$\Rightarrow \frac{\ln 2}{12.3} \times 40 = \ln 5.3 \times 10^{24}$ (N) ✓

⇒

☆ Nth order rxn ☆

$A \longrightarrow P$

$-\frac{d[A]}{dt} = k[A]^n$

$\Rightarrow \int_{[A_0]}^{[A]} \frac{-d[A]}{[A]^n} = \int_0^t k\,dt$

$\Rightarrow -\left[\frac{[A]^{-n+1}}{-n+1}\right]_{[A_0]}^{[A]} = kt$

Imp ✡ $\rightarrow \int_{x_0}^{x} \frac{dx}{x^n} = \left[\frac{x^{-n+1}}{-n+1}\right]_{x_0}^{x}$

$\Rightarrow \left[\frac{[A]}{-n+1}\right]_{[A_0]}^{[A]} = -kt$

$\Rightarrow kt = \left(\frac{1}{n-1}\right)\left[\frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}\right]$

↳ for nth ord rxn, $n \neq 1$

$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1}-1}{[A_0]^{n-1}}\right]$ → nth order

$t_{1/2} \propto \frac{1}{[A_0]^{n-1}}$ → for $n \neq 1$ .. → for reln b/w conc. & $t_{1/2}$.

✡ METHODS FOR DETERMINⁿ of ord. of Rxn

(1) INITIAL RATE METHOD

$A + B \longrightarrow P$.

	$[A]_0$	$[B]_0$	R_0 ($M\ min^{-1}$)	
Expt.-1.	0.01	0.02	(5×10^{-4})	→ Suppose. (1) A = 0.01 M, B = 0.02
Expt.→2	0.01	0.04	2×10^{-3}.	(2) A = 0.01 M, B = 0.04 M (A retained, B changed)
Expt→3.	0.04	0.04	8×10^{-3}	(3) B = 0.04 M, A = 0.04 M (B changed)

$Rate = k[A]^m[B]^n$

$5\times10^{-4} = k(0.01)^m(0.02)^n$

$2\times10^{-3} = k(0.01)^m(0.04)^n$.

$\Rightarrow \frac{1}{4} = \frac{1}{2^n}$

$\Rightarrow n = 2, \quad m = 1$

So, $\text{ord} = 3. \quad (m+n)$

Q. Derive rate law :-

$A + B \longrightarrow P$

$[A_0]$	$[B_0]$	$(\text{Rate})_{\text{initial}}$ ($M\ min^{-1}$)
0.01	0.02	5×10^{-4}
0.02	0.02	10^{-3}
0.04	0.04	8×10^{-3}

(1) Rate law
(2) $k = ?$
(3) R when $[A_0] = 0.03\ M$ & $[B_0] = 0.007\ M$.

$m = 1$

$n = 2.$

$\text{ord} = 3$

(1) Rate law $= k[A][B]^2$ $= (0.01)(0.002)^2$

(2) $k = \frac{1}{(\text{conc})^2} \cdot \frac{1}{t} \cdot \frac{5 \times 10^{-4}}{0.01 \times 0.02 \times 0.02} = k$

$= M^{-2} S^{-1}$ $= \frac{5 \times 10^2}{4} = 125$

$k = 125.$

(3) Rate $= [0.03][0.007]^2 (k)$

$= \frac{3}{100} \times \frac{49}{10^6} \times 125$

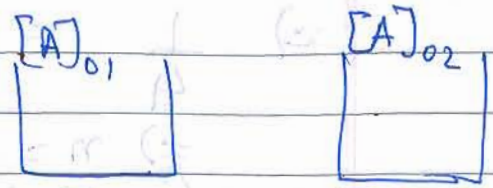
$= \frac{18375}{10^8} \times 10^{-8}$

Rate $= 1.8375 \times 10^{-4}$

249
03
744
125
735
2 94 x
1 47 xx
18375

★ (2) HALF LIFE METHOD

$A \rightarrow P$.



$t_{1/2} = \frac{1}{[A_0]^{n-1}}$

$(t_{1/2})_{01}$ $(t_{1/2})_{02}$

$$\frac{(t_{1/2})_{01}}{(t_{1/2})_{02}} = \left(\frac{[A]_{02}}{[A]_{01}}\right)^{n-1}$$ ★★

Q. Determine ord - ~~of this~~ rxn if $t_{1/2}$ corresponding to initial conc$_s$ → 5×10^{-4} M & 2×10^{-3} M are 20 min & 2.5 min resp.

$\Rightarrow \frac{20}{2.5} = \left(\frac{5\times10^{-4}}{2\times10^{-3}}\right)^{n-1}$

$\Rightarrow 8 = \left(\frac{5\times10^{-4}}{20\times10^{-4}}\right)^{n-1}$

$= \left(\frac{1}{2}\right)^{n-1} = (2^{-2})^{n-1} = 2^3$

$\Rightarrow 2^{-2n+2} = 2^3$

$\Rightarrow -2n+2 = 3$

$\Rightarrow 2n = -1$

$\Rightarrow n = -\frac{1}{2}$

$\frac{20}{2.5} = \left(\frac{2\times10^{-3}}{5\times10^{-4}}\right)^{n-1}$

$\Rightarrow 8 = (4)^{2n-1}$

$\Rightarrow 2^3 = (2)^{2n-2}$

$\Rightarrow 2n-2 = 3$

$\Rightarrow n = 5/2$.

$k\text{-}t_{1/2} = \left(\frac{1}{n-1}\right)\left(\frac{2^{n-1}-1}{[A_0]^{n-1}}\right)$

⟨3⟩ ORDER FROM RXN-MECHANISM

$2A \longrightarrow A_2$

Mechanism

$A + A \longrightarrow A_2$

Product is formed in 1 event
1 step mech.

elementary rxn
molecularity = 2 = ord

molecularity = 2

Mech

$A + h\nu \xrightarrow{fast} A^*$ (molecularity = 1)

$A^* + A \xrightarrow{slow} A_2$ (molecularity = 2)

$R = k[A][A^*]$

Product is formed in 2 consecutive events.
2 step mech.

☆ MOLECULARITY :-

It is the no. of reacting particles (molecules, ions → colliding together to form a specific product.

Properties

1) Rxn may have 1 or more than (1 type) * of molecularities.
   - Type of rxn that complete in 1 single step are called ELEMENTARY or CONCERTED rxn
2) Elementary rxns don't involve reactive intermediates.
3) - Higher molecularities are less probable.
   Practically, molecularity is max. = 3.
   Molecularity > 3 is very very rare.

classmate
Date
Page

☆ In a multistep rxn, slowest step determine (controls) the rate of rxn.
Molecularity of slowest step in multistep rxn determines ord. of rxn.

Elementary rxn

$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$.

↳ balance to simple whole no. coeff.

$H_2 + Cl_2 \longrightarrow 2HCl$.

Molecularity = 2 = order.

☆ For an elementary rxn, sum of stoichiometric coeff. of reactants ~~gives the~~ when the rxn is balanced with simple whole no. ~~of~~ coeff., will be molecularity of that rxn & same will be ord. of rxn.
Order of rxn of elementary rxn is always +ve integer.

Q. Diff. b/w order & molecularity.

order	molecularity
1) It can take any real value (0, +ve, -ve, fⁿ)	1) Always a +ve I
2) There is always single order for a chem. rxn	2) Molecularity of a multistep rxn can be many.

Q. For decompos^n of ozone →

$2O_3 \longrightarrow 3O_2$

Mech

$O_3 \underset{K_c}{\rightleftharpoons} O_2 + [O]$ fast

$O_3 + O \xrightarrow{k} 2O_2$ slow.

Rate = $k[O_3][O]$

Rxn molecularity 1 = uni molecular
2 = bi "
3 = tri "
4 = ter molecular

$$K = \frac{[O_2][O]}{[O_3]}$$

$$[O] = \frac{K_c [O_3]}{[O_2]}$$

$$\Rightarrow R = (kK_c)\frac{[O_3]^2}{[O_2]} \Rightarrow R = k'[O_3]^2[O_2]^{-1}$$

k' = say

product oxygen.
plays role of INHIBITOR

Order = (2 - 1) = 1

☆ In a multistep rxn, if any product term decreases rate, it is called INHIBITOR (see above)

Q. $CH_2Cl_3 + Cl_2 \rightarrow HCl + CCl_4$

Mech

$$Cl_2 \underset{}{\overset{K_1}{\rightleftharpoons}} 2Cl^\bullet$$

$$Cl^\bullet + CHCl_3 \overset{K_2}{\rightleftharpoons} HCl + \dot{C}Cl_3$$

$$\dot{C}Cl_3 + Cl_2 \xrightarrow[k]{\text{slow}} CCl_4 + Cl^\bullet$$

$$R = k[\dot{C}Cl_3][Cl_2]$$

$$K_1 \frac{[Cl^\bullet][CHCl_3]}{[HCl]} = [Cl_4]$$

$$K_2 = \frac{[Cl^\bullet]^2}{[Cl_2]}$$

$$\Rightarrow [Cl^\bullet] = \sqrt{\frac{K_2[Cl_2]}{[\quad]}}$$

$\Rightarrow R = k K_1 \sqrt{\frac{K_2 \sqrt{[Cl_2]}}{[Cl_2]}} [CHCl_3][Cl_2]$

$= k K_1 \sqrt{K_2}\, [Cl_2]^{-3/2} [CHCl_3][HCl]$

$R = k' [Cl_2]^{3/2} [CHCl_3][HCl]$

k' → overall rate constt.

✱ EFFECT OF T & EFFECT OF CATALYST

• EFFECT OF Temp

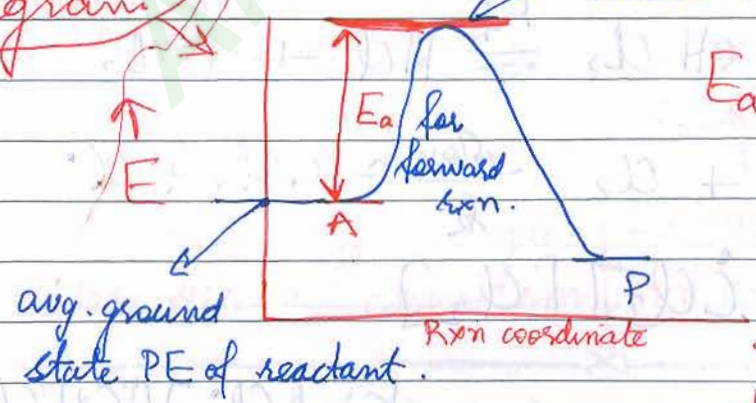
Increasing T increases rate of a chemical rxn., without any excepⁿ.

not radioactive

$\Delta H < 0$.

→ Elementary rxn

Activⁿ E diagram



E_a = ACTIVⁿ Energy

It is the min E which reactant must acquire through colⁿ in order to form product.

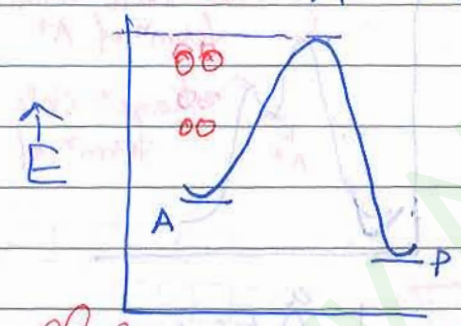
- When 2 molecules collide, their KE converts to PE (at the instt of colⁿ). If PE (sum of KE of reacting molecules) is > Ea, then product is formed.
- Only those colⁿˢ giving E > Activⁿ E to reacting species lead to formⁿ of product.

In,

* Endothermic rxn, backward rxn is very probable ∵ $E_{a_{back}} < E_{a_{forward}}$ So, less E is reqd to convert to reactant.

—∞—

∞ A → P.



EXO, say Increasing T increases avg KE of colliding sys (Kinetic Theory), which in turn increases the no. of colliding sys crossing the Ea barrier per unit time. So, T ↑, no. of molecules crossing E barrier ↑.

—∞—

log k

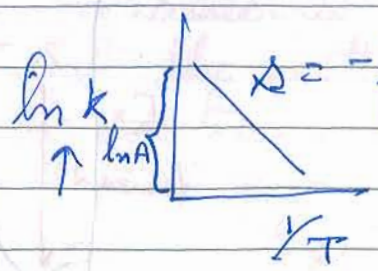
* ARRHENIUS EQN.

$$\ln K = \ln A - \frac{E_a}{RT}.$$

or $$k = A e^{-\frac{E_a}{RT}}$$

(relⁿ b/w T & k)
k → rate constt.
E_a → activⁿ E.
A → Frequency factor or Pre-Exponential Constt or Arrhenius constt.
A > 0

T ↑, ln K ↑
So, k ↑.
Hence, Rate ∝ k, ∀ rxns.

So, 

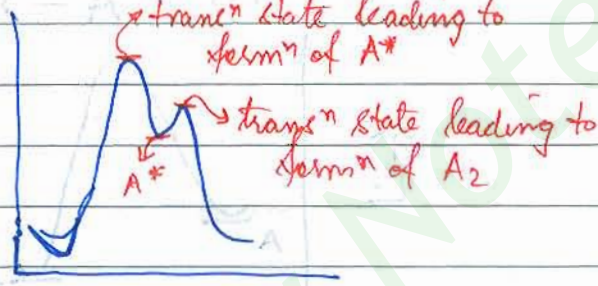
, Intercept = ln A.

- All other colns are unsuccessful. (fail to form product)
- Transⁿ state : State of highest E on Ea diagram. It is the state where transⁿ takes place. In single step rxn → 1 peak.

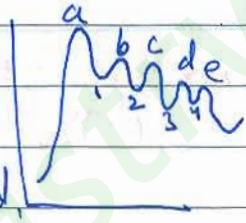
In multistep rxn. →

$A \rightarrow A^*$

$A^* + A \rightarrow A_2$.



Concept So, in a rxn like →



4 intermediates are formed & 5 (a, b, c, d, e) transⁿ states occur.

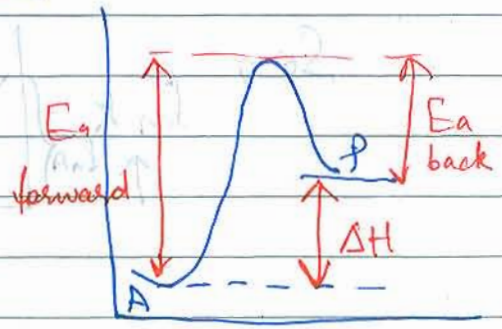
EXO

$\Delta H = E_a$ forward $- E_a$ backward → ∵ here, $\Delta H < 0$.

& ENDO

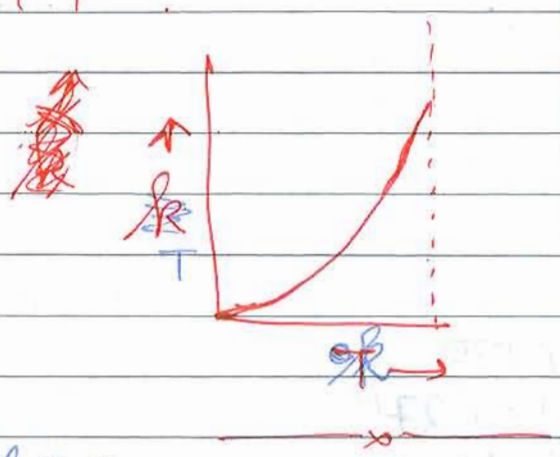
$\Delta H = E_a$ forward $- E_a$ back.

Here, $\Delta H > 0$.



Linear change in T gives exponential change in k.

So, k (rate const^{t}) inc. exponentially with T↑



As $T \to \infty$, $k \to A$.

For 1st ord. rxn $k_{max} = A$

23. April. 2010

~~Effect of Temp~~

Properties of A (Frequency factor)

1) Frequency factor of a rxn is its characteristic const^{t}, independent of physical / chem. parameter of rxn

$$A \xrightarrow[T_1]{} P$$

$$\ln K = \ln A - \frac{E_a}{RT}$$

$$\ln K_1 = \ln A - \frac{E_a}{RT_1} \rightarrow (1) \qquad \ln K_2 = \ln A - \frac{E_a}{RT_2} \rightarrow (2)$$

(2) − (1)

$$\Rightarrow \ln \frac{K_2}{K_1} = \ln \frac{A}{A} - \frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

$$\Rightarrow \ln \frac{K_2}{K_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$k \propto$ Rate

$$\Rightarrow \frac{k_2}{k_1} = \frac{R_2}{R_1}$$

Or $$\ln \frac{R_2}{R_1} = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$\ln K = \ln A - \frac{x}{2.303}$

$\Rightarrow 2.3 \log K = 2.3 \log A - x$

$\Rightarrow \log K = \log A - \frac{x}{2.303}$

1st ord.

Q. $A \rightarrow P$, rate constt (k) can be expressed as

$$\log k\,(hr^{-1}) = 20 - \frac{6270}{T}$$

Determine, (i) E_a of rxn (ii) $t_{1/2}$ at 300 K, (iii) T at which $t_{1/2}$ will be $\frac{1}{10}$th of the same at 300 K

(i) $\frac{E_a}{R} = 6270$

$\Rightarrow E_a = R \times 6270$

$= 8.31 \times 6270$

$= 52103.7$

$= 51.04$ J

(ii) (i) $\frac{E_a}{R \times 2.3} = 6270$

$\Rightarrow E_a = 52103.7 \times 2.3$

$= 119838.51$

(ii) $\log K = 20 - \frac{6270}{300}$

$= -0.9$

$\Rightarrow \log \frac{1}{k} = +0.9$

$\Rightarrow \frac{1}{k} = 8$

$\Rightarrow k = \frac{1}{8} = 0.125$

$\Rightarrow t_{1/2} = \frac{0.693}{0.125} = \frac{693}{125} 5.5$. $t_{1/2} = 0.696$ $\frac{125}{5}$

$= 5.5$ hrs.

(iii) $k \propto \frac{1}{t_{1/2}}$ $\frac{693}{25}$ $\frac{}{68}$

~~$\log \frac{k_2}{k_1} = \frac{E_a}{R}$~~

$\log \frac{K_2}{K_1} = \frac{2090}{6270} \left[\frac{T - 300}{300T} \right]$ $\log K_1 = 20 - \frac{6270}{T_1}$

$\Rightarrow \log \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{20.9}{T} [T - 300]$ $\log K_2 = 20 - \frac{6270}{T_2}$

$\log 10 = \frac{20.9}{T} [T - 300]$ $k \propto \frac{1}{t_{1/2}}$

$\Rightarrow \frac{T}{20.9} = T - 300$

$\Rightarrow T - \frac{T}{20.9} = 300.$

$\Rightarrow T \left\{ 1 - \frac{1}{20.9} \right\} = 300$

$\Rightarrow T = \frac{19.9}{20.9} = 300$

$\Rightarrow T = \frac{21 \times 300}{20}$

$\Rightarrow T = 315$ K

Q → Decompsn of methyl nitrate & ethyl nitrate has following rate consts →

$k_{CH_3NO_3} = 10^{12} e^{-\frac{152.3\ KJ}{RT}}$

$k_{CH_3CH_2NO_3} = 10^{13} e^{-\frac{157.7\ KJ}{RT}}$

Determine the T at which the 2 nitrates start decomposing at same rate.

$\Rightarrow k_1 = k_2$

$\Rightarrow 1 = \frac{1}{10} \frac{e^{\frac{-152.3\,KJ}{RT}}}{e^{\frac{-157.7\,KJ}{RT}}}$

$2.303 \log 10$

$\ln 10 + \ln e^{2...}$

$= 2.303$

$\Rightarrow 10 \times e^{\frac{152.3\,KJ}{RT}} = e^{\frac{157.7\,KJ}{RT}}$

~~$\Rightarrow$ ln 152.3~~

$2.303 + \frac{152.3 \times 1000}{RT} = \frac{157.7 \times 1000}{RT}$

$\Rightarrow 2.3 = \frac{1}{RT}[5.4 \times 10^3]$

$\Rightarrow T = \frac{5.4 \times 10^3}{2.3 \times 8.31}$

$= \frac{5400000}{19113}$

$= \frac{54 \times 10^5}{19113}$

$= 0.0027 \times 10^5$

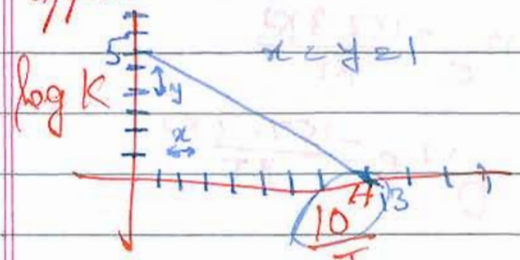
$\Rightarrow T = 2.7 \times 10^2\ K$

$\approx 283\ K$

2
619113
57
13379 1

831
e23
1249 3
16.62 p
119113
e2
38226
13 3840
75 8 22 6
1577 4

Q. For 1st ord rxn $A \to P$, following graph is applicable →



Determine Ea ?

$x = \frac{10^4}{T}$

$\Rightarrow \frac{x}{10^4} = \frac{1}{T}$

$\frac{y}{x} = \frac{y}{x/10^4}$

$\ln K = \ln A - \frac{E_a}{RT}$

x int = 13

y int = 5 units

$\ln A = 5$

$\frac{5}{13} = \frac{-E_a}{R}$. $\frac{3.2}{41.5}$ $\Rightarrow$ $8.3 \times 5 = \frac{41.5}{13}$

$\Rightarrow E_a = 3.2$.

$y = mx + c$

$\log K = -\frac{E_a}{RT} + \log A$

$\log K = -\frac{E_a}{2.3R}\left(\frac{1}{T}\right) + \log A$

~~$\ln K = \ln$~~

$\log K = \log A - \frac{E_a}{2.3RT}$

$\text{Slope} = \frac{-5}{13/10^4} = \frac{-E_a}{2.3R}$

$\Rightarrow \frac{5 \times 10^4}{13} \times 2.3 \times R = E_a$

$\Rightarrow 65$.

183
05.
415

83
023
249
166
190.9

Q. A 1st ord. chem. rxn is started in lab at 9 am at 300 K. by 4 p.m. (7 hrs) rxn was just 20% complete. If scientist has to leave lab at 5 p.m, but he can't leave rxn unless it is 99% complete, determine the T at which the rxn must be carried out after 4 pm.

$E_a = 100$ kJ

$kt = \ln \frac{A_0}{A}$ $\qquad \ln k = \ln A - \frac{E_a}{RT}$

$k(7) = 2.3 \log \frac{100}{80}$ $\frac{5}{4}$ $\frac{3}{1}$

$k = 2.3(0.7 - 0.6) = 2.3(0.1)$

7×10 $\qquad 7 \times 100$

$k = 0.23\ hr^{-1}$ $\Rightarrow$ $k_1 \cdot 7 = \ln \frac{5}{4}$

At T, $k_2(1) = \ln\left(\frac{80}{1}\right) \rightarrow (2)$

$(2) - (1)$

$\Rightarrow k_2 - 7k = \ln\frac{5}{4} - \ln 80$

$\Rightarrow \ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{7\ln 80}{\ln 5/4}\right) = \frac{100\times10^3}{8.3}\left(\frac{T-300}{300T}\right)$

$\Rightarrow \ln\left(\frac{k_2}{k_1}\right) = \ln\left[\frac{(1.9)7}{(-0.1)}\right] = \frac{10^5}{8.31}\times\frac{(T-300)}{300\,T}$

$\Rightarrow \ln 133 = \frac{10^4}{83}\left(\frac{T-300}{3T}\right)$

$\Rightarrow \frac{2.3(2.2)\times83\times3}{10^4} = \frac{T-300}{T}$

$\Rightarrow \frac{23\times22\times83\times3}{10^6} = 1 - \frac{300}{T}$

$\Rightarrow \frac{300}{T} = 1 - x$

$\Rightarrow T = \frac{300}{1-x} = \frac{300}{1-0.126} = \frac{300}{.874}$

$= \frac{8300\times10^3}{874}$

$= 0.340\times10^3$

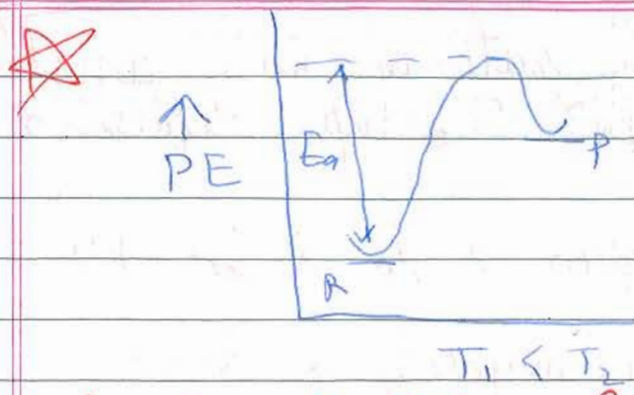
$T = 340\ K$

125994 / 25994 = 0.126

0.126 / .874

Concept

$A \rightarrow P$.

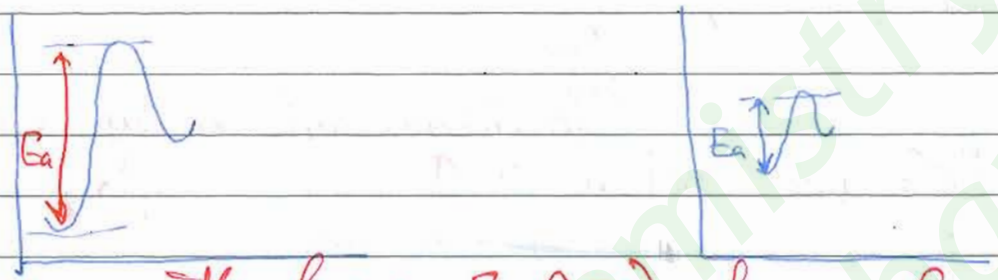


Temp. change has greater impact on the rate of rxn at lower T. than at higher T. ∵ at lower T, more no. of molecules would be ~~be~~ ~~had~~ below Ea line.

& inc. in T would lead to comparitively more no. of molecules crossing the Ea barrier.

Rxn (1) $A \rightarrow P$, Rxn (2) $B \rightarrow Q$.

Concept



A rxn with larger Ea (↑) has greater impact of T change on the rate of rxn than the rxn with smaller Ea (↑)

✱ Temp. Coeff ✱

$A \xrightarrow{T} P$

$\ln K_T = \ln A - \frac{E_a}{RT}$

T ↑ by 10K, $\Rightarrow \ln K_{T+10} = \ln A - \frac{E_a}{R(T+10)}$

(A) constt for an rxn

$\Rightarrow \ln \frac{K_{T+10}}{K_T} = \frac{E_a}{R}\left(\frac{10}{T(T+10)}\right)$

$\Rightarrow \boxed{\frac{k_{T+10}}{k_T} = e^{\frac{E_a}{R}\left(\frac{10}{T(T+10)}\right)} = \text{Temp. Coeff.}}$

ratio of rate constt at 2 diff T, differing by 10°

Collision theory

- Reactant molecule should have $E_{\text{kinetic}} > E_a$.
- Proper orient^{n} should be there for col^{n}

Defin^{n}:- Temp. coeff. is the ratio of rate consts of a rxn at 2 diff^{t} Temp. differing by 10°.

Imp ★ $\frac{k_{T+10}}{k_T}$ lies b/w 2 to 3 at RT for majority of rxns.

Learn

★ $\text{Rate}_{new} = \text{Rate}_{old} \times (\text{Temp. Coeff})^{\frac{\Delta T}{10}}$

→ to know rate & by which Rate inc. when T ↑.

(A) $2NO + O_2 \longrightarrow 2NO_2$.

$O=O \rightarrow \ddot{N}=O \rightarrow \leftarrow O=O$.

∴ O=O bond won't be formed.
Proper orient^{n} is req^{d} even if large amt. of E is supplied

Frequency factor

(A) → accounts for orient^{n} of col^{n} leading to form^{n} of product. So, A is const. for a rxn.
A depends on structure of reactant.

Concept

$A \underset{R_b}{\overset{R_f}{\rightleftharpoons}} P$

Imp

$\ln K_f = \ln A_f - \frac{E_{a_f}}{RT}$; $\ln K_b = \ln A_b - \frac{E_{a_b}}{RT}$.

(1) — (2)

$$\Rightarrow \ln \frac{k_f}{k_b} = \ln \frac{A_f}{A_b} - \frac{1}{RT}\left[E_{af} - E_{ab}\right]$$

$$\rightarrow \ln K = \ln \frac{A_f}{A_b} - \frac{\Delta H}{RT}$$

K : equi. const.

→ for reversible rxn, A will have diff value ∵ structure of reactant & product are diff.

✡ EFFECT OF CATALYST

FACT

✡ Addn of a catalyst inc rate of a chem. rxn.

(Substance that dec. rate of rxn are called Inhibitors, anti catalysts or catalytic poison)

$A \longrightarrow P$

$\Delta H < 0$, elementary

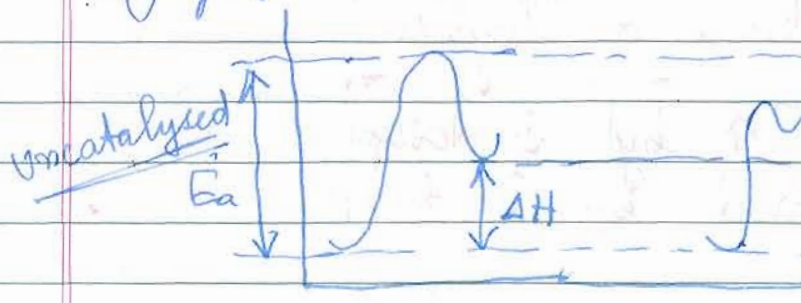
Catalyst 'X'

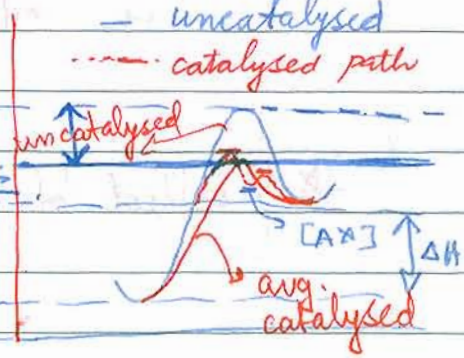
$A + X \longrightarrow [AX]$

$[AX] \longrightarrow P + X$

Catalyst dec. overall Ea of rxn. So, more no. of particles will cross E barrier per unit time. Hence, rate ↑

By graph :-





classmate
Date
Page

* Catalyst doesn't effect ground state PE of either reactant or product. & ∴ catalyst doesn't effect enthalpy (ΔH) of rxn.
Catalyst decreases both rate of forward & backward rxn by same amt..

i.e $K = \frac{k_f}{k_b}$ → remains unaltered.

* In absence of catalyst :-

$\ln K = \ln A - \frac{E_a}{RT}$

Add. catalyst ⇒ k_c, say

$\ln k_{catalyst} = \ln A - \frac{E_c}{RT}$ → E_a of catalysed part (middle portion)

$\Rightarrow \ln \frac{k_c}{k} = \frac{E_a - E_c}{RT}$ → catalysed / uncatalysed

$\frac{k_c}{k_{uc}} = \frac{k_c}{k_{uc}}$ = factor by which catalyst ↑ rate of rxn.

$\ln\left(\frac{k_c}{k}\right) = \left(\frac{E_a - E_c}{R}\right)\left(\frac{1}{T}\right)$

uncatalysed (uc)

→ constt for 1 catalyst & 1 rxn.

So, T ↑, $\ln\left(\frac{k_c}{k}\right)$ ↓.

So, At lower T, catalyst increases rate faster than at higher T.

* Effect of catalyst ↑ by ↓ temp. or ↓ by ↑ temp.

$k \propto \frac{1}{\text{time}}$

rate const

Date 28·4·10

Q: SOURING of Milk At 27°C takes 8 hr under normal condⁿ while presence of a catalyst makes it sour only in 1 hr at 27°C.

Determine Ea of catalysed path if Ea of original path is 120 KJ/mol.

~~ln k~~ = ~~ln~~ $\ln K = \ln A - \frac{E_a}{RT}$

$\ln \frac{8}{1} = \frac{1}{RT}[-E_{a_c} + E_a]$

$\Rightarrow 2.3 \times 8.3 \times 300 = 120 \times 10^3 - E_a$

$\Rightarrow E_a = 12 \times 10^4 + 83 \times 3$

$= 12 \times 10^4 + 2241$

$= 120000 + 2241$

$= 122241$ J

$= 122.24$ KJ

$E_a = 114.6$ KJ/mol Ans

2.3 × 8.3 × 300 = 120 × 10³ − Ea
2483 × 27
17381
4966 ×
241

23 × 83
69
207

✱ ~~Inc. Temp. ↓~~

✱ Increasing T decreases effect of catalyst.

At ↑ T → ∞, the role of catalyst becomes insignificant.

0·3 × 64 = 112

Q 1st ord. rxn A → P, Ea of Uncatalysed part or original part = 120 KJ. If a catalyst is added at 27°C, it inc. rate of rxn by a factor of 1600. Ea of catalysed = ?

$\ln [1600] = \frac{E_a - E_{uc}}{R(300)} = \left(\frac{E_a - 120 \times 10^3}{24.6}\right)^{2.3}$

$\Rightarrow \log 16 + \log 100$

3.2

$\Rightarrow 3.2^{2.3} = \frac{-E_a}{RT} + 120\times10^3$

$\Rightarrow 32 \times 246 + 120\times10^3 = E_a$

$= 342 \times 23 \times 10$

$= 7872 \times 23 \times 10$

$E_{catalysed} = 101$ KJ.

Q. $A \xrightarrow{k} P$ (Multistep rxn)

$A \xrightarrow{k_1, E_1} A_1^*$ $\quad E_1 = 160$ KJ $\quad k_1 = A_1 e^{-E_1/RT}$

$A_1^* \xrightarrow{k_2, E_2} A_2^*$ $\quad E_2 = 40$ KJ $\quad k_2 = A_2 e^{-E_2/RT}$

$A_2^* \xrightarrow{k_3, E_3} P$ $\quad E_3 = 30$ KJ $\quad k_3 = A_3 e^{-E_3/RT}$

$k = \sqrt{\frac{k_1 k_3}{k_2}}$, what is overall Ea of rxn

$\ln k = \ln\sqrt{\frac{k_1 k_3}{k_2}} = \frac{-E_a}{RT}\left[E_1 + E_3 - E_2\right]$

$\ln k = \ln A - \frac{E_a}{RT}$

$\sqrt{\frac{k_1 k_3}{k_2}} = \sqrt{\left(\frac{A_1 A_3}{A_2}\right)} \cdot \left(e^{\frac{-1}{2RT}[E_1 + E_3 - E_2]}\right)$

$\Rightarrow k = A e^{-E_a/RT}$

Comparing $\frac{E_1 + E_3 - E_2}{2} = E_a$

$\Rightarrow 75 = E_a$ Ans.

1246
× 3.2
1492
7380
7872

23
× 3
69

23
× 4
92

$$\int e^{ax} = \frac{e^x}{a}$$

SPECIAL 1ST ORD RXNS

(1) (Parallel Rxn) or (Simultaneous Rxn)

Parallel rxns are those chem. rxns in which a single reactant is involved in more than 1 type of rxns producing more than 1 type of products through diff rxn mechanisms.

* Amts of products are not stoichiometrically related.

$A \longrightarrow B + C$ (elementary → 1 type)

$A \xrightarrow{k_1} B$

$A \xrightarrow{k_2} C$ (2 mechanisms, 2 type of reactions)

$$\frac{d[B]}{dt} = k_1[A]$$

$$\frac{d[C]}{dt} = k_2[A]$$

$$-\frac{d[A]}{dt} = k[A]$$

k acts as const for decay of A

$$\frac{d[B]}{dt} + \frac{d[C]}{dt}$$

$$[k_1 + k_2][A]$$

$$\Rightarrow k[A] = \frac{d[B]}{dt} + \frac{d[C]}{dt} = (k_1 + k_2)[A].$$

$$\Rightarrow k = k_1 + k_2$$

So, $$\boxed{k = \sum_{i=1}^{n} k_i}$$

Now $-\frac{d[A]}{dt} = k[A]$ Integrate $\Rightarrow [A] = [A_0]e^{-kt}$

& $\frac{d[B]}{dt} = k_1[A_0]e^{-kt}$

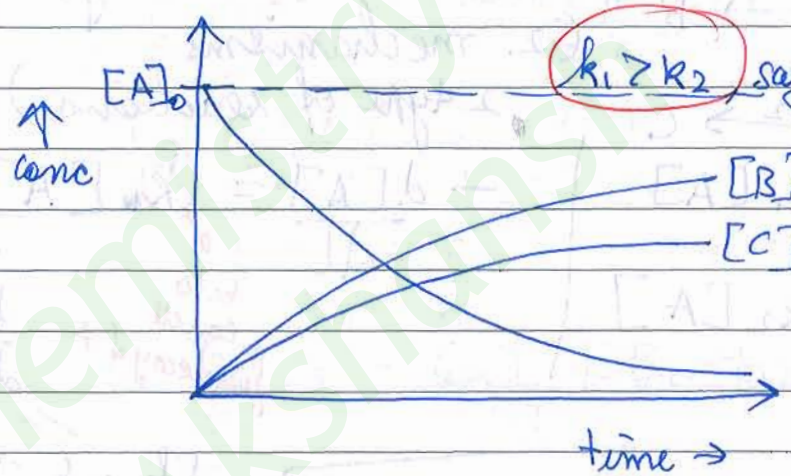
$$\Rightarrow \int_0^{[B]} d[B] = \int_{t=0}^{t=t} k_1[A_0]\left(e^{-kt}\,dt\right).$$

$\ln A = -kt + \ln A_0$

$\Rightarrow [B] = k_1 [A_0] \left(\frac{e^{-kt}}{-k} \right)_0^t$ $\quad \left(\because \int e^{kx} = \frac{e^{kx}}{k} \right)$

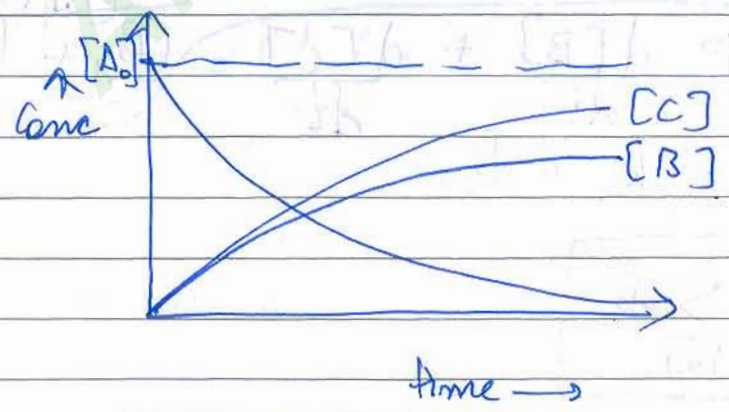
$$[B] = \frac{k_1}{k_1+k_2} [A_0] \left[1 - e^{-(k_1+k_2)t} \right]$$

Similarly, $$[C] = \frac{k_2}{k_1+k_2} [A_0] \left[1 - e^{-(k_1+k_2)t} \right]$$



$k_1 > k_2$ say (So, rate of formⁿ of B > rate of formⁿ of C)

At $t \to \infty$, B & C both tend towards $[A_0]$. Never $> [A_0]$.

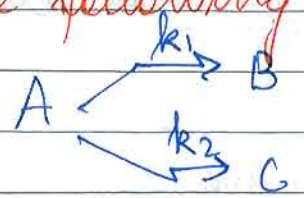


$k_1 < k_2$

Also, $\frac{[B]}{[C]} = \frac{k_1}{k_2}$ → ratio remains same ∀ time

All the above is true ∀ products

Q For the following II Ist ord. rxn with initially only reactant A, mole %age of B & C after 1 hr were found to be 5% & 15% resp. T determine, mole % of B & C after 10 hr at Const. T



At t = 1 hr

$$\frac{5}{15} = \frac{k_1}{k_2} \Rightarrow \boxed{k_2 = 3k_1}$$

$\Delta n = 0$.

$k(1) = \ln \frac{100}{80}$ 5+15 = 20% used.

If A = 100 moles.

So, After t = 1 hr, 80 moles of A left.

Let After t = 10 hrs, x moles of A left.

$k(10) = \ln \frac{100}{x}$

$$\Rightarrow \frac{1}{10} = \frac{\log 5 - \log 4}{\log 100 - \log x}$$

$$\Rightarrow \frac{1}{10} = \frac{0.7 - 0.6}{2 - \log x}$$

$\Rightarrow 2 - \log x = 1$

$\Rightarrow \log x = 1$

$\Rightarrow x = 10$

So, $\frac{x}{90-x} = \frac{1}{3}$

$\Rightarrow 3x = 90 - x$

$\Rightarrow x = 22.5\%$

$90 - x = 67.5\%$

Imp. DERIVATION

JEE

(Q.8) $A \xrightarrow{E_1, k_1} P$; $A \xrightarrow{E_2, k_2}$ Q. $E_a = ?$ in terms of E_1, k_1 & E_2, k_2.

Arrhenious eqn:

$$\ln K = (\ln A) - \frac{E}{RT}$$ → const for 1 rxn

Another form

$$\frac{d(\ln k)}{dT} = \frac{E_a}{RT^2}$$ (Differentiate w.r.t T)

Another form

$$\frac{1}{k}\frac{dk}{dT} = \frac{E_a}{RT^2}$$

$$\Rightarrow k\frac{dk}{dT} = \frac{kE}{RT^2} \quad \rightarrow (1)$$

$$\text{So, } \frac{dk_1}{dT} = \frac{k_1 E_1}{RT^2}$$

$$\& \quad \frac{dk_2}{dT} = \frac{k_2 E_2}{RT^2}$$

(A) $$\frac{dk_1}{dT} + \frac{dk_2}{dT} = \frac{E_1 k_1 + E_2 k_2}{RT^2}$$

$$\Rightarrow \frac{d}{dT}(k_1 + k_2) = \frac{E_1 k_1 + E_2 k_2}{RT^2}$$

$$\Rightarrow \frac{d}{dT} k = \frac{E_1 k_1 + E_2 k_2}{RT^2}$$

$$\Rightarrow \frac{kE}{RT^2} = \frac{E_1 k_1 + E_2 k_2}{RT^2}$$

$$\Rightarrow E = \frac{E_1 k_1 + E_2 k_2}{k_1 + k_2}$$

Or $$\boxed{E = \frac{\sum E_i k_i}{\sum k_i}}$$

(2) Reversible 1st ord. rxn (or Opposing Rxn)

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$$

$t=t$	$a-x$	x
$t=0$	a	0

At equi., $\frac{[B]}{[A]} = K = \frac{k_1}{k_2}$

$$\frac{d[B]}{dt} = k_1[A] \quad , \quad -\frac{d[B]}{dt} = k_2[A]$$

$$\Rightarrow \text{Net change} = \frac{d[B]}{dt} = k_1[A] - k_2[A]$$

$$\Rightarrow \frac{dx}{dt} = k_1(a-x) - k_2(x)$$

$$\Rightarrow \boxed{\frac{dx}{k_1 a - x(k_1+k_2)} = dt}$$

form

$\int \frac{dx}{x} = \ln x$

$\int \frac{dx}{a-bx} \Rightarrow -\frac{1}{b}\ln[a-bx]$

↳ Integrate by ← method & get ans.

$$\int_0^x \frac{dx}{k_1 a - x(k_1+k_2)} = \int_0^t dt$$

$$\Rightarrow \frac{-1}{k_1+k_2} \ln\left[\frac{k_1 a - x(k_1+k_2)}{k_1 a}\right]_0 = t$$

$$\Rightarrow \boxed{(k_1+k_2)t = \ln \frac{k_1 a}{k_1 a - x(k_1+k_2)}} \quad \star$$

Q. Consider following reversible rxn, 1st ord. in both dirn. $K_c = 0.25$ at 27°C.

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \qquad K = 0.25 \text{ at } 27^\circ C$$

$a-x$, x

At same T, rate constt for forward rxn ($k_1 = 0.07\ hr^{-1}$) Determine t reqd for formⁿ of 1/2 of equi. amt. of product.

$$\frac{k_1}{k_2} = K$$

$$\Rightarrow \boxed{k_2 = \frac{0.07}{0.25}} = \frac{7}{25} = 0.28 = k_2$$

$$0.25 = \frac{x}{a-x}, \quad K = \frac{x_e}{a - x_e}$$

$\Rightarrow x_e = \frac{a}{5}$ at equi.

time for $x = \frac{a}{10} = ?$

$$(0.35)t = \frac{\ln (0.07)a}{(0.07)a - \frac{a}{10}(0.35)}$$

$$= \ln \frac{a}{1 - \frac{1}{2}}$$

$$\Rightarrow (0.35)t = \ln 2.$$

$$\Rightarrow t = 2 \text{ hr}.$$

OR

$$\frac{dx}{dt} = k_1(a-x) - k_2 x = k_1 a - 5 k_1 x.$$

$$\Rightarrow \int_0^x \frac{dx}{a-5x} = \int_0^t k_1\, dt.$$

$\Rightarrow \frac{1}{-5}\ln[a-5x] = k_1 t$

$\Rightarrow a\ln\left(\frac{a-5\left(\frac{a}{2}\right)}{a}\right) = -5k_1 t$ (TO2)

$\Rightarrow 5k_1 t = \ln\frac{a}{a-\frac{a}{2}} = \ln 2$

$\Rightarrow t = \frac{\ln 2}{5k_1} = 2$

$= \frac{0.7}{0.35} = 2.$

(3) CONSECUTIVE Rxn (Successive, Sequencial Rxn)

TOUGH

$A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(reacts further : intermediate * not RI.)

Reactant → Product. Product further reacts to form another product.

eg: Radioactive decay

eg: $_{92}U^{238} \longrightarrow {}_{82}Pb^{206}$

$-\frac{d[A]}{dt} = k_1[A] \Rightarrow [A] = [A_0]e^{-k_1 t}$ → (1)

$\frac{d[B]}{dt} = k_1[A] - k_2[B]$

Linear Differential eqn

$\Rightarrow \frac{d[B]}{dt} + k_2[B] = k_1[A]_0 e^{-k_1 t}$ (From (1))

$\frac{dy}{dx} + Py = Qx$

Integrating factor = $e^{\int P dx} = e^{k_2 t}$.

(makes integrable)

$\times (e^{k_2 t})$ both sides

PTO

$\frac{d}{dt}\left(e^{k_2 t}\right) = (e^{ax})(a)$

$\Rightarrow e^{k_2 t}\left[\frac{d[B]}{dt} + k_2[B] = k_1[A_0]e^{-k_1 t}\right]$

$\Rightarrow e^{k_2 t}\frac{d[B]}{dt} + k_2[B]e^{k_2 t} = k_1[A_0]e^{(k_2-k_1)t}$.

$\Rightarrow \frac{d}{dt}\left([B]e^{k_2 t}\right) = k_1[A_0]e^{(k_2-k_1)t}$

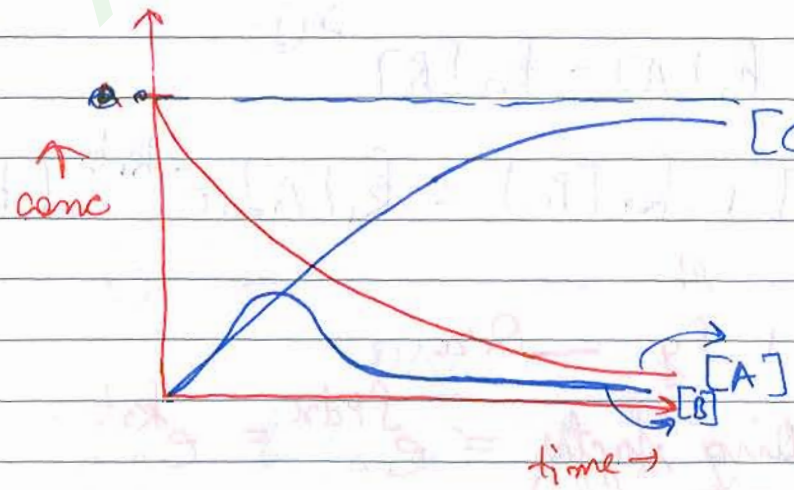
$\Rightarrow \int d\left([B]e^{k_2 t}\right) = \int_0^t k_1[A_0]\, e^{(k_2-k_1)t}\, dt$.

$\Rightarrow [B]e^{k_2 t} = \frac{k_1[A_0]}{k_2-k_1}\left[e^{k_2-k_1 t}\right]_0^t$

$\Rightarrow [B]e^{k_2 t} = \frac{k_1[A_0]}{k_2-k_1}\left[e^{(k_2-k_1)t} - 1\right]$

$\pm e^{k_2 t}$

$\Rightarrow \boxed{[B] = \frac{k_1[A_0]}{k_2-k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right]}$ ★

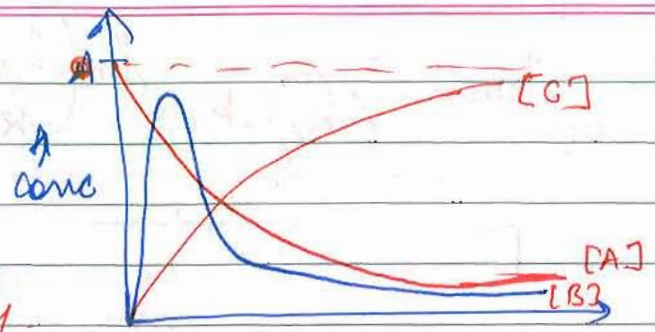


A → decreases continuously. attains maxima & then ↓

Initially, B increases at large rate (∵ it depends on [A] & initially, [A] is max. → see formula ↑)

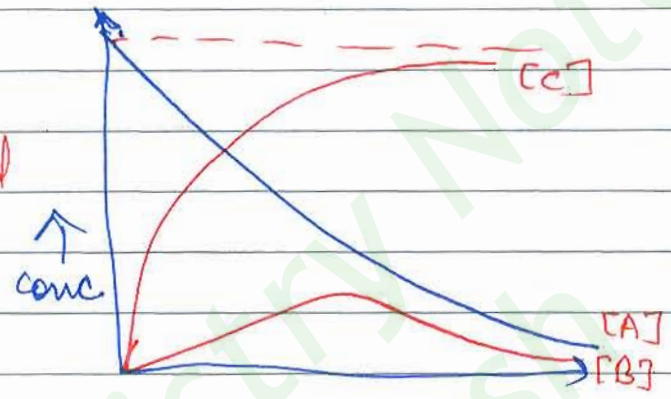
[C] initially = 0. At $t \to \infty$, [C] max.

- If $k_1 >> k_2$



- [B] increases quickly & [C] forms slowly.

- If $k_1 << k_2$
[B] formed slowly (so maxima attained very lately & its value would be less)
- & [C] forms quickly.



★ To attain max. value of [B].

i.e $\frac{d[B]}{dt} = 0$.

i.e $\frac{k_1[A_0]}{k_2 - k_1}\left[-k_1 e^{-k_1 t} + e^{-k_2 t}(k_2)\right] = 0$.

$\Rightarrow \frac{k_1[A_0]}{k_2 - k_1}\left[k_2 e^{-k_2 t} - k_1 e^{-k_1 t}\right] = 0$.

$\Rightarrow k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$ (t → max. ; t → max = t_m, say).

$\Rightarrow \frac{k_1}{k_2} = e^{(k_1 - k_2) t_m}$.

$\Rightarrow \ln \frac{k_1}{k_2} = (k_1 - k_2) t_m$.

$\Rightarrow t_m = \frac{\ln \frac{k_1}{k_2}}{k_1 - k_2} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2}$

classmate
Date
Page

$$t_{max} = \frac{1}{k_2 - k_1} \ln\left(\frac{k_2}{k_1}\right)$$

Now

Put t_m in (B) eqn of [B]

$$[B]_{max} = [A_0] \ln\left(\frac{k_2}{k_1}\right)^{\frac{k_2}{k_1 - k_2}}$$

Chemistry Notes
Akshansh

classmate
Date 30.4.10
Page

Ch: Solid State

Topics:
- Radius ratio
- Packing fr^n.
- Density
- Defects

CLASSIFICATION (depending on array of atoms, molecules/ions in solid state)

Crystalline solids
Those solids in which particles are regularly arranged; there is a well defined pattern of particles.

Amorphous
Those solids in which particles are randomly arranged.
eg: plastic

PROPERTIES

1. Crystalline solids have long range order (regular pattern/array throughout the solid). Amorphous solids → short range order (pattern is there, but in short range)

2. M.Pt :- Crystalline solids have SHARP m.Pt., whereas, amorphous solids have range of M.Pt. i.e they melt b/w lower & upper limit of Temp.

3. Crystalline solids are ANISOTROPIC.
Amorphous " " (ISOTROPIC)

§ Anisotropy: A phenomena in which diff^{t} values of physical properties are obtained when measured through diff^{t} angle of solid.
It is shown by crystalline solids.

§ Isotropy: A phenomena in which same values of physical properties are obtained for a solid if measured through diff^{t} Cs.
Its characteristic of amorphous solids.

4. Crystalline solids: breaks with sharp edge
Amorphous solids break with zig-zag edge.

5. Crystalline solid → hard, amorphous → soft. (generally)

CRYSTALLINE solids.

Based on nature of particles.

① Molecular solids
eg: glucose, urea, sucrose, wax, ice, dry ice ---
all covalent compds
These are those solids in which the basic particles (smallest repeat unit) are covalent molecules, held together by weak intermolecular force of attr^{n} due to which they have low M. Pt (usually).

② Ionic solids
Those solids in which basic particles are ions held together by strong electrostatic attn. giving high M. Pt. to ionic solid.
eg: NaCl (900°C)

③ Metallic
Metallic solids are those solids in which basic particles are metals.
eg: $Al^{3+} + 3e^{-}$
They have very high M. Pt. due to strong electrostatic attr^{n} existing b/w metal ion & e^{-}s.

④ Covalent solids
Silica (SiO_2)
eg. Diamond, (SiC)
These solids in which basic particles are atoms linked together by covalent bonds.
They are usually network solids in which covalent bonding extends infinitely give giant structure. & very high M. Pt. to solids.

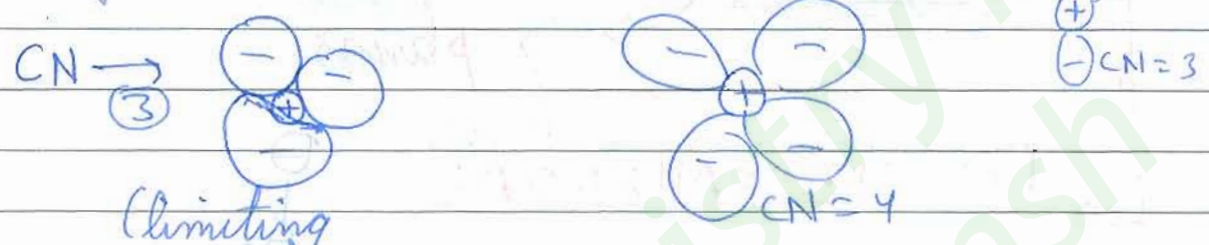
RADIUS RATIO

IONIC SOLIDS : radius ratio = $\frac{r_+ \text{ (radius of cation)}}{r_- \text{ (anion)}}$

For a given coordin^n no. (CN), radius ratio has fixed value in the limiting case.

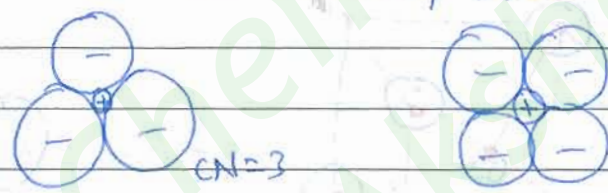
Coordin^n no : It is the no. of nearest neighbours of a central particle (any).

eg: ~~Coordin^n no. of cation here is 3~~



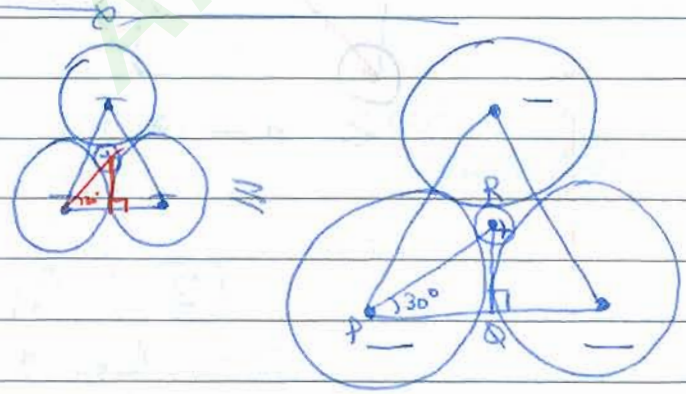
* Limiting case :- It is the case of closest contact.

eg: Limiting cases



CN = 3

Silicon carbide



In $\triangle PQR$

$\cos 30° = \frac{PQ}{PR} = \frac{\sqrt{3}}{2}$

$\Rightarrow \frac{r_-}{(r_+)+(r_-)} = \frac{\sqrt{3}}{2}$

$\Rightarrow \frac{r_+}{r_-} + 1 = \frac{2}{\sqrt{3}} \Rightarrow \frac{r_+}{r_-} = \frac{2}{\sqrt{3}} - 1$

$= \frac{2-\sqrt{3}}{\sqrt{3}}$

CN = 3.

$$\Rightarrow \boxed{\frac{r_+}{r_-} = \frac{2+\sqrt{3}}{\sqrt{3}} = 0.155}$$

↳ radius ratio.

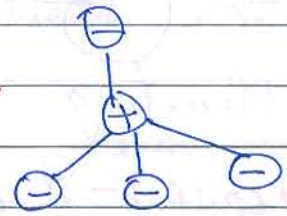
If we increase size of anion (r_-), r_+ will also increase ~~automatically~~ (to maintain radius ratio)

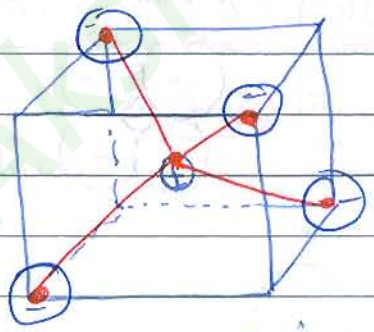
Now, If we ↓ r_+, CN will be 2 ∵ it will lose contact with one of the anions.

CN = 4 → Tetrahedral assay.

→ Sq. planar.

① TETRAHEDRAL.





$2r_- = \sqrt{2}a$ → diagonal of side → ①

$\Rightarrow r_- = \frac{a}{\sqrt{2}}$.

$2(r_- + r_+) = \sqrt{3}a$ → ②

↳ body diagonal

② ÷ ①

$\Rightarrow \frac{r_+}{r_-} + 1 = \frac{\sqrt{3}}{\sqrt{2}}$

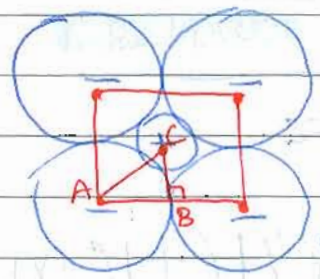
$\Rightarrow \boxed{\frac{r_+}{r_-} = \frac{\sqrt{3}-\sqrt{2}}{\sqrt{2}} = 0.225}$

↳ CN = 4

Tetrahedral assay.

Imp So, radius ratio 0.155 – 0.225 , CN = 3 (provided CN-4 is tetrahedral)

(2) SQUARE PLANAR.



CN = 4

In ΔABC,

~~cos 45~~

$AC^2 = AB^2 + BC^2$

$\Rightarrow [(r_+)+(r_-)]^2 = (r_-)^2 + (r_-)^2$

$\Rightarrow (r_+)+(r_-) = \sqrt{2}\, r_-$

$\Rightarrow \frac{r_+}{r_-} = \sqrt{2} - 1 = 0.414$

↳ CN = 4, square planar

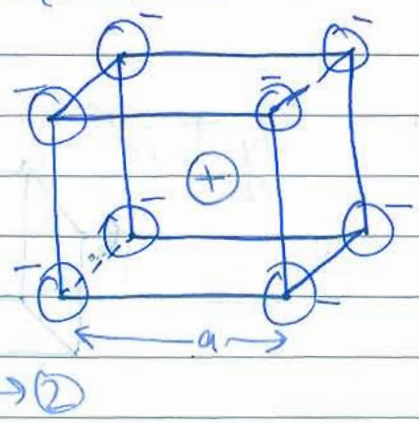
Imp So, radius ratio $\left(\frac{r_+}{r_-}\right)$ ~~0.225 < 0.414~~

= 0.155 – 0.414, CN = 3, provided CN-4 is sq. planar.

CN = 6 (octahedral)

It has same radius ratio value in limiting case as in CN = 4 (sq. planar) = 0.414
(∵ its a modific^n of sq. planar)

CN = 8



$a = 2r_-$ → (1)

$\sqrt{3}a = 2(r_+ + r_-)$ → (2)

(2) ÷ (1)

$\sqrt{3} = \frac{r_+}{r_-} + 1 \Rightarrow$ $r_+ = 0.732$ r_- → octahedral → CN = 8

Packing Fraction (ϕ)

It is the fractional volume of unit all occupied by atoms / molecules / ions

$\phi = N \frac{\text{Vol. of atoms/ions}}{\text{Vol. of unit all}}$

N → no. of atoms per unit cell.

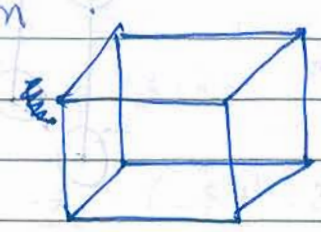
☆ **Unit Cell:** Its the smallest representative elemt of the crystal lattice upto which the characteristics of solid is retained. If solid is broken it its unit cell, it loses its characteristic property.

- 7 types of geometries possible, collectively called crystal lattice of unit cell.

Main ☆
1) Cubic
2) Hexagonal

other 5
3) Tetragonal
4) Trigonal.
5) Rhombohedral.
6) Monoclinic.
7) Triclinic.

<1> CUBIC System.



classmate
Date
Page

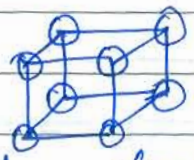
BRAVAIS LATTICE: the specific array of atoms/ions/molecules in a given unit cell.

Total 14 types of bravais lattices are there.

(1) SC (Simple Cubic System):

Atoms are present at corners of ~~cube~~ cube only.

~~Primitive~~

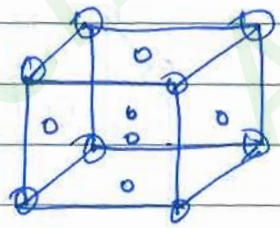


(2) BCC: Body centered:

Contains atoms at all corners as well as at the body centered

(3) FCC ~~or~~ (Face centered) or CCP (Cubic Closest Packing)

Atoms present at corners and all face centers.



Packing Fraction of Simple cubic System.

Limiting case: $a = 2r$

Contribution of atoms from corner = $\frac{1}{8}$

$$N = \frac{1}{8} \times 8 = 1 \quad ; \quad \phi = \frac{\frac{4}{3}\pi r^3}{V} = \frac{4\pi r^3}{3a^3}$$

N = no. of atoms per unit cell

$$= \frac{4\pi r^3}{24 r^3} = \frac{\pi}{6}.$$

+2 Chemistry Notes Akshansh

$\Rightarrow \phi = \frac{\pi}{6} = \frac{3.14}{6} = 0.52$ — Simple cubic sys — Imp

Simple Cubic.

☆ Primitive Cell

Unit cells which contain 1 a particle per unit cell.

eg: Simple cubic sys.

Conclusion → 52% is max occupancy
or 48% is min. vacancy.
0.48 is void fraction.

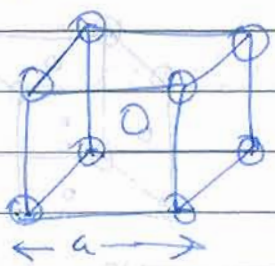
Q. An atom has simple cubic array of atoms. But, due to some defect, 1 corner is left unoccupied per unit cell. Determine PF of solid.

$\frac{7}{8} = N$.

$1 \rightarrow 7/8$

$0.52 \rightarrow \frac{7}{8} \times 0.52 = 0.45$

BCC



$4r = \sqrt{3}a$

$N = 2$

$\phi = \frac{\frac{4}{3}\pi r^3 \times 2}{V} = \frac{\frac{4}{3}\pi r^3 \times 2}{\frac{8}{3\sqrt{3}} r^3}$

$\Rightarrow \phi = \frac{\sqrt{3}\pi}{8} = 0.68$ — BCC — Imp learn

Conclusion:
→ max. occupancy = 68%
min. vacancy = 32%
void fr^n = 0.32.

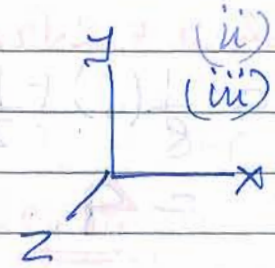
classmate
Date
Page

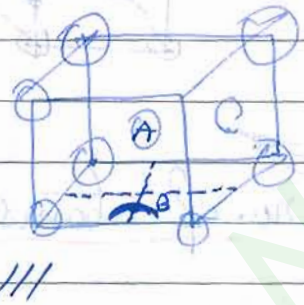
(5) ~~Defn~~ An atomic BCC solid is made of A type of atom & guest ~~as~~ atom B is present at one of the face with its largest possible size without disturbing original unit cell. Coordinate of centre (B) $(\frac{1}{2}, \frac{1}{4}, 0)$

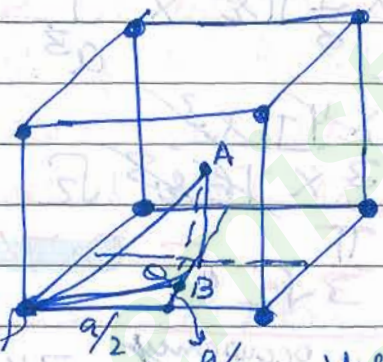
Determine (i) $\frac{r_B}{r_A}$ = ?

(ii) ϕ = ?

(iii) CN = 2







$PQ = r_A + r_B$

$= \sqrt{\frac{a^2}{4} + \frac{a^2}{16}} = \frac{a\sqrt{5}}{4}$ ... → (1)

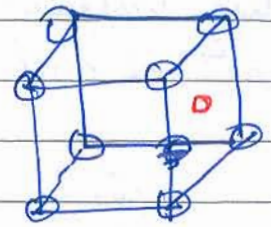
$4r_A = \sqrt{3}a \Rightarrow r_A = \frac{\sqrt{3}a}{4}$ → (2)

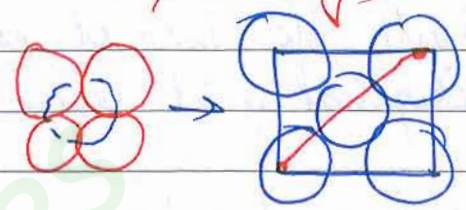
So, $\frac{(1)}{(2)} \Rightarrow 1 + \frac{r_A}{r_B} = \frac{\sqrt{5}}{\sqrt{3}}$

$\Rightarrow \frac{r_B}{r_A} = \frac{\sqrt{5} - \sqrt{3}}{\sqrt{3}} = 0.3$

Type of unit cell : ABCABC -

☆ FCC Atomic Solid (also called CCP → cubic closest packing)





$4r = \sqrt{2}a$.

$\therefore a = 2\sqrt{2}r$

ϕ no. of atoms per unit cell $= \frac{1}{8}(8) + \frac{1}{2}(6)$

$= 4$.

$$\phi = 4 \times \frac{4}{3}\pi r^3 \times \frac{1}{a^3}$$

$$= \frac{4 \times 4\pi r^3}{3 \times 16 r^3 \sqrt{2}}$$

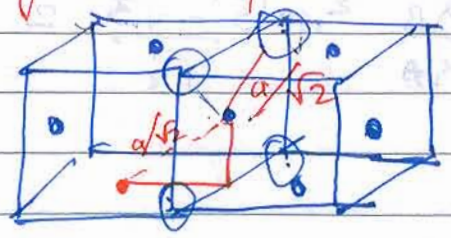
$$\Rightarrow \phi = \frac{\pi}{3\sqrt{2}} = 0.74$$ → FCC

Learn

Max. occupancy = 74 % (max)

~~Max~~ Vacancy = 26 %. (min)

Q. Ca crystallises in FCC array. No. of Ca atoms in nearest neighbour of Ca atoms = ?



12

distance $= \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2}$

$= a/\sqrt{2}$.

distance of all atoms (if $a/\sqrt{2}$), then, CN would be counted.

☆ EMPERICAL FORMULA

Q. An atomic solid made of A & B. A occupy corner & B occupy FCC. E.F of solid.

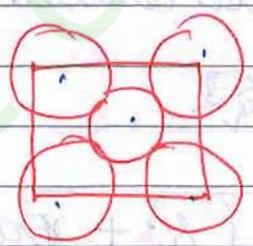
AB_3

Q. An atomic solid made of A & B
A → corner posns.
B → FC posns
Determine EF in following condns:-
(i) If corner is left unoccupied per unit cell. $A_{7/8}B_3 = A_7B_{24}$
(ii) If FC is left unoccupied per unit cell. $A_1B_{3-\frac{1}{2}} = AB_{\frac{5}{2}} = A_2B_5$
(iii) If 1 corner & 1 FC are left unoccupied

$A_{\frac{7}{8}}B_{\frac{5}{2}} = A_7B_{20}$.

Q16 $\phi = ?$

Pg. 195



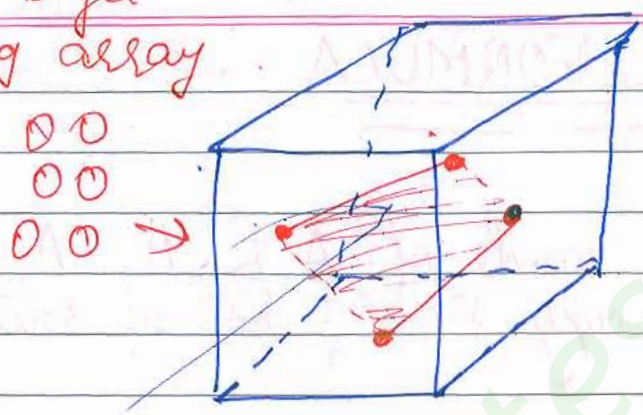
All atoms identical.

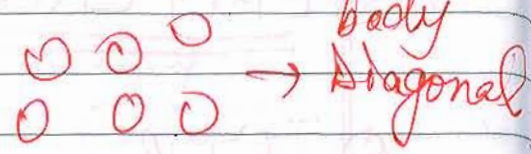
$= \frac{2 \times \pi r^2}{8a^2}$

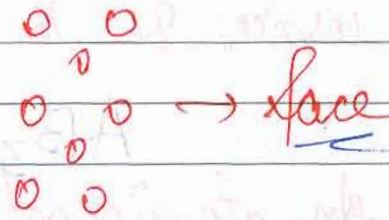
$= \frac{\pi}{4}$.

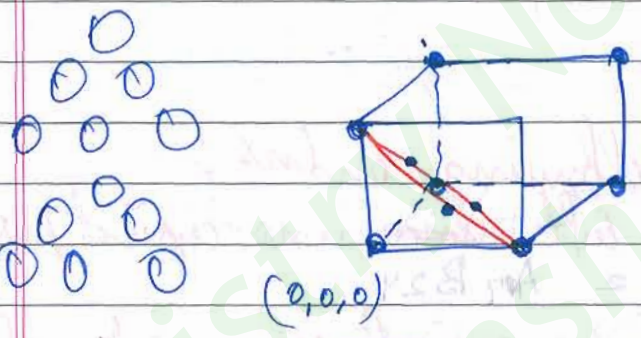
$4r = \sqrt{2}a$
$\Rightarrow a = 2\sqrt{2}r$.

Q. How to get following array







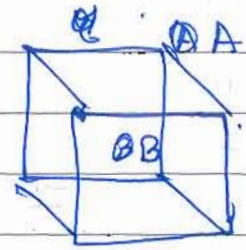


fcc

Q. Determine ϕ of an atomic FCC containing a largest sized guest atom present at body centre of unit cell without disturbing original unit cell. What is its CN?

CN = 6 ↔ face centered (6) : its at a/2 distance

$$\phi = \frac{5 \times \frac{4}{3}\pi\left(r^3 + a^3\right)}{a^3}$$



Radius ratio = 0.414

$4r = \sqrt{2}a$

$\Rightarrow a = 2\sqrt{2}r$

$$= \frac{5 \times 4\pi}{3}\left(\frac{r^3 + 16\sqrt{2}r^3}{(16\sqrt{2})r^3}\right)$$

$$\phi = \frac{20}{3}\pi\left(\frac{1 + 16\sqrt{2}}{16\sqrt{2}}\right)$$

$4R_A = \sqrt{2}a$

$\Rightarrow a = 2\sqrt{2}R$

$\frac{R_B}{R_A} = 0.414$

$\phi = \frac{4}{3}\pi\left(\frac{4R_A^3 + R_B^3}{a^3}\right)$

$= \frac{\pi}{12\sqrt{2}}\left[4 + \left(\frac{R_B}{R_A}\right)^3\right]$

$= \frac{\pi}{12\sqrt{2}}\left(4 + (0.4)^3\right)$

$= \frac{\pi}{3\sqrt{2}} + \frac{0.74}{4}(0.4)^3$

$\frac{\pi}{3\sqrt{2}} \rightarrow 0.74$

$= 0.74 + 0.74\left(\frac{16\times10^{-3}}{4}\right)$

$= 0.74 + 0.74(16\times10^{-3})$

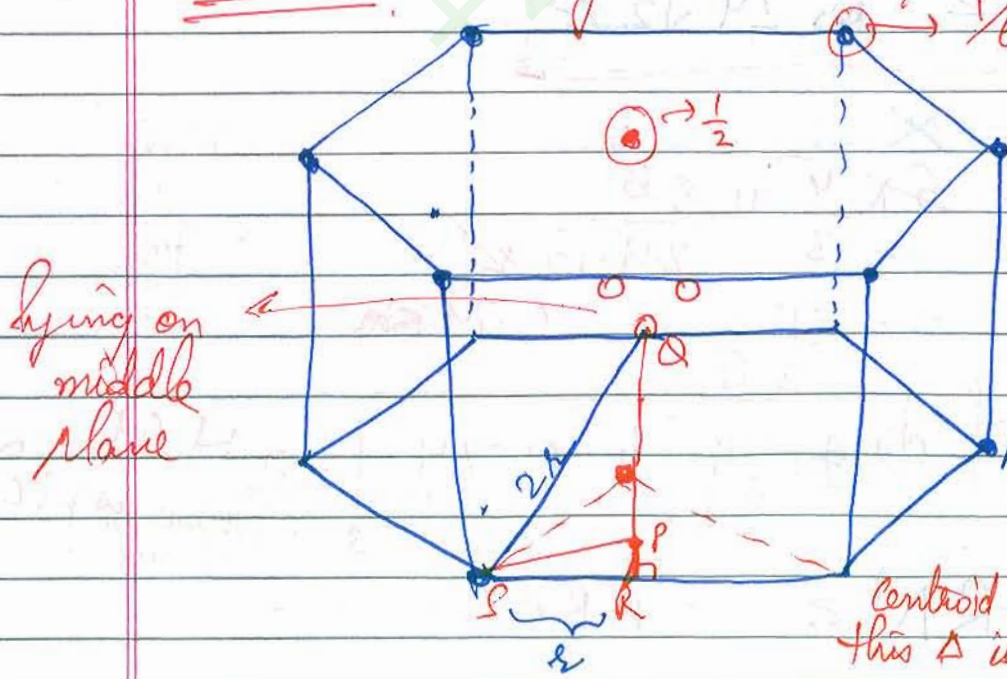
$= 0.74 + 0.01184$

$= 0.07584 \times 100$

$= 75.84\%$

74
16
1184

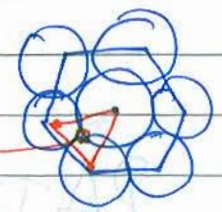
☆ HCP (hexagonal closest packing) N = 6



2+4

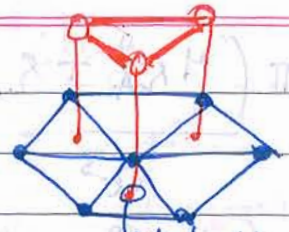
$N = 12\times\frac{1}{6} + \frac{1}{2}(2) + 3 = 6$

$a = b = 2R$



Centroid of this Δ is empty & same everywhere ETC

Δ lies above these voids (adjacent).



Now, $\phi = 6 \times \frac{4}{3} \frac{\pi r^3}{V}$

$V = (A)(h) \rightarrow$ ht.

↓ area

In ΔPRS (See fig previous)

$A = 6 \cdot \frac{\sqrt{3}}{4} a^2 = 6\sqrt{3} r^2$.

$\cos 30^\circ = \frac{SR}{PS} = \frac{\sqrt{3}}{2}$

r

$\Rightarrow \frac{r}{PS} = \frac{\sqrt{3}}{2} \Rightarrow \frac{2r}{\sqrt{3}} = PS$.

In ΔQPS, $PQ = \sqrt{QS^2 - PS^2}$

$= 4r^2 - \frac{4r^2}{3}$.

$\Rightarrow PQ = \frac{2\sqrt{2}r}{\sqrt{3}}$.

$\Rightarrow$ ht. $(h) = 2PQ = 4\sqrt{\frac{2}{3}} r$.

$\Rightarrow V = (6\sqrt{3}) r^2 \times 4 \times \sqrt{\frac{2}{3}} r$

$V = 24\sqrt{2} r^3$

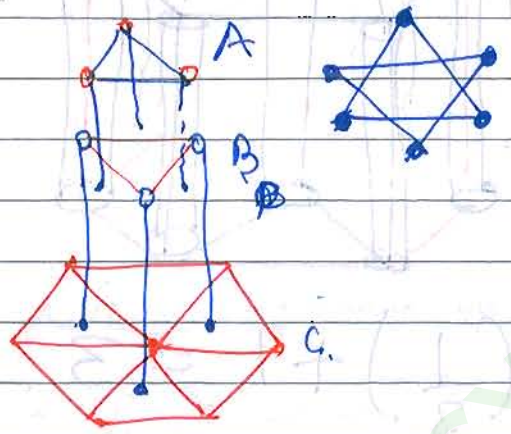
So, $\phi = \frac{6 \times \frac{4}{3} \pi r^3}{24\sqrt{2} r^3}$

$= \frac{\pi}{3\sqrt{2}} = 0.74$

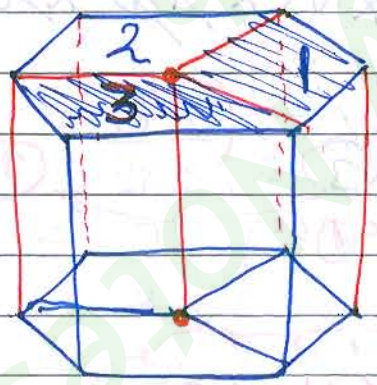
$\Rightarrow \boxed{\phi = \frac{\pi}{3\sqrt{2}} = 0.74} \rightarrow$ HCP (same as FCC or cubic)

PATTERN = --ABAB----

FCC → ABCABC type



HCP structure → volume can be found by adding V of 3 chambers

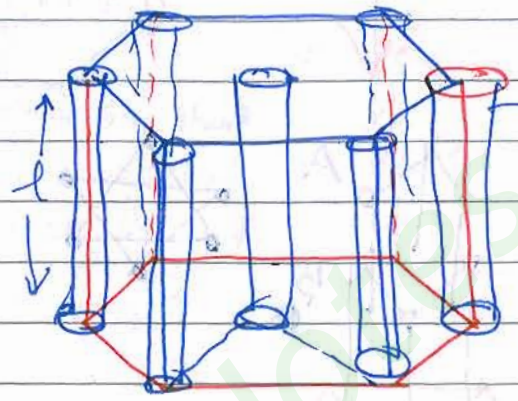


Expected V. Imp

HCP is made of uniform cylindrical atoms. determine Φ of solid.

Expected V. Imp

PTO →



$\frac{1}{3}$ rd contribution.

$$N = 6\left(\frac{1}{3}\right) + 1 = 3.$$

$$\phi = \frac{3[\pi r^2 l)}{6\left(\frac{\sqrt{3}}{4} a^2\right) l} \qquad a = 2r.$$

$$\Rightarrow \phi = \frac{4 \times 3 \pi r^2 l}{6 \times \sqrt{3} \times 4 r^2 \times l}$$

$$\Rightarrow \phi = \frac{\pi}{2\sqrt{3}} \quad \left(FCL = \frac{\pi}{3\sqrt{2}} \text{ don't confuse}\right)$$

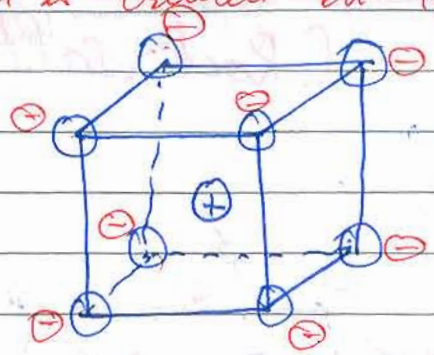
$$= 0.909$$

IONIC SOLID

<1> CsCl (Caesium Chloride)

→ BCC array of ions is in it.

limiting case :- Cs ion has just appropriate size of the void that is created in the hole b/w the ions.



$N_{(CsCl)} = 8$

$$\begin{cases} a = 2r_- \\ 2(r_+ + r_-) = \sqrt{3}a. \end{cases} \quad \text{valid in limiting case.}$$

$$\frac{r_+}{r_-} = 0.732.$$

$$\phi = \frac{\frac{4}{3}\pi\left[(r_+)^3 + (r_-)^3\right]}{a^3}$$

$$= \frac{4\pi}{8\times 3}\frac{\left[(r_+)^3 + (r_-)^3\right]}{(r_-)^3}$$

$$= \frac{\pi}{6}\left\{1 + \left(\frac{r_+}{r_-}\right)^3\right\}$$

$$= \frac{\pi}{6}\left\{1 + (0.73)^3\right\}$$

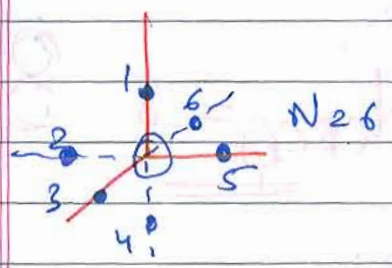
$$\Rightarrow \phi \approx 0.71$$

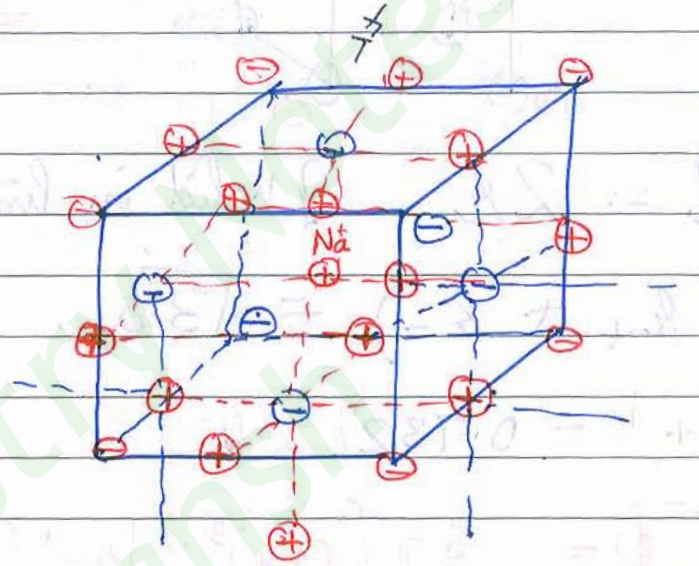
* Packing fr^n of ionic solid is always $>$ ϕ of atomic solid having same array of unit cell (in ionic solid, smaller cations can be accomodated better → more compact)

classmate
Date
Page

imp

(2) NaCl type ionic solid (Rock salt structure)





★ Ions are present at corners, face centres, edge centres & Body centres.
Anions are present at corners as well as face centres.
Cations are present at body centres & edge centres.

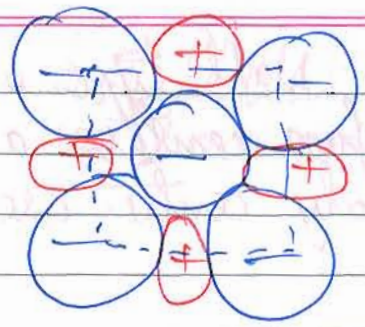
$$Cl^{\ominus} \rightarrow \frac{1}{8}(8) + \frac{1}{2}(6) = 4$$

$$Na^{+} \rightarrow 1 + \frac{1}{4}(12) = 4$$

It is also called interpenetrating FCC of NaCl
(∵ here, Na की FCC, Cl⊖ की FCC में inserted है)

★ • If all anions are removed, its FCC of Cl^-
" " " cations " " " " of Na^+

Face :-



$4r_{\oplus} = \sqrt{2}\,a$.

true only for limiting case.

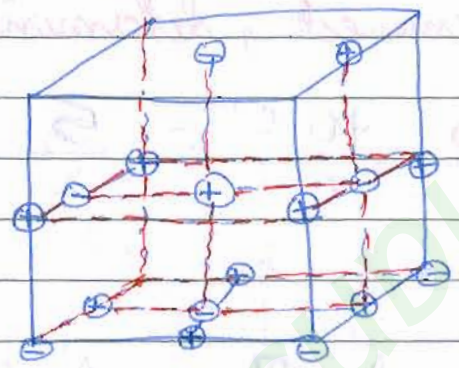
$2(r_{\oplus} + r_{\ominus}) = a$

true ∀ cases (General case)

In limiting case,

$\sqrt{2}a = 4r_-$

$a = 2(r_+ + r_-)$



$\frac{r_+}{r_-} = 0.414$

$\phi = \frac{4\left(\frac{4}{3}\pi\right)\left((r_+)^3 + (r_-)^3\right)}{a^3}$

$= \frac{16\pi\left(r_+^3 + r_-^3\right)}{3 \times 16\sqrt{2}\,(r_-)^3}$

$\Rightarrow \phi = \frac{\pi}{3\sqrt{2}}\left(1 + \left(\frac{r_+}{r_-}\right)^3\right)$ → $(0.414)^3$

$= 0.74\left(1 + (0.414)^3\right)$

$\Rightarrow \boxed{\phi \approx 0.79}$ → NaCl packing fⁿ.

1064
74
4256
74484
78736

97

Q. An AB solid has NaCl type of unit cell. If atoms from face centres along an axis passing through body centre are absent. EF = ?

$A \rightarrow Na \rightarrow 4 \quad AB_3 = A_4B_3$.

$B \rightarrow 3$

(c) If atoms along an axis connecting opp. edge centres & passing through body centres are removed, determine EF.

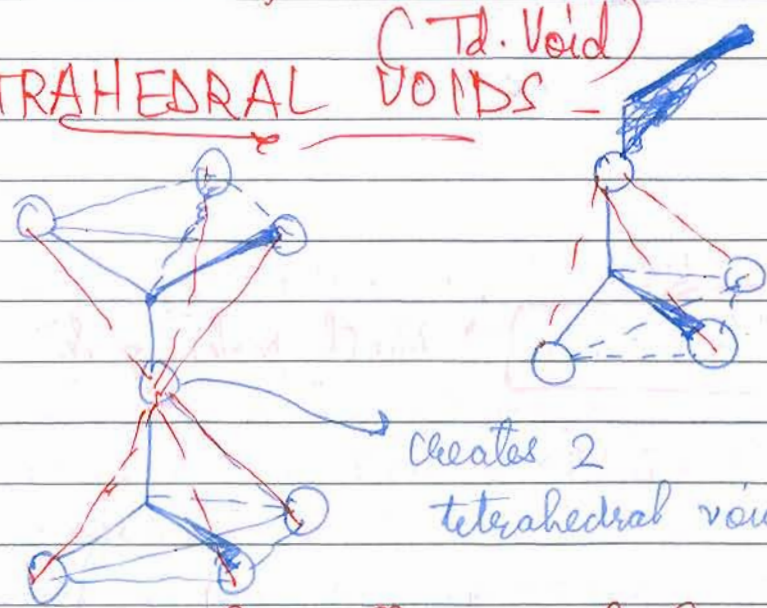
$\frac{+0}{4}\frac{5}{2} = \frac{5}{2} \rightarrow A$.

$B = 4 \rightarrow B_4$.

$= A_{\frac{5}{2}}B_4 = A_5B_8$

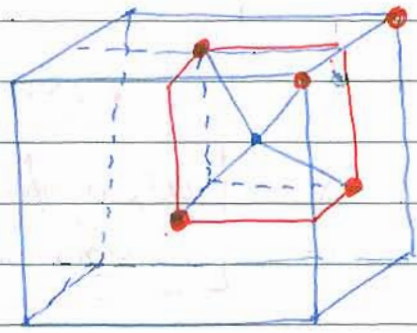
☆ CONCEPT of VOIDS

(I) TETRAHEDRAL VOIDS (Td. Void)



☆ So, in simple cubic cell, 2 tetrahedral voids,
" BCC " 4 " "
FCC " 8 " "

✡ No. of tetrahedral voids = 2 × no. of atoms
(see how many atoms per unit cell.)



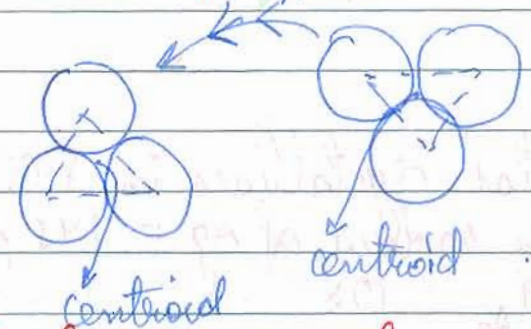
Cube के Body diagonal के alternate corner को join करने से, जो Tetrahedral void बनता है।

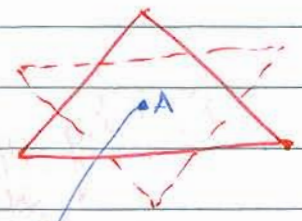
Imp. ✡ In diamond, C atom is present all all FCC positions as well as in the alternate tetrahedral voids.

$\phi_{diamond} = \frac{8(\frac{4}{3}\pi r^3)}{a^3}$; $2r = \frac{\sqrt{3}a}{4}$

$(\frac{1}{4} \times \text{body diagonal})$

(2) OCTAHEDRAL VOID.
(Od. Void)



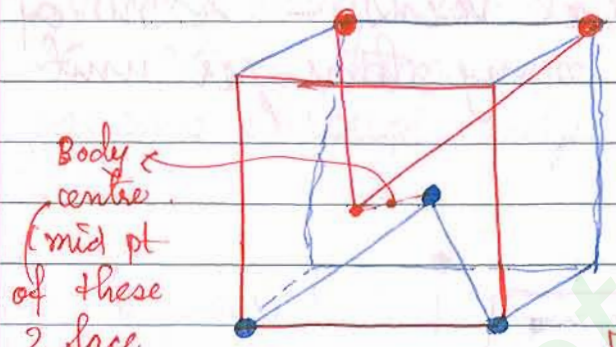


Centroid of equilateral Δ की line का centre A से 1/3 वाँ centre centre of octahedral void है।

- The centroids of these 2 Δ structures are collinear.

✡ no. of octahedral voids = no. of atoms

Hexagon Volume = $24\sqrt{2}\, r^3$



Body centre (mid pt of these 2 face centres. It is the centre of octahedral void also)

Oct. Void = $(12)\frac{1}{4} = 3$

edge centres

★ Mid pt. of edges is also the centre of Oct. Voids.

★ DENSITY of SOLID

If there are N particles per unit cell, mass of unit cell (m) = $\frac{N}{N_A} \times M$ ← atom/molecule/ion

$$\rho = \frac{m}{V} = \frac{N \times M}{N_A \times V}$$

V ← Volume of unit cell.

diff for cubic, hexagonal

Q. Ag metal crystallises in FCC type of unit cell. If radius of Ag = 145 pm, ρ = ? in g/cc. If M_{Ag} = 108.

$4r = \sqrt{2}a$

$a = 2\sqrt{2}r$

$$\rho = \frac{4 \times 108}{6 \times 10^{23} \times 16\sqrt{2}\, r^3}$$

$$\Rightarrow \rho = \frac{4 \times 108 \times 10^{-23}}{6 \times 16\sqrt{2} \times 145 \times 145 \times 145}$$

* In calculations always take radius in form $\times 10^{-8}$

$$\rho = \frac{9}{2\sqrt{2} \times (145)^3} \times 10^{29}$$

$$= \frac{9 \times 10^{29}}{853335}$$

$$= 0.000010$$

OR

$$\rho = \frac{4 \times 108 \times 10}{6 \times 10^{23} (1.45)^3 \times 10^{-29}}$$

$$= \frac{45}{\sqrt{2}(1.45)^3} \text{ g/cc.}$$

Q. Al metal crystallises in cubic array of unit cell & has $\rho = 2.7 \text{ g/cc}$. If edge length of unit cell = 405 pm. determine radius of Al. M = 27

$$\rho = \frac{N \times M}{N_A \times V}$$

$$\Rightarrow \frac{2.7}{27} \times V \times 6 \times 10^{23} = N.$$

$$= V \times 6 \times 10^{23} = N.$$

$$= (405)^3 \times 6 \times 10^{23} = N.$$

$$= (4.05)^3 \times 10^{-25} \times 6 \times 10^{23}$$

$$= 64 \times 6 \times 10 = N.$$

$$= \frac{3840}{10} = 384 = 4.$$

1 m = 100

Chemistry Notes by Akshay

★ OSMIUM → 20 g/cc : Can be used in calcul^n.
Most dense elemt : ρ should be less than 20 g/cc → Remember.

Date
Page

New, $\rho = \frac{N \times M}{N_A \times V}$

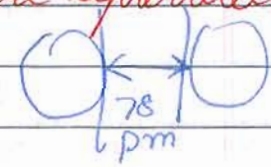
$= \frac{4 \times 27}{6 \times 10^{23} \times 16\sqrt{2}\, a^3}$

$\Rightarrow a^3 = \frac{27 \times 10 \times 4}{27 \times 6 \times 10^{23} \times 16\sqrt{2}}$

$4a = 2\sqrt{2}\, a$

$\Rightarrow a = \frac{a}{2\sqrt{2}} = \frac{405}{2 \times 1.4} = 144.6$ pm.

Q. K crystallises in BCC assay of unit cell & the adjacent atoms on corners are separated by 78 pm (interfacial distance)
K = 39 ρ = ?



$\rho = \frac{2 \times 39 \times 10^{30}}{6 \times 10^{23} \times \left(\frac{4}{\sqrt{3}}\right)^3 \left(\frac{39\sqrt{3}}{2-\sqrt{3}}\right)^3}$

$= \frac{2 \times 39 \times 10^7 \times 3\sqrt{3}\,(2-\sqrt{3})^3}{6 \times 64 \times 3\sqrt{3} \times 39 \times 39 \times 39}$

$= \frac{10^7\,(2-\sqrt{3})^3}{6 \times 32 \times 39 \times 39}$

$= \frac{10^7 (2-\sqrt{3})^3}{292032}$

$\rho = \frac{10^4 \times 27}{292032} = 0.00007 \quad 1600 + 1 - 80 = 1521$

Or

$a - 2r = 78$ pm

$\Rightarrow a - \frac{\sqrt{3}}{2} a = 78$

$\Rightarrow a = \frac{78 \times 2}{0.26}$ pm $= 600$ pm.

$4r = \sqrt{3}a$

$\Rightarrow a = \frac{4}{\sqrt{3}} r$.

$r = \frac{\sqrt{3}}{4} a$

$\Rightarrow (78 + 2r)\frac{\sqrt{3}}{4} = r$

$\Rightarrow \frac{78\sqrt{3}}{4} + \frac{\sqrt{3}r}{2} = r$

$\Rightarrow r\left(1 - \frac{\sqrt{3}}{2}\right) = \frac{78\sqrt{3}}{4}$

$r = \frac{78\sqrt{3}}{4(2-\sqrt{3})}$

$= \frac{39\sqrt{3}}{2-\sqrt{3}}$

☆ In a numerical, if we are finding ρ of alkali metals, then, it would be less than 1 g/cc (∵ they float on water & ρ of water is 1 g/cc)

$\rho = 2 \times 3^{9} \times 10$

Q. He crystallises in HCP array in solid state. If ht of hexagon is 600 pm. Determine ρ of solid He.

$ht = 4\sqrt{\frac{2}{3}}\, r. \Rightarrow \frac{600 \times 10^{-10}}{4} \times \sqrt{\frac{3}{2}} = r.$

$\rho = \frac{N \times 4}{6 \times 10^{23} \times 24\sqrt{2}\, r^3}$

$= \frac{6 \times 24 \times 2\sqrt{2} \times 64}{6 \times 10^{23} \times 24\sqrt{2} \times (600 \times 10^{-10})^3 \times 3\sqrt{3}}$

$= \frac{10 \times 64}{3 \times 36 \times 6 \times 3\sqrt{3}}$

$= \frac{10}{330.12}$

$= \frac{1000}{330312}\ 0.003$

$\rho = 0.192\ g/cc$

$\Rightarrow \rho \simeq 0.2\ g/cc$

Q. KCl has NaCl type of unit cell. Radius of Na^+ ion is $\frac{1}{2}$ (Radius of Cl^- ion). Radius of K^+ is 0.7 times radius of Cl^- ion. If ρ of KCl is 1.8 g/cc, determine ρ of NaCl.

(23, 39, 35.5 → Na, K, Cl)

$2(r_+ + r_-) = a$

$= 2\left(\frac{r_-}{2} + r_-\right) = a$

$= r_- + \frac{a}{3}$

$\sqrt{2}a = 4r_-$

$\Rightarrow \sqrt{2}a = 4\left(\frac{a}{3}\right)$

$\Rightarrow$

So, $\frac{r_+}{r_-} = 0.414$

$\Rightarrow \frac{r_-/2}{r_-} = \frac{1}{2} = 0.$

$\S \cdot 2$

$r_+ = (0.7)\, r_-$

$a_{KCl} = 2(1.7)r_-$

$a_{NaCl} = 2(1.5)r_-$

NaCl → 58.5

KCl → 74.5

$\frac{\rho_{NaCl}}{\rho_{KCl}} = \frac{M_{NaCl}}{M_{KCl}} \left(\frac{a_{KCl}}{a_{NaCl}}\right)^3$

$\Rightarrow \frac{\rho_{NaCl}}{1.8} = \frac{58.5}{74.5}\left(\frac{1.7}{1.5}\right)^3$

$\Rightarrow \rho_{NaCl} = \frac{108}{10} \times \frac{585}{745}\left(\frac{343 \times 17}{225 \times 15}\right)$

≈ 1.4 or 1.3

Solve

225 | 15 | 15

3375 | 3

1125 | 225 | 15 | 15

1125 | 225

3375

Q. Ca crystallises in FCC & its ρ is 2.5 g/cc. Molar mass of Ca = 40. Determine no. of Ca atoms present on surface of $1\,cm^3$ → cubical grain of Ca.

Side = 1 cm

SA of grain = $6cm^2$.

$4R = \sqrt{2}a$

$\Rightarrow a = 2\sqrt{2}R$

M

$$2.5 = \frac{4 \times 40}{6\times10^{23} \times 16\sqrt{2}R^3}$$

$$\Rightarrow R^3 = \frac{4\times40 \times 16 \times 10}{6\times10^{23}\times16\sqrt{2}\times2.5}$$

$$\Rightarrow R^3 = \frac{40}{6\sqrt{2}\times10^{23}}$$

$$\Rightarrow \frac{a^3}{16\sqrt{2}} = \frac{4}{6\sqrt{2}\times10^{23}}$$

$$\Rightarrow a^3 = \frac{4\times16\sqrt{2}}{6\sqrt{2}\times10^{23}}$$

$$= \frac{64\times10^{-23}}{6\cdot3}$$

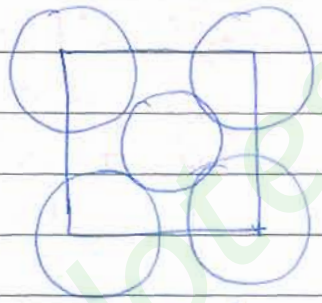
$$\Rightarrow a^3 = \frac{32\times10^{-23}}{3}$$

$$= \frac{4^3}{6}\times10^{-23}$$

$$\Rightarrow a^3 = 10.6\times10^{-24}$$

$$\Rightarrow a = 4.8\times10^{-8}\ cm$$

Now, $a^2 = (4.8)^2\times10^{-16}$



2 atoms on surface.

Now, no. of atoms $= \left[\frac{6}{(4.8)^2\times10^{-16}}\right]\times2$

$\because$ 2 per face.

$$= \frac{12}{4.8\times4.8}\times10^{16}$$

$$= \frac{10^{17}}{0.4\times4.8\times4}$$

no. of atoms $= \frac{10^{17}}{48\times4} \simeq 5\times10^{15}$.

2580+4

—

classmate
Date 12.5.10
Page

SEVEN CRYSTAL SYSTEM

P → Primitive
ECC → edge centered

P 1) TRICLINIC → (nothing equal)
$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$

P, FCC, BCC 2) CUBE
$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$

P 3) HEXAGONAL
$a = b \neq c$ $\alpha = \beta = 90^\circ$. $\gamma = 120^\circ$

P, BCC 4) (T)ETRAGONAL
$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$

P (R)HOMBOHEDRAL
TR $a = b = c$ $90^\circ = \alpha = \beta \neq \gamma$

P, BCC, FCC, ECC (O)RTHORHOMBIC
OM $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$

P, ECC (M)ONOCLINIC
$a \neq b \neq c$ $\alpha = \beta = 90^\circ \neq \gamma$

☆ CRYSTAL DEFECTS

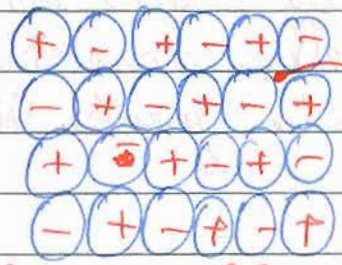
(only Point-Defect would be Studied.)
(Or Stoichiometric defect)

In solid state, atoms, molecules or ions vibrate about a pt. known as normal lattice pt. If all the particles of crystalline solid are vibrating abt its normal lattice pt, the solid is known as Perfectly Crystalline Solid i.e there is no defect.
However, this is impractical.
A crystalline solid is perfectly crystalline only at absolute zero. (cease everything → no motion, So, no E, ? transfer.)

★ ~~Probabil~~ ~~Probabi~~ On increasing T, the probability of formⁿ of pt defect (density of pt. defect) increases ∴ They are also called THERMAL DEFECTS)

Pt. defects
(or Thermal Defects)

SCHOTTKY Defects



If a pair of (oppositely charged) ions are absent from their normal lattice pts, the defect is known as Schottky defect

Ions would be absent in pairs (adjacent are absent → not necessary)

- Schottky defect is more likely to be found in ionic solids in which cations & anions are of comparable size (so that neither of them can be accomodated in the interstitial space)
- eg: KCl (they have comparable size) → likely, pure metal (any)

FRENKEL Defect

If a cation is absent from its normal lattice pt, but occupy the interstitial space, the defect is known as Frenkel defect.

- Frenkel defect is more likely to be found in ionic solids in which cation is much smaller than anion so that cation can be accomodated in the interstitial space
- eg: AgI is likely, alloy (any) → ∵ they have diff^t size of atoms/ions)

classmate
Date
Page

Schottky defect

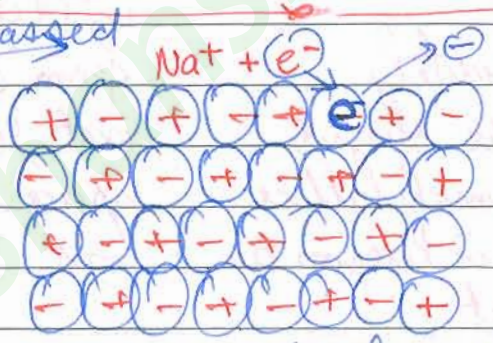
- In case of this, observed density is smaller than the ideal (theoretical) density ∵ some atoms go out, so, mass ↓ Hence $\rho = M/V$, V is same, so, ρ ↓

Frenkel defect

- Frenkel defect has no effect on density of solid

★ Due to coming of some impurities inside voids or interstitial spaces inside unit cell, mass ↑. So, ρ ↑. Hence, Observed ρ can be greater than Theoretical ρ.

Vapours of alkali metal → passed



- Vapourised alkali metal ionises also.

NaCl surface or any gp 1 or gp 2 chlorides.

★ f-centre defect

F : comes from Febri which means colored

★ When vapours of alkali metal is passed over simple salts (NaCl, KCl, $MgCl_2$, $CaCl_2$), some of the anions are substituted by e⁻ from vapour phase giving rise to ANIONIC-HOLE (hole having charge → e⁻) This defect is called F-CENTER defect. The defect makes colorless salt colored (∵ the emission spectrum of trapped e⁻ lies in the visible range)

eg : NaCl becomes yellow on passing vapours of Alkali metal.

Initially its yellow in color (शुरुआत में)

SEMI-CONDUCTOR

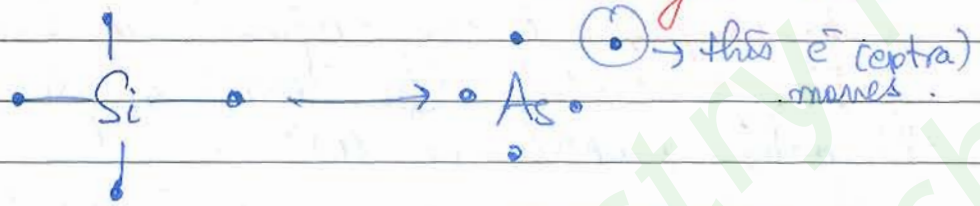
classmate
Date
Page

✡ Semi conductor → phenomena in which charge is carried out by ions or e^-.

✡ n-type & p-type semi-conductor

✡ n-type Semi conductor

When Si is doped by elemts of grp 15, (usually As), it gives rise to n-type semiconductor in which cond^n occurs through e^-s.



✡ p-type

When Si is doped → substituting by elemts of grp 13 (usually Gl → gallium), p-type semiconductor is formed. & cond^n occur through hole.

ऊपर वाले grp से → n type
नीचे वाले grp से - p type

✡ With temp, conductivity [of metal or semi conductor] decreases due to increase in BAND-GAP.

The end

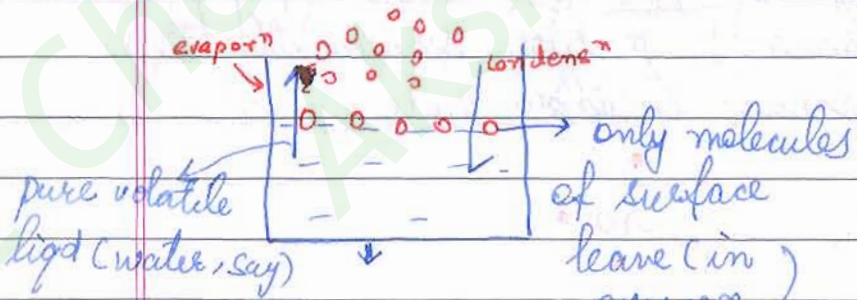
classmate
Date 12.5.10
Page

Ch Solutions

Colligative Properties of Dilute Soln

* COLLIGATIVE PROPERTY : Properties which depends on amt. only, not on nature, is known as colligative properties. In terms of sol^ns → Colligative property of soln is the property which depends on no. of solute particles, not on the nature of solute particles

* VAPOUR PRESSURE (VP) of liqd :-
VP of a volatile liqd is, the equi P exerted by the molecules in the vapour phase on the surface of liqd alw onto the atmosphere.



$H_2O(l) \rightleftharpoons H_2O(v)$

constt = K_p = (P) → vapour pressure

⇒ Property P1 : VP of a given soln or a pure liqd depends on T.

By Vant Hoff eqn, $\ln K_p = C - \frac{\Delta H}{RT}$ (C → constt)

So, for liqd phase → $\ln P = C - \frac{\Delta H}{RT}$

$\Rightarrow$ $P = C' e^{-\frac{\Delta H}{RT}}$ (P → VP of liq^d)

So, VP of liq^d increases exponentially with T.

✱ At molecular level, VP ↑ with T due to →
1. Heating shift equi^n in favour of vapour → forward rxn.
2. On heating, avg. KE of vapour molecules increases

✱ If we heat above limit (1 atm), it starts boiling

• Molecules with greater intermolecular force of attr^n will have less VP.
eg: H_2O has less VP than CH_3OH.

✱ VP of a pure liq^d is characteristic of that liq^d & it depends on the intermolecular force of attr^n
Intermolecular force of attr^n ↑, difficult is evapor^n, Smaller is VP.
Rel^n :- VP more ⟶ B.Pt. less.

✱

If we add some non-volatile solute (eg: sucrose, urea) :- VP of soln decreases.
(∵ some of solute occupies surface of liq^d which prevents max. most of solvent molecules, thus, decreasing VP).

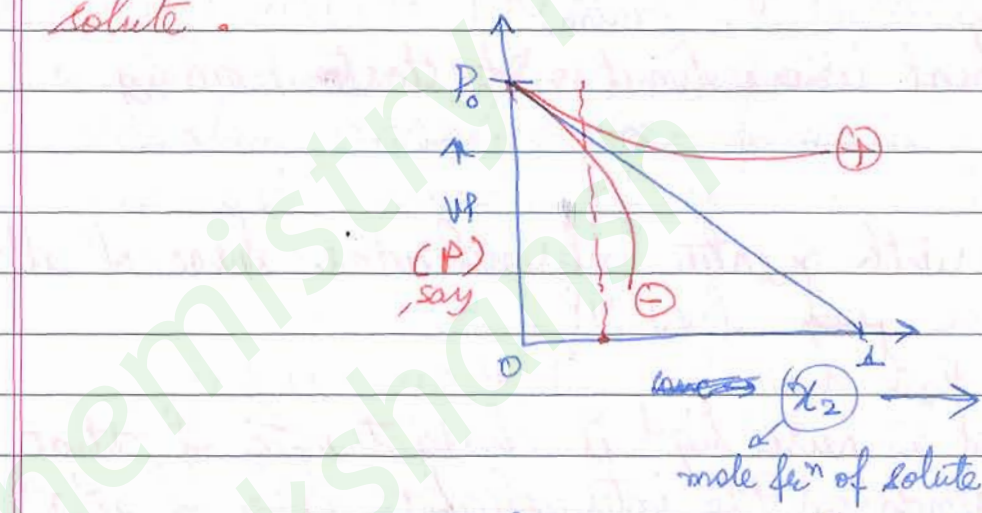
So, We can say that VP of pure liq^d is max.

Symbols used :- 1 → solvent
2 → solute

RAOULT'S LAW

Addⁿ of non-volatile solute to a volatile solvent results in lowering of VP. This happens due to decrease in rate of evaporⁿ by presence of some solute on surface. To restore the equi, no. of molecules in vapour phase, decreasing the rate of condensⁿ, which in turn, decreases VP.

Acc. to Raoult's law, lowering of VP on addⁿ of a non-volatile solute is a linear fⁿ of conc. of solute.



* IDEAL SOLⁿˢ: Solⁿˢ which obey Raoult's law, is known as Ideal solⁿ (very Rare).

In most of the cases, deviation from ideal behaviour is observed.

In case on non-Ideal solⁿˢ :-

1) If observed VP > Ideal VP, deviation is known as +ve deviation.
2) Observed VP < Ideal VP, deviation is known as −ve deviation from Raoult's law.

* If we decrease x_2 (see graph), non-Ideal curve will approach to Ideal curve.

So, extent of deviation from ideal behaviour increases with increase in conc. of solute. &

vice versa. ∴ Raoult's law is STRICTLY applicable only to very dilute sol^ns.

Imp. Increasing conc. increases deviation from Raoult's law.

Acc. to graph, $P = mx_2 + C$ → Intercept

Case (1): If $x_2 = 0$; $C = P_0$ = V.P. of pure solvent.

$\Rightarrow P - P_0 = mx_2$ or $P = P_0 + mx_2$

Case (2): At $x_2 = 1$, $P = 0$

$\Rightarrow 0 = P_0 + m$

$\Rightarrow m = -P_0$

So, eqn becomes:

$P = -P_0 x_2 + P_0$

$\Rightarrow P = P_0(1 - x_2)$

$\Rightarrow P = P_0(x_1)$ ∵ $(1 - x_2 = x_1)$

→ mathematical form of Raoult's Law

☆ VP of pure liq^{d} (P_0) is not a colligative property (∵ it depends on nature)

☆ P is also not a colligative property ∵ it depends on P_0

☆ LOWERING of VP = $P_0 - P$

= $P_0 - P_0 x_1$ (From Raoult's law)

= $P_0(1 - x_1) = P_0 x_2$

$\Rightarrow -\Delta P = P_0 x_2$ → lowering in VP.

☆ lowering of VP: not a colligative property ∵ it depends on P_0 → which itself isn't a colligative property

classmate
Date
Page

☆ Relative lowering of VP (RLVP)

$$\Rightarrow -\frac{\Delta P}{P_0} = x_2 = \frac{n_2}{n_1 + n_2}.$$

It is a colligative property (∵ It doesn't depend on nature of solute & solvent)(∵ It just depends on amt. of solute & solvent).

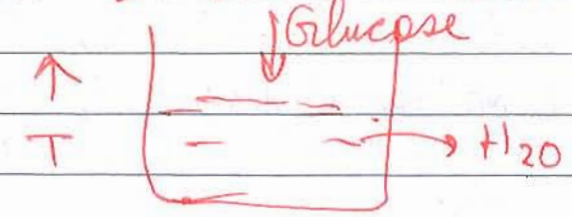
☆ Elevⁿ in B.Pt :-
(Ebullioscopy)
↳ Branch in which we study elevⁿ in B.Pt.

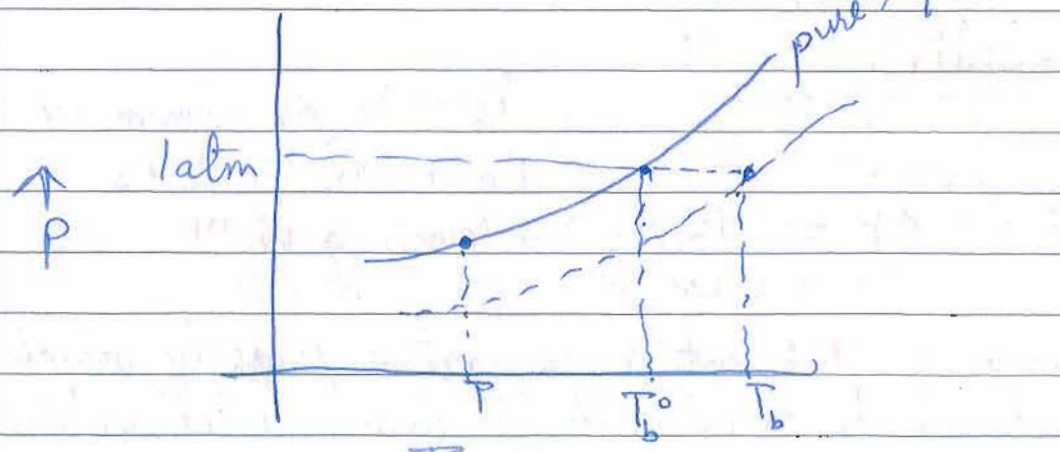
B.Pt. of a liqd is equal to Temp. at which V.P becomes equal to external P.

☆ Normal BPt. (T_b^0)
normal B.Pt. is the B.Pt. when ext. P. is 1 atm.

☆ Addⁿ of a non-volatile solute to a volatile solvent

Due to this, there is decrease in VP of solⁿ which results in elevⁿ in the B.Pt. of solⁿ.





Elevⁿ in B.Pt,

$T_b - T_b^\circ = \Delta T_b$

$\Delta T_b \propto m_2$ (Molality)

$\Delta T_b = K_b \cdot m_2$ → moles of solute / wt. of solvent (in kg) ×1000

K_b = Molal elevⁿ constt.
(Ebullioscopic constt)

$$K_b = \frac{M_1 R (T_b^\circ)^2}{\Delta H^\circ_{1mv}}$$

where M_1 = molar mass of solvt. in kg unit.
$R = 8.314\ J \cdot K^{-1} mol^{-1}$
ΔH°_{1mv} = std. molar (m) enthalpy of vaporisⁿ (v) of solvent (1)

☆ K_b is permanent constt for a solvent.

☆ Special case

If A, B, C solvt. with comparable M, then, whose intermolecular force of attrⁿ more ∴ its T_b° more ∴ its K_b more.

☆ Depression in freezing pt. (CRYOSCOPY)

Addⁿ of a non-volatile solute to a volatile solvt. decreases the freezing pt. of solⁿ.

Dep. in freezing pt is also an outcome of lowering of VP of solⁿ.

$$90 = 100 \times \frac{n_1}{n_1 + n_2}$$

$$90 = 100 \times x_1$$

$$\Rightarrow x_1 = 0.9$$

1 mole soln

0.9 mol H_2O — 0.1 mol solute

18 / 09 / 162

0.9 mol H_2O = 16.2 g H_2O

16.2 g H_2O → 0.1 mole

1000 g → $\frac{0.1}{16.2} \times 1000$

$= \frac{1000}{162} = \frac{500}{81}$ 6.1

$-\Delta T_f = \frac{1.86 \times 1000}{162} = 11.5 = T_f^\circ - T_{f_{H_2O}}$

$T_f^\circ = 4.86$ (81 / 06)

Or

$$90 = 100 \frac{n_1}{n_1 + n_2}$$

$$\Rightarrow \frac{n_2}{n_1} = \frac{1}{9}$$

Now, $-\Delta T_f = 1.86 \frac{n_2}{n_1 M_1} \times 1000$

$= 1.86 \times \frac{1000}{9 \times 18}$

(ii) Determine the wt. of solut. present in 1 Kg of soln.

16.2 g H_2O ⟶ 0.1 mol. Glucose = 18 g.

18 + 16.2 = 34.2 g sol^n contain 16.2 g of H_2O.

⇒ 1000 g sol^n contain → $\frac{16.2 \times 1000}{34.2}$

$= \frac{1710}{19}$

$= \frac{9000}{19} = 472$ g of H_2O.

(iii) What wt. of H_2O must be added to 250 g of above sol^n in order to increase Freezing pt. of sol^n by 5%

250 g of sol^n → $x = 13.2 - 0.590$

$= 12.610$

250 g → 1000 g H_2O

250 → $\frac{472 \times 250}{1000}$

118 g H_2O.

118 g H_2O | 250 g sol^n + H_2O → W_{gm} H_2O, x mole solute

x mole solute

$-\Delta T_f = 11.5$

$11.5 = K_f \times \frac{x}{118} \times 1000$

$\Delta T_f = 6.5$

$6.5 = K_f \times \frac{x}{W} \times 1000$

$\Rightarrow \frac{11.5}{6.5} = \frac{w}{118}$

$\Rightarrow w = \frac{118 \times 23}{13}$

$= 2794.9$

$w \approx 210\,g$.

Initial $= 118\,g\ H_2O$.

Final $= 210\,g$.

Added $H_2O = 92\,g$.

Q. 0.1 mol of a non-volatile Hydrocarbon is dissolved in 0.9 mole of C_6H_6 & cooled to some temp $T^\circ C$, where, some C_6H_6 freezes out. Now, the soln is decanted off & heated to 353 K, where VP is found to be 670 mm of Hg. Also T_b° & T_f° of C_6H_6 are 353 K & 278 K resp.

K_f C_6H_6 $= 5.12\ K\ Kg\ mol^{-1}$.

(i) Determine the mass of C_6H_6 freezed out.

(ii) Also determine the temp ($T^\circ C$) the soln was cooled originally.

Initial moles of $C_6H_6 = 0.9$

After decantn $\rightarrow$ n

$P = P_0^\circ (x_1)$ solvent.

$670 = 760\,(x_1)$

$\Rightarrow x_1 = \frac{670}{760} = 0.8$

Benzene initial = 0.9
final = x mol.

$$670 = 760\left(\frac{x}{x+0.1}\right)$$

$$\Rightarrow \frac{0.1}{x} = \frac{76}{67} - 1 = \frac{9}{67}$$

$$\Rightarrow x = \frac{6.7}{9} = 0.74$$

Freezed out = 0.16 moles
mass of solidified = 0.16 × 78
= 12.48 g

T°C से lower होने पे,
At T°C attained from sol^n, freezing would stop.

$$\Rightarrow T_f = T°C - \frac{128}{256}$$

$$\text{Now, } -\Delta T_f = 5.12 \times \frac{0.1}{0.74 \times 78} \times 1000$$

$$= \frac{128}{1803} \times 10^3$$

$$\approx 8$$

$$\Rightarrow T_f° - T_f = 8$$

$$\Rightarrow T_f = 278 - 8$$

$$= 270°C.$$

* OSMOSIS

8) If P greater than π (Osmotic P) is applied on sol^n chamber, then ~~that~~ net diffusn start occuring from soln to solvt chamber which is known as Reverse Osmosis (RO)

$\pi = hSg$ → density of soln (under ideal condn)

→ difference of ht.

$P = \frac{n}{V} RT = CRT$ → conc./Molality

so, $hSg = CRT$

→ 0.082 take

→ conc. of soln

—x—

Q. 1g of a protein when dissolved in 1L H_2O, & separated from pure H_2O in an osmometer gives a net capillary rise of 4mm at 27°C (300K) If ρ of soln is 1.025 g/cc, determine molar mass of protein.

$273 + 27$

$4 \times 10^{-3} \times 1.025 \times 10 = \frac{1}{M} \times 0.082 \times 300$

$\Rightarrow M = \frac{8.2 \times 3}{61.5} \quad \frac{24.6 \times 10^5}{4 \times 1025 \times 10^{-3}/2}$

$= \frac{246 \times 10^4}{4 \times 1025}$

$= \frac{6150000}{1025}$

$= \frac{615 \times 10^4}{1025} \quad 0.$

6000×10^6

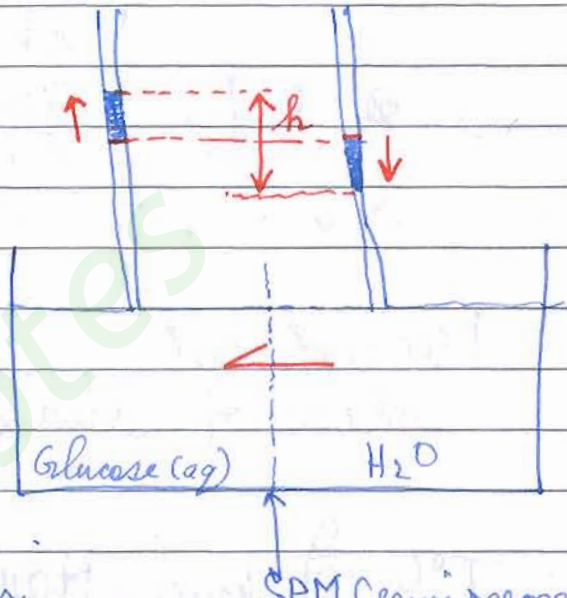
82 e3 246

1025 e6 615

OSMOSIS

OSMOMETER

As solvt. starts moving from towards glucose chamber, sol^n would rise in capillary tube & solvt's capillary level will come down. By time, hydrostatic P of rising capillary sol^n increase. When P epected from dilute sol^n side to conc. sol^n side balances the hydrostatic P, the rise inside capillary stops



(Mainly allows movt. of solvt. molecules eg: skin.

* SPM: * filter of fixed porosity & usually it allows passage for solvt. molecules only.

→ When a pure solvt is seperated from its sol^n, by means of SPM, in an osmometer, there occurs net diffus^n of solvt. molecule from solvt. chamber to sol^n chamber. As a result, level of liq^d in the capillary attached to sol^n chamber rises & the same attached to solvt chamber decreases.

This phenomena of net diff^n of solvt from dilute sol^n to conc. sol^n is called OSMOSIS.

* OSMOTIC P: It is the min. P that must be applied on the sol^n side capillary in order to prevent osmosis is called Osmotic P. It is denoted by (π).

$$M = \frac{W_2}{8kg} \times \frac{RT}{V} = \frac{10^{-3}}{1.025 \times 4 \times 10^{-3} \times 10} \left(\frac{8.314 \times 300}{10^{-3}}\right)$$

$$= \frac{8314 \times 3 \times 10^{-1}}{1025 \times 4 \times 10^{-5}}$$

$$= \frac{8314 \times 3}{1025 \times 4} \times 10^{4}$$

$$= \frac{24942}{4100} \times 10^{4}$$

$$= \frac{24942}{41} \times 10^{2}$$

$$608.34$$

$$\Rightarrow M = 60834 \text{ Kg}$$

8314
e3
24942

1025
e4
4100

246
342
328
140

123
070

✡ COLLIGATIVE PROPERTY OF ELECTROLYTIC SOLⁿ

i → VANT HOFF FACTOR.

i : $\frac{\text{Observed colligative Property}}{\text{Ideal}}$ → Given.
" → (From Raoult's law)

i = no. of ions (particles) obtained from one formula unit of electrolytic solute.

For NaCl ⟶ $Na^+ + Cl^-$
x mole → 2x mole
$i = 2$.

For $Ca(NO_3)_2 \longrightarrow Ca^{2+} + 2NO_3^-$

$i = 3$.

Glucose $\longrightarrow$ no change

$i = 1$.

So, now.

$$\Delta T_b = i K_b m_2$$

$$-\Delta T_f = i K_f m_2$$

$$\Pi = i c R T$$

$$P = P_0 \frac{n_1}{n_1 + i n_2}$$

$$K_a = \frac{c\alpha^2}{1-\alpha}$$

To find (i)

$H_nA \rightleftharpoons n H^+ + A^{n-}$

$1-\alpha \quad n\alpha \quad \alpha$

Total $i = 1 + n\alpha = i$

eg: $CH_3CH_2COOH \rightleftharpoons CH_3COO^- + H^+$

$1-\alpha \quad \alpha \quad \alpha$ $\quad 1+\alpha = i$

Q. 10g of $Ba(NO_3)_2$ is dissolved in 100g of H_2O & resulting sol^n boils at 100.46°C. If $K_{b\,H_2O} = 0.52$. Determine the degree of ionis^n of $Ba(NO_3)_2$, assuming it to be partially ionised.

Ba = 137

$Ba(NO_3)_2 \rightleftharpoons Ba^{2+} + 2NO_3^-$

$1 + 2\alpha = i$

$\Rightarrow$

$0.46 = (1+2\alpha)(0.52)\left(\frac{10 \times 10^3}{137 \times 10^{-1}}\right)$

$\Rightarrow$

$\Rightarrow 0.46 = (1+2\alpha)(0.52)\left(\frac{100}{137}\right)$

$\Rightarrow \frac{0.46 \times 137}{0.52 \times 100} = 1+2\alpha$

$\Rightarrow \frac{46 \times 137}{52 \times 26} = 1+2\alpha$

$\Rightarrow 31.51 \times 10^{-2}$

$\Rightarrow 1+2\alpha = \frac{46}{52} \times 26 \times 10^{-1}$

$= 2.3$

$\Rightarrow 1.3 = 2\alpha$

$\Rightarrow \alpha = 0.65$

$i = 2.3$

Q (a) 0.1 molal urea sol^n 1) max fr. pt.
(b) 0.06 molal NaCl sol^n 2) → same VP
(c) 0.04 molal $CaCl_2$ sol^n 3)
(d) 0.24 molal $Fe(NO_3)_3$ 4) max. B.Pt.

Q. An aq. sol^n of a weak monobasic acid of molarity 0.01 M freezes at $-0.0193^\circ C$. If $K_{f_{H_2O}} = 1.86$ K Kg mol^{-1}
Determine, Ka_{acid}, pH_{sol^n}.

$M = 0.01M$
F.Pt $= -0.0193^\circ C$, -272.9807 K.
$K_{f_{H_2O}} = 1.86$ K Kg mol^{-1}

$K_a = \frac{c\alpha^2}{1-\alpha} = (0.01)$

$HA \rightleftharpoons H^+ + A^-$

$1-\alpha \quad \alpha \quad \alpha \quad 1+\alpha$

$1+\alpha = i$

$-\Delta T_f = i K_f \times m$

$\Rightarrow \frac{0.0193}{1.86 \times 0.01} = i$

$\Rightarrow \frac{193}{186} = i = 1+$

$\Rightarrow 1.04 = 1+\alpha$

$\Rightarrow \alpha = 0.04$

$+0.010$
$-.04$
0.96

$193 - 186 = 700$

$186 \quad 2186$
$06 \quad 04$
$1116 \quad 664$

Now, $K_a = \frac{(0.01)(16\times10^{-4})}{(0.96)}$

$= \frac{16\times10^{-4}}{96}$

$K_a = 0.16\times10^{-4}$

acid $= 16\times10^{-6}$.

$[H^+] = c\alpha = 4\times10^{-4}$

$\Rightarrow pH = 4 - \log 4 = 3.4$.

Q. 1.9 g of TiO_y is dissolved in 0.500 g H_2O & resulting soln is found to be freezing at $-0.186\,^\circ C$. If $K_{f\,H_2O} = 1.86$, deduce molecular formula of salt assuming it to be 100% ionised. $Ti = 48$.

$\frac{1.9}{48 + (35.5)y}$ $\quad \frac{1.9}{0.5\times0.1} =$

$= 3.8$

~~1.86 = 0~~

$0.186 = 1.86 \times m$.

$\Rightarrow m = 0.1$.

Tidal : $i = n+1$.

$M = 48 + (3.5 \cdot 5)y$.

$(0.186) = \overbrace{(n+1)}^{i} (1.86) \frac{1.9}{48+35.5n} \times \frac{1000}{500}$.

$= 0.1 = (n+1) \frac{1.9 \times 2}{48+35.5n}$.

$\Rightarrow 4.8 + 3.5n = 3.8n + 3.8$

$\Rightarrow 1 = 0.1n$

$\Rightarrow 1 = 0.25n$

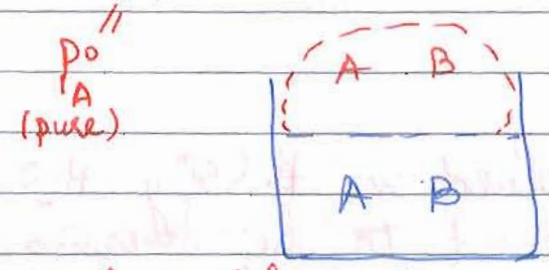
$\Rightarrow n = 4$

✡ BINARY SOLⁿ

↳ Solⁿ of 2 volatile liqds.

A → VP = P_A^0 (pure)

B → VP = P_B^0 (pure)



$V.P_{total} = P_A + P_B$

P_A = Partial VP of A

P_B = " " " B

$P_A = x_A P_A^0$, $P_B = x_B P_B^0$ in liq phase

✡ § • Factors ~~determining~~ :-

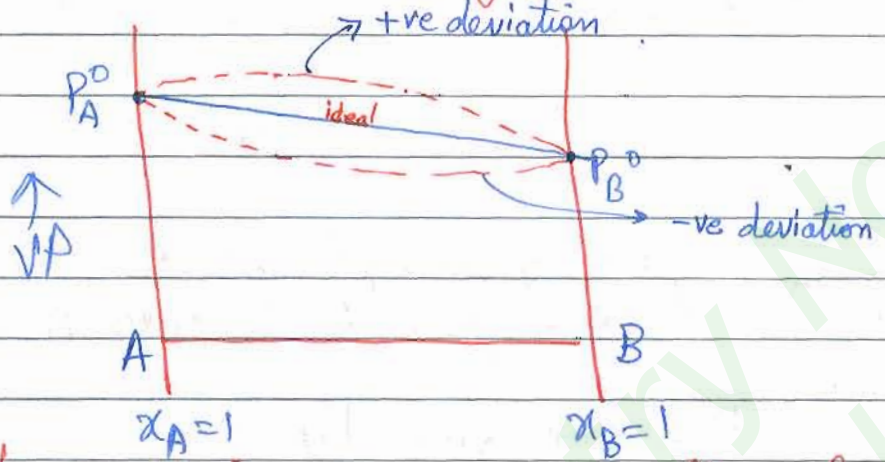
In case of binary mixture, partial VP of component of a mix. depends on 2 factors:

(1) Amt. of that component in the liqd. phase. Greater the amt, greater will be partial VP.

(2) Intermolecular forces of attⁿ. Smaller the

intermolecular force of attrⁿ, greater will be tendency to pass into vapour phase, greater will be partial VP.

let $P_A^0 > P_B^0$ (say)



8. Ideal binary solⁿ: A binary solⁿ whose VP vs mole frⁿ graph is a st. line path is known as Ideal binary solⁿ

As per the graph,

At infinite solⁿ, curves for non ideal solⁿ approaches to the curve of ideal solⁿ & ∴ behaves like an ideal solⁿ.

§ • $\Delta H > 0 \rightarrow$ +ve deviation.

$\Delta H < 0 \rightarrow$ -ve "

$\Delta H = 0 \rightarrow$ no "

• Intermolecular force of attrⁿ b/w 2 solⁿs A & B (similarity)

More ∴ Ideality.

less ∴ Non-Ideality

$$P = P_B^0 + (P_A^0 - P_B^0) x_A$$

$$\Rightarrow \text{Total VP}_{\text{soln}} = P_A + P_B = (P_A^0 - P_B^0) x_A + P_B^0$$

$$y = m \quad x + c$$

$x_A \rightarrow$ mole fr^n in liq^d phase

$y_A \rightarrow$ " " " vapour phase

Let y_A = mole fr^n of A in vapour phase.

$\Rightarrow P_A = y_A P$ (Dalton's law.)

$\Rightarrow y_A = \frac{P_A}{P} = \frac{x_A P_A^\circ}{x_A P_A^\circ + x_B P_B^\circ}$ **

Q. A binary soln contain 2 volatile solvt A & B. VP of soln = 600 mm Hg at 25°C (298K). If x_A (liqd & vapour phase) are (0.7 & 0.35) resp. Determine VP of pure A & pure B in identical cond^n

$P = 600$ mm Hg

$x_A = 0.7$

$y_A = 0.35$.

$P_A^\circ = ?$, $P_B^\circ = ?$

$P = x_A P_A^\circ +$

$0.35 = (0.7)(P_A^\circ)$

$P_A = P_A^\circ x_A$ $\quad 0.35 = \frac{(0.7) P_A^\circ}{600}$

$\Rightarrow \frac{2100}{7} = P_A^\circ$

$\Rightarrow P_A^\circ = 300$

* Now, $600 = 300(0.7) + (0.3) P_B^\circ$

$\Rightarrow 600 = 210 + 0.3 P_B^\circ$

$\Rightarrow \frac{390}{0.3} = P_B^\circ$

$\Rightarrow P_B^\circ = 1300$ mm Hg.

Q. 2 moles of a volatile liqd A is mixed with 3 moles of another volatile liqd B at @ 298 K. VP = 500 mm Hg. If 2 moles of A is added ~~$n_A = 22$~~, further, VP of resulting soln was found to be 400 mm Hg. Find P_A^0, P_B^0. Also determine vapour Phase compos^n above the soln obtained by condensing vapours of orginal soln.

(1) $n_A = 2$, $n_B = 3$. P_A^0, P_B^0 ?

VP = 500 mm Hg.

$P_B = x_A P_A^0 + x_B P_B^0$.

$\Rightarrow 500 = \frac{2}{5}(P_A^0) + \frac{3}{5} P_B^0$.

(2) $n_A = 4$, $n_B = 3$

VP = 400 mm Hg

$\Rightarrow 400 = \frac{4}{7} P_A^0 + \frac{3}{7} P_B^0$.

$\Rightarrow 2800 = 4P_A^0 + 3P_B^0$.

$2500 = 2P_A^0 + 3P_B^0$

$\Rightarrow 300 = 2P_A^0$.

$\Rightarrow P_A^0 = 150$ mm Hg.

$\Rightarrow P_B^0 = \frac{2200}{3}$ mm Hg.

$y_A = \frac{x_A P_A^0}{P} = \frac{2(150)}{500} = \frac{3}{25}$.

$y_A = \frac{3}{25}$, $y_B = \frac{22}{25}$. $1 - \frac{3}{22}$

Now, $x_A = \frac{3}{25}$, $x_B = \frac{22}{25}$.

$P = \frac{1500}{60} \frac{30}{250} + \frac{2200}{3} \times \frac{22 \times 22}{25} = \frac{484 \times 4}{3} + 18$

$18 \quad 10 +$

$$y_A = \frac{\left(\frac{3}{250}\right)\left(\frac{18}{1500}\right)}{\frac{484\times 4}{3}+18}$$

$$= \frac{18}{645.3+18}$$

$$= \frac{180}{6633} \quad 0.027$$

$$\Rightarrow y_A = 0.027$$

$$y_B = 0.973$$

0.99
+.0010
−.027
0.973

3 | 484
84.
1938
3
645.3
18
1663.3
03
1899
16633
02
13266
7334
25
46633
07
46431

Q. C_6H_6 & ~~toluene~~ $C_6H_5CH_3$ forms an ideal binary sol^n. VP of pure C_6H_6 is 60 mm of Hg at 25°C. while VP of $C_6H_5CH_3$ pure = 20 mm Hg. Determine the compos^n of a sol^n of C_6H_6 & $C_6H_5CH_3$, which will start boiling at 25°C, when ext. P = 50 mm Hg.

$P^0_{C_6H_6} = 60$, $P^0_{C_6H_5CH_3} = 20$

$C_6H_6 = A$ $\quad C_6H_5CH_3 = B$

$P = 50$.

$$P = P^0_A x_A + P^0_B x_B.$$

$$\Rightarrow 50 = 60(x) + 20(1-x)$$

$$\Rightarrow 50 = 60x + 20 - 20x$$

$$\Rightarrow 30 = 40x$$

$$\Rightarrow \boxed{x = \frac{3}{4} = 0.75}.$$

$$\Rightarrow \boxed{\text{toluene} = 0.25}.$$

Continued JEE

$= 0.887$ kg/L

- At 300K, $\rho_{C_6H_6} = 0.887$ g/mL & molar volume increases by a factor of 2700 as benzene is vaporised at 300K. $\rho_{toluene} = 0.867$ g/mL at 300K & its molar volume increases by factor of 7700 as it vaporises at 300K.

1 mL C_6H_6 on vaporise करने पर Vol = 2700 mL

At 300K, a binary soln of C_6H_6 & $C_6H_5CH_3$ has VP = 46 torr. Determine mole frns.

$\rho_{gh} = CRT$

$= C(24.6)$

$n = 1$

$V = \frac{2700}{1000}\left(\frac{78}{0.887}\right)$

1 mole C_6H_6 (V) Vol.

$= \frac{2.7(78)}{0.887}$

$= \frac{27 \times 78 \times 100}{887}$

$= \frac{2106}{887}$ 238 lit.

$P = \frac{nRT}{V}$

$= \frac{(1)(0.082) \times 300}{238}$

$= \frac{24.6}{238} = \frac{246}{2380} \times 10$

$= 0.103$ atm

$= 0.103 \times 760$ atm

$P_B^\circ = 78.28$ mm Hg

For toluene

$V = \frac{7700}{1000}\left(\frac{92}{0.867}\right)$

$= \frac{7084 \times 100}{867}$

$= 817$ lit.

Chemistry Notes Akshay

$P_T^\circ = \frac{1 \times 24.6}{817} = \frac{246}{817} \times 10 \times 760$

$= 23$ mm Hg.

$46 = x_B(78) + (1 - x_B)23$

$\Rightarrow 2 = x_B\left(\frac{78}{23}\right) + 1 - x_B$

$\Rightarrow 1 + x_B = x_B\left(\frac{78}{23}\right)$

$\Rightarrow x_B\left(1 - \frac{78}{23}\right) = -1$

$\Rightarrow x_B\left(\frac{-55}{23}\right) = -1$

$\Rightarrow x_B = \frac{23}{55}$

$\Rightarrow x_T = \frac{32}{55}$

246 | 0.3 × 760 | 23

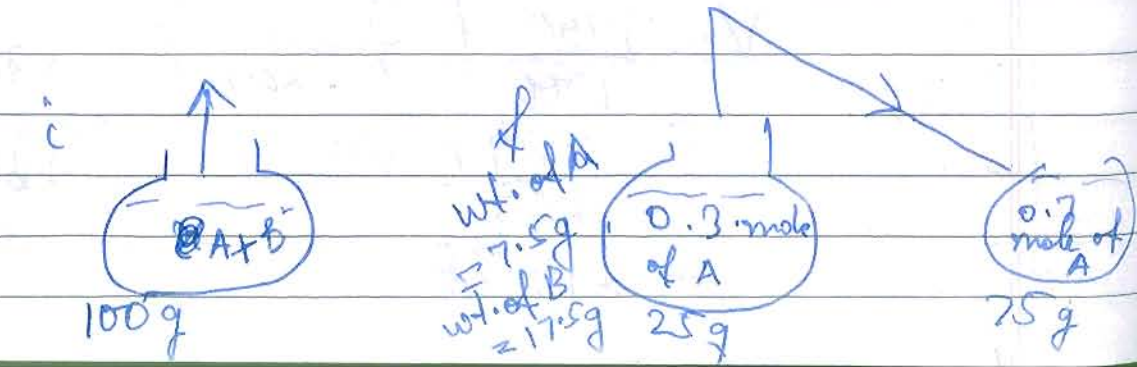
246 | 984 | 4

760 | 23 | 33 | 48

28 | 23 | 55

55 | 23 | 32

Q 2 volatile liqds A & B, have same molar mass. A soln of A & B is prepared in which mole fr^n of A is x_A & $VP_{soln} = 700$ torr at @ 298K. The given soln is distilled without refluxing until 3/4th of the soln is distilled off. The distillate has 0.7 mole fr^n of A, residue has 0.3 mole fr^n of A. $VP_{residue} = 600$ torr at 25°C, determine x_A & P_A°, P_B°.



let i → $W_A + W_B = 100\,g$.

Wt. of A (final) = 75 × (.7)
= 52.5

Wt. of B (final) = 22.5

Total wt

A = 52.5 + 7.5
= 60 g

B = 17.5 + 22.5
= 40 g .

$x_A = \frac{60}{100} = 0.6 =$ Wt. fr.

$x_B = 0.4$.

$700 = 0.6\,P_A^0 + 0.4\,P_B^0$. → (1)

$600 = 0.3\,P_A^0 + 0.7\,P_B^0$.

$\Rightarrow 1200 = 0.6\,P_A^0 + 1.4\,P_B^0$.

$700 = 0.6\,P_A^0 + 0.4\,P_B^0$

$\Rightarrow 500 = P_B^0$

$\Rightarrow P_A^0 = \frac{2500}{3}$.

3 75
525

500
200
5000
0.6 2500/3

JEE

Q. 10 mole of A (VP-300 mm Hg) is mixed with 12 mole of B (VP-500 mm Hg) at 298K. As soon as B is added, A starts polymerising into solid insoluble polymer. Polymerisn follow 1st ord. kinetics. After 100 min 0.525 mole of a non-volatile solute is added which stopped the polymerisn immediately & VP of soln = 400 mm Hg

B acts as a catalyst

Determine $t_{1/2}$ of polymerisⁿ rxn.

$x_A = \frac{10}{22}$, $x_B = \frac{12}{22}$. $P_A^0 = 500$, $P_B^0 = 300$

let x mole of A is remaining after 100 min.

$$400 = (500)\left(\frac{x}{x+10+0.525}\right) + 300\left(\frac{10}{x+12+0.525}\right)$$

$$\Rightarrow 4 = \frac{5x}{x+10.525} + \frac{30}{x+10.525}$$

$$\Rightarrow 4x + 50.1 = 5x + 30$$

$$\Rightarrow x = 14$$

$$\Rightarrow 400 = \frac{300x}{x+12.525} + \frac{5000\,12}{x+12.525}$$

$$\Rightarrow 4x + 50.1 = 3x + 60$$

$\Rightarrow x = 9.9$ moles of A remaining.

$\Rightarrow 0.1$ moles of x polymerised.

$$Kt = \ln \frac{A_0}{A} = \ln \frac{10}{9.9}$$

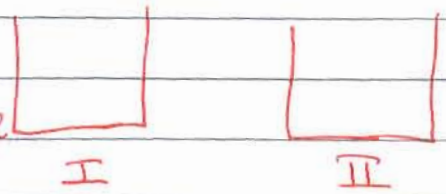
$$\Rightarrow k = \frac{1}{100} \ln \frac{100}{99}$$

$$= \frac{2.3}{100} \log \frac{100}{99}$$

$\longrightarrow \infty \longrightarrow$

classmate
Date 26.5.20
Page

☆ ISOTONIC Sol^n

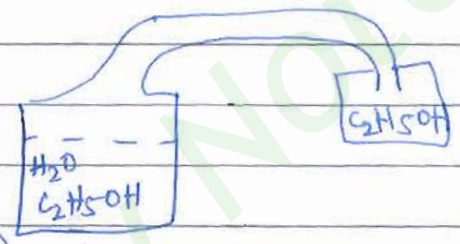


Isotonic sol^{ns} are those sol^{ns} whose π are similar at same T.

☆ AZEOTROPIC sol^n :-

B.Pt $H_2O = 100°C$

$C_2H_5OH \approx 74°C$.



Composn :-

$H_2O : C_2H_5OH = 95 : 5$ (by wt.) ↑ T ≈ 85°C

Azeotropic sol^n is a sol^n of 2 volatile liqds with a specific compos^n at which the sol^n acquire a common B.Pt. which is greater than the more volatile but smaller than the less volatile liqd. If azeotropic mixture is distilled, the vapour phase with same composn as of liqd phase condenses, ∴, components can't be separated by distill^n. Then they can be separated only by chemical methods

— end —

classmate
Date 26·5·10
Page

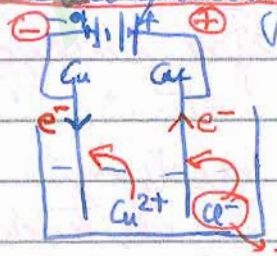
Ch: Electrochemistry

* Electrochemical cells: The means for conversion of chemical E into electrical E. or vice versa using some redox rxns occuring in the cell.

Electrolytic cell

They are the electrochemical cell in which external source of electricity is used to bring about some non-spontaneous redox rxn into the cell.

eg: electroplating



-ve towards +ve electrode.

discharging of ions at electrode

At -ve electrode: Cathode

$Cu^{2+} + 2e^- \rightarrow Cu$.

At +ve electrode: Anode

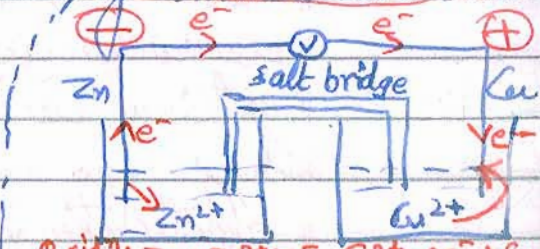
$2Cl^- \rightarrow Cl_2 + 2e^-$

So, e^- movt: Anode to Cathode.

Galvanic cell (Voltaic cell)

The electrochemical cell in which some spontaneous redox rxns occur to produce electricity

eg: commercial cell.



Oxidn: $Zn \rightarrow Zn^{2+} + 2e^-$ $Cu^{2+} + 2e^- \rightarrow Cu$

Spontaneous redox rxn, here:

$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$.

- e^- produced at anode. So, its e^- rich. Hence, its -vely charged.
- Cathode is taking e^- from cathode. So, Cathode becomes +vely charged.

So, e^- movt: anode to cathode

Imp Concept ★ By the time rxn goes, Zn^{2+} (+ve charge) gets accumulated at electrolyte of anode (Zn) so, it would prevent movt. of further e^- from Zn rod & hence rxn would stop.

continued →

★ In order to prevent flow of e^- through internal circuit, 2 chambers are taken in galvanic cell. This is done to conduct electricity by allowing movt. of e^- through external circuit.

★ In both the cells :,
electron movt : anode to cathode

Salt bridge

Since in galvanic cell, electrolysis is carried out in 2 separate electrode chambers, anode chamber becomes +vely charged & cathode chamber becomes -vely charged as soon as electrodes are connected through external circuit & further electrolysis stops. To continue electrolysis, electrolytes in the 2 electrode chambers must be neutralised first. To maintain the electroneutrality, a U-type glass tube filled with highly conc, inert electrolytes of comparable size known as salt bridge is used which provide

Ily, the cathode part would become e^- rich & would prevent further coming of e^-. Hence, Electrolysis would stop.

the desired ions to the respective electrolyte sol^n.

highly conc: otherwise its sol^n will get exhausted soon

* Characteristics of Salt bridge.

1) Salt bridge must contain electrically inert electrolytes: so that it doesn't take part in any spontaneous redox rxn
2) Cations & anions of salt bridge must have comparable ionic radius: so that they have comparable ionic speeds and reaches the 2 electrode chambers simultaneously.
3) The salt bridge must contain highly conc sol^n of salt so that it need not be replaced very frequently.

* 2 common constituents of salt bridge → KCl & KNO_3

KCl: ✓ ionic speed close to K, ✓ Cl may oxidise to Cl_2 → disadvantage.

KNO_3: greater inertness towards electrolysis

* Nowadays Vacuum of ions is made inside salt bridge so that Zn^{2+} ions are absorbed and SO_4^{2-} Cu^{2+} are absorbed.

☆ ELECTROLYTIC CELL

§ FARADAY's Law of electrolysis

LBSE

It relates the amt. of electrolyte discharged with the qty. of electricity passed.

⟨1⟩ FARADAY's 1st law: Acc to this law, the wt. of electrolyte discharged is directly proportional to the qty. of electricity passed. as,

$W \propto Q$

$\Rightarrow W = ZIt$

Q → Coulomb's of electricity.
I → Current strength (ampere)
t → time (second)

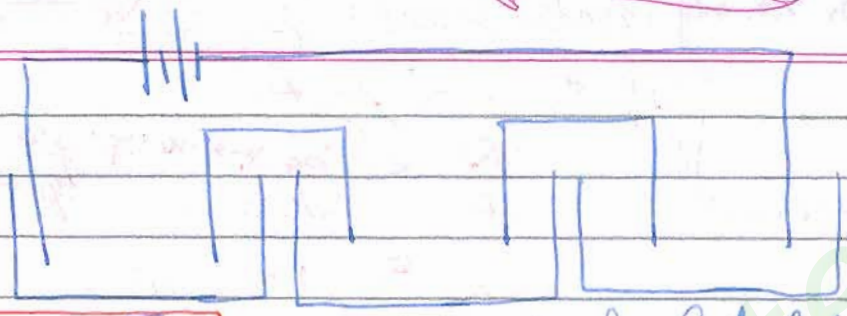
$\because C = A\,s$

Z → Some constt

* Z = Electrochemical equivalence (ECE)
= Wt. of electrolyte discharged on passing 1C of electricity (or passing 1A current for 1 sec)

⟨2⟩ FARADAY's 2nd law: If same qty of electricity is passed through diff^t electrolytic cells connected in series, the ratio of wt. of electrolytes discharged at various electrodes is always = the ratio of their equivalent wts.

Chemistry Notes Akash



So, $\frac{W_1}{W_2} = \frac{E_1}{E_2}$, $W \rightarrow$ wt. of electrolyte discharged.

E_1, E_2 : equivalent wts of electrolytes whose wt. discharged are W_1 & W_2 resp.

For Numerical & JEE :

$Na^+ + 1e^- \rightarrow Na$: 1 mol e^- will discharge 1 mole Na^+

$Mg^{2+} + 2e^- \rightarrow Mg$ " " " $\frac{1}{2}$ mole Mg^{2+}

$Al^{3+} + 3e^- \rightarrow Al$ " " " $\frac{1}{3}$ mole Al^{3+}

$Ti^{4+} + 4e^- \rightarrow Ti$ " " " $\frac{1}{4}$ mole Ti^{4+}

* $\frac{\text{equivalent}}{\text{no. of mole}}$ = n factor.

So, in all above, eq = 1 (1×1, $2\times\frac{1}{2}$, $3\times\frac{1}{3}$ & $4\times\frac{1}{4}$)

Charge on 1 mole of $e^- = 1.6\times10^{-19} \times 6.023\times10^{23}$

$\Rightarrow$ 1 F $\simeq$ ~~960~~ 96500 C.

F → Faraday.

* One faraday = Charge on 1 mole of e^-.

For numerical: No. of faraday = no. of eq. discharged (eq)

Now, eq × EW = wt.

EW → equivalent wt

* Total charge passed = Q = It
* 1 Faraday = 96500 C
So, no. of Faraday passed = $\frac{Q}{96500} = \frac{It}{96500}$ = no. of eq. = $\frac{Wt.}{EW}$

Numerical thought

If Q given / got,

$\frac{Q}{1F}$ = (eq.) → no. of gram equivalent.

eq × EW = wt.

So, nett → no. of faraday passed = no. of gram eq. of electrolyte discharged or deposited

---

Easy ★★ **Electrolysis of molten salt**

$Mg^{2+} \rightarrow Mg$ at cathode
$2Cl^- \rightarrow Cl_2$ at anode

Tough ★★ **Electrolysis of aq. sol^n of electrolyte**

NaCl (aq.), taking it, say.

Electrochem. series (cation)

Grp - I
Grp - II
Al^{3+}
Fe^{3+}
Zn^{2+}
Pb Sn
H^+
Cu^{2+}
Ag^+
Au^{3+}

H^+ more electro +ve. H^+ Gets ~~oxidised~~ reduced instead of them.

Less electro +ve Gets reduced as compared to H^+

H^+ Na^+ HO^- Cl^-

For electro -ve elements (anion)

more electro +ve (oxidised) Cl^- (X-), HO^-

less electro +ve OH^- oxidised instead of them. NO_3^-, SO_4^{2-}

Chemistry Notes Akshansh

classmate
Date 28.5.10
Page

If OH^- is oxidised

$2OH^- \rightarrow O_2 + 2H^+ + 4e^-$

If H^+ is reduced,

$2H^+ + 2e^- \rightarrow H_2$.

✱ At STP.

$32\,g\ O_2 = 22.4\ L$.

$\Rightarrow 8\,g\ O_2 = 5.6\ L$ = Vol. of 1eq at STP

✱✱

$2\,g\ H_2 = 22.4\ L$

$\Rightarrow 1\,g\ H_2 = 11.2\ L$ = Vol eq of H_2

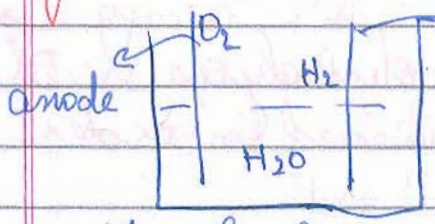
✱✱

$71\,g\ Cl_2 = 22.4\ L$

$\Rightarrow 35.5\,g\ Cl_2 = 11.2\ L$ = Vol. of 1eq of Cl_2

✱✱

Q. How many hrs, the acidified H_2O must be electrolysed in order to produce 50 L of gaseous products at STP & I = 5A.



V vol of H_2

50 - V vol. of O_2.

$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$

V : V : $\frac{1}{2}$V

V ratio = 2 : 1

$\Rightarrow 3V = 50$

$\Rightarrow V = \frac{50}{3}$ L

O_2 $\frac{50}{3}$ H_2 $\frac{100}{3}$.

Charge का ratio vol. का ratio
होता है → Equivalent cond^n

H_2 (vol) = $\frac{100}{3}$

O_2 (vol) = $\frac{50}{3}$.

$geq = \frac{50}{3(5.6)} \times 96500 = It$.

$\Rightarrow \frac{500}{3(56)}(96500) = I(t)$

$\Rightarrow t = \frac{965}{56 \times 3} \times 10^7$

$= \frac{9655.7 \times 10^7}{168 \cdot 36 \times 10^2}$ sec

≈ 16 hrs.

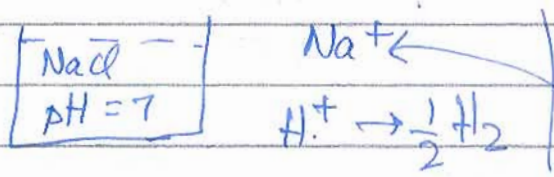
Q. 100 ml of an aq. soln of NaCl is electrolysed at 25°C using I = 2A. How many hrs electrolysis will have to be continued in order to raise pH of soln to 11.

Cathode → H_2

Anode → Cl_2

Soln → OH^-, Na^+

$N = \frac{\text{geq}}{96500 \times 10^{-4}} = \frac{}{2} = 4.8 \text{ sec.}$



geq. of NaOH produced = no. of faraday passed.

pH = 11 ⇒ pOH = 3

⇒ conc. OH^- = 10^{-3} M

= 10^{-3} N.

M = N (here)

$N \times V = \text{meq}$

⇒ meq OH^- = (10⁻³)(100)

= 0.1 meq

Now, $0.1 \times 96500 = 9650 \times 10^{-3}$ C.

= 9.65 C = 2t.

⇒ t = 4.825 sec.

Q. A 500 ml aq. soln of $CuSO_4$ is electrolysed using a current of 5A for 1 hrs. at 25°C. How many ml of 0.1M NaOH soln would be reqd for neutralisn of 30 ml of the above soln

(Assume $CuSO_4$ to be neutral salt)

+2 Chemistry Notes Akshansh

$n_{eq} \left(\frac{eq}{n}\right) = 2$

Wt = 15 g ~~of~~ ~~elect~~ deposited

H_2SO_4 produced is $\frac{15}{98 \times 2}$ ~~mole~~ geq.

$\Rightarrow \frac{7.5}{98}$ geq

$\frac{3}{15(3600)} \times 300 = (0.1)\, x$

$\frac{}{96500}$

1893

$= \frac{36 \times 9 \times 100}{193}$

$= \frac{324 \times 100}{193} = x$

$\simeq 170$ ml

$\simeq 340$ ml

$N_{H_2SO_4} = \frac{108}{193} \times \frac{1}{2}$

$= \frac{54}{193}$ N

$= \frac{216}{193}$

Q A coffee tray of dimension 30 cm × 15 cm is to be silver plated by dipping it into $AgNO_3$ soln. by electrolysis using I = 5A. If thickness of coating is 0.1 mm & $\rho_{Ag} = 10.5$ g/cc, determine the no. of hrs for which electrolysis will have to be continued assuming current

efficiency to be 80% Ag = 108

$I = \frac{4}{5} \times 5 = 4A$.

$I = 4A$.

HNO_3 in sol^n.

$V = 0.01 \times 30 \times 15\ cm^3$.

$= 450 \times 0.01$

$= 4.5\ cm^3$.

$1\ cm^3 = 10.5\ g$

$4.5 \rightarrow 10.5 \times 4.5\ g$.

$Ag = 47.25\ g$.

$n = \frac{m_{Ag}}{eq_{Ag}} = 5103$

$5103 \times 96500 = 4(t)$

$\Rightarrow t = \frac{5103 \times 96500}{4}$

$= 492439500$

$t = 123109875$

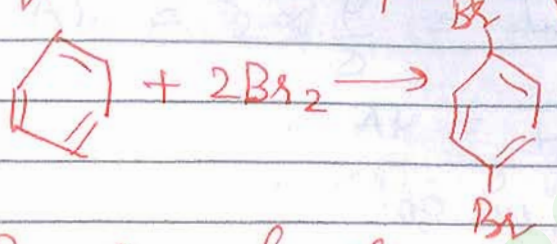
$= \frac{1367887.5}{36} \times 100 + 2$

$= 6839437.5$

$t = 68394.375$ hrs

105
45
525
420
5425
108
10800
13000
1425
5103
965 | 965
515
1255
1306
1827
45927
49243

Q. C_6H_6 is brominated into dibromo benzene acc. to following rxn →



Bromine, for the rxn is obtained by electrolysis of molten KBr. How many hrs, the electrolysis of KBr will have to be carried out using I = 10A in order to produce sufficient Br reqd. for bromin^{n} of 156 g C_6H_6. Br = 80.

$n_{C_6H_6} = 2$, $n_{Br} = 4$ moles.

KOH in eol^{n}.

$eq_{Br} = 4$ eq

$4 \times 96500 = 10(t)$

$\Rightarrow \frac{38600}{3600} \times 2$

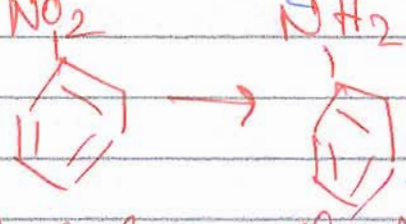
10.7 hrs $= 21.4$ hrs

$2NaBr \rightarrow Br_2$

8 moles

So 8 moles of Br = 8 eq of Br reqd.

Q. Nitrobenzene ($C_6H_5NO_2$) is converted into aniline ($C_6H_5NH_2$)



at cathode in an electrolytic cell. If electrolysis is carried out using I = 15A for 16 hrs. what max wt. of aniline can be formed.

$$\frac{\text{Charge}}{\text{Faraday}} = \frac{15 \times 16}{96500} = \frac{240 \times 3600}{96500} \text{ eq.}$$

n factor = 6

$$wt = \frac{240 \times 3600}{96500} \times 93$$

$$= \frac{803520}{965} \times 6$$

$$= 1832.6 \times \frac{1}{6}$$

$$wt = 4995.6$$

$$\simeq 140\ g$$

Q. 0.52 g of a $TiCl_x$ salt reqd 2 hrs for complete depositn of Ti metal using a current of 1A. determine valency of Ti in compd. Ti = 48

$\Rightarrow$ ~~0.52 = 2(1)x~~

$\Rightarrow$ eq × 96500 = 2(1)

$\Rightarrow$ eq = $\frac{2 \times 3600}{96500}$

$\Rightarrow$ $\frac{0.52\,x}{48 + 35.5x} = \frac{3600}{48250}$

$\Rightarrow$ $25090x = (48 + 35.5x)3600$

$\Rightarrow$ $(250545)x = 48$.

$\Rightarrow$ $x = \frac{48 \times 10}{250545}$

$\Rightarrow$ ~~25090~~ $x = 48 + 35.5x$

~~3600~~ × 10

$\Rightarrow$ $x = 48 + 35.5x$

-35.5

$28.5x = 48$

$x = 1.7$

$TiCl_2$

Ampere hour
= Ah = 3600 C

1 → 1.4 1.4 × 3500
3500 → 1.4 classmate
Date
Page

32
6 4
e 2
98

Q. A lead storage battery has vol. of 3.5 l & contain H_2SO_4 (98) whose ρ = 1.4 g/ml which is 40% H_2SO_4 by wt. during the use of battery, ρ H_2SO_4 decreased to 1.2 g/ml & now it contain only 20% H_2SO_4 by wt. The electrode reaction are as follows

anode $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

cathode $PbO_2 + SO_4^{2-} + 2e^- + 4H^+ \rightarrow PbSO_4 + 2H_2O$

Determine the ampere hour (Ah) for which electricity is used.

(i) Wt. of H_2SO_4 → $104 \times 3500 \times \frac{40}{100} = 1960$ g.

& Wt of H_2SO_4 $= 1.2 \times 3500 \times \frac{20}{100}$

$= 840$ g.

35
140 → 0
12 840
196

no. of moles of H_2SO_4 used = $\frac{1960}{98}$ moles

98
e 2
1960
−840
1120

& = $\frac{1120}{98} \frac{560}{49}$ 11.2

≃ 11.2 moles.

eq

= 44.8 eq.

12 Chemistry Notes Akhtansh

$\Rightarrow 44.8 \times 96500 = Ah$

$= 224 \times 193$

$\Rightarrow \frac{448 \times 965}{56} = A.$

$\Rightarrow A = \frac{193 \times 56}{9}$

$\Rightarrow A = \frac{10708}{9}$

$\Rightarrow A = 1189.7\ A$

$= 297.$

$\approx 300\ A$

Q. 100 mL aq. soln of 0.1M $CuSO_4$ is electrolysed using $I = 5A$. Electrolysis was continued for further 7 min. after the entire Cu was deposited. Determine the total V of gas produced under STP condn.

Cu, OH^- go

H^+ & SO_4^{2-} left.

10 mmol of $CuSO_4$

$5\ meq = 5 \times 10^{-3}$ eq.

$5 \times 10^{-3} \times 96500 = It$

$\Rightarrow t = 96.5$ sec

$= \frac{96.5}{60}$ min.

Cu at cathode
O_2 at anode.

So, 10×2 meq of $CuSO_4$
$= 20$ meq $CuSO_4$.

geq of Cu = geq O_2.

$\Rightarrow$ 20 meq = geq O_2.

$\Rightarrow$

Now, $\frac{7 \times 60 \times 5}{96500} = \frac{2100}{96500} F = X10^3$.
$= 22$ mF.

will give 22 meq O_2 & 22 meq H_2.

Total meq O_2 & meq H_2 $= 42 (22 + 20)$
$= 22$.

Vol. O_2 $= 42$ meq $\times 5.6$ mL
$= 235.2$ mL

Vol. H_2 $= 22 \times 11.2$
$= 22.4\ 246\ 4$
$= 246.4$ mL

Vol. O_2 + Vol H_2 $= 481.6$ mL.

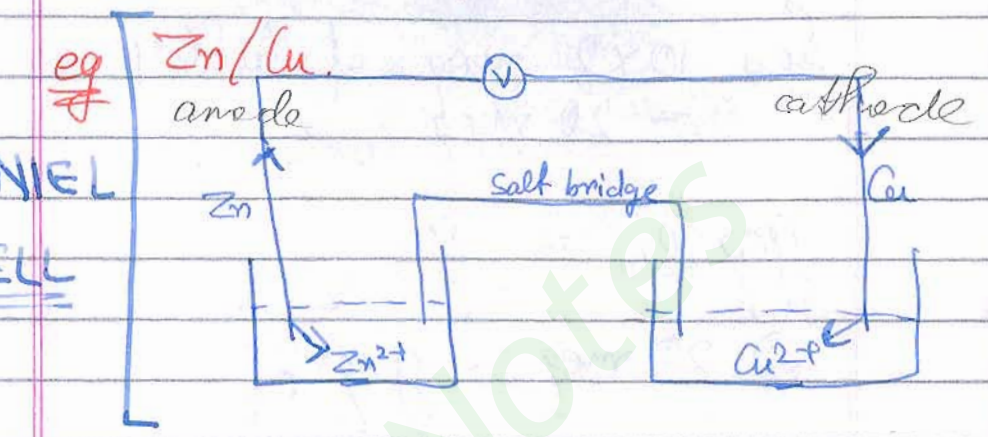
+2 Chemistry Notes Akshesh

Redn takes place at cathode

classmate Date 2·6·10 Page

✡ GALVANIC CELL.

eg: DANIEL CELL



nett rxn: $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$

$Zn \longrightarrow Zn^{2+} + 2e^-$ $\quad Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

$Cu^{2+} + 2e^- \longrightarrow Cu$

✡ In galvanic cell, e^- movt. takes place from higher PE electrode (anode) to lower PE (electrode (cathode) simultaneously.

✡ EPE is measured in terms of electrical PD of electrodes → known as EMF of cell: The electric PD across electrodes in galvanic cell. It is the driving force for spontaneous movt. of e^- from anode to cathode.

$\Delta G = -nEF$ → Faraday = 96500 C

- ΔG → Gibb's free energy change of rxn
- n → no. of e^-s transfer involved in balanced redox rxn
- E → EMF
- F → Faraday

Chemistry Notes Vishnesh

classmate
Date
Page

* For a process to be
Spontaneous $\Delta G < 0$.
non-spontaneous $\Delta G > 0$

* For a cell to be galvanic $E > 0$. (So that ΔG becomes (-ve)

$$E = E^{oxidn}_{anode} + E^{Red}_{cathode}$$

All electrode potential must be in terms of red^n potential → IUPAC convn

$$\therefore E_{cell} = E^{Red}_{cathode} - E^{Red}_{anode}$$

So, $E_{cathode} > E_{anode}$, $\therefore E > 0$

in a galvanic cell,
So cathode is at higher red^n potential than anode in a galvanic cell.

* Std State EMF (E°)

The Std. state EMF of a cell is the EMF of the cell when the all the species are present at unit active mass. (gases at 1 atm & ions at 1 M)

So, $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

Chemistry Notes
AKSharma

✱ Std. Van't Hoff Eqⁿ

$$\Delta G = \Delta G^\circ + RT \ln Q$$

(Q → reaction quotient)

$$\Rightarrow -nEF = -nE^\circ F + RT \ln Q$$

$$\Rightarrow E = E^\circ - \frac{RT}{nF} \ln Q$$

$(\because -nF)$

NERNST's EQⁿ (E, E° depend only on T)

$$\Rightarrow E = E^\circ - \left(\frac{2.303\,RT}{F}\right) \frac{1}{n} \log Q$$

Most of the calculⁿs would be done at 25°C → max no. of times

$$\Rightarrow E = E^\circ - \frac{0.059}{n} \log Q$$

✱✱ → $T = 298\ K$

Imp ✱ When galvanic cell stops working the redox rxn has reached to equi.

So, at equi,

$E = 0$.

$$\Rightarrow E^\circ - \frac{0.059}{n} \log K = 0.$$

$$\Rightarrow E^\circ = \frac{0.059}{n} \log K.$$

Chemistry Notes Akshansh

✱ When cell stops working, Electrode potential becomes equal. So, $Q = K$.
as, all reaches equi.

$$\Rightarrow \log K = \frac{n E^\circ}{0.059}$$ → At equi.

→ T = 298 K = 25°C.

✱ **Std. Half cell red^n potential**

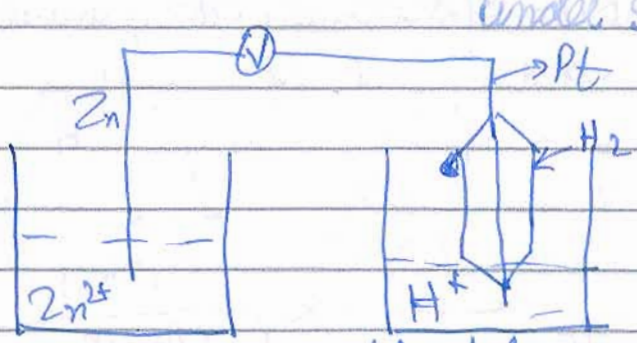
$E^\circ = E^\circ_{cathode} - E^\circ_{anode}$.

So E° is always diff. of electrode potential. So, absolute value of red^n potential of a ½ cell can't be obtained. So, for comparitive study a reference electrode has been set to find electrode potential (red^n) of electrode.

This std. potential is of H-electrode.

By convention →

$E^\circ_{H^+/H_2} = 0$ → Red^n potential of H-electrode under std. conditions



Std. state.

$E^\circ = 0.76\,V = E^\circ_{H^+/H_2} - E^\circ_{Zn^{2+}/Zn}$

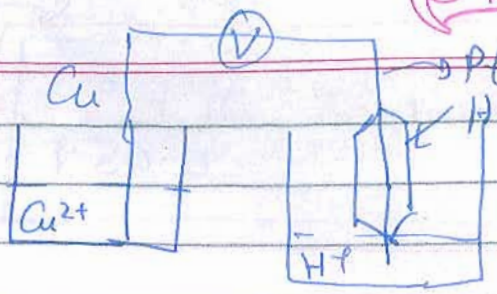
($E^\circ_{H^+/H_2} = 0$)

$\Rightarrow E^\circ_{Zn^{2+}/Zn} = -0.76\,V$, 25°C.

→ i.e red^n potential of Zn is 0.76 V less than H-electrode's red^n poten.

+2 Chemistry Notes Akshansh

classmate
Date
Page



$E^0 = 0.34\,V = E^0_{Cu^{2+}/Cu} - E^0_{H^+/H_2}$ (0)

$\Rightarrow E^0_{Cu^{2+}/Cu} = 0.34\,V$

↳ $\Rightarrow$ Redⁿ potential of Cu is 0.34 times greater than redⁿ potential of H_2.

So, now,

$E^0 = E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}$

$= 0.34 - (-0.76)$

$\Rightarrow E^0 = 1.1\,V$

Imp

★ EMF of cell in std. state is independent of $E^0_{H^+/H_2}$ value. Even if we change H-electrode to some other, E^0_{cell} remains same.

★ Whenever 2 half cells are combined to form a NEW HALF cell, E^0 can't be found algebraically (∵ value of n would be diff^t in every case). If 2 half cells combine to form a complete rxn, E^0 can be found algebraically.

Chemistry Notes

PROPERTY

P1

E° is an intensive thermodynamic property which doesn't depend on amt.

eg: $E^\circ_{Ag^+/Ag} = 0.80\,V$.

$E^\circ_{Zn^{2+}/Zn} = -0.76\,V$

So,

$E^\circ = 0.76$ $Zn/Zn^{2+} \rightarrow Zn \rightarrow Zn^{2+} + 2e^-$

$Ag^+ + 1e^- \rightarrow Ag$]×2

$E^\circ = 0.80\,V$

$\Rightarrow Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

$E^\circ = 0.80 - (0.76)$

$= 1.56$

$= 0.80 + (0.76)$

★ E° is an intensitive qty. So its value can't be algebraically added. So, we change it to extensive (ΔG°) & , manipulate & convert it back to intensive.

Q. eg: $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\,V$.

$E^\circ_{Fe^{2+}/Fe} = -0.44\,V$.

Find $E^\circ_{Fe^{3+}/Fe} = ?$ (changing to extensive)

	$\Delta G^\circ = -nEF$	E°
$Fe^{3+} + 1e^- \rightarrow Fe^{2+}$	$-0.77F$	$0.77\,V$
$Fe^{2+} + 2e^- \rightarrow Fe$	$+0.88F$	$-0.44\,V$
net $Fe^{3+} + 3e^- \rightarrow Fe$	$+0.11F$	$E^\circ = -0.11/3$

$= -nE^\circ F$

$= 0.036\,V$ $= -0.11/3$

E°

Q $Sn^{4+}/Sn^{2+} = 0.15\ V$

$E^\circ_{Sn^{2+}/Sn} = -0.14\ V$.

$E^\circ_{Sn/Sn^{4+}} = ? = -0.005$

$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ $(0.15)2$

$Sn^{2+} + 2e^- \rightarrow Sn$. $(-0.14)2$

$Sn^{4+} + 4e^- \rightarrow Sn$.

$0.3 - 0.28$

$= 0.02$

$= 0.005$

P2 E° & Equi. Const^{n}

At 25°C, $E^\circ_{Ag^+/Ag} = 0.80\ V$.

Another reference electrode other than H-electrode $\left\{ E^\circ_{AgCl/Cl^-,Ag} = 0.22V \right.$

$AgCl + e^- \rightarrow Ag^+ + Cl^-$

$E^\circ = 0.22\ V$.

Determine ~~K~~ solubility product of AgCl.

$\ln K = \frac{n(0.22)}{0.059}$

$\Rightarrow \ln K = 3.6$

Chemistry Notes Akshansh

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq.)} + Cl^-_{(aq)}$ 0.22

$Ag_{(s)} + Cl^- \rightarrow Ag^+ + 1e^-$ −0.80

~~$\ln K = 3.6$~~

Add $AgCl + Ag \rightarrow 2Ag^+ + Cl^-$ $= -0.58V$

$E^\circ = -0.80 + 0.22$

$= -0.58$

$\log K = \frac{nE^\circ}{0.059}$

$= \frac{1(-0.58)}{0.059}$

$= -10$

$\Rightarrow K_{sp} = 10^{-10}$

Q. ~~Determine~~ ~~K_{sp}~~ K_{sp} of $PbSO_4$ is 4×10^{-6} at 28°C. Red^n potential $E^\circ_{Pb^{2+}/Pb} = -0.13V$

Determine $E^\circ_{PbSO_4/Pb,SO_4^{2-}} = ?$

$\log K = \frac{2(E^\circ)}{0.06}$

$\Rightarrow 0.6 - 6 = \frac{E^\circ}{0.03}$

$\Rightarrow (-5.4)(0.03) = E^\circ$

$\Rightarrow E^\circ = .162$

$Pb^{2+} + 2e^- \rightarrow Pb$ $-0.13V$

$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ ( )

$\Rightarrow Pb^{2+} + PbSO_4 \rightleftharpoons 2Pb + SO_4^{2-}$ (-0.162)

$-0.162 = -0.13 + ( )$

$\Rightarrow ( ) = -0.032$

$$E^0 = \frac{0.059}{n} \log K_{sp}$$

$$= \frac{0.06}{2} \log(-5.4)$$

$$= -0.162\ V$$

$$PbSO_4 \rightleftharpoons Pb^{2+} + SO_4^{2-} \qquad E^0 = -0.1$$

$$Pb^{2+} + 2e^- \longrightarrow Pb \qquad -0.13$$

$$PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$$

$$= -0.162 + (-0.13)$$

$$= -0.292\ V$$

$$= -0.3\ V$$

✡ E^0 & Electrochemical Series (at 25°C)

In series,

E^0_{min} = Li^+/Li — E^0 = −3.05 V

Mg^{2+}/Mg — −2.37 V

Zn^{2+}/Zn — −0.76 V

Fe^{2+}/Fe — −0.44 V

H^+/H_2 — 0 V

Cu^{2+}/Cu — 0.34 V

Ag^+/Ag — 0.80 V

Au^{3+}/Au — 1.56 V

E^0_{max} = F_2/F^- — 2.87 V

OA ↓ RA ↑

Chemistry Notes Akshansh

V.V.V.Imp.

classmate
Date
Page

$\Delta G^\circ = -nE^\circ f$.

V.V. Imp

Higher the value of E°, more spontaneous will be red^n. So, F_2/F^- will reduce itself quickly.

★ Smaller the value of E° of $\frac{1}{2}$ cell, easier the oxid^n, stronger the reducing agent.

★ Larger the value of E°, easier will be the red^n. So, it would be a stronger oxidising agent.

62.

★

★

Q. Cu^{2+} (I), Ag^+ (II), Au^{3+} (III), Mg^{2+} (IV)

JEE

Through a sol^n containing equimolar soln of the 4 ions, electric current is passed & voltage is increased gradually. Arrange order in which metals will be deposited at cathode

III > II > I ~~IV~~

Mg^{2+} won't be discharged, H_2 would be ~~oxid~~ reduced instead

Q.

✡ CELL NOTATION

Left: Anode Rt: Cathode

In Galvanic cell

$Zn | Zn^{2+} || Cu^{2+} | Cu$

phase separ^n — salt bridge

LOAN: Left oxid^n anode -ve

$(Pt) | H_2(g) | HCl || KCl, Hg_2Cl_2 | Hg | Pt$

Inert electrode at which gaseous ion takes place.

Ion

$H_2 \rightarrow 2H^+ + 2e^-$

$Hg_2Cl_2 + 2e^- \rightarrow \underset{\text{Pure liq}}{2Hg} + 2Cl^-$

$Q_c = [Cl^-]^2$

—∞—

Q. Determine unknown in the following cell →

$Pt | H_{2(g,\,1atm)} | H^+_{(pH=?)} || Cl^-_{(1M)}, Hg_2Cl_2 | Hg$

Given,

$E^\circ = 0.40\ V$

$E^\circ_{Hg_2Cl_2/Hg,Cl^-} = 0.28\ V$

oxidn: $H_2 \rightarrow 2H^+ + 2e^-$ $E^\circ = 0$

redn: $Hg_2Cl_2 + 2e \rightarrow 2Hg + 2Cl^-$ $E^\circ = 0.2$

$H_2 + Hg_2Cl_2 \rightarrow 2H^+ + 2Hg + 2Cl^-$ $E^\circ = 0.2$

Chemistry Notes Akshansh

$\Rightarrow 0.40 = 0.28 - \frac{0.06}{2} \log [H^+]^2 [a^-]^2$ (1)

$\Rightarrow 0.12 = -0.06 \log [H^+]^2$

$\Rightarrow \frac{-0.12}{-0.06} = \log [H^+]$

$\Rightarrow -\log [H^+] = \frac{0.12}{0.06}$

$\Rightarrow pH = 2$

Q. A Zn electrode in 250 mL, 0.1 M $ZnSO_4$ sol^n is connected to a Ag electrode in 0.05 M $AgNO_3$ sol^n through a voltmeter & salt bridge.

$E^\circ_{Zn^{2+}/Zn} = -0.76\ V$

$E^\circ_{Ag^+/Ag} = 0.80\ V$

Find (i) EMF of cell after 2 hrs if a constt current of 1 A is drawn from the cell.

(ii) Determine conc- of $[Zn^{2+}]$ & $[Ag^+]$ in resp. electrolytes when cell stops functioning.

$Q = It$

$= 1(2)$

$\Rightarrow Q = 2C, = \frac{2}{96500} =$ no. of eqs

$Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag$

0.05 $-2x$ | 0.1 M $+x$ | $E^\circ = 1.56\ V$

$\frac{It}{96500}$ = no. of eq

$0.07 = \frac{2(1)}{96500}$ = no. of eq

$ZnSO_4 + AgNO_3 \rightarrow Zn(NO_3)_2 + Ag_2SO_4$

250 ml, 0.1M | 0.05M

$EMF = E^0 - \frac{0.059}{2}\left(\log \frac{0.1}{(0.05)^2}\right)$

E^0

$ZnSO_4 + 2e^- \rightarrow Zn^{2+} + SO_4^{2-}$ $\quad -0.76$

$AgNO_3 + e^- \rightarrow Ag^+ + NO_3^-$ $\quad \times 2$ $\quad 1.6$

$E^0 = 1.56$

$\Rightarrow E = 1.56 + \frac{0.06}{2}\left[\frac{0.1}{(0.05)^2}\right]$

$\Rightarrow E = 1.56 + 0.03\left(\frac{1\times10^{-1}}{25\times10^{-4}}\right)$

$= 1.56 + 0.03\left(\frac{0.04\times10^3}{}\right)$

$= 1.56 \times 3\left(\frac{40}{100}\right)$

$= 1.56 + 1.2$

$E = 2.76$.

Chemistry Notes Akshansh

$\frac{0.1}{25\times10^{-4}}$ =

$\Rightarrow E = 1.56 - 0.03\left(\log \frac{1}{40}\right)$

$= 1.56 - 0.03(0.6 - 1)$

$= 1.56 - 0.048$

$E = 1.608$ V

$E = E_0 - \frac{0.06}{2}\log\frac{(0.1+x)}{(0.05-2x)^2}$

$\Rightarrow 0.048 = 0.03\log\left(\frac{0.1+x}{(0.05-2x)^2}\right)$

$\Rightarrow \frac{16}{10} = \log\left(\frac{0.1+x}{(0.05-2x)^2}\right)$

1A × 2 hr

$Q = 2\times3600 = 7200$ C.

$Q_{battery}$

$eq = \frac{7200}{96500} \times 1000$ meq $\simeq 75$ meq

$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$

75 meq Ag^+ ↓ (deposited)

75 meq Zn^{2+} ↑ (in soln)

meq Ag^+ remaining $= 25\,(0.05\times2000 - 75)$

meq Zn^{2+} in soln $= 250(0.1)\times2 + 75$.

$= 125$ meq

+2 Chemistry Notes Akshansh

So, $M_{Ag^+} = \frac{25}{2000} = \frac{1}{80}$

Molarity $_{(Zn^{2+})} = \frac{+25 \times 5}{250 \times 2} = 0.25$

$E = 1.56 - \frac{0.059}{2} \log \left(\frac{1/4}{(1/80)^2}\right)$

$= 1.56 - 0.03 \left(\log \left(\frac{80 \times 80}{4}\right)\right)$

$= 1.56 - 0.03 (1.2 + 2)$

$= 1.56 - 0.102$

$E = 1.46$

13.4
e3
102

Cell will stop flowing when it will lose voltage.

$E^0 = \frac{0.06}{2} \log K$

$\Rightarrow \frac{1.56 \times 2}{0.06} = \log K$

$\Rightarrow 26 \times 2$

$\Rightarrow 52 = \log K$

$\Rightarrow K = 10^{52} = \frac{[Zn^{2+}]}{[Ag^+]^2}$

* This rxn will complete

$Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag$

i 0.05 0.1

f $\approx 0 + x$ $0.1 + \frac{0.05}{2} - \frac{x}{2}$

$[Zn^{2+}] = 0.125\ Zn^{2+}$

Chemistry Notes Akhansh

Now, $10^{-52} = \frac{0.125}{x^2}$

$\Rightarrow x^2 = 0.125 \times 10^{-52}$

$= 1.25 \times 10^{-52}$

$\Rightarrow x = \sqrt{0.125 \times 10^{-26}}$

Q. Determine EMF of the following galvanic cell at 25°C →

$Pt / H_2(1\text{ atm}) / HA(0.01M) \| Cl^-_{(0.5M)}, Hg_2Cl_2 / Hg / Pt$

Assume: HA is weak monobasic acid,

$K_a = 2 \times 10^{-5}$

$E^\circ_{Hg_2Cl_2/Hg,Cl^-} = 0.28\ V$

$Hg_2Cl_2 \longrightarrow 2Hg^0 + 2Cl^-$ $E^\circ = 0.28$

$H_2 \longrightarrow 2H^+ + 2e^-$ $E^\circ = 0$

$HA \rightleftharpoons H^+ + A^-$

$0.01 - x \quad x \quad x$

net $H_2 + Hg_2Cl_2 \longrightarrow 2H^+ + 2Hg + 2Cl^-$ $E^\circ = 0.28$

$EMF = E^\circ - \frac{0.06}{2} \log [H^+]^2 [Cl^-]^2$

$= 0.28 - 0.06 \log [H^+][0.5]$

$K_a = \frac{c\alpha^2}{1-\alpha}$

$\Rightarrow 2 \times 10^{-5} < \frac{(0.01)\alpha^2}{1-\alpha}$

2 Chemistry Notes Nilanjan

$HA \rightleftharpoons H^+ + A^-$

$c(1-\alpha) \quad c\alpha \quad c\alpha$

$\Rightarrow \frac{1-\alpha}{\alpha^2} = \frac{0.1}{2} \times 10^8$

$\Rightarrow \frac{1-\alpha}{\alpha^2} = 5 \times 10^2$

$\Rightarrow 1-\alpha = 500\alpha^2$

$\Rightarrow 500\alpha^2 + \alpha - 1 = 0$

$\Rightarrow \alpha = \frac{-1 \pm \sqrt{1+2000}}{1000}$

$\alpha = \frac{-1 + 10\sqrt{20}}{1000}$

$\boxed{\alpha = 3.5 \times 10^{-3}}$

$4 \overline{)20.00}\ (4.5$

-16

$8 \quad 400$

$\Rightarrow E = 0.28 - 0.06 \log (3.5 \times 10^{-3})/(0.5)$

$\Rightarrow E = 0.28 - 0.06 \log (175 \times 10^{-5})$

$= 0.28 - 0.06 [(-5) + 1.4 + 0.85]$

$= 0.28 + 0.1650$

$= 0.5650$

1.4
0.85
2.25

$175 \quad 675.00$
$\quad\quad 2.25$
$\quad\quad 4375$
$\quad\quad 06$

1650
2800
4450

$.2850$

0.28
$.2850$
0.5650

Or

$HA \rightleftharpoons H^+ + A^-$

$c(1-\alpha) \quad c\alpha \quad c\alpha$

$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha^2}{1-\alpha}$

$1-\alpha \approx 1$

$[H^+]^2 = K_a \cdot c$

$[H^+] = \sqrt{K_a \cdot c}$

$= \sqrt{20} \times 10^{-4}$

anode → $Zn \rightarrow Zn^{2+} + 2e^-$

cathode → $2Ag^+ + 2e^- \rightarrow 2Ag$

$Zn + 2Ag^+ \rightarrow Zn^{2+} + 2Ag$ net

Q. A Zn electrode in 0.1 M $ZnSO_4$ sol^n is combined with a Ag electrode in 0.1 M $AgNO_3$ sol^n by means of salt bridge & Voltmeter. If EMF cell was found to be 1.52 V. Now, some solid KCl is added into cathode chamber resulting in Ppt^n of AgCl. After completion of Ppt^n, EMF cell = 1.04 V.

$Zn / Zn^{2+} \,||\, Ag^+ / Ag$ $\quad E^\circ = 1.52\,V$

0.1 M $\quad$ 0.1 M

Also, conc. of $[K^+]$ in cathode chamber was found to be 0.3 M. Assuming V of electrolytes to be 1 L each, determine K_{sp} of AgCl.

$Zn \rightleftharpoons Zn^{2+}_{0.1} + 2e^-$

$[Ag^+_{0.1} + 1e \rightarrow Ag]\times 2$

$1.522 = E^\circ - \frac{0.06}{2} \log \frac{(0.1)}{(0.1)(0.1)^2}$

$= E^\circ - 0.03$

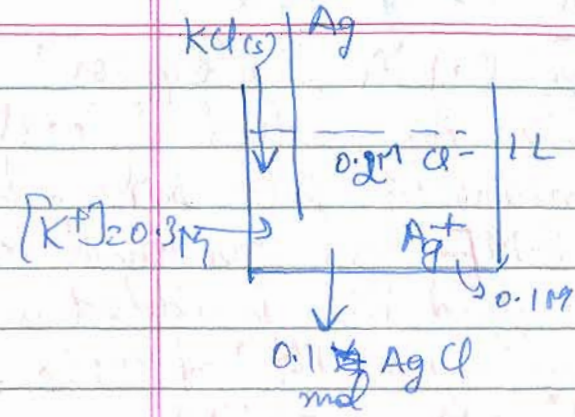
$\Rightarrow \boxed{1.552\,V = E^\circ_{cell}}$

~~$AgBr \rightleftharpoons Ag^+ + Br^-$~~

~~$AgCl \rightarrow Ag^+ + Cl^-$~~

$Zn^\circ + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag$.

Rachna Chemistry Classes Akshansh



$Ag^+ + Cl^- \rightarrow AgCl(s)$

0.1M 0.3M 0.1M

0 0.2M

Now.

$$1.04 = 1.55 - \frac{0.06}{2} \log \frac{0.1}{x^2}$$

$$\Rightarrow \frac{51}{6} x^2 = \log \frac{0.1}{x^2}$$

$$\Rightarrow 8.5 = \log \frac{0.1}{x^2}$$

$$\Rightarrow \frac{0.1}{x^2} = 10^{17}$$

$$\Rightarrow x^2 = 10^{-18}$$

$$\Rightarrow x = 10^{-9}.$$

→ conc. Ag^+ in final soln.

$K_{sp} = [Ag^+][Cl^-]$

$= 10^{-9} \times 0.2$

$= 2 \times 10^{-10}\ mol^2 L^{-2}$.

Chemistry Notes Akshansh

✡ THERMODYNAMICS of cell.

For spontaneity $E^\circ > 0$

$\Delta G^\circ = -nE^\circ F$

In

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ → Std. state entropy change of rxn.

$\Rightarrow -nE^\circ F = \Delta H^\circ - T\Delta S^\circ$

Q. E° for the following cell are 0.24V & 0.20V resp at 17°C (290) & 37°C (310)

$Pt|H_2$ (1atm) | HCl || AgCl, Cl^- | Ag

Determine ΔH°, ΔS° for the cell

Now, $-nE^\circ F = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow -2(0.24)(96500) = \Delta H_1^\circ - 290\Delta S^\circ$

~~$(0.20)(96500)$~~

$\Rightarrow \Delta H_1^\circ - 290\Delta S_1^\circ = -(96500)(0.24)$

$\Delta H_2^\circ - 310\Delta S_1^\circ = -(96500)(0.20)$

$\Delta H^\circ = x$, $\Delta S^\circ = y$.

$x - 290y = -0.24F$.

$x - 310y = -0.20F$.

$\Rightarrow +20y = -0.04F$

$\Rightarrow y = \frac{0.04}{2} \times 96500 \times 100$

$= -1930 = -193\ JK^{-1}$

$\Delta S^\circ = -386\ JK^{-1}$

Now,

$x - 290(-19.3) = -0.24F$

$\therefore x = -0.24F + 5597$

$= -23160 + 5597$

$= -17563$ KJ

$\Delta H^\circ = -79.13$ KJ

$\frac{1}{2}H_2 + AgCl \rightarrow H^+ + Ag^+ + Cl^-$

Q If E° for $Ag^+/Ag = 0.80V$ at 27°C, determine K_{sp} of AgCl at 27°C.

$AgCl(s) \rightleftharpoons Ag^+ + Cl^- \quad E^\circ = -0.58V$

$Ag \rightarrow Ag^+ + e^- \quad -0.80\ V$

$AgCl + 1e^- \rightarrow Ag + Cl^- \quad E_0 = ?$

Now, In the cell.

$Pt/H_2(1atm)/HCl \,||\, AgCl, Cl^-/Ag$

$E^\circ = E^\circ_{H^+/H_2} + E^\circ_{AgCl/Ag, Cl^-}$

$= 0 + E^\circ_{AgCl/AgCl^-}$

At 25°C,

$-(2)(E^\circ)(96500) = (-158.26) + (300)(-386)$

$\Rightarrow E^\circ = 158260 + 115800 + 193000$

15|8260 ⇒ E° = 274060
+11,5800 (183 ×100
27406° ⇒ E° ≈ 0.22 V.

⇒ $E^\circ_{AgCl/Ag,Cl^-}$ = 0.22 V.

So, E°

So, $-0.58 = \frac{0.059}{1} \log K_{sp}$ ...

⇒ $10^{-10} = K_{sp}$.

★ ELECTROLYTIC CONDUCTANCE of Sol^n

$R \propto \frac{l}{A}$, $\boxed{R = \rho \frac{l}{A}\ \Omega}$ ★

$\propto \frac{1}{A}$ Resistance. → Resistivity or specific resistance (Intensive property)

Conductance = $\frac{1}{R} = G$ (or L) = $\frac{1}{\rho}\left(\frac{A}{l}\right)$

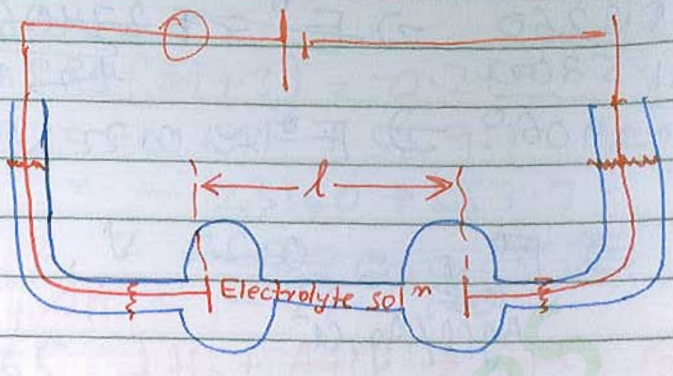
↳ denotion

★★ $\boxed{G = K \frac{A}{l}\ \frac{\Omega^{-1}}{\text{or } \mho}}$

Kappa = Conductivity or specific conductance.

Units: mho or $\boxed{\text{Siemen (S)}}$ → SI.

✡ CONDUCTIVITY CELL



✡ EQUIVALENT CONDUCTANCE (Λ_{eq})

let Normality of electrolyte = C.

⇒ C geq of eq electrolyte in 1000 cc of sol^n.

⇒ 1 geq ---- → $\frac{1000}{C}$ cm^3

⇒ If $l = 1cm$,

⇒ Vol = V = A × l

⇒ $A = \frac{1000}{C}$ cm^2.

$$G = k\left(\frac{1000}{C}\right) = \Lambda_{eq}$$

(C: Normality)

Equivalent conductance of an electrolytic sol^n is the conductance of sol^n containing 1 geq of electrolyte present in a conductivity cell in which electrodes are 1cm apart.

$G = k\frac{A}{l}$ ⇒ $k = G\left(\frac{l}{A}\right)$

= S (S)m^{-1} : SI

Siemens

$S\,cm^{-1}$: otherwise

Now, $\Lambda_{eq} = \frac{S\,cm^{-1}}{eq\,L^{-1}} = \frac{S\,cm^{-1}\,cm^3}{eq}$

$= S\,cm^2\,eq^{-1}$

$\Rightarrow \boxed{\Lambda_{eq} = S\,cm^2\,eq^{-1} = S\,m^2\,eq^{-1}}$: Otherwise : SI.

↳ Imp. learn.

$G = k\frac{A}{l} \Rightarrow k = G\frac{l}{A}$

$\boxed{\frac{l}{A} = \text{cell constt of conductivity cell}}$.

↳ Constt for 1 conductivity cell.

↳ So, can be used to solve k, others of other solns also.

★ MOLAR CONDUCTANCE. (Λ_m) :-

Molar conductance of an electrolytic soln is the conductance of soln containing 1 mole of electrolyte & present in a conductivity cell in which electrodes are 1 cm apart.

$\Rightarrow \Lambda_m = k\frac{1000}{C}$ → Molarity.

So, $\boxed{\frac{\Lambda_m}{\Lambda_{eq}} = \frac{N}{M} = n\text{-factor}}$

V.V. Imp.

★

$k \times 1000 = (0.05)(200)$

Date 9.6.10

Q. Λ_m of 0.05 M aq soln of $MgCl_2$ is 200 $S\,cm^2\,mol^{-1}$ at 25°C. Cell parameters are $A = 1.5\,cm^2$, $l = 0.5\,cm$.
If V across electrodes is 5V, determine strength of I flowing through conductivity cell.

$\Rightarrow \frac{1}{k} = \frac{1000}{0.05 \times 200} = \frac{500}{100} = 5$

$\Rightarrow R = 5 \times 100 \times \frac{0.5}{1.5}$

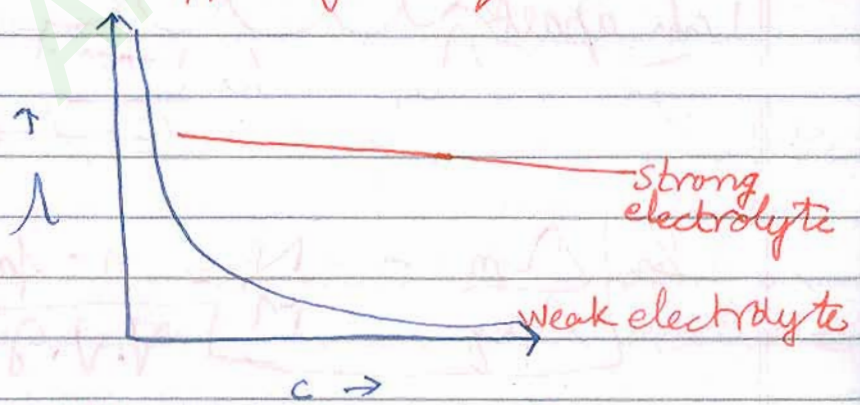
$R = \frac{100}{3}$

$\Rightarrow V = IR$

$\Rightarrow I = \frac{5}{100} \times 3$

$\Rightarrow I = 0.15\,A$

☆ Factors affecting λ_{eq} or Λ_m.



With dilⁿ, conductance increases. Increase is very slow in high conc. But inc. is abrupt as $c \to 0$

classmate
Date
Page

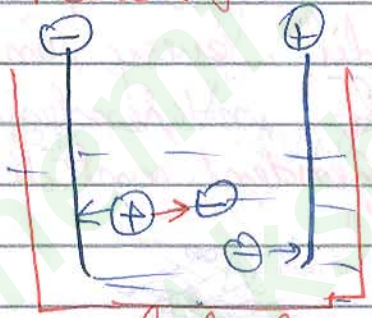
* Conductance inc. with dil^n. The inc. in conductance of sol^n is very slow in higher conc. range. ~~Condu~~

Conductance increases abruptly as $C \to 0$.

* By Ostwal dil^n laws, as very dilute conc $\to 0$, $\alpha = 1$ ($\alpha = \sqrt{\frac{K_a}{C}}$), so more ions, hence, greater conductance...

Weak electrolyte

For strong electrolyte also, $\Lambda \uparrow$ with dil^n. Reason $\longrightarrow$



In a strong electrolyte sol^n, the ions of opposite polarity attract each other & prevent each other from going towards the electrodes. With dil^n, ($F \propto \frac{1}{d^2}$), distance b/w these ions $\uparrow$, so, F $\downarrow$, hence ~~they~~ cond^n $\Lambda \uparrow$.

TEMP :-

* Increasing T $\uparrow$ value of Λ which is opp. to that of metallic conductance

($\because$ Inc $\uparrow$ T, $\uparrow$ avg KE, $\uparrow$ v of ions $\therefore \Lambda \uparrow$ $\because$ quickly go to electrodes)

#2 Chemistry Notes Vikrhansh

* Conductance of single ion can't be known (∵ single ion can't be separated)

Imp

Q. * Metallic conductors → T ↑, Λ ↓
∵ T ↑, band gap ↑ from valence band to cond^{n} band.
So, movt. of e^{-}s through this gap becomes difficult.

* Kohlrausch's law of Independent migration of ions :-
Acc. to Kohlrausch's law of independent migr^{n} of ions, at infinite dil^{n}, every ions moves independently & makes an independent contrib^{n} to total Λ of sol^{n}.

eg:

$\Lambda_c^\infty NaCl = \lambda^\infty_{Na^+} + \lambda^\infty_{Cl^-}$

$KCl = \lambda^\infty_{K^+} + \lambda^\infty_{Cl^-}$

$\Lambda^\infty_{NaCl} - \Lambda^\infty_{KCl} = \lambda^\infty_{Na^+} - \lambda^\infty_{K^+}$

Ans * Λ^∞

$NaNO_3 = \lambda^\infty_{Na^+} + \lambda^\infty_{NO_3^-}$

$KNO_3 = \lambda^\infty_{K^+} + \lambda^\infty_{NO_3^-}$

$\Lambda_{NaNO_3} - \Lambda_{KNO_3} = \lambda^\infty_{Na^+} - \lambda^\infty_{K^+}$

The diff is constt independent of $[Cl^-]$ or $[NO_3^-]$. So, Kohlrausch's law is verified.

Concept :

(a) $\Lambda^\infty_{HCl} = 420 \, S \, cm^2 \, eq^{-1}$.

(b) $\Lambda^\infty_{NaCl} = 126 \, S \, cm^2 \, eq^{-1}$

(c) $\Lambda^\infty_{CH_3COONa} = 91 \, S \, cm^2 \, eq^{-1}$

So, $\Lambda^\infty_{CH_3COOH} = \lambda^\infty_{CH_3COO^-} + \lambda^\infty_{H^+}$

$= (420 + 91 - 126) = 385 \, S \, cm^2 \, eq^{-1}$

① $HCl \rightarrow H^+ + Cl^-$

② $NaCl \rightarrow Na^+ + Cl^-$

③ $CH_3COONa \rightarrow CH_3COO^- + Na^+$

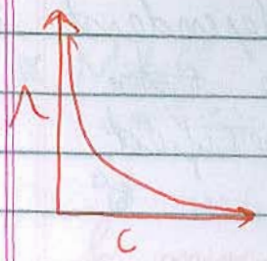
① + ③ − ②

$= 420 + 91 - 126$

$= CH_3COO^- + H^+$ Ans

+2 Chemistry Notes Akshansh

classmate
Date
Page



$\Lambda \propto \alpha$

$\Lambda = k\alpha$

At $\alpha = 1$,

$\Lambda = \Lambda^{\infty}$

$\Rightarrow \boxed{k = \Lambda^{\infty}}$

↳ at ∞ dil^{n}, $\alpha = 1$.

So, $\frac{\Lambda^{c}}{\Lambda^{\infty}} = \alpha$ → alpha → degree of dissociation

conductance at ∞ any ~~∞~~ one.

conductance at ~~any~~ ∞ dil^{n}

Q CH_3COOH sol^{n}, $k = 0.00193\ S\,cm^{-1}$

Det. pH of 0.01 M CH_3COOH.

$\Lambda_{eq}^{\infty} = 385\ S\,cm^{2}\,eq^{-1}$.

$k = 0.002\ S\,cm^{-1}$.

~~$\Lambda_c = 0.770$~~

$\Lambda_e^{c} = \frac{0.00193 \times 1000}{0.01}$

$\Lambda^{c} = 193\ S\,cm^{2}$

$\Rightarrow \alpha = \frac{193}{385} \approx 0.5$

$\Rightarrow [H] = C\alpha = 5 \times 10^{-3}$

$pH = -\log [0.5 \times 0.01]$

$pH = 2.3$.

Chemistry Notes Akshant

classmate
Date
Page

* Saturated soln of a sparingly soluble salt has Λ at ∞ dil^n.
Hence, for it

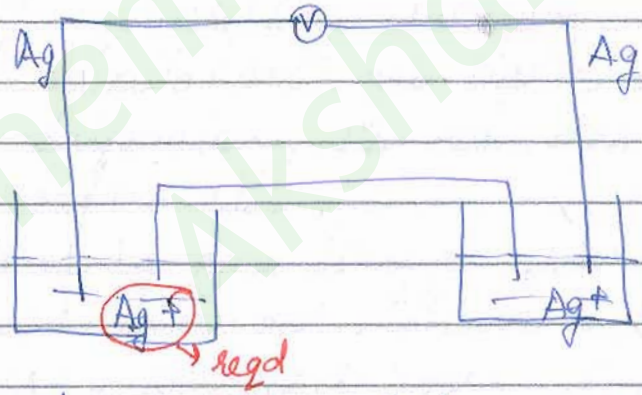
$$\Lambda^{\infty} = \text{@}\, k \times 100$$

(S) → solubility (moles of salt).

So, $K_{sp} = S^2$ @ can be calculated.

GALVANIC CELL:-

* Conc. cell (concept of nernst eq^n)



At anode : $Ag \rightarrow Ag^+_{anode} + 1e^-$ $\quad -E^0$.
cathode : $Ag^+_{cathode} + 1e^- \rightarrow Ag$ $\quad E^0$.

$$Ag^+_{cathode} \longrightarrow Ag^+_{anode} \qquad E^0_{cell} = 0$$

So,

$$E = 0 - \frac{0.059}{1} \log \frac{[Ag^+]_{anode}}{[Ag^+]_{cathode}}$$

$E > 0 \Rightarrow [Ag^+]_{cathode} > [Ag^+]_{anode}$.

when $[Ag^+]_{cathode} = [Ag^+]_{anode}$: Cell stops

+2 Chemistry Notes Akshansh

classmate
Date
Page

★ Conc. cells are galvanic cells in which both cathode & anode are reversible with same ion. The driving force of the cell is conc. diff. of ions in cathode & anode chamber.

Cell stops going when $[Ag^+]$ becomes equal in both half cells

For rxn to occur, $[Ag^+]_{cathode}$ should be $> [Ag^+]_{anode}$

So, that $E > 0$

Chemistry Mate Akshansh

Surface Chemistry

* **COLLOIDAL Sol^n** : A 2 phase heterogeneous sys in which the solute particles of colloidal dimension is distributed evenly in the solvent.

In colloidal sol^n,
Solute : dispersed phase (DP)
Solvt : dispersion medium (DM)

- DP of colloidal sol^n are stable in DM.
- unlike suspension, its not separated when left still.
- Particles of DP pass through ordinary filter paper but not through ultra filter paper, parchment paper, cellophane.

Generally, DP particle size varies from 1 μm to 100 μm.

COLLOIDS

DP	DM	Type
Solid	Liqd.	Sol (syrup)
Liqd.	Solid	Gel (jelly)
Liqd	Liqd	Emulsion (milk)

classmate
Date
Page

PREPARⁿ of SOL

1. CONDENSⁿ
2. DISPERSⁿ

(1) Condensⁿ method : Indirect method of bringing about DP into DM. In this method, diffᵗ solⁿˢ are mixed in right proportion where the DP is produced in SITU chemically in the DM.

The chem. rxn may involve, Oxidⁿ, redⁿ, double decompᵒˢⁿ, neutralisⁿ ---etc.

eg : Gold Sol is prepared by rxn of $AuCl_3$.

$$AuCl_3 \longrightarrow Au^{3+} + 3Cl^-$$

prepared in situ.

eg : $S^{2-} + OA \rightarrow S$

(2) Dispersion method : Direct method of bringing abt. DP in DM.

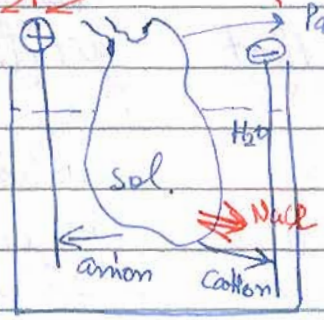
In this method, a larger sized solute particle is dissolved in DM & subjected to mechanical stirring. where, the solute is broken down to colloidal dimension.

Chemistry Notes by Ashish

Heparin

✱ PURIFICATION of SOL

① Dialysis



after equi. of salt & DM, DM (H_2O, here) replaced removed, more salt comes out.

② Electrodialysis :-

Done in manufacturing where electrodes are connected so, anions and cations are quickly separated.

✱ PROPERTIES of SOL

Lyophobic
hate of DP & DM

✓ unstable
✓ DP has hate for DM.
✓ DP are brought into DM with difficulty
✓ DP are separated out from DM by slight change in condⁿ (thermodynamic)

Process name :

✱ Coagulation :
Separⁿ of DP from DM by slight change in condⁿ.

Lyophillic
love of DP & DM

✓ stable
✓ salt in which DP has love/affinity for DM.
✓ DP are easily brought into DM.
✓ Lyophillic salts are not easily coagulated. ∴ They are relatively more stable than lyophobic sol.

Chemistry Notes Akshansh

* Tyndall effect observed in Ultrahigh microscope :→ Invented by ZISGMONDY.

	Lyophobic	Lyophilic
✓	Viscocity : Comparable to that of DM.	✓ Viscocity : much greater than that of DM :: DP is solvated with DM.
✓	DP is at very low conc. & has negligible effect on viscosity of sol^n.	✓ DP is heavily solvated which ↑ apparent particle size resulting in significant inc. in viscosity.
✓ OPTICAL Property	Scatter visible light when passed through it. Process : Tyndall effect.	✓ Very less show tyndall effect :: particle size doesn't come in visible range of light.

* KINETIC PROPERTY

Zig-zag movt :
Brownian motion :

When colloidal particle is observed under ultra high microscope, its found to be moving randomly & ceaselessly. When all external factors like thermal E, ME are eliminated, still the DP particle is found to be moving. The internal chaotic motion of DP particle on a zig-zag path is known as BROWNIAN Motion.

classmate
Date 11.6.10
Page

ELECTRICAL PROPERTY.

✓ lyophobic sols are mostly charged. ∴ conducting, move towards electrodes of opp. polarity in electric field. This charge makes it unstable

✓ lyophilic sols are mostly neutral & less conducting.

Ions bringing coagul^{n} of lyophobic sol is determined by HARDY SCHUELZ rule

Acc. to this rule,

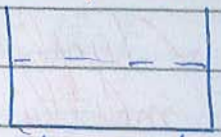
P1 Higher the conc. of electrolytes, greater the coagulating power.

P2 If diff^{t} electrolytes, but at same conc. are used, higher the valency of coagulating ion, greater will be coagulating power.

PROTECTION of lyophobic ~~Salt~~ Sol

Add^{n} of lyophilic sol to a lyophobic sol prevents the latter from coagul^{n} & increases stability of the sol. Protecting power of the lyophilic sol is measured in term of a ~~gg~~ known as Gold no.

mg , 1ml of 10% NaCl soln



10 ml of std. Gold sol (Red colored)

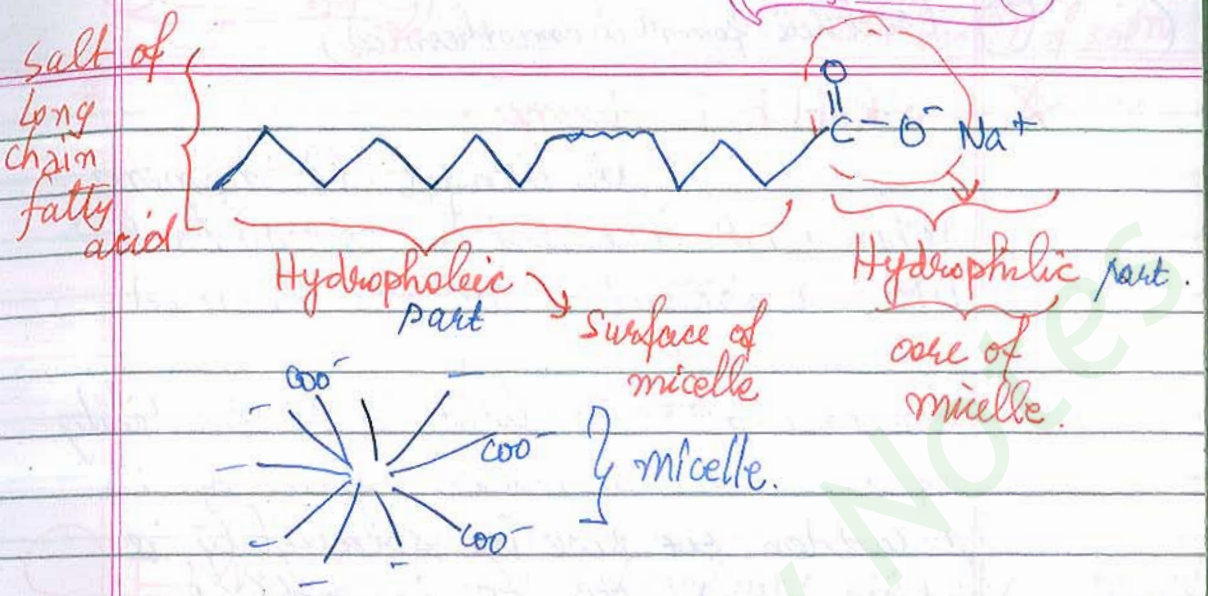
(Turns blue on coagulⁿ)

* Lower the Gold no., higher is the protecting power of lyophilic sol.
* Gold no. of Gelatine is min.
* Gold no. of a lyophilic sol is the min wt. in mg unit of a DP reqd to be added to 10 ml of ~~10% Na~~ std. Gold sol in order to just prevent its turning from Red to Blue (coagulⁿ) on addⁿ of 1 ml, 10% NaCl solⁿ.

MICELLES

When conc. of DP is increased gradually, after a cutain min. value of conc., several DP particles aggregate together to form a bigger solute particle which remains soluble & stable in DM. Aggregates of DP particles is known as MICELLE & phenomena of formⁿ is called MICELLISATION.

classmate
Date
Page



★ Critical Micellisⁿ Conc. (C.M.C.)
≡ It is the min. conc. of DP at which micelle formⁿ takes place.
★ long chain alkyl grp have lower CMC.
~~Higher~~ short " " " " has higher CMC.
§ ★ Once micelle formed & add water (dilute), micelle breaks & add solute, micelle again formed. So, micelle formⁿ is reversible in nature
★ OLEIC ACID → $C_{17}H_{33}$-COO Na & STERIC ACID
★ PALMITIC ACID & LAURIC ACID

C ranges from 15 to 25 or more.

Na or K salt of
Carboxylic acid, sulphonic acid : Anionic micelle

§ Ammonium salt ~~com~~ containing : Cationic micelle.
§ long alkyl chain eg:

$$C_{16}H_{33}-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^{+}}}}}-CH_3\,Br^{\ominus}$$

Cetyl trimethyl ammonium bromide

★ Increasing T ↑ solubility of all organic salts (∵ their formⁿ is endothermic)

★ KRAFFT Temp.

Or Krafft Phenomena

When a DP. is added in excess to a DM, a saturated solⁿ is formed where Solid ⇌ liqd equi. exist. Increasing T ↑ ~~solubility~~ solubility of DP. At a certain value of T, a sudden ~~rise~~ rise in solubility is observed & the T is called KRAFFT temp.

At Krafft T, the solⁿ acquire conc. of DP greater than CMC, micelle formⁿ starts which ↑ solubility greatly. ∵ micelle is more soluble than individual DP particle. In individual DP particle, hydrolohobic fragment is in front of solvent (~~so~~ it is masked in case of micelle), so, its solubility decreases (increases in micelles).

★ Imp: Increasing T increases CMC due to ~~them~~ increased thermal agitation (avg. thermal E of molecules ↑) at high T. So, more solute will have to be added to form micelle.

★ Conductance ↑ with no. of ions.

At CMC, conductance ↓ sharply due to micelle formⁿ that ~~so~~ suddenly decreases no. of ions.

classmate
Date
Page

surface tension

(Surface Active Agent lowering ST of soln)

* MICELLE is also called SURFACTANT or ASSOCIATION COLLOID.

Its cleansing action:
1. By lowering surface tension
2. By occlusion (trapping of oil molecule by hydrophobic portion)

EMULSION: Emulsions are the 2 phase heterogeneous sys of 2 immiscible liqds.

* Oil in Water
  - Oil in water emulsion has oil as DP & H_2O as DM
  - eg: milk

* Water in Oil
  - It has water as DP & oil as DM.
  - eg: butter, paints

* EMULSIFYING AGENT: They maintain the 2 immiscible liqd in same soln. It act as a binder b/w the 2 liqds.

* In milk, the connecting molecule b/w oil & water is a protein called CASEIN.

---

* To differentiate b/w type of emulsions,

1) Add Water: If mixes: oil in water
   not mixes: water in oil
2) Ily add oil.

Chemistry Notes by Akshansh

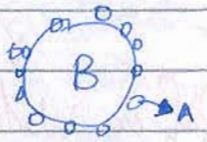
Classmate
Date
Page

* **ADSORPTION** : It is a phenomena which occur at the surface only.

Q Why adsorption ?

Ans- Adsorption occur due to presence of some residual surface E. When a surface is formed some of the sides at the surface are left unbalanced (charged) which makes the surface active & gives rise to spontaneous adsorp".

$$A_{(g)} + B_{(s)} \longrightarrow$$



✓ **ADSORBATE** जो होता है
Substance being adsorbed.

ADSORBENT जिसपे होता है
Substance on whose surface where adsorption occurs.

* **Thermodynamics of adsorption.**

$$A_{(g)} + B_{(s)} \longrightarrow$$

$\Delta G < 0$

$\Delta G = \Delta H - T\Delta S$

* Adsorption decreases entropy of Sys. (∵ Sys. becomes more ordered. Degree of randomness ↓)

Chemistry Notes by Akshansh

$\Rightarrow \boxed{\Delta S < 0}$.

So, for $\boxed{\Delta G < 0, \ \Delta H < 0}$ All < 0.
& $\boxed{|\Delta H| > |T\Delta S|}$.

Process is exothermic process (∵ without providing E, bond is formed & bond form^{n} is exothermic).

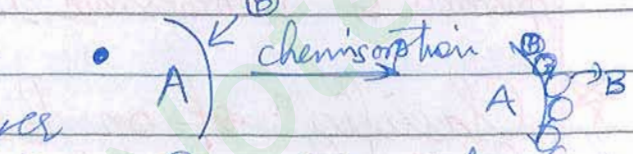
★ Classific^{n} ~~of~~ on basis of type of bond formed b/w adsorbate & adsorbent :

Physical (Physisorption) (or Vanderwall adsorp^{n})	Chemical (Chemisorption)
• Molecules of adsorbate are held at the surface of adsorbent by weak electrostatic attr^{n} which can be one of the following:- H-bond, dipole-dipole attr^{n}, vander wall force.	• Chemical rxn is involved b/w adsorbate & adsorbent & ~~adsorbed~~ ~~adsorbent~~ adsorbate molecules are held with surface through chemical bond which can be ionic or covalent bond.
Properties	
★ Enthalpy of adsorption (ΔH) is less.	• Enthalpy of adsorption is very large due to greater strength of chemical bond.

Chemistry Notes by Akshansh

Inverse of adsorption ⇒ Desorption

- SA of adsorbate, extent of adsorption ↑.

Physisorption	Chemisorption
✱ ~~Desorption~~ It is reversible in nature (substance adsorbed, same is desorbed)	✱ It is irreversible in nature (substance adsorbed is diff^{t} from desorbed substance)
• It is multi-molecular layer in nature (∵ ~~dpole~~ weak interⁿˢ exist b/w same molecules)	•  Once B is adsorbed so, no more layer is adsorbed, so, Chemisorption is monomolecular in nature
✱ It occurs at lower T ∴ It is favoured at low T $A_{(s)} + B_{(g)} \rightleftharpoons A\text{-}B_{(s)}$ $\Delta H < 0$, The process is exothermic	✱ It requires higher T due to large E_a of the chemical bⁿ involved in adsorpⁿ.

✱ Inc. P ↑ extent of adsorption for both ~~adsorption~~ physisorption & chemisorption

same T

✱ FREUNDLICH ADSORPTION ISOTHERM (not in IIT)

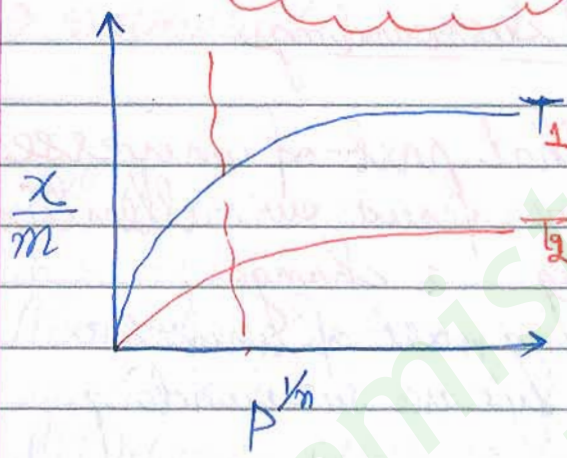
x g adsorbate on m g adsorbent

extent of adsorption ← $\left(\frac{x}{m}\right) \propto (P)^{1/n}$, $n > 1$

Pressure

* Reversible adsorption:
→ Same species is adsorbed & desorbed.
* Irreversible adsorption:
→ Species adsorbed is diff^t from that desorbed. So, there is chem. nature change of adsorbate & adsorbent (eg: charcoal & surface $\xrightarrow{U_2}$ O_2 adsorbed. $\xrightarrow{\text{on heating}}$ O_2 is desorbed)

$$\Rightarrow \frac{x}{m} = k P^{1/n}$$

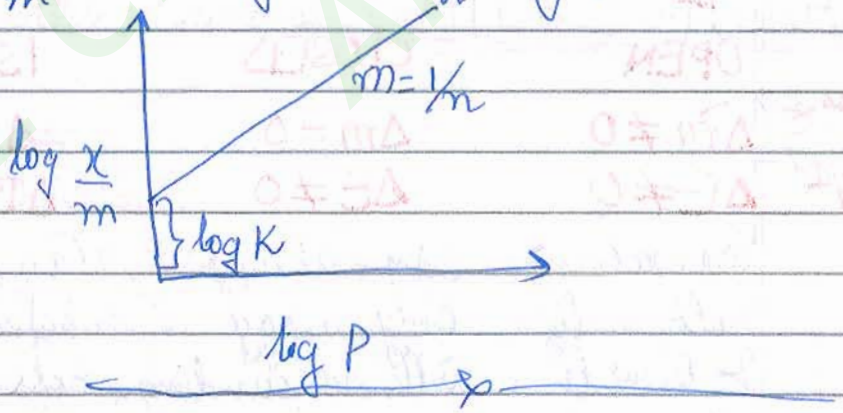


Graph

$T_2 > T_1$

(∵ extent of adsorption higher at lower T)

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log P$$



IIT Chemistry Notes Akshaya

classmate
Date 2·7·10
Page

Ch: Thermodynamics

✱ System and Surroundings

System is that part of universe to which we focus our attention for observing a change.

Remaining part of universe other than sys are surrounding.

SYSTEM

	OPEN	CLOSED	ISOLATED
net mass ←	$\Delta m \neq 0$	$\Delta m = 0$	$\Delta m = 0$
net energy ←	$\Delta E \neq 0$	$\Delta E \neq 0$	$\Delta E = 0$
	Can exchange both matter & E with surrounding	Can exchange only energy with surrounding Can't exchange matter.	Can neither exchange mass nor energy with the surrounding

Chemistry Notes Akshansh

THERMODYNAMIC PROCESSES

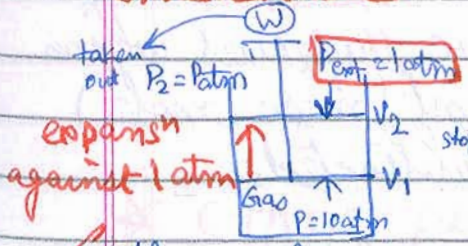
On the basis of CONDITION of change

- Isothermal : Constt T, $\Delta T = 0$.
- Isobaric : Constt P, $\Delta P = 0$.
- Isochoric : Constt V, $\Delta V = 0$.
- Adiabatic : Constt heat, $\Delta Q = 0$.

- All Isochoric process must be carried out in a closed sys :- False
- All adiabatic process occur in isolated sys :- False.
- All process occuring in isolated sys. is simultaneously adiabatic :- TRUE

On the basis of NATURE of CHANGE

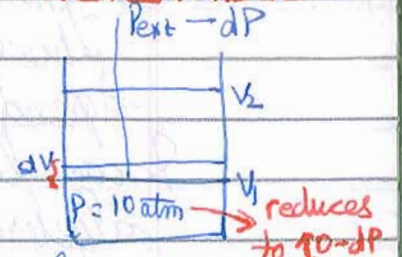
IRREVERSIBLE



✓ Those thermodynamic process which occur against a constt external force (or P)

- P_2 (or P_{final}) $\geq P_{ext}$ (constt)

REVERSIBLE



Those thermodynamic process in which sys remain in equi. with surrounding throughout change. i.e ∞ intermediate equilibria are involved.

Chemistry Notes Akshansh

Irreversible	Reversible
✓ In irreversible process sys attain equi. only at the final state of change. i.e no intermediate equilibria is involved.	The process occur due to infinitesimally small diff. in internal & external cond^{ns}. Reversible process is a combin^{n} of ∞ no. of infinitesimally small irreversible processes.
✓ Irreversible process complete in finite length of time.	Reversible process takes infinite time to complete.
✓ Gas loses its ideal ~~proces~~ behaviour during change	Ideality is maintained throughout the procdss.

✱ Extensive & Intensive Thermodynamic Properties.

Extensive:

Those thermodynamic properties which dpend directly on amt (mass, mole) & can be added (or subtracted) algebraically.

eg: Mass, Volume, all forms of energy (enthalpy, KE, PE, heat, light), all colligative properties (rel. lowering of VP, π, lowering of F. Pt., increase in B. Pt), resistance, conductance.

Intensive :-
Those thermodynamic property which do not depend directly or indirectly on amt. of sample, cannot be added (or subtracted) algebraically.
eg: Temp, ρ, all conc. unit (mole fr^n, PPM, molality, molarity, normality...)
Molar [any] (~~enthe~~ molar enthalpy, molar gibb's free E, molar energy....)
EMF, resistivity, conductivity, RI(μ), Surface tension, Viscosity.

---

* Extensive = Intensive
  Extensive
  eg: mass (extensive) = ρ (Intensive)
  Vol. (")

* Intensive = ~~Extensive~~ Intensive
  Intensive
  eg: Normality = n factor (Intens.)
  Molarity

---

* STATE PARAMETERS.
  Min. no. of variables/parameters reqd to define a state/property/variable.

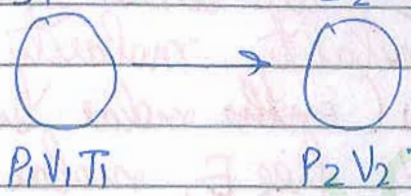
  eg: P, V, T → 3 parameters can define n.
* Min. 3 parameters are reqd to define any state/variable. → P, V & T (to find n)

classmate
Date
Page

✱ STATE fn°

Those fns which are expressed in terms of state parameter.

Value of state fn doesn't depend on path taken

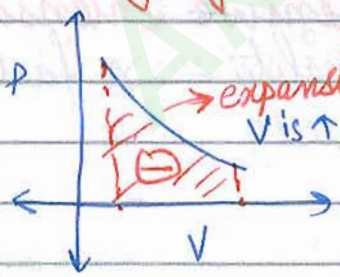


✱ $\Delta S = S_2 - S_1$ = change in state function ∴ It is path independent

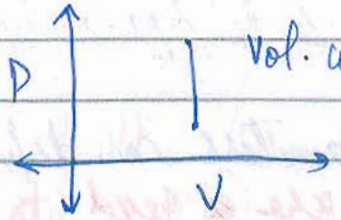
✱ SIGN CONVENTION

WD or anything given

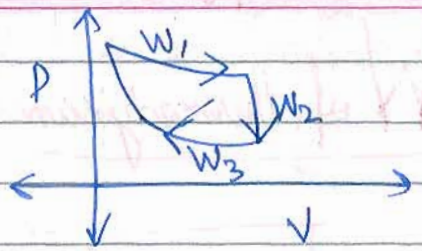
On/To sys from surrounding +VE
By sys to surrounding −VE



✱ Area under P vs V graph is WD.



Chemistry Notes AKS Ghosh



$W_2 =$

$W_1 =$

$W_3 =$ +ve

area under curve for $W_{a1} > W_3$

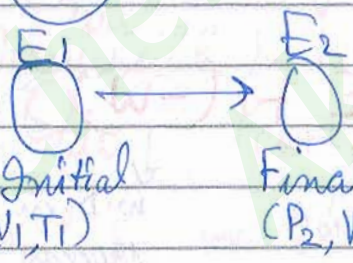
So, net WD -ve.

✱ INTERNAL ENERGY (E → Chemistry, U → Physics)

STATE f^n

Internal Energy = $\sum$ of all forms of E associated with sys.

eg: $O_2(g)$ O=O (bond E, KE, PE, ----)



$E_2 - E_1 = \Delta E$ = Path Independent.

✱ State f^n can't be determined in absolute sense independently. So, always its change is measured. (i.e for a process).

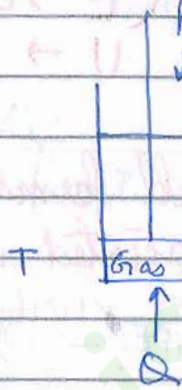
✱ Heat & work are the only 2 non-state f^{ns} in Thermodynamics

* Total degree of freedom for any atom = 3(N) → no. of free atom

FIRST LAW of Thermodynamics

* First law applied to **Ideal Gas**

(i) ✓ For Irreversible isothermal ~~exp~~ expansion/compression



$$-W_{irr} = P_{ext}\,\Delta V$$

W_{irr} → irreversible WD by gas

$P_{ext}\,\Delta V$ → WD on surrounding

* $Q = \Delta E + (-W)$

Q → total heat/E given to sys

ΔE → Internal E change

$-W$ → W.D in ~~irreversible~~ process.

$$\Rightarrow Q_{(irr)} = \Delta E + P_{ext}\,\Delta V$$

→ mathematical stmt. of 1st Law of therms for Irreversible.

If heat is given at constt V.

$$Q_V = \Delta E$$

→ Change in internal E → heat content of sys at constt Vol.

Q_V → heat given to sys.. at constt vol.

Valid ✓ reversible & irreversible

Chemistry Notes AKshamp

* Translation atom = 3 (always in any sys)
* ~~3N-5 (no linear)~~

specific heat

$$q = mS\Delta T = C\Delta T$$

$S = C$ (molar heat capacity)

At constt vol.

$$q_v = C_v \Delta T$$

C_v → molar heat capacity at constt vol. i.e for 1 mole.

$$\Rightarrow q_v = nC_v\Delta T \rightarrow \text{for } n \text{ moles.}$$

$$\Rightarrow \Delta E = nC_v\Delta T$$

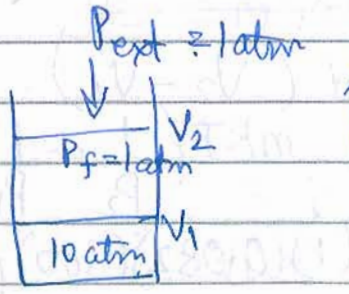
$$\Rightarrow Q_{irr} = nC_v\Delta T + P_{ext}\Delta V$$

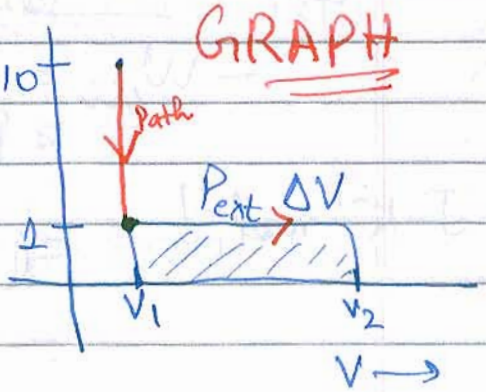
for Irreversible & isothermal

$$Q_{irr} = P_{ext}\Delta V = -W_{irr}$$

* Internal E of any sys of fixed amt. depends only on temp.

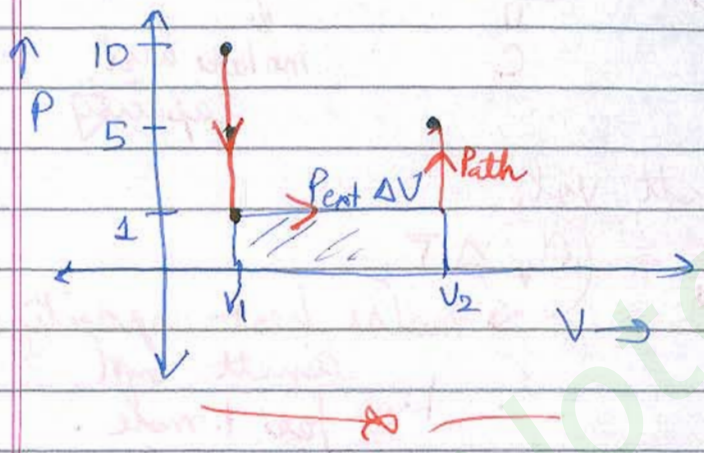
$$\therefore \Delta E = nC_v\Delta T$$





Vibrational degree = 3N-5 (linear)
= 3N-6 (non linear)

P_{ext} = 1 atm. If P_2 = 5 atm.



Q. 1 mole of an ideal gas initially confined in a piston fitted cylinder at 10 atm & 300 K undergo isothermal expansion against 1 atm till P_{gas} decreased to 1 atm. Determine $W_{D_{sys}}$.

$$-W_{irr} = P_{ext}\,\Delta V$$
$$= (1)\left(\frac{(1)(8.314)(300)}{10}\right)$$
$$= 2.46\ J$$
$$= P_{ext}\,(V_2 - V_1)$$
$$= (1)\,(\quad)$$

$$-W_{irr} = P_{ext}\,(V_2 - V_1)$$
$$= P_{ext}\,nRT\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$$

$J\,K^{-1}\,mol^{-1}$

$$= (1)(1)(0.082)(300)\left(\frac{1}{P_2} - \frac{1}{P_1}\right)$$
$$= \left(1 - \frac{1}{10}\right) 8 \cdot 24.6 \times 0.9$$

Chemistry Notes Akshansh

$\Rightarrow -W_{irr} = 22^{\cancel{00}}/4$

Q 2 moles of an ideal gas confined in a piston fitted cylinder at 300 K absorb 5 KJ of heat from surrounding & undergo expansⁿ at against 1 atm till P_{gas} becomes 1 atm. But final T = 400 K.

Determine :- (a) ΔE → monoatomic gas

(b) Initial vol.

$n = 2$, $T = 300$ to 400, $Q = 5$ KJ

$C_V = \frac{3}{2}R$

$\Delta E = n C_V \Delta T$

$= (2)\left(\frac{3}{2}\right)(8.314)(100)$

$= 2494.2$ J

Initial vol.

$Q = \Delta E + P_{ext}\Delta V$

$\Rightarrow P_{ext}\Delta V = 5000 - 2494.2$

$P_{ext}\Delta V \approx 2500$ J

$\Rightarrow V_2 - V_1 = 2507$

$V_2 = \frac{(2)(8.314)(400)}{(1)} \times 10^{-4}$

$= 176 \times 10^{-2}$

$= 1.76.$

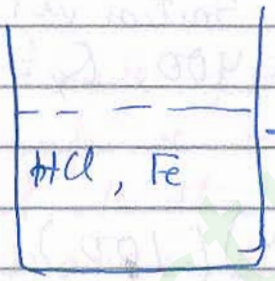
$\Rightarrow V_1 = 1.76 - 2507$

Q. 80g of powdered iron is added to a beaker containing excess of dil. HCl, where following rxn takes place at 300 K (Isothermal)

$$\underset{80/56}{Fe(s)} + \underset{365}{2HCl_{(aq)}} \rightarrow FeCl_2(aq) + \underset{80/56}{H_2(g)}$$

$W_{Dsys} = ?$ $\quad M_{Fe} = 56$

Irreversible



$-W_{Dsys} = P_{ext} \Delta V$

$= (1)\left(\frac{2}{1}\right)(0.082)(300$

$= 24.6 \times 80$

$= 24.6 \times \frac{80}{56} \times 10$

$= 24.6 \times \frac{80}{56} \times 10$

$= 3.5 \text{ J}$

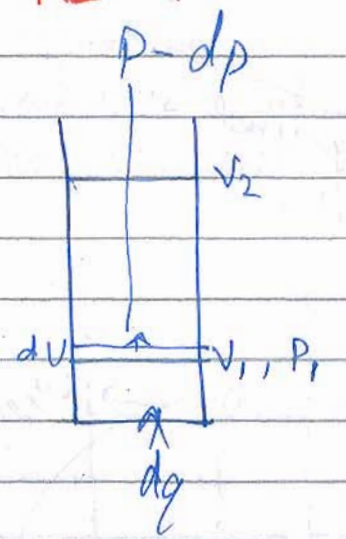
$P_{ext}(V_2 - 0) = P_{gas} \times V_{gas}$

$= 8.314 \times 300 \times \frac{80}{56} \times 10$

$8314 \times 3 = 24942$

$= \frac{24942}{7} = 3563 \text{ J}$

REVERSIBLE PROCESS



$$dq = dE + (-dw)$$

$$= nC_v dt + (P - dp)(dv)$$

$$-w_{rev} = \int -dw = \int P\,dV$$

$$= nRT \int_{V_1}^{V_2} \left(\frac{dV}{V}\right)$$

$$= nRT \ln \frac{V_2}{V_1}$$

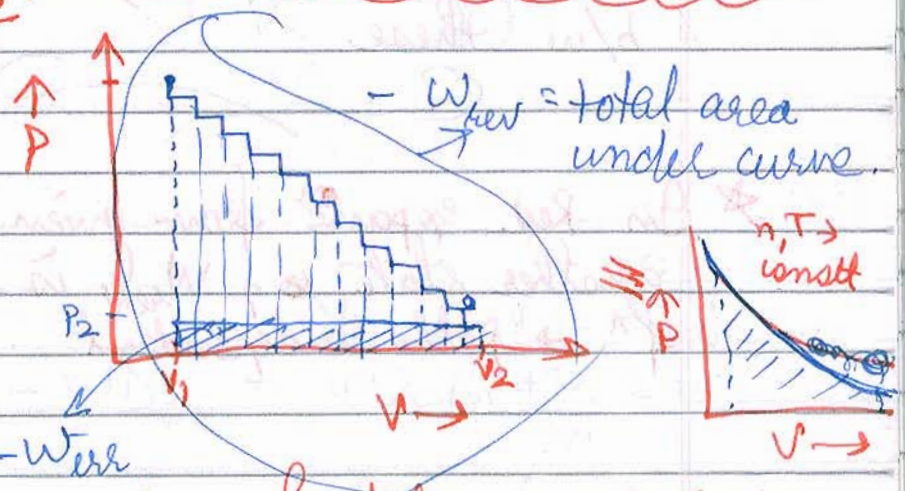
$$-W_{rev} = nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad \left| \begin{array}{l} \Delta T = 0 \\ \Delta n = 0 \end{array} \right\} \text{conditions}$$

W.D in a reversible isothermal process

$$-W_{rev} = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

(∵ It obeys Boyle's law, so, $P \propto \frac{1}{V}$)

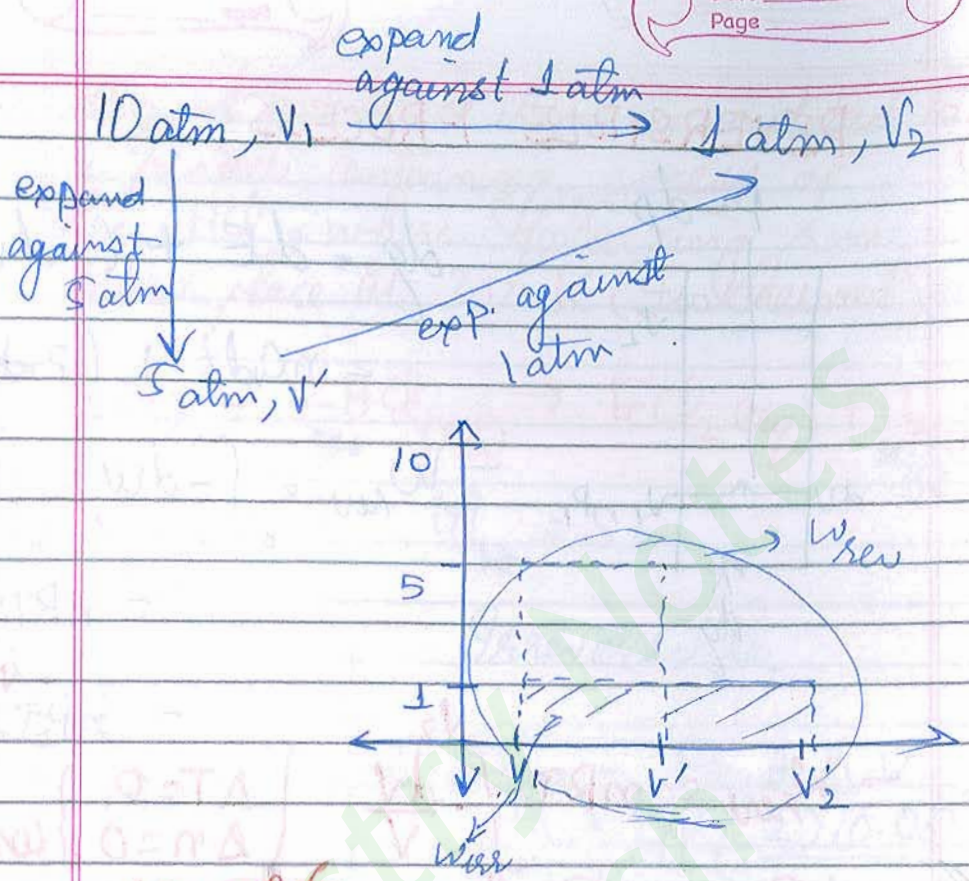
Imp.



★ B/w same i & f states, $W_{rev} > W_{irr}$

Chemistry Notes Assignments

classmate
Date
Page



concept

- W_{rev} : Max.
- W_{irr} : Min

} In isothermal process.

In all other conds, WD is in b/w these

★ In Rev. expansion from given state to another state e.g. W_{rev} is a state fn → path Independent.

Chemistry Notes Akshansh

Q. A 20 L steel cylinder containing 20 moles of He(g) at 300 K starts leaking, but so slowly that T of gas remains const. Determine w_{sys} when cylinder is empty of He.

$w = (20)(0.082)(300) \ln \frac{V_2}{V_1}$ ($V_1 \to 20$)

$\Rightarrow -w_{rev} = (246)(2) \ln \frac{V_2}{20}$

$= 492 \ln \frac{V_2}{20}$.

8.314 J K^{-1} mol

0.082 L atm

246 × 2 = 492

2303 × 492 = 1132476 × 984 = 1131.6

$\ln \frac{V_2}{V_1} = \ln \frac{P_1}{P_2}$.

$\Rightarrow \ln \frac{V_2}{20} = \ln \frac{P_1}{1}$

$\Rightarrow \frac{V_2}{20} = P_1$

$\Rightarrow V_2 = 20 P_1$

$= 20 \frac{(24.6)(20)}{20}$

$V_2 = 492$ L.

$-w_{rev} = 492 \ln \frac{492}{20} \quad 246$

$= 492 \ln 25$

$= 492 (2 \log 5 + 1)$

$-w_{sys} = 492 (2.303)(2.4)$

Q. An ideal gas, initially at 10 atm was taken in a 20 L piston fitted cylinder & allowed to expand through a path which is neither isothermal nor adiabatic, but reversible to 60 L. If $\frac{P}{T}$ is constt, throughout the process, Determine W_{Dsys}

$-W_{Dsys} = nRT \ln$

$-W_{rev} = \int -dw = \int P dV$

$= \int nRT \frac{dV}{V}$

$= nR \int T \frac{dV}{V}$

$P = 10$

$nRT_1 \ln \frac{60}{20} = nRT_2 \ln$

$-W_{rev} = nRT$

$= \int P dV$

$= \int KV dV \quad , \frac{P}{V} = K, \text{say}$

$= K \int V dV$

$= K \left[\frac{V^2}{2}\right]_{20}^{60}$

$(1600) \frac{1}{2} \text{ atm L}^{-1} = K(1800 - 200)$

$= 1600 K.$

Imp: 1 L atm = 104 J
(∵ 0.082 lit atm = 8.3 J)

classmate
Date
Page

$-W = \frac{1}{4}(3600-400)$ lit atm $= 800$ lit atm

$-W_{rev} = 800 \times 104$ J $= 83.2$ KJ

Q. Certain amt. of an ideal gas taken in a piston fitted cylinder is subjected to reversible isothermal expansion from initial ht. of piston = 10 cm to final ht = 50 cm. Determine ht. of piston when work is 1/2 done.

$W_S = nRT \ln 5$.

$W_S = n \times 2.303 RT (0.7)$

Now, $\frac{W_S}{2} = nRT \times 2.3 \log \frac{V_2}{10}$

$= 2 = \frac{0.7}{\log \frac{V_2}{10}}$

$\Rightarrow \log V_2 - 1 = 0.35$

$\Rightarrow \log V_2 = 1.35$

or

$2 \times \log \frac{ht}{10} = n \log 5$

$\Rightarrow \log \left(\frac{ht_2}{10}\right)^2 = 5$

$\Rightarrow ht_2^2 = 500$

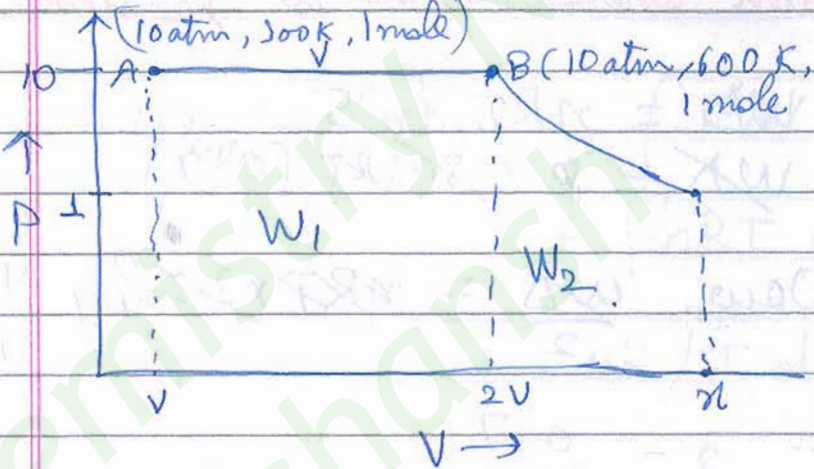
$\Rightarrow ht_2 = 10\sqrt{5} = 22$ cm.

~~$\Rightarrow V_2 = \sqrt{5}$ cm.~~

+2 Chemistry by Akshansh

Q. 1 mole of an ideal gas, initially at 300 K & 10 atm is heated under ~~isobaric~~ isobaric cond^n till T = 25 Then, expanded reversibly & isothermally to 1 atm. Depicting process on P–V diagram, determine, WD

$$-W_{rev} = \int -dw = \int P dV$$



$$WD = P\Delta V$$

$$W_1 = (1)(8.314)(300)\,10(V)$$

$$(10)\left(\frac{nRT}{P}\right) = (10)\left(\frac{8.314 \times 300}{10}\right)$$

~~W_2~~

$$V = \frac{nRT}{P} = (1)(8.314)(600)$$

~~$W_1 = (8.314)(3$~~

$$W_1 = -P\Delta V = -nR\Delta T$$

$$= -(8.314)(300)$$

$$= -2494.2\ J$$

8314
2494.2

$W_2 = -nRT \ln \frac{P_1}{P_2}$

$= -(8.314)(600) \ln \frac{10}{1}$

$= -600R(2.3)$

$\therefore W_2 = -1380\,R.$

$W_1 + W_2 = W_{net} = -1680\,R$

$= -13.9608$

Q. 1 mole of an ideal gas at 300 K and 10 atm is allowed to expand isothermally till final P = 1 atm through a combination of initial reversible expansion to 5 atm followed by irreversible final to 1 atm (a) WD (2) diagram PV (b) Compare the WD calculated with the WDsys if the process is applied in reverse manner i.e initial irr. followed by rev.

$WD_1 = (1)(8.314) \ln \frac{5}{10}$

$= (8.314)(2.3)(-0.3)$

$= 8314 \times 7 \times 10^{-4} \times (-1) = -5.8\,J$

$WD_2 = -(1)(1)(8.314)(300)\left(1 - \frac{1}{5}\right)$

$= (-1)(2494.2)(0.9)$

$= -2244\,J$

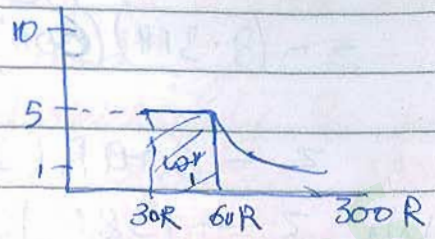
$= -1995.36\,J$

-1740

-3735.36

Now

(b) W_3,



$|W_3'| < W_1$

$\Rightarrow$ $150R <$

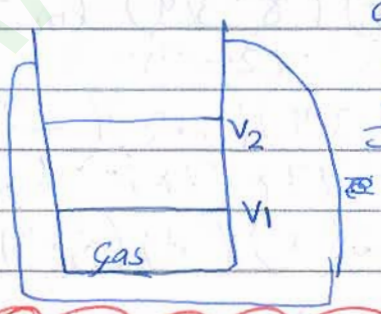
$0.5RT < 0.8RT$

$W_2' = 300R \ln 5 \simeq 2.1R$.

Q.

ADIABATIC PROCESS

(I) REVERSIBLE ADIABATIC PROCESS



$dq = dE + (-dw)$

$= 0 \ (\because dq = 0)$

$\Rightarrow -dw = -dE$

$= -nC_v dT$

$\Rightarrow W = \int -dw = \int_{T_1}^{T_2} -nC_v dT$

☆ Take $C_v \rightarrow$ Independent of $T \rightarrow$ unless specified or given a fⁿ of T

Chemistry Notes Akshansh

$\Rightarrow \boxed{-W = nC_v(T_1 - T_2)}$

Decrease in Internal E

$T_1 > T_2$ ($\because -W > 0$)

So, Cooling takes place.

Hence, adiabatic expansⁿ always lead to cooling (T_1 to T_2 & $T_2 < T_1$)

☆ In adiabatic process :-

WD by sys = $-\Delta E$ of sys

decrease in internal E.

Now, $PdV = -nC_v dT$

$\Rightarrow \frac{nRT}{V} dV = -nC_v dT$

$\Rightarrow \frac{R}{VC_v} dV = -\frac{dT}{T}$

$\Rightarrow \frac{R}{C_v} \int_{V_1}^{V_2} \frac{dV}{\sigma V} = -\int_{T_1}^{T_2} \frac{dT}{T}$

$\Rightarrow \left(\frac{R}{C_v}\right) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2}$

$\gamma - 1$

$\Rightarrow \left(\frac{V_2}{V_1}\right)^{\gamma-1} = \frac{T_1}{T_2}$ ($\because \frac{R}{C_v} = \gamma - 1$)

Or $TV^{\gamma-1} = \text{Constt}$

$\Rightarrow PV \cdot V^{\gamma-1} = \text{Constt}$ (nR)

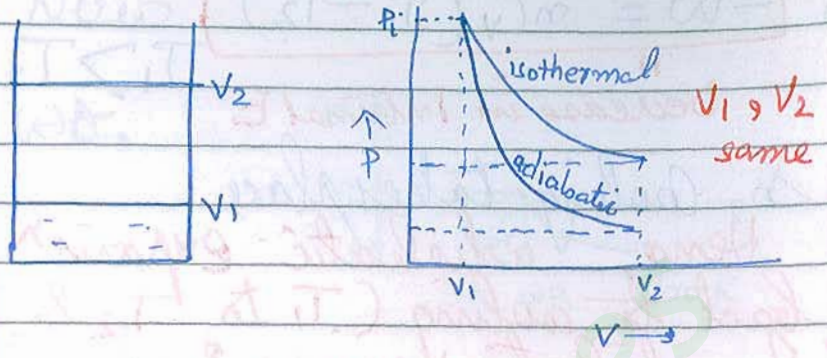
$\Rightarrow PV^{\gamma} = \text{Constt}$

$\Rightarrow P^{1-\gamma} T^{\gamma} = \text{Constt}$

☆ Only for Adiabatic & ☆ Reversible expansⁿ

FZ Chemistry Notes Asmarh

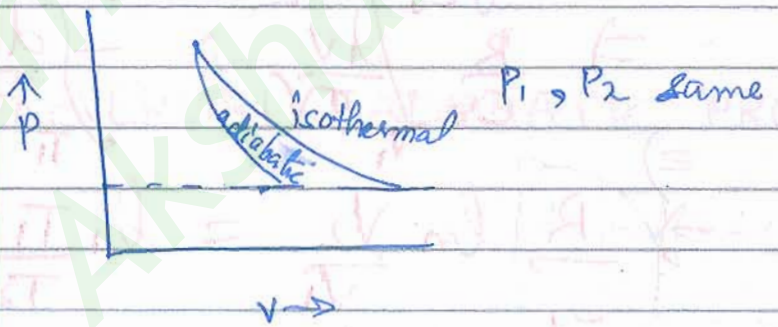
classmate
Date 9.7.10
Page



* If we go from same initial state to same final vol., if we expand →

✓ Isothermally : more WD
✓ Adiabatically : less WD.

* Adiabatic curve : Rate of change (slope) : More
Isothermal curve : " " : less



* P vs V graph :
Slope : Rate of change
Area under curve : WD.

Chemistry Notes Akshansh

Q. 1 mole of a monoatomic ideal gas, initially, at 300 K, is allowed to expand reversibly & adiabatically till volume increased to 5.2 times initial volume, $C_v = \frac{3}{2}R$, WD = ?

$$W = \int_{T_1}^{T_2} (-1)\left(\frac{3}{2}R\right) dt$$

$TV^{\gamma-1}$ = constt. $\quad \gamma = \frac{5}{2}$

$$\Rightarrow (5.2)^{\gamma-1} = \frac{300}{T_2}$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} = (5.2)^{\frac{2}{3}}$$

$$\Rightarrow T_2 = \frac{300}{(5.2)^{2/3}}$$

$$= \frac{300}{(27)^{1/3}}$$

$$\Rightarrow T_2 = 100$$

$$\Rightarrow W = (-1)\left(\frac{3}{2}R\right)(-200)$$

$$W = 300R \text{ Joules}$$

$$= 2500 \text{ J}$$

$$= 2.5 \text{ KJ}$$

2.2

152
52
104
260
270 4

831
3
2493

+2 Chemistry Notes Aishansh

Q. 1 mole of an ideal gas, initially at 10 atm & 300 K is allowed to expand reversibly to a final P = 1 atm T = 150 K. Expansion involve initial isothermal process followed by an adiabatic process. If $C_v = 2R$, $C_p = 3R$, $\gamma = \frac{3}{2} - 1$

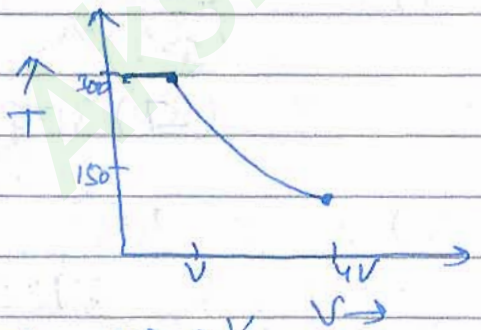
$C_p =$

(i) Draw T - V diagram
(ii) P - V diagram
(iii) Determine net W_{Sys}.

$P_i = 10$ atm $\quad T_i = 300$ K
$P_f = 1$ atm $\quad T_f = 150$ K
$n = 1$

(iii) $-W_{adia.} = (1)(2R)(150)$
$= 300R = 2.5$ KJ.

(i)

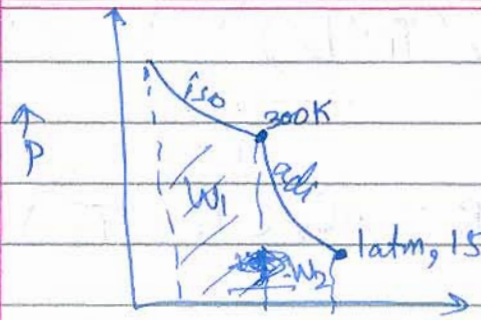


$\frac{300}{150} = \left(\frac{V_2}{V_1}\right)^{1/2}$

$\Rightarrow 4 = \frac{V_2}{V_1}$

$\Rightarrow V_2 = 4V_1$

(ii)



$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$

$\Rightarrow \frac{1}{10} = (4)$

$P^{\frac{1-\gamma}{\gamma}} T = \text{constt}$

$\Rightarrow \left(\frac{P_1}{P_1}\right)^{-1/3} = \frac{T_2}{T_1} \Rightarrow P_1 = 8.$

(iii) $W_{adiabatic} = 2.5\ KJ = 300R$

$W_{isothermal} = (1)(R)(300)\ln\frac{P_1}{P_2} \to 10,\ 8$

$= 300R(2.3)(0.6)$

$= 408R$

$= (2.3)R \times 300(0.7 - 0.6) = 69R$

$W_{Total} = 708R$

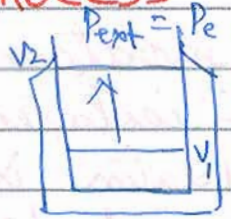
$= 5885.48\ J$

$= 5.88\ KJ$

$W_{Total} = 369R$

$= 3.0747\ KJ$

ADIABATIC IRREVERSIBLE PROCESS



$q = \Delta E + P_e \Delta V$

$q = 0$ (adiabatic)

$\therefore -W_{irr} = P\Delta V = -\Delta E$

$= -nC_v(T_2 - T_1)$

$\Rightarrow -W_{irr} = P_e \Delta V = nC_v(T_1 - T_2)$

classmate
Date
Page

* $P_e(V_2 - V_1) = nC_V(T_1 - T_2)$

$\Rightarrow P_e\left(\frac{T_2}{P_2} - \frac{T_1}{P_1}\right)R = nC_V(T_1 - T_2)$

$\Rightarrow T_2\left(\frac{P_e}{P_2}R + C_V\right) = T_1\left(\frac{P_e}{P_1}R + C_V\right)$

$\Rightarrow T_2 = \left(\frac{\frac{P_e}{P_1}R + C_V}{\frac{P_e}{P_2}R + C_V}\right)T_1$

Understand

If $P_e = P_2$.

$\Rightarrow T_2 = \left(\frac{\frac{P_2}{P_1}R + C_V}{R + C_V}\right)T_1$

$\Rightarrow T_2 = \left(\frac{\frac{P_2}{P_1}R + C_V}{C_P}\right)T_1$

To find T_2

Q. 1 mole of an ideal monoatomic gas present in a 10 L isolated flask, initially at 10 atm is allowed to expand against 1 atm till $P_f = 1$ atm. Determine WD by sys

$C_V = \frac{3}{2}R$

12 Chemistry Notes Akshansh

$n = 1$, $V_2 = 10\,L$, $P_1 = 10\,atm$, $P_2 = 1\,atm$.

$C_V = \frac{3}{2}R$

$P_e \Delta V = -nC_V(T_2 - T_1)$

$T_2 = \frac{PV}{nR} = \frac{(10)(10)}{(1)(8.3R)}$

$T_1 = \frac{100}{R}$

$T_2 = \frac{1}{R}\left(\frac{R + \frac{3}{2}R}{\frac{10}{R} + \frac{3}{2}R}\right)\frac{100}{R}$

$= \frac{1 + \frac{15}{10}}{\frac{9}{2} + \frac{3}{2}} = \frac{\frac{16}{10}}{\frac{5}{2}} = \frac{16}{25}$

$T_2 = \frac{64}{R}$

$T_2 - T_1 = \left(\frac{64}{R} - \frac{100}{R}\right) = \left(\frac{6400}{R} - \frac{100}{R}\right)$

$= \frac{64R - 100}{R} = \frac{6300}{R}$

0.082
8.314

$\Rightarrow W = nC_V \Delta T$

$= (1)\left(\frac{3}{2}R\right)\left(\frac{36}{R}\right) \times 100$

$-W = 5.4\,kJ$

$= \frac{3R}{2}\left(\frac{6300}{R}\right)$

✡ ENTHALPY (H)

✡ $H = E + PV$ = state f^n

$\Rightarrow dH = dE + P\partial V + V\partial P$

$\Rightarrow \Delta H = \Delta E + \underbrace{P\Delta V}_{(1)} + \underbrace{V\Delta P}_{(2)}$

MASTER EQN.

(1) P को constt रखकर V को change किया

(2) जो V की value आई उसे constt रखकर P को change किया

If P = constt.

$\boxed{\Delta H = \Delta E + P\Delta V = q_p} = nC_p\Delta T$

only for ideal

$\Delta H = \Delta E + P\Delta V = nC_p\Delta T = q_p \neq q$

If P is assumed constt

Q 1 mole of an ideal gas initially at 300 K, 5L is heated, till V_f = 8L under isobaric cond^n. Determine ΔH, $C_V = 20\ J\ K^{-1}\ mol^{-1}$

Chemistry Notes Aksmansh

$\Delta H = n\Delta T(-R) + P(-3)$

$= (1)(\Delta T)(-R) +$

$P(5) = 300R$

$P(8) = TR$

$\Rightarrow \frac{5}{8} = \frac{300}{T}$

$\Rightarrow T_2 = 480\ K.$

$\Rightarrow \Delta H = (1)(20+R)(180)$

$= (20 + 8.314)(180)$

$= (28.314)(180)$

$= 5.0958$

$= 5.1\ KJ$

6 2831
18
12 26 48
2831
5 0 9 5 8

Q. At 100°C, 1 atm $\Delta H_{vap}(H_2O) = 40.6\ KJ/mol$

$\Delta E_{vap}(H_2O)$ → same condⁿ = ?

$\Delta H_{vap}(H_2O) = 40.6\ KJ/mol$

$T = 373K$, $P = 1\ atm$

$\Delta E_{vap}(H_2O) = ?$

$H_2O(l) \rightarrow H_2O(v)$

$\Delta H = \Delta E + P\Delta V$

$\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$

$\Rightarrow \Delta E = \Delta H - \Delta n_g RT.$

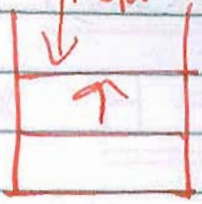
$= (1-0)R(373)$

$\Rightarrow \Delta H - \frac{373R}{1000} = \Delta E.$

$\Rightarrow \Delta E = 37.7\ KJ.$

+2 Chemistry Notes Akshansh

★ Expansion against zero P = Free expansion



$q = \Delta E + P\Delta V = 0$

In case of free expansn
→ Process is adiabatic ✗
isothermal
✓ either both
✓ or none.

★ 2ND LAW
(determines dirⁿ of spontaneous change)

Acc to 2nd law,
Heat cannot be transferred completely from a colder to a hotter reservoir without doing some external work & vice versa.

OR

A spontaneous process leads to ↑ increase in entropy of UNIVERSE (sys + surrounding)

V.V Imp

★ ENTROPY : defined in reversible process as

$$dS = \frac{dq_{rev}}{T}$$

$$dq_{rev} = dE + PdV$$

$$\Rightarrow \frac{dq_{rev}}{T} = \frac{dE}{T} + \frac{PdV}{T}$$

Chemistry Notes Wykansa

* All changes in surrounding occur reversibly

classmate Date Page

$$\Rightarrow \int dS = \int \frac{nC_v\,dt}{dT} + \int \frac{nRT\,dV}{V \times T}$$

$$\Rightarrow \boxed{\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}}$$

→ MASTER Eqn → valid everywhere
→ state fn
→ defined for reversible process

Q. 1 mole of an ideal gas, initially at 10 atm & 300K is allowed to expand against 1 atm till P_f = 1 atm. Determine ΔS_{sys} = ?, $\Delta S_{surrounding}$ = ? Process is isothermal

$$\Rightarrow \Delta S_{sys} = (1)(R) \ln \frac{10}{1}$$

$$\Rightarrow 2.303R = \Delta S$$

$$\Rightarrow \Delta S_{sys} = 19.13793 = 19.13$$

2.303 × 8.31 = 23.03 + 16.9224 + 184.24 = 191.3793

$$q_{sys} = P_{ext}\,\Delta V = (1 - 0.1)\,nRT = 270R$$

$$q_{surr} = -q_{sys} = -270R$$

$$= (q_{rev})_{surr}$$

$$\Delta S_{surr} = \frac{-270R}{300} = -0.9R = -7.3$$

$\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr}$

$= 1.4R$

⁂ In isothermal irreversible expansion process is always spontaneous
In it $\Delta S_{sys} > \Delta S_{surr}$
So, $\Delta S_{universe}$ always +ve.

⁂ In isothermal reversible expansion,

$\Delta S_{universe} = 0$, ∵ entropy ↑ on one side = entropy ↓ in other process (Sys in equi with surr)

Q. For an ideal gas, its $C_V = 20 - 10^{-3}T$ (SI)
If 1 mole of this gas is heated at constt volume from 300 to 400 K, determine, $\Delta S = ?$

$\Delta S = n C_V \ln \frac{T_2}{T_1}$

$= (1) C_V \ln \frac{4}{3}$

$= (20 - 10^{-3}T)(2.3)(0.12)$

$= (0.1)$

$20 - 0.4$
$= 19.6 - 19.$
$19.7 - 19.6$

60
48

3 2 2 3
1 2
2 7 6 2
5 5 2

$dS = n C_V \frac{dT}{T}$

$\int dS = \int (20 - 10^{-3}T) \frac{dT}{T}$

$\ln \frac{400}{300}$

$\ln(400) - \ln(300)$

$\Rightarrow \Delta S = 20 \ln \frac{T_2}{T_1} - 10^{-3} \Delta T$

$= 20(2.3)(0.12) - (0.1)$

$= 5.52 - 0.1$

$\Rightarrow \Delta S = 5.42 \text{ J/K}$

$\Delta S = n C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

$P \propto \frac{1}{V}$, n, T const.

~~$\Delta S = nR \ln \frac{P_1}{P_2}$~~

$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$\Rightarrow \frac{V_2}{V_1} = \left(\frac{P_1}{P_2}\right)\left(\frac{T_2}{T_1}\right)$

$\Rightarrow \Delta S = n \left[C_V \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \right]$

$\Rightarrow \Delta S = n C_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$

* → If initial & final P is given, ΔS can be found.

+2 Chemistry Notes Akshansh

Entropy : Physical Significance

- ✓ Entropy is the measure of randomness (disorderness, chaos)
- ✓ More ordered Sys, Entropy ↓
- ✓ entropy of sys ↑, with ↑ in randomness.
- ✓ For a given substance, its solid state has min. entropy & gaseous state has max. entropy. Liq^{d} state has intermediate value b/w them.

✱ MOLAR ENTROPY of a PURE substance
→ for 1 mole

- ✓ For the same state of matter, the harder substance has lower entropy than softer substance
- ✓ For the same state & atomicity (no. of atoms) higher the molar mass, greater the entropy.
  eg: in noble gas, He : Entropy min
  Rd : Entropy max.
- ✓ For comparable molar mass & same state, greater the atomicity, higher the entropy.
  ∵ atomicity ↑, no. of bonds ↑,
  so, no. of orient^{ns} in 3D ↑,
  so, entropy ↑.

Chemistry Notes Branch

classmate
Date 14·7·10
Page

✓ If In same state, greater the intermolecular force of attⁿ, smaller the entropy.

Ionic solids : Comparing molar entropy

In case of ionic solids, greater the electrostatic attⁿ b/w the oppositely charged ions, smaller the molar entropy.

- First compare charge.
- If |charge| is same, then see size. $F \propto \frac{1}{r^2}$, $F \propto q$.

eg: $\overset{+1}{Na}\overset{-1}{F}$, $\overset{+1}{K}\overset{-1}{F}$ $\quad MgO < NaF < KF$
charge high, size less, size more

$\overset{+2}{Mg}\overset{-2}{O}$.

Heat change without T-change

atm $\quad H_2O(l) \longrightarrow H_2O(v) \quad \Delta H = 40.6\ KJ/mol$

VIP

H_2O ... dq

100°C

$$\Delta S_v = \frac{q_{rev}}{T} = \frac{\Delta H_v}{T_b^\circ}.$$

$$\Rightarrow \Delta S_{transⁿ} = \frac{\Delta H_{transⁿ}}{T_{transⁿ}}$$

Only at transⁿ & temp., heat supplied gives full transⁿ. So, $\Delta S_{transⁿ}$ can be effectively evaluated.

Chemistry Notes by Akshansh

eg: If $T < T_{transn}$, then 1st thy, T would ↑ to T_t. Then, phase change would occur.

Q. $\Delta S = ?$ for formⁿ of $n=1$ ice at $-3°C$ for sys, surr., universe
$\Delta H_{fus}(ice) = 6$ KJ/mol.

$\Delta S = \frac{dq_{rev}}{T}$ $\quad \Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}}$

$H_2O(l) \rightarrow H_2O(s)$ $\quad \Delta S_{tr} = -\frac{6000}{273} 22$

$\Rightarrow \Delta S_{tran\ of\ sys} = -22 \text{ J K}^{-1}\text{mol}^{-1}$

$q_{sys} = -600$ J

$q_{surr} = -q_{sys} = 6000$ J

$\Delta S_{surr} = \frac{6000}{T_{surr}} = \frac{6000}{270} = 22.2$ J K^{-1}mol^{-1}

$\Delta S_{universe} = 2$ J K^{-1} mol^{-1}. > 0
So, process is spontaneous.

Q. Determine ΔS for transformⁿ of 1 mole of H_2O at $-10°C$. to 1 mole of ice at $-10°C$.
$C_p(H_2O)_l = 75$ J K^{-1} mol^{-1}
$\Delta H_{fus} = 6$ KJ K^{-1} mol^{-1}
$C_p(H_2O)_{(s)} = 60$ J K^{-1} mol^{-1}

12 Chemistry Notes Akshansh

$H_2O(l) \longrightarrow H_2O(s)$

$-10^\circ C$ $\quad$ $-10^\circ C$

path ↓

~~ΔS~~ ~~$\Delta S_1 + \Delta S_2$~~

$H_2O(l) \xrightarrow{\Delta S_1} H_2O(l) \xrightarrow{\Delta S_2} H_2O(s) \xrightarrow{\Delta S_3} H_2O(s)$

$-10^\circ C$ $\quad$ $0^\circ C$ $\quad$ $0^\circ C$ $\quad$ $-10^\circ C$

$\Delta S_1 = (1)(75) \ln \frac{273}{263}$ $\quad \left(nC_p \ln \frac{T_2}{T_1}\right)$

$\Delta S_2 = \frac{-6000}{273}$

$\Delta S_3 = (1)(60) \ln \frac{263}{273}$

$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$

✡ Std. Molar Entropy (S_m°) & ΔS° of rxn.

* A perfectly crystalline substance has 0 entropy.
* At absolute zero, entropy of a subs. = 0 ∵ subs. is perfectly crystalline.

S_1 $\quad$ S_2

eg: $Fe \longrightarrow Fe$

$0\ K$ $\quad$ $298\ K$

$\Delta S = S_2 - S_1 = S_2 = S_m^\circ$

($S_1 = 0$)

Assume: At absolute zero, entropy of subs = 0.

Std. molar entropy of a substance.

Defin^n: S_m° is the entropy change when 1 mole of the substance in its std. state is heated from 0 K to the given temp.

—— ∞ ——

Useful for numerical

$$\Delta S^\circ_{\text{of sys}} = \sum S_m^\circ(\text{Product}) - \sum S_m^\circ(\text{reactant})$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

$$= \Delta S^\circ + \left(\frac{-\Delta H^\circ}{T}\right)$$

(* ΔH° can be found from $A + B \rightarrow P + Q$)

$$\Rightarrow -T\,\Delta S_{\text{univ}} = \Delta H^\circ - T\Delta S^\circ = \Delta G^\circ$$

$\Delta S_{\text{univ}} > 0$, $T > 0$.

So, $-T\Delta S_{\text{univ}} < 0$

For a process to be spontaneous $-T\Delta S_{\text{univ}} < 0$ so that $\Delta H - T\Delta S^\circ < 0$. $\Rightarrow \Delta G^\circ < 0$.

$$\Rightarrow -T\Delta S_{\text{univ}} = \Delta H^\circ - T\Delta S^\circ = \Delta G^\circ$$

Std. state Gibb's free Energy of rxn.

Q. Determine the ΔG° for following rxn:

$C_{(gr)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H^\circ = -83\ KJ\ mol^{-1}$

ΔS_m° $C_{(gr)} = 6\ J\ K^{-1}$

$(H_2) = 131\ J\ K^{-1}$

$(CH_4) = 212\ J\ K^{-1}$

$\Delta S_m^\circ = (212) - (268)$

$= -56\ J\ K^{-1}$

$\Delta G^\circ = (-83 \times 1000) + (56)(298)$

$= -83000 + 18688 = -64312\ J\ K^{-1}\ mol^{-1}$

$= -64.3\ KJ\ K^{-1}$

Spontaneous ✓

Q. Consider the following rxn →

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

ΔH_f° : $CO_2 \rightarrow -394\ KJ\ mol^{-1}$

$CaO \rightarrow -656\ KJ\ mol^{-1}$

$CaCO_3 = -1170\ KJ\ mol^{-1}$

ΔS_m° $CaCO_3 = 93\ J\ K^{-1}$

$CaO = 46\ J\ K^{-1}$

$CO_2 = 186\ J\ K^{-1}$

$\frac{22}{7} = 3.142857$

T = ? at which rxn will turn spontaneous from non spont.

$\Delta S_m^\circ = +139\ J\ K^{-1}\ mol^{-1}$

$\Delta H_f^\circ = +120\ KJ\ K^{-1}\ mol^{-1}$

$\Delta G^\circ = +120 - T(+140)$

$= +120 - \frac{140T}{1000}$

$+120 - 140T < 0$

$\Rightarrow 140T < 120000$

$\Rightarrow T < \frac{120}{140} \approx 0.8571$

$\Rightarrow T_{max} = 0.8\ K$

$T = 857.142857\ K$

If $T > 857\ K$, spontaneous

$T < 857K$, non spont.

✱ EQUI & 2nd LAW

$A + B \rightleftharpoons X + Y$

Rxn Quotient (Q):

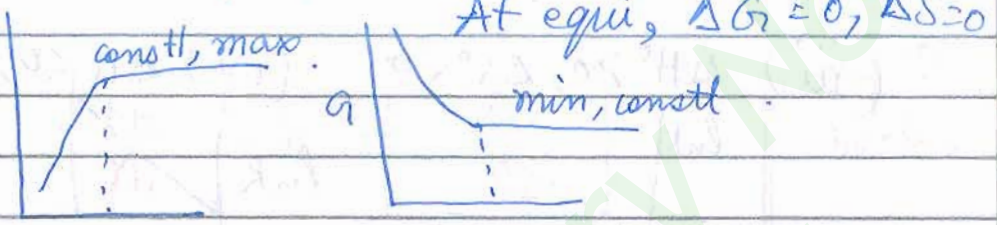
Spontaneous dirⁿ is the one in which Q tends to K, $Q \to K$

Chemistry Notes Akram

classmate
Date
Page

✱ At equi, S becomes max
G becomes min.
$\Delta G \geq 0$, $\Delta S = 0$.
S & G stop changing their values.

From Graph,



At equi, $\Delta G = 0$.
To find ΔG at other pts,

✱✱ $\Delta G = \Delta G^\circ + RT \ln Q$

At equi,
$0 = \Delta G^\circ + RT \ln K$
$\Rightarrow \Delta G^\circ = -RT \ln K$ ✱✱

Now, $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$
$\div -RT$
$\Rightarrow \ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$

✱✱ $\Rightarrow \ln K = \left(\frac{-\Delta H^\circ}{R}\right)\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$

↳ K vs $\frac{1}{T}$ graph,
Slope $= \frac{-\Delta H^\circ}{R}$, Intercept $= \frac{\Delta S^\circ}{R}$

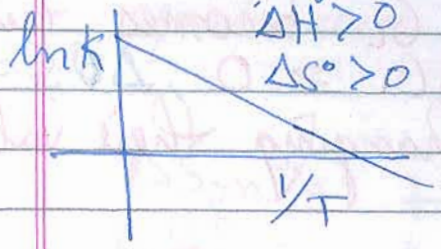
✱ $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$ ✱✱

+2 Chemistry Notes Akshansh

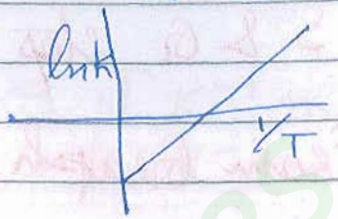
classmate
Date
Page

Graphs

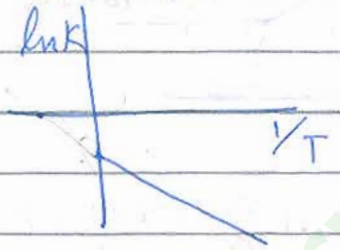
(i) $\Delta H^\circ > 0$, $\Delta S^\circ > 0$



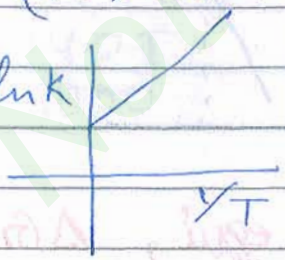
(ii) $\Delta H^\circ < 0$, $\Delta S^\circ < 0$



(iii) $\Delta H^\circ > 0$, $\Delta S^\circ < 0$



(iv) $\Delta H^\circ < 0$, $\Delta S^\circ > 0$



Q For a reversible rxn,

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ ~~K_{eq}~~

~~K~~ $\log K_{p(atm)} = 4.2 - \frac{120}{T}$ (SI)

Q Determine ΔH°, ΔS° & (ΔG° at 500K)

$\frac{\Delta S^\circ}{R} = 4.2$

$\Delta S^\circ = (4.2)(8.314)(2.3)$

$\Delta S^\circ = 34 \text{ KJ mol}^{-1}$

$\frac{\Delta H^\circ}{R} = 120$

$\Rightarrow \Delta H^\circ = 120(8.3)(2.3)$

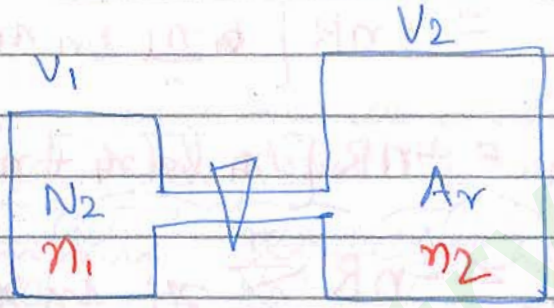
$= 2760 \times 2.3 = 329.08$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= 2300 - 500(80)$$

$$= -37.7 \text{ KJ K}^{-1} \text{ mol}^{-1}$$

Spontaneous.



On mixing
S_{N_2}, S_{Ar} ↑ both.

Entropy change in mixing of non-reacting ideal gas at constt P, T,

$$\Delta S_1 = n_1 R \ln \frac{V_1+V_2}{V_1}$$

$$\Delta S_2 = n_2 R \ln \frac{V_1+V_2}{V_2}$$

$$\Delta S_{mix} = \Delta S_1 + \Delta S_2$$

$$\Delta S_{mix} = R\left[n_1 \ln \frac{V_1+V_2}{V_1} + n_2 \ln \frac{V_1+V_2}{V_2} \right]$$

> 0 (+ve)

Since, P, T → constt, so, By Avogadro Hypothesis
$n \propto V \Rightarrow V_1 + V_2 \propto n_1 + n_2$.

$$\Rightarrow \Delta S_{mix} = R\left[n_1 \ln \frac{1}{x_1} + n_2 \ln \frac{1}{x_2} \right]$$

x_1 → mole fraction

P, T constt
entropy change.

gas constt.

$\Rightarrow \Delta S_{mix} = -(R) \sum (n_i \ln x_i)$

n_i : no. of moles.

x_i : mole fr^n

Change in entropy at constt T, P on mixing n gases.

$= -nR \left[\frac{n_1}{n} \ln x_1 + \frac{n_2}{n} \ln x_2 \right]$

$= -nR \left[x_1 \ln x_1 + x_2 \ln x_2 \right]$

$$\Delta S_{mix} = -nR \sum_{i=1}^{n} x_i \ln x_i$$

The End

F2 Chemistry Notes Akshansh

Classmate
Date 16.7.10
Page

CH - COORDINⁿ COMPOUNDS

(or Complex Salt/Compd)

✓ Chapter deals with discussion of SALTS.

✱ Coordinⁿ compds are the salts which when dissolved in H_2O, ionise into a simple & an complex ion

Simple salts : Ionise completely in aq. form.

eg: $NaCl \rightarrow Na^+ + Cl^-$

$NaCN \rightarrow Na^+ + CN^-$

$Al_2(SO_4)_3 \rightarrow Al^{3+} + SO_4^{2-}$

Double Salts : More than 1 salts together, ionise completely

MOHR SALT $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O \rightarrow Fe^{2+} + SO_4^{2-} + NH_4^+$

eg $FeSO_4 + (NH_4)_2SO_4$

eg $KCl \cdot MgCl_2 \cdot 6H_2O \rightarrow K^+ + Cl^- + Mg^{2+}$

CARNALITE

eg 2 $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O \rightarrow K^+ + SO_4^{2-} + Al^{3+}$

non poisonous

$K_3[Fe(CN)_6] \rightarrow \underset{\text{Simple ion}}{3K^+} + \underset{\text{complex ion.}}{[Fe(CN)_6]^{3-}}$

Complex ion.

It won't give property of all the 3 ions present in it.

✱ Coordinⁿ compd. doesn't give independent tests of all individual ions present in the compd.

LATER TOPICS : ✓Bonding Theory
✓Isomerism
✓Magnetic Prop.
✓Color & Spectra
✓Metal Carbonyls

classmate
Date
Page

Complex salts
eg : $[Co(NH_3)_6]Cl_3$, $[Cu(NH_3)_4]SO_4$,
$K_3[Fe(CN)_6]$, $K_4[FeF_6]$ ----

✡ IUPAC NAMING.

General Conventions

$K_3[Co(CN)_6] \rightarrow 3K^+ + [Co(CN)_6]^{3-}$

Co : central metal

$C\equiv N$, NH_3, F^- } They are attached to the central metal. They are all lewis bases, called as LIGANDS.

Ligand : They are LB which form dative (coordinate) bond with the central metal in complex. It can be neutral, anionic, cationic (rare) ($\ddot{N}=O$ (only one))

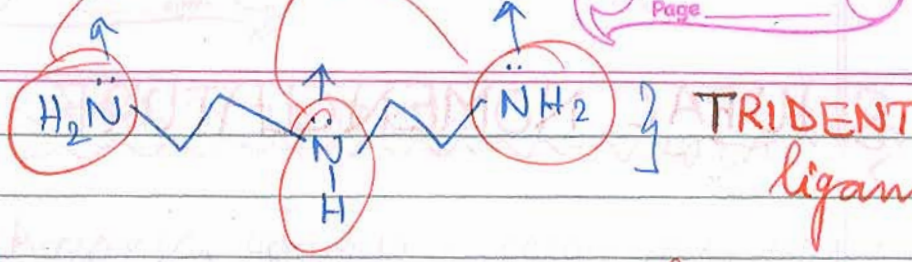
✡ 1 grp can donate only 1 lone pair

$H_2\ddot{O}:$, $\ddot{N}H_2-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$
$\ddot{N}\equiv\bar{C}:$
$O=\ddot{N}-\ddot{O}:$
} can donate only 1 lone pair to central metal. Hence, they are called MONODENTATE LIGAND.

CH_2-CH_2 (each NH_2 donates a lone pair)
$O=C-O:$, $O=C-O:$
} 2 separate grps are here. So, they can donate 2 LP's

BIDENTATE LIGAND

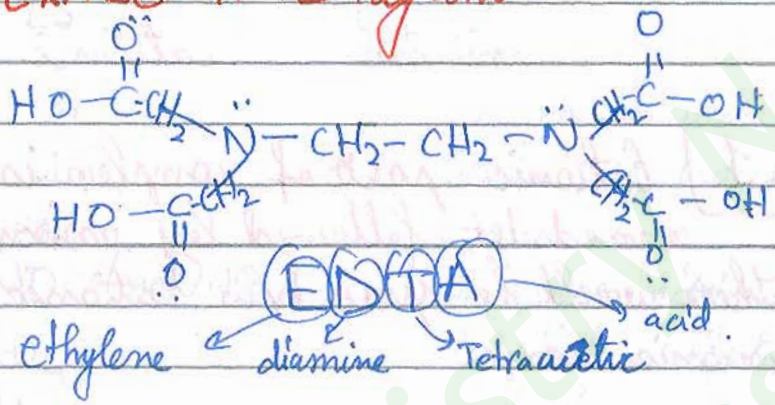
3 separate grps. Can donate 3 LPs



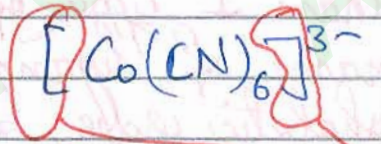
TRIDENTATE ligand.

Mono, bi, tri - - - - hexadentate

HEXADENTATE ligand :-



* Coordin^{n} no:- No. of coordinate bonds formed by ligand with the central metal. In case of monodentate ligand, coordin^{n} no. = no. of ligands attached to central atom.



Coordin^{n} sphere : Signifies nothing goes out of it.

+2 Chemistry Notes Akshansh

8 IUPAC NOMENCLATURE

$[Ni(CO)_4]$ $Na_3[Cu(CN)_4]$ $[Co(NH_3)_6]Cl_3$

$Na_3[Cu(CN)_4] \rightarrow 3Na^+ + [Cu(CN)_4]^{3-}$

$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3Cl^-$

$[Ni(CO)_4]$ — neutral

$[Cu(CN)_4]^{3-}$ — anionic

$[Co(NH_3)_6]^{3+}$ — cationic.

Rule 1 Cationic part of complex is named 1st followed by anionic part.

✓ There would be space b/w cationic & anionic name.

Rule 2 Naming Complex Part :-

In writing name of complex part of salt, ligands will be named 1st.

Name : Ligands → then → central metal.

When more than 1 type of ligands are present, name of ligands are written in alphabetic order, irrespective of their charge.

In alphabetical order, original name of ligand are considered, not initial prefixes (like di, tri ....).

eg: in this → $[Cr(H_2O)ClBr(NH_3)_2NO]I$.

Rule 3 : Naming ligands.

NAMING LIGANDS

(a) Anionic ligands : name ends in –'o'

Ligands	Name
F^-	Fluoro or fluorido
Cl^-	Chloro or chlorido
Br^-	Bromo or bromido
I^-	Iodo or iodido
CN^-	Cyano
NO_2^- (not NO_3^-)	Nitro or nitrito-N-
SO_4^{2-}	Sulphato / sulfato
H^-	hydrido
OH^-	hydroxo
NH_2^-	amido (not amino)
* N^{3-}	nitrido
* N_3^-	azido
$C_2O_4^{2-}$	oxalato
O^{2-}	oxo
O_2^{2-}	peroxo
$S_2O_3^{2-}$	thiosulphato
* HS^-	mercapto
S^{2-}	thio
ONO^-	nitrito-O-
NH^{2-}	imido
$C_5H_5^-$	cyclopentadienyl
SCN^-	thiocyanato
~~CNS^-~~ *	

classmate Date Page

NAMING LIGANDS

(a) Anionic ligands : name ends in –'o'

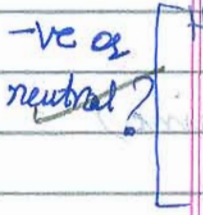
ligands	Name
F^-	Fluoro or fluorido
Cl^-	Chloro or chlorido
Br^-	Bromo or bromido
I^-	Iodo or iodido
CN^-	Cyano
NO_2^- (not NO_3^-)	Nitro or nitrito-N-
SO_4^{2-}	Sulphato / sulfato
H^-	hydrido
OH^-	Hydroxo
NH_2^-	Amido (not amino)
* N^{3-}	nitrido
* N_3^-	azido
$C_2O_4^{2-}$	oxalato
O^{2-}	oxo
O_2^{2-}	peroxo
$S_2O_3^{2-}$	thiosulphato
* HS^-	mercapto
S^{2-}	thio
ONO^-	nitrito-O-
NH^{2-}	imido
$C_5H_5^-$	cyclopentadienyl
SCN^-	thiocyanato
~~ARS~~	

Chemistry Notes Akinnsn

amine → organic name ammine → inorganic name.

(b) Neutral ligands

** NO^+ — nitrosonium

Ligands	Name
CO	carbonyl
NO	nitrosyl
NH_3	ammine If $(NH_3)_4$, then tetraamine ✗ tetrammine ✓
H_2O	aqua
O_2	dioxygen
CH_2NH_2 CH_2NH_2 CH_2-NH_2	ethylenediamine (en)
CH_3NH_2	methylamine
	dimethylglyoxime (DMG)

-ve or neutral?

* NO_2^+ — nitronium

Rule 4 : CENTRAL ATOM

(I) If complex is +ve or neutral then →

common name of central metal (oxidn no. in Roman I & II)

eg: $[Co^{*}(H_2O)_4(NH_3)_2]Cl_3$ (Co: +3)

↓

$[Co(H_2O)_4(NH_3)_2]^{3+} + 3Cl^-$

diamminetetraaquacobalt(III) chloride

$[Co(NH_3)_6]^{3-}$

central metal — ligand — complex (-ve here)

classmate
Date
Page

$[Cr(NH_3)_4Cl_2]_2SO_4 \rightarrow 2[Cr(NH_3)_4Cl_2]^+ + SO_4^{2-}$

(Cr: +3)

tetraamminedichlorochromium(III) sulphate

$[Co(en)_3]Cl_3 \rightarrow [Co(en)_3]^{3+} + 3Cl^-$

(Co: +3)

tris(ethylenediamine)cobalt(III) chloride

2 = bis(name)
3 = tris( )
4 = tetrakis( )

to be used if its name itself contains (di, tri) in name.

eg: en, PPh_3 (triphenyl phosphine)

$[Cu(NH_3)_4]_3(PO_4)_2$ (Cu: +2)

tetraamminecopper(II) phosphate

TOLLEN'S reagent

$[Ag(NH_3)_2]_2SO_4$ (Ag: +1)

diamminesilver(I) sulphate

(II) When complex is -ve (anion)

↑ ligands in alphabetic order, "Metallate".

↓

central a metal name ends in 'ate', name: Original name.

Chemistry Notes by Akshansh

Hg : Hydrogynum

Central metal	Original	Name
Fe	Ferrum	Ferrate
Sn	Stannatium	Stannate
Pb	Plumbatum	Plumbate
~~Hyd~~		
Ag	Argentium	Argentate
Au	Aurus	Aurate

$K_4[Fe^{+2}(CN)_6^{-6}]^{-4}$

potassium hexacyanoferrate (II)

$Li^{+1}[Al^{+3}H_4^{-1}]^{-1}$

lithium tetrahydridoaluminate (III)

$Ca_3[Ag^{+1}(S_2O_3)_2^{-4}]_2^{-6}$

Calcium dithiosulphatoargentate (I)

O_2 : dioxygen

$(O)_2$: dioxo

(O_2) : peroxido peroxo

Chemistry Notes Akshansh

$$\overset{+6}{Na_2}\left[\overset{-4}{Cr}\overset{-2}{(O)_2}\ \overset{-2}{(O_2)}\ \overset{0}{(NH_3)}\ \overset{-1}{(CN)}\ \overset{-1}{Cl}\right]$$

Sodium ammine chlorocyanodioperoxy chromate(VI)

$$\overset{+1}{Cu_2}\left[\overset{+2}{Fe}\overset{-6}{(CN)_6}\right]^{-4}$$

If Cu → +1, Fe comes +4 → not possible.

Copper(II) hexacyanoferrate(II)

$$[Ni(CN)_4][Ni(NH_3)_4]$$

✱ Naming of complex in which both cation & anion are complex

⊛ Common O.N. of 1st row transⁿ elemts

(oxidⁿ no.)

	$4s^2 3d^1$	d^2	d^3	$3d^5 4s^1$	$3d^5 4s^2$					
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+2,	+2	+2	Cr^{2+},	Mn^{2+},	$3d^6 4s^2$	d^7	d^8	$3d^{10} 4s^1$	$3d^{10} 4s^2$
+3	+3	+3	Cr^{3+}	Mn^{4+},	+2	+2	+2	+1	+2
+4	+4	+4			+3	+3		+2	
		+5	Cr^{6+}	Mn^{7+}					

$$\overset{+2}{[Ni}\overset{-4}{(CN)_4}][\overset{+2}{Ni}\overset{0}{(NH_3)_4}]$$

−ve = −4

So, +ve = +4

$[Ni(CN)_4]^{-2} + [Ni(NH_3)_4]^{+2}$ So, +2, +2 is distributed on Ni

tetraammine nickel(II) tetracyano nickelate(II)

classmate
Date 21.7.10
Page

$\overset{+3}{[Ag}\overset{-2}{(CN)_2]_3}\overset{+3}{[Co}(H_2O)_6] \quad -3$

$-3 \qquad +3$

hexaaquacobalt (III) dicyanoargentate (I)

$\overset{+2}{[Fe}\overset{-6}{(CN)_6]}\ \overset{+2}{[Cu}(NH_3)_4]_2$

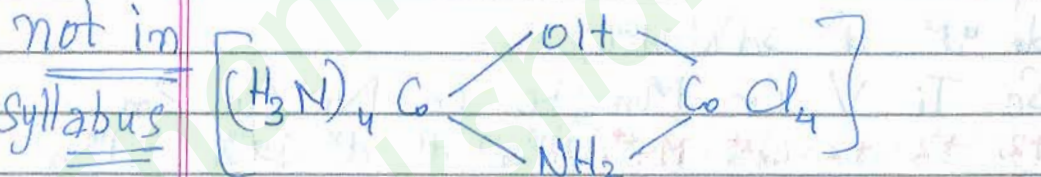
$-4 \qquad +4$

tetraamminecopper (II)
hexacyanoferrate (II)

$\overset{+4}{[Ti}\overset{-6}{(CN)_6]}\ \overset{+2}{[Ni}(NH_3)_6]$

hexaamminenickel (II)
hexacyanotitanate (IV)

not in syllabus



12 Chemistry Notes Akshansh

classmate
Date 21.7.20
Page

✡ Bonding theories of complexes

* THEORY - I : WERNER's theory of coordinⁿ

$Cr(H_2O)_6Cl_3$.

CN = 6.

He said 2 types of valencies :-

* Primary (ionisable) Charge / valency of central metal.
* Secondary (non-ionisable)

Acc. to Werner's theory a complex salt possesses 2 type of valencies known as Primary & Secondary valencies.

→ Primary valency (or Ionisable valency)
It is ionic valency of central metal (Charge/ON) i.e the valency of central metal assuming it to be a simple salt.

→ Secondary valency (or non-Ionisable valency)
It is the no. of dative bond to the central metal by the ligands.

eg: $[Cr(H_2O)_6]^{3+}Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$,

Both of them have Primary valency = 3
Secondary valency = 6

But, they have entirely diff Physical & Chem. Prop.

Chemistry Notes by Krishnansh

THEORY-II: VALENCE BOND THEORY (VBT)

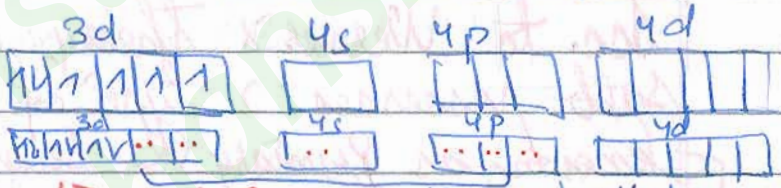
Acc. to VBT, strong ligands forces the e⁻s of d orbital of the central metal to pair up against Hund's rule of max. multiplicity.

In case of weak ligand d-orbitals are occupied acc. to Hund's rule.

eg: $K_4[Fe(CN)_6]$

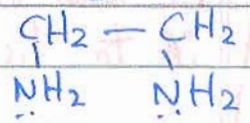
Fe : $3d^6 4s^2$

Inner orbital complex



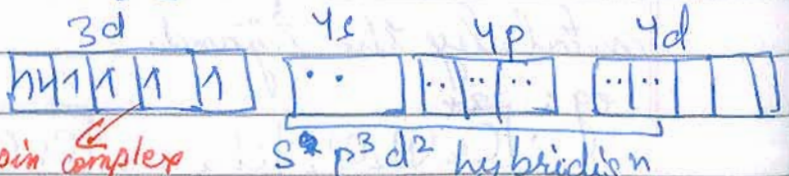
★ Strong Ligands :-

CO, CN^-, NO_2^-, NH_3, en



$K_4[FeF_6]$ F^- : Weak ligand.

Outer orbital complex.



★ d^2sp^3 & sp^3d^2 are diff types of hybridisn. But they correspond to octahedral geometry.

* All dentates except monodentates are called CHELATING LIGANDS. (∵ they form a closed loop ~~not~~ by making dative bond (more than 1) with central metal).

* All Chelating ligands are strong ligands.

eg: CH_2-CH_2 (loop)

NH_2 NH_2

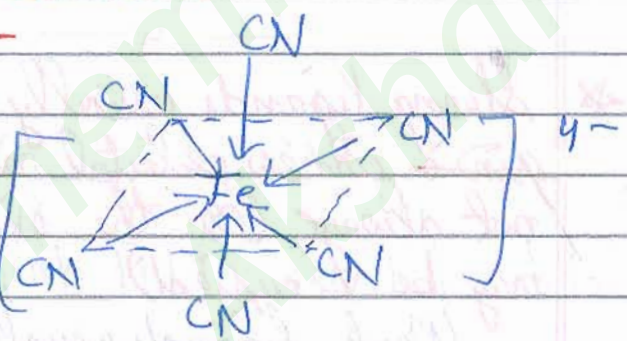
Cn

M^{n+}

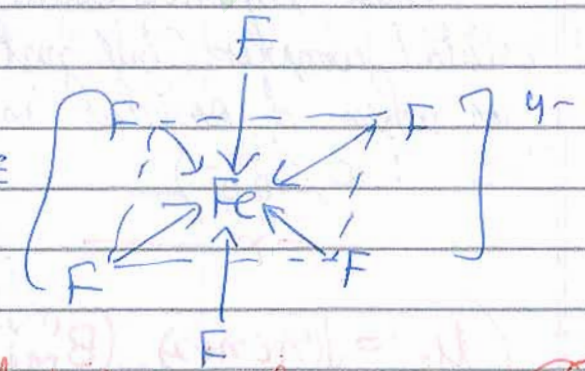
* d^2sp^3 or sp^3d^2 :-

geometry : octahedral

shape :-

in $[Fe(CN)_6]^{4-}$ ≡ 

d^2sp^3

$[Fe(F)_6]^{4-}$ ≡ 

sp^3d^2

** The d orbitals in above $sp^3(d^2)$ & $(d^2)sp^3$ are → $d(x^2-y^2)$ & dz^2 & not dx, dy.

classmate
Date
Page

✡ Inner Orbital complex: Complex in which use inner d-orbital for bonding.

✡ Outer Orbital complex: Complex in which use outer d-orbital for bonding.

✡ Inner orbital complexes are usually more stable than outer orbital ∵ in inner orbital complex low E (more stable) d-orbitals are involved in bonding.
(reverse in outer orbital)

✡ Strong ligands usually give inner orbital complex. But not always (as the inner d-orbitals may be occupied)
Weak ligands usually give outer orbital complex (but not necessarily when d orbital is empty almost i.e $1e^-/10e^-$)

—x—

$\mu_s = \sqrt{n(n+2)}\ B_M$

n → no. of unpaired e^-
B_M → Bohr magneton.
μ_s → Spin only magnetic moment.

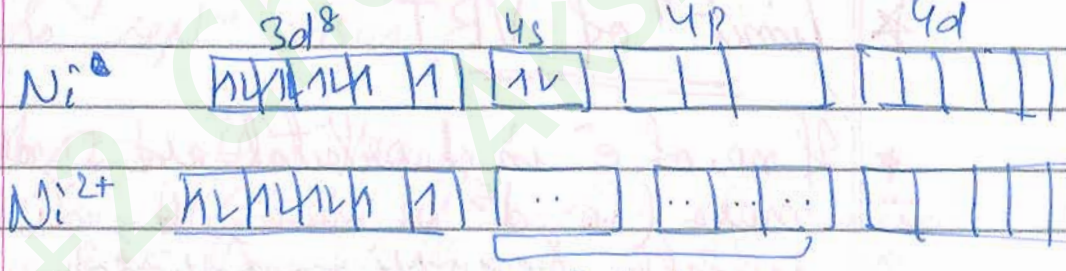
$\mu_s = 0$: Diamagnetic
$\mu_s \neq 0$: Paramagnetic.

Chemistry Notes Akanksh

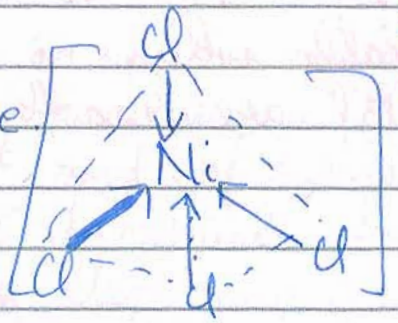
* Low Spin complex : Complex in which there is min. possible no. of unpaired e⁻s are present in valence shell of central metal are called Low Spin complex or SPIN-PAIRED (they need not be only in Strong ligands) (d^1).
* Strong ligands usually form low spin complex
* High Spin complex : Those complex in which there are max. possible no. of unpaired e⁻s present in the valence shell of central metal (they need not be only in weak ligands (d^{10}).
  Also called SPIN-FREE complexes.
* Weak ligands usually form high spin complex.

—x—

Q. $Na_2[NiCl_4]$ 28



Shape

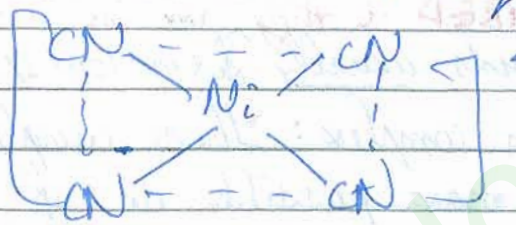


+2 Chemistry Notes Akshansh

Q. $Na_2[Ni(CN)_4]$

Ni^{2+} : 3d | 4s | 4p | 4d

$dsp^2 \rightarrow$ sq. planar shape.



Q. $[Ni(CO)_4]$

Ni : 3d | 4s

$Ni(CO_4)$: $3d^{10}$ $4s^0$

$3d^{10}$ | sp^3

★ Limitⁿ of VBT

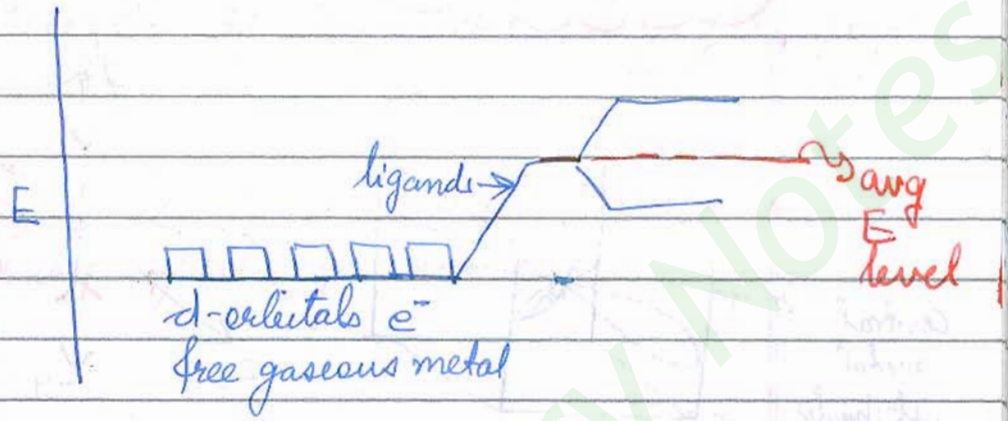
* If no. of e^- in d orbital are 5 or more (i.e. d^5 or more) then it is applicable. (eg. Ni, not Ni^{2+})
* Its not applicable when no. of e^-s in d orbital are less than 5.

Chemistry Notes by Akshansh

classmate
Date
Page

9-mp.

✡ CRYSTAL FIELD THEORY (CFT)

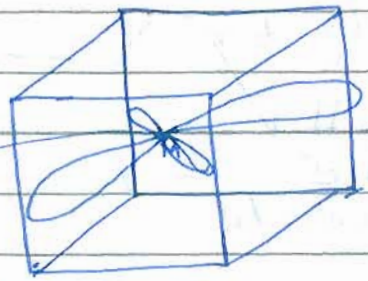


On approach of ligands to free metal, its LP repel the free e⁻s of orbital. ∴ E ↑, Stability ↓.
The repulsion is not uniform because they have diff^t orient^ns in 3D. So, repl^n varies.

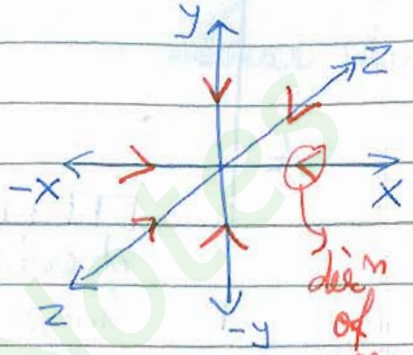
Acc. to this theory,
when ligands approaches the central metal, it repels the d e⁻s & ∴ ↑ avg. E of d-orbitals.
However, diff^t d-orbitals receive diff^t amt. of repulsion. As a result, the 5 d-orbitals, ~~do no~~ loses their degeneracy (same E) under influence of ligands.
Orbitals suffering greater repul^n occupy higher E state & one suffering smaller repuls^ns occupy lower E state.

Chemistry Notes by Akshansh

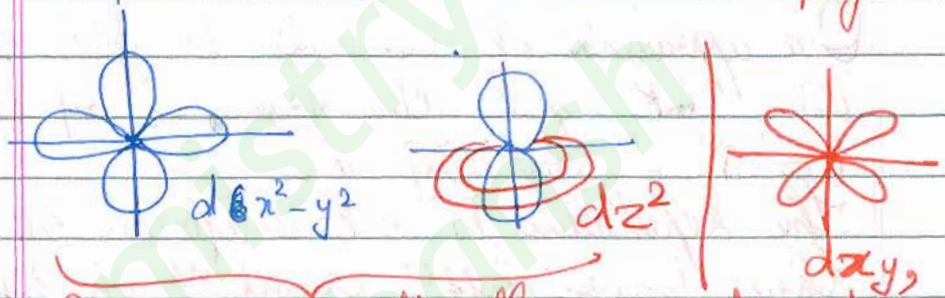
CFT in CN=6 Octahedral complex



Central metal at body centre & ligands at 6 face centres.



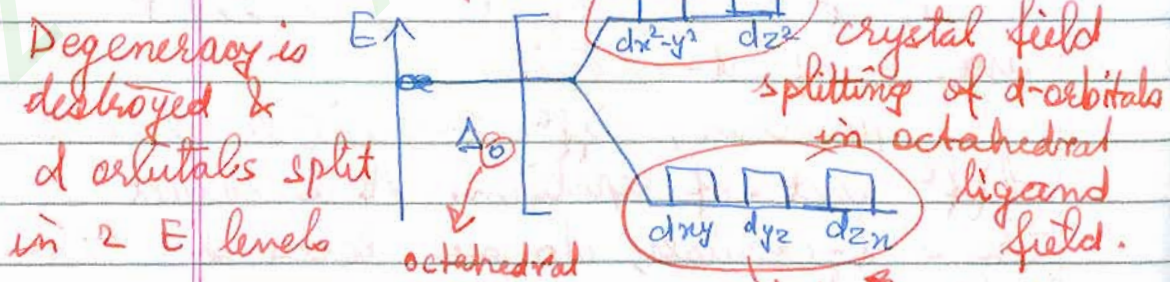
dirⁿ of approach of ligand



these orientⁿs directly lie on path of approach of ligands. So, they have high E.

low E

eg: Grind level



Degeneracy is destroyed & d orbitals split in 2 E levels

crystal field splitting of d-orbitals in octahedral ligand field.

The E gap b/w orbitals of low & high E is called: Crystal Field ~~Splitting~~ Splitting Energy (CFSE). Denoted: Δ_o

* Pairing or Promotion requires E. So, process is endothermic.

* Magnitude of Δ_o (E gap) b/w e_g & t_{2g} level depends on the strength of ligand. Stronger ligand gives greater splitting, larger E gap (CFS(E) & weaker ligand gives small splitting, smaller E gap.

eg. (i) $K_3[\overset{+3}{Co}\overset{-6}{F_6}]^{-3}$ (ii) $K_3[\overset{+3}{Co}(CN)_6]$

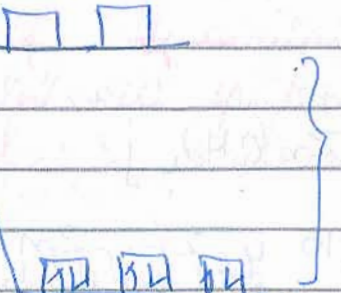
$Co^{3+} \rightarrow 3d^6$

(iii) $K_4[\overset{+2}{V}(CN)_6]^{-4}$

(i) $K_3[CoF_6]$ d^6

Weak ligand field. So, Pairing E > Trans" E. So, it goes up 1st & the 6th e^- is down due to less E req^d.

(ii) $K_3[Co(CN)_6]$ d^6

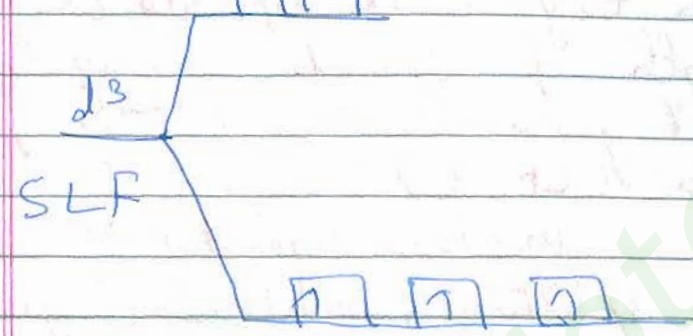


Strong ligand field. So, Pairing E << Trans^n E.
So, after 6th e^- it goes up.

★ Weak ligand field → WLF

★ Strong " " → SLF

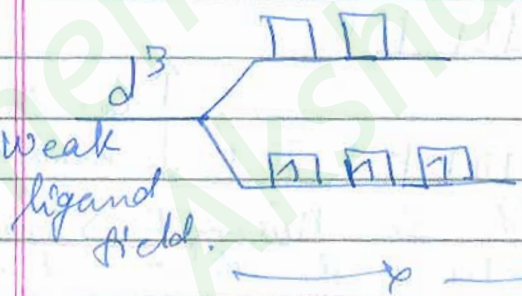
(iii) $K_4[V(CN)_6]$ (+2)



* whether its WLF or SLF

Ans = same.

(iv) $K_4[V(Cl)_6]$ (+2)

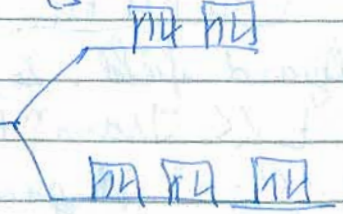


★ d_1, d_2, d_3 are all high spin complex.

$Na_2[Zn(OH)_4]^{-2}$ (+2)

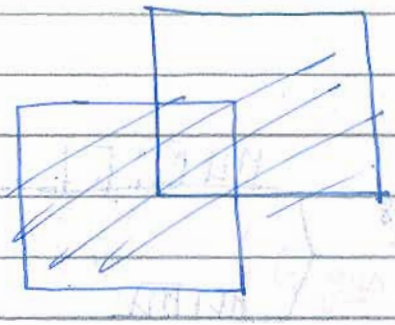
Zn: $3d^{10}\ 4s^2$ $Zn^{2+} = 3d^{10}\ 4s^0$

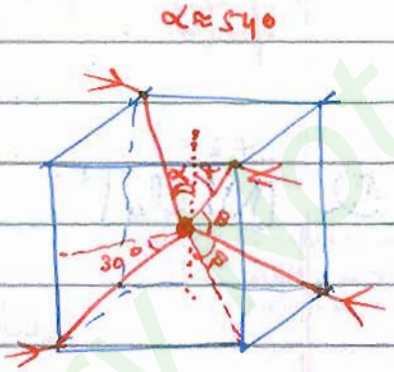
CFT d^{10}



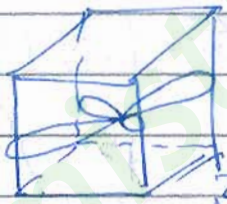
VBT: sp^3

CFT in CN = 4 → tetrahedral complex





$d_{x^2-y^2}$



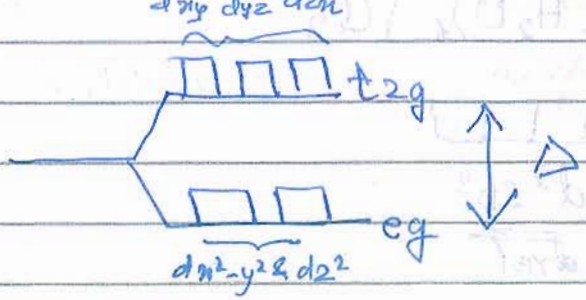
d_{xy}

$2\alpha + 2\beta = 180°$

$\Rightarrow 108 + 2\beta = 180°$

$\Rightarrow \beta = 36°$.

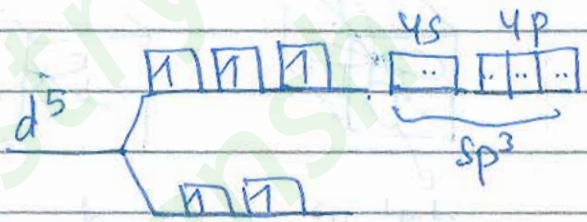
* In tetrahedral ligand field, no d-orbitals lie directly along the path of ligands.
  ∴ avg. repulsion is less.
* In tetrahedral ligand field, once again, degeneracy of d-orbital is destroyed. So, d orbital will split into 2 levels with 2 below & 3 above.



* In tetrahedral ligand field, no lobes lie directly on the path of ligand. So, their Δ E gap is less than in octahedral ligand field.

Q. $[Ni^{+2}Cl_4]^{2-}$

Q. $[Mn^{+2}Cl_4]^{2-}$



Q. $[Mn(CN)_4]^{2-}$

dsp^2

Sq. planar complex

Q. $[\overset{3d^2}{\underset{+3}{V}}(H_2O)_6]Cl_3$

d^2sp^3

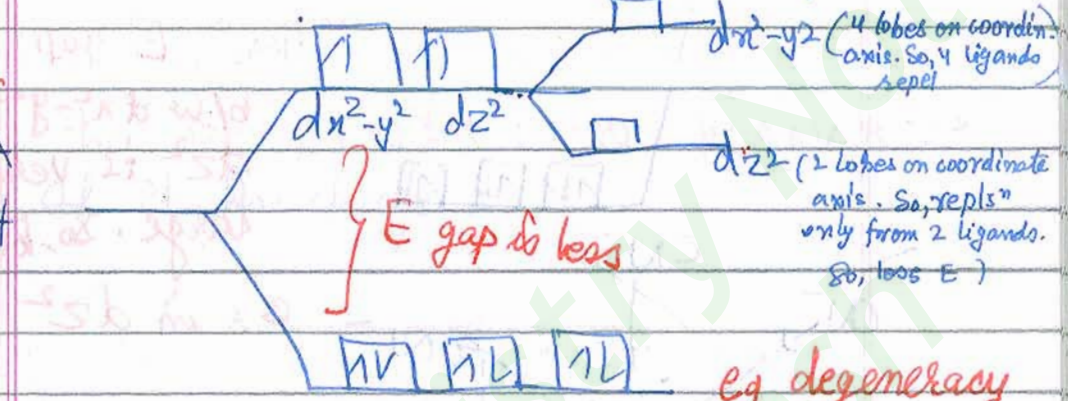
Octahedral

SQUARE PLANAR COMPLEX

~~Weak~~ ~~Strong~~ ~~Weak~~ ~~Unformed~~

* Ni^{2+} $(3d^8)$ → Attempts to form an octahedral complex.

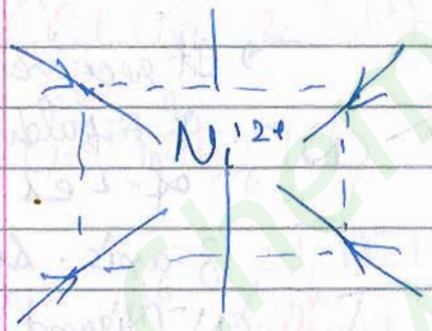
JAHN TELLER



(dx^2-y^2 (4 lobes on coordin. axis. So, 4 ligands repel)

(dz^2 (2 lobes on coordinate axis. So, repls" only from 2 ligands. So, loos E)

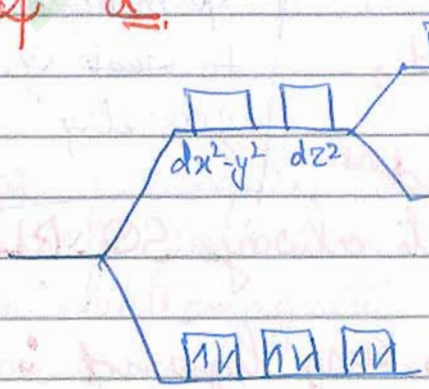
eg degeneracy is destroyed here.



Tetragonal compression - length is distorted.

DISTORTION

* If d^7



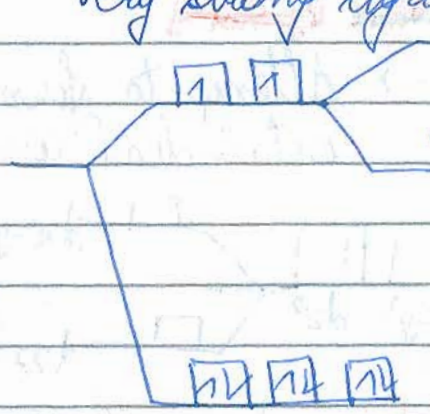
Tetragonal compression.

Chemistry Notes by Akshada

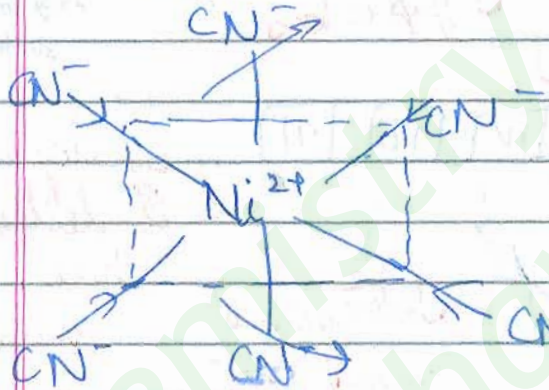
Ni^{2+} $(3d^8)$

↓

very strong ligand.



Here, E gap b/w dx^2-y^2 & dz^2 is very large. So, both e^-s in dz^2



→ It receives lot of repulsion of 2 e^-s from z-axis. So, CN^- (ligand) on z-axis doesn't form bond leading to ~~weak~~ sq. planar geometry.

Learn

* d^8, strong ligand, $CN = 4$ ∴
** If these cond^ns are satisfied, its always SQ. PLANAR.

* d^9, $CN = 4$, any ligand ∴
i.e in Cu^{2+} → $[Cu(NH_3)_4]^{2+}$, $[Cu(CN)_4]^{2-}$, $[Cu(H_2O)_4]^{2+}$ } SQ PLANAR geometry.

E gap b/w dx^2-y^2 & dz^2 rises so much that e^- doesn't go in dx^2-y^2. It goes in 4s

12 Chemistry Notes Akshansh

classmate
Date
Page

* d^7, CN = 4, strong ligand :-
  SQ. PLANAR ✓

* d^4, CN = 4, weak ligand :-
  SQ. PLANAR → only ex: $[Cr Cl_4]^{2-}$

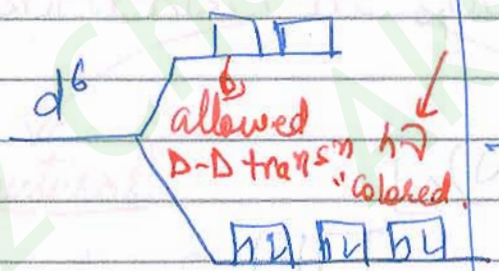
* $[Pt(L)_4]$ (L → ligand) :- eg: $Pt(NH_3)_2 Cl_2$:-
  In Pt, CN = 4 : SQ. PLANAR →
  If Pt has charge.

---

* COLOR & SPECTRA of COMPLEX.

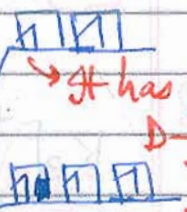
$[Fe^{+2}(NH_3)_6]Cl_2$

d^6



$K_3[Fe^{+3}F_6]$

d^5



Shows no color, ∴ Colorless

Imp For a complex to be colored, it must absorb some ~~radiations~~ of from ~~the~~ electromagnetic radiation leading ~~for~~ to an electronic transn from lower D level (t_{2g}) to higher D level (e_g) → known as D D transn without violating Pauli Exclusion Principle.

+2 Chemistry Notes Akshansh

classmate
Date
Page

★ During D-D transⁿ change of spin is not allowed.

★ In case of d^5, weak ligand is colourless. It will always be colourless.

d^0 : It will always be colourless.
d^{10} : Cu^{+1} & Zn^{+2} :→ It will always be colourless.

★ To see colourless, see whether if we take an e^- from lower to higher, without changing spin, Pauli Exclusion principle is violated or not.

Q $K_3[Fe^{+3}(CN)_6]$
d^5

& it would be colourless ∵ e^- is not absorbing E in visible range. It is absorbing UV- rays → not visible.

2 Chemistry Notes
Akshansh

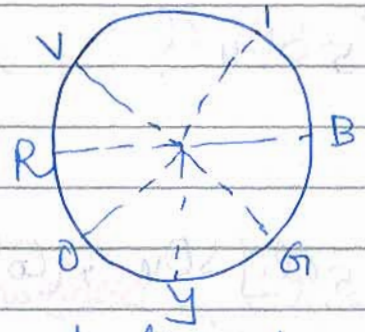
* The color seen in shorter λ, absorbs color of larger λ & vice versa ; $E = \frac{hc}{\lambda}$ ⇒ $E \propto \frac{1}{\lambda}$

speed of light classmate Date Page → Energy

h → Plank's const

Q. MA_6 ↓ Blue } longer λ absorbed

MB_6 ↓ Red } shorter λ absorbed.



A is weak ligand

B is strong ligand

* CN = 2 $[CuCl_2]^-$: $3d^{10}$: sp → linear

∀ CN = 2

$Ag[(NH_3)_2]^+$: sp, linear, $[Ag(CN)_2]^-$: sp, linear.

$[Au(CN)_2]^-$

* ISOMERISM IN COMPLEXES.

Structural

① Ionisation Isomerism
② Hydrate Isomerism
③ Linkage Isomerism
④ Coordin^n Isomerism
& more (not in IIT)
⑤ Polymerisation Isomerism

Stereo

✱ IONISATION ISOMERISM

$Co(NH_3)_5SO_4Cl$, CN = 6

↓

$[Co(NH_3)_5Cl]SO_4$, $[Co(NH_3)_5SO_4]Cl$

fixed because its gaseous form. So, if outside, it goes off.

(same formula)

Isomers producing diff ions in soln are known as ionisn isomers. Ionisn isomers have ions interchanged b/w inside & outside coordin sphere.

⊗ $Cr(H_2O)_5Cl_2Br$

↳ $[Cr(H_2O)_5Cl_2]BrCl$

$[Cr(H_2O)_5Br]Cl_2$

~~$Cr(H_2O)_6Cl_3$~~

2 Chemistry Notes Akshansa

★ If 2 donor atoms are present in one group, then that ligand is called ⇔ AMBIDENT LIGAND

★ HYDRATE ISOMERISM

Loss of wt. = 0

$Co(H_2O)_6Cl_3 \rightarrow$ (a) $[Co(H_2O)_6]Cl_3$ (max no. of ions)

Loss of wt. ← (0.9)

(b) $[Co(H_2O)_5Cl]Cl_2 \cdot H_2O$

Loss of wt. ← (1.8)

(c) $[Co(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (min. no. of ions)

a, b & c are hydrate but not ionisⁿ isomers

Isomers with diffᵗ no. of water molecules of crystallisⁿ outside coordinⁿ spheres are called Hydrate Isomers.

★ LINKAGE ISOMERISM

✓ complex containing ~~at less~~ atleast 1 only shown by Ambident ligands.

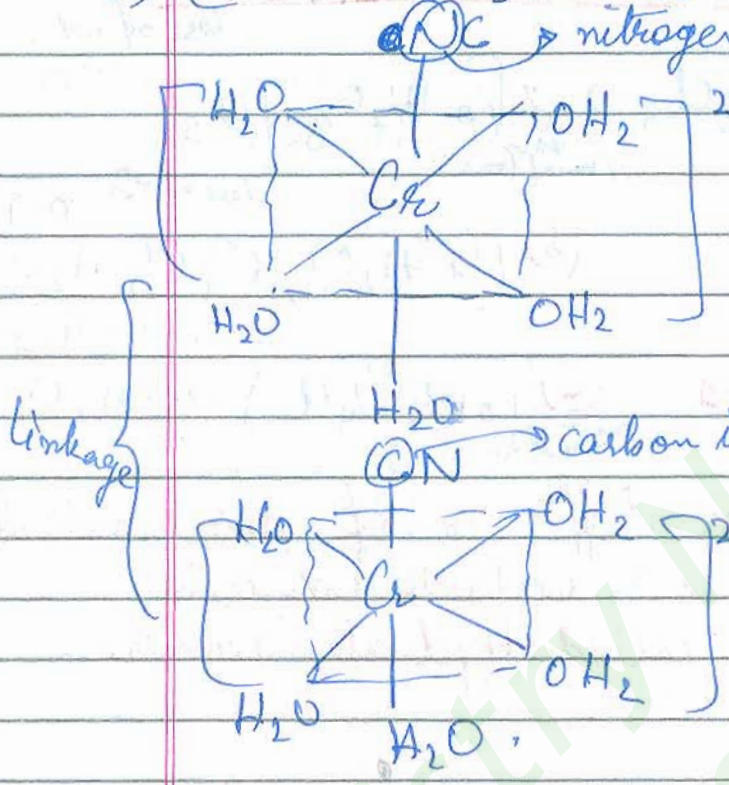
eg;

main
- $:C\equiv N^-$ cyanide.
- $^-O-\dot{N}=O$ nitro
- $S-C\equiv\dot{N}$ thiocyanide.
- $^-O-C\equiv N$ cynate.

★ Isomers having same donor grp but diffᵗ donor atom bonded to central metal are known as linkage isomers. ~~bio~~ linkage isomers have diffᵗ IUPAC names.

classmate
Date
Page

Q $[Cr(H_2O)_5(CN)]Cl_2$ (+3)



← $C \equiv N$: cyano

← $N \equiv C$: isocyano (name ~~iso~~ is considered in naming)

← $O-N=O$: nitrito or nitrito -O-

← NO_2 : nitro or nitrito -N-

← $S-C \equiv N$: thiocyano or thiocyanato

← $N \equiv C-S$: ~~cyanato~~ isothiocyanato
isothiocyano.

← $O-CN$: cyanato

← $N \equiv C-O$: isocyanato.

* $Cr(H_2O)_5(CN)Cl_2$ → Shows Ionisⁿ, Hydrⁿ, linkage isomerism.

12 Chemistry Notes Akshansh

$Na[Ag(CN)(NC)]$

Sodium ~~cyano isocyano~~ cyano isocyano argentate (I)

$[Co(H_2O)_5ONO]Cl_2$

~~Pentaqua~~ pentaaquanitritocobalt (III) chloride

✱ COORDINATION ISOMERISM

✓ both part complex.

✓ Interchange of ligands b/w complex ions.

eg: $[Pt(NH_3)_4][Ni(CN)_4]$; $[Pt(CN)_4][Ni(NH_3)_4]$

✱ Coordin^n isomerism arises due to inter-change of ligands b/w complex ions.

∴ This isomerism is observed only in complex where both cation & anion are complex. Amt. of exchange can be any → not fixed.

$\underbrace{[Pt(NH_3)_2(CN)_2]^0[Ni(NH_3)_2(CN)_2]^0}$

they are not coordin^n isomers ∵ both have 0 charge. So, they would separate.

its ions get discharged at cathode

eg: $[Pt(NH_3)_3CN]^{+1}[Ni(CN)_3(NH_3)]^{-1}$

$[Pt(NH_3)C(CN)_3]^{-1}[Ni(CN)(CNH_3)_3]^{+1}$

its ions get discharged at cathode.

$[Ag(CN)_2]$ → $[NC-Ag-CN]^-$, $[CN-Ag-NC]^-$, $[CN-Ag-CN]^-$

3 isomers possible.

classmate Date 28·7·10 Page

★ POLYMERISATION ISOMERISM

B Isomers have diff molecular formula, but same emperical formula. Its not true isomerism. Only some rel^n holds.

Eg: $[Pt(NH_3)_2Cl_2]$ $[Pt(NH_3)_4][PtCl_4]$

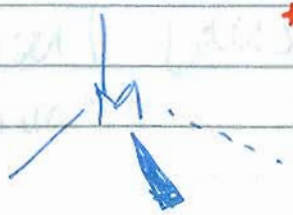
It is a polymer of

Stereo Isomerism

Geometrical Optical

★ GEOMERICAL ISOMERISM

ML_4 (tetrahedral : known)



★ CN=4, tetrahedral geometry : Geometrical isomerism doesn't take place in it.

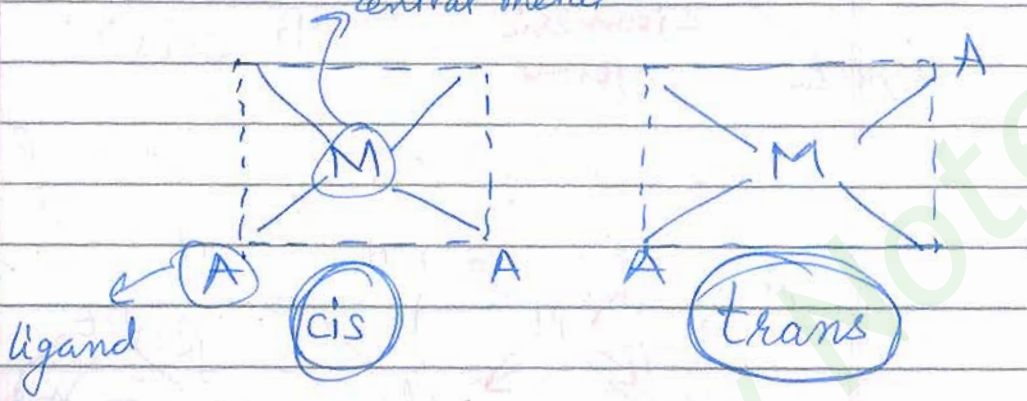
2 Chemistry Notes Akshansh

$K[Ag(CN)(SCN)]$ (4)

fix C → N, S.

fix N → C, S.

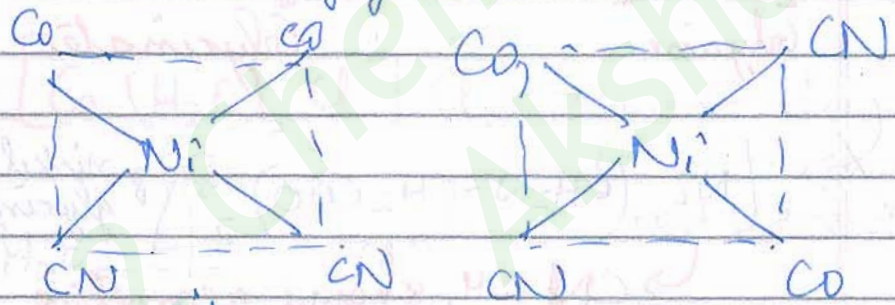
* CN = 4, Sq. planar geometry.



* CN = 4, Sq. planar geometry may show geometrical isomerism

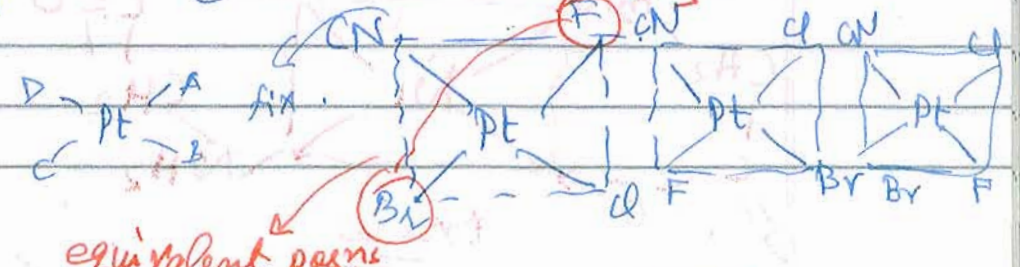
eg: $[Ni(CN)_2(CO)_2]$ } can also show polymerism, linkage isomerism

d^8, strong ligand, CN = 4



* $[Pt^{+2}L_4]$ Pt(II), CN = 4, always sq. planar.

eg: $K_2[Pt^{+2}ClFBr(CN)]$ } 3 stereo isomers



Chemistry Notes Akshansh

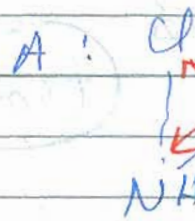
classmate
Date
Page

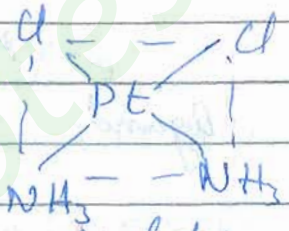
Q. $Pt(NH_3)_2Cl_2$ → A (trans), B (cis)

2 isomeric forms

cisplatin.

A is not deflected by electric field.

A: 

B → 

cisplatin

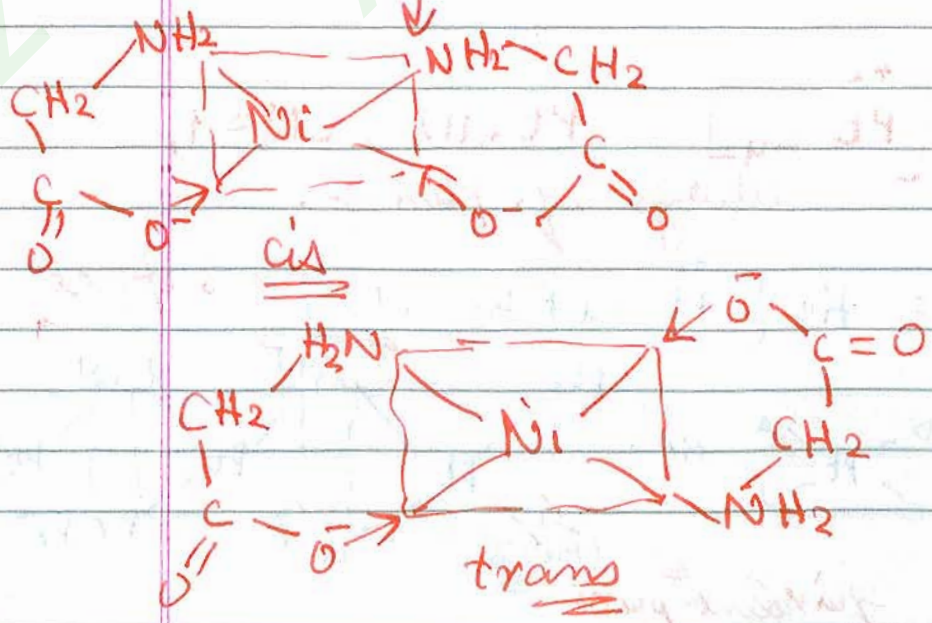
Q. H_2N-CH_2-COOH (glycine)

$H_2N-CH_2-COOH \rightarrow H_2\ddot{N}-CH_2-\overset{\overset{O}{\|}}{C}-O^-$

Glycine → Glycinate

$\rightarrow \left[Ni\left(\ominus H_2N-CH_2COO\right)_2\right]^0$ nickel glycinate

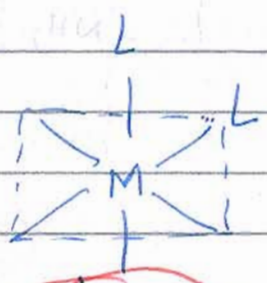
↳ CN = 4, shows geometric isomerism.



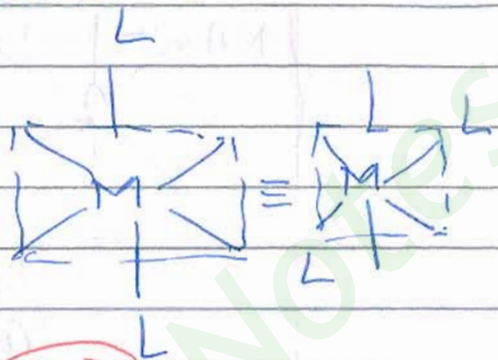
cis

trans

CN = 6, octahedral geometry



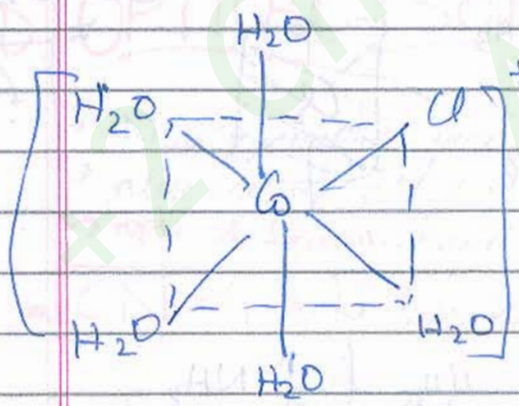
cis
Identical ligands at 90°



trans
Identical ligands at 180°

* If it exists, trans should independently exist

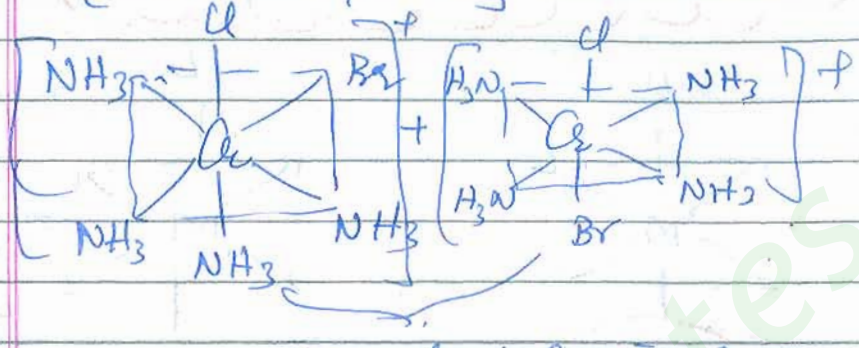
Q. $[Co(H_2O)_5Cl]Cl_2$ → won't show.
(∵ cis & trans don't exist independently)



But, if given, its hydrate isomer shows geometrical, then the complex will show geometrical isomerism.

* $[MA_5B]$ → such complex won't ever show geometrical isomerism.

Q $[Cr(NH_3)_4ClBr]Cl$



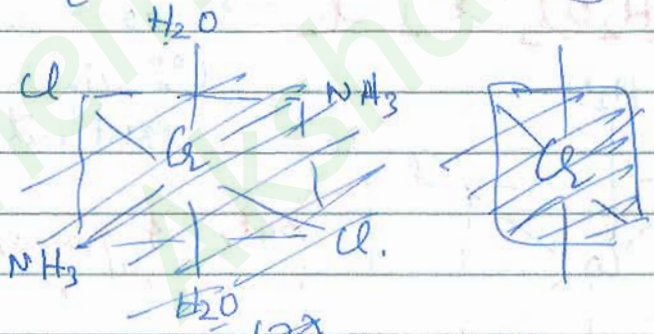
geometrical isomerism.

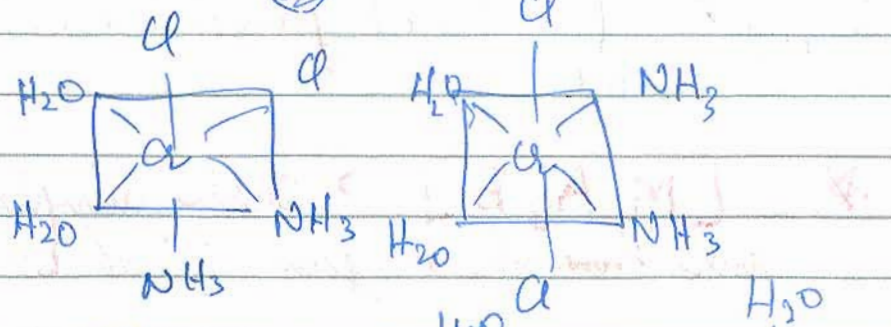
shows → E-Z (here)

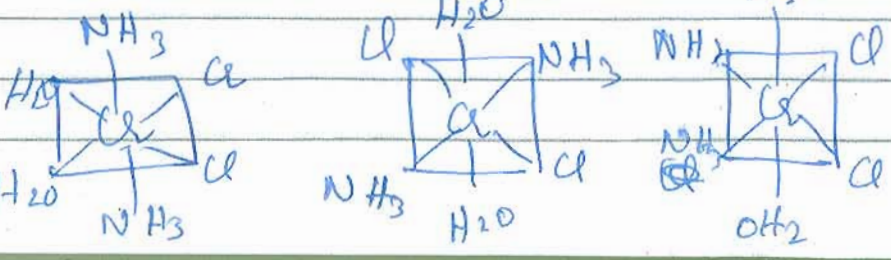
* $[MA_4B_2]$ or $[MA_4BD]$

both complexes show geometrical isomerism.

Q $[Cr(H_2O)_2(NH_3)_2Cl_2]Cl$ → 5 isomers





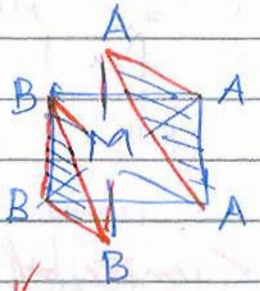


classmate
Date
Page

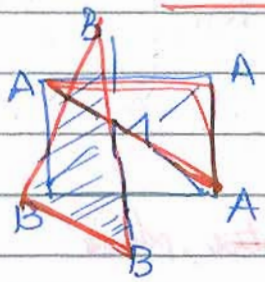
* $[MA_2B_2C_2]$ shows 5 geometric isomerism.

Q $[Cr(NH_3)_3Cl_3]$ i.e $[MA_3B_3]$ CN = 6

Another type of Geometrical Isomerism



Facial: 'fac'
∥ planes (Δles) containing identical ligands.

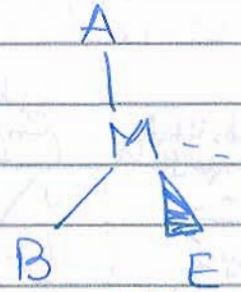


Meridianal: 'mer':
⊥ planes (Δles) containing identical ligands

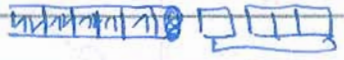
OPTICAL ISOMERISM in complexes.

→ N_{sp} on mirror image.
→ absence of either plane or centre of symm.
→ axis of symm. doesn't affect optical isomerism.

• CN = 4 : Tetrahedral geometry.



eg: $Na_2[NiFClBrI]$



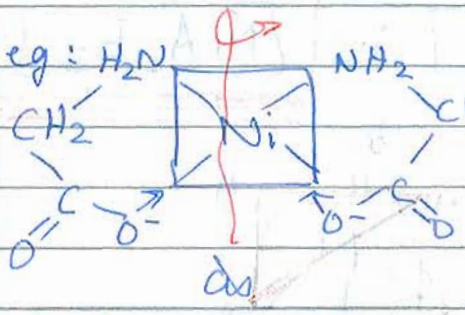
sp^3

Shows optical

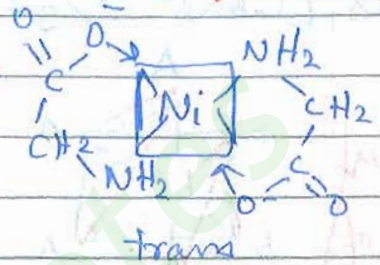
* If 4 diff^t ligands are bonded to central metal, it will essentially show OPTICAL ISOMERISM

Chemistry Notes by Akshansh

CN = 4 → Sq. planar } not optical isomerism

eg: 

cis



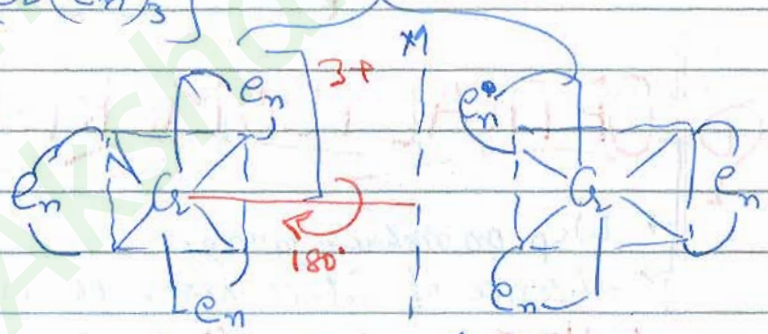
trans

✓ ~~optical~~ centre, plane of symm
✓ axis of symm

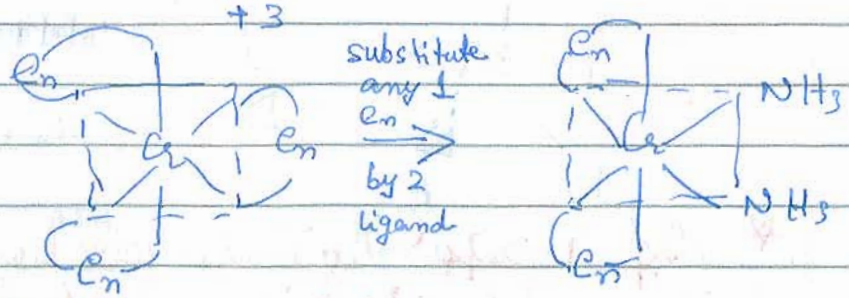
✓ centre of symm
✓ plane of sym.
✓ axis of sym

CN = 6

eg: $[Cr(en)_3]^{3+}$ enantiomers.

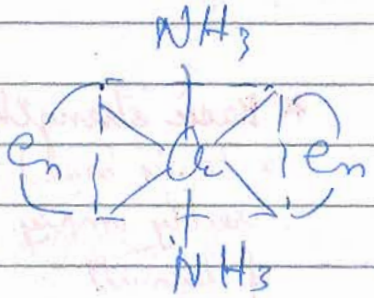


N_{SP} on mirror image, so, its optically active, axis of symm ✓; chiral compd.



★ If we substitute a brige by 2 monodentate ligands (same or diff ▷),

Chirality is not lost.



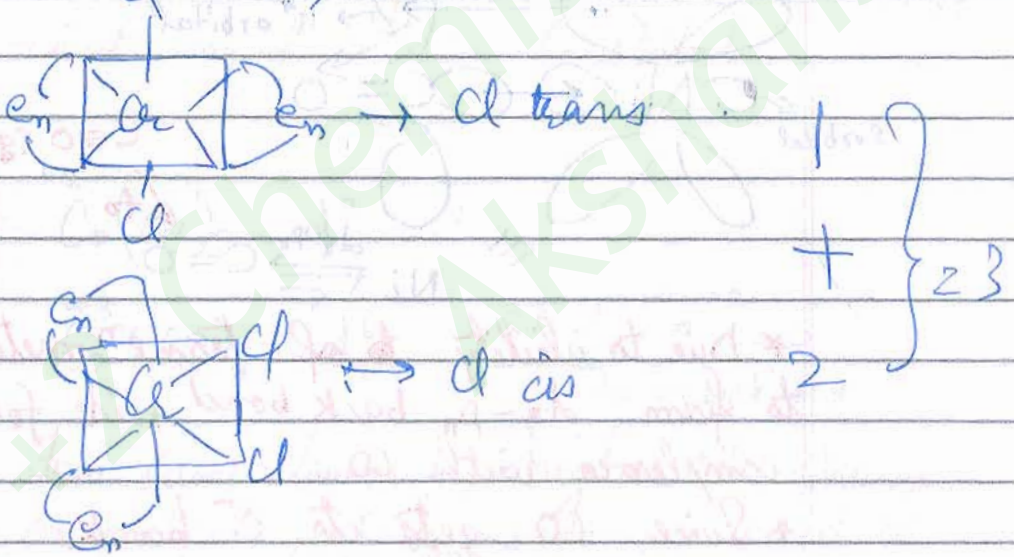
: Achiral (Got plane of symm.)

Q. $[Cr(en)_2Cl_2]^+$: has 3 stereo isomers.

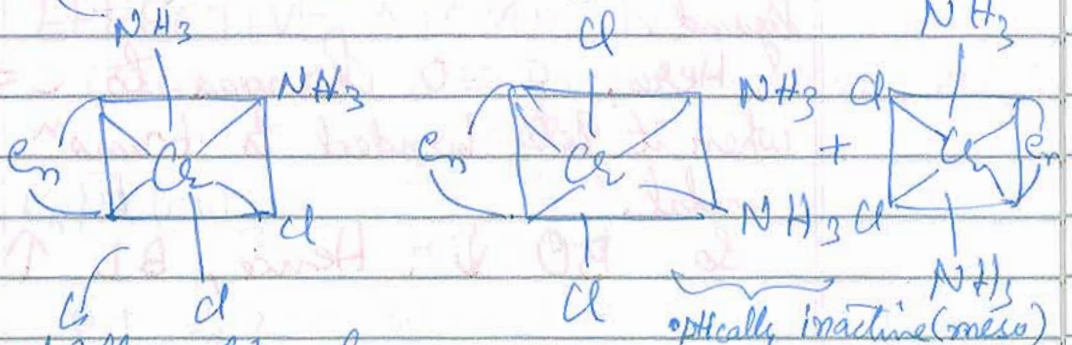
distereo Cl → trans

mers: Cl → cis (optically active also)

So, total 3



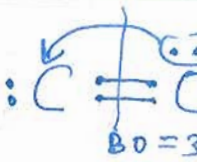
Q. $[Cr(NH_3)_2Cl_2(en)]^+$



2 = optically active also,

(2) + (1) + (1) = 4

Acid = ~~3HCl~~



} not a Lewis Base

classmate Date Page

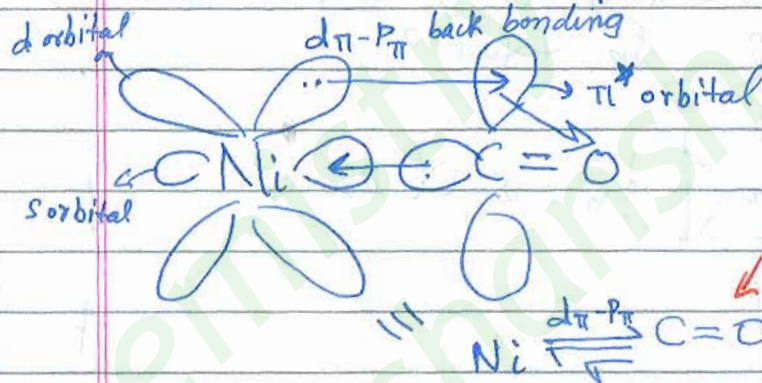
✱ BONDING IN METAL-CARBONYLS

$[Ni(CO)_4]$

✱ Basic strength (being a lewis base) doesn't directly imply strength of ligand.

CO = 14

$\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_x^2$ | $\pi 2p_y^1$ | $\pi^* 2p_y$
$\pi 2p_z^2$ | $\pi^* 2p_z$



C≡O (g) ↓ to

✱ Due to ability of transⁿ metal to form $d\pi - p_\pi$ back bond, it forms complexes with CO.

✱ Since CO gets its e⁻ back immediately after it give its e⁻ to transⁿ metal. so, it's strong ligand.

Here, C≡O changes to C=O when it gets bonded to transⁿ metal.

So, BO ↓. Hence, BL ↑.

Chemistry Notes Akshansh

* All non metallic oxides are acidic except :
NO, H_2O, CO, ~~NH_3~~, N_2O

classmate
Date
Page

Now, $[Cr(CO)_6]$

$d_\pi - P_\pi$ back bond

$Cr \rightleftharpoons C=O$ → $BO_{Cr} > BO_{Ni}$

$BL_{Cr} < BL_{Ni}$

* Ability to form strong back bond depends on no. of e^- in d-orbital. Greater $d_\pi - P_\pi$ back bond, smaller is C=O BO, greater is its BL.

* Sc^{+3}, V^{+4} or Sc, V don't form back-bond efficiently due to inefficient no. of e^-s in d-orbital.

—×—

§ $Co(CO)_6^{+2}$ d^7 :

$Co(CO)_6^{+3}$ d^6 Co^{+3} ← strong C=O

$d_\pi - P_\pi$ back bond.

For same element, higher the charge on central metal, stronger bond it will form with carbonyl.

—×—

§ EFFECTIVE ATOMIC NO.
(EAN Rule) or (SIDWICK-POWEL Rule)

$K_4[Fe(CN)_6]$ $3d^6 4s^2$

$Fe^{2+} = 3d^6$

6 + 6(×2) = Valence shell e^- } total 36 e^- noble gas confi (Kr)

18 e^- in core shell.

Chemistry Notes Akshansh

classmate
Date
Page

at. no. of central metal → Z
oxidn no. → ON
coordin no. → CN

$$EAN = Z - ON + 2(CN)$$

eg $K_3[Fe(CN)_6]$ → total $e^- = 35$ = EAN

however, $K_3[Fe(CN)_6]$ is more stable than $K_4[Fe(CN)_6]$

$[Cu(NH_3)_4]Cl_2$

$3d^9\ 4s^2$

$= 3d^9$

$29 - 2 + 2(4) = 35 = EAN$

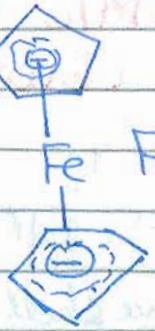
$[Cu(CN)_4]^{3-}$ EAN = 36

* π-donation may also take place from ligand to central metal.
eg: In C_6H_6, its tridentate (3 π-bonds to donate)

In ≡ (common name: ferrocene)

cyclopentadienyl — tridentate.

π-donor



Fe Ferrocene.

$[Fe(cyclopentadienyl)_2]$

Chemistry Notes Akshansh

Trans^{n} Elements

* Trans^{n} elements are the elemts which have incompletely filled d-or orbitals → either IN ITS ATOMIC STATE OR IN THE FORM OF IONS.

Period 4 (3d series): ~~Sc Ti V Cr Mn Fe Co Ni~~
" 5 (4d ")
" 6 (5d ")

Period 4:- (3d series)	Sc $(n-1)d^1ns^2$	Ti	V	Cr $(n-1)d^5ns^1$ $3d^5 4s^1$	Mn	Fe	Co	Ni $3d^8 4s^2$	Cu $(n-1)d^{10}ns^1$	Zn
Period 5:- (4d series)	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd $4d^{10} 5s^0$	Ag	Cd
Period 6:- (5d series)	La	Hf	Ta	W $5d^4 6s^2$	Re	Os	Ir	Pt $5d^9 6s^1$	Au	Hg

→ densest among them.

penultimate : 2nd from outermost

classmate
Date
Page

✡ Metallic Properties

§ Trans" elements are all metals. Their metallic property are due to the presence of unpaired e^-_s in their valence shell which takes part in metallic bonding.

Metallic property ↑ from left to right upto Mn & then ↓ till Cu acc. to no. of unpaired e^-

✡ → Zn is not considered as trans" metal ∵ it doesn't have incompletely filled d-orbital either in atomic or ionic state.

Properties of Zn has greater similarity with metals of grp 2.

§ **Density**

Density of trans" metals are very high (usually > 5 g/cc). Its ∵ of their very small size & very large atomic wt.

§ **Atomic/ionic radii :-**

Shielding effect :-

s > p > d > f

Size of atom ↓ as we move from left to rt. in a period. Its ∵ of e⁻s are being added in the penultimate

shell, which shield the nucleus negligibly increasing effective nuclear charge significantly.

Zn is slightly bigger than its adjacent atom (Ni & Cu). Its due to the last e⁻ being filled in 4s orbital.

Atomic size ↑ as we move down in a group. Its due to add^{n} of a new shell everytime as we move 1 step down the groups.

Variation in size is non-uniform in group. There is a greater diff. in size b/w 3d & 4d series elemts. Whereas, in 5d elements & 4d elemts have comparable size & in some case size of 5d elemts is even smaller than that of 4d elemts of same gep.

* Size of Zr > Size of Hf ($5d^2 6s^2$)
before Hf the 4f orbitals are filled which contain 14 e⁻s. The filled 4f orbital e⁻ give very poor shielding but add 14 unit of +ve charge on nucleus, ↑ effective nuclear charge greatly. So, its size contracts to such a level that it becomes even less than Zr.

classmate
Date
Page

Ionisation energy (IE)

IE ↑ as we move from left to rt. in a period.

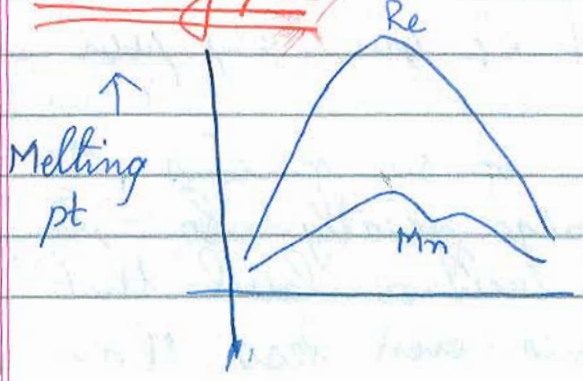
IE of transⁿ elements are usually larger than that of representative elemts of same period.

Although, IE ↑ from left to rt. & Zn has max. in 1st row, increment is very small. However, there is a large diff in IE of Cu & Zn.

Reason:- For elemts other than Zn, e⁻s are removed from d-orbital during ionisⁿ & readjustment of e⁻ occur b/w 4s & 3d orbital. Some 4s e⁻s are exchanged to 3d orbital releasing E which compensate to some extent the I.E.

In case of Zn, e⁻ is removed from 4s orbital only & larger E is reqd.

Melting pts.



Hg : melting pt → −38°C

Trans^{n} metals have high M Pt. compared to representative metals. Its ∵ of their smaller size & strong metallic bond. In general, M Pt. ↑ from left to rt. in period upto centre & then ↓ gradually due to variation in no. of unpaired e^- (more unpaired e^-, less M. Pt.).

Mn has anomalous behaviour.

* Hg is the only metal i.e liq^{d} at RT. It is due to following 2 reasons :-

(1) It has very high IE due to completely filled 4f & 5d orbitals & ∵ its 6s e^-s are not ionised for metallic bonding.

(2) It has completely filled d-orbital. So, no unpaired e^- for bonding.

So, Hg fail to form metallic bond & has very low M. Pt.

* Hg is highly carcinogenic. So, its stored in Toluene.

Toluene doesn't allow Hg to vapourise. (Hg being liq^{d} would have VP. Now, if left in open, it may go inside body in gaseous phase).

§ Colour :-

Trans^{n} metals usually form coordin^{n} compds whose aq. sol^{ns} are usually colored due to allowed d-d trans^{n} in visible range of EMR.

§ Oxid^{n} state :-

Trans^{n} metals show variable oxid^{n} state.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
2	2	2	2	1			(2)	1	(2)
3	3	3	(3)	2	(2)	2	(2)	(2)	
	4	4	4	(3)	(3)	(3)			
		5	5	4	4				
			(6)	5					
				6					
				7					

(*) → stable oxid^{n} state

* IE down the grp ↓. So, in period, it won't lose e^{-}s.

But, down the group, e^{-}s would be lost even when it has 6 e^{-}s

* Cr^{4+} is a Reducing agent (RA) because it reduces others and oxidises itself to a stable oxid^{n} state Cr^{+6}.
* Hg is exception regarding IE principle (trend)

Chemistry Notes Akshansh

classmate
Date
Page

✡ Mn^{3+} is an ~~redus~~ oxidising agent. So, it reduces to its stable oxid^{n} state → Mn^{2+}.

✡ Formation of Interstitial compds :-

Interstitial compds are those compds which contain some physically trapped (Occluded) smaller atoms like H_2, C, N etc in ~~ther~~ their voids.

Interstitial compds are mainly, non Stoichiometric (eg $FeH_{1.4}$) i.e atoms don't bear simple whole no. ratio (eg. $FeO_{0.97}$)

Interstitial compds have some characteristic features which make them imp. commercially :-

✓ Interstitial compds are very hard, used for making cutting tools

✓ Interstitial compds have higher S than pure metal.

✓ Interstitial compds are more ~~conductu~~ conductive ~~that~~ than the metal from which it formed.

✡ Due ~~to~~ to ~~fol~~ filling of voids in the interstitial spaces, they give color. So, interstitial compds are colored.

✡ COMPOUNDS

⟨1⟩ $KMnO_4$

§ PREPARATION

1. $KMnO_4$ is prepared from pyrolusite ore which contain (MnO_2).
The purified ore is fused with KOH in presence an Oxidising agent (usually KNO_3) where following rxn takes place :-

S1 $MnO_2 + KOH + O_2 \rightarrow K_2MnO_4$
(KNO_3 ↑)
Potassium manganate
(Green in color)
(Solid in state)

S2 Converting manganate to permanaganate
(A)

~~S2~~ $K_2MnO_4 + CO_2 + H_2O \rightarrow KMnO_4 + MnO_2 + K_2CO_3$

(B)

$K_2MnO_4 + H_2SO_4(dil) \rightarrow K_2SO_4 + KMnO_4 + MnO_2 + H_2O$.

i.e K_2MnO_4 on acidificⁿ undergo ~~dis~~ DISPROPORTIONATION RXN.

Chemistry Notes Akshansh

* HCl is not used as an acid here bcz Cl is further oxidised by permanaganate.

(C) Passing stream of $Cl_2(g)$ on dry, hot K_2MnO_4.

$$K_2MnO_4 + Cl_2 \longrightarrow KMnO_4 + KCl$$

(D) Treatment of sol^n of K_2MnO_4 with $O_3(g)$

$$K_2MnO_4 + O_3 + H_2O \rightarrow KMnO_4 + O_2 + KOH$$

PROPERTIES

1) Heating

$KMnO_4$ is thermally unstable & on simple heating, it decomposes forming the following

$$KMnO_4 \rightarrow \underset{\text{green}}{K_2MnO_4} + \underset{\text{black}}{MnO_2}\downarrow + O_2\uparrow$$

* The above rxn is also light initiated rxn. So, its kept in black container to prevent decompos^n from sunlight.
* It has to be standardised before titration to know what is its net strength (in case its decompos^n takes place).

#Chemistry Notes Akshansh

classmate
Date
Page

(2) $K_2Cr_2O_7$

PREPARATION

$K_2Cr_2O_7$ is prepared from Chromite steel ($FeO.Cr_2O_3$)

Chromite steel is 1st roasted with Na_2CO_3 in presence of O_2 (heat) where →

S1 $FeO.Cr_2O_3 + Na_2CO_3 + O_2 \xrightarrow{\Delta} Fe_2O_3 + Na_2CrO_4 + CO_2\uparrow$

(Sodium chromate)

~~Na~~ Soln containing ~~Na_2CO_3~~ sodium chromate is treated with H_2SO_4 (conc) where sodium dichromate is produced →

S2 $Na_2CrO_4 + H_2SO_4 \xrightarrow{(conc)} Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Soln containing $Na_2Cr_2O_7$ is treated with KCl (aq) →

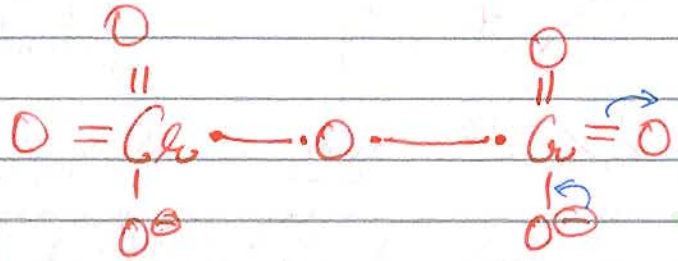
S3 $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7\downarrow + 2NaCl$

(crystallization)

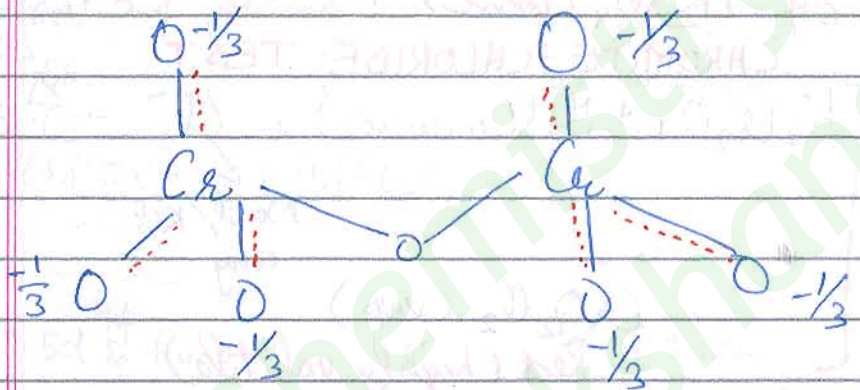
12 Chemistry Notes Akshansh

$K_2Cr_2O_7 \rightarrow 2K^+ + Cr_2O_7^{2-}$

covalent ion.



III



$Cr_2O_7^{2-}$ has 6 strong bonds b/w Cr & O & 2 weak bonds relatively.

CHEMICAL PROPERTIES → Cr_2O_7

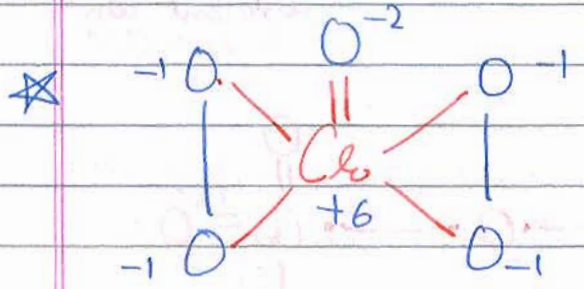
1) With H_2O_2

$K_2Cr_2O_7 + H_2O_2 \rightarrow \overset{+6}{Cr_2}O_5^{4-} + O_2 \uparrow$

Intense blue colored soln (water soluble)

Chemistry Notes by Akshansh

CrO_5 : Chromium peroxide.



peroxide linkage
Cr → +6 oxidn state.

2) Rxn with chloride salt in presence of H_2SO_4 (conc).

CHROMITE-CHLORIDE TEST

Test of Cl.

$K_2Cr_2O_7 + H_2SO_4$ (conc.) + Cl^- $\xrightarrow{\Delta}$

Cl^- ← NaCl/KCl.... any

CrO_2Cl_2 (vap.)
Red (highly volatile)

$CrO_2Cl_2 \xrightarrow{NaOH} Na_2CrO_4$.
Yellow

$Na_2CrO_4 \xrightarrow{conc.\ H_2SO_4} Na_2Cr_2O_7$
Orange

2 Chemistry Notes Akshansh

f-Block elements

↳ Elements in which f-orbitals are partially occupied. There are 2 periods of f-block elements known as
4f-series &
5f series

$^{57}La(5d^1 6s^2)$ →

4f :-

58	59	64	65	71
Ce	Pr	Gd		Lu
$(4f^1 5d^1 6s^2)$	$4f^3 6s^2$	$4f^7 5d^1 6s^2$	$4f^9 6s^2$	$4f^{14} 5d^1 6s^2$
5d is there		5d is there		5d is there

5f :-

89	90	91	92	96	103
Ac	Th	Pa	U	Cm	Lr
$6d^1 7s^2$	~~$5f^1$~~ $6d^2 7s^2$	$5f^2 6d^1 7s^2$	~~$6f^3 7s^2$~~ $5f^3$	$5f^7 6d^1 7s^2$	$5f^{14} 7s^2$
5f not there	5f not there	5f & 6d exist		5f & 6d exist	

Chemistry Notes Akshansh

classmate
Date 4.8.10
Page

ORGANIC CHEMISTRY

XII

Topics:

- ✓ Alkyl halides.
- ✓ Alcohols, Ethers, Epoxides
- ✓ Aldehydes & ketones.
- ✓ Carboxylic acid and its derivatives
- ✓ Amines
- ✓ Aromaticity and aromatic hydrocarbon
- ✓ Aromatic Electrophilic Substitution rxn.
- ✓ Nitrobenzene, Aniline, Diazonium compds.
- ✓ Aromatic aldehydes, ketone acids
- ✓ Aryl halides and phenols.

BIO CHEMISTRY
- ✓ Carbohydrates
- ✓ Amino acids / Proteins
- ✓ Polymers

XII Chemistry Notes Aryansh

Ch: Alkyl Halides (R-X)

✱ PREPARATION

(1) From Alcohols

Treatment of alcohol with :-

(a) HX

$$R\text{-}OH + HX \longrightarrow R\text{-}X + H_2O$$

(X → Cl, Br, I)

Mechanism

$$CH_3CH_2OH + HCl \longrightarrow CH_3CH_2Cl + H_2O$$

$$CH_3\text{-}CH_2\text{-}\ddot{O}\text{-}H + H^+ \longrightarrow CH_3\text{-}CH_2\text{-}\overset{+}{O}(H)(H)$$

(oxonium ion)

highly unstable intermediate

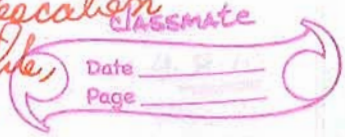
$$CH_3\text{-}CH_2^+ + H_2O \leftarrow$$

carbocation intermediate

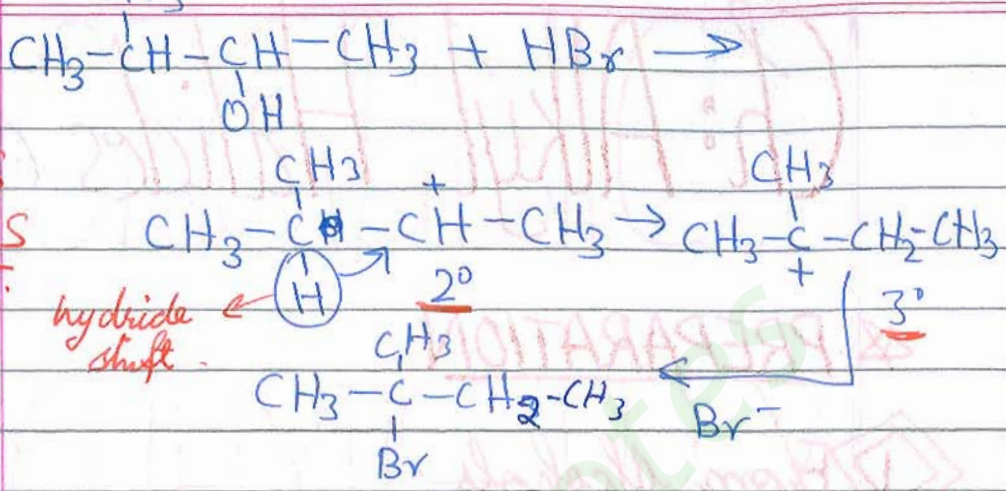
$$CH_3\text{-}CH_2^+ + Cl^- \longrightarrow CH_3CH_2Cl$$

Chemistry Notes Akhansh

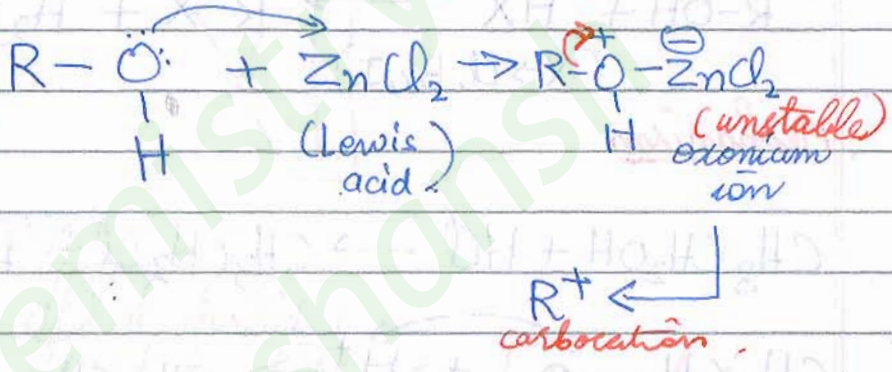
* In previous mechanism, carbocation intermediate was formed. So, if possible, its rearrangement may take place ↓



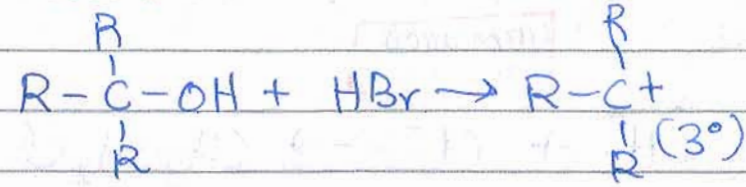
Eg



* The rxn is catalysed by lewis acid
* lewis acid helps in form of carbocation



* Tertiary alcohols may not require any lewis acid due to stability of tertiary carbocation :-



★ MK's rule:

MARKOVNIKOV's RULE
or MARKOWNIKOFF's RULE

b) $R\text{-}OH + PCl_5 \rightarrow R\text{-}Cl + POCl_3 + HCl$

$3R\text{-}OH + PCl_3 \rightarrow 3R\text{-}Cl + H_3PO_3$ (l)
phosphorous acid

Usage: ✓ PBr_3 ✗ PBr_5

c) $R\text{-}OH + SOCl_2 \rightarrow R\text{-}Cl + SO_2\uparrow + HCl\uparrow$
(Thionyl chloride)

Advantage: Both gaseous bi-products are gaseous at Room temp. So, they needn't be separated. Moreover So, byproducts need not be isolated in any additional step.

Moreover, gaseous nature of bi-product drive rxn to completion (Le-Chatelier principle)

Disadvantage: ✓ $SOCl_2$ most suitable for primary alcohol.
✓ $SOCl_2$ doesn't work with tertiary alcohol, weakly with 2° alcohol.

2) Addition of H-X to alkene

$>C=C< + HCl \rightarrow -\overset{H}{\underset{|}{C}}-\overset{Cl}{\underset{|}{C}}-$ (MK's rule)

eg: $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 + HBr \rightarrow CH_3-\overset{CH_3}{\underset{+}{C}}-\underset{CH_3}{CH}-CH_3$

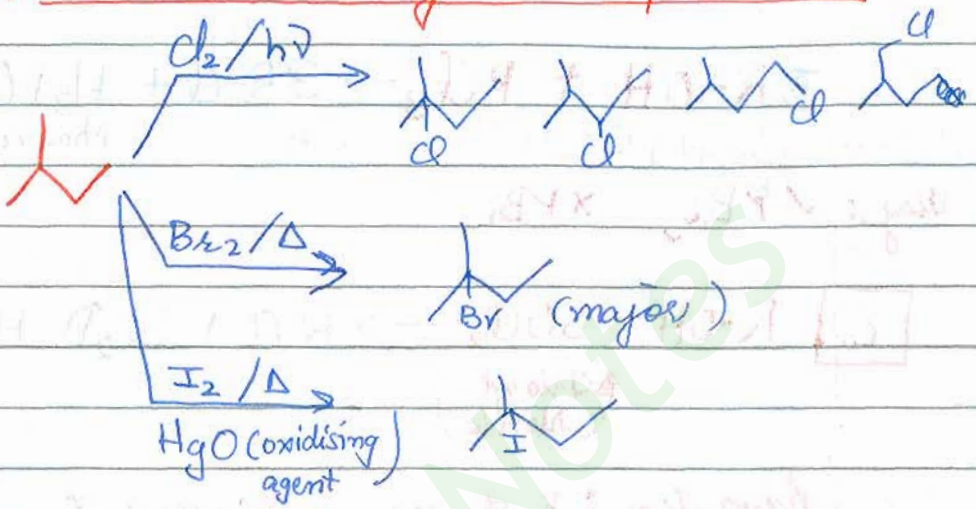
$\downarrow$

$CH_3-\overset{CH_3}{\underset{Br}{C}}-\underset{CH_3}{CH}-CH_3$ (major) (by methyl shift)

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{Br}{CH}-CH_3$ (minor)

* Chlorin^{n} is highly reactive, but very less selective.
* Bromin^{n} is less reactive, highly selective, occur at highest degree carbon.

3 Free-Radical Halogenation of Alkanes



4

$$RCOOH \xrightarrow[\Delta]{Ag_2O(aq)} R-\overset{O}{\overset{\|}{C}}-OAg + Br_2 \xrightarrow[\text{(non aq. solvent)}]{CCl_4 \text{ or ether}} R-Br + CO_2\uparrow + AgBr\downarrow$$

Silver salt of carboxylic acid.

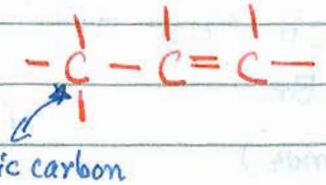
* Reduces one carbon from carboxylic acid.

($R-Br$ contains a C less than original compd)

* Above rxn is valid only for Br.
* Name of above rxn is HUNDSDIEKER'S rxn.
* Above rxn follow free radical mechanism.

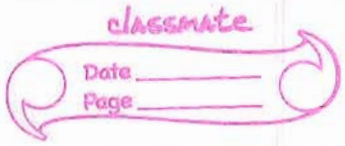
* Rxn occuring through $h\nu$ or Δ are mostly following free radical mechanism.

5 Allylic Bromination

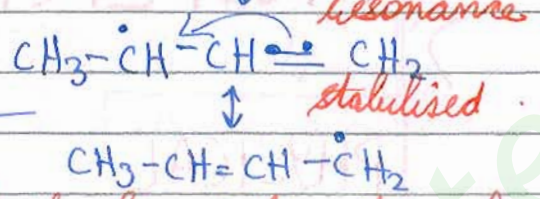


12 Chemistry Notes Nishant

* Allylic carbon : sp^3 carbon at α posⁿ of sp^2 carbon.



$CH_3-CH_2-CH=CH_2$ $\xrightarrow{Br_2/\Delta}$



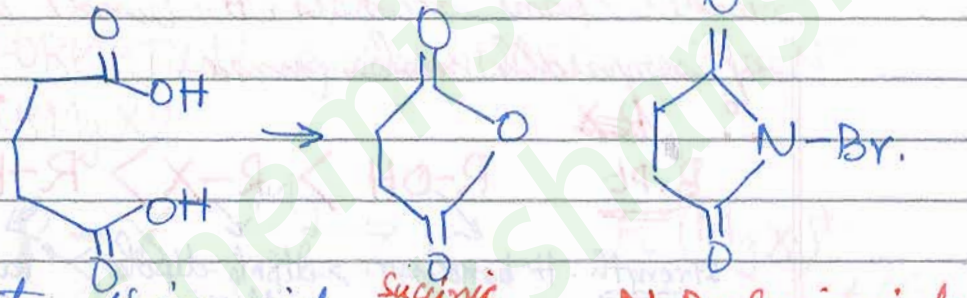
$CH_3-\dot{C}H-CH=CH_2 \leftrightarrow CH_3-CH=CH-\dot{C}H_2$

$CH_3-\underset{Br}{CH}-CH=CH_2$ (major)

Other products may also be formed by action of Br_2 on double bond to form dibromide.

$\xrightarrow[\Delta \text{ or } h\nu]{NBS/CCl_4}$ $CH_3-\underset{Br}{CH}-CH=CH_2$ (only allylic bromine)

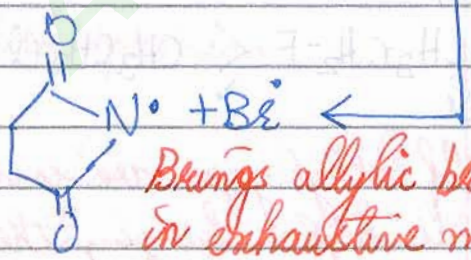
* NBS : N-Bromo Succinimide



Butanedioic acid or Succinic acid

Succinic anhydride.

N-Br-Succinimide



Brings allylic bromination in exhaustive manner.

+2 Chemistry Notes Akshansh

& PROPERTIES

PHYSICAL

1. R-X is a polar covalent bond.

$$-\overset{|}{\underset{|}{C}}-\overset{\delta+}{\underset{}{}}\ \overset{\delta-}{X}$$

The intermolecular force of attrⁿ among R-X molecule (~~H-bond~~ dipole-dipole) is stronger than hydrocarbons (Vander wall) but weaker than alcohols (H-bond) in case of comparable molar mass.

∴ ~~R-X~~

B.Pt R-OH > R-X > R-H.

Strength: H-bonding > dipole-dipole attrⁿ > Vander wall attrⁿ.

B.Pt. $CH_3CH_2-F < CH_3CH_2-Cl < CH_3CH_2-Br < CH_3-CH_2-I$

dipole-dipole

If alkyl grps are same, and molar mass is high change, then, vander wall exceeds over dipole-dipole attrⁿ.

2. Solubility: Solubility of R-X parallels the polarity i.e ~~R-F~~ R-F is most soluble & R-I is least soluble in H_2O.

(R-F forms H-bond)

FZ Chemistry Notes Akshansh

Ether: ✓ acts as inert solvent
✓ stabilises $RMgX$.

3. Density:
Fluoro & Chloro alkanes (~~R-F & R-Cl~~) floats over water, i.e lighter than H_2O.
Bromides & iodides are denser than H_2O.
Dihalides (any combin^n) are all denser than H_2O.

CHEMICAL

1) FORMATION of GRIGNARD REAGENT ($RMgX$)

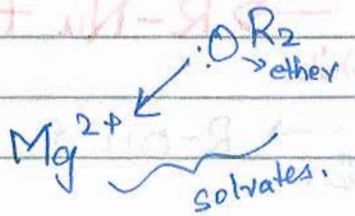
$$R-X \xrightarrow[\text{Ether } (C_2H_5OC_2H_5) \text{ or THF } (\square O)]{Mg} R^-(Mg X)^+$$

$(X \rightarrow Cl, Br, I)$ not F

Organometallic

Tetra Hydro Furan

* $RMgX$ is highly reactive, cannot be stored for longer time. It is prepared in Situ.
* Ether is used to reduce its reactivity a bit to control rxn. Dil e
* Ether solvates $RMgX$ by process of solv^n & thus, ↑ ~~solubility~~ stability.



classmate
Date
Page

3) REDUCTION

R-Cl (or R-Br) $\xrightarrow[\text{dil } H^+]{Zn-Cu}$ R-H } Zinc catalysed reduction.

$LiAlH_4$ → 1°, 2° to alkane
3° to alkene

$NaBH_4$ → 2°, 3° to alkane
1° → X

Ph_3SnH (Triphenyl Tin hydride) → 1°, 2°, 3° → all to alkane.

ALKYL HALIDES.

(main reactions)

- Nucleophilic Substitution
- Elimination Reaction

1 Nucleophilic Substitution.

leaving grp (it has to leave)

$R-\overset{\text{SUBSTRATE}}{X} + \overset{\text{Nucleophile}}{Nu^-} \longrightarrow R-Nu + X^-$

eg: $R-Cl + \underset{\text{nucleophile}}{OH^-} \longrightarrow R-OH + Cl^-$

classmate
Date
Page

* Nucleophile : The e^- rich species containing atleast a lone pair of e^-. It can be neutral (like H_2O, NH_3, R-OH) or can be -vely charged (like ^-OH, Cl^-, R^-).

* These rxns are also called (SN) rxns (substitution, nucleophilic).

* On the basis of nature of substrate, nucleophile, solvent etc., SN rxns are further classified into 2 categories known as

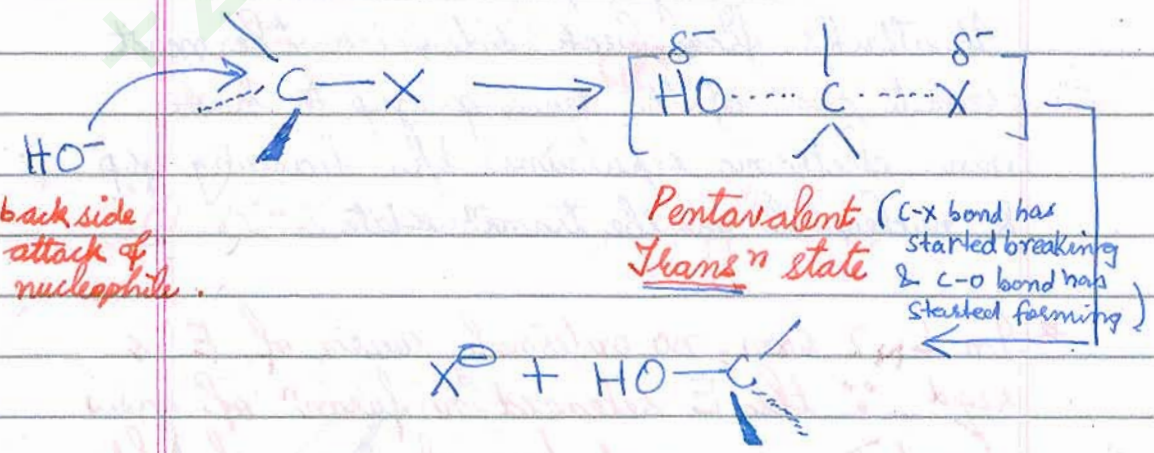
(i) BIMOLECULAR nucleophilic substitution (S_N2)

(ii) ~~U~~ ~~ECULAR~~ UNIMOLECULAR nucleophilic substitution (S_N1)

(i) S_N2 reaction

[~~also called~~ it is a CONCERTED Rxn i.e elementary Rxn]

Mechanism



back side attack of nucleophile.

Pentavalent Transn state (C-X bond has started breaking & C-O bond has started forming)

classmate
Date
Page

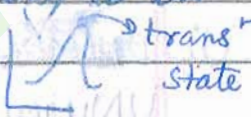
(1) Elementary rxn : ∵ S_N2 is a one step concerted rxn

(2) Nucleophile attacks from back side ∴ to form a pentavalent transⁿ state

(3) Involves pentavalent transⁿ state ∵ in which old bond has started breaking & new bond has started forming.

(4) Its order = 2, molecularity = 2 : The rxn is bimolecular, 1st order in each, nucleophile & substrate & 2nd order overall.

(5) Transⁿ state is the state of highest PE because C forms 5 bonds leading to its unstability & hence, high E.



Q. Why nucleophile ($N\ddot{u}^{\ominus}$) attacks from back side?

Ans: In order to have min. repulsion b/w $N\ddot{u}^{\ominus}$ & leaving group at transⁿ state. It attacks from back side, i.e the most remote posⁿ of the leaving grp to have min. electronic repulsions b/w leaving grp & nucleophile in the transⁿ state.

* In S_N2 rxn, no external source of E is reqd. ∵ the E released in formⁿ of new bond is consumed for cleavage of old bond. ∴ Stronger nucleophile is always reqd so that more E is released in making than the E reqd in breaking of bonds.

Chemistry Notes
Akshansh

In a nutshell,

* In S_N2 rxn, strongest nucleophile will replace the weaker nucleophile.

§ Kinetics : Rate = $R = k[RX][Nu^{\ominus}]$

* # Reactivity

(i) R–X (Same R but diff^t X)

$CH_3-F < CH_3-Cl < CH_3-Br < CH_3-I$.

** If all other cond^{ns} are same, then, the leaving ability follow the order : $F \ll Cl < Br < I$
(∵ in Rate determining step, cleavage of C–X bond will be tough in C–F, easy in C–I)

So * Iodide is the best leaving gp.

* In S_N2 rxn, C–X bond is broken in rate determining step. So, weaker the bond, stronger the cleavage.
* R–F is practically inert in S_N2 reaction.

(ii) R–X (Same X, diff^t R)

classmate
Date 6·8·10
Page

PRIORITIES

1st ✱ Attack of nucleophile on α carbon would depend on size of grps attached i.e the STERIC HINDERANCE.

2nd ✱ Electro +ve character of α-carbon.
More the +ve charge on α-carbon, more efficient will be attack of $Nu^{\ominus}$

✱ Reactivity on an alkyl halide in S_N2 rxn depends on 2 prime factors (if all other condns are same)
1) Steric hinderance
2) Electropositivity of α-carbon.

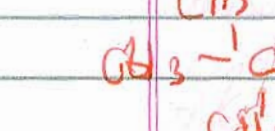
Steric hinderance: larger the size of final grps at α-C, greater the steric hinderance, small the reactivity in S_N2.

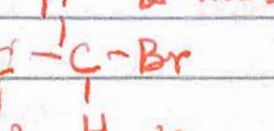
$$CH_3X > R-CH_2-X > R-\underset{R}{\underset{|}{C}}H-X >> R-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}-X$$

1° 2° 3°

✱ So, CH_3I is best leaving group.
✱ Bring alkyl grp to α-C decreases reactivity also due to +I effect from alkyl grp to reduce δ+ charge of C.

✱ Steric hindrance produced by 1 ter-butyl grp is more than that by 2 methyl grp. So Here, Reactivity 2° > 1°





* Some rxns (Situations) They are to understand

classmate Date Page

✓ $CH_3CH_2Cl \xrightarrow{aq.\ NaOH} CH_3-CH_2-OH + NaCl$

Feasible rxn → O-c bond strong than c-cl

✓ $CH_3CH_2Cl + NaCN \longrightarrow CH_3CH_2CN + NaCl$

c-cl bond weaker than c-c bond.

So, rxn is feasible.

✓ $CH_3CH_2Cl + CH_3ONa \rightarrow CH_3CH_2OCH_3 + NaCl$

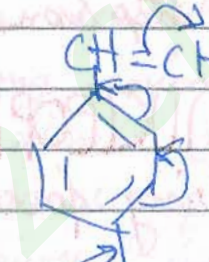
methoxy ethane.

✓ $CH_2=CH-\ddot{Cl} \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{Cl}$

S_N2 rxn not feasible. Stable ↑ due to resonance → Partial (=) bond character

✓ $R-CH=CH-\ddot{Cl} \longleftrightarrow \overset{\ominus}{R}=CH-\overset{\oplus}{C}H=Cl$

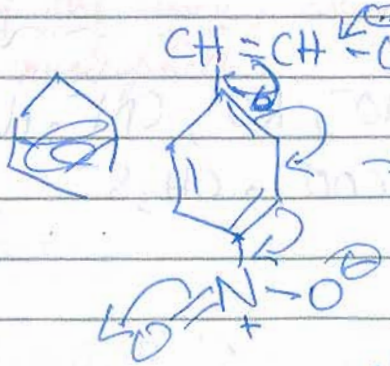
* Sometimes, resonance gives partial double bond character. So, then, it becomes difficult to break.

* 

→ reduces resonance ability of Cl. So, C-Cl bond would remain single bond.

Relative Comparison

Vinyl halide. Easy substitution

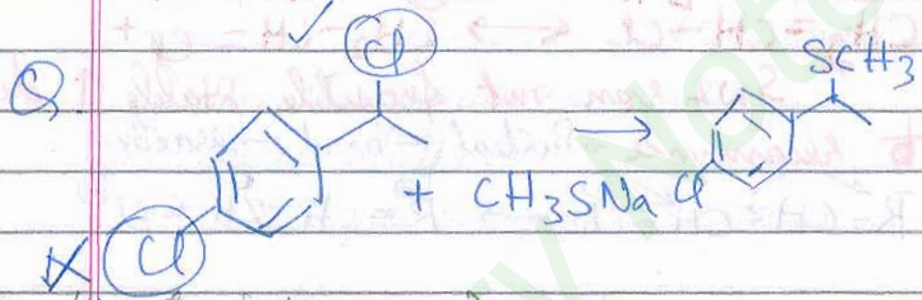


→ Cl in exhaustive resonance. So, C-Cl bond will have (=) bond character. Tough substitution.

→ High resonance

ARYL HALIDE

* Vinyl & Aryl halide are Inert in S_N2 rxn (due to resonance stability)



(participates in resonance / partial (=) bond character)

* S_N2 rxn is devoid of rearrangement (∵ no Reactive intermediate is involved, it's a single step rxn).

** EFFECT of Strength of NUCLEOPHile.

For S_N2 rxn, the driving force is strength of nucleophile.

neutral: $\ddot{N}H_3$ $H_2\ddot{O}:$ R–$\ddot{O}$H $CH_3-C(=\ddot{O})-\ddot{O}H$

Nucleophile:

anionic: HO^-, RO^-, CN^-, HS^-, $R-C\equiv C^-$, R^-, $RCOO^-$, CH_3S^-

Chemistry Notes Arshdeep

classmate
Date
Page

* **Basic strength** tells : Rxn ~~fast~~ ~~slow~~ How much amt. of product will be formed at equi.

Stronger base gives large amt of product. Basic strength pertains to thermodynamics of rxn.

* **Nucleophilic strength** : Gives how fast the rxn is taking place.

eg: Its possible to have a weak base, which is a strong nucleophile. So in it, rxn will occur quickly, but ~~rxn~~ product will be less formed.

Imp

1 * Anionic nucleophiles are always stronger than neutral nucleophile.

2 * Among anionic $Nu^{\ominus}$,

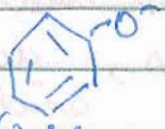
If donor atoms are same (eg O, O;)
& donor grps are from diff^t family, stronger base are always stronger nucleophile.

eg : $CH_3-CH_2-O^- > CH_3-\overset{\overset{O}{\|}}{C}-O^-$

** Most of the time, stronger base are strong nucleophile.

8.

Strength :

$CH_3-CH_2-O^- >$  $> CH_3-\overset{\overset{O}{\|}}{C}-O^-$

resonance is not only criterion.

Q. CH_3-CH_2-Cl + C_2H_5ONa → base
+ C_6H_5OH (excess) → acid

$$C_6H_5OH + C_2H_5O^- \rightleftharpoons C_6H_5O^- + C_2H_5OH$$

St. acid (excess) | st. base, limiting reagent | weak base | wk. acid

In the end, $C_6H_5O^-$ is only left & C_6H_5OH & C_2H_5OH are neutral. So, $C_6H_5O^-$ ($Nu^\ominus$) will react with CH_3-CH_2-Cl.

2 ★ (ii) If nucleophiles are from same family, then donor atom is same (They don't have much diff in acidic & basic strength. So, size matters) Smaller nucleophiles are stronger nucleophiles.

A ← $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-O^-$ SB	$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH$ WA
B ← CH_3-O^- WB	CH_3-OH SA

Though A is SB, still B is more reactive ∵ now, size comes.

3 ★ If donor atoms are from same gp of periodic table, nucleophilicity ↑ from top to bottom.

★★ In any group, down the gp :-
acidic strength ↑
basic strength ↓

Chemistry Notes by Akshay

HO^- ; NH_2^-

HS^- ; PH_2^-

WA H_2O HO^- SB

SA H_2S HS^- WB

So, HO^- ~~is more~~ should be reactive than HS^-. But, by previous rule, HS^- is more reactive. Hence, here, it disproves that stronger base is not always strong nucleophile.

Larger anions are more polarisable. It shares e^- density more easily & aids the form^n of bond.

Q (A) HO^- (C) CH_3O^-

(B) NH_2^- (D) CH_3^-

Basically (D) ✓ most reactive → carbanion;
2nd most reactive → NH_2 (see ↙)

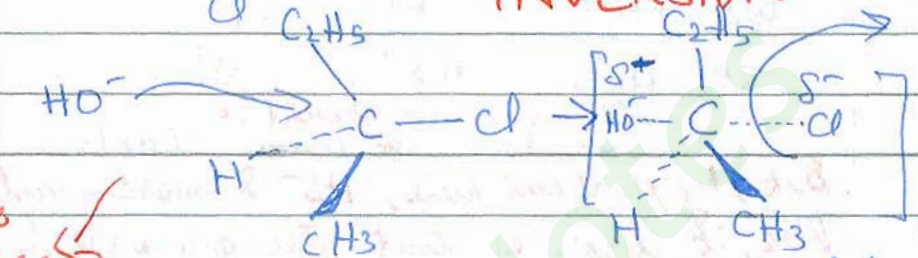
✱ Order of acidity

$RH < RCH=CH_2 < NH_3 < R-C\equiv CH < ROH < H_2O < \cdots$
$\cdots < PhOH < RCOOH < RSO_3H$

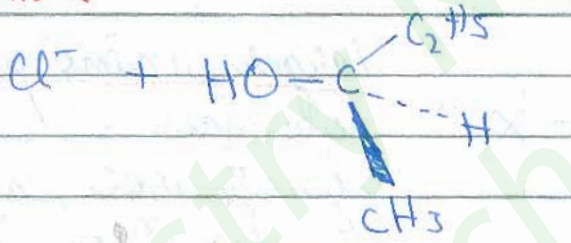
classmate
Date 11.8.10
Page

✱ Stereochemistry of S_N2 rxns

$CH_3CH_2-CH(Cl)-CH_3$ WALDEN INVERSION



They are not isomers so, ⊗ Isomerism can't be seen here.

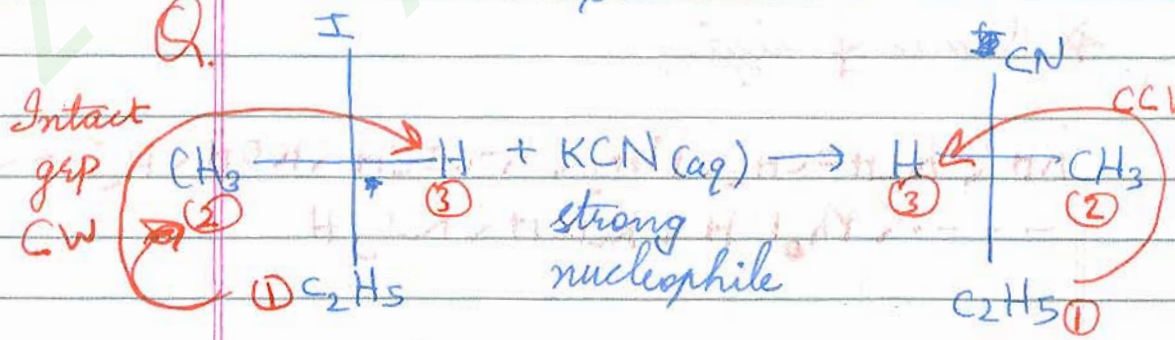


Walden inversion

✱ S_N2 rxn leads to inversion of confi. at chiral carbon possessing the leaving grp which is commonly known as Walden inversion.

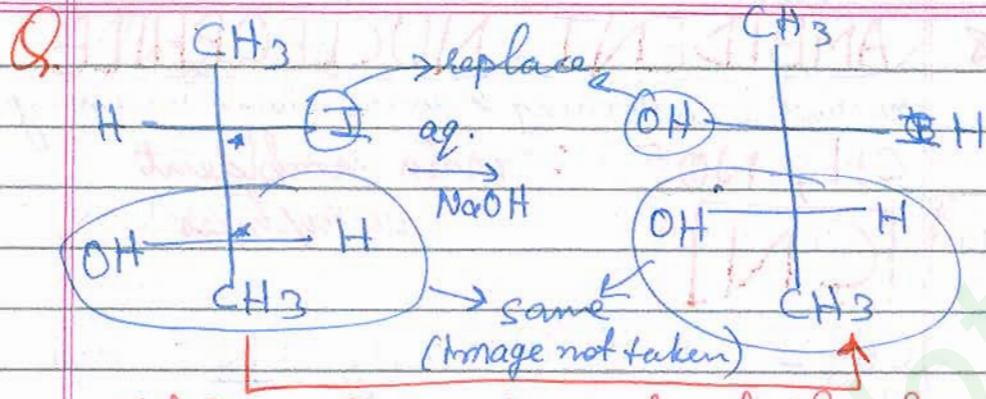
✱ Isomeric rxn: No chance here ∵ substance has changed.

Q.



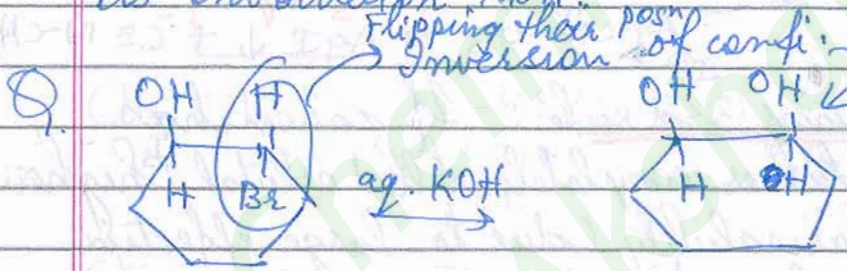
Taking mirror image & replacing I by CN⁻

* OH is never a leaving grp



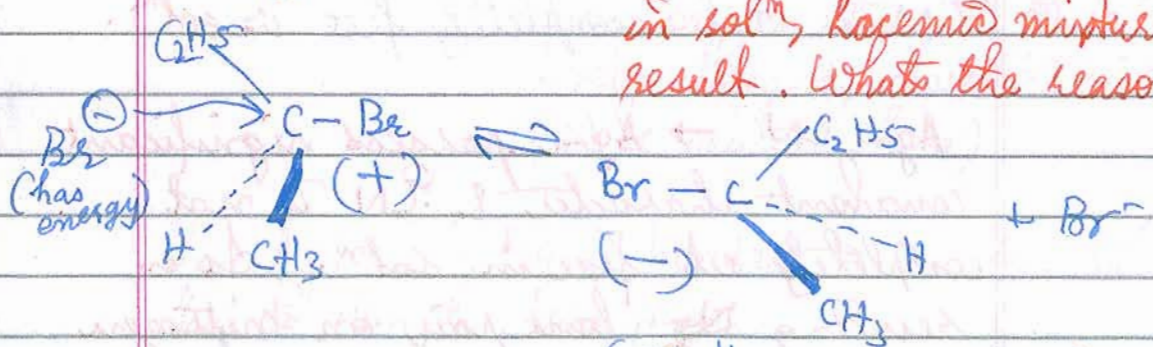
Taking mirror image only of the above α-carbon which undergoes change. The grps attached to lower α-C don't involve in rxn. So, its mirror image isn't taken.

* Confi. is inverted of the α-C only when its involved in rxn.



Q. $CH_3CH_2-\overset{*}{C}H-CH_3$
|
Br

When an enantiomerically pure 2-bromobutane is treated with NaBr (Br^-) in sol^n, Racemic mixture result. What's the reason?



* The 2 enantiomers occur in equal amt by equi. So, racemic
* Reactant & products are thermodynamically stable. So, its K = 1.

☆ All nucleophiles are ligands.

☆ **AMBIDENT NUCLEOPHILE**

nucleophile containing 2 donor atom in same grp

CN^-, NO_2^- : main ambident nucleophiles.

$:\overset{\ominus}{C}\equiv N$ ↳ carbon is stronger donor ∵ its less electro -ve.

CN (or Ba, K, Na(CN))

$CH_3-I + KCN \rightarrow CH_3-CN + KI$

CH_3-I: Strongest reactivity in SN2 reaction.

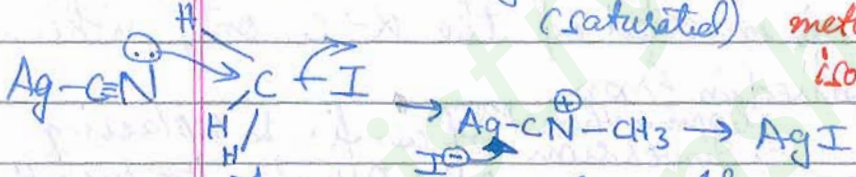
KCN (aq): Highly soluble cyanide.

CH_3-CN: methyl cyanide (major)

(Other minors may also exist)

$CH_3-I + AgCN \longrightarrow CH_3NC + AgI\downarrow$

(saturated) methyl isocyanide (major)



Fajans 3rd rule :- If cation has partial or completely filled orbital, its higher polarisability (due to large effective nuclear charge) increases. eg in Ag-CN, Ag has high polarising power, ∴ in AgCN, Ag-C bond has sufficient covalent character & $:CN^-$ is not completely free in sol^n.

Ag-CN → Ag-C possess significant covalent character & $:CN^-$ is not completely set free in sol^n. As a result, lone pair on nitrogen is more effective in donating to α-C of alkyl halide.

Chemistry Notes

★ Other ambident nucleophiles

→ SCN^- } with K, Na ... → S & O react
OCN^- } with Ag → N react.

classmate

Date
Page

Isocyanide

Resonance structures

$C\equiv\overset{\oplus}{N}-CH_3 \longleftrightarrow \ddot{C}=\ddot{N}-CH_3$

✓ octet complete ✓ C octet incomplete
✓ more bond ✓ less bond

eg: $Hg(CN)_2$ with CH_3I

$N\equiv C-Hg-C\equiv N$ (lone pair) → $C-I$

same logic as before.

$NO_2^{\ominus}$

$CH_3-CH_2-I + KNO_2 \xrightarrow{(aq)} CH_3-CH_2-ONO$ (major) ethyl nitrite

$CH_3-CH_2-I + AgNO_2 \xrightarrow{(aq)} CH_3CH_2-NO_2$ (major) nitroethane

(Ag bonded with O)

$\ddot{O}-\ddot{N}=O$ ∴ Attack occur predominantly from oxygen atom ∵ ⊖ is -vely charged, more e^- rich. (N is neutral, here)

In $AgNO_2$, Ag is bonded to O. So, N has to donate lone pair.

$CH_3-CH_2-I + :N(=O)-OAg \rightarrow CH_3-CH_2-\overset{\oplus}{N}(=O)-O^- + AgI\downarrow$

I. ↙

classmate
Date
Page

* $C = C^{14}$ here

$CH_3-\overset{*}{C}H_2-Cl + NaOH \rightarrow CH_3-\overset{*}{C}H_2-OH$ ✓

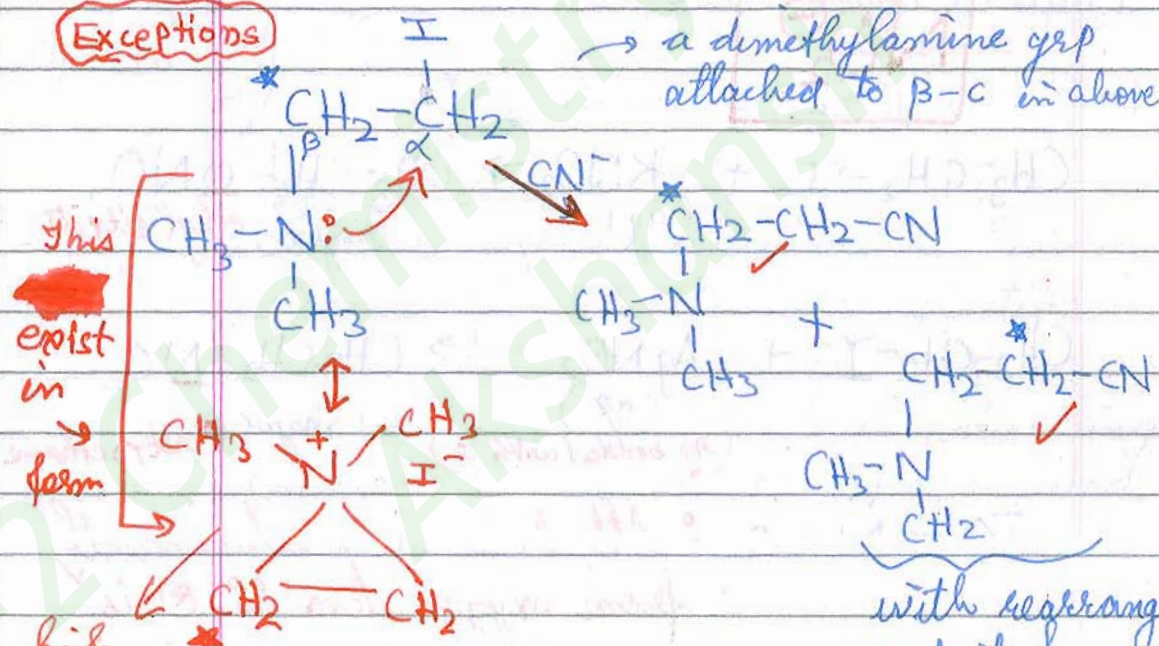
Radioactive labelling.

not $CH_3-\overset{*}{C}H_2-OH$ ✗

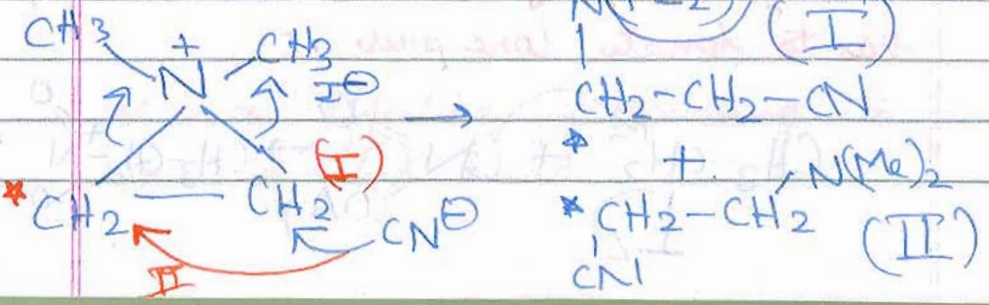
↳ as rearrangement doesn't take place (its a one step rxn, no RI is formed)

* In S_N2 rxn, $Nu^{\ominus}$ attach only to α-C in the final product.

Exceptions



→ a dimethylamine grp attached to β-C in above



classmate
Date
Page

* This condⁿ ↙ can also take place if CH_3S- is connected instead of $CH_3-N(CH_3)-$.

* ↙ This rxn is called SN(i) rxn. (not as S_N2 rxn) — intramolecular

* ↙ case is called as case of neighbouring grp participation
or
(ANCHIMERIC ASSISTANCE)

---

* S_N2 rxn: EFFECT of SOLVENT

Solvents

Polar (related to dipole moment) — polarity

Non-polar
eg: CCl_4, CS_2

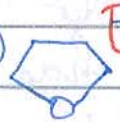
Polar Protic — from proton
eg. H_2O, $R-OH$, $R-\overset{O}{\overset{\|}{C}}-OH$, $R-NH_2$
Having atleast one H bonded to N or O
Polar

Polar Aprotic
Polar, but H is not bonded to electro-ve atom.

1) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ Acetone

2) $H-\overset{O}{\overset{\|}{C}}-N(CH_3)-CH_3$ DMF dimethyl formamide or N,N-dimethyl methanamide

3) $CH_3-\overset{O}{\overset{\|}{S}}-CH_3$ (S: sp^2) DMSO dimethylsulphoxide

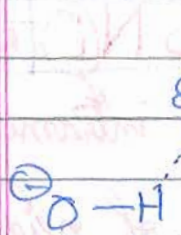
4)  THF: tetra hydrofuran

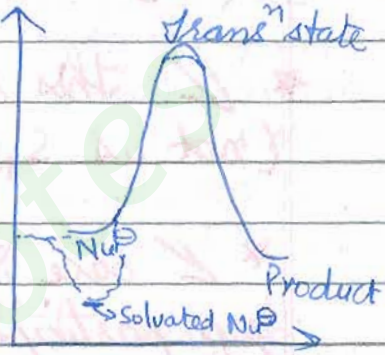
classmate
Date
Page

* Polar Protic solvent decreases the rate of S_N2 rxn (no exception)

$$R-X + OH^{\ominus} \xrightarrow{H_2O}$$

Polar Protic





Polar protic solvent solvate the $Nu^{\ominus}$
Since a type of bond is formed, So, E_{sys} is reduced ∴ E is released from sys. So, PE of $Nu^{\ominus}$ is decreased. So, Ea of reactant ↑, So rate ↓

* Polar protic solvent solvate $Nu^{\ominus}$ which is a reactant. ∴ increases Ea for forward rxn decreasing rate of rxn.

* Polar protic solvent solvates ~~Nu~~ $Nu^{\ominus}$ more than transⁿ state (∵ $Nu^{\ominus}$ has −ve charge but transⁿ state has less −ve charge). So, net Ea ↑. reactivity ↓

* If ions are not solvated, then, their basic strength parallels nucleophilicity.

Chemistry Notes by Arshdeep Singh

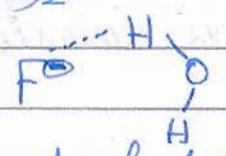
nucleophilicity

classmate
Date
Page

H_2O ⟶

Q. F^- Cl^- Br^- I^-

$(CH_3)_2CO$ ⟵



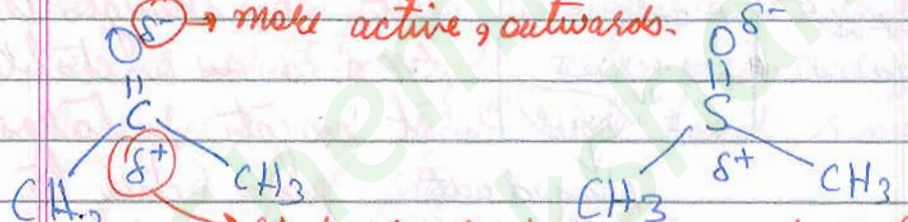
~~with water~~

with $(CH_3)_2CO$, ↖ their basic strength ∥ parallels nucleophilicity (F^- → most basic)

most solvated by water than Cl, Br, I

So, it would be largest in size. So, its attack ↓. But I is very less solvable. Hence, its size is less, so, its attack would be easy.

★ Polar Aprotic solvent increases rate of S_N2 rxn greatly (true)



$R-X + NaOH \longrightarrow R-OH + NaX$

$NaOH \rightarrow Na^+ + OH^-$

Na^+ goes with δ⁻ terminal

★ +ve terminal are sterically hindered. Not effective in solvating -ve Nu^-

★ -ve terminal are more exposed. & solvate cationic part of Nu^- more effectively & make anionic part of Nu^- more free, thus ↑ rate of S_N2 rxn.

IIT Chemistry Notes Akshansh

* Halogen exchange rxn

FINKELSTEIN'S RXN

classmate Date 20.8.10 Page

$$R\text{-}Cl \;(1^\circ \text{ or } 2^\circ) + NaI \xrightarrow[\text{acetone}]{(CH_3)_2CO} R\text{-}I + NaCl$$

* Here, a poor $Nu^\ominus$ (I^-) is substituting a stronger $Nu^\ominus$

NaI has smaller %age ionic character than NaCl. (Fajan's Rule)
So, NaCl is more soluble in H_2O
So, NaI is more soluble in Acetone.
So, NaI is more soluble in Acetone than NaCl.

Some amt of I replaces Cl.

Acetone
RCl + NaI
R-I + (NaCl)
↓
phased out (small solubility in acetone)

It is the insolubility of NaCl, it is phased out. So, though this rxn is unstable, it exists & takes place (due to Le Chatelier Principle)

SN1 Rxns. (Solvolysis)

$$R\text{-}X + \underset{\text{Poor } Nu^\ominus}{H_2O} \xrightarrow[\text{essential requirement}]{\Delta} R\text{-}OH + HX$$

✓ SN1 rxn require high T & weak $Nu^\ominus$
✓ SN1 rxn is a 2 step rxn.

Chemistry Ambition

Mechanism

S1 $R-X \xrightarrow[\text{slow}]{\Delta} R^+ + X^-$

S2 $R^+ + :\ddot{O}(H)(H) \xrightarrow[\text{fast}]{} R-\overset{+}{O}(H)(H) \xrightarrow{-H^+} R-OH$

oxonium ion

Rate = $K[RX]$

- ✓ S_N1 rxn is unimolecular rxn.
- ✓ In this rxn, rate depends only on conc. of RX.
- ✓ $Nu^\ominus$ is not involved in rate determining step, so, its strength is unimportant. But weak $Nu^\ominus$ is req^d, strong isn't req^d. Moreover, any $Nu^\ominus$ will react samely ∵ its a fast step.
- ✓ This rxn is called solvolysis rxn ∵ solvent itself is the / acts as the $Nu^\ominus$.

S_N2: $CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2-Cl \xrightarrow{C_2H_5ONa} CH_3-\underset{}{\overset{CH_3}{CH}}-CH_2-OC_2H_5$ (Major)

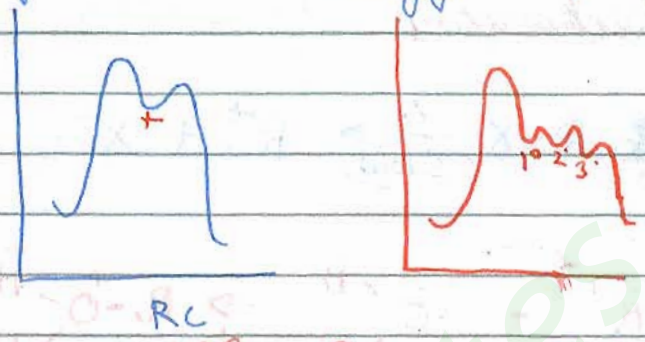
S_N1: $CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2-Cl \xrightarrow[\Delta]{C_2H_5OH} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OC_2H_5$

$CH_3-\underset{H}{\overset{CH_3}{C^+}}-CH_2 \longleftrightarrow CH_3-\underset{}{\overset{CH_3}{C^+}}-CH_3$

Chemistry Notes Akash

classmate
Date
Page

Ea diagram (or Energy Profile)



* In Energy profile, there would be atleast 2 peaks & one valley.

* REACTIVITY

(i) Diff^t halides : RF < RCl < RBr < RI

(ii) Diff^t alkyl gaps : 1° < 2° < 3°

Reactivity: S_N1 ⟶ 1° 2° 3° ⟵ S_N2

Q. $CH_3CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2I + CH_3ONa \xrightarrow{\Delta}$ S_N2 rxn takes place.

✓ In case of strong $Nu^{\ominus}$, even if heat is supplied, S_N2 rxn takes place (the rxn becomes faster).

Chemistry Notes Akshansh

classmate
Date
Page

✓ Allyl halides are highly reactive in S_N1 rxn.

$CH_2=CH-CH_2-X \longrightarrow CH_2=CH-\overset{+}{C}H_2 + X^-$

allyl ↕ allyl.

$CH_2=CH-\underset{\text{Allylic}}{\underset{|}{CH}}-R \longrightarrow CH_2=CH-\overset{+}{C}H-CH_3$

allylic

Stability:- Allylic carbocation > Allyl carbocation.

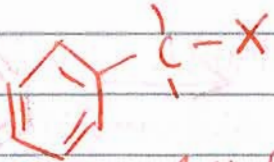
So, net stability/reactivity for S_N1 rxn:-

$1° < 2° <$ (Allyl $<$ $3°$ close relⁿ) $<$ Allylic.

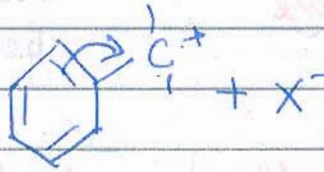
$CH_2=CH-\underset{R}{\overset{R}{\underset{|}{\overset{|}{C}}}}-X \quad < \quad CH_2=CH-\underset{X}{\overset{R}{\underset{|}{\overset{|}{C}}}}-CH=CH_2$

Reactivity order: monoallyl < diallyl < triallyl.

Phenyl halide



Benzyl Halide.



Very reactive :- $Ph-\underset{Ph}{\overset{Ph}{\underset{|}{\overset{|}{C}}}}-X$

at in S_N1 rxn

classmate
Date
Page

✱ $CH_3-O-\overset{\alpha}{C}H_2-Cl$: Highly reactive.

α-halo ethers.

Reason

$CH_3-O-CH_2-Cl \xrightarrow[\Delta]{C_2H_5OH} CH_3-O-CH_2-O-C_2H_5$

$CH_3-\ddot{O}-\overset{+}{C}H_2 \longleftrightarrow CH_3-\overset{+}{\ddot{O}}=CH_2$

complete octet

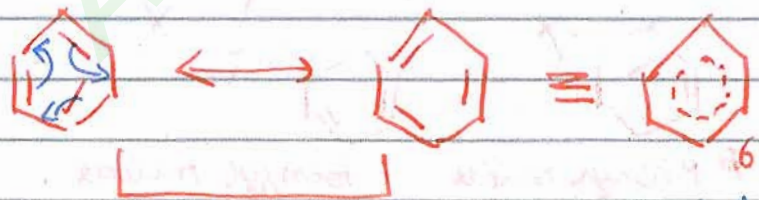
So, more stable.

Hence, substrate highly reactive.

✱ AROMATICITY

✓ Aromaticity is a phenomenon providing addnal stability to sys by lowering PE

✓ It is a stronger factor than resonance



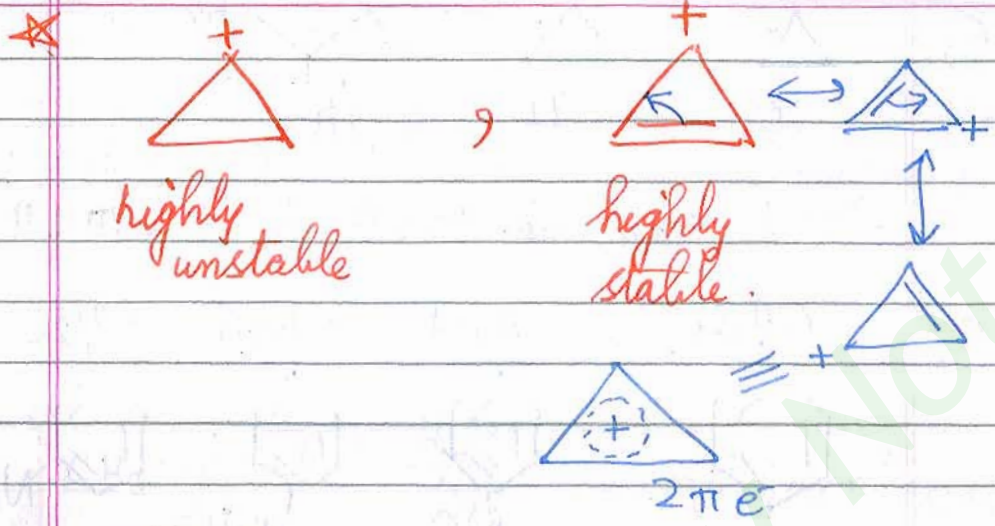
Kekule benzene

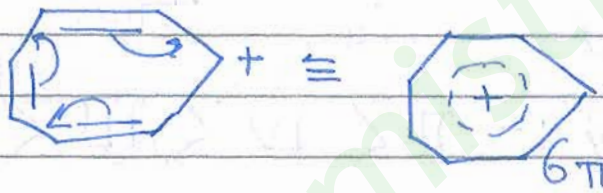
Actual benzene.

✓ Ultimate Criterion :- There must be a loop of delocalised $(4n+2)\ \pi\ e^-s$ where $n \in W$

Chemistry Notes Akshansh

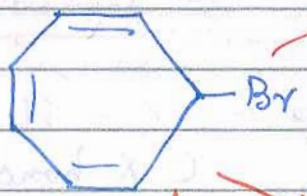
classmate
Date
Page



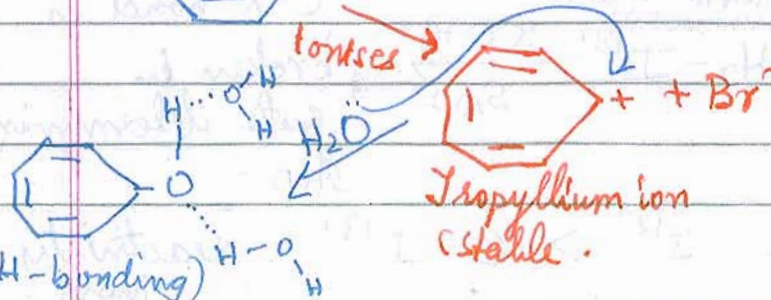


cycloheptatrienium ion
or TROPYLLIUM ION

Loop of delocalised 4nπ e⁻s
→ ANTI AROMATIC
(destabilises the sys greatly)



→ Though being an alkyl halide, its highly soluble in H_2O.

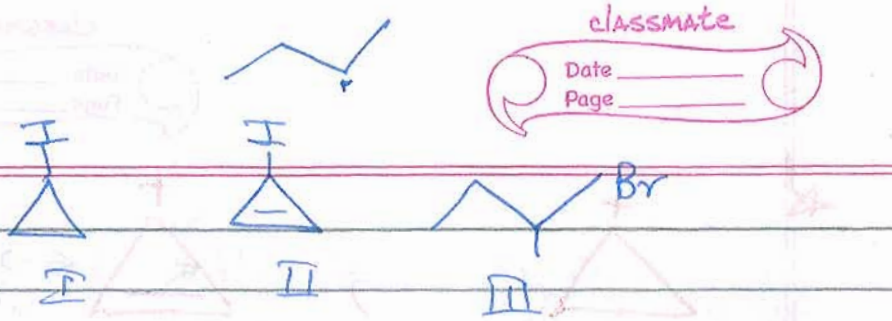


Tropyllium ion
(stable.

+2 Chemistry Notes
Akhilansh

classmate
Date
Page

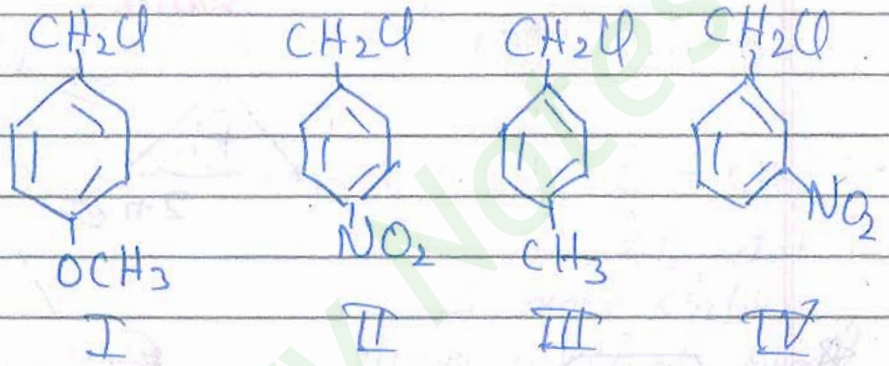
Ask Q.



I II III

S_N1 rxn ~~slow~~ reactivity I < III < II

Q.



I II III IV

S_N1 reactivity :- II < IV < III < I

—×—

* Isotopes have same chemical behaviours ∵ e^-s are involved in chemical bonding which are identical for both isotopes. But A heavier isotope forms stronger covalent bond.

eg : $CH_3-I^{127} < CH_3-I^{131}$: Strength of bond formed

—×—

Q $CH_3-CH_2-I^{127} \xrightarrow[S_N2]{KOH}$ identical condⁿ

$CH_3-CH_2-I^{131} \xrightarrow[S_N2]{KOH}$

C-X bond is broken in rate determining step -

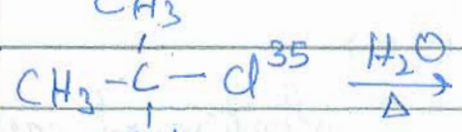
So, $C-I^{127} > C-I^{131}$: reactivity Here.

Chemistry Notes Anshuman

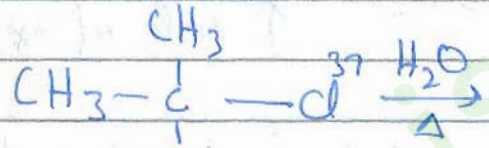
classmate
Date
Page

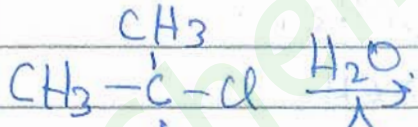
Q. $CH_3-CH_2-I \xrightarrow[S_N2]{KOH}$

$CH_3-CH_2-I \xrightarrow{K^{18}OH} O^{18}$ → stronger bond with C. So, its reactivity would be more.

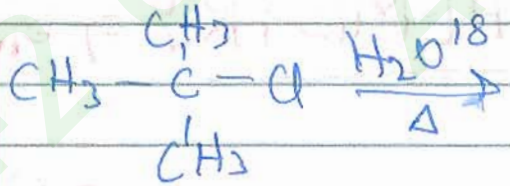
Q.


$Cl^{35} > Cl^{37}$ reactivity here
∵ cleavage of bond in Cl^{37} is easy.
Cl^{37} forms stronger bond.



Q.


: Same reactivity



✱ Presence of lewis acid catalyses S_N1 rxn.

$R-\ddot{X}: + ZnCl_2 \rightarrow R^+ + (ZnCl_2X)^{\ominus}$

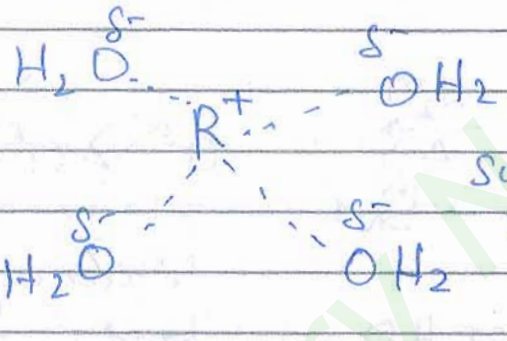
facilitate S_N1 rxn.

Chemistry Notes by Akshansh

ROLE OF SOLVENT

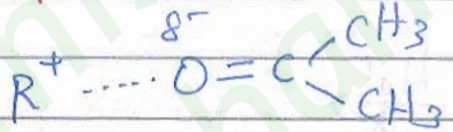
* **Polar protic solvent ↑ rate of S_N1 rxn.**

$$R-X \longrightarrow R^+ + X^-$$

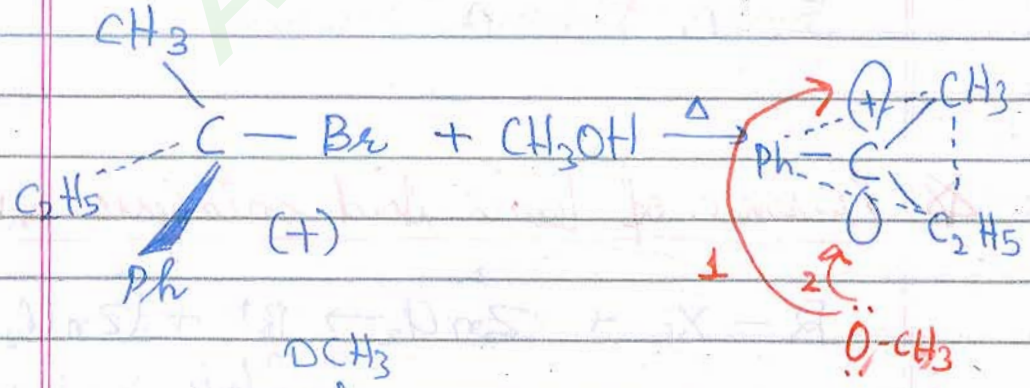


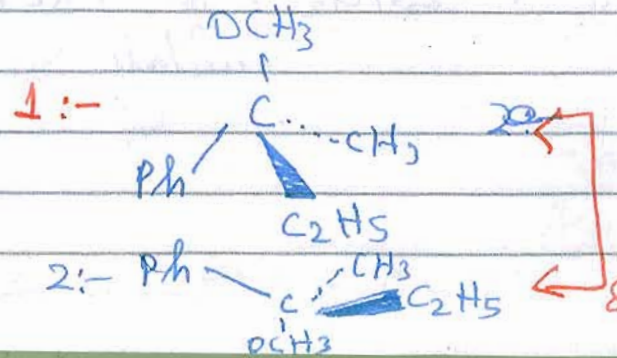
solvation of carbocation stabilises R^+, ↑ rate of rxn.

* **Polar aprotic solvent & also ↑ rate of rxn.**



STEREOCHEMISTRY of S_N1 rxn.



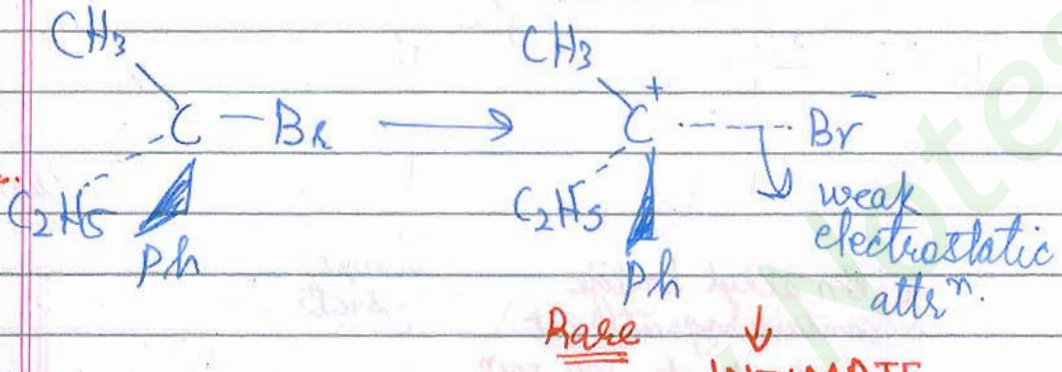


equal probability, gives 2 products in equal amt. So, RACEMIC MIXTURE

Chemistry Notes Akshansh

* S_N1 rxn leads to racemisⁿ of product if the α-C is chiral.

Some rare cases.



Rare

↓

INTIMATE ION PAIR.

* $Nu^{\ominus}$ can't react from front side here, so, there occurs partial racemisation with net inversion (the concept properly exists only 1% or 2% → mainly equal racemic mixture is formed).

---

§ ELIMINATION Rxn :-

$$R-X + \underset{\text{Base}}{B^-} \longrightarrow HX + \text{Alkene}$$

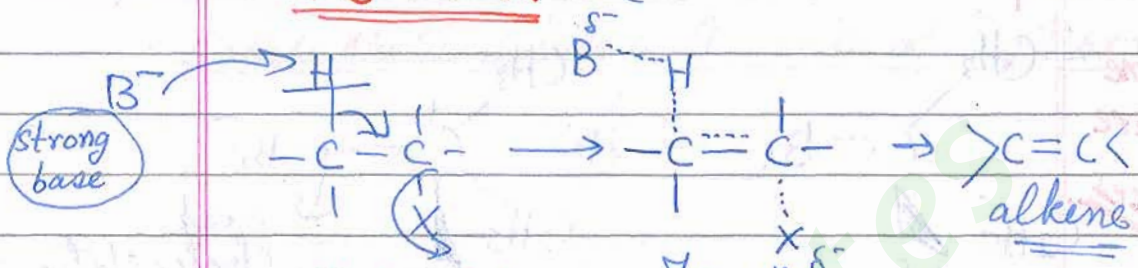
Depending upon the nature of R-X & B^- (base), elimination rxns are of further 2 categories :-

(I) BIMOLECULAR Elimination (E2)

(II) Unimolecular Elimination (E1)

One Step Concerted Rxn

✱ E2 Rxn (β-Elimination)



✱ An alkyl halide containing atleast 1 β-H at anti posⁿ

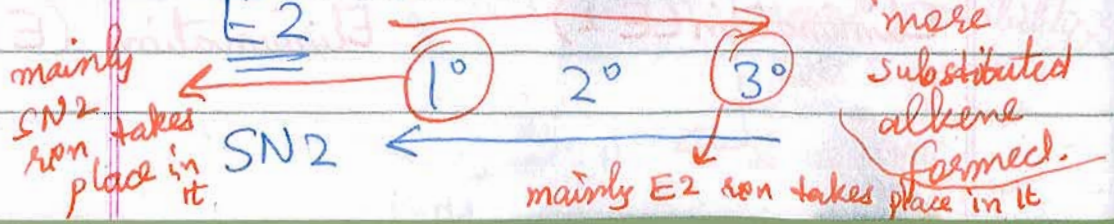
Imp
- ✱ E2 rxn is a one step concerted rxn
- ✱ E2 rxn is bimolecular
- ✱ E2 rxn is 2nd order. (1st ord. w.r.t each halide & base)

§ REACTIVITY

(i) Different Halides :-
C-X bond is broken in rate determing step. ∴, stronger the C-X bond, less reactive will be the alkyl halide in E2 rxn. ∴

RF < RCl < RBr < R-I

✓ E2 rxn reactivity depends on stability of alkene. More substituents on alkene, more stability. So, ∵ more R grp on α-C, more substituted alkene formed.



Q $CH_3CH_2-Cl + C_2H_5ONa/C_2H_5OH \rightarrow CH_3CH_2-O-CH_2CH_3$

SN2 takes place.

∵ 1° is more reactive in SN2 rxn.

Q $CH_3-\underset{Cl}{\overset{CH_2}{C}}-CH_3 + C_2H_5ONa/C_2H_5OH \rightarrow CH_3-\overset{CH_3}{C}=CH_2$

E2 rxn takes place

∵ $C_2H_5O^-$ plays role of base ∵

3° is more reactive in E2

Q. Which is better method to prepare methyl tert-butyl ether

Q $CH_3-O-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ methyl tert-butyl ether.

I: $CH_3ONa + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$

II: $CH_3Cl + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-ONa$ (no β-H, no E2)

In II, only SN_2 rxn takes place, but in I, chances E2 is predominant rxn, although some SN_2 product is formed.

Q $CH_3-\underset{D}{\overset{D}{C}}-\underset{Cl}{CH}-CD_3 \xrightarrow{C_2H_5OK/C_2H_5OH}$

I

II $CH_3-CH_2-\underset{Cl}{CH}-CH_3 \xrightarrow{II}$

I < II

D heavier than H

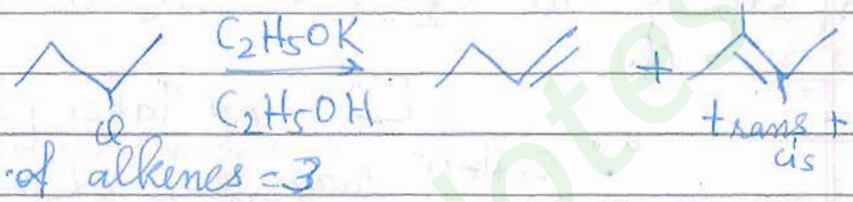
So, C-D stronger than C-H.

So, I < II.

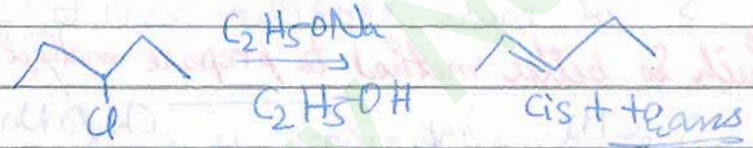
classmate
Date 25.8.10
Page

✱ KINETIC ISOTOPIC EFFECT (KIE):

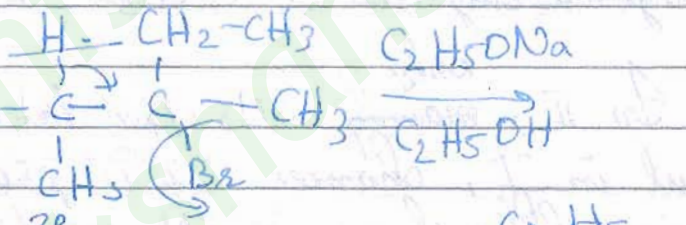
If rate of rxn changes by changing isotope, it leads to KIE.

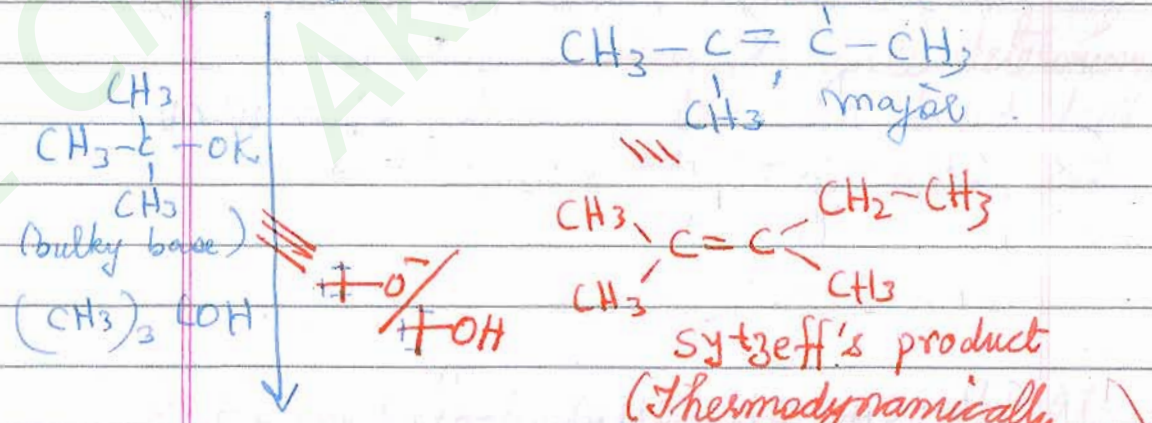


→ No. of alkenes = 3



→ no. of alkenes = 2





Chemistry Notes Akshansh

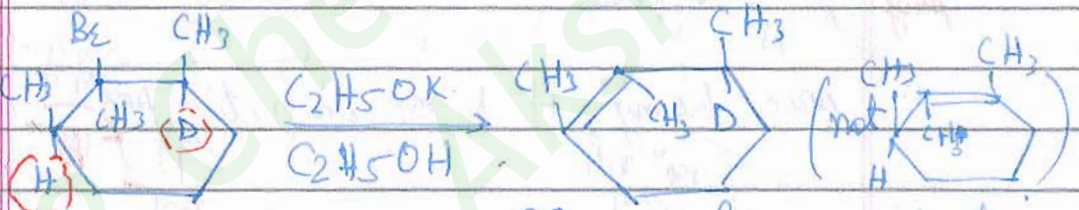
classmate
Date
Page

* If base is not very bulky, stability of product determine the orient^{n} of elimin^{n}.
* If base is bulky, (3°) then, the factor of steric hinderance determines nature of product & diminates β-H from C having min. steric hinderance.

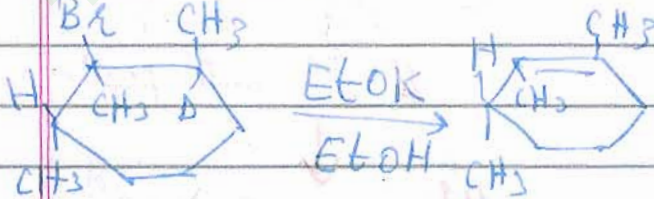
§ Role of SOLVENT.

Polar protic solvent decreases reactivity of E_2 rxn (solvates the base)
whereas, polar aprotic solvent ↑ reactivity (solvates the cation)

* STEREOCHEMISTRY of E_2 rxn :-



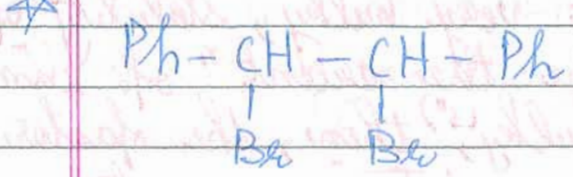
2° C-H bond is broken in rate determining step



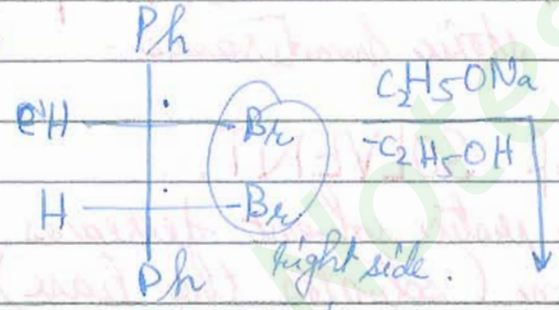
(∵ H is not at anti pos^{n})

FZ Chemistry Notes Akshansh

classmate
Date
Page



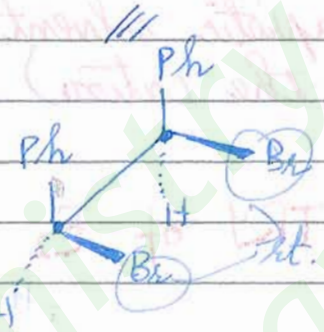
meso →



fischer projection.

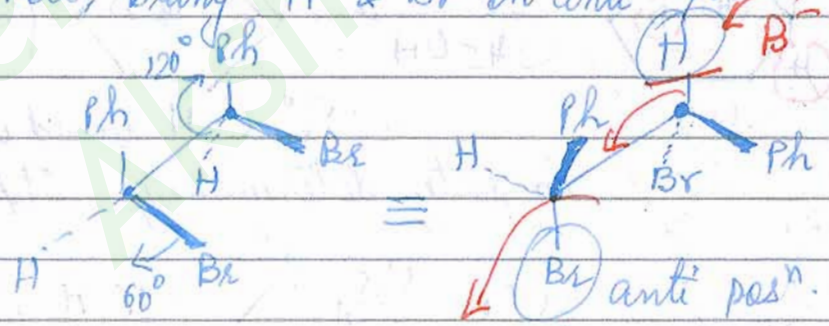
convert to

Saw horse projn



Rt. side.

now, bring H & Br in anti - posn

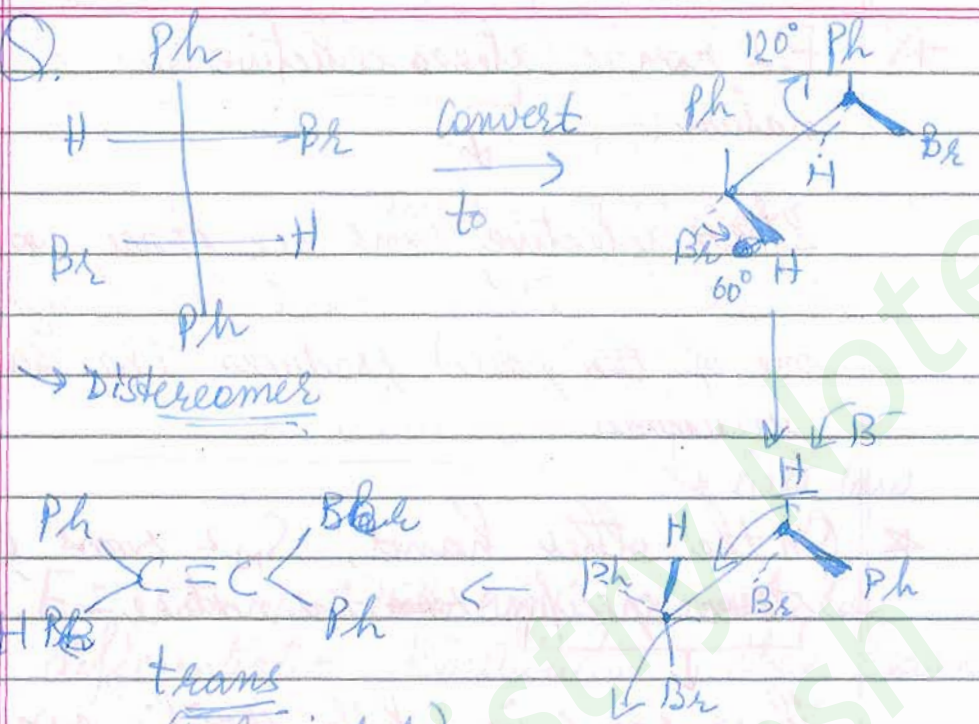


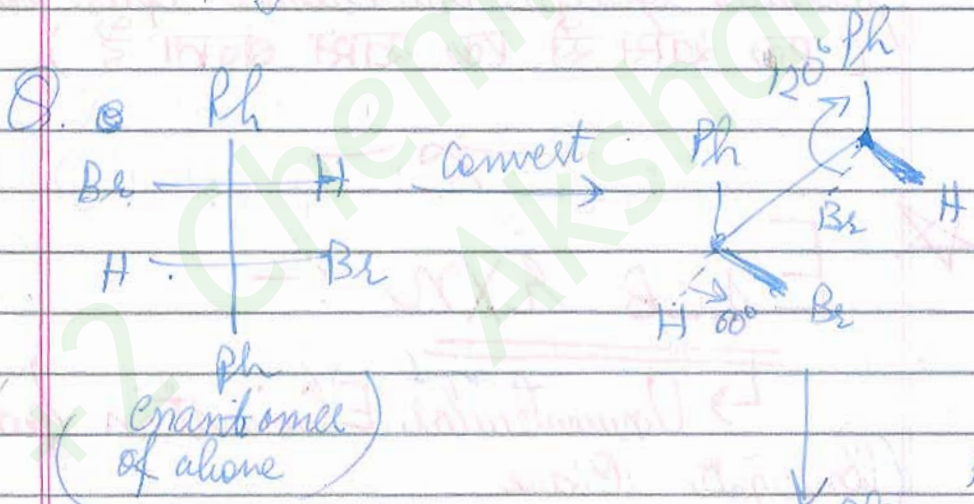
anti posn.

cis. (only product)

Chemistry Notes Abhilash

classmate
Date
Page

Q. 

Q. 

#2 Chemistry Notes Akshansh

Classmate
Date
Page

* E2 rxn is stereoselective in nature.

Stereoselective rxns are those rxns in which either enantiomers (any one of the pair) produces the same stereomer.

* On the other hand, S_N2 rxns are stereospecific in nature.

These rxns in which specific enantiomer produces specific enantiomer after rxn. (एक खास से एक खास बनता है)

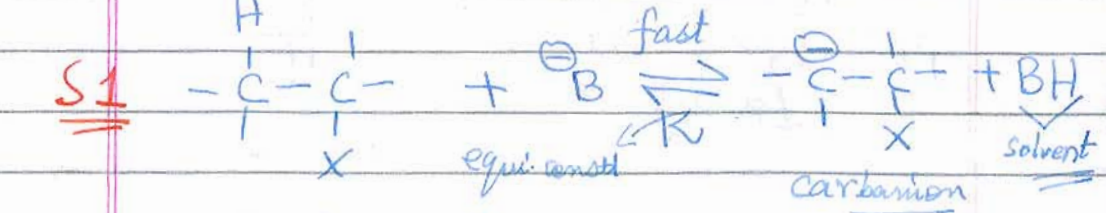
→

* E_{1cB} RXN :-

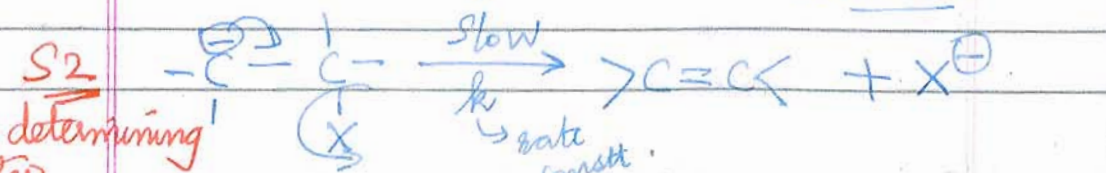
↳ Unimolecular (E)limination from (C)onjugate (B)ase

Mechanism ✓ 2 step elimin^n

S1



S2 Rate determining step.



Chemistry Notes Akshansh

classmate
Date
Page

Kinetics

$$R = k[C^-] = \left(k \frac{K[RX][B^-]}{[BH]}\right)$$

const. $\left(\because K = \frac{[C^-][BH]}{[RX][B^-]}\right)$

$$\Rightarrow \boxed{R = k'[RX][B^-]} \rightarrow \text{Rate law.}$$

* E2 rxn & ElCB rxns cannot be differentiated kinetically ∵ they have same rate law.

In this rxn,

Q $C_6H_5-CH_2-\underset{Br}{CH}-CH_3 \xrightarrow[C_2H_5OD]{C_2H_5OK}$,

(i) $C_6H_5CH=CH-CH_3$ is produced.

(ii) Neither reactant, nor product has radioactivity. What is its mechanism.

Ans: Its E2 only.

∴ Had (ii) $C_6H_5-\underset{D}{CH}-CHBr-CH_3$ is also obtained.

(i) In 1st case, D is not involved in reactant or product, so, no role of solvent. Hence, 1 step. So, E2.

Chemistry Notes Akshansh

(ii) Had it been E1CB, Cl^- formed reversibly forms reactant taking back D instead of H. Then,

$C_6H_5-\underset{\underset{D}{|}}{\overset{\overset{H}{|}}{C}}-CHBr-CH_3$ is obtained.

This reactant undergoes E1CB rxn to give $C_6H_5-\overset{\overset{D}{|}}{C}=CH-CH_3$ & hence giving both radioactive reactant & product

Q. $R-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3$ (I) $\qquad$ $R-CD_2-\underset{\underset{Br}{|}}{CH}-CH_3$ (II)

Stmt 1 Given: Rate of rxn is same.
Then, its E1CB ∵ S1 is fast.

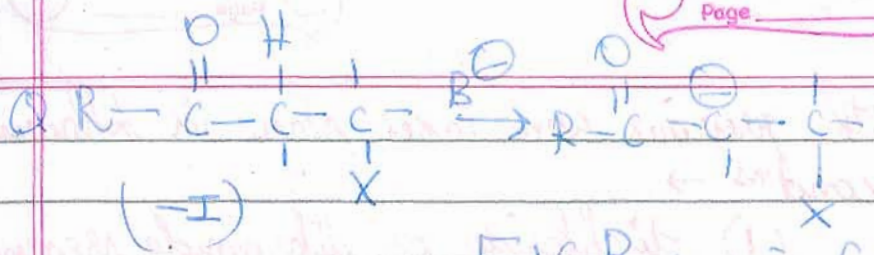
Stmt 2: Given Rate of 1 > Rate of 2
Then, its E2 ∵ breaking of bond occurs in rate determining step.

* E1CB rxn doesn't show KINETIC ISOTOPIC rxn.

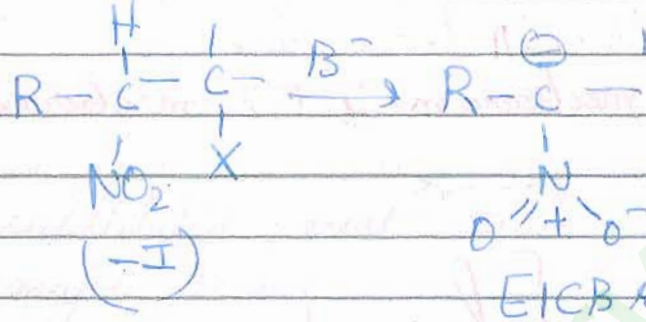
* Formⁿ of E1CB rxn would depend on the stability of carbanion formed. (Condⁿs to see → −I effect, −R effect, 1°, 2°, 3°)

Chemistry Notes Akshansh

classmate
Date
Page

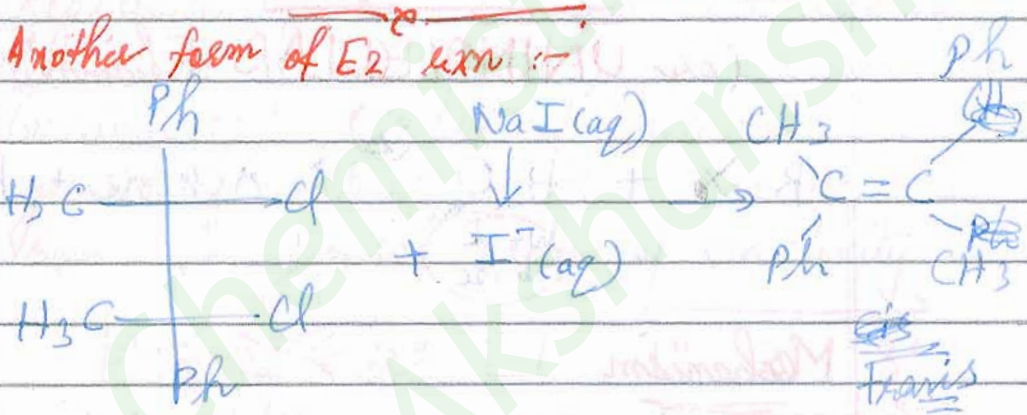
Q 

E1cB rxn is favoured.

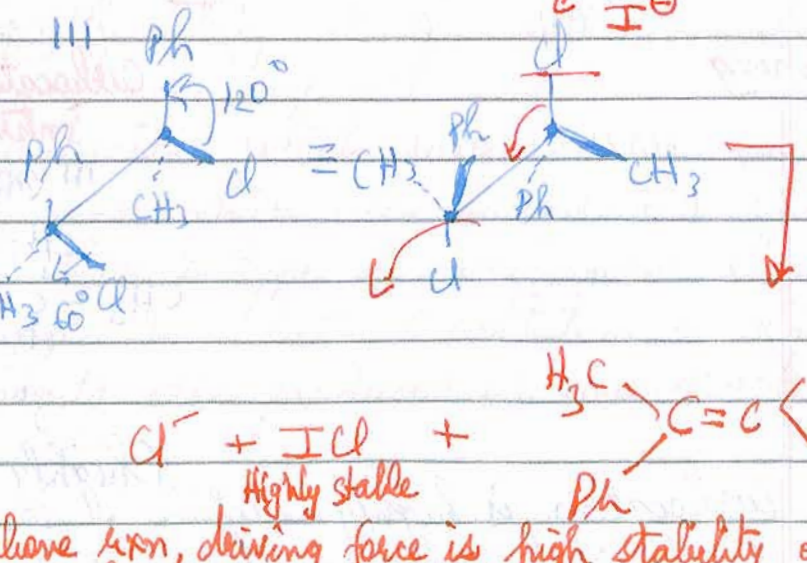
Q 

E1cB ~~rxn is promoted~~.

* Another form of E2 rxn :-

Q 

(meso)
(we can also take enantiomeric)



* In above rxn, driving force is high stability of interhalogen bond formed.

Chemistry Notes Akshansh

* The previous reaction takes place in following conditions →
  (i) dichloride or dibromide presence is treated with NaI, dichlorination & dibromin takes place
  (ii) mechanism is E2 mechanism.

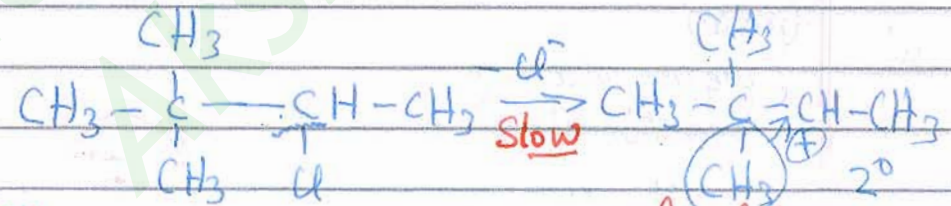
☆ E1 Elimination

(or UNIMOLECULAR Elimination)

$$R-X + H_2O \xrightarrow{\Delta} \text{Alkene} + HX$$

(H_2O: weak base)

Mechanism

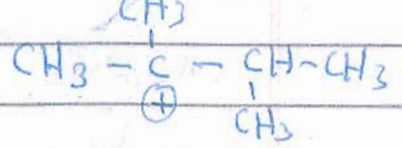


S1

Rate determining step.

Carbocation intermediate

1,1 methyl shift



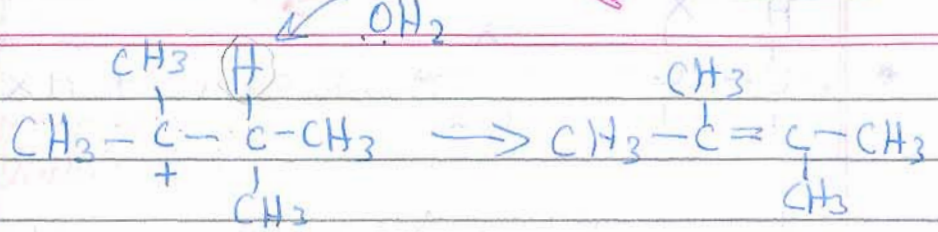
(highly reactive)

* Carbocation is highly reactive, so, it reacts with weak or strong base.

Chemistry Notes Akshansh

classmate
Date
Page

S2



In the 2nd fast step, carbocation loses a proton from the α-posⁿ containing min. no. of H in order to give most substituted, most stable alkene as the major product.

* Reactivity of R-X towards E1 rxn is determined from stability of carbocation. Greater the stability of carbocation, greater is reactivity of R-X towards E1 rxn. ∴ general order of reactivity.

1° ~~2°~~ ~~3°~~ E1 1° 2° 3°

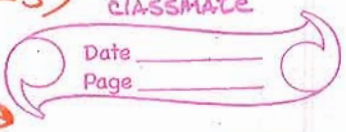
Same order SN1

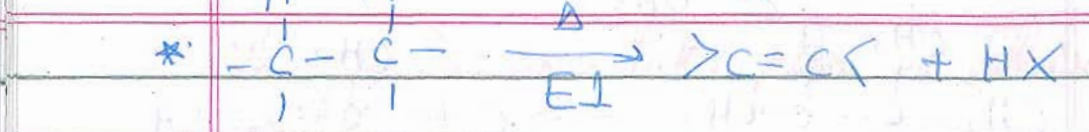
* Both E1 rxns & SN1 rxns are equally likely. Hence, both product are formed in comparable amts.
& Factors which favour SN1 rxn are the same which also favour E1 rxn.
∴ These 2 type of mechanism always compete & both substitution & elimin^n products are produced in comparable amt.

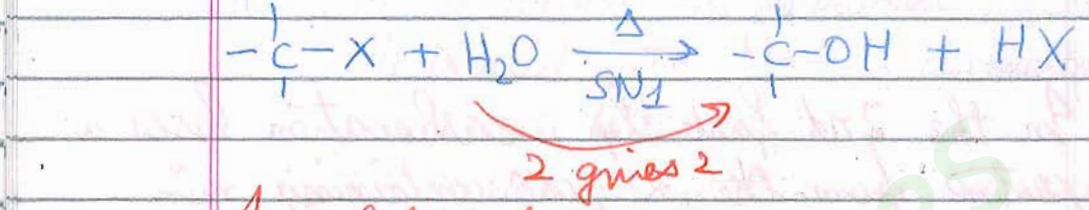
Chemistry Notes Akshansh

(has more +ve ΔS)

Δ gives 2



* 



In relative terms,

high heating : E1 takes place

moderate heating : S_N1 takes place

* E1 ron has more +ve ΔS°, So,

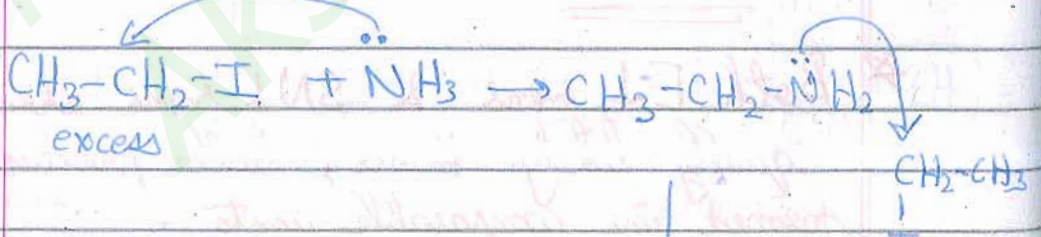
by $\Delta G = \Delta H^\circ - T\Delta S^\circ$,

T ↑, ΔG becomes more -ve.

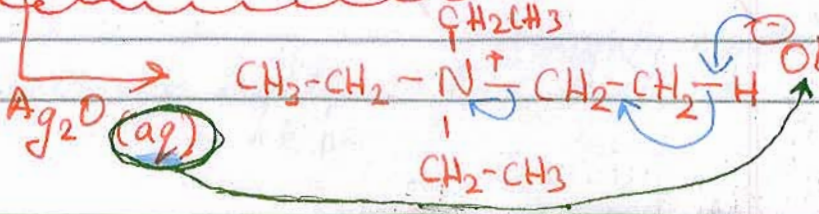
So, E1 ron is favored at high T.

---

another form



Quartenary ammonium salt



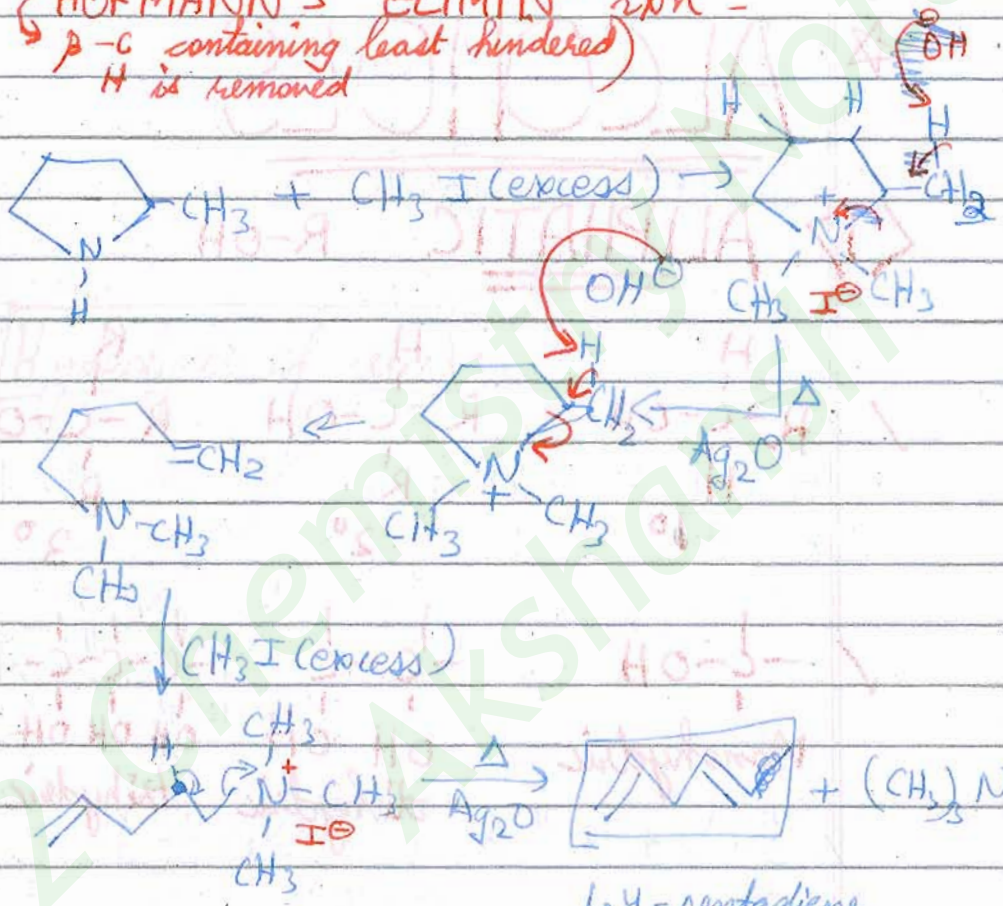
Chemistry Notes Akshansh

classmate
Date
Page

$\xrightarrow{\Delta}$ $(CH_3(CH_2)_3)_3N + CH_2=CH_2$

Hoffmann's elimin^n.

* The above rxn is called HOFMANN'S ELIMIN^n rxn - (↳ β-C containing least hindered H is removed)



1,4-pentadiene (diene grp)

EXCEPTION

* CH_3I + NH_3 → $(CH_3)_4N^+$ or $CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_3$ $I^\ominus$

excess

$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_3$ $\xrightarrow{OH^\ominus,\ \Delta,\ Ag_2O\ (aq)}$ $N(CH_3)_3 + CH_3OH$

SN2

* Above rxn is an exception of Hoffmann elimin^n rxn. It takes place when there is no β-H.

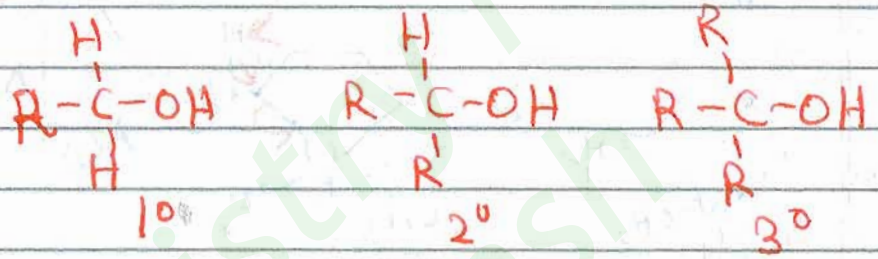
Chemistry Notes by Akshara

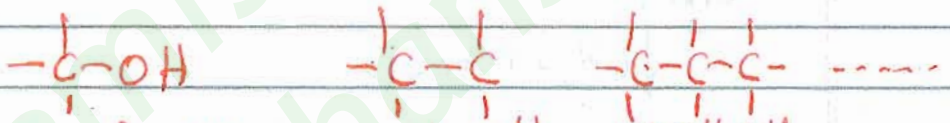
classmate
Date 27.8.10
Page

Ch: Alcohols, Ethers, Epoxides

✡ ALCOHOLS

(i) ALIPHATIC R-OH

✓ 

✓ 

§ PREPARATIONS (monohydric)

1) **By S_N2 rxn of R-X** :-

$$R\text{-}CH_2\text{-}Cl + aq.\ OH^{\ominus} \rightarrow R\text{-}CH_2\text{-}OH + Cl^-$$

Alcohol.

* Above method is not suitable for prepar^n of 3° alcohol (E_2 rxn will take place). Most suited for 1° alcohol.

Chemistry Notes Akshansh

Acyl grp – C(=O)–

In 3° alkyl halide

$$R-\underset{R}{\overset{R}{C}}-Cl + AgOOCR \xrightarrow{-AgCl} R-\underset{R}{\overset{R}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

Silver salt of Carboxylic acid — Ester

$$R-COOH + R-\underset{R}{\overset{R}{C}}-OH \underset{\text{or } OH^-/H_2O}{\overset{H^+/H_2O}{\rightleftharpoons}} \text{Hydrolysis}$$

Alcohol

2) **Hydrolysis of ester :-**

$$R-\overset{O}{\overset{\|}{C}}-OR' \xrightarrow[H^+ \text{ or } OH^-]{H_2O} RCOOH + R'OH$$

Alcohol

$$R-\overset{O}{\overset{\|}{C}}-\overset{OH}{\underset{H}{O}}-R' \quad (H, OH \text{ leave})$$

$$R-\overset{O}{\overset{\|}{C}}-\overset{\cdot\cdot}{O}-R' \xrightarrow[\text{or } HO^-/H_2O]{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-OH + R'-\overset{\cdot\cdot}{O}-H$$

* In hydrolysis of ester, acyl-oxygen bond breaks (& not alkyl-oxygen bond)

3) **Hydrolysis of ethers :**

$$R-\underset{OH}{\overset{H}{O}}-R + \underset{H_2O}{H_2SO_4\,(dil)} \rightarrow 2\,ROH.$$

$$R-\underset{OH}{\overset{H}{O}}-R' + \underset{H_2O}{H^+} \rightarrow R-OH + R'-OH$$

Chemistry Notes by Akshansh

classmate
Date
Page

4) Red^n of carbonyl compds.

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2/Ni} R-CH_2OH$$

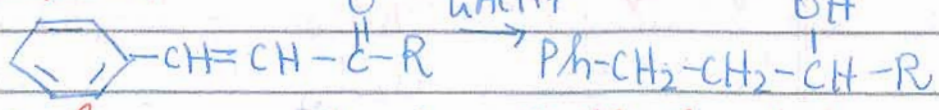
$$R-\overset{O}{\overset{\|}{C}}-R \xrightarrow{H_2/Pt} R-\underset{OH}{\underset{|}{CH}}-R$$

@ $R-CH=CH-CH_2-CHO \xrightarrow{Ni/H_2} R-CH_2-CH_2-CH_2-CH_2OH$

* H_2/Pt, H_2/Ni reduces olefins (compds containing double or triple bonds) also alongwith carbonyls.
* To protect removal of double & triple bonds:—

$R-CH=CH-CH_2-CHO$

$LiAlH_4$, $NaBH_4$ are used ∵
- ✓ Strong RA but weaker than H_2/Pt
- ✓ $LiAlH_4$ is ~~of~~ slightly stronger R.A than $NaBH_4$
- ✓ None of them reduces olefins
- ✓ Exception: of $LiAlH_4$.



in above case, it reduces double bond of CH=CH (not of Phenyl grp).

Chemistry Notes by Ishan

aldehyde $R-\overset{O}{\overset{\|}{C}}-H$

ketone $R-\overset{O}{\overset{\|}{C}}-R$

Derivatives

acid $R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR$ Ester

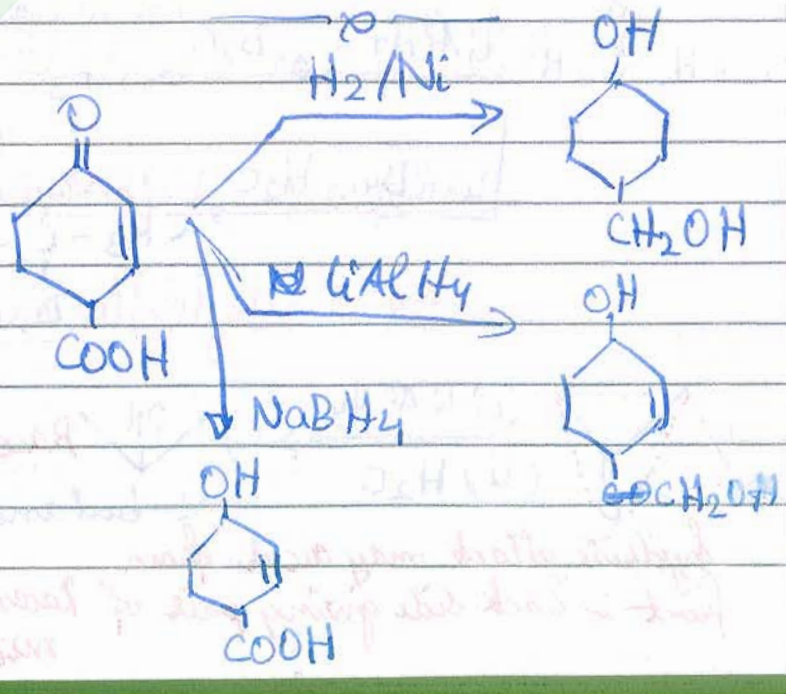
$R-\overset{O}{\overset{\|}{C}}-NH_2$ Amides

$R-\overset{O}{\overset{\|}{C}}-Cl$ Acid chloride

$(RCO)_2O$ Anhydride

* $LiAlH_4$ reduces aldehydes, ketones, acids, acid derivatives → into alcohols (amide is reduced to amine).
* $NaBH_4$, being weaker than $LiAlH_4$, reduces aldehydes & ketones → into alcohols. But fails to reduce acids & its derivatives

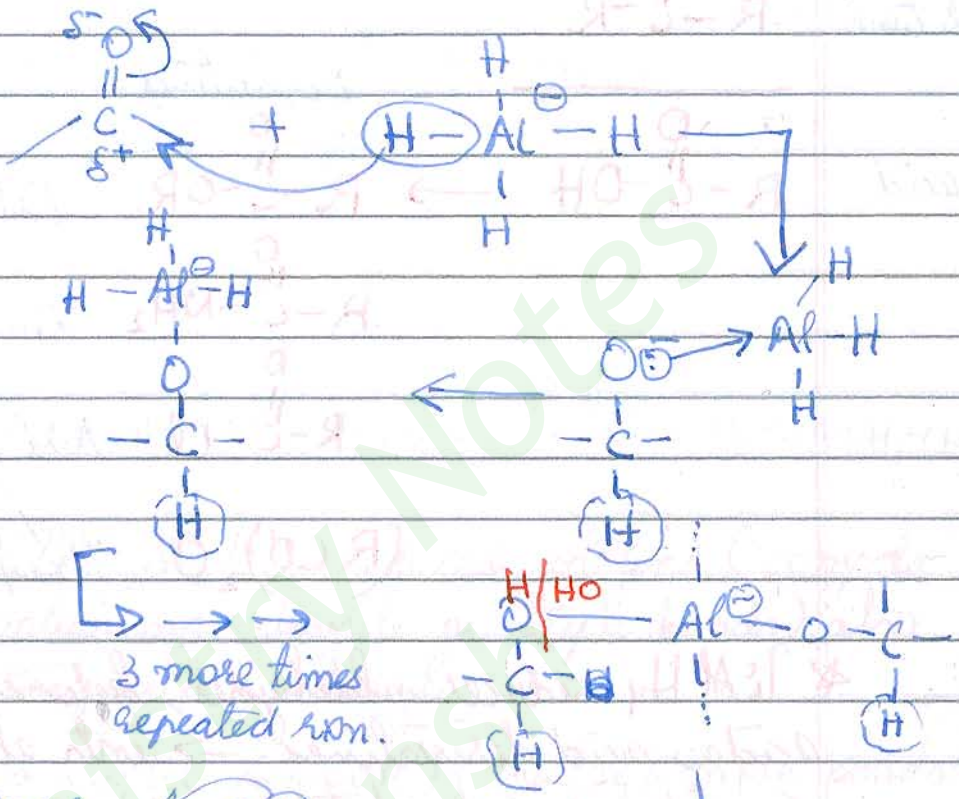
Q.

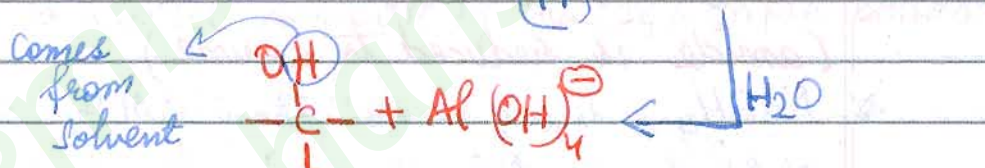


classmate
Date
Page

MECHANISM of redⁿ with $LiAlH_4$ or $NaBH_4$.

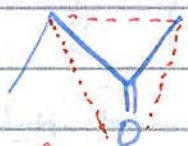
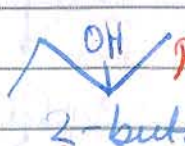
HYDRIDE TRANSFER





eg. $CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow{LiAlH_4} \xrightarrow{D_2O} CH_3-\underset{H}{\overset{OD}{C}}-H$

$LiAlD_4 \xrightarrow{H_2O} CH_3-\underset{D}{\overset{OH}{C}}-H$

Q.  $\xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4}$  Racemic mix

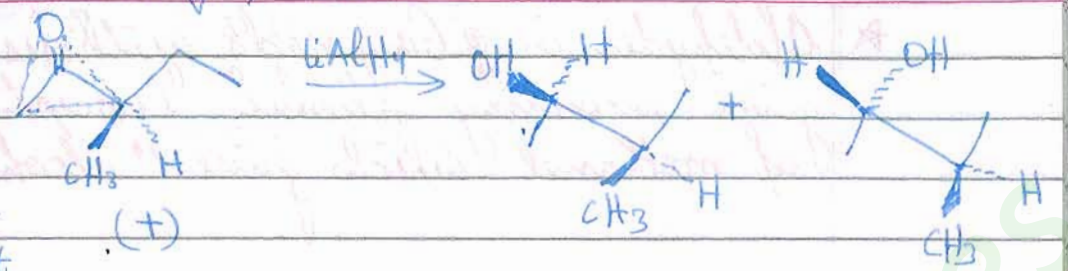
2-butanol

hydride attack may occur from front & back side giving pair of racemic mixture.

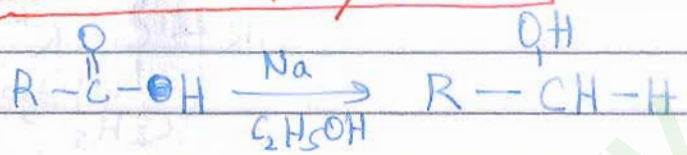
Chemistry Notes by Akshansh

How many products? → 2

Q. Attack from back & front



5) Redⁿ with Na/EtOH



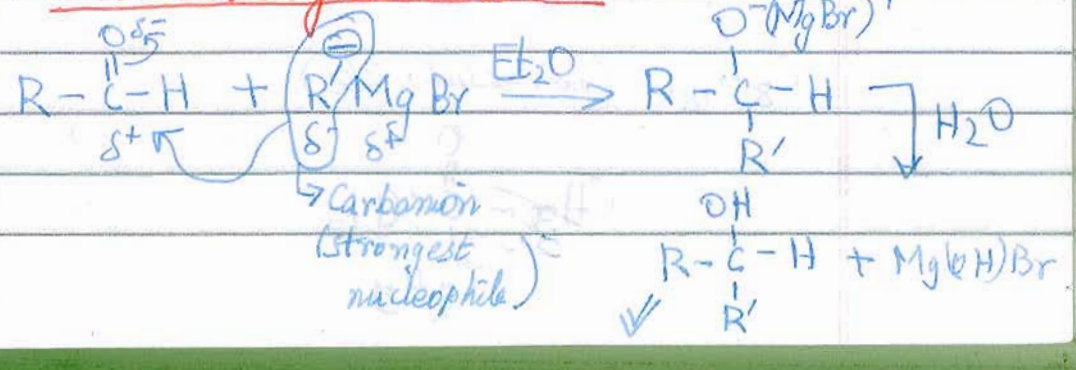
* Na/EtOH never reduces → olefins, cyanides

reduces → aldehydes, ketones, acids, acid derivative to ale alcohols.

* BAUREAULT BLANC REDⁿ.
  ↳ B-B Redⁿ.
  ✓ Rxn proceeds through free-radical mechanism
  ✓ It doesn't reduce olefins.

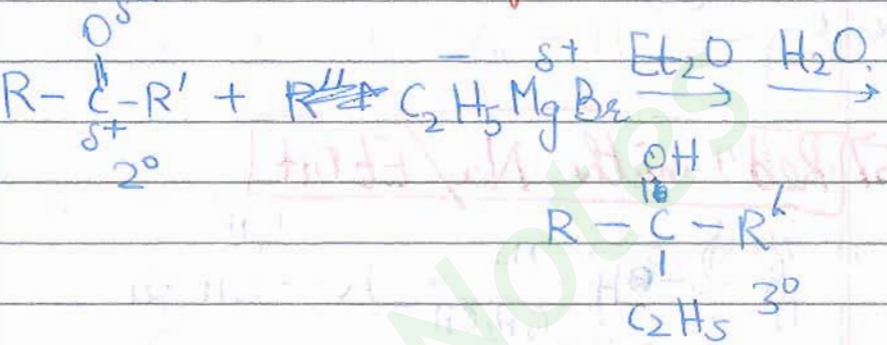
*6) GRIGNARD's Synthesis

(A) From Aldehydes & Ketones



classmate
Date
Page

* Aldehydes in Grignard's synthesis gives secondary alcohol (exception of methanal which gives 1° alcohol)



* All ketones in Grignard's Synthesis always gives tertiary (3°) alcohol.

* If, in Grignard Synthesis, α-C becomes chiral, then, there would be Racemic mixture of products.

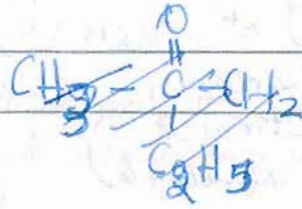
* Separⁿ of Racemic mixture is called RESOLUTION (i.e resolvable products are formed)

* For non-resolvable products → optically inactive

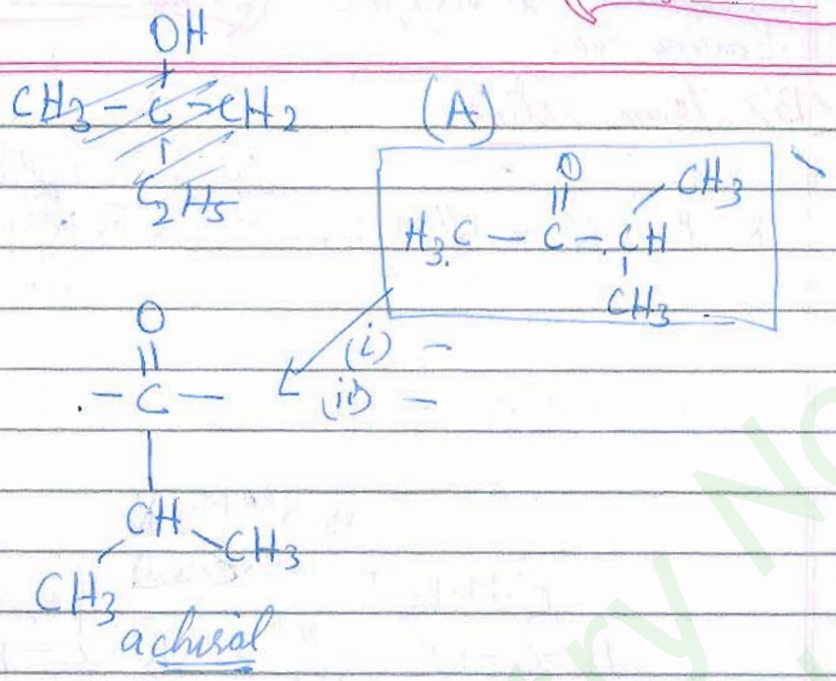
Q. $A(C_5H_{10}O) \xrightarrow{LiAlH_4} \xrightarrow{H_2O}$ Resolvable products

(i) $(CH_3)_2CHMgBr$
(ii) H^+/H_2O

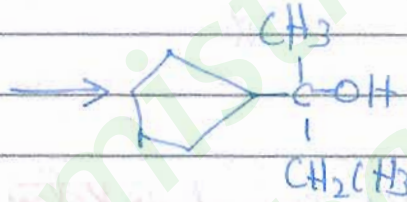
$C_8H_{18}O$ (non resolvable)



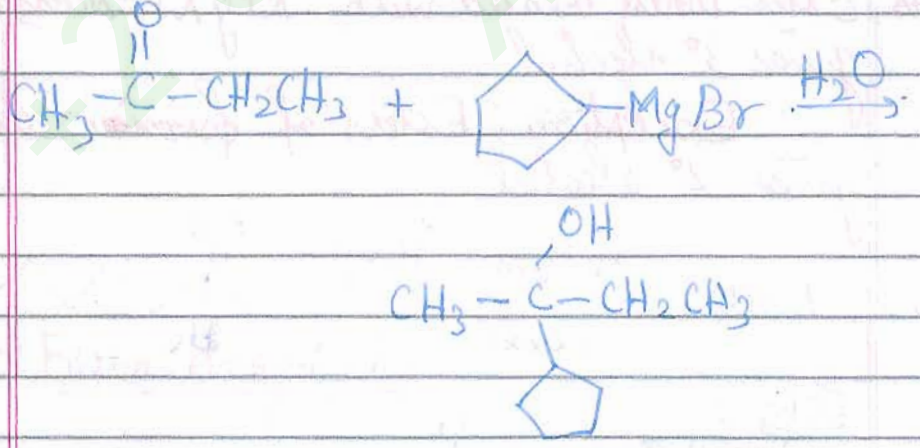
classmate
Date
Page



achiral

Q. 

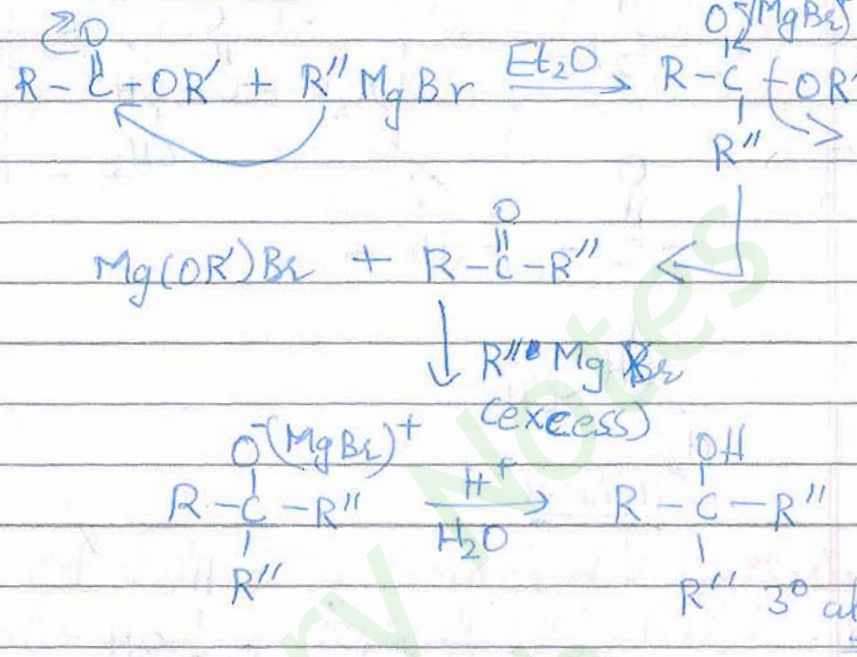
Prepare → alcohol starting from compds not containing more than 5 C, start from RMgX



2 Chemistry Notes Akshansh

H^-, R^- are strongest nucleophiles. So, very poor leaving grps.

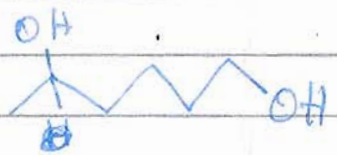
(B) From esters



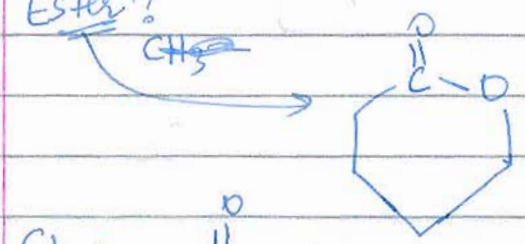
* To stop rxn at → Ketone, take excess of ester (to consume RMgX)
alcohol, take RMgX excess (to consume ester 1st)

* Ester when treated with RMgX (excess) gives 3° alcohol.
Exception: Esters of formic acid gives 2° alcohol.

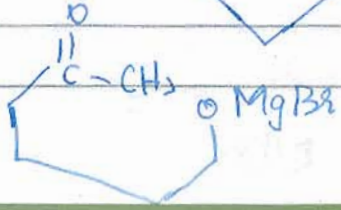
Q. Ester $\xrightarrow[\text{excess}]{MeMgBr}$ $\xrightarrow{H_2O}$



Ester?



S1 →

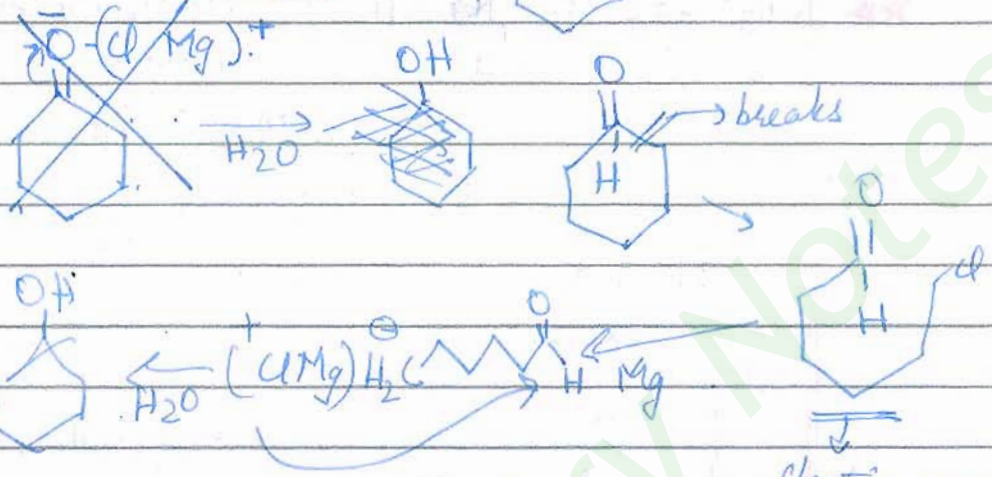


S2 → react further with MeMgBr

12 Chemistry Notes Akshansh

classmate
Date
Page

Q. $C_6H_{11}OCl \xrightarrow[Ether]{Mg} \xrightarrow{H_2O}$



(c) From Acid chloride $R-\overset{O}{\overset{\|}{C}}-Cl$

$$R-\overset{O}{\overset{\|}{C}}-Cl + R'MgCl \longrightarrow R-\underset{R'}{\overset{O(MgCl)^+}{\overset{|}{C}}}-Cl$$

* To stop even at ketone ✓ $R-\overset{O}{\overset{\|}{C}}-Cl$ excess.
alcohol ✓ $R'MgCl$ excess. (3°)

$$R-\overset{O}{\overset{\|}{C}}-R' + MgCl_2$$

(i) $R'MgCl$ (excess) (ii) H_2O

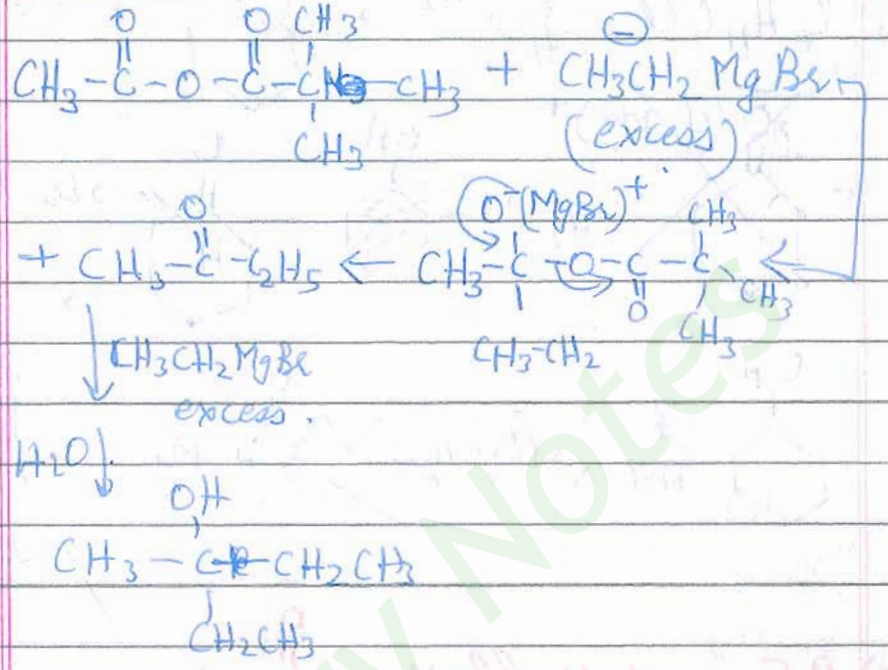
$$R-\underset{R'}{\overset{OH}{\overset{|}{C}}}-R'$$

(b) From Anhydrides

$$R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + R'(MgCl)^+ \rightarrow R-\overset{O}{\overset{\|}{C}}-O-\underset{R'}{\overset{O(MgCl)^+}{\overset{|}{C}}}-R$$

$$Mg(RCOO)Cl + R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow[(excess)]{R'MgCl} \xrightarrow{H_2O} R-\underset{R'}{\overset{OH}{\overset{|}{C}}}-R' \quad 3^\circ$$

Chemistry Notes by Akshansh



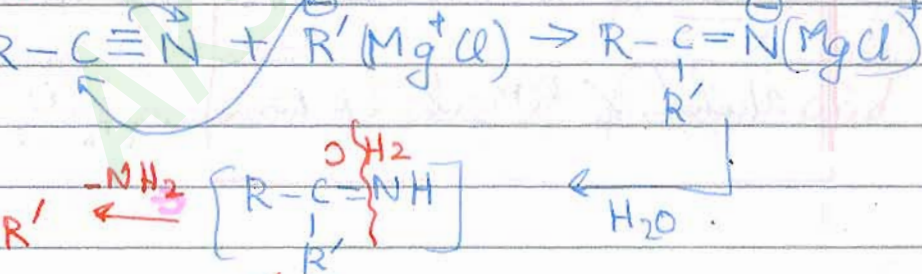
Biproduct

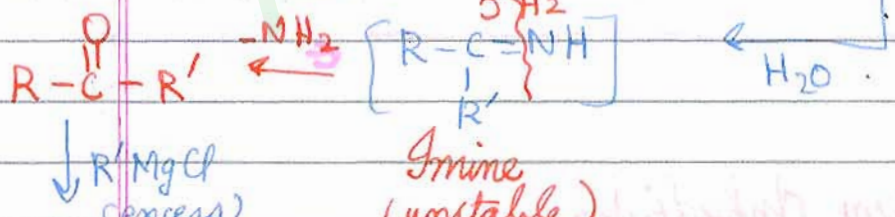
CH_3CH_2MgBr excess.

H_2O

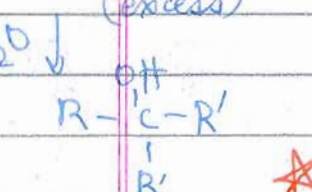
* To stop rxn / control rxn at ketone : anhydride in excess.
alcohol (3°) : RMgX excess.

(E) Cyanides





Imine (unstable)

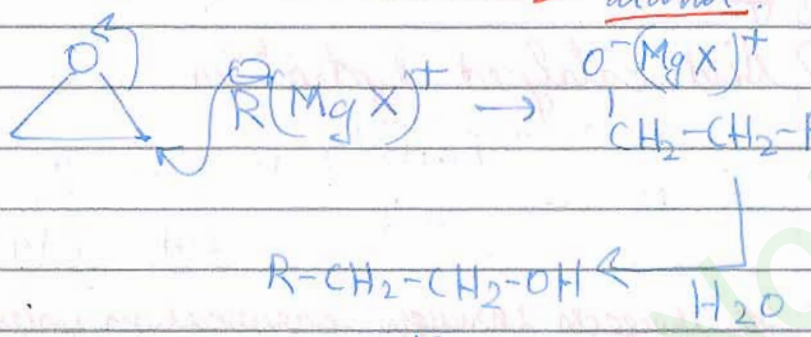


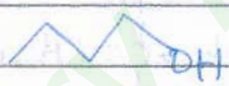
* The type of alcohol (3°) can be varied by using some other alkyl grp in (R)MgX in 2nd step.

Chemistry Notes Akshansh

3 membered cyclic ether

(F) From Epoxides ( ) → For making 1° alcohol. ★★



Q. CH_3-CH_2-OH → 

$CH_3-CH_2-OH \xrightarrow{SOCl_2} CH_3CH_2Cl \xrightarrow[(ii)\ \text{epoxide}]{(i)\ Mg/Et_2O} \xrightarrow[(iii)\ H_2O]{} \text{Product}$

Q. $H-C\equiv C-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 + \overset{\ominus}{C}H_3MgBr \xrightarrow{Et_2O} \xrightarrow{H_2O}$

neutralisation 1st

not possible CH_4 is evolved

$H-C\equiv C-CH_2-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3$

★ If reactant contains any acidic final grp, it fails in Grignard Synthesis.
The acidic grp may include →

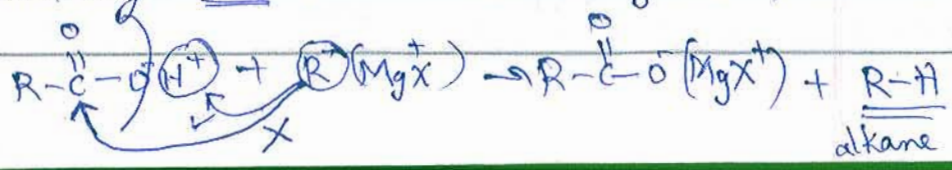
$-C\equiv C-H$

$-O-H$

$-N-H$

$-\underset{H}{\overset{|}{N}}-H$

So, alkanes can be prepared on rxn with $RMgX$ and any acid (or acidic grp). :— (neutralizn rxn)



Acetyl group : $(CH_3-\overset{O}{\overset{\|}{C}}-)$
(Ac)

classmate
Date 1-10-17
Page 1·9·10

(1) Hydration of alkenes

(A) Acid catalysed hydration.

$$R-CH=CH_2 \xrightarrow[\text{boil}]{\text{dil. } H_2SO_4} R-\underset{OH}{CH}-CH_3 \quad (\text{MK's rule})$$

Limitⁿ : * It proceeds through carbocation intermediate so, rearrangement may occur.

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2 + \text{dil. } H_2SO_4 \xrightarrow{\text{boil}} CH_3-\overset{CH_3}{\overset{|}{C}}-\overset{+}{C}H-CH_3$$

$(CH_3)_2^0$

$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH-CH_3 \xleftarrow{-H^+} CH_3-\overset{CH_3}{\overset{|}{C}}-\underset{\overset{+}{O}H_2}{CH}-CH_3 \xleftarrow{Me\text{-shift}} CH_3-\overset{CH_3}{\overset{|}{C}}-\overset{+}{C}H-CH_3$$

Alcohol.

(B) Oxy-mercuration-demercuration of alkene :-

✓ Brings about MK's addⁿ of H_2O without rearrangement ; Reagent :- $(CH_3COO)_2Hg$: Mercuric acetate

O_2 $(CF_3COO)_2Hg$: Rare, but better

$$CH_3-CH=CH_2 \xrightarrow[\text{Mercuric acetate}]{(CH_3COO)_2Hg} \xrightarrow[\text{redⁿ}]{NaBH_4} CH_3-\underset{OH}{CH}-CH_3$$

H_2O

MK's rule

$$CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow[(ii)\,NaBH_4]{(i)\,(CH_3COO)_2Hg\,(aq)} CH_3-\underset{CH_3}{CH}-\underset{OH}{CH}-CH_3$$

$$\xrightarrow[\text{boil}]{\text{dil. } H_2SO_4} CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_3$$

Mechanism :-

OXYMERCURATION

$$Hg(OAc)_2 + H_2O \rightarrow \overset{+}{Hg}(OAc) + CH_3COOH + HO^-$$

Mercurinium ion

$$CH_3-CH=CH_2 + \overset{+}{Hg}(OAc) \rightarrow \left[CH_3-\overset{+}{C}H-CH_2 \leftrightarrow CH_3-CH-\overset{+}{C}H_2 \right] \quad (:Hg(OAc))$$

H_2O attacks the more substituted carbon:

$$CH_3-CH(OH)-CH_2-Hg(OAc)$$

Cyclic mercurinium ion.

* Above ion doesn't proceed through carbocation intermediate, but through cyclic mercurinium ion, so, it doesn't undergo rearrangement.

$$\xrightarrow[H_2O]{-H^+} CH_3-CH(OH)-CH_2-Hg(OAc)$$

DEMERCURATION

Steps above

$$\xrightarrow{NaBH_4} CH_3-CH(OH)-CH_2-H$$

Q. $CH_3-CH=CH_2 \xrightarrow[H_2O]{Hg(OAc)_2} \xrightarrow{NaBD_4} CH_3-CH(OH)-CH_2-D$

$CH_3-CH=CH_2 \xrightarrow[D_2O]{Hg(OAc)_2} \xrightarrow{NaBH_4} CH_3-CH(OD)-CH_2-H$

classmate
Date
Page

(c) Hydroboration oxidation

$R-CH=CH_2 \xrightarrow[HO^- \text{(alkaline medium)}]{B_2H_6 \text{ (diborane)}} R-CH(H)-CH_2(OH)$ (Anti MK's rule)

H_2O_2

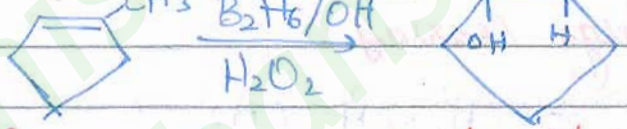
comes from solvent

comes from B_2H_6

$R-CH=CH_2 \xrightarrow[H_2O_2]{B_2D_6 / HO^-} R-CH(D)-CH_2(OH)$

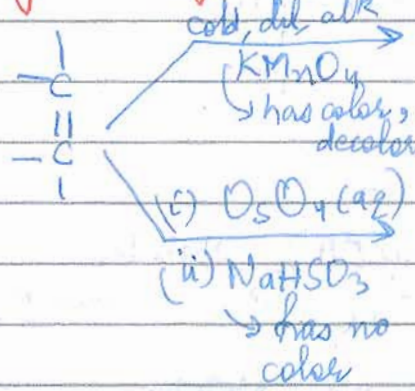
✓ In above rxn:-

- Anti MK's rule is followed.
- It goes through syn hydr^n.

eg: 

- ~~No~~ no rearrangement doesn't occur.

(8) When an alkene is treated with Bayer's Reagent (cold, dil, alkaline $KMnO_4$), it gives syn vicinal diol.



✡ PROPERTIES

1) Physical Properties.

B.Pt

Alcohols have higher B.Pt. than hydrocarbons, R-X, aldehydes, ketones of comparable molar mass due to its ability to form intermolecular H-bond. [except Methanol]

Its isomer

C_2H_5OH (l) at RT CH_3-O-CH_3 (g) at RT

Alcohol has higher B.Pt than its isomeric ether.

CH_3CH_2-OH ethanol B.Pt : 78°C

↓ Big gap.

CH_2-CH_2 (OH, OH) ethylene-glycol B.Pt → 180°C

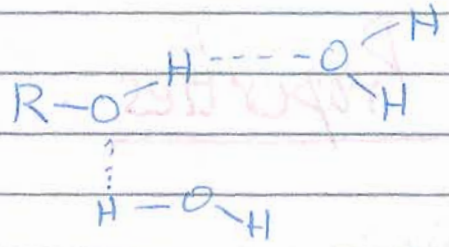
CH_2-OH, $CH-OH$, CH_2-OH glycerol B.Pt ≈ 300°C (degrades before boiling ∵ decompos^n Temp < boiling pt.)

✡ ↑ no. of OH grp, ↑ B.Pt greatly.

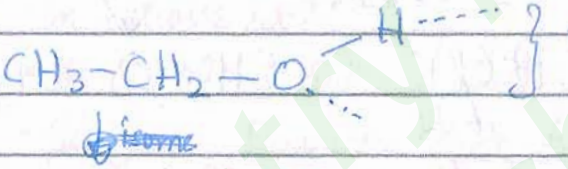
Chemistry Notes Alshamsh

classmate
Date
Page

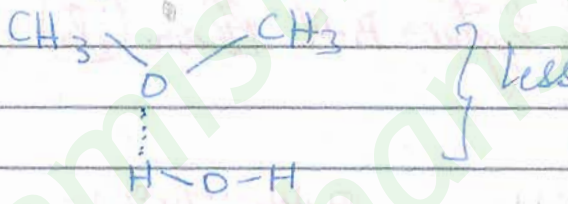
Solubility : (due to H-bonding :- R-OH are soluble in H_2O)



- Alcohols are more soluble than either hydrocarbons or R-X due to its ability to form intermolecular H-bond with H_2O



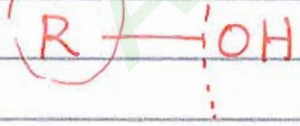
} more exhaustive H-bonding more soluble



} less exhaustive H-bonding less soluble (Comparatively)

Isomeric ethers

Hydrophobic — Hydrophilic



$CH_3 - OH$ → more soluble

$CH_3CH_2CH_2CH_2 - OH$ less soluble.

$N = \frac{m}{M} \times N_A$

(N: no. of molecules; M: molar mass)

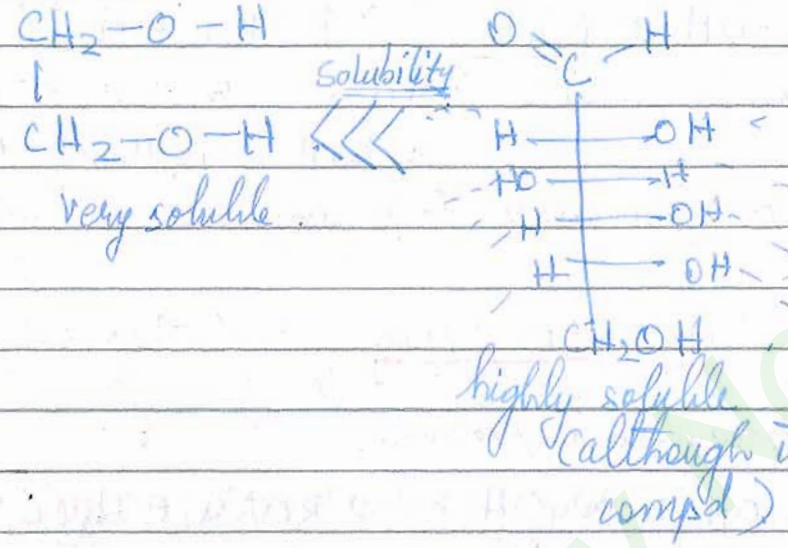
So, for a given mass of compd, lower chain alcohols contain more no. of atoms & Hence, more no. of OH bonds, & hence, more soluble.

★ Increasing the alkyl fr^n ↓ solubility ∵ alkyl is hydrophobic fraction.

12 Chemistry Notes Akshansh

* CH_3OH is slightly more acidic than H_2O. All other unsubstituted aliphatic alcohols are weaker acids than H_2O.

classmate
Date
Page



2> Chemical Properties.

* CHEMICAL RXNS. of ALCOHOLS

<A> Acidity of Alcohols.

$$R-OH + Na \xrightarrow{\Delta} RO^-Na^+ + \frac{1}{2}H_2\uparrow$$

effervescence

$$C_4H_{10}O + Na \xrightarrow{\Delta} H_2\uparrow : \text{alcohol}$$

Al Kal Na/Δ
ii os Ca → no effervescence : ether
drains ...

- It can't differentiate b/w alcohols & carboxylic acids, phenols — ∵ they too release $H_2\uparrow$.

$$\underset{SA}{R-OH} + \underset{SB}{NaNH_2} \rightarrow \underset{WB.}{RONa} + \underset{WA}{NH_3}$$

Rxn is feasibility is high ∵ NH_3 is weak acid than ROH & So, $NaNH_2$ is SB than RONa

So, $NaNH_2$ will also form effervescence.

+2 Chemistry Notes Akshansh

SA SB WB WA

- $R-OH + NaH \longrightarrow RONa + H_2\uparrow$

Rxn is feasible ∵ H_2 is WA than ROH
So, NaH is SB than RONa
So, effervescence is produced.

- $R-OH + C_2H_5-MgBr \rightarrow R-O-MgBr + C_2H_6\uparrow$
  ↳ neutralisⁿ occurs instead of Grignard synthesis
  effervescence is produced.

Distinction of ALIPHATIC & AROMATIC alcohols

- $R-OH + NaOH \longrightarrow RONa + H_2O$ ✗
  WA WB SB SA
  ↳ Rxn is not feasible (∵ H_2O is stronger acid than ROH)

- $PhOH + NaOH \longrightarrow PhONa + H_2O$ ✓
  SA SB WB WA
  ↳ Rxn is feasible ∵ H_2O is weaker acid than phenol.

ROH / PhOH | aq. NaOH → ether | ROH (ether) / $(PhO^-)(Na^+)$ aq.

fractional distillation

ether ROH | aq PhONa (insoln)

- ether is lighter than H_2O & ROH goes in ether layer & PhO^-Na^+ goes in H_2O. So, they are separated
- R-OH goes in ether ∵ with exception of methanol & ethanol, all alcohols are not soluble in H_2O.

$PhONa + HCl \rightarrow PhOH + NaCl$

distillation at B.Pt. of phenol. So, phenol is separated

Chemistry Notes Akshansh

* No grp ⊖ / $Nu^{\ominus}$ can directly substitute OH grp

eg $R-OH + NH_2^{\ominus} \not\rightarrow R-NH_2 + HO^{\ominus}$

$\rightarrow R-O^- + NH_3 \uparrow$

Nucleophilicity $NH_2^{\ominus} > HO^{\ominus}$.

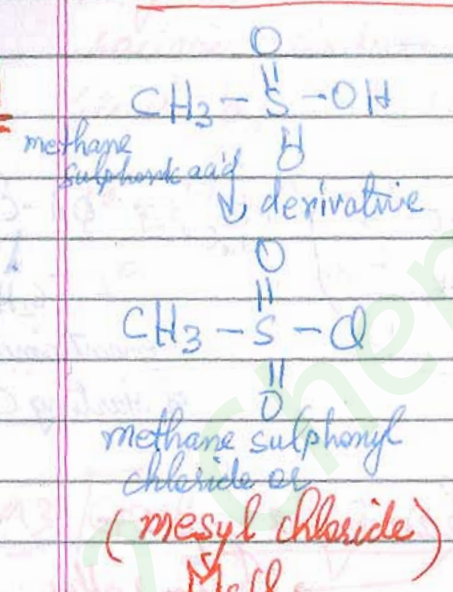
$NH_2^{\ominus}$ is stronger $Nu^{\ominus}$ than $HO^{\ominus}$ & at the same time, its stronger base than $HO^{\ominus}$.

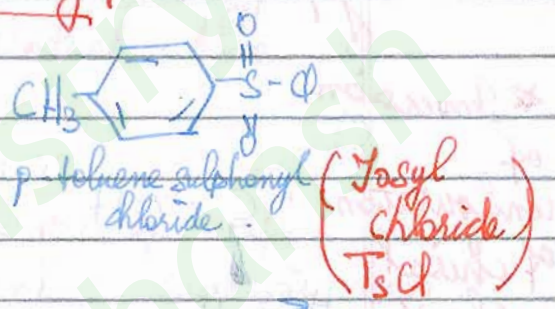
So neutralisⁿ occurs 1st.

* So, direct substitution fail even with strong $Nu^{\ominus}$.

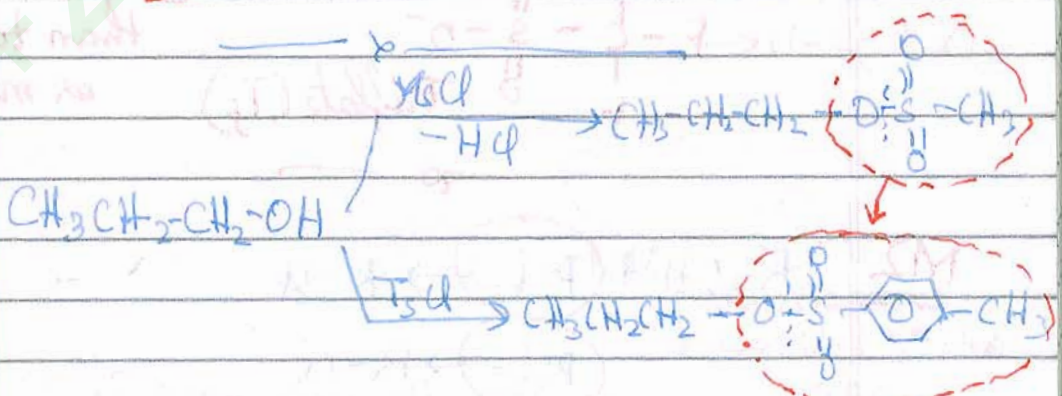
* SUBSTITUTION of OH-grp.

M1





2 main grps used for substitution.

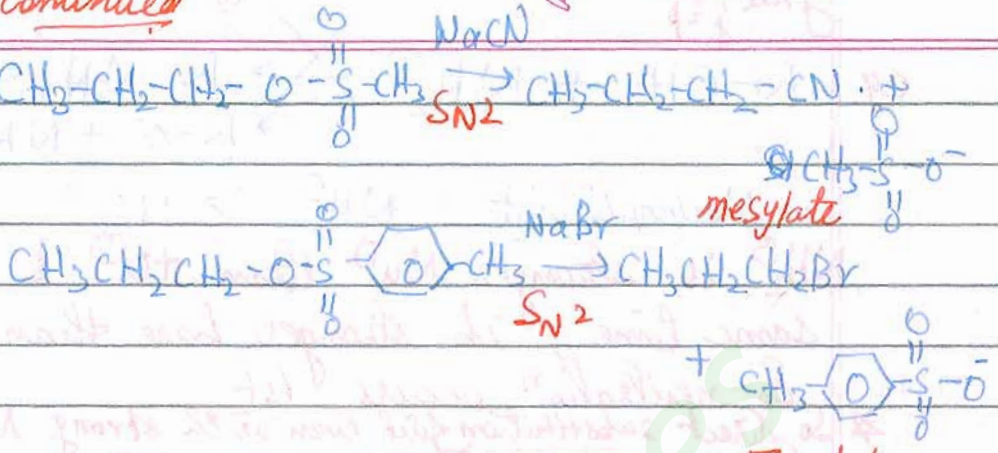


excellent leaving grp. ∴ any $Nu^{\ominus}$ can substitute them.

continued....

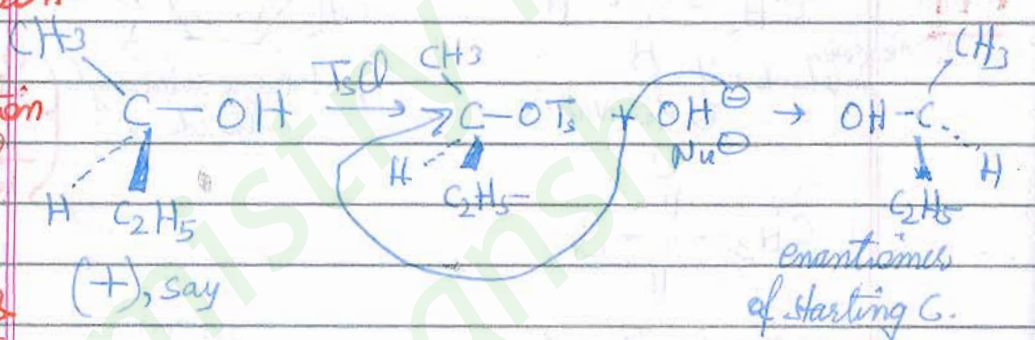
Chemistry Notes by Akshansh

Continued

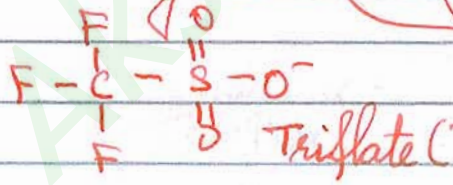


* Mesylates & tosylates are very good leaving grps due to resonance

* Inversion of configuration of chiral carbon using tosylate & mesylate



* Another great leaving grp :-

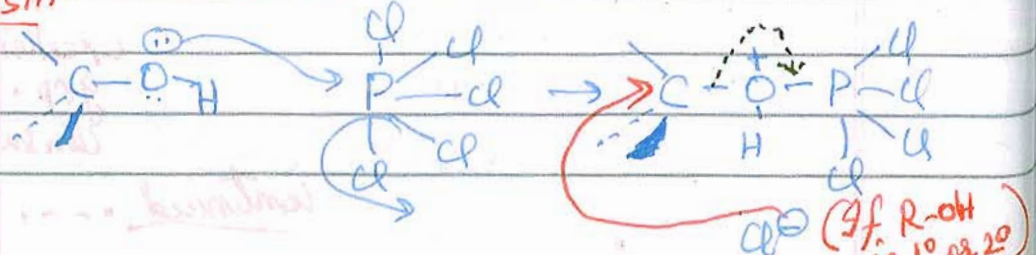


better than tosylate or mesylate.

M2 $R-OH + PCl_3 \rightarrow R-Cl$

$PCl_5 \rightarrow R-Cl$

Mechanism



Possibility :- ✓ If alcohol is 1° or 2°, halogenⁿ with PCl_5 or PCl_3 leads to S_N2 rxn & inversion of configurⁿ is observed.

✓ If alcohol is 3°, it becomes sterically hindered, hence, ~~attack~~ carbocation is formed instead & so, its rearrangement may also occur. Moreover, it gives racemic mixture in product. Also, it reacts by S_N1 rxn.

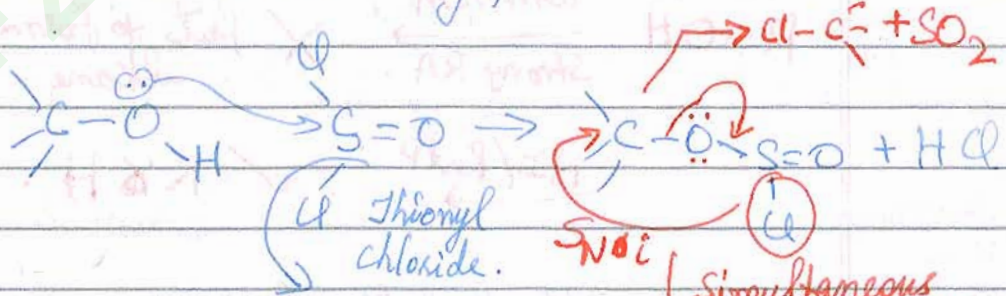
1° or 2° $\xrightarrow{S_N2}$ inversion of confi.

3° $\xrightarrow{S_N1}$ racemizⁿ, rearray may take place.

—x—

M3 $\boxed{SOCl_2}$: doesn't work with 3° alcohol.

→ suitable only for 1° alcohol.



* ∵ S_Ni takes place, its necessary for grps at C to be small. So, its not suitable for 3°.

* It results in inversion of confi. Once Cl comes, it can be substituted for any desired thing.

Chemistry Notes Akshansh

How to convert?

Q. $CH_3-CH_2-CH_2-OH \longrightarrow CH_3-CH_2-CH_2-C\equiv C-CH_3$

(i) PCl_5 or $SOCl_2$ or $TsCl$ or $MsCl$

(ii) $CH_3-C\equiv C^- Na^+$

$CH_3CH_2CH_2Cl$

(2) REDUCTION Rxn

** $R-H \xrightarrow{[O]} R-OH \xrightarrow{[O]} \underset{\text{or Ketone}}{\text{Aldehyde}} \xrightarrow{[O]} \text{Acid} \xrightarrow{[O]} CO_2 + H_2O$

* Pattern :- The difficulty of oxidⁿ decreases in the following pattern (series). Reverse is true in reverse dirⁿ ie. R-OH is difficult (most) to reduce to R-H.

$R-OH \xrightarrow[\text{Strong RA.}]{\text{common}}$ ✗ fails to form alkane

$\xrightarrow{HI/Red\,P}$ ✓ R-H.

* Method to work with alcohols selective reduction.

$ROH \rightarrow R-OTs \xrightarrow{LiAlH_4} R-H$

$ROH \rightarrow R-Cl \xrightarrow{LiAlH_4} R-H.$

Chemistry Notes Akhansh

3.9.10

* Another method of red^{n} of alcohol.

* $R-OH \xrightarrow[TiCl_3]{LiAlH_4} R-H$

$TiCl_3$ → co-catalyst (improves reactivity or action of catalyst)

(3) OXIDATION OF ALCOHOLS.

(A) Oxid^{n} with $KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$

$R-CH_2-OH \xrightarrow{[O]} [R-C(=O)-H] \xrightarrow{[O]} R-C(=O)-OH$

(1°)

formed but gets oxidised ∵ its oxid^{n} is easier.

$R-CH(OH)-R \xrightarrow{[O]} R-C(=O)-R$ → no further oxid^{n} ∵ no more C-H bond.

(2°) Ketone

* $CH_3OH \xrightarrow{[O]} H-C(=O)-H \xrightarrow{[O]} H-C(=O)-OH \xrightarrow{[O]} CO_2 + H_2O$ (carbonic acid)

* 3° alcohol $\xrightarrow{[O]}$ X

* C-H bond can easily be oxidised than C-C
* $K_2Cr_2O_7/H^+$ has orange color. It can be used in ben tests. PTO
* The C bearing OH grp will get oxidised only when it has some/one atleast H attached to it. The no. of H attached to it, the same no. of times it can be oxidised.

classmate
Date
Page

$$R-\underset{1^\circ}{CH_2}-OH \xrightarrow{Cr_2O_7^{2-}/H^+} R-COOH + \underset{\text{Green}}{Cr^{3+}}$$

$$R-\underset{\underset{H}{|}}{\overset{\overset{R}{|}}{C}}-OH \xrightarrow{Cr_2O_7^{2-}/H^+} R-\overset{\overset{O}{||}}{C}-R + \underset{\text{Green}}{Cr^{3+}}$$

2°

$$R-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-OH \longrightarrow X$$

* $K_2Cr_2O_7/H^+$ can be used to distinguish b/w 3° & (1° or 2°) alcohol ∵

1° or 2° $\xrightarrow{K_2Cr_2O_7/H^+}$ Orange changes to green

3° $\xrightarrow{K_2Cr_2O_7/H^+}$ no reaction - orange color persists.

To differentiate b/w 1° & 2°

Now, 1° or 2° $\xrightarrow{NaHCO_3}$ $CO_2 + \underset{1^\circ}{RCOONa}$

~~X~~ X

2°

* $R-CH=CH-CH_2-OH \xrightarrow[\text{or } H^+/K_2Cr_2O_7]{H^+/KMnO_4}$ not suitable oxidising agent ∵ it affects olefinic bonds.

* To prevent Olefins from oxidising:-

Jone's Reagent is used

↳ CrO_3/aq. acetone

classmate
Date
Page

* Jone's reagent doesn't affect olefine. Rest, it does all work of $KMnO_4/H^+$ or $K_2Cr_2O_7/H^+$.
* Jone's reagent doesn't affect olefinic bonds.

$$R-CH=CH-CH_2-OH \xrightarrow[\text{Reagent}]{\text{Jones}} R-CH=CH-COOH$$

$$CH_3-CH_2-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3 \xrightarrow[\text{hot, conc, } H^+/KMnO_4]{\text{exhaustive oxid}^n} 2\,CH_3CH_2COOH$$

alcohol → aldehyde → acid

$$\left[CH_3CH_2CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CH_3\right]$$

to → acid

of unsymmetrical ketone, C=O goes with smaller alkyl group.

PARTIAL OXIDⁿ of ALCOHOLS

$$R-CH_2-OH \xrightarrow[+\text{ Pyridine}]{CrO_3/HCl} R-\overset{\overset{O}{\|}}{C}-H$$

1° — aldehyde

CrO_3/HCl + Pyridine → PCC (Pyridinium Chlorochromate)

* PCC reacts with 1° alcohol & after oxidⁿ, forms a complex with aldehyde. & after hydrolysis, this complex gives aldehyde.

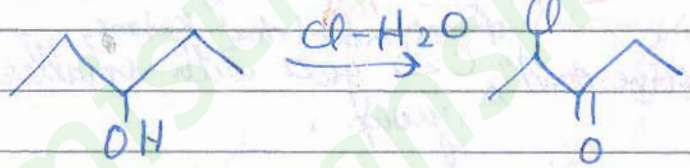
[B] Oxidⁿ with X_2/H_2O

Oxidising strength ↓ decreases down the group.

F
Cl
Br
I

$$R-CH_2-CH_2OH \xrightarrow[\text{or } Br_2-H_2O]{Cl_2-H_2O} R-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{Cl_2} R-\underset{Cl}{\overset{\alpha}{C}}H-\overset{O}{\overset{\|}{C}}-H$$

✓ Inspite of its oxidⁿ, its not used due to its α-halogenⁿ of aldehyde formed after oxidⁿ.



[C] Dehydrogenation

$$\underset{1^\circ}{R-CH_2-OH} \xrightarrow[\Delta,\ T>300^\circ C]{CuO} R-\overset{H}{\overset{|}{C}}=O + Cu + H_2O$$

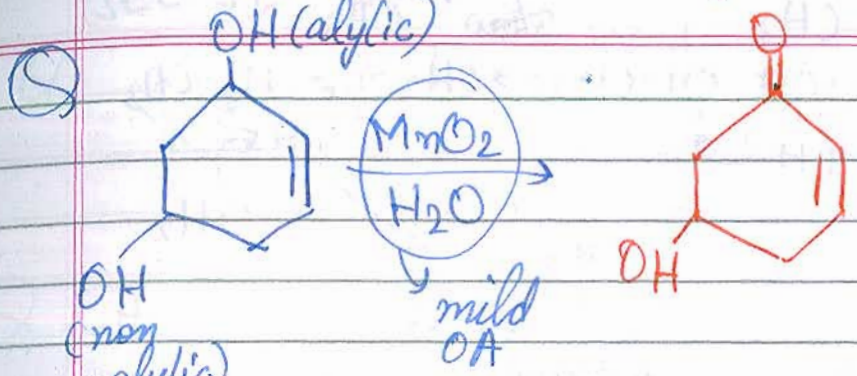
$$\underset{2^\circ}{R-\underset{OH}{\underset{|}{CH}}-R} \xrightarrow[\Delta,\ T>300^\circ C]{CuO} R-\underset{O}{\overset{\|}{C}}-R + Cu + H_2O$$

Dehydⁿ with 3°:

$$\underset{3^\circ}{R-\underset{H}{\underset{|}{CH_2}}-\underset{OH}{\overset{R}{\overset{|}{C}}}-R} \xrightarrow[\Delta]{CuO} R-CH=\overset{R}{\overset{|}{C}}-R + H_2O$$

* CuO require high T for oxidⁿ. & most of the organic compds degrade & high T. So, this method is practically not used for synthesis of aldehyde or ketone or alkene.

classmate
Date
Page



* Mild OA, MnO_2/H_2O oxidises only at allylic posns so as to bring the alkene sys. in conjug^n.

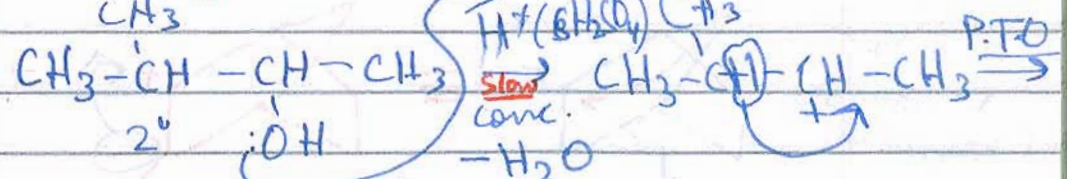
D) DEHYDRATION of ALCOHOLS

(i) Acid catalysed Dehydration

When an aliphatic alcohol is heated (not boiled → above boiling → ≈ 300°C) with conc. soln of H_2SO_4 or H_3PO_4, dehydration takes place to give alkene.

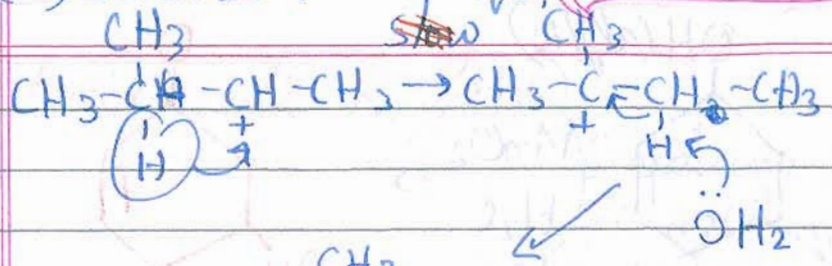
(high heating)

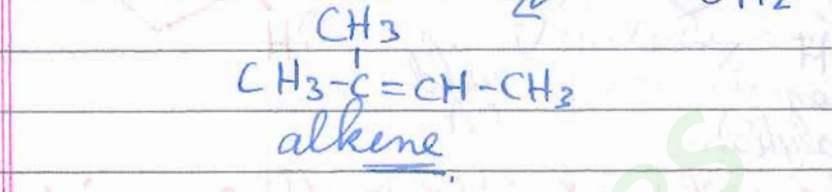
CAUTION:- If 3° alcohol, it gets dehydrated with dil. H_2SO_4 only; conc. would do something else.

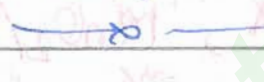


* Why H_2SO_4 only & not HCl ?
  - Sulphate grp. resonance stabilised.
  - Cl a good $Nu^\ominus$ gives R-X

★ In bridge structure, the bridge head carbon can never have (=) bond at +ve charge.

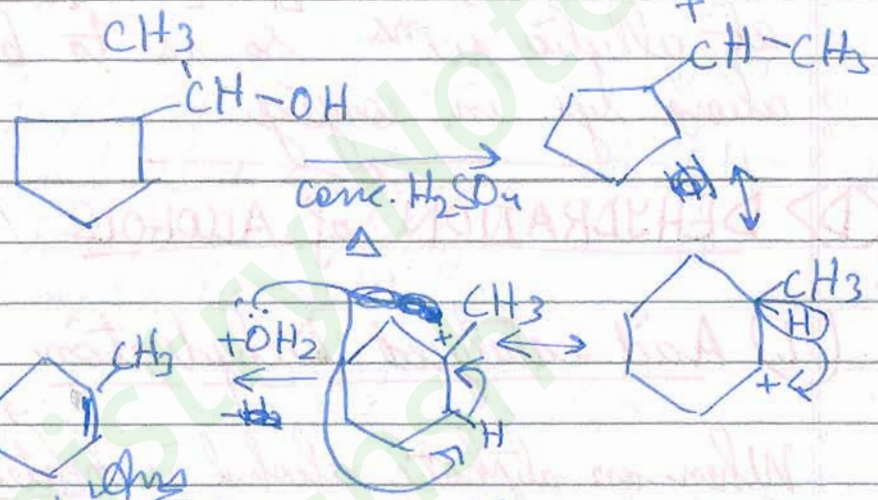






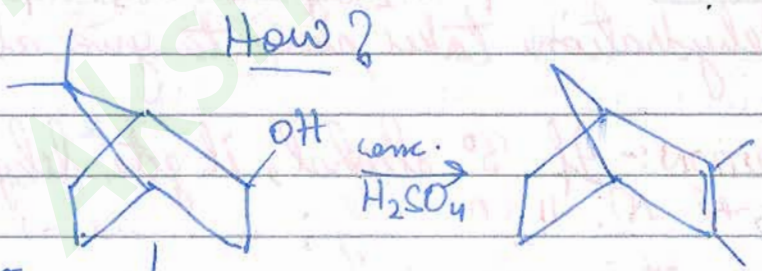
alkene

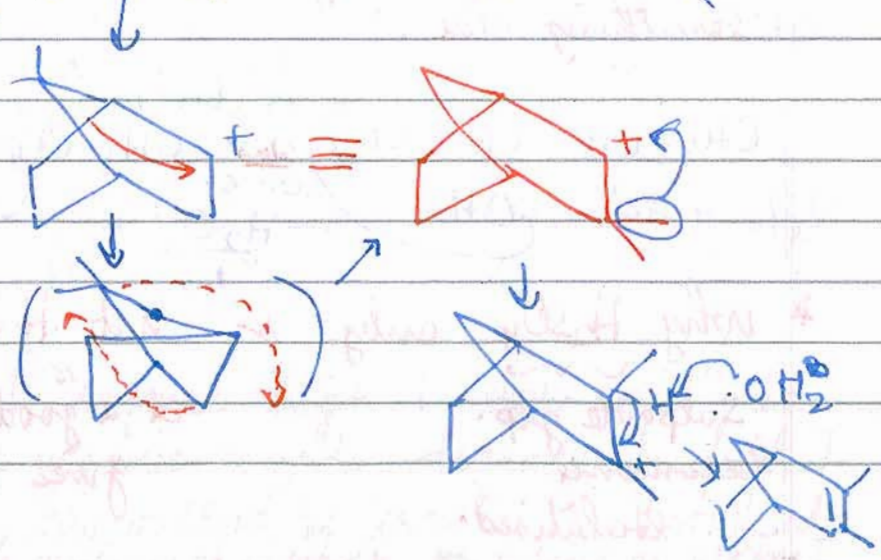
Q Major Product & most imp. RI :-



most stable & most reactive

Q How ?





JEE 97

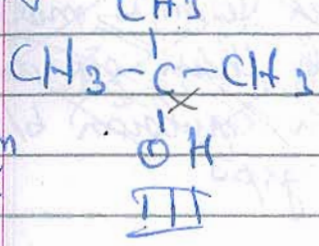
Q. + $CHBr_3$ $\xrightarrow{KOH}$?

Q. $CH_3-CH_2-CH_2-OH$, $CH_3-CH_2-\underset{OH}{CH}-CH_3$

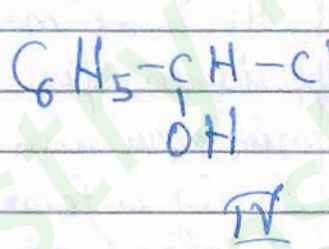
I II

Order of reactivity of dehydrⁿ

I < II < III < IV



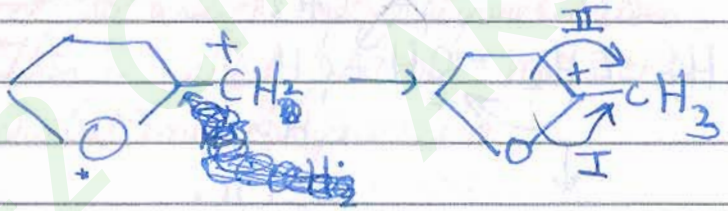
III

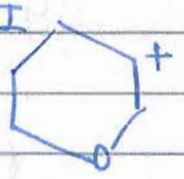
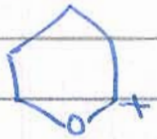


IV

Q. $\xrightarrow{H^+/H_2O}$

most imp. RI, product ?



Way I  Way II 

(resonance stabilised)

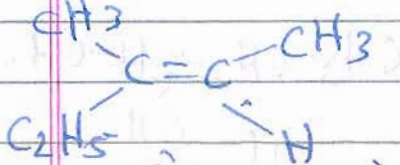
X

(more reactive than the 4 options in above ques.)

+2 Chemistry Notes Akshansh

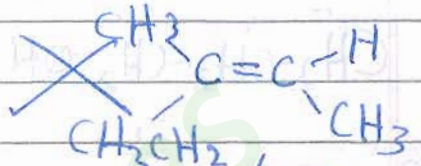
Q. $CH_3-CH_2-\underset{OH}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{C}}H-CH_3 \xrightarrow{H^+}$

$CH_3-CH_2-\overset{*}{\underset{CH_3}{\underset{|}{C}}}=CH-CH_3$



cis

here, bulky grp C_2H_5 is at max. distance for min repulsion. So, cis is formed instead of trans.



~~trans~~

it'll be formed : trans form is more stable than cis due to min repulsion b/w bulky grps.

Q. $C_6H_5-CH_2-\underset{OH}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{C}}H-CH_3 \xrightarrow{H^+/\Delta}$

$\rightarrow C_6H_5-CH_2-\overset{+}{C}H-\overset{CH_3}{\overset{|}{C}}H-CH_3$

$\downarrow$

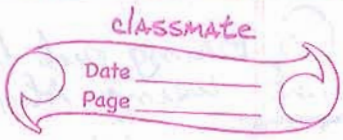
$C_6H_5-\underset{+}{C}H-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_3$

$\downarrow$

(∵ Benzylic carbocation is more stable than 3° carbocation & after deprotonation, it gives resonance stabilised product)

Chemistry Notes by Akshansh

* 3° alcohol dehydrⁿ



$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2CH_3$ → forms highly stable 3° carbocation, So even with dil. H_2SO_4 (200°C), rxn occurs. where Temp acts as driving force.

$\xrightarrow[\approx 200^\circ C]{\text{dil. } H_2SO_4}$

$CH_3-\overset{CH_3}{C}=CH-CH_3$

* If conc. H_2SO_4 is used: Cationic Polymerisⁿ of alkene takes place

$CH_3-\overset{CH_3}{C}=CH-CH_3 \xrightarrow{H^+}$ $CH_3-\overset{CH_3}{\overset{+}{C}}-\underset{C_2H_5}{}$ $CH=\overset{CH_3}{C}-CH_3$

$CH_3-\overset{CH_3}{\underset{C_2H_5}{C}}-\underset{CH_3}{CH}-\overset{CH_3}{\overset{+}{C}}-CH_3$ ← goes on

* To avoid this polymerisⁿ of 3° carbocation, dil. H_2SO_4 acid is used.

~~→ To avoid this polymerisation,~~

This is called CATION-INDUCED POLYMERISⁿ or Cationic Polymerisⁿ.

Q $CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}-\underset{OH}{CH}-CH_3$

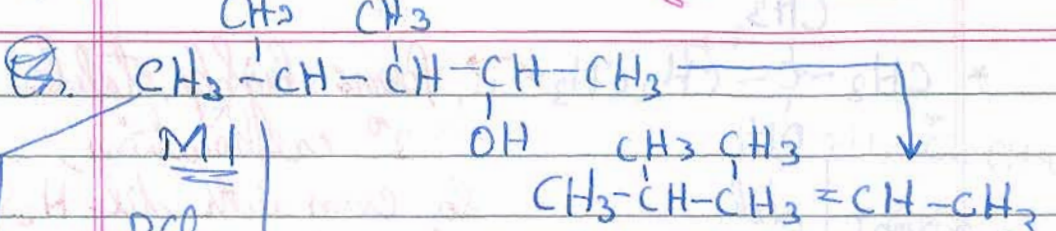
$\xrightarrow[\Delta]{\text{Alumina } (Al_2O_3)}$ $CH_3-\overset{CH_3}{CH}-\overset{CH_3}{CH}=CH-CH_3$ ← Sytzeff dehydrⁿ (But without rearray)

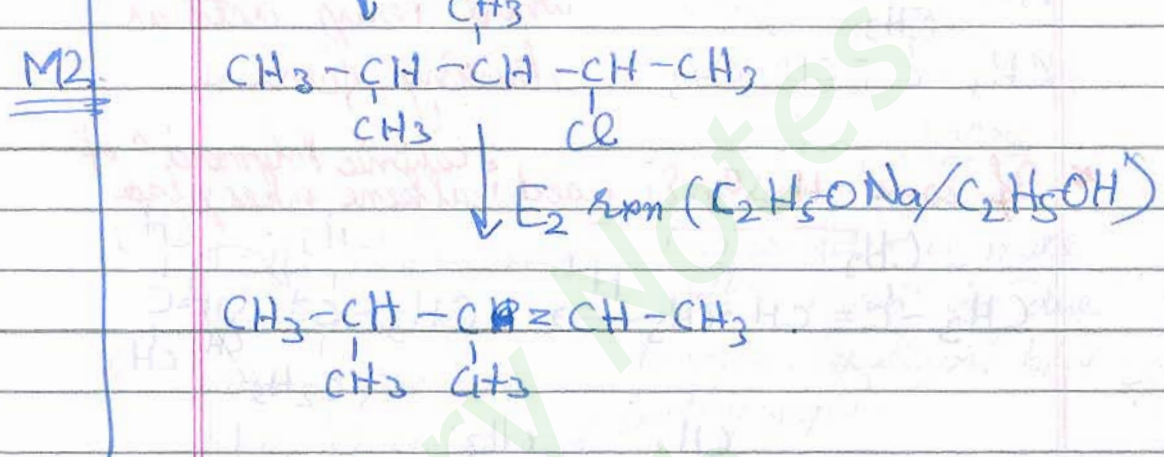
$\xrightarrow{\text{conc. } H^+/H_2SO_4}$

$CH_3-\overset{CH_3}{C}=\overset{CH_3}{C}-CH_2-CH_3$

(with rearrangement)

Q. Bring out the conversion not using Alumina ⇒





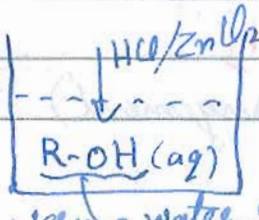
—×—

✱ DISTINCTION of 1°, 2°, 3° Alcohol.

1) Oxidⁿ rxn with $Cr_2O_7^{2-}$ (done before)

2) $ZnCl_2$/conc. HCl : LUCAS REAGENT.

Lucas Test



R-Cl formed.
(makes sol^n TURBID → i.e translucent)

very → water soluble Cas compared to R-X

Chemistry Notes Akshansh

If only P : Red phosphorus.
P_4 : White phosphorus

NITROUS ACID :- O=N-OH

Reactivity with HCl. 3° > 2° > 1°

alcohol 3° → immediate turbidity.
2° → slow reacts, but, it also reacts completely So, Delayed turbidity.
1° → very very slow reacts. So, to solubility limit, hours take. So, no turbidity is observed.

---

37) Victor Mayer's Test

don't confuse with HI/red P

$R-CH_2-OH$ (1°) $\xrightarrow{I_2/P\text{-red}}$ $R-CH_2-I$ $\xrightarrow{AgNO_2}$ $-AgI$

I_2/P-red plays same role of PCl_3.

$R-CH_2-I \xrightarrow{HNO_2} R-CH_2-NO_2 + HNO_2$

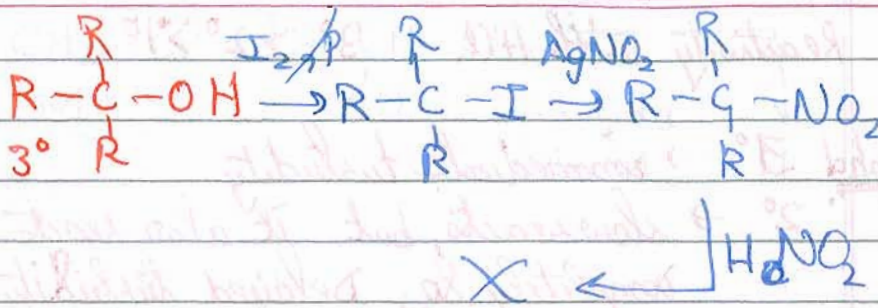
$R-CH_2-NO_2$ (Nitrolic acid (blue)) $\xrightarrow{NaOH}$ $R-C(=N-O^-Na^+)-NO_2$ (red on making alkaline)

$R-CH_2-NO_2$ (Nitrolic acid (blue)) $\xrightarrow{HNO_2}$ $R-C(=N-OH)-NO_2$

$R-CH(R)-OH$ (2°) $\xrightarrow{I_2/P}$ $R-CH(R)-I$ $\xrightarrow{AgNO_2}$ $R-CH(R)-NO_2$ $\xrightarrow{HNO_2}$ $R-C(R)(N=O)-NO_2$

Pseudonitrol (blue) — remains blue on making alkaline

classmate
Date 8.9.10
Page



* Victor Mayer test can be used for distinction of
1°, 2°, 3° → R-X, R-NO$_2$ or R-OH (mainly)

4) $[Ce(NH_3)_6]^{4+}$ + 1° alcohols → RCOOH + Ce^{3+} blue
Red ↑ 2° alcohols → Ketone

$Ce(NO_3)_4 + NH_3(aq.)$

* Turning of Red to blue of ceric ammonium nitrate indicate the presence of 1° or 2° alcohols.
So, it can distinguish b/w (1° & 2°) & 3° alcohols.

Chemistry Notes Akshanth

ETHERS

R-O-R or R-O-R'
Symmetrical Unsymmetrical

PREPARATION

1. Industrial Prepar^{n} of ether :-

$$R\text{-}\underset{1^\circ}{OH} \xrightarrow[\approx 140^\circ C]{\text{conc. } H_2SO_4} \underset{\text{ether}}{R\text{-}O\text{-}R}$$

Remember the diff.

$$\underset{1^\circ}{ROH} + \left(\xrightarrow[\approx 180^\circ C]{\text{conc. } H_2SO_4}\right) \rightarrow \text{alkene}$$

eg

$$CH_3CH_2\text{-}OH + H\text{-}O\text{-}CH_2CH_3 \xrightarrow[\approx 140^\circ C]{H_2SO_4}$$

2 reactant give 2 product

$$H_2O + CH_3CH_2\text{-}O\text{-}CH_2CH_3 \quad (\text{major})$$

1 reactant gives 2 product

$$\underset{[H \cdots OH]}{CH_2\text{-}CH_2} \xrightarrow[\text{conc. } H_2SO_4]{180\text{-}200^\circ C} CH_2=CH_2 + H_2O$$

So, ΔS is more +ve in 2nd rxn.

* At relatively lower temp, inter molecular dehydr^{n} is favoured.
* At relatively higher T, intramolecular dehydr^{n} is favoured.

Continued → Also, $\Delta G = \Delta H - T\Delta S$; At higher T, entropy always favour intramolecular dehydr^{n}. At relatively lower T, inter molecular dehydr^{n} takes place ∵ ΔH drives its rxn due to form^{n} of stable (C-O bond)

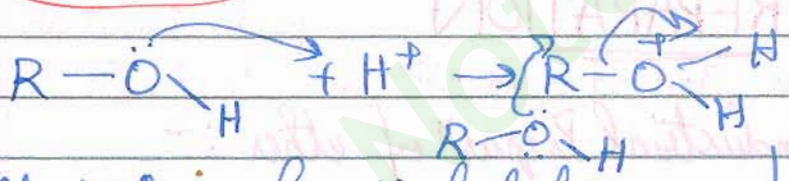
Chemistry Notes Akshansh

classmate
Date
Page

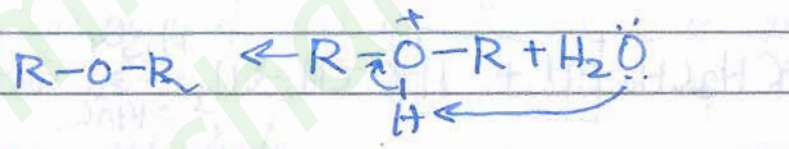
$$2\text{-}R\text{-}OH \xrightarrow[\Delta/140^\circ C]{H^+} R\text{-}O\text{-}R$$

The previous method is not suitable for prepar^n of ether if alcohol is 2° or 3° (∵ 2° & 3° alcohols dehydrate even with dil. H_2SO_4 to give alkene)

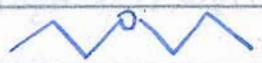
Mechanism



At 140°C, when 1° alcohol is there, protonated alcohol act as substrate & 1° alcohol act as $Nu^{\ominus}$ & S_N2 rxn takes place



✱ Imp. Distinction

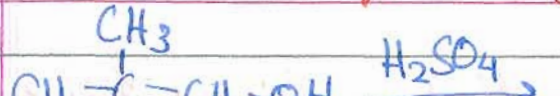
✱ $CH_3CH_2CH_2OH \xrightarrow[\Delta/140^\circ C]{Conc.\ H_2SO_4}$ 

$\left(CH_3\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}O\text{-}CH_2CH_2CH_3\right)$

↳ This do never formed ∵ above rxn doesn't take through carbocation intermediate

Since → is not formed, it proves the presence of 1° alcohol forming ether.

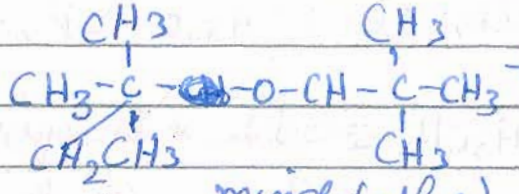
* In I method, see the carbocation stability & temp taken. Then accordingly make (alkene & ether) major or minor.



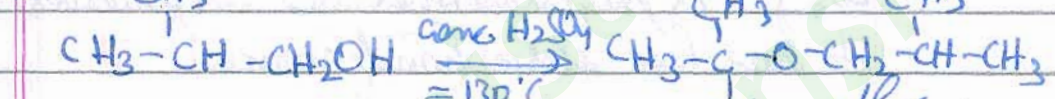
neopentanol

major

(∵ carbocation is formed accompanied by ~~methyl~~ hydride shift)



minor (ether)



ether.

(Carbocation + Hydride shift + alcohol Nu⊖ attack & + deprotonation)

LIMITATION

(Cross condens^n product) ← R–O–R′ ← Condens^n Rxn ← R–OH + R′–OH

unsymmetrical

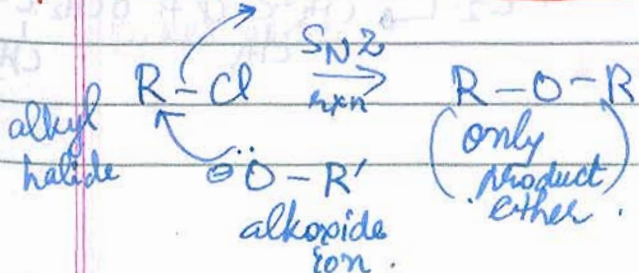
(R–OH HO–R′)

+ R′–O–R′ + R–O–R

↳ bipoducts (Self condens^n product)

* ← Method is not suitable for preparing of unsymmetrical ether.

2> WILLIAMSON'S ETHER SYNTHESIS :-



classmate
Date
Page

Advantage:-

* The previous method can be used for preparing unsymmetrical ether as only product.

Q. $CH_3I + CH_3CH_2ONa \xrightarrow{①} CH_3-O-CH_2-CH_3$

$CH_3ONa + CH_3CH_2-I \xrightarrow{②} CH_3-O-CH_2-CH_3$

CH_3I is most reactive R-X in SN_2 rxn So, ① is preferred over ②. Moreover it has less steric hindrance.

Q. $CH_3-ONa + CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br \rightarrow CH_3-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$ (not formed)

$+ E_2$ (predominate)

$CH_3-I + CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-ONa \xrightarrow[\text{only}]{SN_2}$ + ~~xx~~ E_2 (not occurs) (no β-H)

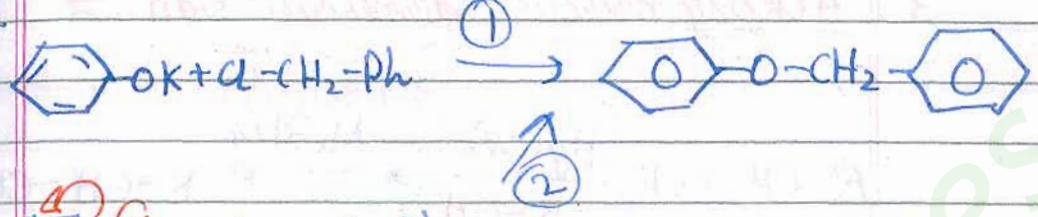
Q. $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$

only SN_2 ① $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-Cl + {}^{+}OK$

mainly E_2 ② $CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Cl + {}^{-}O-CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_3$

Chemistry Notes Arshan

Q.

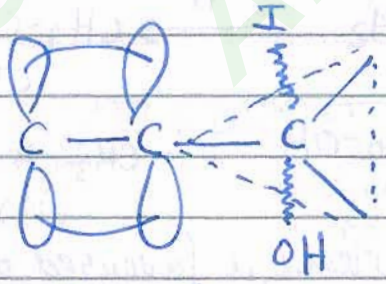


partial (=) bond of C=Cl, so, very touch to substitute.

In ①, $Nu^{\ominus}$ is weaker than in ②. But, the leaving ability of halide is seen 1st. which occurs in ①. So, ① will give product.

★ ~~Alk~~ Allylic halide is preferred in S_N1 & S_N2 rxn :—

Reason



In pentavalent transⁿ state of C, the π-bond of orbital is not completely filled in allylic carbon. So, its stabilises the pentavalency of carbon. So, S_N2 rxn takes place.

+2 Chemistry Notes Akshansh

classmate
Date
Page

3. Alkoxy mercuⁿ demercuⁿ rxn :-

$$R-CH_2=CH_2 \xrightarrow[R-OH]{Hg(OAc)_2} \xrightarrow{NaBH_4} R-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_3$$

RO { H
(MK's rule)

(In oxymercuⁿ demercuⁿ, H_2O was used instead of ROH)

- ✓ No rearray takes place.
- ✓ Very efficient method of prepaⁿ from alkene.
- ✓ Make symmetrical or unsymmetrical by choice of (R)-OH

(4) Alcoholysis of Alkene

$$CH_3-CH=CH_2 + R-OH \xrightarrow[\text{MK's rule}]{H^+} CH_3-\underset{\displaystyle OR}{\underset{|}{CH}}-\underset{\displaystyle H}{\underset{|}{CH_2}}$$

eg

$$CH_3-CH=CH_2 \xrightarrow{H^+} CH_3-\overset{+}{C}H-\ddot{O}-CH_2CH_2CH_3$$
$$\quad\quad\quad

* Had it been alkoxymercuration demercuration rxn

$CH_3-\underset{CH_3}{CH}-CH=CH_2 + CH_3-CH_2-OH$

$CH_3-\underset{CH_3}{CH}-\underset{O-CH_2CH_3}{CH}-CH_3$

5. $R-OH + :CH_2$

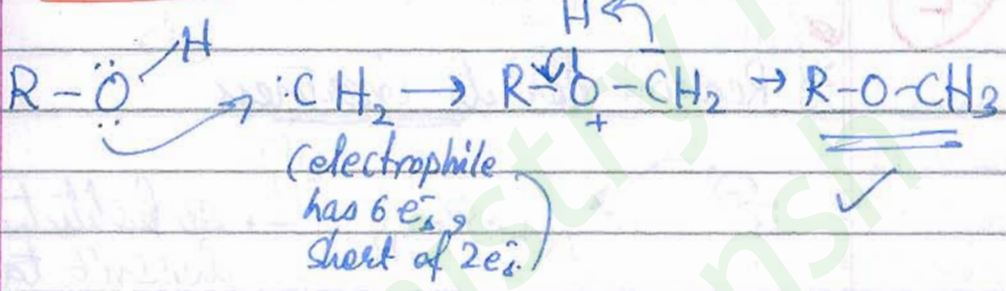
CARBENE

$R-OH + CH_2N_2 \xrightarrow{\Delta} R-O-CH_3$

methyl ether.

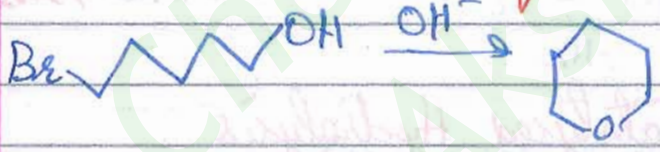
✓ Via - carbene, only methyl ether can be obtained

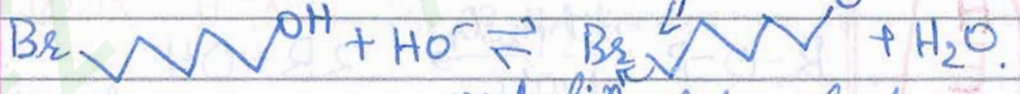
Mechanism



(electrophile has 6 e⁻s, short of 2 e⁻s.)

* Under Williamson's Synthesis:-





neutralisation. Intramolecular S_N2 rxn.

(one gives ⊗ 2 product. So, entropy ↑. Hence it is favoured over intermolecular S_N2 rxn)

✓ So, its a type of Williamson's Synthesis.

✓ This rxn is not S_Ni rxn ∵ adjacent grp is not involved.

R Chemistry Notes ARSHansh

✱ PROPERTIES

PHYSICAL

- highly volatile
- very inert towards any strong base.
- doesn't react with dil acid & react only with conc- sol^{n} of H-X (not HF)
- used as a common solvent due to its inertness

✱ Reason for its inertness

→ substitution doesn't takes place ∵ O-R bond can't be broken/substituted

CHEMICAL

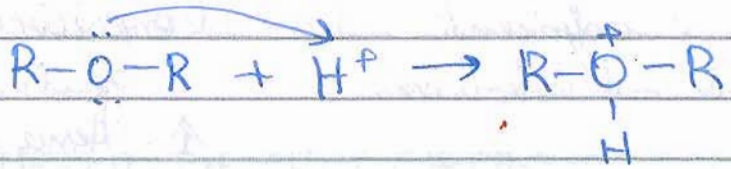
① Acid-Catalysed Hydrolysis.

$$R-O-R \xrightarrow[\text{140° C (refluxing)}]{\text{dil } H_2SO_4} 2R-OH \text{ (by hydrolysis)}$$

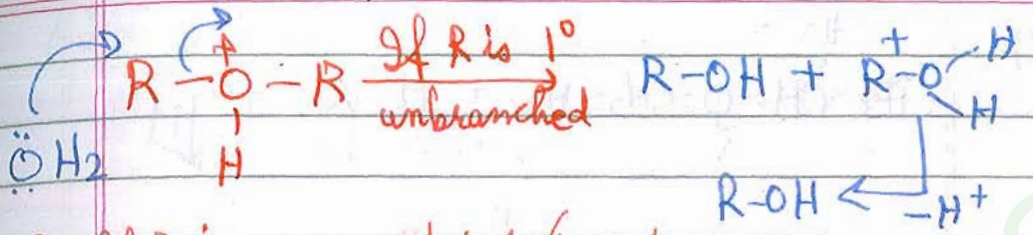
not high heating

(conc. $H_2SO_4 + H_2O$)

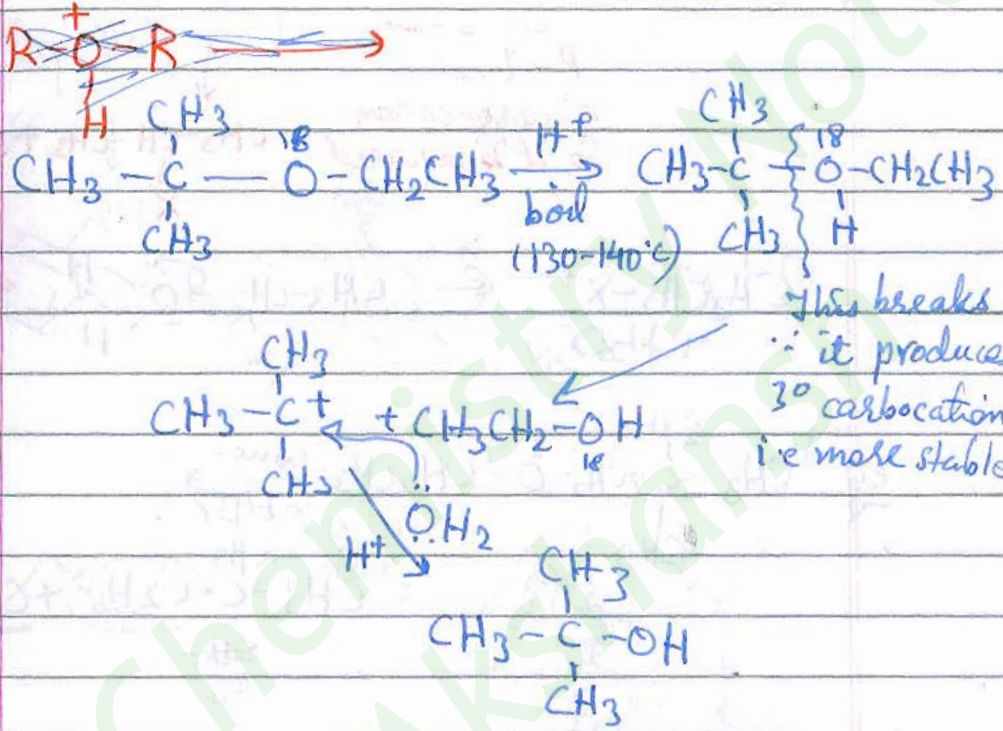
Mechanism



Case ①



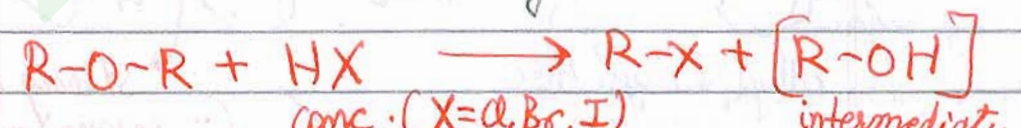
Case ② : If R is unsymmetrical & branched



This breaks ∴ it produces 3° carbocation i.e more stable.

---

② With H-X (reverse of Williamson's Ether synthesis)



2RX

(RX + ROH + HX → R-X → 2RX)

Chemistry Notes by Akshansh

eg $CH_3-\underset{CH_3}{\underset{|}{CH}}-\ddot{O}-CH_2-CH_3 + H^+X^-$ →

$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{+}{O}(H)-CH_2CH_3 + X^-$

Produces 2° carbocation. So, it is favoured

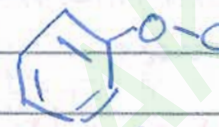
$CH_3-\underset{X}{\underset{|}{CH}}-CH_3 + CH_3CH_2OH$ (H+)

$CH_3-CH_2-\overset{+}{O}(H)-H$ (X⁻) ← $CH_3CH_2-X + H_2O$.

eg $CH_3-\underset{CH_3}{\underset{|}{C}}(CH_3)-CH_2-O-CH_2CH_3$ $\xrightarrow{\text{conc. HBr}}$ (H^+ $Br^\ominus$)

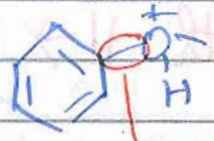
$CH_3-\underset{CH_3}{\underset{|}{C}}(Br)-C_2H_5 + CH_3CH_2Br$

eg



ethylphenylether

$\xrightarrow[HBr]{\text{conc.}}$



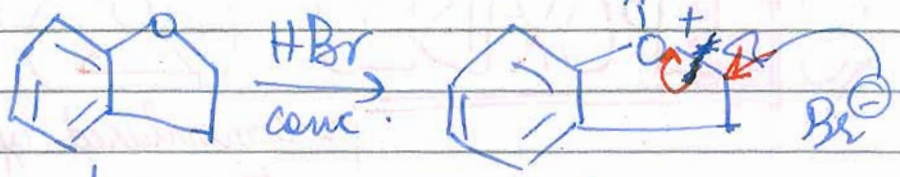
Strong bond (∵ resonance stabilised & if broken, it brings +ve charge on a phenyl grp thats never possible)

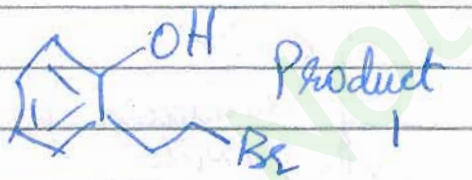
+ CH_3CH_2Br

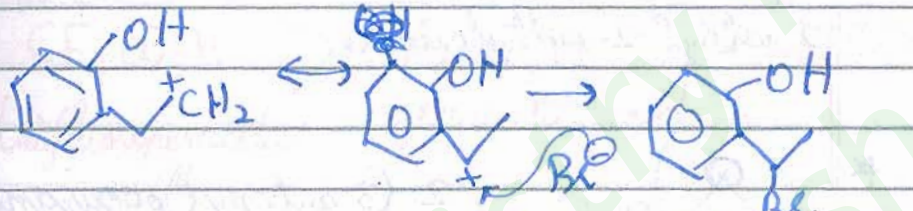
Phenol (necessary to form)

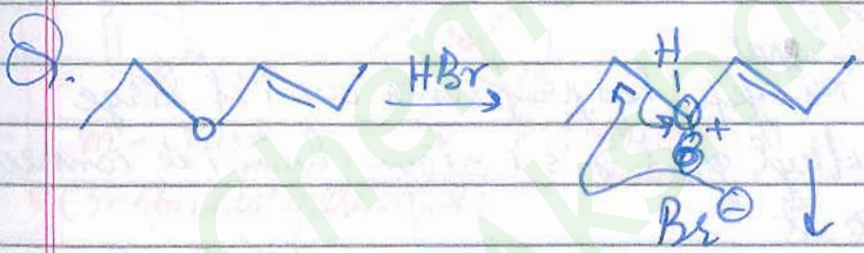
Chemistry Notes Akshanda

classmate
Date
Page

Q. 





Q. 

Q.

EPOXIDES (△)

→ 3 membered cyclic ether's common name.

→ IUPAC name: oxirane (If substituted, take no. 1 & on oxygen)

(Substituted epoxide.)

2-ethyl-2-methyloxirane

* : 2-(3-butenyl)oxirane

↓

Principal functional grp., has preference even if large alkyl grp (> 3 C atom chain) is connected to it.

* → OXITANE (common name)

OXIPANE (IUPAC)

OXANE (IUPAC)

*

* PREPARATION

1) From ALKENE: Prileschive's Rxn.

$$R-CH=CH_2 \xrightarrow{RCO_3H} R-CH(O)-CH_2$$

Source of [O] ← $R-\overset{O}{\overset{\|}{C}}-O-O-H$ i.e Peroxyacid or Peracid

Chemistry Notes Akshara

★ Peroxy acid :- Very unstable

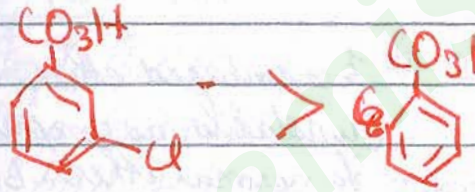
unstable

★ $CH_3-C(=O)-O-O-H$ peraceticacid.

★ $C_6H_5-C(=O)-O-O-H$: perbenzoic acid.

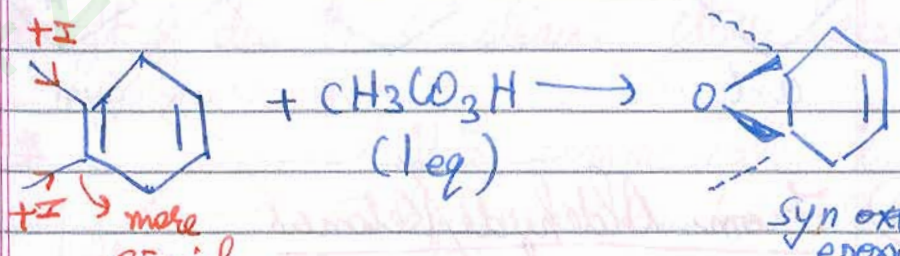
its stable form

★ $CF_3CO_3H > CH_3CO_3H$: Stability.
trifluoroperacetic acid — peracetic acid.

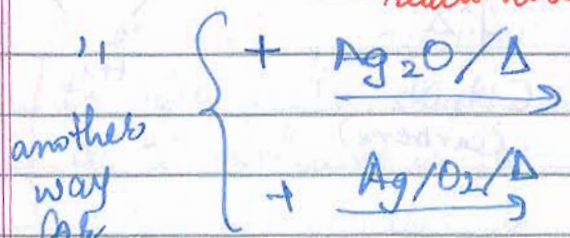


m-CPBA (metachloroperbenzoic acid)

perbenzoic acid.

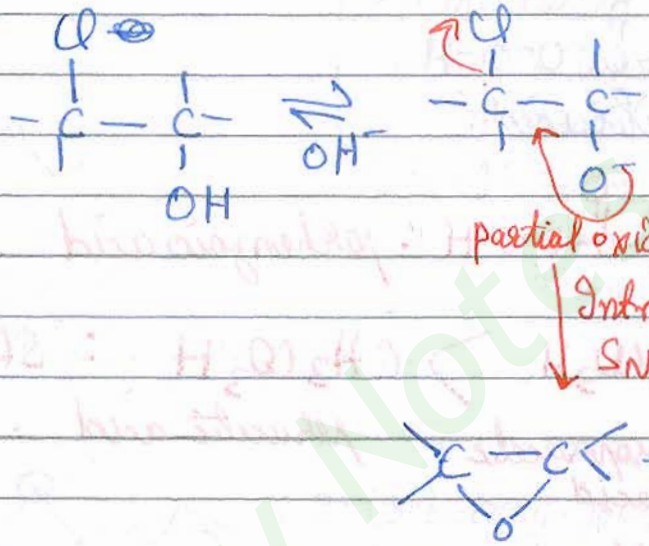


another way for Syn epoxidn.

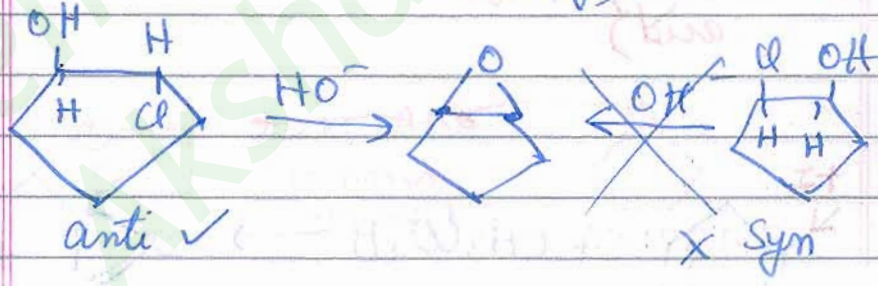


classmate
Date 10.9.20
Page

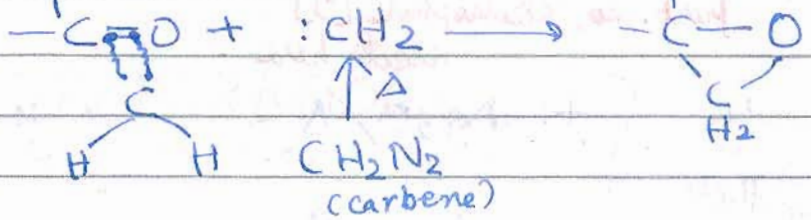
(2) From Vicinal-antihalohydrin :-



3 membered ether (unstable as compared to normal ether. But, its favoured due to entropy)

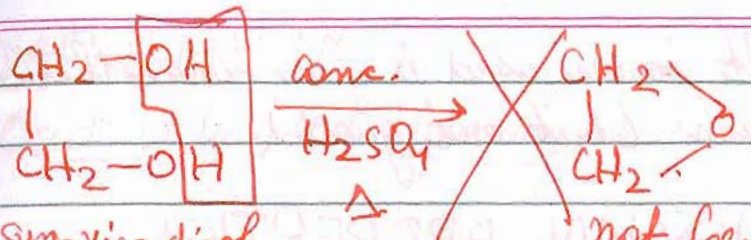


(3) From Aldehyde/Ketones



Chemistry Notes Akshansh

classmate
Date
Page



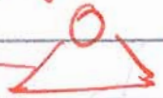
syn-vic-di-ol — not formed.

Reason:- In same condⁿ, syn-vic-diol reacts in slightly diffᵗ manner:-

Instability of 3 membered ring ∝ lets this happen.

Had it been 5 membered, then H₂O could take place (dehydⁿ)

PROPERTIES

* It is due to < strain, ether becomes highly reactive.
*  → It is commercially known as ethyleneoxide (ETO)

It is gas at RT.

→ used in ripening of fruit (conventionally CaC_2, calcium carbide, was used to ripe fruits, but, its not a good method ∵ acetylene is formed from it.) But, in ETO, hydrolysis gives ethylene glycol which is not hazardous.

→ Surgical appliances are sterilised by it.

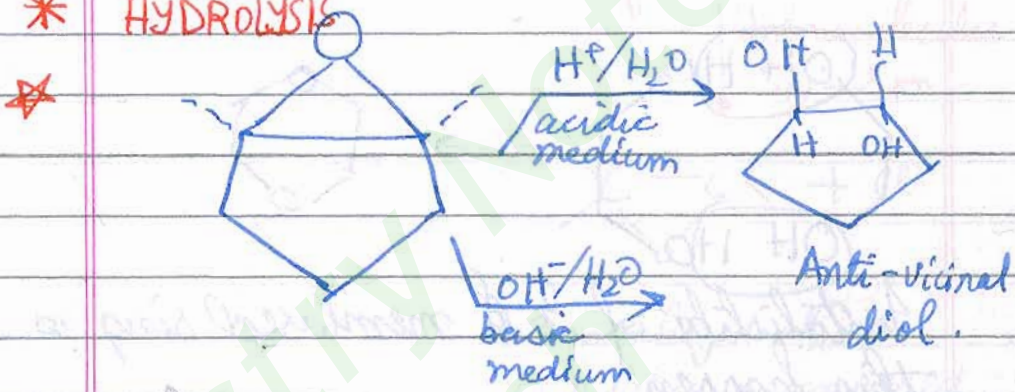
classmate
Date
Page

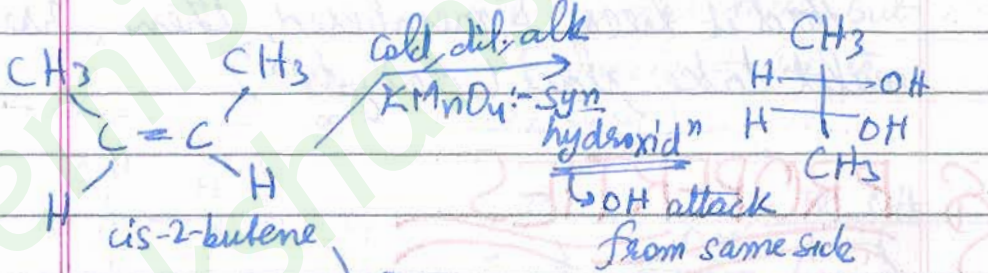
↳ It is was used to give anaesthetic gas (but not good)

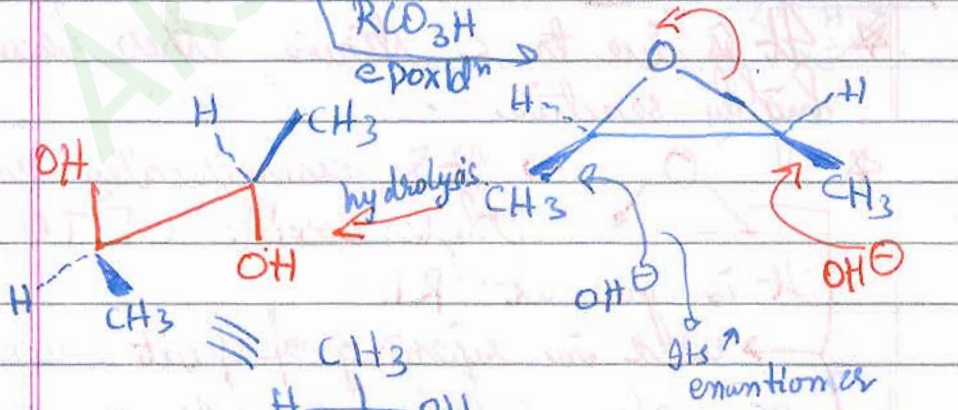
CHEMICAL PROPERTIES

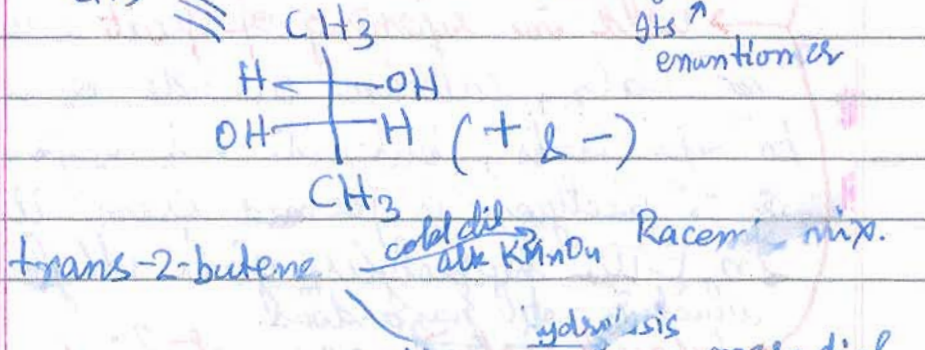
REACTIONS

* HYDROLYSIS





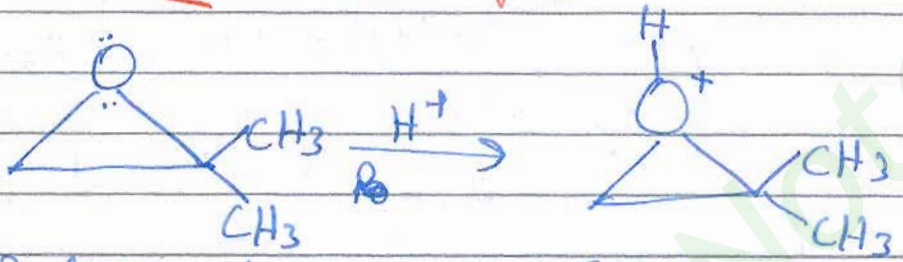




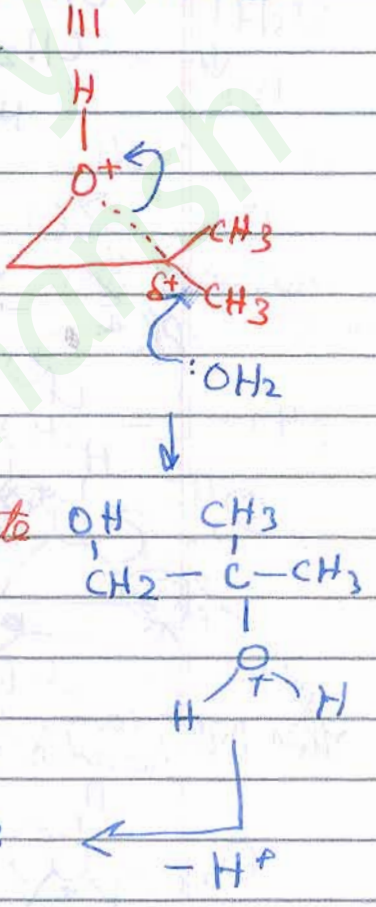
Chemistry Notes Akshansh

MECHANISM

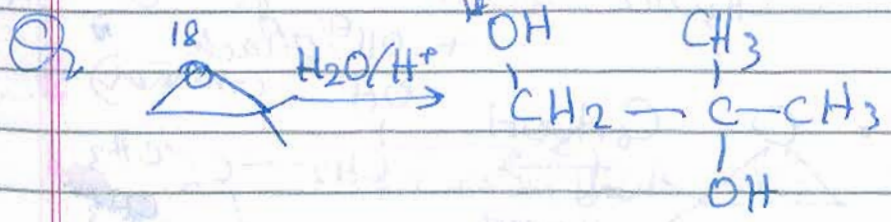
Acid Catalysed Hydrolysis



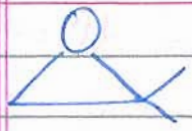
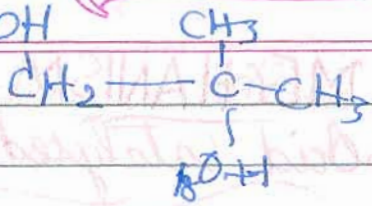
* Protonⁿ makes epoxide further more reactive for $Nu^{\ominus}$ attack
* Driving force → +ve charge on O.
* In acidic medium, $Nu^{\ominus}$ attack occurs at more sterically hindered carbon of protonated oxygen.
* That bond is broken in which the carbocation produced can better accomodate the +ve charge.
* Attack on O takes occurs from anti-posⁿ.

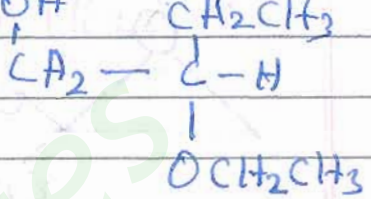


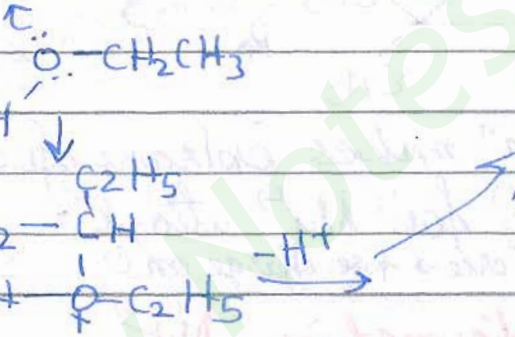
anti-vicinal diol.



classmate
Date
Page

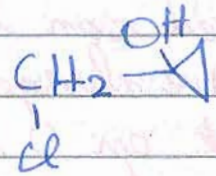
Q.  $\xrightarrow{H_2O^{18}/H^+}$ 

Q. $\xrightarrow{CH_3CH_2OH/H^+}$ 

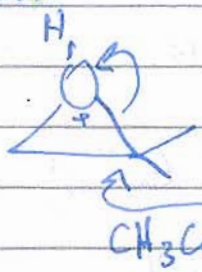
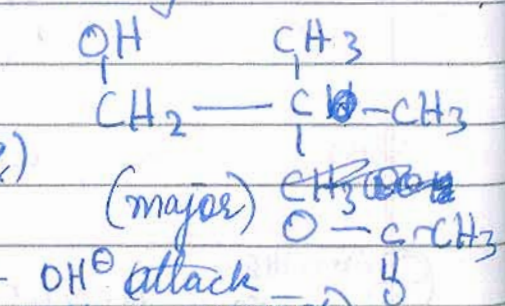


Q.

anti-halohydrine

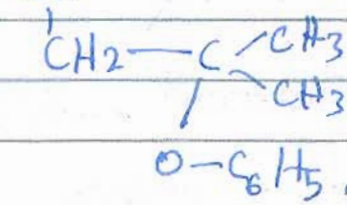
Q. $\xrightarrow{HCl}$ 

This part can handle +ve charge more nicely

Q  $\xrightarrow[H^+ (aq)]{CH_3COO^-}$ 

(major)

$+ OH^\ominus$ attack (minor)

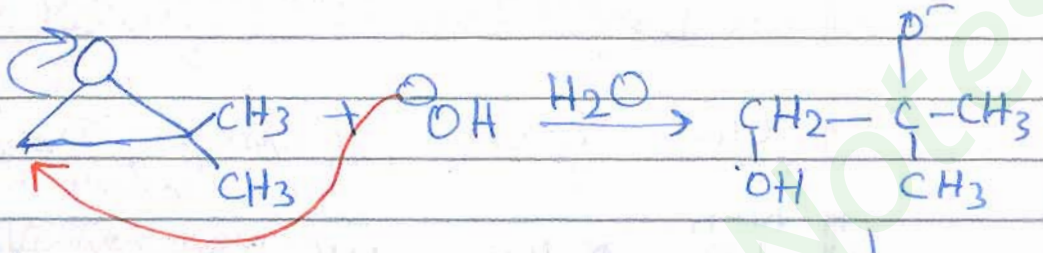
Q. C_6H_5OH $\rightarrow$ 

stronger acid than H_2O

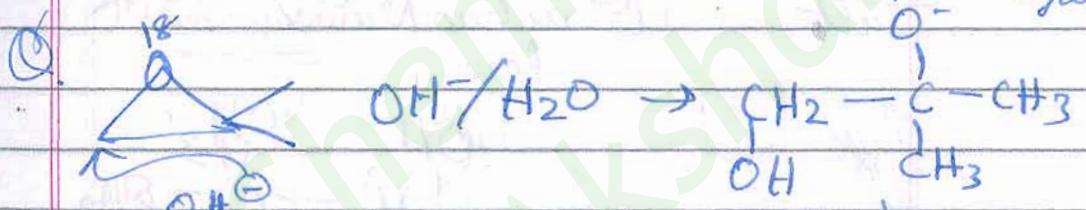
Chemistry Notes Akhansh

MECHANISM

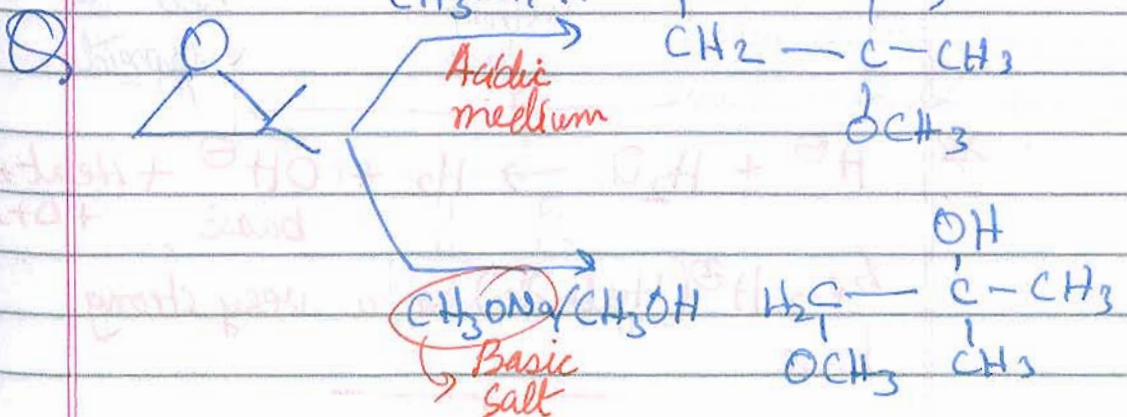
Basic catalysed hydrolysis
↳ alkaline



* ~~Hydrogen~~ Proton" doesn't takes place. So, $Nu^{\ominus}$ always attacks at less substituted / hindered C



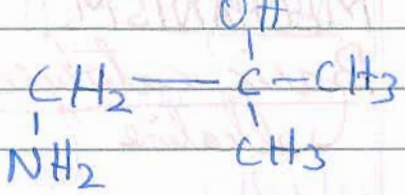
* $Nu^{\ominus}$ attack occurs at less hindered carbon.
⇒ Alkaline medium

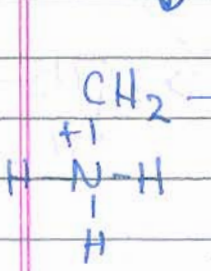


✱ $LiAlH_4$, $NaBH_4$ → source of $H^{\ominus}$ (Basic) ion.

Q.

$NH_3(aq)$ → basic medium





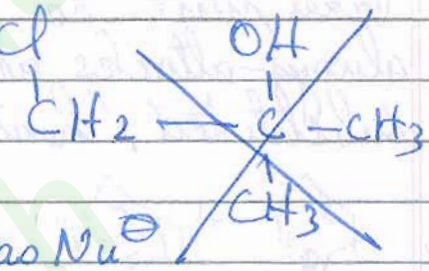
internal neutralisation → amine ol = amino ✱ amino

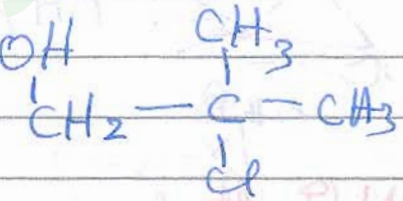
✱ Here, NH_3 is active $Nu^{\ominus}$ & not $OH^{\ominus}$.

Q.

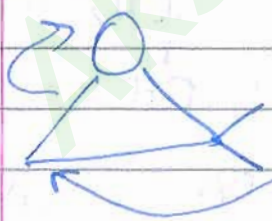
acidic salt

$NH_4Cl(aq.)$ ($Cl^{\ominus}$ act as $Nu^{\ominus}$ here.)



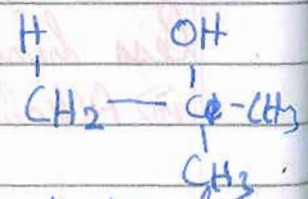


Q.



$LiAlH_4$ → source of $H^{\ominus}$ ion. → strong base

H_2O →



Red^n of epoxide.

✱ $H^{\ominus} + H_2O \rightarrow H_2 + OH^{\ominus}$ (basic) + Heat → Δ + Δ + Δ

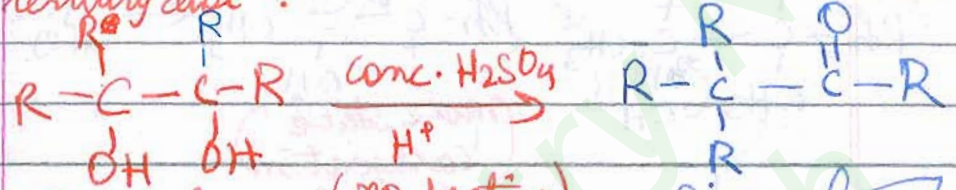
So, $H^{\ominus}$ (Hydride) is a very strong base.

Chemistry Notes Akshansh

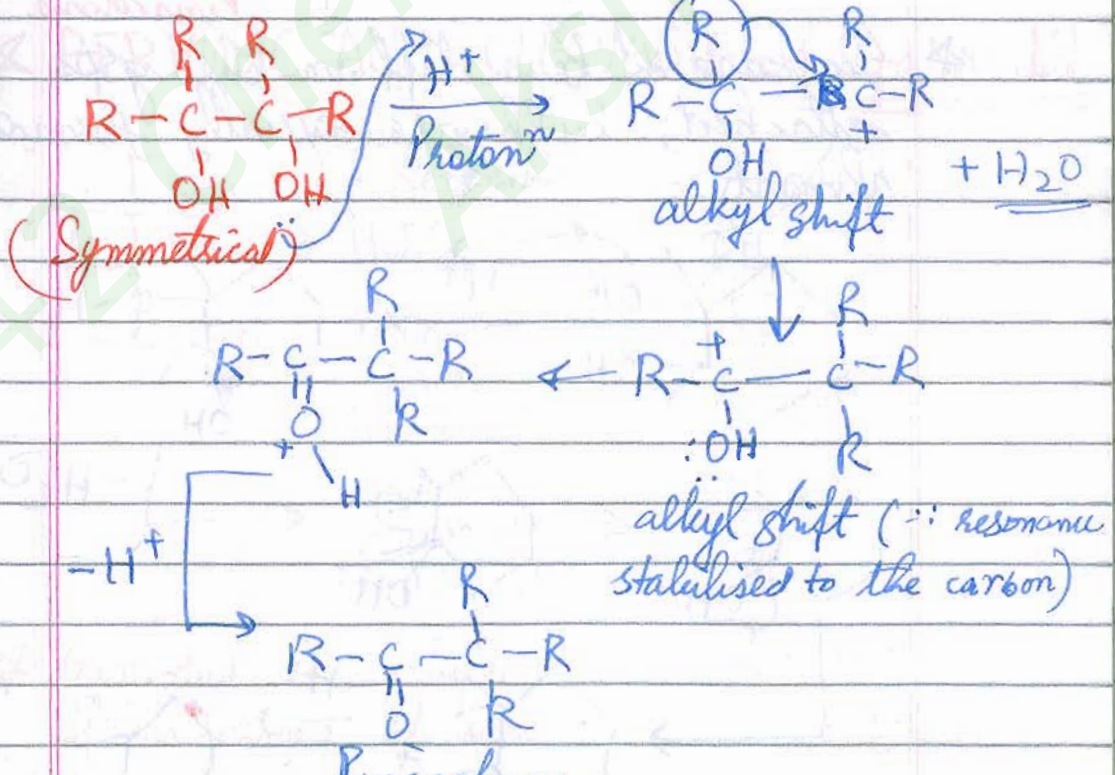
✱ RXNS of DIOL

✱ PINACOL-PINACOLONE rearrangement

name given to vicinal tertiary diol.

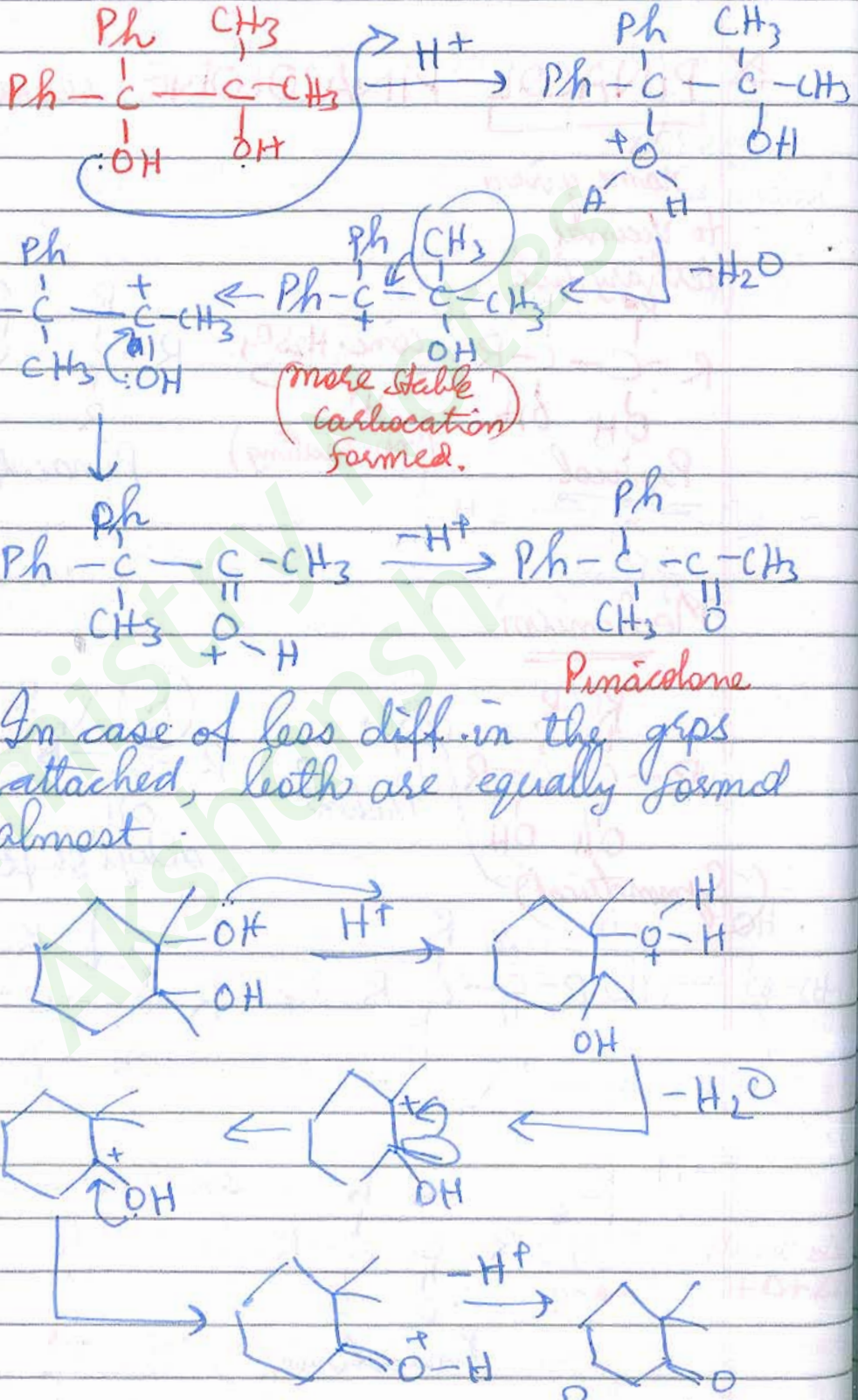


Mechanism



classmate
Date
Page

In case of unsymmetrical,



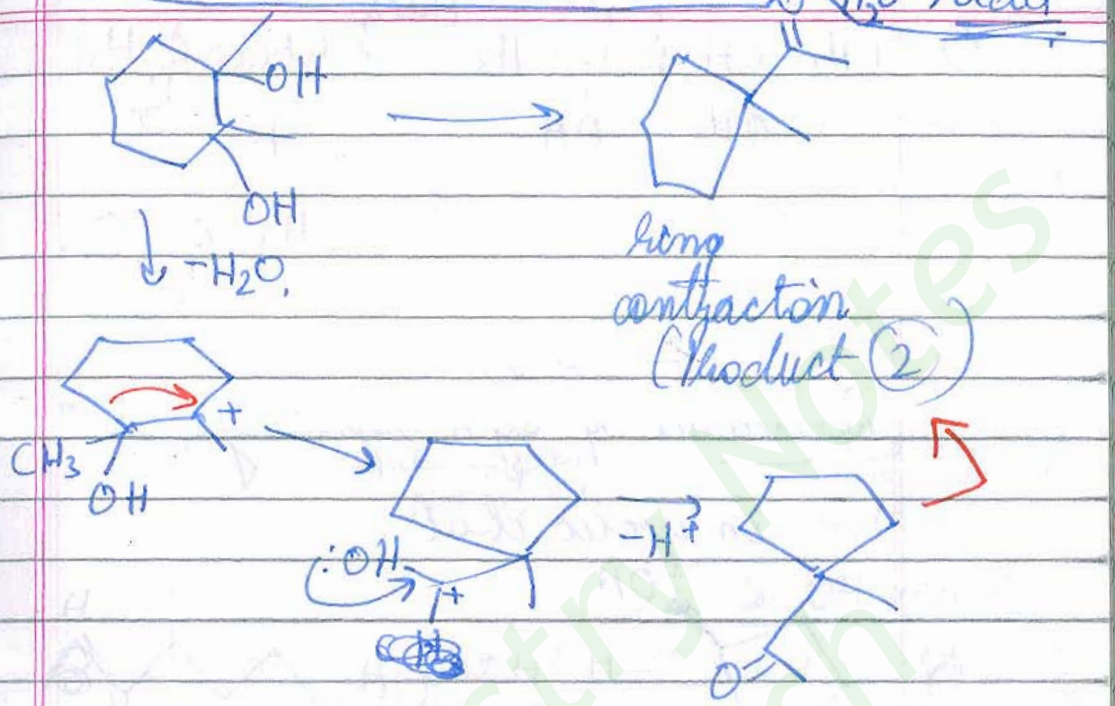
Pinacolone

* In case of less diff. in the grps attached, both are equally formed almost.

Product 1

✱ HOX, HXO_2, HXO_3, HXO_4 Forms of with $H_2O \rightarrow$ acid

hypohalous ↓ halic halous ↓ hallic perhallic

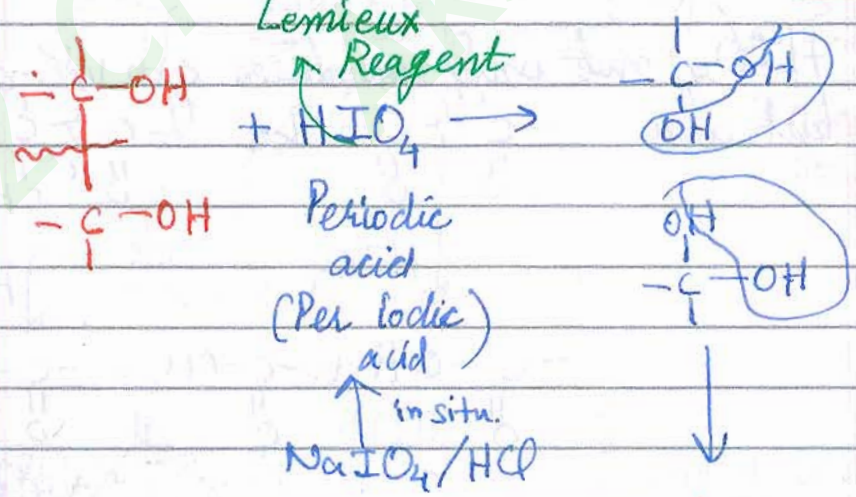


$\frac{24}{14} \times 100$

$2\frac{12}{7} \times 100$

$2\ 1.714$

✱ PERIODIC ACID CLEAVAGE of Syn-vic diol



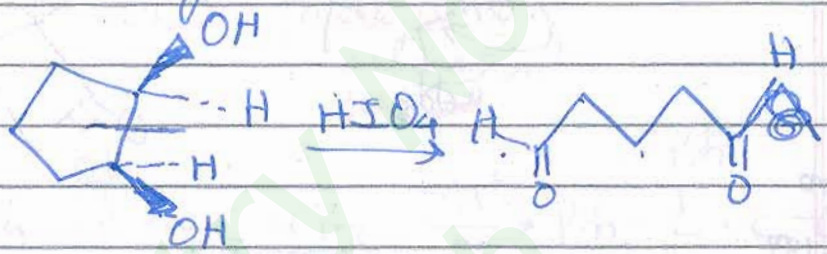
✱ Gem-diol is unstable. If its formed, it loses H_2O molecule to become stable.

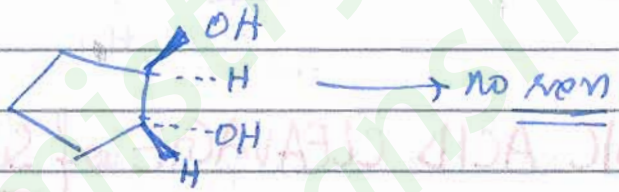
$-\overset{|}{C}=O + \quad -\overset{|}{C}=O$.

classmate
Date
Page

Q. $CH_3-CH(OH)-C(CH_3)(OH)-CH_3 \xrightarrow{HIO_4} CH_3-CHO + CH_3-C(=O)-CH_3$.

Relevance of syn hydrolysis in cyclic diol.

Q. 

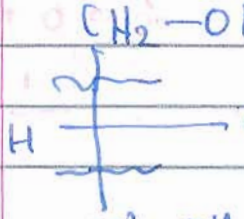


→ no reaction.

* HIO_4 not only oxidises syn vic-diol, but also $-C(=O)-C(=O)-$ and $-C(=O)-C(OH)-$

$-C(=O)-C(=O)-$ $\xrightarrow{HIO_4}$ $-C(=O)-OH + -C(=O)-OH$

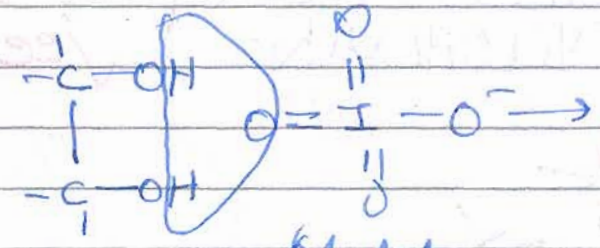
$-C(=O)-C(OH)-$ $\xrightarrow{HIO_4}$ $-C(=O)-OH + C=O$

Q. 

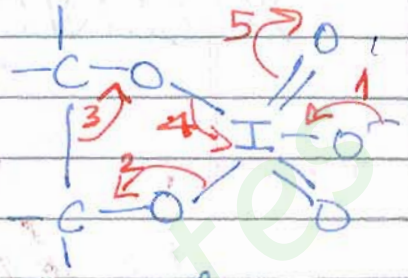
syn-vic-triol

$\rightarrow 2CH_2=O + H-C(=O)-OH$ ($H-C(OH)_2-OH$)

Mechanism



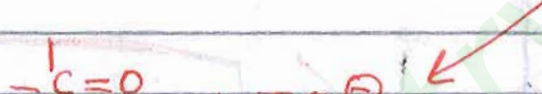
Iodate ion (From HIO_4)



cyclic intermediate with diol.

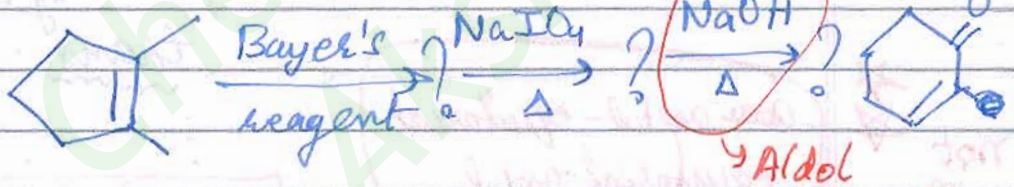
So, OH must be on same side

So, syn-vic diol is there

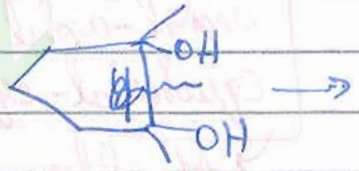


JEE '86

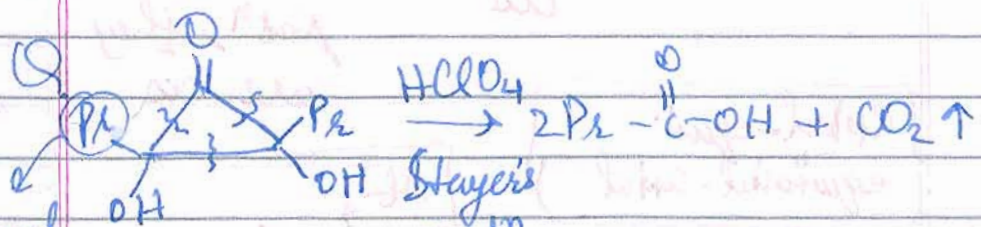
Q.



Aldol condensation



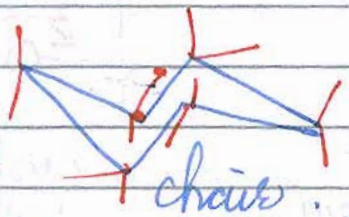
Q



Propyl grp.

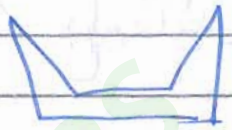
Stayer's oxidn.

☆ CONFORMERS of CYCLOHEXANE. (not in jee)

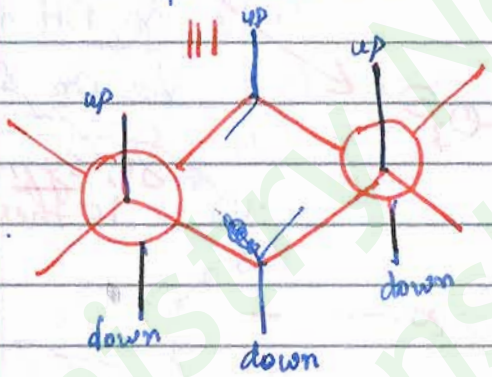


109° 28'

chair. (most stable) conformer.



boat structure.



Newman's projection.

axial - axial
or
equitorial - equi

↳ At adj. posⁿ they are trans.

☆ ☆ not in jee

~~axial~~ axial - equitorial
equitorial - axial

↳ At adjacent posⁿ, they are ~~trans~~ cis.

axial - axial
equitorial - equi

↳ At alternate posⁿ, they are cis.

axial - equi.
equitorial - axial

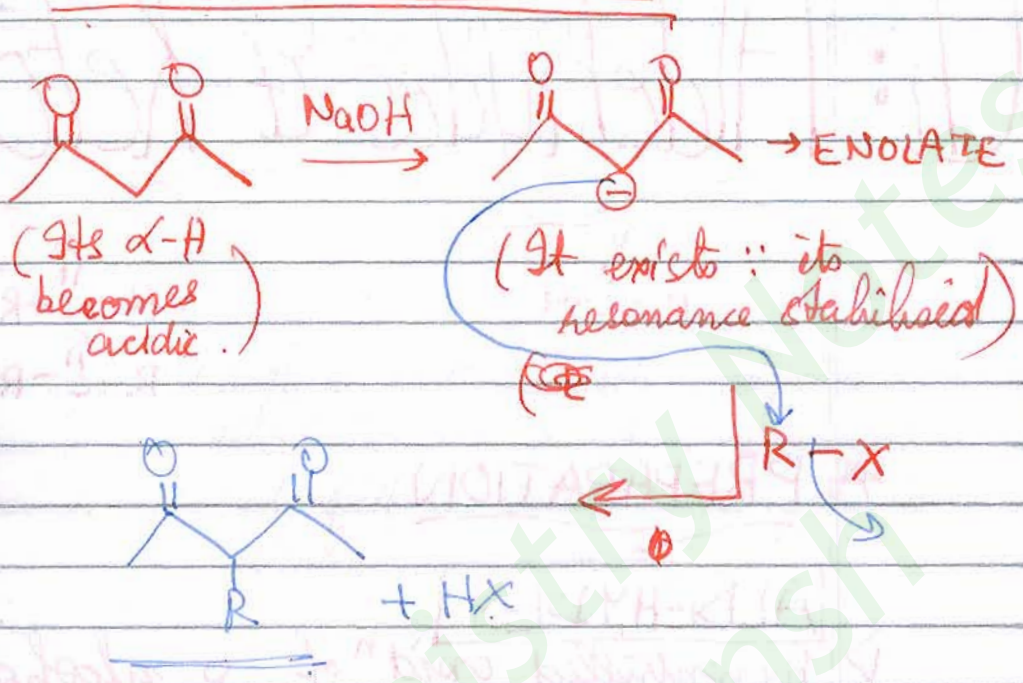
↳ At alternate posⁿ, they are trans.

At 1, 4 posⁿ →

a a
e e] trans

a e
e a] cis.

✱ ENOLATE ALKYLATION

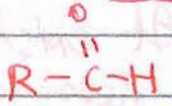


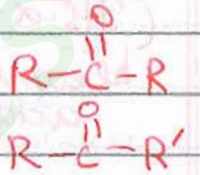
✱ AZO BENZENE Ph – N = N – Ph

+2 Chemistry Notes Akshansh

classmate
Date 15.9.10
Page

Ch: Aldehydes & Ketones





✱ PREPARATION

ALDEHYDES

1) By controlled oxidⁿ of 1° alcohols :-

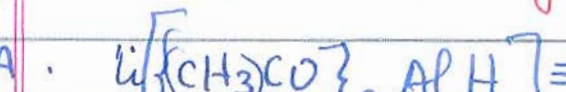
2) By Controlled Redⁿ of Acid Derivatives :-

- Acid chloride
- Acid anhydride
- Ester

✱ Imp. Reagents

1) Lithium tri-tert-butoxy Aluminium hydride

mild RA.

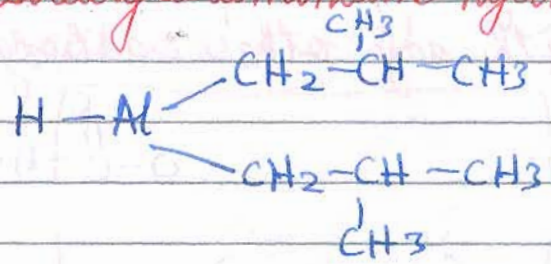


4-tri-t-BuOAlH

✓ sterically hindered.
✓ e⁻ withdrawing group, ↓ $H^{\ominus}$ donating ability of Al., ∴ ↓ reducing power

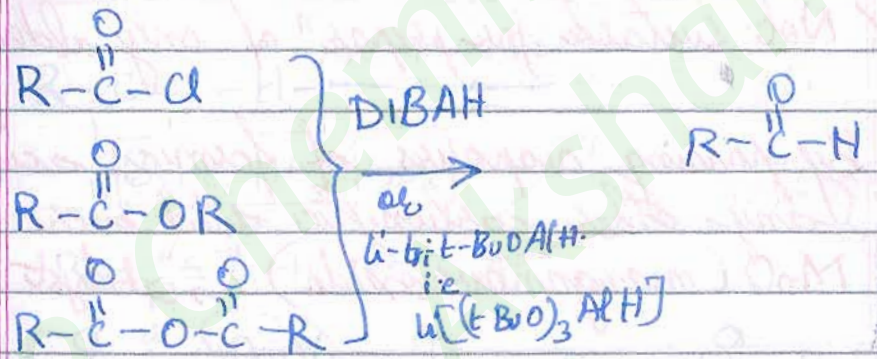
✓ The above reagent can't reduce ketones to alcohols.

2) diisobutylaluminium hydride (DIBAH)



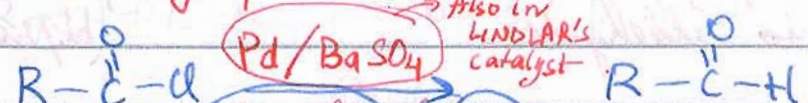
✓ Above 2 reagents :-

✓ reduce acid chloride, anhydrides & esters into corresponding aldehydes, but fail to reduce aldehyde to alcohol.



3) ROSENMUND red^{n} rxn :-

↳ Only for Acid-chloride red^{n}.



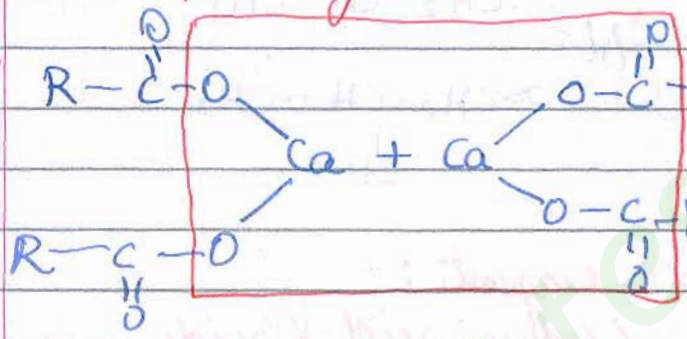
↳ Catalytic Poison :- ∴ prevent red^{n} of aldehyde to alcohol.

Solvent :- derivative of benzene (dimethyl benzene)

Chemistry Notes by Rishansh

4. By heating mixture of Ca salt formic acid with any other carboxylic acid.

Condensⁿ Rxn



$$\rightarrow \underset{\text{cross}}{2R-\overset{O}{\overset{\|}{C}}-H} + 2CaCO_3 + R-\overset{O}{\overset{\|}{C}}-R + H-\overset{O}{\overset{\|}{C}}-H$$

biproducts (self condensⁿ)

✓ Not suitable for prepar^n of only aldehyde.

5. By passing vapours of formic acid & any other carboxylic acid over hot MnO (manganous oxide) → catalyst

Condensⁿ Rxn

$$H-\overset{O}{\overset{\|}{C}}-OH + R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{MnO} \underset{\text{cross}}{R-\overset{O}{\overset{\|}{C}}-H} + H_2O + CO_2 + R-\overset{O}{\overset{\|}{C}}-R + H-\overset{O}{\overset{\|}{C}}-H$$

self condensⁿ biproducts

✓ It is also not suitable for prepar^n of only aldehydes.

M4 & M5 are industrial methods.

6. STEPHAN'S METHOD

↳ applicable for CN.

$$R-CN + \text{conc. HCl} \xrightarrow{SnCl_2} R-\overset{O}{\overset{\|}{C}}-H$$

↳ Stephan's reagent

$$[R-CH=NH] \xrightarrow{\text{hydrolyse (source of oxygen)}}$$

forms through : Imine (intermediate)

✓ Above method is not for prepar^n of ketones.

7. From terminal alkynes.

$$R-C\equiv C-H \xrightarrow{\text{Anti MK's add}^n} R-CH_2-CHO$$

$$R-C\equiv C-H \xrightarrow{B_2H_6/HO^-/H_2O_2} R-C(H)=C(OH)-H$$

(enol) $\xrightarrow{\text{tautomerism}}$ aldehyde.

HYDROBOR^n RxN.

* HBO of internal alkyne will produce ketone.

8. From alkene : Reductive ozonolysis

$$R-CH=\overset{R}{C}-R \xrightarrow[\text{or } O_3/(CH_3)_2S]{O_3/Zn-H_2O} R-\overset{O}{\overset{\|}{C}}-H + R-\overset{O}{\overset{\|}{C}}-R$$

↳ Zinc hydrolysis

↳ better.

Chemistry Notes Arsmnsir

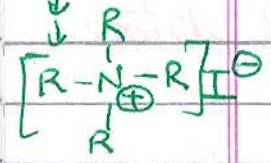
classmate
Date
Page

9. Quartenary ammonium salt of 1° amine.

SOMLET RXN

To prepare Quartenary Ammonium salt ↓

$R-I + \ominus NH_3$ ↓ ↓ ↓



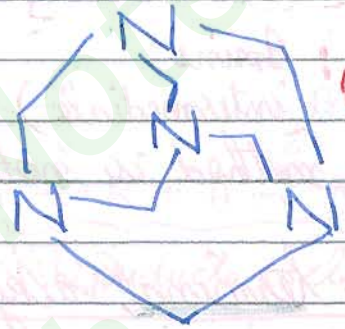
$$R-CH_2-\overset{\oplus}{N}H_4-Cl^- + (CH_2)_6N_4 \xrightarrow{H_2O} R-CHO$$

Quartenary ammonium salt.

hexamine. (CN:- ~~ecto~~ euro tropine)

commercial name

$(CH_6)N_4 \equiv$



Urotropine

✓ ancient explosive

10. OXO-PROCESS (Alkene → Aldehyde)

Industrial method.

tetra carbonyl cobalt hydride

$$R-\underset{\text{CHO}}{\overset{(2)}{CH}}=\underset{\text{CHO}}{\overset{(1)}{CH_2}} + CO + HCl \xrightarrow{[Co(CO)_4H] \text{ or } [Co[CO]_8]} R-CH_2-CH_2-CHO + R-\underset{\text{CHO}}{\overset{(2)}{CH}}-CH_3$$

* Formyl^n of C=C takes place.

∴ 2 units of H−C=O + H are added

11. GRIGNARD'S SYNTHESIS.

ester (of formic acid) (excess)

major + biproduct alcohols (∵ aldehyde is more prone to $Nu^\ominus$ add^n than ester)

* If RMgX excess, then, it reacts to form alcohol.

* Aldehyde is ~~also~~ more prone to nucleophilic add^n than ester

∵ → 1) Steric hinderance of OR grp in ester than
2) Electrophile character of ester is reduced du

KETONES | Preparⁿ

1. Oxidⁿ of 2° alcohol OA : PCC, NBS

$$R-\underset{OH}{\underset{|}{CH}}-R \xrightarrow[\text{oxidⁿ}]{[O]} R-\overset{O}{\overset{\|}{C}}-R$$

(use any OA)
another oxidising agent :- $(t\text{-}BuO)_3Al$ (aq.) : very mild → RA or OA?

If this OA is used, its called.
(OPPENAUER OXIDⁿ)

2. Oxymercurⁿ-demercurⁿ.

$$Ph-C(OH)=C(H)-CH_3 \xrightarrow{\text{tautomerises}} Ph-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

enol

* Modificⁿ of above reagent → $Hg^{2+}/HgSO_4$

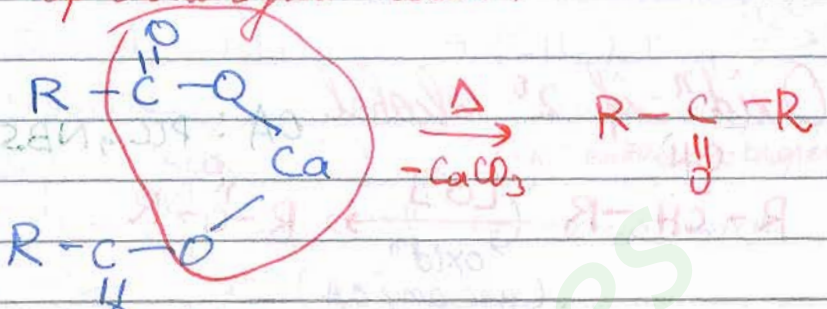
Mercuric ion is enough (Mercuric acetate is not reqd)

$$R-C\equiv C-H \xrightarrow[HgSO_4]{Hg^{2+}} R-\overset{O}{\overset{\|}{C}}-CH_3$$

* Note :- Oxymercurⁿ-demercurⁿ of H-C≡C-H will produce aldehyde.

resonance.

3. By thermal decompos^n of Ca salt of carboxylic acid.



✓ not suitable for prepar^n of unsymmetrical ~~alkene~~ ketone

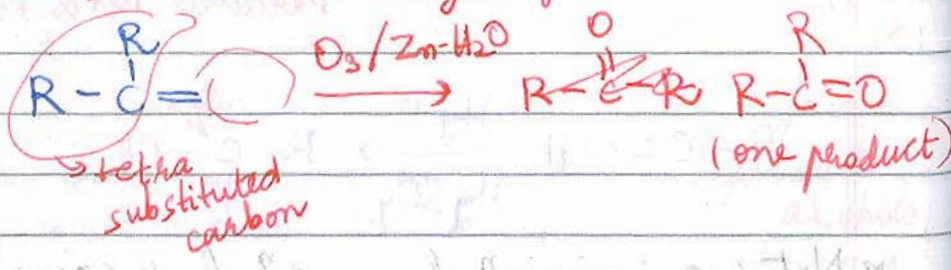
$$(RCOO)_2Ca + (R'COO)_2Ca \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-R + R'-\overset{O}{\overset{\|}{C}}-R' + R-\overset{O}{\overset{\|}{C}}-R'$$

4. By passing vapours of carboxylic acid over heated MnO.

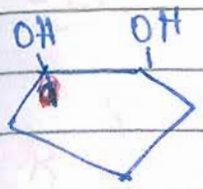
$$R\text{-}COOH + MnO \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-R + CO_2 + H_2O$$

✓ not suitable for unsymmetrical ketone : mixed acid will have to be taken

5. From alkene : Ozonolysis.



classmate
Date
Page



$\xrightarrow{HIO_4}$ OHC ⟋⟍⟋⟍ CHO

(LEMIEUX Reagent)

5. GRIGNARD'S SYNTHESIS.

acid chloride, ester, anhydride } excess
cyanide

↓ Ketone (major)

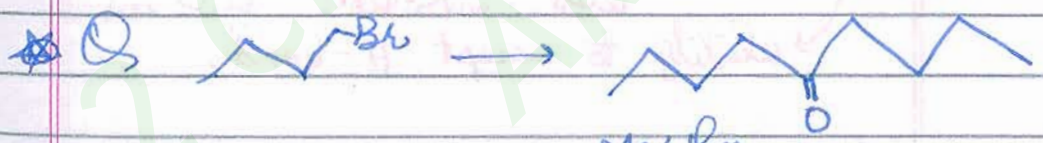
$R-C\equiv N + R'MgX \rightarrow \left[R-C(R')=N^{\ominus}MgX^{\oplus}\right]$

(excess)

$\left[R-C(R')=N^{\ominus}MgX^{\oplus}\right] \xrightarrow{H^{\oplus}/H_2O}$ $R-C(=O)-R'$

$\left[R-C(R')=NH\right] \xrightarrow{H^{\oplus}/H_2O}$ $R-C(=O)-R'$

Imine (undergoes self hydrolysis in H_2O at RT)



$CH_3CH_2CH_2CH_2-Br \xrightarrow{Mg/ether} CH_3CH_2CH_2CH_2-MgBr$

$CH_3CH_2CH_2CH_2-MgBr + (I)$.

$\downarrow KCN$

$\xrightarrow{I} \xrightarrow{H_2O}$

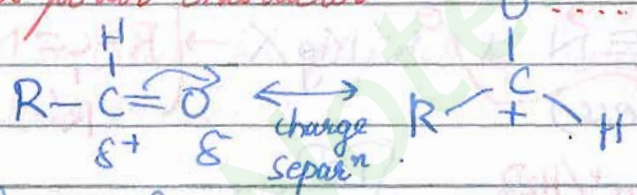
Pentane nitrile.

+2 Chemistry Notes Akshansh

§ PROPERTIES

⟨1⟩ PHYSICAL

✓ Both aldehyde & ketone have C=O giving it a polar character.



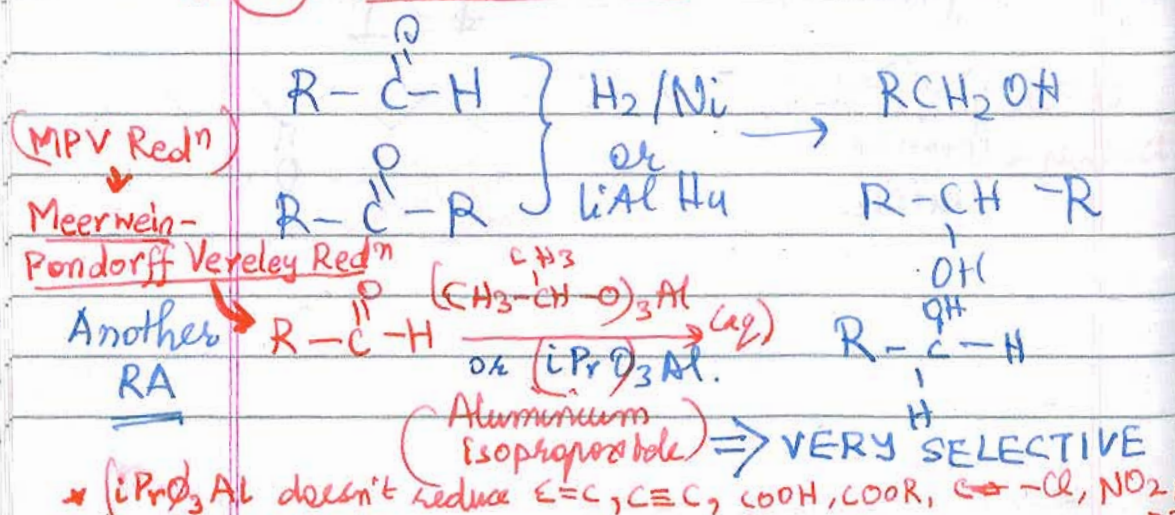
✓ Above charge separⁿ provide Addⁿal polarity to them (more polar than ethers, esters, R–X)

✓ B.Pt :- More than: ether, R–X, ---
less than: R–OH (H-bonding)

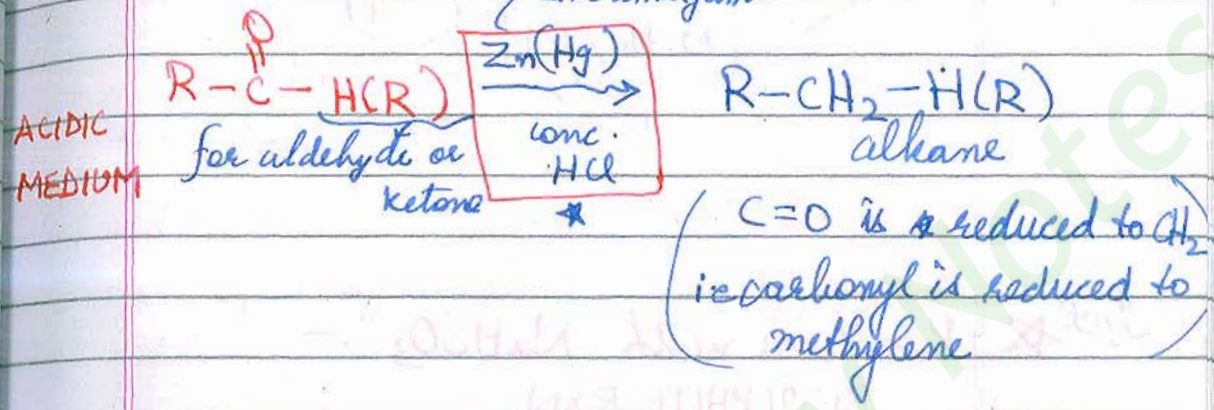
✓ Solubility :- More: R–X, ether } in H_2O
less: R–OH
↳ ability to accept H-bond.

⟨2⟩ CHEMICAL REACTIONS

(i) REDUCTION

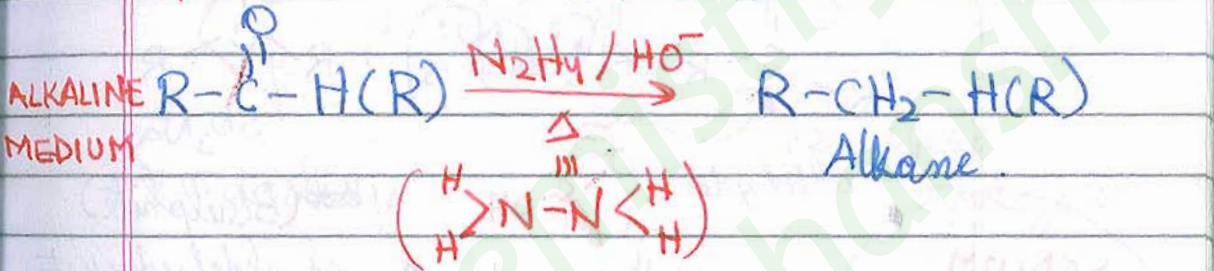


✱ CLEMMENSON'S Red^{n} :- (Ald. or ketone → Alkane)



(C=O is reduced to CH_2 i.e carbonyl is reduced to methylene)

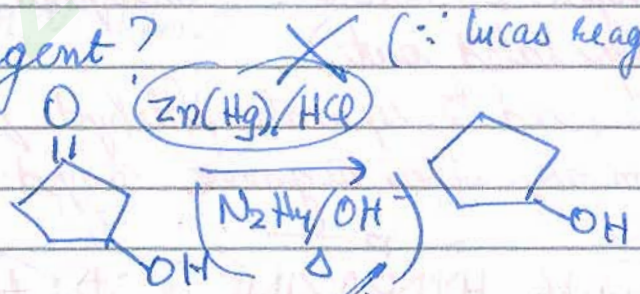
✱ WOLF-KISCHNER Red^{n}



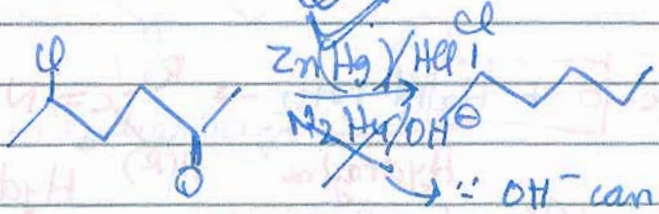
✱ Alone 2 rxns have same purpose but occur in diff^{t} mediums.

→

Q. Reagent? (∵ lucas reagent is formed)

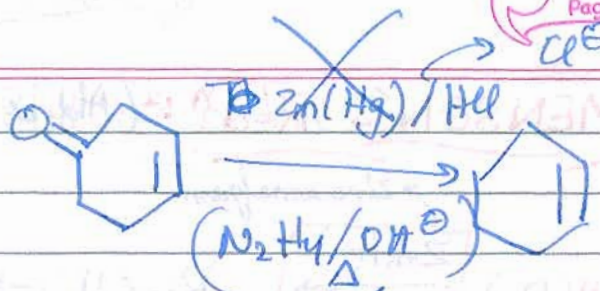


Q.



→ ∵ OH^- can react as a $Nu^{\ominus}$.

12 Chemistry Notes Akshara

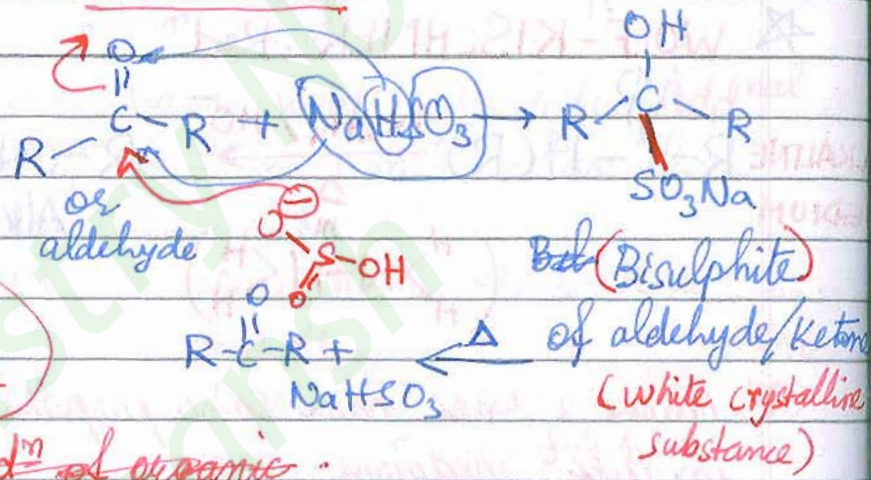
Q. 

$Cl^\ominus$ addⁿ ryn on double bond occurs

Base & $OH^\ominus$ don't react.

Imp ✱ Reaction with $NaHSO_3$:-

BISULPHITE RXN



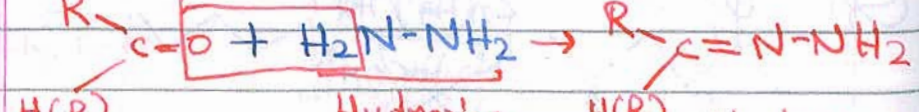
SODIUM BISULPHITE TEST

~~Addⁿ of organic~~.

DISTINCTION ✓ Above method is used to detect Aldehyde or ketone (∵ Bisulphite formed is separated out).

SEPARATION ✓ It is used to separate Aldehyde / Ketone from any other organic compd.

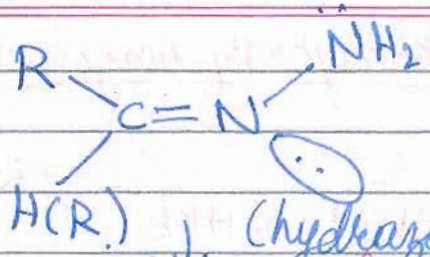
✱ Rxn with HYDRAZINE & its derivatives

(a) 

(Its not wolf Kishner ryn because alkali medium isn't there)

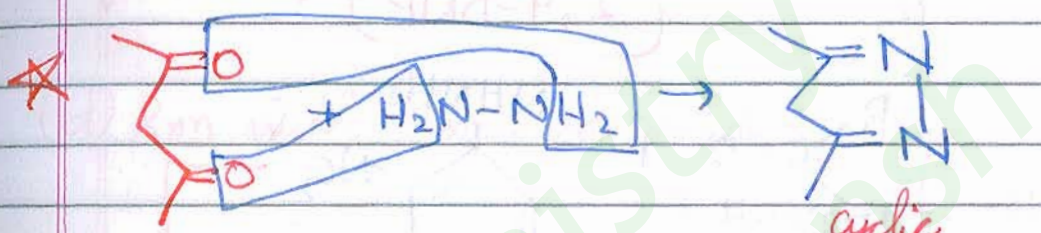
It is beginning of wolk ✱ Kischner red"

classmate
Date
Page



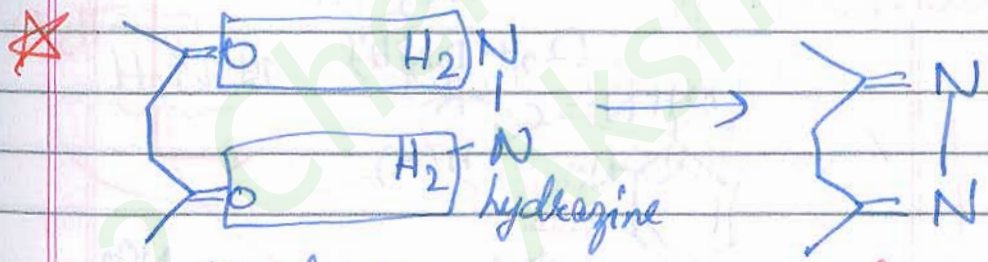
(hydrazone)

It can be optically active & so, no. of hydrazone formed would be varied.
If unsymmetrical → 2 hydrazone.



1,3 dicarbonyl

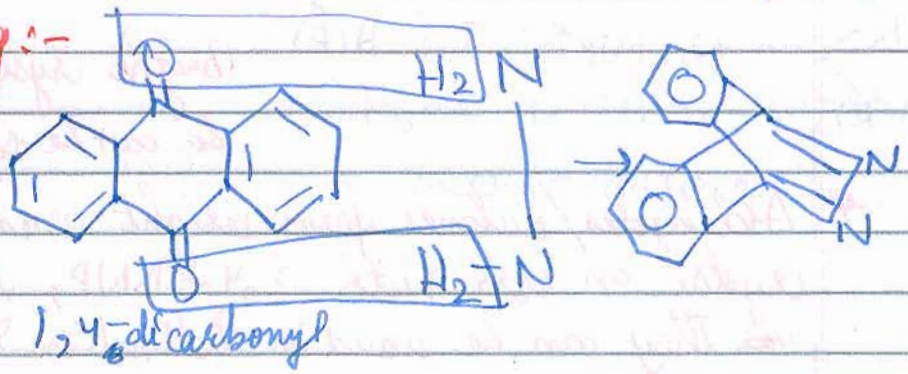
cyclic hydrazone.



1,4 dicarbonyl

cyclic hydrazone

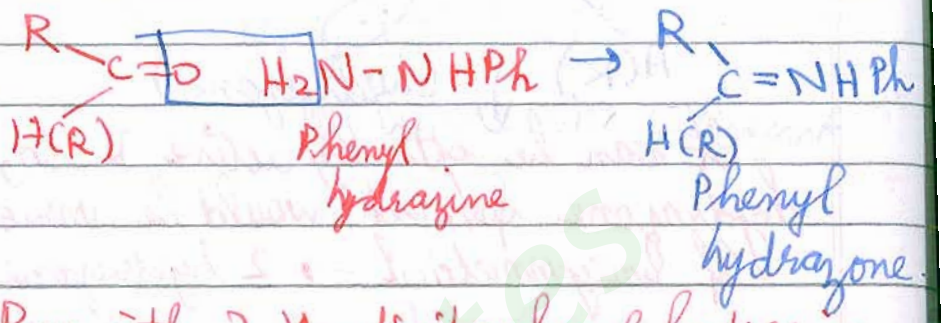
eg:-



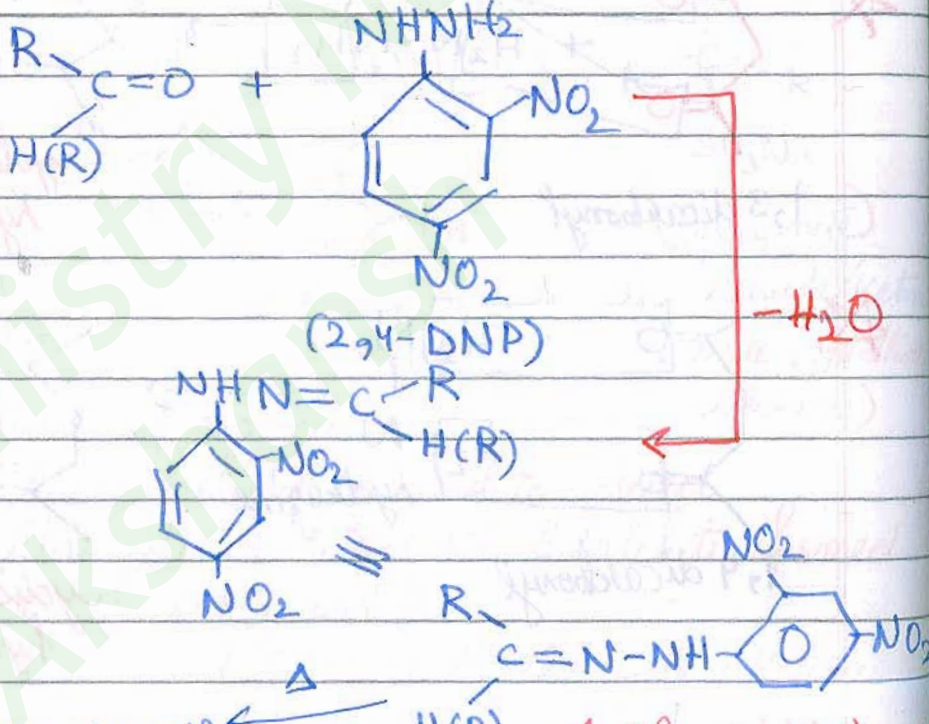
1,4-dicarbonyl

+2 Chemistry Notes Akshansh

(6)* Rxn with Phenyl Hydrazine



(c) ** Rxn with 2,4-dinitrophenyl hydrazine (2,4-DNP)



(Bright crystal) so, can be separated

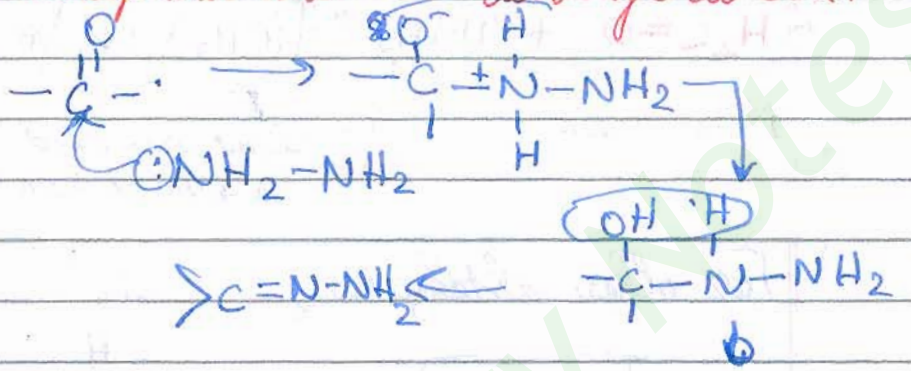
* Aldehydes/Ketones form bright orange crystal on rxn with 2,4-DNP, so, they can be used in distinction & separ^{n}.

Chemistry Notes by Akshansh

$CH_3-\overset{O}{\overset{\|}{C}}-$ grp: aceto

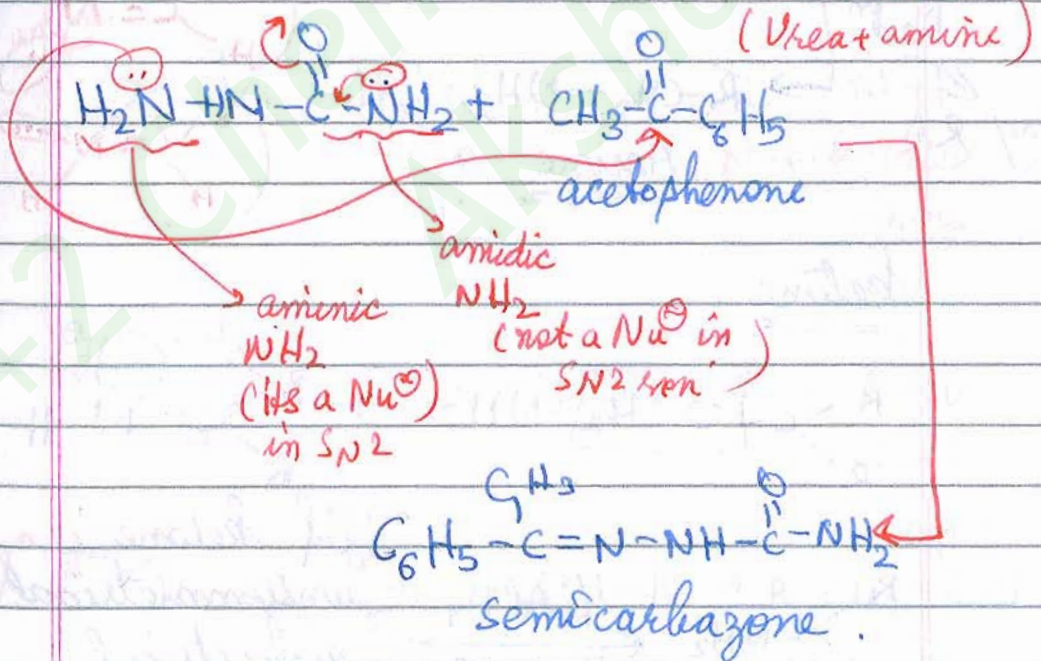
Mechanism : ~~known as~~

S1 : Nucleophilic add^n at carbonyl carbon.



(d) Rxn with Semi-carbazide → ($H_2N-HN-\overset{O}{\overset{\|}{C}}-NH_2$)

↓ Uramine (Urea + amine)



$C_6H_5-\overset{C_6H_5}{\overset{|}{C}}=N-NH-\overset{O}{\overset{\|}{C}}-NH_2$

semicarbazone.

+2 Chemistry Notes Akshansh

classmate
Date 17.9.10
Page

✱ Reactions with NH_3 & $R-NH_2$

With NH_3

SPECIAL CASE

$$6\,H_2C{=}O + 4NH_3 \xrightarrow{\Delta} \boxed{(CH_2)_6N_4} + 6H_2O$$

formaldehyde

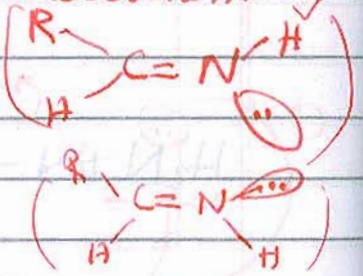
urotropine
(Same was used in Sommelet-Hon)

For other aldehydes,

$$R-CH{=}O + H_2NH \longrightarrow R-\underset{H}{\overset{H}{C}}{=}N-H$$

Imine.

(It can show stereochemistry



)

$$RCH{=}NH \xleftarrow{\text{Red}^n} \text{any RA}$$

$$RCH{=}NH \longrightarrow R-CH_2-NH_2$$

Amine

Ketone

$$R_2C{=}O + H_2NH \longrightarrow R_2C{=}N-H$$

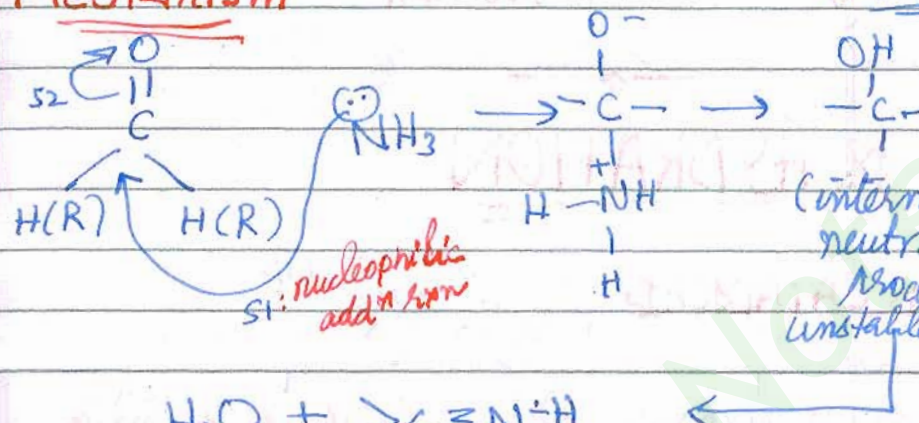
(If ketone is unsymmetrical geometrical isomerism will come into play)

$$R_2CH-NH_2 \xleftarrow[\text{Red}^n]{LiAlH_4}$$

Amine

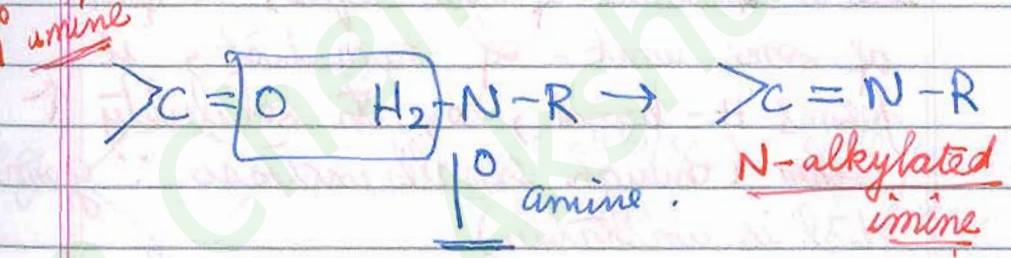
Chemistry Notes Akshansh

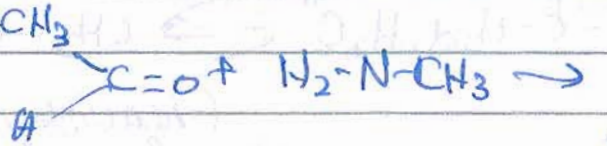
Mechanism

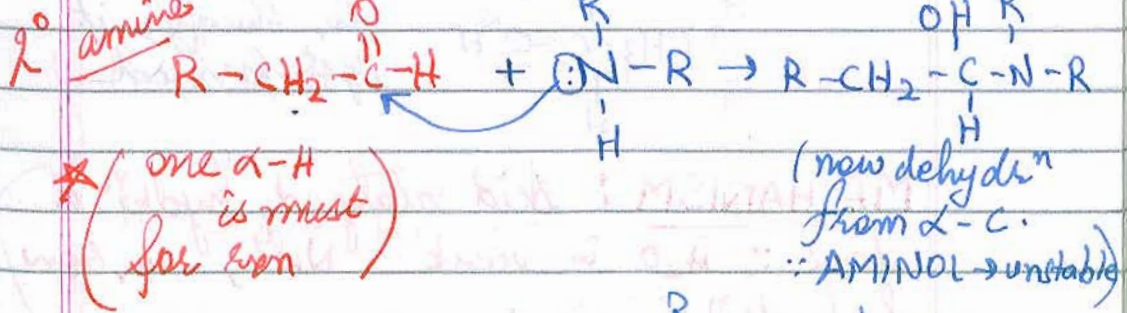


* In above rxn:- aldehyde > ketone : Reactive
∵ its nucleophilic addⁿ rxn (steric hinderance)

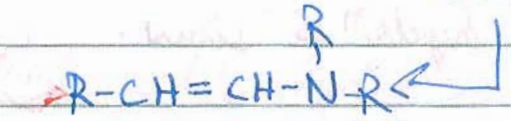
With $R-NH_2$



eg: 

2° amine 

* (one α-H is must for rxn)



3° amine :- No rxn.

✡ HYDRATION

ACID CATALYSED

$$-\underset{\underset{H(R)}{|}}{C}=O + H_2O \underset{\text{equi}}{\overset{\text{hydrate}}{\rightleftharpoons}} -\underset{|}{\overset{OH}{\overset{|}{C}}}-OH$$

hydrate (of aldehyde or ketone)

Gem diol
↳ very unstable & so, equi favour reactant.

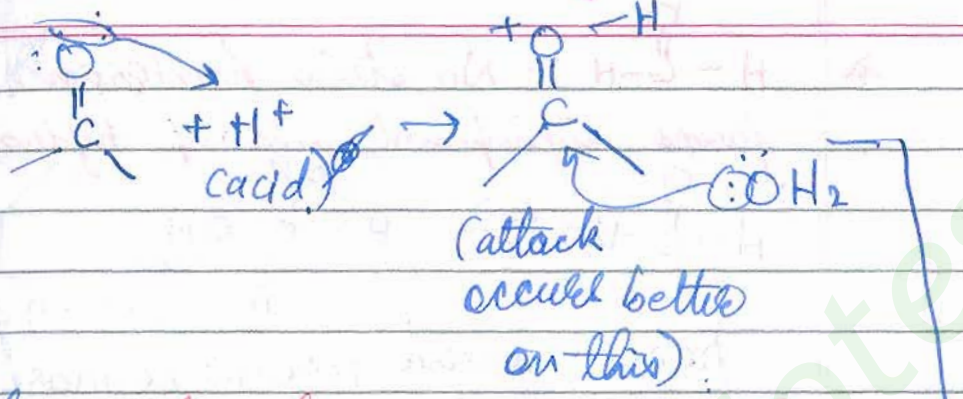
Due to existence of this equi, & formⁿ of some amt of Gem diol, it forms H-bond, so, its solubility ↑ (though small increase ∵ gem diol is unstable)

$$CH_3-\overset{O}{\overset{\|}{C}}-H + H_2O^{18} \rightleftharpoons CH_3-\overset{O^{18}}{\overset{\|}{C}}-H$$

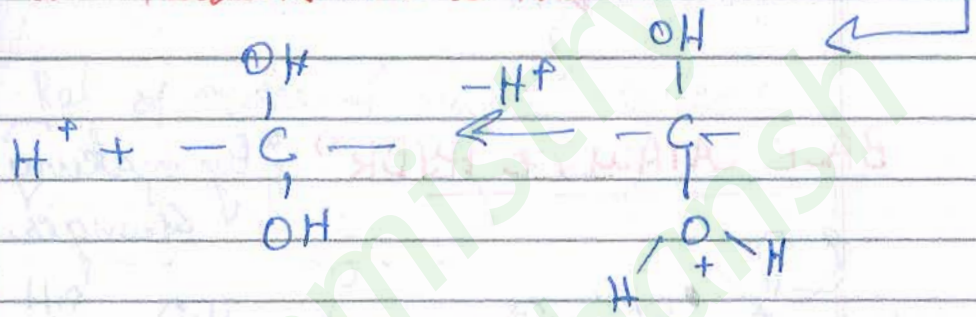
(heavier isotope form stronger bond) So, slowly, it gets formed

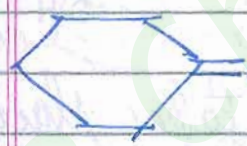
$$CH_3-\underset{\underset{H}{|}}{\overset{OH}{\overset{|}{C}}}-O^{18}H$$

MECHANISM : Acid catalysed hydrⁿ is done ∵ H_2O is weak $Nu^{\ominus}$, so, rxn of hydrⁿ is slow.

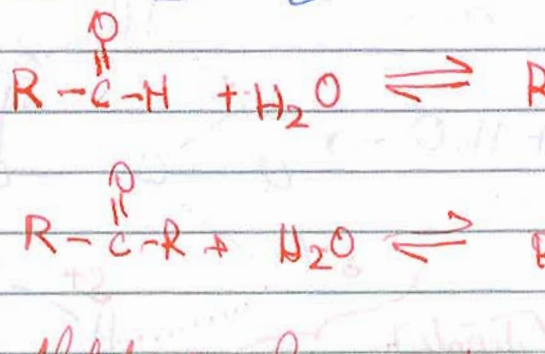


So, protonⁿ of carbonyls make them highly reactive. So, even H_2O can ~~ad~~ attack as a $Nu^{\ominus}$.



eg  $+ H_2O^{18} \xrightarrow[\text{slow}]{\text{very}}$ O^{18} presence not seen

$+ H_2O^{18} \xrightarrow[\text{acid}]{H^+}$ very fast. O^{18} presence seen.



Aldehyde has greater hydrate content at eqlm. than ketone. Both have $K < 1$ But, comparitively, $K_{ald} > K_{ketone}$.

+2 Chemistry Notes Akshansh

classmate
Date
Page

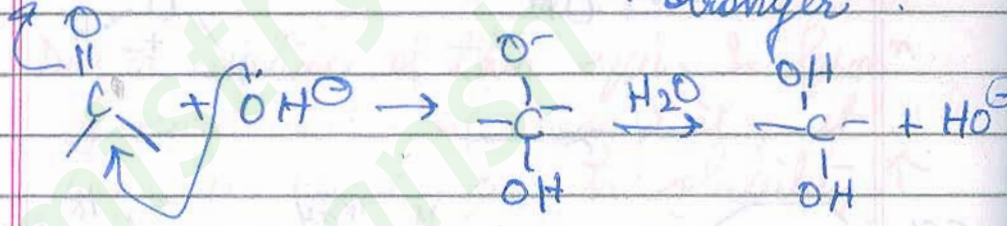
* $H-\overset{O}{\overset{\|}{C}}-H$:- No steric hindrance. It forms significant amt. of hydrate.

$$H-\overset{O}{\overset{\|}{C}}-H \rightleftharpoons H-\overset{OH}{\overset{|}{C}}-OH \quad (H)$$

hence, ~~metha~~ $H-CHO$ (2 OH grp) is more reactive than ethanol (one OH)

* HCHO (aq) :- FORMALIN (common name)

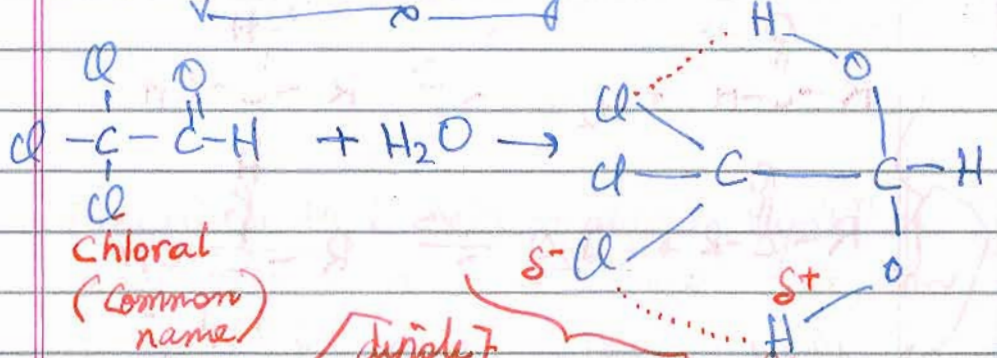
BASE CATALYSED HYDR^{n} : By making $Nu^{\ominus}$ stronger.



** Acid catalysed hydr^{n} takes place by making aldehyde/ketone stronger (by add^{n} of $H^{\oplus}$/acid).

Imp.

** Base catalysed hydr^{n} takes place by making $Nu^{\ominus}$ stronger.



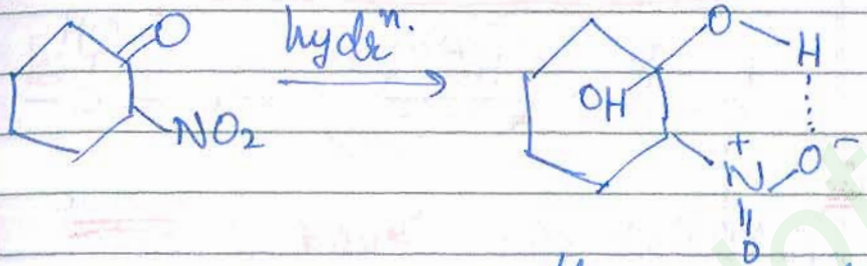
Chloral (common name)

Chloral hydrate is stabilised to high extent due to dipole dipole attr^{n}

Stability acquired due to form^{n} of ring (So, hydrate is most existent)

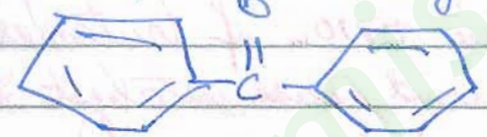
classmate
Date
Page

☆ Ist case



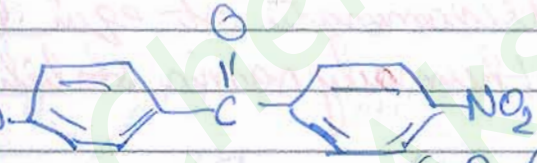
Its content at equi is a lot due to high hydrⁿ (H-bonding)

Q. Rel. order of hydrⁿ content?



II > I > III ✓

II < ~~I~~ < III

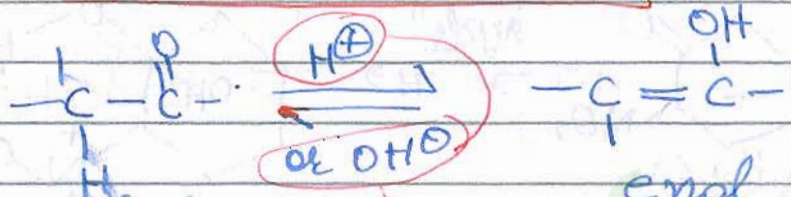


(-R effect : ↑ electrophilic character of C=O
∴ so, reactivity ↑

(+R effect. so, electrophilicity ↓)

Chemistry Notes Akshansh

KETO enol Tautomerism



(aldehyde or Ketone having atleast one α-H)

→ used for establishing equi. faster.

* An aldehyde / ketone containing atleast 1 α-H remain in dynamic equi with its ENOL & tautomer. Presence of acid / base catalyst catalyses tautomerism. Under normal cond", KETO form predominate at equi. (due to greater thermodynamic stability of it).

* $CH_3-CHO \underset{D_2O}{\overset{aq.\ NaOD}{\rightleftharpoons}} D-\underset{D}{\overset{D}{C}}-CHO.$

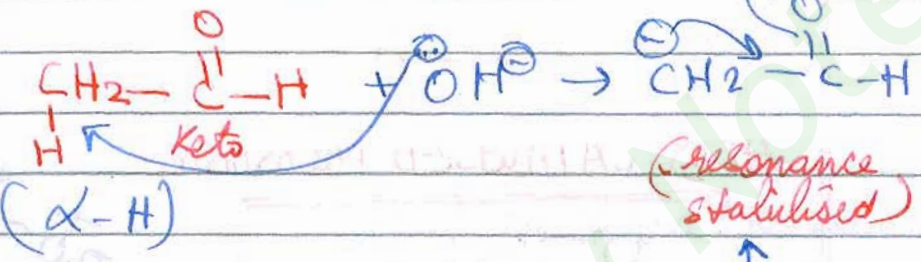
3 unit gain in molar mass occurs in one exchange (−1 for H, +2 for D)

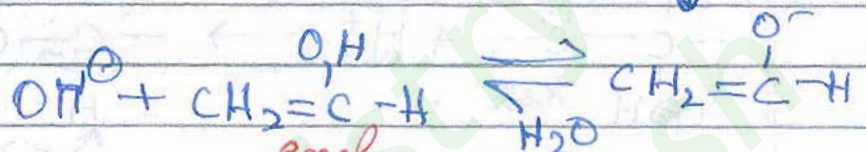
It proves dynamic equi. occurs b/w keto & enol form.

* α-H is reqd ∵ in mechanism, its conjugate base formed is resonance stabilised.

Mechanism

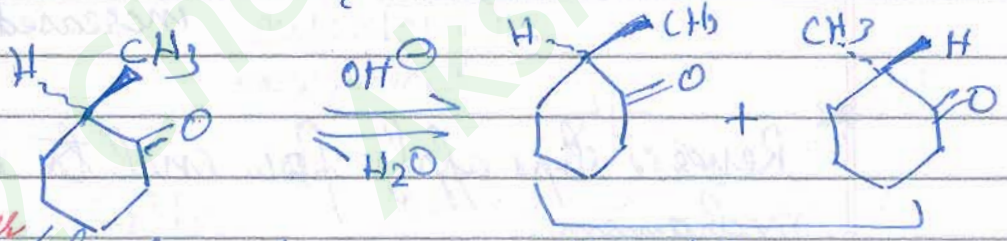
BASE CATALYSED





** Reverse mechanism of this occurs for enol to keto.

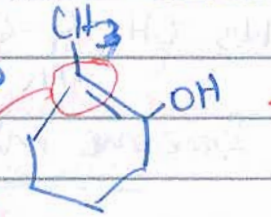
Concept



Pure enantiomer (+ or −) / chiral C ✓ / optically active ✓ / 2 enantiomer ✓

Racemisⁿ occurs

50 %. 50 %.



Racemic.

Planarity (Or extraction of H⁺ from any side is equally likely)

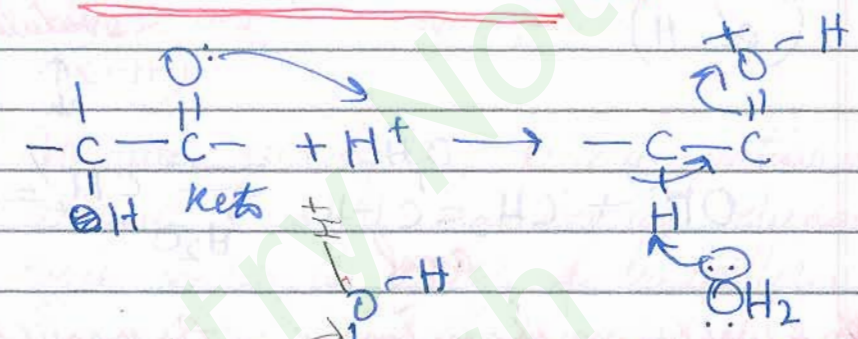
* Same occurs in acidic medium.

Chemistry Notes Akshansh

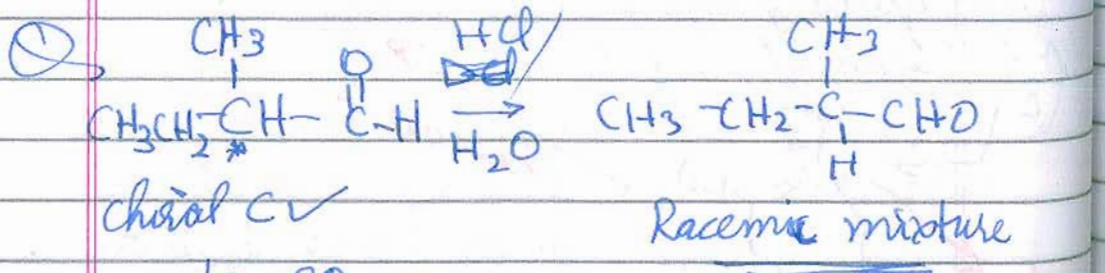
classmate
Date
Page

* If α-C in keto form (C=O compd) contains 1H (atleast) & chiral carbon racemises to produce 2 product (racemisⁿ) through keto-enol tautomerism.

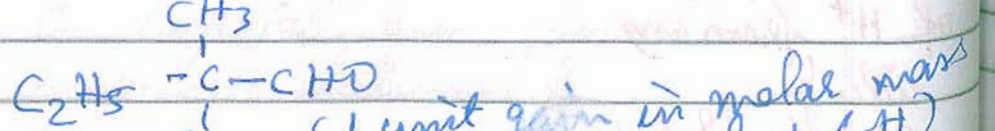
ACID CATALYSED Mechanism



* Reverse steps apply for enol to keto mechanism.



D_2O | D_2SO_4 dil



D. (1 unit gain in molar mass occurs due to only 1 α-H)

Chemistry Notes Akshansh

Q. $CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[NaOD]{D_2O} CD_3-\overset{O}{\overset{\|}{C}}-CD_3$

all H-replaced

Relative Stability & Rel. enol content

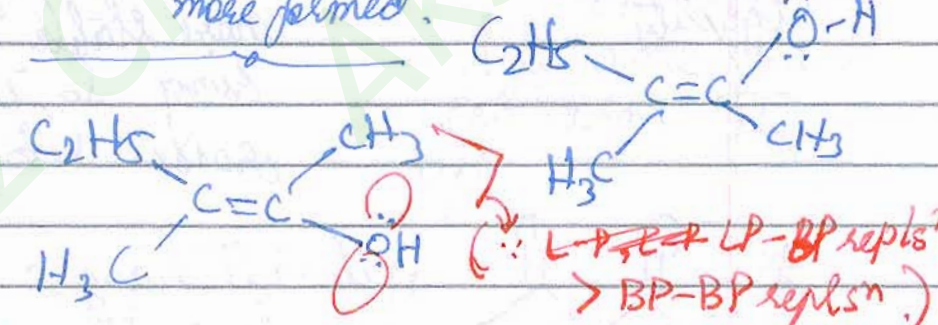
$CH_3-CH_2-\underset{CH_3}{CH}-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow$

less substituted (less stable) $\rightarrow$ $CH_3-CH_2-\underset{CH_3}{CH}-\underset{OH}{C}=CH_2$ (no stereo isomerism, single compd)

+

more substituted alkene (more stable) more formed $\rightarrow$ $CH_3-CH_2-\underset{CH_3}{C}=\underset{OH}{C}-CH_3$ (cis + trans, 2 compds.)

net, 3 compds formed.

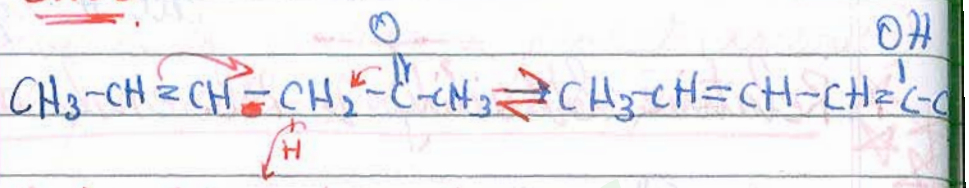


(∵ L-P-BP repln > BP-BP repln.)

* If no special factor of stability is present, more substituted enol is always more stable enol & has the largest enol content at equi. (in rel. terms & not > keto)

classmate
Date
Page

★ Conjugation increases stability of enol.

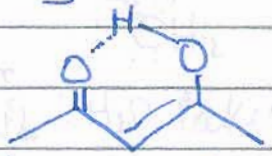


★★ Conjugated enol is always more stable than non-conjugated enol (but not keto)

Imp compd

1,3-dicarbonyl

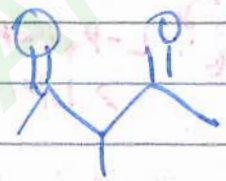
(mono enol)

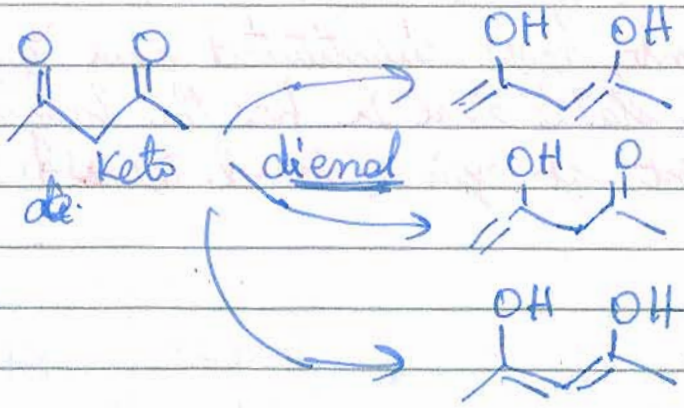


1,3 dienol > keto form

Stability.

Intramolecular H-bond also comes. So more stable 6-membered ring. So, it creates keto stability.

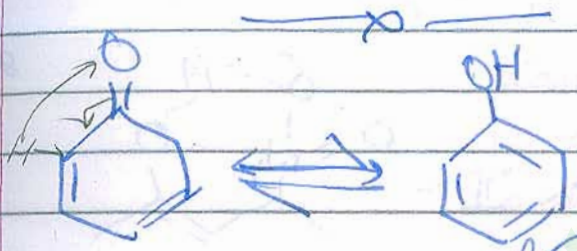
★  → it will have > enol content than ↑.



classmate
Date
Page

★ Dienol of any compd is always less stable than mono enol (∵ enol is unstable so, 2 OH group ↓ stability)

★ 2 $-C=C=C-$ such a compd is called CUMULATED.

★ 

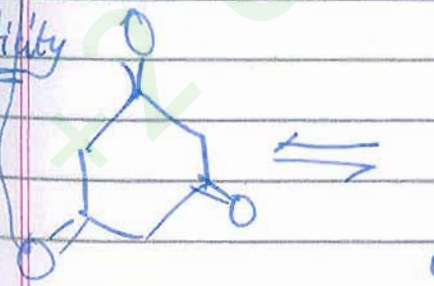
∴ enol tautomer of phenol occurs 99% than ketone (∵ 1) resonance 2) aromaticity)

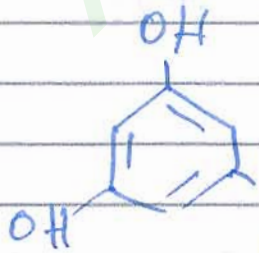
★ phenol.

I

exists more than keto form II

Effect of aromaticity





OH Exist

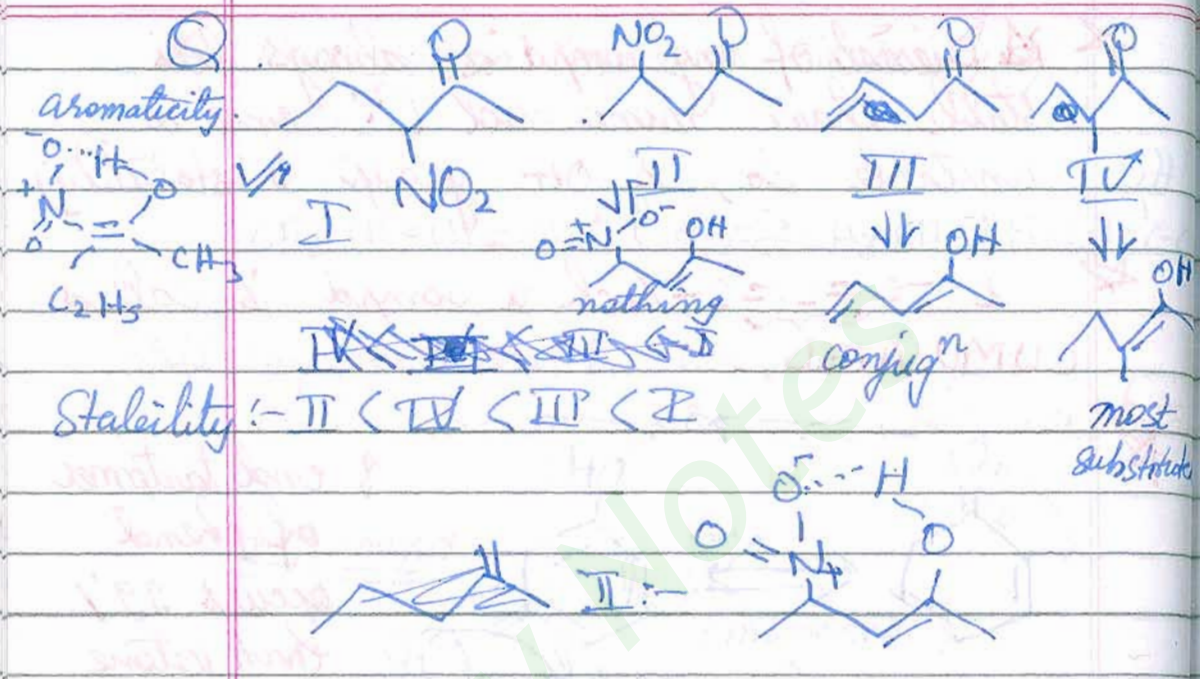
III

I > II > III : Stability.

(∵ as OH no. ↑, Stability ↓)

classmate
Date
Page

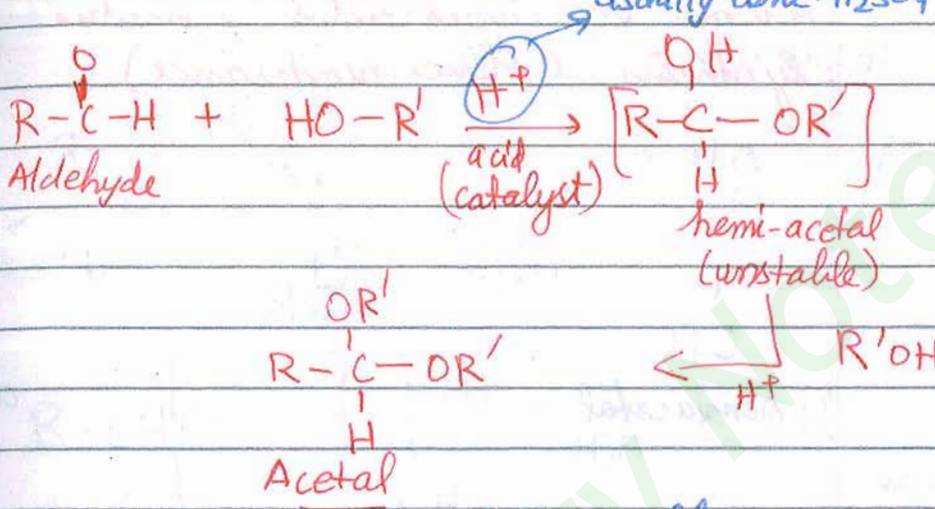
Q.



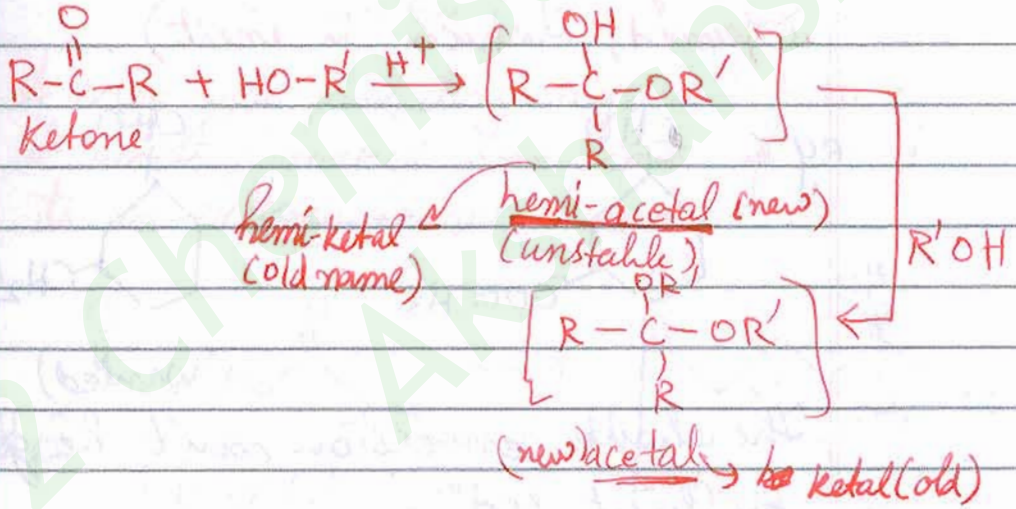
Chemistry Notes Akshansh

classmate
Date 24·9·10
Page

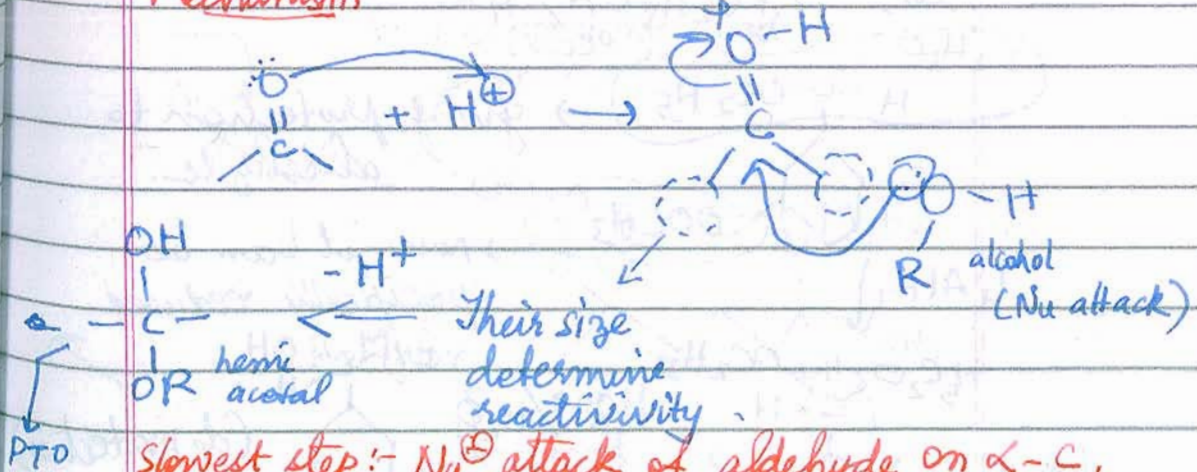
✡ Reaction with Alcohols



✡ Aldehyde or Ketone + excess alcohol $\xrightarrow[\text{catalyst}]{\text{acid}}$ hemiacetal $\longrightarrow$ acetal.



Mechanism

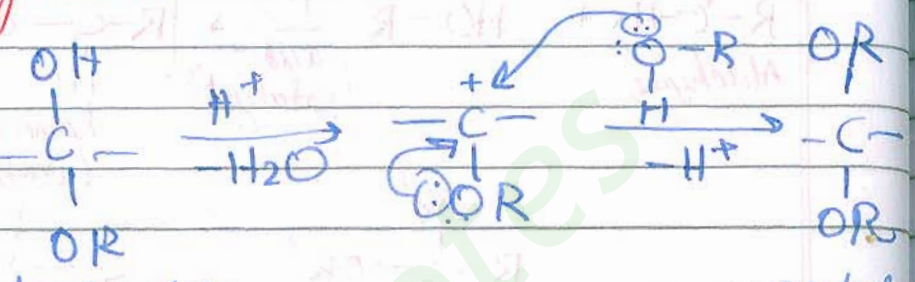


Slowest step :- $Nu^{\ominus}$ attack of aldehyde on α-C.
So, size of substituents determine reactivity.

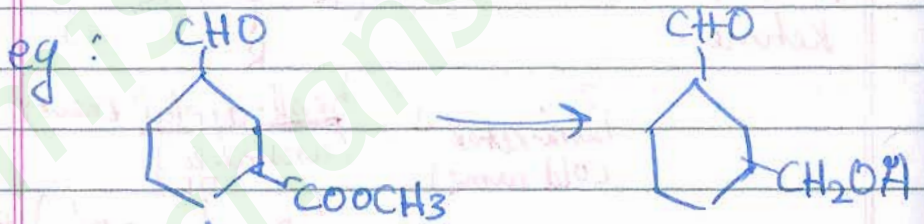
PTO

classmate
Date
Page

* Aldehydes are more reactive than ketones in hemi-acetal — acetal synthesis (steric hindrance)

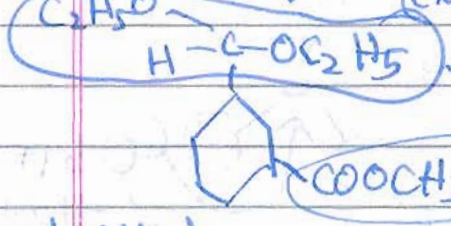


* Acetal grp is used for protection of aldehyde grp. (∵ in acetal, ether is formed, which is inert).



The above conversion can't be got by direct redⁿ.

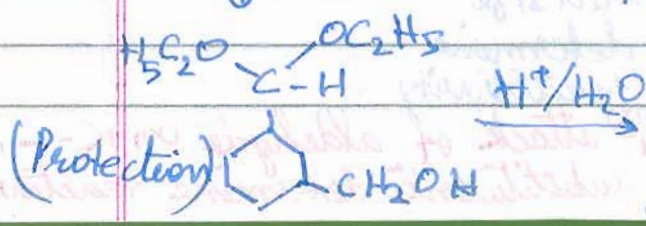
So, C_2H_5OH/H^+ (excess)



→ gives protection to aldehyde.

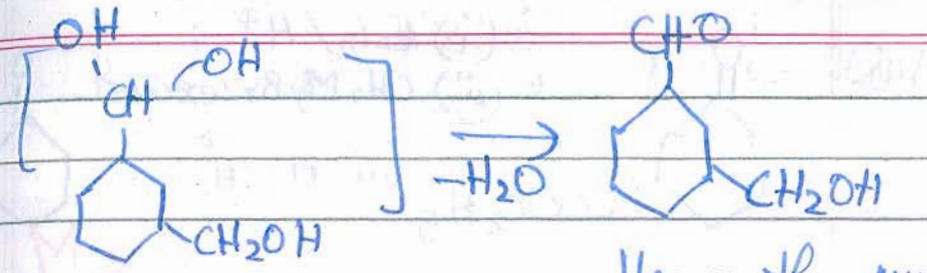
→ now it can be specifically reduced.

$LiAlH_4$

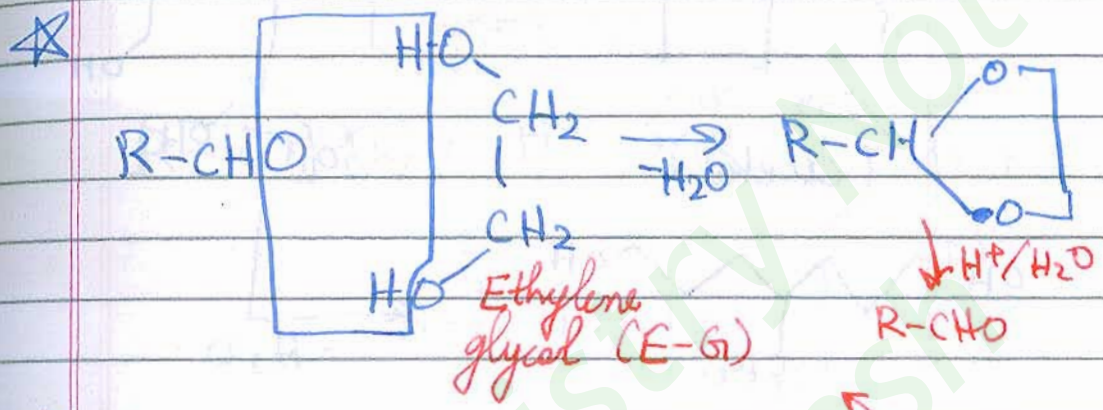


(deprotection)

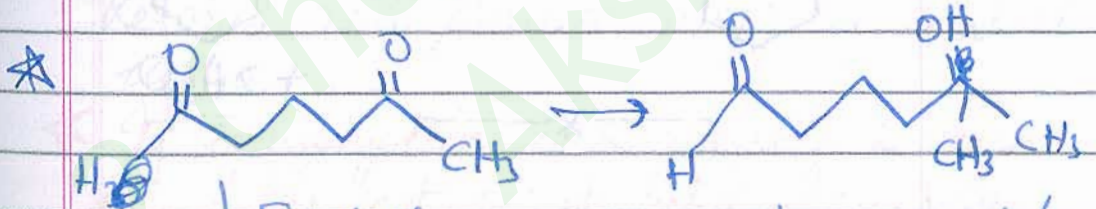
classmate
Date 1
Page



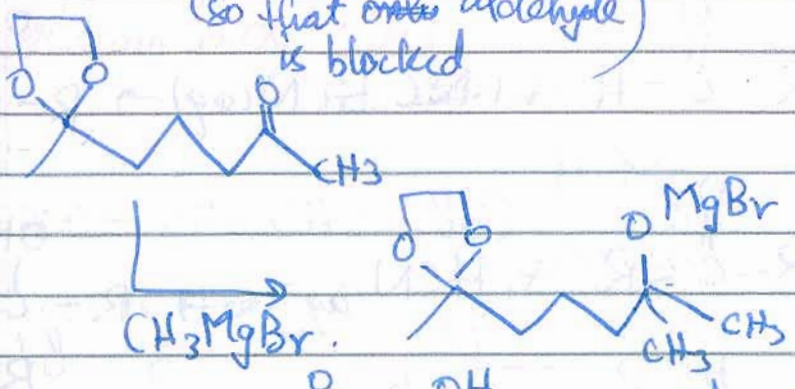
Hence, the product



A very good protecting agent :- E-G :
It reacts / makes bon fast :- ∵
its an entropy favoured rxn.



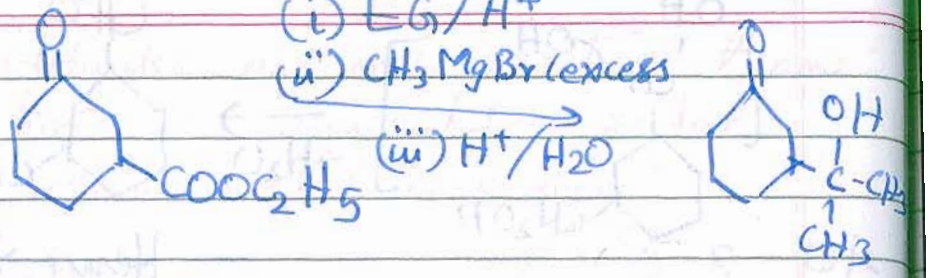
EG/H^+
(1 eq)
(So that only aldehyde is blocked)

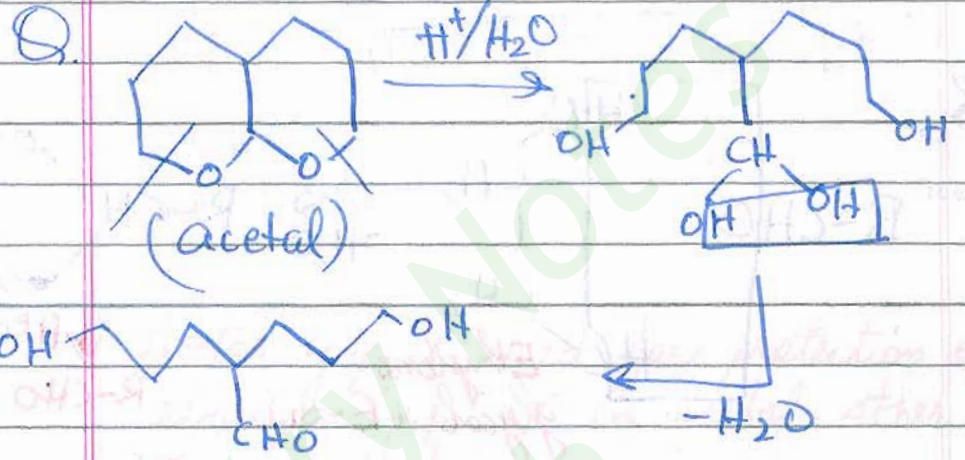


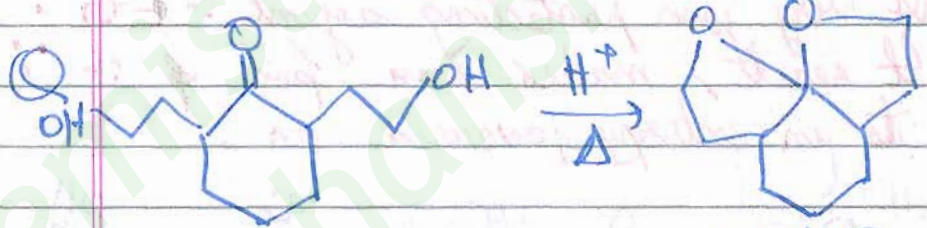
how to get here

Chemistry Notes
Akshansh

classmate
Date
Page

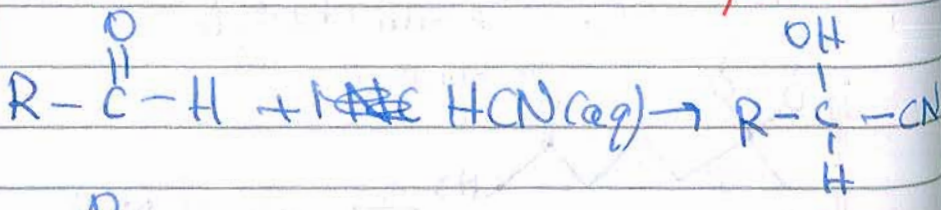
Q. 

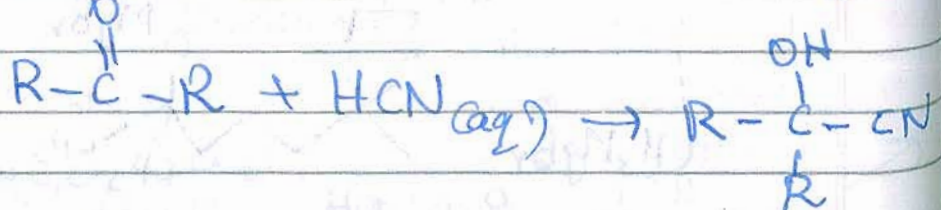
Q. 



—— x ——

★ **Reaction with HCN**: Cyanohydrin is produced

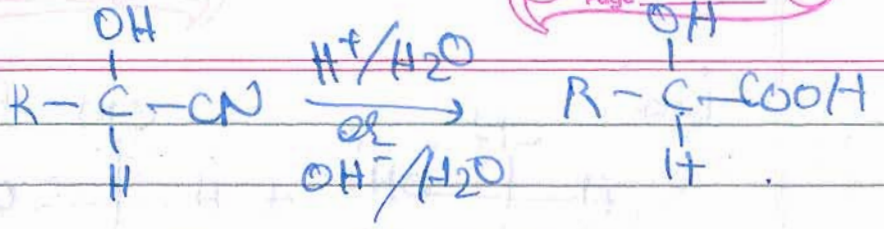




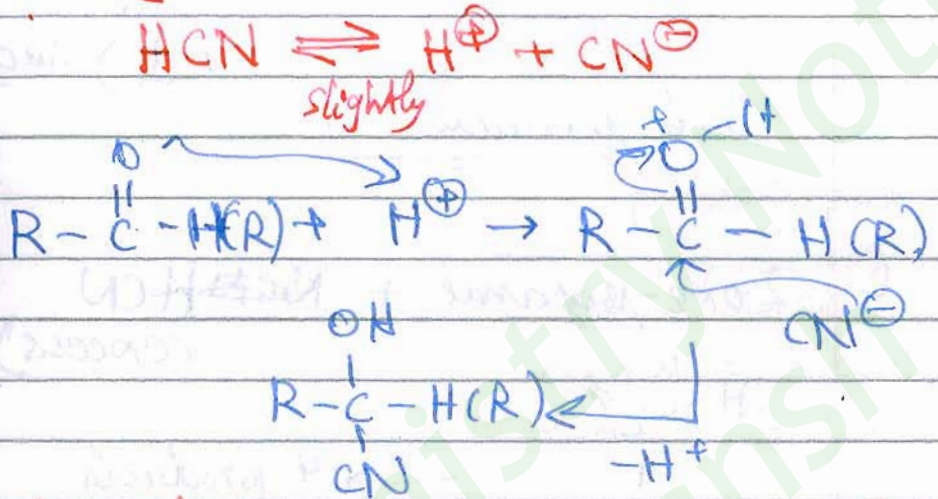
Cyanohydrin
[CN & OH on same]

Chemistry Notes Akshansh

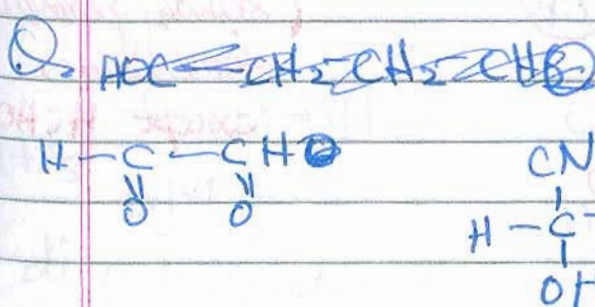
Ethane-dial : CN: glyoxal



* Mechanism

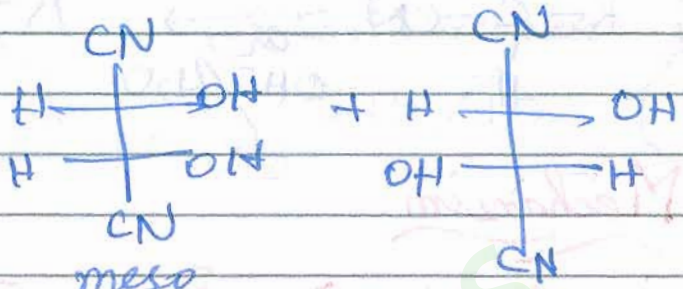


* So, Aldehyde is more reactive than Ketone (steric)
* Except HCHO, all aldehydes or ketones will produce (may) a chiral carbon.
* If cyanohydrin can generate a chiral C, the net result will always be form^{n} of racemic mixture ($\because$ $CN^{\ominus}$ has equal probability to react on sp^2 carbon from both sides).

Q. 

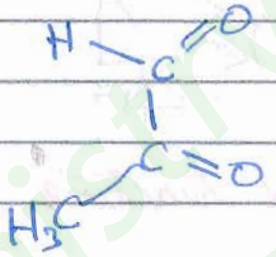
classmate
Date
Page

i.e



net products = 3

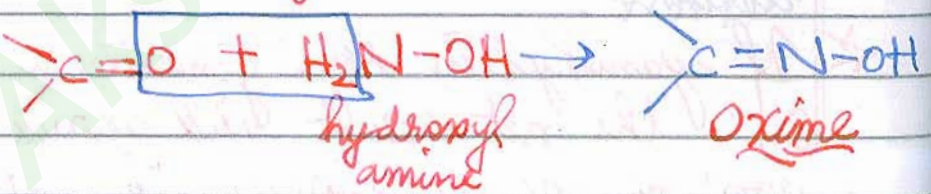
Q. 2-oxo-propanal + ~~NaCN~~ HCN (excess)

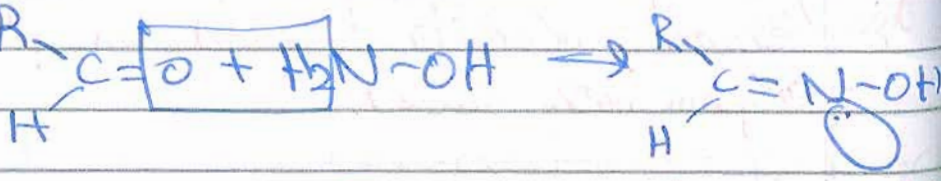


→ 4 products
(2 pair of enantiomers)

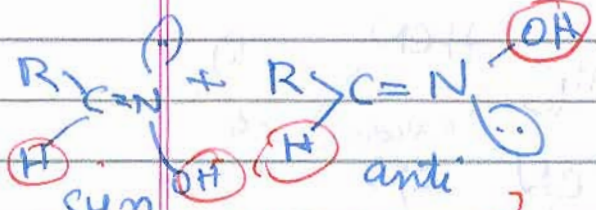
—x—

✡ With Hydroxyl Amine





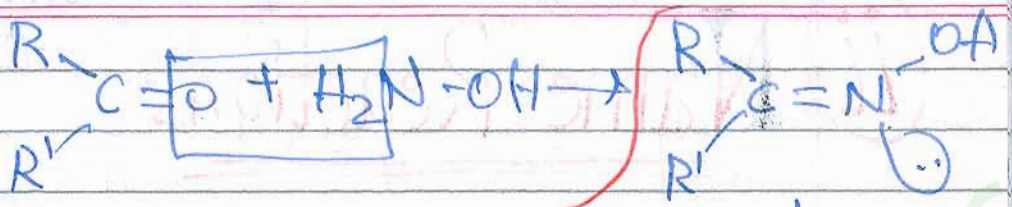
(shows geometrical isomerism → except HCHO)



aldoxime.

Chemistry Notes Akshansh

classmate
Date
Page



Ketoxime

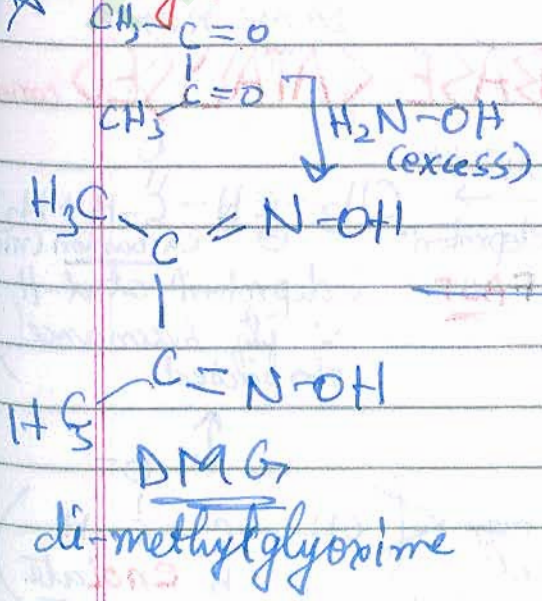
(nothing such as syn or anti)

But, we can say,
syn w.r.t R' or R
or anti w.r.t R' or R

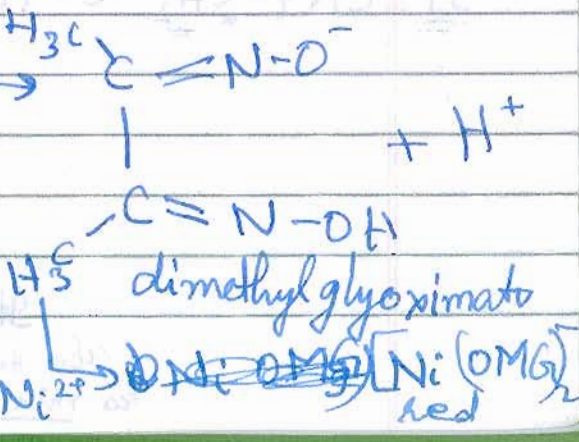
✱ Hydroxyl amine is unstable. So its prepared in situ

$$H_3\overset{\oplus}{N}OH\,Cl^{\ominus} \xrightarrow{-HCl} H_2N-OH$$

✱ Glyoxal (diethanal) $\xrightarrow[\text{amine (excess)}]{\text{hydroxyl}}$ Glyoxime (or di-methyl glyoxime) (DMG)



DMG
di-methylglyoxime



dimethylglyoximato

Ni^{2+} → $Ni(DMG)_2$ red

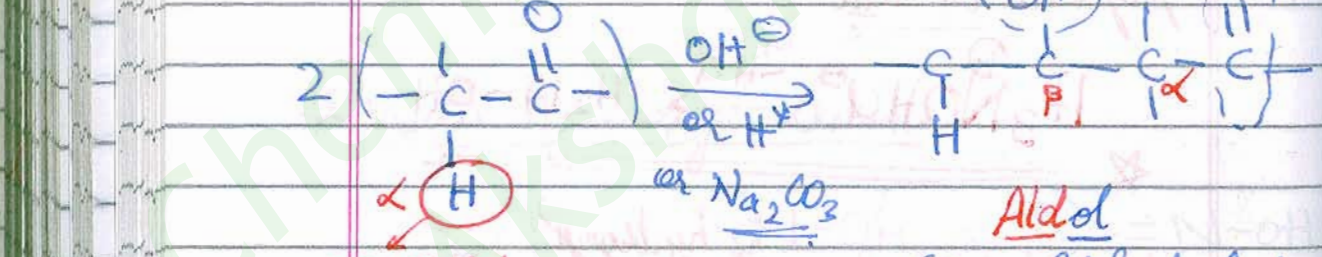
, H-C(=O)-H :- don't have α-H. So, they don't undergo aldol condensⁿ.

(ii) Name Reactions

[A] ALDOL CONDENSATION

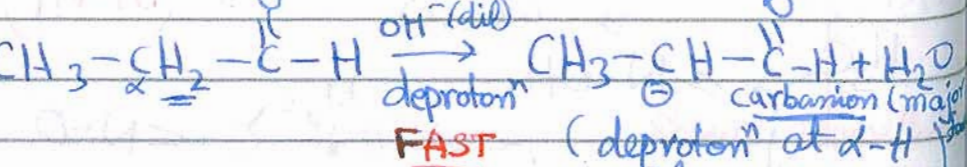
Imp * An aldehyde / ketone containing atleast one α-H when treated with dil. solⁿ of strong base or dil. H_2SO_4 (strong acid), condensation takes place to produce β-hydroxy aldehyde / ketone as the final product.

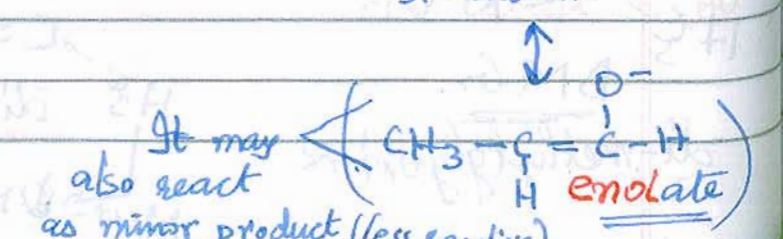
* It can occur in both presence of acid or base.

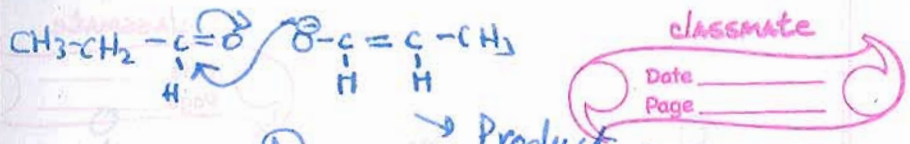


(For aldehyde/ketone) Same name

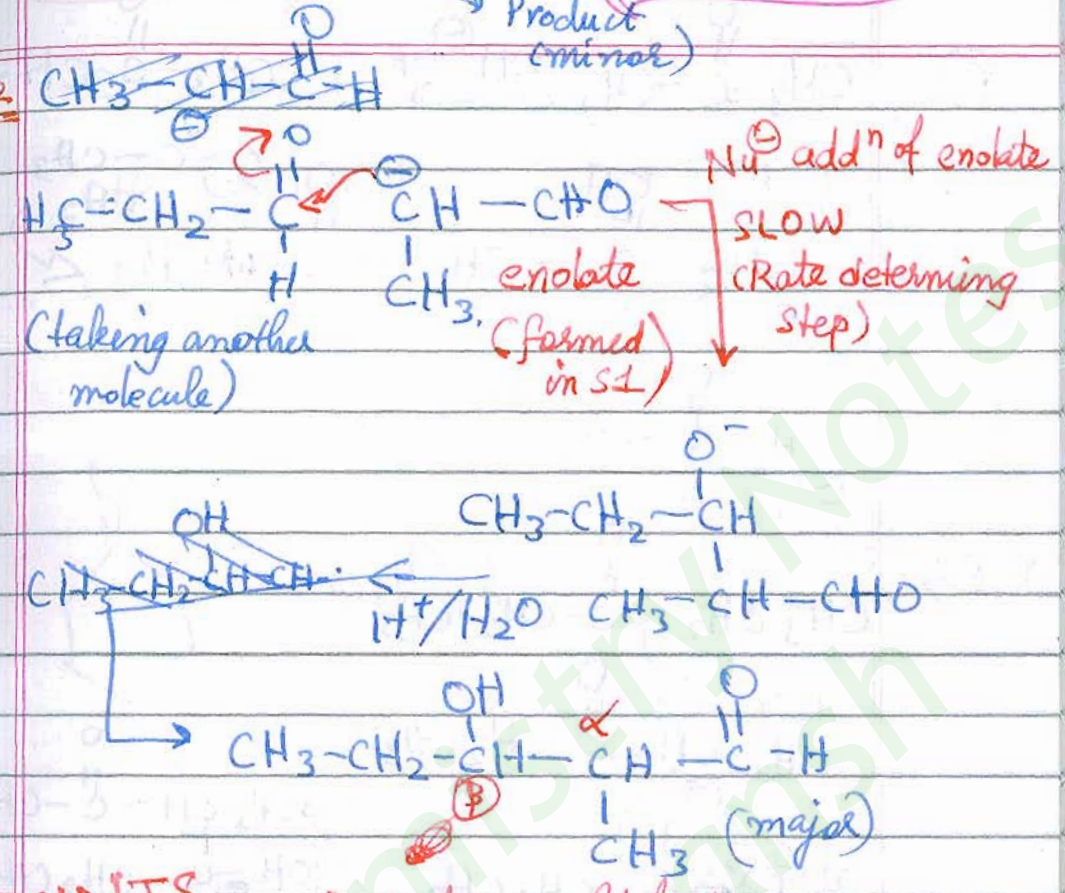
MECHANISM : BASE CATALYSED condensⁿ

S1 





S2



β-hydroxy aldehyde.

KEY POINTS

- Here also, aldehydes are more reactive than ketones.
- Its an example of nucleophilic add^n at carbonyl carbon

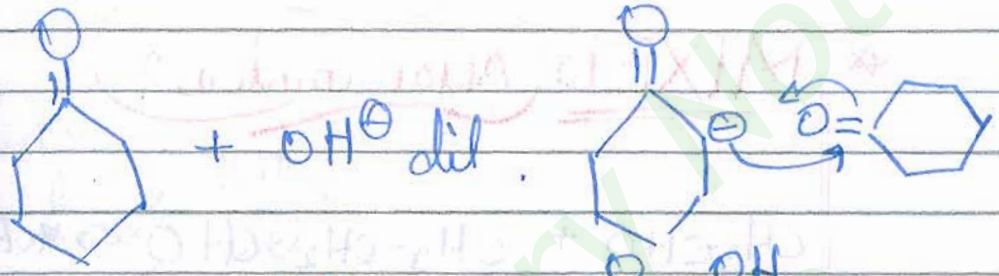
K = ? of above rxn

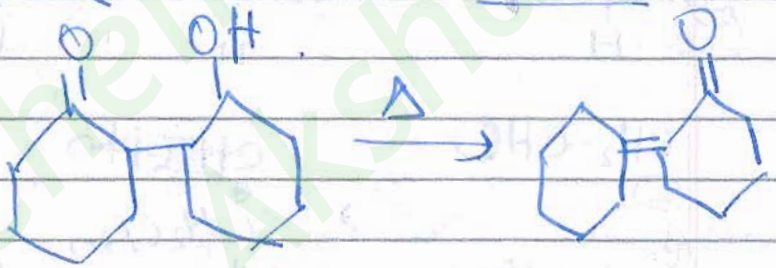
classmate
Date
Page

$CH_3-CH(OH)-CHO$ i.e $CH_3CH_2-C(OH)(H)-C(=O)-H$

$OH-C(H)-CH_2CH_3$

$CH_3CH_2-C(H)=C(CH_3)-C(=O)-H \xleftarrow{\Delta}$

Q) 



III < I < II

Q) CH_3CH_2-CHO (I) CH_3CHO (II) $CH_3-CO-CH_3$ (III)

II < I < III

classmate
Date
Page

Q) $CH_3-\overset{O}{\overset{\|}{C}}-H$ $\xrightarrow{\ominus}$ $\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H \leftrightarrow CH_2=\underset{O^-}{\underset{|}{C}}-H$ → aldol condensⁿ

$CH_2=\underset{O^-}{\underset{|}{C}}-H \rightarrow CH_3-\underset{H}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-O-CH$

✱ MIXED Aldol Condensⁿ

$CH_3CHO + CH_3-CH_2-CHO \rightarrow$ Pos^nal isomer & chain isomer

CH_2-CHO $\xrightarrow{\ominus}$ $\overset{\ominus}{C}H_2-CHO \leftrightarrow O=C-CH_3$ (H)

$H-CH_2-CHO$ / $OH-C-CH_3$ (H) (1) Self (major)

CH_2-CHO $\xrightarrow{\ominus}$ $\overset{\ominus}{C}H_2-CHO \leftrightarrow O=C-C_2H_5$ (H)

~~CH_2CHO~~ / CH_2CHO / $OH-C-C_2H_5$ (H) (2) Cross

CH_3-CH_2-CHO $\xrightarrow{\ominus}$ $CH_3-\overset{\ominus}{C}H-CHO \leftrightarrow O=CH-CH_2$ (CH_3)

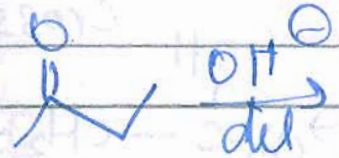
$CH_3-CH-CHO$ / $OH-C-CH_2$ (CH_3) (3) Self

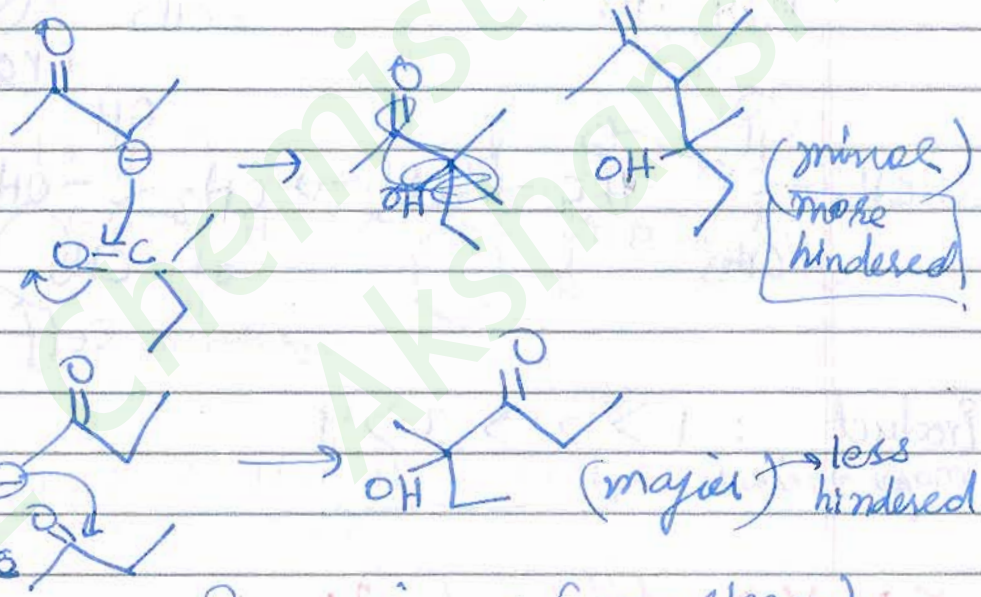
$CH_3-CH-CHO$ $\xrightarrow{\ominus}$ $CH_3-\overset{\ominus}{C}H-CHO \leftrightarrow O=C-CH_3$

$CH_3-CH-CHO$ / $OH-C-CH_3$ (4) Cross

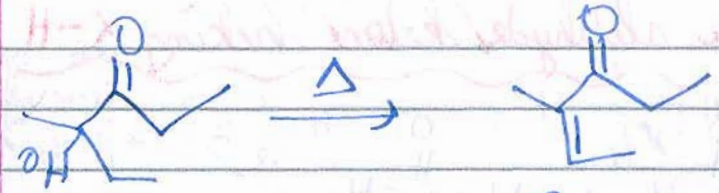
Here
major to minor :- 1 > 4 > 2 > 3

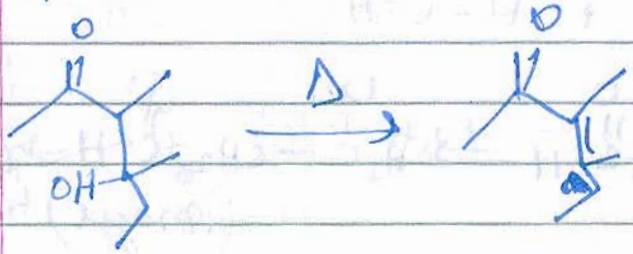
* See steric hinderance at site of attack, not at the size of $Nu^{\ominus}$.

Q. 

(1) 

2 * isomers (non stereo)





Chemistry Notes Akshansh

classmate
Date
Page

Q $CH_3-CHO + CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{HO^-(aq.)}$

$CH_3-\overset{O}{\overset{\|}{C}}-H \;\; CH_2-\overset{O}{\overset{\|}{C}}-H \rightarrow CH_3-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-H$ (1) Self

$CH_3-\overset{O}{\overset{\|}{C}}-H \;\; H_2C-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\underset{H}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (2) Cross

$\overset{CH_3}{\underset{CH_3}{C}}=O \;\; CH_2-\overset{O}{\overset{\|}{C}}-H \rightarrow CH_3-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-H$ (3) Cross

$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \;\; H_2C-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (4) Self

Product : 1 > 2 > 3 > 4
major → minor

✡✡ Mixed Aldol Condens^n :-

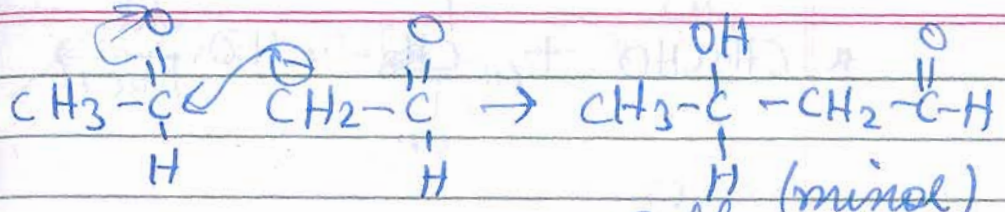
One aldehyde/ketone lacking α-H

$CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H$

$H-\overset{O}{\overset{\|}{C}}-H \;\; CH_2-\overset{O}{\overset{\|}{C}}-H \rightarrow H_2C-CH_2-\overset{O}{\overset{\|}{C}}-H$ Cross (major)

Chemistry Notes by Akshansh

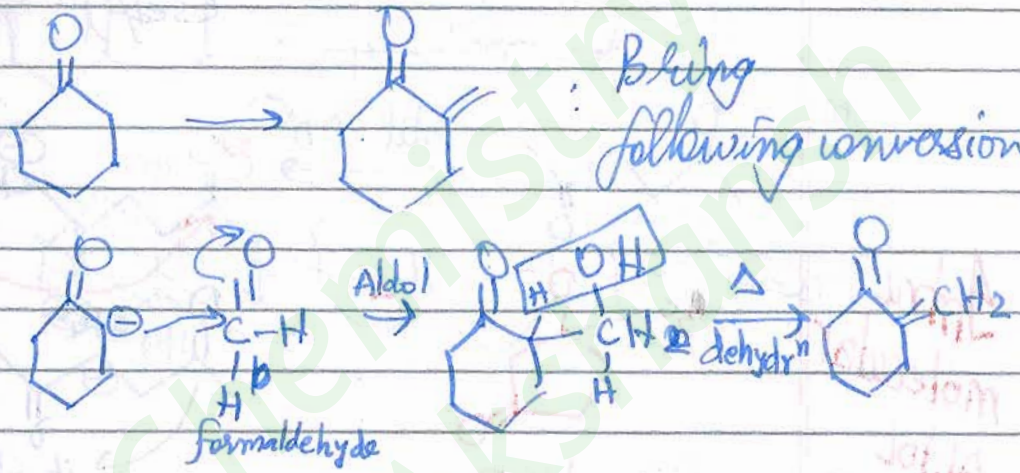
classmate
Date
Page



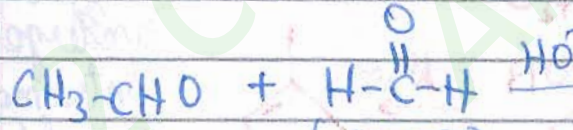
Self

* In above case,
If formaldehyde is one of aldehyde, then, cross condens^n gives major product.

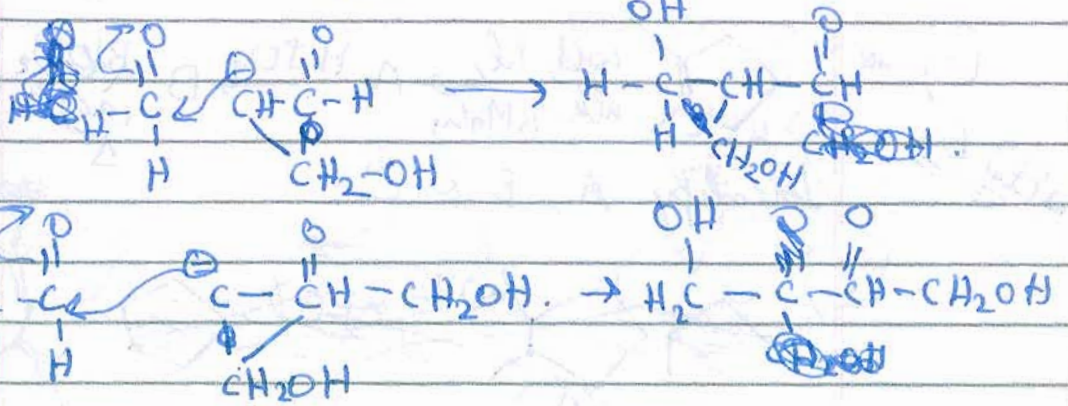
Q. : Bring following conversion



Q



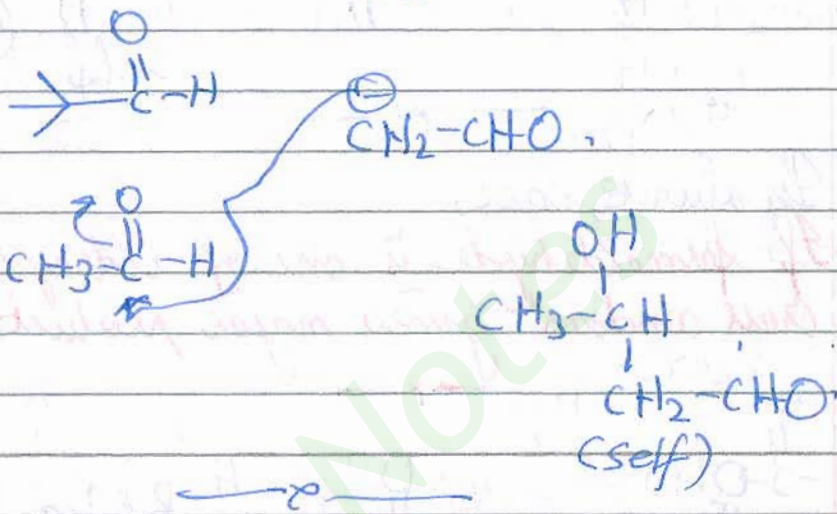
If excess.



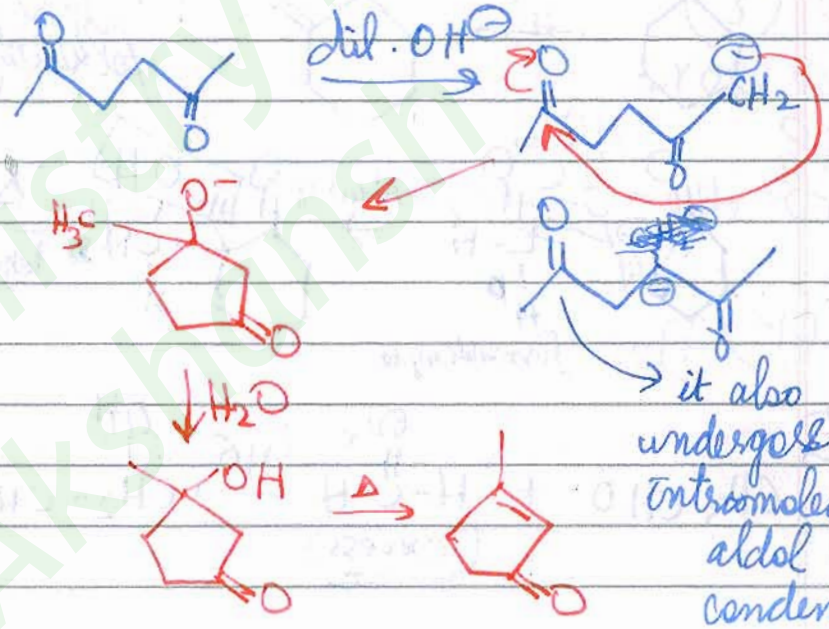
+2 Chemistry Notes AKSunish

classmate
Date 29.9.10
Page

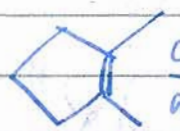
* $CH_3CHO + (CH_3)_3C-CHO \xrightarrow[NaOH]{dil.}$



* Intra molecular Aldol condens'n



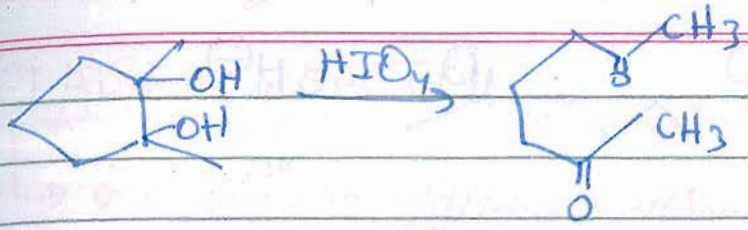
Q6

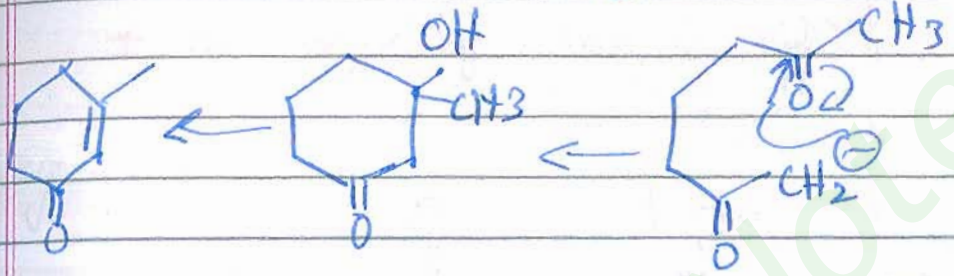
* 

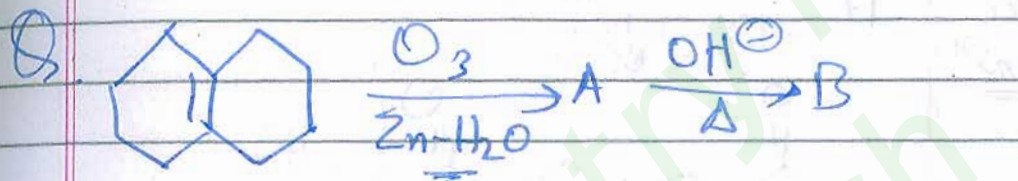
Identify A, B & C.

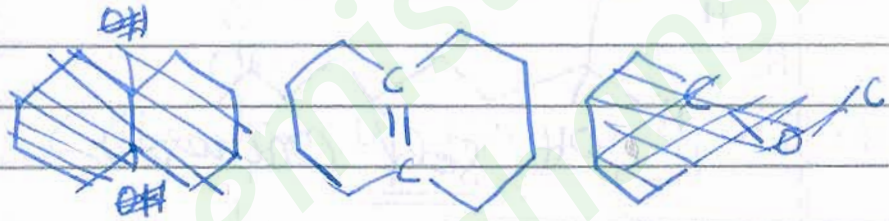
Chemistry Notes Akshansh

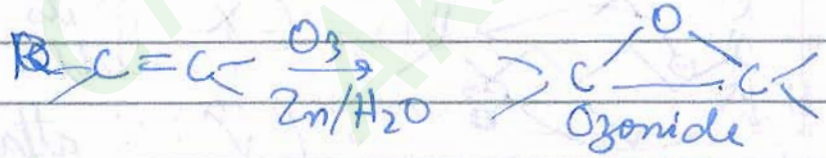
classmate
Date
Page

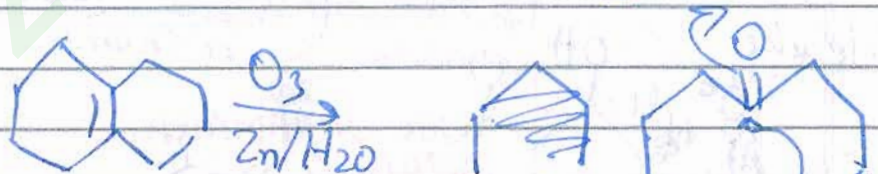


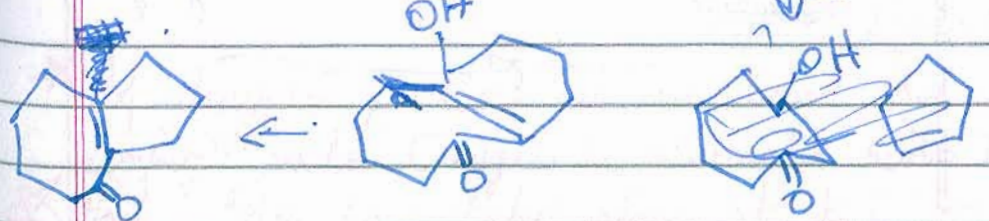










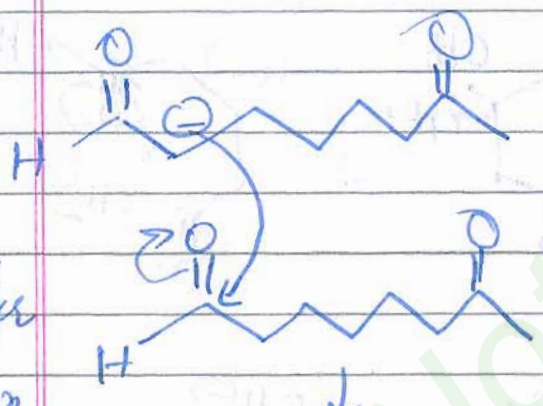


+2 Chemistry Notes
Akshansh

classmate
Date
Page

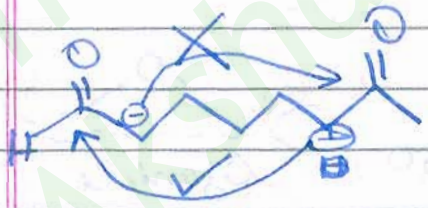
Q.

Inter molecular Aldol Condensⁿ



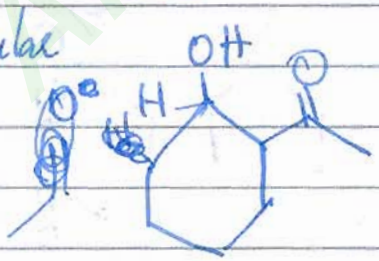
self (minor)

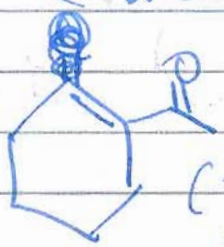
Cross



(X : ∵ its Nu⊖ addn
(✓ : ∵ attack is easier

Intramolecular Aldol Condensⁿ





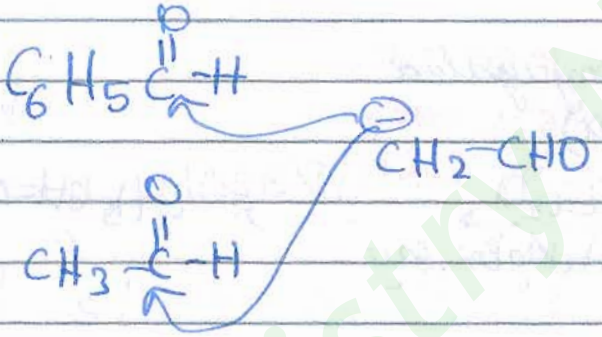
(= — =) conjugⁿ

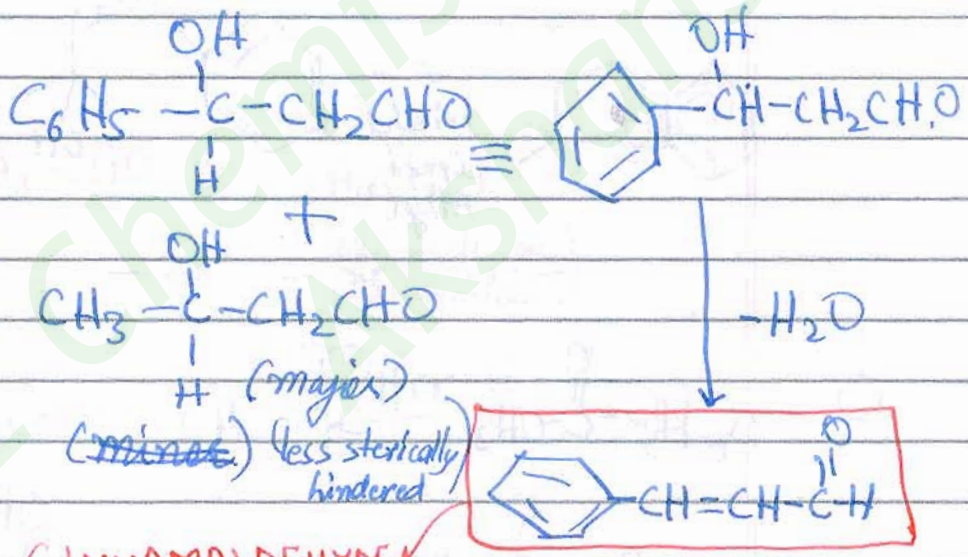
Chemistry Notes Akshansh

✡ CLAISEN REACTION (part of Aldol condensⁿ)

↳ one aromatic aldehyde (containing no α-H) + one aliphatic aldehyde (containing α-H)

eg: $C_6H_5CHO + CH_3CHO$





(minor) less sterically hindered

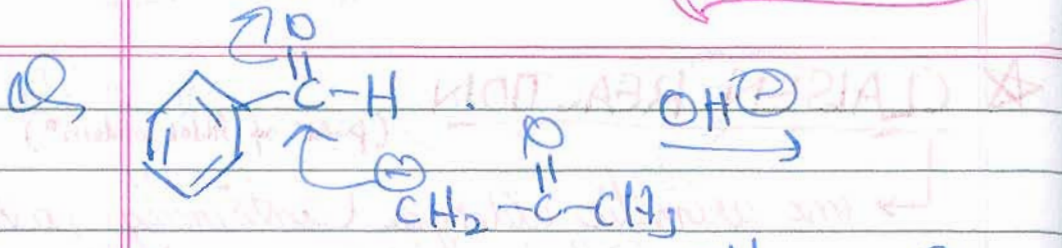
CINNAMALDEHYDE ~~CINNAMIC~~

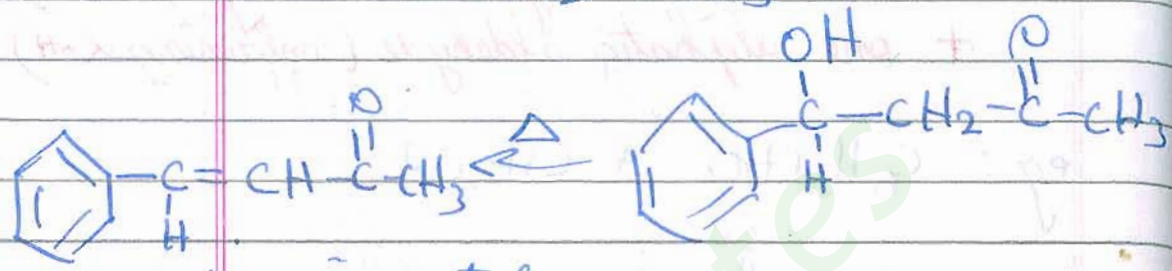
(addnal conjugⁿ ∞ of π bond with ring) → Imp product (opted)

~~major~~

✡ If dehydrⁿ produces double bond having conjugⁿ with Oxygen & aromatic ring both, then, this rxn takes place at RT (no heat reqd). ~~Its major product~~

classmate
Date
Page

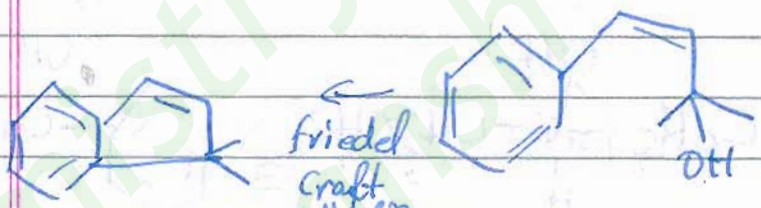




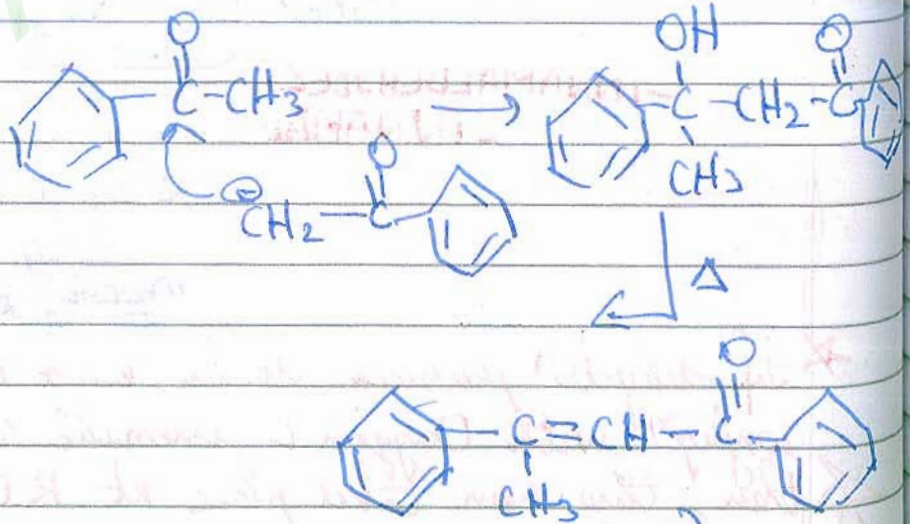
again conjugated
(major)

$\xrightarrow[CH_3MgBr,\ say]{Et_2O}$ $\xrightarrow{H^{\oplus}/H_2O}$ $C_6H_5CH=CH-C(CH_3)_2(OH)$

i.e



Q. $C_6H_5-C(=O)-CH_3 \xrightarrow{OH^{\ominus}}$



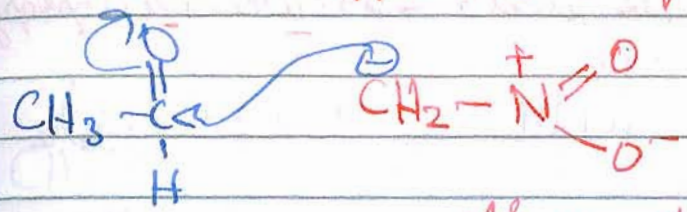
(E-Z)

Chemistry Notes
Akshansh

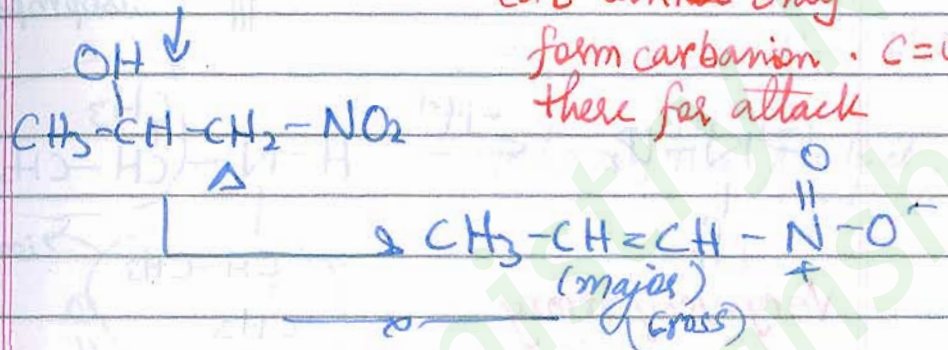
★MODIFIED ALDOL CONDENSⁿ

★ $CH_3-CHO + CH_3-NO_2 \xrightarrow{NaOH(aq)}$?

(CH_3NO_2 has acidic H, forms carbanion effectively (conjugation more effective than CH_3CHO))

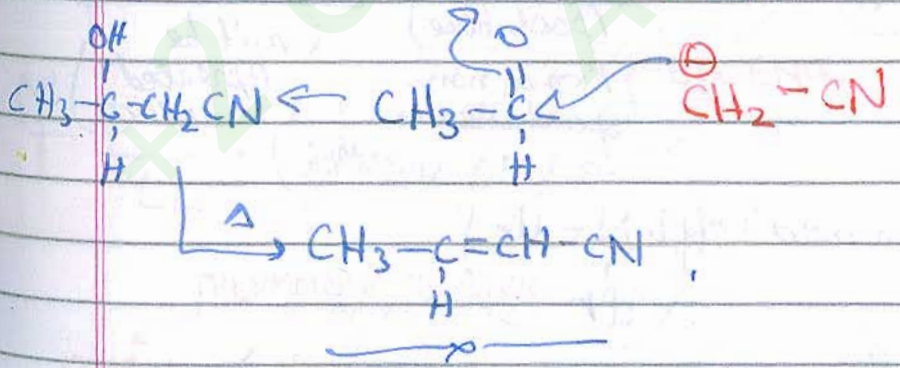


(CH_3CHO cannot only form carbanion. C=O not there for attack)



★ $CH_3-CHO + CH_3-CN \xrightarrow{OH^-}$

(CH_3CN α-H is also acidic)



classmate
Date
Page

✱ TARGETED ALDOL CONDENSⁿ RXN

↳ when a single selective product (reqd.) is formed

↳ Base used : LDA : Lithium diisopropylamide

i.e $LiNH_2 \longrightarrow LiN(iPr)_2$

iPr ||| Isopropyl

$\ominus N-iPr \xleftarrow{-H^+} H-N-(CH(CH_3)-CH_3)$

iPr

Very-very strong base

(Stronger than Amine)

isopropyl: $CH(CH_3)-CH_3$, CH_3

$CH_3-\overset{O}{\overset{\|}{C}}-H + OH^{\ominus} \rightleftharpoons \overset{\ominus}{C}H_2-CHO + H_2O$

(poor base) (can't be separated as such)

(Rxn is non spontaneous. So, rxn is reversible.)

On addⁿ of $LiN-iPr$ (iPr)

$(CH_3-\overset{O}{\overset{\|}{C}}-H + LiN(iPr)_2 \rightarrow \overset{\ominus}{C}H_2-CHO)$

(Strong base)

$Li^+ \overset{\ominus}{C}H_2-CHO + (iPr)_2NH$

Lithium salt (Can be separated)

Chemistry Notes Akshansh

Q. $CH_3CHO \rightarrow CH_3CH_2CHO \rightarrow CH_3CH_2CH=CH-CHO$

how?

$CH_3CHO + LDA \rightarrow [CH_2CHO]^{\ominus} Li^{\oplus}$

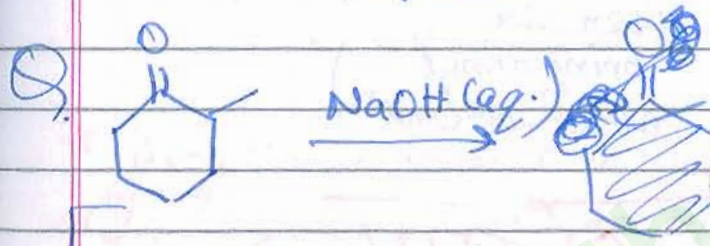
LITHIUM ENOLATE

$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-H \quad {}^{\ominus}CH_2-CHO \xrightarrow{\Delta}$

$CH_3CH_2-\underset{\underset{H}{|}}{C}=CH-CHO$

(hence, the product reqd singly)

Q.

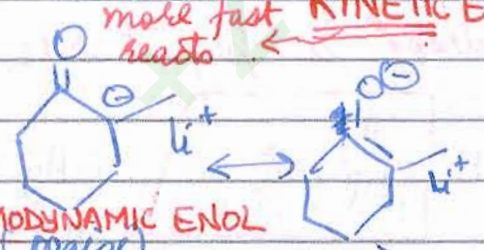


M1

M2

LDA

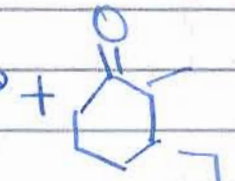
more fast reacts KINETIC ENOL



THERMODYNAMIC ENOL (major)

more stable

∵ carbanion on more substituted. (Thermodynamically more stable)



Single reqd Product.

Exceptions

☆ $CH_3-CHO + CH_3-\underset{H}{\overset{|}{N}}-H \longrightarrow CH_3-\underset{OH}{\overset{|}{C}}H-CH_2-CHO$

(aq.)

(2° amine → very high basic)

can bring about aldol condensⁿ with small carbonyl grps

* In above rxn, enamine can also be produced. So, work acc. to options given.

☆ $CH_3CHO + Na_2CO_3(aq) \rightarrow CH_3-\underset{OH}{\overset{|}{C}}H-CH_2-CHO$

basic (can also bring about aldol condensⁿ)

§ ACID CATALYSED Aldol Condensⁿ Rxn

✓ α-H req'd

✓ β-hydroxy is formed here also

eg S1 FAST step.

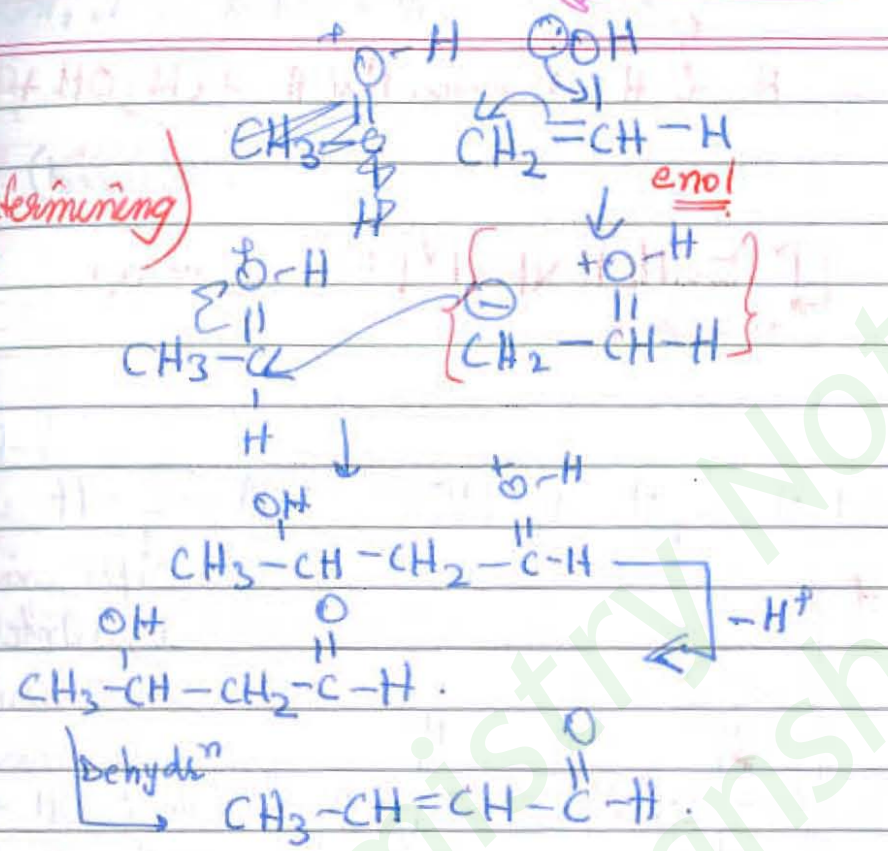
$CH_3-\overset{O}{\overset{\|}{C}}-H \xrightarrow[(dil.\ H_2SO_4)]{H^+}$ FAST (Protonⁿ–Deprotonⁿ)

$CH_2=\overset{+O-H}{\overset{|}{\underset{\|}{C}}}-H$ ⟷ $CH_2-\overset{O-H}{\overset{|}{\underset{\|}{C}}}-H$

$CH_2=CH-H$

$\ddot{O}H$

enol



★ Dehydration product is must in acid catalysed.
★ In slow step, ₂ₚₙ takes by ~~Nu~~ neutral enol.
★ Driving force is protonated aldehyde/ketone.
★ Dehydⁿ takes place by acid (here).

B CANNIZARO'S REACTION

Condⁿˢ:-
- Only for Aldehydes
- given by aldehydes lacking α-H.
- conc. solⁿ of strong base reqd.

On aldehyde lacking α-H, when treated with conc. solⁿ of strong base, mutual oxidⁿ redⁿ takes place as follows:—

QTD

eg $C_6H_5-\overset{O}{\overset{\|}{C}}-H$ + conc. NaOH → ~~$C_6H_5CH_2OH + C_6H_5COONa$~~

→ $C_6H_5CH_2OH + C_6H_5COONa$

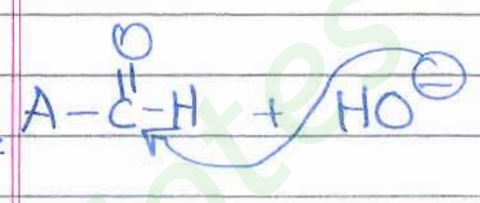
eg $H-\overset{O}{\overset{\|}{C}}-H$ + conc. NaOH → $\underset{-2}{CH_3OH} + H-\underset{+2}{\overset{O}{\overset{\|}{C}}}-ONa$

(reduced) (oxidised)

MECHANISM : cannizaro rxn

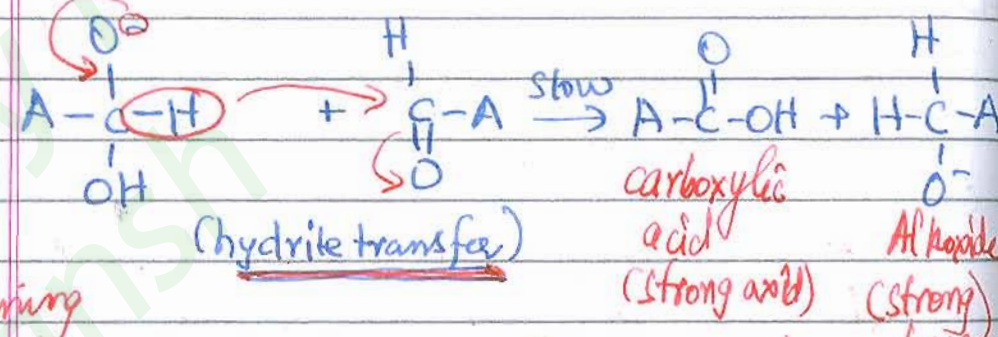
2 step rxn

S1 (fast)



(I) → Intermediate

S2 (slow rate determining step.)



(hydride transfer)

carboxylic acid (strong acid)

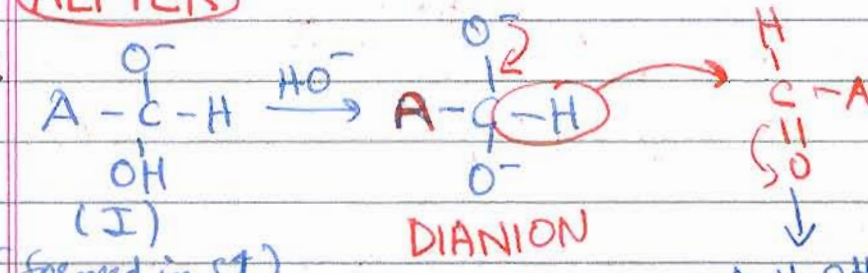
Alkoxide (strong base)

Neutralisⁿ

$ACH_2OH + A-\overset{O}{\overset{\|}{C}}-O^-$ (Salt) is given by it.

ALITER

S1



(I) (formed in S1 above.)

DIANION (I undergoes further neutralisⁿ (better hydride donor)

$ACH_2OH + A-\overset{O}{\overset{\|}{C}}-O^-$

* The carbonyl carbon on which conc. base attacks, after rxn, it forms acid.

* B/w like molecules, Cannizaro rxn act/is a disproportionation reaction

CROSS-CANNIZARO

$$H-\overset{O}{\overset{\|}{C}}-H + C_6H_5-CHO \xrightarrow[(conc)]{HO^-} C_6H_5-CH_2OH + HCOOH$$

* Since Formaldehyde is very reactive, it makes rate determining step (S1) instead of S2. So, 2
* Formaldehyde is always oxidised in cross condensⁿ rxn. So, the other one is reduced.

Way 1 ✓

$$H-\overset{O}{\overset{\|}{C}}-H + HO^{\ominus} \rightarrow H-\underset{OH}{\overset{O^-}{C}}-H$$

All $Nu^{\ominus}$ used

: Rate determining step.

$$H-\underset{OH}{\overset{O}{C}}-H + \underset{O}{\overset{H}{C}}-\phi \rightarrow H-\overset{O}{\overset{\|}{C}}-O^- + \phi-CH_2OH$$

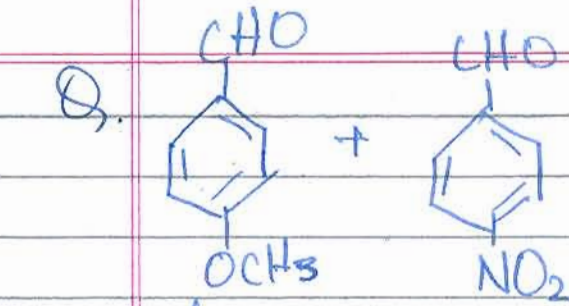
Here

Way 2 ✗

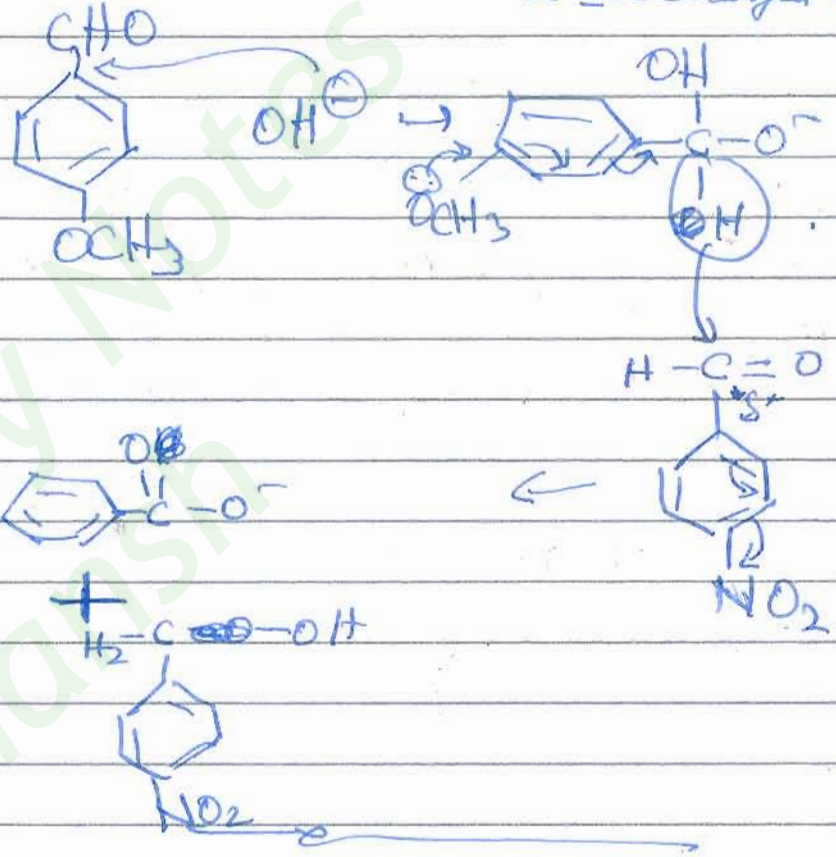
$$\phi-\overset{O}{\overset{\|}{C}}-H + HO^{\ominus} \rightarrow \phi-\underset{OH}{\overset{O^-}{C}}-H$$

$$\phi-\underset{OH}{\overset{O^-}{C}}-H + \underset{H}{\overset{O}{C}}=O \rightarrow \phi-\overset{O}{\overset{\|}{C}}-O^- + CH_3OH$$

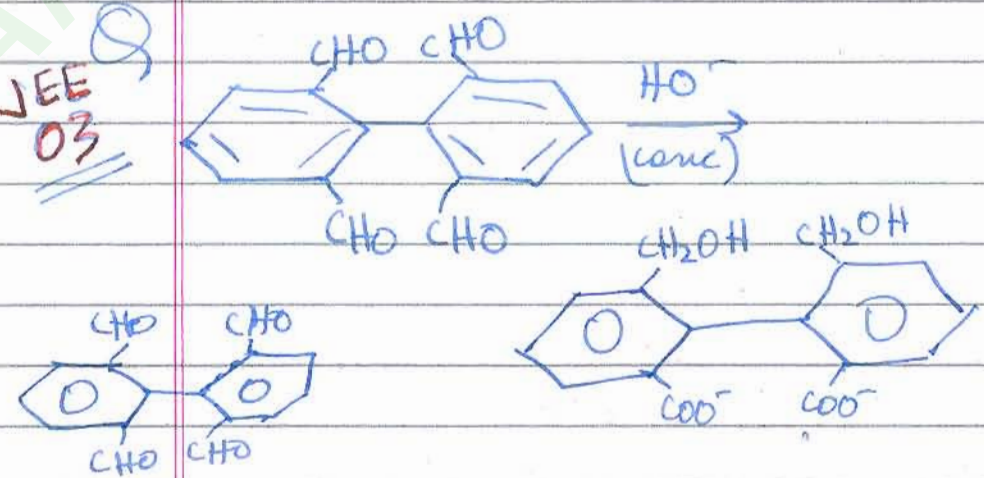
* In all other cross-Cannizaro rxn, imp. step will be S2. Condⁿ:- there should be better hydride donor & better hydride acceptor. See, which is what & make product.

Q. 

donor, acceptor (See resonance & ±ve charged CHO)

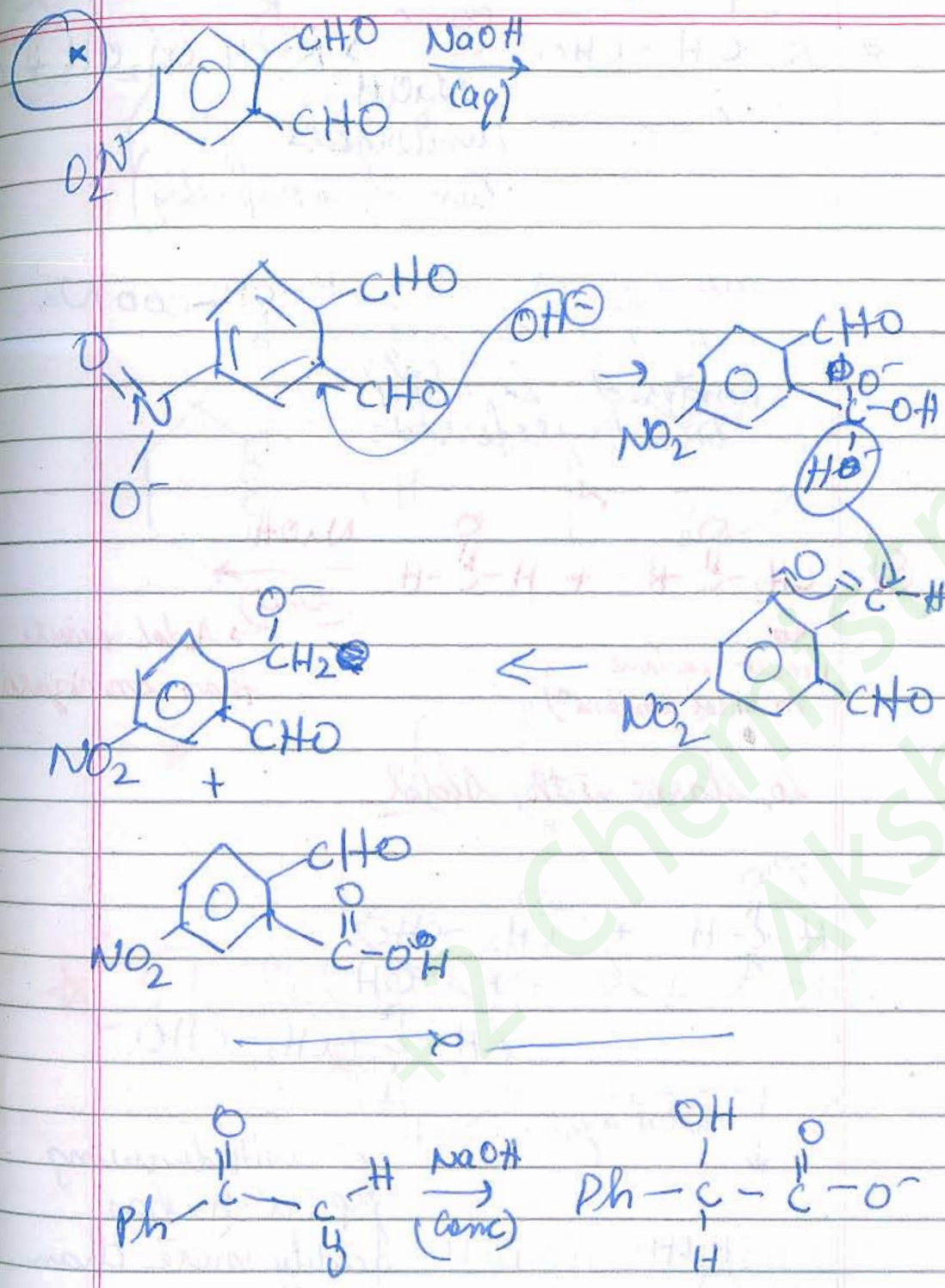


Q. JEE 03



due to being in ⊥ plane, H-transfer from one ring to other (b/w planes) is not possible.

classmate
Date
Page



classmate
Date
Page

* $R-\underset{\underset{R}{|}}{CH}-CHO \xrightarrow[NaOH]{conc.} R-\underset{\underset{R}{|}}{CH}-CH_2OH +$ undergoes Cannizaro preferably

although it has α-H, but sterically hindered. So, aldol is not preferred.

$R-\underset{\underset{R}{|}}{CH}-COONa$.

Q. $CH_3-\overset{O}{\overset{\|}{C}}-H + H-\overset{O}{\overset{\|}{C}}-H \xrightarrow[(conc.)]{NaOH}$ Aldol easier than Cannizaro.

~~No~~ (most reactive in aldol condensn)

So, starts with Aldol

$H-\overset{\ominus O}{\overset{\|}{C}}-H + \overset{\ominus}{C}H_2-CHO \rightarrow H-\underset{\underset{H}{|}}{\overset{OH}{\overset{|}{C}}}-CH_2-CHO$.

Aldol again

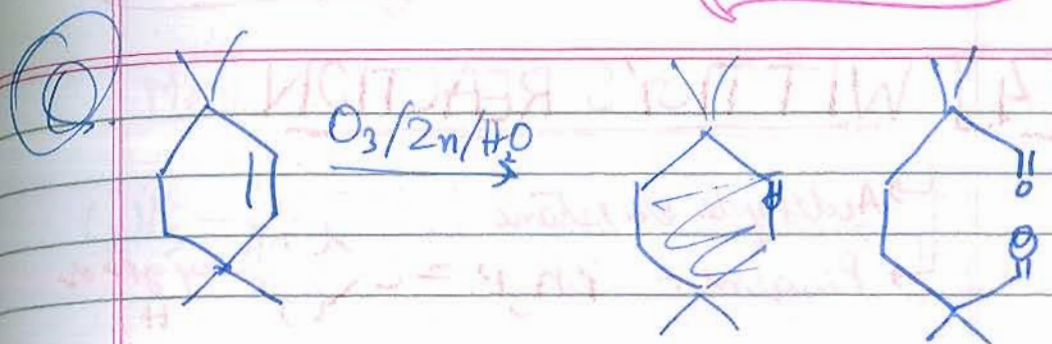
e^- withdrawing grp. α-H has acidity more than CH_3CHO.

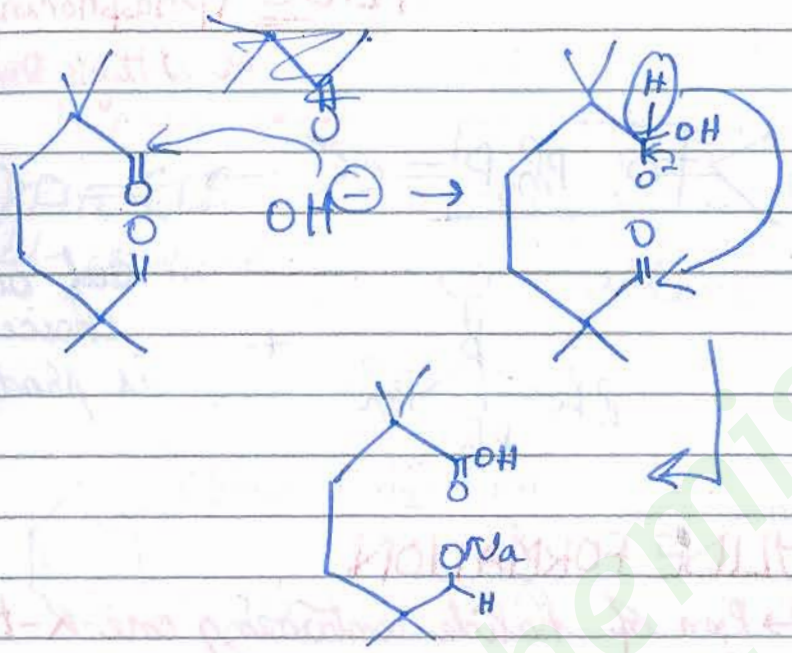
$HOCH_2-\underset{\underset{CH_2OH}{|}}{CH}-CHO$

Again Aldol

$HOCH_2-\underset{\underset{CH_2OH}{|}}{\overset{CH_2OH}{\overset{|}{C}}}-CHO$ — now Cannizaro

$HCOONa + HOH_2C-\underset{\underset{CH_2OH}{|}}{\overset{CH_2OH}{\overset{|}{C}}}-CH_2OH$





[3] TISCHENKO REACTION

$CH_3-CHO \xrightarrow[H_2O]{Al(C_2H_5O)_3}$ Forced to undergo Cannizaro rxn.

$[\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{CH_3CH_2OH}]$

↓ Esterification

$CH_3COO-C_2H_5 + H_2O$

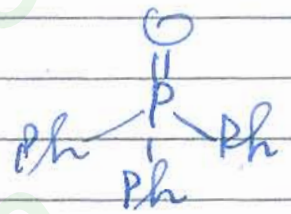
[4] WITTIG'S REACTION

↳ Aldehyde or ketone

↳ Reagent :- $Ph_3P=C\begin{matrix}(\ )\\(\ )\end{matrix}$ any grp or H.

YLIDE (phosphorane)

or Wittig's Reagent



+ ~~Out~~ our choice alkene is produced

* YLIDE FORMATION

↳ Rxn of halide containing one α-H.

i.e

S_N2

eg : $Ph-\underset{Cl}{CH}-CH_3$ $\xrightarrow{Ph_3P}$ $Ph-\underset{H}{C}-CH_3$

TRIPHENYL PHOSPHENE

Ph_3P → $R\,Li$ (strong base) (alkyl lithium)

C_4H_9Li or BuLi → common.

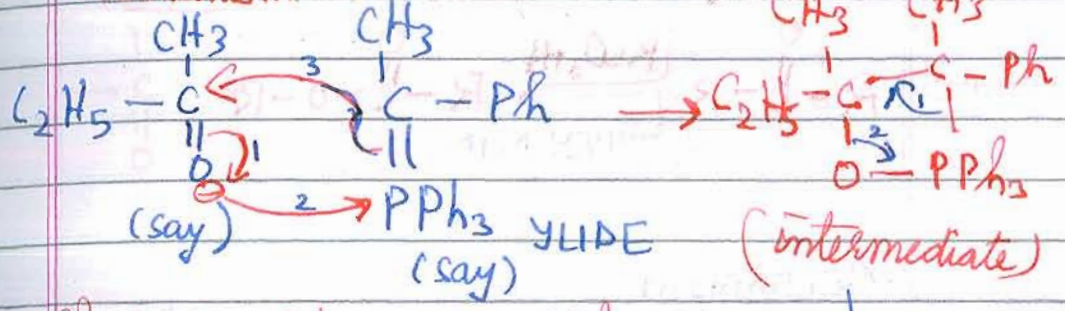
H_3C, Ph — $C=PPh_3$ YLIDE $\equiv$ $Ph-\underset{R}{\overset{\overset{PPh_3}{\|}}{C}}-CH_3$

* SHORT CUT TO MAKE YLIDE

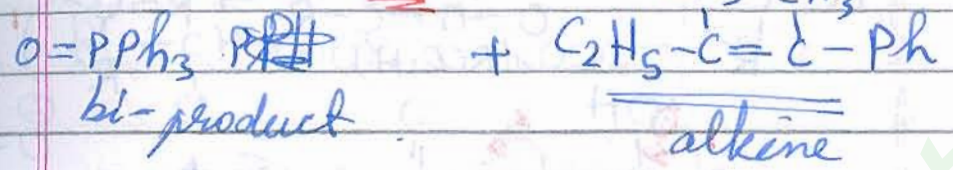
i.e Remove H-X from α-C and add PPh_3 with double bond to that C.

$Ph-\underset{Cl}{CH}-CH_3$ $\xrightarrow[(ii)\ BuLi]{(i)\ PPh_3}$ $H_3C-\underset{Ph}{C}=PPh_3$

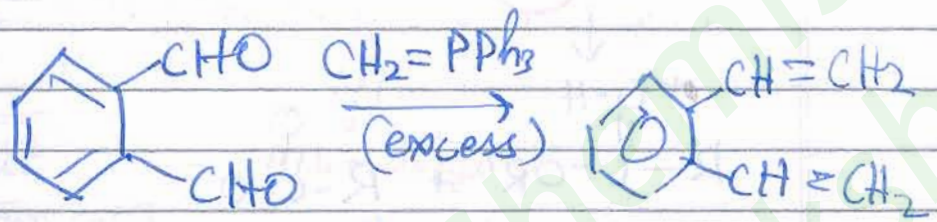
Mechanism

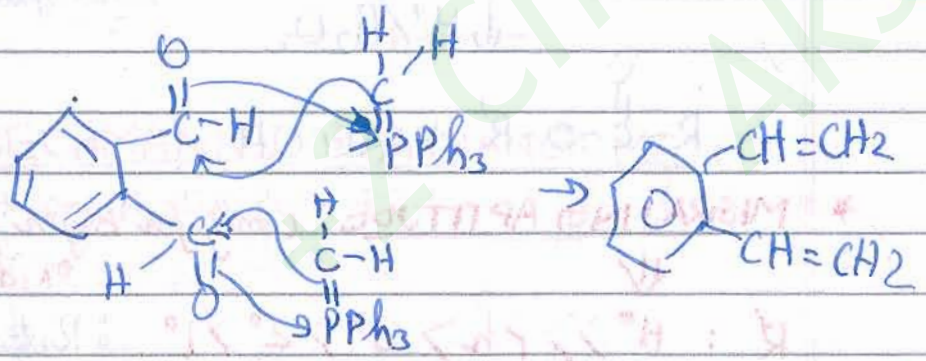


Shortcut :- Take out O-PPh3 & make alkene

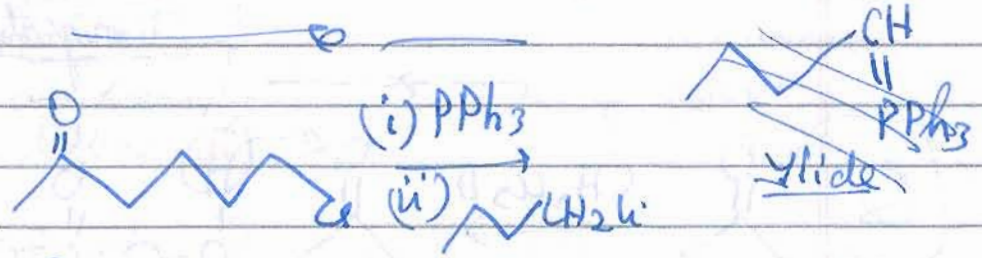


Q.





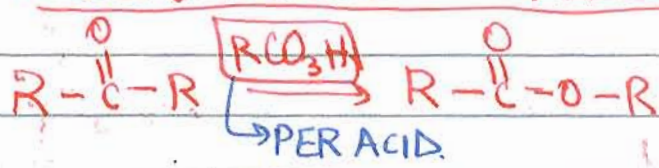
Q.



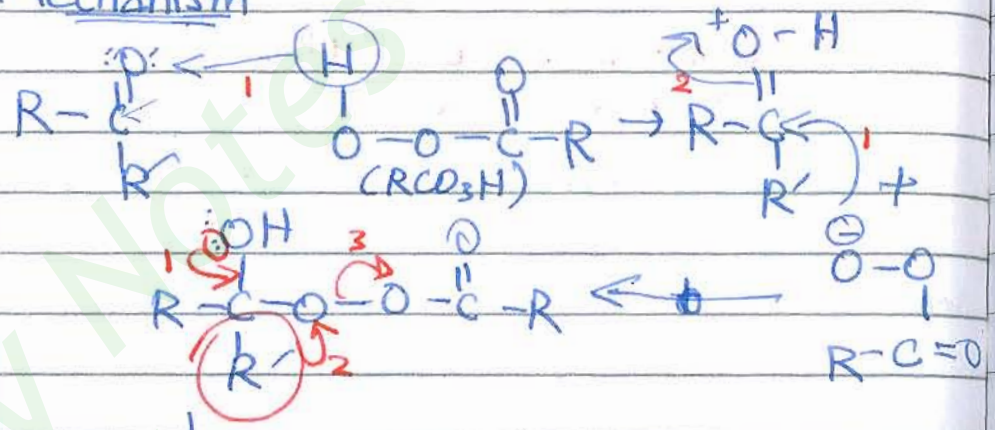
→ Aldehyde gives acid
→ Ketone gives ester.

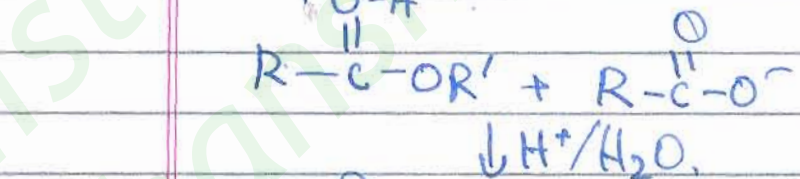
classmate
Date
Page

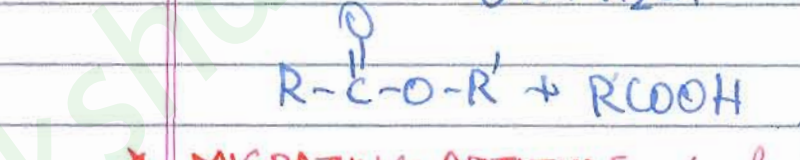
[5] BAYER VILLIGER OXIDATION



Mechanism

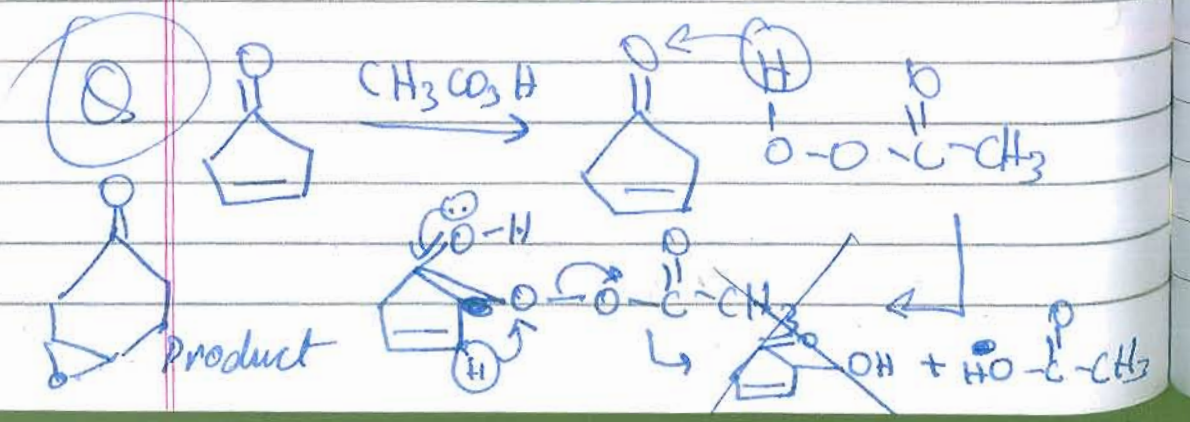




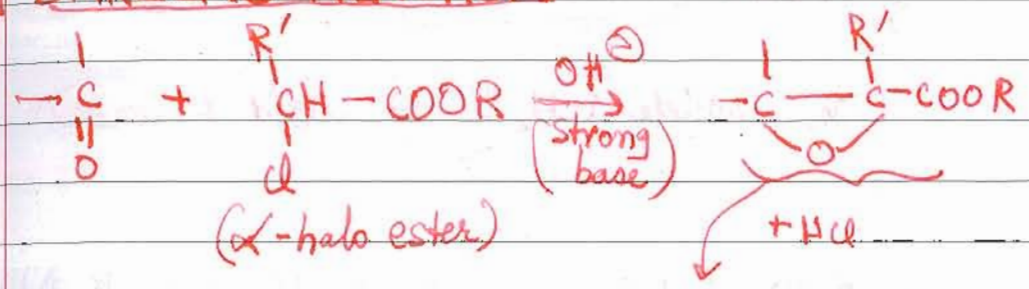


* MIGRATING APTITUDE. (only for Bayer Villiger oxidn)

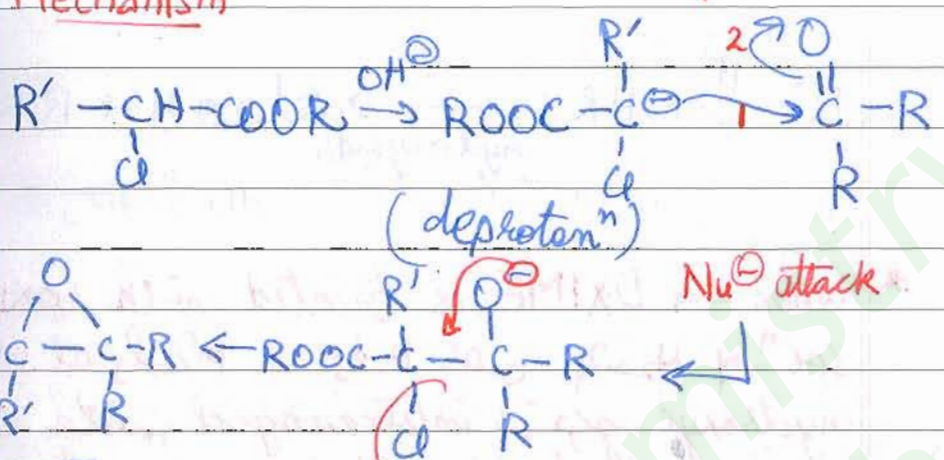
R' : H° >> Ph > 3° > 2° > 1° . ∴ Rate of migrating ability.



[6] DARZEN'S REACTION

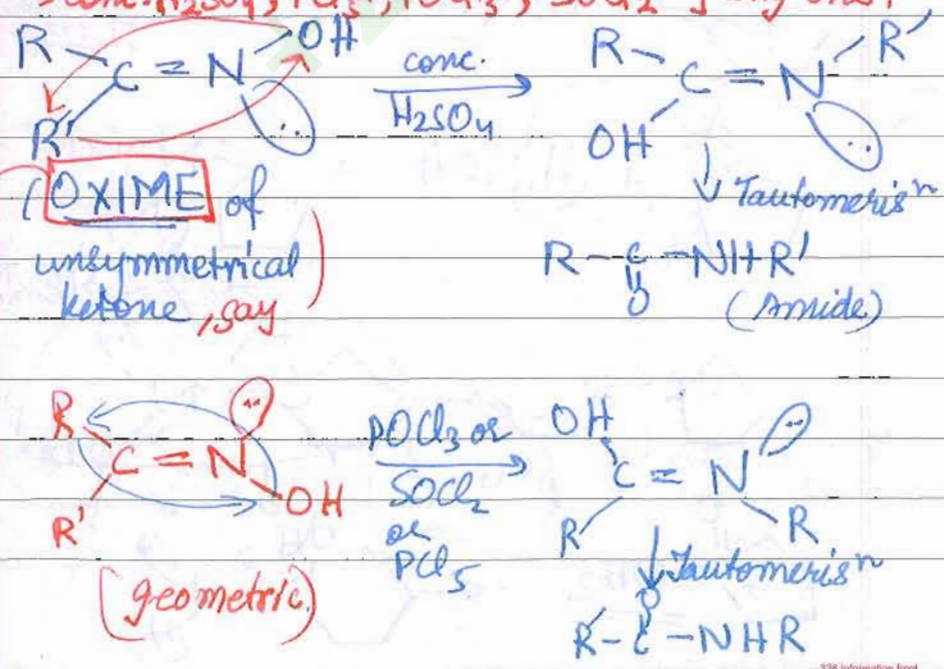


Mechanism



[7] BECHMANN'S REARRANGEMENT

→ conc. H_2SO_4, PCl_5, $POCl_3$, $SOCl_2$ } any one.



Chemistry Akshar

classmate
Date
Page

Acid + Amine → Amide + H_2O

So, amide + H_2O → Acid & amine

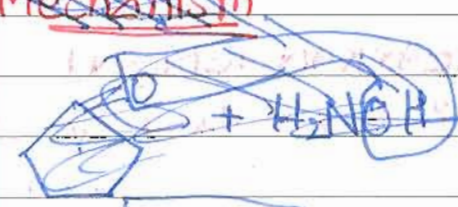
Eg

$$R-\underset{\underset{O}{\|}}{C}-NHR' \xrightarrow[\text{or } OH^-/H_2O]{H^+/H_2O} RCOOH + R'NH_2$$

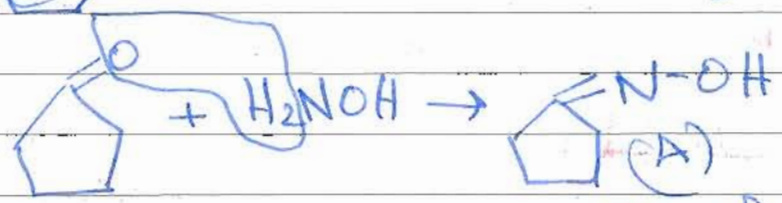
$$R'-\underset{\underset{O}{\|}}{C}-NHR \xrightarrow[\text{hydrolysis}]{''} R'COOH + RNH_2$$

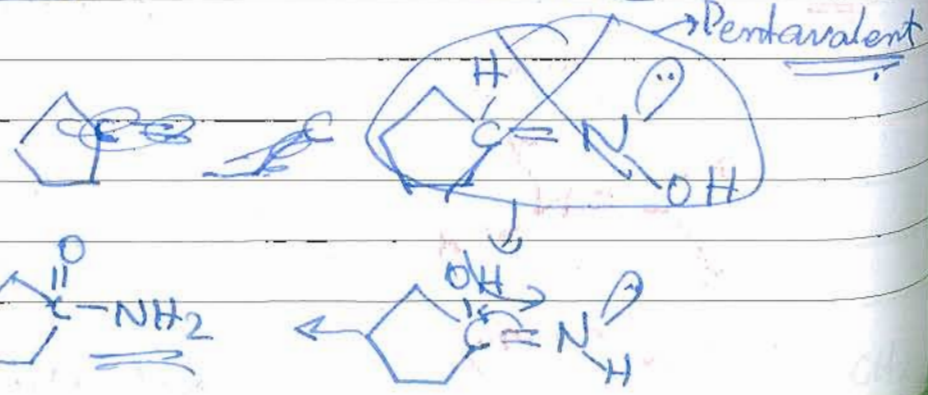
* When an OXIME is treated with conc. sol^n of H_2SO_4 (or PCl_5 or $POCl_3$ or $SOCl_3$), hydroxyl grp is interchanged with the grp ante to it, giving an enol, which tautomerises to give stable amide.

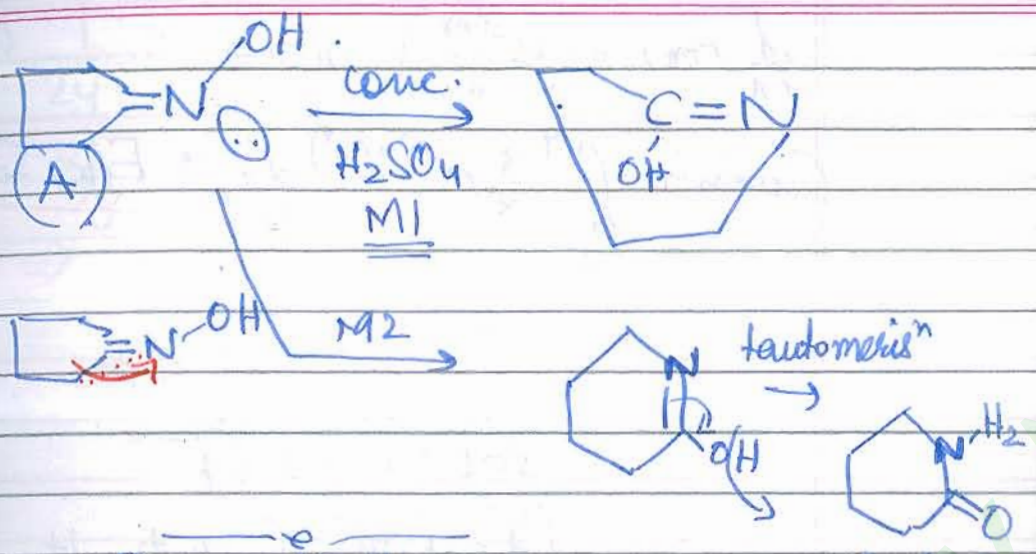
Mechanism



Q.





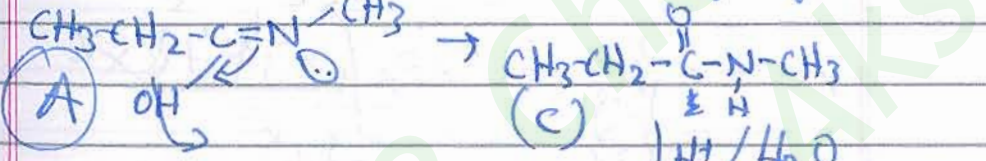


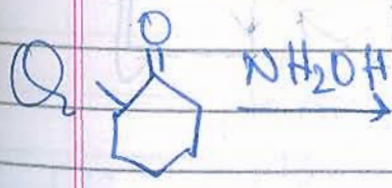
Q. $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{NH_2OH} A + B$

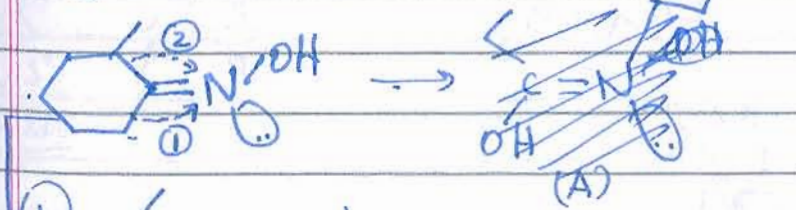
B:- $CH_3-CH_2-C(=N-OH)-CH_3$

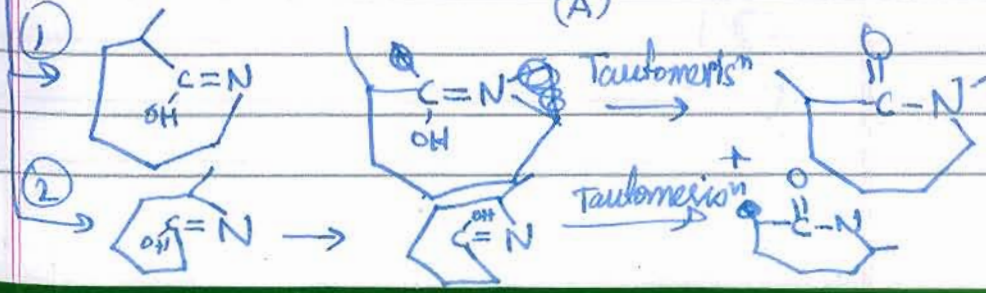
(A) $CH_3-CH_2-C(=N-OH)-CH_3$ oxime

$A \xrightarrow[PCl_5]{} C\ (C_4H_9NO) \xrightarrow{H^+/H_2O} CH_3NH_3^+$ as one of the products of hydrolysis.



Q.  $\xrightarrow[H_2SO_4]{NH_2OH,\ conc.}$ A + B.



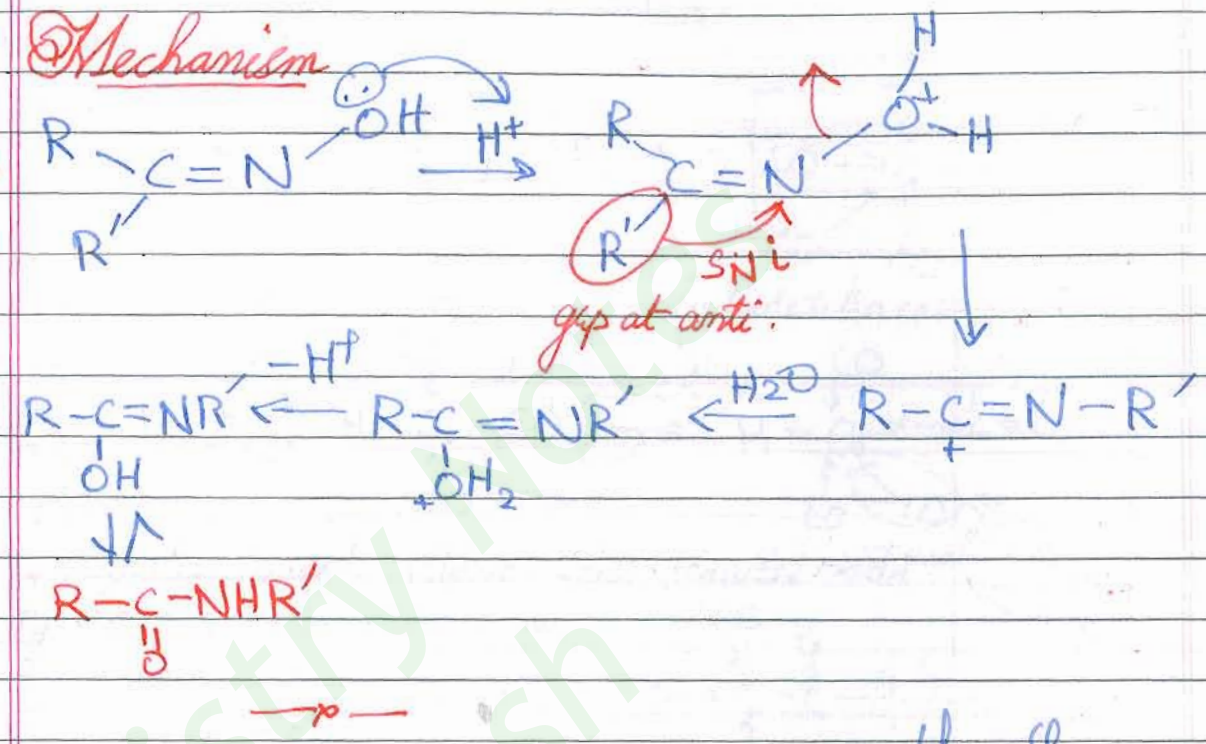


classmate
Date
Page

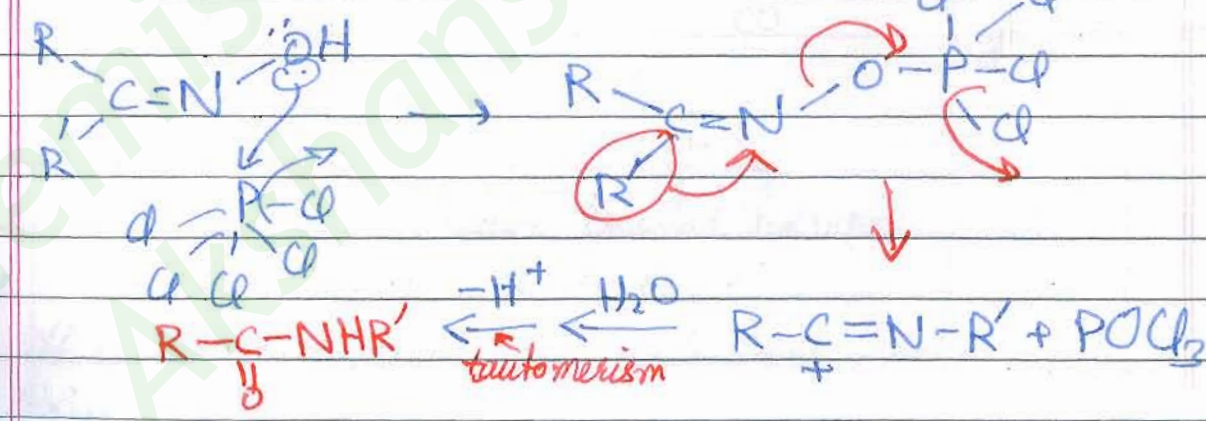
★ Beckmann's rearrangement

Mechanism

• Rxn with conc. H_2SO_4



• Rxn with PCl_5



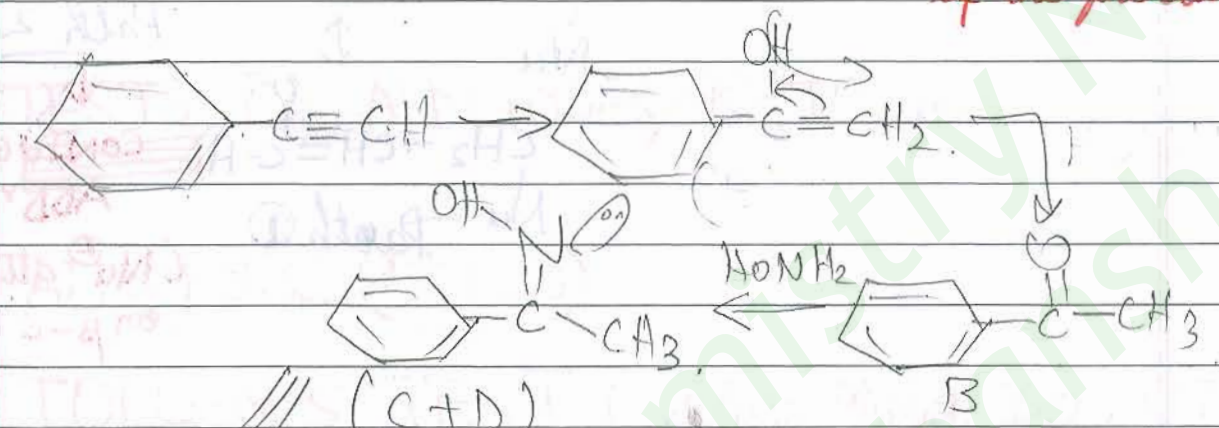
CONTINUED

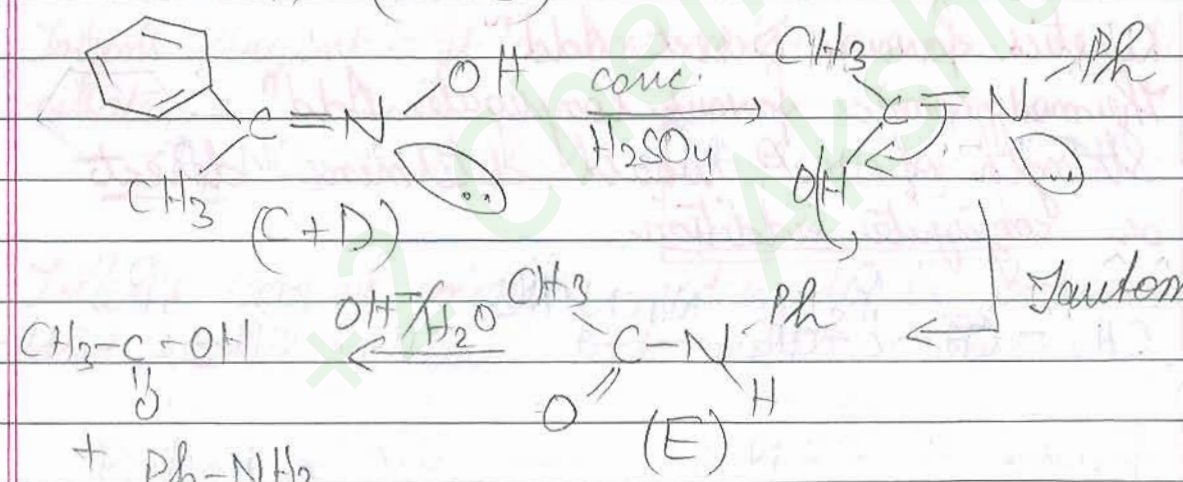
Ch: Aldehyde, Ketones.

JEE 2000

Q. $A(C_8H_6) \xrightarrow[H_2SO_4]{HgSO_4} B(C_8H_8O) \xrightarrow{HONH_2} \underbrace{C + D}_{C_8H_9ON}$.

$C \xrightarrow{conc.H_2SO_4} E$ (stable product) $\xrightarrow{HO^-/H_2O}$ Aniline as one of the product.





C :- CH_3, Ph, C=N, OH

, D :- Ph, CH_3, C=N, OH

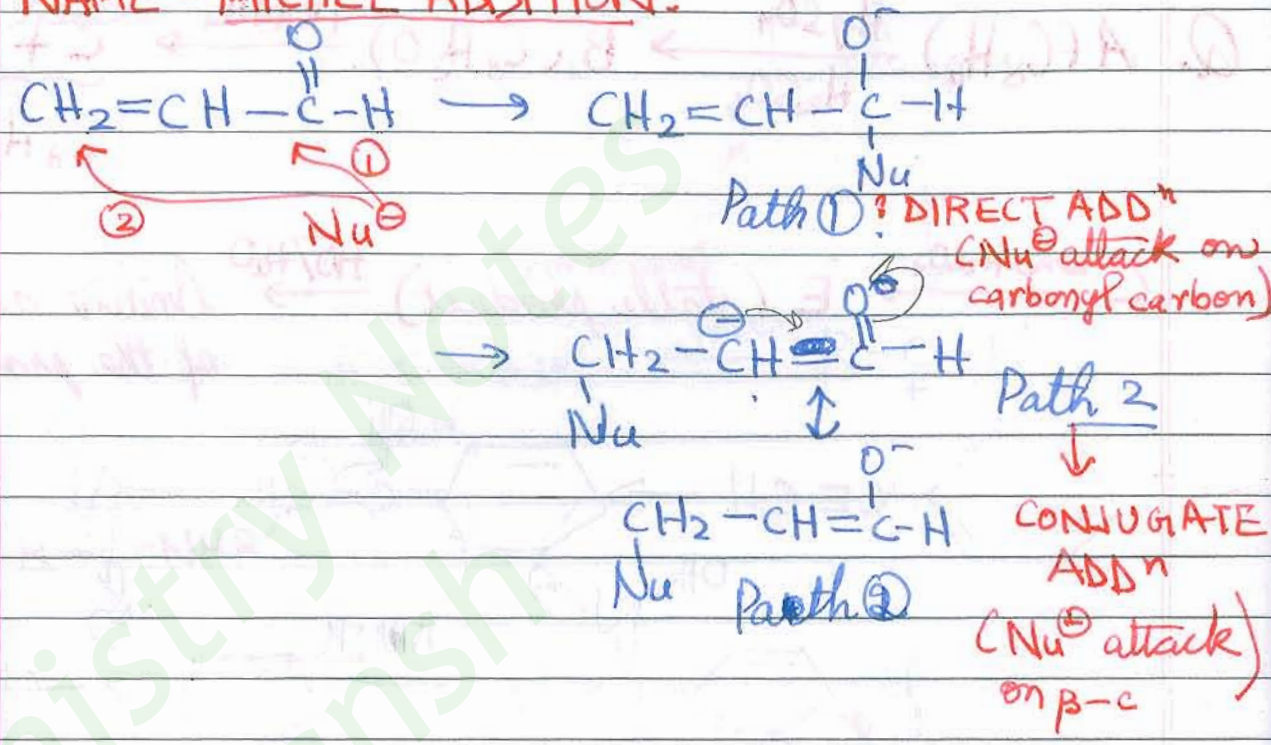
A :- C≡CH

B :- C(=O)–CH_3

Name rxns (continued)

[8] CONJUGATE vs DIRECT ADDITION on α, β - Unsaturated Aldehyde / Ketone.

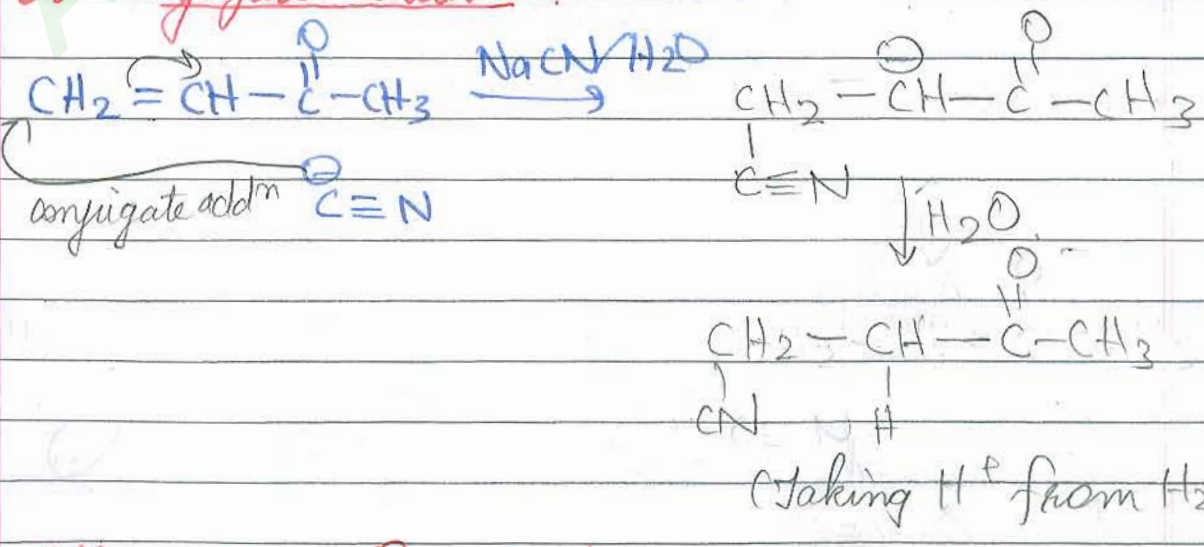
NAME - MICHEL ADDITION.



★ Kinetics favour Direct Addⁿ

★ Thermodynamics favour Conjugate Addⁿ.

★ Strength of $Nu^{\ominus}$ would determine direct or conjugate addition.

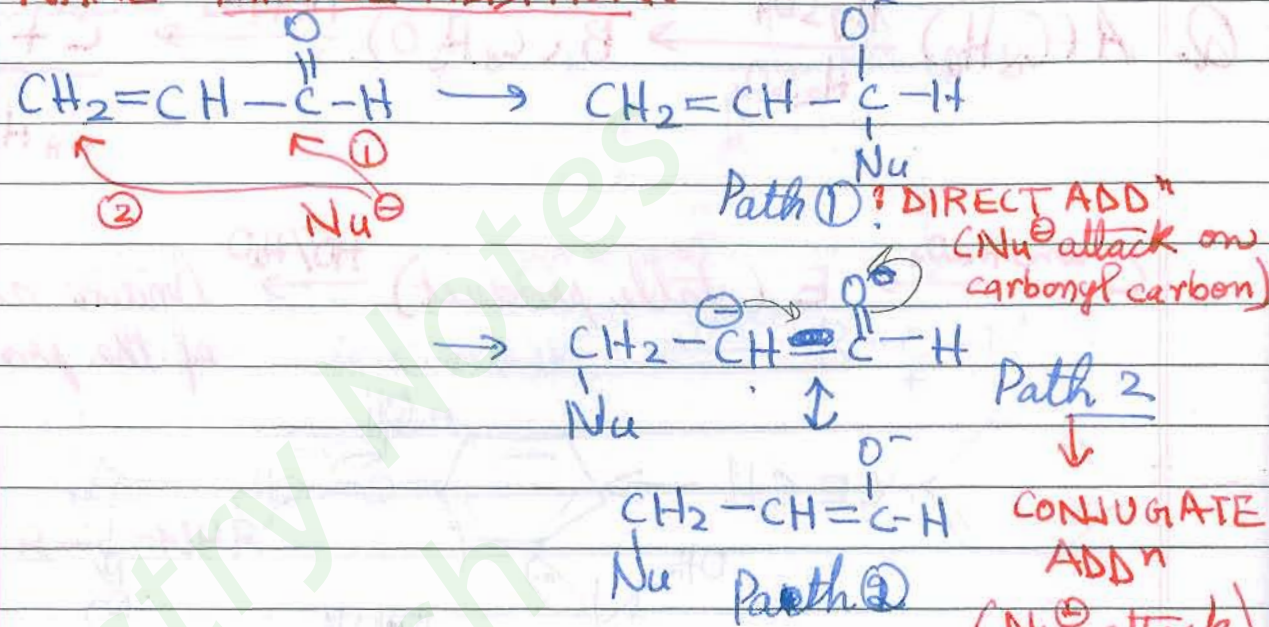
Q. 

★ All weaker $Nu^{\ominus}$ prefer to undergo conjugate addⁿ Whereas, stronger $Nu^{\ominus}$ prefer to undergo direct addⁿ.

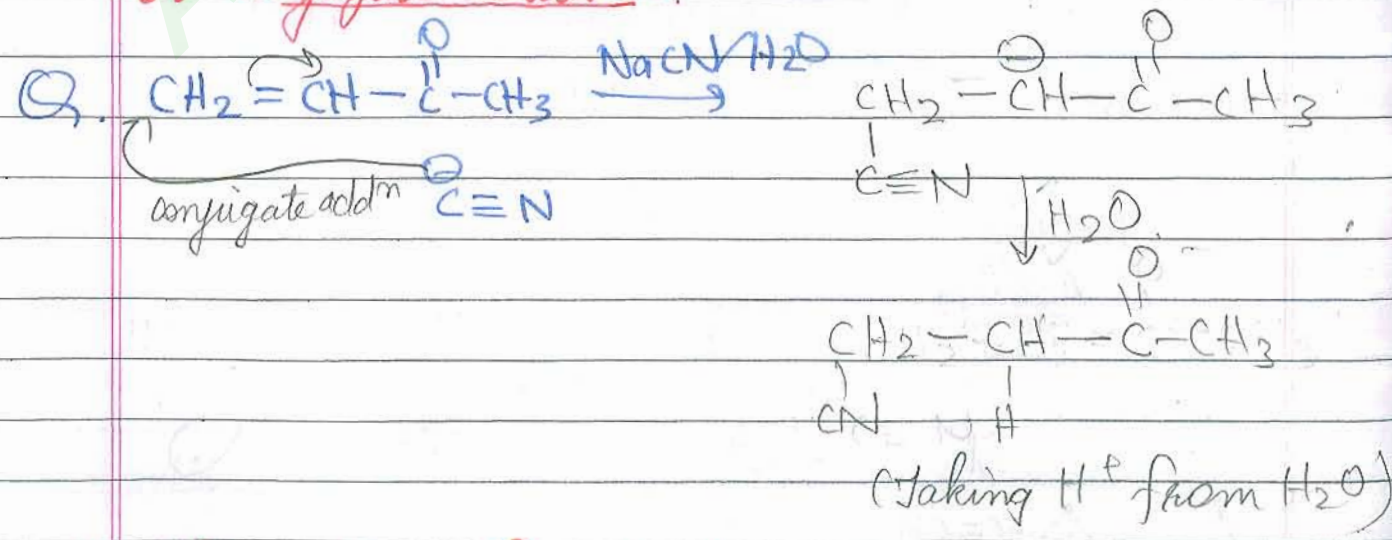
8 Name rxns (continued)

[8] CONJUGATE vs DIRECT ADDITION on α, β - Unsaturated Aldehyde / Ketone

NAME - MICHEL ADDITION.



- Kinetics favour Direct Addⁿ
- Thermodynamics favour Conjugate Addⁿ.
- Strength of $Nu^{\ominus}$ would determine direct or conjugate addition.

Q. 

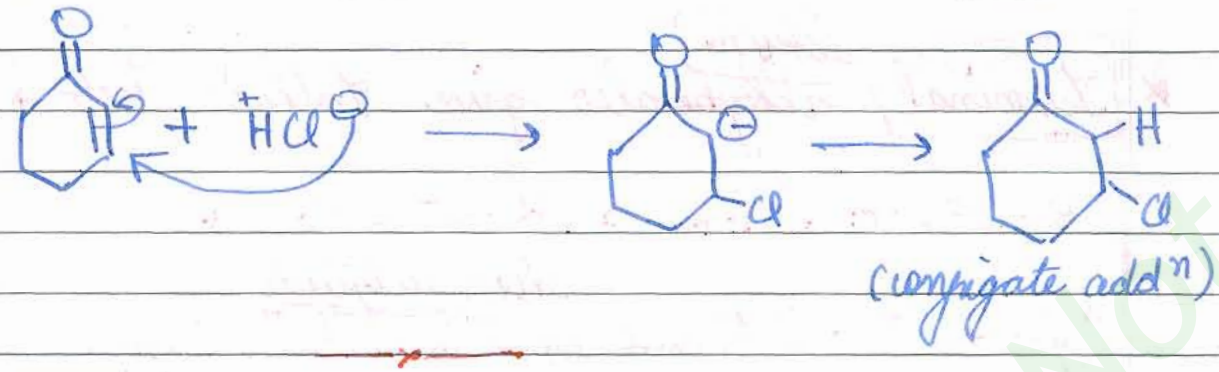
- All weaker $Nu^{\ominus}$ prefer to undergo conjugate addⁿ Whereas, stronger $Nu^{\ominus}$ prefer to undergo direct addⁿ.

From $LiAlH_4$, $NaBH_4$ or NaH

classmate Date 6.10.10 Page

* Only $RMgX$, RLi, $H^{\ominus}$:- are the only ones that undergo direct add^{n} in this reaction.

Q.



(conjugate add^{n})

* TESTS OF ALDEHYDES/KETONES

* ALDEHYDE ONLY

1) TOLLEN'S TEST (Silver Mirror Test) (T.R.)

Tollen's Reagent :- It is ammonical solution of silver nitrate.

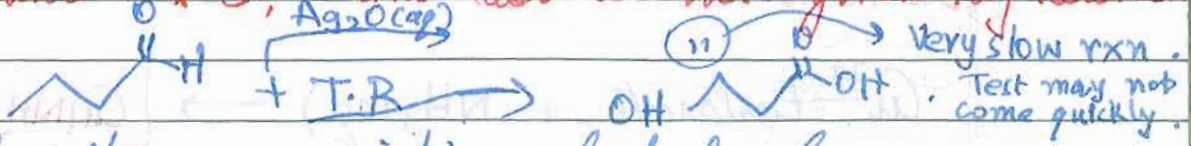
$$AgNO_3 + 2NH_3 \rightarrow \underbrace{[Ag(NH_3)_2]^{+}}_{\text{Tollen's Reagent}} + NO_3^{-}$$

* Tollen's reagent oxidises aldehyde to carboxylic acid, reducing itself into metallic silver.

$$R-\overset{O}{\overset{\|}{C}}-H + T.R \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + \underset{\text{Silver}}{2Ag\downarrow}$$

* Tollen's reagent is a very mild oxidising agent — oxidises aldehyde to acid, leaving all other grp intact. i.e, this test is not given by Ketone.

eg:



✓ It doesn't even oxidise alcohol. So, we can get oxidised product without affecting hydroxy grp.

* Ag_2O may also be used for this test. But, rxn is very slow. Test may not be seen immediately.

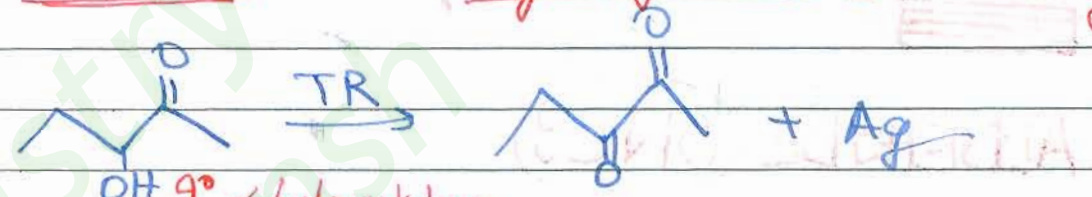
* Terminal alkyne also give Tollen's Test +ve.

$R-C\equiv C-H + T\cdot R \rightarrow R-C\equiv C-Ag\downarrow$

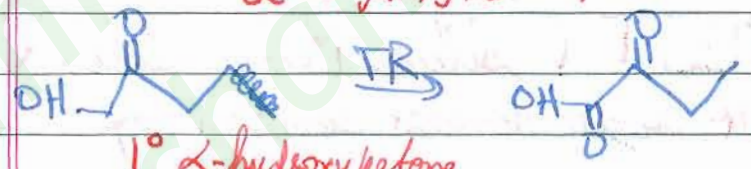
Silver acetylyde

→ gives same test but rxn is not the same.

§ EXCEPTIONS :- α-hydroxy ketone [1° & 2° only]



2° α-hydroxy ketone.



1° α-hydroxy ketone

✓ Tollen's Test given by
- Aldehyde
- 1° or 2° α-hydroxy ketone
- Alkyne : Terminal. (but we can't say that Tollen's reagent reduces alkyne)

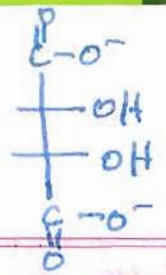
2) FEHLING'S TEST

(F.S) Fehling soln :- It is ammonical soln of Cupric tartarate.

Cu^{2+} tartarate + $NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}$

Fehling's reagent.

★ tartarate:-



classmate
Date
Page

$$R-\overset{O}{\overset{\|}{C}}-H + F.S. \rightarrow R-\overset{O}{\overset{\|}{C}}-OH + \underset{\text{RED}}{Cu_2O}\downarrow$$

cuprous

(cupric → cuprous reduction)

★ Terminal alkyne

$$R-C\equiv C-H + Cu^{2+}\text{-tartarate}(NH_3) \rightarrow \underset{\text{Red}}{R-C\equiv C-Cu}\downarrow$$

(Copper tartarate)

✓ It is a redox rxn (unlike in T.R.)
✓ So, Aldehyde can't be differentiated from terminal alkyne.

★ Fehling's Test given by
✓ All aldehydes.
✓ 1° & 2° α-hydroxy ketone
✓ Terminal alkynes.

★ Aromatic aldehydes : T.R ✓ F.S ✗
Aliphatic aldehydes : T.R ✓ F.S ✓
So, F.S can differentiate b/w aromatic & aliphatic

3) BENEDICT TEST.

Benedict's solution :- It is ammonical solution of cupric citrate

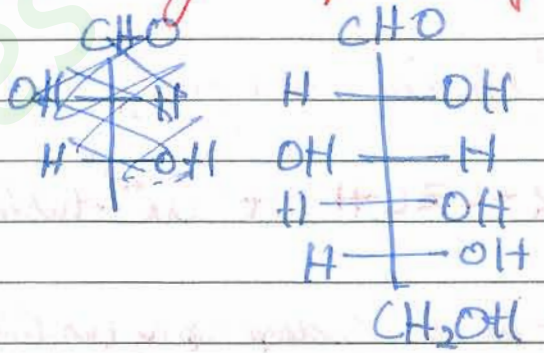
$$Cu^{2+}\text{-citrate} + NH_3(aq) \rightarrow \underbrace{[Cu(NH_3)_4]^{2+}}_{\text{same as Fehling's Reagent.}}$$

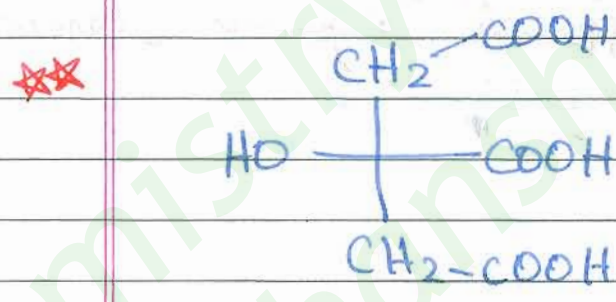
★ It is same as Fehling's sol^n. (just vary due to complexing ability of citrate & tartarate).

✓ It also doesn't react with benzaldehyde (just as Fehling's sol^n).

✓ Benedicts sol^n ~~is used to d~~ :- Behaves in the same manner ~~wd~~ as F.S with normal aldehydes But, it also reacts with sugar of aldehyde.

eg :- D-glucose :-





: CITRIC ACID

* 4) SCHIFF's TEST

↳ exclusively for aldehyde (Aliphatic & Aromatic)

Schiff's Reagent (: a type of organic dye)

= ROSANILINE : magenta color.

SO_2 (g) ~~(a reducing agent)~~ (acts as a reducing agent) $\xrightarrow{\text{react with}}$ (Rosaniline + HCl) aq
magenta color

↓ makes.

Rosaniline ⟶ Aldehyde.
colorless.

↓

Color restored.

~~Aldehyde~~

* Aldehyde restore magenta color of ~~Sch~~ Schiff's reagent.

* $X_2 + H_2O \rightarrow HOX + HX$. : halogen oxidises.
eg: HOCl, $OCl^{\ominus}$ reacts

* This test is not given by Ketones or Terminal Alkyne.
* Schiff's test doesn't react with α-hydroxy ketone (1° & 2°)

IODOFORM TEST → given by ketone & acetaldehyde.

$$R-\underset{\text{ACETO}}{\underset{\|}{C}(=O)-CH_3} + I_2 \xrightarrow[(aq.)]{NaOH} R-\underset{\|}{C}(=O)-ONa + CHI_3\downarrow$$

Iodoform (yellow ppt.) bright.

* This test is given by
  - ✓ Methyl ketone
  - ✓ Acetaldehyde (exception).

* It can be used to differentiate b/w methyl ketones and — ketones (others), aldehyde (except acetaldehyde).

* CH_3CH_2-OH gap also gives this test.

$$CH_3CH_2OH \xrightarrow{I_2} CH_3-\underset{\|}{C}(=O)-H \rightarrow CHI_3\downarrow + H-\underset{\|}{C}(=O)-ONa$$

✓ carbonyl carbon → acid is given by it
carbon of methyl → CHI_3 is given by it

Mechanism

~~NaOI + I~~

$NaOH + I_2 \rightarrow NaOI + NaI + H_2O$.

Now, α-halogenation takes place on aceto final gap.

$$R-\underset{\|}{C}(=O)-CH_3 \rightarrow R-C(:OH)=CH_2 + I-I \rightarrow R-\overset{+}{\underset{\|}{C}}(-OH)-CH_2 \; (I^{\ominus})$$

enol tautomer (intermediate → (not RI))

$$R-\underset{\|}{C}(=O)-CH_2I \rightarrow R-\underset{\|}{C}(=O)-CHI_2 \rightarrow R-\underset{\|}{C}(=O)-CI_3$$

classmate
Date
Page

(produced as intermediate or previous rg.)

Iodoform

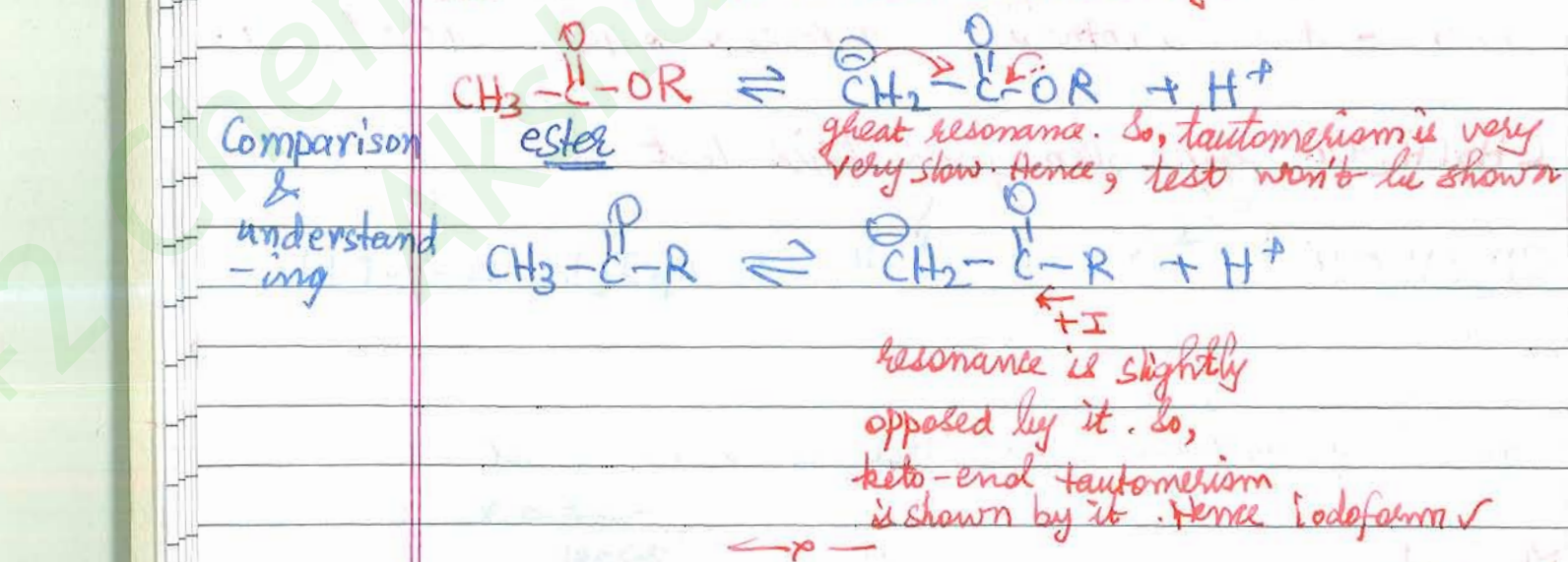
✓ If methyl ketone grp had not been there, 2 I grps would have been attached/replaced by H's instead of 3 (see mechanism). So, ~~—CI_3~~ won't be produced. So, CHI_3 won't be produced.

✓ Iodoform test NOT given by.

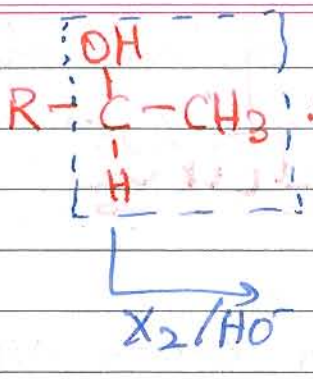
$CH_3-C(=O)-OH$: ∵ it doesn't give/show keto-enol tautomerism. So, SI of mechanism is not followed. Its enol is not formed (∵ its α-H is not acidic)

✓ This test is NOT RESPONDED by.

Comparison & understanding



✱ On reaction with Cl & Br, test would take place, but, distinction won't occur ∵ $CHCl_3$ & $CHBr_3$ are colorless. So, no visible change.

E ✱ 
:- gives haloform even & Iodoform test also.

$R-C(=O)-CH_3 \xrightarrow{X_2/HO^-}$ rest is same as in mechanism.

✱ Iodoform test given by :-

- ✓ methyl ketone
- ✓ acetaldehyde
- ✓ ethanol
- ✓ 2° alcohol with one α-methyl.

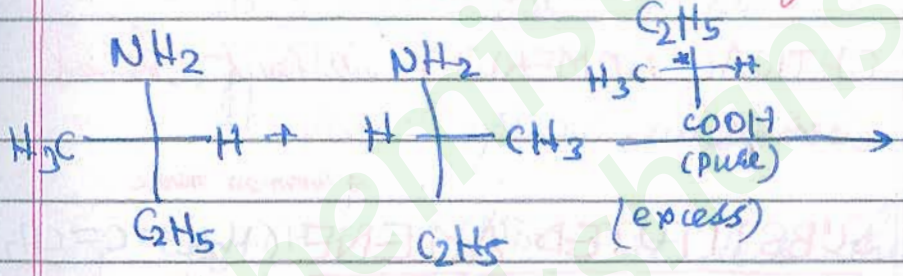
+2 Chemistry Notes Akshansh

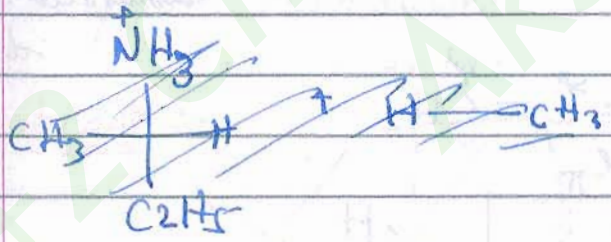
classmate
Date 19.9.10
Page

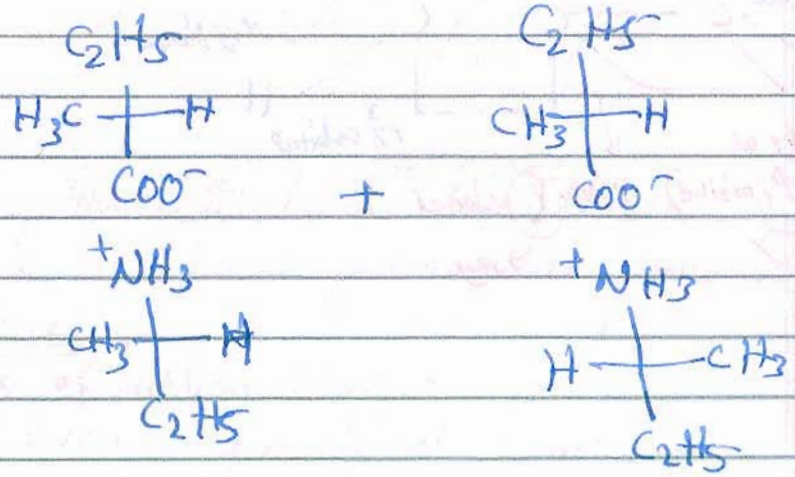
Stereo Isomerism

✡ Separation of ENANTIOMER

* Enantiomers have same chemical properties with optically inactive substance. Hence, its tough to separate them chemically.
* They have same physical properties. So, they can't be separated by physical means.







diastereomers → diff't properties. Can be easily separated.

classmate
Date
Page

* Diastereomeric salts can be separated from fractional crystallisⁿ.

* If reactant given (enantiomers) is

Case (1) → an amine
use acid (pure) as a reagent

Case (2) → an acid
use amine (pure) as a reagent

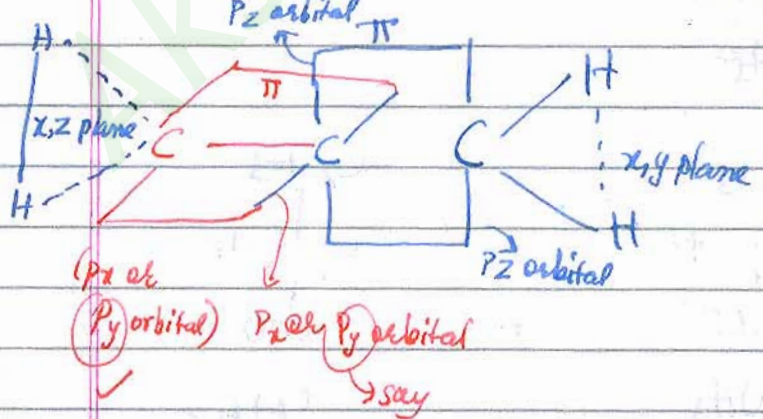
* They react to give pair of diastereomers (as before) & hence can be separated.

→

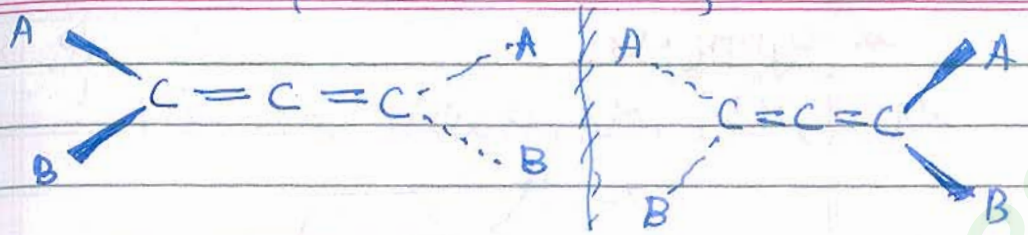
8) OPTICAL ISOMERISM without Chiral Carbon.

* SUBSTITUTED ALLENE ($H_2C=C=CH_2$) → common name
(cumulated ~~diene~~ diene)

$$H_2\overset{sp^2}{C}=\overset{sp}{C}=\overset{sp^2}{C}H_2$$



enantiomers



(If same carbon doesn't have identical grps, it becomes Nsp on its mirror image)

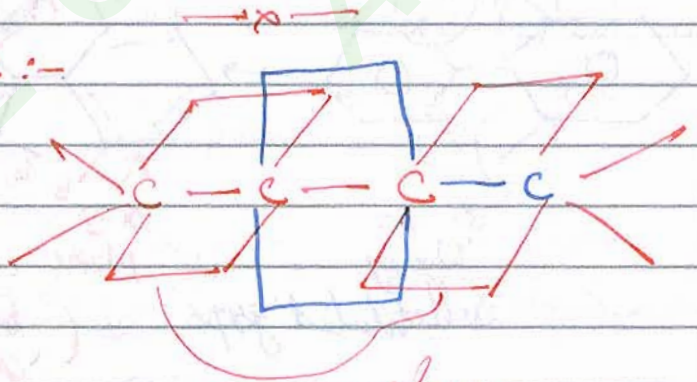
eg: ClHC=C=CHCl :- It won't show geometrical isomerism.

→ Its always polar :- Cl are not in same plane.

→ It shows optical isomerism.

eg: $CH_3-CH=C=CClBr$:- It does show optical isomerism

A case :-



Its substituents are in same plane. (same plane.)

So, it shows geometrical isomerism.

Hence,

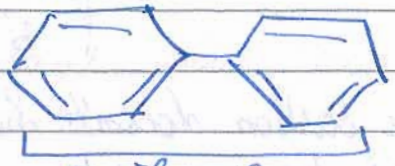
no. of carbon atoms :-

even :- geometrical isomerism

odd :- optical "

classmate
Date
Page

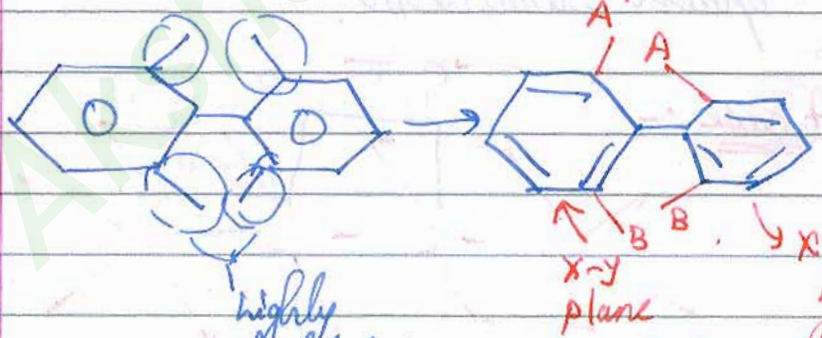
✱ BIPHENYL



Biphenyl grp.

✱ If Biphenyl grp is unsubstituted, then, phenyl grps are in same plane.

✱ If Biphenyl is substituted at all ortho pos^{ns} by a bulky grp :-



Highly substituted grps

(One phenyl grp turns ⊥ to other to minimise steric repulsion b/w grps at ortho pos^{n})

Resonance destroyed

(C-C B.L ↑) → (BE ↓, BO ↓)

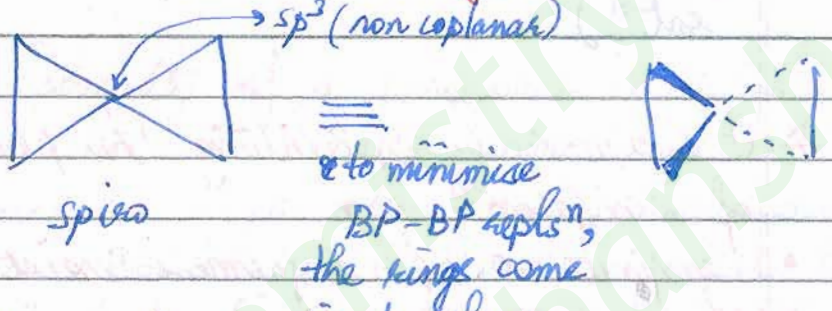
Chemistry Notes Akshansh

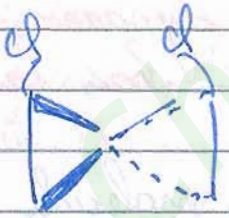
classmate
Date
Page

★ If the bulky grps attached are
A & B = $COOH$, NO_2, CH_3, CN, SO_3H,
Then, it becomes same as Allene &
i.e, it becomes Optically Active.

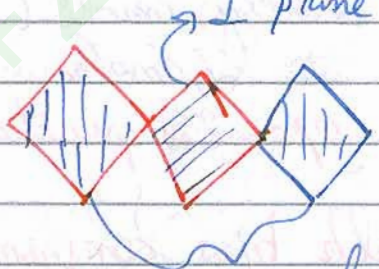
→ SPYRO compd

★ SPYRENE : compds in which only 1 C is common to both rings.





:- It becomes optically active (same as case of Allene)



★ :- It shows geometric isomerism.

+2 Chemistry Notes Akshansh

Conformation:

Temporary molecular shape arising due to rotⁿ of grps about a covalent bond are known as conformers.

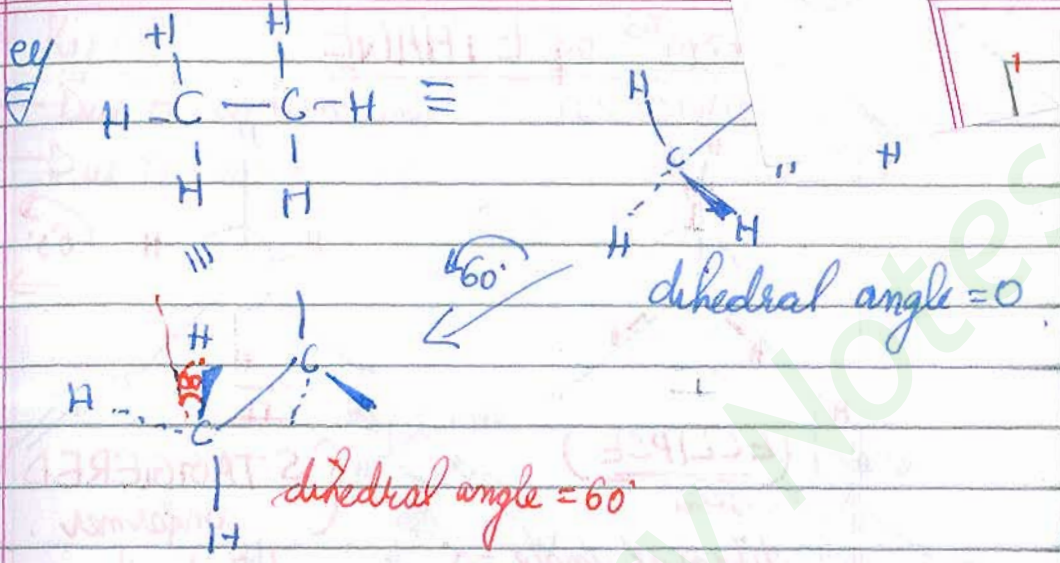
The phenomena is called conformⁿ (or ROTAMERS: Isomers formed due to rotⁿ).

✱ For a molecule exhibiting the phenomena of conformⁿs →

- Infinite no. of conformers exist. All the conformers remain in dynamic equi. & the most stable conformer has largest fraction
- Diffᵗ conformers of a molecule differ in their PE & ∴ stability; however, the diff in P.E. is very small (in the range of 10-50 KJ/mole
- Conformers can't be separated practically.

✱ Max. E gap possible b/w conformers is 10-50 KJ/mole.

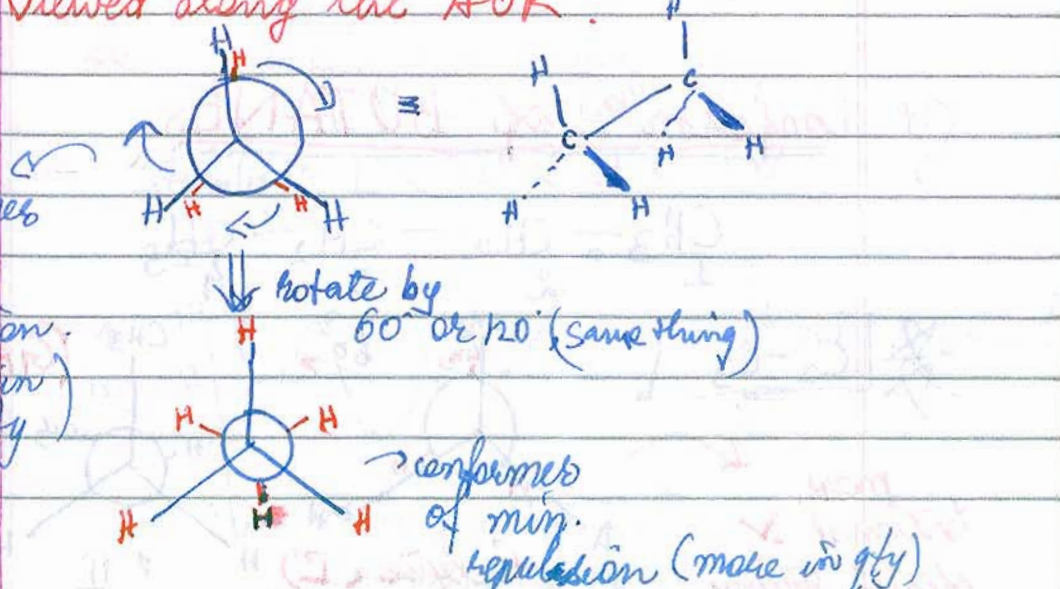
✱ DIHEDRAL ANGLE :- Dihedral angle is the angle b/w bonds (or grps) on the adjacent atoms along the line of rotⁿ.



* PE / stability of a conformer is determined from the BP - BP repulsion b/w the bonds on adjacent atoms (∵ on same atom, Bond angle is fixed). Greater the dihedral angle, smaller the BP - BP repulsion, greater the stability, lower the PE.

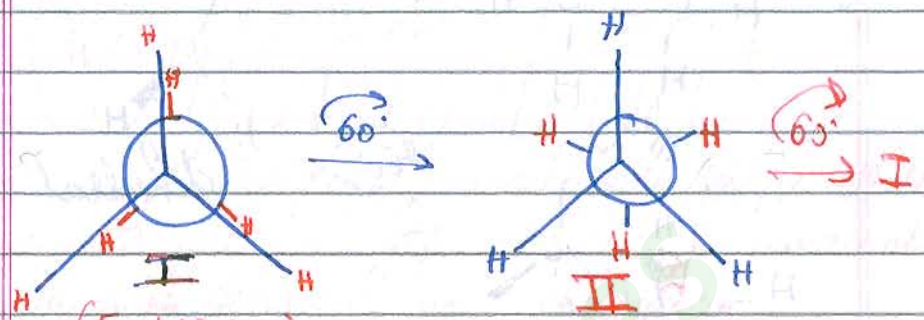
* NEWMAN'S PROJECTION

It is depiction of a molecule when viewed along the AOR.



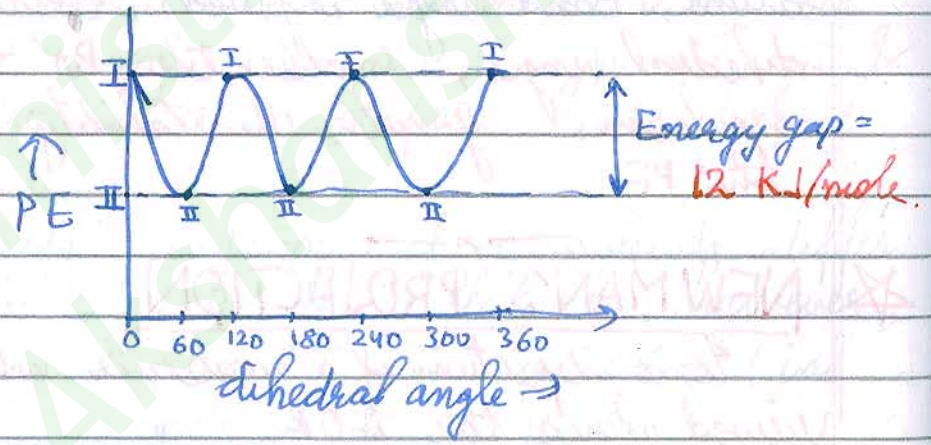
classmate
Date
Page

Conformⁿˢ of ETHANE



(ECLIPSE) form
dihedral angle = 0°
✓ least stable
✓ min. fraction at equi.

(STAGGERED) conformer.
dihedral angle = 60°
✓ most stable
✓ max. fraction at equi.

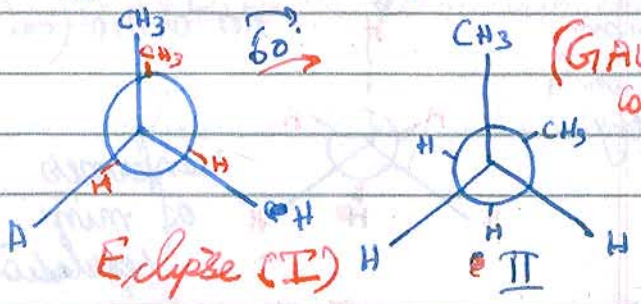


Conformⁿˢ of BUTANE

$$\overset{1}{CH_3}-\overset{2}{CH_2}-\overset{3}{CH_2}-\overset{4}{CH_3}$$

C_2-C_3

max. torsional & steric strain



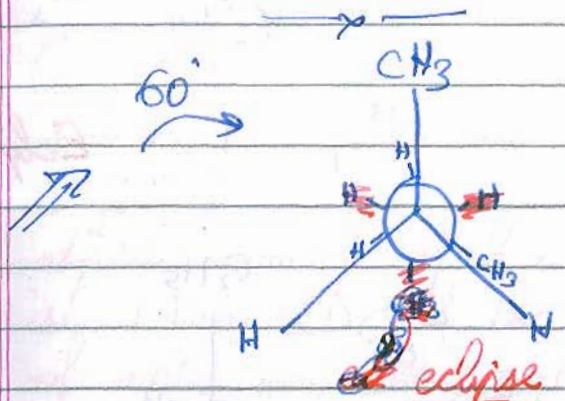
Chemistry Notes Akshansh

classmate
Date
Page

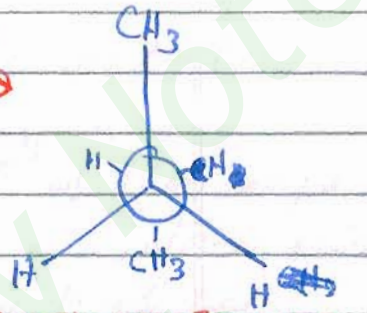
★ Repulsion — Bond angle - Bond or STRAIN

∴ Due to BP-BP angle : TORSIONAL repulsion.

— Due to size of compds : STERIC repulsion



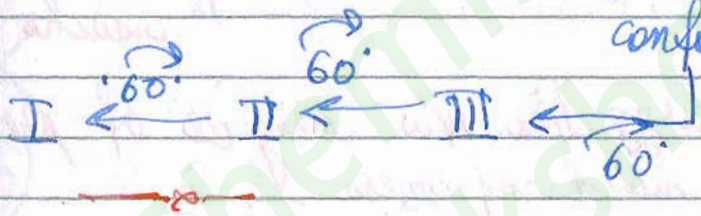
III.



ANTI-CONFORMER

IV

(most stable conformer of butane)



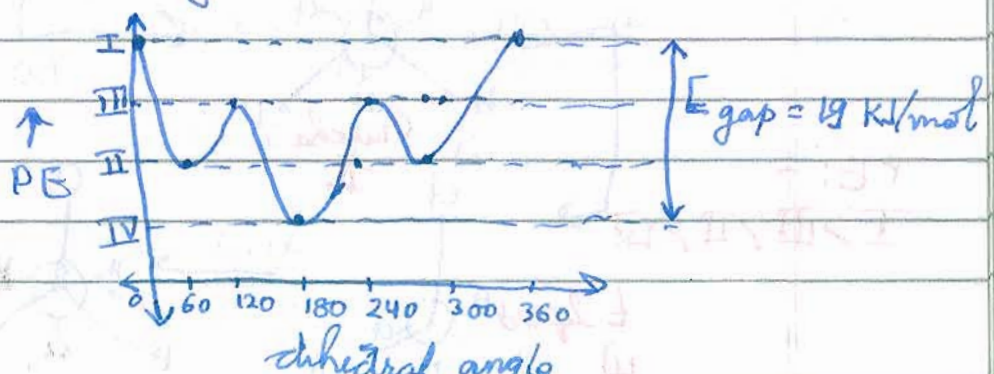
★ Torsional strain is always greater in magnitude than steric strain.

So, $PE_{Gauche} < PE_{any\ Eclipse}$.

So, Start Eclipse > Eclipse > Gauche > Anti

PE :- I > III > II > IV

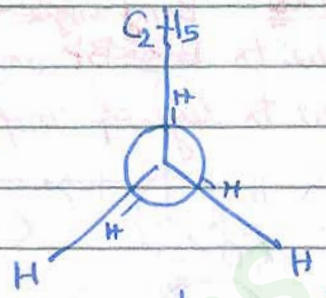
Stability :- I < III < II < IV



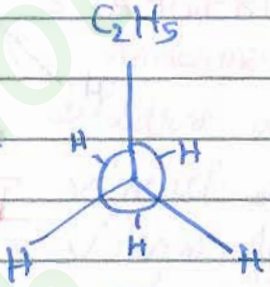
B/w

☆ C_1C_2 bond

$CH_3-CH_2-C_2H_5 \equiv$



I ↓ 60° Eclipsed



I (Eclipsed) ← 60°

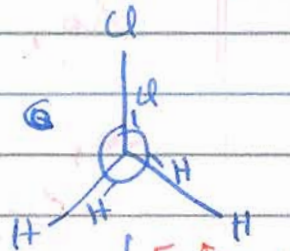
II Gauche

* ↑ energy lies b/w energies of previous C_2C_3 bond conformers.

Q) ☆ 1,2-dichloroethane :- diff^t conformers

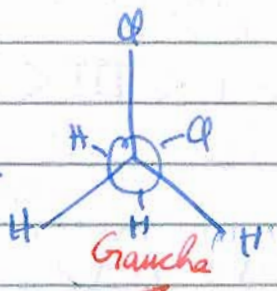
CH_2-CH_2 : Rest

Cl Cl



Eclipsed I

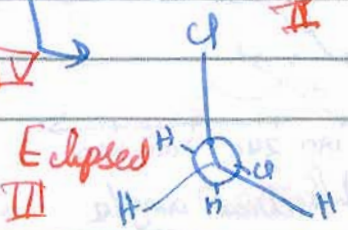
60°



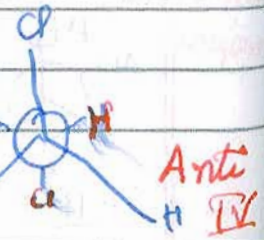
Gauche II

PE:-

I > III > II > IV



Eclipsed III



Anti IV

Dr. Chemistry Notes Akshansh

Q Dipole moment $(\mu) = \sum \mu_i x_i$; μ_i is dipole moment of the stable conformer of i^{th} component & x_i is its mole fraction. Consider that a sample of 1,2-dichloroethane, has only 2 ~~conformers~~ of the most stable conformers → anti & gauche form & dipole moment of a sol^n of this sample is 1 Deby = 1 D. If the sample contain 82% of anti conformer, determine μ of gauche conformer.

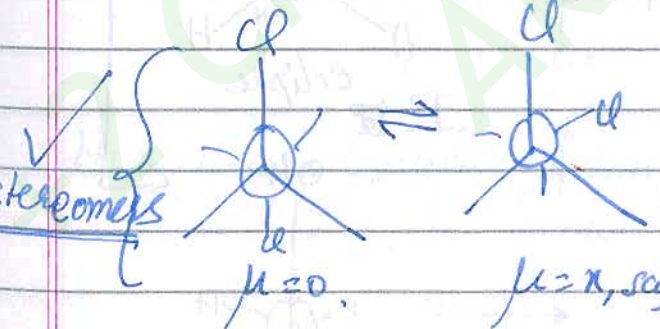
$$1 = \mu\left(\frac{\cdot 82}{1}\right) + (1-\mu)(0.18)$$

$\mu_{anti} = 0$ ✗

$$\Rightarrow 1 - 0.18 = \mu(0.82 - 0.18)$$

$$\Rightarrow \frac{0.82}{0.64} = \mu$$

7.82 / 18 / .64



distereomers ✓

$\Delta H > 0$ (∵ from more stable to less stable)

So, mole fr^n of 2nd ↑ So, its μ ↑.

$\mu_{cis} = 0$ $\quad \mu_{trans} = x$, says

$$\mu = 1 = (0 \times 0.82 + x \times 0.18)$$

$$\Rightarrow x = \frac{1}{0.18} = \frac{100}{18} = 5.5\ D.$$

$$\Rightarrow x = 5.5\ D.$$

$$K_c = \frac{0.18}{0.82}$$

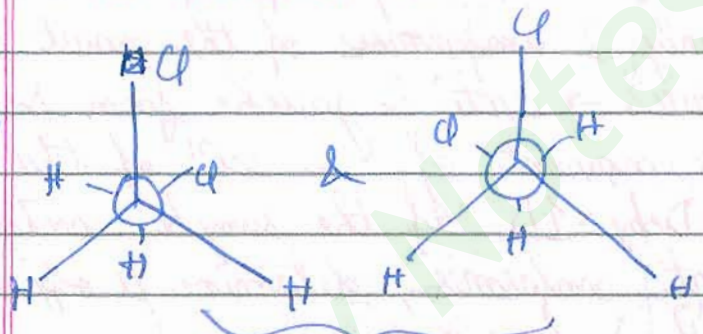
Chemistry Notes Ashish

classmate
Date
Page

★ Conformⁿ is a type of Stereoisomerism. But that isomerism is dynamic in nature.

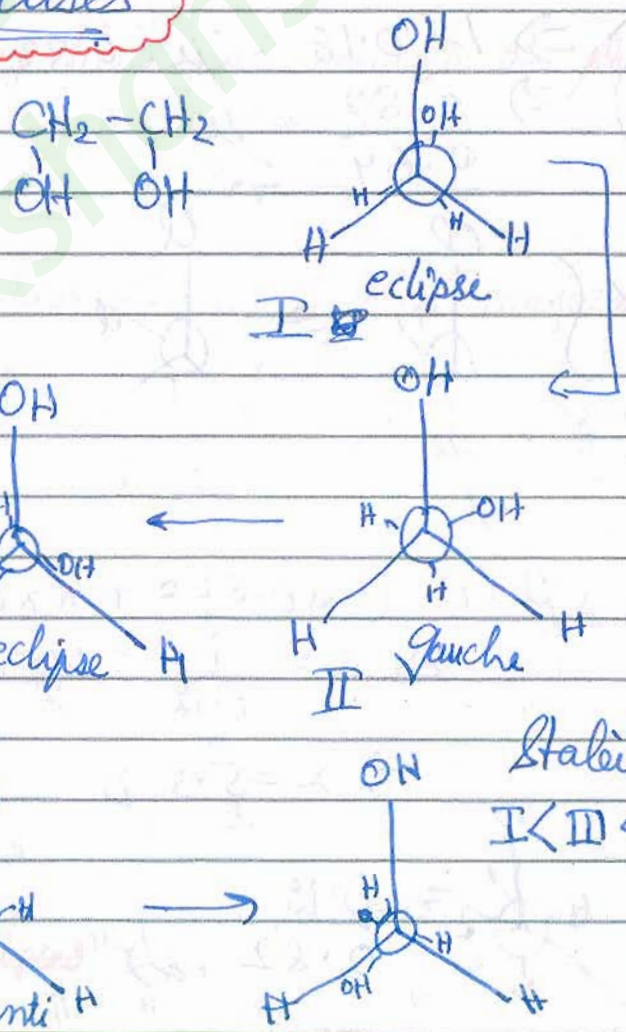
★ All conformers are DISTEREOMERS of one another.

Q. Relⁿ ?



They are identical.

★★ Other cases



Stability :-

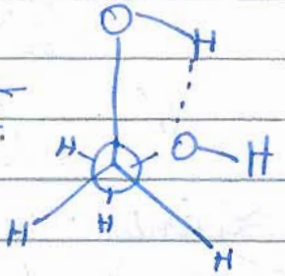
I < III < IV < II

Chemistry Notes Akshansh

classmate
Date
Page

* By convention, IV > II :- Stability.
But actually, II > IV : Stability
Reason:- Intramolecular H-bonding in II

II



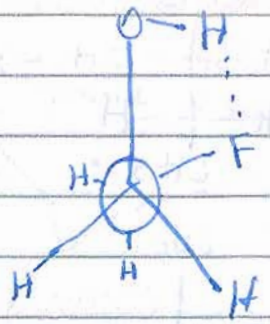
: 5 membered ring.
↑ Stability.

* H-bond doesn't take place in eclipsed form due to high LP-LP repulsion of O-O.
* Had NH_2 been in place of OH,
Check NH_2 doesn't form H-bond (based on reference)

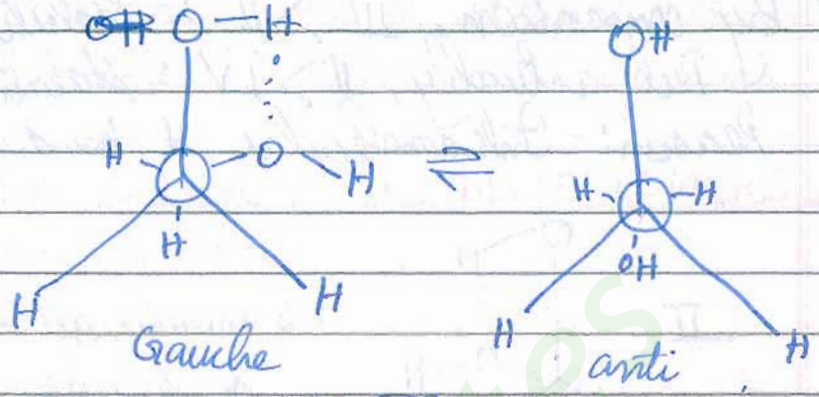
* In case of

$$CH_2(F)-CH_2(OH)$$

Here also, Gauche form is more stable than anti form (H-bonding)



IIT Chemistry Notes Akshesh



Gauche ⇌ anti

Ant Gauche ≈ anti

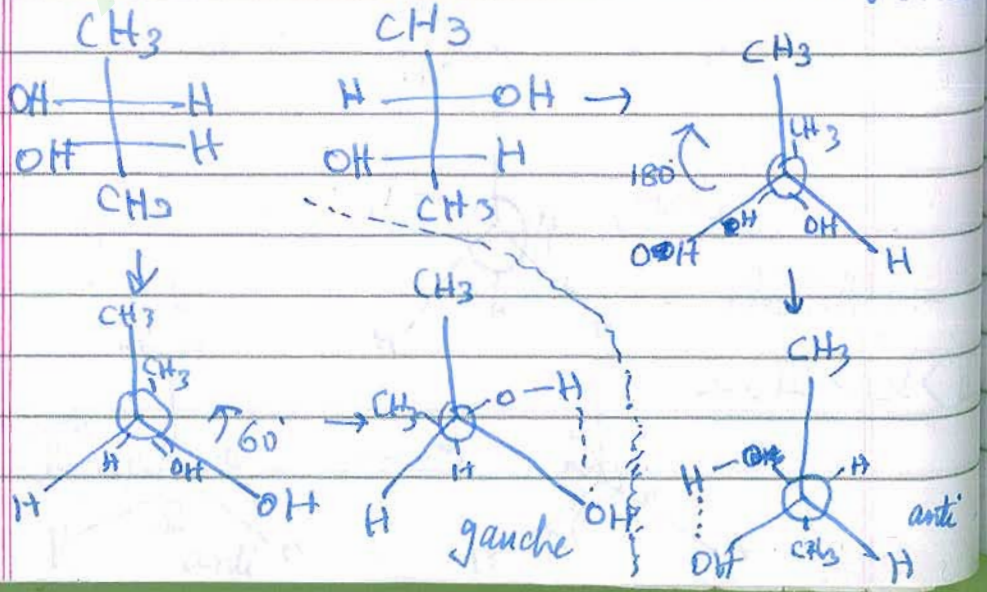
→ almost equal, gauche greater.

★ In water, anti form has greater amt. than Gauche form (∵ it forms less H-bond with water; Gauche busy in intra)

In non-aq. solvent or organic compd. Gauche form is in more amt. than anti form. (H-bond of Gauche form)

★ $CH_3-\overset{*}{C}H-\overset{*}{C}H-CH_3$ (OH, OH) : 3 stereomers

1 meso + 2 enantiomers



anti posⁿ forms stronger

Enantiomeric butane 2,3-diol forms stronger H-bond than meso 2,3 diol

(∵ 2 methyl grp at anti posⁿ bring OH-OH bond closer & hence ↓ BL, ↑ BE)

* Repelling force in meso 2,3 diol is not as much as increase of enantiomeric 2,3 diol.

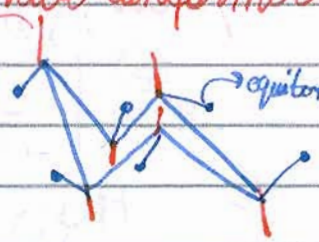
✱ CONFORMⁿ of CYCLOHEXANE

↳ Bond flipping can be done easily (In other 3 membered, 4 membered ring, it not possible due to rigidity)

* Cyclohexane is smallest ring from where bond flipping start to occur.

2 MAIN CONFORMERS.

- Chair conformer (More stable)



✓ More stable than boat conformer (reason ↓)

- Boat conformer

1,4-steric replⁿ b/w H-H. Stability ↓.

classmate
Date
Page

★ In Adjacent

AA or EE : Trans.
AE or EA : Cis

★ In Alternate.

AA or EE : Cis
AE or EA : trans.

★ 1,4 posn

AA or EE : trans
AE or EA : cis.

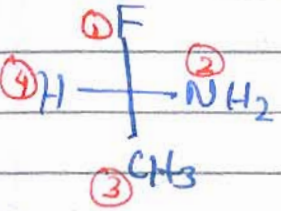
★ In case of substituted cyclohexane, where should it be placed?

Ans: In case of single substituent, grp is placed on equitorial posn (to avoid steric repulsion from 3 & 5 axial posns)

Chemistry Notes Akshansh

Cahn
or ~~Chan~~-Ingold-Prelog
configuration.

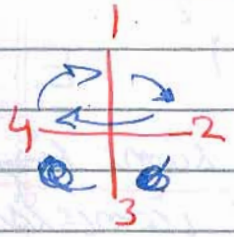
R & S Configuration



S1 : Give priority to the 4 grps at chiral carbon.

⇓

Heavier atom (in terms of molar mass) directly bonded to chiral carbon has higher priority.

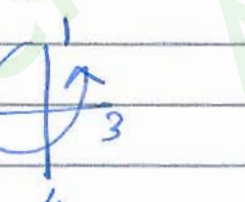


S2:- lowest priority grp must be on vertical.

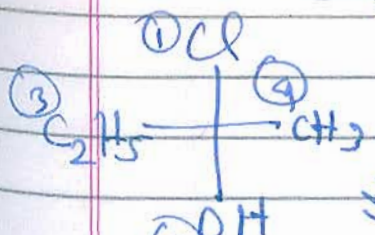
S3 : Hide 4 (not to see it).

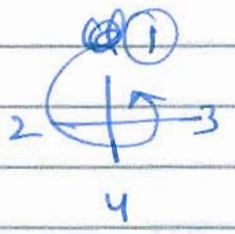
S4: See dirⁿ of rotⁿ of 1, 2 & 3.

Anticlockwise : S confi
Clockwise : R confi.



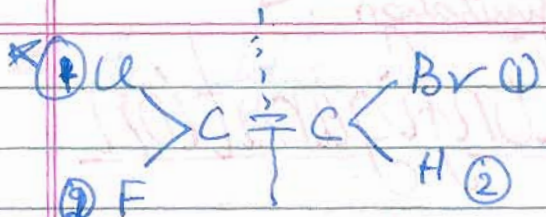
* If 1st atom is found identical, see next atom.



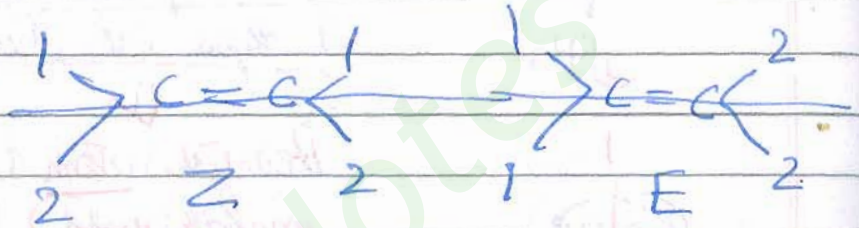


S confi

★ Prioritise each side



E-Z isomerism.



★ Like priority on same side :- Z isomerism

★ Like priority on opp side :- E isomerism.

Chemistry Notes Akshansh

Ch: Acids & Derivatives

$RCOOH$ — carboxylic acid.

$R-\overset{O}{\overset{\|}{C}}-X$

$X: Cl, OR, O-\overset{O}{\overset{\|}{C}}-R, NH_2$

CARBOXYLIC ACID.

✱ PREPARATION

1. Preparation from natural source:

(a) By hydrolysis of Glycerides.

glycerides family: CH_2-O / $CH-O$ / CH_2-O : basic framework.

esters of long chain fatty acid ← glyceride:

$CH_2-O-\overset{O}{\overset{\|}{C}}-R$
$CH-O-\overset{O}{\overset{\|}{C}}-R$
$CH_2-O-\overset{O}{\overset{\|}{C}}-R$

OH^-/H_2O or H^+/H_2O

✓ Ester of glycerol and aldehyde)
✓ found in oil seeds.

CH_2-OH / $CH-OH$ / CH_2-OH $+ 3R-COOH$ carboxylic acid.

✓ Acids obtained are long chain fatty acids — Stearic acid, Palmic acid, Oleic acid, Lauric acid: whose Na salts are used for soap preparation.

(b) By bacterial fermentation of Sugar:

$$\text{Sugar } (C_{12}H_{22}O_{11}) + \text{Enzyme (Acetobacter)} \rightarrow CH_3COOH$$

2. Industrial Preparation

(a) By oxidation of hydrocarbon.

$$R\text{-}CH_3 + O_2 \xrightarrow[\Delta]{\text{catalyst}} R\text{-}COOH \quad (\text{oxidn directly in air})$$

(b) Oxo Process

$$R\text{-}CH=CH_2 \xrightarrow[\text{i.e Water gas}]{H_2/CO} R\text{-}CH_2\text{-}CH_2\text{-}CHO + R\text{-}\underset{CHO}{CH}\text{-}CH_3$$

$[Co(CO)_4H]$ or $[Co(CO)_3H]$

$\downarrow H^+/K_2Cr_2O_7$

$$R\text{-}CH_2CH_2COOH + R\text{-}\underset{CH_3}{CH}\text{-}COOH$$

(c) By passing CO (g) through Alcohol at very high pressure:

$$R\text{-}OH + CO \xrightarrow[Rh/I_2]{\text{high P}} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH.$$

✓ Carbonation of alcohol takes place.

(x) Synthetic Reactions

(i) By oxidation of aldehyde or 1°-alcohol.

$$R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-OH$$

$$R-CH_2-OH \xrightarrow{[O]} R-\overset{O}{\overset{\|}{C}}-OH$$

(ii) Grignard Synthesis:-

Passing $\xrightarrow{DRY} CO_2(g)$ through Grignard reagent, followed by hydrolysis, gives carboxylic acid.

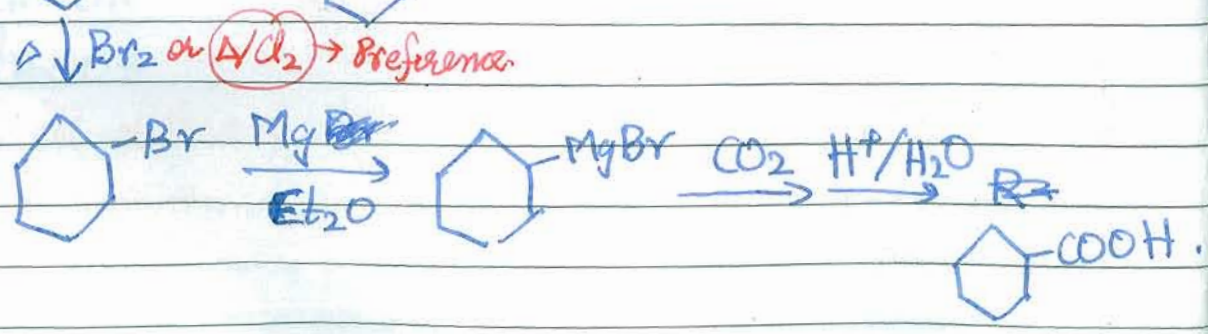
$$R-MgX + (CO_2(dry)) \xrightarrow{Et_2O} \xrightarrow{H^+/H_2O} R-COOH.$$

Mechanism:-

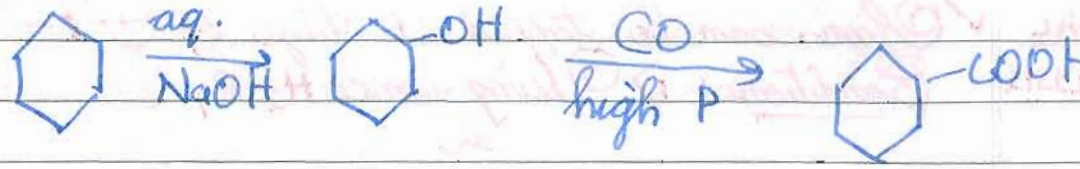
$$R^{\ominus} \text{ (from } RMgX) \longrightarrow \overset{O}{\overset{\|}{C}}=O \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^-Mg^+X \xrightarrow{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-OH.$$

/ $CO_2(g)$ should be dry. ∵ $CO_2(g)$ wet i.e. will react with H_2O first to produce H_2CO_3.

Q. to ?



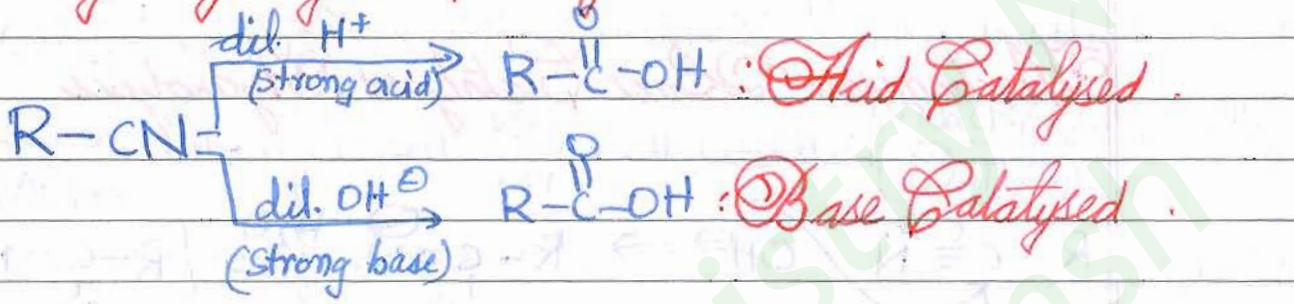
M2 ═



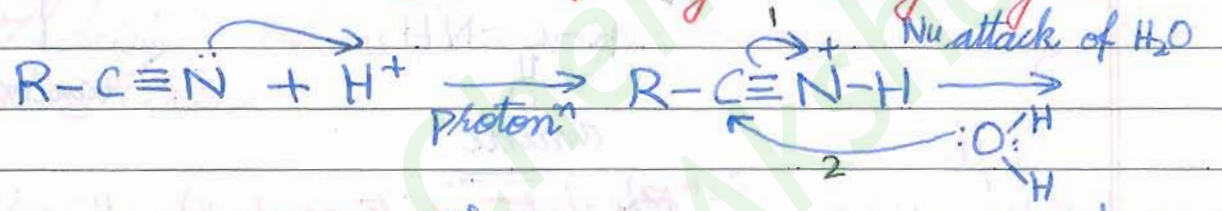
✓ Grignard method is an effective method of bringing $-COOH$ to C_6H_6.

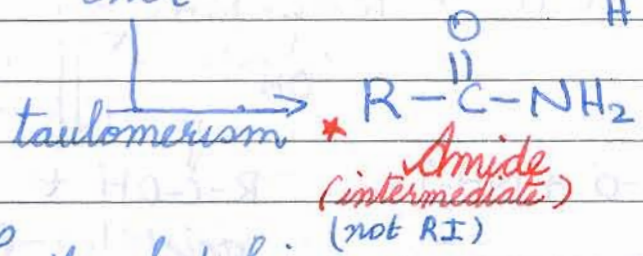
Imp:

(iii) By hydrolysis of Cyanide (Nitrile).

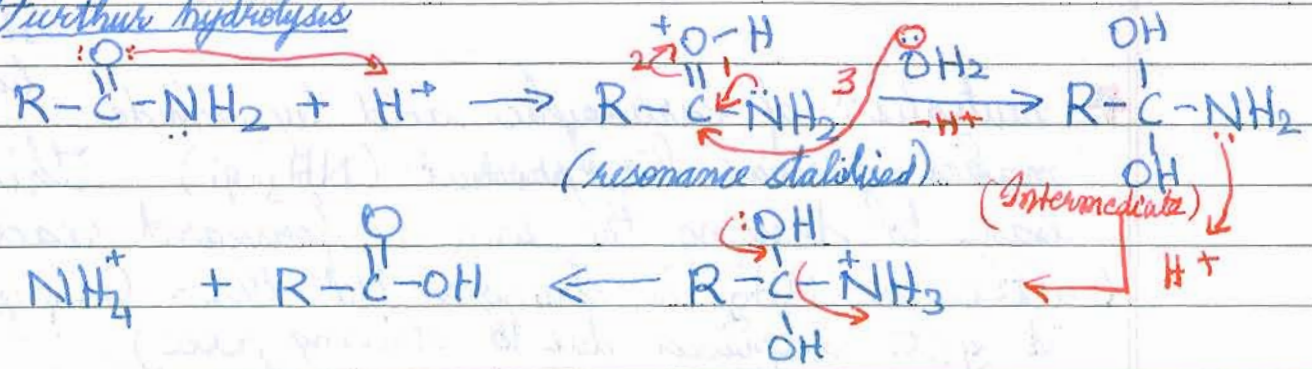


Mechanism : Acid Catalysed Hydrolysis.





* Further hydrolysis



classmate
Date 8-10-20
Page

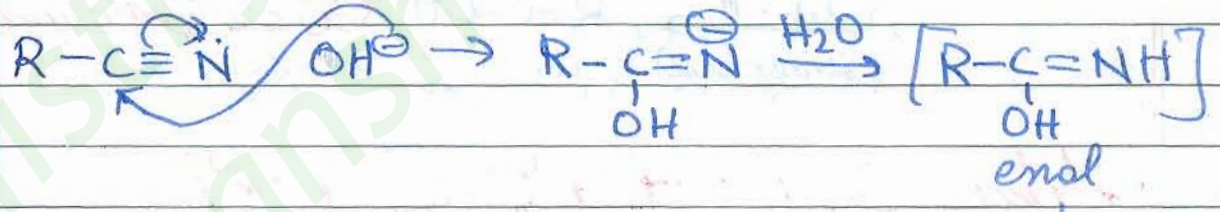
PARTIAL HYDROLYSIS

✓ Rxn. can be stopped at stage of Amide:
Condition: 1) Using conc. H_2SO_4.
or
2) Cold, conc. HCl.

✓ Amide produced from cyanide hydrolysis can only be produced primary. Secondary & tertiary can't be produced.

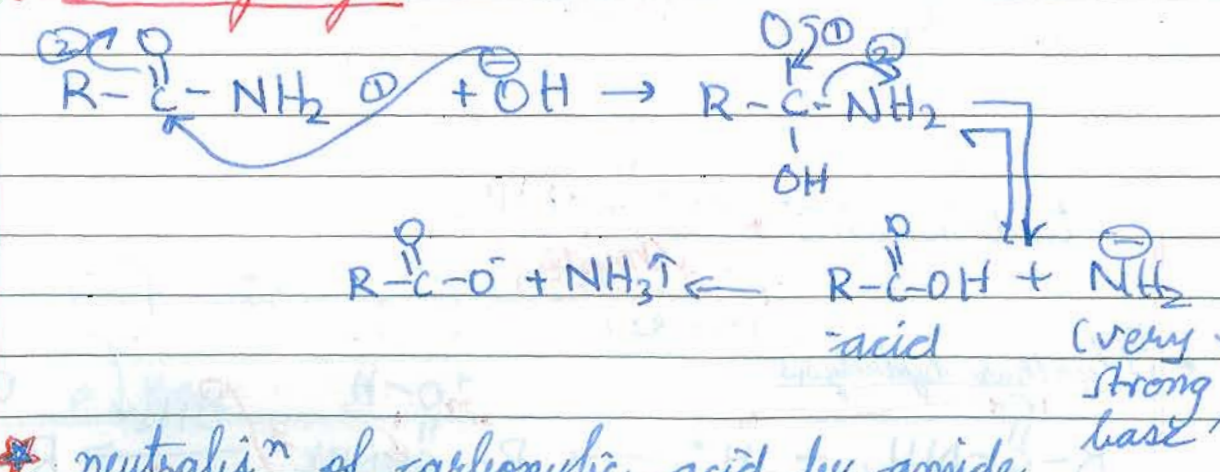
—x—

Mechanism: Base Catalysed Hydrolysis



(Intermediate product)

Further hydrolysis



* neutralisⁿ of carboxylic acid by amide makes gaseous bi-product ($NH_3(g)$). This leads to driving the rxn in forward reaction. (although NH_2^- is stronger $Nu^\ominus$ than $O.$, yet it gets displaced due to driving force).

* To prevent further hydrolysis (base catalyzed) of cyanide at amide level by adding
  * H_2O_2 (hydrogen peroxide) — catalyst

Q. CH_3CH_2COOH to $CH_3CH_2CH_2COOH$.

$CH_3CH_2COOH \xrightarrow{H_2/Pt \text{ or } LiAlH_4} CH_3CH_2CH_3 \xrightarrow{CN^\ominus} CH_3CH_2CH_2CN \xrightarrow{H^+} CH_3CH_2CH_2COOH$

$CH_3CH_2COOH \xrightarrow{LiAlH_4} CH_3CH_2CH_2OH \xrightarrow[M1]{PCl_5} CH_3CH_2CH_2Cl \xrightarrow[(ii)\ H^+/H_2O]{(i)\ NaCN/KCN,\ H^+/H_2O} CH_3CH_2CH_2COOH$

$CH_3CH_2CH_2OH \xrightarrow[M2]{CO/\text{high } P} CH_3CH_2CH_2COOH$

(iv) Addition of a Carboxylic acid containing α-H to Alkene.

$CH_3-CH=CH_2 + CH_3CH_2-COOH \xrightarrow[\Delta]{H_2O_2} CH_3-\underset{H}{CH}-CH_2-\underset{CH_3}{CH}-COOH$

Mechanism

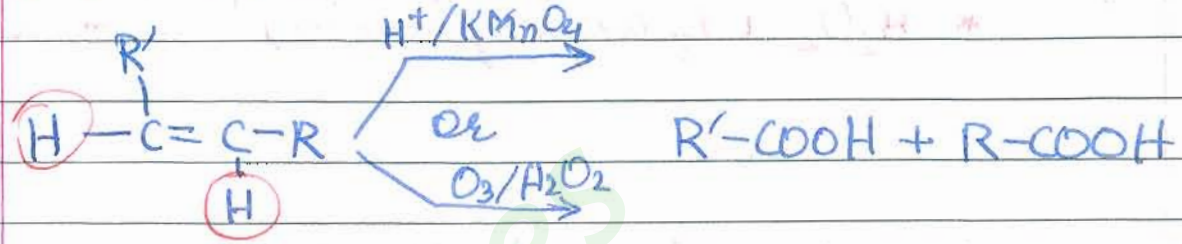
$HO^\cdot$ (from H_2O_2) $+ H-CH(CH_3)-COOH \longrightarrow {}^\cdot CH(CH_3)-COOH$

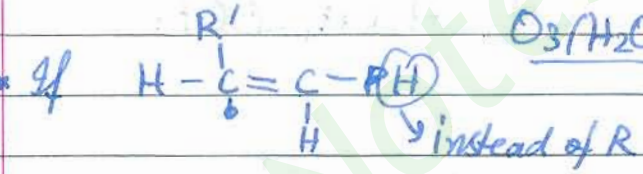
$CH_3-CH=CH_2 + {}^\cdot CH(CH_3)-COOH \rightarrow CH_3-\dot{C}H-CH_2-CH(CH_3)-COOH$

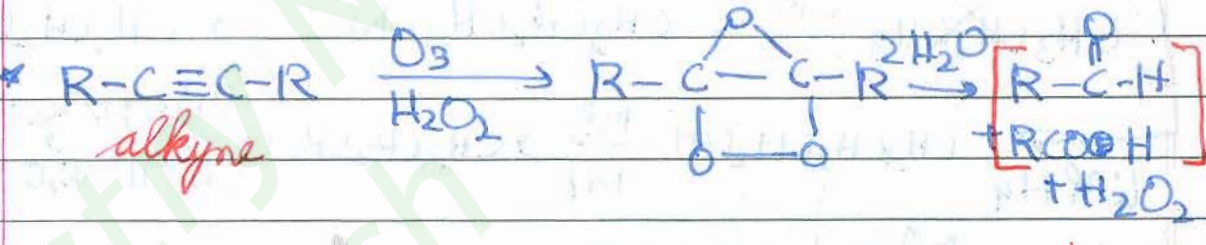
$\dot{O}H + CH_3-CH_2-CH_2-CH(CH_3)-COOH \leftarrow H_2O.$

★ Previously done methods

(v) ★ ~~Oxidic~~ Acidic cleavage of C=C in presence of $H^+/KMnO_4$ or O_3/H_2O_2 : OXIDATIVE OZONOLYSIS

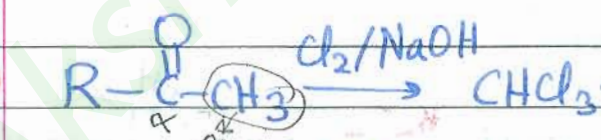


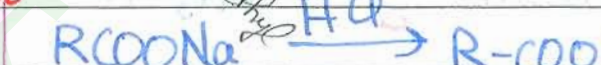
* If 

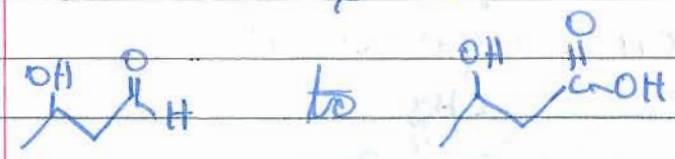
(vi) ★ 

* had it been terminal alkyne, CO_2 would be produced.

(vii) Haloform reaction





Q. 

M1 :- Tollen's Reagent (or $Ag_2O_{(aq)}$)

M2 :- Fehling's solution

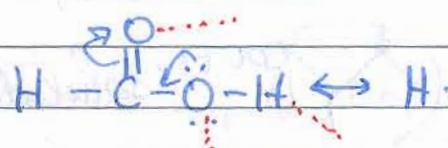
★ Properties

(1) Physical properties.

(a) Boiling point :

Except formic acid (HCOOH), all other carboxylic acids have higher B.Pt. than H_2O.

B.Pt. : $HCOOH < H_2O$.

Reason :- 

So,

H-bonding ability of one oxygen is reduced due to resonance. So, it has B.Pt $< H_2O$.

With same no. of C, ~~R-COOH~~

B.Pt :- $RCOOH > ROH > R-O-R > R-CHO > R-CO-R > RCl > R-X$

It is because of exhaustive bonding (H-bonding) ability of acids.

Among acid, B.Pt. : increases with molar mass (∵ of increase in Van-der-wall fore of attraction).

* All di-acids are SOLID at RT.

High jump in B.Pt occurs with ↑ in carboxylic functional group.

* Branching lowers B.Pt.

(b) Solubility (in H_2O)

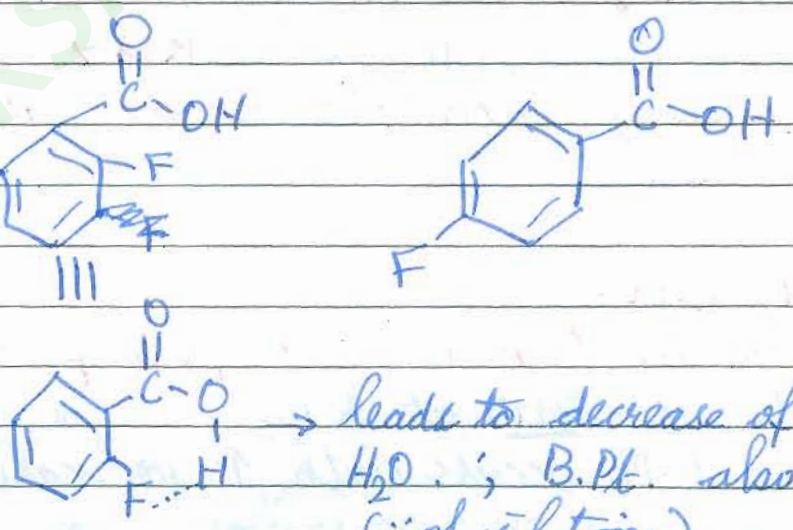
Starting from C_1 to C_4, carboxylic chain (aliphatic) has infinite solubility in H_2O. (due to their ability to form intermolecular H-bond with H_2O).

Solubility decreases on further increase of no. of carbons (∵ of increasing dominance of hydrophobic part).

Q.

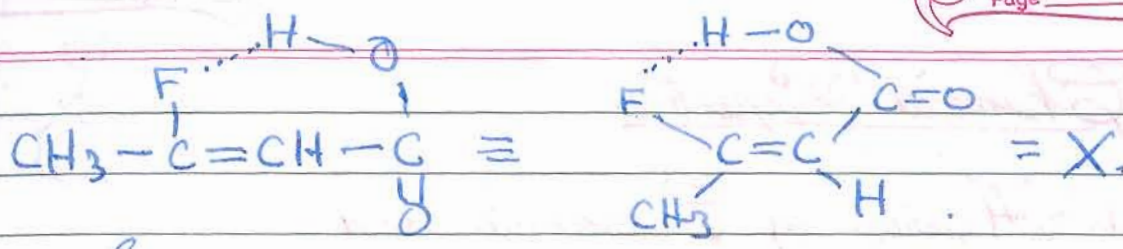
→ smaller fⁿ of hydrophobic area
: Solubility
larger surface area of hydrophobic part

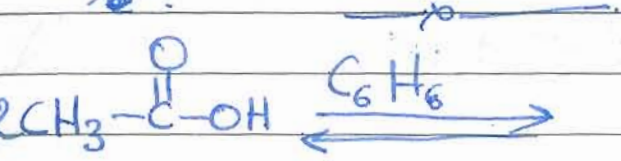
* Branching increases solubility (see surface area increase or decrease of hydrophobic fraction).

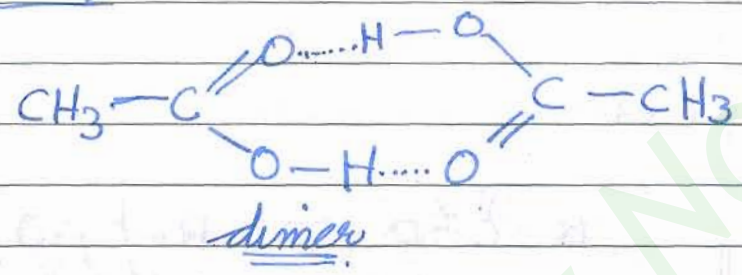
Q. 

→ leads to decrease of solubility in H_2O.; B.Pt. also DECREASES. (∵ of isolation)

Q. $CH_3-\overset{F}{C}H=CH-COOH$. It has 2 isomers X & Y. X is more volatile than Y.







dimer

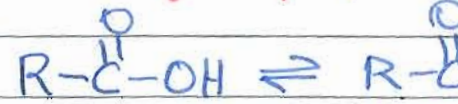
* In organic solvents (C_6H_6, CF_4, THF, DMF), carboxylic acid remain partially DIMERISED (↑)
* In aqueous solvent (H_2O), carboxylic acid remains as a monomer (∵ of H-bonding with H_2O)

* Hydroxylic solvents (alcohol, carboxylic acid) add^n ↓ equi. content of DIMER (by forming H-bond with monomer acid, reducing its dimer content).

* Carboxylic acid has both hydrophobic and hydrophillic part. So, it would be soluble both in oil and water

(2) Chemical Properties

(a) Acidity of Carboxylic acid.



* carboxylic acid is stronger acid than any alcohol (aromatic or aliphatic).

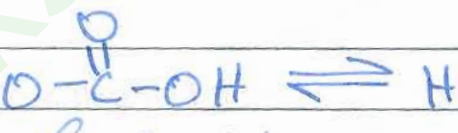
∵

(resonance stabilised conjugate base).

Although resonance also occurs in alcohols :-

resonance.

But, by the rule (-ve charge on electro -ve atom), carboxylic acid is stronger.

* 

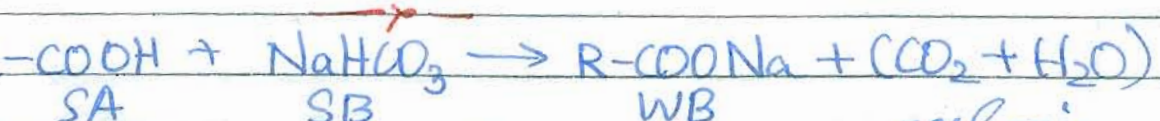
carbonic acid.

resonance stabilised.

resonance opposition reduces acidity as O^- compared to carboxylic acid.

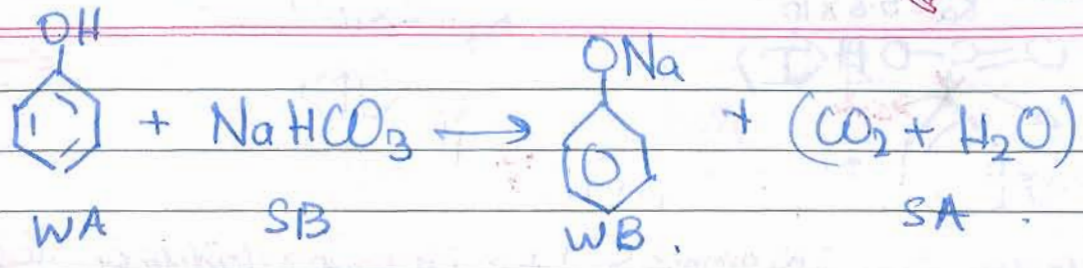
* ~~for~~ Acidity :- Phenol < Carbonic acid < Carboxylic acid

↳ No exception.

* 

This rxn is spontaneous.

classmate
Date
Page



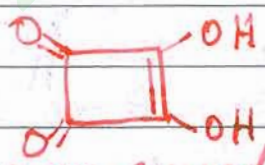
The above reaction is non-spontaneous.

* **$NaHCO_3$ test**:- It is used to detect presence of carboxylic acid.
It is also used to distinguish carboxylic acid and any other compound (except sulphonic acid).
It is used to separate mixture of carboxylic acid and phenol :-

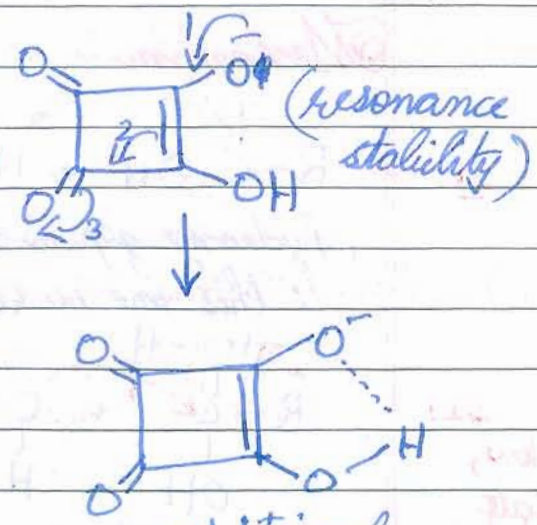
RCOOH, PhOH } in ether —aq. $NaHCO_3$→ PhOH (ether) / RCOONa (aq)

* Exceptional case: compound (phenol) having nitro grp (o, m or p) increases its acidity greatly (more than carbonic acid). So, then, it would show $NaHCO_3$ test.

* Squaric acid

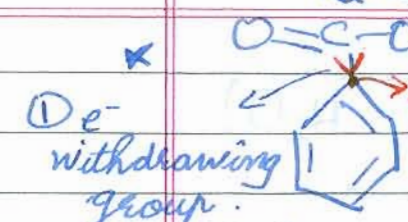


↳ Its acidity even exceeds normal carboxylic acid.



§ Very big exception

$K_a = 5.6 \times 10^{-5}$ (I) $\quad$ $K_a = 2 \times 10^{-5}$ (II)



① e^- withdrawing group.
② Resonance factor

$\uparrow R \; \downarrow -I$; $CH_3 \xrightarrow{+I} C-OH$

$\Downarrow$

$\uparrow R$ overall $<$ $+I$ of Me. So, Acidity of I > II.

* Greater s character, increases E_N. (except formic acid)

$H-C(=O)-OH$ III . So, net acidity :- III > I > II

$K_a = 2 \times 10^{-4}$

§ Chemical Reactions

1) With Alcohol : FISCHER ESTERIFICATION.

When an aliphatic OR aromatic acid is treated with an alcohol in presence of conc. H_2SO_4 as catalyst, at slightly elevated temp (50-60°C), condensation takes place to give ester.

$$R-C(=O)-OH + R'OH \xrightarrow[\text{conc. } H_2SO_4]{H^+,\ \Delta} R-C(=O)-O-R' + H_2O$$

Mechanism

S1 $\quad R-C(=O)-OH + H^+ \underset{}{\overset{\text{fast}}{\rightleftharpoons}} R-C(=O^+-H)-OH$

(hydroxy grp is not hydrolysed ∵ this one is resonance stabilised)

S2: Slow, Rate determining $\quad R-C(OH)_2 + :O-R' \xrightarrow{-H^+} R-C(OH)_2-O-R' \xrightarrow{H^+} R-C(OH)(O^+H_2)-OR' \rightleftharpoons R-C(OH)_2-OR'$

($Nu^\ominus$ attack at carbonyl carbon) $\quad$ Tetrahedral Intermediate (gem-diol)

classmate
Date
Page

→ $R-\underset{\underset{\underset{+}{O}-H}{\|}}{C}-OR' \xrightarrow{-H^+} R-\overset{O}{\overset{\|}{C}}-O-R'$ ester.

* Imp :- Oxygen of alcohol gets retained in the ester (in esterification).

i.e $R-\overset{O}{\overset{\|}{C}}-\boxed{O:H \quad H}O-R'$ ☐ X ☐ ✓

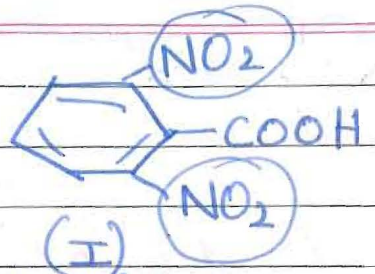
eg : $CH_3CH_2COOH + CH_3CH_2-{}^{18}OH \xrightarrow{H^+} CH_3CH_2-\overset{O}{\overset{\|}{C}}-{}^{18}OC_2H_5$

eg : $CH_3-\overset{O}{\overset{\|}{C}}-{}^{18}OH \leftrightarrow CH_3-\overset{{}^{18}O}{\overset{\|}{C}}-OH + CH_3CH_2OH \xrightarrow{H^+/\Delta} CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5 + CH_3-\overset{{}^{18}O}{\overset{\|}{C}}-OC_2H_5$

(minor) (major)

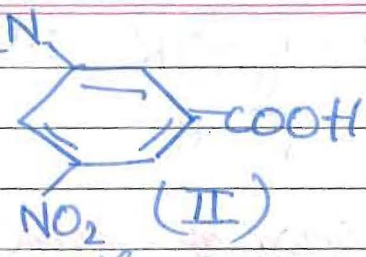
* Note :- Electron withdrawing group present in acid (specially aromatic) increases reactivity, whereas, e⁻ donating grp ↓ reactivity of acid towards Fischer Esterification.
* ~~If we~~ HCl
* Conc. ~~H_2SO_4~~ is considered to be a better cata catalyst especially when alcohol is 2° or 3°.
(∵ in 2° or 3° alcohol, conc. H_2SO_4 will bring out its dehydration to produce alkene).
* With common acid, under identical cond^n (catalyst, T..) less hindered alcohol undergo faster esterific^n (∵ small sized $Nu^\ominus$ is more reactive) than more hindered alcohol.

Q. Reactivity



(I)

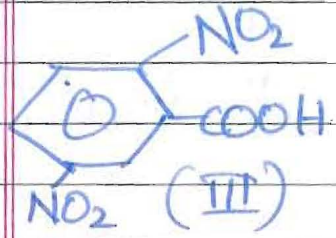
steric hinderance finishes possibility of $Nu^{\ominus}$ attack.



(II)

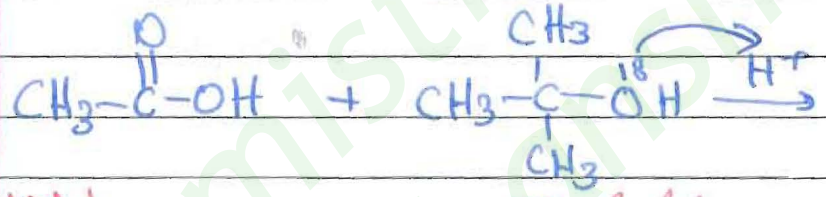
Although no R effect shown but steric hinderance effect will dominate R effect in FER

↳ Fischer Esterification rxn



(III)

net reactivity : III > II > I

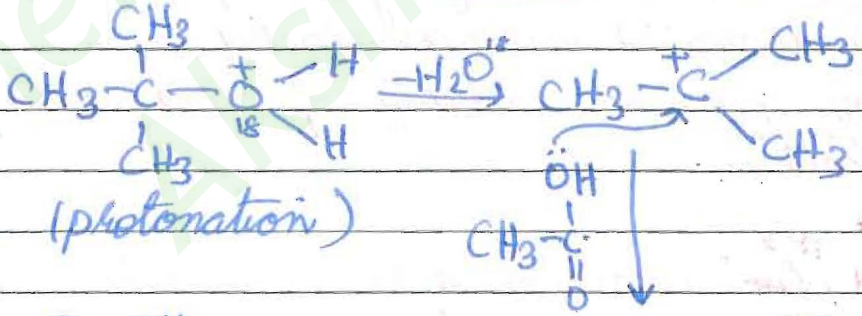
Q. 

EXCEPTION

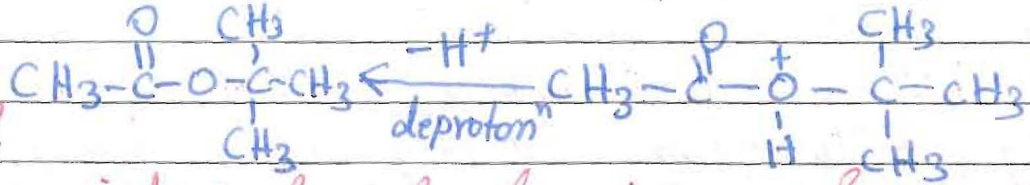
↓

If 3° alcohol is used in esterification rxn, protonation of alcohol takes place, instead of carboxylic acid and hence, oxygen of alcohol no longer remains in ester.

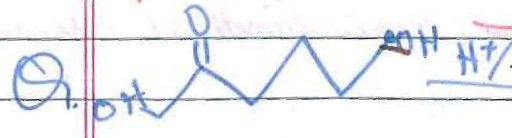
3° alcohol



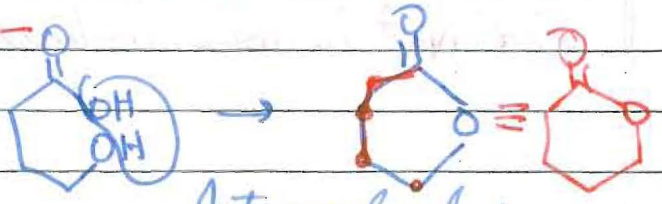
(protonation)



deprotonation

Q. 

LACTONISATION



Intramolecular esterification.

Chemistry Notes Akshansh

* Note:- Every cyclic ester is called LACTONE

classmate Date 13.10.20 Page

* 4 or 5 carbon chain of hydroxy acid gives Lactone.

2) Rxn with PCl_5, PCl_3 or $SOCl_2$ or $(COCl)_2$ (or $\underset{COCl}{\overset{COCl}{|}}$ oxyl chloride)

$$R-\overset{O}{\overset{\|}{C}}-OH + PCl_5 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

(aliphatic or aromatic) carboxylic acid — acetyl chloride do acid chloride

$$+ PCl_3 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

$$+ SOCl_2 \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + HCl\uparrow$$

$$+ \underset{COCl}{\overset{COCl}{|}} \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + CO\uparrow + CO_2\uparrow + HCl\uparrow$$

acid chloride — one of most reactive f.g.

3) Dehydration Rxn.

$$R-\overset{O}{\overset{\|}{C}}-OH + H-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\Delta]{P_2O_5} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + H_2O$$

anhydride.

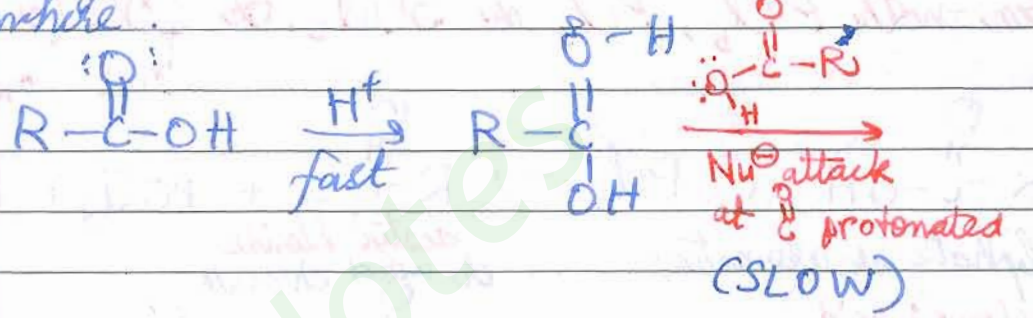
* In this rxn, drying agent(s) are reqd.
Main drying agents: ✓ P_2O_5
✓ V_2O_5
✓ conc. H_2SO_4

* when carboxylic acid is heated with either P_2O_5/V_2O_5 or H_2SO_4 (conc.), intermolecular dehydrn takes place & anhydride is formed.

classmate
Date
Page

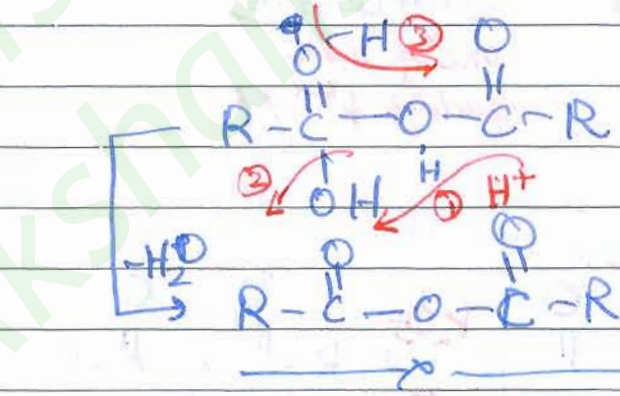
Mechanism

* Rxn is acid catalysed. All reactant, catalyst, everywhere is acid. So, take H^+ from any where.

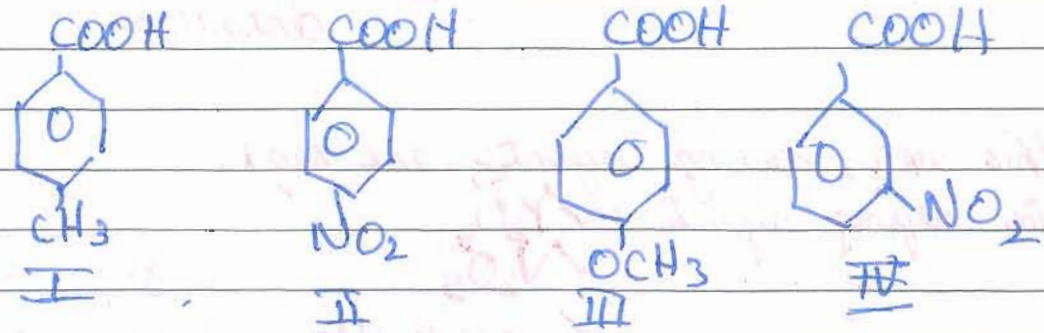


* Keep in mind :-
  - Smaller alkyl grp in carboxylic acid ↑ reactivity
  - e^- withdrawing grp in carboxylic acid ↑ reactivity.

→ on which nucleophilic attack takes place



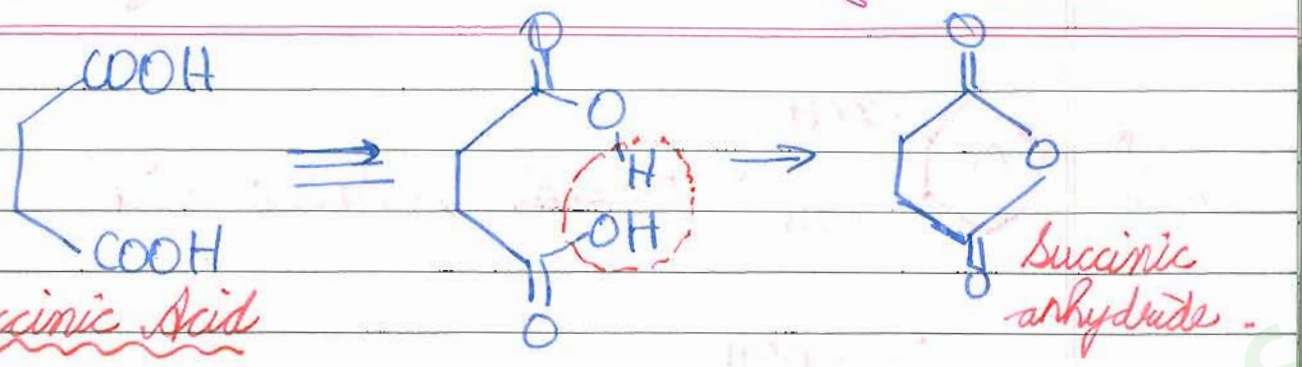
Q.



Reactivity in dehydrⁿ rxn :- II > IV > I > III

: Xylene

classmate
Date
Page

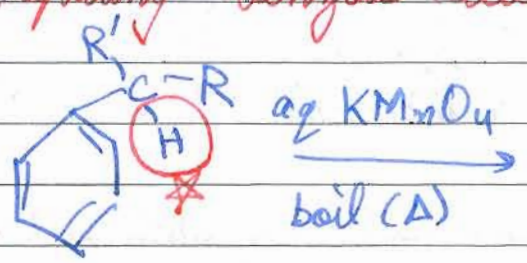


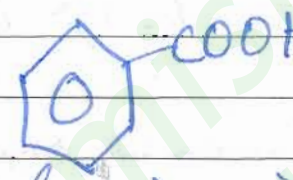
Succinic Acid

Succinic anhydride.

* If 1,4 or 1,5 diacid is heated, it dehydrates intramolecularly to give 5 or 6 membered cyclic anhydride even in absence of any drying agent as catalyst.

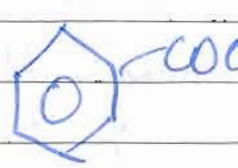
* Preparing benzoic acid.





benzoic acid.

* Benzoic acid is always formed, no matter what alkyl gps are present
* In above rxn, presence of atleast one α-H is necessary.

3. * $A(C_8H_{10}) \xrightarrow[\Delta]{KMnO_4(aq)}$ 

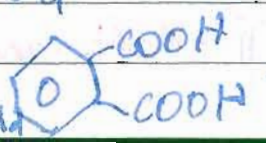
$\Rightarrow A =$

Q. $A(C_8H_{10}) \xrightarrow[\Delta(boil)]{KMnO_4} C_8H_6O_4$ ~~Cdimeth~~

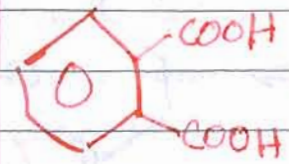
$\Rightarrow A =$ dimethyl benzene.

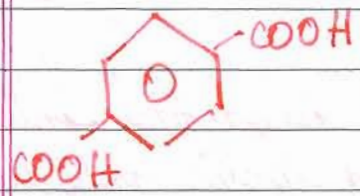
→ posⁿ of methyl can be known from 2nd rxn.

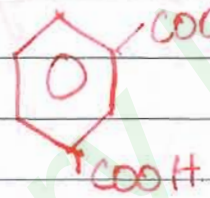
Q. $C_8H_6O_4 \xrightarrow{\Delta} C_8H_4O_3 + H_2O$

$\Rightarrow$ 

o-Phthalic acid

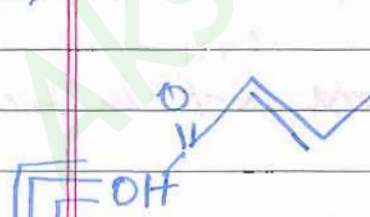
* ortho  → ~~O-phthalic~~ O-phthalic acid

* para  :- terphthalic acid

* meta  :- isophthalic acid.

* M.Pt :- ter > isophalic acid

Q. but-2-enedioic acid.

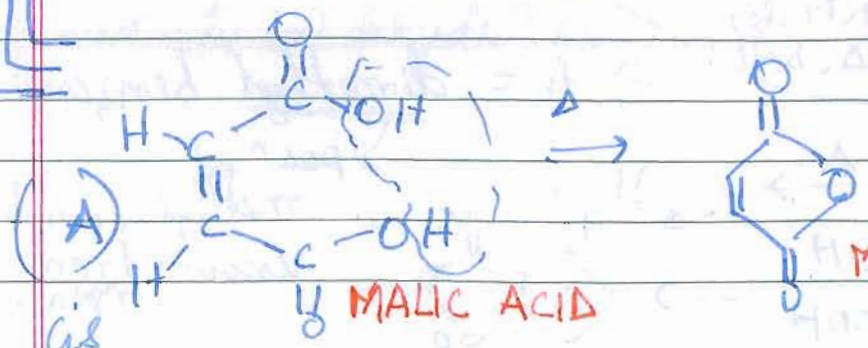


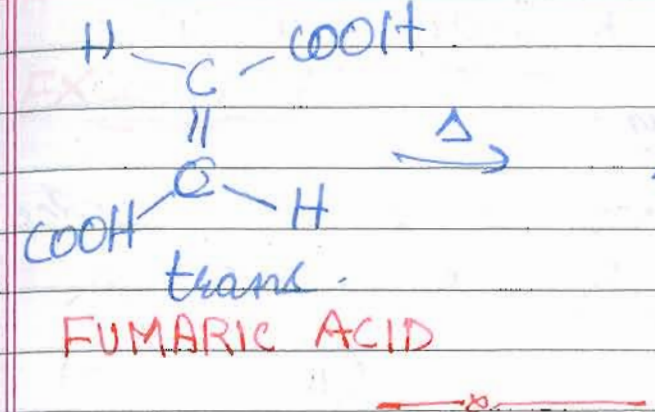
exists in 2 stereoisomeric forms A & B

A $\xrightarrow{\Delta}$ loses H_2O forming anhydride of 4 carbon.

B $\xrightarrow{\Delta}$ doesn't hydrate.

A :- cis, B : trans.





FUMARIC ACID

4) Decarboxylation of Acids.

When a carboxylic acid is heated with soda lime, decarboxylⁿ takes place & alkane is produced.

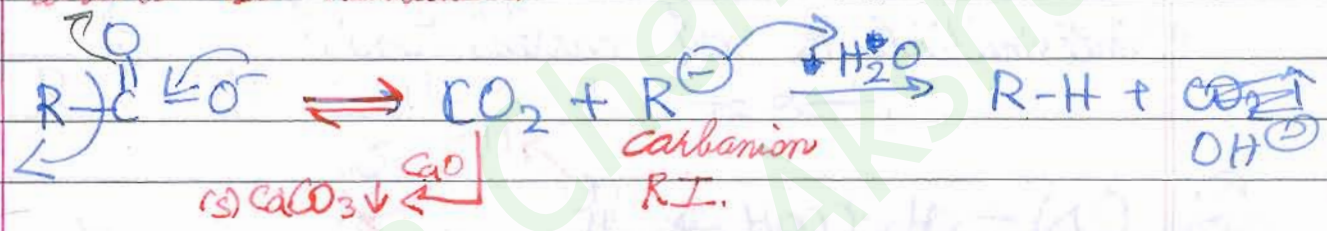
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NaOH/CaO} R-H + CO_2\uparrow$$

(NaOH/CaO above the arrow)

alkane.

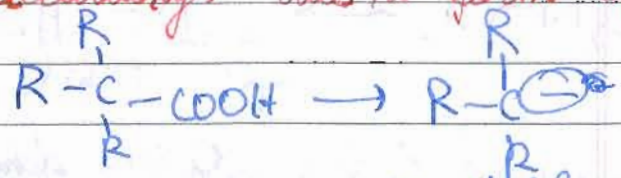
* Rxn takes place in strongly basic medium & hence, acid is 1st neutralised.

Rxn mech:

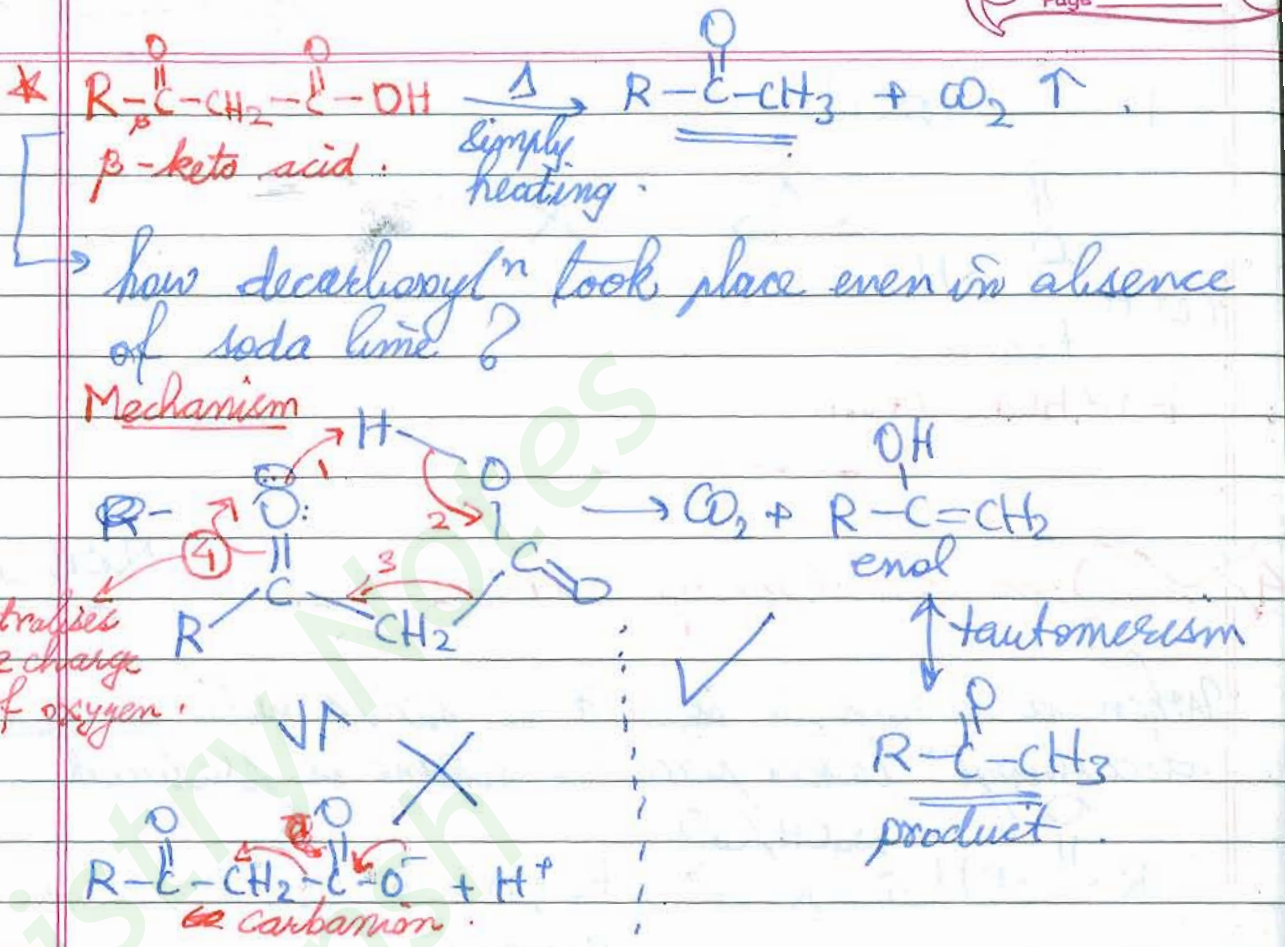


* CaO is reqd to react with CO_2 to give $CaCO_3$ (ppt.) & hence, helps in completion of rxn (Le chatelier principle).

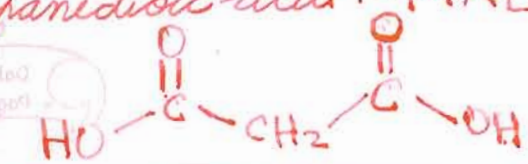
* Tertiary acid fails in decarboxylⁿ due to formⁿ of 3° carbanion (unstable).



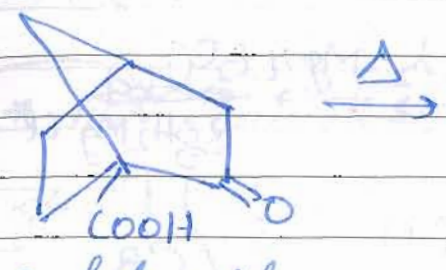
* Presence of e⁻ withdrawing grp ↑ reactivity & vice-versa.
* Aromatic acids are less reactive than aliphatic in decarboxylⁿ (resonance) →


R–C(=O)–CH2–C(=O)–OH
β-keto acid.
Δ
simply heating.
R–C(=O)–CH3 + CO2 ↑
how decarboxylⁿ took place even in absence of soda lime?
Mechanism
neutralises +ve charge of oxygen.
CO2 + R–C(OH)=CH2
enol
tautomerism
R–C(=O)–CH3
product.
R–C(=O)–CH2–C(=O)–O⁻ + H⁺
ex carbanion.
α alkyl" of β-keto acid ↑ its reactivity indicating that it proceeds through enol intermediate & not carbanion.
O2N–CH2–COOH
O2N–CH3 ⟷ N(OH)=CH2
enol.
+ CO2 ↑
dehydr"
highly strained
decarboxyl"
Propanedioic acid
or Malonic acid.
CH3–C(=O)–OH

★ Propanedioic acid :- MALONIC ACID



★ EXCEPTION

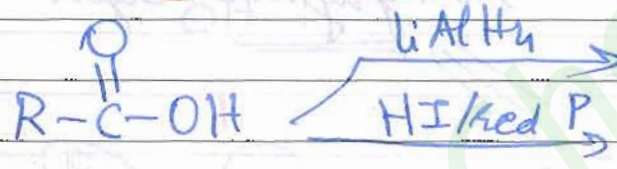


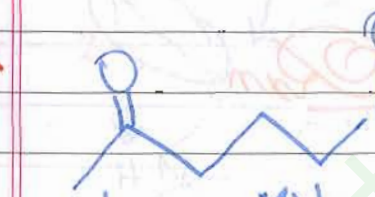
β-keto acid

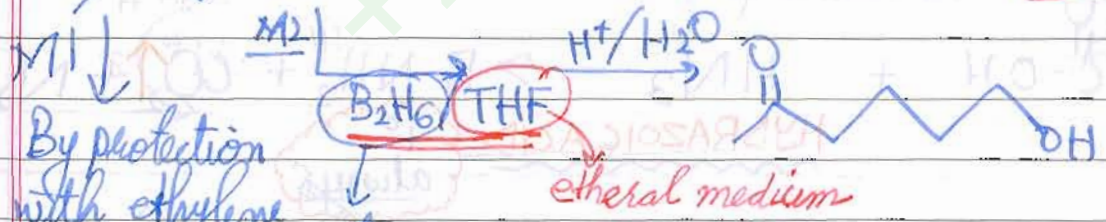
This product is itself not formed ∵ bridge-head carbon can't be sp^2 hybridised

★ Planarity can't be acquired on heating.
★ It decarboxylates with difficulty.

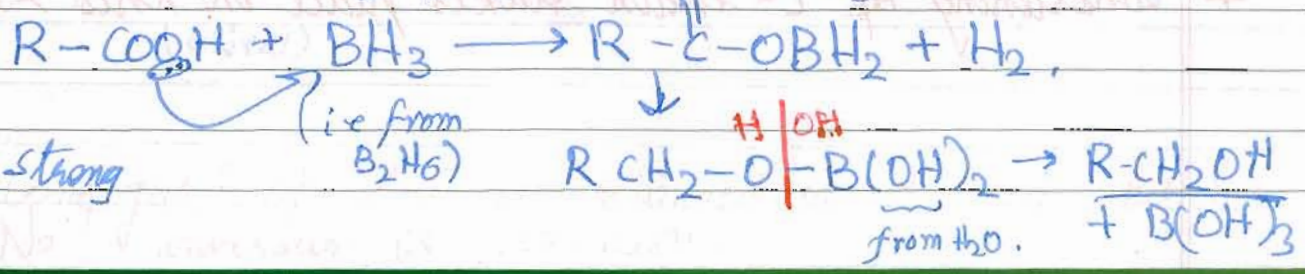
5) Reduction Rxn.



★  : If we want to reduce acid selectively



Mechanism → Rxn comes into play due to reactivity of COOH towards BH_3.



Q $R-COOH \longrightarrow RCH_2CH_2COOH$?

M1 Reduce → CO / high P → Reduce → CO / high P

M2 $RCOOH \xrightarrow{LiAlH_4} RCH_2OH \xrightarrow{SOCl_2} \xrightarrow{Mg/Et_2O} RCH_2MgCl$

$RCH_2CH_2CH_2OH \xrightarrow{[O]} RCH_2CH_2COOH$

Q $CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH \longrightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_3$

$CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{Mg/Et_2O} CH_3CH_2CH_2MgCl$ (from grignard reagent)

6) SOMLET RXN

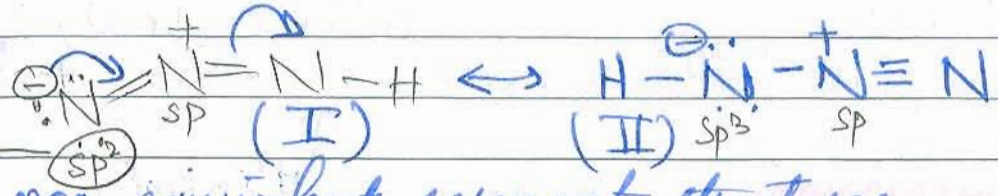
or Somlet-Schmidt Rxn

$R-\overset{O}{\overset{\|}{C}}-OH + HN_3 \longrightarrow R-NH_2 + CO_2\uparrow + N_2$

HYDRAZOIC ACID → 1° always

* It is a ~~distinguishing~~ distinguishing test for carboxylic acid (gases evolved)
* Shortening of C-chain takes place in this rxn

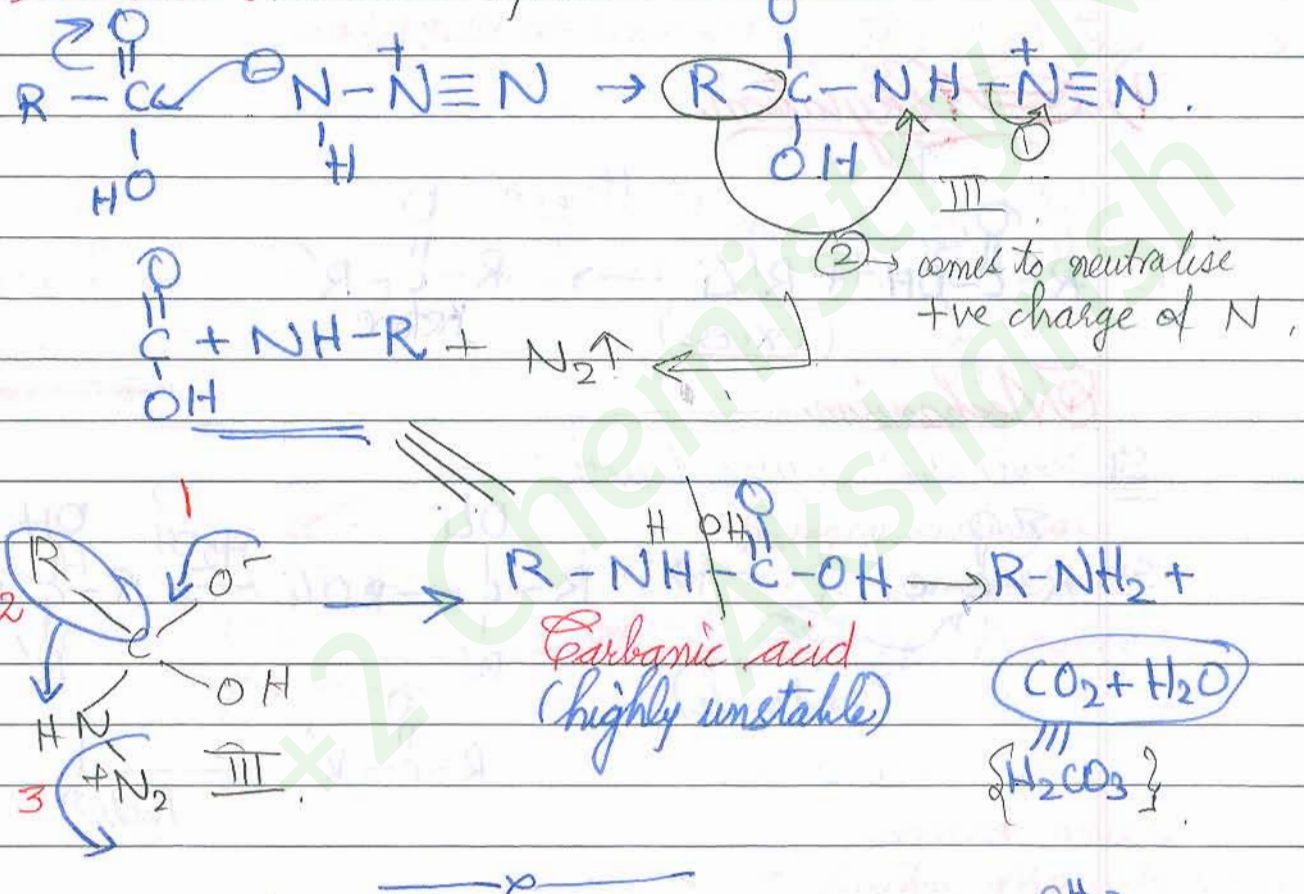
Structure of N_3H.



* non equivalent resonant structures.

→ greater s character of this N. So, greater EN than its other resonance structure. Hence, (I) is more stable than (II).

* Mechanism: Condensed form



Q. $CH_3CH_2-\underset{H}{\overset{CH_3}{C^*}}-COOH + HN_3 \rightarrow CH_3CH_2-\underset{H}{\overset{CH_3}{C}}-NH_2$

(chiral)

* Configuration at α-C is retained if α-C is chiral. No inversion or racemisation.

Q. $R-CH_2-COOH \longrightarrow R-COOH$?

M2 / $LiAlH_4$

Sonlet Rxn ↓ HN_3

RCH_2NH_2 (1°) $\xrightarrow{HONO}$ RCH_2OH $\xrightarrow{[O]}$ $H^+/K_2Cr_2O_7$

$RCH_2OH \xrightarrow{H^+/KMnO_4}$ $R-COOH$

$RCH_2CH_2OH \xrightarrow[\Delta]{Al_2O_3}$ $RCH=CH_2$

$RCH_2CH_2OH \xrightarrow{PCl_5}$ $RCH_2CH_2Cl \xrightarrow{alc.\ KOH/EtOH\ (E2\ Rxn)}$ $RCH=CH_2$

7) Alkylation

$$R-\underset{\underset{O}{\|}}{C}-OH + R'Li \xrightarrow{R^{\ominus}\ (Strong\ base)} R-\underset{\underset{O}{\|}}{C}-R'$$

(excess) — Ketone

Mechanism

S1 Neutralisⁿ → uses 1 mole.

S2 $R-\underset{\underset{O}{\|}}{C}-OLi \xrightarrow{R'^{\ominus}\ (2nd\ mole)} R-\underset{\underset{R'}{|}}{\overset{\overset{OLi}{|}}{C}}-OLi \xrightarrow{H_2O} R-\underset{\underset{R'}{|}}{\overset{\overset{OH}{|}}{C}}-OH$ (gem diol)

$R-\underset{\underset{R'}{|}}{\overset{\overset{OH}{|}}{C}}-OH \xrightarrow{hydrⁿ} R-\underset{\underset{O}{\|}}{C}-R'$

8) α- halogenation

* carboxylic acid containing α-H.

(HVZ Rxn i.e Hell Volhard Zelensky Rxn.)

$$R-\underset{\underset{H}{|}}{CH}-COOH \xrightarrow[I_2\ (rare)\ +\ Red\ P]{Cl_2\ or\ Br_2\ or\ (common)} R-\underset{\underset{Cl\ (or\ Br\ or\ I)}{|}}{CH}-COOH$$

Mechanism

S1 $Cl_2 + \underbrace{P\text{-red}}_{\text{:. } Cl_2 \text{ is reacting with Phosphourous halide produced from P-red.}} \longrightarrow PCl_5$ (or PBr_3 if Br is attacking)

$PCl_5 \xrightarrow{RCH_2COOH}$ $R-CH_2-\overset{O}{\overset{\|}{C}}-Cl$ ⇌ $R-\overset{2}{CH}=\overset{1}{C}(OH)-Cl$

Acid chloride (It is the one that undergoes α-halogen") — (slight tautomerism shown) — This end tautomer is halogenated

$R-CH(Cl)-\overset{O}{\overset{\|}{C}}-Cl \xleftarrow{Cl^-} R-CH(Cl)-\overset{+OH}{\overset{\|}{C}}-Cl \xleftarrow{} R-\overset{\oplus}{C}H-\overset{+OH}{\overset{\|}{C}}-Cl$

$Cl-Cl$

S2 $R-CH(Cl)-\overset{O}{\overset{\|}{C}}-Cl + R-CH_2-\overset{O}{\overset{\|}{C}}-OH \rightarrow R-CH(Cl)-COOH +$ Product

(highly reactive) — halogen exchange

$+ R-CH_2-\overset{O}{\overset{\|}{C}}-Cl$

(Produced which further proceeds rxn)

★ Product may/would undergo $Nu^{\ominus}$ attacks.

$R-CH(Br)-COOH + NaCN \rightarrow R-CH(CN)-COOH \xrightarrow[H_2O]{H^+} R-CH(COOH)-COOH$

basic salt

$NaSH$ ↓

$R-CH(SH)-COOH$.

★ Iodenⁿ is easy for SN2. So, mainly I_2/P is used.

★ If HVZ rxn produces α-C chiral, then, product will be a racemic mixture.

★ If $Nu^{\ominus}$ is made to attack the product in previous rxn, & if, its a strong base, neutralisⁿ also takes place.

Q $CH_3-COOH \xrightarrow{I_2/P} CH_2(I)-COOH$

Its basic & hence undergoes neutralisⁿ first

$\xrightarrow{Na/Et_2O/\Delta}$ $CH_2(CH_2COONa)-COONa \xrightarrow{HCl}$ (COOH)(CH2COOH)

Its not basic & also enable to undergo Wurtz rxn

$\xrightarrow{Zn/\Delta}$ $CH_2(CH_2COOH)-COOH + ZnI_2$

9) Hundsdiecker rxn

$R-COOH \xrightarrow[\text{saturated (∵ its solubility is less)}]{Ag_2O\ (salt)} R-COOAg \xrightarrow[\text{non aqueous medium}]{Br_2/CCl_4,\ \Delta \text{ or } h\nu} R-Br + CO_2 + AgBr$

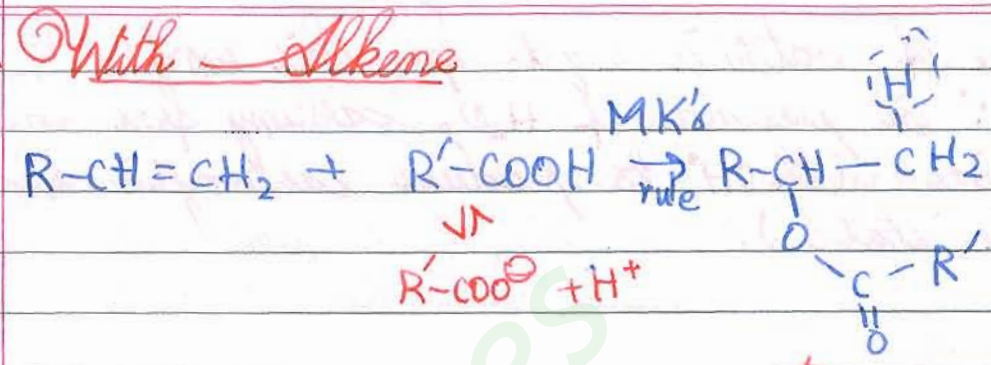
Mechanism -

Precipitation :- $R-COO^{\bullet}Ag + Br^{\bullet}-Br \rightarrow R-COO^{\bullet} + Br^{\bullet} + AgBr$

$R-COO^{\bullet} \xrightarrow{-CO_2} R^{\bullet} + Br^{\bullet} \rightarrow RBr$

(unstable although, less stable than $R^{\bullet}$)

11. With Alkene

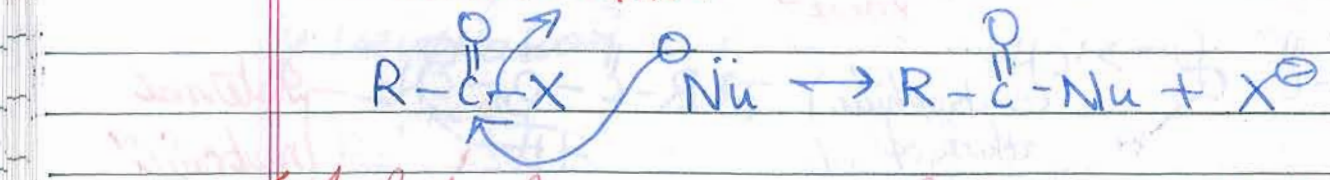


§ Acid Derivatives

→ derived from acids.
→ don't exist in nature as such
→ prepared in laboratory.

★ Key Points:

✓ All acid derivatives undergo nucleophilic substitution rxn.



✓ A better leaving grp would be one which is weaker base or its conjugate acid is stronger acid.

* Absence of water is reqd. for this rxn.
(∵ in presence of H_2O, carboxy free radical combines with $OH^\bullet$ to produce carboxylic acid to become stable).

⟶

Q $RCH_2COOH \longrightarrow R-COOH$?

Hundsdiecker $\downarrow Ag_2O/Br_2/\Delta$ ← [O]

$R-CH_2Br + \ldots + NaOH \xrightarrow{S_N2} R-OH \rightarrow RCH_2OH$

(aq)

⟶

* Cu_2O is used to catalyse decarboxylⁿ of benzoic acid.

⟶

* Decarboxylⁿ can also be done by Hundsdiecker rxn.
Method :- ✓ Remove CO_2 ($Ag_2O/Br_2/CCl_4/\Delta$)
✓ React with MgBr
✓ Hydrolyse.

⟶

10 With Diazomethane

$R-\overset{O}{\overset{\|}{C}}-OH + CH_2N_2 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O-CH_3$ + N_2

(diazomethane) → ester

$:CH_2$ Methyl carbene or $CH_2=C=O$ Ketene } Source of carbene.

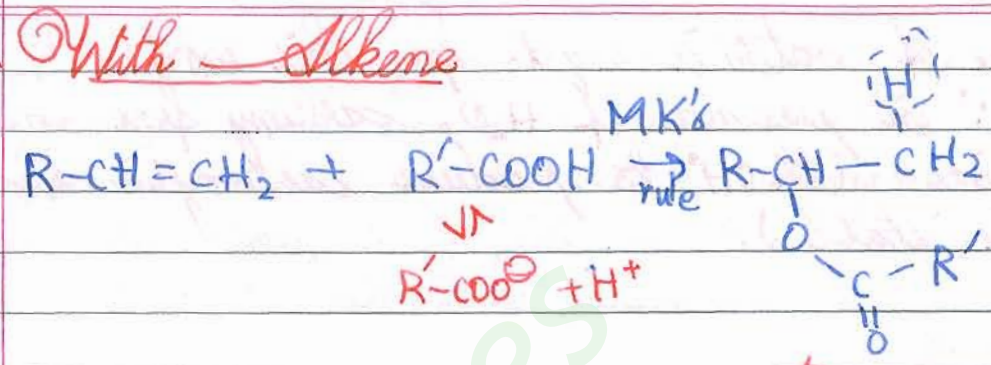
Mechanism

$R-\overset{O}{\overset{\|}{C}}-\ddot{O}-H \rightarrow :CH_2$ (electrophilic attack of carbene)

$\rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{+}{O}-\overset{\ominus}{C}H_2$ — Internal neutralisⁿ

$R-\overset{O}{\overset{\|}{C}}-O-CH_3$

11. With Alkene

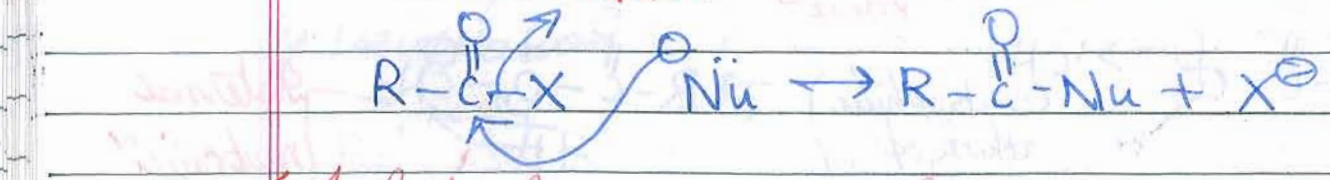


§ Acid Derivatives

→ derived from acids.
→ don't exist in nature as such
→ prepared in laboratory.

★ Key Points:

✓ All acid derivatives undergo nucleophilic substitution rxn.



✓ A better leaving grp would be one which is weaker base or its conjugate acid is stronger acid.

So, HCl (I) ROH (II) RCOOH (III) NH_3 (IV)

Strength of conj. acid :- I > III > II > IV

So, basic strength :- $Cl^- < RCOO^- < RO^- < NH_2^{\ominus}$

So, reactivity of acid derivatives towards $Nu^{\ominus}$ substitution rxn :- $Cl^- > RCOO^- > RO^- > NH_2^{\ominus}$ or Acid chloride > Anhydride > Ester > Amide

Q. $R-\overset{O}{\overset{\|}{C}}-OCH_3 + NH_2^{\ominus} \rightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + CH_3O^{\ominus}$ ✓ Spontaneous

$R-\overset{O}{\overset{\|}{C}}-OCH_3 + NaCl \rightarrow R-\overset{O}{\overset{\|}{C}}-Cl + CH_3ONa$ ✗ non-spontaneous.

** ester more stable than acid chloride. So, rxn is non spontaneous or spontaneous in reverse dir^n.

Acid Chloride.

$R-COOH \xrightarrow[PCl_3]{PCl_5,\ SOCl_2,\ (COCl)_2} R-\overset{O}{\overset{\|}{C}}-Cl$: only method.

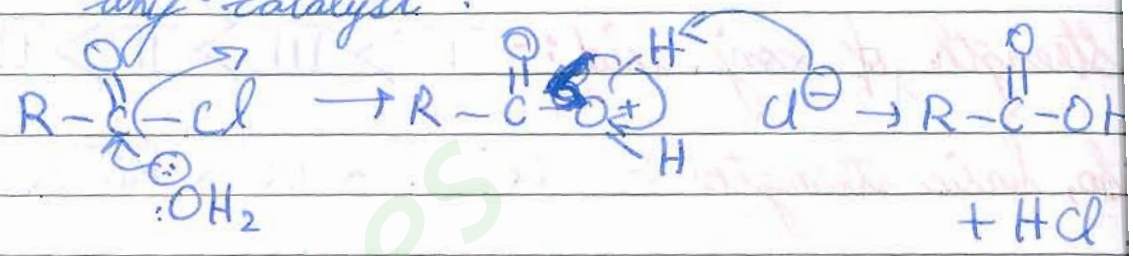
Properties

$R-\overset{O}{\overset{\|}{C}}-Cl$ (I) and $R-CH_2-Cl$ (II) with $CN^{\ominus}$. Reactivity :- I > II.

- Greater electrophilic character of leaving grp.
- Less hinderance.

* ✓ **Hydrolysis**

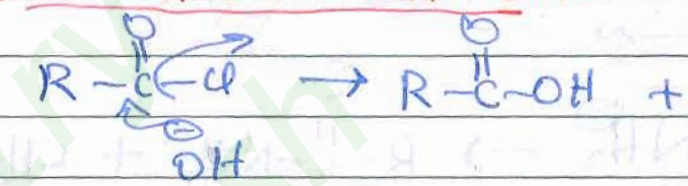
↳ hydrolysis takes place even in absence of any catalyst.



✓ 1 mole acid chloride hydrolysis requires 2 moles of H_2O. (1 → acid & 1 HCl)

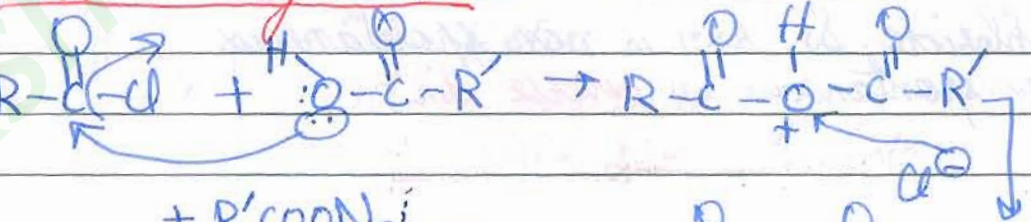
✓ If Base is added, rxn is catalysed.

BASE CATALYSED HYDROLYSIS

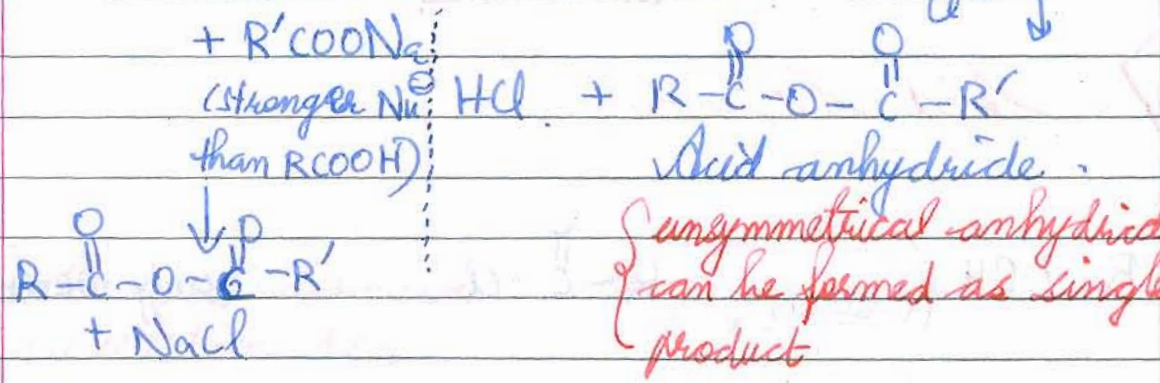


: Single step.

* ✓ **with carboxylic acid**



+ R′COONa (Stronger Nu⊖ than RCOOH)



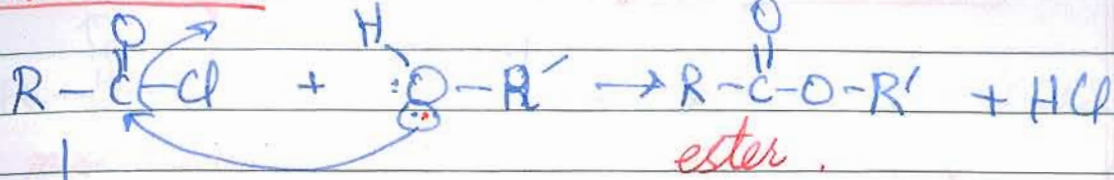
Acid anhydride.

{ unsymmetrical anhydride can be formed as single product

* So, ~~best~~ best method to prepare unsymm. ahydride is treating acid chloride with sodium salt of carboxylic acid.

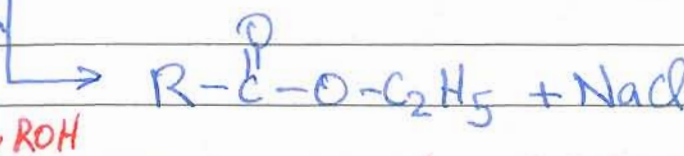
* On reacting, see 1st: Steric hinderance.
2nd: Size of Nu⊖.

✓ with alcohol

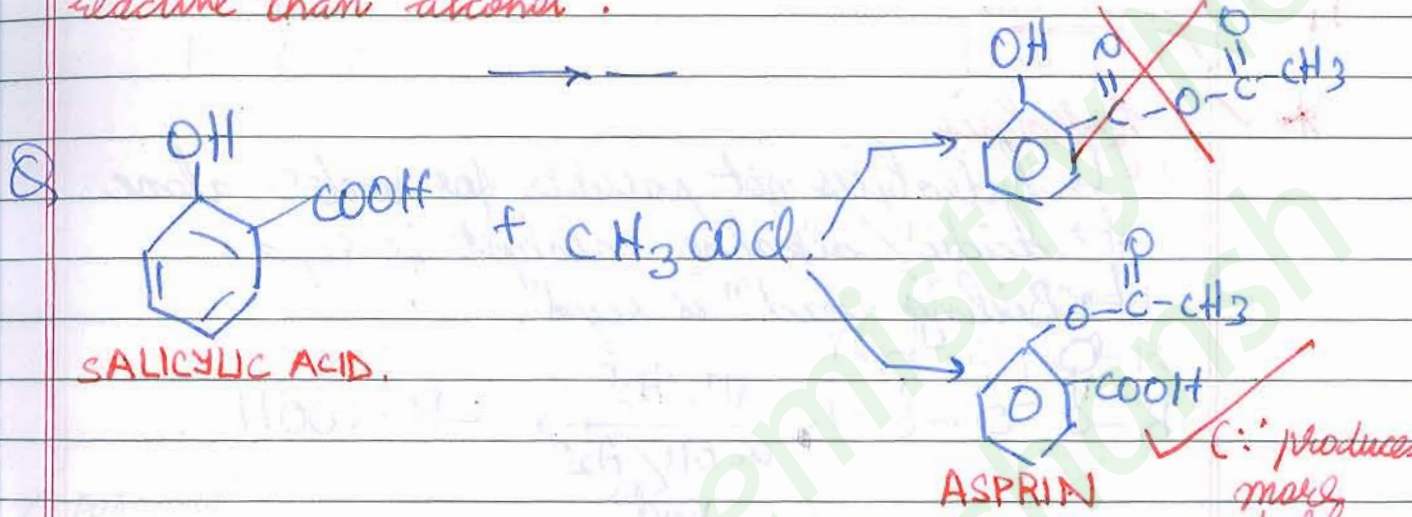


ester.

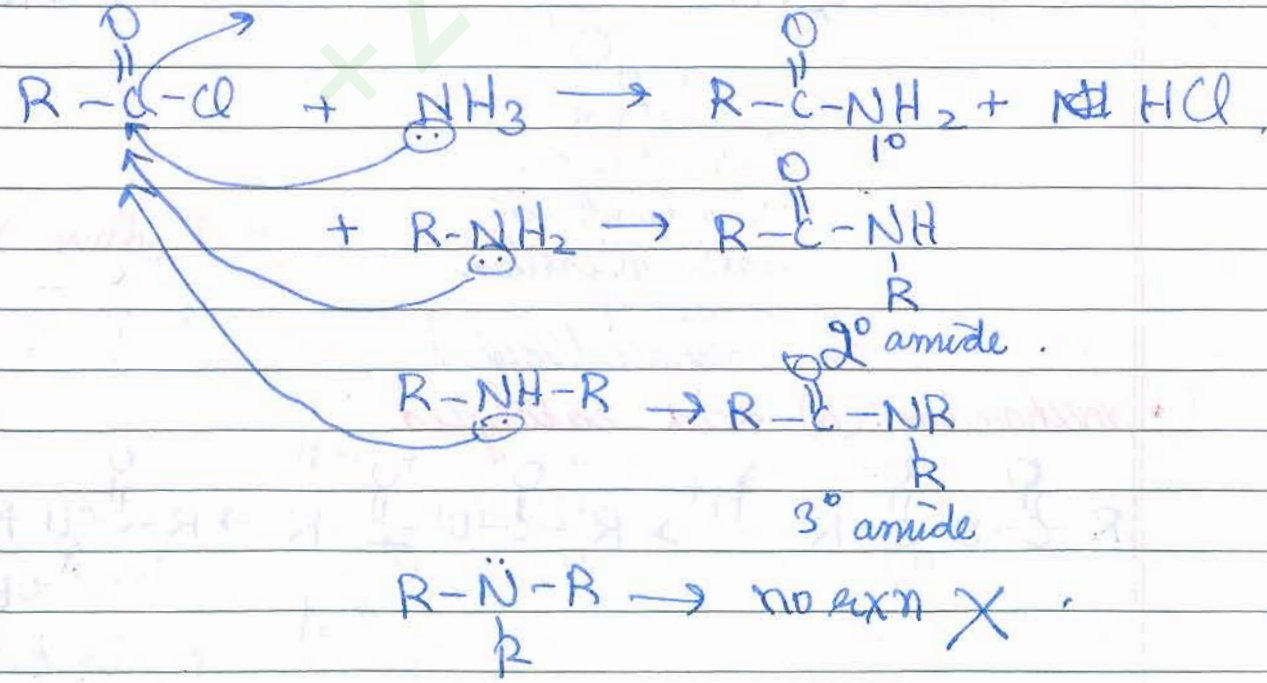
C_2H_5ONa strongu Nu than ROH



* Rxn with sodium salt of ethanol (alcohol) is more reactive than alcohol.



* ✓ with NH_3 or $R-NH_2$



* ✓ Rosenmund reduction (done in aldehydes earlier)

→∞←

(2) Anhydride

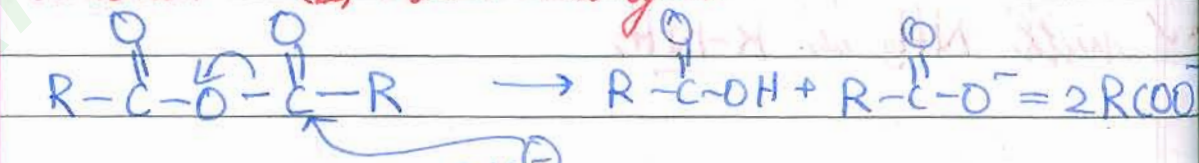
✓ prepar^{n} :- done before in terms of acid.

* Properties

* ✓ Hydrolysis
  - → hydrolysis not possible for water alone.
  - → acidic / alkaline catalyst is reqd.
  - → Boiling cond^{n} is reqd.

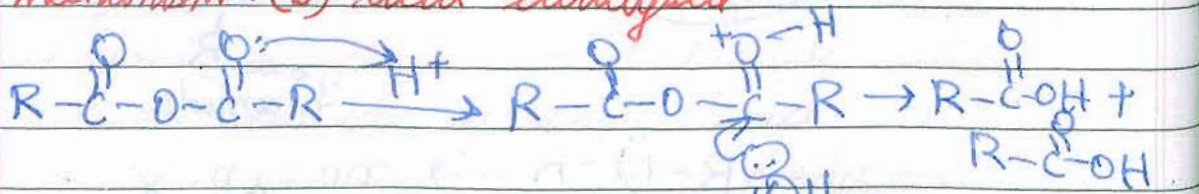
$$R-C(=O)-O-C(=O)-R \xrightarrow[\text{or } OH^-/H_2O,\ \text{boil}]{H^+/H_2O} 2R-COOH$$

- mechanism :- (a) base catalysed.



(its attack would be on less hindered carbonyl carbon in case of unsymmetrical)

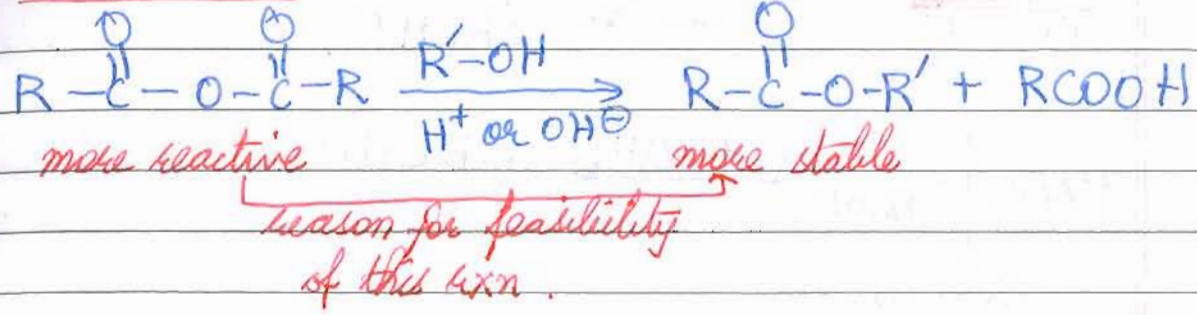
- mechanism :(b) acid catalysed



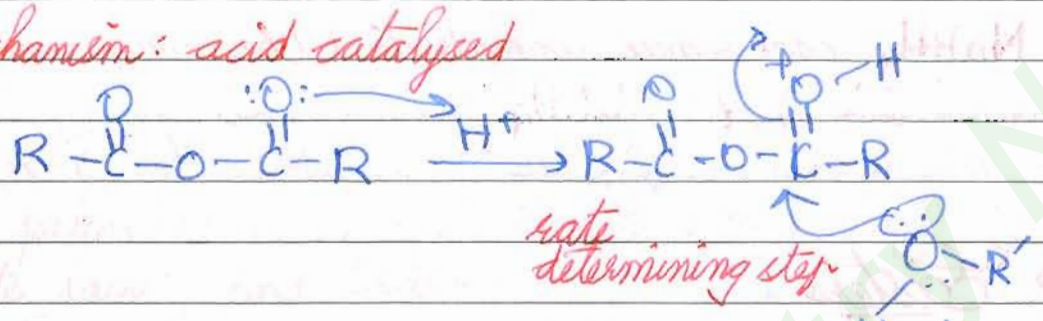
(see where it attacks in unsymmetrical case)

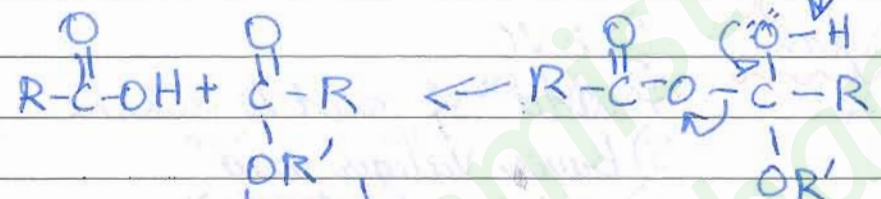
☆ Acid catalysed :- Protonⁿ → followed by Nu⊖ attack (solvent) on protonated C.

✱ ✓ with alcohol



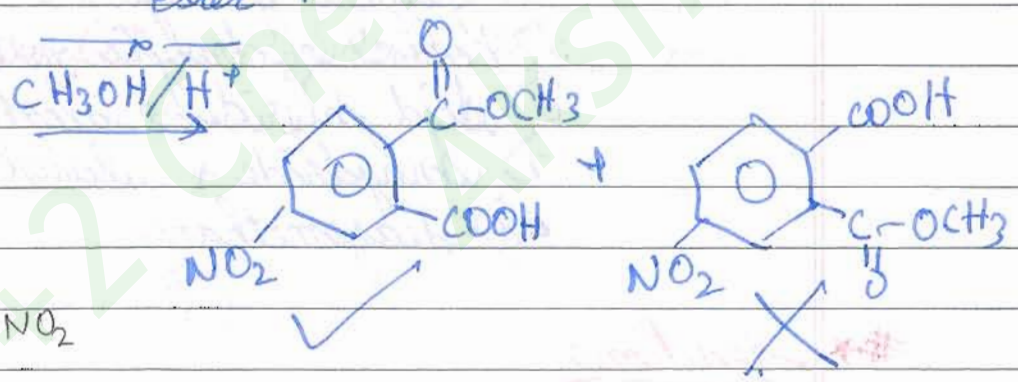
• mechanism : acid catalysed



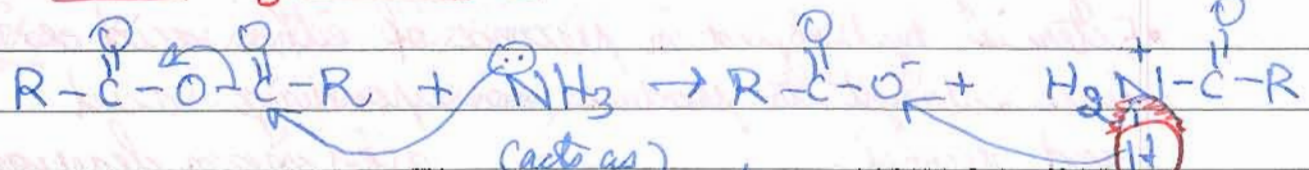


✓ para posⁿ w.r.t NO_2

✗ meta posⁿ w.r.t NO_2

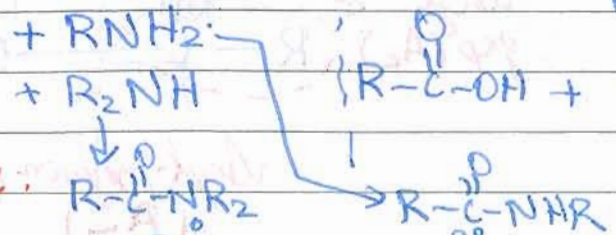


✱ ✓ with NH_3 & RNH_2



+ RNH_2
+ R_2NH

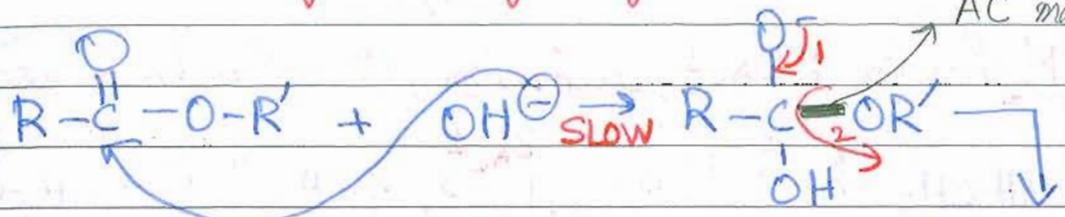
✱ Ily with amine :

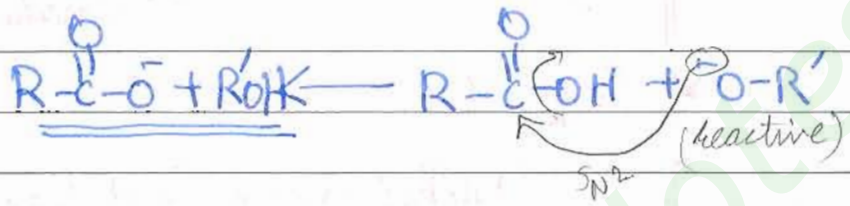


Amide . IO

classmate
Date 20.10.10
Page

(a) base catalysed hydrolysis





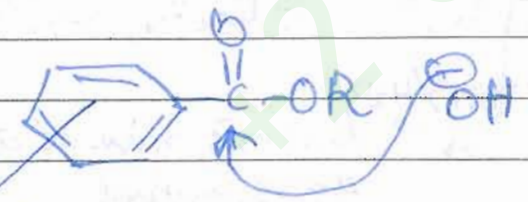
- If α-C of alcohol is 1° or 2°, a bimolecular mechanism is followed (as above) in rate determining step.
- Rate law :- 2nd Order.

$$R = k[R\text{-}COOR'][OH^-] \equiv {}^{*}B_{AC}2$$

→ bimolecular.

Base catalysed → Acyl oxygen cleavage

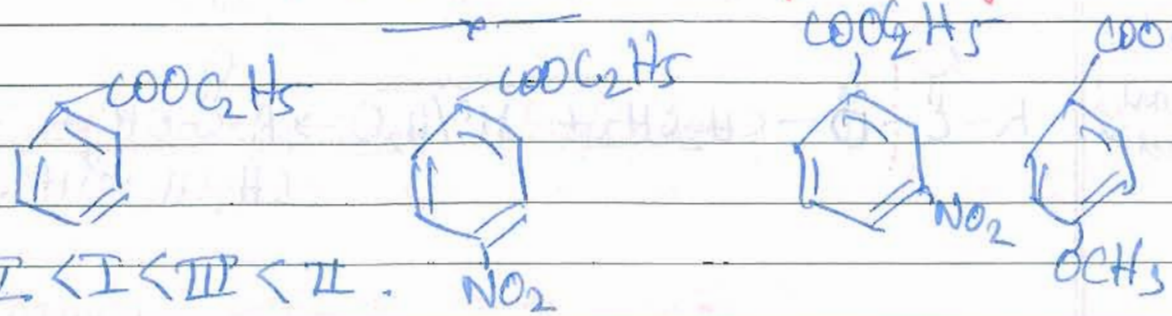
- Above rxn is also called SAPONIFICATION rxn.
  & hence, Saponific^{n} rxn follows $B_{AC}2$ rxn.



Group.

In case of $B_{AC}2$ mechanism,

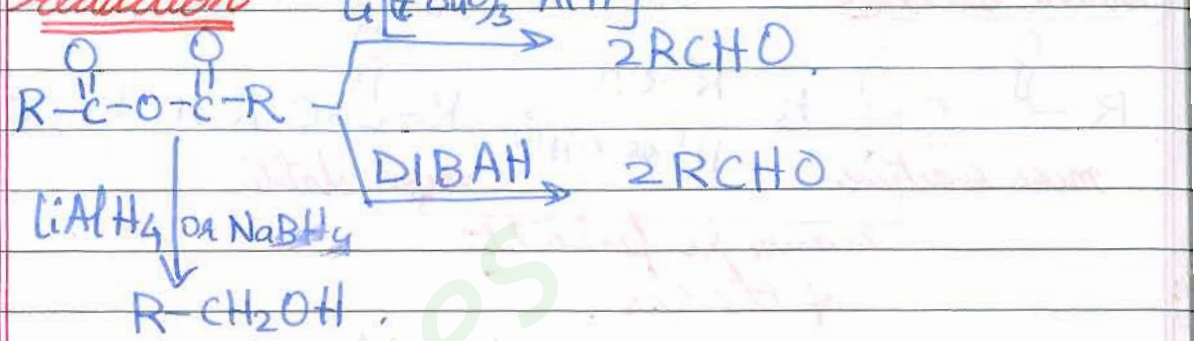
* Grp. e⁻ withdrawing (in acid fragment) ↑ reactivity of acyl carbon.
  e⁻ donating (in acid fragment) ↓ reactivity of acyl carbon.



Q.

activity: IV < I < III < II.

* ✓ **reduction**



EXCEPTION * $NaBH_4$ can reduce anhydride (the only acid derivative that $NaBH_4$ can reduce) giving $R-CH_2OH$

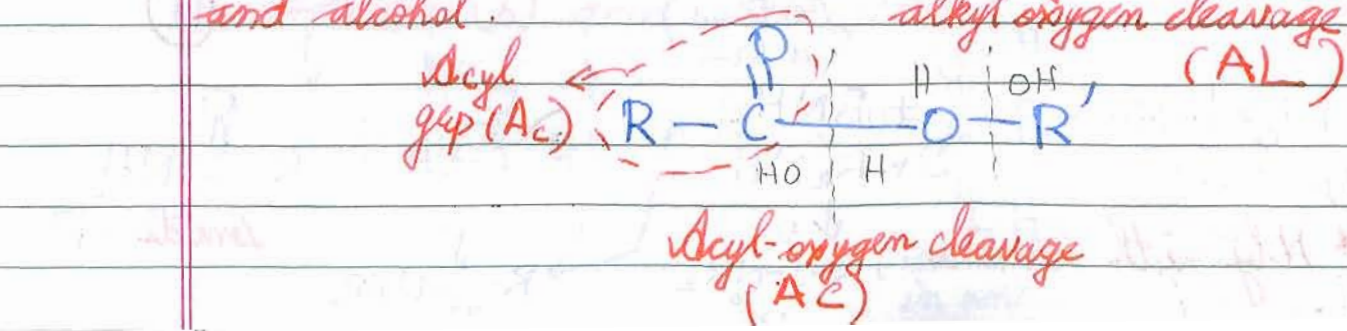
<3> Esters

* prepare^n :- 1) BVO
2) Add^n of acid to alkene
3) Bayer villiger oxid^n
4) Fischer esterific^n.
5) Kolbe's electrolytic method (bi-product as)
6) Acid chloride + alcohol
7) Anhydride + alcohol.
8) Diazomethane.

** reactions

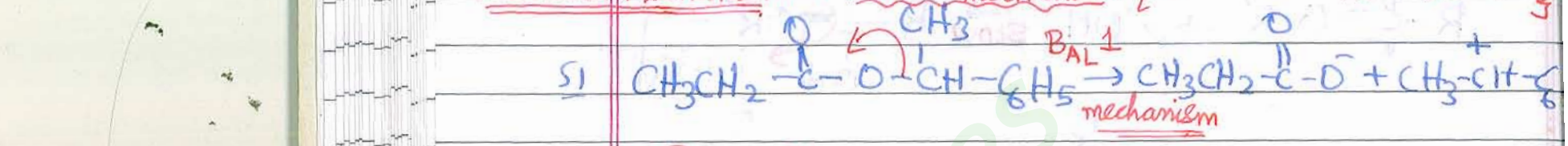
* ✓ Hydrolysis

• Ester is hydrolysed in presence of either acid or base catalyst to produce corresponding acid and alcohol.



Different from usual

Alternate Mechanism : $B_{AL}1$ mechanism {other than $B_{AC}2$ mech.}

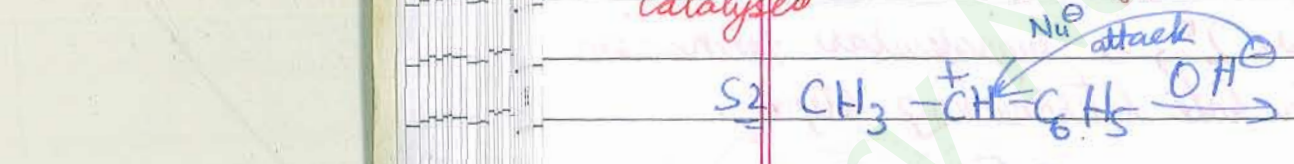
S1 

mechanism

* B AL 1 → unimolecular.

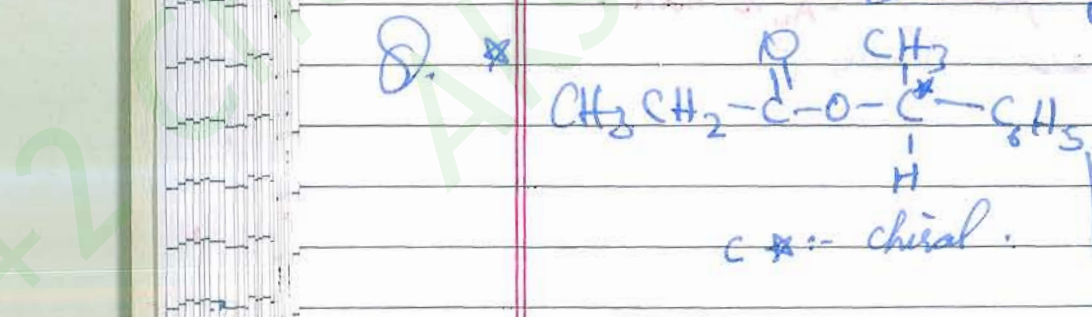
Base catalysed

Alkyl-oxygen bond cleavage.

S2 

* Don't follow this mechanism (↑) unless in the question. In general, use $B_{AC}2$ mechanism.

More chances of $B_{AL}1$ { * $B_{AL}1$ mech. can also be used if carbocation is very stable (3° or benzylic & polarising solvent)

Q. * 

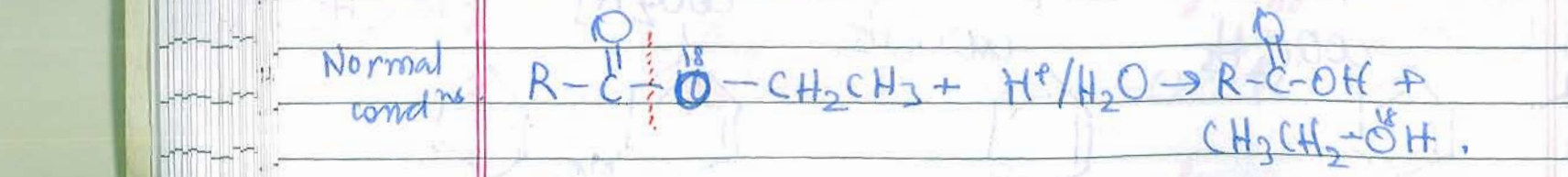
with retention of confi. at chiral carbon
⇒ $B_{AC}2$.

C * :- chiral.

Racemic mix. of alcohol are obtained.
⇒ $B_{AL}1$.

(b) Acid catalysed hydrolysis

Normal conditions



H^+ conc conc. is kept constt practically
Ok PSEUDO UNIMOLECULAR

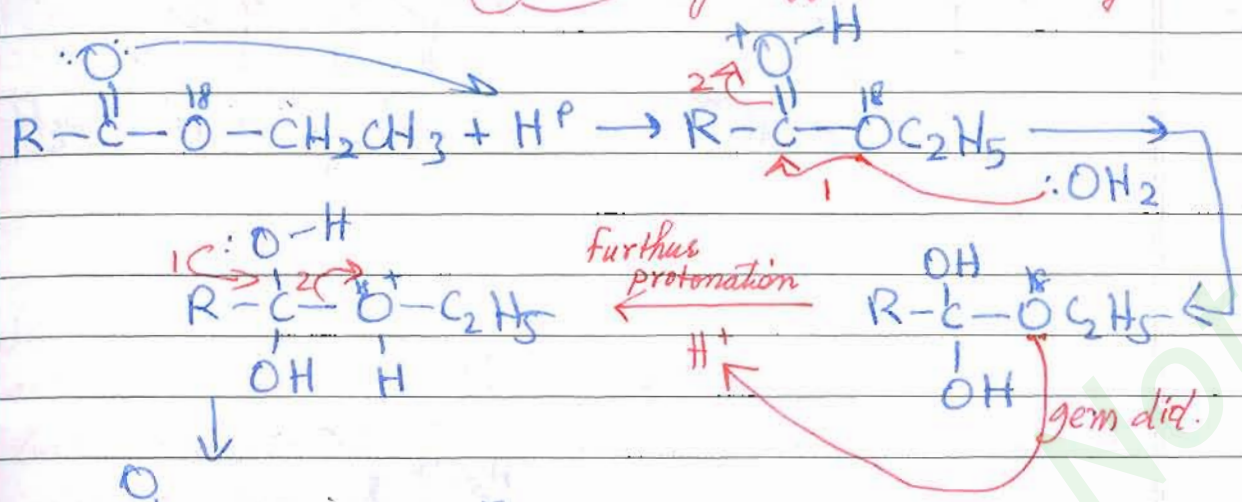
Acid catalysed

bimolecular

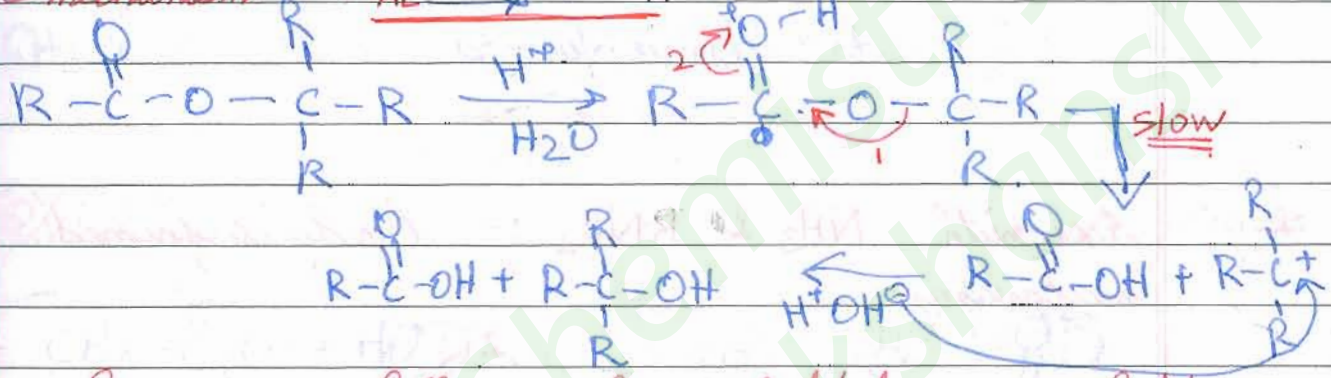
A AC 2

acyl oxygen bond cleavage

1) • mechanism :-



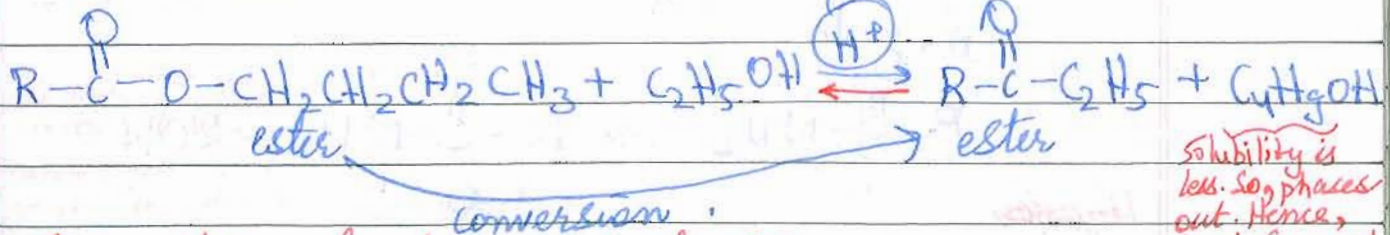
2) • mechanism :- $A_{AL}1$ mechanism



✓ mechanism (2) is followed when ~~substitution is~~ substituted group is 3° or benzylic

✓ If α-C is chiral :- Retention of confi. : $A_{AC}2$
Racemic mix formed : $A_{AL}1$.

*✓ trans esterification



Solubility is less. So, phases out. Hence, rxn is favoured by le Chatelier principle.

✓ Conditions for trans esterification

• In trans esterification rxn, small alcohol replaces the higher alcohol.

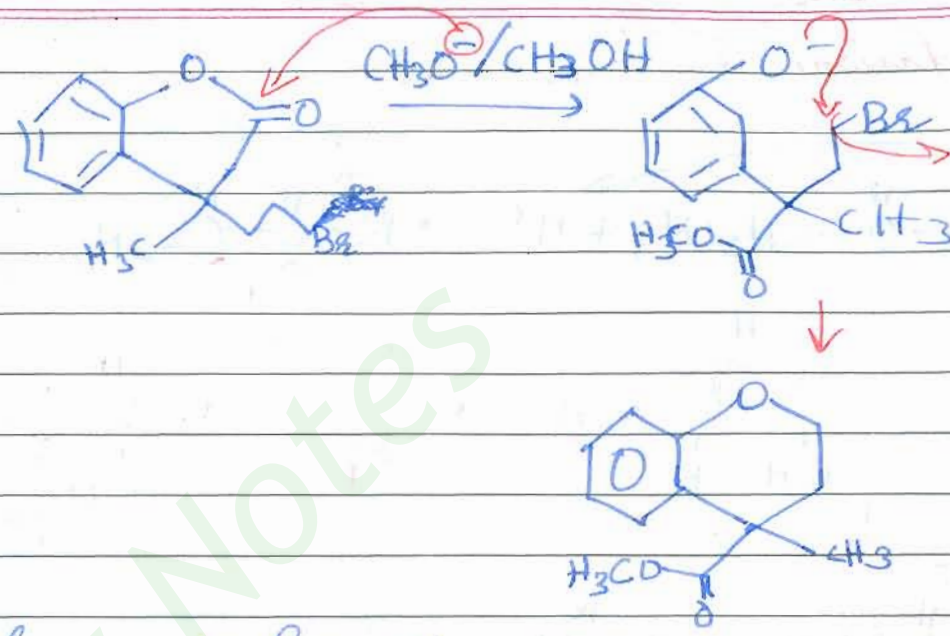
• Mechanism :- same as Fischer esterific^n.

Chemistry Notes Akshansh

* $Nu^{\ominus}$ attack preference :

• Acid derivative > R-X : Reason- ± character

JEE



✓ above rxn is favoured

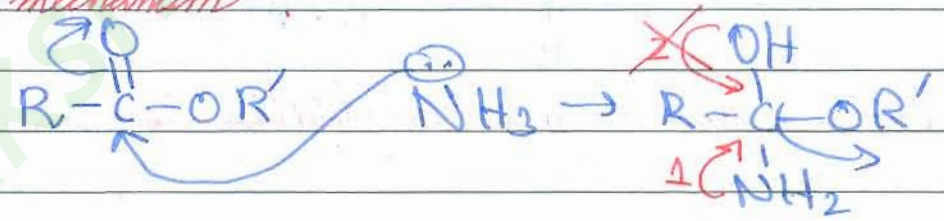
∵ → 1) 5 to 6 membered ring

2) add^n ether is formed.

---

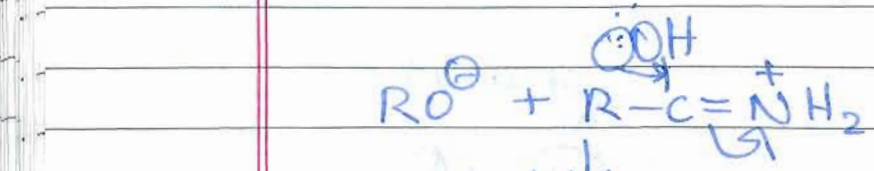
*✓ Rxn with NH_3 & RNH_2 :- Amide is formed.

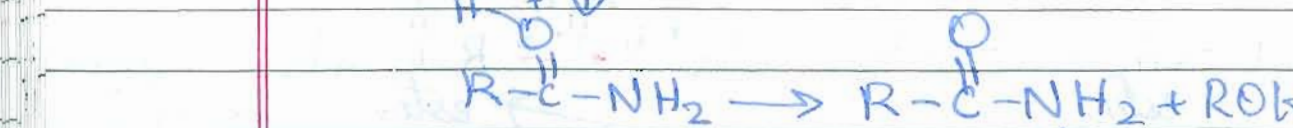
mechanism.



1✓ +ve on N(less E_N)

2✗ +ve charge on O(more





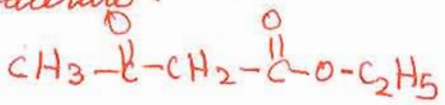
Hydrolysis

• $R-\underset{\underset{H}{|}}{C}(=O)-OR' + RNH_2 \rightarrow R-\underset{\underset{H}{|}}{C}(=O)-\underset{2^{\circ}}{NHR} + R'OH$

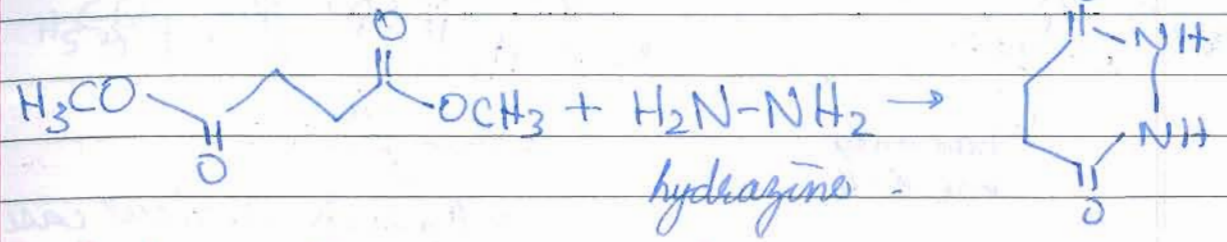
• $R-\underset{\underset{H}{|}}{C}(=O)-OR' + R_2NH \rightarrow R-\underset{\underset{H}{|}}{C}(=O)-\underset{3^{\circ}}{NR_2} + R'OH$

• $+R_3N \rightarrow X$

* Ethyl aceto acetate :-

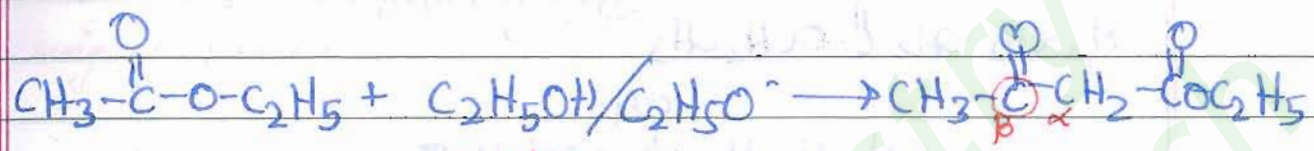


In case of diester

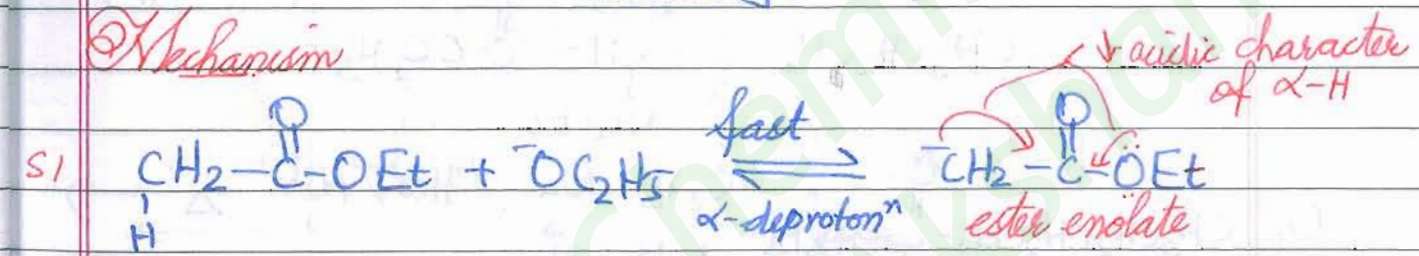


* ✓ Claisen Condensation of Ester

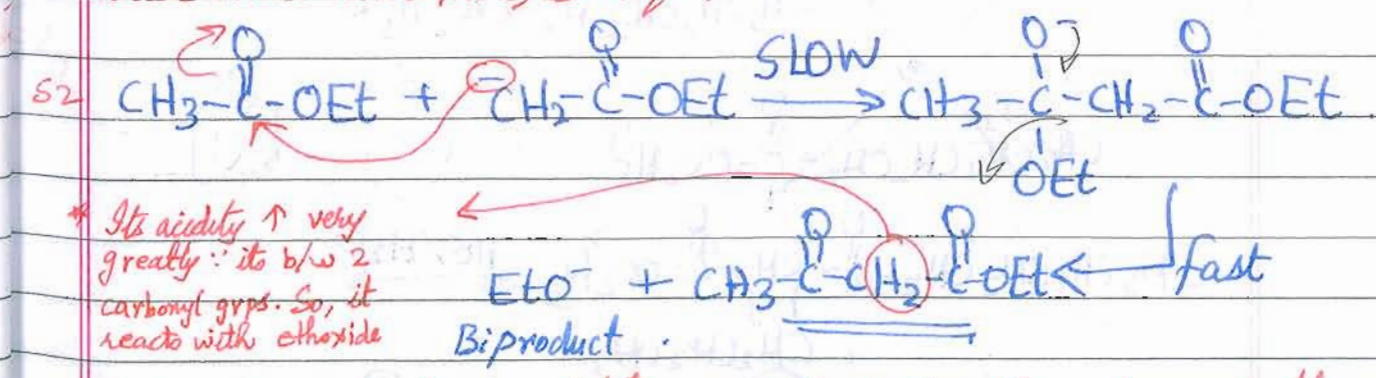
when an ester containing α-H is treated with a strong base, usually ethoxide – ethanol, condens^n takes place to give β-keto-ester.



Mechanism



✓ Red^n with NaOH or KOH can't be done in this rxn (∵ α-H of ester is less acidic than ald. or ketones). So, further strong base (like alkoxide) is req^d.



* Its acidity ↑ very greatly ∵ it b/w 2 carbonyl grps. So, it reacts with ethoxide

* rxn proceeds to completion even if S2 is thermodynamically non-spontaneous [Reason: very high acidity of H surrounded by 2 carbonyl gaps. So, the product formed reacts with ethoxide & it gets precipitated out. Hence → favoured → le Chatelier.

Contd. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow{C_2H_5ONa} CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{C}H-\overset{O}{\overset{\|}{C}}-OEt \; Na^+$

$R-\underset{\text{has only one } \alpha\text{-H.}}{\underbrace{CH}}-COOC_2H_5 \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-\overset{R}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-OEt$ (R)

(R) — no H, as in previous case. So, thermodynamically unstable.

** Condⁿ: starting ester must contain atleast 2 α-H.

—x—

Q. $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-OCH_2CH_3 \xrightarrow{C_2H_5ONa/C_2H_5OH}$

$CH_3CH_2CH_2-\underset{OCH_2CH_3}{\overset{OH}{\overset{|}{C}}}-CH-\overset{O}{\overset{\|}{C}}-OC_2H_5$

$CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-\underset{CH_2CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OC_2H_5$

Q. $CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow[C_2H_5OH,\ 70^\circ C]{C_2H_5ONa} \xrightarrow{HO^-/H_2O} \xrightarrow{\Delta} ?$

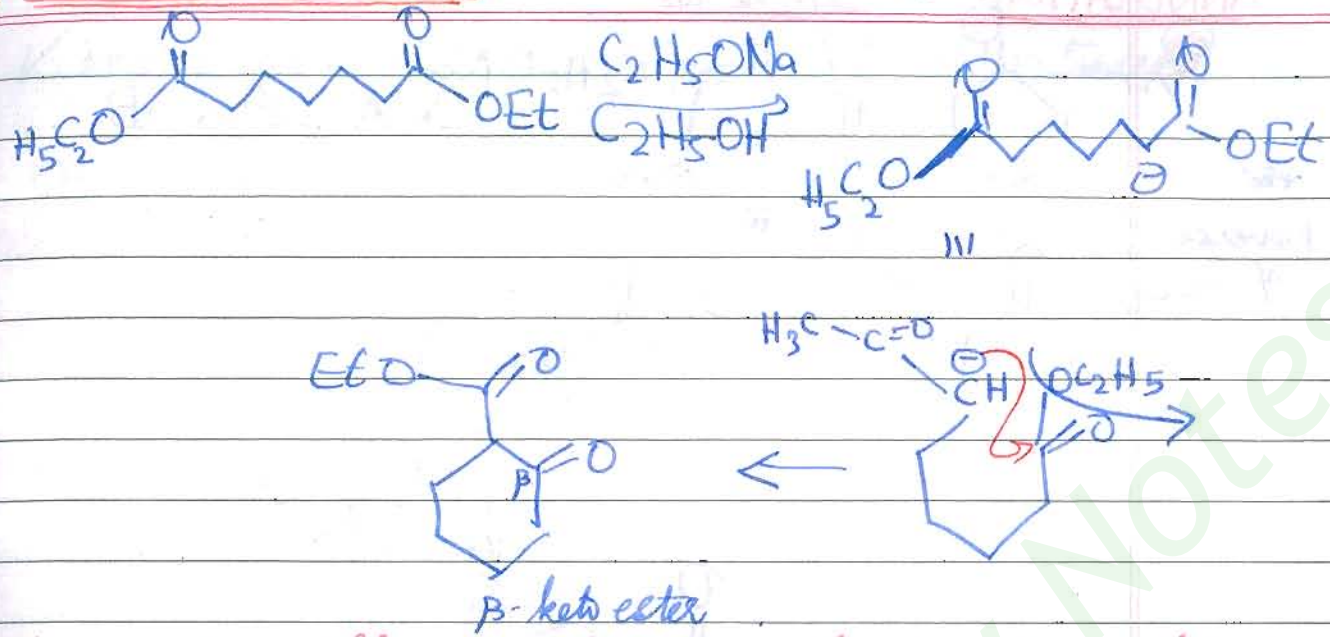
$CH_3CH_2CH_2CH_2-\overset{O^-}{\overset{|}{C}}-OC_2H_5$

$CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-\underset{CH_2CH_2CH_3}{CH}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \xrightarrow{HO^-/H_2O}$

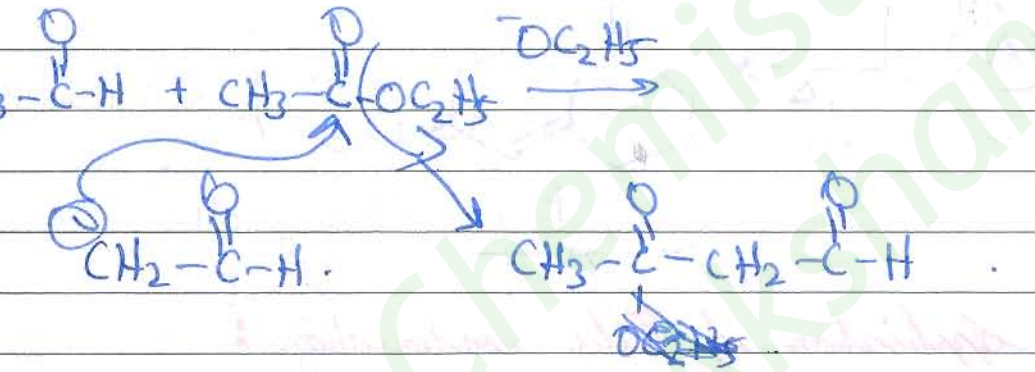
$Bu-\overset{O}{\overset{\|}{C}}-\underset{Pr}{CH}-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\Delta} Bu-\overset{O}{\overset{\|}{C}}-\underset{Pr}{CH_2}$

5-nonanone.

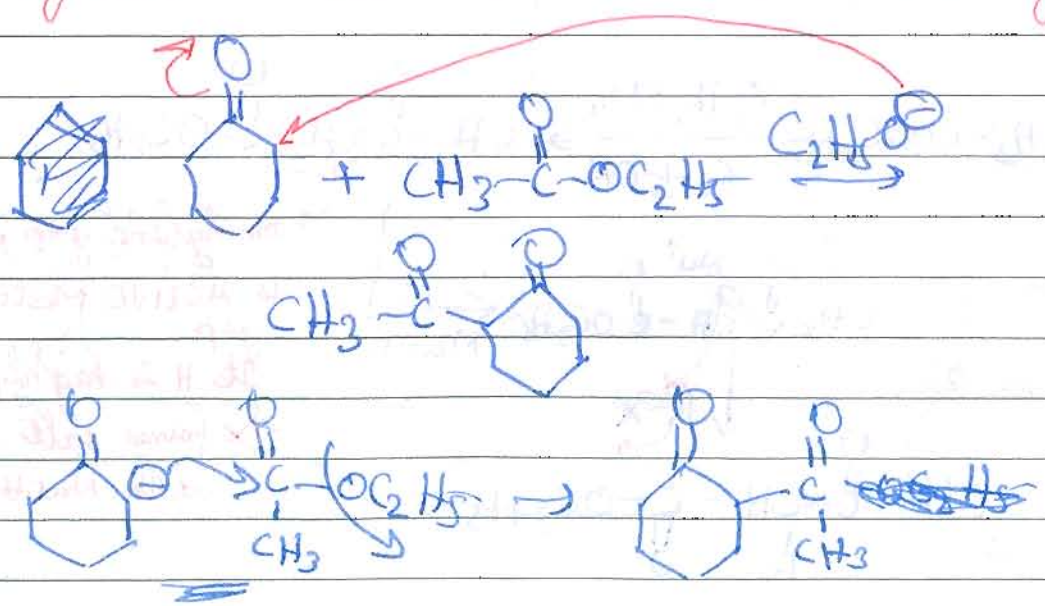
DIECKMANN'S RXN



* This rxn is possible only when 5 membered or 6 membered ring is formed.



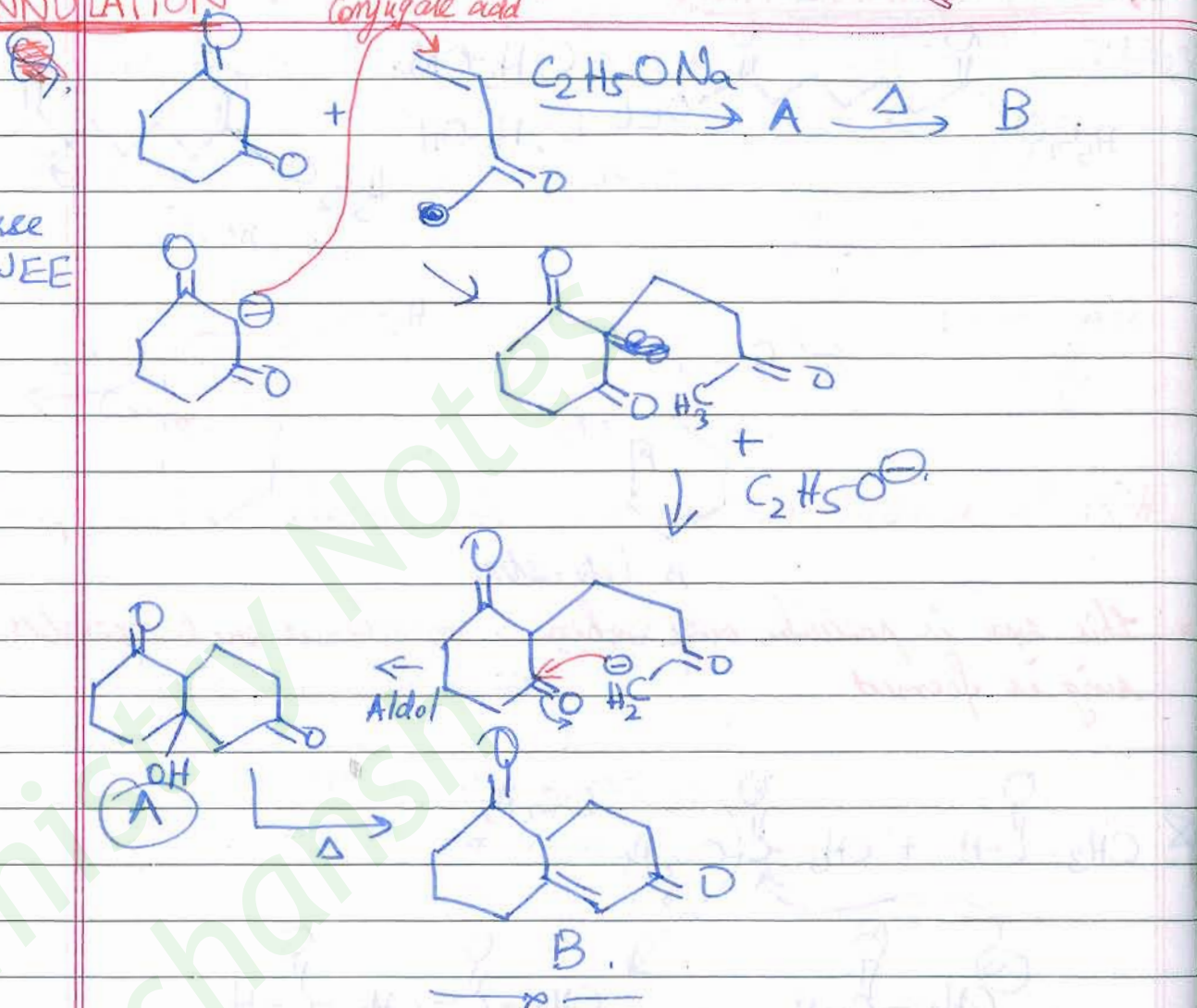
* In case of a mixture of aldehyde/ketone & ester, aldehyde/ketone forms $Nu^{\ominus}$ & attacks carbonyl of ester



ROBBINSON ANNULATION

(∵ it's not that strong $Nu^{\ominus}$)

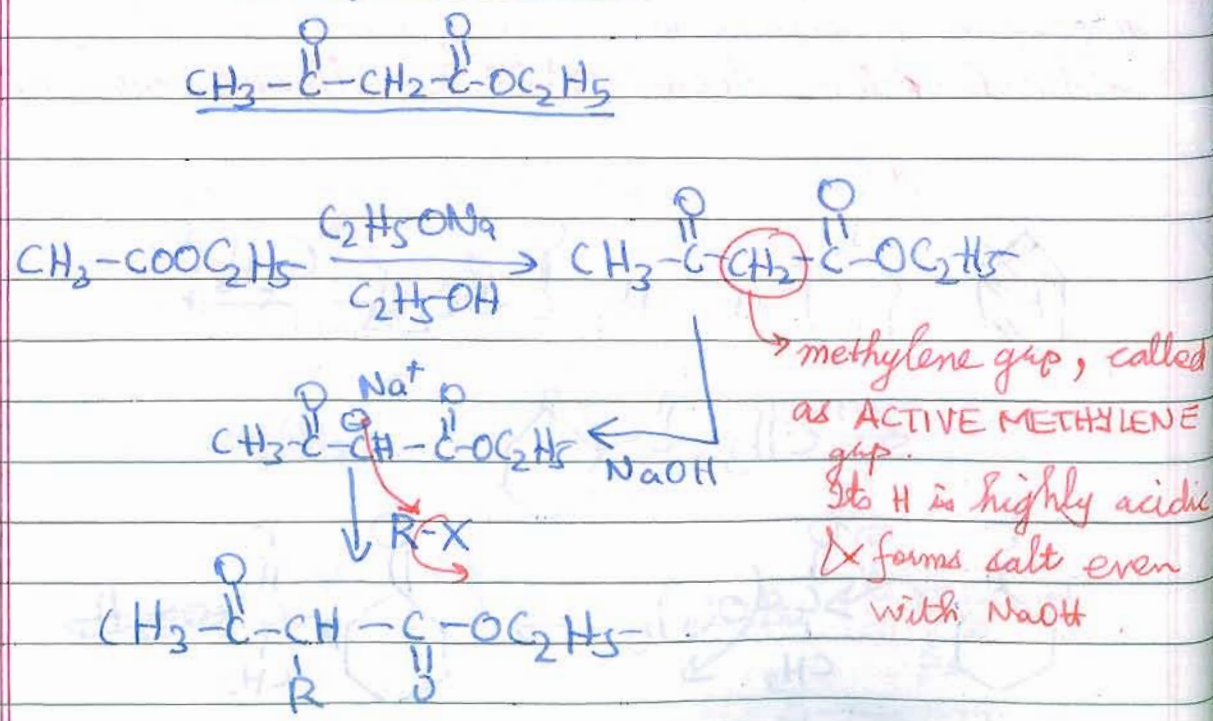
conjugate addⁿ



Reverse of JEE

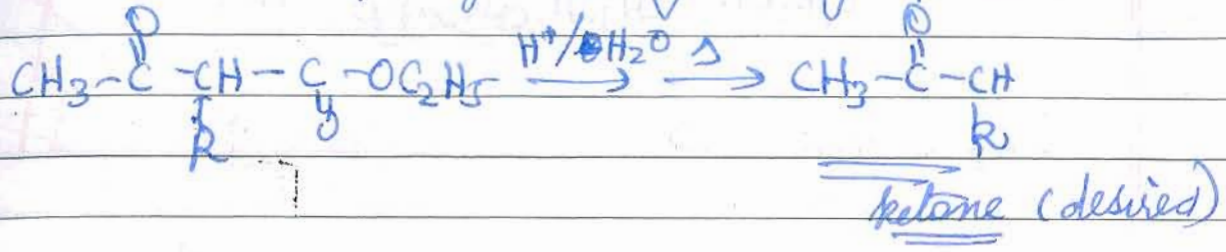
Application of Ester-condensation :

ACETOACETIC ESTER SYNTHESIS

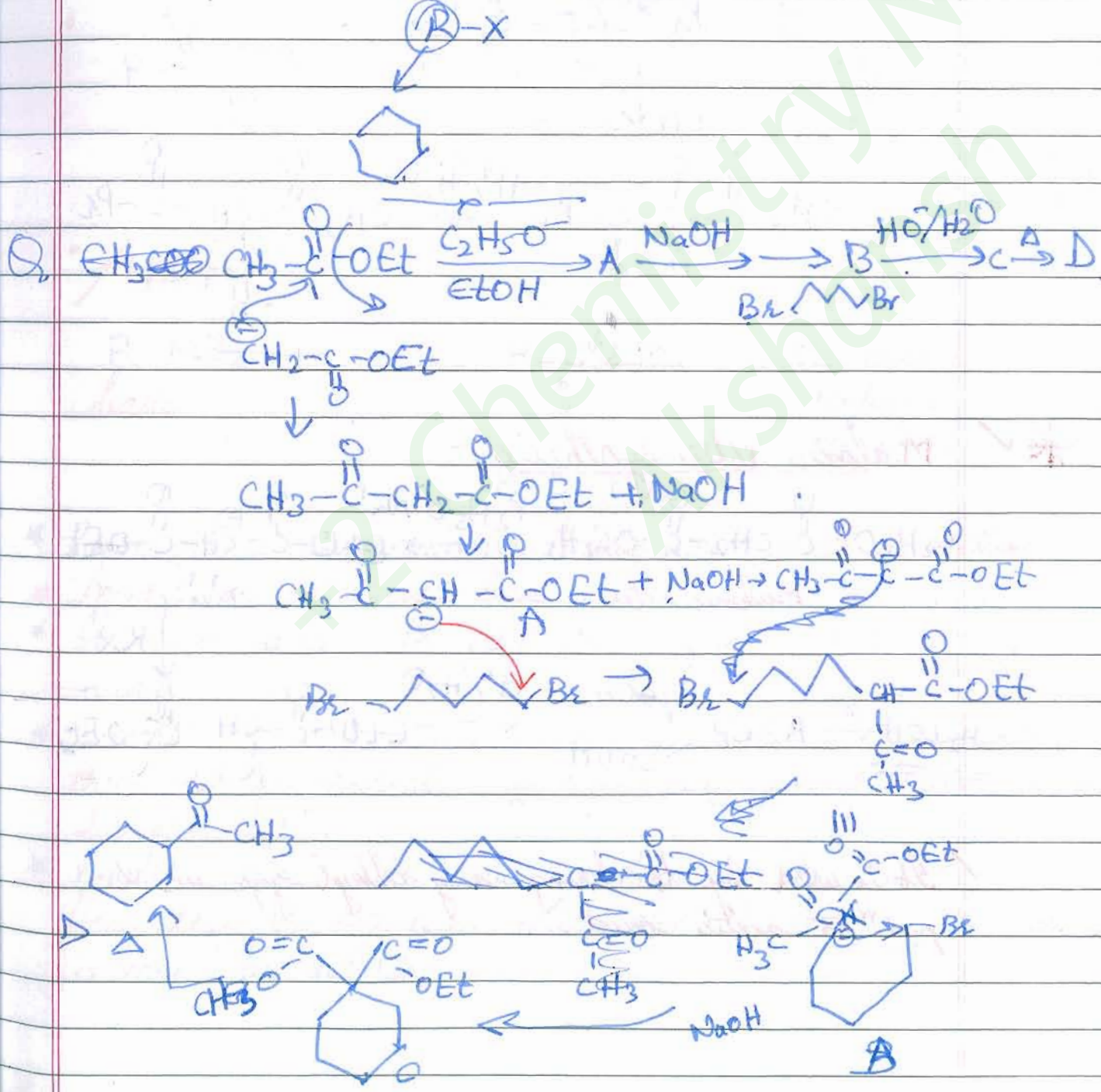


methylene grp, called as ACTIVE METHYLENE grp.
Its H is highly acidic & forms salt even with NaOH.

✓ ✓ rxn is used for synthesising variety of ketones:-



Q. $CH_3COOC_2H_5$ $\xrightarrow[C_2H_5OH]{C_2H_5ONa}$ $CH_3C(=O)-CH_2-C_6H_5$?



Propane dioic acid : Malonic acid

classmate
Date 22·10·20
Page

Q. $CH_3-\underset{\underset{O}{\|}}{C}-OEt \xrightarrow{C_2H_5O^-} A \xrightarrow{HO^-} \xrightarrow{\Delta}$

$A = (CH_3CH_2CH_2CO)_2O$; C_2H_5OH ; H_2O

$CH_2^{\ominus}-\underset{\underset{O}{\|}}{C}-OEt \longleftrightarrow$

$CH_3-\underset{\underset{O}{\|}}{C}-\underset{(A)}{CH_2}-\underset{\underset{O}{\|}}{C}-OEt$

$Pr-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-Pr$

$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{\underset{OEt}{\underset{|}{C=O}}}-\underset{\underset{O}{\|}}{C}-Pr \xrightarrow{H^+/H_2O} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{C-OEt}{\underset{\|}{O}}}{CH}-\underset{\underset{O}{\|}}{C}-Pr$

---

* ✓ **Malonic ester synthesis :-**

$C_2H_5O-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-OC_2H_5 \xrightarrow{C_2H_5O^-Na^+} EtO-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{CH}-\underset{\underset{O}{\|}}{C}-OEt$

Malonic ester

$EtO-\underset{\underset{O}{\|}}{C}-\underset{\underset{R}{|}}{CH}-\underset{\underset{O}{\|}}{C}-OEt \xleftarrow{H^+/H_2O} \xleftarrow{RX}$

$R-CH_2COOH \xleftarrow{\Delta} R-CH(COOH)_2$

(like β-keto acid)

✓ It is used to bring any alkyl grp on α-pos^n to acetic acid.

Chemistry Notes Akshansh

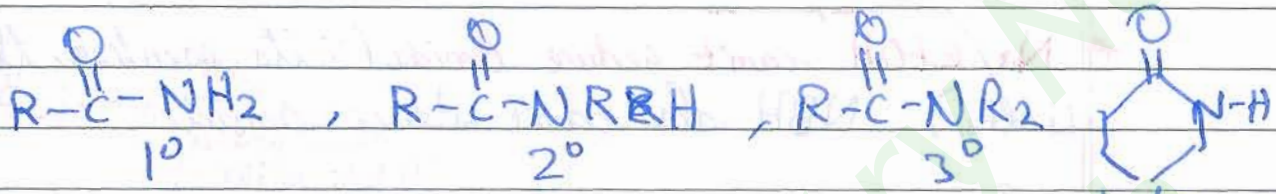
* All cyclic amides are called LACTUM

classmate
Date
Page

<4> Amide

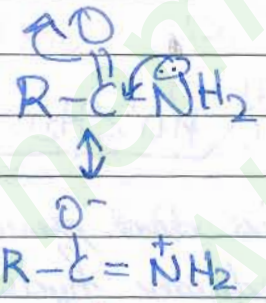
Preparation:-

- prepared by condensⁿ of acid or derivative with NH_3.
- Beckmann Beckmann's rearrangement
- controlled hydrolysis of $-CN$.



properties

$R-NH_2$ basic



: neutral even in aq. medium. (∵ of strong resonance)

* Resonance is maximum in Amides among Acid derivatives.
* Amides are not Lewis base.
* It forms salt with very strong base. It is weakly acidic.
* Except , all amides are solid at R.T. due to their dipolar character by resonance giving them strong dipolar attrⁿ.
* Amides behave like ionic compds i.e. like salts. Hence, they are soluble in water. eg:- $H_2N-\underline{CO}-NH_2$, i.e urea is very water soluble.

classmate
Date
Page

*** Chemical Rans.

(a) Reduction

* Amide is most difficult to reduce among acid derivatives

* $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Red}^n]{LiAlH_4} R-CH_2-NH_2$
Amide. Amines

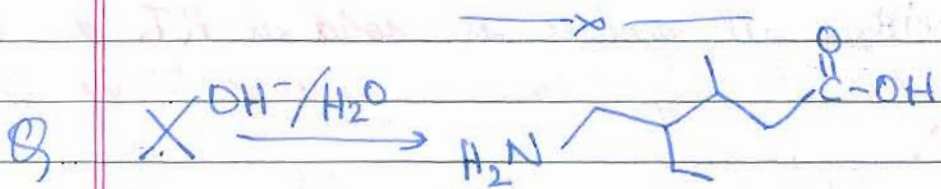
* $Na/EtOH$ can't reduce Amide (∵ its weaker than $LiAlH_4$). NBH also can't reduce amide.

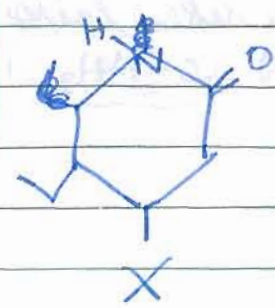
(b) Hydrolysis

$$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-OH + NH_3$$
(OH, H)

$$\xrightarrow{HO^-/H_2O}$$

- Its mechanism is done previously.
- The alkaline medium hydrolysis gives effervescence due to $NH_3(g)$. So, its used as a test for Primary amide. (it doesn't take place with acid ∵ NH_3 forms salt in acidic medium).

(c) 



X

** X_2 in H_2O ⟶ HOX (acid)
hypohalous acid.

(c) dehydration :- ONLY 1° AMIDE (∵ 2 hydrogen with N are req^d to remove H_2O)

$R-\overset{O}{\overset{\|}{C}}-NH_2$ —(P_2O_5/Δ or $POCl_3/\Delta$)→ $R-C\equiv N$.

↳ drying agents

* (d) Hofmann's Bromamide rxn : ONLY 1° AMIDE

$R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Strong base (KOH or NaOH) or ....}]{Br_2} R-NH_2$

Mechanism

$Br_2 + NaOH \longrightarrow NaOBr + HBr$.

S1 $R-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{..}{N}}-H$ (1: H, 2: N, 3: OBr) $\rightleftharpoons R-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-Br + HO^-$

an Intermediate (not RI)

S2 $R-\overset{O}{\overset{\|}{C}}-\underset{..}{\overset{Br}{N}}-H + \overset{\ominus}{O}H \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{\underset{..}{N}}-Br + H_2O$

(from base) a RI (not intermediate)

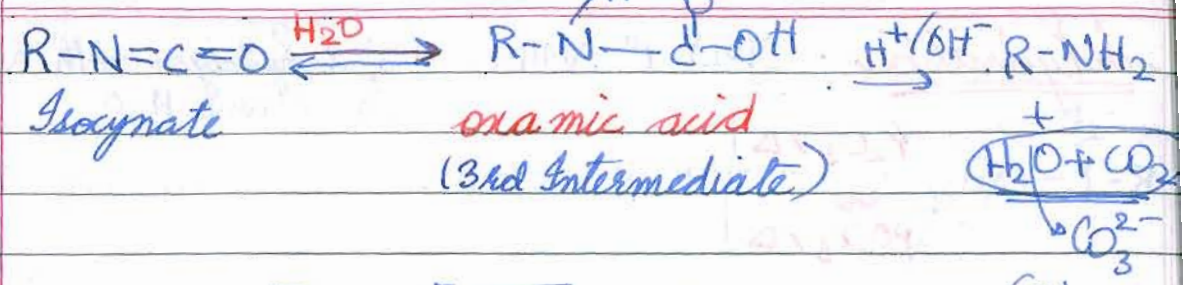
S3 (1: $:N^\ominus$, 2: $C=O$, 3: $O^\ominus$, 4: R, 5: Br) SLOW ⟶ $N\equiv C=O + Br^\ominus$

R Isocyanate

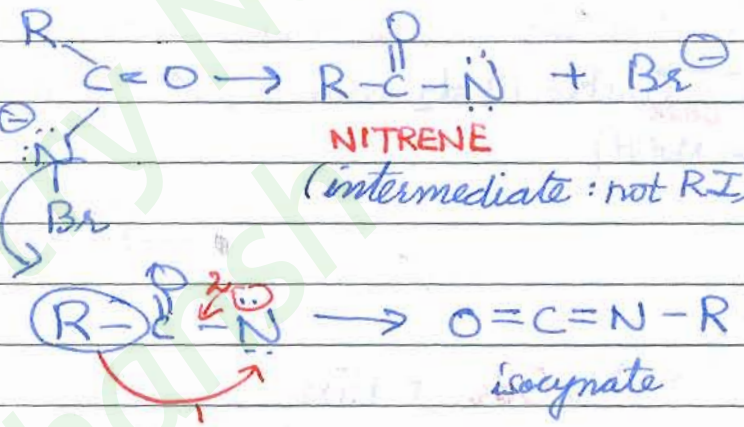
an intermediate (not RI)

• above Isocyanate is formed through UNIMOLECULAR elimin^n of Br^- forming in the slow rate determining step.

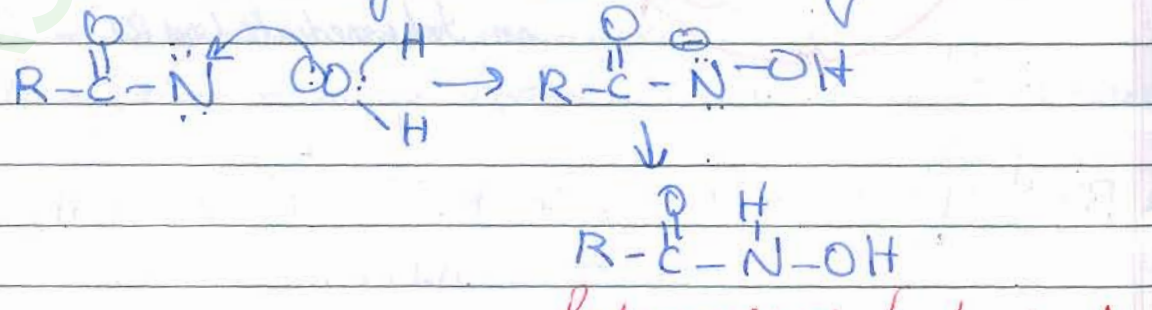
S4 hydrolysis in steps



• Alternate mechanism :- WRONG



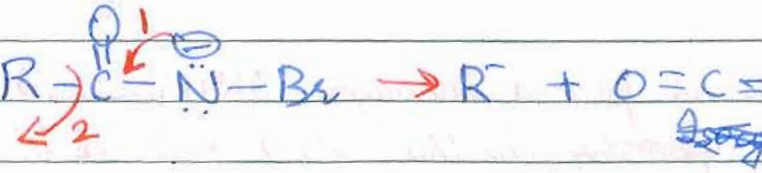
Above rxn is wrong ∵ nitrene is reacting with H_2O



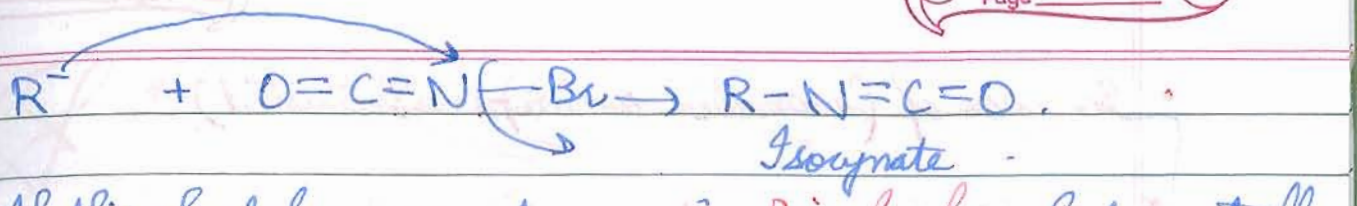
hydroxamide or hydroxamic acid

• absence of hydroxamic acid in medium indicates that rxn doesn't proceed via Nitrene

• Another alternate mechanism :- WRONG

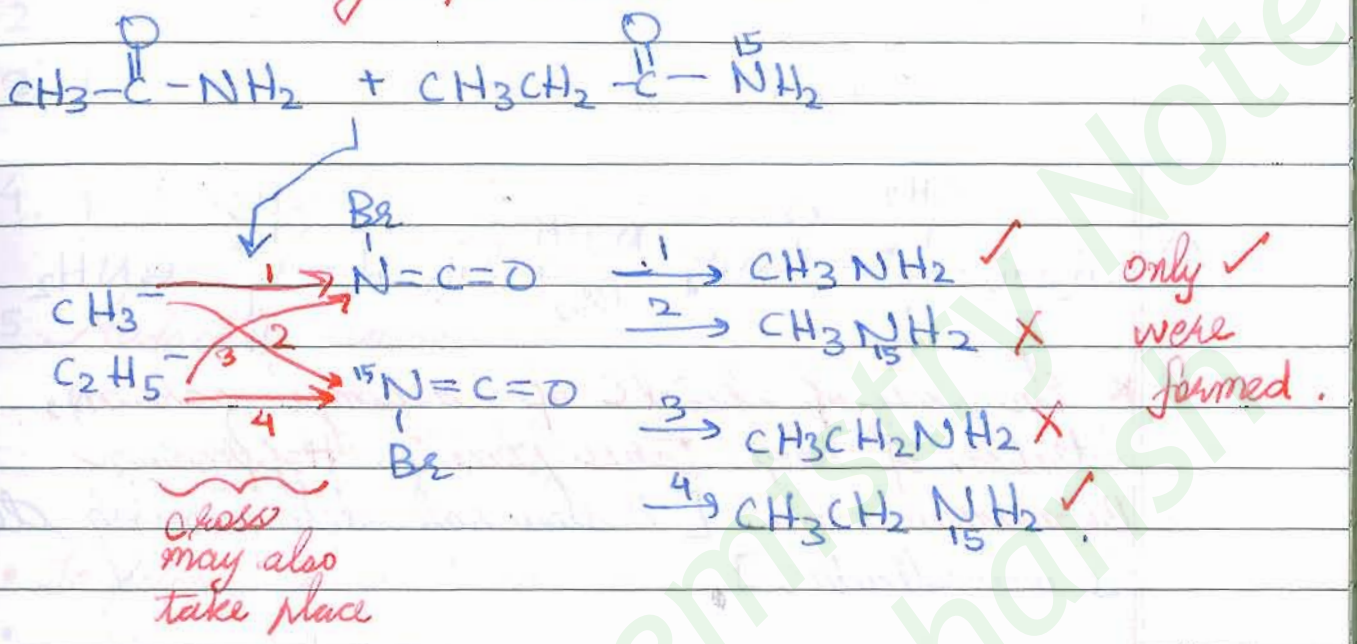


classmate
Date
Page

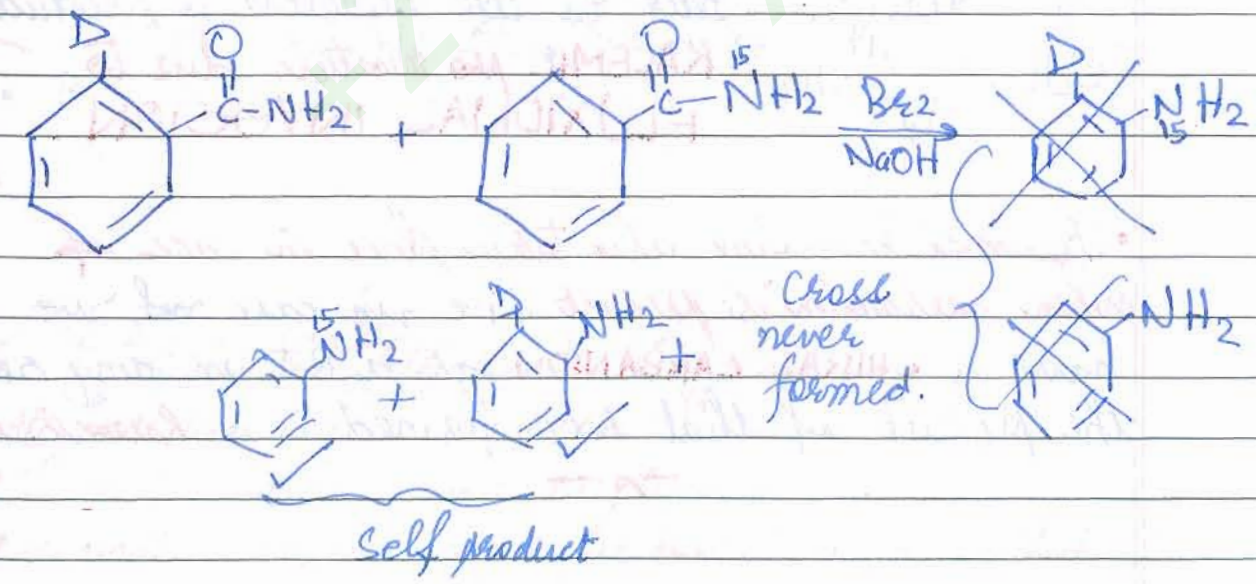


- If this had been correct, rxn is Bimolecular, but, actually its Unimolecular.

- Correction made by Hofmann Lis:-

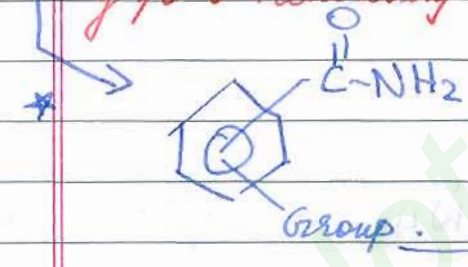


- failure of isotopic exchange b/w amide shows rxn proceeds by unimolecular elimination.



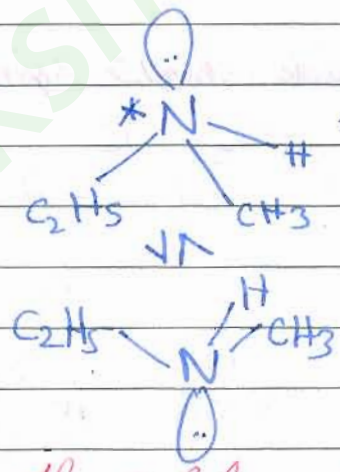
- In case of (aromatic amide)-(substituted).

* e^- donating grp ↑ reactivity & e^- withdrawing grp ↓ reactivity.



Q. $CH_3CH_2-\overset{*}{\underset{H}{\underset{|}{\overset{CH_3}{\underset{|}{C}}}}}-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[Br_2]{NaOH} CH_3CH_2-\overset{*}{\underset{H}{\underset{|}{\overset{CH_3}{\underset{|}{C}}}}}-NH_2$

* In case of chiral C of carbonyl carbon, retention of confi. takes place in Hoffmann Bromamide rxn. [∵ slow rate determining step is unimolecular].



* :- Though it should behave as a chiral carbon. But, the lone pair e's are movable & produces RACEMIC mixture due to FLUXIONAL INVERSION.

- Fluxional Inversion also takes place in case ~~of~~ when carbanion is present. (i.e., in case we have a CHIRAL CARBANION as a RI in any rxn, the product of that rxn formed is a Racemic mix)

✱✓ Aliphatic Amines

• Preparation

1. $R-CN \xrightarrow{LiAlH_4} R-CH_2NH_2$ (1°)

2. $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{LiAlH_4} R-CH_2NH_2$ (1°)

3. $R-NO_2 \xrightarrow{LiAlH_4} R-NH_2$ (1°)

4. $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{Hoffmann.}]{NaOH,\ Br_2} R-NH_2$ (1°)

5. Reductive amination

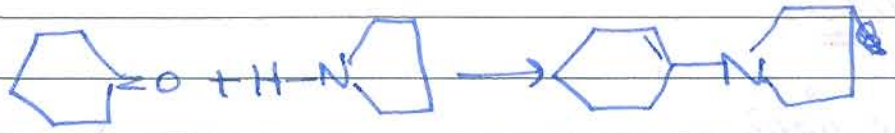
$$R_2C{=}O + H_2NH \xrightarrow{\Delta} R_2C{=}NH \xrightarrow{H_2/Pt} R-\underset{R}{\overset{|}{C}}H-NH_2 \quad (1^\circ)$$

• To prepare 2° or 3° amine.

2° $R-\overset{O}{\overset{\|}{C}}-NHR \xrightarrow{LAH} R-CH_2NHR$ (2°)

3° $R-\overset{O}{\overset{\|}{C}}-NR_2 \xrightarrow{LAH} R-CH_2-NR_2$

2°/3° $R_2C{=}O + H_2NR \xrightarrow{\Delta} R_2C{=}NR \xrightarrow{H_2/Pt} R-\underset{R}{\overset{|}{C}}H-NHR$ (2°)



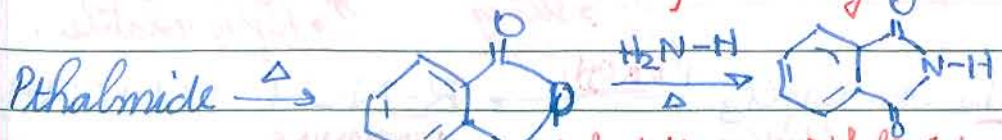
3°

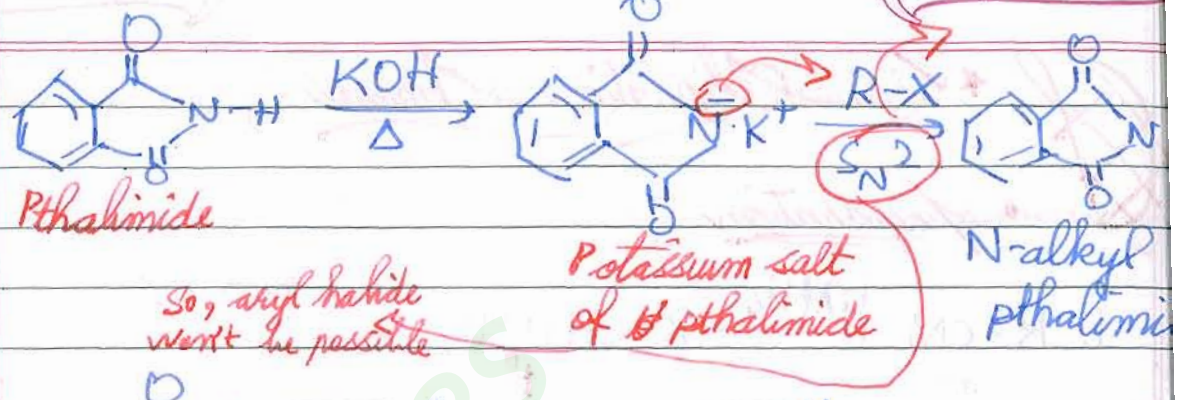
6. Gabriel Phthalimide Synthesis

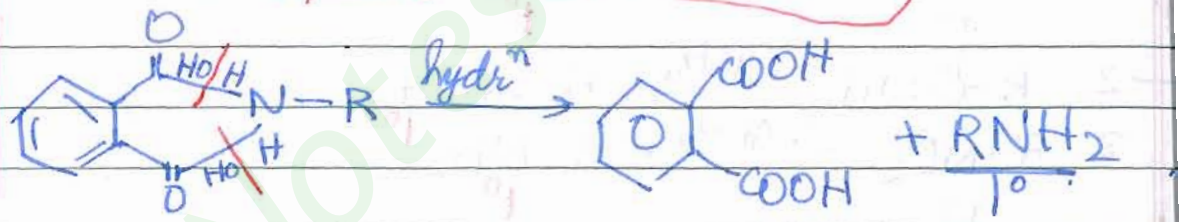
• Its industrial method to prepare 1° amine

• 2° or 3° amines can't be prepared

• aromatic amines can't be formed by this method.

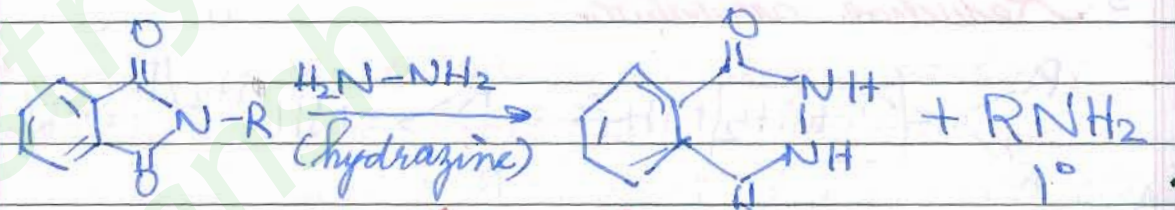






—∞—

• **modification** : better method to prepare 1° amine.



—∞—

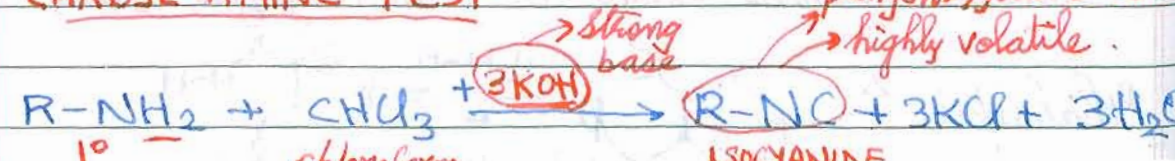
• **properties**

• amines are basic.

⊙ DISTINCTION OF 1°, 2°, 3° AMINES.

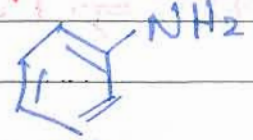
→ distinction of 1° amines from others (2° or 3°)

(1) CARBYL-AMINE TEST



- In carbylamine test
  foul smell ✓ 1°
  X 2° or 3°.

- carbylamine test is also given by AROMATIC 1° AMINE



$+ CHCl_3 + KOH \longrightarrow$

aniline.

—∞—

$R-NH_2 + CH_3I$ (excess) $\longrightarrow \longrightarrow \longrightarrow R-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_3\ I^-$

$R-NH_2 \xrightarrow{CHCl_3/KOH} R-\overset{+}{N}\equiv C^- \xrightarrow[\text{or } H_2/Pt]{LiAlH_4} R-NH-CH_3$

enables exclusively one methyl grp to get attached to 1° amine.

(2) HOFMANN'S MUSTARD OIL TEST

$R-NH_2 + S=C=S \longrightarrow R-\underset{H}{N}-\underset{S}{\overset{S}{C}}-SH$

(plays role of a specific ligand)

↓ ~~$FeCl_3$~~ Mercuric chloride.

A complex formed ~~w~~ by

~~$FeCl_3$~~ + $RNH-\underset{S}{\overset{S}{C}}-SH$

$HgCl_2$ → Mercuric chloride

~~smell of~~ repelling/eye irritating product/complex is formed.
(just like as in mustard oil)

classmate
Date 27·10·20
Page

(3) NITROUS ACID TEST

$R-NH_2$ + $\underbrace{NaNO_2+HCl}_{HONO.}$ → $R-OH + N_2\uparrow + H_2O$

1°. (in situ)

effervescence.

• amine giving effervescence with HONO ⟹ 1°.

PROCEED THROUGH CARBO-CATION INTER-MEDIATE

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-NH_2 + O=N-OH \rightarrow CH_3-\underset{CH_3}{\underset{|}{CH}}-N=N-OH$

$CH_3-\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\overset{+}{C}H_2 + N_2\uparrow \leftarrow CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-N=N-OH$

carbocation. (unstable)

$CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_3$

→ distinction/test of 2° amine

$R_2NH + HONO. \rightarrow R_2N-NO.$ (in situ)

NITROSAMINE
(formed only by 2° amine)
→ OILY, YELLOW colored

✓ above test is given ONLY by 2° amine.

Contd: test of PHENOL

$R_2N-NO + PhOH \xrightarrow{H_2SO_4}$ complex dye (GREEN) $\xrightarrow{NaOH}$ Salt of N (BLUE)

& CRUX

1° 2° 3° amine

HONO → effervescence 1°

" → no effervescence ⟹ 2° or 3°

→ Oily yellow 2°

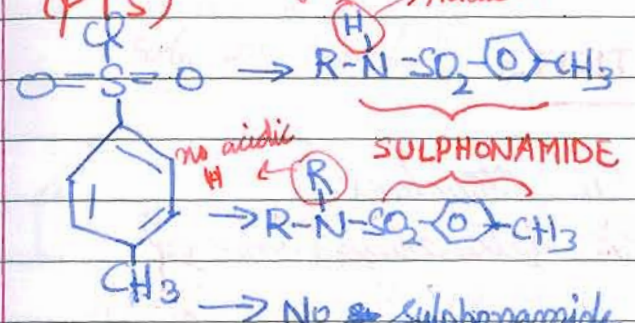
→ no oily yellow color 3°.

Separation of Amines

✓ Separⁿ of 1°, 2°, 3° amines

By HINSBERG'S METHOD

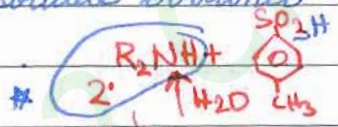
✓ Separating agent :-
p-toluenesulphonylchloride
(PTS)



→ No Sulphonamide

✓ Sulphonamide :- water insoluble

• So, 3° separated from 1° & 2°
∵ 3° remains soluble obtained by distillation.



Sulphonamide (Formed above) $\xrightarrow[NaOH]{aq.}$ $R_2N-SO_2-C_6H_4-CH_3$ (s) + $R-\overset{\ominus}{N}-SO_2-C_6H_4-CH_3$ (Na^+) (aq)

comes in soln.

$\xrightarrow{+HCl}$ $R-NH-C_6H_4-CH_3$ $\xrightarrow{H_2O/H^+}$ $R-NH_2$ (1°) + $HO_3S-C_6H_4-CH_3$

1° + 2° + 3° $\xrightarrow{PTS}$ liq + Solid

liq → distillⁿ → 3°

Solid $\xrightarrow{aq. NaOH}$ Soln $\xrightarrow{HCl}$ $\xrightarrow[H_2O]{}$ distillⁿ → 1°

Solid → $\xrightarrow{H_2O}$ 2°

✓ Separⁿ from other non-aminic compds

→ they should be non acidic, otherwise amine + acid → salt (base)

$R-NH_2$ + $R-CONH_2$ $\xrightarrow{dil. HCl}$ $R-CONH_2$ (ether) + $R-\overset{+}{N}H_3Cl^-$ (aq)

in presence/dissolved in ETHER.

Separate them

$R-\overset{+}{N}H_3Cl^-$ (aq) + NaOH

H_2O + NaCl + RNH_2

↓ Distillation

★ RNH_2

★ any non-aminic compd taken (which is not an acid).

Aromatic Organic Chemistry

Imp: ★ **Aromaticity**

Aromaticity is a phenomena which provides addⁿᵃˡ stability to the sys. Stability gained by aromaticity is greater than stability gained by resonance alone.

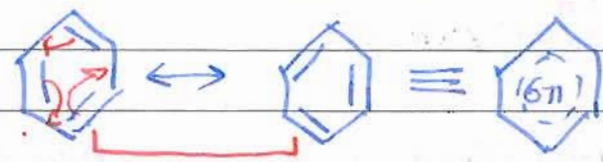
CRITERION FOR AROMATICITY

"Hückel" Rule

1. There must be a CYCLIC structure.
2. There must be a cyclic delocalization of $(4n+2)\ \pi\ e^-_\Delta$; $n \in W$
   i.e, there must be a closed loop of $(4n+2)\ \pi\ e^-_\Delta$.
3. Atoms involved in aromatic ring must be co-planar.

—x—

eg:



KEKULE BENZENE

(earlier predictions of Benzene

DEEWAR benzene

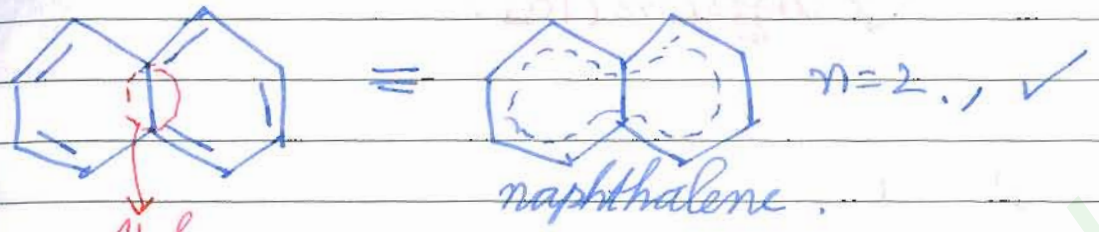
WOHLER → father of ORGANIC CHEMISTRY. (synthesised UREA)

• Brought benzene from Whale.)

* For a compd. to be aromatic, it should be planar.
FALSE

* For a compd. to be aromatic, the electrons of aromatic ring must be planar. TRUE.

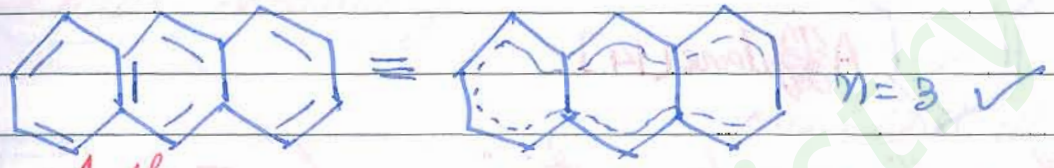
—x—



$n=2$, ✓

naphthalene.

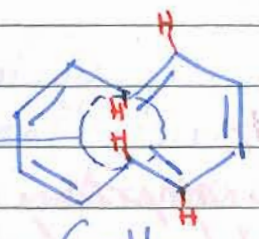
It has no role on delocalisⁿ



$n=3$ ✓

Anthracene.

—x—



$n=2$

≡ NOT AROMATIC.

↳ although it satisfies all condⁿˢ given.

$C_{10}H_{10}$

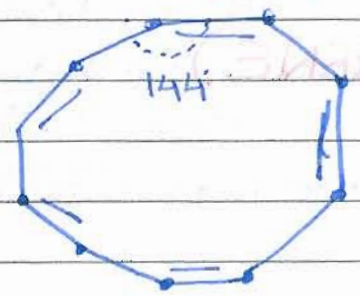
e.g. 2 trans

REASON

undergo steric repulsion. So, they move in & out of plane. Hence, loss of planarity. The loop of $(4n+2)\pi$ e^-_δ is broken.

—x—

• Another structure of $C_{10}H_{10}$. :- NON AROMATIC.



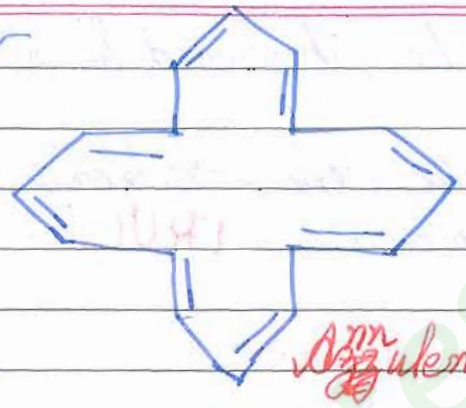
$C_{10}H_{10}$

:- Strain of 24° on each carbon. (144 − 120 = 24°)
So, it overcomes the factor of aromaticity.

ANNULENE

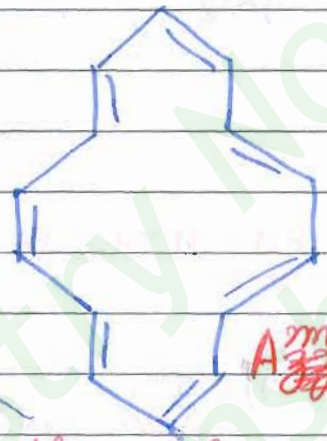
~~AZZULENE~~

FAMILY OF Compds.



: An anti-aromatic compd. (~~not~~ will be done later).

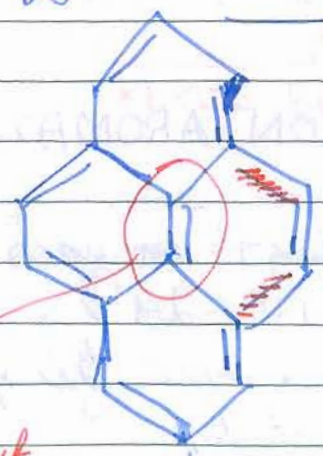
~~Azz~~ annulene [16].



Annulene [14]

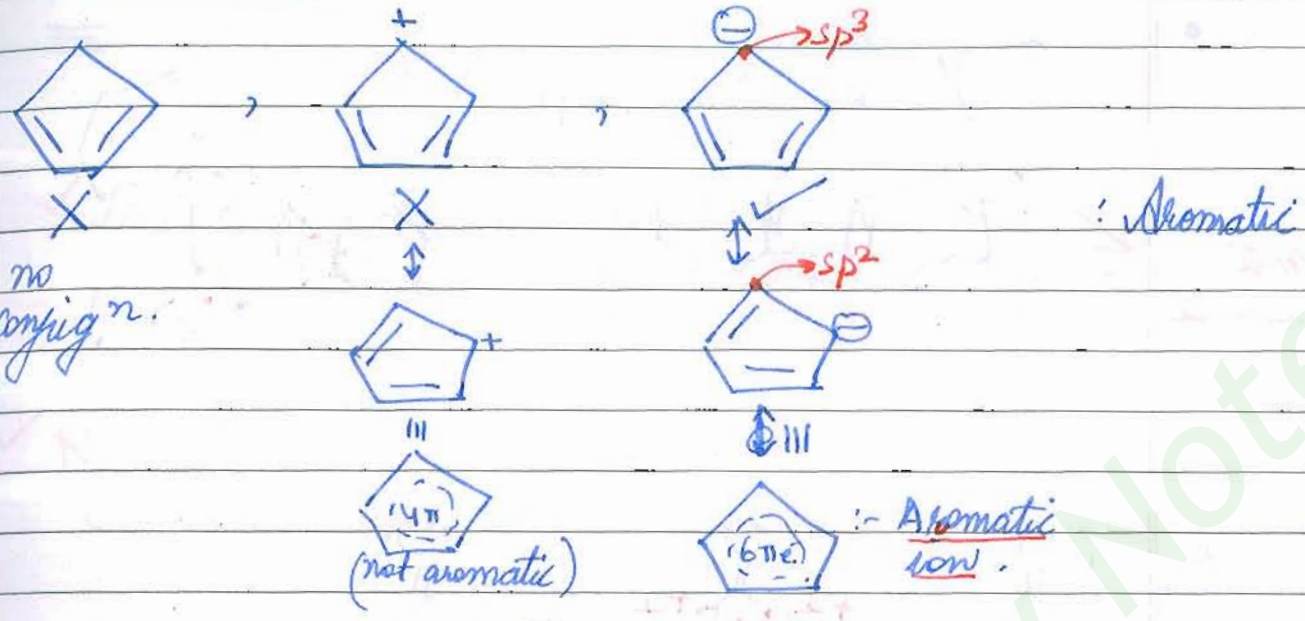
- All cyclic compds containing alt. = – = bonds are in the family of
  * ~~AZZULENES~~ * ANNULENES
- ✓ smallest ~~azzulene~~ annulene :- BENZENE
- ✓ except annulene [10], all cyclic compds. having alt. → = – bonds & odd no. of π-e⁻s are Aromatic.

annulene [10] :- non aromatic



:- AROMATIC (PYRENE)

doesn't participate, it will behave like alkene & hence, would also undergo add^{n} & oxn



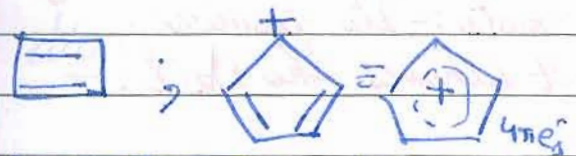
no conjugⁿ.

: Aromatic

(not aromatic)

:- Aromatic ion.

☆ Anti-Aromaticity



satisfy all condⁿs except $(4n+2)\pi$ e^-_s.

In anti-aromatic sys. satisfy all criterions of aromaticity except the HÜCKEL RULE & CONTAIN A CLOSED LOOP OF $4n\ \pi$ e^-_s.

☆ As much as Aromaticity stabilises, in same way, Anti-Aromaticity Destabilises (Reason MOT).

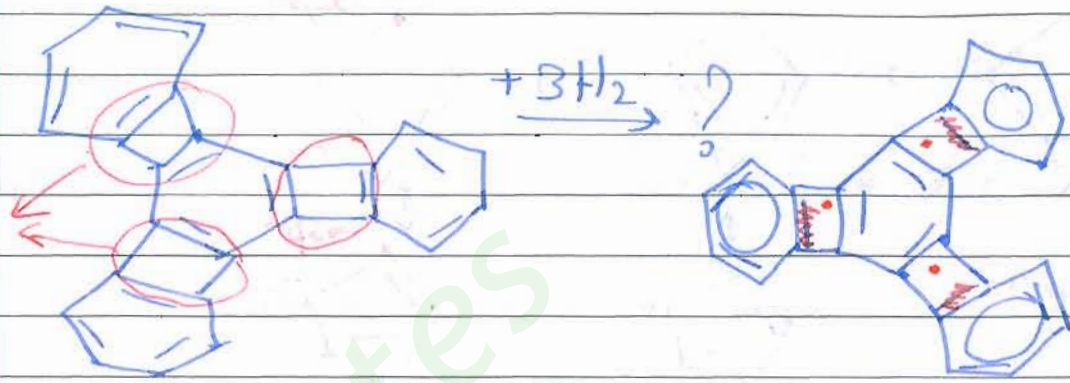
Non-Aromaticity:

compd that is neither aromatic nor anti-aromatic are non-aromatic.

eg:- CH_4.

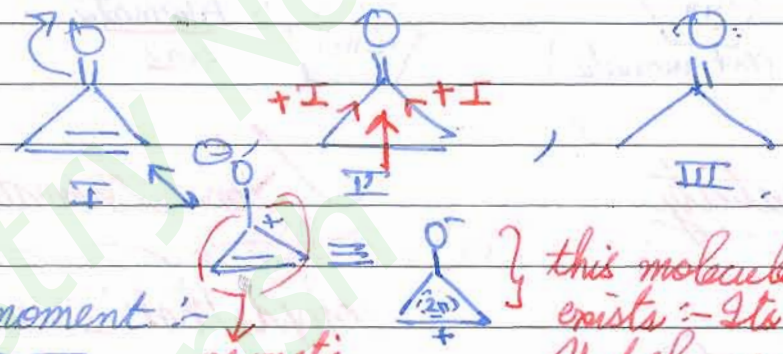
99

Q.



Anti aromatic

Q.



Dipole moment :- I > II > III

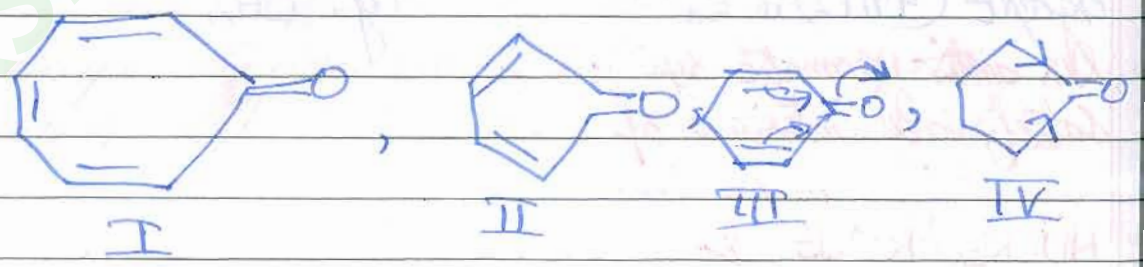
I → aromatic

II → +I effect & vector addⁿ

III → anti aromatic

} this molecule predominantly exists :- Its dipolar. It behaves like NaCl.

Q.



Dipole moment :- I > III > IV > II

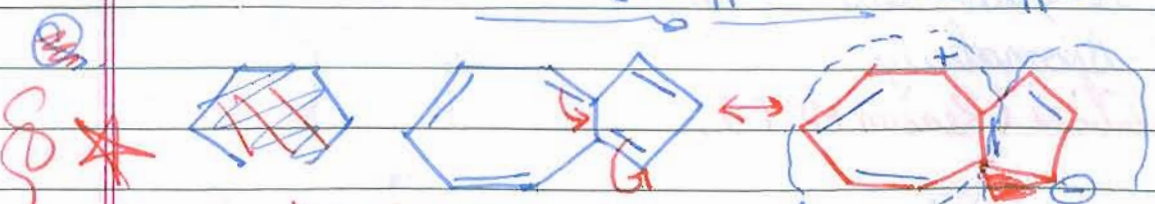
I → aromatic

III → supplement by R-effect

IV → supplement by +I-effect

II → anti aromatic

Q.



AZZULENE

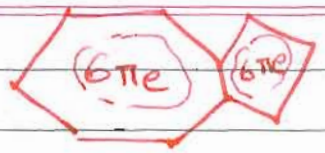
- ✓ water soluble.
- ✓ conducting in aq. solⁿ

tropyllium ion

cyclopentadienyl ion

SEPARATELY AROMATIC

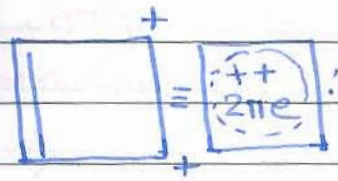
classmate
Date
Page

≡ 

:- These 2 are independently aromatic sys.

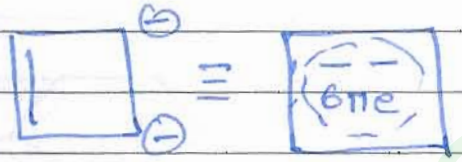
✓ This gives it Ionic character
→ water soluble
→ highly conducting

✓ Non-ionic form of azzulene is non-aromatic
(Reason:- expt. based:- solubility, conductivity seen).



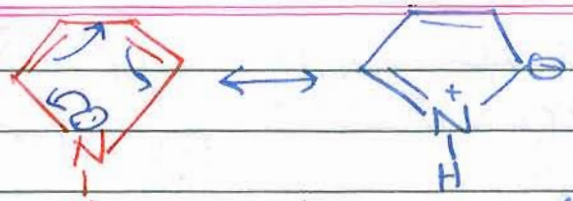
:- EXISTENT.
Reason:- Aromaticity.

dicarbocation



:- EXISTENT
Reason:- Stability due to aromaticity.

+2 Chemistry Notes Akshansh

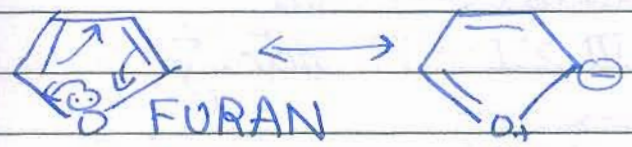


PYRROLE :- Aromatic (taking lone pair)

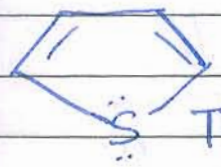
: Aromatic (without taking lone pair)

PYRIDINE

* HETEROCYCLIC COMPDS.
contain ring & atleast one atom of ring is not carbon



FURAN : Aromatic

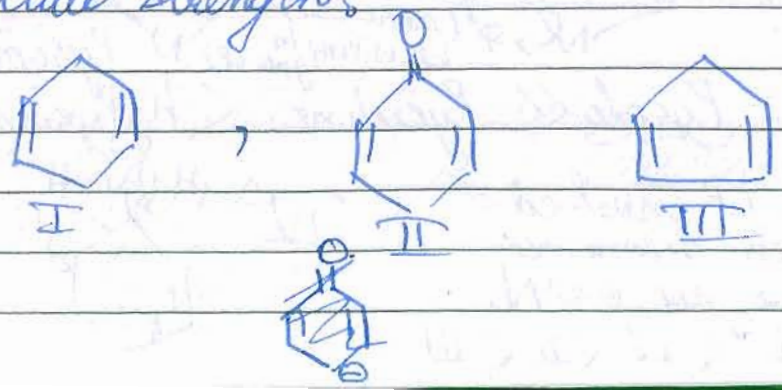


THIOPHENE : Aromatic

Q Thiophene is less aromatic than Furan.
Reason:- S & C are of diff^t periods & so, effective overlap won't occur of p orbitals & there would be more difference in energy.

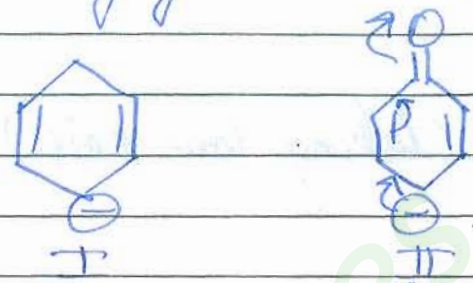
—×—

Q. Acidic Strength?



I , II , III

Their conjugate bases are



I

Non aromatic

II

(most stable conj. base)

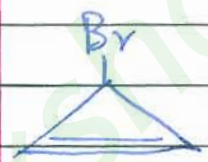
Aromaticity + (-ve) on E_N

III

Aromatic

So, order II > III > I :- Acidity.

—∞—



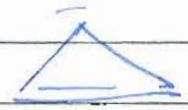
I :- Homolytic.

II :- Heterolytic (Br^-)

III :- Heterolytic (Br^+)

So,

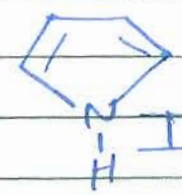
:- most likely.



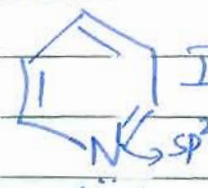
:- least likely.

—∞—

Q.



I



II

sp^2 (more E_N, less willing to give LP)

III

sp^3 (more willing to give LP)

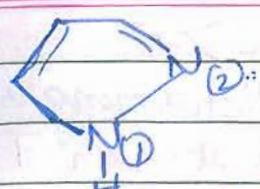
Pyrimidine

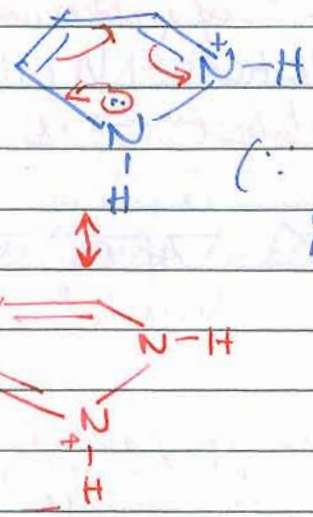
Basicity :- Pyrole << Pyridine < Pyrimidine

LP involved in resonance. So, not on N.

IV

Basicity :- I < IV < II < III.

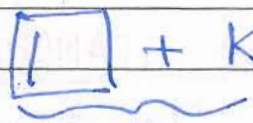
Q.  $\xrightarrow{HCl}$?

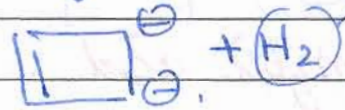


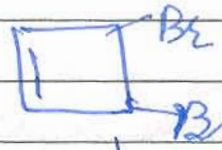
imidazole

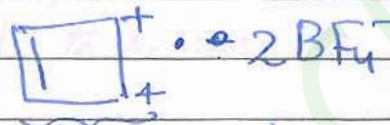
Reason ② equivalent resonance structure ∴ most stable.

Reason ① (∵ Basicity of $N_{(2)} > N_{(1)}$)

Q.  $+ K \xrightarrow{\Delta} H_2 \uparrow$



Q.  $+ AgBF_4 \longrightarrow$ Ppt. of AgBr.



Its aromatic ($n=0$)

—x—

✱✱ BENZENE & SUBSTITUTED BENZENE

• Preparation of benzene.

Benzene or alkyl benzene is obtained mainly by destructive distillⁿ of crude oil.

1. By polymerisation of acetylene.

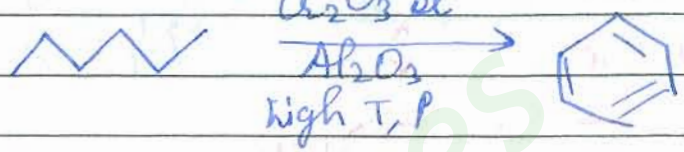
$3C_2H_2 \xrightarrow[\text{i.e red hot Cu tube}]{Cu/\Delta\Delta}$

(not bi, or tetra merisⁿ ∴ benzene is aromatic, stable)

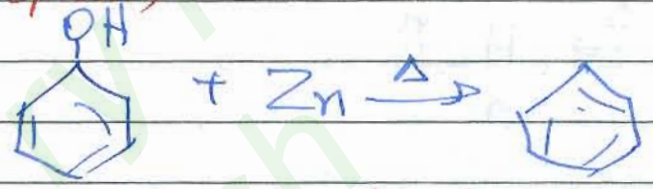
(trimerisation)

St. chain

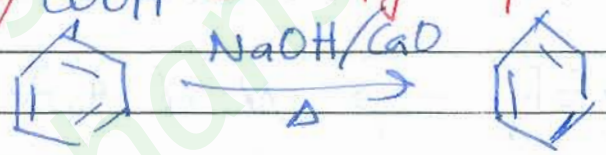
2. Aromatisⁿ of alkane with no. of C ≥ 6.
or DEHYDROGENATION RXN or Reforming rxn
↳ catalyst :- Cr_2O_3 or Al_2O_3 } at high T, P



3. Distillation of phenol (produced as a major product in destructive distillⁿ of crude oil) by using Zn (pwdr.)



4. By decarboxylⁿ of Benzoic acid.



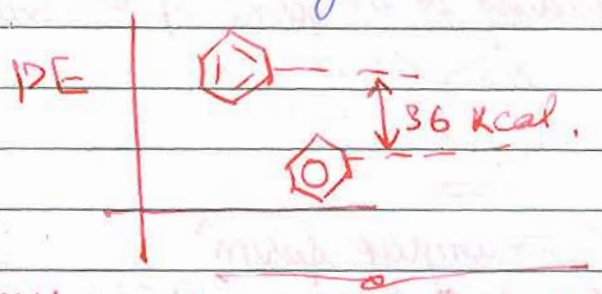
- Properties of BENZENE

1. Although it has 3° of unsaturation, yet it doesn't show property of alkene :-
π bonds in benzene are involved in aromaticity & thus, are not free for rxns. of alkene.
2. It doesn't decolorise Br-H_2O. } ↓ loss of aromaticity occurs.
3. It doesn't decolorise Bayer's Reagent
4. Alkene undergoes MK's addⁿ with HCl, but, benzene shows no rxn with HCl. (loss of aromaticity)
5. $\xrightarrow[H_2SO_4]{\text{cold. dil}}$ not absorbed.

6. All C=C bonds are identical with bond order (1.5), bond energy.

Resonance energy of benzene ≈ 150 KJ
= 36 k.cal.

P.E diff. b/w cyclohexatriene & benzene = 36 Kcal.

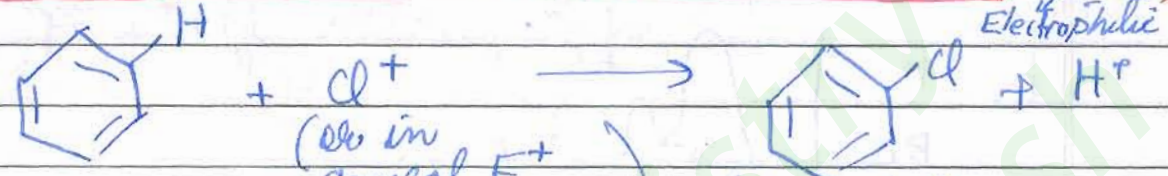


★ AROMATIC ELECTROPHILIC SUBSTITUTION RXN ((S$_E$Ar))

Imp.

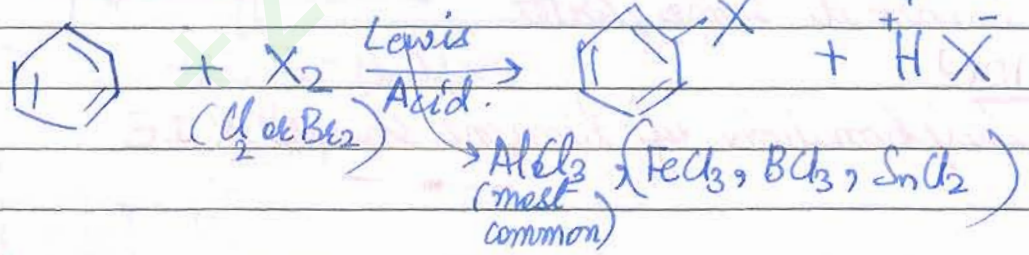
Substitution — Aromatic

Electrophilic

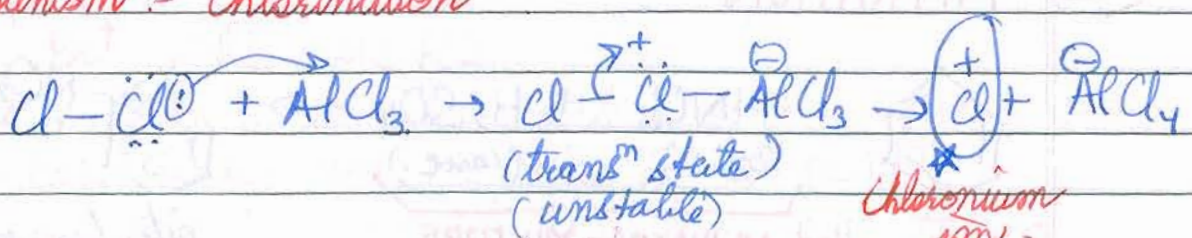


★ Benzene or aromatic sys PREFER to undergo, electrophilic substitution rxn rather than electrophilic addn to retain its stability, aromaticity.

(1) HALOGENATION OF BENZENE

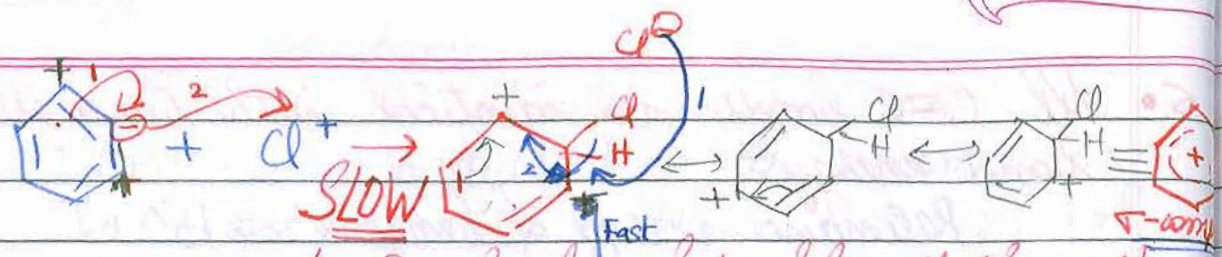


Mechanism :- Chlorination

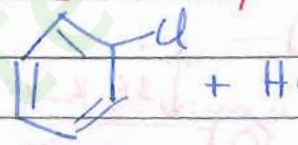


classmate
Date
Page

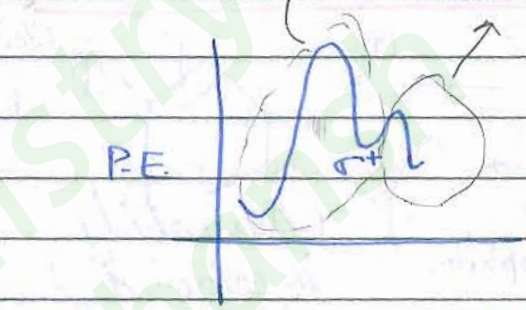
S2



↳ Bimolecular electrophilic attack :- The rate determining determining step leading to form^{n} of σ-complex.



Effectively → ✓ σ-complex form^{n}
✓ return to aromaticity



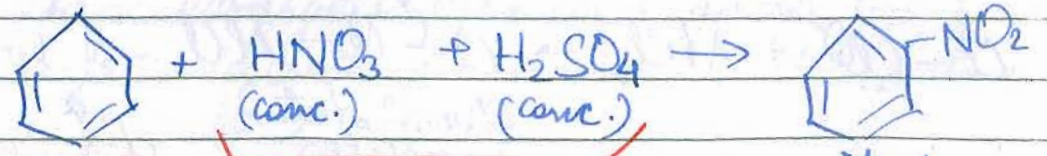
Q. C_6H_6, C_6D_6 :- Rate of rxn :- $C_6H_6 = C_6D_6$
(∵ C-D or C-H bond is not broken in slowest step)

* S_EAr rxn doesn't show KIE (kinetic isotopic effect) i.e C_6H_6 or C_6D_6 (deuterated benzene) react at same rate.

EXCEPTION

* Sulphonation of benzene shows KIE.

(2) NITRATION



called NITRATING MIXTURE
(i.e mixture used in nitr^{n})
or MIXED ACID (MA)

nitrobenzene.

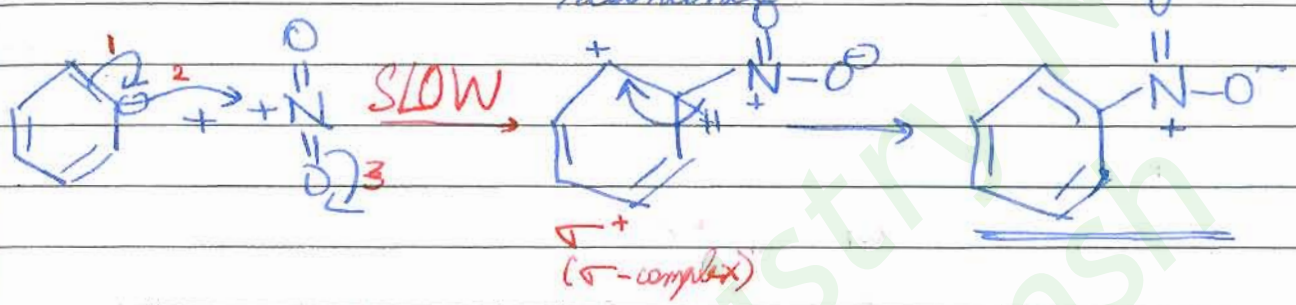
* Only neutral electrophile :- SO_3

Mechanism

1. $HNO_3 + 2H_2SO_4 \rightarrow \overset{+}{N}O_2 + 2HSO_4^- + H_3O^+$

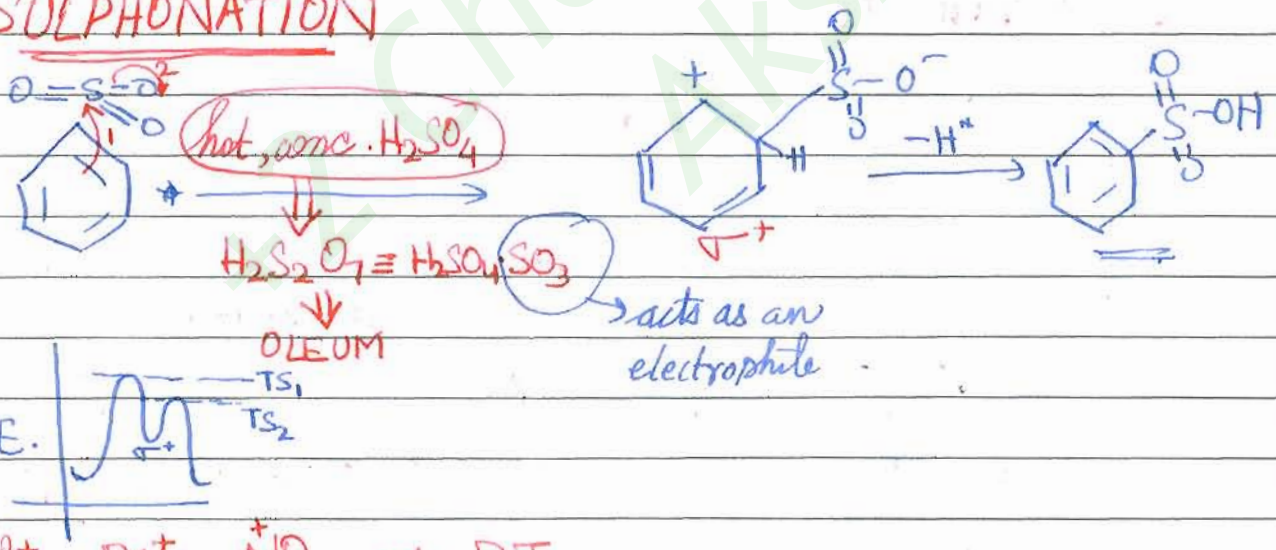
nitronium ion (electrophile).

- (when H_2SO_4 & HNO_3 react, HNO_3 acts as a base)
- NO_2^+: $O=\overset{+}{N}=O$:- linear ; doesn't show resonance.



✓ nitr~ doesn't show KIE.

(3) SULPHONATION



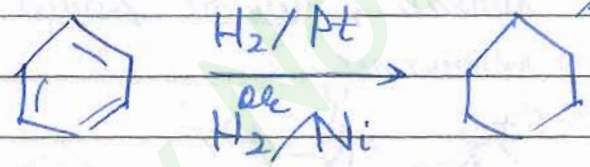
* Cl^+, Br^+, $\overset{+}{N}O_2$ are RI.
but, SO_3 is an intermediate. So, σ+ formed from it is more stable, less PE. than in Cl^+ or NO_2^+
* Sulphon^n rxn is reversible in nature due to very close PE to 2 trans^n states.

$Cr_2O_4^{2-}$:- chromite.

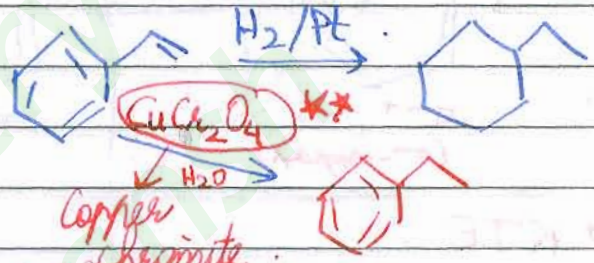
* Sulphonation can be reversed by dilution of acid i.e Desulphonation.

* Deutrated benzene undergo decreased sulphonation rxn
∵ TS_2 PE ↑ & becomes ≈ TS_1 PE.
So, it shows KIE.

⟨4⟩ REDUCTION :- Only rxn where benzene and alkene show same rxn. But reactivity of benzene < reactivity of alkene.

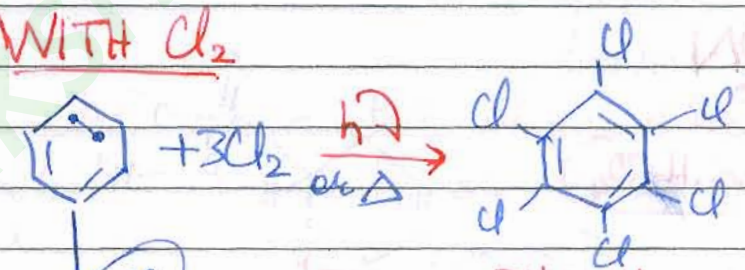


• eg :-



Copper Chromite (mild RA)

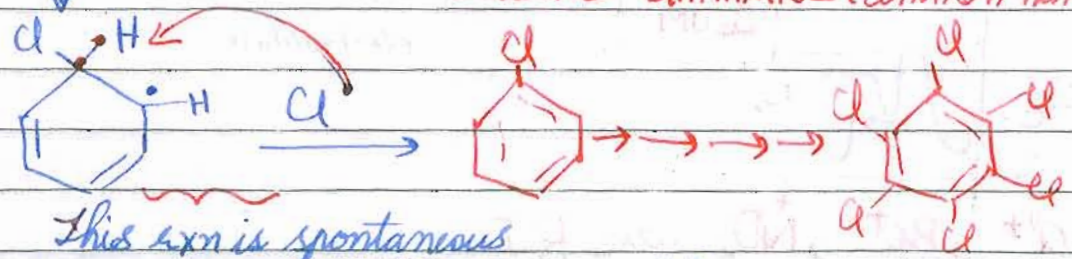
⟨5⟩ WITH Cl_2



: By free radical substitution mec

called as GAMAXINE (common name)

by homolytic fission of Cl_2



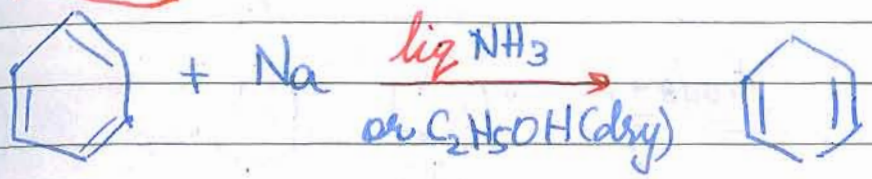
This rxn is spontaneous because benzene tries to retain its aromaticity quickly.

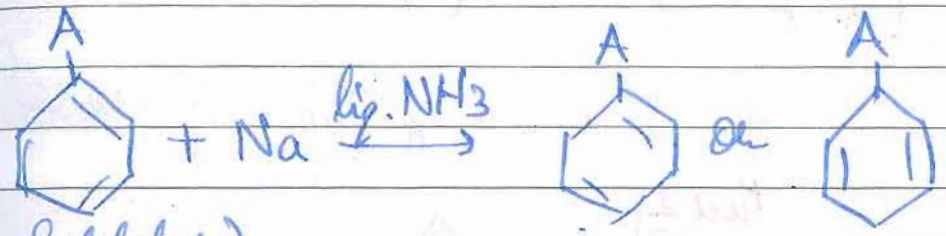
—∞—

(6)

✡ PARTIAL Red^{n} of Benzene & derivatives

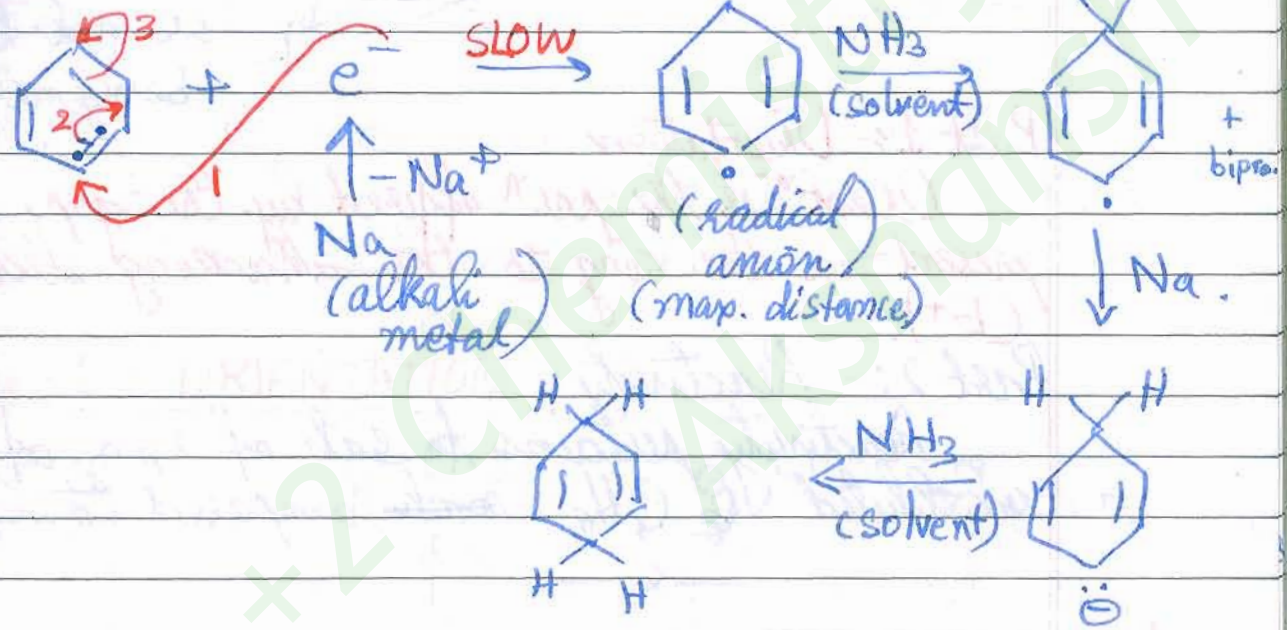
Birch's Red^{n}



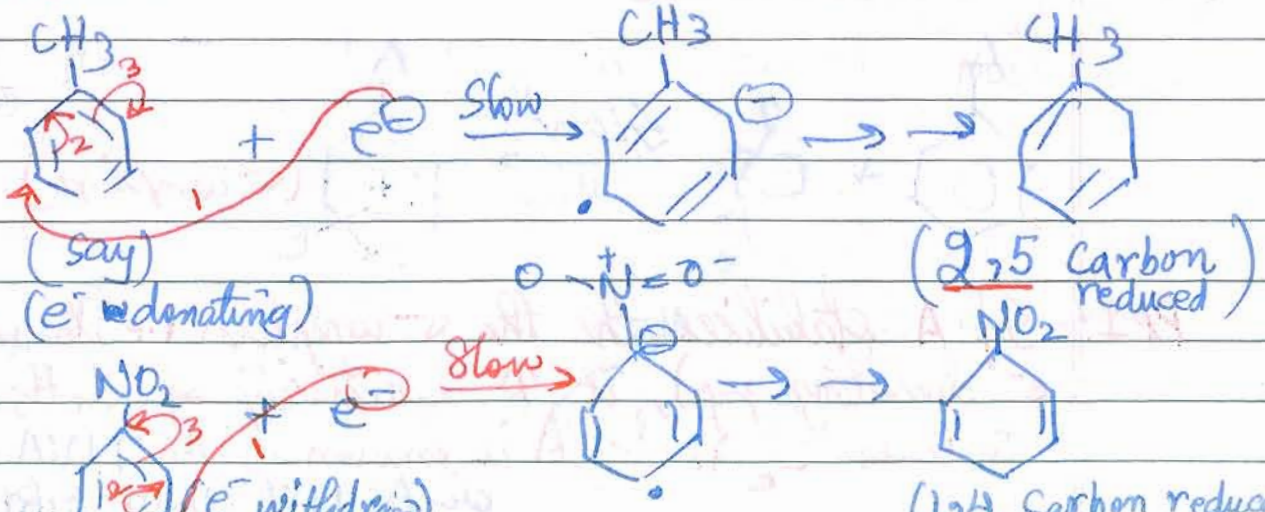


(substituted)

Mechanism



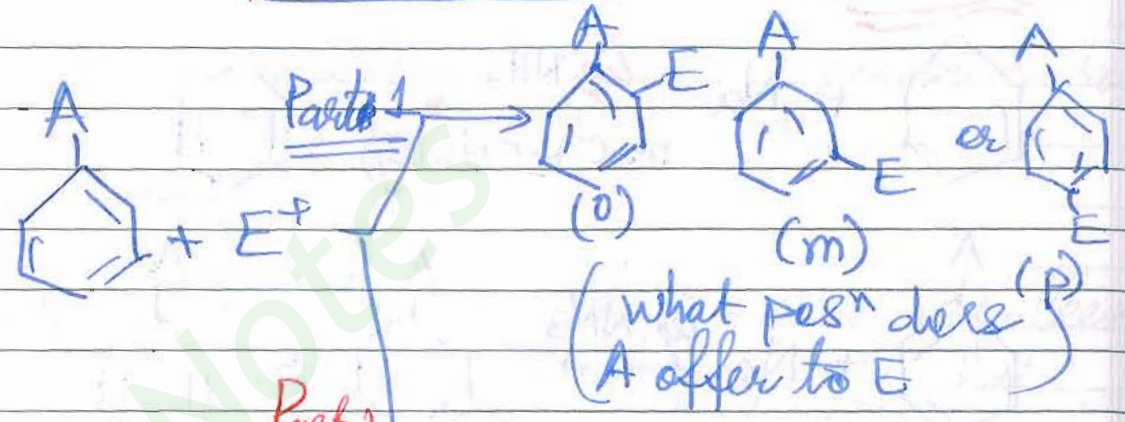
Substituted



(S_EAr)

✡ AROMATIC ELECTROPHILIC SUBSTITUTION RXN

REACTIVITY & ORIENTATION



Part 1:- Orientation.

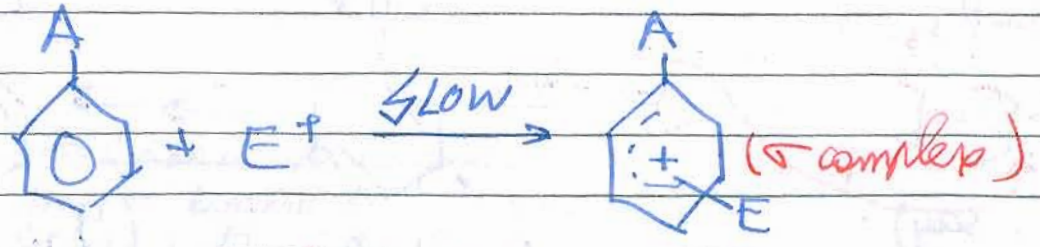
Orient^n is the pos^n offered by the grp present on the ring to the attacking electrophile (E^+).

Part 2:- Reactivity.

Reactivity pertains to rate of rxn of substituted C_6H_6 compared to C_6H_6

—x—

✳ PART-2 : REACTIVITY



Pt 1:- If A stabilises the the ↓ complex (i.e its an e^- donating grp), it ↑ reactivity of C_6H_6 towards S_EAr & A is known as ACTIVATOR or ACTIVATING GROUP

C.2:- For A to be activator, it must be an e^- donating grp.

C.3:- If A destabilises the σ complex, it ↓ the reactivity of C_6H_6 towards S_EAr rxn. & A is known as DEACTIVATOR or DEACTIVATING GROUP.

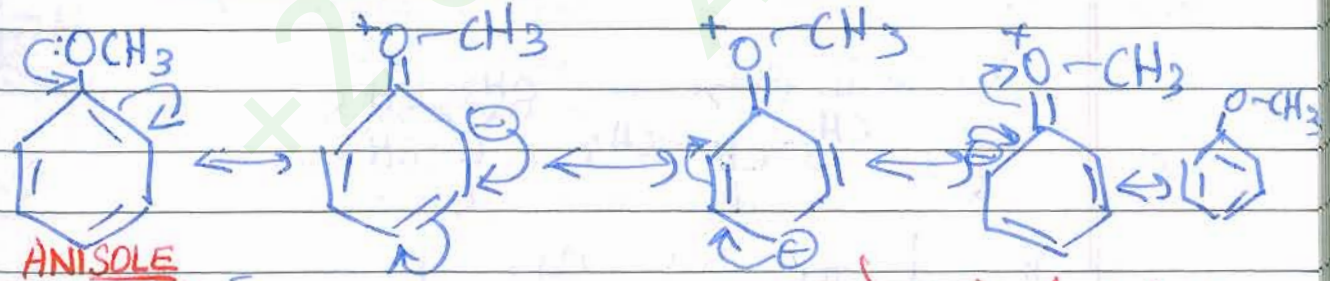
C.4:- For A to be deactivator, it must be an e^- withdrawing grp. (I, R, H-effect → any)

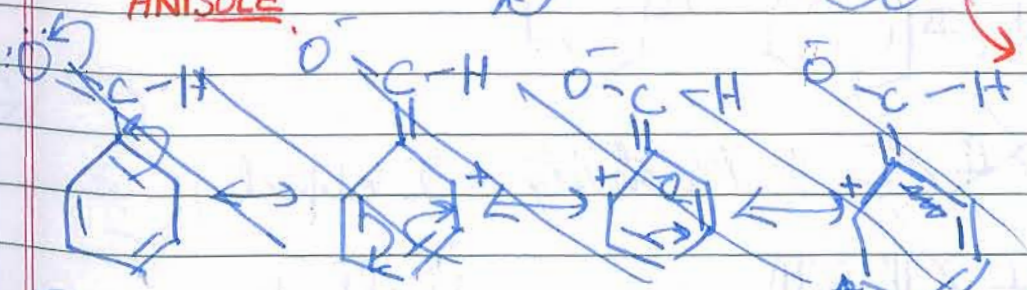
eg: In & , II is more reactive
∵ Me is e^- donating (+I & +H effect)

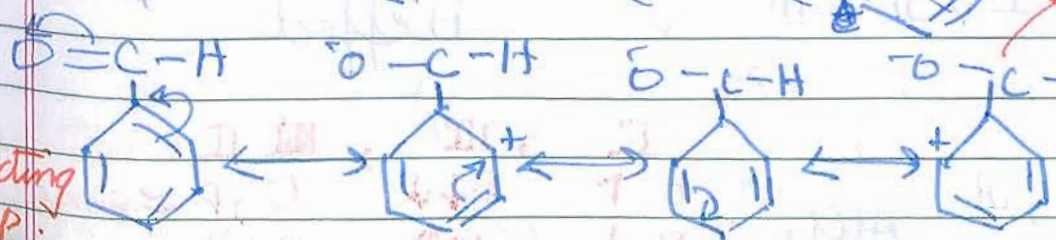
III least reactive
∵ NO_2 is e^- withdrawing (-I & -R effect)

II > I > III :- reactivity.

PART-1 : ORIENTATION




→ E^+ at O & P posn only


→ E^+ at m posn only.

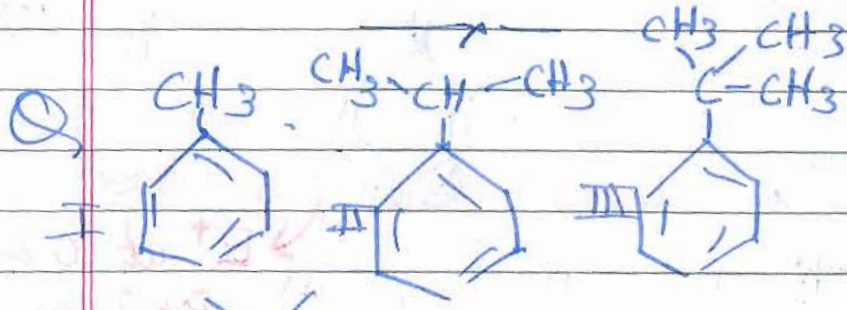
★ Common Activating - Deactivating Gp

Activators	Deactivators
o-p directing: $-R$, $-OR$, $-\ddot{N}H_2$, $-\ddot{O}H$, $-NHCOR$ (i.e $-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-R$)	m-directing: $-NO_2$, $-CN$, $-CHO$, $-C(O)R$, $-SO_3H$, $-\overset{O}{\overset{\|}{C}}-NH_2$, ~~$-NH_3^+$~~, $-\overset{O}{\overset{\|}{C}}-OR$
	o-p directing: $-X$

aniline part — carboxylic acid part

ANILIDE

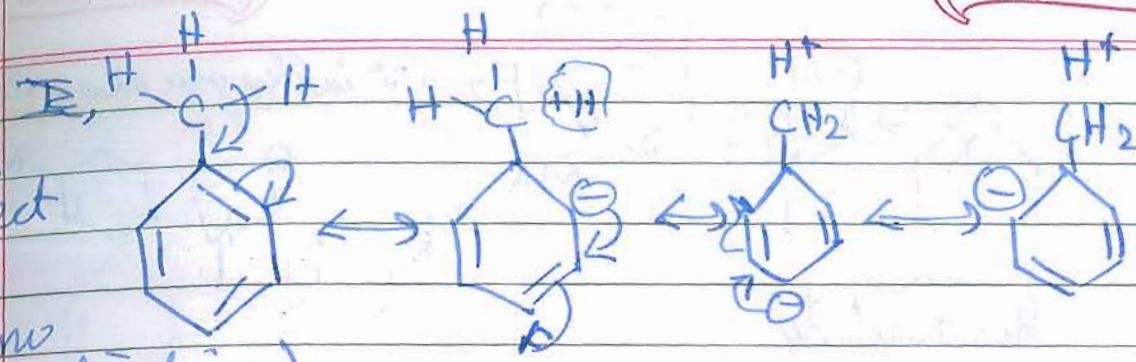
★ All activators are USUALLY o-p directing.
★ All deactivators are USUALLY m directing.
Exception:- halides are o-p directing & deactivating.

Q. 

III ~~>~~ II > I :- Reactivity I effect

Reactivity :- I > II > III. ✓ H effect

$I, II, III \xrightarrow[AlCl_3]{Cl_2}$ I , III , II
o ↑ , o ↓↓ , o, p ≈ same
p ↓ , p ↑ , p bit more

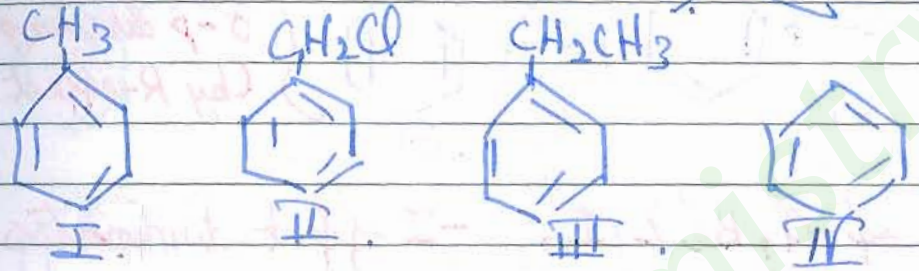


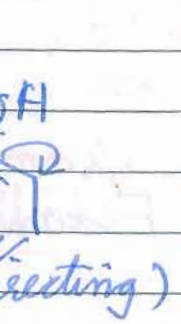
effect
(o-p directing)

Q. ↑ order of reactivity towards sulph

H effect

II < IV < III < I or IV < II < I < III .



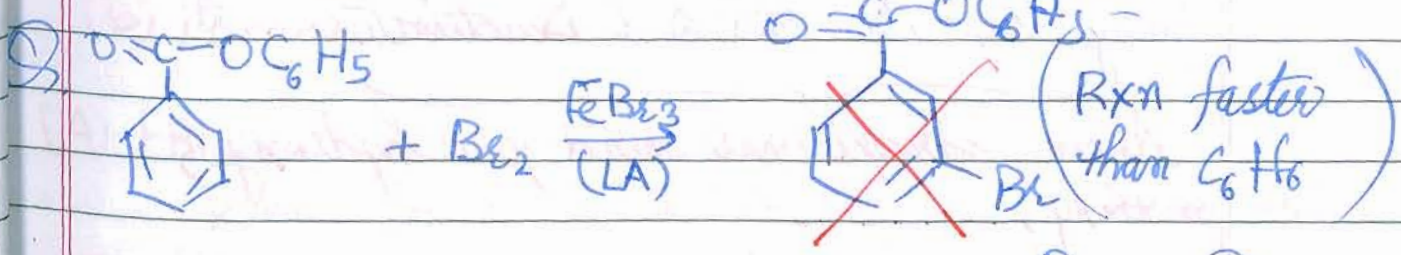


Ph–CH₂–Cl

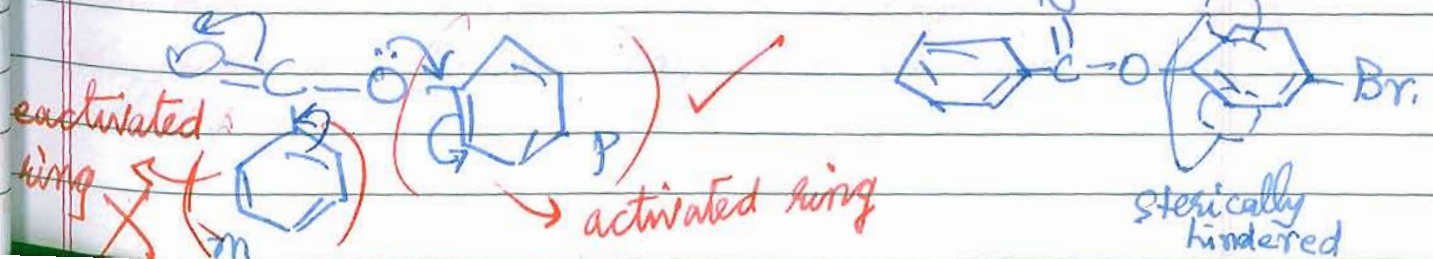
Cl e⁻ withdrawing → withdraws e⁻ from C–Cl bond. So, CH₂ withdraws e⁻ from Ph. So, CH₂Cl as a whole is e⁻ withdrawing.

Here, H-effect is weaker than I-effect.
So, II < IV.

(o-p directing)



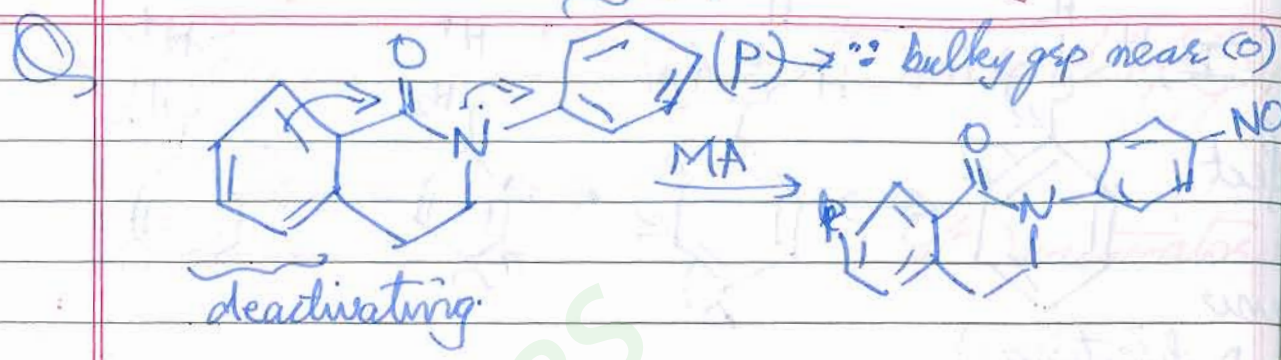
(Rxn faster than C_6H_6)



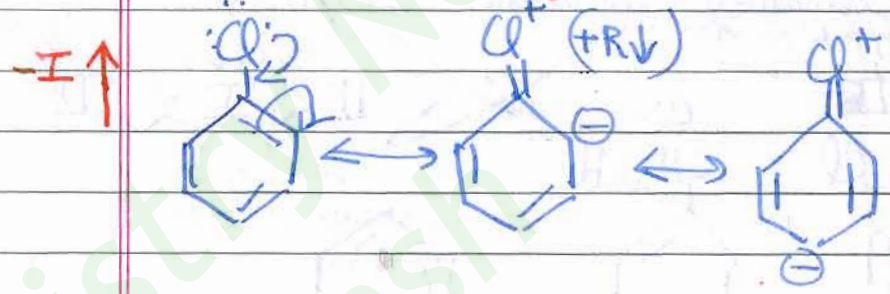
deactivating

activated ring

sterically hindered



* Imp concept :- Why halogen is deactivator?

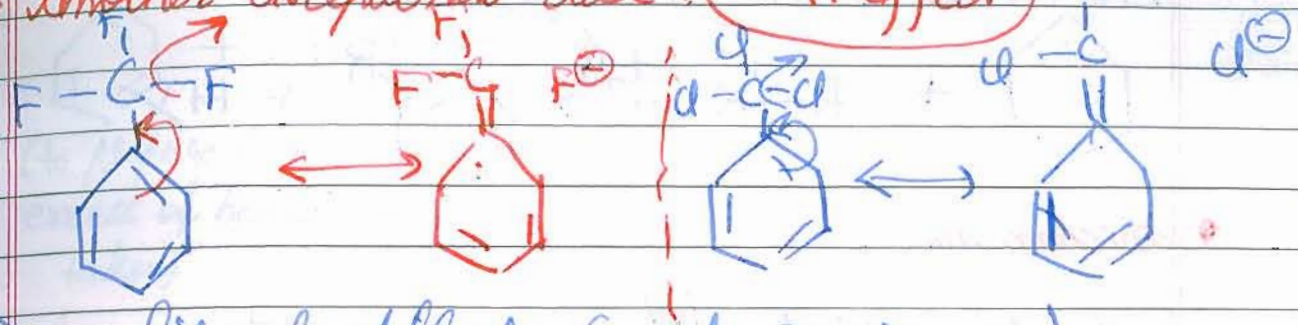


- In case of Cl, Br & I, -I effect dominates over +R effect (∵ of effective ~~overlap~~ not occuring b/w orbitals of like energy. Here Cl & C are from different energy)
  So, Halogens are deactivators.

- In case of F (although F & C are from same period — same energy), but, F can never bear a +ve charge. So, it never donates by +R effect. Hence, among halogens, its the best deactivator.

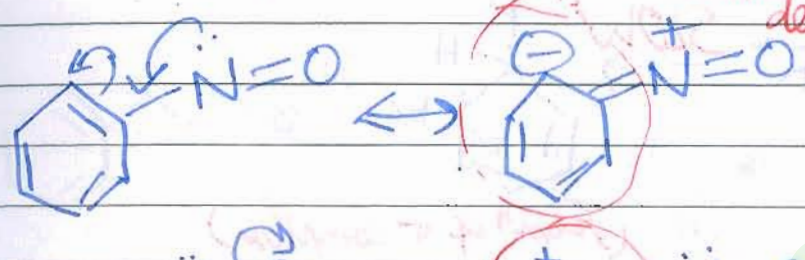
Above concept not valid for hydroxy, methoxy, ...

* Another exceptional case : **−H effect**



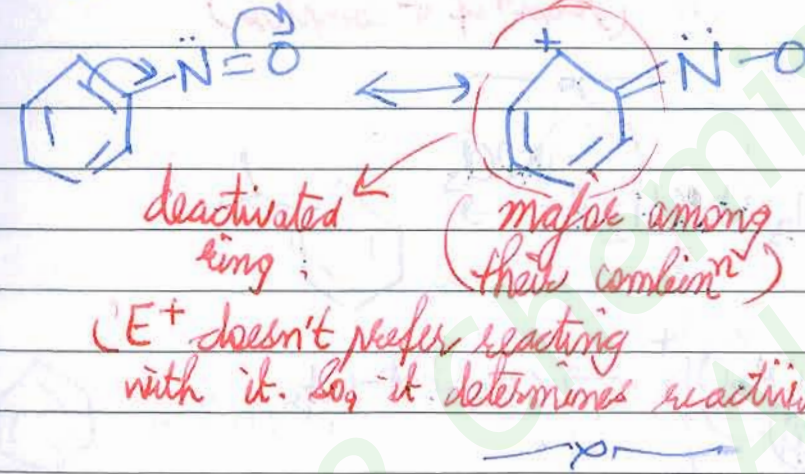
→ valid only till Cl. (not for Br, I)

* Another exception.



activated ring (so, E^+ prefers attacking it & hence, it determines orientation)

⇒ It is o-p directing grp.



deactivated ring; (E^+ doesn't prefer reacting with it. So, it determines reactivity)

major among their combinⁿ

⇒ It is deactivating grp.

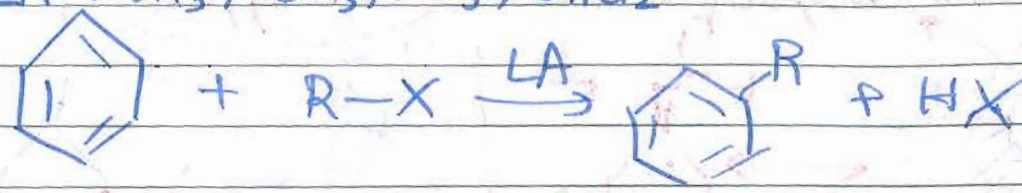
FRIEDEL CRAFT RXN

(A) FRIEDEL CRAFT ALKYLATION (FCA)
(B) FRIEDEL CRAFT ACYLATION. (FCA_c)

(A) FRIEDEL CRAFT ALKYLATION (FCA)

When C_6H_6 or substituted benzene is treated with an RX, in presence of a LA catalyst, alkyl benzene is produced. Alkylⁿ may also be done using alcohol or alkene.

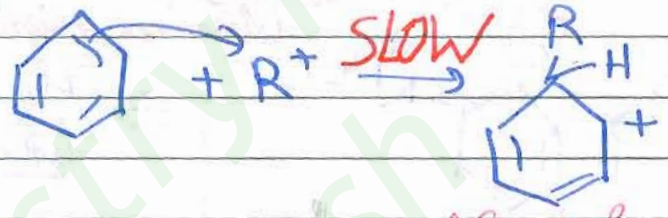
LA: $AlCl_3$, $FeCl_3$, BCl_3, $SnCl_2$



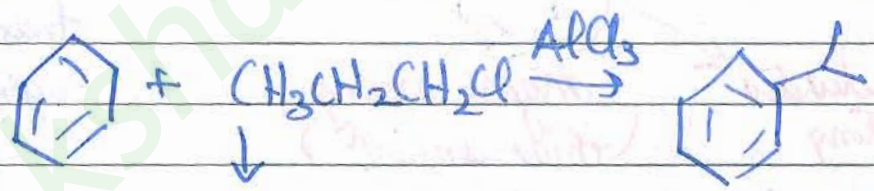
- mechanism

$$R\text{-}Cl + AlCl_3 \xrightarrow{fast} R^+ + AlCl_4^-$$

carbocation (rearray, if possible)

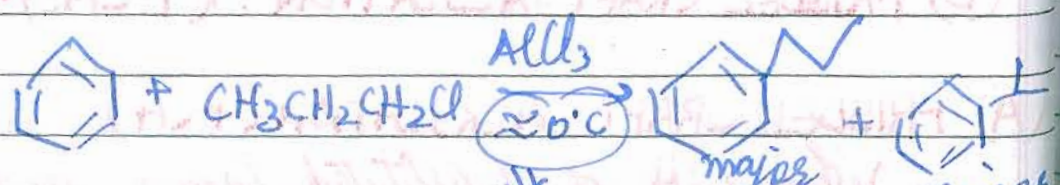


(form^n of σ complex)

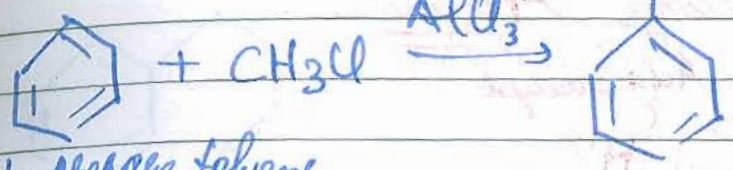


* hence, under ordinary cond^n, FCA can't be used to introduce a St. chain hydrocarbon to benzene ring.

To minimise rearray.

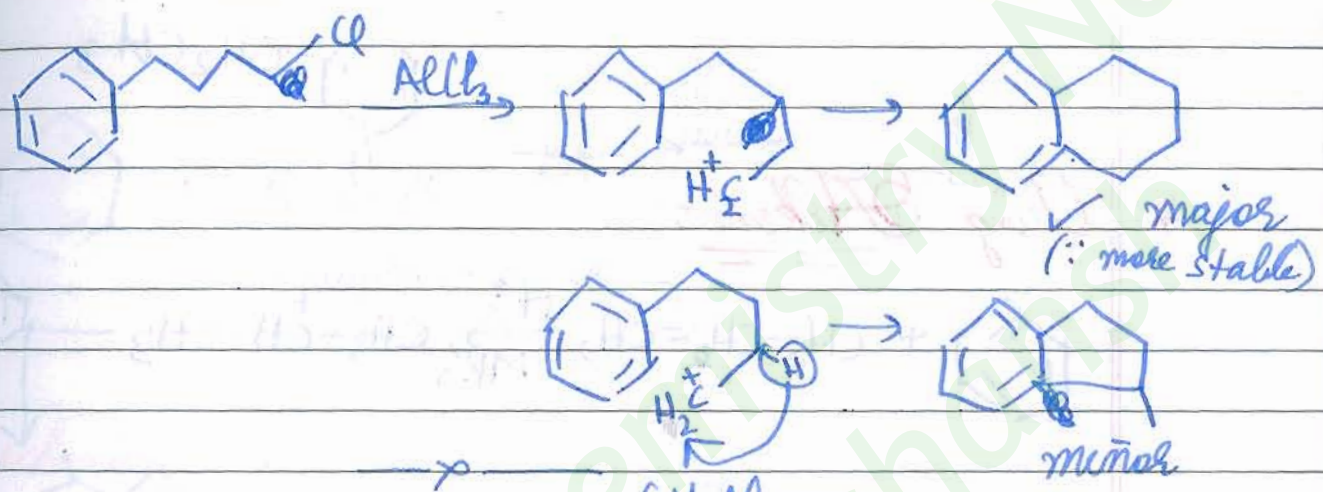


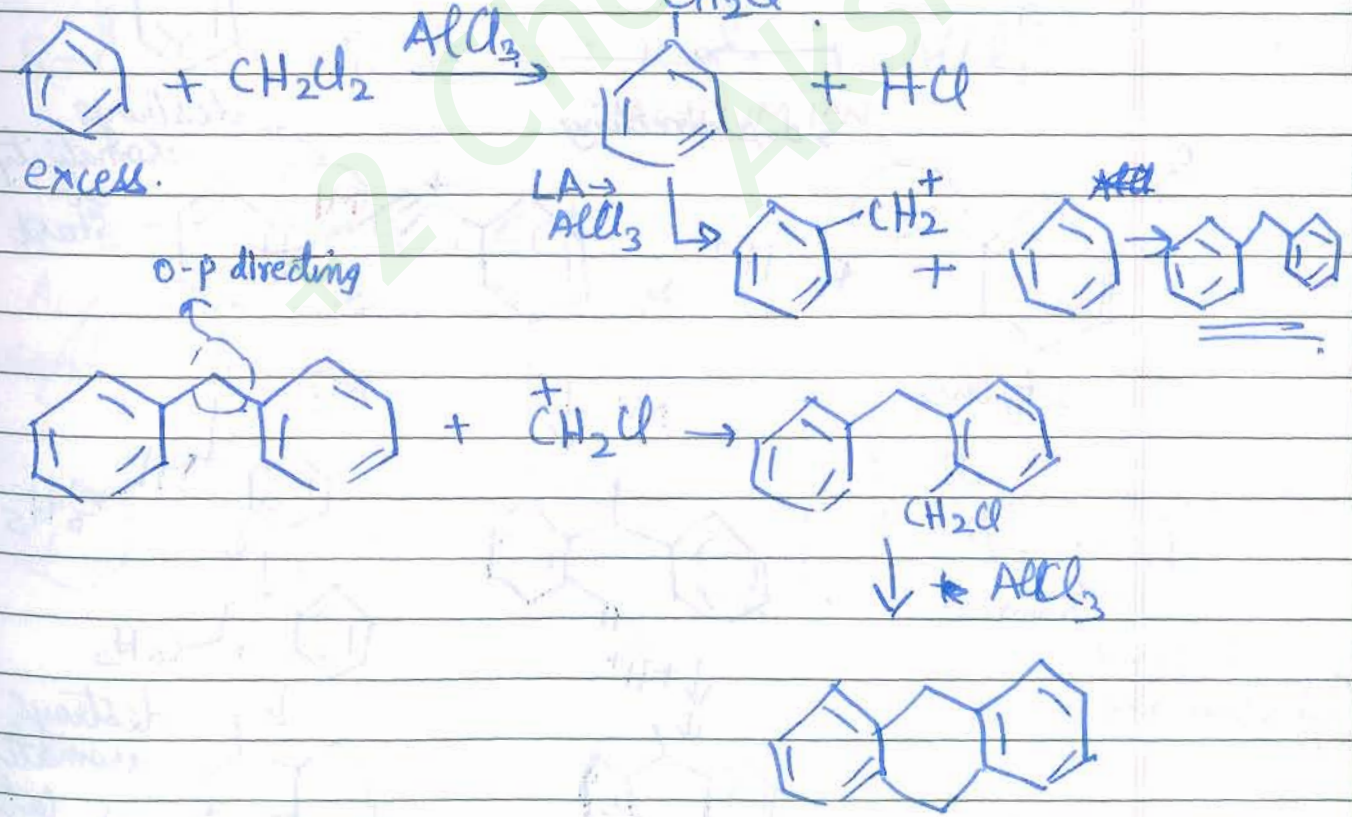
i.e very low temp. (So that rearray doesn't take place almost)

Q) 

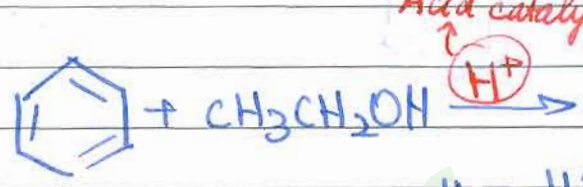
(to prepare toluene, excess of benzene is taken)

* In FCA, product is more reactive than reactant towards S_EAr giving di, tri alkylation. Hence, excess of reactant is reqd for desired single substituted product.

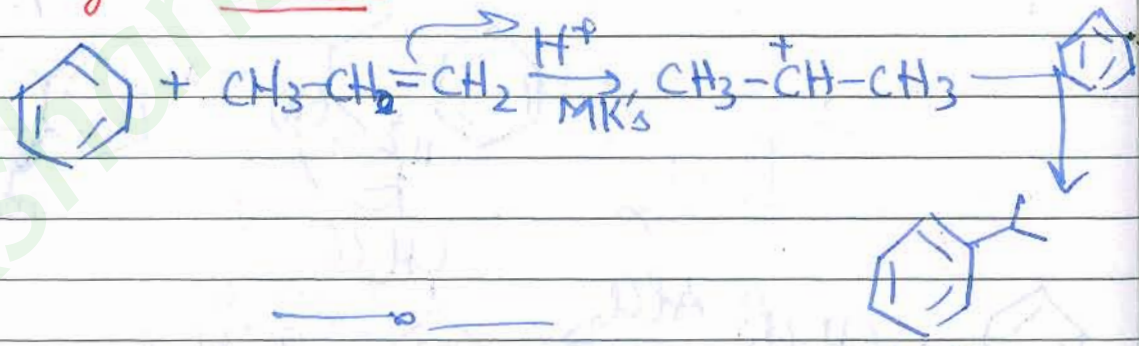
Q) 

Q) 

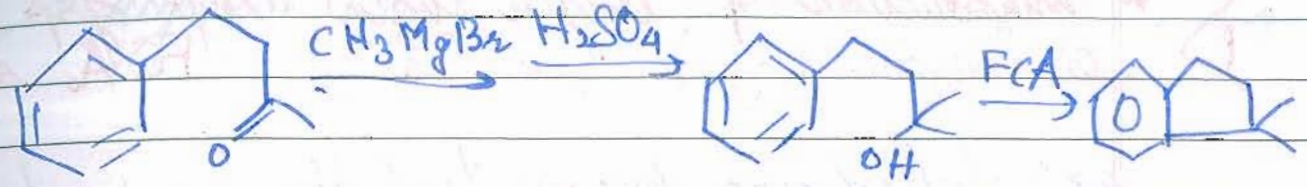
★ Alkylation using Alcohols



★ Using Alkenes

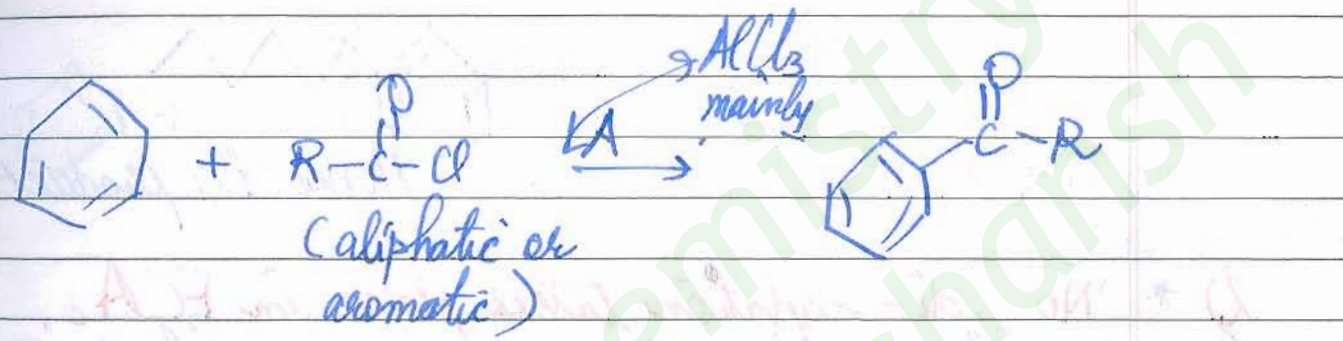


JEE

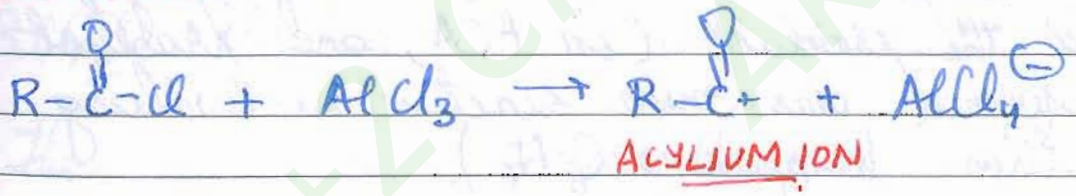
Q. 

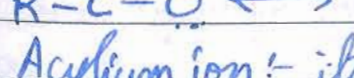
(B) FRIEDEL CRAFT ACYLATION (FCAc)

When Benzene or substituted benzene is treated with acid chloride or acid anhy anhydride in presence of LA catalyst, acylation takes place & aromatic ketone is obtained.

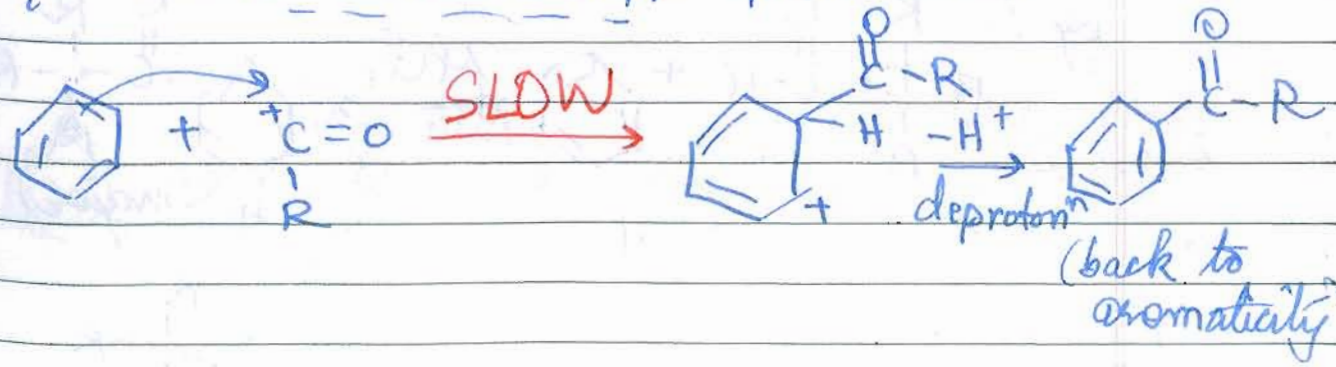


• mechanism





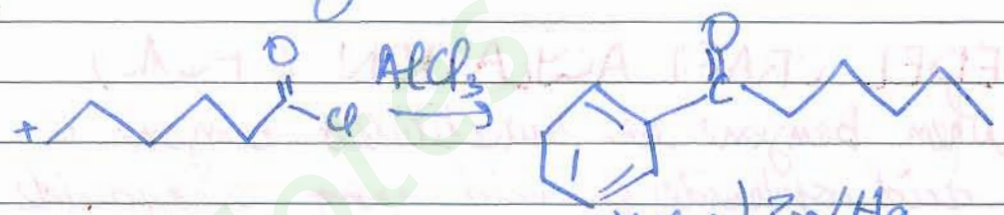
Acylium ion :- itself very stable. So, no rearrangement (here comes a diff. from FCA)

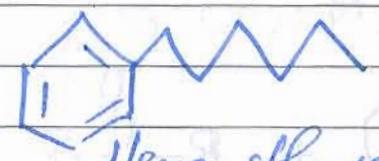


Applications

1) * Introduction of longer chain alkyl grp. to benzene ring is possible by FCAc rxn.

eg :- Introducing hexane to C_6H_6

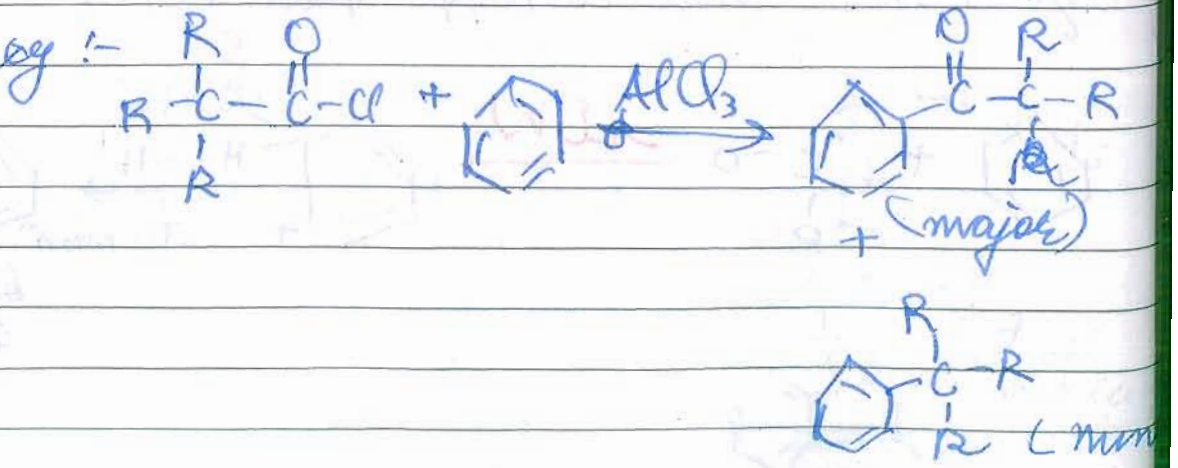




Hence, the product

2) * No di-acylation takes place in FCAc. (unlike FCA). So, no over acylation takes place → ∵ deactivating grp is the product. (in FCA, ~~as~~ product formed was more reactive → activating than benzene → C_6H_6).

3) No extra benzene is req^d for rxn →



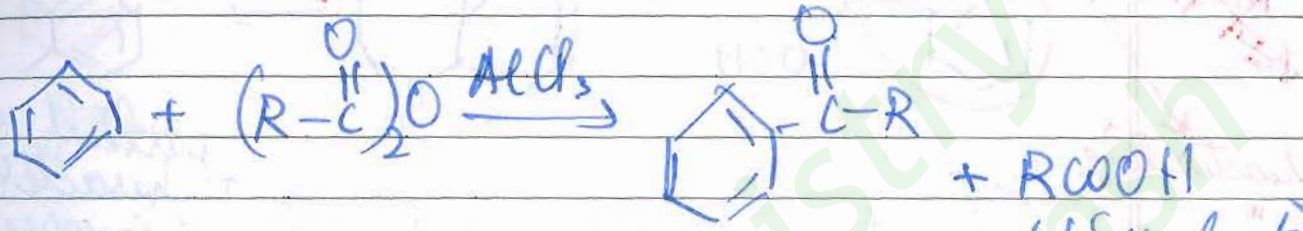
→ acylium ion → $R-\overset{R}{\underset{R}{C}}-\overset{+}{C}=O \rightleftharpoons R-\overset{R}{\underset{R}{C}}^{+} + CO\uparrow$ (minute)

3° carbocation

↳ This possibility occurs only when its 3° or very stable possibility of carbocation formed. So, etc

---

★ With Anhydride

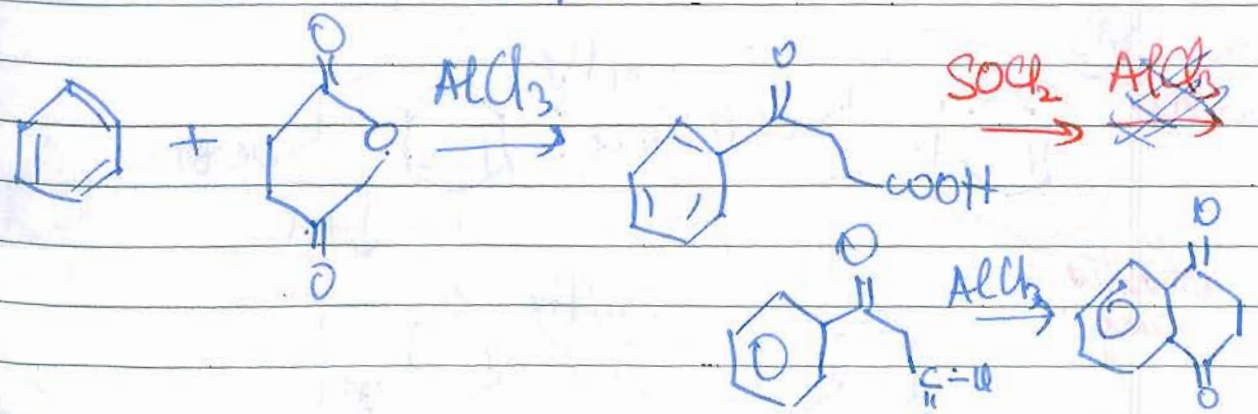


Mechanism

$(RCO)_2O + AlCl_3 \rightarrow R-\overset{+}{C}=O + \overset{\ominus}{AlCl_3}(RCOO)$

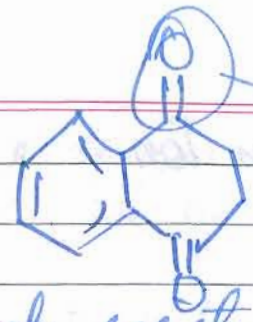
↳ Then, Friedel craft take place

↳ The exact form of acylium ion would depend on the alkyl grp → giving stability to the ion. More stability, more product.



classmate
Date
Page

In previous ampd, → meta directing

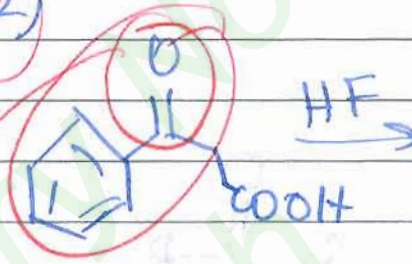


So, the rxn was ~~not~~ resulting towards its formⁿ. But, all intra molecular rxns are entropy favoured. Hence, the above product is formed.

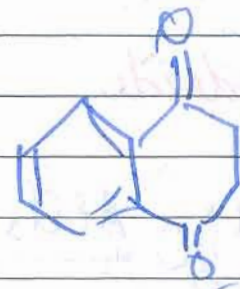
M2

Better than M3

deactivating (Rough :-

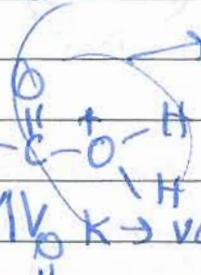


HF →



Clemmensen →

decaline



partial = character (favoured)

$$R-\overset{O}{\overset{\|}{C}}-\ddot{O}H + H^+ \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{+}{O}(H)(H)$$

$\frac{1}{V_0}$ K → very small

$$R-\overset{O}{\overset{\|}{C}}{}^+ + H_2O$$

Why HF ?

Its an ~~under~~ intermediate strength acid — plays role only of catalyst.

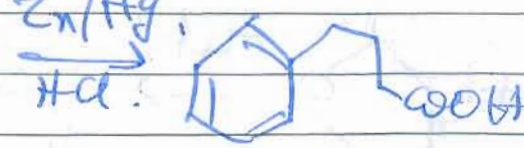
* Above rxn takes place only ∵ its intramolecular (Entropy favoured)

(H_2SO_4 will lead to sulphonation)

better than M2

M3

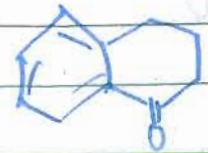
activated ring



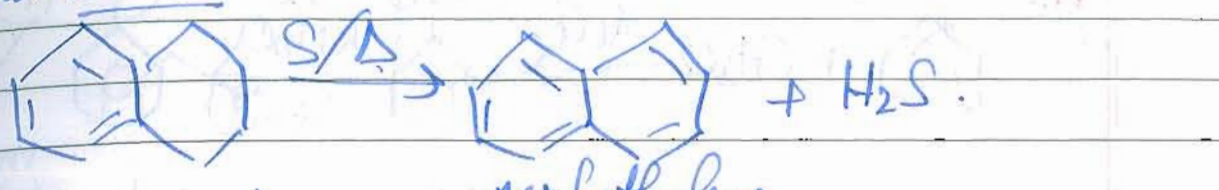
Zn/Hg
HCl

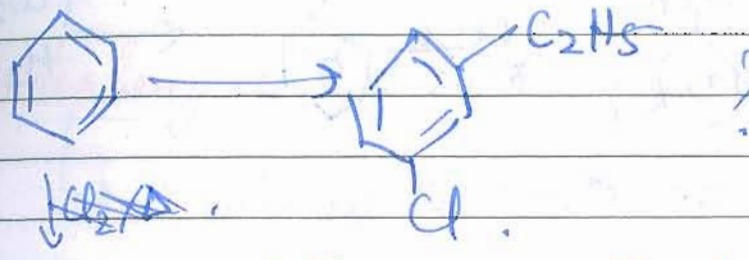
↓HF

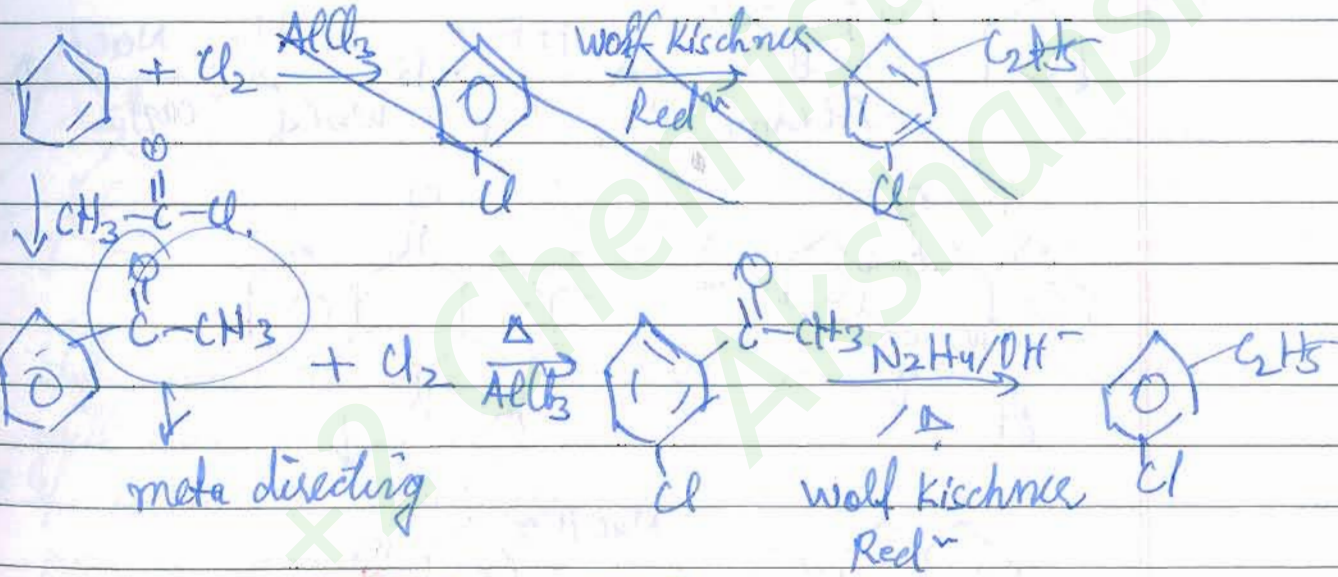
Zn/Hg
HCl

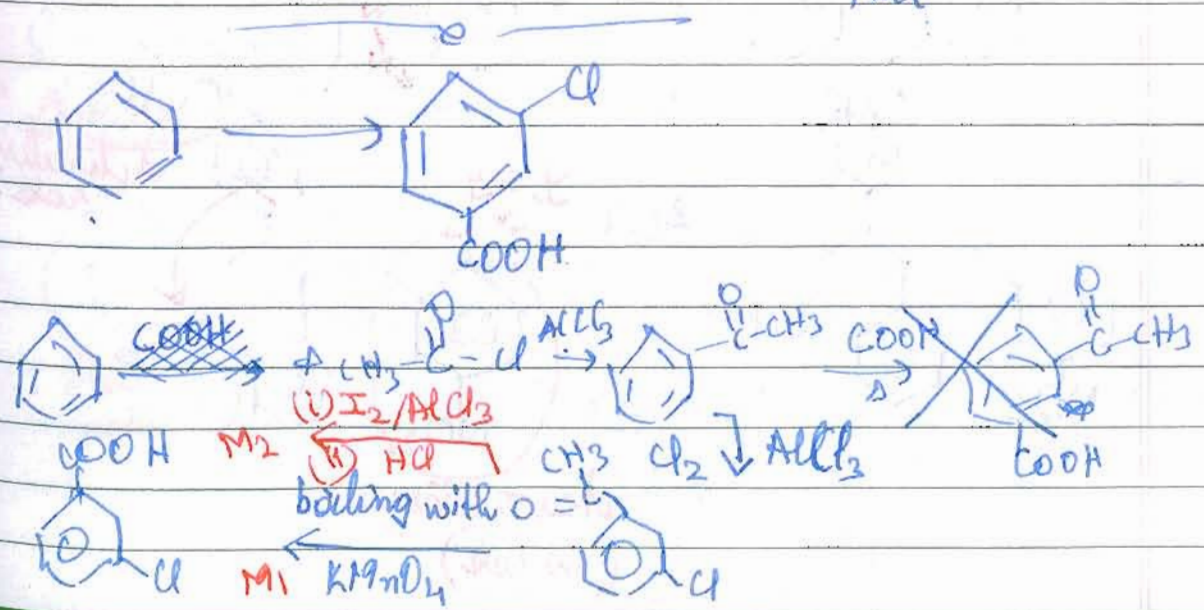


Further upon



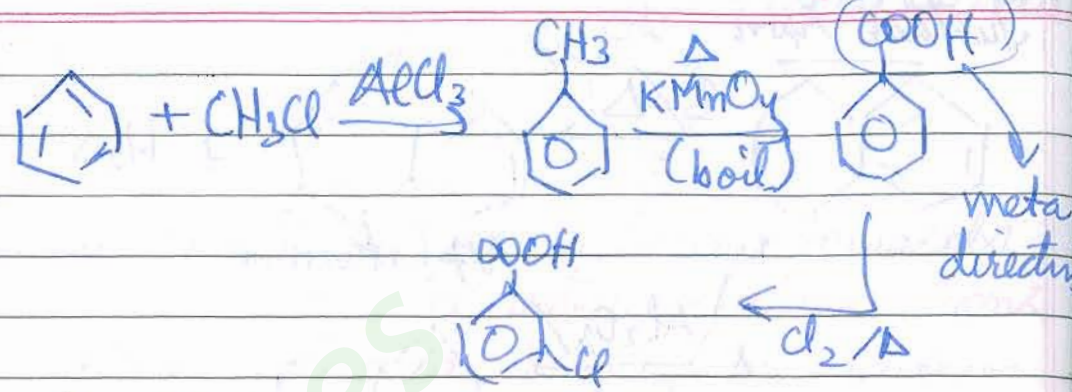




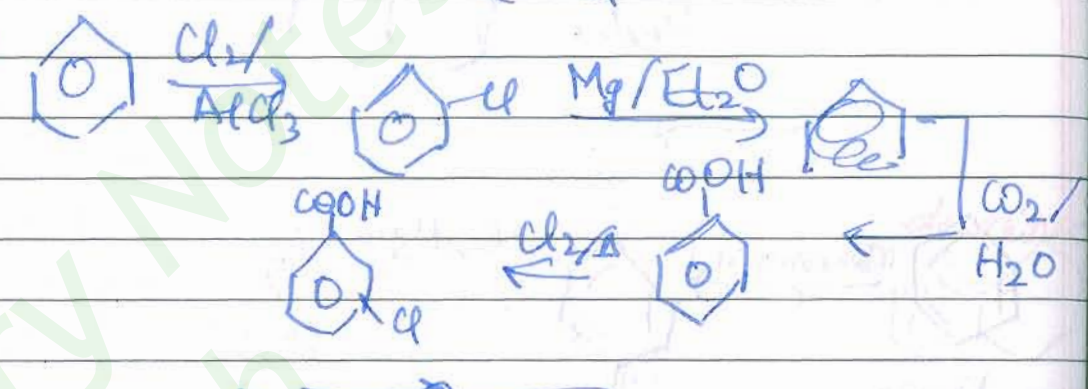


classmate
Date
Page

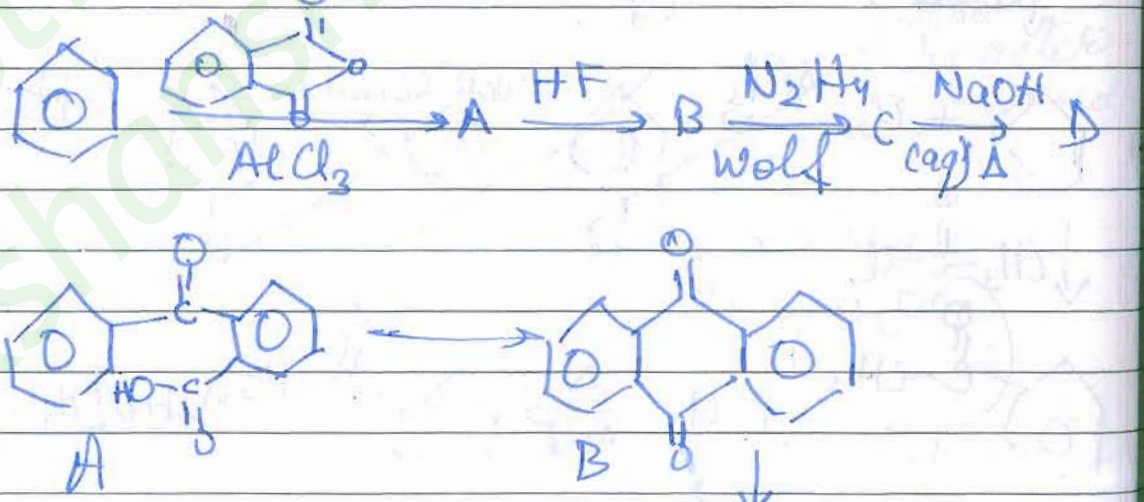
M3



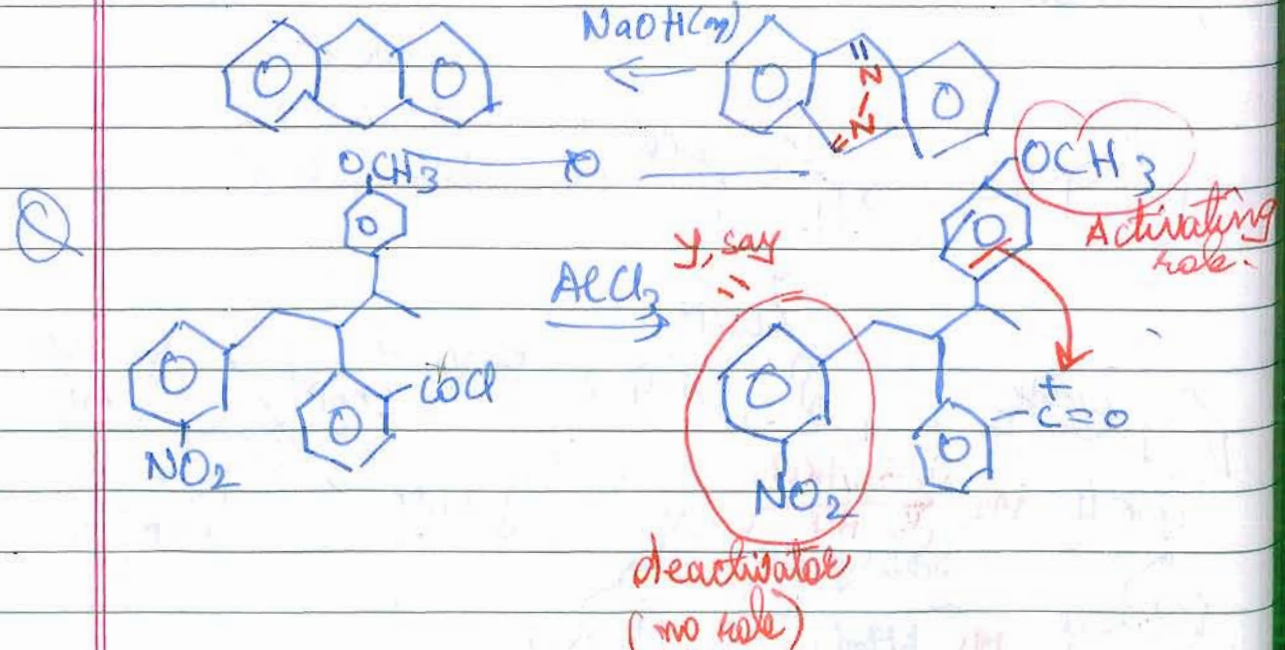
M4

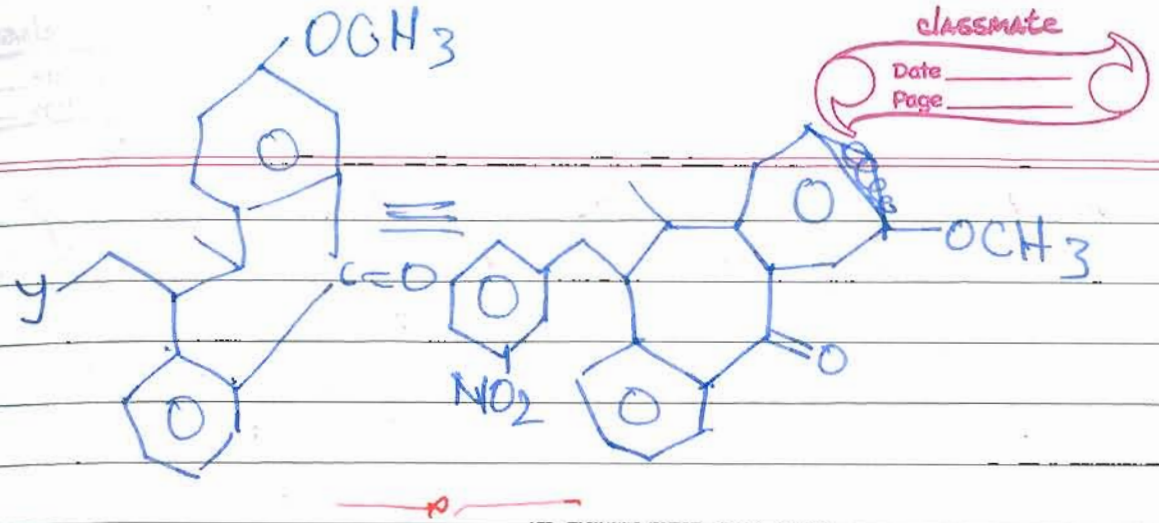


8



9

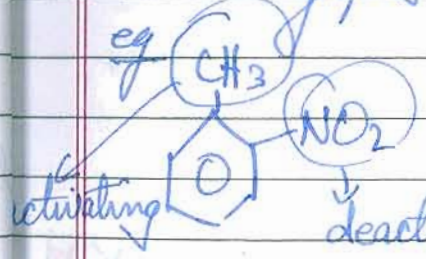




★ LIMITATIONS → FC Rxn.
(Alkylation & Acylation)

1) Nitrobenzene fail in Friedel Craft Rxn.

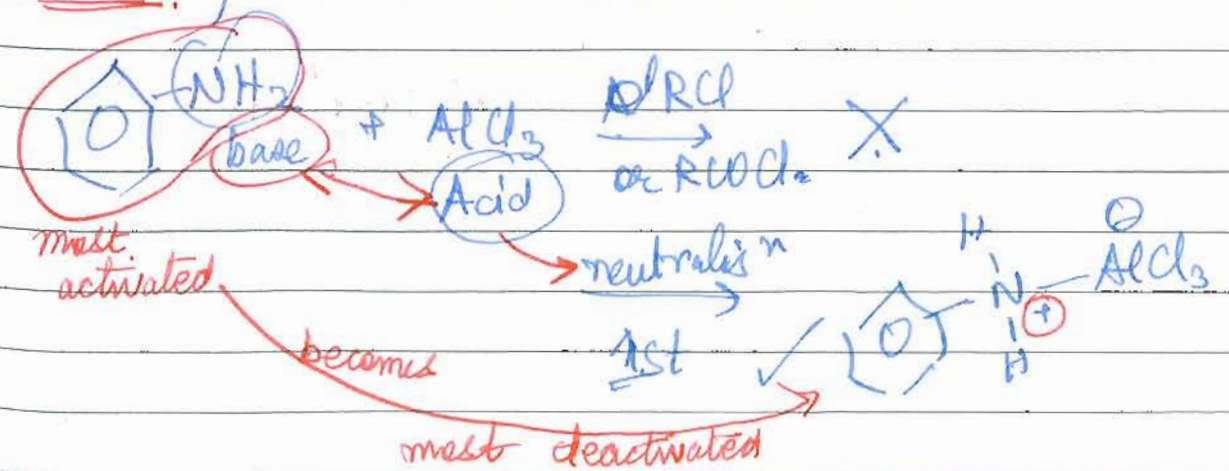
→ ∵ nitro grp is very very strong deactivating grp

eg 

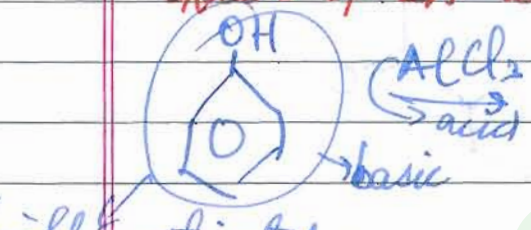
: E^+ will move w.r.t activating grp. CH_3 is o-p directing. Here, it'll react at para.

* If both grps are activating, more activating will governs orientn
* If both are deactivating, less deactivating governs orientn

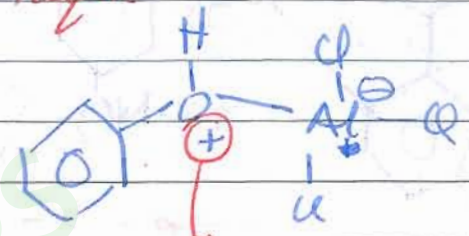
2) Aniline fails in FC rxn.



3) Phenol undergo FC rxn with difficulty & excess of LA is reqd.



highly activated ring (after aniline)



+ve on oxygen (not poss

↓ -HCl.

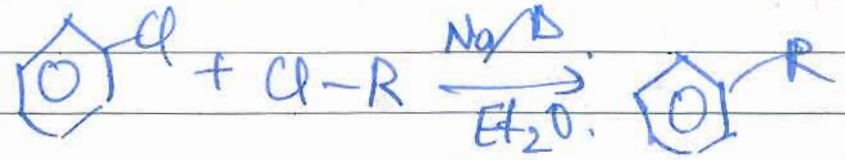
→ e⁻ withdrawing

1 mole $AlCl_3$ consumed

If excess LA is used, then, it would bring about substitution on phenol. Hence, tough, but possible.

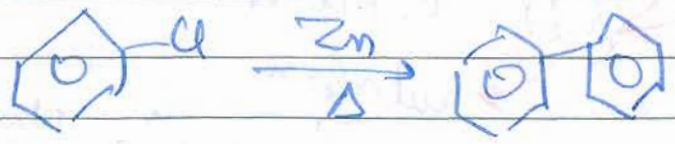
→

* Another reaction: WURTZ-FITTIG'S RXN



Coupling of 2 aryl halides is tough ∵ S_N2 rxn on aryl halide isn't possible.

For this to happen i.e for making aryl halides react :- FITTIG'S RXN



• can di-protonate a base

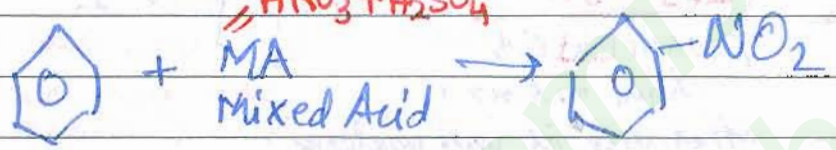
Ch: Nitrogen containing compounds.

→ NITROBENZENE
→ ANILINE
→ BENZENE - DIAZONIUM SALTS

NITROBENZENE

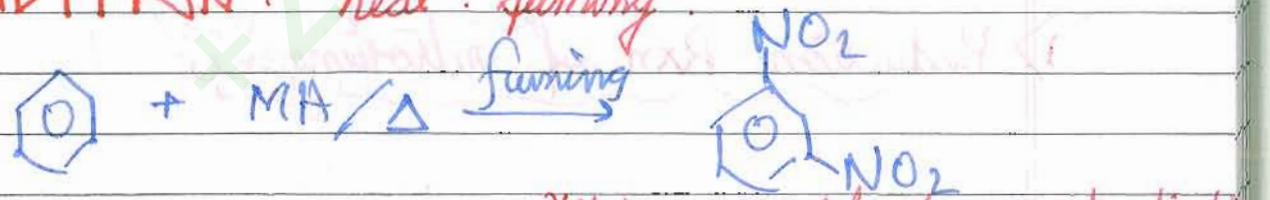
• preparation

→ M1) : Direct nitration of benzene



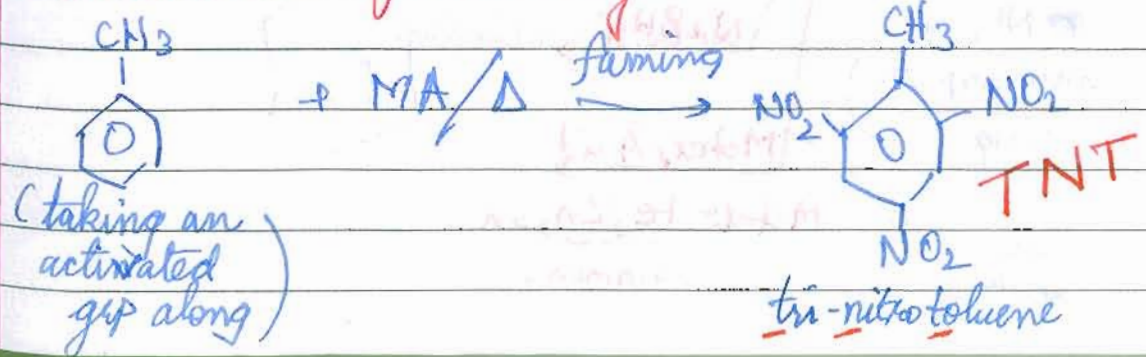
★ Dinitration : single nitration makes ring very deactivating. Hence, dinitration has very less chances of formⁿ

CONDITION :- heat : fuming.

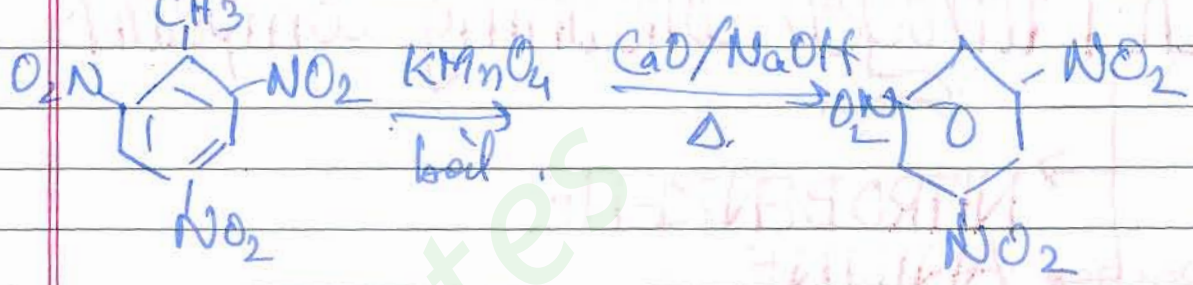


very common solvent : very deactivated in organic synthesis

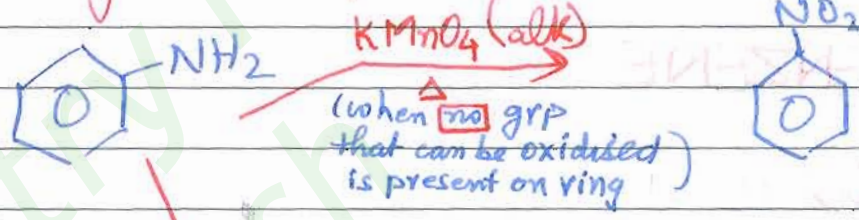
★ Trinitration :- further tough.

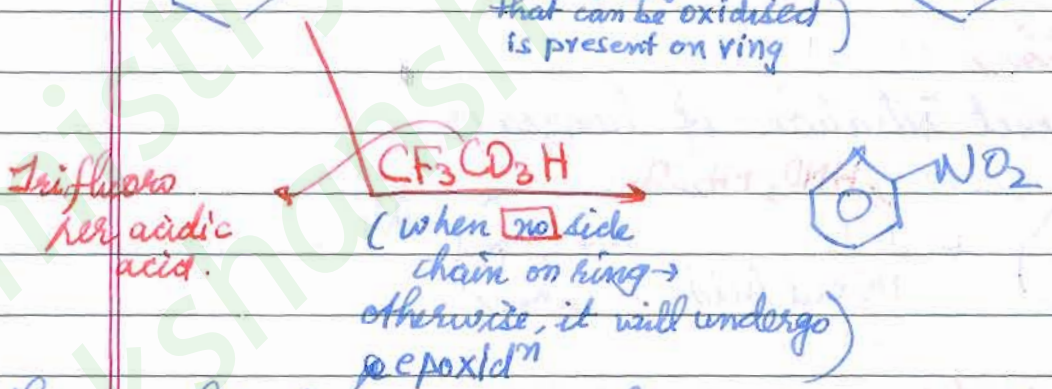


- Removing CH_3 from TNT



→ M2) By oxidⁿ of aniline & its derivatives.





Both ✓ valid for any no. of NH_2 grp on ring.

✱ PROPERTY

1) Reduction Rxn of nitrobenzene

• NOTE :- $SnCl_2$ reduces NO_2 leaving side gaps → CHO, COR.. intact. Other RA's ↙ reduce all side gaps.

★ NO_2 → (Zn, weakly acidic medium. i.e use of NH_4Cl (aq)) → $NH-OH$ (N-phenyl hydroxylamine) — PARTIAL RED^n

→ (Zn, OH^-(aq) (i.e reduce further acidity)) → hydra azobenzene

→ (Zn/OH^-(aq) + Alcoholic sol^n (CH_3OH) (i.e more reduce acidic medium)) → azobenzene

→ ✗

★ NITRO → (Zn/HCl) → NH_2

NITRO → ($SnCl_2/HCl$ (common)) → NH_2

(Specific) → Na_2S, $(NH_4)_2S$, $NaHS$, NH_4HS → Sulphides - bisulphides

+2 Chemistry Notes Akshansh

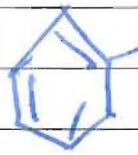
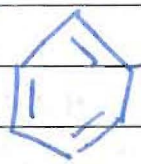
classmate
Date 17.11.10
Page

✱ Aniline

- **preparation:**

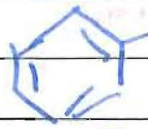
1) $C_6H_5-NO_2 \xrightarrow{Red^n} C_6H_5-NH_2$

2) From chloro benzene (bromo or iodo) : Aryl ha

M1)  + $NH_3(g)$ $\xrightarrow{High\ T,P}$  NH_2 + H

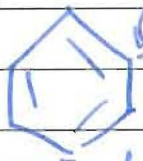
(S_N rxn., small amt.)

M2)

+ $NaNH_2$ $\xrightarrow{at\ RT}$  NH_2 + NaCl

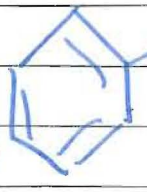
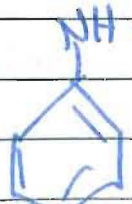
$NH_2^{\ominus}$ is strong $Nu^{\ominus}$ → Rxn is favourab

- **properties**

(a)  NH_2 vs $R-NH_2$

Lewis base (weaker than aliphatic amine)

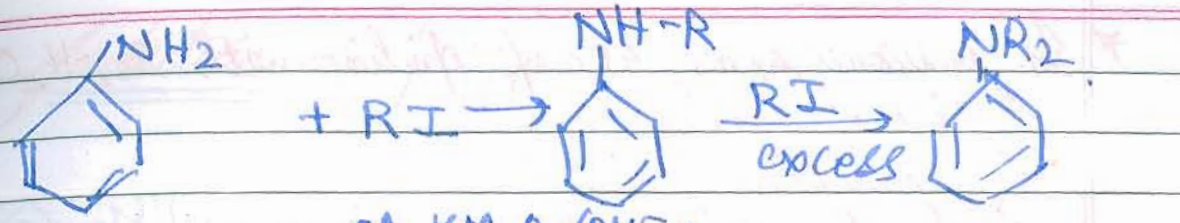
(b) halogen^n & alkylation of Aniline ✱

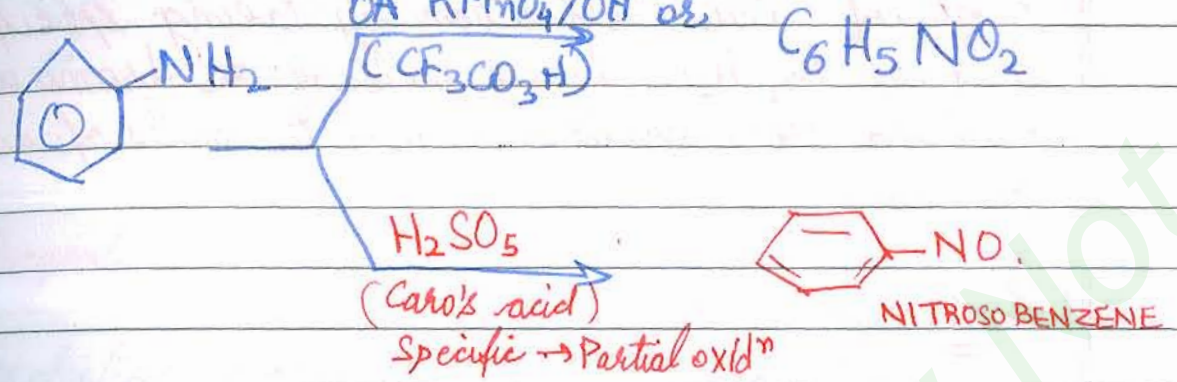
 NH_2 + $Cl_2(g)$ →  $NH-Cl$ + HCl

N-Chloro aniline

NH_2Cl_2

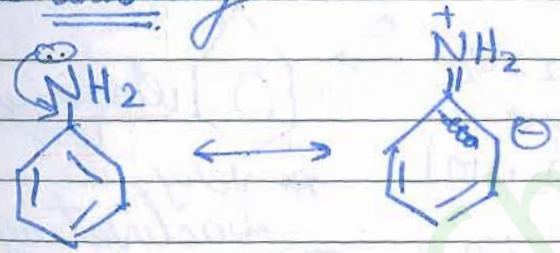
+2 Chemistry Notes Akshansh





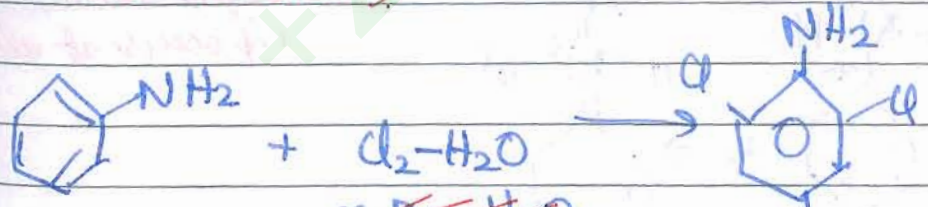
$S_E Ar$

1) Reactivity



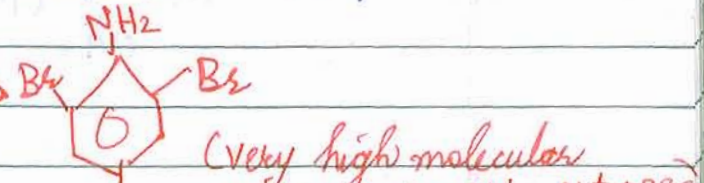
(most activated compd towards S_EAr rxn for mono substitution)

Reactivity :- Aniline > Phenol



(mono chlorin^n not possible → ∵ rxn is very vigorous. Electrophilic attack of Cl_2 to ▽ complex)

TEST FOR ANILINE



(Very high molecular

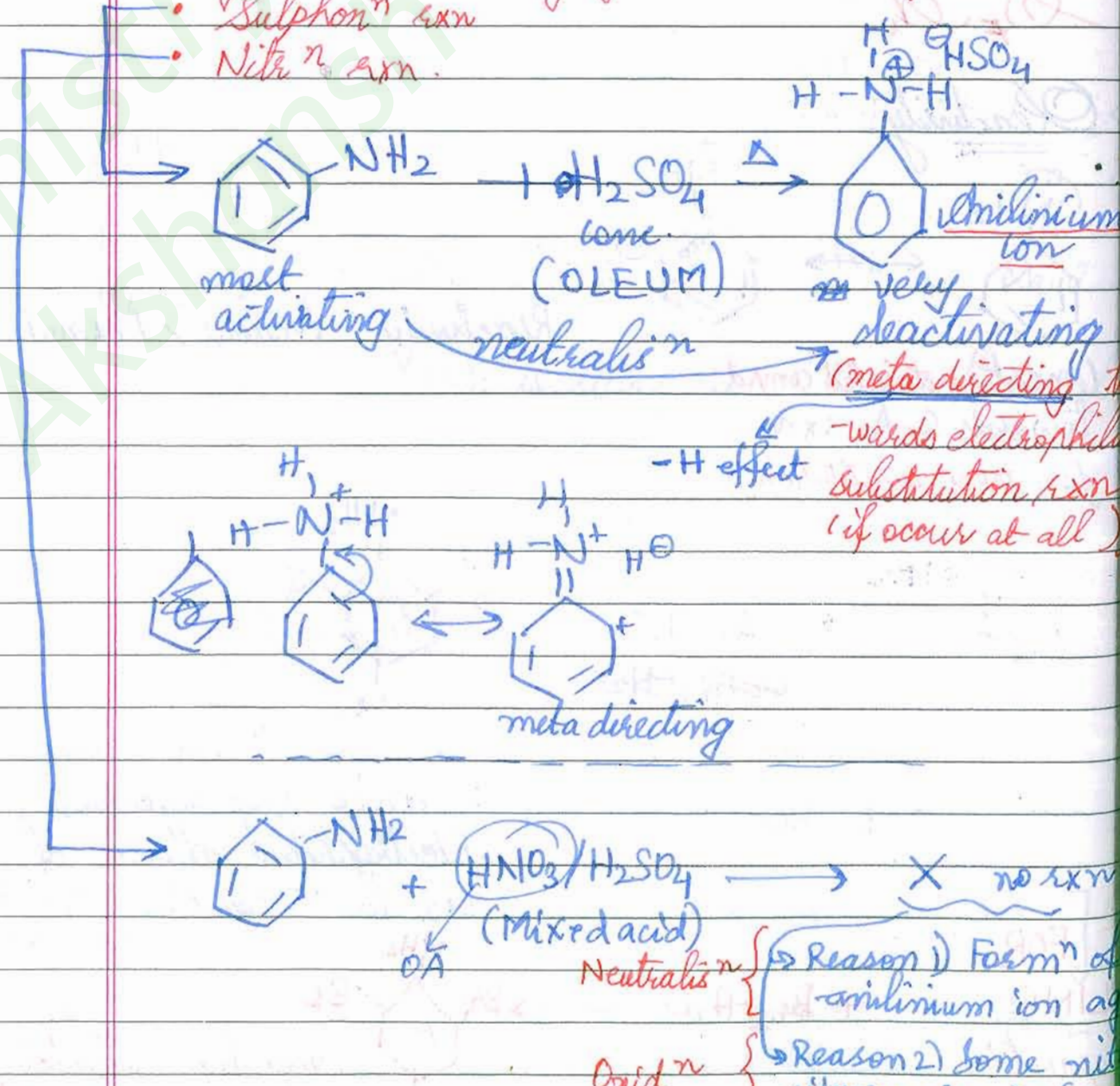
Separation

classmate
Date
Page

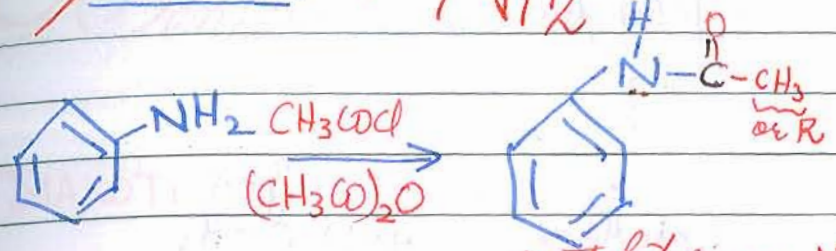
* In previous expn, rxn of aniline with Br_2-H_2O.
✓ Test of aniline
✓ separation of aniline.
✓ qty. of aniline estimation by taking specific amt. of Br_2-H_2O & see moles of tri-bromo anil produced. They would be equal to moles of anilin present

Failure

- Although aniline is highly activated, it fails in
  - Sulphon^n expn
  - Nitr^n expn.



☆ Protection of NH_2 in aniline.



} conjugating on both sides, still o-p directing

Acetylation on Nitrogen forming amide → most stable acid derivative)

Reagents :- Most commonly :- Anhydride $(CH_3CO)_2O$

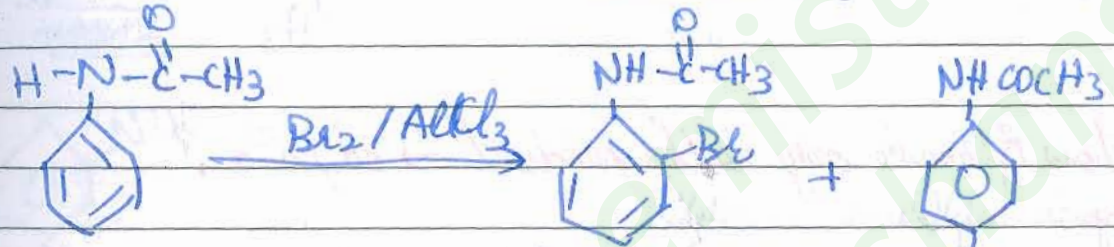
Most reactive :- CH_3COCl (tough to handle)

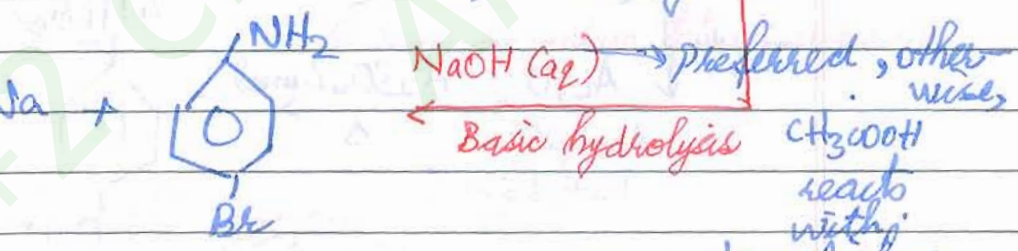
• protection makes it INERT towards conc. acid.

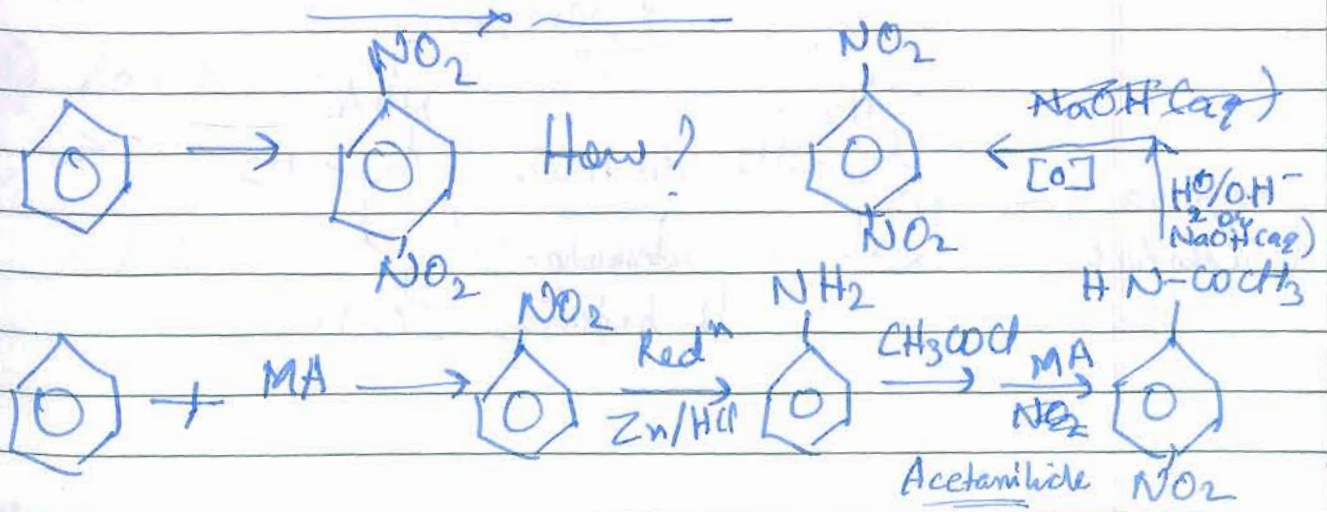
Now, it no longer holds feature of aniline.

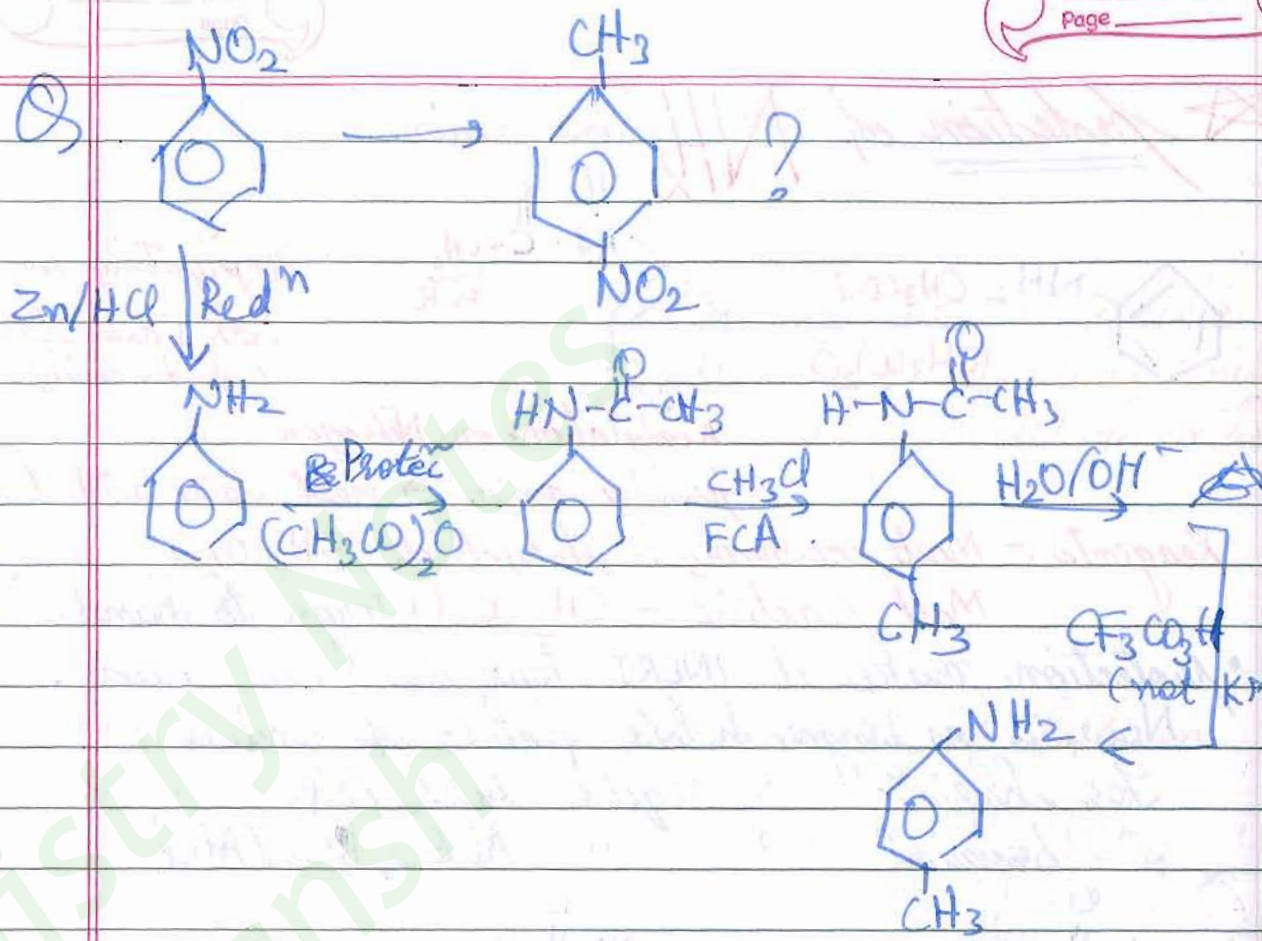
For chlorin^n → require $AlCl_3/Cl_2$

bromin^n → " ~~$AlBr_3$~~ $Br_2/AlCl_3$

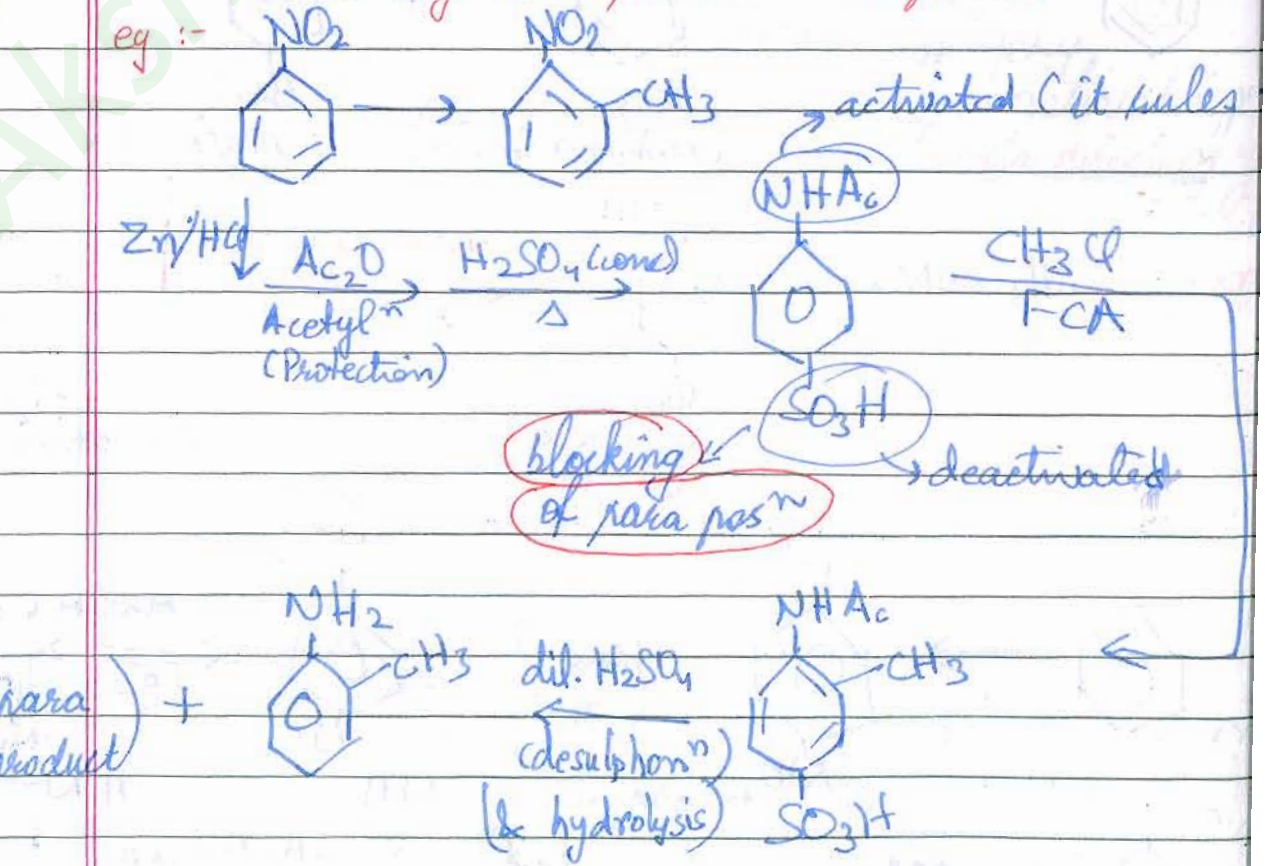






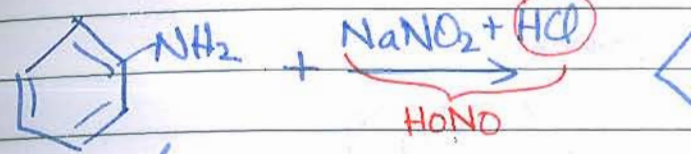


Imp. ★ How to make only ortho product → no para ?



Benzene Diazonium Salts.

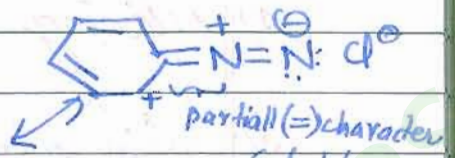
DIAZOTIZATION RXN



aromatic amine.

or $C_6H_5N_2Cl$

or Benzene diazonium chloride

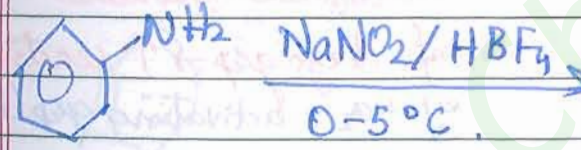


$R-NH_2$ aliphatic amine. $\xrightarrow{HNO_2}$ $R-N^+\equiv N\ Cl^- \rightarrow R^+ + N\equiv N\uparrow \rightarrow$ Alcohol.

(doesn't exist → highly unstable)

$C_6H_5N_2^+HSO_4^-$

Benzene diazonium ~~deed~~ bisulphate.



$C_6H_5N_2^+BF_4^-$

Benzene diazonium tetrafluoroborate.

Use: distinguishing b/w diff^t compds in which benzene is having Nitrogen on ring.

(1) Add Zn/HCl → Aniline $\xrightarrow[\text{or any other.}]{NaNO_2/HCl}$ $Ph\ N_2^+$

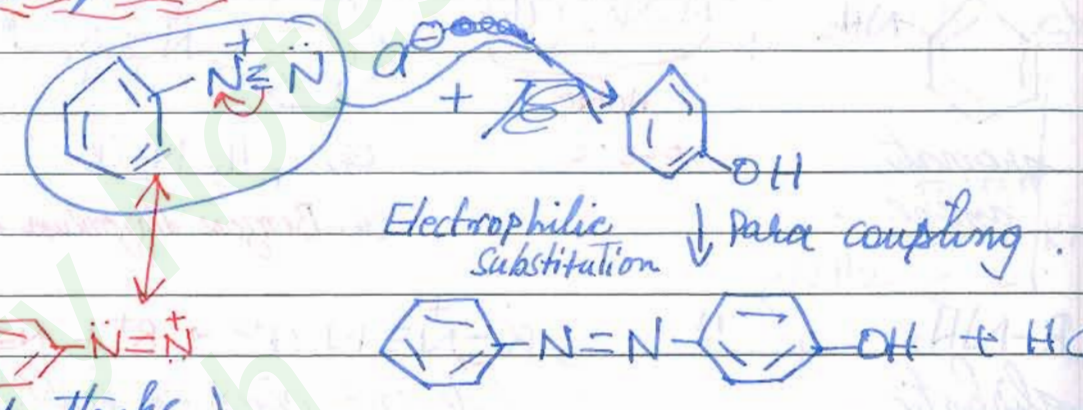
Red dye. ← β-naphthol + $Ph\ N_2^+$ (diazonium salt)

APHTHOL
EST

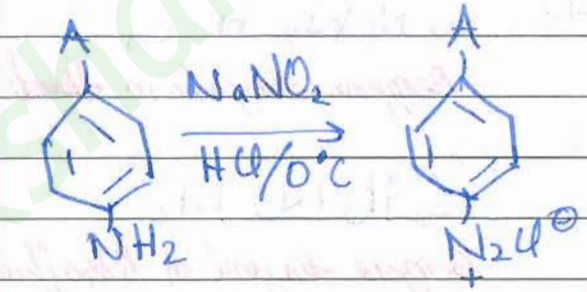
* Reactions of benzene diazonium Chloride ($C_6H_5N_2^+Cl^-$)

(a) retaining diazo (N≡N) gp.

(i) With phenol:



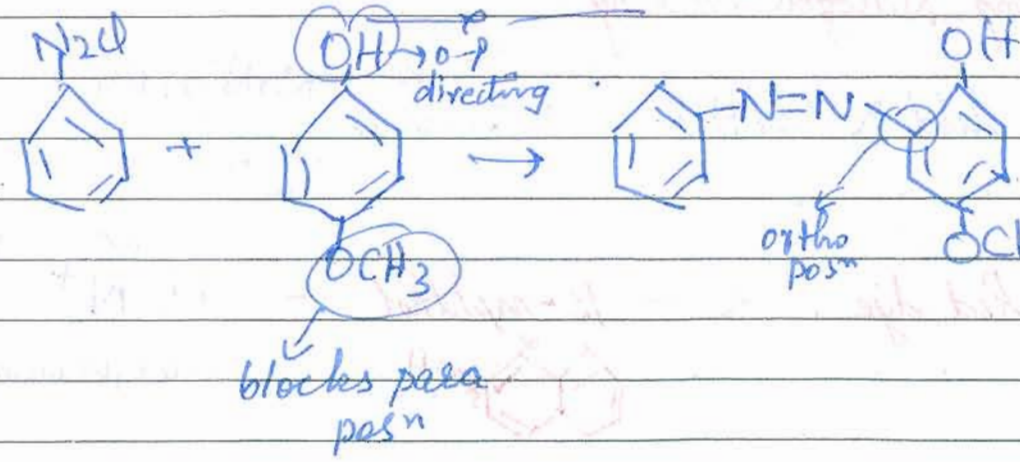
(electrophilic) (it attacks on ring)



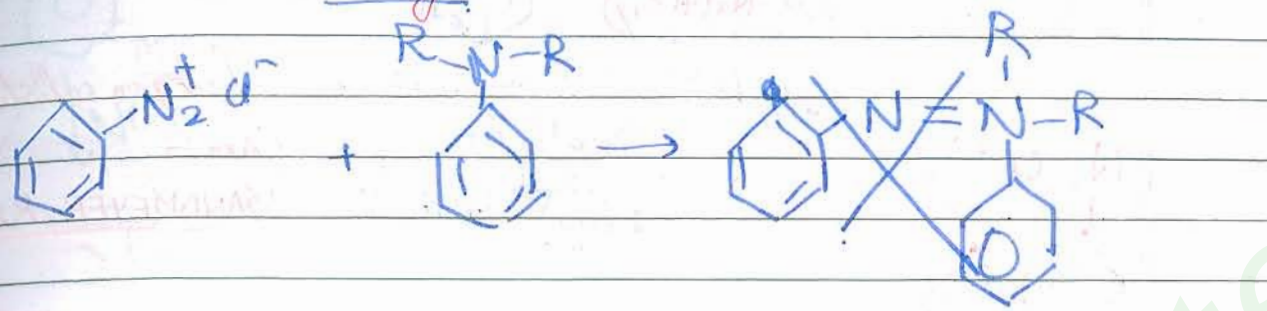
A: e^- withdrawing → ↑ electrophilic character of diazo gp → ↑ reactivity
eg: NO_2 → activating gp (h

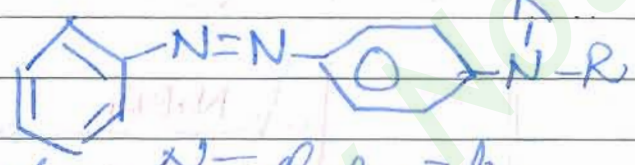
A: e^- donating gp:- ↓ electrophilic character of diazo gp → ↓ reactivity

↓EE of $\ominus$



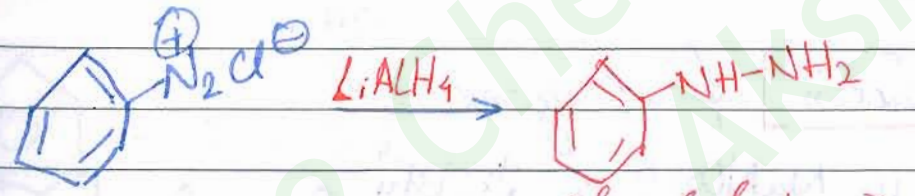
(ii) With N_3N-dialkyl aniline.





* If even a single H is present on N- alkyl aniline, it would remove HCl to give $-N=N-N-$ bond which is more stable.
* In phenol, however, it doesn't take place ∵ it would lead to +ve charge on Oxygen atom.

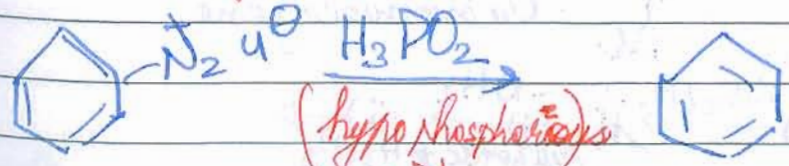
(iii) Redⁿ :-



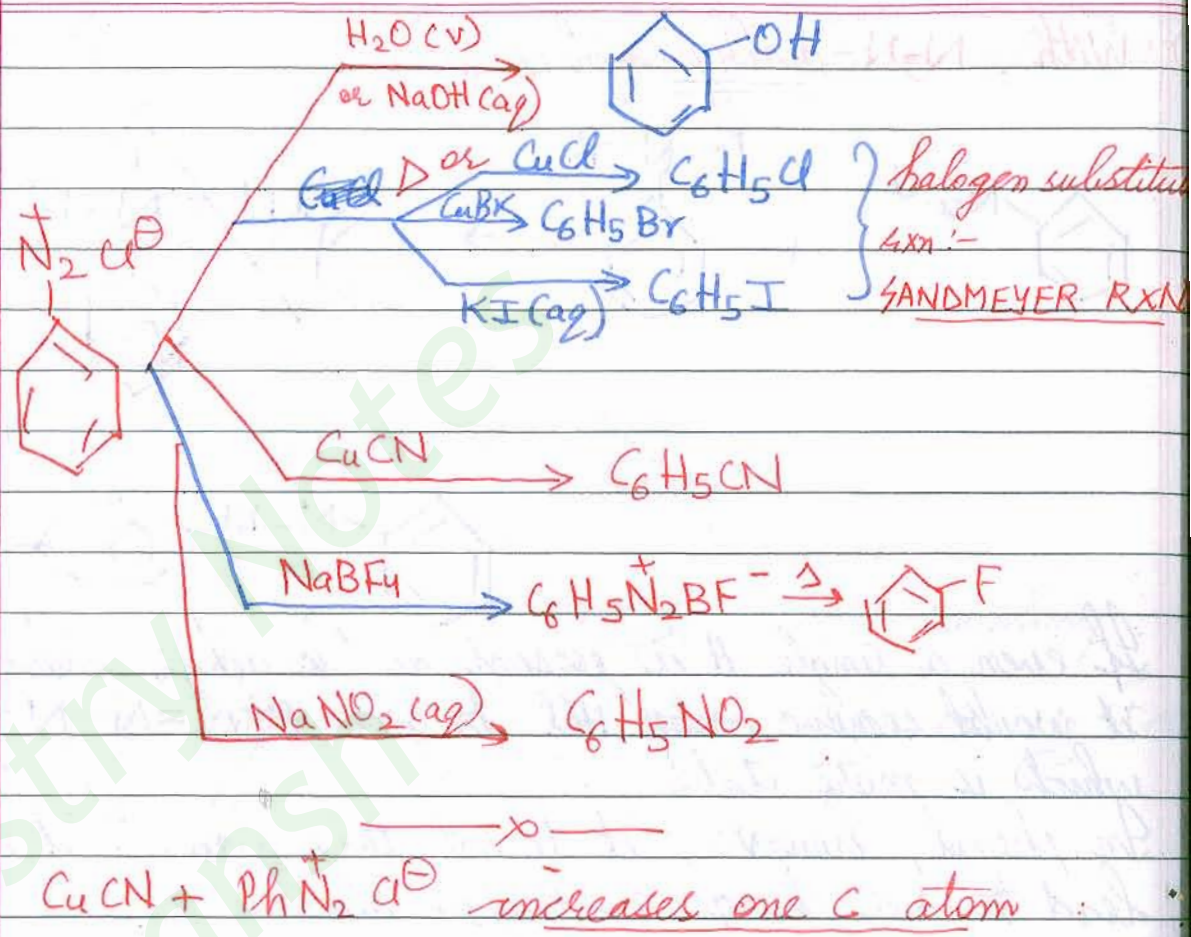
Phenyl hydrazine

* Substitution of diazo gp.

(i) Replacement by H

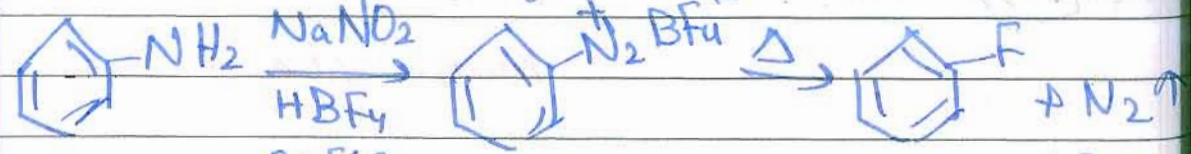


(ii)



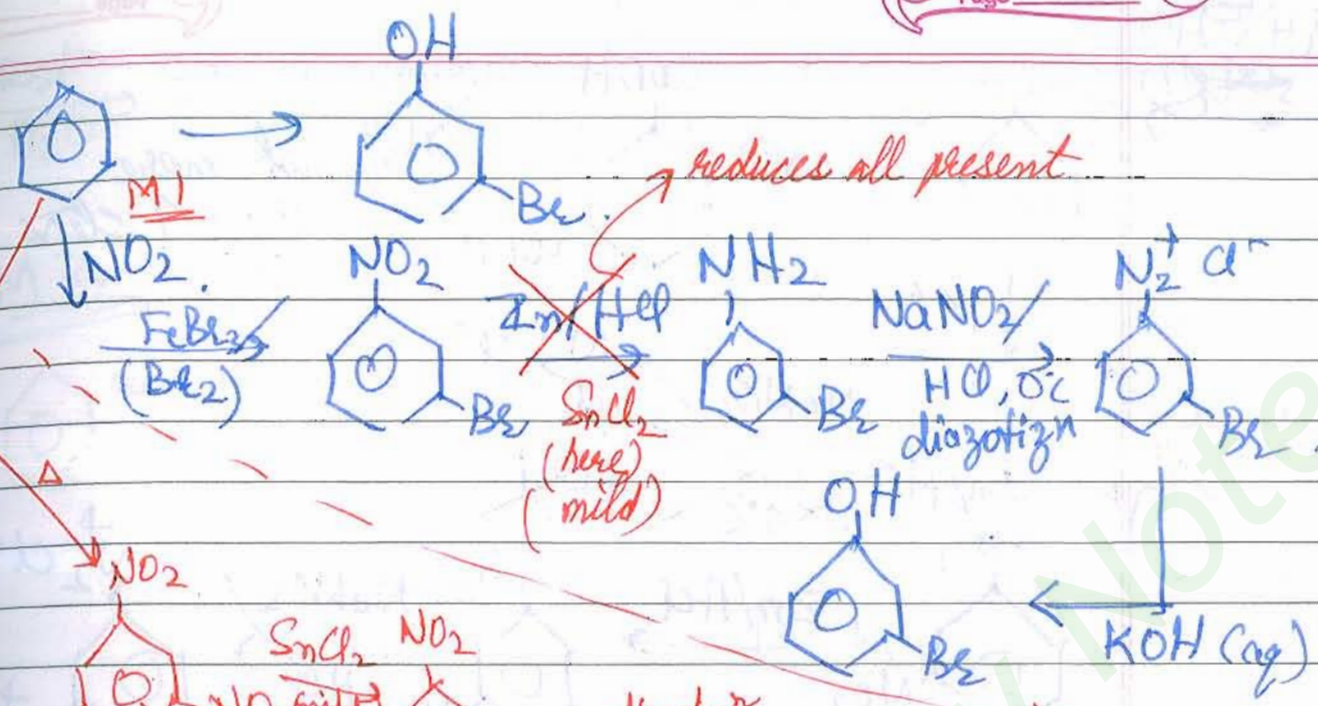
* $CuCN + PhN_2^+Cl^-$ increases one C atom.

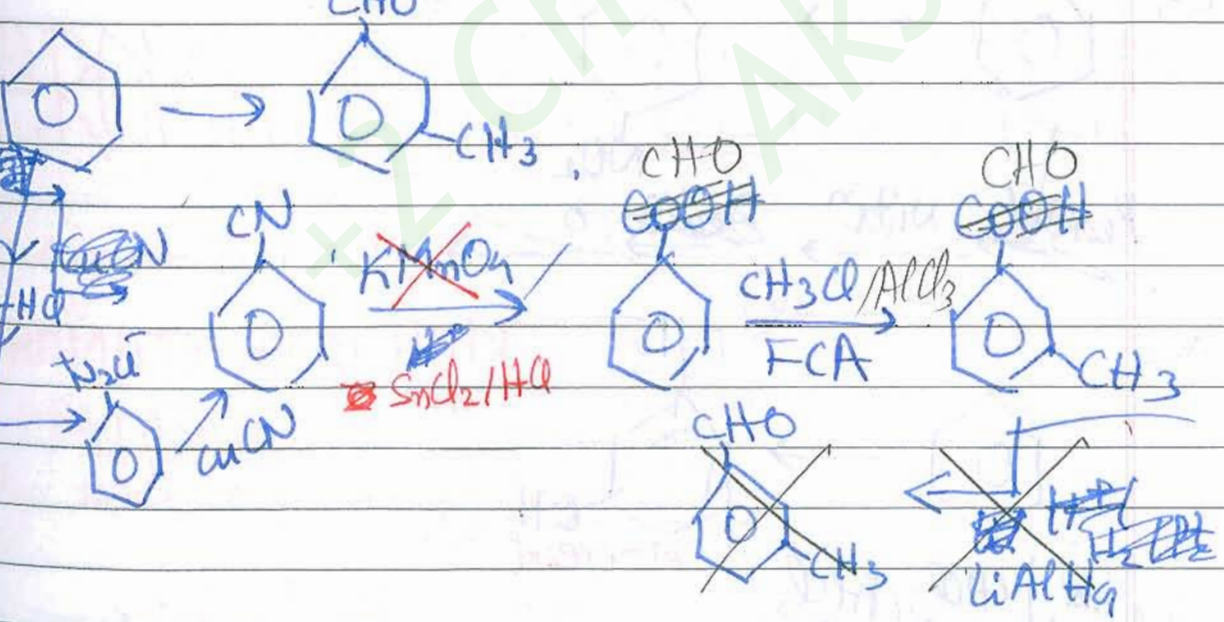
* Fluorin^n of benzene.

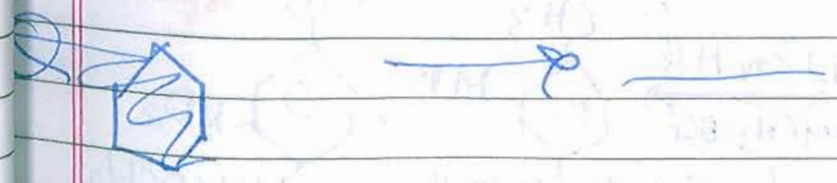


Q.

classmate
Date
Page

Q) 

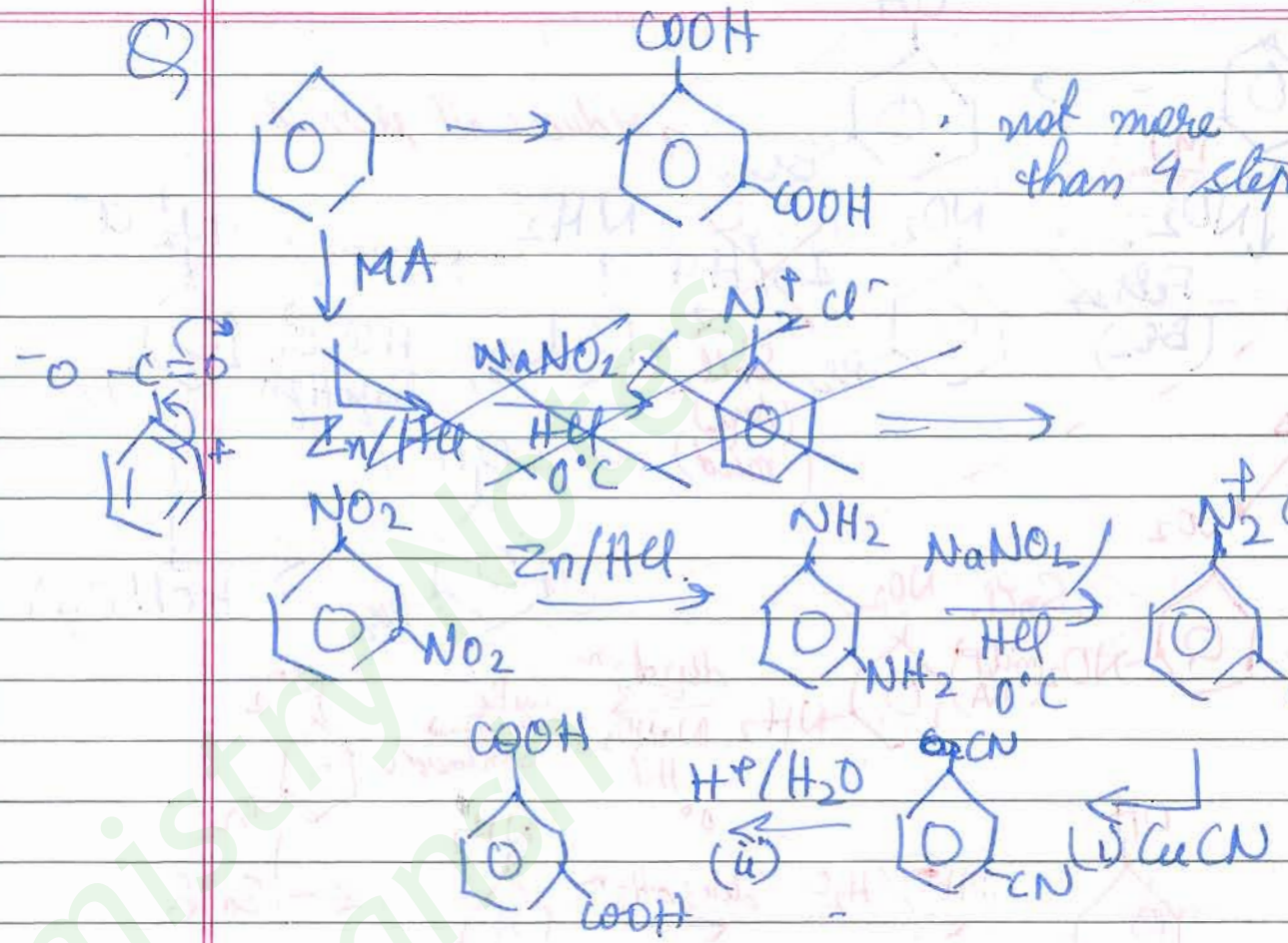
Q) 

Q) 

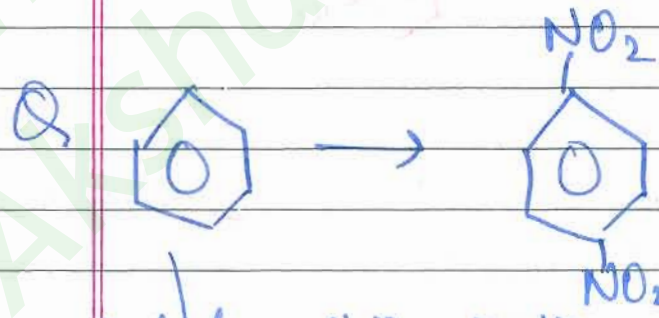
If OH & Methyl on 1 benzene ring → CRESOL

classmate Date Page

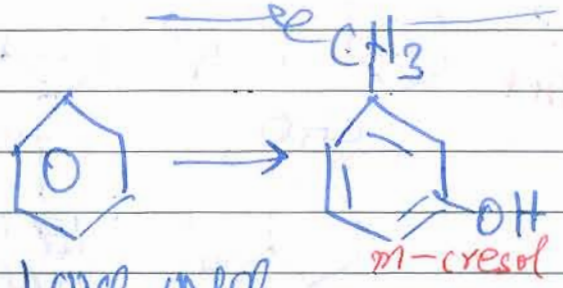
Q

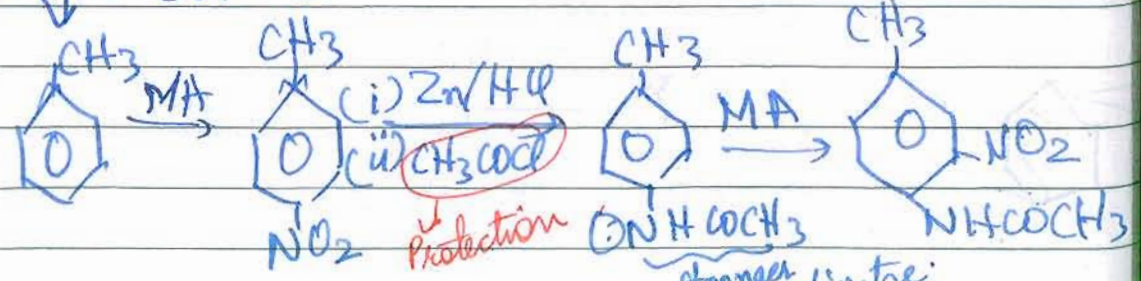


Q



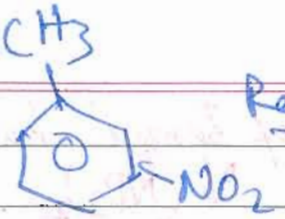
Q





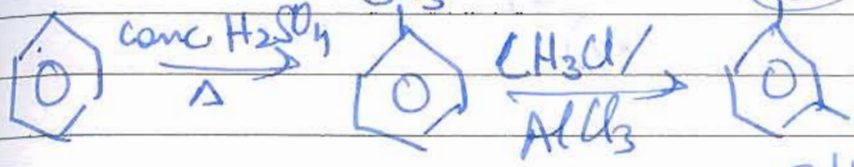
✱ Ar-CHO : called as OIL OF BITTER ALMOND

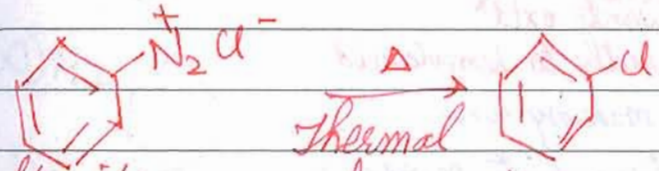
classmate Date Page

Red^{n} H_2O → Diazotis^{n} → Hydrolysis H_3PO_2 → 

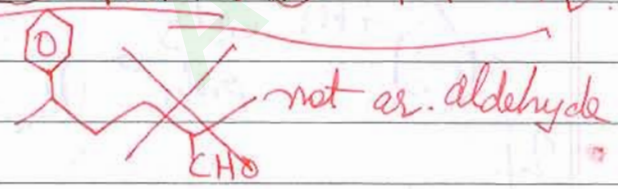
Red^{n} → diazotis^{n} H_3PO_2 →

M2



✱ 

AROMATIC-ALD-KETO-ACID



• ring contains CHO not ar. aldehyde

① AROMATIC ALDEHYDE

✱ PREPARATION

एक ही C-पर दो Cl आ जाए

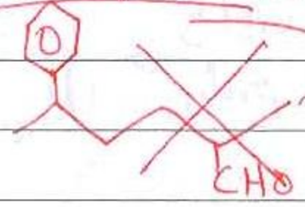
1. By treatment of benzylidene chloride.

CH_2 → (Δ free radical, sunlight) → $Ph-CH-Cl_2$ → ($OH^{\ominus}$ aq) → gem diol → ($-H_2O$) → $Ph-CHO$

most convenient way.

AROMATIC-ALD-KETO-ACID

- ring contains CHO



not ar. aldehyde

① AROMATIC ALDEHYDE

✱ PREPARATION

एक ही C-पर दो Cl आ जाए

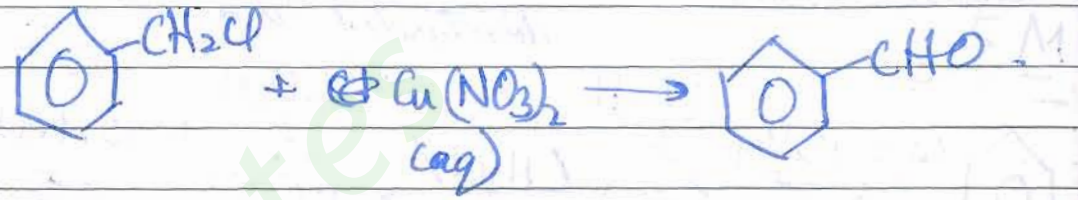
1. By treatment of benzylidene chloride.

$$Ph-CH_3 \xrightarrow[\text{free radical}]{Cl_2,\ \Delta,\ \text{sunlight}} Ph-\underset{\leftarrow}{CH}-Cl_2 \xrightarrow[aq]{OH^{\ominus}} \text{gem diol} \xrightarrow{-H_2O} Ph-CHO$$

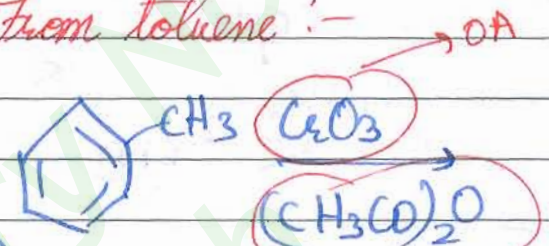
most convenient way.

Chemistry Notes by Akshansh

(ii) Treatment of Benzyl chloride with aq. sol^n of $Cu(NO_3)_2$ or $Pb(NO_3)_2$.



(iii) From toluene :-

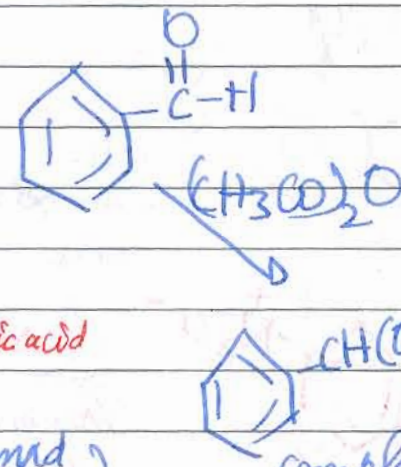


CONTROLLED OXID^n

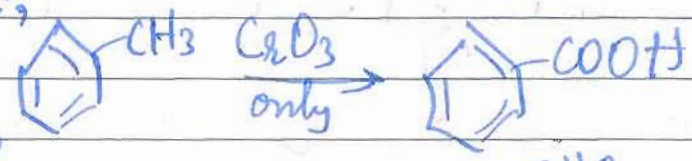
PROTECTION

(by making an intermediate compd with benzaldehyde)

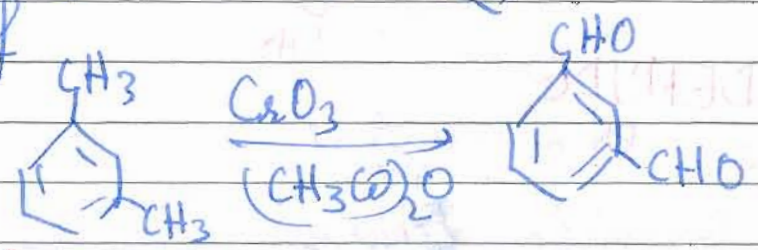
solvent prevents oxid^n directly to benzoic acid



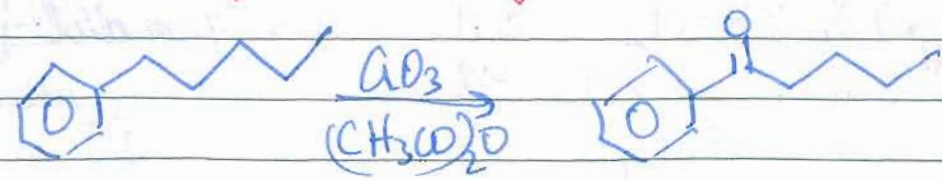
- But,



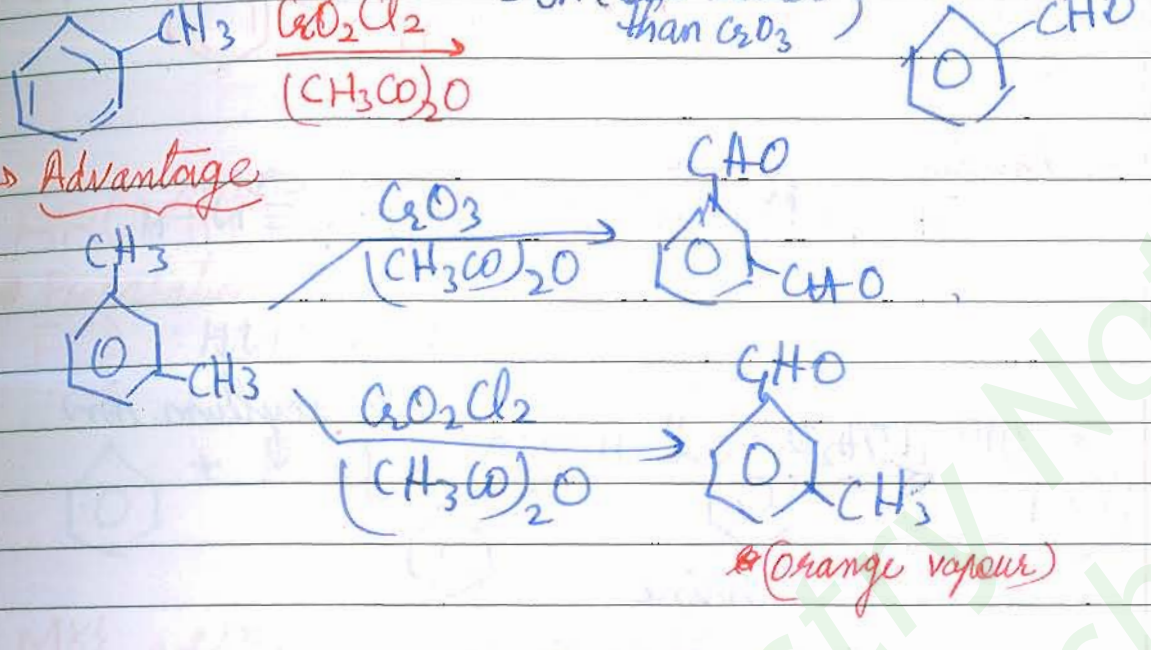
- If



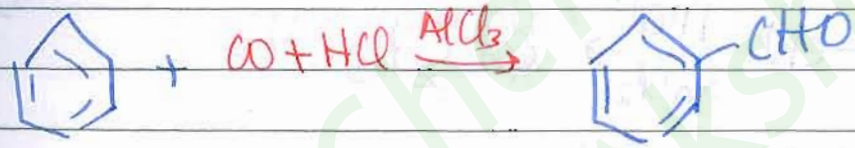
- If α-C on benzene is CH_2 (just) : Ar-ketone



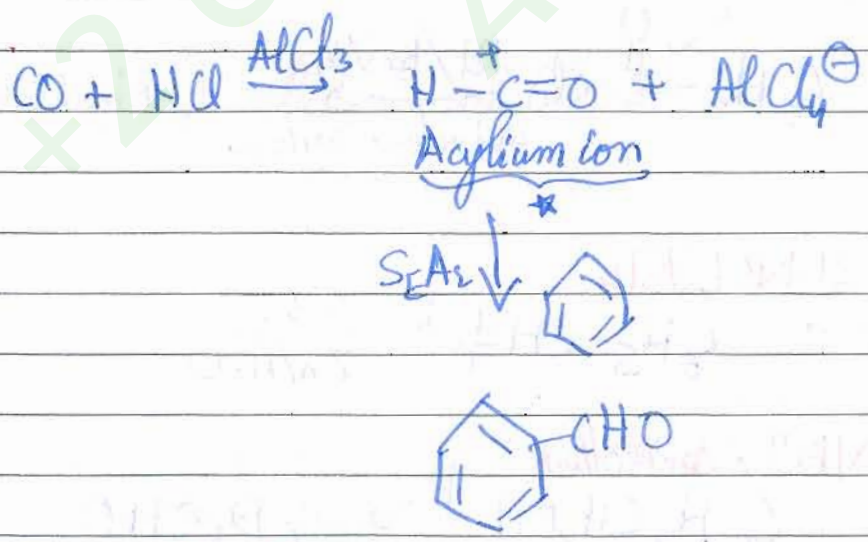
(iv) ETARD'S RXN.



V) GATTERMAN KOTCH RXN. : modific^n of friedel craft rxn.



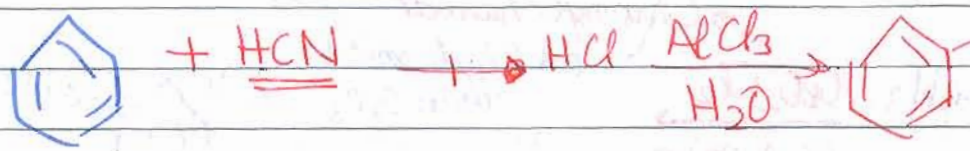
mechanism.



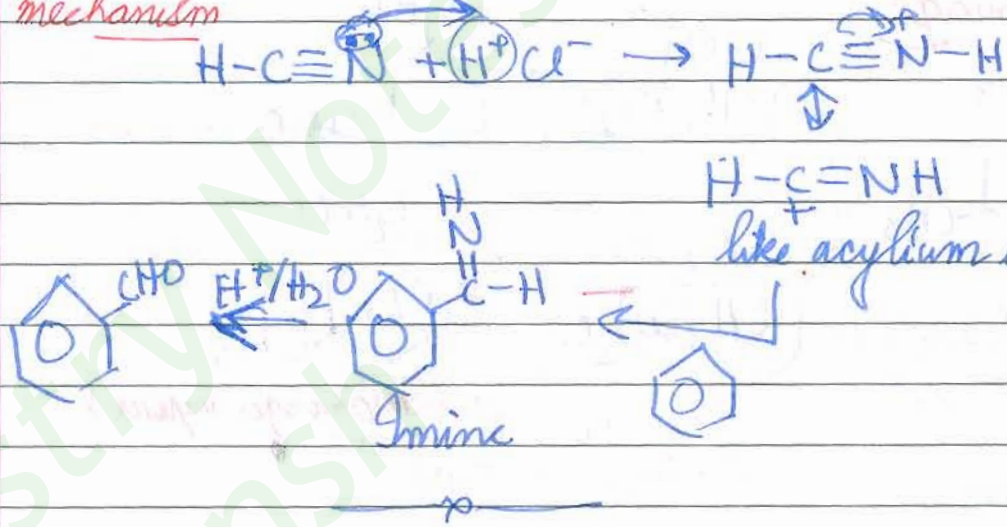
- rxn fails in case of nitro-benzene.

classmate
Date
Page

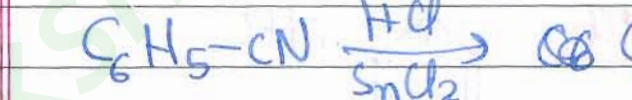
(vi) GATTERMAN'S RXN



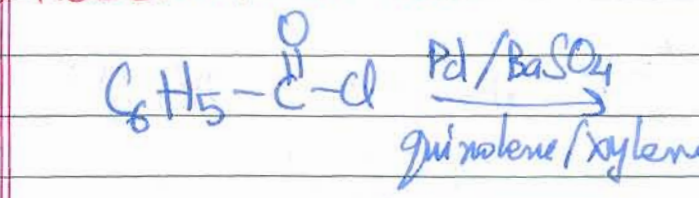
mechanism



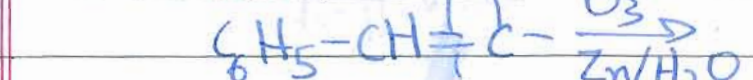
(vii) STEPHAN'S RXN



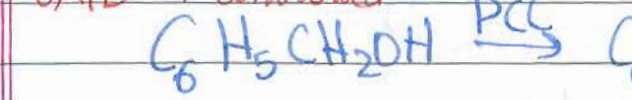
(viii) ROSENMUND Red^{n} :-



(ix) OZONOLYSIS



(X) OXID^{n} : controlled



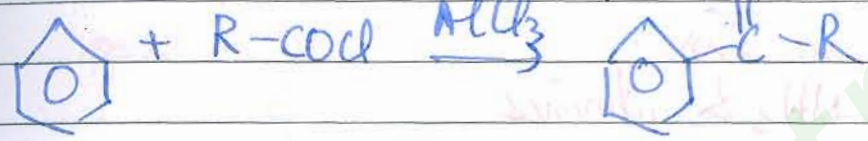
xi) $(CH_2)_6N_4$: urotropene hexamine

$Ph-CH_2-NH_2 \xrightarrow[aq.]{(CH_2)_6N_4} Ph-CHO$

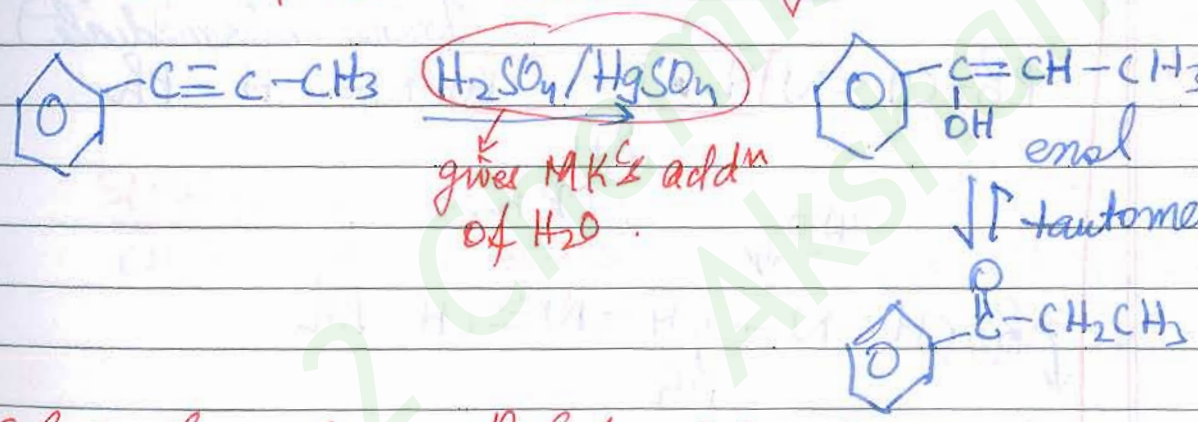
AROMATIC KETONES.

- Preparation

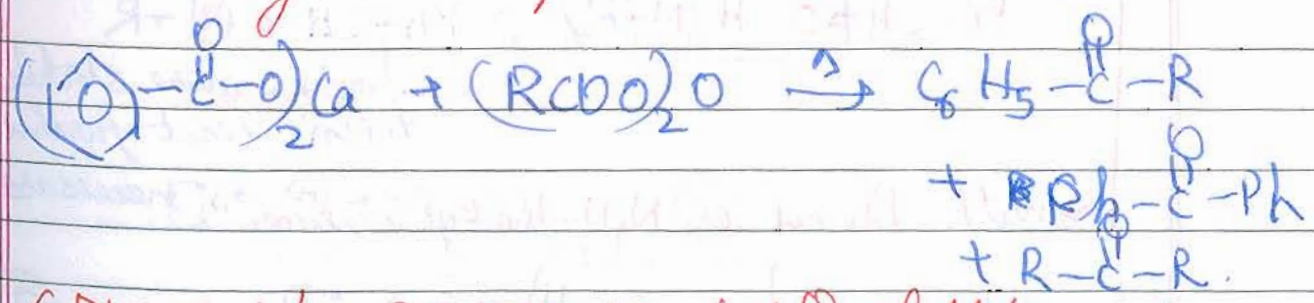
1) FCA$_c$: Friedel Craft Acyl^n.



2. MK's add^n of H_2O on aromatic alkyne.



3. Calcium benzoate + Aliphatic ~~acid~~ Ca salt



4. GRIGNARD'S SYNTHESIS ($Nu^{\ominus}$ substitution rxn)

$Ph(Mg^+X)$ + Acid derivative

classmate
Date
Page

- Properties

Aromatic aldehyde
- → gives Schiff's test
- → gives Tollen's test
- → forms insoluble bisulphide (with $NaHSO_3$)
- → doesn't give Fehling's Test → can differentiate b/w aliphatic & aromatic.

→ REACTIONS
- → Cannizaro exn.
- → With NH_3 & Amines

$$Ph-CH=O \;\; H_2N-H \rightarrow Ph-CH=NH$$
(Imine (intermediate))

$$Ph-CH=N-H \;\; O=CH-Ph \;\; H-N=CH-Ph$$

$$-H_2O \downarrow$$

$$Ph-CH=N-CH(Ph)-N=CH-Ph$$

If

$$Ph-CH=O \;\; H_2N-R \rightarrow Ph-CH=N-R$$
Imine (more stable, doesn't react further)

→ with Phenol (or) N,N-dialkyl aniline → 3° necessary

$$C_6H_5-CH=O + 2\,C_6H_5OH \rightarrow \text{dye}$$

$$Ph-CH=O + 2\,C_6H_5N(CH_3)_2 \rightarrow Ph-CH(C_6H_4N(CH_3)_2)_2$$

→ PERKIN'S RXN (for any aromatic)

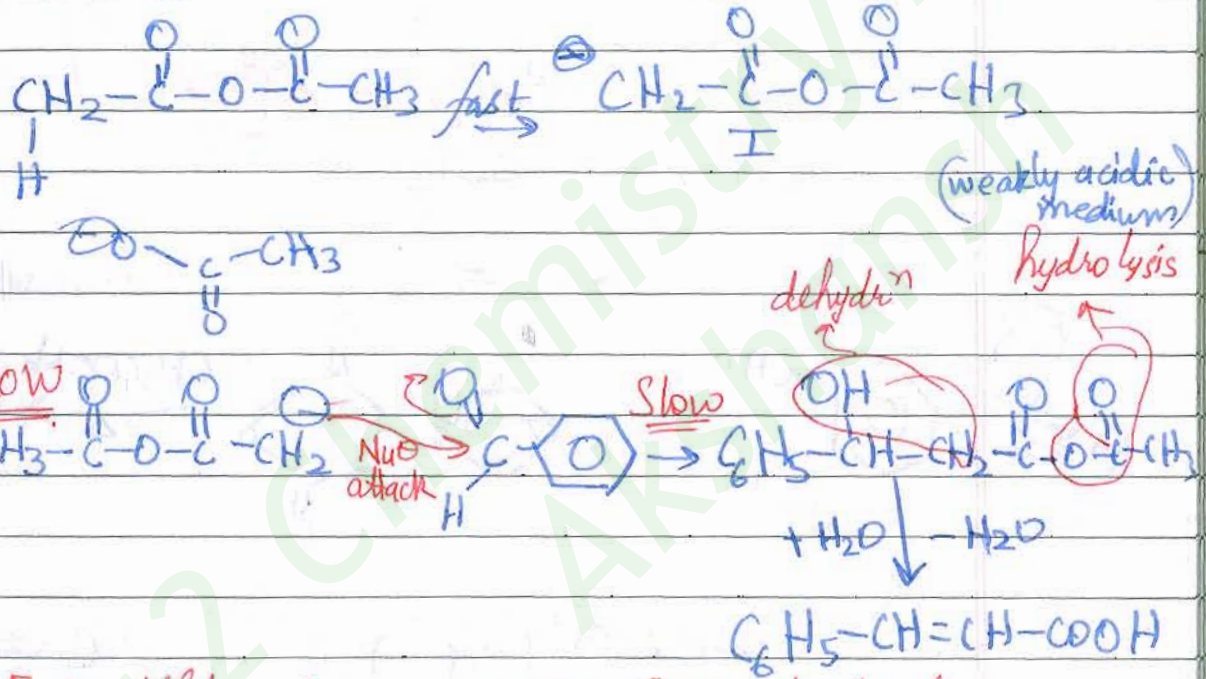
When an aromatic aldehyde is treated with anhydride of an aliphatic acid containing α-H, at about 180°C, condensⁿ (Perkin's condensⁿ) takes place to give α,β-unsaturated acid as major product.

Catalyst :- Na salt of aliphatic acid as basic catalyst

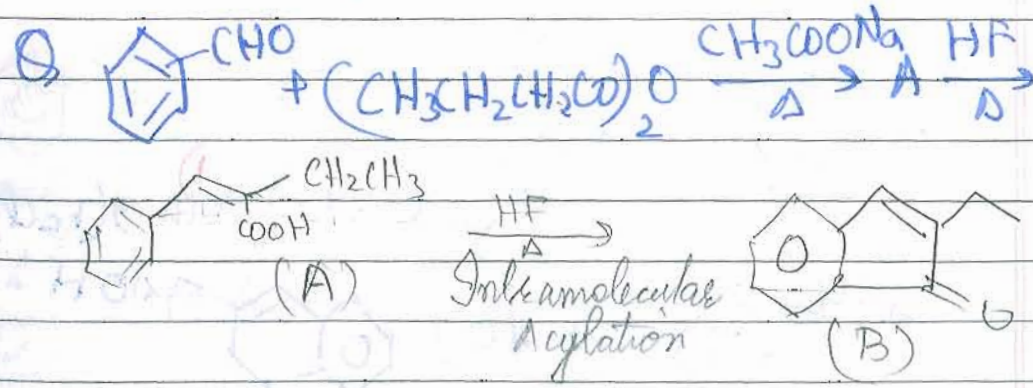
$$C_6H_5-CHO \xrightarrow[+\ CH_3COONa,\ \approx 180^\circ C]{(CH_3-\overset{O}{\overset{\|}{C}})_2O} \underset{\text{unsaturated}}{C_6H_5-\overset{\beta}{C}H=\overset{\alpha}{C}H-COOH}$$

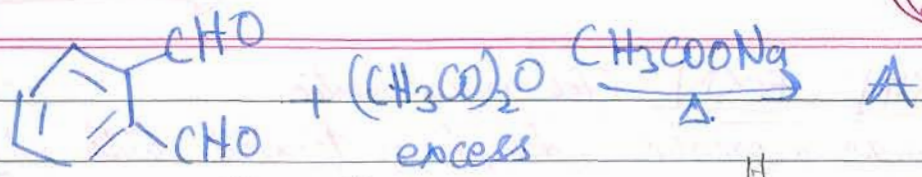
CINNAMIC ACID.

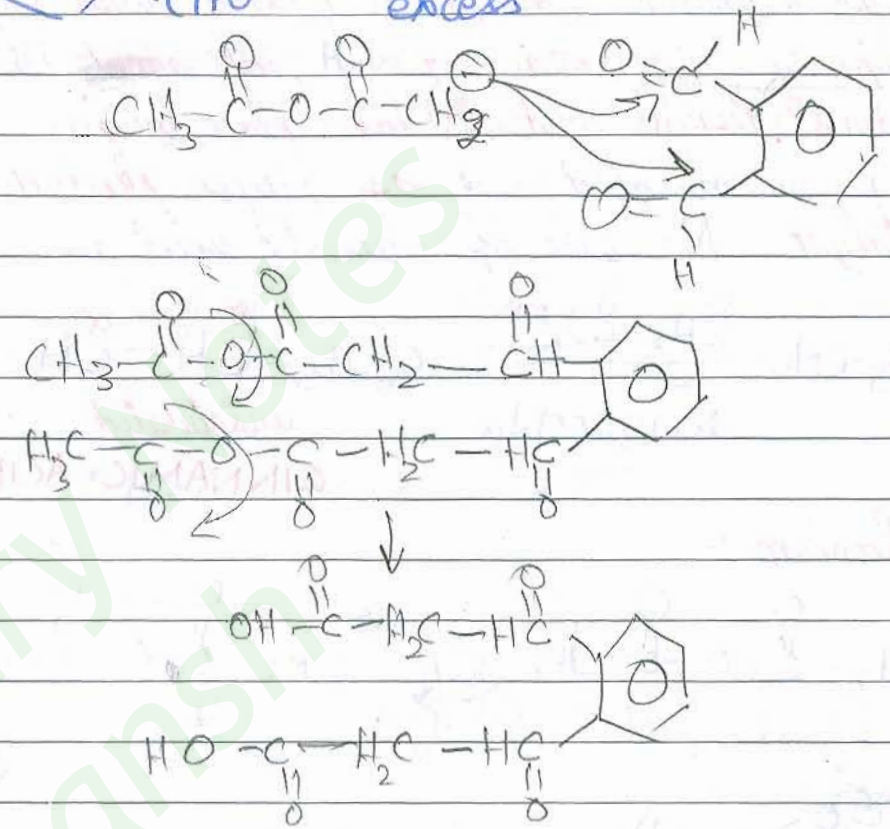
mechanism :-

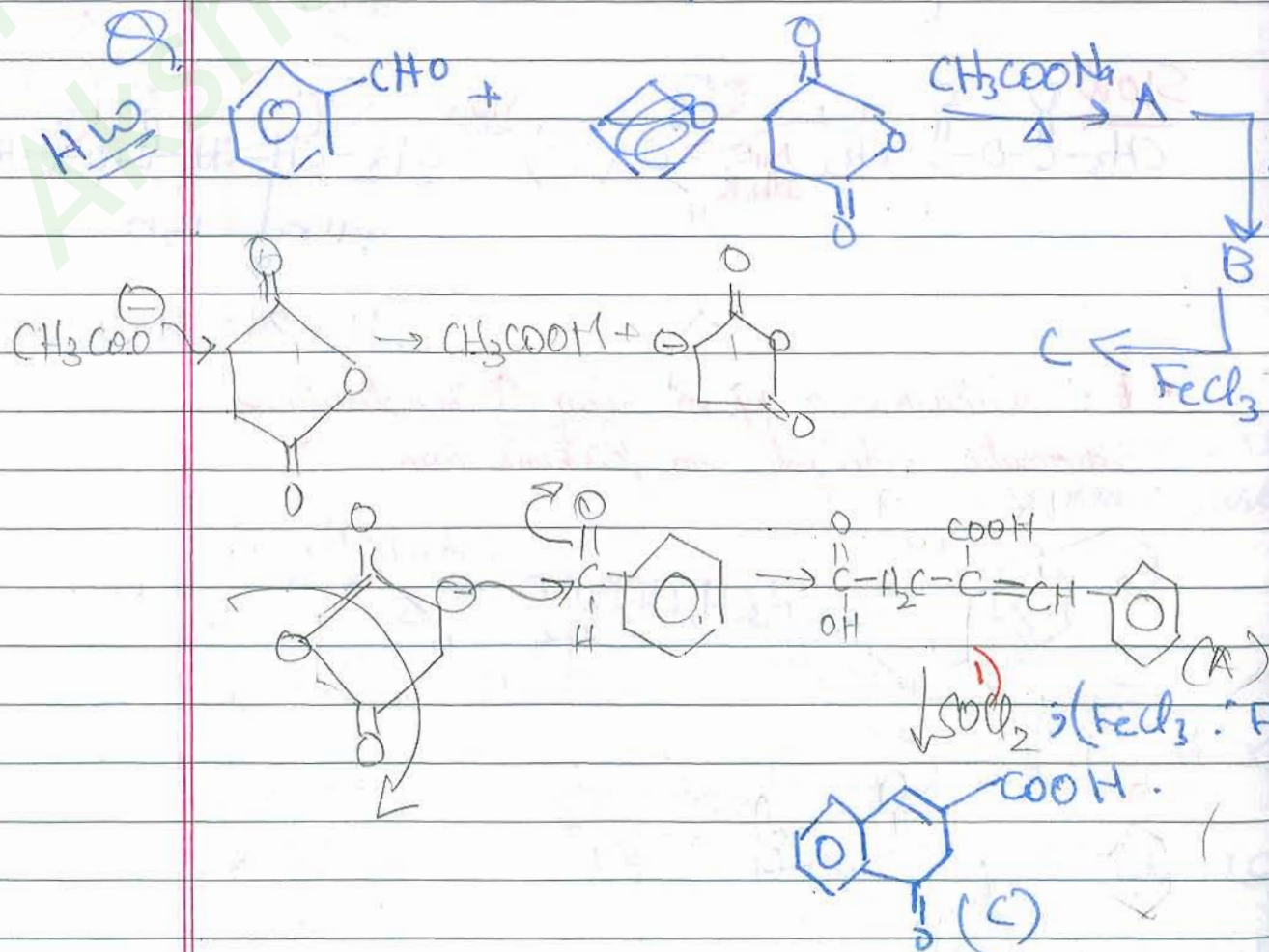


- ⊖ e⁻ withdrawing grp in ring ↑ reactivity of aromatic aldehyde in Perkin's rxn.



Q. 
CHO
CHO
+ (CH3CO)2O
excess
CH3COONa
Δ
A

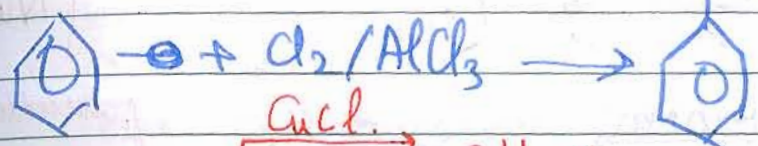

CH3
C
O
CH2
H
O

Q. 
CHO
CH3COONa
A
B
C
FeCl3
CH3COO
CH3COOH
COOH
(A)
SOCl2 ; (FeCl3 . F
COOH
(C)

classmate
Date 24·11·20
Page

ARYL-HALIDE

• preparation:

(i) 

(ii) $C_6H_5N_2Cl$ —CuCl→ C_6H_5Cl

$C_6H_5N_2Cl$ —CuBr→ C_6H_5Br

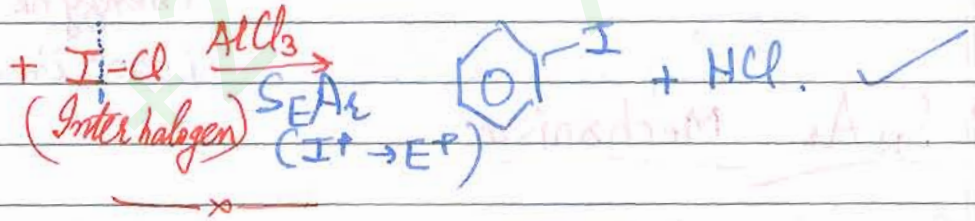
$C_6H_5N_2Cl$ —KI→ C_6H_5I

→ Iodination

: fails

(RA → strong)

Aliter



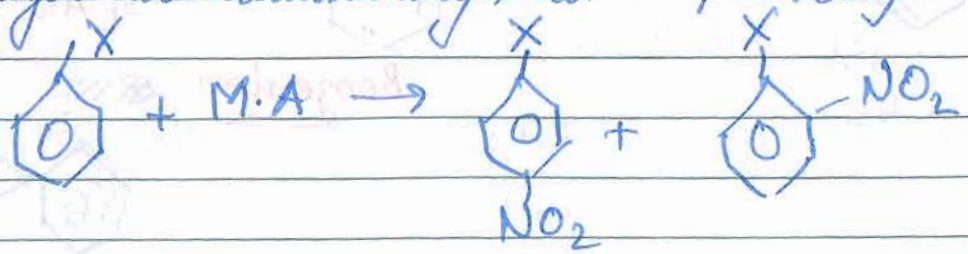
(Inter halogen)

S_EAr ($I^+ \rightarrow E^+$)

+ HCl. ✓

Properties

1. halogens are deactivating, but o-p directing.



* $Cl_3-C-CHO$ (chloral) + 2 C_6H_5Cl $\xrightarrow[-H_2O]{\Delta}$ $Cl_3-C-CH(C_6H_4Cl)_2$ DDT

2. $C_6H_5\overset{\oplus}{I}$ only $\xrightarrow[\Delta]{Cu}$ $Ph-Ph$; Ullman's Rxn
Coupling

3. $C_6H_5Cl \xrightarrow[\approx 300°C]{NaOH}$ C_6H_5ONa → ∵ medium is alkaline
(very less ≈ 5% formed)

$C_6H_5Cl \xrightarrow[\Delta, high\ P]{NH_3}$ $C_6H_5NH_2$ (very less)

$C_6H_5Cl \xrightarrow{CH_3ONa}$ $C_6H_5OCH_3$ ANISOLE (very less)

$Nu^\ominus$ substitution rxn (if occur at all)

** § NUCLEOPHILIC AROMATIC SUBSTITUTION
↳ only for aryl halide

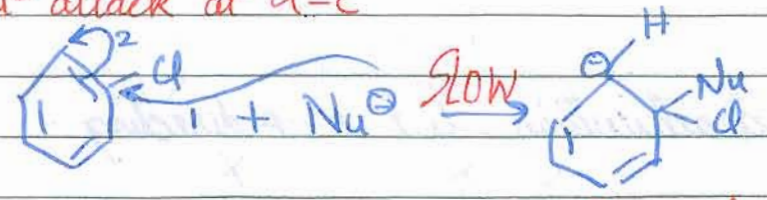
Addition-Elimination Mechanism (S_NAr)

Elimination-Addition Mechanism (Benzyne mechanism) (not in JEE)

S_NAr Mechanism

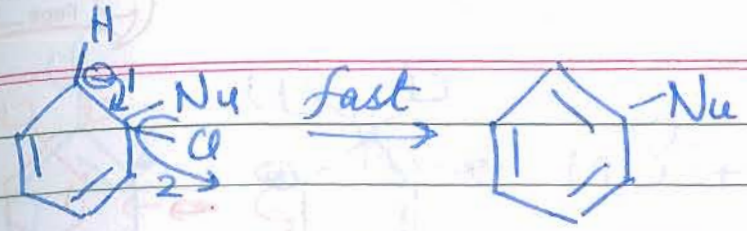
• General mechanism

S1: $Nu^\ominus$ attack at α-C



(+ve charge comes in S_EAr)

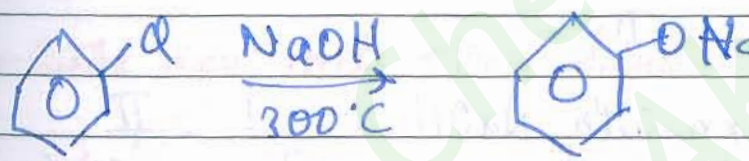
Benzenion

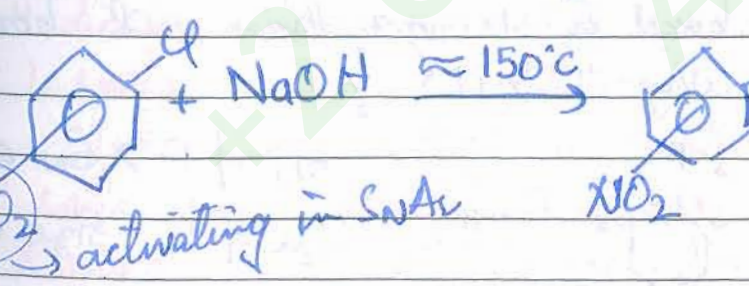
S2) 

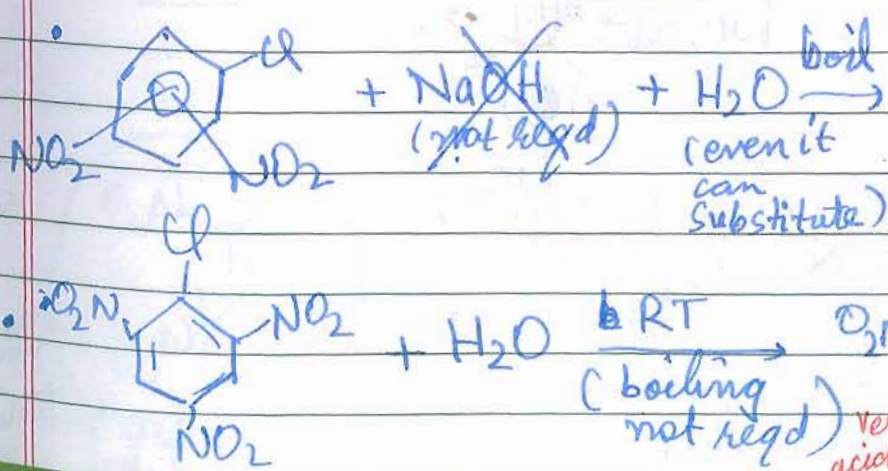
- Rate determining : Addition } S_NAr.
  non Rate determining : Elimination }
  ↳ opp. in Benzyne Substitution

1. • e^- withdrawing grp on the ring catalyses S_NAr rxn by stabilising the intermediate anion.
     eg: NO_2, SO_3, X, $COO^\ominus$
   • e^- donating grp on the ring retards S_NAr rxn by destabilising the intermediate carbanion.

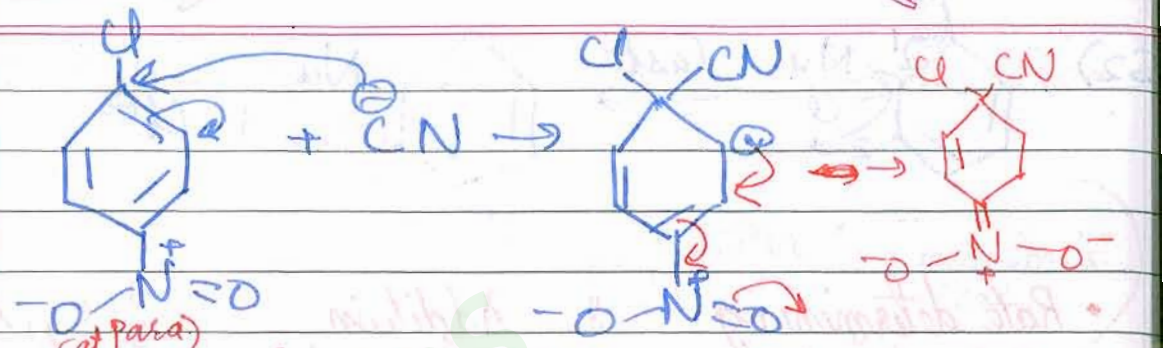
2. All activators of S_EAr are DEACTIVATORS in S_NAr
   " deactivators " S_EAr " ACTIVATORS. " S_NAr







classmate
Date
Page

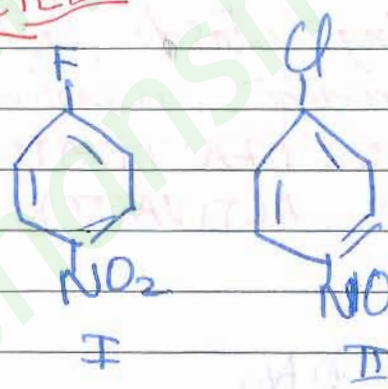


(at para)
↳ Stabilises intermediate carbanion by resonance

→ -R & -I

- On activating grp activates o & p substitution more than meta substitution
  → -I

Q. ✱EXPECTED



NaOH →

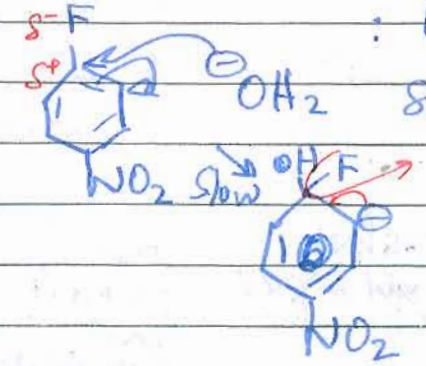
Ily,

✱ NO_2-Ph-F > NO_2-Ph-Cl > NO_2-Ph-Br > NO_2-Ph-I

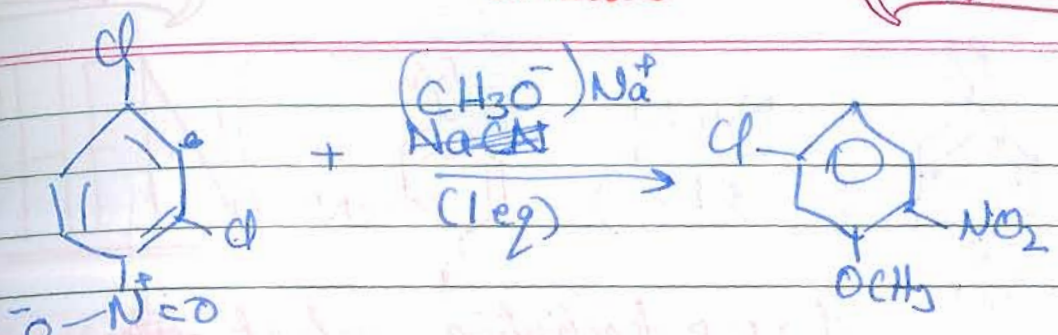
Reactivity in rxn with NaOH :- I > II

Q. C-F bond is stronger than C-Cl bond
Then why I > II ?

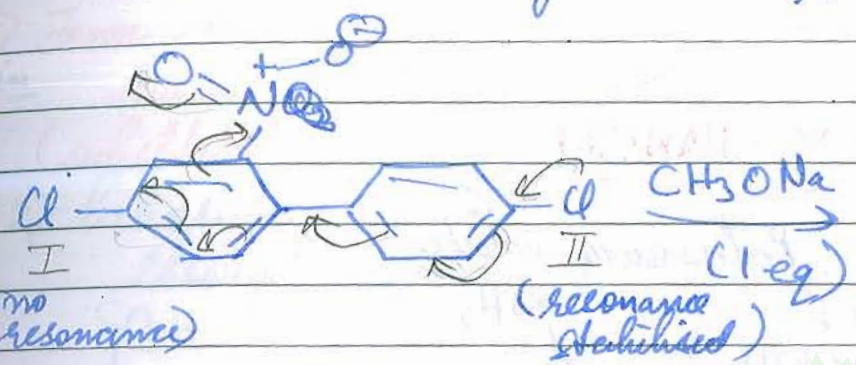
Ans → ① : E_N of F > E_N of Cl
Size of F < Size of Cl



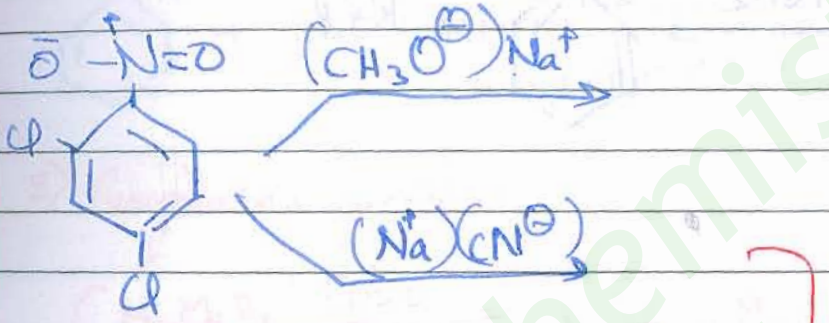
• Mostly :- I-effect > Steric hindrance
see its strength & decide

Q) 

O > P :- greater I effect

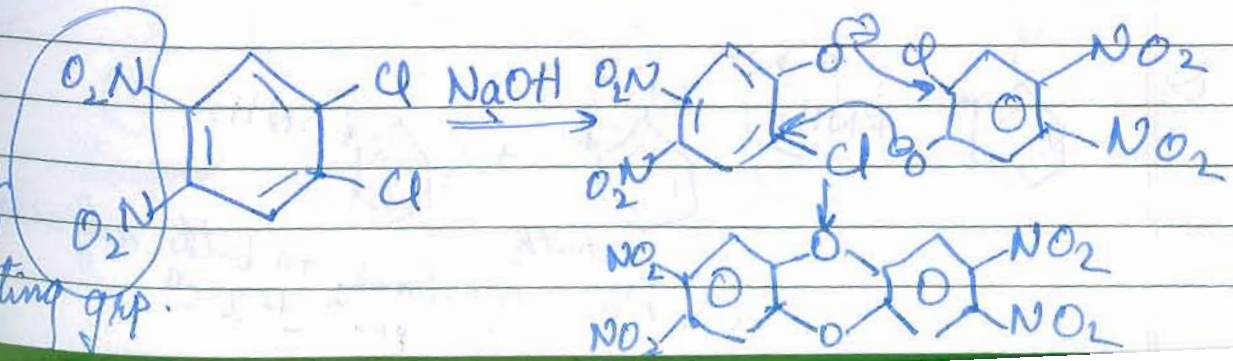
Q) 

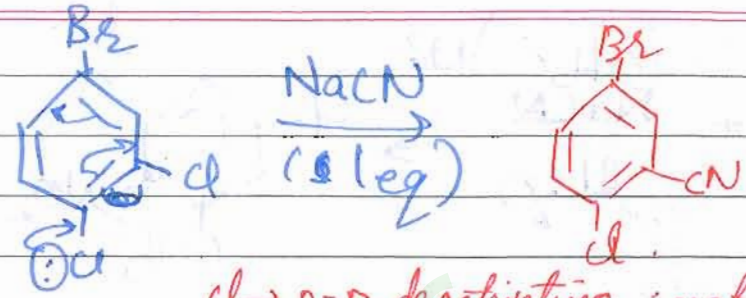
II is substituted.

Q) 

In S_NAr rxn with OMe, disub

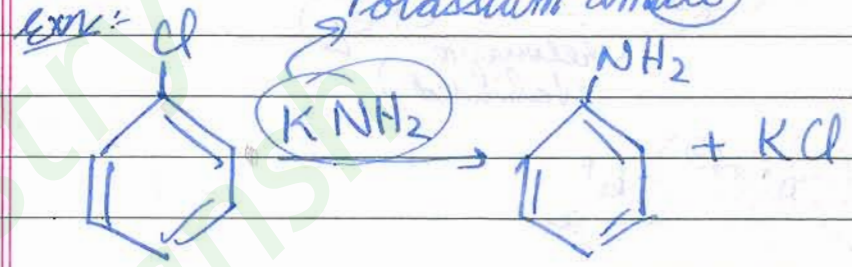
3. 2, 4 dichloro nitrobenzene when treated with NaOMe in 1:1 ratio → no disubstitution.
When same substrate is treated with NaCN in 1:1 ratio, some disubstitution product is formed.
Reason: OMe deactivates after coming once.
CN activates " " "



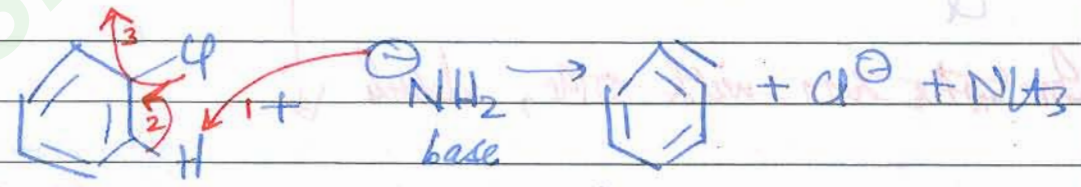
Q. 

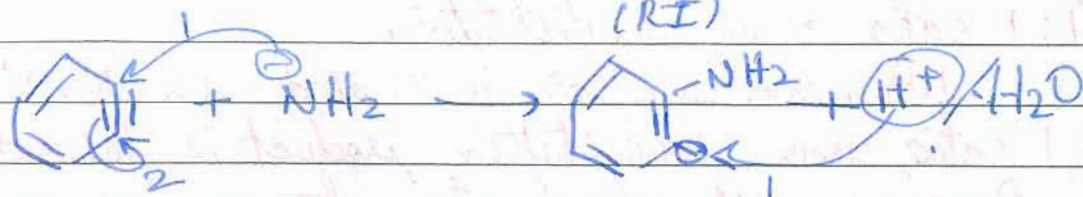
Cl → o-p deactivating ; not at meta.
So, substitution at meta.

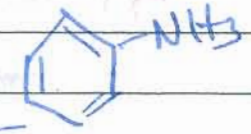
✱ BENZYNE - MECHANISM

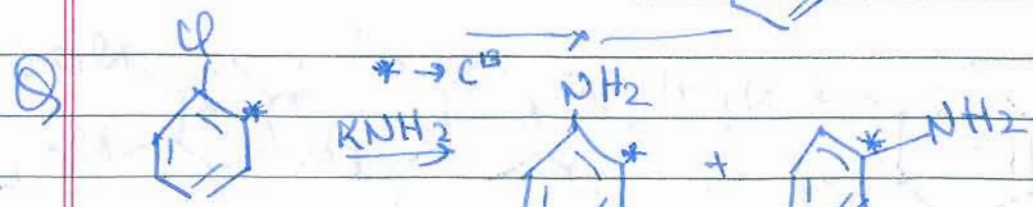
Ex:- 

mechanism :-







Q. 

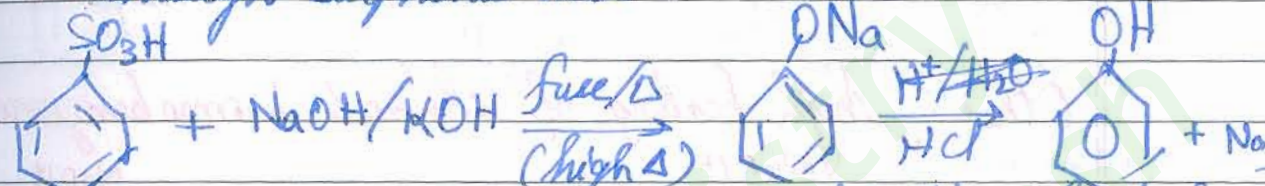
both
(∵ ⊖NH2 may attack on both adjacent pos^n C12 & C13

PHENOL

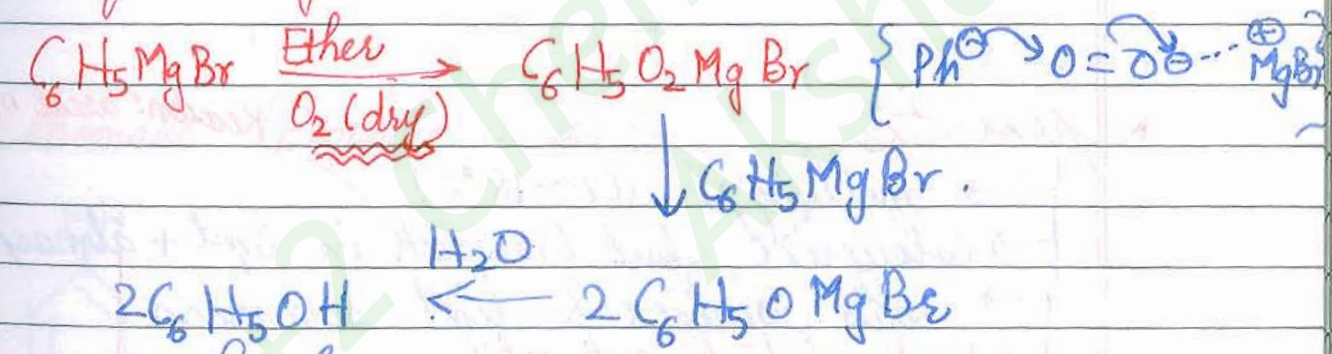
- Preparation

1) From crude oil :-
Main — during destructive distill^{n} of crude oil, some phenols (substituted also) in middle oil fraction.

2) laboratory method :-
through sulphonic acid.



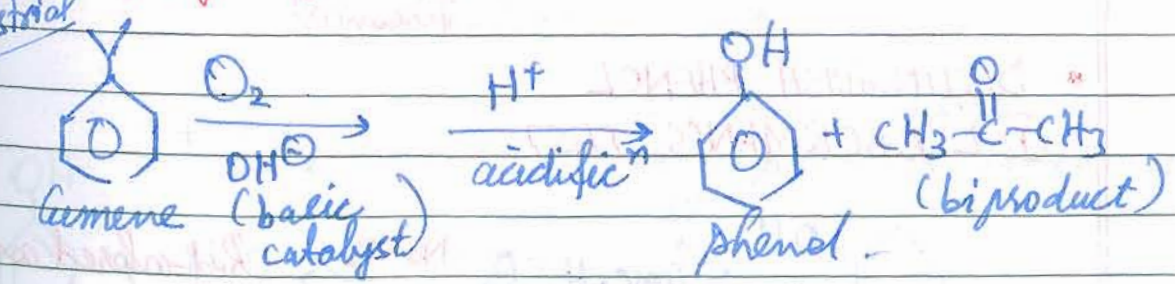
3) Grignard's synthesis :



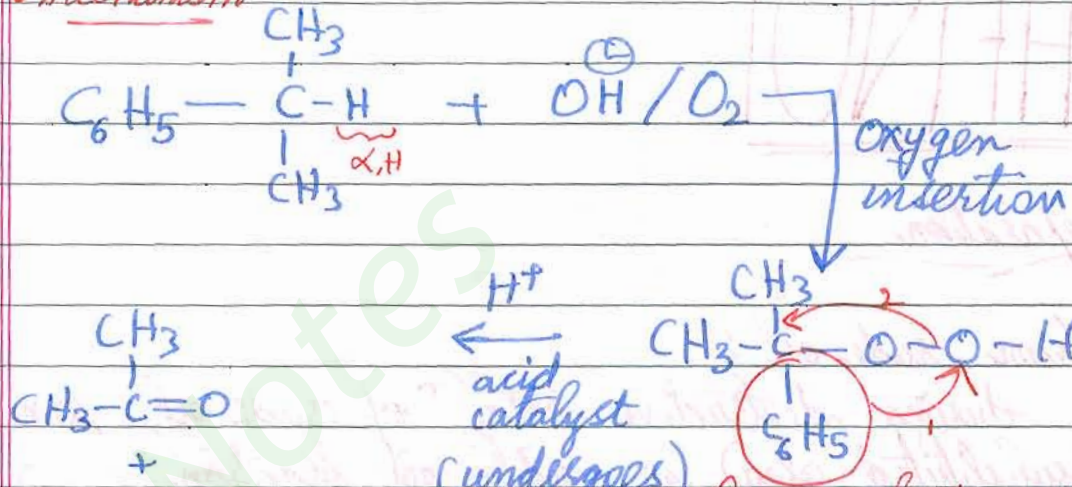
- calculated amt. of O_2 (dry) must be used → NOT excess.

4) CUMENE PROCESS :-
Isopropyl benzene

Industrial



• mechanism



Cumene-hydro peroxide

Intermediate

Other :- high heating of chloro & bromo benzene with NaOH

✓ with Benzene diazonium salts → NaOH → H⊕/H2O

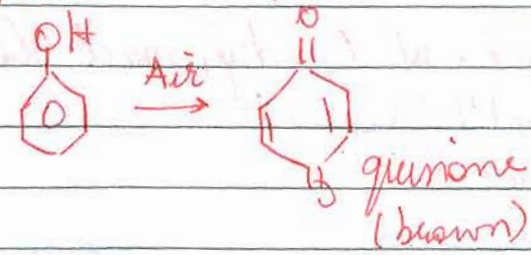
* properties

→ melting pt (17~18°C) — Reason: areal ox

→ colourless (but brownish in liqd + atmosp

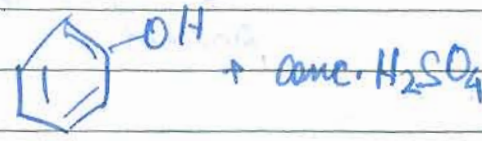
→ solid: winters & liqd: summers

→ ~~dun~~ disinfectant, antiseptic.



• DISTINGUISH PHENOL

① LIBBERMAN'S TEST



→ Na

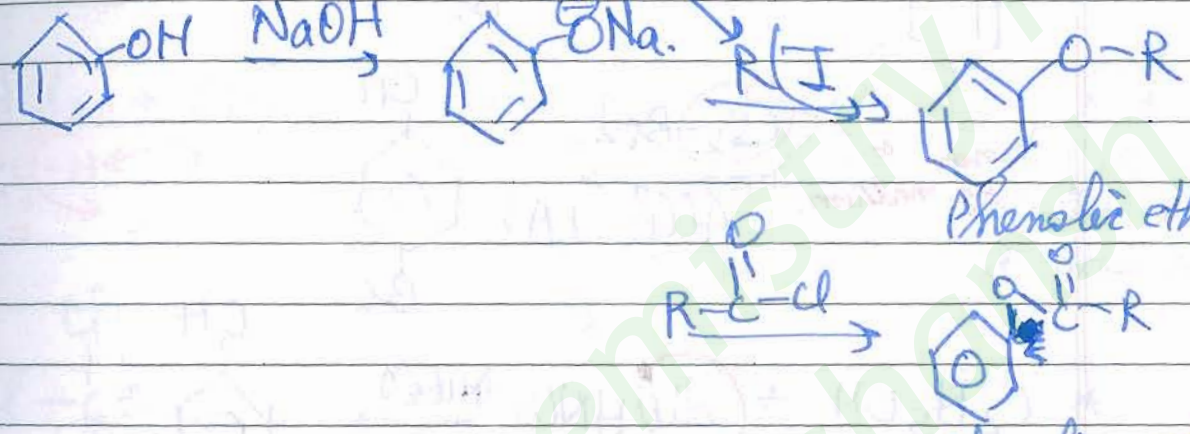
Blue ←

② FERRIC CHLORIDE TEST

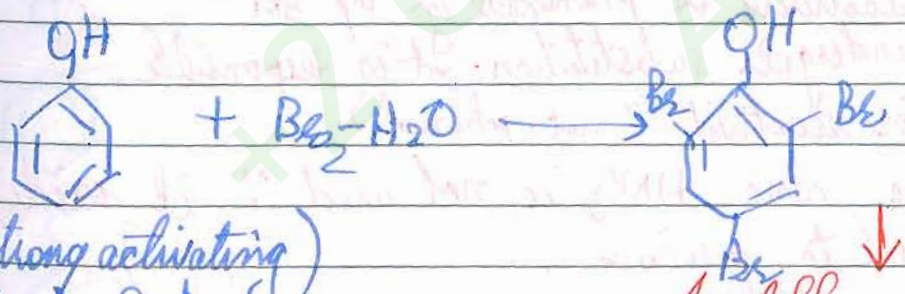
$PhOH + FeCl_3 \longrightarrow$ violet colored complex

✱ Reactions

① Acidity :- Phenol is stronger acid than H_2O.



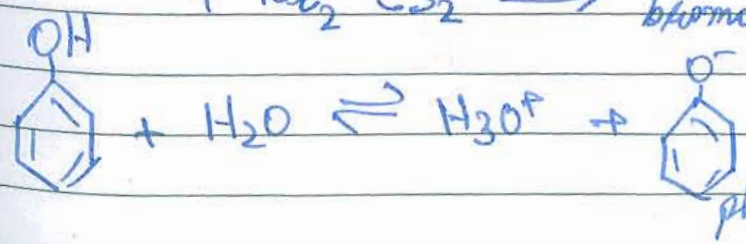
② Aromatic electrophilic substitution

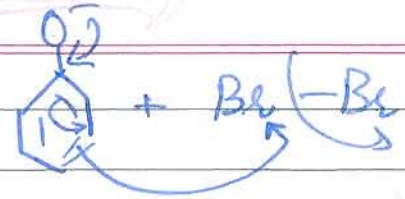


(Strong activating grp in S_EAr)

• used for detection of amt. of phenol used (∵ product is equally formed)

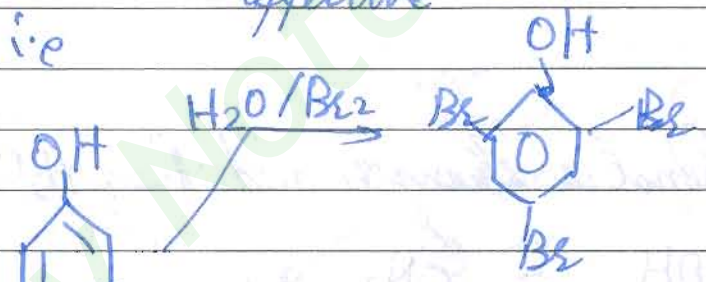
+ Br_2-CS_2 → not even a single bromo phenol is formed without LA

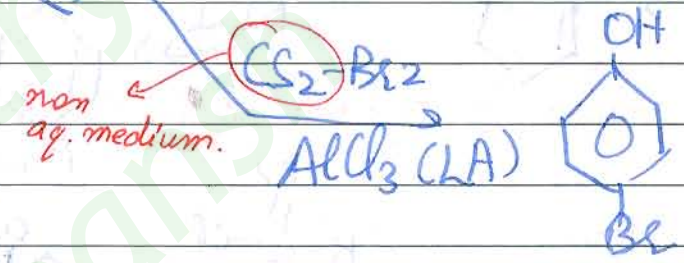




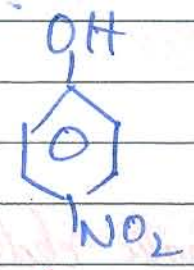
In non aq. solvents :- no proton acceptor, so benzonium on phenol (not phenoxide) → not effective -

i.e





* C_6H_5OH + (dil) HNO_3 $\xrightarrow{Nitr^n}$



very (reactive)

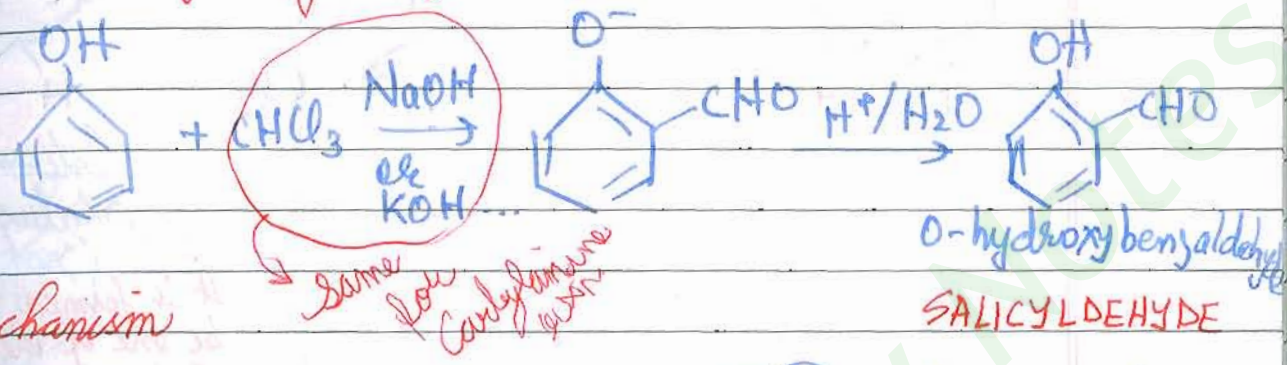
↳ reactivity of phenoxide in aq soln undergoes substitution. It is responsible for reactivity (not phenol)

- MA or conc. HNO_3 is not used ∵ it oxidises phenol to quinone.

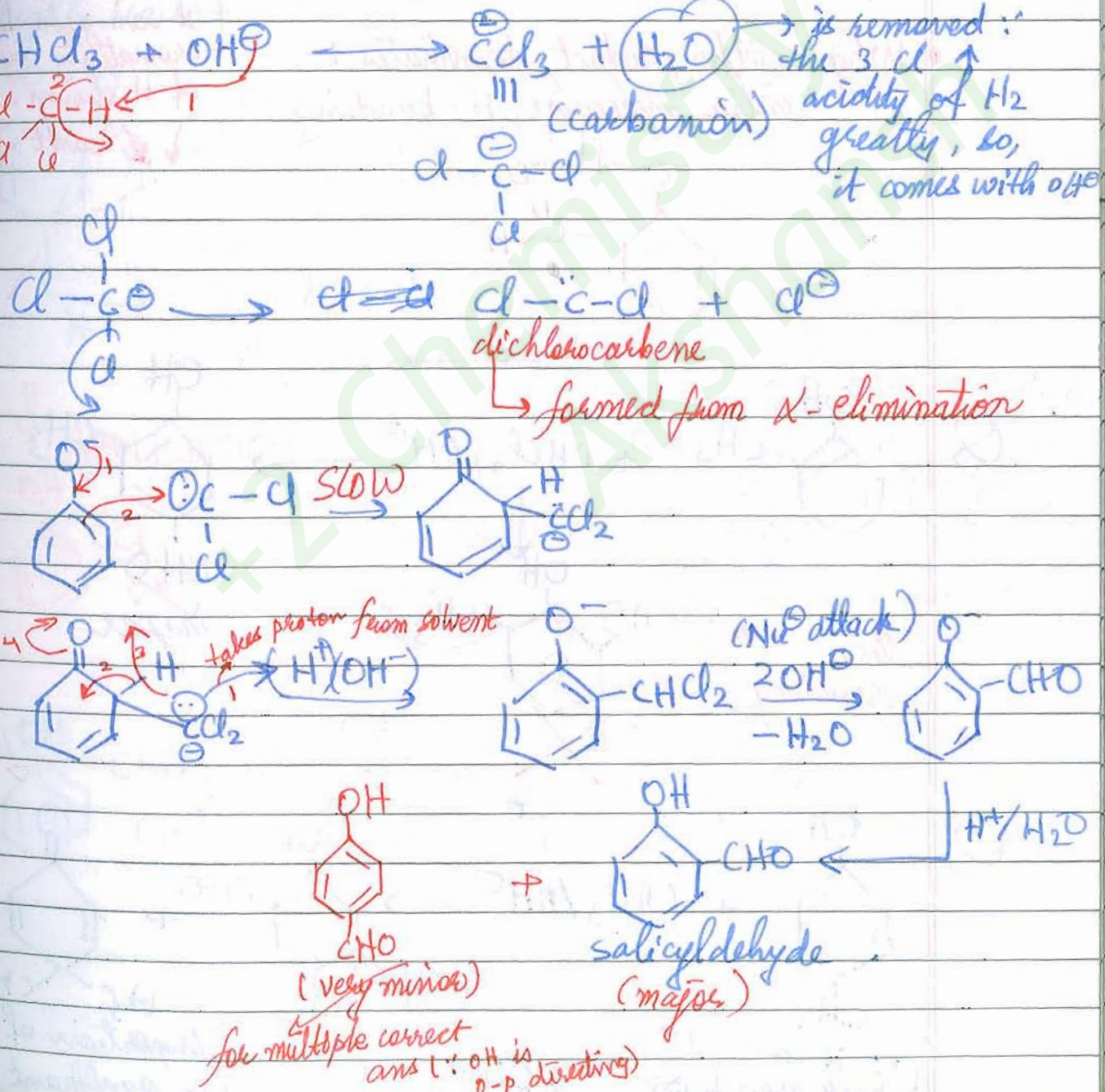
classmate
Date 26·11·20
Page

✡ RIEMER TIEMAN'S RXN

↳ when Phenol is treated with $CHCl_3$ (Chloroform), in presence of a strong base, followed by acidific^{n}, gives o-hydroxy benzaldehyde.

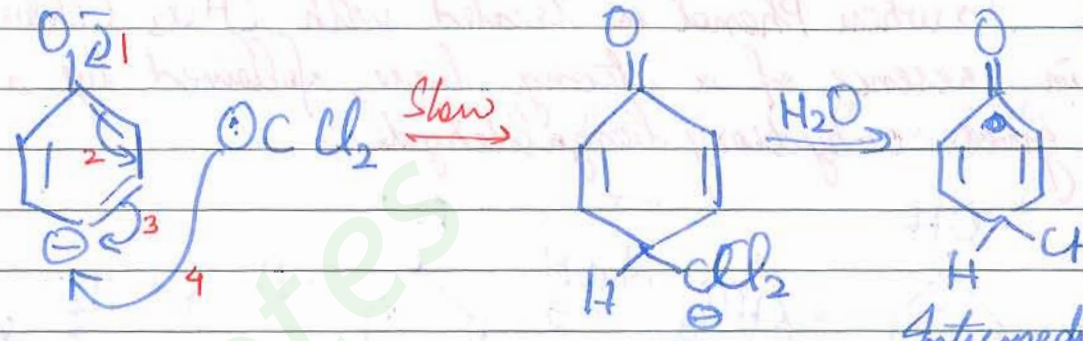


• mechanism



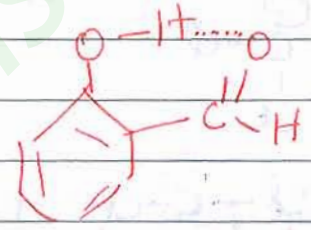
classmate
Date
Page

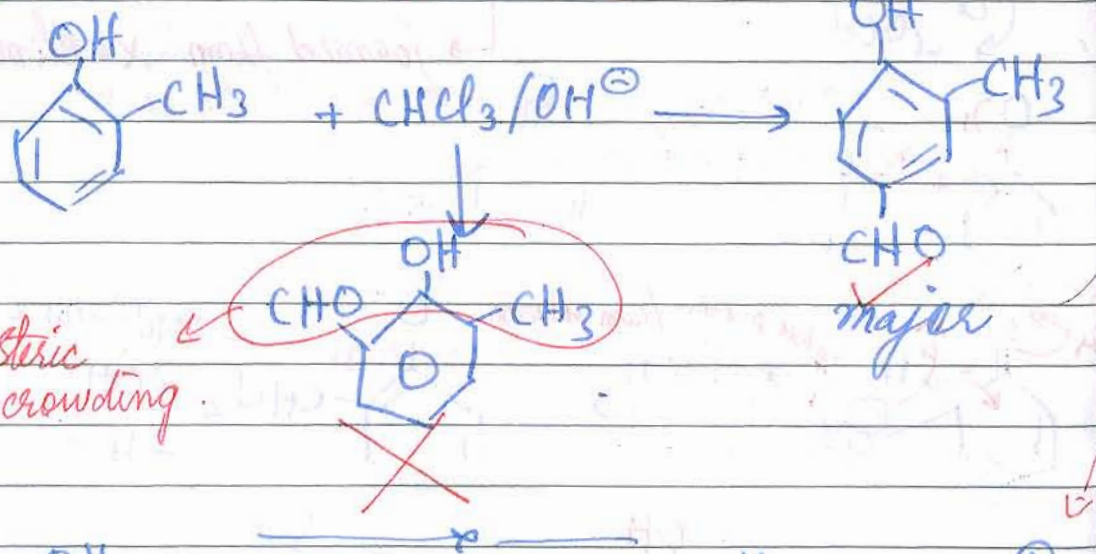
para attack :-



It is formed & w
be one of the prod
[It can gain ba
aromaticity by
of H shown. B
can't.)

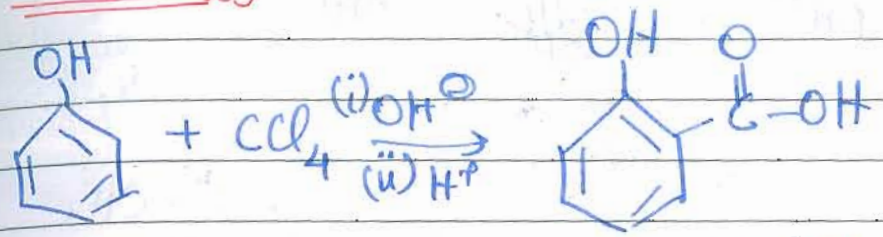
- Why ortho product dominates :-
intra molecular H-bonding



Q 

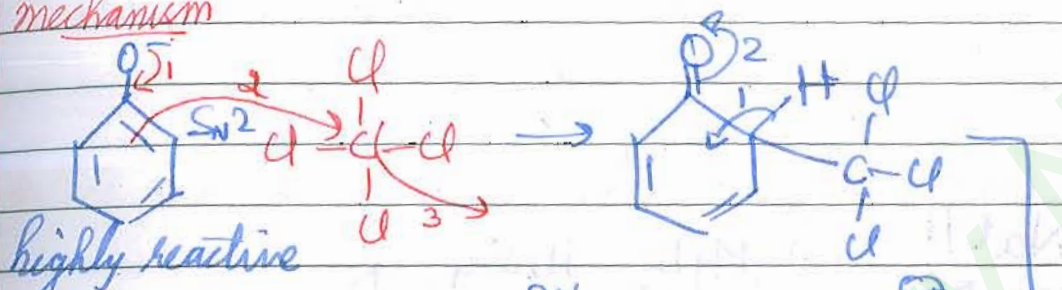
Q

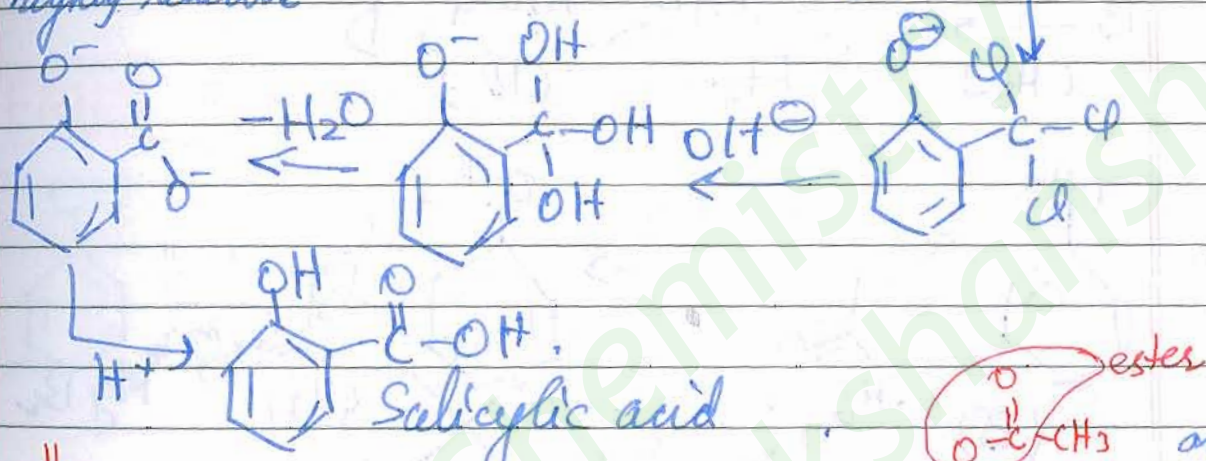
- Related Stuff :-



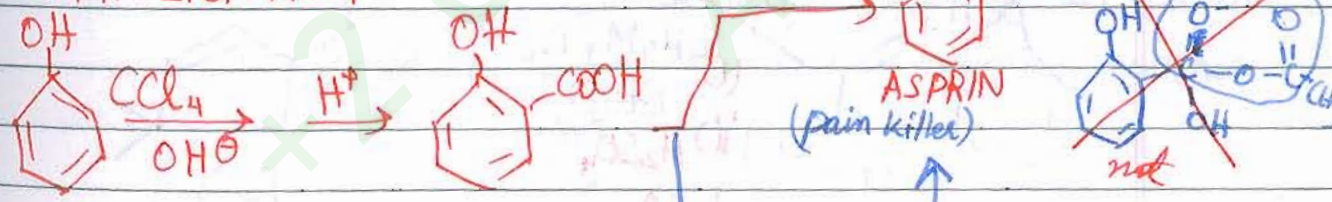
SALICYLIC ACID

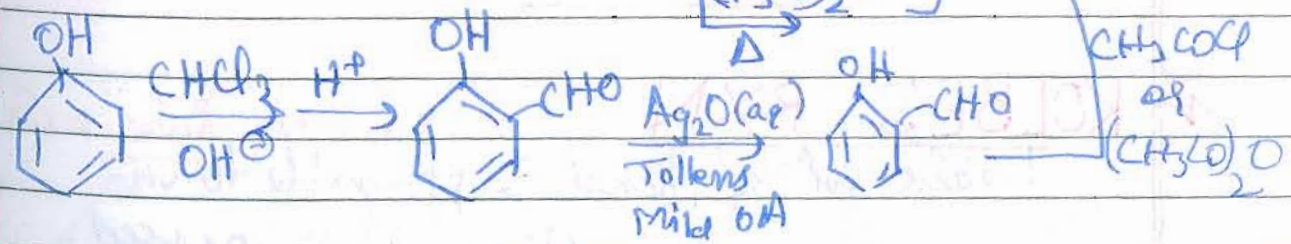
mechanism



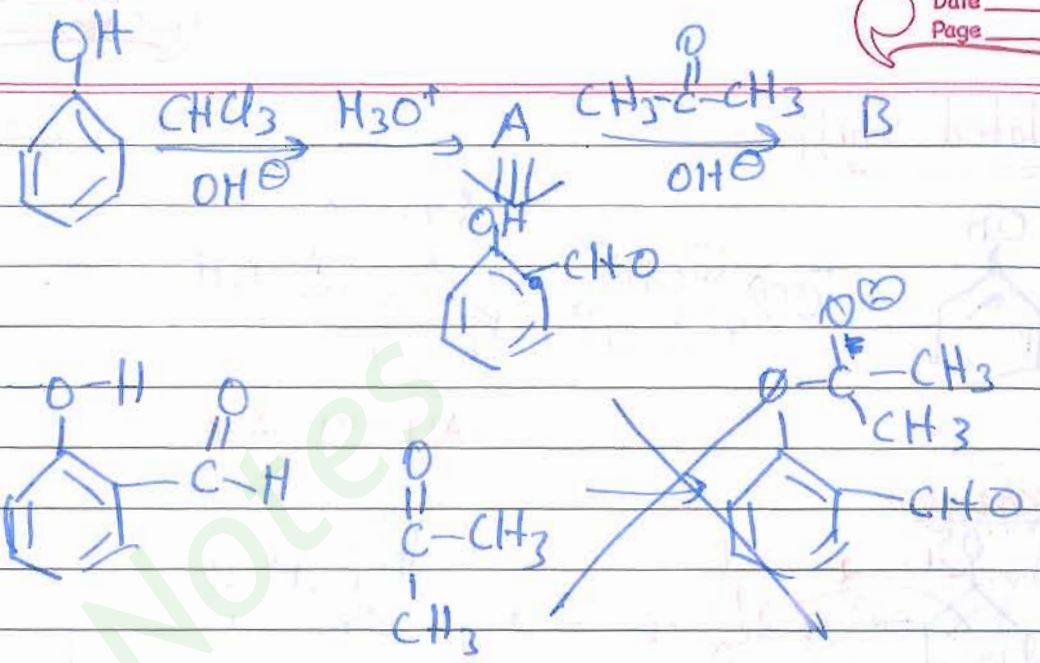


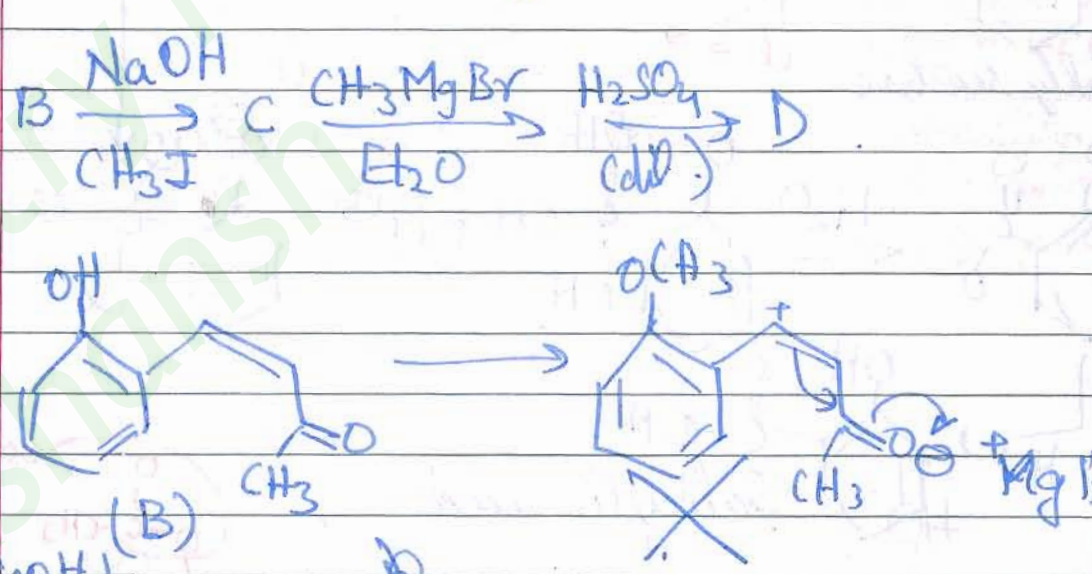
APPLICATION





Q)



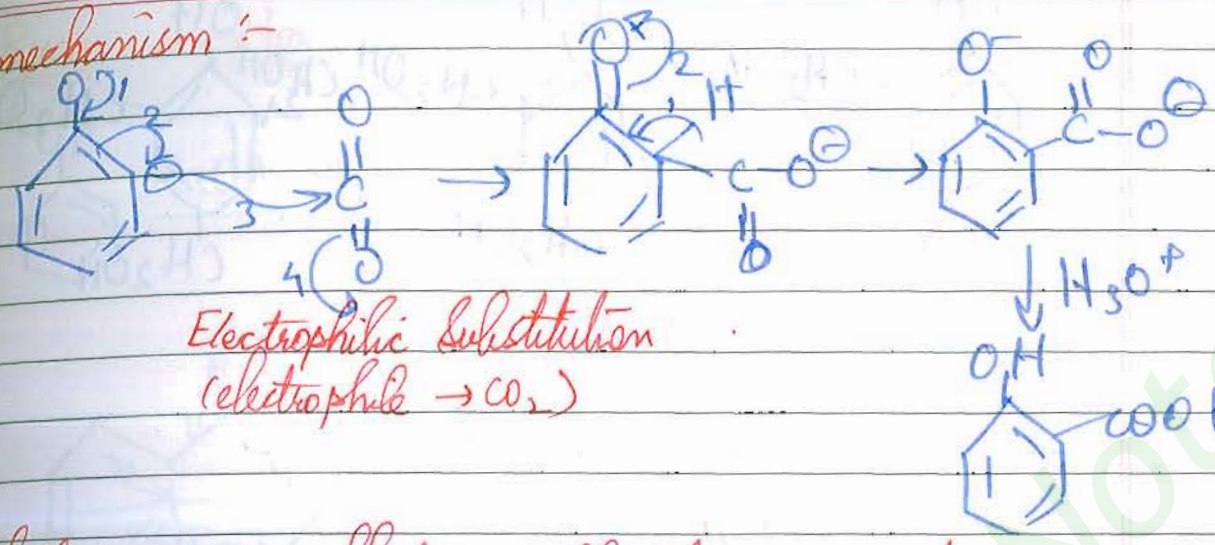


✱ KOLBE'S RXN

↳ alk. sol^n of phenol ⇒ phenoxide ion.

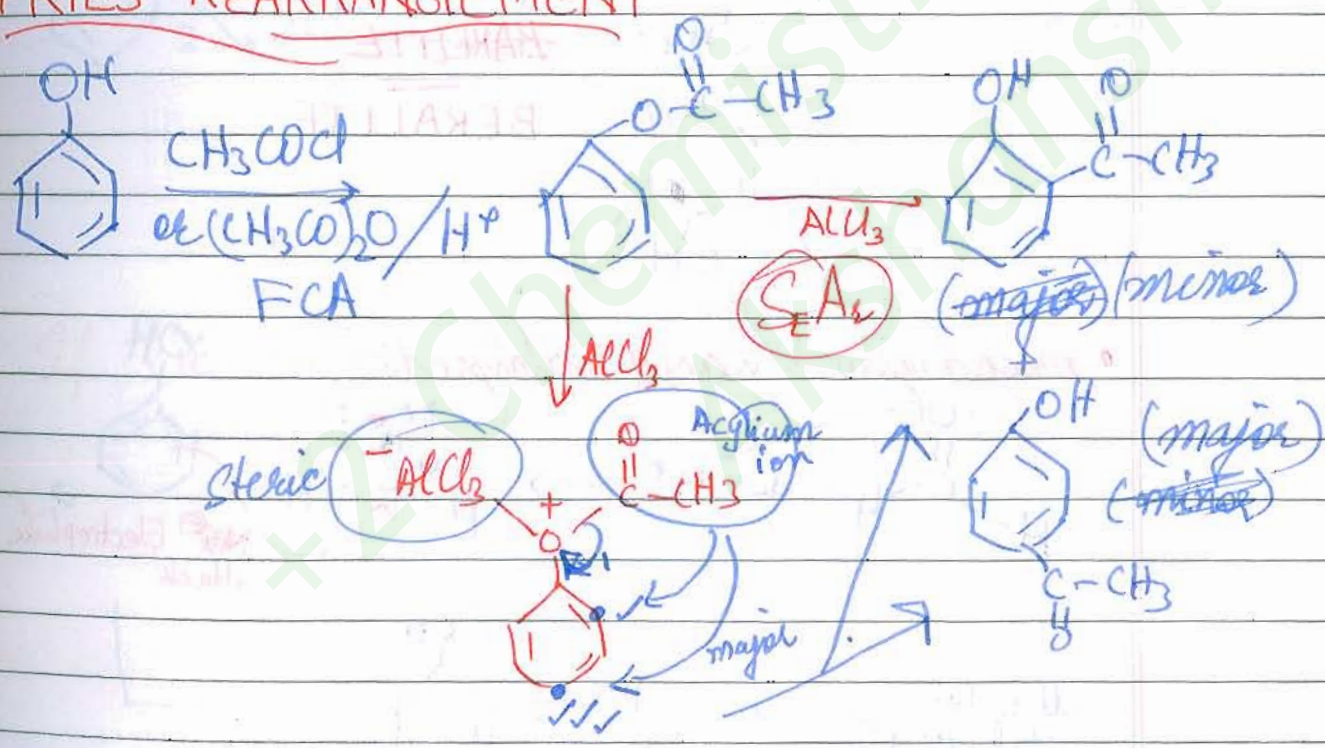
Salicylic acid addition $\xrightarrow{CO_2 \text{ passed.}}$ Salicylate is formed $\xrightarrow{H^+}$

- mechanism :-

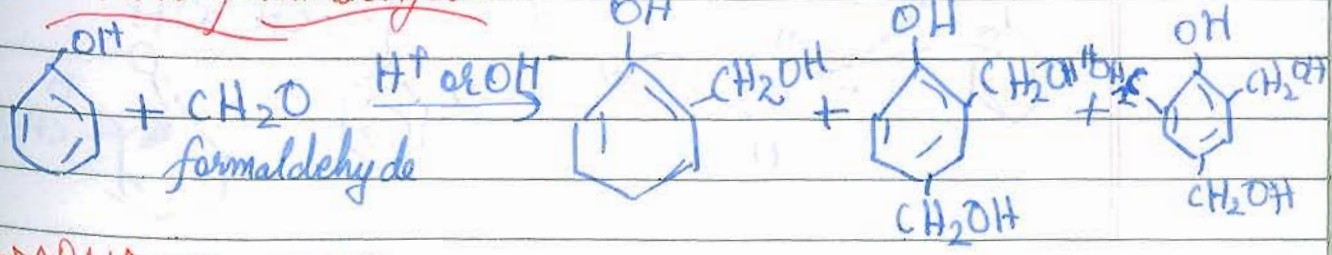


- kolbe's rxn is effective method to prepare Aspirin. (see previous page)

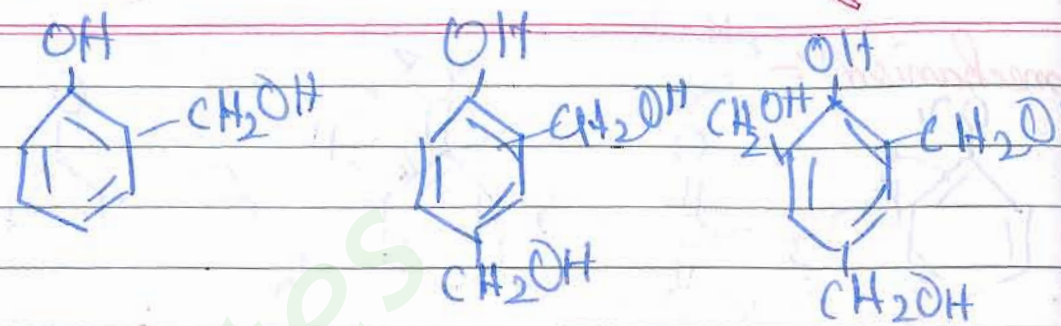
✱ FRIES REARRANGEMENT



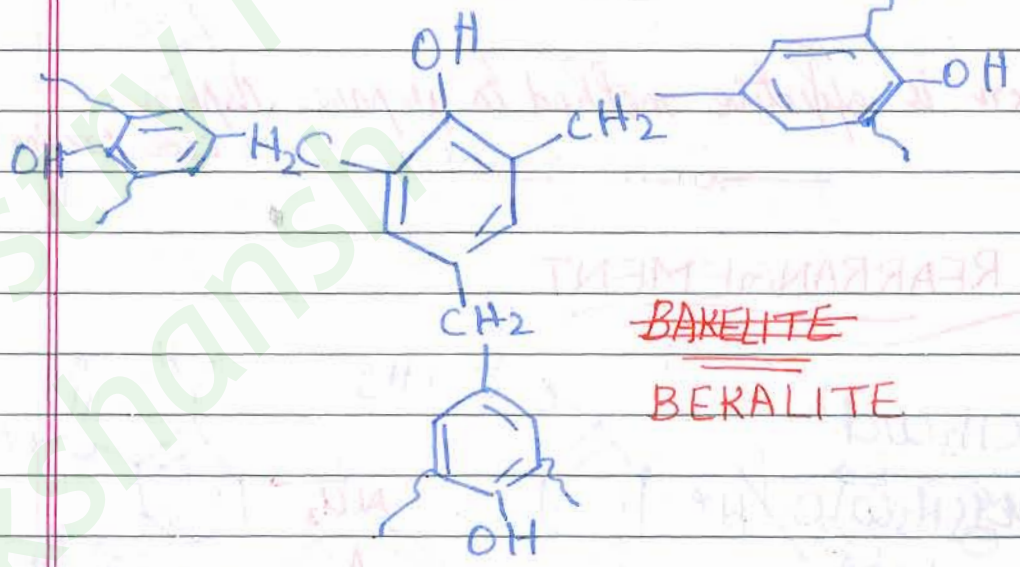
- Rxn with formaldehyde



✱ DER-MANASSE RXN.



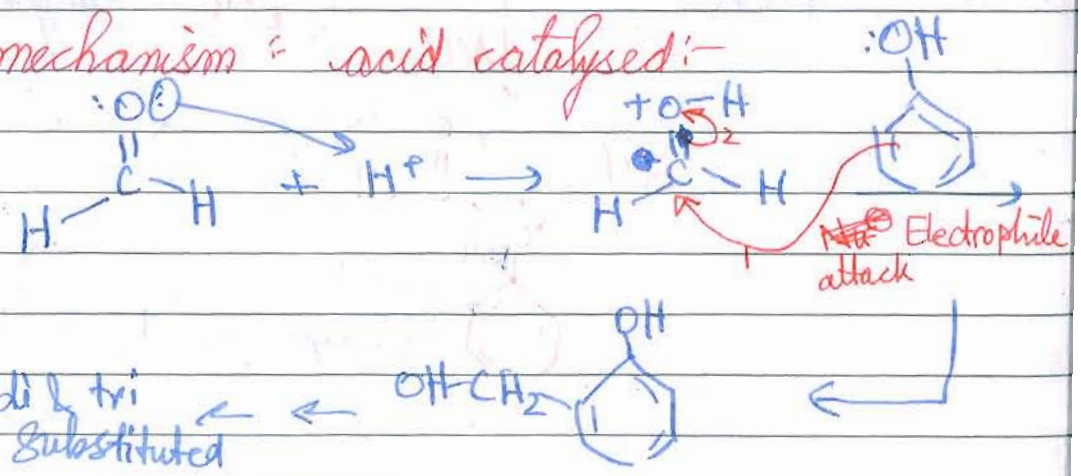
FCA repeated



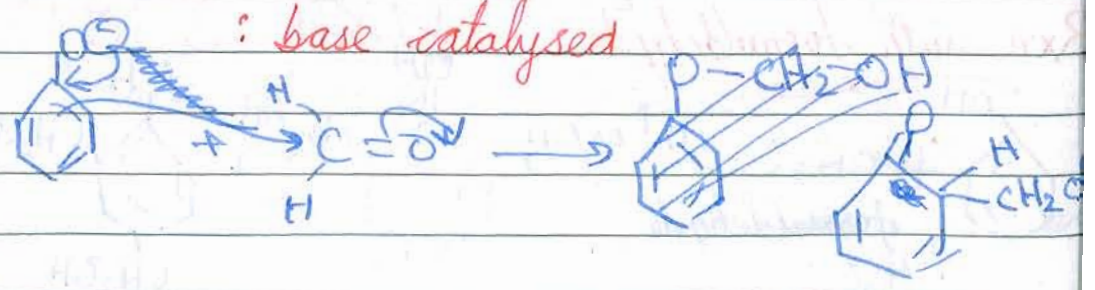
BAKELITE

BEKALITE

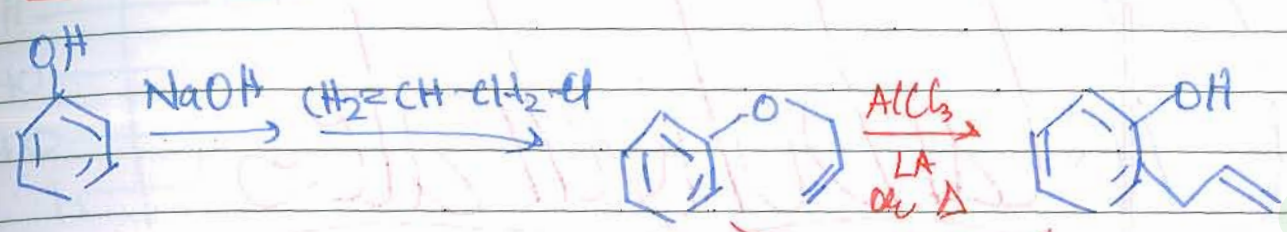
- mechanism :- acid catalysed :-



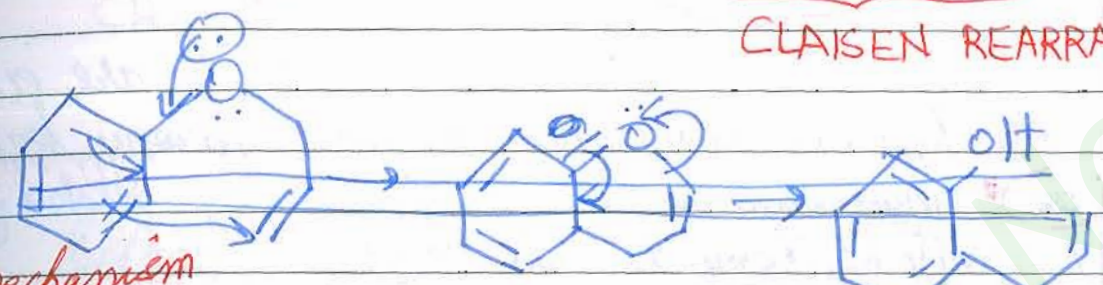
: base catalysed



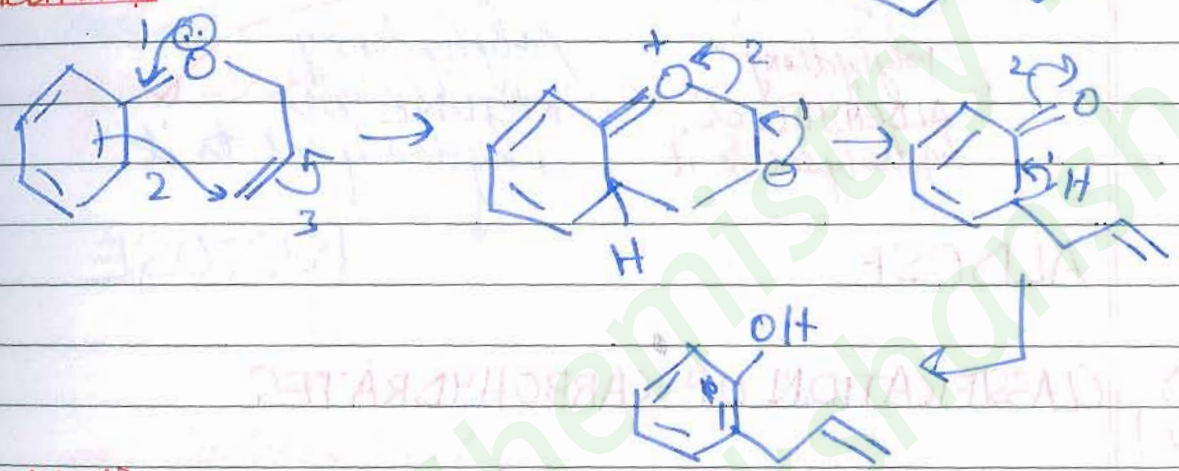
- Rxn :- extra



CLAISEN REARRAY



mechanism



If $^{13}CH_2=CH-CH_2-Cl$, it would be on ring
↳ confirmation

Ch: Carbohydrates

Carbohydrates are the compds which are either poly hydroxy aldehydes or poly hydroxy ketones or hydrolysee into polyhydroxy aldehydes or poly hydroxy ketones

polyhydroxy ALDEHYDE or hydrolyses to it → ALDOSE

polyhydroxy KETONE or hydrolyses to it → KETOSE

CLASSIFICATION OF CARBOHYDRATES

ON THE BASIS OF HYDROLYSIS RXN

1. MONOSACCHARIDES (1)
2. DISACCHARIDES (2) * OLIGOSACCHARIDES (3)
   ↳ also a part C but not LI
3. POLYSACCHARIDES (10 onwards)

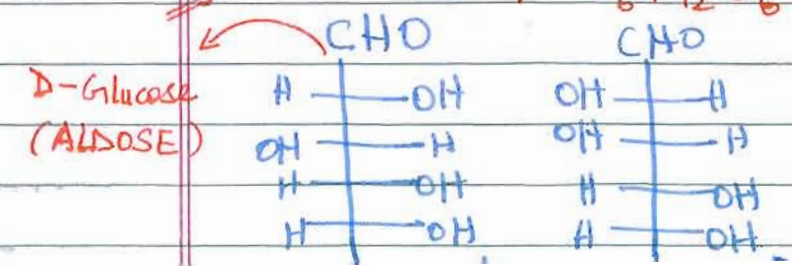
① Monosaccharides are the smallest unit of carbohydrates which is not hydrolysed further into the lower carbohydrate molecule.

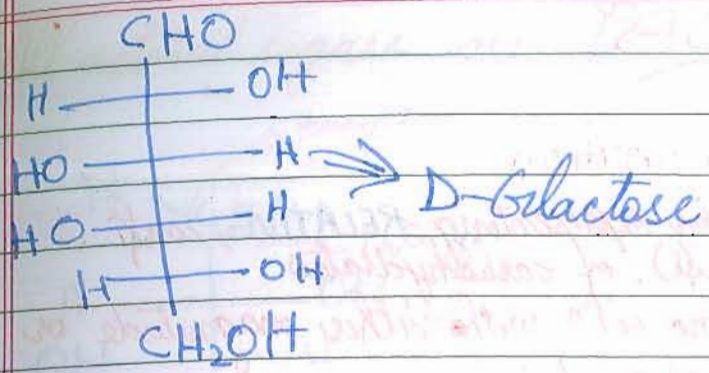
All monosaccharides have molecular formu

* $C_6H_{12}O_6$

eg

D-Glucose (ALDOSE)





⇒ D-Galactose

② Disaccharides are carbohydrates which on hydrolysis produces 2 monosaccharides per molecule are known as disaccharides

eg :- SUCROSE → $C_{12}H_{22}O_{11}$ ≡ Table Sugar

$+H_2O$

↓

$C_6H_{12}O_6 + C_6H_{12}O_6$

D-Glucose D-Fructose

eg: Lactose, Maltose

$C_{12}H_{22}O_{11}$ → diff^t structures.

③ Polysaccharides are carbohydrates which on complete hydrolysis gives many monosaccharides are called polysaccharides.

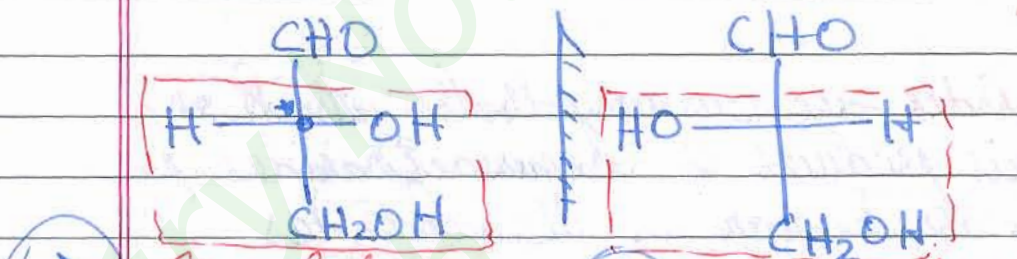
eg :- STARCH, CELLULOSE

MONOSACCHARIDES

(1)* D-L Configuration

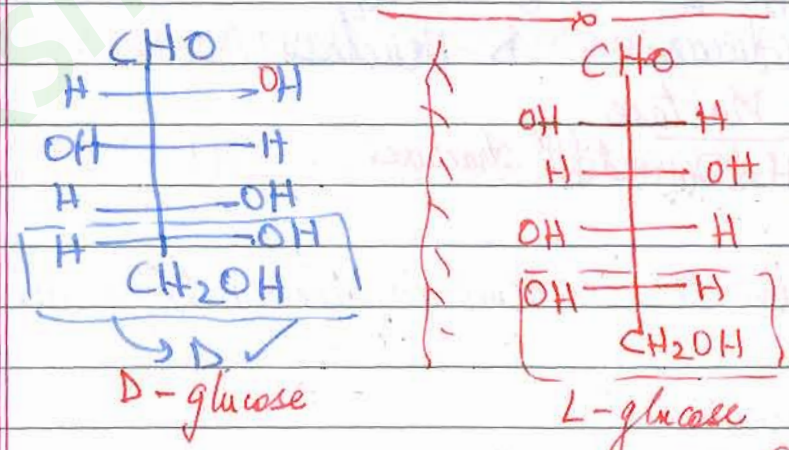
a notation used for representing RELATIVE confi. (not absolute confi) of carbohydrates.

They have no relⁿ with either magnitude or sign of optical rotation.

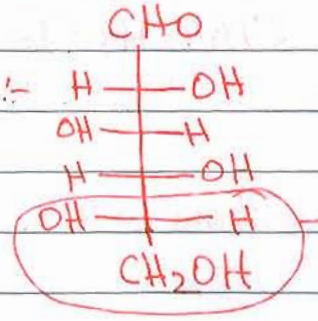


• To remember
D: दाहिना : d
L: left : l

chosen arbitarily. But, the [---] grp. decides whether its D or L confi.



* But :- L form of glucose :-

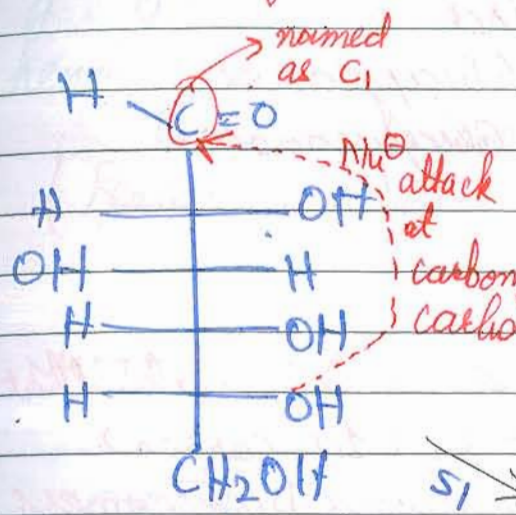


* D-L h
no interm
with eryt

:- Common name → PYRANE

classmate Date 1·12·10 Page

* All natural sugars are D -sugar

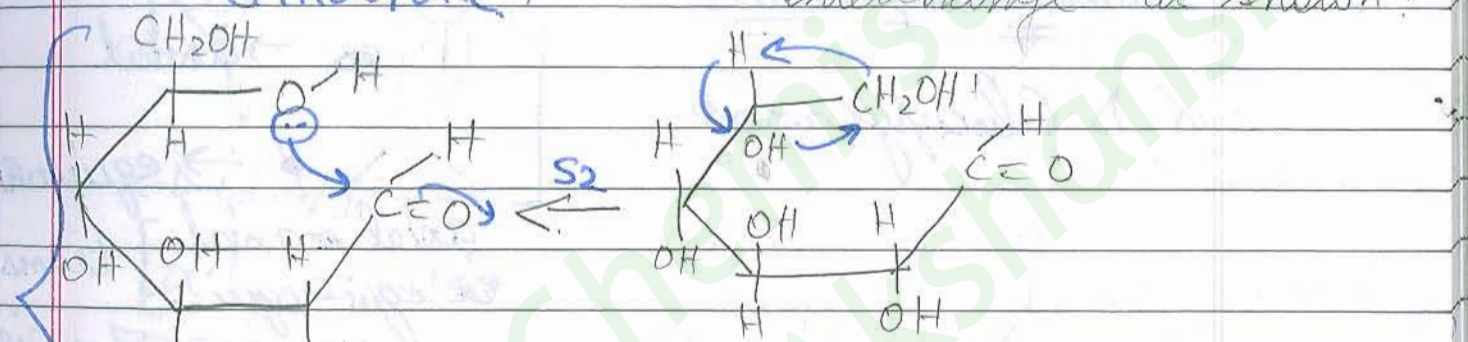


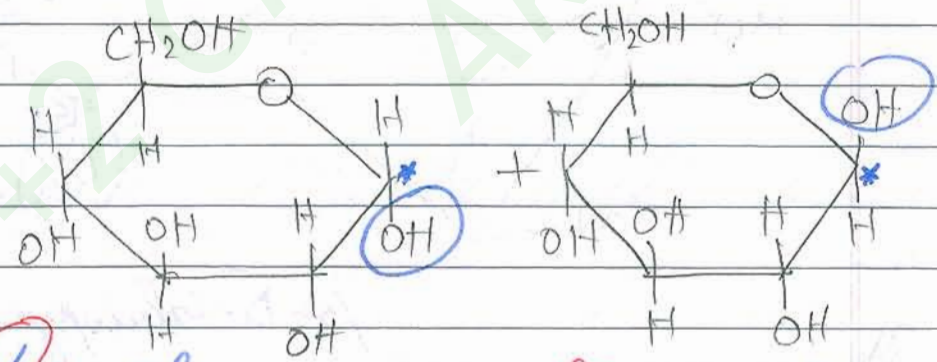
* D-glucose in solid state exists in cyclic hemi-acetal form.

S1 :- Turn ↖ structure ↗ to make horizontal & make a ring

S2 :- Then, make a 3 group interchange as shown.

D-glucose (OPEN-CHAIN STRUCTURE)





α-D-Glucopyranose

OH downwards

β-D-Glucopyranose

OH - upwards.

* cyclic hemiacetals of D-glucose called as (collectively) → PYRANOSE

From pyrane — From aldose

* α-D-Glucopyranose & β-D-Glucopyranose are DISTEREOMERS. In carbohydrate chemistry, they are called ANOMERS (PTO)

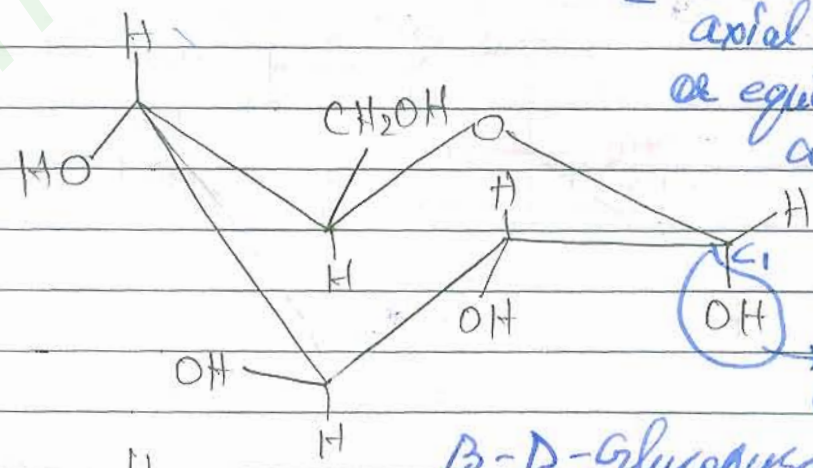
* In Solid State,
D-Glucose exists as either
only 100% α-D-Glucopyranose
or only 100% β-D-Glucopyranose.

* ~~ANOMERS~~
* ANNOMERS
The ~~cyclic~~ cyclic structures of carbohydrate that differ in confi ONLY at C_1 (1st carbon).
Hence, Annomers are always Diastereomers.

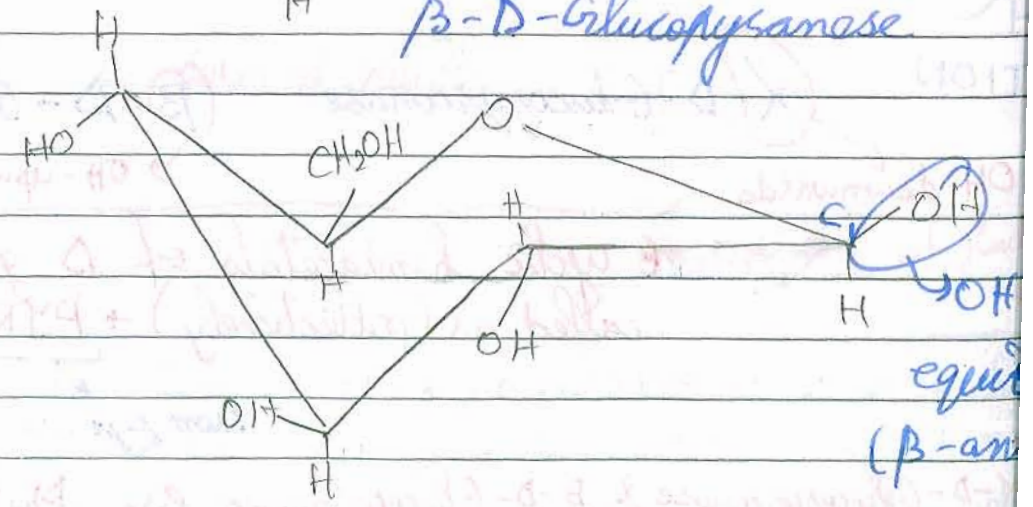
Chair conformer

st. line
[① → axial
/ \ ② → equ
axial-axial]
or equi-equi.
ae or ea]

α-D-Glucopyranose

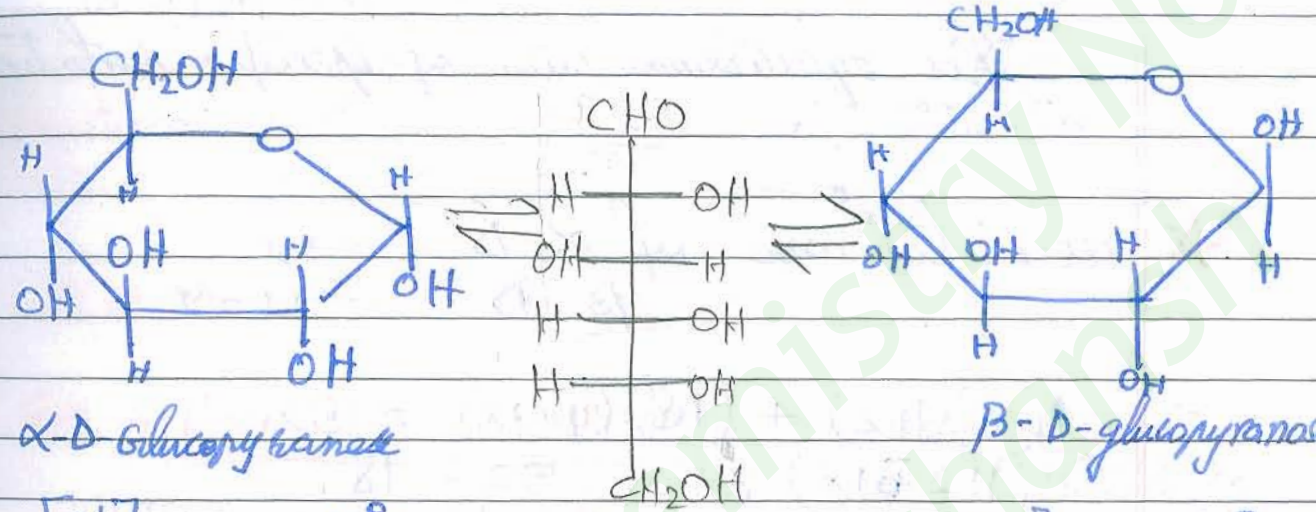


β-D-Glucopyranose



- larger grps are more stable at equitorial pos^{n} - hence, β-anomer of glucose is more stable than α-anomer.
(Reason:- less steric repulsion)

* MUTAROTATION



$[\alpha]_{25^{\circ}C} \approx +112^{\circ}$

specific rotn at 25°C

$[\alpha]_{25^{\circ}C} = +18^{\circ}$

α-D-Glucopyranose, in its aq. soln, establishes a reversible equilibrium with its open chain form. This open chain form, in turn, can form both α-D---- & β-D---- Hence, this open chain form ~~can~~ ~~form~~ establishes a relation with β-D-form.

Same would happen when β-D---- is dissolved in H_2O. Hence, an equi. is established b/w α-D-form & β-D-Glucopyranose form.

K = Rate constt = $\frac{[\beta]}{[\alpha]} = 2$

8. Mutarotation

When a pure ~~anomer~~ annomer of D-Glucose (α or β) is dissolved to make its aq. sol^n, specific rot^n of sol^n, initially changes (decreases with α & increases with β) & finally reaches to a constt value when equi. is established b/w the 2 annomers via open chain structure. This phenomena of change in specific rot^n to a constt value is known as MUTAROTATION.

This equilibrium value of specific rotation at 25°C is 52°.

* Let initial conc. of α-D ⟶ x
β-D ⟶ (1-x)

$\Rightarrow (x)(112) + (18)(1-x) = 52$

$\Rightarrow (112-18)x = 52 - 18$

$\Rightarrow x = \frac{34}{94} = \frac{17}{47} \approx \frac{1}{3}$

$\Rightarrow x \approx \frac{1}{3}$.

So, at equi. at 25°C :- $\alpha = 1/3$

$\beta = 2/3$ $(1 - 1/3)$

So, they are formed at 1:2 ratio.

Hence, β annomer is more stable.

Hence, Proved.

So, $K = \frac{[\beta]}{[\alpha]} = \frac{2/3}{1/3} = (2)$

* We have ignored open chain form at e
∵ it contributes ≈ < 0.02 % at equi

- Finding enthalpy when entropy given

$$\Delta G = -RT \ln \frac{[\beta]}{[\alpha]} = \Delta H - T\Delta S$$

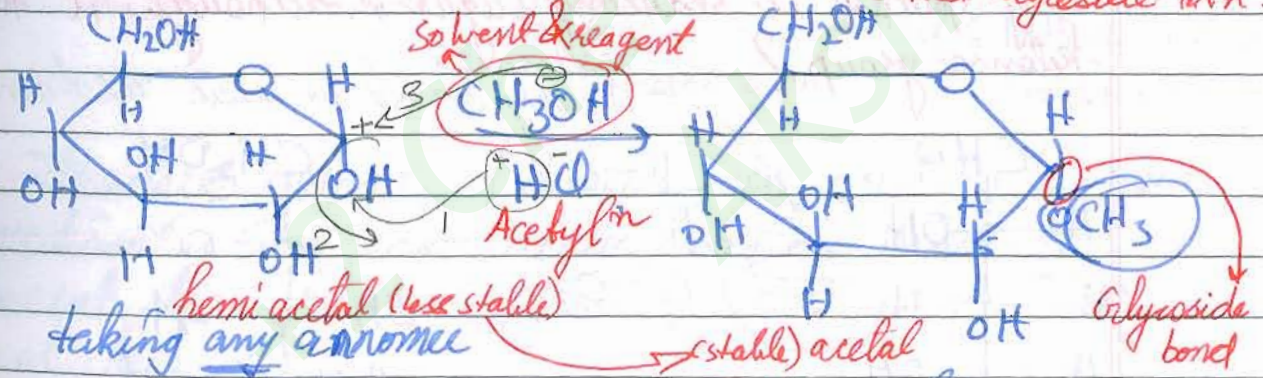
✓ ? ✓

* Crystallizⁿ temp :- α = 17°C, β = 33°C. ~~At~~ b/w 17 – 33°C, only α (β also gives α → le Chatelier)

* Pure form of any anomer can be formed by fractional crystallizⁿ (see above)

CHEMICAL REACTIONS of D-GLUCOSE

I GLYCOSIDE FORMATION: Below process of acetylⁿ is called Glycoside rxn.



methyl-α-D-glucopyranoside
+
methyl-β-D-glucopyranoside
(∵ rxn involves carbocation intermediate. So, attack from any side)

* Glycosides do NOT show mutarotⁿ
∵ they are acetals, highly stable, do not open in solⁿ

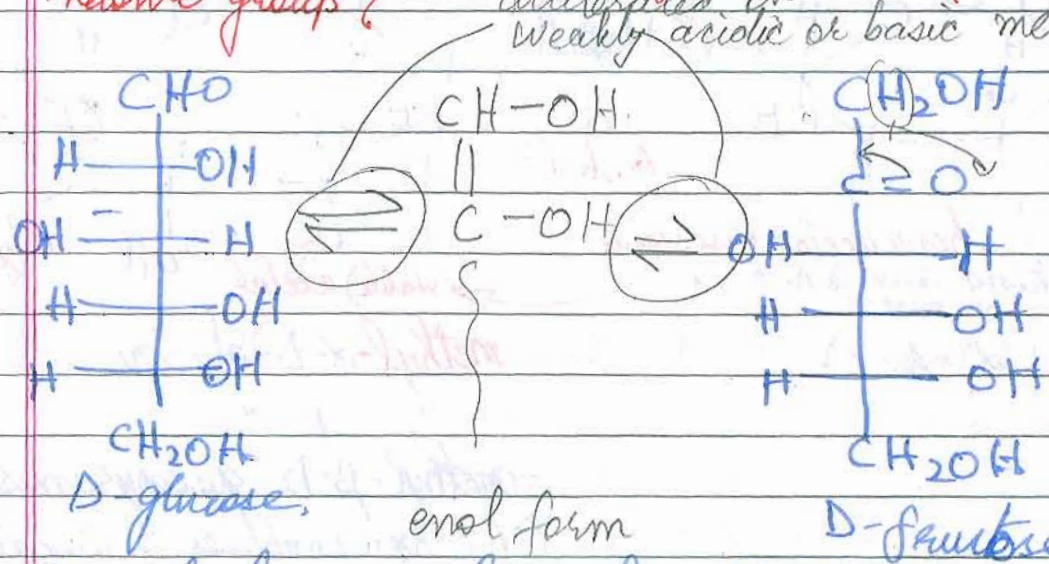
★ REDUCING AND NON-REDUCING SUGARS

Valid ∀ saccharides

- **Reducing Sugars :-**
  Carbohydrates which reduce Tollens Reagent, Fehling Sol^{n} & Benedicts sol^{n} are known as Reducing Sugars.
  eg D-glucose, D-fructose, D-manose are all reducing sugars.

- **Non-reducing Sugars :-**
  Carbohydrates which ~~so~~ don't reduce, either of TR, FS ~~&~~ Benedicts sol^{n} are Non-Reducing Sugars.
  eg :- Sucrose. (no eg in monosaccharides)

- Why Glucose is reducing sugar, although it has ketonic group?

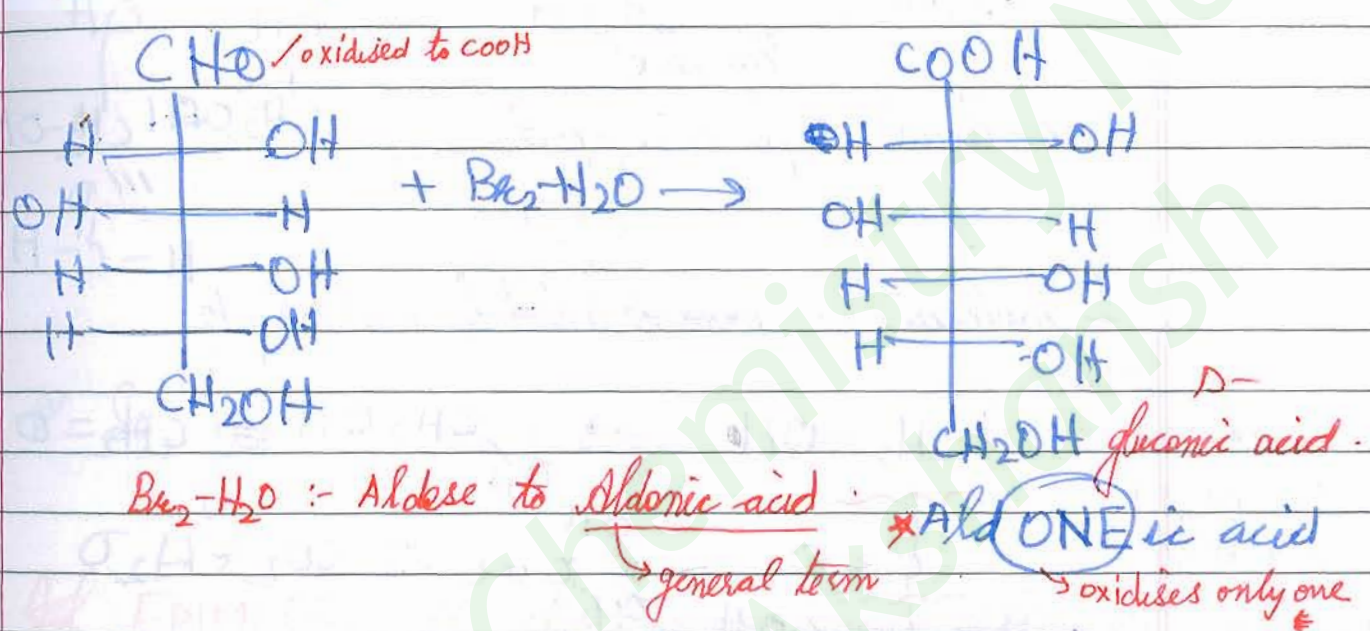


Due to basic nature of TR, FS, Benedicts, glucose ~~to~~ establishes rapid eqlm. with enol form. This enol form converts rapidly to D-glucose, & D-glucose gives the desired

* Glucose differs from aliphatic or aromatic aldehydes in terms of SCHIFF'S TEST & BISULPHITE TEST. Glucose doesn't give either of above 2 tests.

* OXIDATION

◇ With Br_2-H_2O : OXIDISE ALDEHYDE ONLY

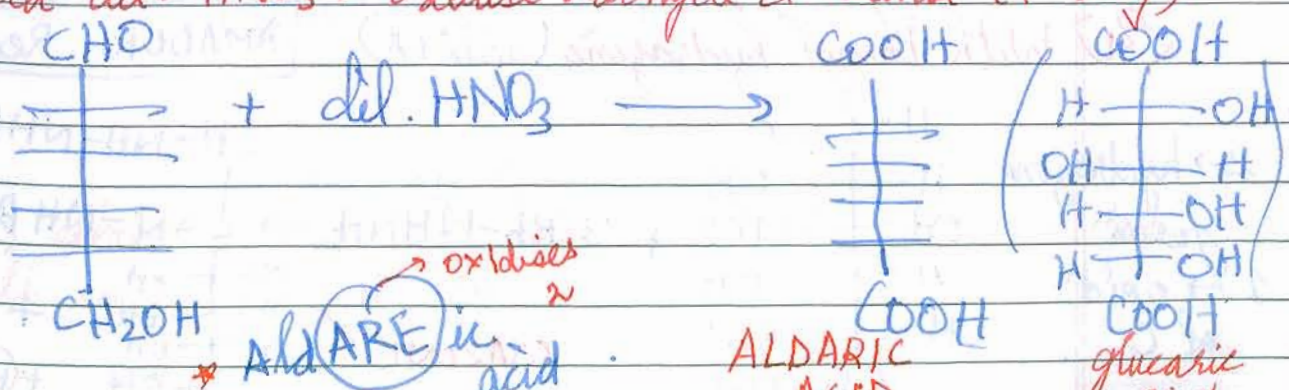


Br_2-H_2O :- Aldose to Aldonic acid.
(Aldonic acid: general term)

* Ald(ONE) ic acid (ONE: oxidises only one)

* Fructose doesn't decolorise Br_2-H_2O (∵ now, medium is not that acidic/basic. Hence, it doesn't turn to end form & so, glucose is not formed.) So,
→ Test to differentiate b/w glucose & fructose

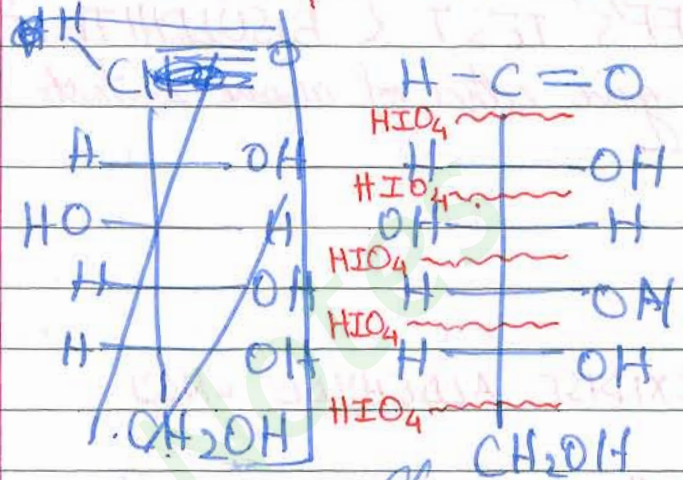
(2) With dil. HNO_3 :- Oxidise Aldehyde & alcohol (1° only)



* Ald(ARE) ic acid (ARE: oxidises 2)

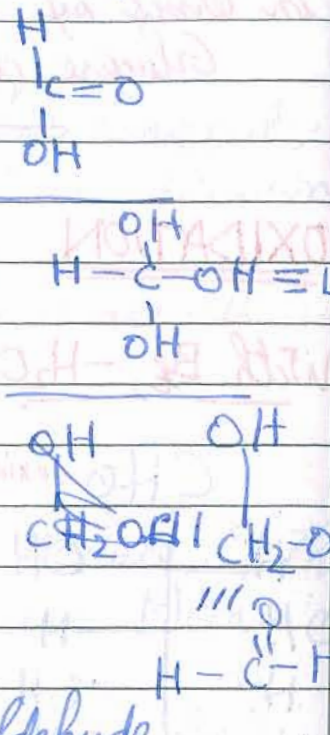
classmate
Date
Page

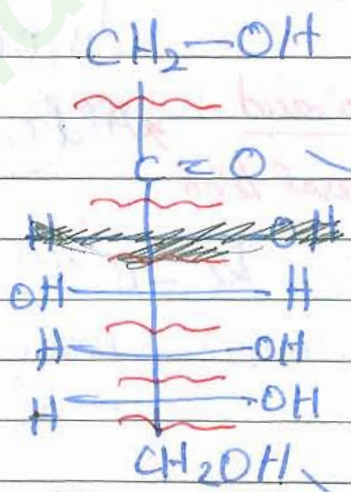
(3) With HIO_4 :- Periodic acidic cleavage.

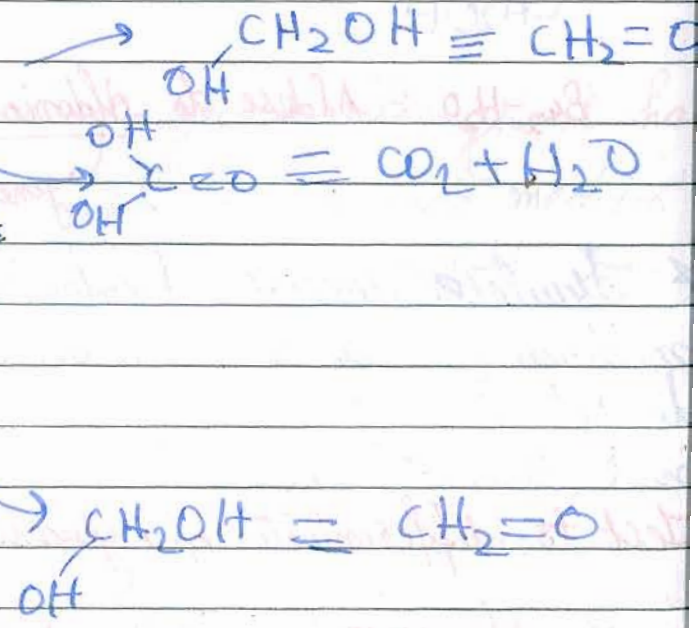


5 molecules :- formic acid

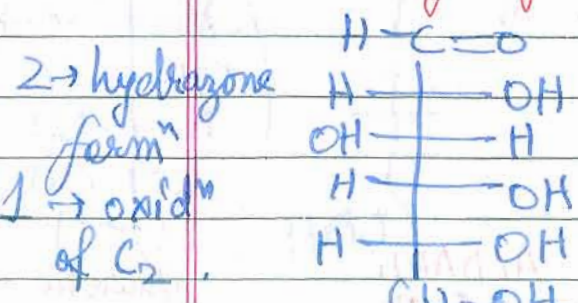
1 molecule :- ~~formic acid~~ formaldehyde

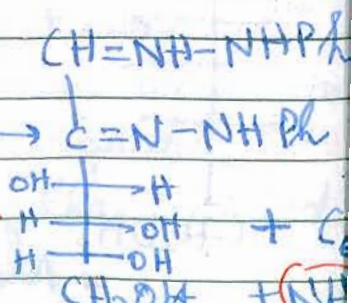


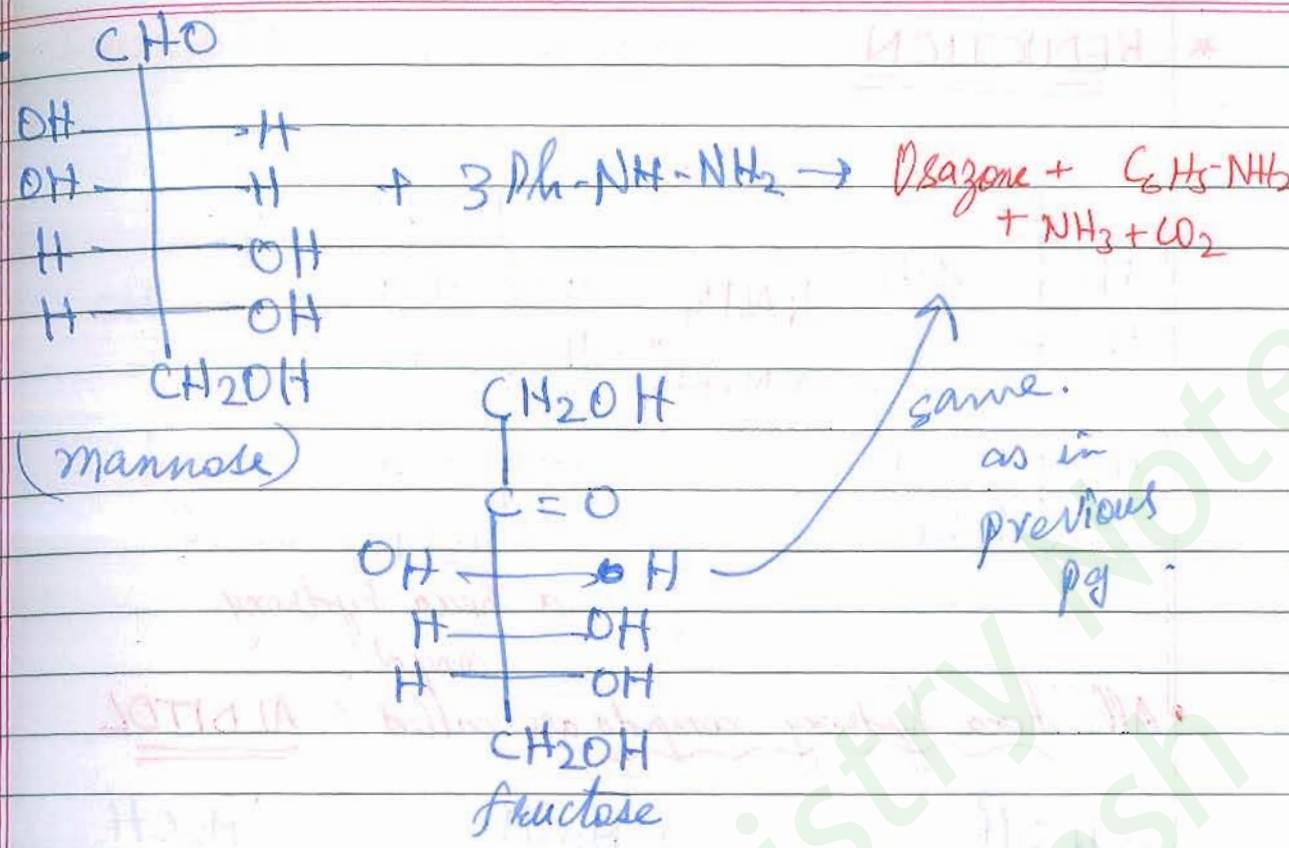




(4) With Phenyl hydrazine (mild OA) AMADORI Rear



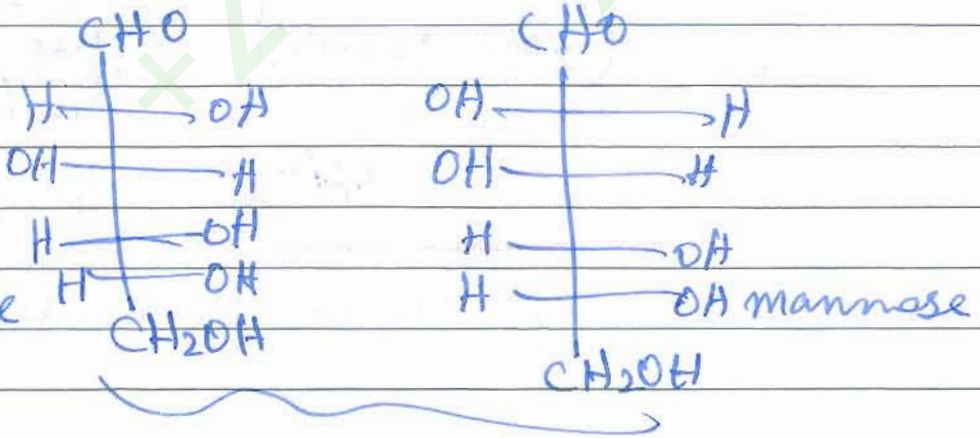




* So, glucose, mannose, fructose $\xrightarrow{3PhNHNH_2}$ osazone + $C_6H_5NH_2$ + NH_3 + CO_2.

* EPIMERS :- The stereoisomers which differ in confi. ONLY at one chiral carbon in open chain structure form.

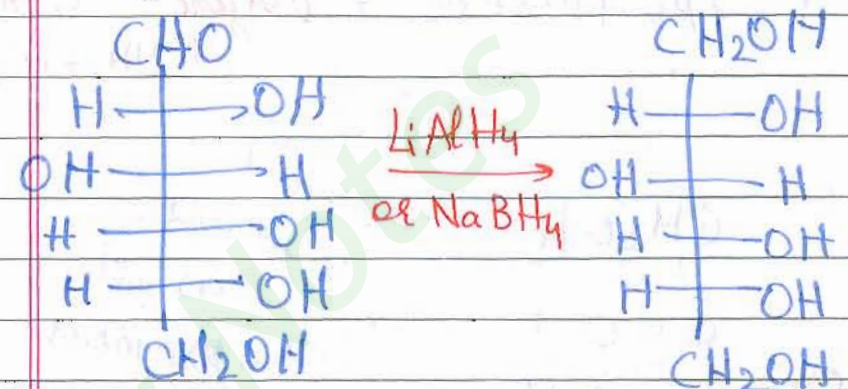
eg :-



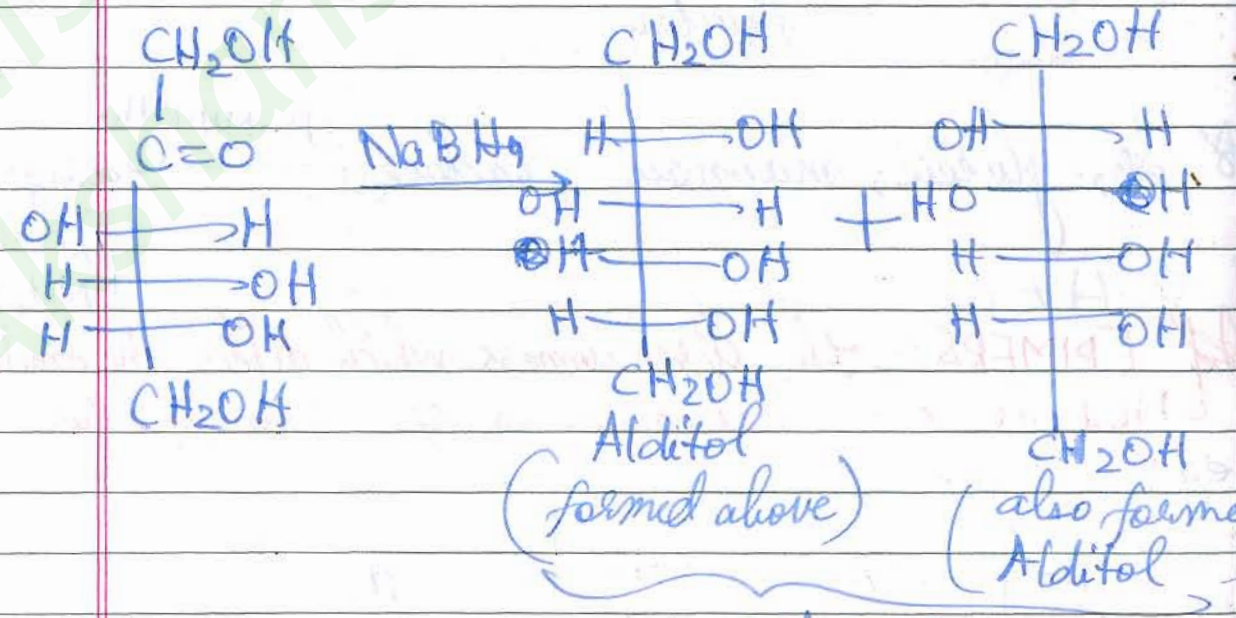
C_2 epimers.

• C_2 epimers always give same OSAZONE when treated with excess Ph-NH-NH_2

* REDUCTION

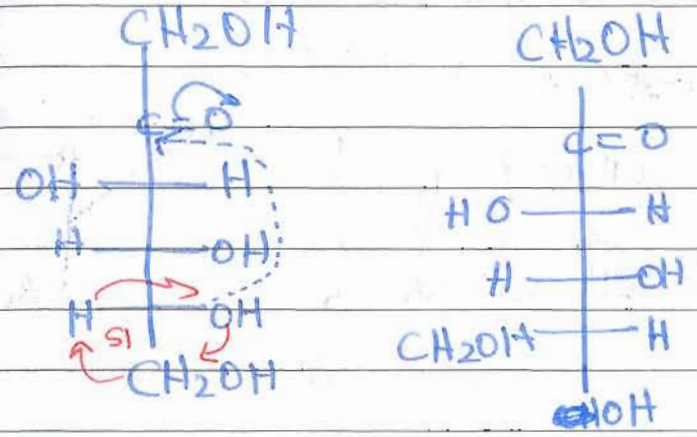


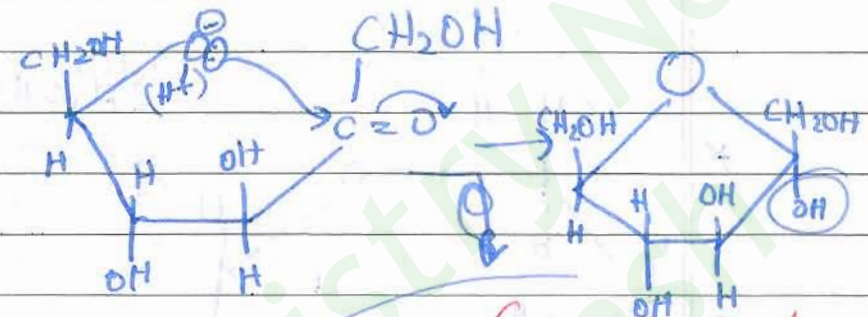
• All hexa hydroxy compds are called :- ALDITOL

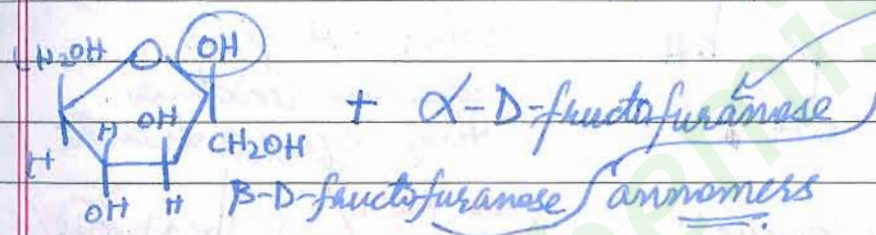


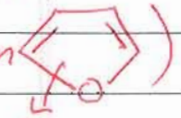
classmate
Date 3/12/10
Page

★ FRUCTOSE :- cyclic structure :- hemiacetals





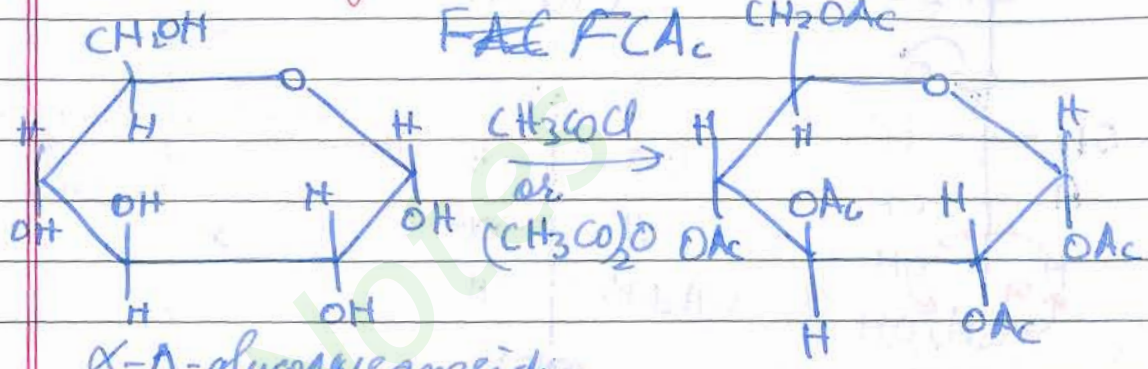


furanose structure (comes from  furan.)

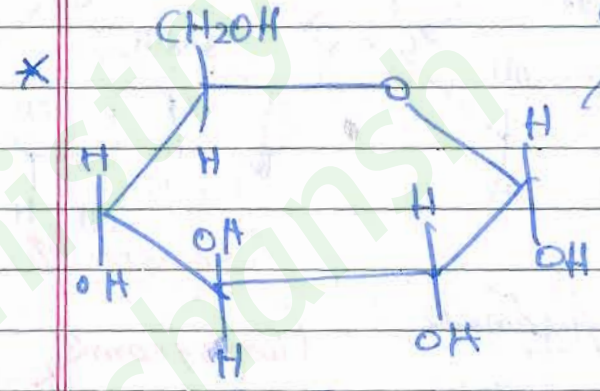
* hemiacetal of fructose is furanose (not pyranose)
* C_2 carbon is involved in hemiacetal formⁿ (from bottom) → ALWAYS.
- α :- CH_2OH both on same side.
  β :- CH_2OH both on opp. side.
- The above hemiacetal also shows Mutarotⁿ.
- All properties of Glucose are also valid here, except, it doesn't give Br_2+H_2O test. (do written previously).

classmate
Date
Page

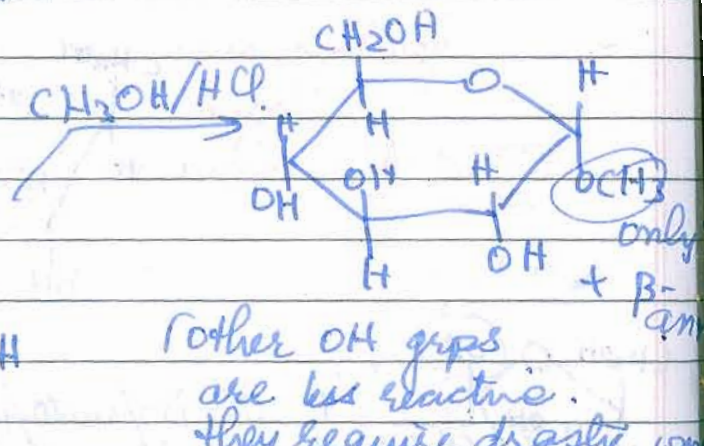
- Rxns with an acid chloride or acid anhydride
  → valid for glucose & fructose BOTH.



α-D-glucopyranoside



α-D-glucopyranose



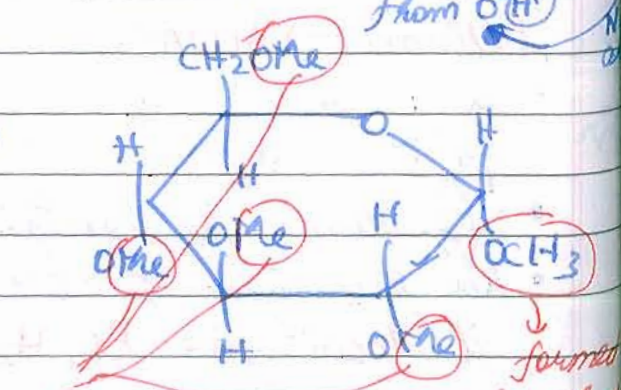
only + β-an

Rather OH grps are less reactive. they require drastic con

or NaOH/ $(CH_3)_2SO_4$

NaOH takes H^+ from O

$NaOH/CH_3I$



formed from S_N2 → no change in confi.

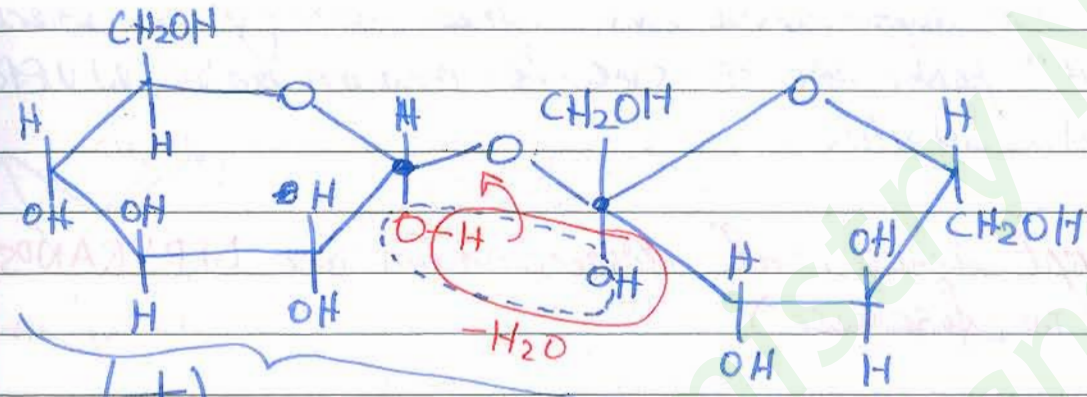
formed from S_N

☆ DISACCHARIDES

Sucrose $C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$

(+) — D-glucose (+) — D-fructose (−)

→ α-D-glucopyranosyl-β-D-fructofuranoside



(+) Sucrose

↳ dextrorotatory

(β-D-fructofuranose ↳ flipped)

- Sucrose is a non reducing sugar
  ↳ ∵ it has become acetal (from hemi acetal)
  Hence, it doesn't establish equi. with open chain structure when dissolved in H_2O. Hence, it doesn't show MUTAROTATION

☆ Br_2-H_2O ✗
☆ dil. HNO_3 ✗
☆ Osazone formⁿ ✗
☆ Mutarotⁿ ✗

} for alone compd.

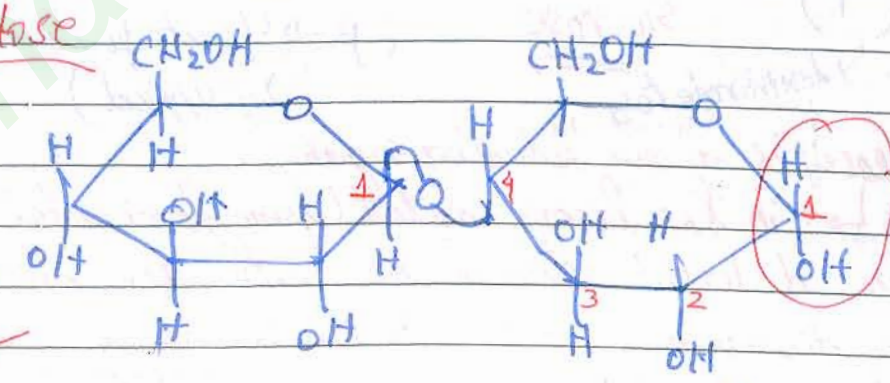
✱ Inversion of Sugar: valid only for Sucrose

Sucrose is a dextro-rotatory compd. When pure sucrose is dissolved in H_2O & hydrolysed in presence of an acidic catalyst, specific rotⁿ of the solⁿ becomes FINALLY -ve.

It is ∴ of the greater magnitude of specific rotⁿ of levo-D-fructose formed in the hydrolysis rxn. This turning of specific rotⁿ from +ve to -ve is known as INVERSION OF SUGAR.

- except sucrose, all disaccharides are DIPYRANOSIDE (no furanose)

✱ Maltose



Reducing sugar
Mutarotⁿ ✓
Osazone formⁿ ✓
forms anomeric glycoside ✓

β-D-glucopyranose α-D-glucopyranose.

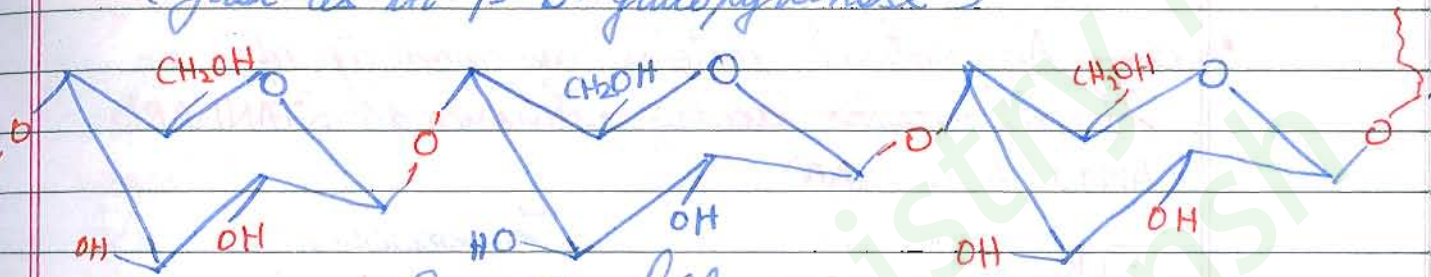
Maltose

- In Sucrose, $C_1 - C_1$ interact to remove H_2O
- In other disaccharides, $C_1 - C_4$ interact. So, one C_1 of pyranose is left free to make it a reducing sugar.

✡ POLYSACCHARIDES :-

Cellulose & Starch

- Cellulose is a polymer of ~~gluco~~ β-D-glucopyranose.
- It is poly-β-D-glucopyranoside linked together with ~~1,2~~ 1→4 linkage.
  - ✓ All OH, CH_2OH are at equitorial posⁿ (just as in β-D-glucopyranose)



$C_1 - C_4$ linkage

- rxn with conc. HNO_3.
  replacement of OH with NO_3 grp.
  - ✓ mild condⁿ → cellulose mononitrate
  - ✓ medium condⁿ → cellulose dinitrate
  - ✓ extreme condⁿ → Cellulose trinitrate
    → called as GUNCOTTON
    ↳ an explosive.
- In mononitrⁿ :- Preference to 2° over 1°.
  1° difficult to nitrate.

Ch: Amino Acids Et Proteins

- Protein :- They are BIOPOLYMERS of amino acids joined together by amide bonds, commonly known as peptide linkage.

- ~~Amo~~ All natural proteins are made up of 20 α-amino acids - known as STANDARD AMINO ACIDS (AA)

FIRST 5)

ESSENTIAL ⇓ α-amino acid i.e NH_2 & COOH grps kept fixed

To remember:- G, AVLI (Don)

1) H_2N-CH_2-COOH Glycine (M=75)

2) $H_2N-\underset{CH_3}{\underset{|}{CH}}-COOH$ Alanine

3) $H_2N-\underset{(iPr)}{\underset{|}{CH}}-COOH$ Valine

4) $H_2N-\underset{(iBu)}{\underset{|}{CH}}-COOH$ Leucine.

5) $H_2N-\underset{(1\text{-methyl propane})}{\underset{|}{CH}}-COOH$ Isoleucine.

- except glycine, rest all 4 above are CHI

- All std. AA are L-amino acids (except glycine : it itself isn't chiral)

✱ Essential & non-essential Amino acids :-

Essential AA (10) : Those AA, which aren't produced in the body & supplied through diet.

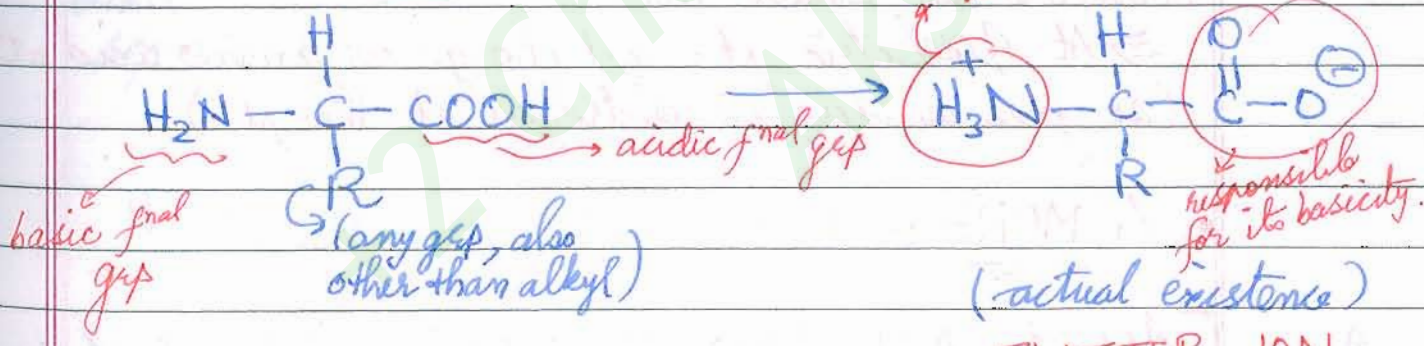
Non Essential (10) : AAs synthesised in the body, needn't be supplied externally are called non essential.

✱ Complete & Incomplete proteins :-

Complete :- Food which is contains all 10 essential AAs & exactly in the proper^{n} as req^{d} by body are called complete proteins. eg :- all non veg, milk

Incomplete :- Food with deficiency of 1 or more essential AAs or with inexact proportion of essential AAs are called Incomplete proteins

✱✱ Properties of Amino Acids

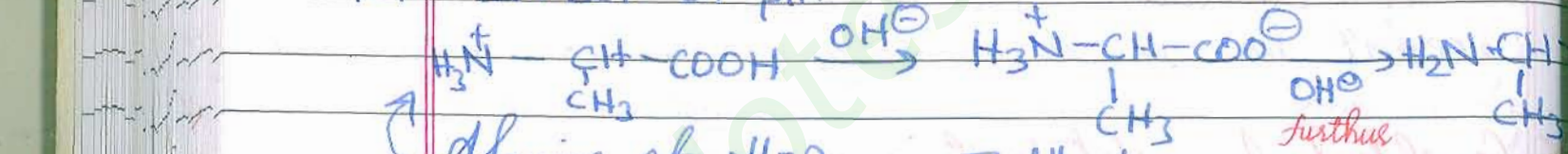


P1 :- AAs have very high MPts compared to general organic compds. Its due to its existence as Zwitter ion which gives a very strong inter ionic attr^{n}.

P2 :- Unlike organic compds, AAs are highly soluble in H_2O & very less soluble in common organic solvents (like ether). (due to its salt like property → Zwitter ion)

P3:- Acidic grp. of AA is NH_3^+ (not COOH) & basic grp is $COO^\ominus$ (not NH_2) ∴ AAs are (usually) weaker acid than RCOOH & weaker base than an RNH_2 (amine)

P4:- EFFECT OF pH:-



Alanine at pH=2, say

⇓ Strongly acidic medium

★ At low pH, amino acids behave as CATIONIC

Zwitter ion At pH = ISOELECTRIC pH of Amino Acid

⇒ pH = 7 (most of amino acids)

Alanine at pH, say

⇓ Strong basic

★ At high pH, amino acids beh as ANIONIC

Isoelectric pH :- pH of sol^n at which AA exist completely as Zwitter ion.

⇒ At Isoelectric pt; net charge on amino acid = 0 (So, goes nowhere in electrolysis at this pt.)

• 4 MORE:-

A G L A ⇓ AGLA

- Aspartic Acid ($H_2N-CH(CH_2COOH)-COOH$)
- Glutamic Acid ($H_2N-CH(CH_2CH_2COOH)-COOH$)

} Isoelectric pH ≈ 3.

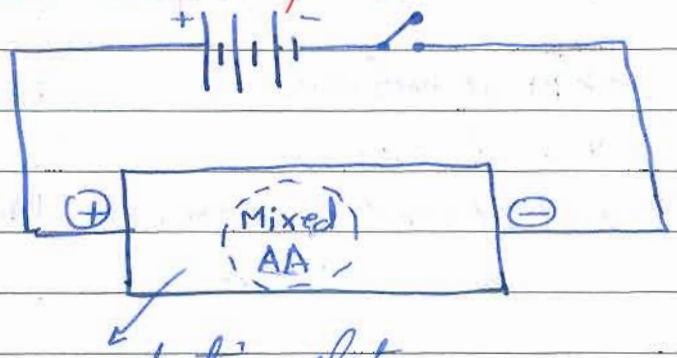
- Lysine ($H_2N-CH(CH_2CH_2CH_2CH_2NH_2)-COOH$)
- Agrinine ($H_2N-CH(CH_2CH_2CH_2-NH-C(=NH)NH_2)-COOH$)

} Isoele pH ≈

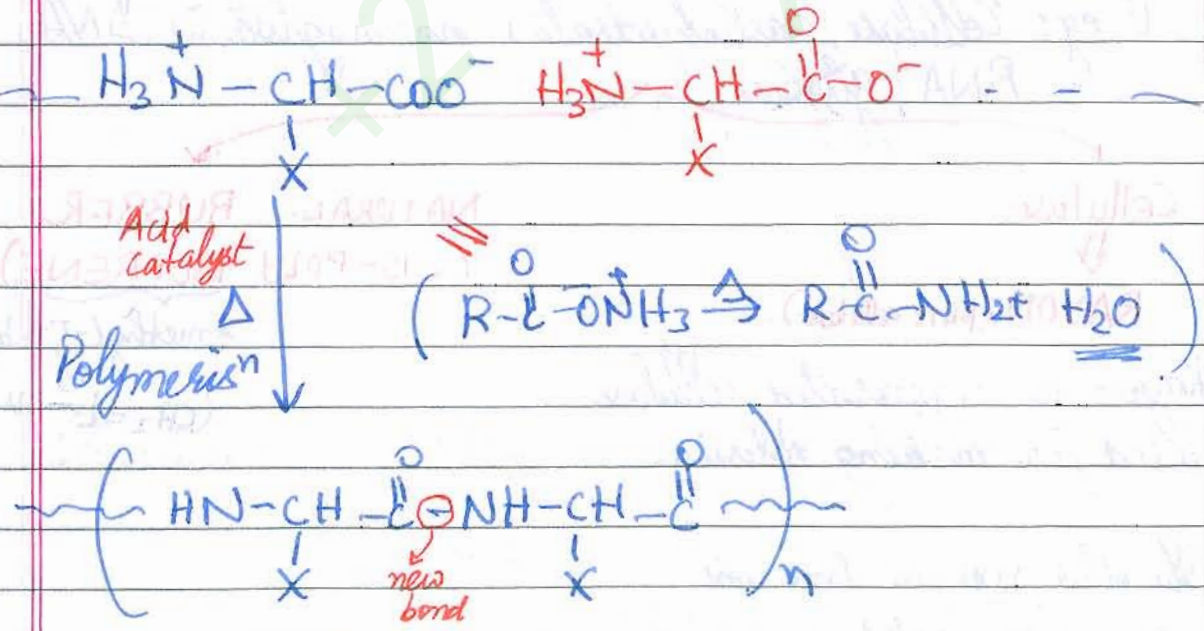
classmate
Date 8·12·10
Page

ELECTROPHORESIS

↳ it is a method of separ^{n} & isol^{n} of a specific amino acid from the mixture of amino acids.



A mixture of AA is put at centre of ELECTROPHORESIS PLATE and BUFFERED with a buffer whose pH equals isoelectric pH of the AA to be separated. On completing the circuit, AA with net +ve charge move towards -ve electrode, while, the one to be separated doesn't move towards either electrode due to no net charge. Hence, separated.



• During polymerisⁿ, amide linkage (C–N bond) is formed. Amide in chemistry of protein is called PEPTIDE BOND

* low molecular wt. polymer of α amino acids (≈ 40000 Molar mass) is known as PEPTIDES

Peptides further polymerise to give huge polymer molecule with molar mass in range of 40,000 – 4,00,00000

* Peptide classification
  - N at both ends : N STRUCTURE
  - C at both ends : C STRUCTURE
  - N at one & C at one end : NC STRUCTURE

(f) POLYMERS

* NATURAL POLYMERS

Polymers produced in nature.

eg: Cellulose, carbohydrates, haemoglobin, DNA, RNA, glucose

- Cellulose ⇓ RAYON (pure cellulose)

  Rayon is regenerated cellulose used for making fabrics.

- NATURAL RUBBER (CIS-POLY ISOPRENE)

  2-methyl-1,3-butadiene

  $CH_2=C(CH_3)-CH=CH_2$

- No other rxns are done in ch-carbohydrates.

* low molecular wt. polymer of α amino acids (≈ 40000 Molar mass) is known as PEPTIDES

Peptides further polymerise to give huge polymer molecule with molar mass in range of 40,000 – 4,00,00000

* Peptide classification
  - N at both ends : N STRUCTURE
  - C at both ends : C STRUCTURE
  - N at one & C at one end : NC STRUCTURE

(f) POLYMERS

* NATURAL POLYMERS

Polymers produced in nature.

eg: Cellulose, carbohydrates, haemoglobin, DNA, RNA, glucose

- Cellulose ⇓ RAYON (pure cellulose)

  Rayon is regenerated cellulose used for making fabrics.

- NATURAL RUBBER (CIS-POLY ISOPRENE)

  2-methyl-1,3-butadiene

  $CH_2=C(CH_3)-CH=CH_2$

- No other rxns are done in ch-carbohydrates.

• Isolation of Rayon

Imp ☆ JEE2011

$$\text{Wood-pulp } (R{-}OH) \text{ (crushed)} + CS_2 \xrightarrow{NaOH} R{-}O{-}\overset{\overset{S}{\|}}{C}{-}\bar{S}\,Na^{+} \downarrow$$

cellulose

Sodium xanthate

$$R{-}O{-}\overset{\overset{S}{\|}}{C}{-}\bar{S}\,Na^{+} + NaHSO_4\,(aq) \rightarrow \underset{\text{cellulose (recovered) (water insoluble)}}{R{-}OH\downarrow} + \underset{\text{(separated)}}{CS_2} + \underset{\text{(from } NaHSO_4\text{)}}{Na_2SO_4}$$

Sodium xanthate — Sodium bisulphate

↓

SPINNERET (a machine) ↳ gives

RAYON FIBRE

Use :- ∴ Rayon is an important raw material for cloth ∵ its a polyhydroxy compd (H-bond), so, resous.

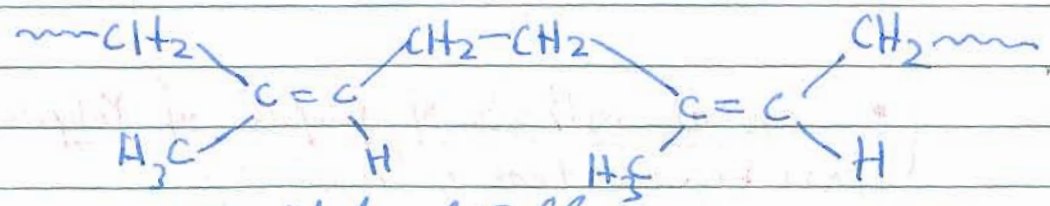
Natural Rubber :-

$$n\ CH_2{=}\underset{\underset{\text{isoprene}}{}}{\overset{CH_3}{\overset{|}{C}}}{-}CH{=}CH_2 \rightarrow \left[CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}CH_2\right]_n$$

Polyisoprene (without confi)

III

Structure :-



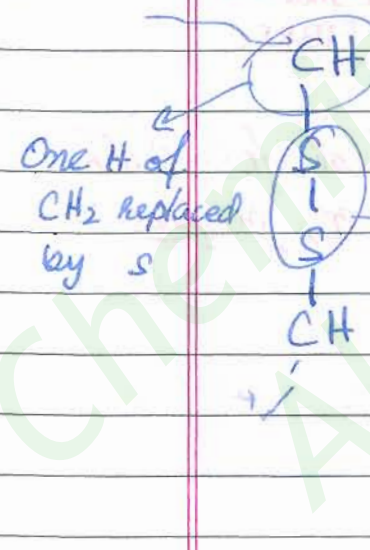
Natural Rubber.

- Properties of natural rubber :-
  - Very low MPt. (due to very weak vander wall force of attr^{n})
  - very low strength. → ∴ of no use

↓ To increase strength

VULCANIZATION of rubber.

Vulcaniz^{n} is a process in which natural rubber is heated with RHOMBIC SULPHUR, where chains are interlinked through -S-S- linkage giving a cross-linked rubber. Vulcaniz^{n} improves mechanical properties of rubber.



Extent of cross-linking determine strength of rubber.

Extent ↑ ∴ tensile strength ↑

★ SYNTHETIC POLYMERS (or Man-made)

PVC — Teflon — Nylon

- General methods of prepar^{n} of Polymer : POLYMERISATION
  - (i) Free-radical polymeris^{n}

In this rxn, polymer is formed through chain rxn involving no. of free radical RI.

→ (ii) Condens^{n} polymeris^{n} :-
In condens^{n} polymeris^{n}, monomers are heated to polymerise & some smaller molecules (eg HCl, H_2O, CH_3OH) are produced as bi-product in the rxn.

→ (iii) Ionic polymeris^{n} :- (or Living Polymeris^{n})
In this, the growing polymer chain are either cation or anion.

★ PVC : Poly vinyl chloride

↳ Obtained by FREE-RADICAL polymeris^{n} of VINYL CHLORIDE ($CH_2=CH-Cl$)

$$n\ CH_2=\underset{Cl}{CH} \longrightarrow \left(CH_2-\underset{Cl}{CH}\right)_n$$

PVC

mechanism :-

- Polymeris^{n} requires an initiator.
  Initiators can be — LIGHT (γ-ray polymeris^{n})
  — FREE RADICAL INITIATOR
    - most common polymeris^{n} → BPO (Benzoyl peroxide) $\left(C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5\right)$
      - symbolised as (ROOR)
        ↳ don't confuse with alkyl grp.
    - other (rare) $CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3$
      (Azobis Iso Butyro nitrile — AIBN)

• For a monomer :-
If α-C containing final grp is said to have HEAD posⁿ. & β-C is said to be in TAIL posⁿ.

S1. Initiation

$$ROOR \longrightarrow 2RO^{\bullet}$$

S2. Propagation

$$RO^{\bullet} + CH(Cl)=CH_2 \longrightarrow RO-CH(Cl)-\dot{C}H_2$$

(α = CH, β = CH_2)

e⁻ withdrawing grp, destabilises free radical. So, $RO^{\bullet}$ attacks at α posⁿ so, that radical goes to CH_2

$$RO-CH(Cl)-\dot{C}H_2 + CH(Cl)=CH_2 \rightarrow RO-CH(Cl)-CH_2-CH(Cl)-\dot{C}H_2$$

S3:- Termination

✓ large chains combining with each other
✓ other combinⁿs also possible

↓ after this step
PVC is obtained

★ Most Imp. property of PVC
✓ very low thermal conductivity of PVC. It catches fire very slowly ⇒ fire resistant.
✓ poor conductor of electricity.
✓ PVC has slightly greater M.Pt, than polyethylene & has superior mechanical property due to dipole-dipole attrⁿ (or add'n to van der wall)
$(\delta^{+}C-\delta^{-}Cl)$

classmate
Date
Page

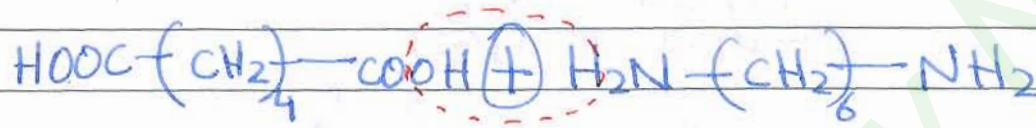
NYLON { NY → New York , LON → London }

↳ a polyamide

- NYLON 6,6 ★★★
- NYLON 6 ★★
- NYLON 6,10 ★

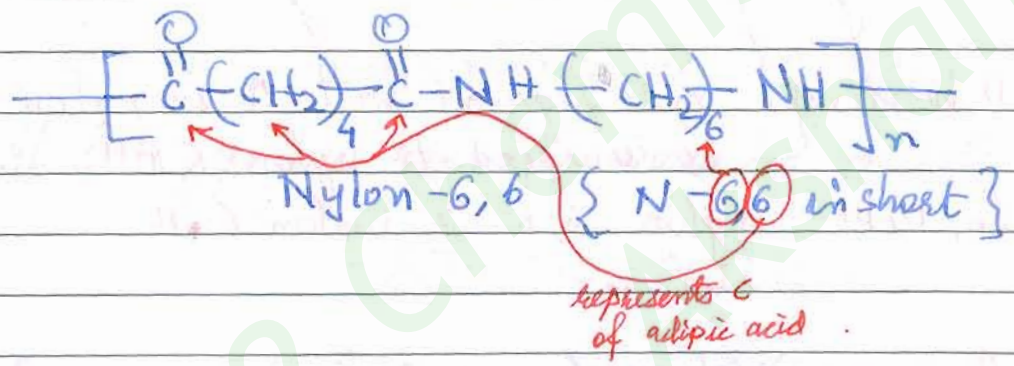
Nylon 6,6

Obtained by condensⁿ polymerisⁿ of



hexane di oic acid (ADIPIC ACID) — 1,6-hexanediamine

↓ $-H_2O$



★ Nylon is obtained by condensⁿ polymerisⁿ of

diamine + diacid (or diacid chloride or diacate - - - -)

* Proteins ≡ Polyamides ≡ Natural nylons.
* Nylon + cotton = Terylene.

* Nylon-6,10

$HOOC\text{-}(CH_2)_8\text{-}COOH + H_2N\text{-}(CH_2)_6\text{-}NH_2$

Sebacic acid

$\downarrow \Delta, -H_2O$

$-\left[C(=O)\text{-}(CH_2)_8\text{-}C(=O)\text{-}NH\text{-}(CH_2)_6\text{-}NH\right]_n$

Nylon-6,10

* Properties :-

(intermolecular)

- Nylon :- very high mechanical strength : H-bonding.
- H-bonding : more frequent pattern in nylon-6,6 as compared to nylon-6,10.

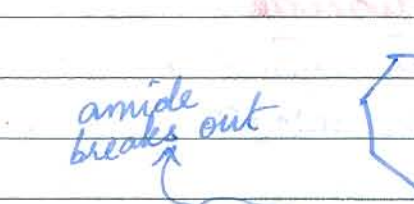
So, M.Pt nylon-6,6 > nylon-6,10

* Nylon-6 → polymer of 6-amino hexanoic acid

Present in

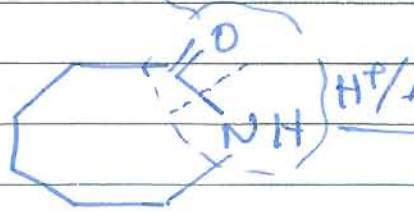
max. vol. found

obtained by ring opening polymerisⁿ of CAPROLACTUM (its monomer)



(present in oil seeds, other natural sources)

amide breaks out



$\xrightarrow{H^+/\Delta} -\left[HN\text{-}(CH_2)_5\text{-}C(=O)\right]_n$

Nylon-6

★ Stereo chemistry of Polymer

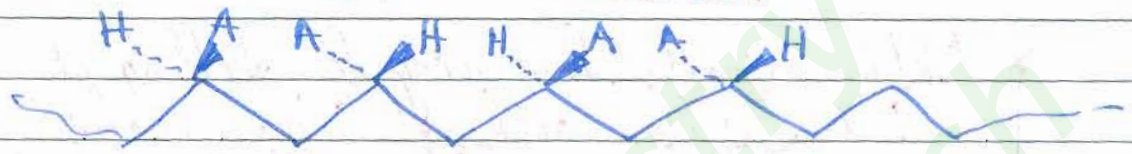
$CH_2=CH$ (A) —free radical initiator→ $+(CH_2-CH)_n+$ (A)

any grp ← (~~poly vinyl~~)

(all (A) on same side of polymer chain's plane, say)

↓

ISOTACTIC POLYMER



(A → one in front, other at back - - - -)

↓

SYNDIOTACTIC POLYMER

- If final grps are randomly distributed on both sides of plane

↓

ATACTIC POLYMER.

- Polymers which have a fixed pattern of final grp

↓ collectively called

STEREO-REGULAR POLYMERS eg. natural rubber, PVC, ;-;-;-;-

(i.e regular pattern in stereo chemistry)

- Free radical rxn always gives ATACTIC POLYMERS.
- Stereo regular polymers are used with a specific catalyst

↓

ZIGLAR-NATTA Catalyst (ZN Catalyst)

$TiCl_4/(C_2H_5)_3Al$ → for synthesis of stereo regular polymer.

→ firstly was used to synthesise natural rubber.

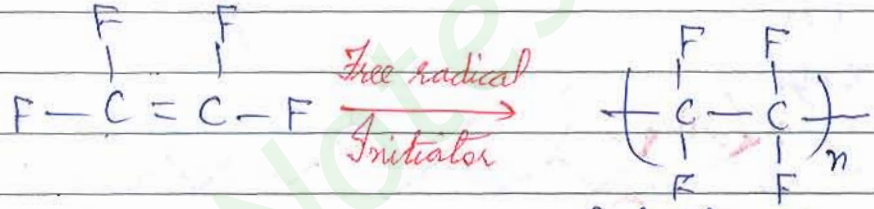
an eg. of heterogeneous catalysis in which polymerisⁿ occur at surface of catalyst

ethene ≡ ethylene
ethyne ≡ acetylene .

classmate
Date 10/12/10
Page

★ **Teflon:** ≡ Polytetrafluoroethylene

It is produced by free radical polymerisⁿ of tetrafluoroethylene.



Polytetrafluoroethylene
TEFLON

★ Olefins usually have very low melting pt.
But, Teflon although being an olefine
→ has very high M.P (> 450°C)
→ very high thermal stability (C–F bond → very stable)
→ possesses properties of plastic
→ Its stable → doesn't degrade thermally (no rxn with acid. →)
★ → used to make surgical equipments (doesn't melt in sterlization)
→ used in fire fighting (teflon is permeating not ~~permitting~~ heat)

Ch: Nuclear Chemistry

Nuclear Stability

Nucleus ~~acquires~~ acquires a stability by converting SUM ~~Some~~ of the masses of Nucleons into energy during its form^{n}. & the same amt. of energy is released when nucleus is completely formed. The energy released in the form^{n} of a nucleus is known as NUCLEAR BINDING ENERGY (B.E.)

Binding Energy is much greater in magnitude than bond energy.

$$\underbrace{n_s + p_s}_{\text{nucleons}} \longrightarrow \text{nucleus} + + + E$$

Mass-defect

Mass loss for nucleons when a nucleus is formed

Mass defect (Δm) = $\sum$ mass(nucleons) − mass(nucleus) = Δm (deration)

Einstein mass-energy rel^{n}

$$E = mc^2$$

$$\equiv \boxed{B.E. = \Delta m \cdot c^2}$$

Q. Determine nuclear BE of He giving the following masses.

m_p = 1.0076 amu

m_n = 1.00866 amu

m_{He} = 4.0026 amu

Ignore m_{e^-} in compared to p & n.

* $1\,amu = \frac{1}{N_A}\,g = 931.5$ MeV

* $1eV = 1.6 \times 10^{-19}$ J

MeV → Mega electron volt

classmate Date Page

$_2^4He = 2p + 2n$

$= \Delta$

$\Rightarrow \Delta m = 2(1.00726 + 1.00866) - 4.0026$

$\Delta m = 0.02924$ amu

$BE = \left[\frac{(0.02924)}{6.023 \times 10^{23}} \times (10^{-3})\right] kg \times \left[(3 \times 10^8)^2\right] = J$

4.0026

592

1.00726

+ 1.00866

2.01592

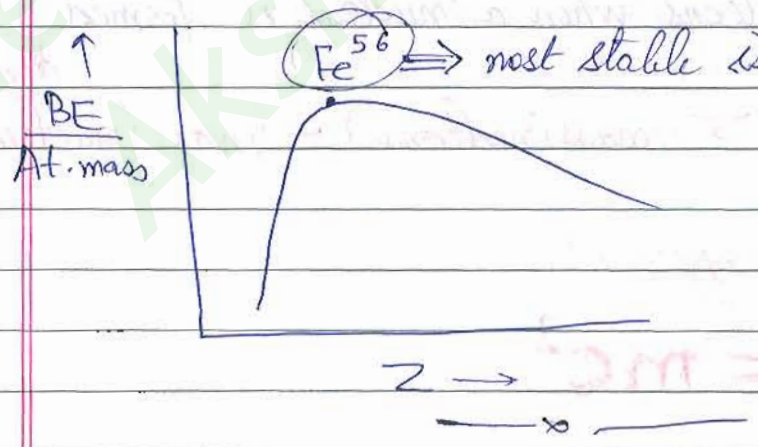
4.00260

2.00

* Avg $\left(\frac{\text{nuclear B.E}}{\text{At. mass}}\right)$ of all isotopes $\in [8, 9]$ MeV

said as Nuclear B.E per nucleon.

→ Nuclear B.E per nucleon is responsible for Nuclear stability



* Nuclear Stability : Qualitative Analysis

1) ODD-EVEN RULE :- If n & p are both even,

⇓

MOST STABLE (∵ both n & p will be having spin completely paired)

If n & p are both odd

⇓

LEAST STABLE

2) MAGIC-NUMBER :-

2, 8, 20, 28, 50, 82, 126 : no. of nucleons.

If n or p has any one of this no., its more stable than corresponding ones with no (or less) no. of magic nos.

eg : $^{4}_{2}He$:- 2 p, 2 n :- both magic nos.
so, highly stable

EXCEPTION :-

Stability :- $^{12}_{6}C$ > $^{14}_{6}C$

(no magic no.) (1 magic no → (8)n)

among heavier isotopes, $^{208}_{82}Pb$ → 82+126 has both magic no. so, it is most stable. (In later period, all radioactive elements will decay to this).

3) n/p ratio

Nuclear instability (Radioactivity) arises due to imbalance b/w neutrons & protons. For a stable nucleus, there must be a proper proportions of nucleons.

In case of unstable nucleus, stability is acquired by inter conversion b/w nucleons. During this interconversion, radioactive rays are emitted.

Neutrons shield (not prevent) repulsion (electrostatic) of protons. Hence, makes nucleus stable.

p (n) p → shields.

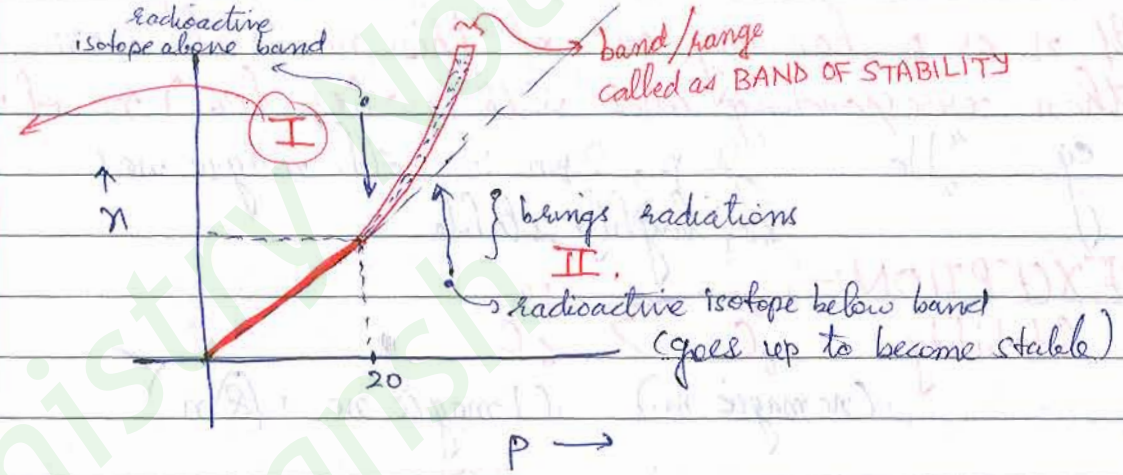
N

classmate
Date
Page

Ca
** Upto $Z = 20$, $\frac{n}{p}$ ratio req^d for stability = (1)

* $\left\{ \frac{n}{p} = 1 \right\}$ upto $Z = 20$

For $Z > 20$ $\left\{ \frac{n}{p} > 1 \right\}$ for stability



§ If $\frac{n}{p}$ not in band of stability

(Area) (I) : Neutron Rich Isotope : β-decay

$${}^{1}_{0}n \longrightarrow {}^{1}_{1}H + {}^{0}_{-1}e \left({}^{0}_{-1}\beta \right)$$

neutrons → protons

e^- emission or β emission

⇒ neutron rich species ⇒ β emission

eg: ${}^{14}_{6}C \longrightarrow {}^{0}_{-1}\beta + {}^{14}_{7}X$

${}^{22}_{10}Ne \longrightarrow n > p$:- β emission

$(^{0}_{+1}e)$ +ve e ≡ positron $(^{0}_{+1}\beta)$

Area (II) : Proton rich isotope

$$^{1}_{1}H \longrightarrow {}^{1}_{0}n + {}^{0}_{+1}e\ (^{0}_{+1}\beta)$$

positron emission

or

$$^{0}_{-1}e + {}^{1}_{1}H \longrightarrow {}^{1}_{0}n$$

e^- capture

✱ γ - emission

γ-ray emission occurs when a radioactive isotope decays to a stable isotope, but, with nucleons in the higher energy level. Such state is known as META-STABLE STATE, which, when returned back to stable state, energy is emitted in the form of γ-rays without any change in either at. no. or mass no.

- most common source of γ-ray :- Co^{60m}

$$Co^{60m} \longrightarrow Co^{60} + h\nu\ (\gamma\text{-ray})$$

Its formⁿ in hospitals :-

$$Fe^{59} + {}^{1}_{1}H \longrightarrow Co^{60m}$$

✱ α - decay

α-rays are emitted only by heavier radio-active isotopes with at. no. > 82.

• Radioactivity uses :- ✓MRI
✓ medical sciences
✓ power ~~xxxx~~ gener^{n}
✓ nuclear reactor

classmate
Date 15/12/10
Page

Q. $_{92}U^{238}$ decays $\longrightarrow$ $_{82}Pb^{206} + 8\,_{2}He^{4} + 6\,_{-1}e^{0}$

through a no. of intermediate steps emitting α & β rays. Determine no. of α & β particles produced per atom of $_{92}U^{238}$

X

Q. $_{5}B^{8} + {}_{-1}e^{0} \longrightarrow {}_{4}Be^{8}$

K-capture

K : capture from K shell.

other name of e^{-} capture

✡ NUCLEAR Trans Mutation (Artificial Radioactivity)

In nuclear transmut^{n}. a stable isotope is bombared by α rays, β-rays, neutron or proton in order to produce a radioactive isotope.
This requires a large amt. of energy, usually done in cyclotron

• most common :- $_{13}Al^{27} + {}_{2}He^{4} \longrightarrow {}_{15}P^{30} + {}_{0}n^{1}$
radioactive
↳ used in brain mapping.

• $_{12}Mg^{24} + {}_{1}H^{2} \longrightarrow {}_{11}Na^{22} + {}_{2}He^{4}$
↳ used in MRI.

✡ Nuclear fission

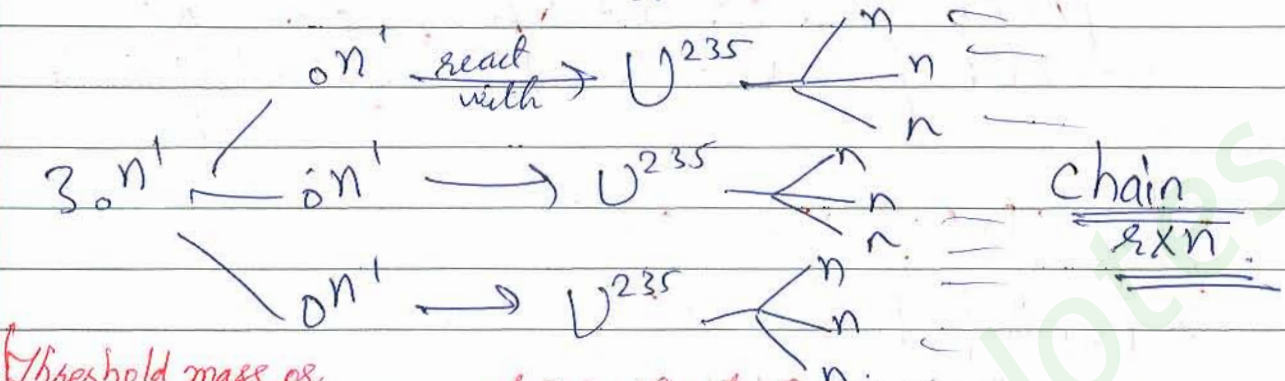
Heavier radioactive isotopes, when bombarded by slow moving neutrons (thermal neutrons) undergo dissociation into smaller stable isotopes producing large amt. of energy. The splitting phenomena

not fissionable

above is called nuclear fission.

eg:

* $U^{235} + {}_0n^1 \longrightarrow {}_{56}Ba^{139} + {}_{36}Kr^{94} + 3\,{}_0n^1$



* Threshold mass or
* Critical mass :- Min. mass of fissionable material req^d to induce a chain rxn i.e sufficient for explosion
- For controlled nuclear fission, neutron absorbers (moderator) are used.

Common neutron absorbers → heavy water
→ Cd rod

* ${}_{92}U^{235} + {}_2He^4 \longrightarrow {}_{94}Pu^{239}$: BREEDER reactor produces more fissile material from less.
more dangerous.

* ≈ 200 MeV energy is produced in Nuclear fission rxn

NUCLEAR FUSION

- natural fusion at Sun :- ${}_1H^2 + {}_1H^2 \longrightarrow {}_2He^4$.
- H-bomb is based on principle of nuclear fusion.

In nuclear fusion, lighter isotopes combine to produce a heavier isotope releasing a large amt of energy >> than energy released in fission.

A huge amt of E is req^d to initiate fusion.
∵ large electrostatic repulsion b/w like charge nuclei as they come closer.

• Radioactivity uses :- ✓ MRI
✓ medical sciences
✓ power ~~xxxx~~ gener"
✓ nuclear reactor

classmate
Date 15/12/10
Page

Q $_{92}U^{238}$ decays $\longrightarrow$ $_{82}Pb^{206} + 8\,_{2}He^{4} + 6\,_{-1}e^{0}$

through a no. of intermediate steps emitting α & β rays. Determine no. of α & β particles produced per atom of $_{92}U^{238}$

X

Q $_{5}B^{8} + {}_{-1}e^{0} \longrightarrow {}_{4}Be^{8}$

K-capture

K :- capture from K shell.

other name of e^- capture

✡ NUCLEAR Trans Mutation (Artificial Radioactivity)

In nuclear transmutn. a stable isotope is bombared by α rays, β-rays, neutron or proton in order to produce a radioactive isotope

This requires a large amt. of energy, usually done in cyclotron

• most common :- $_{13}Al^{27} + {}_{2}He^{4} \longrightarrow {}_{15}P^{30} + {}_{0}n^{1}$ (radioactive)

↳ used in brain mapping.

• $_{12}Mg^{24} + {}_{1}H^{2} \longrightarrow {}_{11}Na^{22} + {}_{2}He^{4}$

↳ used in MRI.

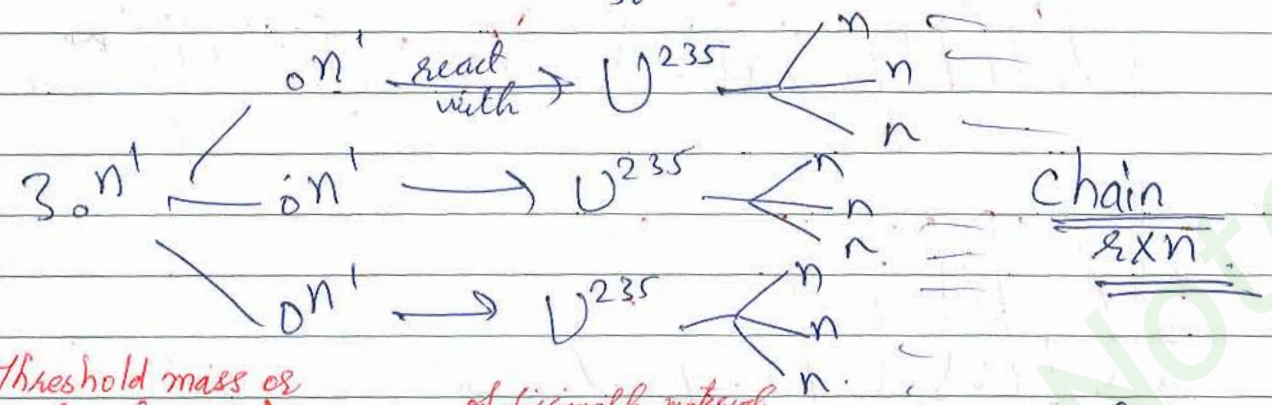
✡ Nuclear fission

Heavier radioactive isotopes, when bombarded by slow moving neutrons (thermal neutrons) undergo dissociation into smaller stable isotopes producing large amt. of energy. The splitting phenomena

$U^{238}, U^{234}, U^{}$: not radioactive → not fissile i.e. not fissionable

above is called nuclear fission.

eg: $_{92}U^{235} + {}_0n^1 \longrightarrow {}_{56}Ba^{139} + {}_{36}Kr^{94} + 3\,{}_0n^1$



★ Threshold mass or

★ Critical mass :- Min. mass of fissionable material req^d to induce a chain rxn i.e sufficient for explosion.

• For controlled nuclear fission, neutron absorbers (moderator) are used.

Common neutron absorbers → heavy water

→ Cd rod

★ $_{92}U^{235} + {}_2He^4 \longrightarrow {}_{94}Pu^{239}$: BREEDER reactor

more dangerous. produces more fissile material from less.

★ ≈ 200 MeV energy is produced in Nuclear fission rxn

NUCLEAR FUSION

• natural fusion at Sun :- $_1H^2 + {}_1H^2 \longrightarrow {}_2He^4$

• H-bomb is based on principle of nuclear fusion

In nuclear fusion, lighter isotopes combine to produce a heavier isotope releasing a large amt of energy >> than energy released in fission.

A huge amt of E is req^d to initiate fusion.

∴ large electrostatic repulsion b/w like charge nuclei as they come closer.

Inorganic Chemistry

GROUP-15

NITROGEN

colorless, tasteless, odourless, non-poisonous, non-combustible, non supporter of combustion.

PREPARATION OF NITROGEN (N_2)

M(1) By thermal decompos^n of Ammonium nitrite (NH_4NO_2)

$$NH_4NO_2 \xrightarrow{\Delta} 2H_2O + N_2(g)$$

NH_4NO_2 can cause explosion if formed directly.

in situ

$NH_4Cl + NaNO_2$

ammonium salt

M(2) By oxid^n of NH_3 → also a rxn of NH_3

(a) $8NH_3 + 3Cl_2 \xrightarrow{\text{Oxid}^n} N_2 + 6NH_4Cl$

ammonia in excess necessarily. chlorine OR

- If NH_3 not in excess →

$$NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$$

(b) $2NH_3 + 3\underset{\text{bleaching pwd.}}{\underset{\text{OA}}{CaOCl_2}} \xrightarrow{\text{Oxidn}} N_2\uparrow + 3CaCl_2 + 3H_2O$

(c) $2NH_3 + 3CuO \longrightarrow N_2(g) + 3Cu + 3H_2O$

M(3) By thermal decompos^n of metal azide :- method to prepare purest form of N_2

$2\underset{\text{salt}}{NaN_3} \xrightarrow{\Delta} \underset{\text{solid}}{2Na} + 3N_2(g)$

$\underset{\text{salt of } HN_3}{Ba(N_3)_2} \xrightarrow{\Delta} \underset{\text{solid}}{Ba} + 3N_2(g)$

✓ N_2 gas can be collected easily

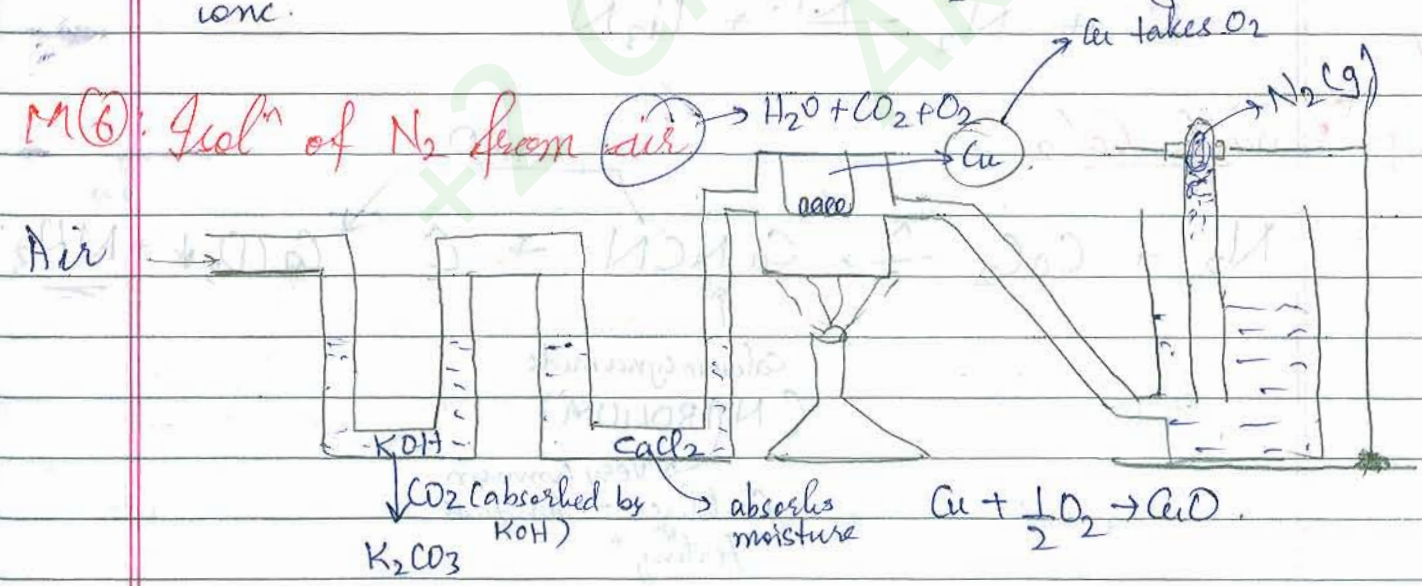
M(4) :- Redn of oxides of N_2.

eg. $N_2O + Cu \xrightarrow{\Delta} CuO + N_2\uparrow$

* M(5) Passing "hot vapours of HNO_3(conc.) over Cu.

$\underset{\text{conc.}}{HNO_3}(v) + Cu \xrightarrow{\Delta} Cu(NO_3)_2 + N_2(g)$

M(6): Isol^n of N_2 from air



* Nitrogen obtained from air is usually heavier than pure N_2. (due to presence of other heavier components → Noble g impurity still present in air)

* After noble gas, nitrogen is the next most unreactive gas. Hence, its so abundant in air.

PROPERTIES

- With non-metals.

$$N_2 + F_2 \longrightarrow NF_3$$

(F_2: most reactive element)

$$N_2 + O_2 \xrightarrow{2200^\circ C} NO$$

(O_2: 2nd most reactive) — during lightning

- With metals

Li, Al, Be, Mg, Ca, Sr, Ba, Ra (Grp 2)

They react with N_2 forming metal nitrides.

$$Ba + N_2 \xrightarrow{\Delta} Ba_3N_2$$
$$Al + N_2 \xrightarrow{\Delta} AlN$$
$$Li + N_2 \xrightarrow{R.T.} Li_3N$$

Imp: * - With CaC_2

$$N_2 + CaC_2 \xrightarrow{\Delta} CaNCN + C \xrightarrow{H_2O} CaCO_3\downarrow + NH_3$$

$CaNCN$: calcium cyanamide (NITROLIUM) → very common fertilizer → for fast fertilizn

- Urea is an amide → slowly ~~hydrolyse~~ react to give NH_3 (base) to make it fertile.

imp

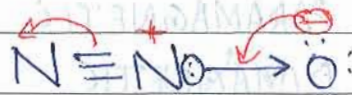
Oxides of Nitrogen

- N_2O
- NO
- N_2O_3
- NO_2 ($\equiv N_2O_4$)
- N_2O_5

imp

PROPERTIES of oxides of N_2

(1) STRUCTURE

- $N_2O \longrightarrow$ 

unsymmetric oxide of N_2

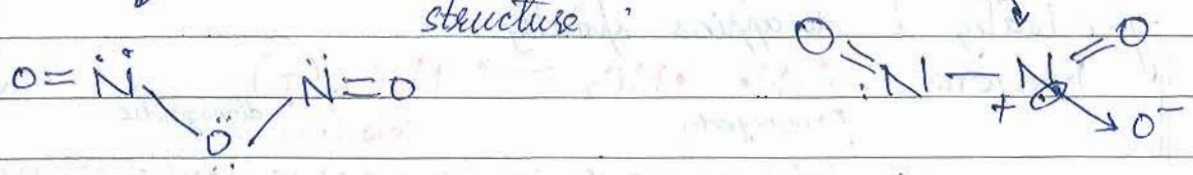
- ✓ linear oxide (sp hybridisⁿ)
- ✓ shows resonance
- ✓ highly polar oxide
- ✓ also called as ~~laughing gas~~ → only by name.

- $NO \rightarrow$

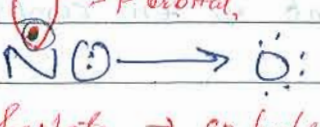
- ✓ odd e^- species
- ✓ neither N nor O have complete octet
- ✓ free radical behaviour ⇒ highly reactive ⇒ very strong electrophile

- N_2O_3 : existence only below −80°C. So, its existence not defined

2 proposed structure



- ✓ symmetric
- ✓ unsymmetric

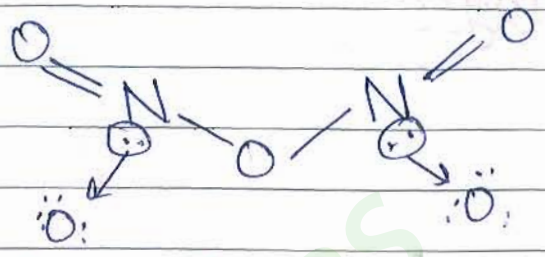
- $NO_2 \rightarrow$ 

p orbital

- ✓ central Nitrogen → hybrid → sp hybridisⁿ.
- ✓ LP–BP repulsion → Angular structure (not linear)

NH_3

* N_2O_5 →



↓ another symmetric structure.
↓ O-N-O & N-O-N bond present.

(2) MAGNETIC PROPERTY

odd no. of e^-s → PARAMAGNETIC
even no. of e^-s → DIMAGNETIC → this property is applicable only for oxides of N_2 (don't generalise)

⇒ $\underbrace{NO}_{7+\text{even}(8)}$ & $\underbrace{NO_2}_{\text{odd}}$ are paramagnetic
$7+\text{even}(8)$ $7+\text{even}(16)$

(3) COLOR

- At RT, only NO_2 shows DEEP BROWN COLOR.
- N_2O_3 (below $-80^\circ C$) → blue crystal
  (Above $-80^\circ C$) (it to $N_2O_3 \rightarrow NO + (NO_2)$ → brown
  → brown
- $NO_2(g)$, when compressed (piston), brown color fades gradually & disappear finally.

Reason:- $O_2N\cdot \cdot NO_2 \rightleftharpoons N_2O_4(g)$
($O_2N\cdot$ Paramagnetic; N_2O_4 colorless, dimagnetic)
more crowded to less crowded → Le Chatelier → favours.
⇓
Magnetic moment ↓ on compressing NO_2 (or (NO) also)
↓
$ON\cdot \cdot NO \rightleftharpoons N_2O_2$

N nitrogen : ON ⇝ -3 to +5

classmate Date 17/12/20 Page

(4) ACIDIC PROPERTY

Neutral: N_2O, NO

N_2O_3 (+3) + H_2O → HNO_2 (+3)

NO_2 (3+5=4, 2) + H_2O → HNO_2 (+3) + HNO_3 (+5)

N_2O_5 (+5) + H_2O → HNO_3 (+5)

acidic

mixed anhydride

↳ eg: $\overset{3+5=4}{\underset{2}{}}NO_2 + NaOH\ (aq) \longrightarrow ?\ NaNO_2 + NaNO_3$

(5) OXIDISING/Red. Prop.

- Among same element, oxidising power increases with ↑ in ON.
- N_2O, NO, N_2O_3, NO_2, N_2O_5, are all good oxidising agents. (Same is true for other non-metallic oxides BUT → compare b/w oxides of same element).
- Except N_2O, oxides of N_2 are also good RA. Reducing power ↓ with ON

§ N_2O

PREPARATION

* (1) Thermal decompos" of ammonium nitrATE
  ↳ leaves nothing as residue producing 2 gaseous products

$NH_4NO_3\ (s) \xrightarrow{\Delta,\ >100^\circ C} N_2O\ (g) + 2H_2O$

white → $2H_2O$ evaporates; N_2O → laughing gas

(2) Treatment of Zn metal with dil HNO_3

$$Zn(s) + \text{dil. } HNO_3 \rightarrow N_2O + Zn(NO_3)_2 + H_2O$$

BALANCING A RXN → VERY QUICK (Inorganic / Redox any)

HYDROGEN method of balancing

$$2HNO_3 + Zn \rightarrow Zn(NO_3)_2 + 2H \quad] \times 4$$

leaving at. H as it es

$$8H + 2HNO_3 \longrightarrow N_2O + 5H_2O$$

$$10HNO_3 + 4Zn \rightarrow 4Zn(NO_3)_2 + N_2O + 5H_2O$$

(3) Redⁿ of nitrate salt with Hg in acidic (H^+) medium.

$$Hg + KNO_3 + H_2SO_4 \rightarrow HgSO_4 + K_2SO_4 + H_2O + N_2O$$

(mild RA; acidic medium)

(4) Controlled Redⁿ of higher oxides

$$\overset{+2}{NO} + \overset{+4}{SO_2} + H_2O \rightarrow \overset{+1}{N_2O} + \overset{+6}{H_2SO_4}$$

SO_2 reduces 1 unit of ON

★ PROPERTIES

(6) Oxidising Action : Same for other oxides of N_2 also.

$$N_2O + \overset{0}{S_8} \rightarrow \overset{+6}{SO_3} + N_2$$

N_2O ← or other oxides of N_2

• Oxides of N_2 oxidise the corresponding or a non metal reacting with it to max. oxidⁿ no. state.

$N_2O + P_4 \longrightarrow P_4O_{10} + N_2$

$+ C \longrightarrow CO_2 + N_2$

$+ Cl_2 \longrightarrow Cl_2O_7 + N_2$

$+ Li \longrightarrow Li_2O + N_2$ } Li_2O_2 & Na_2O are other bi products

$+ Na \longrightarrow Na_2O_3 + N_2$

• $N_2O_{(g)}$ + $NaNH_2(aq)$ → $NaN_3 + H_2O$ (absorbs completely)

sodamide — Sodium azide (Metal azide)

Thermal decompos^n ↓ Δ

$NaN_3 \rightarrow Na + N_2\uparrow$

• NO nitric oxide.

✱ PREPARATION

<1>

$Cu + \underline{dil.}\ HNO_3 \rightarrow Cu(NO_3)_2 + NO_{(g)} + H_2O$

$Pb + \underline{dil.}\ HNO_3 \rightarrow Pb(NO_3)_2 + NO_{(g)}$

✱ <2> By redⁿ of nitrate & nitrite salts with acidic $FeSO_4$ (RA)

Brown Ring Test

$FeSO_4 + KNO_3 + H_2SO_4 \rightarrow NO + K_2SO_4 + Fe_2(SO_4)_3 + H_2O$

(or nitrite) (both) (acidic med.)

<3>

$KNO_3 + KI + H_2SO_4 \rightarrow K_2SO_4 + NO + I_2 + H_2O$

(or nitrite) (RA)

<4> $N_2(g) + O_2(g) \xrightarrow[\text{lightning only}]{2200^\circ C} 2NO$

✱ PROPERTIES

✓ very poisonous gas

✓ With elements, N_2 gas is evolved & elem is oxidised in highest oxidⁿ state.

classmate
Date
Page

(7) With Cl_2

$$NO + Cl_2 \xrightarrow{RT} 2NOCl \equiv Cl-\dot{\underset{\cdot\cdot}{N}}=O$$

Add^n comp^d
Nitrosyl chloride

fixation of alkene eg.

$$\overset{\delta-}{Cl}-\overset{\delta+}{N}=O + CH_3-CH=CH_2 \xrightarrow{MK} CH_3-\underset{Cl}{CH}-CH_2NO$$

↳ rearray may also occur.

(8) NO gas fully gets absorbed in ferrous sulphate soln

$$NO + FeSO_4(aq) \rightarrow Fe(NO)SO_4$$

↳ $[Fe(H_2O)_5NO]SO_4$
✓✓ in soln
(it is formed at junction in brown ring test)

- N_2O_3

✓ doubtful existence

PREPARATION

EXPECTED

- only prepar^n

$$\overset{+5}{HNO_3} + As_2O_3 \longrightarrow \overset{+3}{N_2O_3} + H_3AsO_4$$

conc.
↳ only RA
to reduce to +3 oxid^n state

PROPERTY

✓ It a blue crystal at low (-80°C below) temp.
N_2O_3 is solid at $T < -80°C$.
(blue)

✓ most of properties of N_2O_3 are of NO & NO_2 because it

N_2O_5

↳ very strong dehydrating agent

PREPARATION

(1) HNO_3 (conc.) + P_4O_{10} (P_2O_5 dimer of) ⟶ N_2O_5 + HPO_3 (meta phosphoric acid.)

↳ P_2O_5 ↳ strongest dehydrating agent than HNO_3

(2) $2AgNO_3(s) + Cl_2(g) \xrightarrow{\Delta} 2AgCl + N_2O_5 + \frac{1}{2}O_2(g)$

↳ not aq.

(3) $N_2O_4 + O_3 \longrightarrow N_2O_5 + O_2$

NO_2

PREPARATION

* (1) conc. HNO_3 + Cu / Pb / Fe / Sn (Heavy metal.) ⟶ $Cu(NO_3)_2 + NO_2 + H_2O$

(2) Catalytic oxidⁿ of NO → discussed in Ostwald's method

$NO + \frac{1}{2}O_2 \xrightarrow{\text{Catalyst}} NO_2$

PROPERTIES

✓ Strong OA when treated with pure elements, N_2 gas is evolved. Elements go in highest oxidⁿ state.

- ~~It is~~ It is a highly reactive, brown colored, poisonous gas at RT
- NO_2 on compression dimerises to N_2O_4
- i.e, liq^d NO_2 is existing as N_2O_4 (its dimer → colorless)

NH_3

- Lab Preparation

∧ By treatment of ammonium salts with conc sol^N of strong base.

<1> NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3 + NaOH (basic) → (neutralisation) $NH_3(g) + NaCl + H_2O$

→ (neutralisation) $+ Na_2SO_4 + H_2O$

→ (neutralisation) $+ NaNO_3 + H_2O$

salts of SA, WB ⇒ Acidic.

∧ By treatment of nitrates/nitrites with Al or Zn in strongly basic medium

<2> $Al + NaNO_3$ or $NaNO_2 + NaOH \rightarrow NaAlO_2 + NH_3$

$Zn + NaNO_3$ or $NaNO_2 + NaOH \rightarrow Na_2ZnO_2 + NH_3$

∧ By hydrolysis of nitrides

<3> metals of grp II: $Li_3N + H_2O \longrightarrow NH_3$

$Mg_3N_2 + H_2O \longrightarrow$ (neutralisation)

- Industrial Preparⁿ

** Haber's Process

$$N_2(g) + H_2(g) \underset{\text{high P}}{\overset{\text{Catalyst (Fe pwd.)},\ \approx 500^\circ C}{\rightleftharpoons}} 2NH_3(g) \qquad \Delta H < 0$$

Promoter → Mo

Q. above rxn is exothermic, So, it should be favoured at low temps (Le Chatelier). But, we are using high temps. Why?
T is ↑ to ↑ rate of rxn (∵ it has low equi. constt)
So, thermodynamics is neglected over kinetics
Moreover :- High temp → more crowded to less ~~crowded~~ crowded

- above rxn is heterogeneous process (Fe → solid pwd. & N_2 (gas))
Still not desirable formed. Fe pwd. is favoured over Fe block : more SA
- Promoter : Improves efficiency of catalyst

* Original Haber's Process used catalyst
actual but very old : Fe_2O_3 / Al_2O_3 → alumina

- WD by Mr. Haber to separate N_2 from air → to give N_2

Air : $N_2 + O_2 + C_{(g)} \xrightarrow{\text{heat}} \underbrace{CO + N_2}_{\text{called as PRODUCER GAS.}}$

CO : substance less reactive with N_2

- WD by Mr. Haber to get H_2

$$H_2O(v) + C_{(g)} \longrightarrow \underbrace{CO + H_2(g)}_{\text{WATER GAS}}$$

→ to give H_2

- To improve efficiency of this ancient method

$$\underbrace{N_2 + CO}_{\text{produces gas.}} + H_2O(v) \longrightarrow CO_2 + N_2 + H_2$$

N_2 ✓ Additional H_2.

PROPERTIES of NH_3

✓ some done earlier,

- DRYING OF NH_3

Drying agents

as well as strong acidic oxides

So, neutralise NH_3

- N_2O_5 ✗
- P_4O_{10}

- $CaCl_2$ ✗ → $\downarrow NH_3$ → $[Ca(NH_3)_8]Cl_2$ complex → So, can't be used.

- ✓ CaO (base) $+ H_2O$ (takes H_2O) $\rightarrow Ca(OH)_2$

- alkali & alkaline earth metals dissolve in LIQUID (not aq.) NH_3 to form deep blue colored sol^n.

Oxy Acids of Nitrogen

→ NITROUS ACID :

Prepar^n ⟨1⟩ Gr Grp 1 / Grp 2 metal nitrite on treatment with dil sol^n of HCl / H_2SO_4 in cold cond^m → (∵ HNO_2 is unstable) HNO_2 is formed

✓ $NaNO_2 + HCl \longrightarrow NaCl + HNO_2$

✓ $NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + HNO_2$

✓✓ $Ba(NO_2)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2HNO_2$ (white ppt)

properties

- HNO_2 is a weak monobasic acid.

- $H-O-\underset{\curvearrowright}{N}=O$

- $H-O-\ddot{N}=O \rightleftharpoons H^+ + \ddot{O}-N=O$:- Partially ionised in H_2O
- HONO is highly unstable & decomposes on simple heating giving NO + NO_2
  $HONO \xrightarrow{\Delta} NO + NO_2$
- It is a good OA as well as RA → ∵ ~~less reactive~~ very unstable, so, quickly converts or reduces/oxidises itself.

$HNO_2 + Cu \rightarrow Cu(NO_2)_2 + NO + H_2O$

$+ Ag \rightarrow AgNO_2 + NO + H_2O$

oxidising action → reduces itself

$HNO_2 + KMnO_4 + H_2SO_4 \rightarrow K_2SO_4 + MnO_4 + HNO_3$

Strong OA or Cr_2O_7 or H_2O_2 or other strong OAs

reducing action, oxidises itself.

→ NITRIC ACID

prepar^n

① OSTWALD's method

- successive oxid^n of NH_3.
- multi-step process
- heterogeneous catalysis

catalyst: Pt

S1) $NH_3 + O_2 \rightarrow NO + H_2O$

S2) $NO + O_2 \xrightarrow[\text{high T, P}]{\Delta} NO_2$

S3) $NO_2 + H_2O \rightarrow HNO_3 + NO + NO_2$

($NO + NO_2$ came from HNO_2 which decomposed due to high T.)

properties

- colorless, strong monobasic acid, strong OA.
- if left for long time, HNO_3 decomposes to NO_2 giving it brown color. NO_2 is poisonous and also makes high P development inside the bottle. So, physical & chemical damage can take place.

PHOSPHORUS

3 imp. allotropes :- White Phosphorus, Red phosphorus, Black Phosphorus

most abundant allotrope

§ Extraction :

Imp. minerals containing phosphorus (mainly in phosphate form) :- (a) Phosphate rock containing $Ca_3(PO_4)_2$
→ made of animal bones
→ called as BONE ASH
:- (b) Fluorapatite :- containing $[Ca_3(PO_4)_2 \cdot CaF_2]$
:- (c) Aluminium phosphate $AlPO_4$

★ Extraction from PHOSPHATE ROCK

(M1) RETORT PROCESS

- Purified phosphate rock is boiled (refluxed) with conc. H_2SO_4 where insoluble $CaSO_4$ ppt. out leaving behind H_3PO_4 (phosphoric acid) in soln. The filtrate is heated strongly where H_3PO_4 dehydrate into P_4O_{10} which is finally heated with C (acts as a RA) giving vapours of white phosphorus & CO gas. These vapours are condensed under water (∵ it catches fire in open air)

The rxn :-

$$\underset{\text{basic}}{Ca_3(PO_4)_2} + \underset{\text{acidic}}{\text{conc. } H_2SO_4} \longrightarrow \underset{\text{insoluble}}{CaSO_4\downarrow} + H_3PO_4$$

$$H_3PO_4 \xrightarrow{\Delta\,\Delta.} P_4O_{10}.$$

$$\overset{+5}{P_4O_{10}} + 10\overset{0}{C} \xrightarrow{\Delta} 10\overset{+2}{CO} + \underset{\text{white phosphorus.}}{P_4}$$

carbon red^{n} takes place.

* White phosphorus is active allotrope.

(M2) Electric Spark Method :-
↳ or PARKER-ROBINSON Method

$$Ca_3(PO_4)_2 + SiO_2 \xrightarrow{\text{Electricity}} CaSiO_3 + P_4O_{10}$$

SiO_2: silica {excess} (sand)
- quite stable. Made to react with spark
- plays role of flux

$CaSiO_3$: Slag (Calcium silicate)

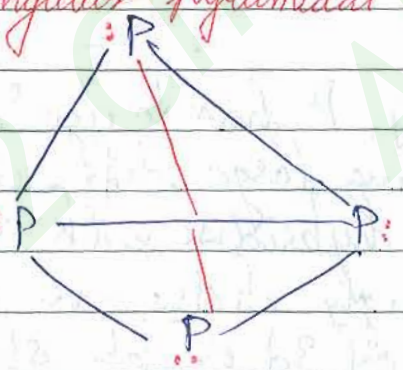
Note :- $CaCO_3$ is flux in Fe extraction to react with silica producing $CaSiO_3$ (slag) (same as above)

$$P_4O_{10} + C \xrightarrow{\Delta} P_4 + CO$$

* PROPERTIES

P1 STRUCTURE

* Keep 4 P at 4 corners of tetrahedron & develop P-P bond b/w each of them
- It is triangular pyramidal in structure
- sp^3
- PPP bond angle = 60°



- highly strained
  - should have been 109°
  - actually its 60°
- Highly reactive
- starts burning at 35°C & ∴ stored under H_2O

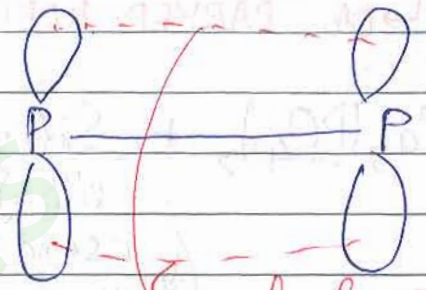
- $P_4 + O_2 \xrightarrow[\text{starts burning.}]{T > 35^\circ C} P_4O_{10}$. $\Delta H < 0$
  ↳ ΔH is quite less.

MAGIC — So, in open air, heat is not much accumulated. Hence, it burns itself, not sufficient to burn others

classmate
Date
Page

~~Comparison in~~ terms of

Q. In abundance, N_2 is diatomic but P_4 is tetratomic. Why?



↳ not feasible
∵ size is large so, BL is high so, BE is low (BL $\propto \frac{1}{BE}$)
So, π bonds don't get established

** Same is true ∀ elements of 3rd & higher periods. i.e elements of 3rd period don't form π bonds with elements of 3rd or higher period.

** EXPECTED

Q. P forms both PF_3 & PF_5 (sp^3d)
⇒ P is both trivalent & pentavalent.

However, inspite of this,
P forms only PH_3 but not ~~PH_5~~. Why?
Moreover, SF_2, SF_4, SF_6 ✓ but H_2S ✓ ~~SH_4~~ ~~SH_6~~
& NO_3^- ✓ but ~~PO_3^-~~
& N_2O_5 ✓ but ~~P_2O_5~~ Why?

Ans:-
P: $3s^2\ 3p^3\ 3d^0$
To show pentavalency, P has to use 'd' orbital.
3p & 3d orbitals have large diff in size. So, 3p orbitals does not hybridise with 3d orbitals.
However, when strongly electro-ve atom like F, Cl approaches P, size of 3d orbitals starts contracting & becomes comparable to size of 3p & hybridisⁿ takes place.
But, less electro-ve atom like H can't do this.

Reason:-

large +ve charge leads to coming of e⁻s of P from its higher orbitals to compensate the charge.

Same reason for others.

* Under normal condns, treatment of anything (almost) with conc. HNO_3 (OA) gives away NO_2 vapours.

★ REACTIONS of white phosphorus :

(1) With water :

Does NOT react with water at RT. However, when treated with hot water, following rxn takes place →

$$\overset{0}{P_4} + H_2O(v) \xrightarrow{\text{disproportion}^n} \overset{-3}{PH_3} + \overset{+1}{H_3PO_2}$$

hypophosphorous acid → earlier used to get benzene from benzene diazonium chloride.

Similar **With alkali** sol^n

$$P_4 + NaOH(aq) \xrightarrow{\text{at RT}} PH_3 + NaH_2PO_2$$

(with base) (salt of Hypophosphorous acid)

(2) With conc. HNO_3

$$P_4 + \text{conc. } HNO_3 \longrightarrow NO_2 + H_3PO_4$$

(3) With oxygen (O_2)

$$P_4 + O_2(g) \xrightarrow{\Delta} P_4O_6 \xrightarrow[\text{further heated}]{\Delta, O_2} P_4O_{10}$$

(formed 1st)

So, to produce P_4O_{10}, oxygen (excess) is necessary.

(4) With halogens

$$P_4 + F_2(g) \xrightarrow{\text{at RT}} \underbrace{PF_3 \longrightarrow PF_5}_{\text{both are formed}}$$

$$P_4 + Cl_2(g) \xrightarrow{\Delta} PCl_3 \longrightarrow PCl_5$$

$$+ Br_2(l) \xrightarrow{\Delta} PBr_3 \xrightarrow[Br_2]{\Delta} PBr_5$$

HPO_3 → Phosphite
H_3PO_2 :- Hypophosphorous acid
H_3PO_4 :- Phosphoric acid

$P_4 + I_2(s) \longrightarrow PI_3 \checkmark \longrightarrow \cancel{PI_5}$

(∵ EN of I ≈ EN of H, also, it doesn't allow formation of such compounds -

[5] With metals → Grp 1, grp 2, Al
Phosphorous + reactive metals → metal phosphide
↓ $+H_2O$
phosphine gas.

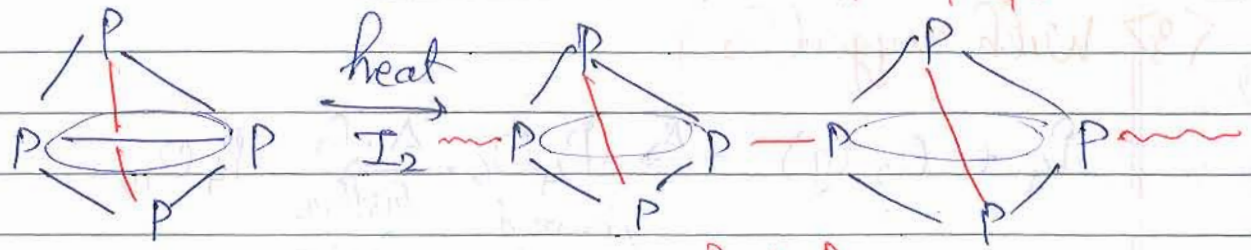
$Na + P_4 \longrightarrow Na_3P$
$Ca + P_4 \longrightarrow Ca_3P_2$
$Al + P_4 \longrightarrow AlP$
Phosphide
$\xrightarrow{H_2O}$ $PH_3\uparrow$ + - - -
phosphine gas.

Allotropy

P_4 (white) $\xrightarrow[I_2\text{-catalyst}]{heat\ (250^\circ C)}$ Red-P $\xrightarrow[at\ high\ P]{heat\ (500^\circ C)}$ Black-P

Inc. Stability : W → R → B

W : least stable, most abundant
B : most stable, least abundant
(E_A is higher than that of P_4 (white))



Red P
(less angle strains than P_4 (white))
no. of

Use :- • match stick
• crackers
] of Red-P

* Do not confuse
PH_3 : phosphine
$COCl_2$: phosgene

* **Black** Phosphorous is a cross linked polymer of red phosphorous. So, Black phosphorous is free from any angle strain.

* OXIDES OF P

P_4O_6 — trioxide

P_4O_{10} — pentaoxide

Preparation :

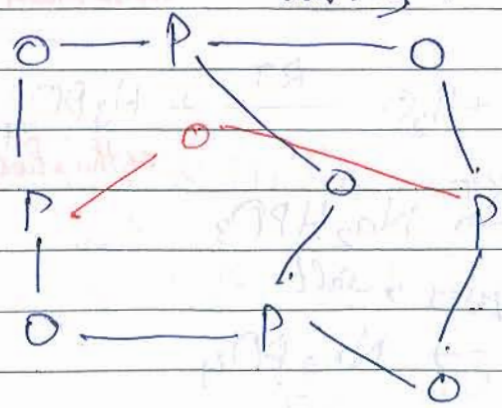
① Direct oxidⁿ of elements :

P_4 + dry air ⇓ less amt. of O_2 (no H_2O) $\xrightarrow{heat}$ P_4O_6 (predominant)

$$P_4 + O_2 \text{ (dry)} \xrightarrow{\Delta} P_4O_{10}$$

P_4O_{10} is also obtained during extraction of P by Retort's Process & electric spark process.

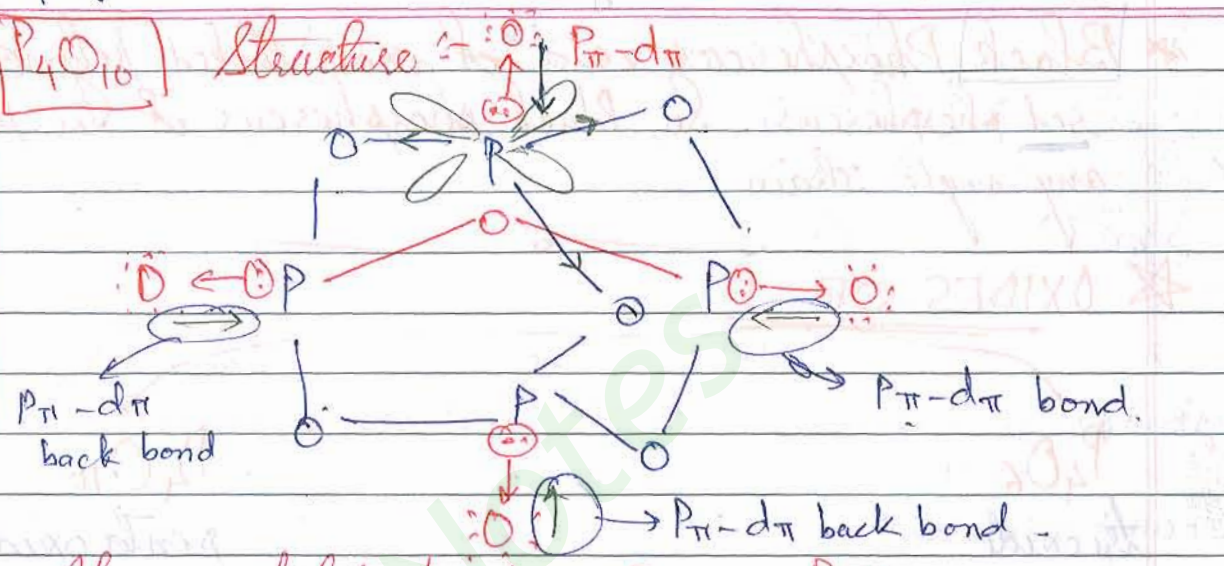
P_4O_6 Structure : Keep 4 P at 4 corners of tetrahedron & make P–O–P bond b/w every one of them in a type of non planar array.



- all atoms are sp^3 hybridised.
- P try avoiding π bond. So, its dimer is more stable than monomer. So, P_4O_6 ✓ ~~P_2O_3~~.

P_4O_7
P_4O_8
P_4O_9 } less stable.

P_4O_{10} Structure :-



If one dative bond on P : P_4O_7
two " : P_4O_8
three " : P_4O_9
4 " : P_4O_{10} (very stable)

* no. of double bonds in P_4O_{10} : not zero
they are ↓
$P_\pi - d_\pi$ back bonds

PROPERTIES

- Both oxides are strong OAs.
  OA strength :- $P_4O_{10} > P_4O_6$
- With H_2O $P_4O_6 + H_2O \xrightarrow{RT} H_3PO_3$ (*)
  anhydride of H_3PO_3 ; hydride of P_4O_6 ; orthophosphorous acid

$P_4O_{10} + H_2O \xrightarrow{RT} H_3PO_4$
orthophosphoric acid

Salt case: $P_4O_6 + aq.NaOH \xrightarrow{RT} Na_2HPO_3$
base gives → salt.

$P_4O_{10} + aq.NaOH \xrightarrow{RT} Na_3PO_4$
base ; salt.

classmate
Date
Page

$\overset{+3}{P_4O_6} + H_2O \xrightarrow{\Delta} \overset{+3}{PH_3} + \overset{+5}{H_3PO_4}$ (4)

disproportionⁿ

↳ subcase

$P_4O_6 + NaOH(aq) \xrightarrow{\Delta} PH_3 + Na_2HPO_3$ (3)

basic — disproportionⁿ — salt

gives

$P_4O_{10} + 6PCl_5 \longrightarrow 10POCl_3$

OXY-ACIDS of Phosphorus

all reducing acids.

Phosphoric Acid Series

1. H_3PO_4 (orthophosphoric acid or phosphoric acid)
2. $H_4P_2O_7$ (pysophosphoric acid)
3. $H_4P_2O_6$ (hypophosphoric acid)
4. HPO_3 (meta phosphoric acid) or phosphate

Phosphorous Acid Series.

1. Orthophosphorous acid (H_3PO_3)
2. Hypophosphorous (H_3PO_2)

Orthophosphoric acid (H_3PO_4)

Lab Preparation

<1> $Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4\downarrow + 2H_3PO_4$

Phosphate rock

<2> Hydrolysis of P_4O_{10} or PCl_5

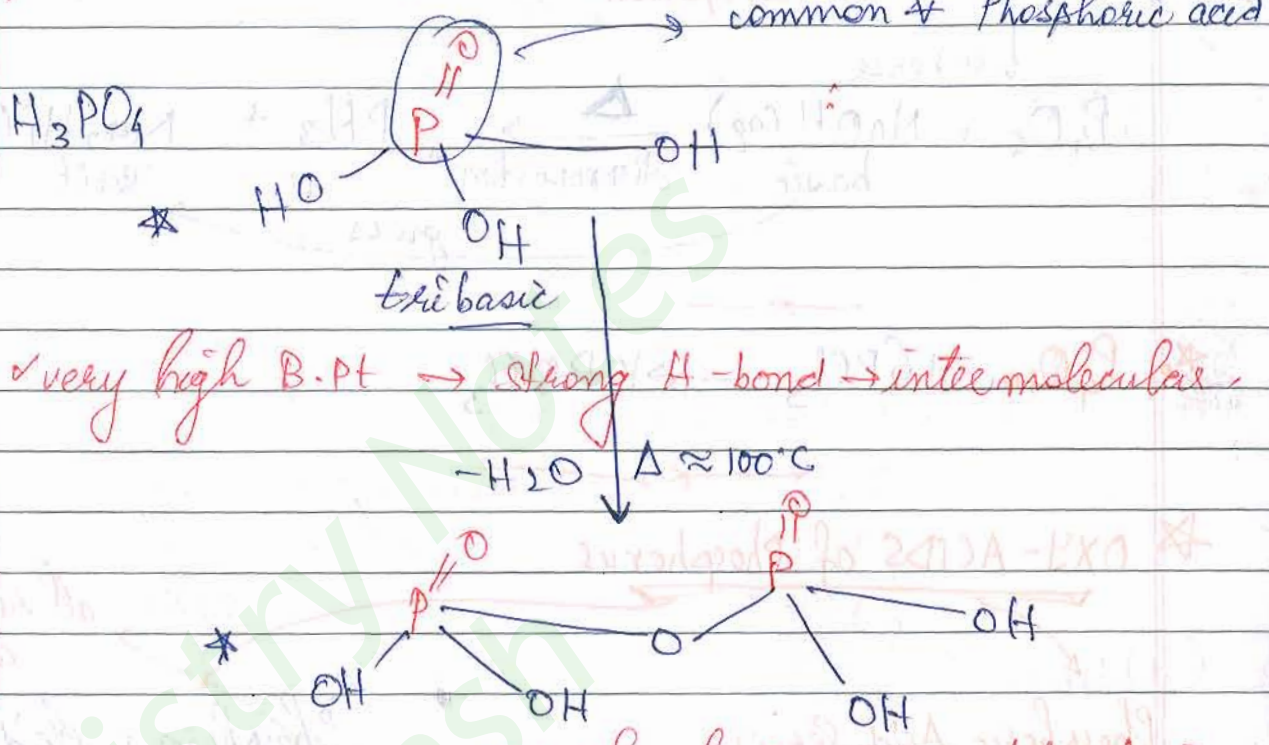
$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

$PCl_5 + 4H_2O \longrightarrow H_3PO_4 + 5HCl$

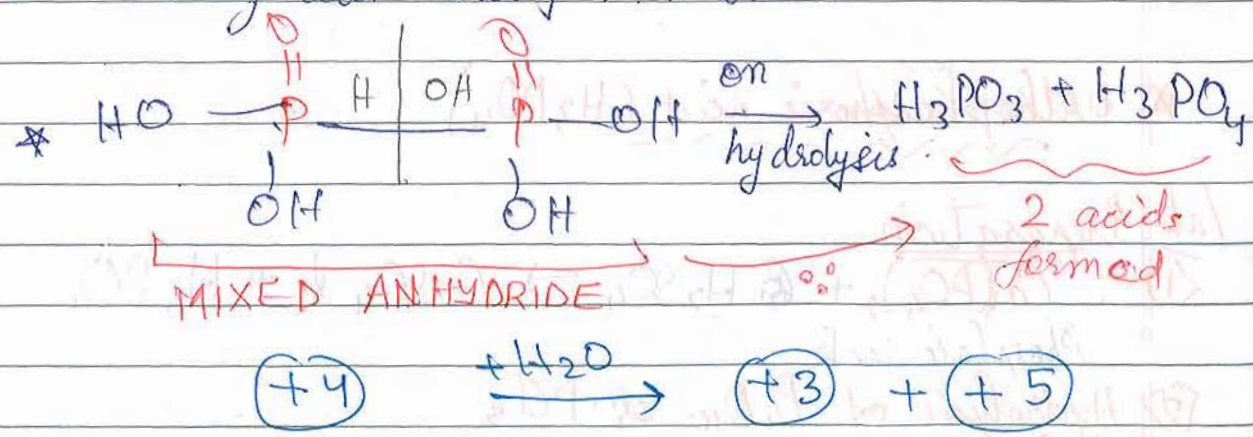
+2 Chemistry Notes Akshat

classmate
Date
Page

- properties → orthophosphoric acid



* Hypophosphoric acid ($H_4P_2O_6$)
  ↳ only acid having P-P bond.



✱ Meta Phosphoric acid

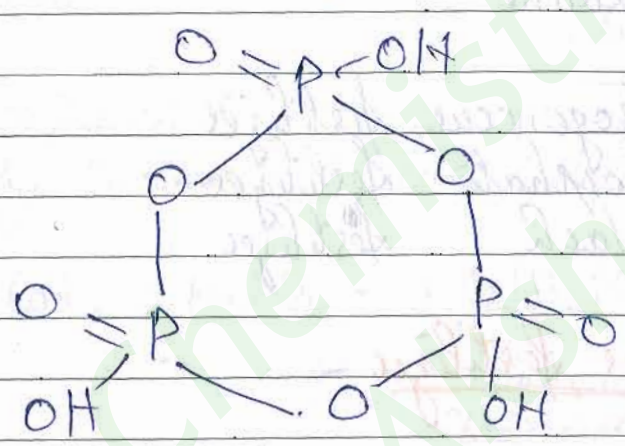
$H_3PO_4 \xrightarrow[\text{heating}]{\text{strong}} \underbrace{2H_2O}_{2H_2O \text{ removed.}} + HPO_3 = (HPO_3)_3$

meta phosphoric acid.

(in pyrophos. — acid 1 H_2O was removed.)

✱ meta phosphoric acid exist as a cyclic trimer

Structure :- Make a structure like C_6H_6 &
keep P–O–P at alt. corners.
Then, at every P → a =O & an OH.



• cyclic trimer ✓
monomer ✗
(∵ HPO_3 tries to minimise π bonds.)

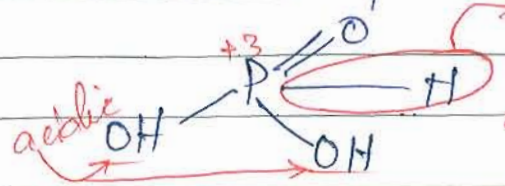
✱ Orthophosphorous acid : Reducing acid (∵ P in +3, so can go in +5 i.e.)

Hydrolysis • $P_4O_6 \xrightarrow[RT]{H_2O} H_3PO_3$

• $PCl_3 + H_2O \longrightarrow H_3PO_3 + HCl$

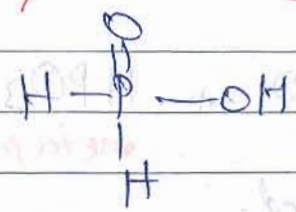
• properties

Structure :- Make a P=O.
& Make OH from left Oxygen



can be used to reduce other.
dibasic.

2. Hypophosphorous (H_3PO_2)



mono basic
Reducing acid.

Reducing power :- H_3PO_2 (2 hydrides to reduce) > H_3PO_3 (1 hydride to reduce)

✱ FERTILIZER

For a fertile soil, pH ≈ > 7 i.e it must be slightly alkaline.

✱ N : nitrogeneous fertilizer
✱ P : phosphate fertilizer
K : potash fertilizer

✱ Nitrogeneous fertilizer :-

→ Urea

$2NH_3(g) + CO_2(aq) \rightarrow H_2N-\overset{O}{\overset{\|}{C}}-\bar{O}NH_4^+$
(CO_2 = H_2CO_3)
salt (ammonium carbamate)

$\downarrow -H_2O$

$H_2N-\underset{O}{\overset{\|}{C}}-NH_2$ (Urea) $\xleftarrow[H_2O]{Slow}$ $NH_3(aq)$

Urea → amide → undergoes slow hydrolysis in soil.

$NH_3(aq)$ → reason for making soil alkaline

or NITROLIUM

→ $CaNCN$ (Calcium cyanamide)

$$CaNCN + H_2O \longrightarrow CaCO_3 + (NH_3\,aq)$$

✱ Phosphate fertilizer

→ Super phosphate

Super phosphate is obtained by treatment of ~~fluoro~~ fluor-apatite $[Ca_3(PO_4)_2 \cdot CaF_2]$ with conc. H_2SO_4

(kept as such in compd → inert → otherwise rate high)

$$\underset{\text{fluorapatite}}{Ca_3(PO_4)_2 \cdot CaF_2} + \underset{\text{conc.}}{H_2SO_4} \longrightarrow \underbrace{Ca(H_2PO_4)_2 \cdot CaSO_4}_{\text{Super phosphate (contains } CaSO_4 \text{ inert impurity)}} + HF$$

→ Triple Super phosphate

Obtained by treatment of fluorapatite with conc. H_3PO_4

$$Ca_3(PO_4)_2 \cdot CaF_2 + H_3PO_4 \longrightarrow \underbrace{Ca(H_2PO_4)_2}_{\text{triple super phosphate (basic salt)}} + HF$$

↳ very slowly hydrolyse to make soil alkaline

✱ Triple super phosphate (pure) better Super phosphate : fertilizer action (& impurity is there → $CaSO_4$)

Group - 16

OXYGEN

✱ OZONE (O_3)

§ Preparation

- Ozone is obtained by passing silent electric discharge (≡ low P) through pure O_2 (g) where O_2 is ozonised.

$$3O_2 \rightleftharpoons 2O_3$$

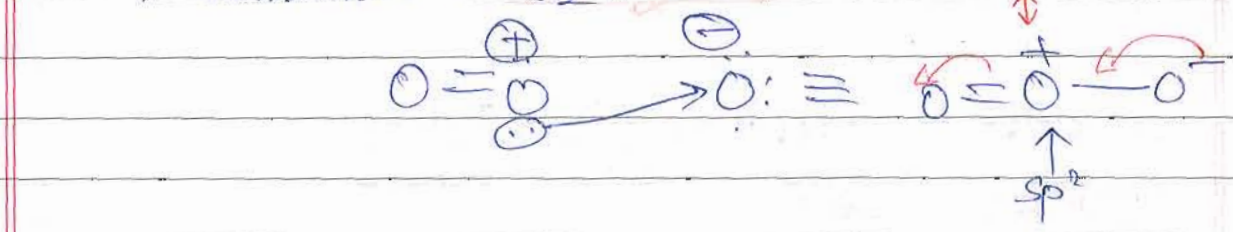
Ozoniser types.

- Siemen ozonisers
- Brodie ozonisers

§ Properties

1. STRUCTURE :

To remember :- $O_2 + O$



2. Chemical property :-

Ozone is a very strong OA.

$$O_3 \longrightarrow O_2 + [O]$$

Action of oxidⁿ of ozone.

$O_3 \longrightarrow$ ∴ $X^- \rightarrow X_2$

∴ $Fe^{2+} \rightarrow Fe^{3+}$

∴ $Sn^{2+} \rightarrow Sn^{4+}$

∴ $SO_3^{2-} \rightarrow SO_4^{2-}$

∴ $S^{2-} \rightarrow S$

In gas phase, see the ON

i.e eg. $\overset{+4}{SO_3^{2-}} \rightarrow$ in gas phase $\overset{+4}{SO_2}$

- $\overset{-1}{H_2O_2} + \overset{0}{O_3} \longrightarrow \overset{-2}{H_2O} + 2\overset{0}{O_2}$
- $\overset{+7}{KMnO_4} + \overset{0}{O_3} \longrightarrow \overset{2+}{Mn^{2+}} + \overset{0}{O_2}$

Stronger OA — Strong OA

∴ red^n of O_3 takes place

- To see which is stronger OA ?

red^n ½ rxn of $MnO_4^- \longrightarrow Mn^{2+}$

$8H^+ + (5e^-) + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

red^n ½ rxn of $O_3 \rightarrow O_2$

$(2e^-) + O_3 \longrightarrow O_2 + O^{2-}$

MnO_4^- takes $5e^-$ & O_3 takes $2e^-$

So, $KMnO_4$ is stronger OA than O_3.

classmate
Date
Page

- $Hg_{(l)} + O_3 \xrightarrow{RT} HgO_{(solid)} + O_2$: called as :- Tailing of Hg

SULPHUR

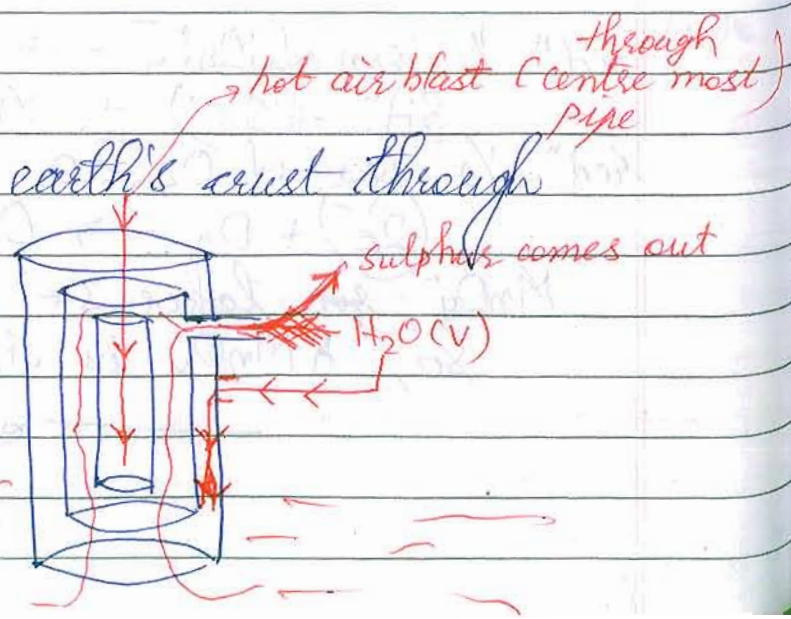
Sulphur exists in free state in earth crust. Besides, it also exists in the form of several compds., mainly as a metal sulphide & metal sulphate. eg:

SULPHIDE
1. Pyrite (mineral containing FeS_2) (fool's gold)
2. Copper glance (" " Cu_2S)
3. Iron Pyrite (" " $CuFeS_2$)
4. Cinnabar (" " HgS)
5. Zinc blende (" " ZnS)

SULPHATE
- Gypsum (" " $CaSO_4 \cdot 2H_2O$)
- Epsom salt (" " $MgSO_4 \cdot 7H_2O$)
- Glauber's salt (" " $Na_2SO_4 \cdot 10H_2O$)
- Mohr's salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$)
- Potash alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$)

Preparation

S is obtained from earth's crust through Frasch Process

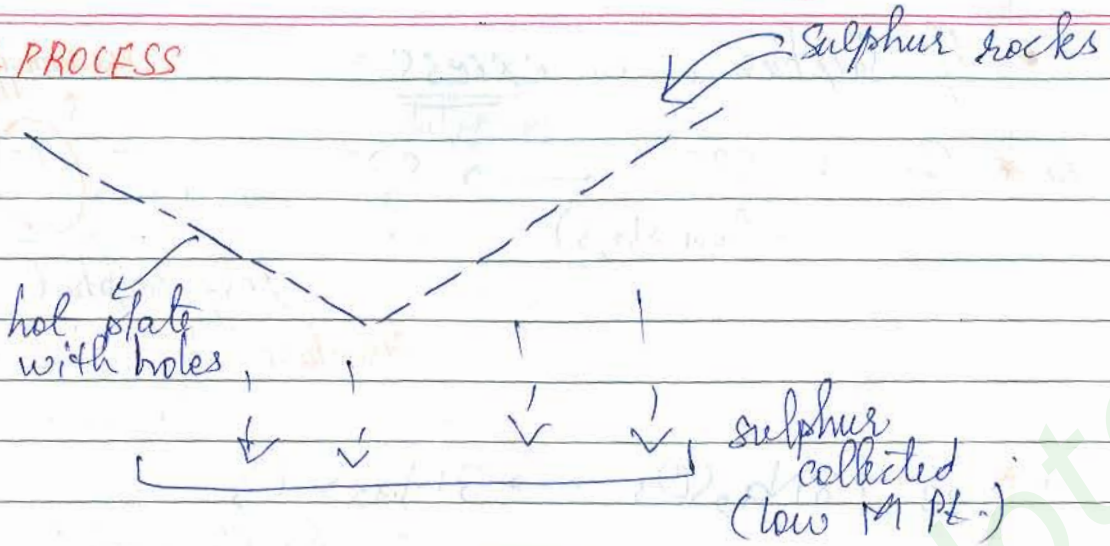


melts by hot air (creates high P on S)

Sulphur deposited.

classmate
Date
Page

- GILL PROCESS



- Properties

1. Structure :- → not most stable

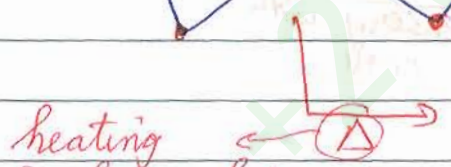
most abundant allotrope :- α-sulphur (Rhombic sulphur)

⇓

S_8 (solid → white) at RT

Way to remember :-
write a stylish W

: Puckered ring structure



- So, Sulphur changes from di to para magnetic on heating

2. Reactions

(a) Rxn with alkali — disproportion

S1 $S_8 + NaOH \xrightarrow[\text{cold} \equiv RT]{\text{(strong base any)}} Na_2S + Na_2SO_3$

• If Sulphur is in excess

predominant among them (पूछो क्यों)

S2 ✱ $S_8 + S^{2-} \longrightarrow S_2^{2-}, S_3^{2-}, S_4^{2-}, S_5^{2-}, \ldots S_n^{2-}$

(from Na_2S)

poly sulphide form^n

Structure $^{\ominus}S-S-S\ldots-S^{\ominus}$

-ve on terminals

S2 ✱ $S_8 + 8Na_2SO_3 \longrightarrow 8Na_2S_2O_3$

Sodium hypothio sulphate

✱ $S_8 + NaOH \xrightarrow{\Delta} Na_2S + Na_2S_2O_3$

conc

(or with conc. NaOH formed in 1st step. But with NaOH (cold) formed in 2nd step)

✱✱ (b) With conc. HNO_3

$S_8 + HNO_3 \not\longrightarrow H_2SO_4 + NO_2\uparrow$

conc

necessary with CONC

✱ (c) With conc. H_2SO_4

$S_8 + H_2SO_4 \longrightarrow SO_2\uparrow$.

strong RA → driving force

(conc) weak OA

(d) With halogens

✱ $S_8 + F_2(g) \longrightarrow SF_2 \xrightarrow{F_2 \text{ more}} SF_4 \xrightarrow{\text{more } F_2} SF_6$

sp^3d sp^3d^2

i.e $S_8 + F_2(g) \longrightarrow SF_6$

excess

* S → used in vulcanization of rubber.

* $S_8 + Cl_2(g) \longrightarrow S_2Cl_2$
sulphuryl chloride.
$+ Br_2(g) \longrightarrow X$
$+ I_2(g) \longrightarrow X$

(c) With $H_2(g)$
$S_8 + H_2(g) \xrightarrow{\Delta} H_2S(g)$

$S_8 + O_2(g) \xrightarrow{\Delta} SO_2(g)$ {not SO_3}
colorless
its formⁿ requires catalyst

Δ | O_2 → $S_2 + O_2 \rightleftharpoons SO_2$
blue

i.e S_8 burns in O_2 in blue coloration, but giving product SO_2 i.e colorless.

(d) S_8 + Na $\xrightarrow{\Delta}$ Na_2S
acts as an OA
K $\xrightarrow{\Delta}$ K_2S
Ca $\xrightarrow{\Delta}$ CaS
Al $\xrightarrow{\Delta}$ Al_2S_3
→ Grp 1, grp 2 & Al.

COMPOUNDS of Sulphur

H_2S highly poisonous

Preparation
- $H_2(g) + S_8 \xrightarrow{\Delta} H_2S(g)$
(boiling sulphur)
- MS + dil. $H_2SO_4 \rightarrow MSO_4 + H_2S\uparrow$
metal sulphide
basic
acid

for acidic property, most common DEHYDRATING AGENTS

i.e SO_3, conc. H_2SO_4, conc. HNO_3, Cl_2O_7, P_2O_5.

- In previous exp, HNO_3 is not suitable ∵ H_2S produced is strong RA & HNO_3 is strong OA. So, they react further.

- **Lab preparation**

(a) KIPP'S PROCESS

$$FeS + H_2SO_4 \xrightarrow{\text{rxn at very slow rate}} FeSO_4 + H_2S$$

FeS: sparingly soluble

H_2SO_4: (dil)

H_2S: formed at very slow rate (salt tests of gp II & gp IV)

- **properties**

✓ H_2S is a weak dibasic acid, gas at RT

✓ H_2S is sufficiently (intermediately) soluble in H_2O (∵ of polarizability of S)

✓ H_2S is always containing some moisture as impurity. So, it has to be dried.

- **Drying of H_2S**

✗ • CaO, MgO can't be used ∵ of neutralizⁿ

✗ • $MgCl_2$ doesn't work

$$MgCl_2 + H_2S \longrightarrow MgS + 2HCl$$

✗ • $H_2S + \underbrace{\text{conc. } H_2SO_4}_{\text{won't work}} \longrightarrow SO_2 + H_2O$

✓ • P_2O_5 or Al_2O_3

- H_2S is a strong RA.

- H_2S reduces $X^- \rightarrow X_2$, $MnO_4^- \rightarrow Mn^{2+}$, $Cr_2O_7^{2-} \rightarrow Cr^{3+}$, $H_2O_2 \rightarrow H_2O$ + ... $\Big\}$ + SO_2 (gas)

OXIDES of S

(1) SO_2

- Preparⁿ

① $Cu + \text{conc. } H_2SO_4 \xrightarrow{\Delta} CuSO_4 + H_2O + SO_2\uparrow$

$Ag + \text{conc. } H_2SO_4 \xrightarrow{\Delta} Ag_2SO_4 + H_2O + SO_2\uparrow$

② By oxidⁿ of metal sulphides

$Cu_2S + O_2 \xrightarrow{\Delta} Cu_2O + SO_2\uparrow$

$PbS + O_2 \xrightarrow{\Delta} PbO + SO_2\uparrow$

$HgS + O_2 \xrightarrow{\Delta} HgO + SO_2\uparrow$

③ Decomposⁿ of $FeSO_4$

$2FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

- $FeSO_4$ on decomposⁿ gives both oxides of S → SO_2 & SO_3

④ S_8 or $H_2S \xrightarrow{+} \text{conc. } H_2SO_4 \xrightarrow{\Delta} SO_2 + H_2O$

- Properties

✓ SO_2 is an acidic oxide dissolved in H_2O to give solⁿ of H_2SO_3

$H_2O + \overset{+4}{SO_2} \longrightarrow \overset{+4}{H_2SO_3}$

✓ ON of S → −2 to +6

✓ SO_2 acts both as an OA & RA

↳ $\overset{+4}{CO_2}$ + acid. $KMnO_4$ (strong OA) + $H^+ \longrightarrow MnSO_4 + \overset{+6}{K_2SO_4}$

$\overset{+4}{SO_2} + KI$ (strong RA) $+ H^+ \longrightarrow \overset{0}{S} + I_2$

* SO_2 acts as a Temporary bleaching agent → It bleaches by redⁿ

classmate
Date
Page

[2] SO_3

• Preparation

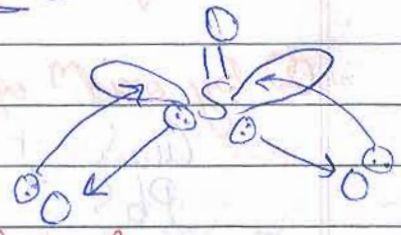
oxidⁿ of SO_2

$$SO_2 + \frac{1}{2}O_2 \xrightarrow[\Delta]{V_2O_5} SO_3$$

Ferrous gives both ✓
Ferric gives SO_3 ✓ only

$$FeSO_4 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$



• Properties

[1] ** SO_3 in GAS phase is triangular planar.

STRUCTURE

sp^2

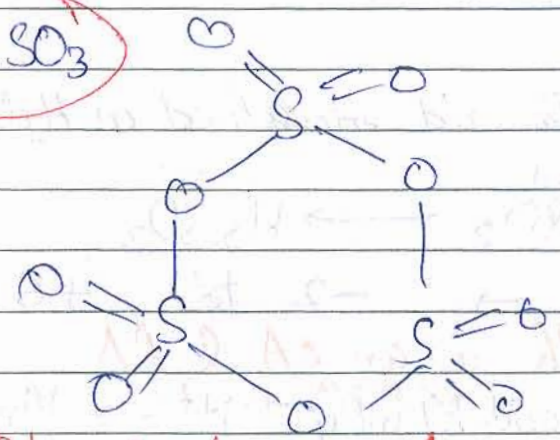
(g) (non polar)
($d\pi - p\pi$ back bonding exists b/w S & O here)

$SO_3(g)$ when condensed ⇒ $\gamma - SO_3$ allotrope i.e $(SO_3)_3$ trimer of SO_3 (S_3O_9)

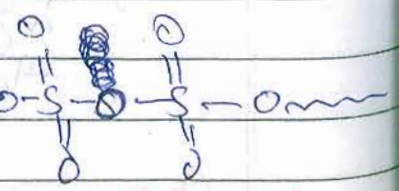
most abundant.

Y.V. Imp.

$\gamma - SO_3$

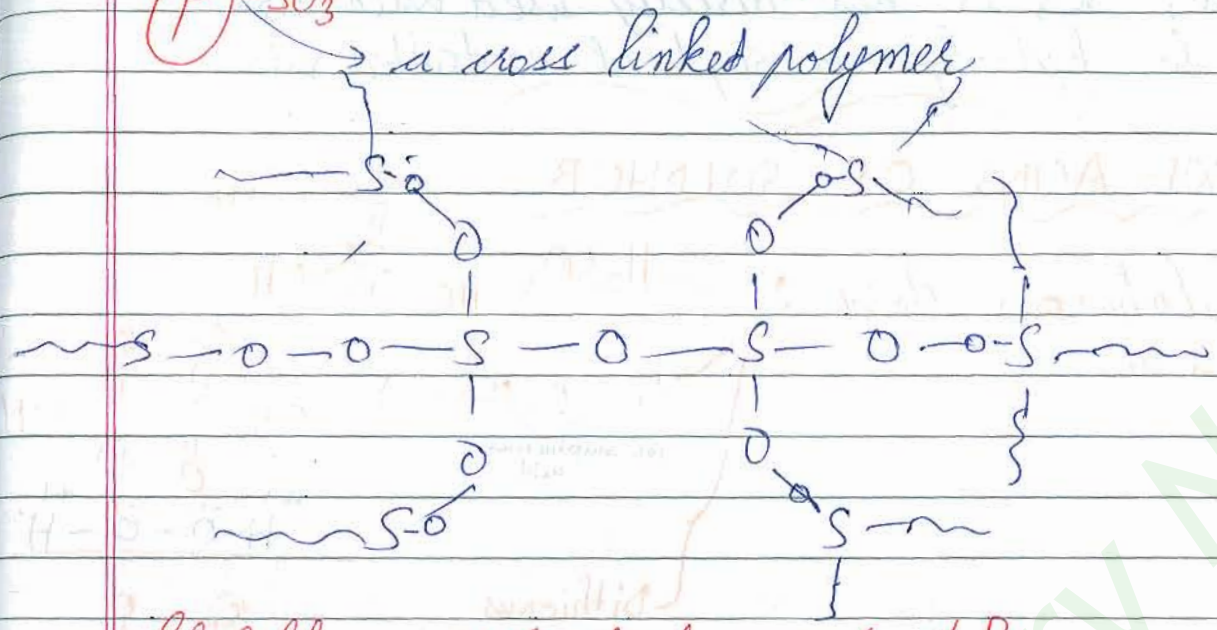


• $\gamma - SO_3$ Polymerises when left for long time ⇒ $\alpha - SO_3$



linear chain polymer of SO_3

If (α)-SO_3 / (β)-SO_3 is heated at high T, its converted into a cross linked polymer



Stability γ < αβ < α.β

Existence γ > βα > αβ

---

(2) SO_3 is anhydride of H_2SO_4, acts as a very strong dehydrating agent. SO_3 has very high affinity for moisture.

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

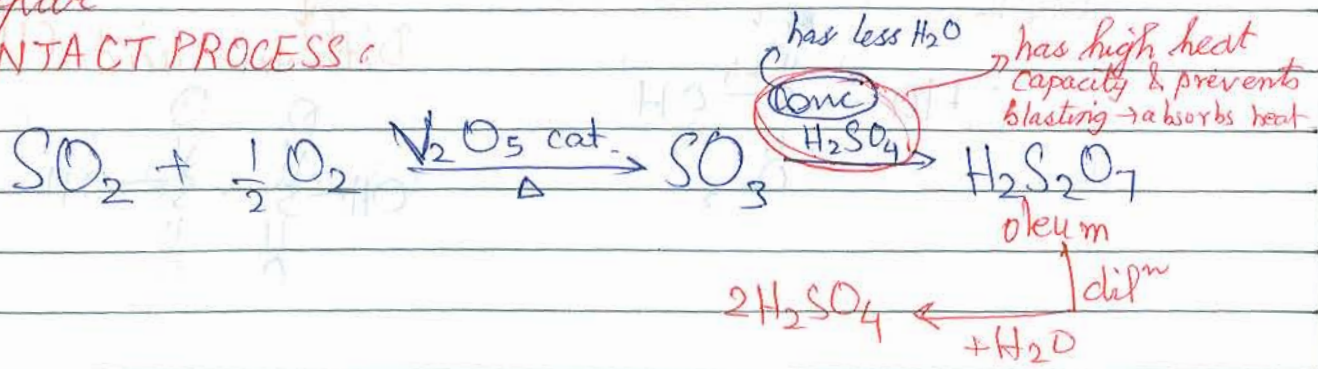
used for drying of ONLY acidic compd.
(basic compd → neutralizn)

---

(3) H_2SO_4

§ preparⁿ

CONTACT PROCESS:



Oxidⁿ state : of individual elements (in terms of contribⁿ)

ON : of overall.

$SO_3 + H_2O \longrightarrow H_2SO_4 \quad \Delta H < 0$.

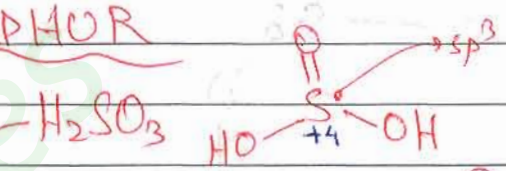
So, SO_3 is not directly used with H_2O.

So, hydrolysis is reqd at controlled rate.

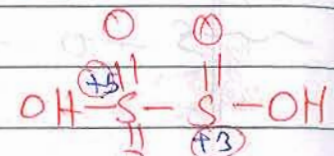
• OXY-ACIDS OF SULPHUR

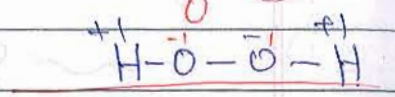
Sulphurous Acid series :

- H_2SO_3

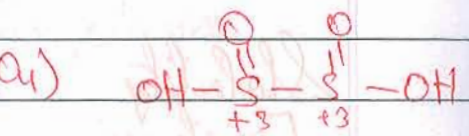


- $H_2S_2O_5$ (has S-S bond)
  pyro sulphurous acid



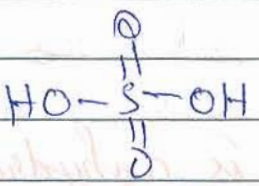


- Dithionus acid ($H_2S_2O_4$)
  (S-S bond)

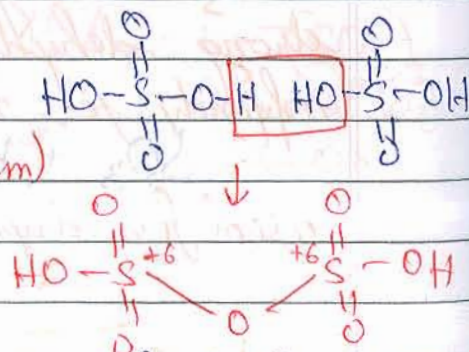


Sulphuric Acid Series :

- H_2SO_4

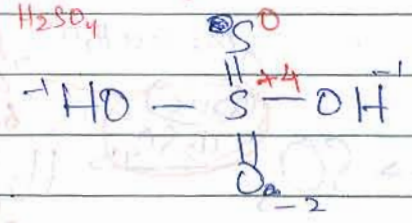


- Pyrosulphuric acid ($H_2S_2O_7$) (oleum)
  (S-O-S bond)

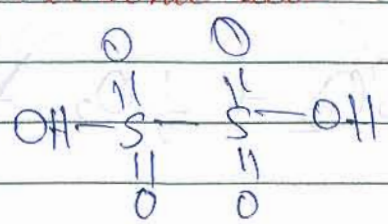


~~of~~ anhydride of H_2SO_4
(just as SO_3)

- Thiosulphuric acid
  $H_2S_2O_3$
  (replace one oxygen with sulphur of H_2SO_4)



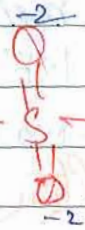
- Dithionic acid ($H_2S_2O_6$)



classmate
Date 5.1.11
Page

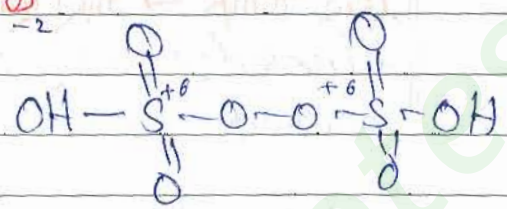
✱ Peroxy acids of S

✓ H_2SO_5 (Caro's acid)



Strong OA

✓ $H_2S_2O_8$ (persulphuric acid)



(commonly: MARSHAL ACID)

GROUP 17 : HALOGENS

Halogen's don't exist in nature in free state. They exists mainly in the form of their salts.

FLUORINE

✓ EXTRACTION

It exists in Fluorapatite (which contains $Ca_3(PO_4)_2 \cdot CaF_2$)
Cryolite (Na_3AlF_6)
Fluorspar (CaF_2)

• problems in extraction of fluorine.

- F being the most reactive elemt., combines with electrode material & material of electrolytic cell.
- Chemical OA, are not available for oxidn of fluoride (∵ F is strongest OA) → non ionisable.
- HF is almost non-electrolytic. ∴ It can't be electrolysed directly.

classmate
Date
Page

- **extraction by MOISSON METHOD**

In Moisson method, anhyd. HF was passed through dry KF & the Fermy salt (KHF_2) thus produced, was electrolysed at $-23°C$ (very low temp → molten state) in a bad retort, where fluorides were oxidised at Pt-Cu electrode giving $F_2(g)$

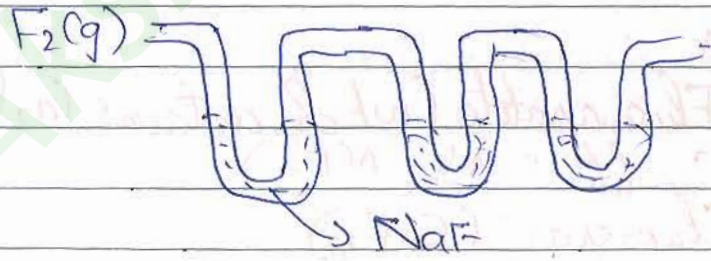
$$HF + KF \longrightarrow \underset{\text{Fermy salt}}{KHF_2} \xrightarrow[-23°C]{\text{electrolysed}} K^+ + H^+ + 2F^-$$

Pt-Cu electrode, $-23°C$:

$$2e^- + F_2(g)$$

- Low T is maintained to avoid the rxn of fluorine with electrode & its material.

The produce $F_2(g)$ is passed through U-tube containing NaF to absorb any HF if produced after electrolysis.



- **DENNIS METHOD**

In this method, Fermy salt is electrolysed in graphite chamber at ≈ 120°C & the fluorides were oxidised at graphite electrode.

Some CF_4 formed were isolated from the product mixture.

$NaClO_3$, $NaIO_3$: very strong OA

common

F_2 oxidises even them.

① $2F_2 + 2H_2O \xrightarrow{RT} 4HF + O_2$

$3F_2 + 3H_2O \xrightarrow{RT} 6HF + O_3$

$2F_2 + 2H_2O \xrightarrow{\Delta} 4HF + O_2$ only

- **With alkali**

$F_2 + \underset{\text{DILUTE}}{NaOH} \longrightarrow \overset{(+2)}{OF_2} + NaF + H_2O$

(only compd with Oxygen in +ve oxidn state) → unstable

$F_2 + NaOH \xrightarrow[(\text{or dil.} + \Delta)]{\text{CONC}} NaF + O_2 + H_2O$

- **With non-metals** (F_2 doesn't react with N_2 & O_2 at RT)

$H_2 + F_2 \rightarrow HF$

$P_4 + F_2 \rightarrow PF_5$

$S_8 + F_2 \rightarrow SF_6$

$C + F_2 \rightarrow CF_4$

$Cl_2 + F_2 \rightarrow ClF \xrightarrow[\text{excess}]{F_2} ClF_3$ ③

$Br_2 + F_2 \rightarrow \rightarrow \rightarrow BrF_5$ ⑤

$I_2 + F_2 \rightarrow \rightarrow \rightarrow \rightarrow IF_7$ ⑦

- **With metals**

With exception of Ir, Pt & Au, F_2 combines with all metals at RT producing fluorides.

$Fe + F_2 \rightarrow FeF_3$

$Sn + F_2 \rightarrow SnF_4$

$Cu + F_2 \rightarrow CuF_2$

} all in their highest oxidn state ∴ F_2 is strongest OA

$NaClO_3 + F_2 \xrightarrow{+H_2O} NaClO_4 + 2HF$

$NaIO_3 + F_2 \xrightarrow{+H_2O} NaIO_4 + 2HF$.

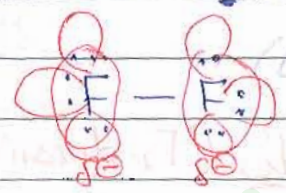
* Properties of F_2

- $F_2(g)$ → light yellow colored gas at RT
  - → Strongest OA
  - → most electro -ve element in P. table.

• BE – BL relationship

	F–F	Cl–Cl	Br–Br	I–I
BL	F–F <	Cl–Cl <	Br–Br <	I–I
BE	Cl–Cl >	Br–Br >	F–F >	I–I

(Note, ~~BE ∝ 1/BL~~ only case)

Reason:-  : High electrostatic repulsion. Bond becomes strained. So, BE ↓

- Similar case :- Peroxide —O—O— : very less BE.

• Oxidising property

Oxidising power F_2 (strongest) $> Cl_2 > Br_2 > I_2$

So, It displaces halides of lower grp elements from its solution.

$$F_2 + 2X^- \longrightarrow X_2 + 2F^-$$

$X = Cl, Br, I$

Illy, Cl oxidises Br, I, Br oxidises I, I oxidises none AMONG this group. Otherwise, they all are OAs.

* Reactions of F_2

• Rxn with water

F_2 in water $\xrightarrow[+H_2O \text{ at } RT]{\text{oxidises}}$ $O_2 + O_3 \xrightarrow[\text{heat}]{\text{~~high~~}}$ O_2 only (O_3 → unstable, breaks into O_2)

CHLORINE

Chlorine is present in the form of chloride salts in sea water.

Cl_2 in earth crust in ores

Carnalite ($KCl \cdot MgCl_2 \cdot 6H_2O$)

Horn Silver ($AgCl$)

- **extraction of chlorine**

DECON'S PROCESS

Industrial

$NaCl + H_2SO_4 \longrightarrow Na_2SO_4 \uparrow HCl$

(or any chloride salt) — CONC

$HCl + MnO_2 \longrightarrow MnCl_2 + Cl_2 + H_2O$

anhyd. Pyrolusite

Mineral having MnO_2

Lab

$Cl_2(g)$ is produced –

(a) By oxidⁿ of chloride salts with strong OA, like $KMnO_4/H^+$, $K_2Cr_2O_7/H^+$, $NaClO_3/H^+$

(b) By action of bleaching pwd. with dil H_2SO_4 or dil HCl.

$CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$

$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + Cl_2$

(c) Electrolysis of aq or molten chloride salt :- purest form is obtained.

- **Properties**

$Cl_2(g)$ ⟶ Yellowish-green gas at RT

⟶ neither burns nor supports combustion. So, chlorinated polymer (like PVC) is used in high fire areas

⟶ non-porsonous. → max. E_a (electron affinity)

$Ca(OCl)Cl$ → Responsible for Bleaching action

Relate

- **chemical property :-**

(a) Rxn with water

$$Cl_2 + H_2O \longrightarrow \overset{-1}{H}Cl\uparrow + H\overset{+1}{O}Cl$$

→ also does bleaching.

$\Rightarrow Cl_2$ disproportionate in H_2O.

(b) With alkali

$$Cl_2 + NaOH(aq) \xrightarrow{RT} NaCl + NaOCl + H_2O$$

base → any

also bleaching agent

If left for long time

$$NaOCl \longrightarrow NaCl + NaClO_3$$

i.e $$Cl_2 + NaOH(aq) \xrightarrow{boil} NaCl + NaClO_3 + H_2O$$

- $Cl_2 + Ca(OH)_2$ (alkali)

$\xrightarrow{40°C}$ $Ca(OCl)Cl + H_2O$ → bleaching pwd.

$\xrightarrow{RT}$ $Ca(OCl)_2Cl_2 + H_2O$

→ crystallizⁿ temp. of $Ca(OCl)Cl$.

(c) With CO, SO_2, NO

$$Cl_2 + CO \longrightarrow COCl_2 \text{ (phosgene)}$$

$$Cl_2 + 2NO \longrightarrow 2NOCl$$

$$Cl_2 + SO_2 \longrightarrow SO_2Cl_2$$

$$Cl_2 + SO_3 \longrightarrow SOCl_2 + O_2$$

(d) With metals

$$Cl_2 + \underset{\text{hot iron}}{Fe} \xrightarrow{\Delta} \underset{\text{ANHYD}}{FeCl_3}$$

only method for anhyd. metal chloride

(F reacted with metals at RT)

$$Fe_2O_3 + HCl \rightarrow FeCl_3 + H_2O$$

HYDROUS

$$Cl_2(g) + Sn \xrightarrow{\Delta} SnCl_4 \text{ (not } SnCl_2\text{)}$$

anhyd.

(e) With non metals

$Cl_2 + H_2 \xrightarrow{\Delta} 2HCl$

$Cl_2 + P_4 \xrightarrow{\Delta} PCl_3 + PCl_5$

$Cl_2 + S_8 \xrightarrow{\Delta} S_2Cl_2$

BROMINE

Occurs mainly as bromide salts → NaBr, $MgBr_2$ in sea water & some bromates → $NaBrO_3$ in earth crust

Its extracted by oxidⁿ of bromide with MnO_2, $Cr_2O_7^{2-}$, MnO_4^-, ——— etc.

Rxns of Br

↳ match with Cl. Same.

Properties

Br_2 → B.Pt. → 35°C ⇒ At RT (25°) → highly volatile brown colored liqd.

→ like Cl_2, Br_2 disproportionate in H_2O with dil. NaOH, NaOBr is formed which on standing / boiling disproportionate further to BrO_3^- & Br^-

→ doesn't form bleaching pwd. but possesses bleaching properly. (i.e its an OA).

IODINE

Source :- • Chile Salt Petre ($NaIO_3$) (or Salt petre)
• Sea weeds (Kelps)

Iodine is obtained by chemical redⁿ method of salt petre.

$\overset{+5}{NaIO_3} + 3\overset{+5}{NaHSO_3} \longrightarrow 3\overset{+6}{NaHSO_4} + \overset{-1}{NaI}$

(limiting Reagent)

The acidic iron flushes reacts with NaI giving

$$HI + HIO_3 \longrightarrow I_2 + H_2O$$

- **Properties**

I_2 (s) → deep violet, solid at RT

→ very low solubility in water. However, solubility is increased greatly if NaI or KI is added (∵ I_2 doesn't dissolve in H_2O in free state)

Improve solubility

$$I_2 + NaI \longrightarrow NaI_3$$

It is present in NaCl, which is water soluble.

with alkali

$$I_2 + NaOH(dil) \longrightarrow NaI + NaOI$$

Alkali (any)

left or boiled.

$$NaI + NaIO_3$$

with $Na_2S_2O_3$ → oxidising action of I_2

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$$

($I^0 \rightarrow I^{-1}$; $S^{+2} \rightarrow S^{+10/4}$)

Sodium di-thionate

→ highly antiseptic, forms deep blue colour water soluble complex with Starch

In hospitals:- Starch + Iodine ⇒ Blue soln.

☆ Acids of Halogens

§ HF

- **preparation**

HF is obtained by distillⁿ of CaF_2 (fluorspar) in [conc] H_2SO_4

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$$

conc

HF produced always contain some moisture as impurity (H-bonding → HF has high affinity for H_2O)

classmate
Date 7/1/11
Page

preduce dry HF :- ~~dt~~ dried with common acidic oxides → N_2O_5, P_2O_5, Cl_2O_7, SO_3

• anhyd. HF is also obtained directly by distillⁿ of Fermi salt

• Properties

HF → a gas at RT, has highest solubility in H_2O (among HX) (∵ H-bonding)

→ weak monobasic acid (∵ strong covalent character b/w H & F)

→ ETCHING of Glass → i.e designing of glass.

HF attack glass.

$HF + SiO_2 \longrightarrow SiF_4 + H_2O$: Softening action.

$SiF_4 + 2HF \longrightarrow H_2SiF_6$: glass dissolves.

Hydrofluorosilicic acid

i.e HF (excess) + Glass (SiO_2) → glass dissolves.

Oxides of Chlorine

Cl_2O

ClO_2

Cl_2O_6

Cl_2O_7

(1) Cl_2O

• preparation

$2Cl_2 + HgO \xrightarrow{\Delta} Cl_2O^{(g)} + HgCl_2 \downarrow$

(HgO: mercuric oxide)

• properties

$Cl-O-Cl$ (g) (Cl_2O: +1 on each Cl)

$Cl_2O + H_2O \longrightarrow 2HOCl$ (+1) : simple hydrolysis

$+ NaOH\ (dil.) \longrightarrow NaOCl \xrightarrow{\text{long standing}} NaCl + NaClO_3$

$+ NaOH\ (conc.) \longrightarrow NaCl + NaClO_3$

• all oxides of Cl are strong OA. Their oxidising power ↑ with ON.

Oxy acids of Cl :- $\overset{+1}{HOCl}$, $\overset{+3}{HClO_2}$, $\overset{+5}{HClO_3}$, $\overset{+7}{HClO_4}$

<2> ClO_2

• prepar^n $NaClO_3 + \underset{\text{oxalic acid}}{(COOH)_2} \longrightarrow ClO_2 + Na_2C_2O_4 + CO_2 + H_2O$

$+ \underbrace{SO_2 + H_2O}_{\text{Reduce ON by one}} \longrightarrow ClO_2 + NaHSO_4$

• property $O=\dot{\underset{\cdot}{Cl}}^{118°}=O$ ⇒ paramagnetic ; polar covalent molecule

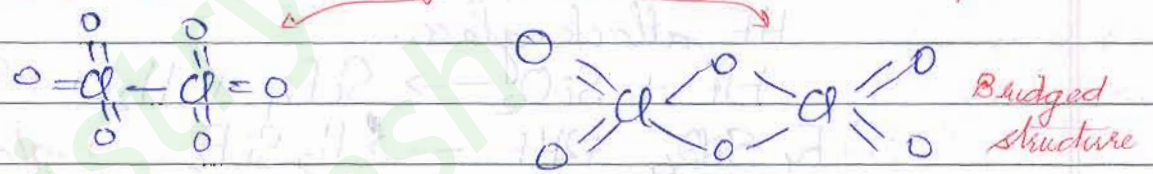
$2\overset{+4}{Cl}O_2 + H_2O \longrightarrow \overset{+3}{HClO_2} + \overset{+5}{HClO_3}$ ⇒ ClO_2 is a mixed anhydride

$+4 \rightarrow \frac{(+3)+(+5)}{2}$

<3> Cl_2O_6

• prepar^n $2ClO_2 + 2O_3 \xrightarrow{\Delta} Cl_2O_6 + 2O_2$

• property → Cl_2O_6 : stable at very low Temp. So, has 2 proposed st.



✓ Cl-Cl bond & Cl-O-Cl bond.

$\overset{+6}{Cl_2O_6} + H_2O \longrightarrow \overset{+5}{HClO_3} + \overset{+7}{HClO_4}$

$+6 = (+5)+(+7)$

Hy. $Cl_2O_6 + NaOH \xrightarrow{2} NaClO_3 + NaClO_4$

* • $Cl_2O_6 + \frac{1}{2}N_2O_4 \longrightarrow ClO_2 + [NO_2^+][ClO_4^-]$.

Salt : nitronium perchlorate

✓ white solid ✓ volatile.

<4> Cl_2O_7

• prepar^n $HClO_4 + \underset{\text{dehydrating agent}}{P_4O_{10}} \xrightarrow{\Delta} Cl_2O_7 + HPO_3$ (always produced)

• property ⇒ Cl-O-Cl bond present.

✓ strong OA, anhydride of perchloric acid ($HClO_4$)

Inter

INTER HALOGENS : Compd of more than 1 type of halogens.

eg : ICl, ClF, ClF_3, IF_5, IF_7, ICl_4

formed by direct combin^n of elements. - F, learns max. no. of inter halogens (most electro -ve)

PSEUDO HALIDES:

Mono -ve anion (i.e charge -1) which do not contain halides, but resemble halides in some of their chem. rxns.
eg: CN^-, SCN^-, NCO^- : most common ; resemble with properties of Cl^-
* Presence of N is necessary for pseudohalides. The -1 charge is on N.

PSEUDO HALOGENS: Properties similar to halogen.

eg: $(CN)_2 \equiv (N\equiv C-C\equiv N)$.·. Cl – Cl .
→ cyanogen ; gas at RT like Cl_2, has single covalent bond like Cl–Cl .

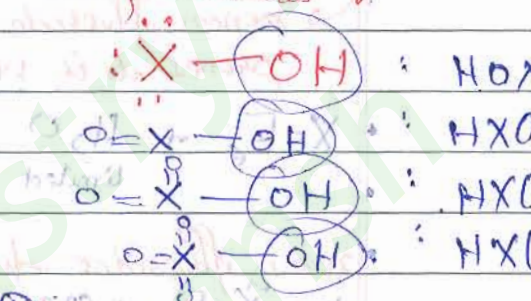
OXY ACIDS OF HALOGENS

HOX
HXO_2
HXO_3
HXO_4
} forms.
⇒ All have +ve oxidn state on E X.

NO oxy acids of F exist (∵ +ve charge on F is not possible. Moreover, (For HFO_2, HFO_3 & HFO_4 octet of F will be violated)

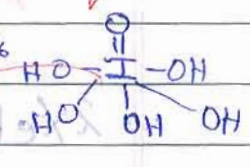
§ Structures ↓

HOCl	HOBr	HOI	: HOX
$HClO_2$	$HBrO_2$	HIO_2	: HXO_2
$HClO_3$	$HBrO_3$	HIO_3	: HXO_3
$HClO_4$	$HBrO_4$	HIO_4	: HXO_4



• For comparing acidic strength, give preference to ① no. of oxygen.
(∵ More oxygen, more e^- withdrawing effect → more acidity ! & with more no. of O_2, its conj. base will have more no of resonance str.)
② E_N of halogen. E_N ↑, acidity ↑ (–I effect)

• Q. On basis of above preference order, $HClO_4$ should have been strongest acid. But, HIO_4 is strongest. R. Why?
A: $HIO_4 + 2H_2O \longrightarrow H_5IO_6$ (due to larger size of I_2) ≡ H_5IO_6



more no. of e^- withdrawing grp.

So, $HIO_4 > HClO_4$: acidity.

GROUP – 18

XENON

• Xenon Fluorides : XeF_2, XeF_4, XeF_6
Although Xe is inert, it is having very low IE. So, F attacks it to form compds.

$$Xe + F_2(g) \xrightarrow{2:1} XeF_2$$
(2 : 1 — molar ratio)

$Xe + F_2(g) \xrightarrow{1:5} XeF_4$

$\xrightarrow{1:20} XeF_6$

These rxns are reversible. So, its form^n is very weak. So, XeF_4, XeF_6 (higher fluorides of Xe) are produced from XeF_2 by heating with F_2 ($XeF_2 + F_2(g) \xrightarrow{\Delta} XeF_4, XeF_6$)

Property :- hydrolysis

$XeF_2 + H_2O \longrightarrow Xe + HF + O_2$

$XeF_4 + H_2O \longrightarrow XeO_3 + (Xe + HF + O_2)$ } $\Delta H < 0$

$XeF_6 + H_2O \xrightarrow{(excess)} XeO_3 + HF$

→ xenon fluoride is oxidising water in all 3 rxns which proves it is very strong oxidising agent

$XeF_6 + H_2O \xrightarrow{\text{limited}} XeOF_4 + 2HF$

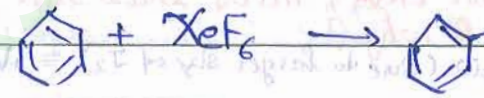
xenon oxo fluoride

- xenon fluorides displace halides from their aq. sol^n

ie $XeF_4 + Cl^- \longrightarrow Xe + F^- + Cl_2$

$+ Br^-/I^- \rightarrow Xe + F^- + Br_2/I_2$

- Alkane (or benzene) + XeF_6 ⟶ Mono fluorin^n of Alkane (or benzene)



- $2XeF_6 + SiO_2 \longrightarrow 2XeOF_4 + SiF_4$