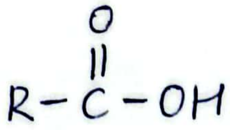
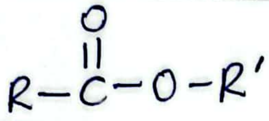
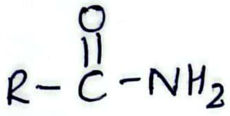
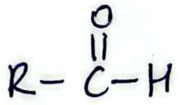
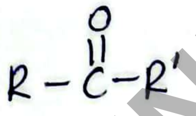
Surendra Sharma

Organic Chemistry.

Functional Group	Structure	Suffix	Prefix
Carboxylic acid	 $R-\overset{O}{\overset{\|}{C}}-OH$	-oic acid -carboxylic acid	Carboxy
Sulphonic acid	$R-SO_3H$	-sulphonic acid	Sulpho
Ester	 $R-\overset{O}{\overset{\|}{C}}-O-R'$	-oate (alkyl alkanoate)	Alkoxy carbonyl
Acid amide	 $R-\overset{O}{\overset{\|}{C}}-NH_2$	- amide - carboxamide	Carbamoyl
Acid chloride	 $R-\overset{O}{\overset{\|}{C}}-Cl$	- oyl chloride	Chloro formyl
Iso cyanide Nitrile/Cyanide	$R-N\equiv C$ $R-C\equiv N$	- nitrile	Cyana
Aldehyde	 $R-\overset{O}{\overset{\|}{C}}-H$	-al	Aldo or formyl or OXO
Ketone	 $R-\overset{O}{\overset{\|}{C}}-R'$	- one	Keto or OXO
Alcohol	$R-OH$	- ol	Hydroxy
Thiol	$R-SH$	-thiol	Mercapto
Amine	$R-NH_2$	- amine	Amino
Ether	$R-O-R'$	×	Alkoxy
Halogen	$R-X$	×	Halo
Nitro	$R-NO_2$	×	Nitro

Decrease in Priority of primary functional group ↓

Test of elements in organic compounds:

— Lassaigne's method.

Q. Reason for preparing sodium extract?

Org. compounds are covalent compounds & common laboratory reagents are ionic compound. So, organic compounds are fused with sodium metal so that covalently bonded org. compounds convert to ionic compound and can easily detected by common lab. reagents.

* Sodium extract is generally alkaline because during prep. of sod. extract excess sod. metal used reacts with water forming alkali. $2Na + H_2O \longrightarrow 2NaOH + H_2$

dirty green ppt.

$$6NaCN + Fe(OH)_2 \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$$

sodium ferrocyanide

(iv) Few drops of ferric chloride solution is added and then acidified with dil. HCl. Appearance of prussian blue or

(1) Detection of Nitrogen

(i) Preparation of sodium extract: $Na + C + N \xrightarrow{\Delta} NaCN$

(ii) Take 1ml of sodium extract in test tube and make it alkaline by adding NaOH if not alkaline:

$$2Na + H_2O \longrightarrow 2NaOH + H_2$$

(iii) 1 ml of freshly prepared ferrous sulphate solution is added into it, boiled and cooled.

$$FeSO_4 + 2NaOH \longrightarrow \underset{\text{dirty green ppt.}}{Fe(OH)_2\downarrow} + \cancel{H_2}\ Na_2SO_4$$

$$6NaCN + Fe(OH)_2 \longrightarrow \underset{\text{sodium ferrocyanide}}{Na_4[Fe(CN)_6]} + 2NaOH$$

(iv) Few drops of ferric chloride solution is added and then acidified with dil. HCl. Appearance of prussian blue or green color ~~precipitate~~ indicates presence of nitrogen in organic compound.

$$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\substack{\text{Ferric ferrocyanide}\\ \text{(prussian blue or green colour)}}}{Fe_4[Fe(CN)_6]_3} + 12NaCl$$

Role of HCl is to dissolve dirty green precipitate of ferrous hydroxide which otherwise masks the color.

$$\underset{\text{dirty green ppt.}}{Fe(OH)_2\downarrow} + HCl \longrightarrow FeCl_2 + H_2O$$

(2) Detection of nitrogen and sulphur together

If nitrogen and sulphur both are present in the organic compound, they may give NaCNS as sod. extract.

$$Na + C + N + S \longrightarrow \underset{\text{(sod. sulphocyanide)}}{NaCNS}$$

Few drops of sod. extract when treated with ferric chloride solution, blood coloration of ferric sulphocyanide is formed.

$$3NaCNS + FeCl_3 \longrightarrow \underset{\text{blood.}}{\underline{Fe(CNS)_3}} + 3NaCl$$

(3) Detection of Sulphur

Sodium extract: $2Na + S \rightarrow Na_2S$ (sodium sulphide)

① Lead acetate test: By adding few drops of lead acetate over 1ml of sod. extract. Formation of black color lead sulphide.

$$Na_2S + \underset{\text{Lead acetate}}{(CH_3COO)_2Pb} \longrightarrow \underset{\text{Lead sulphide (black ppt)}}{PbS\downarrow} + 2CH_3COONa$$

⑪ Sodium nitroprusside test.

Few drops of freshly prepared sod. nitroprusside solution is added to 1ml of sod. extract. Appearance of violet colour indicates the presence of S.

$$\underset{\text{sodium nitroprusside}}{Na_2S + Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{violet colour}}{Na_4[Fe(CN)_5NOS]}$$ [sodium thionitroprusside]

(4) Detection of Halogens

Sodium extract: $Na + X \longrightarrow NaX$

Before detection of ~~sodium~~ halide ion sodium extract is boiled with ~~Ha~~ HNO_3, why?

To remove interferring ions like CN^-, S^-, OH^-, etc. which would otherwise masks the colour and make difficulty for detection of halide ion:

For eg:- $CN^- + AgNO_3 \rightarrow \underset{\text{(white ppt.)}}{AgCN\downarrow} + NO_3^-$

$$Cl^- + AgNO_3 \rightarrow \underset{\text{(white ppt.)}}{AgCl\downarrow} + NO_3$$

So,

$$CN^- + HNO_3 \xrightarrow{\text{boil}} HCN\uparrow + NO_3^-$$

$$S^- + HNO_3 \xrightarrow{\text{boil}} H_2S\uparrow + NO_3^-$$

$$OH^- + HNO_3 \xrightarrow{\text{boil}} H_2O + NO_3^-$$

Halide ion is detected by silver nitrate test:-

Take few sodium extract in test tube and add aqueous silver nitrate after treating it with HNO_3.

i. $Cl^- + AgNO_3 \longrightarrow AgCl\downarrow + NO_3^-$. [white ppt. is obtained]

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Diammine silver chloride}}{[Ag(NH_3)_2]Cl} + 2H_2O$$ [soluble in NH_4OH]

$$[Ag(NH_3)_2]Cl + 2HNO_3 \longrightarrow AgCl\downarrow + 2NH_4NO_3$$ [white ppt. reappers on adding HNO_3]

(ii) $Br^- + AgNO_3 \longrightarrow AgBr\downarrow + NO_3^-$ [Pale yellow ppt sparingly soluble in NH_4OH & reappers slowly to give pale yellow ppt.]

(iii) $I^- + AgNO_3 \longrightarrow \underset{\text{(Yellow ppt.)}}{AgI} + NO_3^-$ [Yellow ppt. insoluble in NH_4OH]

Preparation of alkanes:- (Paraffins: little affinity)

1. Decarboxylation [Removal of CO_2 as CO_3]

$$R-\overset{\overset{O}{\|}}{C}-ONa + NaOH \xrightarrow[\Delta]{CaO} R-H + Na_2CO_3$$

2. Catalytic hydrogenation : [Ni, Pt or Pd]

$$R=R + H_2 \xrightarrow[\Delta]{Ni} R-R$$

$$R\equiv R + 2H_2 \xrightarrow[\Delta]{Ni} R-R$$

3. Removal of Halides:- [Reducing agents → H, H_2/Ni, HI, $LiAlH_4$, HI, red P hsw]

$$R-X + 2[H] \xrightarrow{Zn/HCl} R-H + H-X$$

(Hydrogenhalide)

4. Wurtz reaction:

$$R-X + 2Na + X-R \xrightarrow[\Delta]{dry\ ether} R-R + 2NaX$$

5. Grignard's reagent (Alkyl Magnesium halide) [RMgX]

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

Active Hydrogen (H_2O, alcohol, ether, etc) or hydrogen bonded with more electronegative atom

6. Kolbe's electrolysis:

$$2RCOONa_{(aq)} \rightleftharpoons 2RCOO^- + 2Na^+$$

Sodium salt of fatty acid

At anode (Oxidation):-

$$2RCOO^- \longrightarrow 2RCOO + 2e^-$$

$$2RCOO \longrightarrow \underline{R-R} + 2CO_2$$

At cathode (Reduction):

$$2Na^+ + 2H_2O + 2e^- \longrightarrow 2NaOH + H_2\uparrow$$

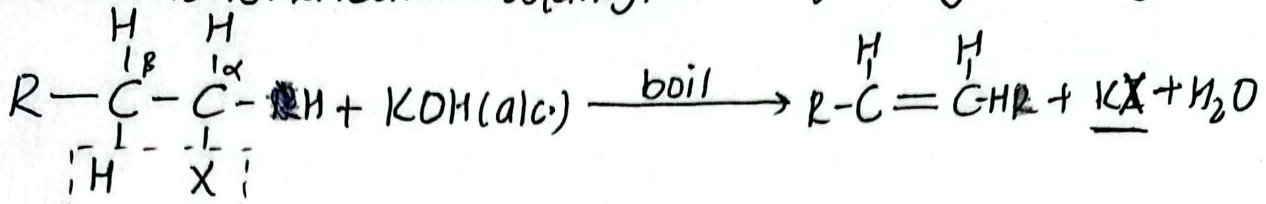
7. From Aldehydes and Ketones:-

$$* \quad R-\overset{\overset{O}{\|}}{C}-H + 4[H] \xrightarrow{Zn\text{-}Hg + conc\ HCl} \underline{R-CH_3} + H_2O$$

$$* \quad R-\overset{\overset{O}{\|}}{C}-R + 4[H] \xrightarrow{Zn\text{-}Hg + Conc.\ HCl} \underline{R-CH_2-R} + H_2O$$

Preparation Of Alkene

1. From monohaloalkanes(alkyl halides): Dehydrohalogenation



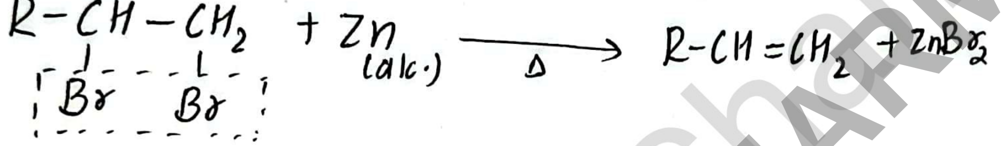
$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H + KOH(alc.) \xrightarrow{boil} R-\overset{H}{C}=\overset{H}{C}HR + \underline{KX} + H_2O$$

[α- attached with X
β- attached with H]

[I > Br > Cl
3° > 2° > 1°]

* Saytzeff rule: (i) Alkene with higher number of Alkyl Groups is major product formed and
(ii) lesser number of alkyl group (less substituted alkene) is minor product.

2. From 1,2-dihaloalkanes: Dehalogenation (-X)



$$R-\underset{Br}{CH}-\underset{Br}{CH_2} + Zn_{(alc.)} \xrightarrow{\Delta} R-CH=CH_2 + ZnBr_2$$

3. From alkynes: Catalytic hydrogenation

$$R-C\equiv C-H + H_2 \xrightarrow[\text{(Partially poisoned)}]{Pd/BaSO_4} R-\overset{H}{C}=\overset{H}{C}-H$$

$Pd/BaSO_4$ → Lindlar catalyst

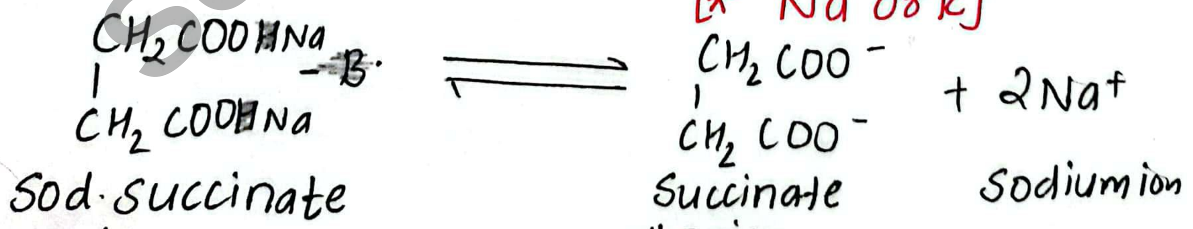
4. From alcohol: Dehydration

$$R-\underset{H}{CH}-\underset{OH}{CH_2} \xrightarrow[Al_2O_3,\,170°C]{acid\,(conc.\,H_2SO_4)} R-CH=CH_2 + H_2O$$

* Ease of dehydration of alcohol: 3° > 2° > 1°

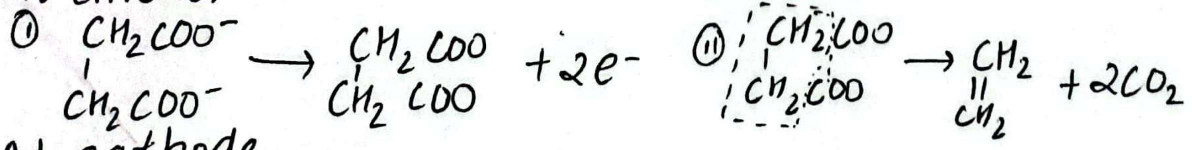
5. From Sodium succinate: Kolbe's electrolytic decarboxylation

[* Na or K]



$$\begin{matrix} CH_2COONa \\ | \\ CH_2COONa \end{matrix} \rightleftharpoons \begin{matrix} CH_2COO^- \\ | \\ CH_2COO^- \end{matrix} + 2Na^+$$

#At anode:



$$① \begin{matrix} CH_2COO^- \\ | \\ CH_2COO^- \end{matrix} \longrightarrow \begin{matrix} CH_2COO \\ CH_2COO \end{matrix} + 2e^- \qquad ⓘⓘ \begin{matrix} CH_2COO \\ | \\ CH_2COO \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO_2$$

#At cathode

$2Na^+ + 2e^- + H_2O \rightarrow 2NaOH + H_2$

Laboratory preparation of ethene/ethylene.

→ When ethanol is heated with excess of conc. sulphuric acid at 160° to 170° ethene gas is obtained. Reaction is completed in two steps:

(i) At 100°c, ethyl alcohol reacts with conc. H_2SO_4 to give ethyl hydrogen sulphate.

$$CH_3CH_2OH + H_2OSO_3H \xrightarrow{100°C} CH_3CH_2OSO_3H + H_2O$$

(ii) At 170°c, ethyl hydrogen sulphate decomposes to ethene with release of sulphuric acid.

$$CH_3-CH_2-O-SO_3H \xrightarrow{170°} CH_2=CH_2 + H_2SO_4$$

Therefore, overall reaction is:

$$CH_3CH_2OH \xrightarrow[170°C]{Conc. H_2SO_4} CH_2=CH_2 + H_2O$$

Note: If the temperature is below 170°c and alcohol is excess then diethyl ether is formed as major product.

$$\underset{(excess)}{2\,CH_3CH_2OH} \xrightarrow[140°]{Conc. H_2SO_4} \underset{(Diethyl\ ether)}{CH_3CH_2-O-CH_2CH_3} + H_2O$$

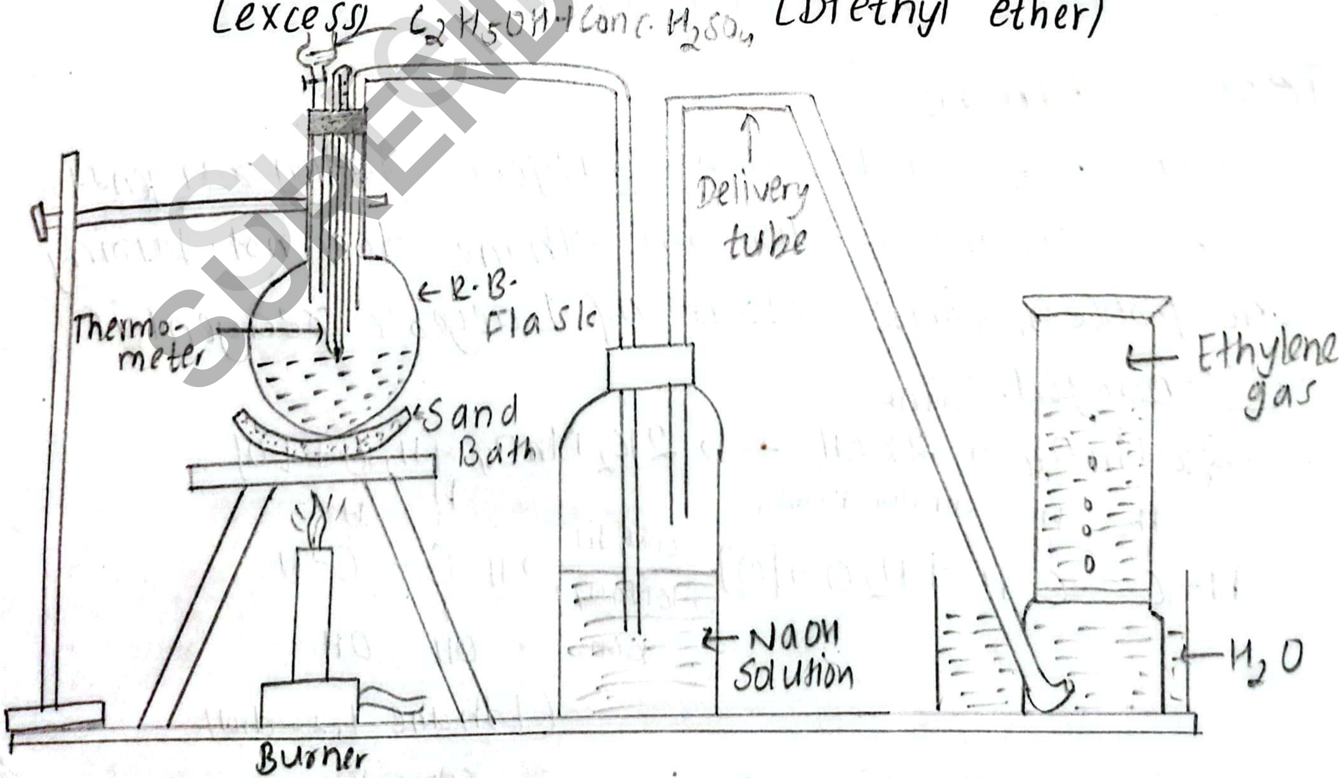


Fig: Laboratory preparation of ethene

Procedure:

Mixture of ethanol (50ml) and conc. H_2SO_4 (100ml) is taken in R.B. flask fitted with dropping funnel, thermometer and delivery tube as shown in the figure. Small amount of aluminium sulphate and sand are added to R.B. flask to prevent frothing (fizz) and facilitate dehydration. and heated to 170°C. Ethene gas is formed with impurities like SO_2, CO_2, etc

$$\text{Conc. } H_2SO_4 \longrightarrow SO_2 + H_2O + [O]$$

$$C_2H_5OH + 6[O] \longrightarrow 2CO_2 + 3H_2O$$

The mixture of gas is passed through bottle containing NaOH solution and absorbs CO_2 and SO_2 while undissolved ethene gas is collected in gas jar by downward displacement of water.

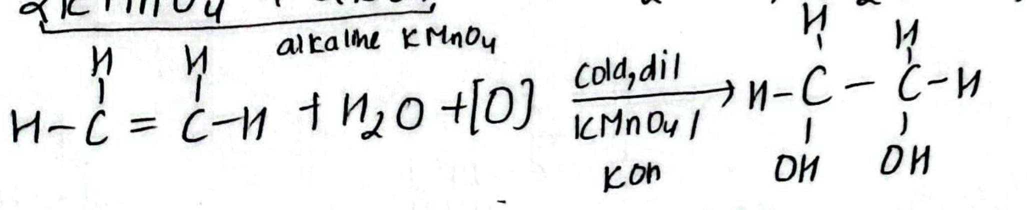
$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

Test of Ethene:

Ethene reacts with Baeyer's ~~solution~~ reagent to give ethane-1,2-diol but ethane does not. During the process, pink colour of Baeyer's reagent is discharged.

$$\overset{\text{pink}}{\underbrace{2KMnO_4 + 2KOH}_{\text{alkaline } KMnO_4}} \longrightarrow 2K_2MnO_4 + H_2O + [O]$$



$$H-\overset{H}{C}=\overset{H}{C}-H + H_2O + [O] \xrightarrow[KMnO_4/KOH]{\text{Cold, dil}} H-\underset{OH}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H$$

(Ethane-1,2-diol)
colourless

Chemical properties of Alkenes:-

* Addition reaction

(i) With H_2 (Catalytic hydrogenation)

$$>C=C< + H_2 \xrightarrow[\Delta]{Pt, Ni or Pd} -\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- + energy$$

(Alkane)

(ii) Halogenation (X_2 : Cl_2, Br_2, I_2]

$$-\overset{|}{C}=\overset{|}{C}- + X_2 \xrightarrow{inert solvent} -\overset{|}{\underset{X}{C}}-\overset{|}{\underset{X}{C}}-$$

[Inert solvent: CCl_4, $CHCl_3$]

(Dihaloalkane)

(iii) Hydrohalogenation (HX: HCl, HBr, HI)

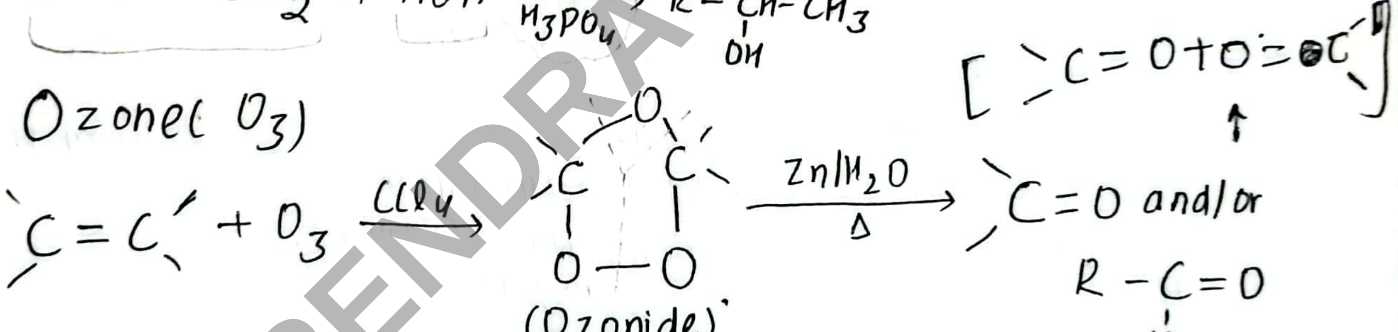
$$-\overset{|}{C}=\overset{|}{C}- + HX \longrightarrow H-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-H$$

[Follows Markovnikov's rule] (Haloalkane)

(iv) Hydration (H_2O)

$$R-CH=CH_2 + HOH \xrightarrow[H_3PO_4]{H_2SO_4 or} R-\underset{OH}{CH}-CH_3$$

(v) Ozone(O_3)



(Ozonide)

(Aldehyde and/or ketone)

(vi) H_2SO_4

$$RCH=CH_2 + H-OSO_3H \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OSO_3H}{C}}- \xrightarrow[\Delta]{H_2O} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- + H_2SO_4$$

(Alkene) (conc.) (Alkyl hydrogen sulphate) (alcohol)

* Oxidation with alkaline $KMnO_4$ (Baeyer's reaction) (unsaturation test)

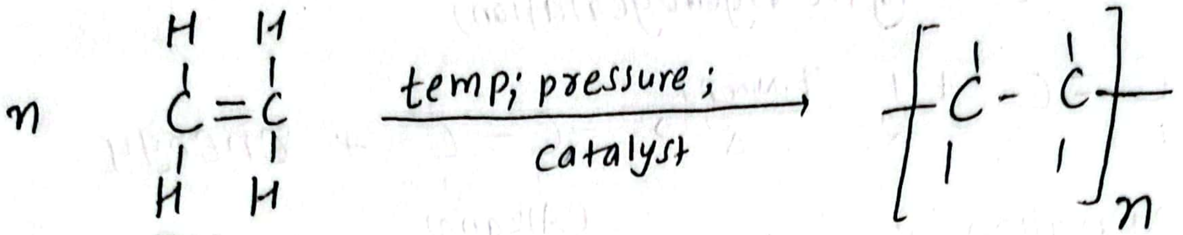
$$\underline{2KMnO_4 + 2KOH} \rightarrow 2K_2MnO_4 + H_2O + [O]$$

[Alkaline $KMnO_4$] → Pink colour

$$>C=C< + H_2O + [O] \xrightarrow[OH^-]{cold/dil\ KMnO_4/} -\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{OH}{C}}-$$

(1,2-diol) [colourless]

* Polymerization:



$$n\;\begin{matrix}H & & H\\ | & & |\\ C & = & C\\ | & & |\\ H & & H\end{matrix}\xrightarrow[\text{catalyst}]{\text{temp; pressure;}}\left[\begin{matrix} & | & & | & \\ - & C & - & C & -\\ & | & & | & \end{matrix}\right]_n$$

Ethene
(Monomer)

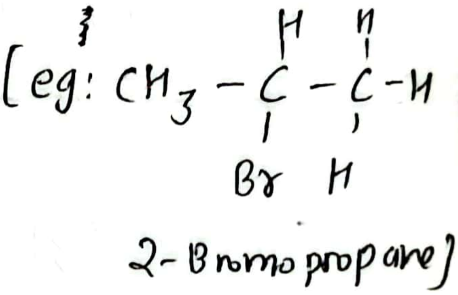
Polyethene
(Polymer

Markovnikov's rule

$$R-\overset{H}{\overset{|}{C}}=CH_2+\overset{\delta+}{H}-\overset{\delta-}{X}\longrightarrow \cancel{CH_3}\;R-\underset{X}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}H_3$$

(unsymmetrical unsaturated org. compound
↓
cannot be divided into two equal halves

(unsymmetrical reagent; cannot be divided into two equal halves)
↓
negative part added to unsaturated Carbon with less number of hydrogen)



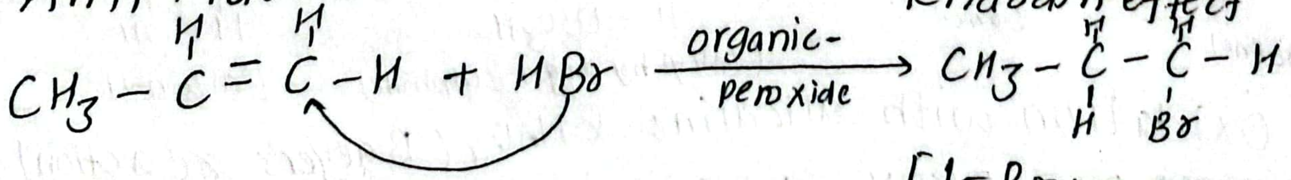
$$[\text{eg: } CH_3-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

2-Bromopropane]

$$\left[H-\overset{H}{\overset{|}{C}}\;\vdots\!=\;\overset{H}{\overset{|}{C}}-H\qquad CH_3-CH\;\vdots\!=\;CH_2\right]$$

Symmetrical unsymmetrical)

Anti Markovnikov's rule peroxide effect or Kharash effect



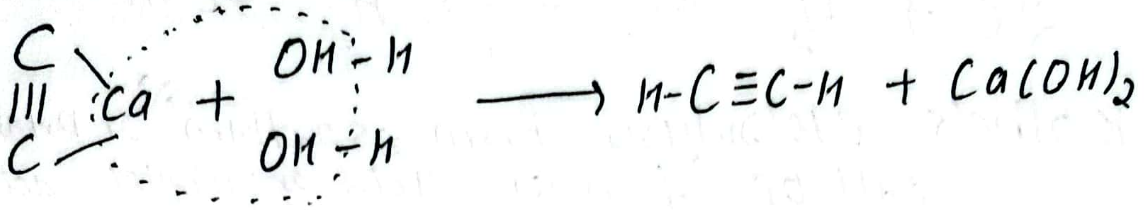
$$CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-H+HBr\xrightarrow[\text{peroxide}]{\text{organic-}}CH_3-\underset{H}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-H$$

[1-Bromo propane)

[Bromine added to unsaturated carbon having more number of hydrogen in presence of traces of organic peroxide]

Preparation of Alkyne (Acetylene)

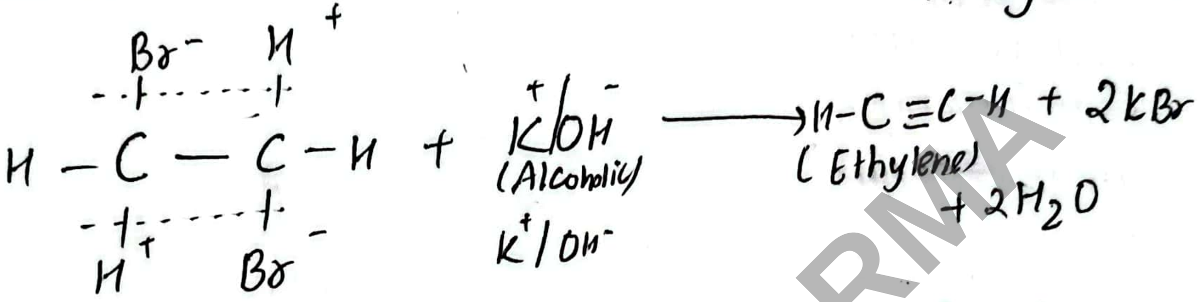
* Laboratory Preparation:



$$\begin{matrix}C\\ |||\\ C\end{matrix}\!\!>Ca + \begin{matrix}OH-H\\ OH-H\end{matrix} \longrightarrow H-C\equiv C-H + Ca(OH)_2$$

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

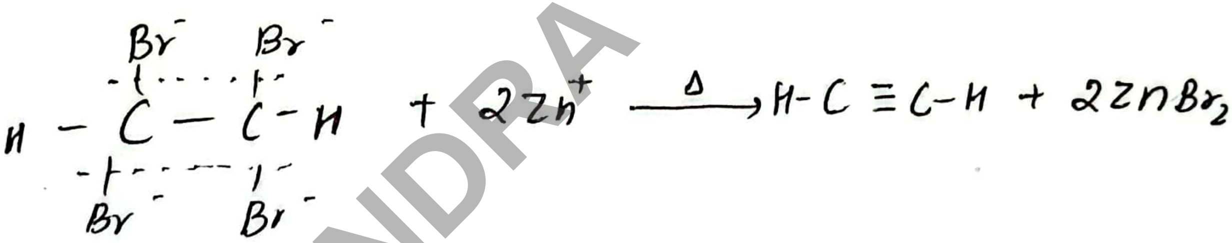
1. From 1,2-dibromo ethane (Elimination) (Dehydro-halogenation)



$$H-\overset{\overset{Br^-}{|}}{\underset{\underset{H^+}{|}}{C}}-\overset{\overset{H^+}{|}}{\underset{\underset{Br^-}{|}}{C}}-H + \underset{\substack{(Alcoholic)\\ K^+/OH^-}}{\overset{+\ \ -}{K/OH}} \longrightarrow \underset{(Ethylene)}{H-C\equiv C-H} + 2KBr + 2H_2O$$

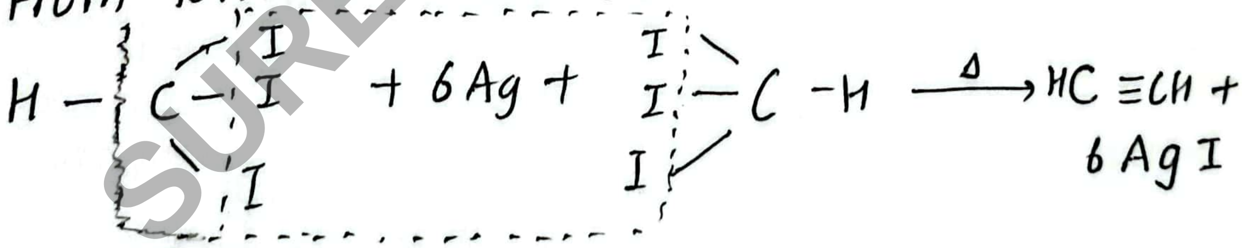
$$C_2H_4Br_2 + \underset{(alc)}{2KOH} \longrightarrow \underset{(Acetylene)}{C_2H_2} + 2KBr + 2H_2O)$$

2. From tetrahaloalkanes: Dehalogenation



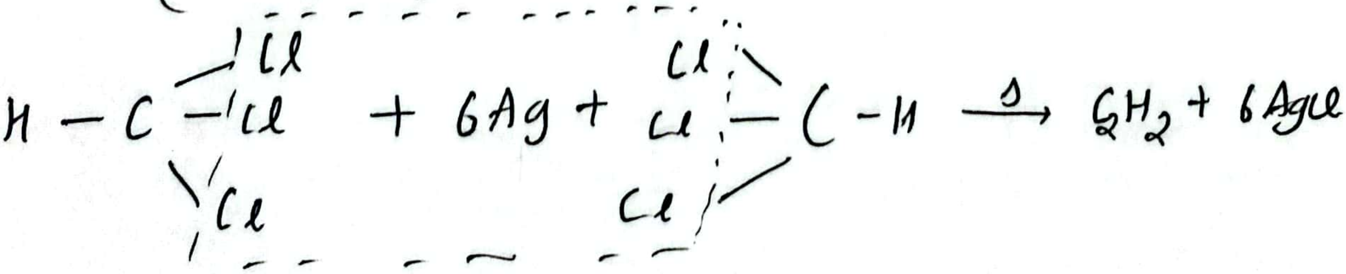
$$H-\overset{\overset{Br^-}{|}}{\underset{\underset{Br^-}{|}}{C}}-\overset{\overset{Br^-}{|}}{\underset{\underset{Br^-}{|}}{C}}-H + 2Zn^+ \xrightarrow{\Delta} H-C\equiv C-H + 2ZnBr_2$$

3. From trihalomethane (haloform)



$$H-\overset{I}{\underset{I}{C}}-I + 6Ag + I-\overset{I}{\underset{I}{C}}-H \xrightarrow{\Delta} HC\equiv CH + 6AgI$$

(Iodoform)



$$H-\overset{Cl}{\underset{Cl}{C}}-Cl + 6Ag + Cl-\overset{Cl}{\underset{Cl}{C}}-H \xrightarrow{\Delta} C_2H_2 + 6AgCl$$

(Chloroform)

4. From carbon and hydrogen

$$2C + H_2 \xrightarrow{\text{electric spark}} H-C\equiv C-H$$

5. Kolbe's eletrolysis: From sodium or potassium salt of fumaric acid or maleic acid

$$\begin{array}{l} CHCOONa \\ \| \\ CHCOONa \end{array} \rightleftharpoons \begin{array}{l} CHCOO^- \\ \| \\ CHCOO^- \end{array} + 2Na^+$$

(Sod. maleate or sod. fumarate)

At anode:

$$\begin{array}{l} CHCOO^- \\ \| \\ CHCOO^- \end{array} \rightarrow CH\equiv CH + 2CO_2 + 2e^-$$

At cathode

$$2Na^+ + 2e^- + 2H_2O \rightarrow 2NaOH + H_2\uparrow$$

APPENDICES

APPENDIX A 1

THE GREEK ALPHABET

Alpha	Α	α	Iota	Ι	ι	Rho	Ρ	ρ
Beta	Β	β	Kappa	Κ	κ	Sigma	Σ	σ
Gamma	Γ	γ	Lambda	Λ	λ	Tau	Τ	τ
Delta	Δ	δ	Mu	Μ	μ	Upsilon	Υ	υ
Epsilon	Ε	ε	Nu	Ν	ν	Phi	Φ	φ, φ
Zeta	Ζ	ζ	Xi	Ξ	ξ	Chi	Χ	χ
Eta	Η	η	Omicron	Ο	ο	Psi	Ψ	ψ
Theta	Θ	θ	Pi	Π	π	Omega	Ω	ω

APPENDIX A 2

COMMON SI PREFIXES AND SYMBOLS FOR MULTIPLES AND SUBMULTIPLES

Multiples			[illegible]		
Factor	Prefix	Symbol	Factor	Prefix	symbol
10^{18}	Exa	E	10^{-18}	atto	a
10^{15}	Peta	P	10^{-15}	femto	f
10^{12}	Tera	T	10^{-12}	pico	p
10^{9}	Giga	G	10^{-9}	nano	n
10^{6}	Mega	M	10^{-6}	micro	μ
10^{3}	kilo	k	10^{-3}	milli	m
10^{2}	Hecto	h	10^{-2}	centi	c
10^{1}	Deca	da	10^{-1}	deci	d

Laboratory preparation of Ethyne:-

Principle: Ethyne(Acetylene) is prepared in laboratory by dropping water over calcium carbide.

$$\underset{\text{Calcium carbide}}{CaC_2} + H_2O \longrightarrow \underset{\text{Ethyne}}{H-C\equiv C-H} + Ca(OH)_2$$

Instrumentation:

Acetylene is colourless gas with etheral odour which is insoluble in water but soluble in org. solvent and is somewhat poisonous

Fig: Laboratory prep. of acetylene gas.

Procedure: Apparatus are set as in the figure. Pieces of calcium carbide are taken in a conical flask and water is added from dropping funnel. Calcium carbide reacts with water giving acetylene gas. Calcium carbide always contains small amount of impurities like CaS, Ca_3P_2, etc, hence smaller amount of H_2S, PH_3 and NH_3 are also produced.

Purification:

$$CuSO_4 + H_2S \longrightarrow CuS\downarrow + H_2SO_4$$

$$3CuSO_4 + 2PH_3 \longrightarrow \underset{\text{(Cupric phosphide)}}{Cu_3P_2} + 3H_2SO_4$$

$$NH_3 + HCl \longrightarrow NH_4Cl$$

Acetylene is collected in gas jar by downward displacement of water.

Test reaction: Ethyne can be tested in laboratory by passing it through ammonical cuprous chloride solution. It will form a red precipitate of copper acetylide.

$$CH\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{[copper acetylide]} \\ \text{(red ppt.)}}}{Cu^+C^-\equiv C^-Cu^+\downarrow} + NH_4Cl + H_2O$$

Chemical properties of Ethyne (Acetylene)

C_2H_2 +

$$H_2 \xrightarrow[\text{addition of Hydrogen}]{Pd-BaSO_4} CH_2=CH_2$$

(Ethene)

$$2H_2 \xrightarrow{Ni} CH_3-CH_3 \text{ (Ethane)}$$

$$X_2 \xrightarrow{CCl_4} H-\underset{X}{C}=\underset{X}{C}-H \xrightarrow{X_2} H-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-H$$

X_2 [Cl_2 or Br_2]

(1,2-dihalo ethene)

[1,1,2,2-tetrahalo ethane]

$$Cl_2 \xrightarrow{dark} C_2H_2Cl_4$$

$$HX \longrightarrow H-\overset{H}{C}=\overset{X}{C}-H \xrightarrow{HX} H-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-H$$

HX [HCl, HBr, HI]

(Vinyl halide)

[1,1-Dihaloethane]

$$H_2O \xrightarrow[\text{Catalytic hydrogenation}]{HgSO_4 / H_2SO_4, \Delta} H_2C=\overset{OH}{CH}$$

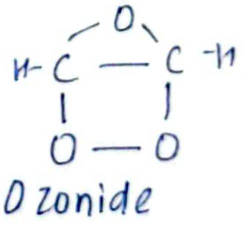
[Ethenol]

↓ Tautomerization

$$H_3C-\overset{O}{\overset{\|}{C}}-H$$

[Ethanal]

$$O_3 \xrightarrow[\text{Ozonolysis}]{CCl_4}$$



Ozonide

$$\xrightarrow{H_2O, Zn} H-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-H$$

Ethane-1,2-dial [Glyoxal]

$$AgNO_3 / NH_4OH \longrightarrow AgC \equiv CAg\downarrow$$

(Tollens reagent) (Ammonical Silver nitrate)

[Silver acetylide] white ppt

$$Cu_2Cl_2 / NH_4OH \longrightarrow CuC \equiv CCu\downarrow$$

(Ammonical cuprous chloride)

copper acetylide (red ppt.)

Test of acidic nature of ethyne

$$4[O] \xrightarrow[\text{Oxidation}]{KMnO_4 \text{ (alc.)}/OH^-} (COOH)_2$$

[oxalic acid]

[Bayer's Test] [Test of unsaturation Since, pink colour of alk. $KMnO_4$ is

$$\xrightarrow[\text{Aromatization}]{\text{red hot tube (Cu), (Fe)}}$$

[Benzene]

$$HC \equiv CNa \xleftarrow{Na}$$

[Monosodium acetylide]

$$NaC \equiv CNa \xleftarrow{2Na, \Delta}$$

(Disodium acetylide)

$$CO_2 + H_2O + \text{Energy} \xleftarrow[\text{Combustion}]{O_2}$$

Unit-9 Haloalkanes and Haloarenes

They are the organic compound formed by the replacement of one or more atoms of hydrogen by halogen from a hydrocarbon.

* If hydrogen atom is removed or replaced from an aliphatic hydrocarbon by a halogen, then the compound formed is known as haloalkanes.

alkyl groups (CH_3, C_2H_5, etc.)

halogens - Cl, Br, I, etc.

$$\underset{\text{alkane}}{R-H} \xrightarrow[-H]{+X} \underset{\substack{\text{Haloalkane}\\ \text{(Alkyl halides)}}}{R-X}$$

* If one or more hydrogen atom is replaced by halogen from an aromatic hydrocarbon (arenes), then the compound formed is known as haloarenes.

$$\underset{\substack{\text{Aromatic hydrocarbon}\\ \text{(arenes)}}}{Ar-H} \xrightarrow[-H]{+X} \underset{\substack{\text{Halo arenes}\\ \text{(Aryl halides)}}}{Ar-X}$$

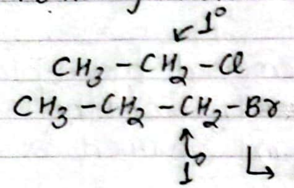
9.1 Haloalkanes

classification and nomenclature of Haloalkane.

⇒ They are classified on the basis of.

(a) Type Of carbon atom to which the halogen atom is bonded

~~eg~~ (i) Primary haloalkane [$R-CH_2-X$]



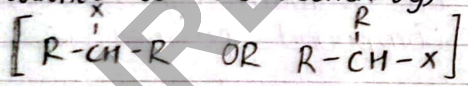
CH_3-CH_2-Cl – Chloroethane (ethylchloride)

$CH_3-CH_2-CH_2-Br$ ↳ Bromopropane (Propyl bromide)

Primary haloalkanes are the organic compound in which the halogen atom is attached to 1° (primary) carbon atom.

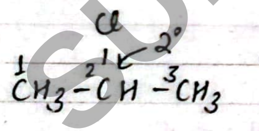
(ii) Secondary haloalkane

In this type of haloalkane, halogen atom is attached to 2° (secondary) carbon atom.

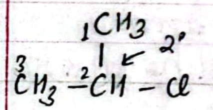


$[R-\overset{X}{CH}-R$ OR $R-\overset{R}{CH}-X]$

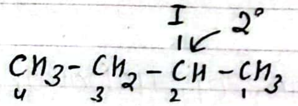
eg-



$\overset{1}{C}H_3-\overset{2}{\overset{Cl}{C}}H-\overset{3}{C}H_3$ → 2Chloropropane (Isopropyl chloride)

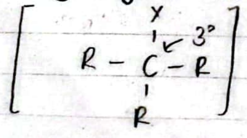


$\overset{3}{C}H_3-\overset{2}{\overset{^1CH_3}{C}}H-Cl$ → 2-chloropropane



$\underset{4}{CH_3}-\underset{3}{CH_2}-\underset{2}{\overset{I}{CH}}-\underset{1}{CH_3}$ → 2-Iodobutane (sec-butyl iodide)

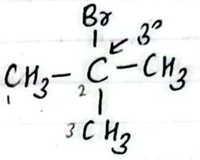
(iii) Tertiary ~~hydr~~ haloalkane



$[R-\overset{X}{\underset{R}{C}}-R]$

In this type of haloalkane, halogen atom is attached to 3° (tertiary) carbon atom.

eg-

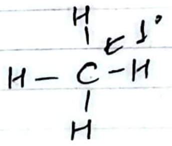


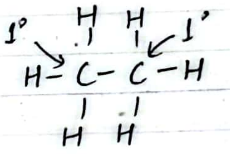
$\underset{1}{CH_3}-\overset{Br}{\underset{^3CH_3}{\underset{2}{C}}}-CH_3$ 2-Bromo-2-methylpropane (tert-butyl bromide)

Note-1

* Primary or 1° Carbon atom

A carbon atom attached to one or no other carbon atom is called primary carbon atom.

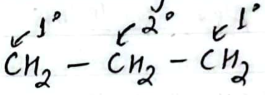




* Secondary or 2° carbon atom

A carbon atom attached to two other carbon ato

is called secondary carbon atom.

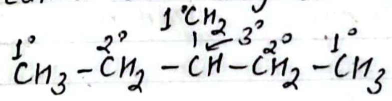


$\overset{1°}{C}H_2-\overset{2°}{C}H_2-\overset{1°}{C}H_2$

* Tertiary or 3° carbon atom

A carbon atom attached to 3 other carbon atom

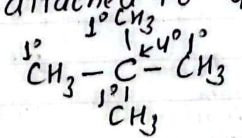
is called tertiary carbon atom.



$\overset{1°}{C}H_3-\overset{2°}{C}H_2-\overset{^{1°}CH_3}{\overset{3°}{C}}H-\overset{2°}{C}H_2-\overset{1°}{C}H_3$

* Quaternary or 4° carbon atom

Carbon atom attached to 4 other carbon atoms



$\overset{1°}{C}H_3-\overset{^{1°}CH_3}{\underset{^{1°}CH_3}{\overset{4°}{C}}}-\overset{1°}{C}H_3$

Note-2

(b) No. of halogen present per molecule

(i) Monohaloalkane

- One halogen atom per molecule

eg

CH_3Cl , CH_3CH_2I , $CH_3CH_2CH_2Br$, CH_3Br, etc.

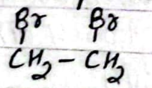
Chloro methane, Iodo ethane, 1-Bromo propane, Bromo methane

(ii) Dihaloalkane

-Two halogen atoms per molecule

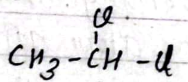
eg- CH_2Cl_2 ,

1,1-dichloro methane



$BrCH_2-CH_2Br$,

1,2-dibromo ethane (vicinal)



$CH_3-CHCl-Cl$

1,1-dichloro ethone (Geminal)

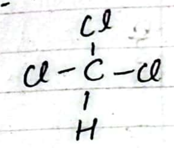
vicinal→ adjacent carbon atom ma ~~[illegible]~~ halogen added xa vane

Geminal→ Eutai (single) carbon atom ma ~~[illegible]~~ halogen added xa vane.

(iii) Polyhaloalkane

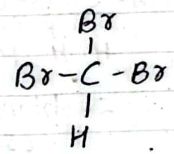
-More than two halogen atom per molecule

eg-



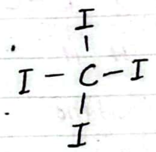
$CHCl_3$

Trichloromethane (chloroform)



$CHBr_3$

Tribromomethane (Bromoform)



CI_4

(Tetraiodomethane) [Carbon tetraiodide]

Isomerism in Haloalkane

Two or more compound having same molecular formula but different structural formula are called isomers and the phenomenon is called isomerism.

Following types of two isomerism is only possible in haloalkane-

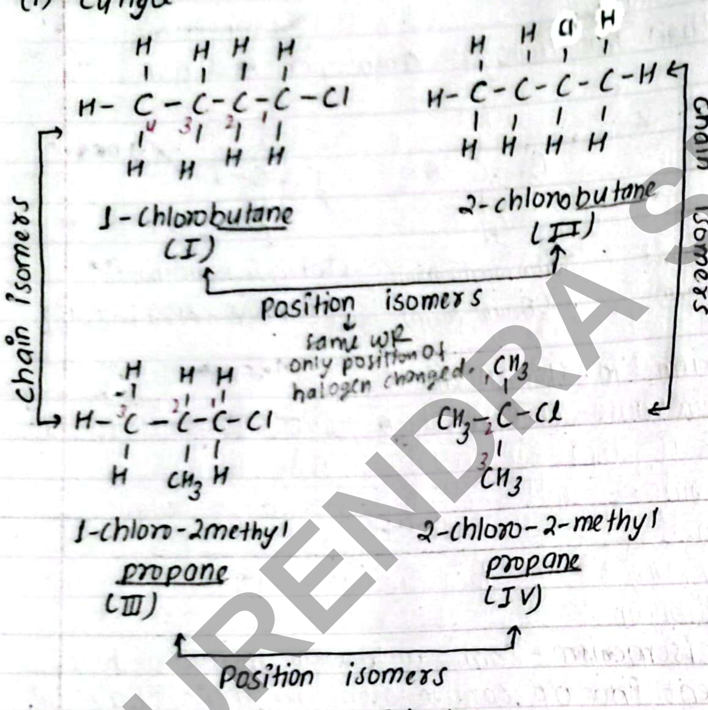
(a) Chain Isomerism - Same molecular formula but different no. of carbon atom in main chain OR different length of chain.
Haloalkanes consisting at least 4 carbon atoms gives chain isomers.

(b) Position isomerism - Same molecular formula but different position of functional group i.e. halog

(Isomers banauda straight chain bata suru garne

Examples

(i) C_4H_9Cl



* I and II are position isomers (III and IV)

* (I and III)/(I and IV)/(II and III/IV) are chain isomers.

General methods of preparation of monohaloalkanes

F_2, Cl_2, Br_2, I_2

(violently reacts) Reactivity decreases.

(a) From direct halogenation of alkane

$$\underset{\text{(alkane)}}{R-H} + X_2 \xrightarrow[\Delta\ \text{catalyst}]{h\nu\ \text{(sunlight)}} \underset{\text{haloalkane}}{R-X} + HX$$

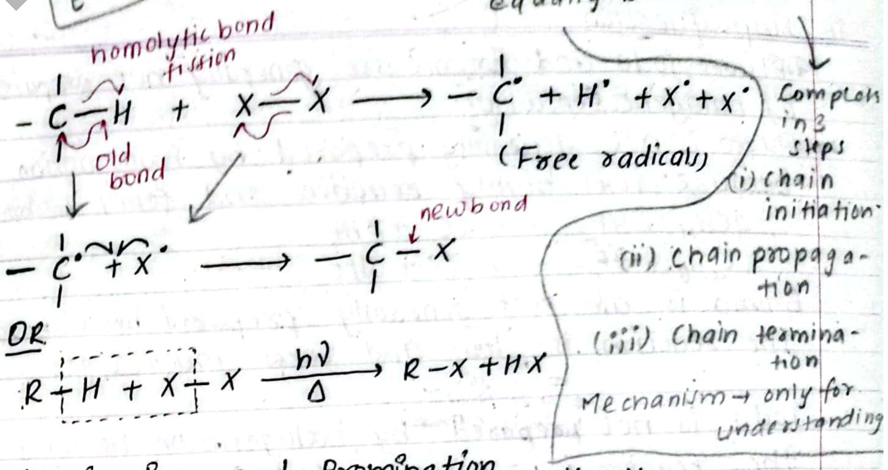
(Free radical substitution rxn)

$h\nu, \Delta$ → Free radical substitution

uvlight

homolytic bond fission: equally bond break

$E = h\nu$

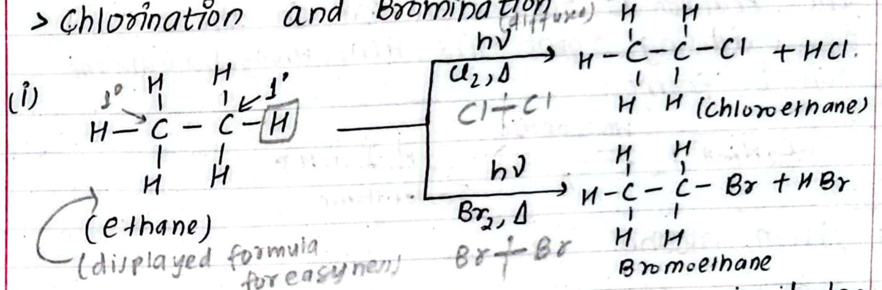


OR

$$R-H + X-X \xrightarrow[\Delta]{h\nu} R-X + HX$$

> Chlorination and Bromination

(i)

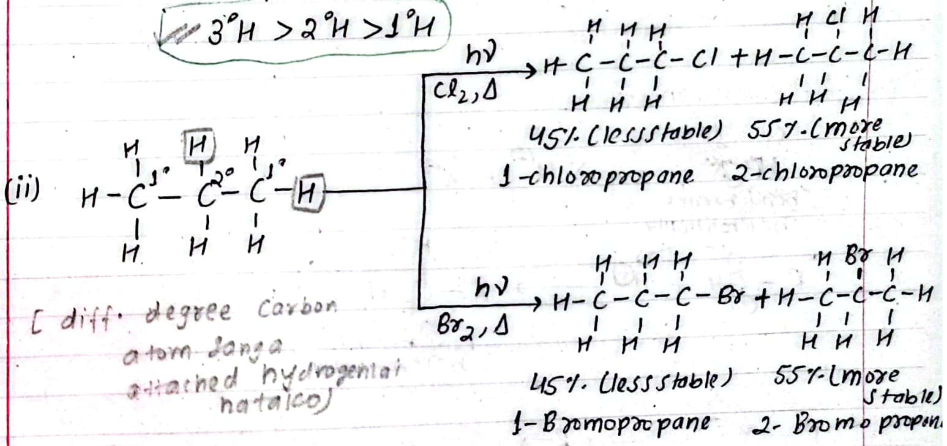


(ethane) (displayed formula for easyness)

* The rate of abstraction of hydrogen in halogenation

$3°H > 2°H > 1°H$

(ii)



[diff. degree carbon atom danga attached hydrogen lai hatalco]

3°H

halogen Cl_2

Imp. question

(Q) Fluoro, iodo and Bromo are generally not prepared by halogenation, why?

→ Fluoro is not generally prepared by halogenation because it is highly reactive and forms carbon as

$$2CH_4 + 4F_2 \longrightarrow 2C + 8HF$$

$$C_2H_6 + 3F_2 \longrightarrow 2C + 6HF$$

Bromo is also not generally prepared because the reaction is slow and takes much time.

Iodo is not prepared by halogenation because the reaction is reversible. But in the presence of oxidising agent like HIO_3, HNO_3, haloalkane can be formed.

$$C_2H_6 + I_2 \underset{\Delta}{\xrightleftharpoons{HNO_3 \text{ or } HIO_3}} \underset{\text{Iodoethane}}{C_2H_5I} + HI$$

(b) From alcohol

$$\overset{\delta+}{R} - \overset{\delta-}{\ddot{O}H} + \overset{\delta+}{H} - \overset{\delta-}{X} \longrightarrow \underset{\text{haloalkane}}{\overset{\delta+}{R} - \overset{\delta-}{X}} + H_2O$$

- Mechanism

X = Cl, Br, I

$$\overset{\delta+}{H} - \overset{\delta-}{X} \longrightarrow H^{\oplus} + \ddot{X}^{\ominus}$$

bond breaks heterolitically

$$R - \ddot{O}H + H^{\oplus} \longrightarrow R - \overset{H}{\overset{|}{\dot{O}^{\oplus}}} - H \longrightarrow R^{\oplus} + H_2O$$

can't break as H is small and O attracts H strongly

Bond breaks heterolytically

$$\overset{\oplus}{R} + \ddot{X}^{\ominus} \longrightarrow R-X \text{ (haloalkane/alkyl halide)}$$

e-pair acceptor → electrophile

nucleophile ← lone pair donor

Lonepair pair imp role in OC chem. rxn

(i) Reaction with HCl

$$\underset{\text{(Ethanol)}}{CH_3 - \overset{\delta+}{CH_2} - \overset{\delta-}{OH}} + \underset{\text{(conc.)}}{\overset{\delta+}{H} - \overset{\delta-}{Cl}} \xrightarrow[\Delta]{\text{anhydrous } ZnCl_2} \underset{\text{chloroethane}}{CH_3 - \overset{\delta+}{CH_2} - \overset{\delta-}{Cl}} + H_2\ddot{O}:$$

dehydrating agent (absorbs H_2O molecule formed during rxn)

haloalkane, polar molecule EN $\boxed{O>C}$

- Mechanism

① $HCl \longrightarrow H^{\oplus} + \ddot{Cl}^{\ominus}$

② $CH_3CH_2 - \ddot{O}H + H^{\oplus} \longrightarrow CH_3 - CH_2 - \overset{H}{\overset{|}{\ddot{O}^{\oplus}}} - H$ [C—O]

$$CH_3 - CH_2 - Cl \xleftarrow{\ddot{Cl}^{\ominus}} \underset{\text{ethyl carbocation}}{CH_3CH_2^{\oplus}} + H_2O$$

*Lucas reagent → conc. HCl : $ZnCl_2$ → 1 : 1

Reactivity) HCl > HBr > HI

→ Bond energy decrease

→ Reactivity in.

1° alcohol $\xrightarrow[HCl]{ZnCl_2}$ No turbidity at room temp (25°) ↙ halo alkane don't form.

2° alcohol → 5 min turbidity

3° alcohol → immediate turbidity ↓ formation of haloalkane.

(ii) Reactivity with HBr

$$\underset{\text{(or KBr)}}{2NaBr} + H_2SO_4 \longrightarrow Na_2SO_4 + 2HBr$$

$$CH_3\overset{\delta+}{CH_2} - \overset{\delta-}{\ddot{O}H} + \overset{\delta+}{H} - \overset{\delta-}{Br} \xrightarrow{\Delta} \underset{\text{Bromoethane}}{CH_3\overset{\delta+}{CH_2} - \overset{\delta-}{Br}} + H_2\ddot{O}$$

(iii) Reaction with HI

$$H_3PO_4 + KI \longrightarrow 3HI + K_3PO_4$$

$$CH_3\overset{\delta+}{CH_2} - \overset{\delta-}{OH} + \overset{\delta+}{H} - \overset{\delta-}{I} \longrightarrow \underset{\text{Iodoethane}}{CH_3CH_2I} + H_2\ddot{O}:$$

Alcohol → e^- rich species

(iv) Reaction with PCl_5, PCl_3, PBr_3, PI_3

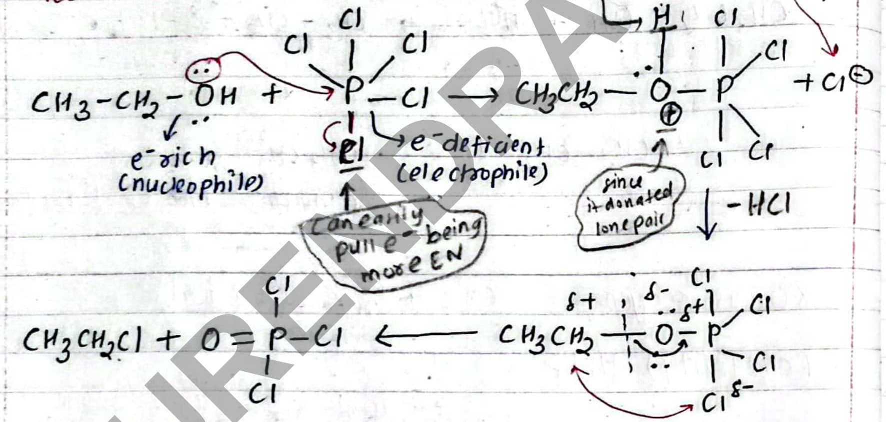
* With PCl_5

$$CH_3-CH_2-\underline{OH} + P\underline{Cl}_5 \xrightarrow[\Delta]{} CH_3CH_2Cl + POCl_3 + HCl$$

ethanol — Chloroethane

[OH replaced by Cl]

Mechanism-

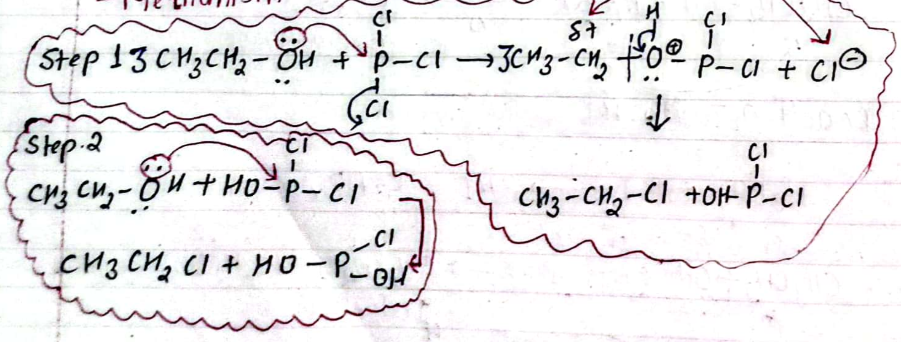


* with PCl_3

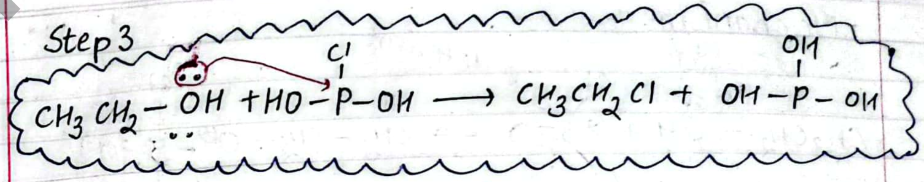
$$3CH_3-CH_2-\boxed{OH} + PCl_3 \xrightarrow{\Delta} 3CH_3CH_2\boxed{Cl} + H_3PO_3$$

ethanol — Chloroethane

- Methanism



Why 3 steps??
↳ 3Cl to be replaced by 3OH



* with PBr_3 & PI_3

→ unstable at room temp to needed to produce in situ. "in situ" → Jun bela rxn garne ho teti belai tyo compound banaune condition.

$$P_4 + 6Br_2 \xrightarrow{\Delta} 4PBr_3$$

$$P_4 + 6I_2 \xrightarrow{\Delta} 4PI_3$$

$$CH_3-CH_2-\boxed{OH} + PBr_3 \xrightarrow[\Delta]{} CH_3CH_2\boxed{Br} + H_3PO_3$$

ethanol — Bromoethane

$\boxed{PBr_3 \text{ or } P_4 + Br_2}$

$$CH_3-CH_2-OH + PI_3 \xrightarrow[\Delta]{} CH_3CH_2I + H_3PO_3$$

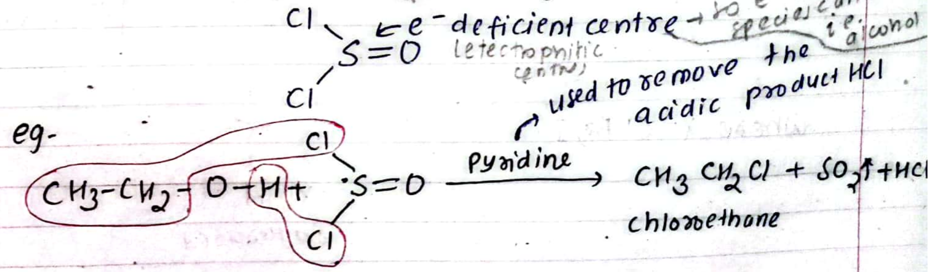
ethanol — Iodoethane

$\boxed{PI_3 \text{ or } P_4 + I_2}$

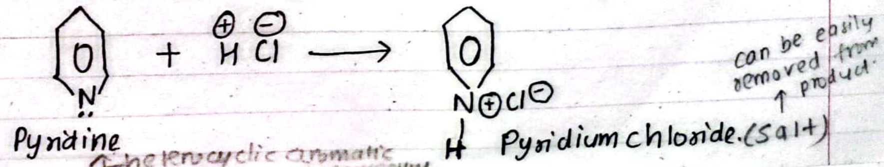
- Mechanism for both same as for PCl_3

(v) Reaction with $SOCl_2$ (Thionyl chloride)

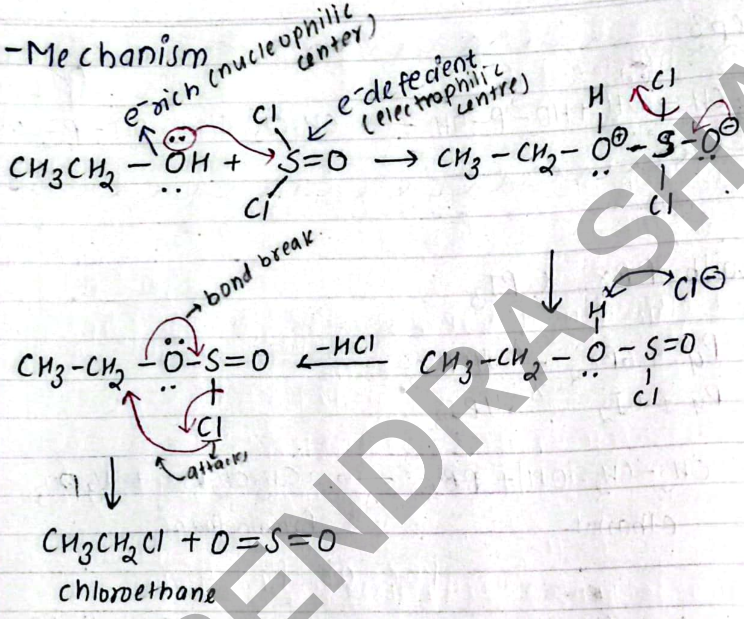
→ Sulphur



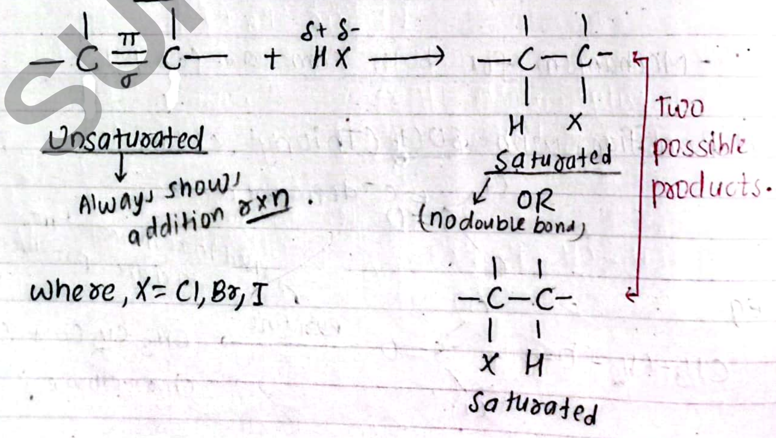
$$CH_3-CH_2-O-H + SOCl_2 \xrightarrow{Pyridine} CH_3CH_2Cl + SO_2\uparrow + HCl$$



-Mechanism

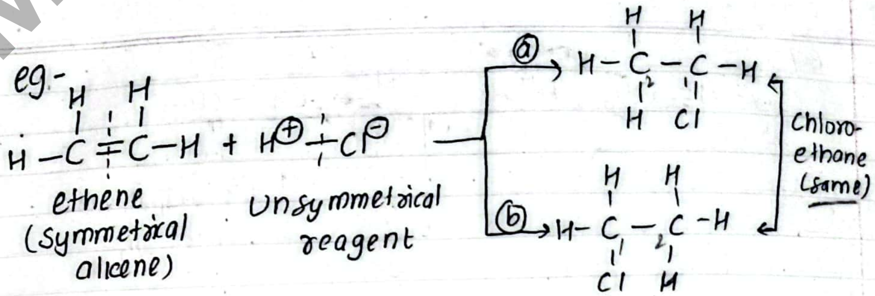


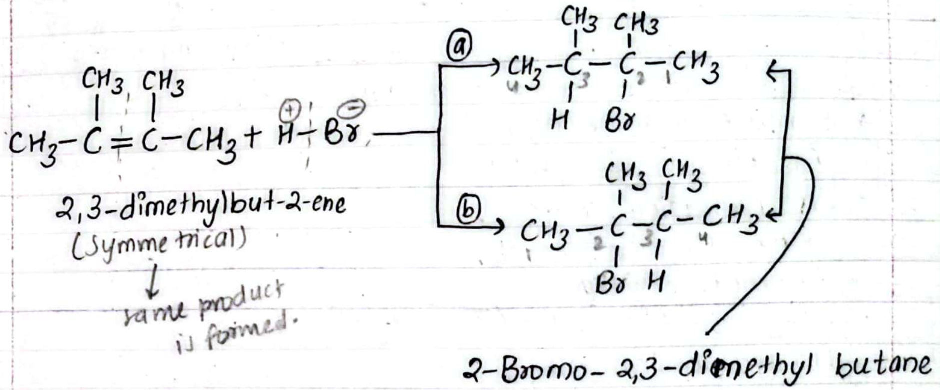
(C) From Alkene



where, X= Cl, Br, I

eg.-



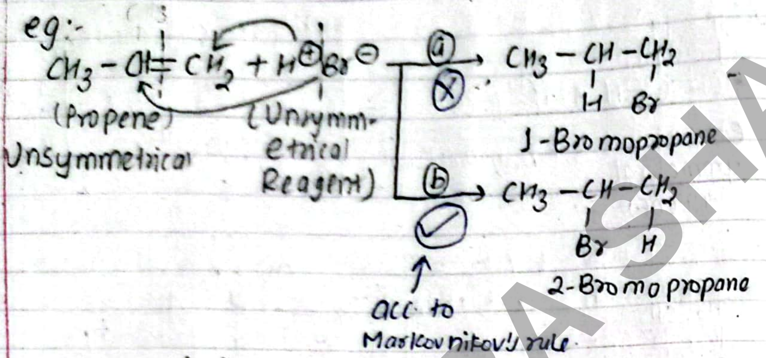


★ Markovnikov's rule

- When unsymmetrical alkene reacts with unsymmetrical reagent, then the addition follows ~~mo~~ Markovnikov's rule.
- Markovnikov's rule states that when halo acid or other unsymmetrical reagent is added to an unsymmetrical alkene or alkyne, negative part of the reagent goes to the carbon atom of = or ≡ bond having lesser no. of hydrogen atom and positive part goes to the carbon atom of double or triple bond having more no. of hydrogen atom.

(Alkene ma add gardai xau vane jaile double bond ma aakha laune)

eg:-



$CH_3-CH=CH_2 + H^{\oplus}Br^{\ominus}$

(Propene) Unsymmetrical (Unsymmetrical Reagent)

ⓐ ✗ $\rightarrow CH_3-\underset{H}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$ 1-Bromopropane

ⓑ ✓ $\rightarrow CH_3-\underset{Br}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH_2}}$ 2-Bromopropane

↑ acc to Markovnikov's rule

* Symmetrical reagents
$Br-Br$, $Cl-Cl$, $H-H$

- Unsymmetrical reagents
HBr, HCl, H_2SO_4, H_2O

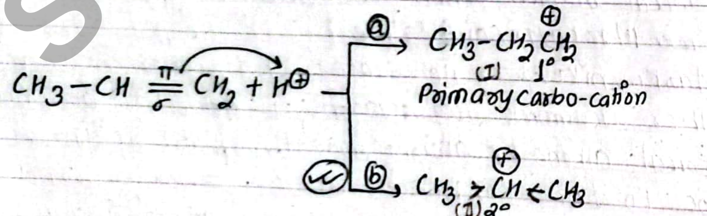
- Symmetric alkenes
$CH_2=CH_2$, $CH_3-CH=CH-CH_3$

- Unsymmetrical alkene
$CH_3-CH=CH_2$, $CH_3CH_2CH=CH_2$

- Mechanism

I $H-Br \longrightarrow H^{\oplus} + Br^{\ominus}$

II



$CH_3-CH \overset{\pi}{\underset{\sigma}{=}} CH_2 + H^{\oplus}$

ⓐ $\rightarrow CH_3-CH_2\overset{\oplus}{C}H_2$ (I) 1° Primary carbo-cation

✓ ⓑ $\rightarrow CH_3 \rightarrow \overset{\oplus}{C}H \leftarrow CH_3$ (II) 2° Secondary carbocation

ⓑ is more stable than ⓐ

(I) < (II) (1° < 2° carbocation)
$\xrightarrow{\text{stable increases}}$

III. $CH_3-\overset{\oplus}{C}H-CH_3 + Br^{\ominus} \longrightarrow CH_3CHBrCH_3$

3° carbocation > 2° carbocation > 1° carbocation
$\xrightarrow{\text{stability decreases}}$

[Alkene $e^{\ominus}$ rich] ↳ due to π bond

Stable product dherai banxa (major)

2° carbocation ma 2 tira bata symmetrically e^- donate hunxa to e^- deficient group so it is more stable than 1° carbocation as donation ek tira bata matra vairaxa

→ denotes heterolytic bond fission

$\rightharpoonup$ or $\leftharpoondown$ denotes homolytic bond fission

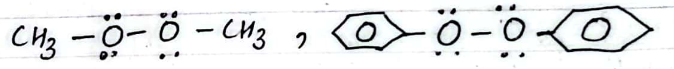
★ Antimarkovnikov's rule (Peroxide effect)

It states that when an unsymmetrical reagent such as $\boxed{HBr}$ is added to an alkene or alkyne in the presence of organic peroxide, then -ve part of reagent goes to C-atom having more no. of H-atom and +ve part goes to C-atom of double or triple bond having less no of H-atom.

H-Cl > H-Br > H-I
$\xrightarrow{\text{Bond strength}}$

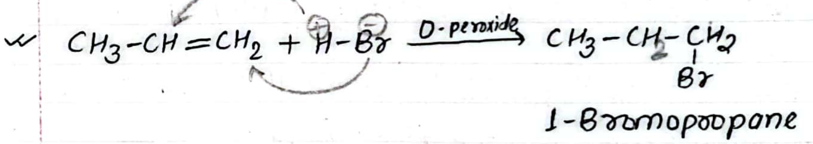
- AMR is shown by HBr

Examples of peroxide:-



$CH_3-\ddot{O}-\ddot{O}-CH_3$,

eg-



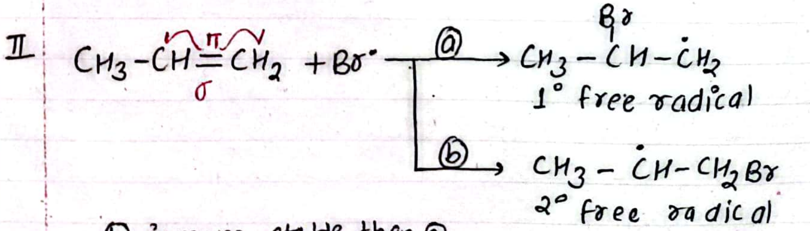
✓ $CH_3-CH=CH_2 + \overset{\oplus}{H}-\overset{\ominus}{Br} \xrightarrow{O\text{-peroxide}} CH_3-CH_2-\underset{Br}{\underset{|}{CH_2}}$

1-Bromopropane

- Mechanism

I $R-\ddot{O}-\ddot{O}-R + 2H-Br \longrightarrow 2R-\ddot{O}\cdot + 2H^{\cdot} + Br^{\cdot}$

II



$CH_3-CH \overset{\pi}{\underset{\sigma}{=}} CH_2 + Br^{\cdot}$

ⓐ $\rightarrow CH_3-\overset{Br}{\overset{|}{C}H}-\dot{C}H_2$ 1° free radical

ⓑ $\rightarrow CH_3-\dot{C}H-CH_2Br$ 2° free radical

ⓑ is more stable than ⓐ

III $CH_3-\dot{C}H-CH_2Br + H-Br \longrightarrow CH_3-CH_2-CH_2Br + Br^{\cdot}$

(solubility & M P/BP)

Physical propeoties of monohaloalkane (R-X)

(a) State

- Lower haloalkanes are gases
- C_2-C_8 haloalkanes are colourless sweet smelling liquid
- Higher haloalkanes are colourless

(b) Boiling point

$R-X > R-H$

Haloalkanes boil at higher temperature than corresponding alkanes.
Moreover the boiling point increases with an increase in their molecular weight

$CH_3I > CH_3Br > CH_3Cl$ → Boiling point decreases [Same alkyl group but diff X]

$CH_3CH_2CH_2Cl > CH_3CH_2Cl > CH_3Cl$ → B.P. decreases [same X but diff R]

$R-Cl < R-Br < R-I$ → Boiling point increases (vanderwaal's force increases as there is inc in size of halogen atom makes R-X molecule larger)

$Cl < Br < I$ → size of atom

$CH_3CH_2CH_2CH_2\boxed{Br} > CH_3CH_2\overset{Br}{C}HCH_3 > CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$ →

surface area inc. ↓ vanderwaal's force increases.

Boiling point decreases, as branching increases the size of molecule decreases and hence surface area of molecule also decreases & vanderwaal's force also decreases and BP decreases.

Linear chain isomers have higher boiling point than branched isomers because as branching starts the surface area decreases and Vanderwaal force also hence decreasing the boiling point.

(c) Solubility → in water [H-bond]

Even if haloalkanes are polar compounds they are insoluble in water due to incapability of forming hydrogen bond with water molecules.

$\overset{\delta+}{R}-\overset{\delta-}{X}$ effective intermolecular

Polarity in haloalkane

$\overset{\delta+}{H}-\underset{H\delta+}{\overset{\delta-}{O}}$ $\quad \underset{R\delta+}{\overset{\delta-}{Cl}}$ → big atom ↓ can't form int. H-Bo

They are however soluble in organic solvent like benzene, chloroform ($CHCl_3$), Carbon tetrachloride (CCl_4).

Cl, Br, I → E.N. decreases

Chemical properties of monohaloalkanes.

$-\overset{\delta+}{C}-\overset{\delta-}{Cl} > -\overset{\delta+}{C}-\overset{\delta-}{Br} > -\overset{\delta+}{C}-\overset{\delta-}{I}$ → Bond energy decreases, reactivity increases, size increases.

$\overset{\delta+}{R}-\overset{\delta-}{X}$

X = Cl, Br, I → EN decreases, size increases

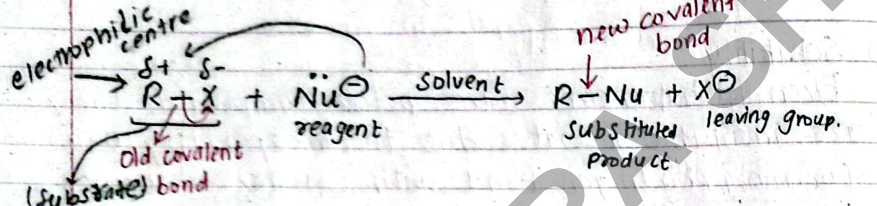
$\overset{\delta+\delta+\delta+}{C}-\overset{\delta+\delta+}{C}-C-\overset{\delta+}{C}-\overset{\delta-}{Cl}$

↑ more reactive carbon

Nucleophile → e⁻ pair donar (e⁻ rich)

1. Nucleophilic substitution reaction

- Nucleophiles are those species having either negative charge (Cl^-, Br^-, CN^-, OH^-) or containing the lone pair of electron. It is denoted by $Nu^\ominus$


$$\overset{\delta+}{R}-\overset{\delta-}{X} + \ddot{N}u^\ominus \xrightarrow{\text{Solvent}} R-Nu + X^\ominus$$

Examples of nucleophiles-
Cl^-, Br^-, $:OH^-$, CN^-, NH_2^-, RO^- (alkoxide ion), HS^- (hydrosulphide ion), O^{2-} (oxide ion), S^{2-}, etc.

Neutral nucleophiles- $\ddot{N}H_3$, $R\ddot{N}H_2$, $H_2\ddot{O}:$, $R-\ddot{O}-H$, $R-\ddot{O}-R$, $R_3\ddot{N}$, $R_2\ddot{N}H$, etc.

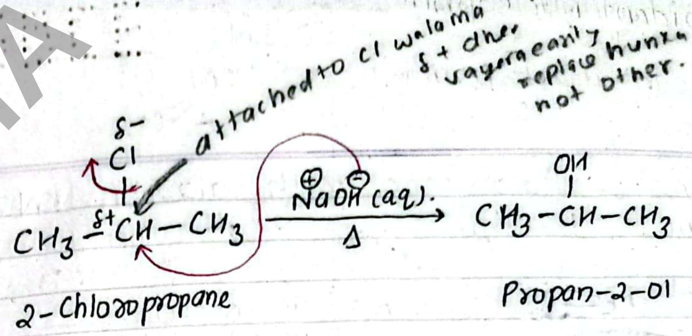
→ Some typical nucleophilic reaction of haloalkanes

(a) Reaction with aqueous NaOH or KOH
→ solution prepared in water

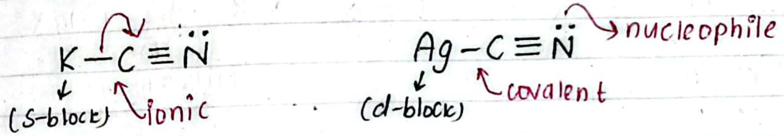
$$NaOH \longrightarrow Na^+ + :\ddot{O}H^\ominus$$
→ Nucleophile
↳ actually in O
↳ lone pair attacks not ⊖ charge.

$$\overset{\delta+\delta+}{CH_3}\overset{\delta+}{CH_2}-\overset{\delta-}{I} + \overset{\oplus}{Na}-\overset{\ominus}{OH} \xrightarrow{\Delta} CH_3-CH_2-OH + NaI$$
Iodoethane (aq) ethanol Sod. iodide

$$\overset{\delta+\delta+}{CH_3}\overset{\delta+}{CH_2}-\overset{\delta-}{I} + \overset{\oplus}{K}-\overset{\ominus}{OH} \xrightarrow{\Delta} CH_3-CH_2-OH + KI$$
Iodoethane (aq) Pott. iodide

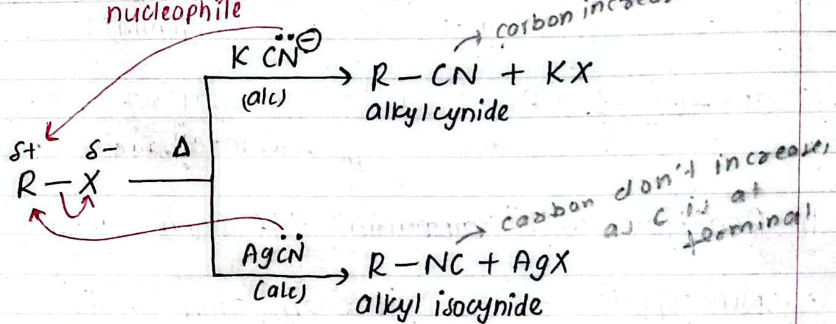

$$CH_3-\overset{\delta+}{CH}(\overset{\delta-}{Cl})-CH_3 \xrightarrow[\Delta]{\overset{\oplus}{Na}\overset{\ominus}{OH}\text{(aq).}} CH_3-CH(OH)-CH_3$$
2-Chloropropane Propan-2-ol

(b) Reaction with alcoholic KCN & alcoholic AgCN


$$K-C\equiv\ddot{N} \qquad Ag-C\equiv\ddot{N}$$

s → d → p
covalent bond tendency increases →
E.N.↑↑

$K^\oplus \; :\overset{\ominus}{C}\equiv N$
nucleophile

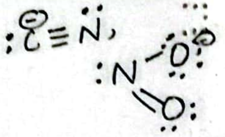

$$\overset{\delta+}{R}-\overset{\delta-}{X} \xrightarrow[\Delta]{K\ddot{C}N^\ominus \text{ (alc)}} R-CN + KX$$
alkyl cynide
$$\overset{\delta+}{R}-\overset{\delta-}{X} \xrightarrow[\Delta]{Ag\ddot{C}N \text{ (alc)}} R-NC + AgX$$
alkyl isocynide

Example-

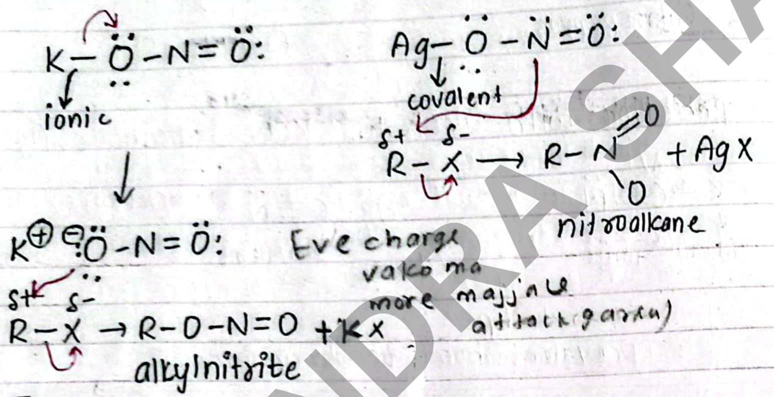
$$CH_3\overset{\delta+}{CH_2}-\overset{\delta-}{I} + K-\overset{\ominus}{C}\equiv\ddot{N} \longrightarrow CH_3CH_2-CN + KI$$
Iodoethane (alc) Propanenitrile (ethyl cynide)

$$CH_3\overset{\delta+}{CH_2}-\overset{\delta-}{I} + Ag-C\equiv\ddot{N} \longrightarrow CH_3CH_2NC + AgI$$
(alc.) ethyl isocyanide

* ambident nucleophile -
↓
can attack from two side



(c) Reaction of haloalkane with alcoholic KNO_2 & alcoholic $AgNO_2$.



-ve charge vako ma more majjale attack garxu)

Example -

$\overset{\delta+}{CH_3-CH_2}-\overset{\delta-}{I} + K-\ddot{\underset{..}{O}}-N=\ddot{\underset{..}{O}} \longrightarrow CH_3CH_2ONO + KI$
(alc)
ethyl nitrite

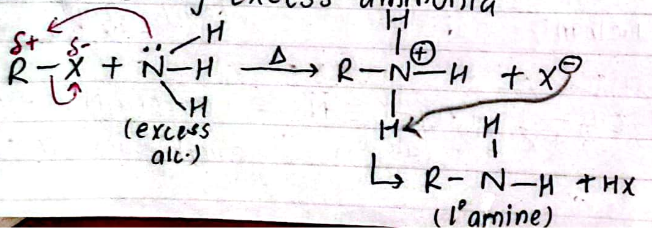
$CH_3-\overset{\delta+}{CH_2}-\overset{\delta-}{I} + Ag-\ddot{\underset{..}{O}}-\ddot{N}=\ddot{\underset{..}{O}} \longrightarrow CH_3CH_2NO_2 + AgI$
(alc.)
nitroethane

(d) Reaction with ammonia (Haffmann's ammonolysis system)

Nucleophile → $\ddot{N}H_3$ (nitrogen atom with lone pair)

→ $R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$

Case I - Using excess ammonia



~~Excess~~ Example -

$CH_3-\overset{\delta+}{CH_2}-\overset{\delta-}{I} + \ddot{N}H_3 \xrightarrow{\Delta} CH_3CH_2-NH_2 + HI$
(alc.) excess
Iodoethane
ethanamine
high +ve charge so can act as electrophile.

Case II - Using excess haloalkane

Step 1 $\overset{\delta+}{R}-\overset{\delta-}{X} + \ddot{N}H_3 \xrightarrow{\Delta} R-\ddot{N}H_2 + HX$
(excess) (alc.)
1° amine

Step 2 $\overset{\delta+}{R}-\overset{\delta-}{X} + R-\ddot{N}H_2 \longrightarrow R_2\ddot{N}H + HX$
2° amine

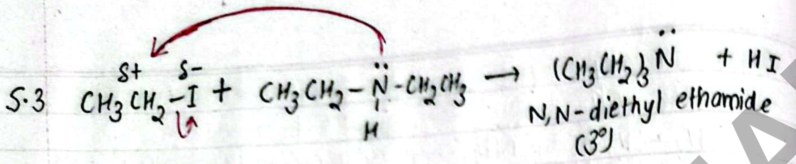
Step 3 $\overset{\delta+}{R}-\overset{\delta-}{X} + R_2\ddot{N}H \longrightarrow R_3\ddot{N} + HX$
3° amine

Step 4 $\overset{\delta+}{R}-\overset{\delta-}{X} + R_3\ddot{N} \longrightarrow R_4N^{\oplus}X^{\ominus}$
4° (Quaternary ammonium halide)

Example -

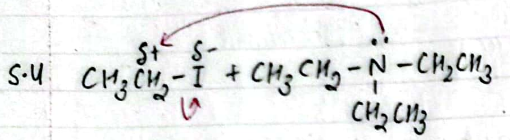
S.1 $CH_3\overset{\delta+}{CH_2}-\overset{\delta-}{I} + \ddot{N}H_3 \longrightarrow CH_3CH_2-\ddot{N}H_2 + HI$
excess
(Iodoethane)
ethanamide
(1°)

S.2 $CH_3\overset{\delta+}{CH_2}-\overset{\delta-}{I} + CH_3CH_2-\ddot{N}H_2 \longrightarrow CH_3CH_2-\overset{H}{\overset{|}{N}}-CH_2CH_3 + H$
$(CH_3CH_2)_2NH.$
N-ethyl ethanine
(2°)



S.3 $\overset{\delta+}{CH_3CH_2}-\overset{\delta-}{I} + CH_3CH_2-\underset{H}{\underset{|}{\ddot{N}}}-CH_2CH_3 \longrightarrow (CH_3CH_2)_3\ddot{N} + HI$

N,N-diethyl ethamide
(3°)



S.4 $\overset{\delta+}{CH_3CH_2}-\overset{\delta-}{I} + CH_3CH_2-\underset{CH_2CH_3}{\underset{|}{\ddot{N}}}-CH_2CH_3$

$\downarrow$

$(CH_3CH_2)_4N^{\oplus}I^{\ominus}$
(tetraethyl ammonium iodide)
(4°)

(e) Reaction with sodium or potassium alkoxide

Preparation of alkoxide

$R-OH + NaOH \longrightarrow \boxed{R\bar{O}}\overset{+}{Na} + H_2O$

(slightly acidic) (base) (alkoxide ion) → nucleophile

sodium alkoxide

$R-OH + KOH \longrightarrow \boxed{R\bar{O}}\overset{+}{K} + H_2O$

slightly acidic (base) → nucleophile

Potassium alkoxide

Example-

* $CH_3-OH + NaOH \longrightarrow \boxed{CH_3\bar{O}}\overset{+}{Na} + H_2O$ → nucleophile

Methanol base sod. methoxide

* $CH_3-OH + KOH \rightarrow \boxed{CH_3\bar{O}}K^+ + H_2O$ → nucleophile

base Pot. methoxide

* $CH_3CH_2OH + NaOH \longrightarrow \boxed{CH_3CH_2\bar{O}}Na^+ + H_2O$ → nucleophile

ethanol Sodium ethoxide

* Williamson's ether Synthesis (Imp.)

Nucleophile
$R\ddot{\underset{..}{O}}:^{\ominus}$ or $RO^{\ominus}$

$\overset{\delta+}{R}-\overset{\delta-}{X} + R'\bar{O}\overset{+}{Na} \xrightarrow{\Delta} R-O-R' + NaX$

haloalkane (alkyl halide) alkoxy alkane (ether)

R, R → may be same or different

[dissimilar → unsymmetrical ether
similar → symmetrical ether]

When,
R=R' eg-1

$\overset{\delta+}{CH_3}-\overset{\delta-}{Cl} + CH_3\overset{\ominus}{O}\overset{\oplus}{Na} \xrightarrow[\Delta]{} CH_3-O-CH_3 + NaCl$

methoxy methane
(symmetrical ether)

$CH_3\overset{\delta+}{CH_2}-\overset{\delta-}{I} + CH_3CH_2\overset{\ominus}{O}K^{\oplus} \xrightarrow[\Delta]{} CH_3CH_2-O-CH_2CH_3 + KI$

ethoxy ethane
(Symmetrical ether)

When
R≠R' eg-2

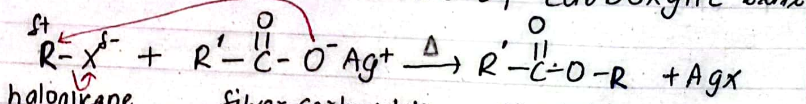
$\overset{\delta+}{CH_3CH_2}-\overset{\delta-}{Cl} + CH_3\overset{\ominus}{O}\overset{\oplus}{Na} \xrightarrow[\Delta]{} CH_3CH_2-O-CH_3 + NaCl$

chloroethane sod. methoxide methoxyethane
(Unsymmetrical ether)
Take O with short chain & do naming.

Advantage:
Willamson's ether synthesis is useful for the synthesis of symmetrical as well as unsymmetrical ether.

[$RCOO^-Ag^+$].

(f) Reaction with silver salt of carboxylic ~~salt~~ acid.



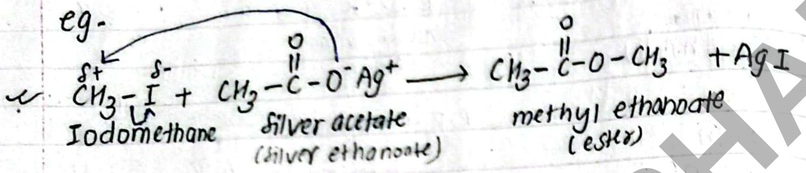
$\overset{\delta+}{R}-\overset{\delta-}{X} + R'-\overset{O}{\overset{\|}{C}}-O^-Ag^+ \xrightarrow{\Delta} R'-\overset{O}{\overset{\|}{C}}-O-R + AgX$

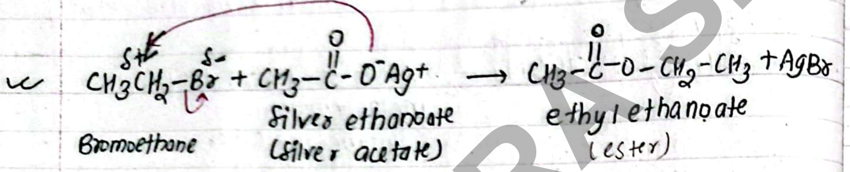
haloalkane silver carboxylate alkyl alkanoate
→ coming from alkyl halide.

R, R may be same or different

electronegativity)

eg-


$CH_3-I + CH_3-\overset{O}{\overset{\|}{C}}-O^-Ag^+ \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3 + AgI$


$CH_3CH_2-Br + CH_3-\overset{O}{\overset{\|}{C}}-O^-Ag^+ \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_3 + AgBr$

Application of alkyl cyanide & alkyl isocyanide in organic synthesis.

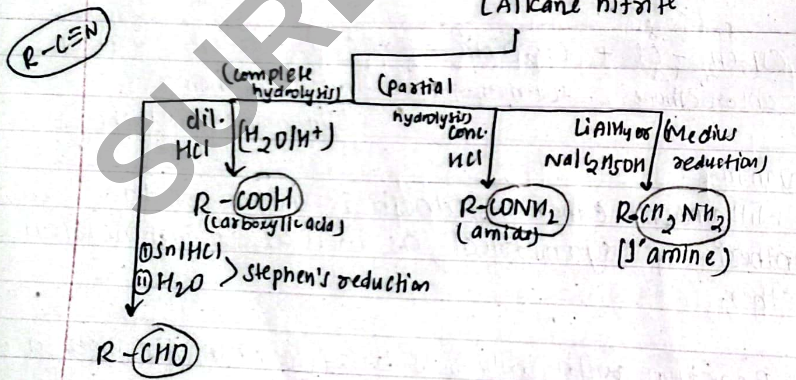
$R-X + K\bar{C}N \text{(alc.)} \xrightarrow[(-KX)]{\Delta} R-CN$

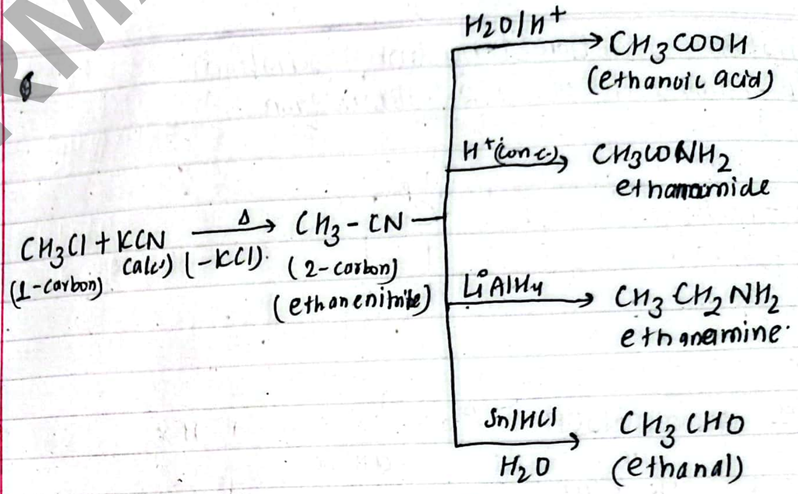
δ+ δ-

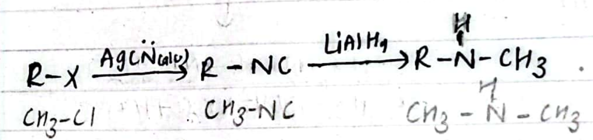
(carbon no. increase with one than given haloalkane)

Alkyl cyanide

(Alkane nitrile






$R-X \xrightarrow{AgCN(alc)} R-NC \xrightarrow{LiAlH_4} R-\overset{H}{N}-CH_3$

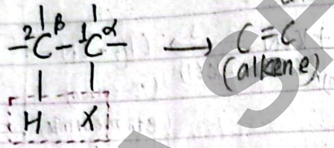
$CH_3-Cl \quad CH_3-NC \quad CH_3-\overset{H}{N}-CH_3$

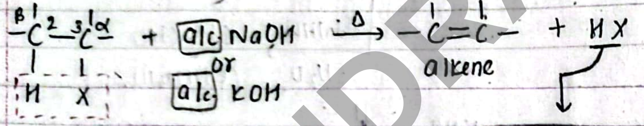
2. Elimination reaction (Dehydrohalogenation) or β-elimination or 1,2-elimination → hydrogen & halogen are removed from adjacent (1,2) carbon atom.

Dehydrohalogenation:- ↳ Removal of β hydrogen

De → removal
hydro → hydrogen
halo → halogen

(Removal of hydrogen & halogen from adjacent carbon atom)



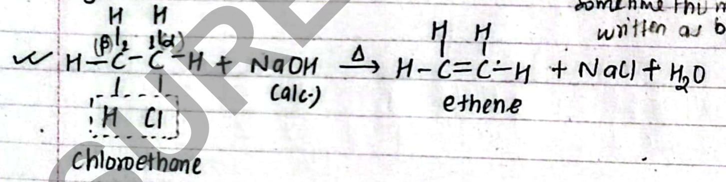


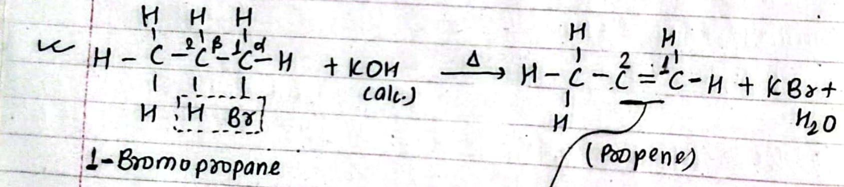
[Not aq.]

$HX + NaOH \rightarrow \underline{NaX + H_2O}$
OR $HX + KOH \rightarrow \underline{KX + H_2O}$

Sometime this may be written as byproduct.

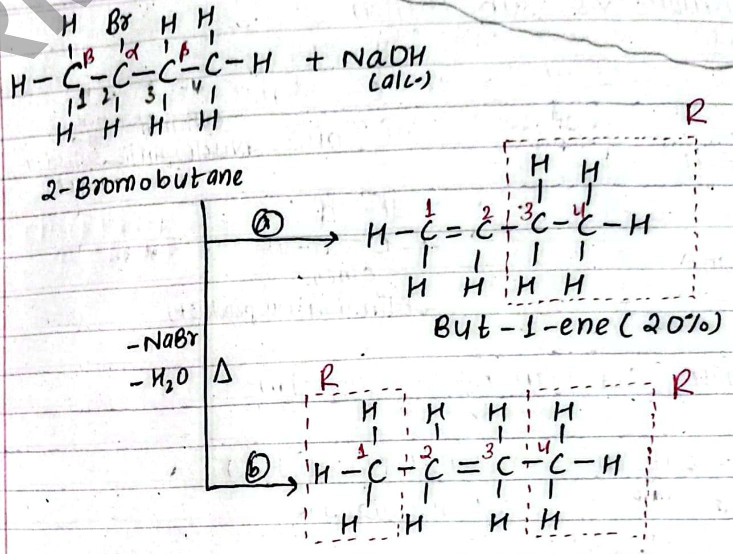
eg-





Jaha bata hatya xa tyahi = aauxa.

α → Jun ma X atom jodiyekoxa
Carbon
β → adjacent to α carbon
α, β, Hydrogen → H attached with α, β-carbon



- Saytzeff's rule:

More alkyl substituted alkene is formed as a major product in dehydrohalogenation reaction.

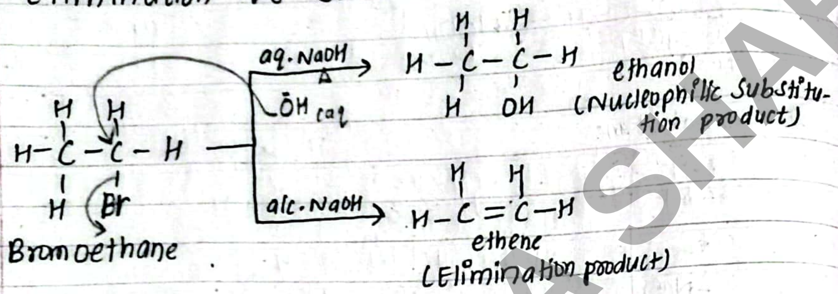
OR

- If more than one elimination product is possible, the most substituted alkene (containing more no. of R) is the most stable product (major product)

- $CH_2=CHR < RCH=CHR < R_2C=CHR < R_2C=CR_2$

$\xrightarrow{\text{Stability increases.}}$

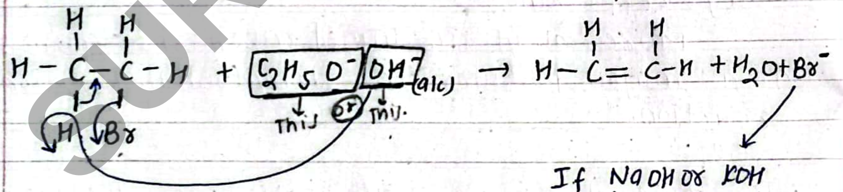
* Elimination vs substitution



→ Mechanism of elimination reaction

$NaOH + C_2H_5OH \longrightarrow C_2H_5O^-Na^+ + H_2O$
sodium hydroxide (alc.) sodium ethaoxide

- ethaoxide ion is a powerful base → proton
base reacts with proton



If NaOH or KOH is used, this $Br^{\ominus}$ will attack $N^{\oplus}$ or $K^{\oplus}$

C. Reaction with metals

3. Wurtz's reaction (Rx^n with Na metal)

$R-X + 2Na + X-R \xrightarrow[\Delta]{\text{dryether}} R-R + 2NaX$

haloalkane haloalkane alkane

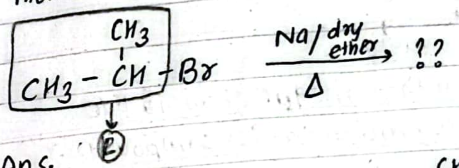
Useful for syn (n.x) of even no. carbon.

Na → very reactive so might react with moisture. so, dry ether is used.

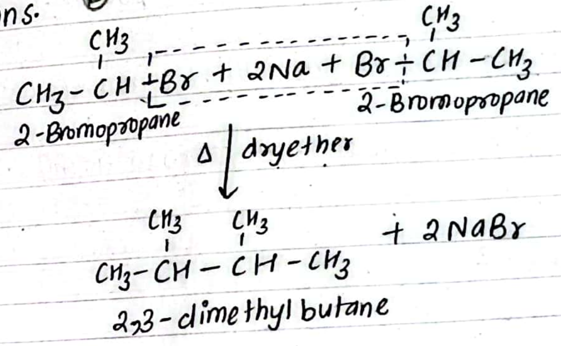
eg-

$CH_3-Cl + 2Na + Cl-CH_3 \xrightarrow[\Delta]{\text{dryether}} CH_3-CH_3 + 2NaCl$

Chloro methane Chloro methane Ethane.



Ans.



* Limitations of Wurtz. reaction

- CH_4 (Methane) cannot be prepared.
- Alkane with even no. of C-atom can be prepared but not the alkane with odd no. of C-atoms.
- The Wurtz coupling method generally fails when tertiary alkyl halides are used.
- commonly only symmetric alkanes can be synthesized via this method, since a mixture of alkane products are formed when dissimilar alkanes are reacted. (this mixtures are difficult to separate).

For eg-

$CH_3-Cl + CH_3CH_2-Cl + 2Na \xrightarrow[\Delta]{\text{dryether}}$

→ $CH_3-CH_2-CH_3 + 2NaCl$ ⓷C (expected product)
+
→ CH_3-CH_3 ⓶C
+
→ $CH_3CH_2-CH_2CH_3$ ⓸C

In this way a mixture of alkanes is obtained and they cannot be separated easily.

4. Grignard's reaction (victor Grignard)

$$R-X + Mg \xrightarrow[\text{inert atm.}]{\text{dry ether}} R-Mg-X$$

halo alkane

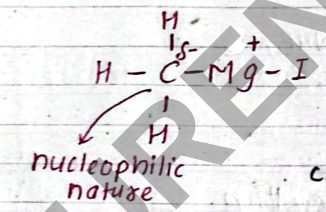
alkyl magnesium halide (Grignard reagent)

$$CH_3-I + Mg \xrightarrow[\text{inert atm}]{\text{dry ether}} \overset{\delta+}{CH_3}-\overset{+}{Mg}-\overset{-}{I}$$

methyl megnesium iodide (Organometallic compound)

* Grignard reagent- Organometallic compound

[metal directly bonded with carbon atom]



$$H-\overset{H}{\underset{H}{\overset{|}{\underset{|}{\overset{\delta-}{C}}}}}-\overset{+}{Mg}-I$$

precautions

(i) Moisture free

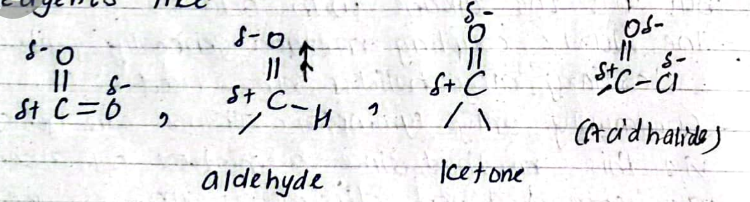
$$\overset{\delta+}{CH_3}-\overset{+}{Mg}-\overset{-}{I} + \overset{+}{H}-\overset{-}{OH} \longrightarrow CH_3-H$$

(moisture)

(ii) Inert atmosphere

$$CH_3-Mg-I + O_2 \longrightarrow CH_3-O-O-Mg-I$$

- The grignard C-atom is nucleophilic in nature and can react with other organic electrophilic reagents like



* Application of Grignard reagent in organic synthesis

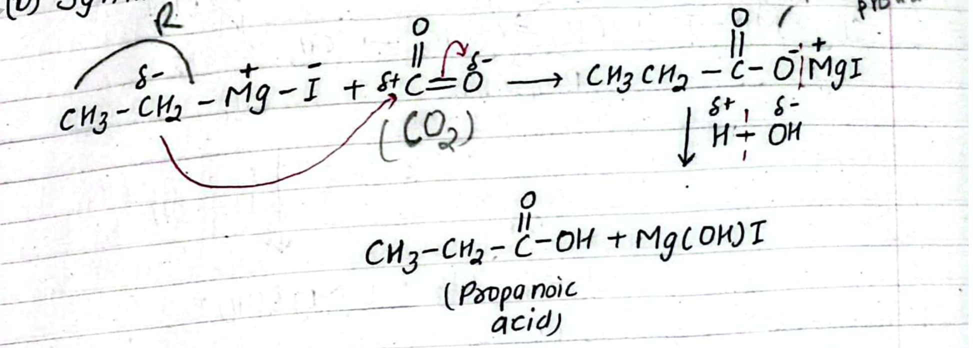
(a) Synthesis of Alkane

$$\underset{R}{\overset{\delta-}{CH_3CH_2}} - \underset{Mg}{\overset{+}{Mg}} - \underset{X}{\overset{-}{I}} + \overset{\delta+}{H} - \overset{\delta-}{OH} \longrightarrow CH_3-CH_3 + Mg(OH)I$$

(ethyl magnesium Iodide) ethane (magnesium hydroxy iodide)

[R-Vary product vary]

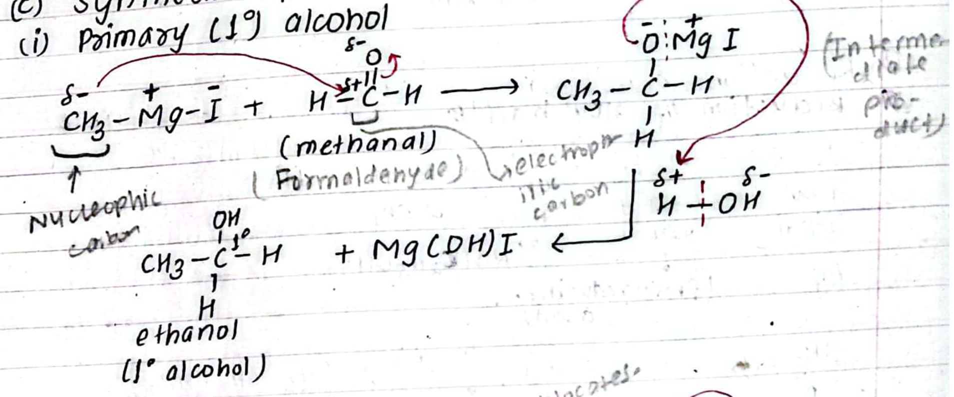
(b) Synthesis of carboxylic acid



$$\overset{\delta-}{CH_3-CH_2}-\overset{+}{Mg}-\overset{-}{I} + \overset{\delta+}{C}(=\overset{\delta-}{O})=O \longrightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Mg}I \xrightarrow{\overset{\delta+}{H}-\overset{\delta-}{OH}} CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH + Mg(OH)I$$

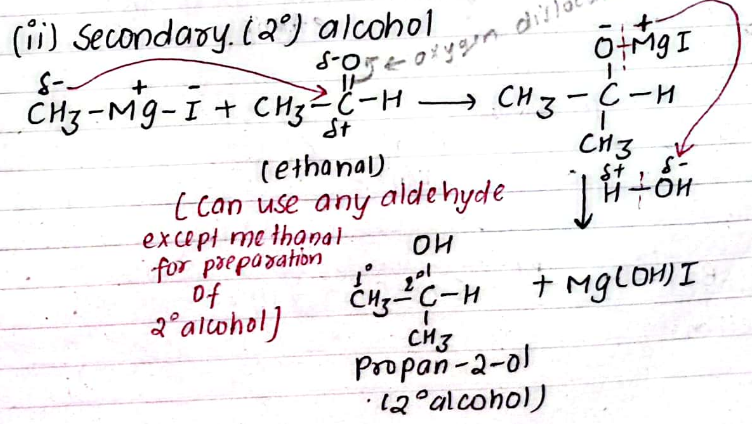
(c) Synthesis of Alcohol (1°, 2°, 3°)

(i) Primary (1°) alcohol



$$\overset{\delta-}{CH_3}-\overset{+}{Mg}-\overset{-}{I} + H-\overset{\overset{\delta-}{O}}{\overset{\|}{\overset{\delta+}{C}}}-H \longrightarrow CH_3-\overset{\overset{-}{O}\overset{+}{Mg}I}{\overset{|}{C}}-H \xrightarrow{\overset{\delta+}{H}-\overset{\delta-}{OH}} CH_3-\overset{OH}{\overset{|}{C}}-H + Mg(OH)I$$

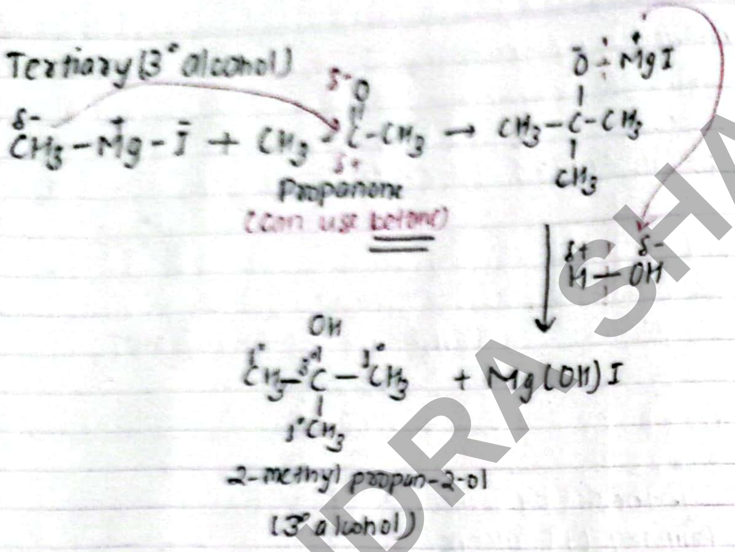
(ii) Secondary (2°) alcohol



$$\overset{\delta-}{CH_3}-\overset{+}{Mg}-\overset{-}{I} + CH_3-\overset{\overset{\delta-}{O}}{\overset{\|}{\underset{\delta+}{C}}}-H \longrightarrow CH_3-\overset{\overset{-}{O}\overset{+}{Mg}I}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-H \xrightarrow{\overset{\delta+}{H}-\overset{\delta-}{OH}} \overset{1°}{CH_3}-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{\overset{2°}{C}}}}}-H + Mg(OH)I$$

[Can use any aldehyde except methanal for preparation of 2°alcohol]

(iii) Tertiary (3° alcohol)



(5) Reduction reaction

(5) Reduction of alkyl halide

$R-X + 2[H] \xrightarrow[\text{OR } LiAlH_4 \text{ or } Na/C_2H_5OH]{Zn/HCl} R-H + HX$

alkyl halide, nascent hydrogen (from reducing agent), alkane

eg-

$CH_3CH_2-Br + 2[H] \xrightarrow{Zn/HCl} CH_3-CH_3 + HBr$

Bromoethane, ethane

$R-X + H_2 \xrightarrow[\Delta]{Pd \text{ or } Ni/Pt} R-H + HX$

alkyl halide, alkane

eg-

$CH_3CH_2Br + H_2 \xrightarrow[\Delta]{Pd} CH_3-CH_3 + HBr$

Bromoethane

$R-I + HI \xrightarrow[\text{Pressure}]{\Delta} R-H + I_2$

alkyl halide, hydroiodic acid, alkane

eg-

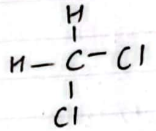
$CH_3-I + HI \xrightarrow[\text{Pressure}]{\Delta} CH_4 + I_2$

Iodo ethane, hydro-iodic acid, Methane

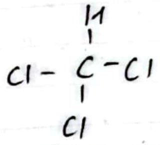
Polyhaloalkane

Poly → many, halo → halogen

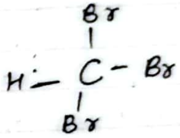
Examples:-



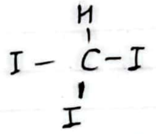
Dichloromethane



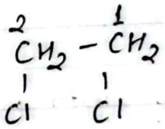
Trichloromethane (Chloroform)



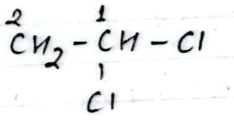
Tribromomethane (Bromoform)



Triiodomethane (Iodoform)



1,2-Dichloroethane (vicinal dichloride)



1,1-dichloroethane (Geminal dichloride)

Note:-

- descriptor vicinal [From latin vicinus- neighbour] abbreviated vic, describes any two functional group bonded to two adjacent C-atom.
- descriptor Geminal refers to the relationship between two atoms of functional group that are attached to same C-atom.

Laboratory preparation of trichloromethane (Chloroform)

- Molecules formula - $CHCl_3$
- IUPAC Name - Trichloromethane
- Common name - Chloroform

Principle- Chloroform can be prepared in lab by heating ethanol or propanone (acetone) with moist bleaching powder.

(a) By using ethanol (C_2H_5OH)

(i) Hydrolysis of bleaching powder

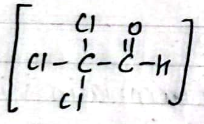
$$CaOCl_2 + \overset{H-OH}{H_2O} \longrightarrow \underset{\text{(Hydrolyzing agent)}}{Ca(OH)_2} + \underset{\text{(O.A) [Chlorinating agent]}}{Cl_2}$$

(ii) Oxidation of Ethanol into Ethanal by Cl_2

$$\overset{(R.A)}{\underset{\text{ethanol}}{C_2H_5OH}} + \underset{\text{(O.A)}}{\overset{0}{Cl_2}} \xrightarrow[\Delta]{\text{oxidation}} \underset{\text{ethanal}}{CH_3CHO} + 2HCl$$

(iii) Chlorination of ethanal into chloral

$$\underset{\text{ethanal}}{CH_3CHO} + \underset{\downarrow \text{ chlorinating agent}}{3Cl_2} \xrightarrow[\Delta]{\text{chlorination}} CCl_3CHO + 3HCl$$



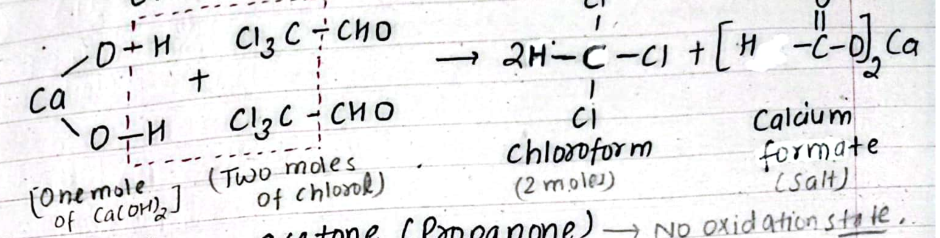
Chloral [Trichloroethanal]

$HCOO^- \rightarrow$ Formate, Methanoate
$CH_3COO^- \rightarrow$ acetate

(iv) Hydrolysis of Chloral by $Ca(OH)_2$

$$\underset{\text{chloral}}{2\,CCl_3-CHO} + \underset{\text{Hydrolyzing agent}}{Ca(OH)_2} \xrightarrow{\text{hydrolysis}} \underset{\text{Trichloromethane (Chloroform)}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

OR



(b) By using acetone (Propanone) → No oxidation state.

(i) Hydrolysis of Bleaching powder

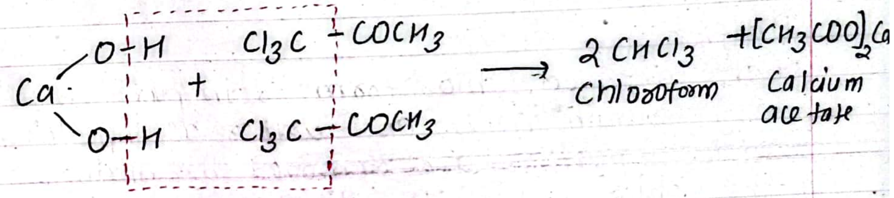
$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

(ii) Chlorination of acetone into trichloro acetone

$$\underset{\text{acetone (Propanone)}}{CH_3COCH_3} + 3Cl_2 \longrightarrow \underset{\text{Trichloroacetone}}{CCl_3-CO-CH_3} + 3HCl$$

(1,1,1-Trichloropropanone)

(iii) Hydrolysis of trichloroacetone by $Ca(OH)_2$



Procedure-

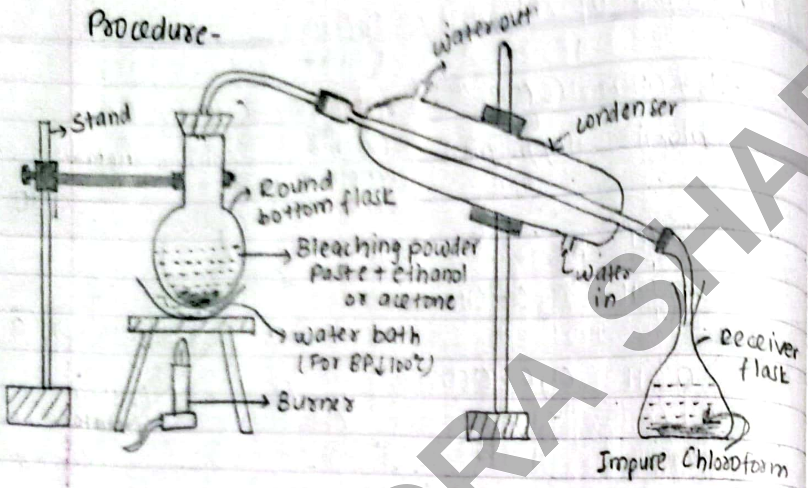


Fig:-Laboratory Preparation Of Chloroform.

First of all paste of bleaching powder is prepared by mixing 100g of bleaching powder with 200ml of water in 1 litre round bottom flask. 25ml ethanol or acetone is added to it and the mixture is distilled. Then the chloroform obtained in the receiver funnel is impure and transferred in the separating funnel to separate the lower dark layer of chloroform.

Purification-

Lab prepared chloroform is impure and may contain acids and water as impurities. Acidic impurities are removed by mixing the chloroform with dilute NaOH/ Na_2CO_3.

$$\underset{(dil.)}{NaOH} + HCl \longrightarrow NaCl + H_2O$$

Water soluble impurities are removed by washing the chloroform with cold water. Then it is dried over anhydrous $CaCl_2$

$$CHCl_3 + H_2O + \underset{anhydrous}{CaCl_2} \longrightarrow \underset{Chloroform}{CHCl_3} + CaCl_2 \cdot H_2O$$

Finally, chloroform is refined by distillation process carried at about 60°C–62°C [Since boiling point of $CHCl_3$ is 61°C].

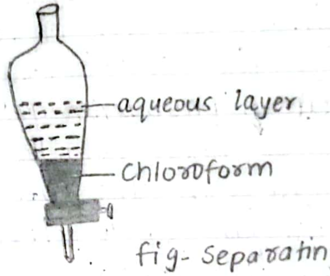


fig- Separating funnel.

Physical properties of Trichloromethane (Chloroform)

(a) It is colourless and sweet smelling liquid.

(b) Freezing point and boiling point of chloroform are −63°C and 61°C respectively

(c) It is insoluble in water and soluble in non-polar organic solvent.

(d) Although chloroform is non poisonous ~~gas~~, it forms a poisonous compound (phosgene) in air.

(e) It is heavier than water.

(f) It dissolves fat, oil, waxes, etc.

Chemical properties of chloroform

1. Oxidation reaction

Chloroform is oxidised is the air in presence of sunlight to form a poisonous compound called phosgene. → highly poisonous.

wargas (in IInd WW)

$$CHCl_3 + O_{2(air)} \xrightarrow{sunlight} 2COCl_2 + 2HCl$$

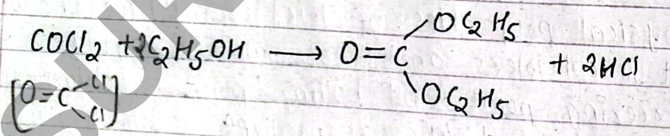
Chloroform   Phosgene (Carbonyl chloride)

*Why chloroform is stored in dark brown bottle?

→ Chloroform is stored in a dark brown bottle with a tight lid so as to prevent the formation of ~~8~~ phosgene gas.

(upto the stopper) ↓ so O_2 gas donot enter.

- Chloroform containing bottle is often supplied with a small amount of ethanol since it converts phosgene into diethyl carbonate which is non-poisonous.



$$COCl_2 + 2C_2H_5OH \longrightarrow O=C(OC_2H_5)_2 + 2HCl$$

$[O=C(Cl)_2]$

*Why Impure $CHCl_3$ gives white ppt with $AgNO_3$?

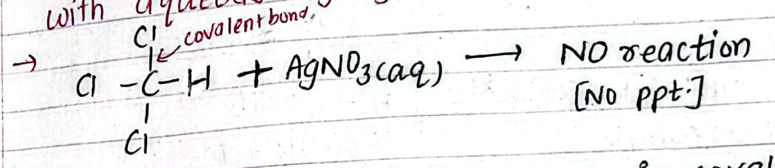
→ Test of purity of $CHCl_3$ [aq. $AgNO_3$ Test]

$$HCl \longrightarrow H^{\oplus} + \underset{free}{Cl^{\ominus}}$$

$$Cl^{\ominus} + \underset{(aq)}{Ag^{\oplus}NO_3^{\ominus}} \longrightarrow \underset{white\,ppt}{AgCl\downarrow} + NO_3^{\ominus}$$

Impure chloroform contains significant amount of free chloride ion. The free chloride ion (Cl^-) reacts with aqueous $AgNO_3$ to give white ~~rest~~ ppt of AgCl.

* Why pure chloroform does not gives ppt with aqueous $AgNO_3$?



covalent bond

→ $CHCl_3 + AgNO_{3(aq)} \longrightarrow$ NO reaction [No ppt.]

The C-Cl bond in chloroform is covalent in nature which does not ionize in the aqueous solution and there is no any free chloride ion (Cl^-) to produce white ppt of AgCl.

2. Reduction reaction

Chloroform is reduced to dichloro methane in acidic medium and to methane in neutral medium respectively.

Acidic medium : $\underset{Chloroform}{CHCl_3} + 2[H] \xrightarrow{Zn/HCl} \underset{dichloro-methane}{CH_2Cl_2} + HCl$

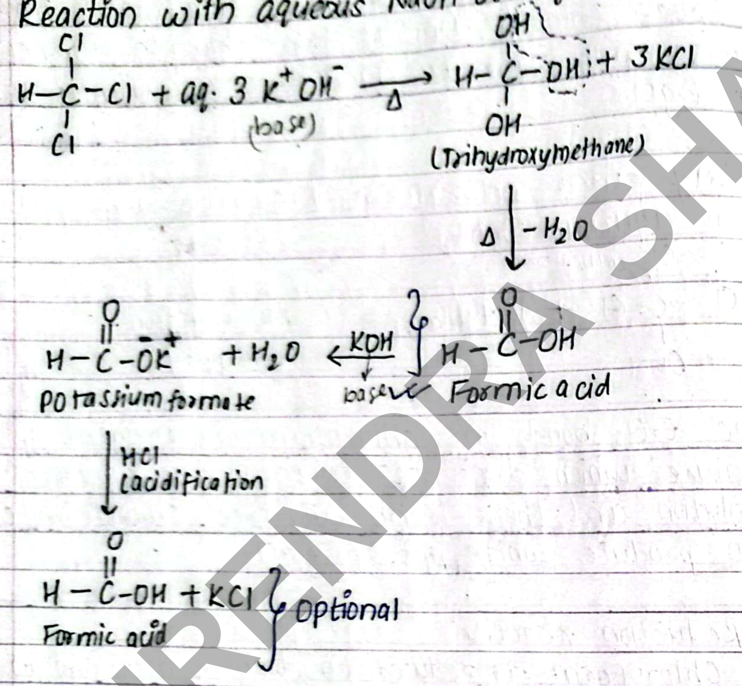
$Zn + 2HCl \rightarrow ZnCl_2 + 2[H]$

Neutral medium: $\underset{Chloroform}{CHCl_3} + 6[H] \xrightarrow{Zn/H_2O} \underset{Methane}{CH_4} + 3HCl$

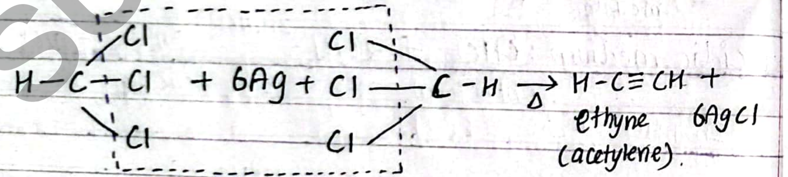
$Zn + H_2O \rightarrow Zn(OH)_2 + [H]$

[redacted]

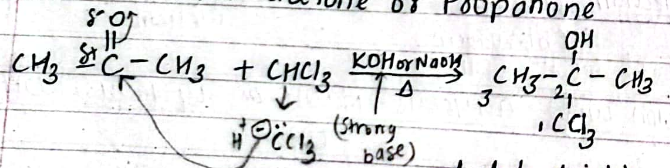
3. Reaction with aqueous NaOH or aqueous KOH



4. Reaction with Silver powder



5. Reaction with acetone or Propanone

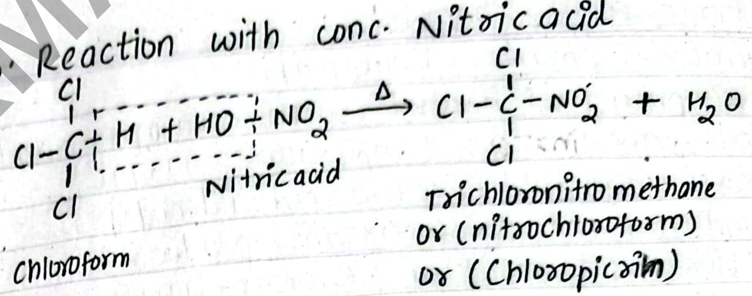


1,1,1-trichloro-2-methyl propan-2-ol

Uses- Sleep inducing drug ← (Chloretone)

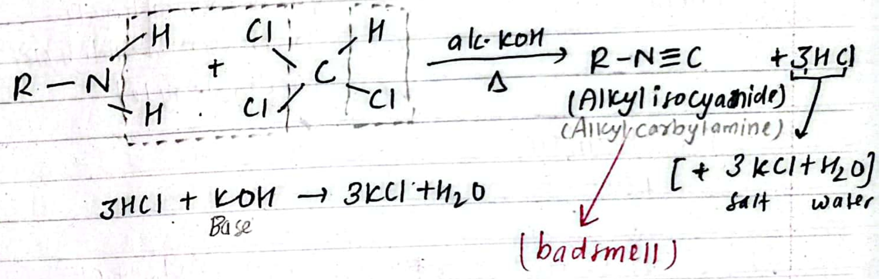
(hypotonic drug) [Chloro + acetone]

6. Reaction with conc. Nitric acid



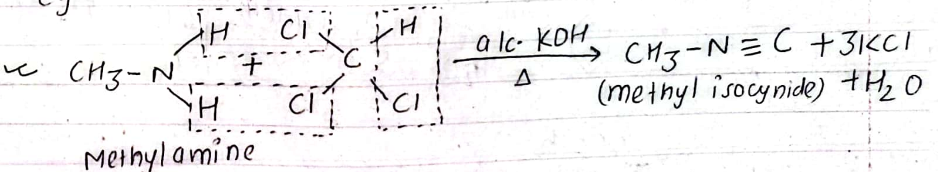
Uses- Tear/war gas
- Insecticide.

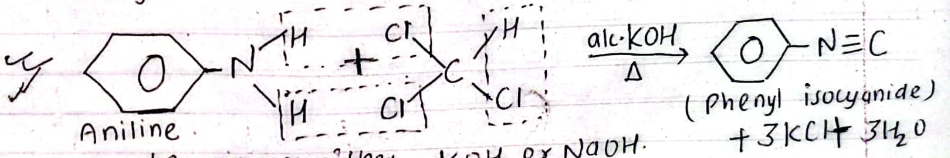
(7) Reaction with primary amine [Carbyl amine reaction test]



Chloroform produces an offensive smelling carbyl amines or isocynides when warmed with the primary amine ($R-NH_2$) in presence of an alkali (NaOH or KOH). This reaction is known as carbyl amine reaction.

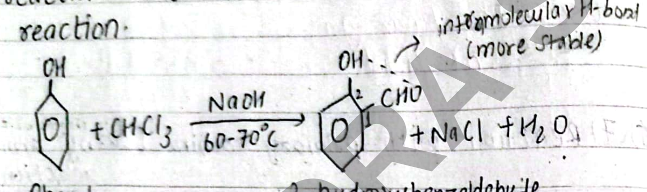
eg-





* We can use either KOH or NaOH.

8. Reactions with Phenol
[Reimer-Tiemann's Reaction]
When phenol is heated with chloroform and aqueous alkaline at temperature 60-70°C, hydroxy benzaldehyde [Salicyl aldehyde] is formed as the chief organic product. This reaction is termed as Riemer-Tiemann reaction.

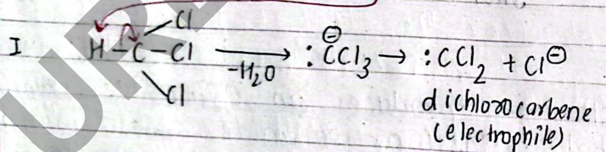


2-hydroxybenzaldehyde
or [O-hydroxybenzaldehyde]
or [Salicylaldehyde]
(Major)

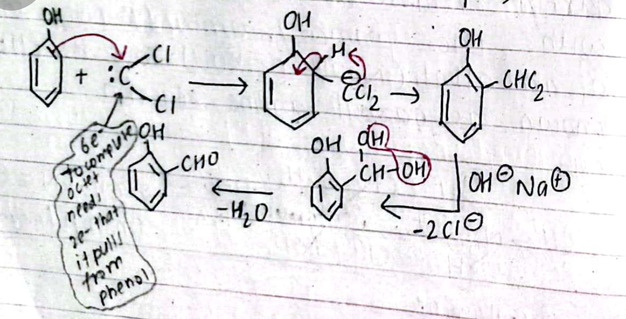
Mechanism

$Na-OH \longrightarrow Na^{\oplus} + OH^{\ominus}$

I



II.



Uses of Chloroform [Trichloromethane]

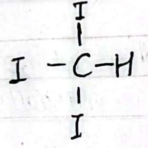
(a) Chloroform is used as a solvent for iodine, alkaloids, fats, etc.

(b) Chloroform is majorly used for the manufacture of Freon refrigerant R-22.

(c) It was used as a prominent anaesthetic during medical surgeries even since it effects were discovered.

~~(d). For~~ (d) For preparation of chloropicrin, chloretone, etc.

Iodoform [Triiodo methane] → similar properties to Chloroform.



$$I-\overset{\displaystyle I}{\underset{\displaystyle I}{C}}-H$$

OR CHI_3 → Yellow crystaline solid.

* Preparation of iodoform

In laboratory iodoform is prepared by the action of iodine on ethyl alcohol or acetone in the presence of an alkali. The reaction is known as iodoform reaction.

1. From ethyl alcohol

iodoform → yellow precipitate or characteristic hospital smell

I. $2NaOH + I_2 \rightarrow \underset{\text{Sodium hypoiodite (Iodizing agent) (Oxidising agent)}}{NaOI} + NaI + H_2O$

II. $\underset{\text{ethanol}}{CH_3CH_2OH} + NaOI \xrightarrow{\text{oxida-tion}} \underset{\text{ethanal}}{CH_3CHO} + NaI + H_2O$

III. $CH_3CHO + NaOI \xrightarrow{\text{Iodization}} \underset{\text{Triiodoethanal}}{CI_3CHO} + 3NaOH$

IV. $CI_3\boxed{CHO + NaOH} \xrightarrow{\text{hydrolysis}} \underset{\text{Iodoform}}{CHI_3\downarrow} + \underset{\text{Sodium formate.}}{HCOONa}$

(2) From acetone (Propanone) → No oxidation.

I. $NaOH + I_2 \longrightarrow NaOI + NaI + H_2O$

II. $CH_3COCH_3 + NaOI \xrightarrow{\text{Iodization}} CI_3COCH_3 + 3NaOH$

Acetone (Triiodoacetone)

III. $NaOH + CI_3COCH_3 \xrightarrow{\text{hydrolysis}} CHI_3\downarrow + CH_3COONa$

(Triiodopropanone) Iodoform (yellow crystalline precipitate) (Sodium acetate)

* Overall reaction

1. $CH_3CH_2OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3\downarrow + 5NaI + 5H_2O + HCOONa$

ethanol Iodoform

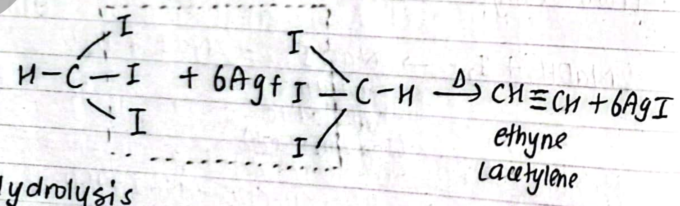
2. $CH_3COCH_3 + 3I_2 + 4NaOH \xrightarrow{\Delta} CHI_3\downarrow + 3NaI + CH_3COONa + H_2O$

acetone Iodoform

* Chemical reaction of Iodoform

(a) With Silver powder

Iodoform on heating with Silver powder forms acetylene.



(b) Hydrolysis

Iodoform on boiling with alcoholic or conc. aqueous solution of KOH gives potassium formate.

$CHI_3 + 3KOH_{(aq.)} \xrightarrow{\text{Boil}} HCOOH + 3KI + H_2O$

(formic acid)

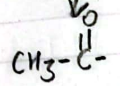
(Main chemical properties similar to chloroform)

$HCOOH + KOH \longrightarrow HCOOK + H_2O$

(Potassium formate)

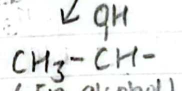
Iodoform Test (V.V.I) [CHI_3 → Yellow/ hospital like smell]

Iodoform test is used to check the presence of carbonyl compounds with the structure $R-CO-CH_3$ or alcohols with the structure $R-CH(OH)-CH_3$ in a given unknown reaction



$CH_3-\overset{O}{\overset{\|}{C}}-$

(in aldehyde or ketone)



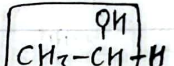
$CH_3-\overset{OH}{CH}-$

(In alcohol)

necessary condition for +ve iodoform test. [$CH_3-\overset{OH}{CH}-$ group]

Examples:-(1) Alcohol

① CH_3OH & CH_3CH_2OH /



$\boxed{CH_3-\overset{OH}{CH}}-H$

Methanol Ethanol

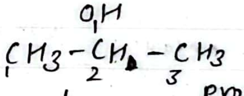
Here H so HCOONa as by product if CH_3 then CH_3COONa as byproduct.

↳ respond to positive iodoform test while methanol doesn't.

Distinguish Methanol & Ethanol ⇅

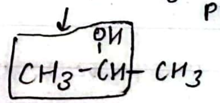
$CH_3-CH_2-OH + NaOH + I_2 \xrightarrow[\text{60°C-70°C (waterbath)}]{\Delta} CHI_3\downarrow + NaI + HCOONa$

(ii) $\overset{3}{C}H_3-\overset{2}{C}H_2-\overset{1}{C}H_2-OH$ &



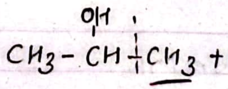
$\underset{1}{C}H_3-\underset{2}{\overset{OH}{CH}}-\underset{3}{CH_3}$

Propan-1-ol Propan-2-ol



$\boxed{CH_3-\overset{OH}{CH}}-CH_3$

→ Propan-2-ol respond the iodoform test.

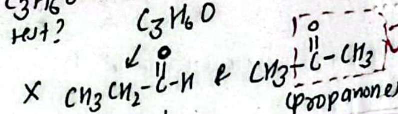


$CH_3-\overset{OH}{CH}-CH_3 + NaOH + I_2 \xrightarrow{\Delta} CHI_3\downarrow + NaI + CH_3COONa + H_2O$

Propan-2-ol Iodoform

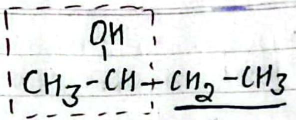
For 2 marks question of iodoform test you can write simply above rxn & for 4 marks you can extend as given in prepⁿ rxn.

Write isomers of C_3H_6O & distinguish which of them give iodoform test?



C_3H_6O ✗ $CH_3CH_2-\overset{O}{\overset{\|}{C}}-H$ & $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ → Methyl keto group.

Propanal (Propanone)



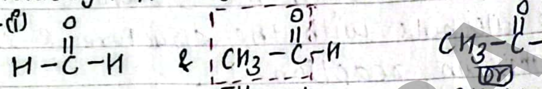
$CH_3-\overset{OH}{\overset{|}{CH}}-CH_2-CH_3$ & $CH_3-CH_2-CH_2-CH_2-OH$

Butan-2-ol Butan-1-ol

↓

doesn't contain $CH_3-\overset{O}{\overset{|}{CH}}-$ group so don't give Iodoform test.

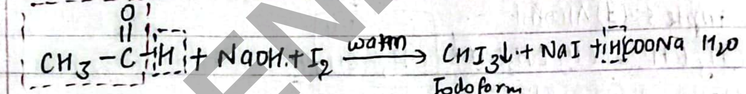
(2) Aldehyde/ketone ⟶ should contain



\# Eg:-(i) $H-\overset{O}{\overset{\|}{C}}-H$ & $CH_3-\overset{O}{\overset{\|}{C}}-H$ $CH_3-\overset{O}{\overset{\|}{C}}-$ group to give Iodoform test. (or) CH_3CO- (Methyl keto group)

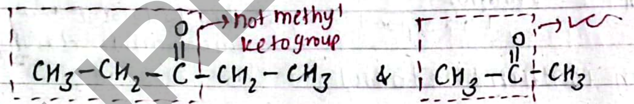
Methanal (Formaldehyde) Ethanal (Acetaldehyde)

→ Ethanal gives +ve iodoform test while Methanal doesn't.



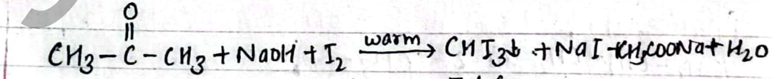
$$CH_3-\overset{O}{\overset{\|}{C}}-H+NaOH+I_2\xrightarrow{warm}CHI_3\downarrow+NaI+HCOONa\ H_2O$$

Iodoform



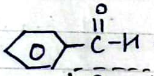
(ii) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ → not methyl keto group & $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ → ✓

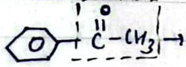
pentan-3-one Propanone (Acetone) → gives +ve iodoform test

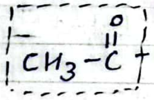


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3+NaOH+I_2\xrightarrow{warm}CHI_3\downarrow+NaI+CH_3COONa+H_2O$$

Iodoform

 → doesn't gives iodoform test.

 → gives +ve iodoform test.



$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$ → gives +ve iodoform test

---

→ prepⁿ of haloarene from

(i) Benzene (ii) Benzenediazonium salt

→ phy. prop → chem prop.

• Nucleophilic subⁿ (comparision imp.)

9.2. Haloarenes

Haloarenes are the halogen derevatives of aromatic hydrocarbon in which halogen is directly attached to C-atom of the benzene ring. These are obtained by replacing hydrogen by alphahydrogen atom.

$$Ar-H \xrightarrow{-H/+X} Ar-X$$

Aromatic substitution Haloarene

where, Ar → aryl eg-phenyl (C_6H_5) or 

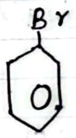
X → F, Cl, Br, I

Halobenzene

Nomenclature of Haloarenes

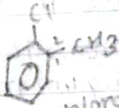
(a) Monosubstituted haloarenes

Chlorobenzene



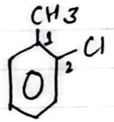
Bromo benzene

Fluoro benzene

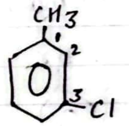


2-chlorotoulene

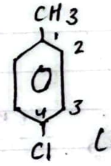
(b) Disubstituted and polysubstituted haloarenes



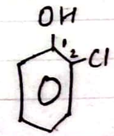
2-chlorotoulene (o-chlorotoulene)



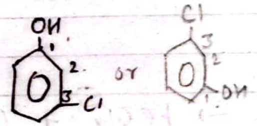
3-Chlorotoulene (m-chloro toulene)



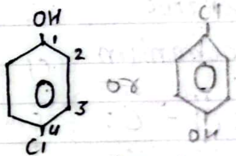
(4-chlorotoulene) (p-chloro toulene)



2-Chlorophenol (o-chlorophenol)

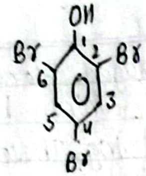


3-chlorophenol (m-chlorophenol)

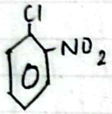


4-chlorophenol (p-chlorophenol)

(OH more priority, CH_3 more priority)



2,4,6-Tribromophenol



2-nitrochloro benzene
(o-nitrochloro benzene)

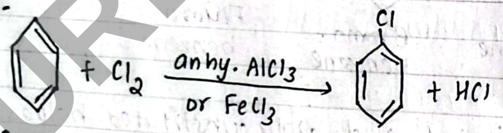
General method of preparation of Halo arenes

1. By direct halogenation of aromatic hydro carbon (Benzene)

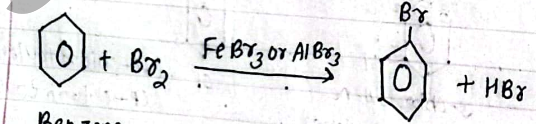
$Ar-H + X[Cl_2 \text{ or } Br_2 \text{ or } I_2] \xrightarrow[\text{to generate electrophile}]{\text{lewis acid}} Ar-X + HX$

aromatic hydrocarbon (halo arene)

eg-

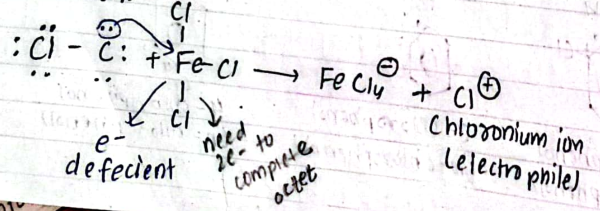


Benzene Chlorobenzene

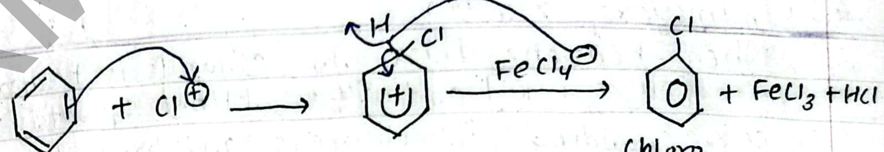


Benzene Bromobenzene

- Mechanism

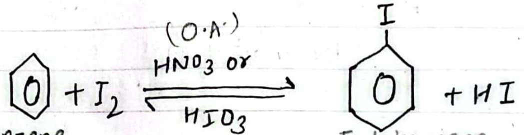


$HCl > HBr > \boxed{HI} \leftarrow (O.A)$
Reducing character increases



Chloro benzene

The reaction of an aromatic hydrocarbon with iodine is reversible. Therefore, iodination is carried out in presence of oxidation agent like HNO_3, HIO_3, etc. with accelerate the rate of forward reaction.

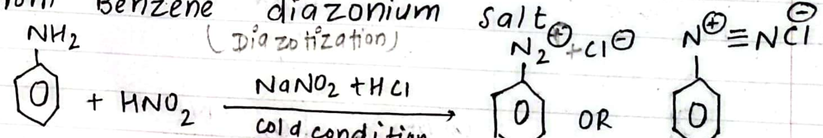


Benzene Iodobenzene

$HI + HNO_3 \rightarrow H_2O + NO_2\uparrow + I_2\uparrow$
(R.A.) (O.A.)

$HCl > HBr > HI$
Reducing character increases.

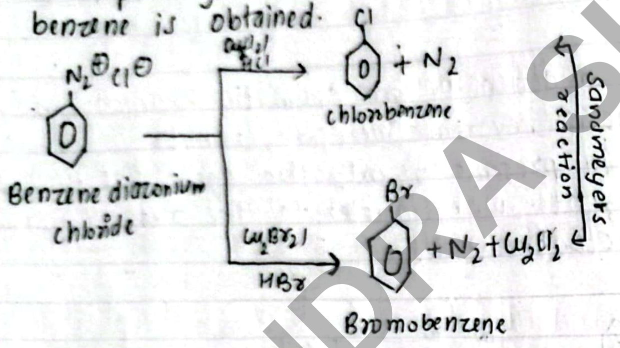
2. From Benzene diazonium salt (Diazotization)



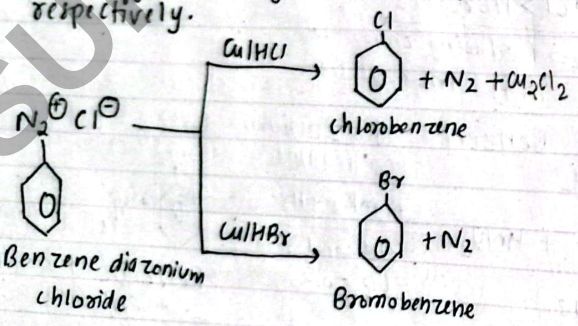
Aniline

Benzene diazonium chloride

* Sandmeyers reaction
When benzene diazonium chloride is treated with [Cu_2Cl_2 + HCl] and [Cu_2Br_2 + HBr] seperately corresponding chlorobenzene and bromo, benzene is obtained.

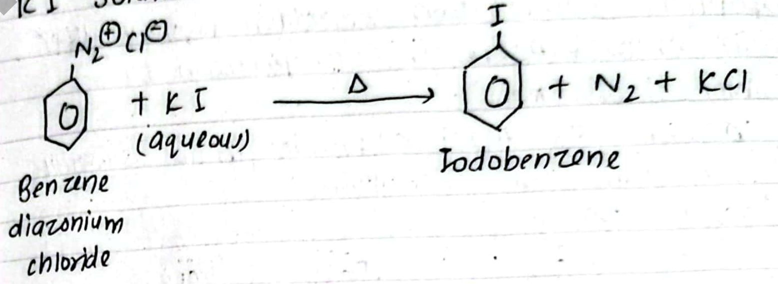


* Gattermann reaction
Gattermann reaction is used for obtaining chlorobenzene or bromobenzene from benzenediazonium chloride by treating it with Cu/HCl or Cu/HBr respectively.



Main organic product is important than By product.

* Iodobenzene is obtained by adding aqueous KI solution to benzene diazonium chloride

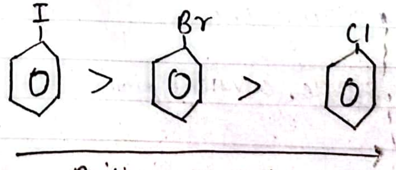


Physical properties of Haloarenes

(a) State
Haloarenes are colourless liquid or crystaline solids.

(b) Solubility
Haloarenes are the non polar compound which cannot form the hydrogen bond with water molecules. As a result, they are insoluble in water but soluble in organic solvent.
cannot form intermolecular H-Bond

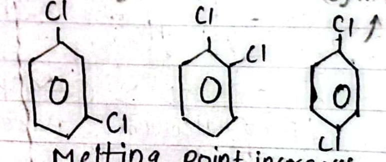
(c) Melting and Boiling point
Boiling points of haloarenes increase with an increase in their molecular weight.



Boiling point decrease due to decrease in vanderwaal force
[I - Molecular size increase
↓
Vanderwaal's force increases]

Symmetrical Molecular
↓
Better packing in crystal lattice & High M.P.

can fit in lattice points.
↑
(symmetry
↑



Melting point increases.

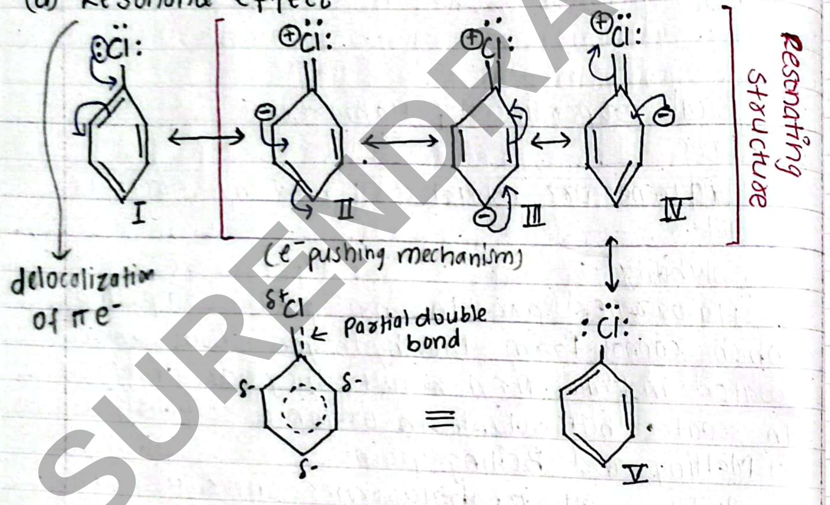
Chemical properties of Haloarene [Chlorobenzene]

1. Nucleophilic substitution reaction in chlorobenzene [Comparision with halo alkane]

✓ Nucleophilic substitution reaction is very difficult in chlorobenzene in comparision to haloalkane (chloroethane).

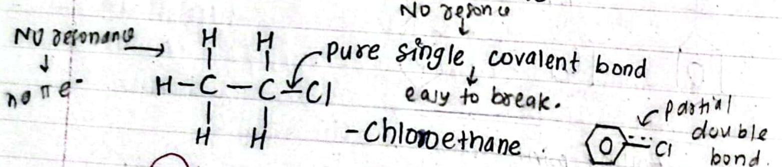
Key reasons of unactive nucleophilic substitution reactions are as follows-

(a) Resonance effect



Resonance hybrid

- Resonance in chlorobenzene



- Chloroethane

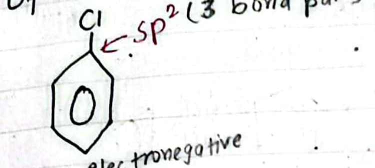
C---Cl > C–Cl

Partial covalent bond — Pure single covalent bond

- Difficult to break by nucleophile — - Easily breakable by nucleophile

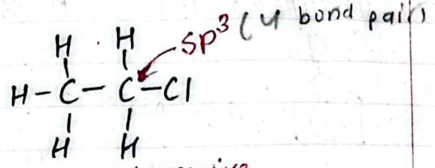
More polar → more reactive
(more EN diff)
↓
More % s-character.

(b) Hybridization state of Carbon atom and polarity of C–Cl bond



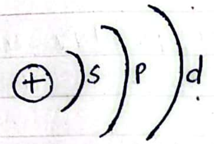
more electronegative
↑
C–Cl → more electronegative
sp^2 ↳ less polar

% S-character = 33.3%
Bond length = 1.69A°
→ Less reactive

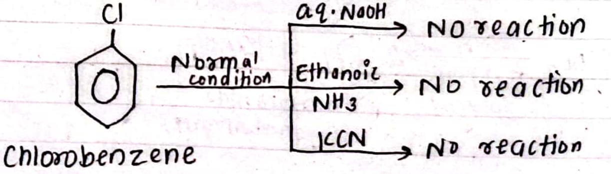


less electronegative
↑
C–Cl → more electronegative
sp3 ↳ more polare

% s-character = 25%
Bond length = 1.77A°
→ More reactive



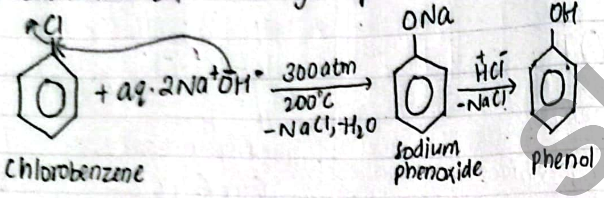
Since 's' orbital is much closer to the nucleus in comparision to 'p' and 'd'. The % s character of carbon in C–Cl bond of chlorobenzene is more than that of the C–Cl bond of chloroethane. Due to this C atom of chlorobenzene attracts incoming electrons more strongly then C-atom of chloroethane i.e. C-atom of chlorobenzene is more electronegative than C-atom of chloroethane. Similarly the difference in electronegativity of C-atom and Cl-atom of C-Cl bond in chloroethane is high, hence making the bond polar and the compound chloroethane more reactive.



Drastic → High T ✓
High P ✓
catalyst ✓

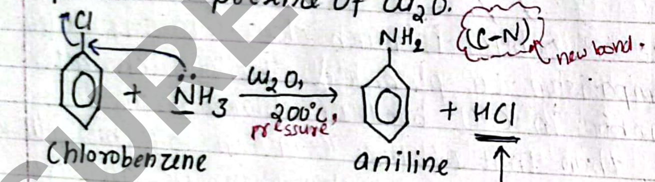
1. Nucleophilic substitution reaction in chloro benzene [Under drastic conditions]

(a) Substitution of –OH group ((C–OH))



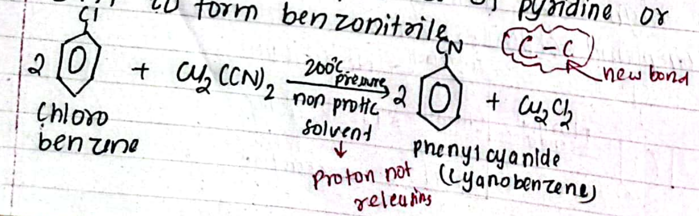
When chlorobenzene is heated with caustic soda at 200°c and 300 atm pressure, sodium phenoxide is formed which on acidification gives phenol.
→ For manufacture of phenol in large scale.

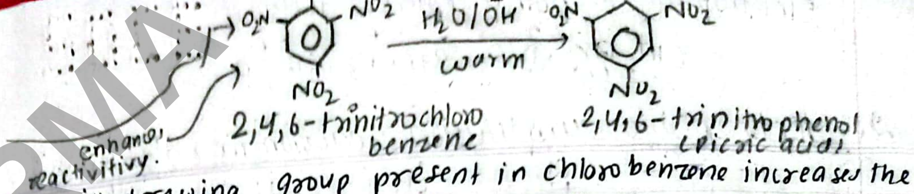
(b) Substitution by –NH_2 group
Haloarenes (eg- chlorobenzene) produce aniline on heating with ammonia at 200°c under pressure in presence of Cu_2O.



$Cu_2O + HCl \rightarrow Cu_2Cl_2 + H_2O$
cuprous oxide (basic oxide)
cuprous chloride

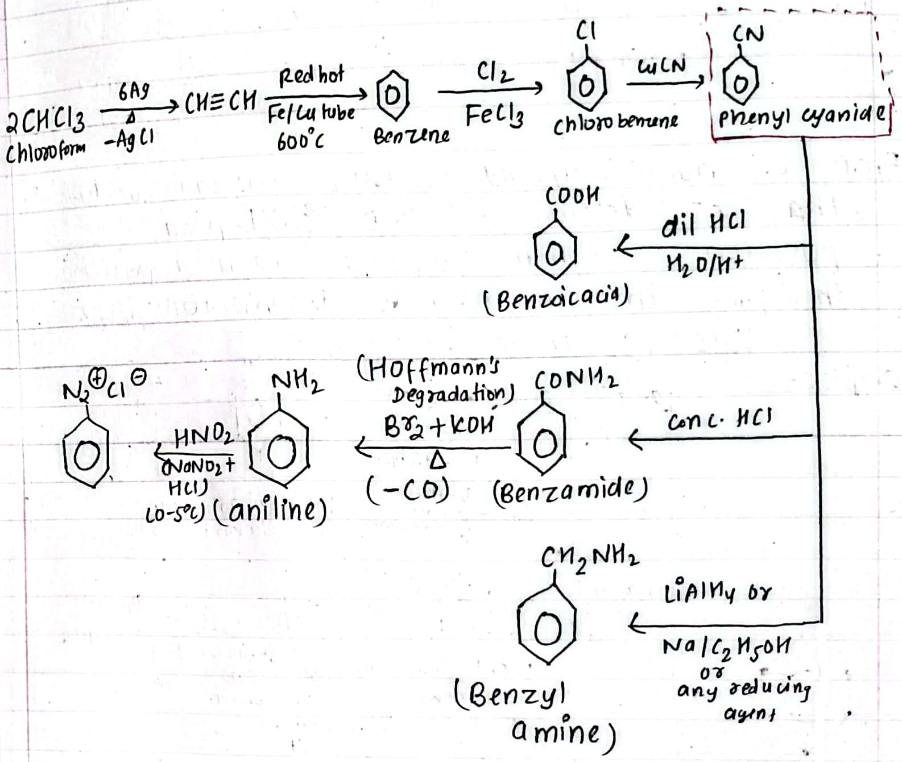
(c) Substitution of –CN group
Haloarenes react with cuprous cyanide at 200°c under pressure in presence of pyridine or DMF to form benzonitrile.





e- withdrawing group present in chlorobenzene increases the reactivity towards nucleophilic substitution rxn.

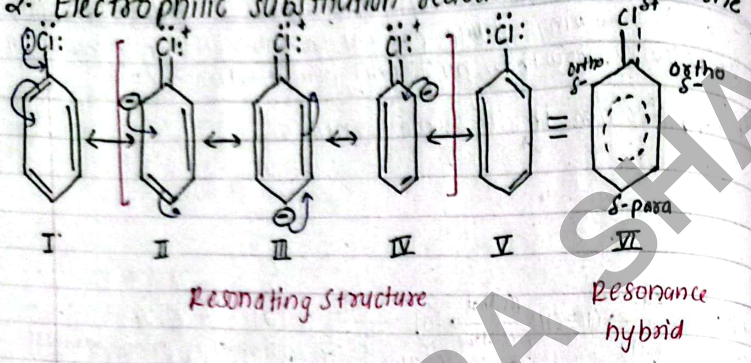
Application in organic synthesis



Electrophile : e⁻ pair acceptor / e⁻ deficient

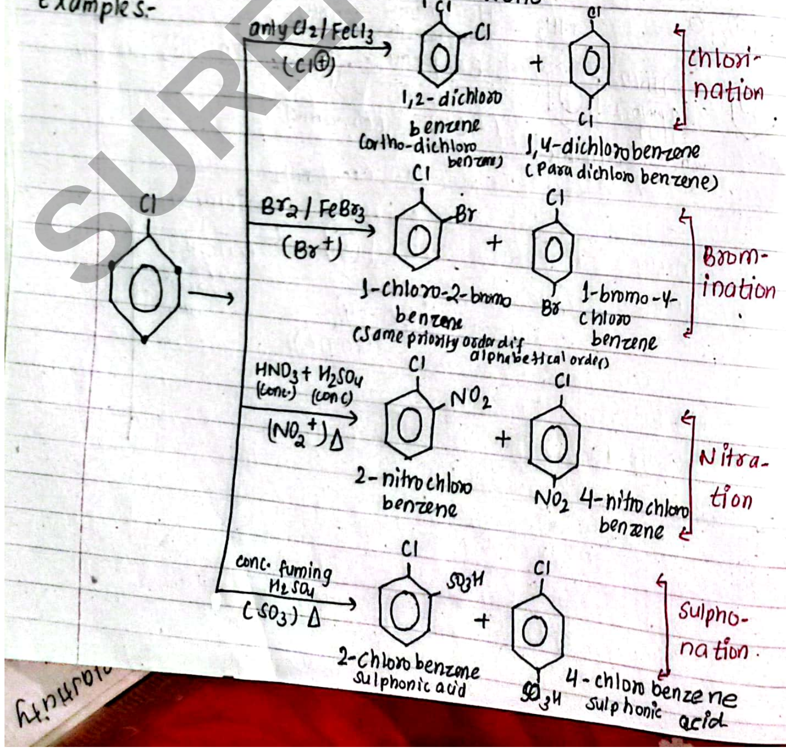
$Cl^+, Br^+, \overset{+}{N}O_2, SO_3, \overset{+}{C}H_3, CH_3\overset{+}{C}O$

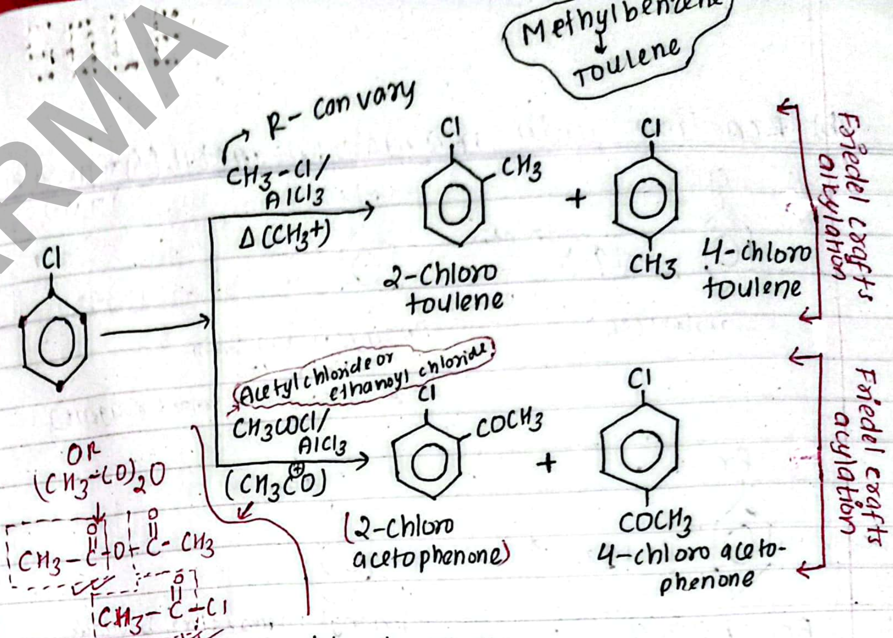
2. Electrophilic substitution reaction in chlorobenzene



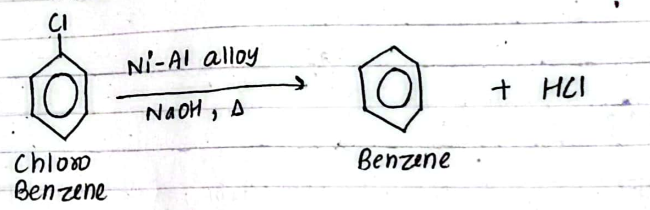
From resonance hybrid structure we can conclude that e⁻ density at ortho and para position is high in comparision to meta position. Therefore the incoming electrophile will prefer to attack at these positions.

Examples:-



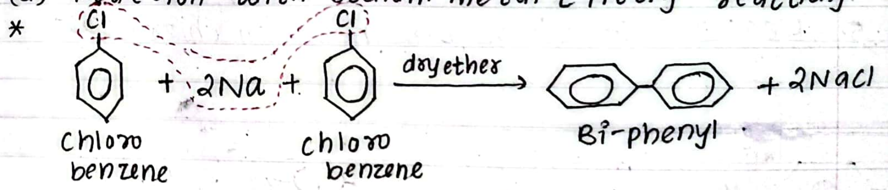


3. Reduction of chlorobenzene

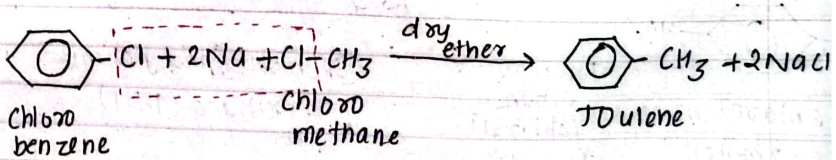


4. Reaction with metal

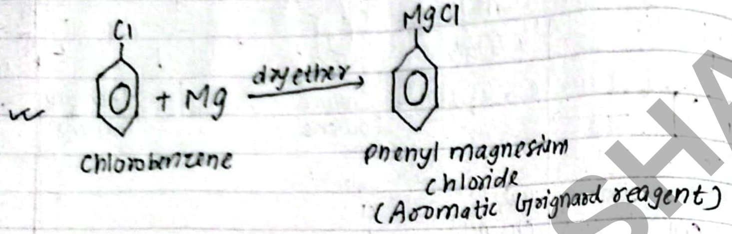
(a) Reaction with sodium metal [Fittig reaction] → aromatic-aromatic combination

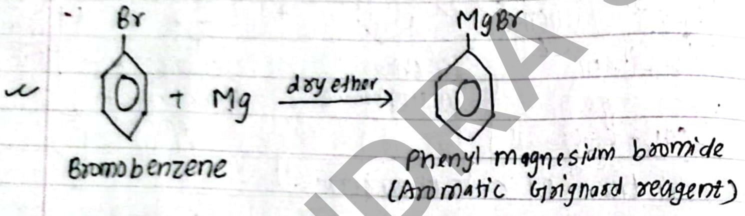


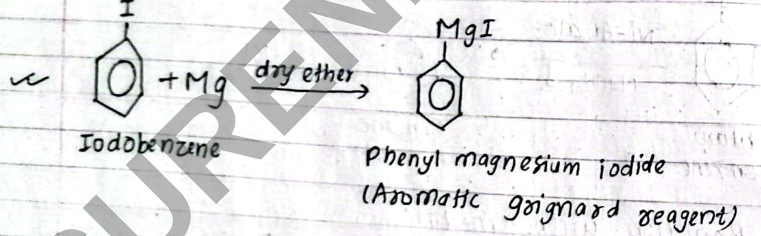
* Wurtz Fittig reaction → aromatic-aliphatic



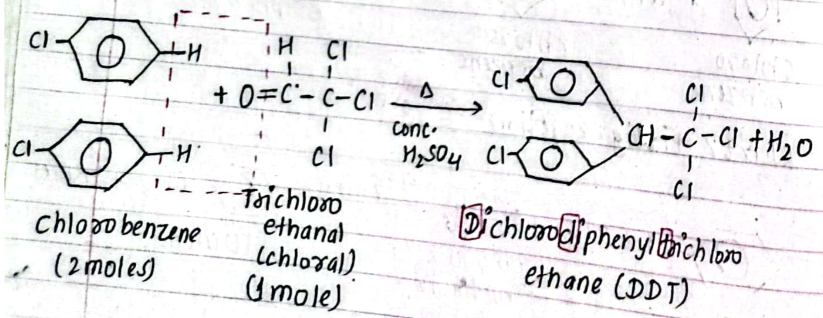
(b) Reaction with magnesium metal (Grignard's rxn)







5. Reaction of chlorobenzene with chloral



Uses of Haloarenes

(a) Dichlorodiphenyl trichloro ethane (DDT) is used as an insecticide.

(b) Used to synthesize (prepare) phenol, aniline, phenyl cyanide, etc.

→ Alcohols (R-OH) and ether (R-O-R) are functional isomers of each other. $\boxed{C_nH_{2n+2}O}$

→ Victor Meyer's method - distinguish 1°, 2° and 3° alcohol

- $\boxed{OH}$ (i) Alcohol is treated with PI_3 (red $P_4 + I_2$) + Δ,

↓

- $\boxed{I}$ (ii) Iodoalkane treated with alcoholic $AgNO_2$ to obtain nitro Alkane ($-NO_2$)

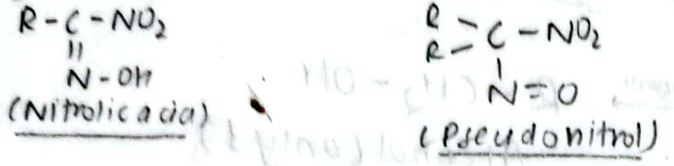
↓

- $\boxed{NO_2}$ (iii) Nitro Alkane treated with nitrous acid ($NaNO_2$ + HCl) ↓ HNO_2 (O=N-OH)

↓ $-H_2O$

(iv) then with aqueous alkali (NaOH)

1° → blood red colour; 2° → blue colour; 3° → colourless solution.


$R-\underset{\underset{N-OH}{||}}{C}-NO_2$ (Nitrolic acid)

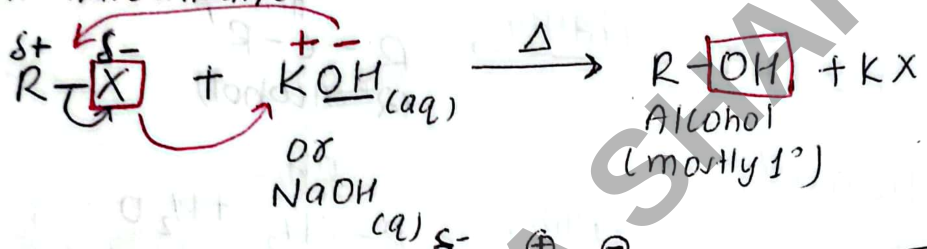
$R_2C(NO_2)-N=O$ (Pseudonitrol)

3° ↓ No reaction

P	A	N	N
PI_3	alc. $AgNO_2$	HNO_2	aq. NaOH
R	B	C	
Red	Blue	Colourless	

Preparation of Monohydric alcohol.

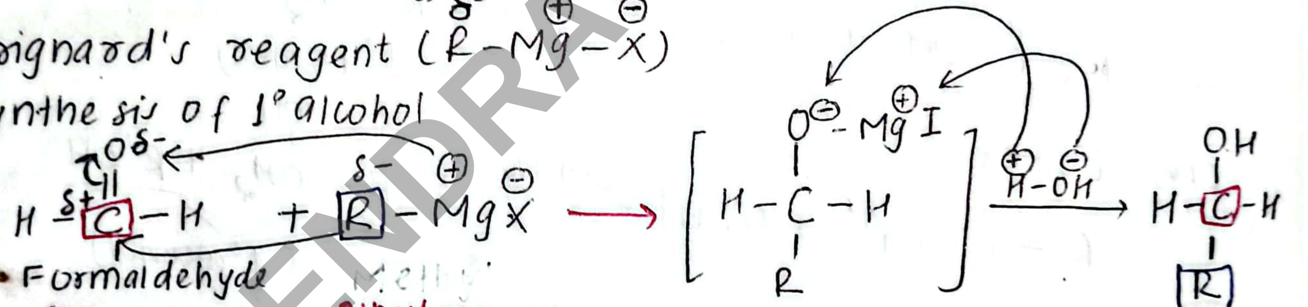
(1) From haloalkanes


$$\overset{\delta+}{R}-\overset{\delta-}{\boxed{X}} + \overset{+}{K}\overset{-}{OH}_{(aq)} \text{ or } NaOH_{(aq)} \xrightarrow{\Delta} R-\boxed{OH} + KX$$

Alcohol (mostly 1°)

(2) Grignard's reagent ($\overset{\delta-}{R}-\overset{\oplus}{Mg}-\overset{\ominus}{X}$)

(i) synthesis of 1° alcohol


$$H-\overset{\overset{O^{\delta-}}{||}}{\overset{\delta+}{\boxed{C}}}-H + \overset{\delta-}{\boxed{R}}-\overset{\oplus}{Mg}\overset{\ominus}{X} \longrightarrow \left[H-\underset{R}{\overset{O^{\ominus}-\overset{\oplus}{Mg}I}{C}}-H\right] \xrightarrow{\overset{\oplus}{H}-\overset{\ominus}{OH}} H-\underset{\boxed{R}}{\overset{OH}{\boxed{C}}}-H$$

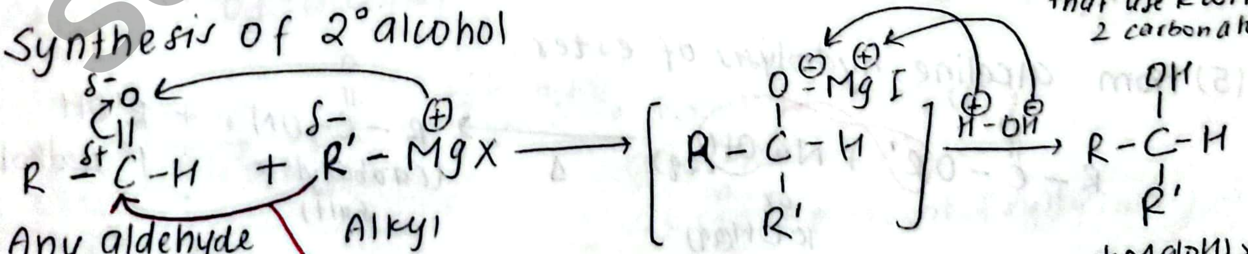
Formaldehyde (Methanal) [Must]

Alkyl magnesium halide

+ Mg(OH)X

R can be varied to obtain desired 1° alcohol of (ie. If 3 carbon needed in product that use R with 2 carbon atom)

(ii) Synthesis of 2° alcohol


$$R-\overset{\overset{\delta-O}{||}}{\overset{\delta+}{C}}-H + \overset{\delta-}{R'}-\overset{\oplus}{Mg}X \longrightarrow \left[R-\underset{R'}{\overset{O^{\ominus}-\overset{\oplus}{Mg}I}{C}}-H\right] \xrightarrow{\overset{\oplus}{H}-\overset{\ominus}{OH}} R-\underset{R'}{\overset{OH}{C}}-H$$

(Any aldehyde except formaldehyde acc. to req. product)

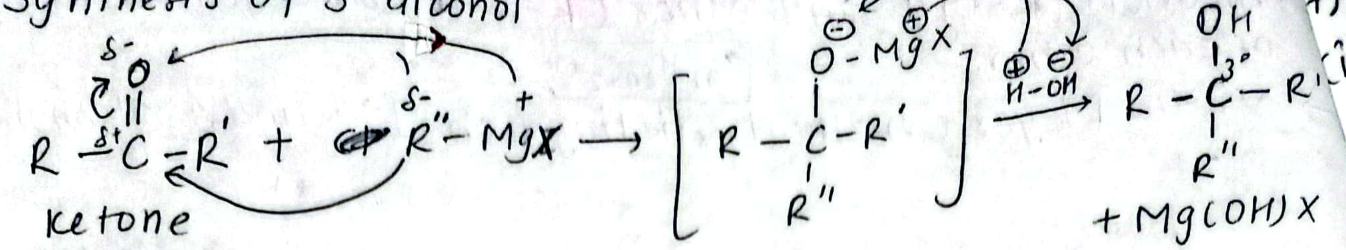
Alkyl Magnesium halide

+ Mg(OH)X

R & R' can be varied to obtain desired 2° alcohol.

Attach C attached with Mg as that C is more δ- than other.

(iii) Synthesis of 3° alcohol



$$R-\overset{\overset{\delta-}{O}}{\overset{\|}{\overset{\delta+}{C}}}-R' + \overset{\delta-}{R''}-\overset{+}{MgX} \longrightarrow \left[R-\underset{R''}{\underset{|}{\overset{\overset{\ominus}{O}-\overset{\oplus}{Mg}X}{\overset{|}{C}}}}-R' \right] \xrightarrow{\overset{\oplus\ \ominus}{H-OH}} R-\underset{R''}{\underset{|}{\overset{OH}{\overset{|}{\overset{3^\circ}{C}}}}}-R' + Mg(OH)X$$

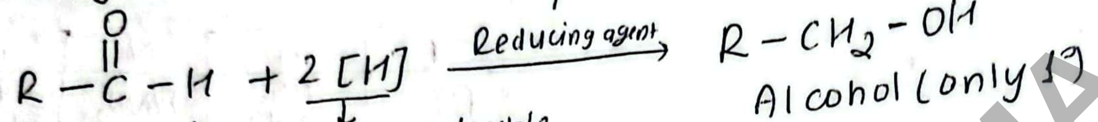
ketone (always)

R, R' and R'' can be varied.

(3) From reduction of aldehyde, ketone, carboxylic acid, ester.
↳ +H & −O

(i) Aldehyde

$LiAlH_4$, H_2/Ni, Na/C_2H_5OH



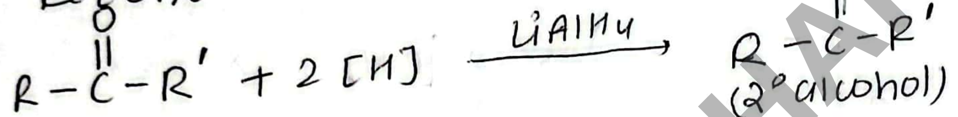
$$R-\overset{O}{\overset{\|}{C}}-H + 2[H] \xrightarrow{\text{Reducing agent}} R-CH_2-OH$$

Alkanal

↓ 1 removes double bond & one form −OH

Alcohol (only 1°)

(ii) ketone



$$R-\overset{O}{\overset{\|}{C}}-R' + 2[H] \xrightarrow{LiAlH_4} R-\overset{OH}{\overset{\|}{C}}-R'$$

(2° alcohol)

(iii) Carboxylic acid

$$R-\overset{O}{\overset{\|}{C}}-OH + 4[H] \xrightarrow{LiAlH_4} R-\overset{OH}{\overset{|}{CH_2}} + H_2O$$

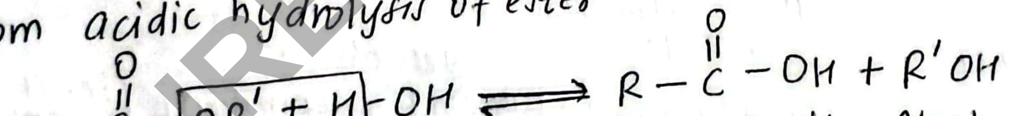
(1° alcohol)

(iv) Ester

$$R-\overset{O}{\overset{\|}{C}}-OR' + 4[H] \xrightarrow{LiAlH_4} R-\overset{OH}{\overset{|}{CH_2}} + R'OH$$

(1° alcohol)

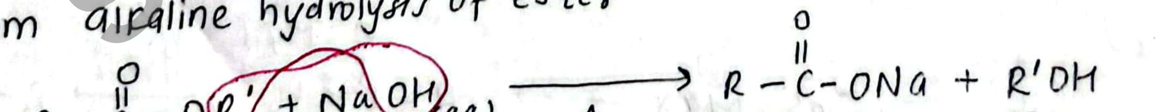
(4) From acidic hydrolysis of ester



$$R-\overset{O}{\overset{\|}{C}}-\boxed{OR' + H}-OH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-OH + R'OH$$

Carboxylic acid   Alcohol (1°)

(5) From alkaline hydrolysis of ester



$$R-\overset{O}{\overset{\|}{C}}-OR' + NaOH_{(aq)} \xrightarrow[\Delta]{} R-\overset{O}{\overset{\|}{C}}-ONa + R'OH$$

or KOH(aq)

(Carboxylate salt)   1° alcohol

(6) From primary amines

$$R-NH_2 + HNO_2 \xrightarrow[\substack{(0-5^\circ C)\\(cold)}]{NaNO_2 + HCl(conc)} R-OH + N_2\uparrow + H_2O$$

(Nitrous acid)

alcohol (1°)

R ⁞ N ⁞ H_2
HO ⁞ N = O

But not CH_3- group.

7) Fr

(i) F

7) From Alkenes

(i) From hydration of alkene

$$CH_3-CH=CH_2 + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[H_3PO_4 \text{ or } H_2SO_4]{H^+} CH_3-\overset{OH}{CH}-CH_3$$

Propan-2-ol
(2° alcohol)

(Markovnikov's rule)

(ii) From hydroboration oxidation reaction

$$3CH_3-CH=CH_2 \xrightarrow{BH_3} (CH_3CH_2CH_2)_3B$$

(Markovnikov's rule) Tri propyl borane

$(BH_3)_2$ → diborane

$$\Big\downarrow [O]\ 3H_2O_2 / OH^-$$

→ Anti-Markovnikov's rule.

$$3CH_3-CH_2-CH_2-OH + H_3BO_3$$

Propan-1-ol
(1° alcohol)

[Industrial prepⁿ] → Book/copy

[Physical properties] → copy

Test of alcohol: (Majorly Ethanol)

(a) Iodoform test → alcohols with structure (i) $R-\overset{O}{\overset{\|}{C}}-\textcircled{X}$ → any group not containing lone pair (ii) $CH_3-\overset{OH}{CH}-$ gives positive iodoform test.

Such alcohols on heating with excess I_2 and aq. alkali (NaOH) give yellow precipitate of iodoform.

$$\boxed{CH_3-\overset{OH}{CH}}-R \xrightarrow[\Delta]{I_2 / NaOH} CHI_3\downarrow + R-\overset{O}{\overset{\|}{C}}-\overset{-}{O}\overset{+}{Na} + 5NaI + 5H_2O$$

(R → H, CH_3, ...)

Iodoform
(Yellow ppt.)

(b) Esterification test : Reaction of alcohol with carboxylic acid : Basic nature of Alcohol

$$R-COOH + HOR' \xrightarrow[\Delta]{conc.\ H_2SO_4} RCOOR' + H_2O$$

carboxylic acid, alkanol

alkyl alkanoate (Ester - pleasent fruity smell)

Ethanol → only primary alcohol giving Iodoform test

Chemical properties of Monohydric alcohol

A. Reaction involving the cleavage of O–H bond or reaction due to H-atom of alcohols.

(a) Reaction with active metals (Na, K, Li, Mg etc.)

$$2R-\ddot{O}H + 2Na \longrightarrow 2R-\bar{O}\overset{+}{Na} + H_2\uparrow$$

Sodium alkoxide.

(b) Esterification reaction

(i) Reaction with carboxylic acid

$$\underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Alkanol}}{H-O-R'} \xrightleftharpoons[\Delta]{conc.\ H_2SO_4} \underset{\text{(Ester)}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O$$

(ii) Reaction with acid chlorides and acid anhydride : Acylation

$$\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + \underset{\text{Alcohol}}{H-O-R'} \xrightarrow[\Delta]{Pyridine} \underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + HCl$$

pyridine

$$\underset{\text{Acid anhydride}}{R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R} + \underset{\text{Alkanol}}{H-O-R'} \xrightarrow{\Delta} \underset{\text{ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH}$$

(c) Reaction with Grignard reagent

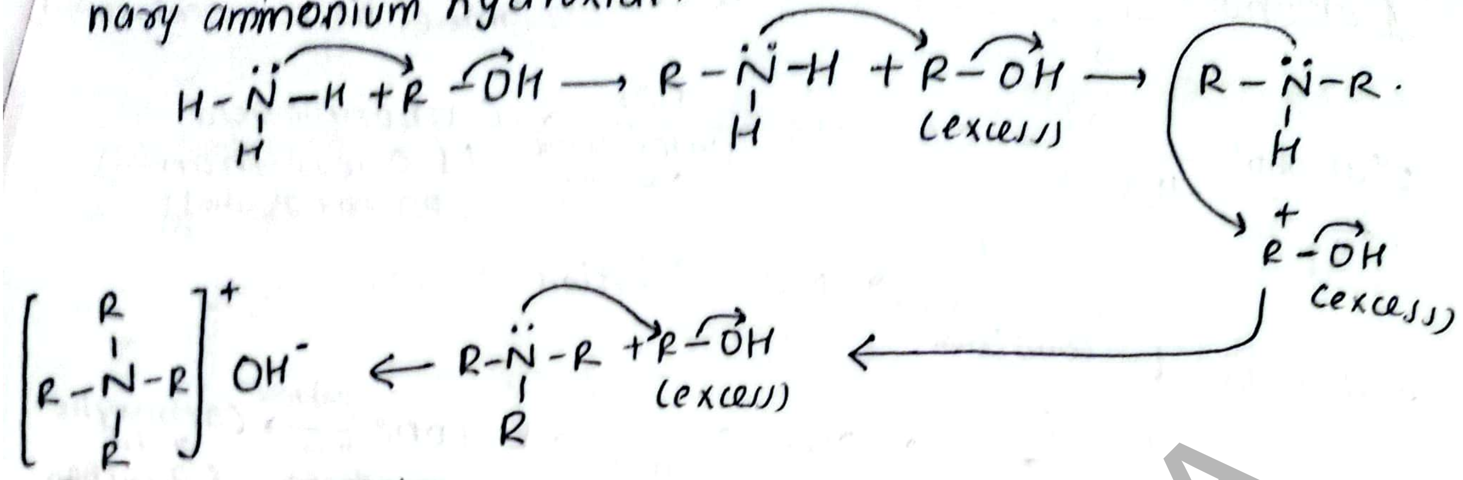
$$\underset{\text{Grignard reagent}}{\overset{\delta-}{R}-\overset{+}{Mg}X} + \overset{\delta+}{H}-\overset{\delta-}{O}R' \longrightarrow \underset{\text{Alkane}}{R-H} + \underset{\text{Magnesium alkoxy halide}}{Mg(OR')X}$$

B. Reaction involving breakage of C–O bond or Reaction due to –OH group of alcohol (Nucleophilic substitution reaction).

(a) Reaction with ammonia

$$\overset{\delta+}{R}-\overset{\delta-}{O}H + \underset{\text{(excess)}}{H-\ddot{N}H_2} \xrightarrow[\Delta]{Al_2O_3} \underset{\text{(1° amine)}}{R-\ddot{N}H_2} + H_2O$$

However, if alcohol is in excess, the 1° amine formed at first stage of reaction as given above further reacts with excess alcohol to form 2° amine and 3° amine and finally quaternary ammonium hydroxide.



$$H-\ddot{N}(H)-H + R-OH \rightarrow R-\ddot{N}(H)-H + \underset{(excess)}{R-OH} \rightarrow R-\ddot{N}(H)-R + \underset{(excess)}{R-OH} \rightarrow R-\ddot{N}(R)-R + \underset{(excess)}{R-OH} \rightarrow \left[R-\overset{R}{\underset{R}{N}}-R\right]^+ OH^-$$

Quaternary ammonium hydroxide

(Tetraalkyl ammonium hydroxide)

(b) Reaction with PCl_5, PCl_3, PBr_3, PI_3, $SOCl_2$

$$R-OH \xrightarrow{PCl_5/\Delta} R-Cl + POCl_3 + HCl$$

$$R-OH \xrightarrow{PCl_3/\Delta} R-Cl + H_3PO_3$$

$$R-OH \xrightarrow[(Pyridine)]{SOCl_2/\Delta} R-Cl + SO_2\uparrow + HCl\uparrow$$

Alcohol

$SOCl_2$
↓
thionyl chloride.

$$R-OH \xrightarrow{PBr_3\ (P_4+Br_2)} 3R-Br + H_3PO_3$$

$$R-OH \xrightarrow{PI_3(P_4+I_2)} 3R-I + H_3PO_3$$

Reaction with hydrogen halides

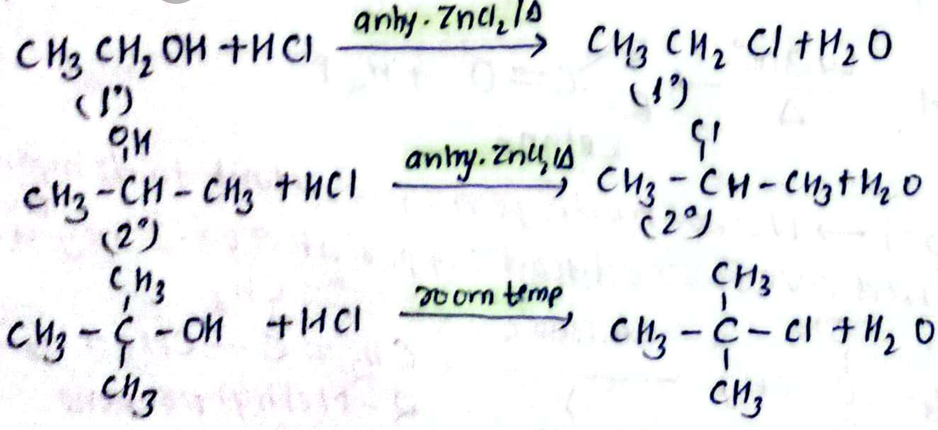
$$R-OH + H-X \longrightarrow R-X + H_2O$$

✓ Reactivity sequence

✓ 3° alcohol > 2° > 1°

✓ HI > HBr > HCl

Eg:-



$$\underset{(1°)}{CH_3CH_2OH} + HCl \xrightarrow{anhy.\ ZnCl_2/\Delta} \underset{(1°)}{CH_3CH_2Cl} + H_2O$$

$$\underset{(2°)}{CH_3-\overset{OH}{CH}-CH_3} + HCl \xrightarrow{anhy.\ ZnCl_2/\Delta} \underset{(2°)}{CH_3-\overset{Cl}{CH}-CH_3} + H_2O$$

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH + HCl \xrightarrow{room\ temp} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl + H_2O$$

Mixture of hydrogen chloride and anhydrous $ZnCl_2$
↓
Lucas Reagent.

With HBr:
1° → Reagent Conc. H_2SO_4
2° → Room Temp.
With HI:
1° → Room temp.

2) D

(a)

C. Reaction involving both alkyl part and -OH part.

(a) Oxidation of alcohol: [redacted] using $KMnO_4/H^+$ or K_2Cr_2 / CeO_2/H^+ [O] agent

$$1^\circ \text{alcohol} \xrightarrow[-H_2O,\ \Delta]{[O]} \text{Aldehyde} \xrightarrow[-H_2O,\ \Delta]{[O]} \text{Carboxylic acid}$$

(same C no. as parent alcoho

$$2^\circ \text{alcohol} \xrightarrow[-H_2O,\ \Delta]{[O]} \text{Ketones} \xrightarrow[\text{Under drastic conditions}]{[O]} \text{Carboxylic acid}$$

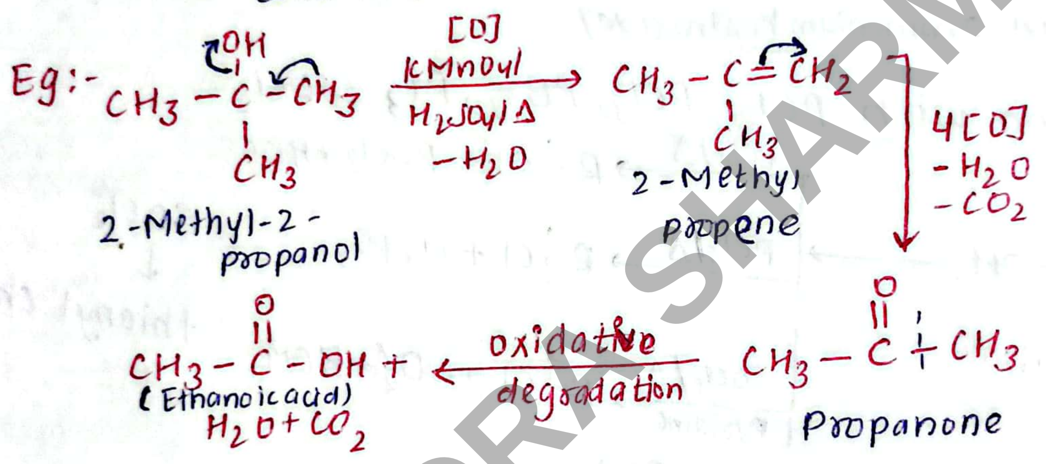
(1 C less than parent alcohol)

$$3^\circ \text{alcohol} \xrightarrow[\text{Under normal condition}]{[O]} \text{NO oxidation}$$

$$3^\circ \text{alcohol} \xrightarrow[\text{drastic condition}]{[O]} \text{alkene} \xrightarrow[-H_2O,\ -CO_2]{[O]} \text{Ketone} \xrightarrow[\text{tive degradation}]{\text{oxida-}} \text{Carboxylic acid}$$

(2 carbon less than parent alcohol)

Eg:-



$$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3 \xrightarrow[H_2SO_4/\Delta,\ -H_2O]{[O]\ KMnO_4/} CH_3-\underset{CH_3}{C}=CH_2$$

2-Methyl-2-propanol

2-Methyl propene

$$\xrightarrow[-H_2O,\ -CO_2]{4[O]} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

Propanone

$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{\text{oxidative degradation}} CH_3-\overset{O}{\overset{\|}{C}}-OH + H_2O + CO_2$$

(Ethanoic acid)

(b) catalytic dehydrogenation of alcohols: (Removal of H_2).

When vapour of alcohol passed over heated copper at 300°C.

(i) $CH_3-OH \xrightarrow[\Delta]{Cu,\ 300^\circ C} HCHO + H_2\uparrow$

Methanol — Methanal

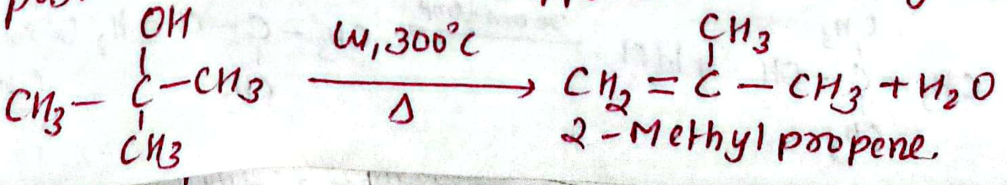
(ii) $R-CH_2-OH \xrightarrow[\Delta]{Cu,\ 300^\circ C} R-CHO + H_2\uparrow$

1° alcohol — Aldehyde

(iii) $R_2CH-OH \xrightarrow[\Delta]{Cu,\ 300^\circ C} R_2C=O + H_2\uparrow$

Ketone.

Tertiary alcohol → NO α-hydrogen → resistant to dehydrogenation. But, when passed over reduced copper at 300°C, they are dehydrated.



$$CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_3 \xrightarrow[\Delta]{Cu,\ 300^\circ C} CH_2=\overset{CH_3}{C}-CH_3 + H_2O$$

2-Methyl propene.

(2) Dehydration of alcohol: Removal of H_2O

(a) Dehydration of alcohols into ethers with catalytic amount of conc. H_2SO_4 at 140°C:

[R-OH Ethanol]

$$2\,R-OH \xrightarrow{conc.\,H_2SO_4,\,\Delta} R-O-R + H_2O$$

(b) Dehydration of alcohols into alkenes with excess of conc. H_2SO_4 at 170°C:

$$CH_3CH_2-\boxed{OH + H}O-SO_3H \xrightarrow[-H_2O]{conc.\,H_2SO_4,\ \Delta\,100^\circ C} CH_3CH_2-O-SO_3H + H_2O$$

$$CH_3CH_2-O-SO_3H \xrightarrow{\Delta,\,170^\circ C} CH_2=CH_2 + H_2SO_4$$

(c) Passing the vapour of ethyl alcohol over heated alumina (Temp < 300°C)

$$\underset{Ethanol}{2\,CH_3CH_2-OH} \xrightarrow[250^\circ C]{Al_2O_3} \underset{(Ethoxyethane)}{CH_3CH_2-O-CH_2CH_3} + H_2O$$

(d) Passing the vapour of ethyl alcohol over heated alumina as a catalyst (Temp > 300°C)

$$\underset{Ethanol}{CH_3CH_2-OH} \xrightarrow[350^\circ C]{Al_2O_3} \underset{(Ethene)}{CH_2=CH_2} + H_2O$$

cold and Alkaline $KMnO_4$
or
$KMnO_4/OH^-$ (O.A
(Baeyer's reagent)

Ethane-1,2-diol (Ethylene glycol)

Preparation:

(1) By hydroxylation of alkene (addition of $-OH$ in $C=C$)

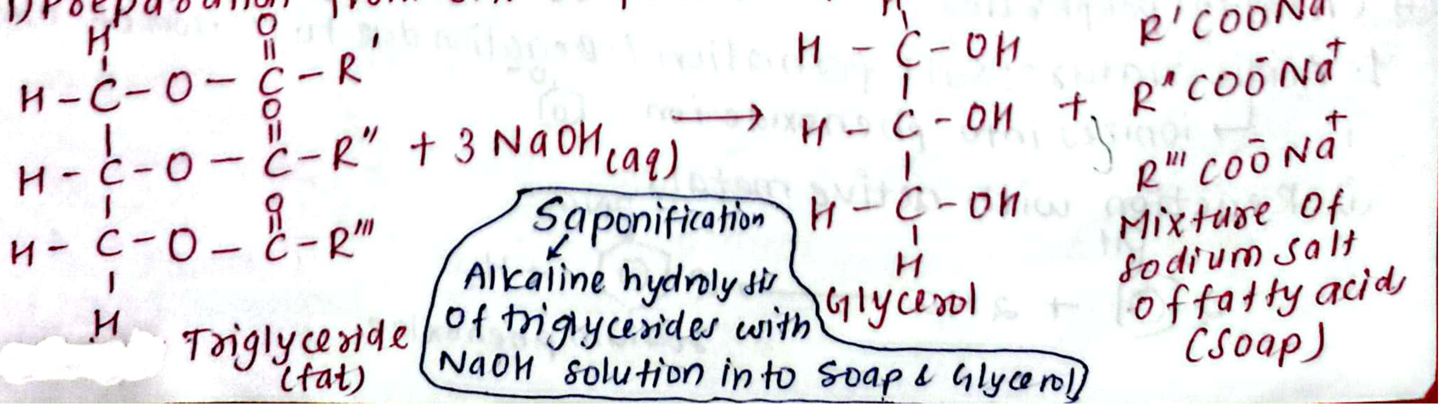
$$\underset{Ethene}{CH_2=CH_2} + \underset{Pink}{2KMnO_4} + 2KOH \longrightarrow \underset{colourless}{K_2MnO_4} + \underset{Ethylene\ glycol}{\underset{OH\qquad OH}{CH_2-CH_2}}$$

(2) By hydrolysis of ethylene chlorohydrin

$$\underset{OH\qquad Cl}{CH_2-CH_2} \xrightarrow{aq.\,Na_2CO_3} \underset{OH\qquad OH}{CH_2-CH_2}$$

Trihydric alcohol [Propane-1,2,3-triol (Glycerol)]

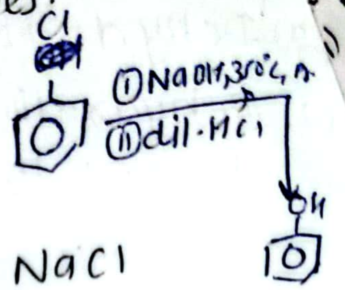
(i) Preparation from oils or fats (Saponification)



$$\underset{\text{Triglyceride (fat)}}{\begin{matrix} H-\overset{H}{C}-O-\overset{O}{\overset{\|}{C}}-R' \\ H-C-O-\overset{O}{\overset{\|}{C}}-R'' \\ H-\underset{H}{C}-O-\overset{O}{\overset{\|}{C}}-R''' \end{matrix}} + 3\,NaOH_{(aq)} \longrightarrow \underset{Glycerol}{\begin{matrix} H-\overset{H}{C}-OH \\ H-C-OH \\ H-\underset{H}{C}-OH \end{matrix}} + \underset{\text{Mixture of sodium salt of fatty acid (Soap)}}{\begin{matrix} R'COO^-Na^+ \\ R''COO^-Na^+ \\ R'''COO^-Na^+ \end{matrix}}$$

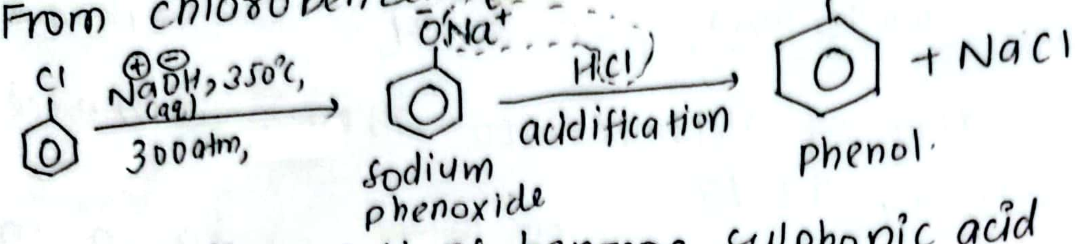
Saponification
Alkaline hydrolysis of triglycerides with NaOH solution into soap & Glycerol

#Phenols → Hydroxy derivatives of arenes.

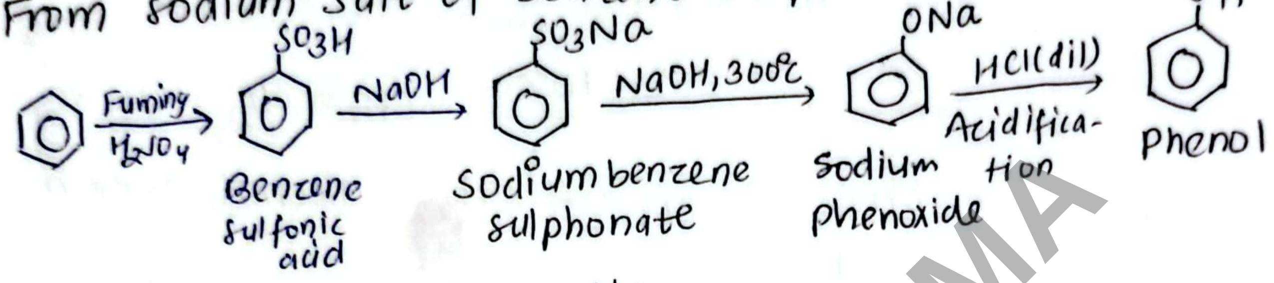


Methods of preparation.

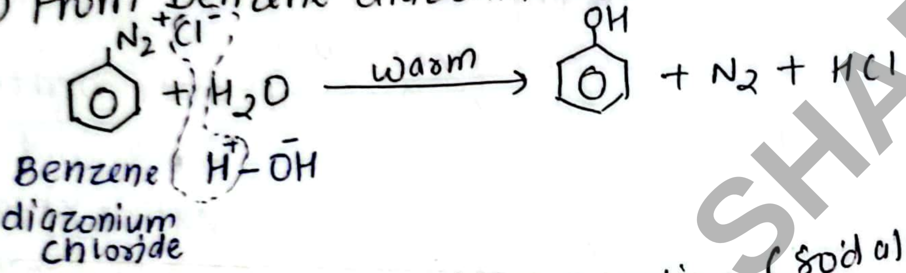
(1) From chlorobenzene (Dow Process)



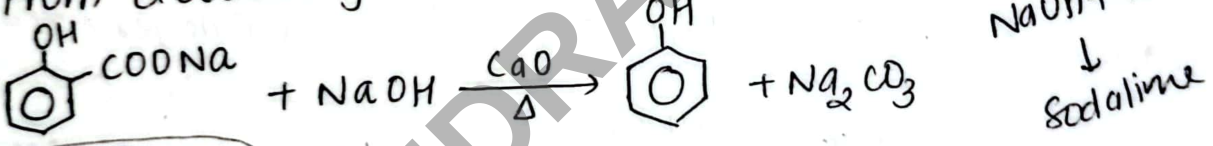
(2) From sodium salt of benzene sulphonic acid



(3) From Benzene diazonium salt:-



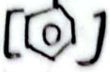
(4) From decarboxylation reaction (sodalime decarboxylation)



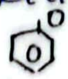
Salt of Salicylic acid → sodium salicylate

Physical properties:

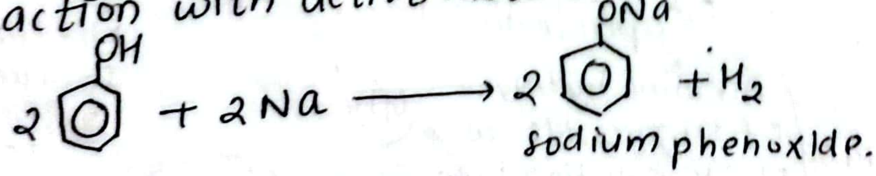
(i) High boiling point: Strong intermolecular H-bonding b/w phenols

(ii) Moderately soluble in water:
↳ can form intermolecular H-bond with water
↳ Due to non-polar hydrophobic part → []

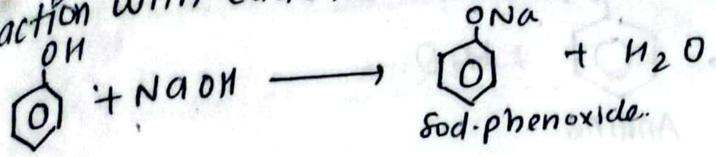
Chemical properties

1. Acidic nature: Salt formation (Reaction due to H-atom of -OH group)
↳ ionizes into phenoxide ion 

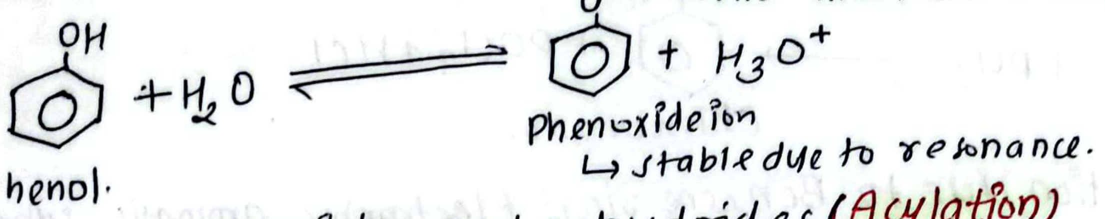
(i) Reaction with active metals:-



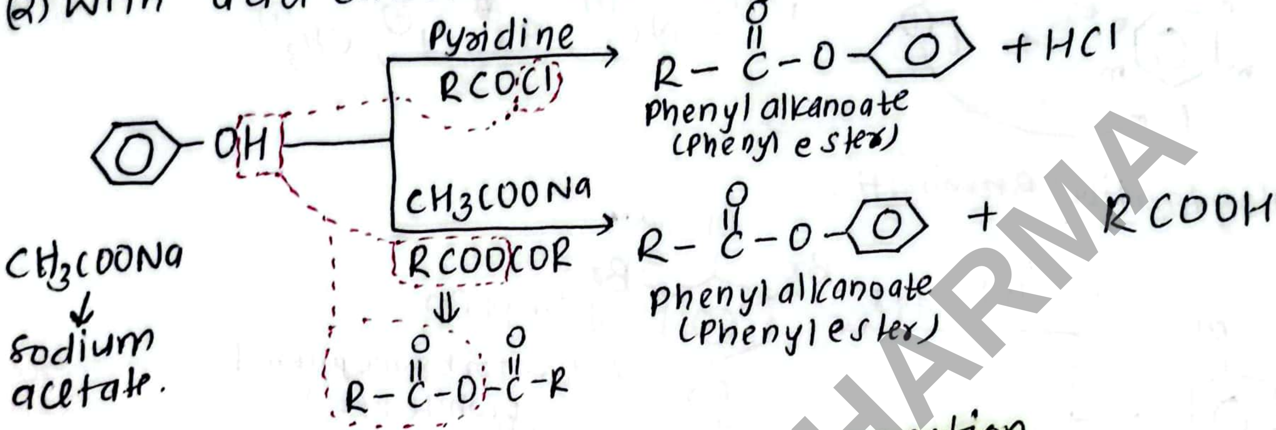
Reaction with caustic alkalies (NaOH, KOH):



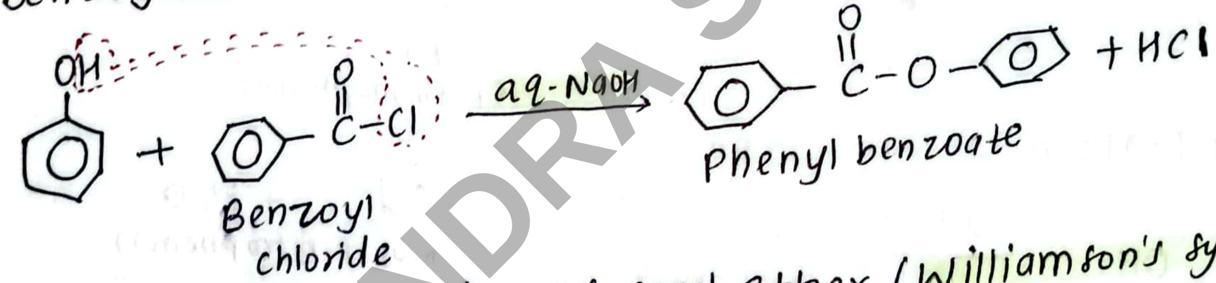
(iii) litmus test: ionizes into aqueous solution to give H_3O^+ ion due to which it turns moist blue litmus into faint red.



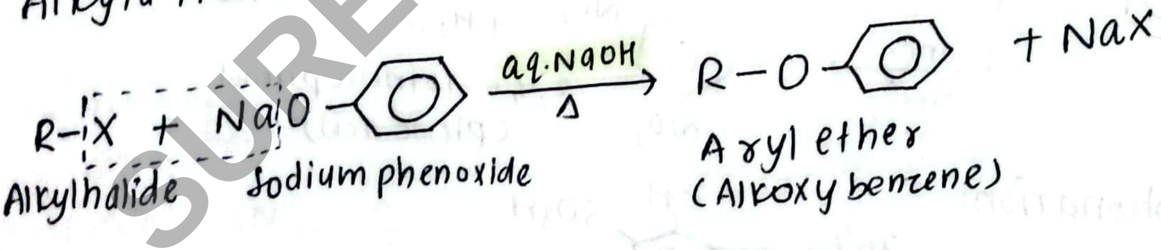
(2) With acid chlorides and anhydrides (Acylation)



(3) Benzoylation: Schotten-Baumann reaction

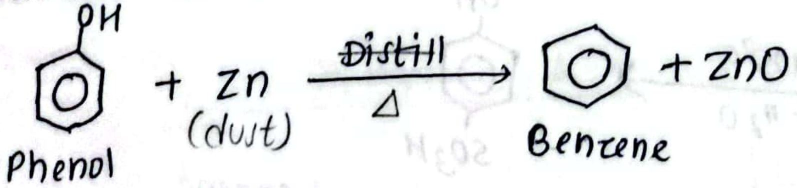


(4) Alkylation: Formation of aryl ether (Williamson's synthesis)

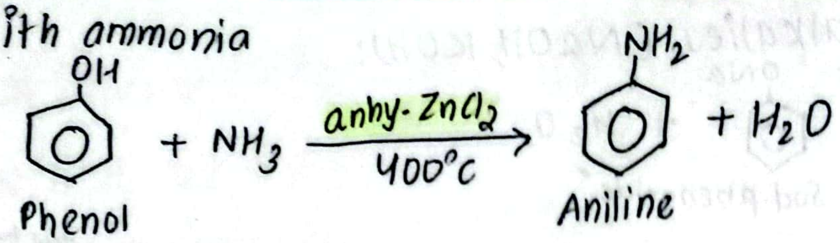


5. Reaction due to phenolic –OH group

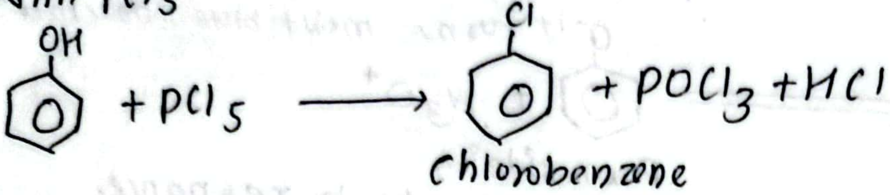
(a) Reaction with zinc dust:



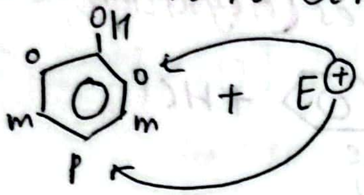
(b) With ammonia



(c) With PCl_5

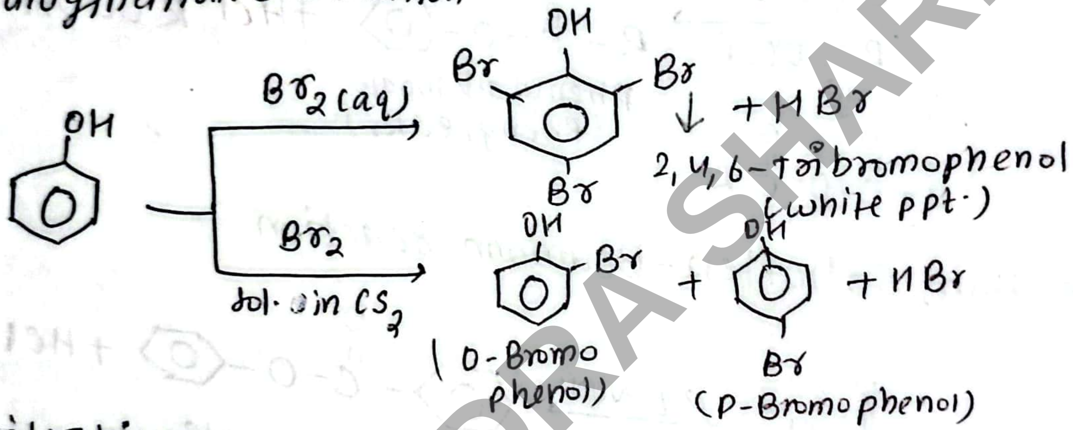


(6) Reaction due to Benzene ring: Electrophic aromatic subs^n rxn.

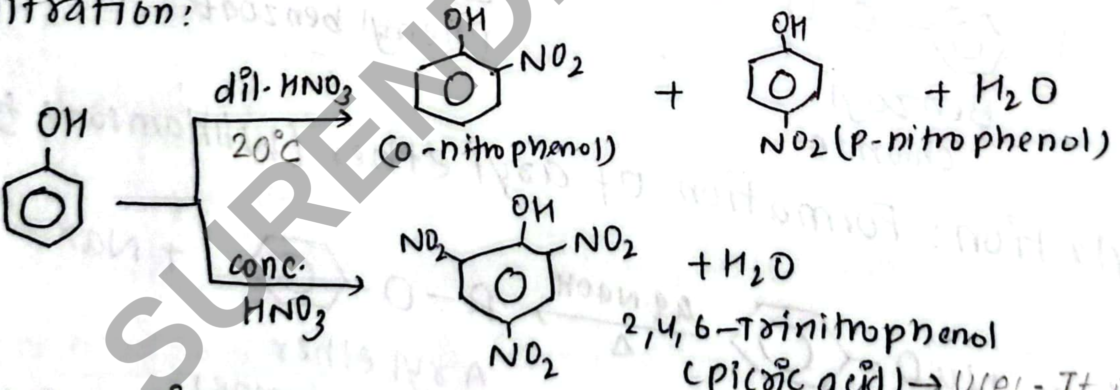


$E^{\oplus}$: $NO_2^{\oplus}$, $Br^{\oplus}$, $Cl^{\oplus}$, $CH_3^{\oplus}$

(a) Halogination: Bromination

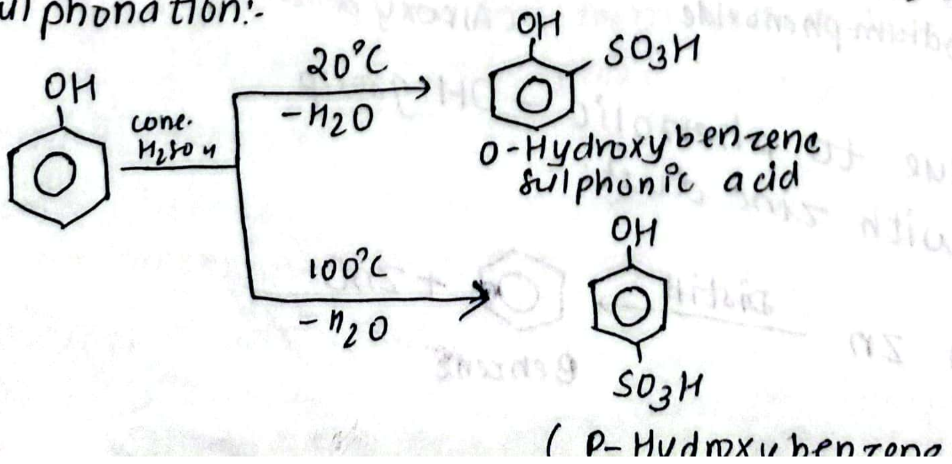


(b) Nitration:

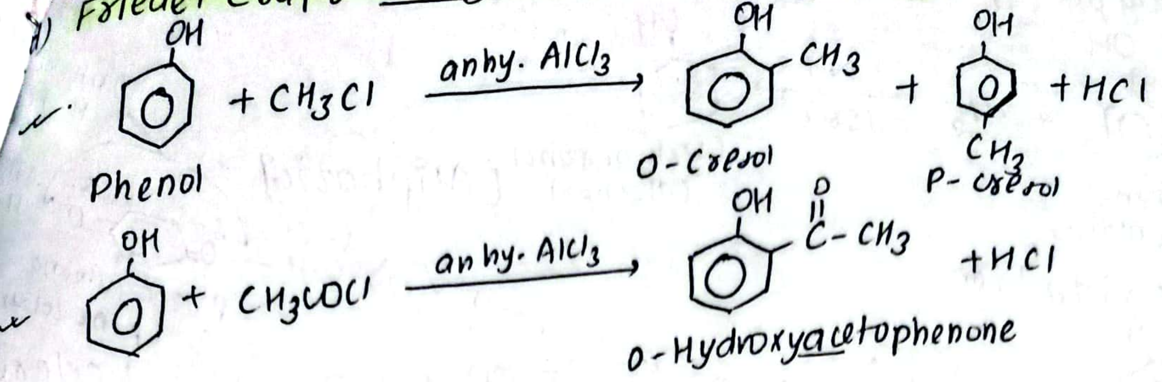


→ Uses - It is primary used as an explosive.

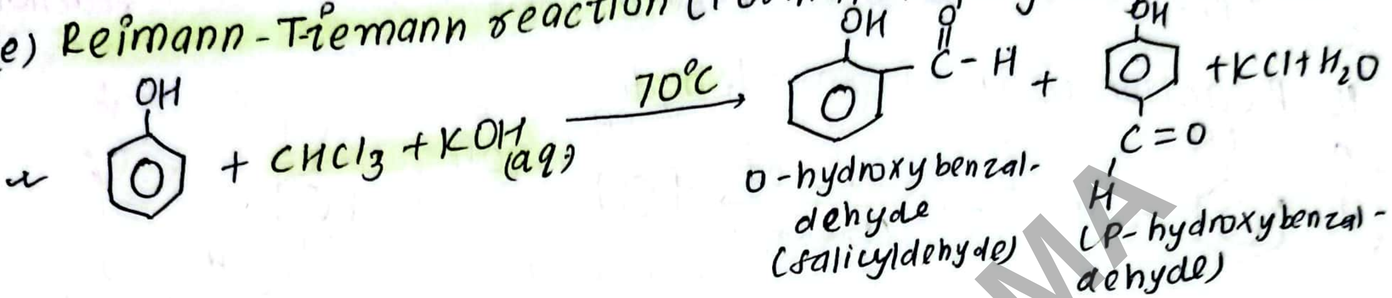
(c) Sulphonation:-



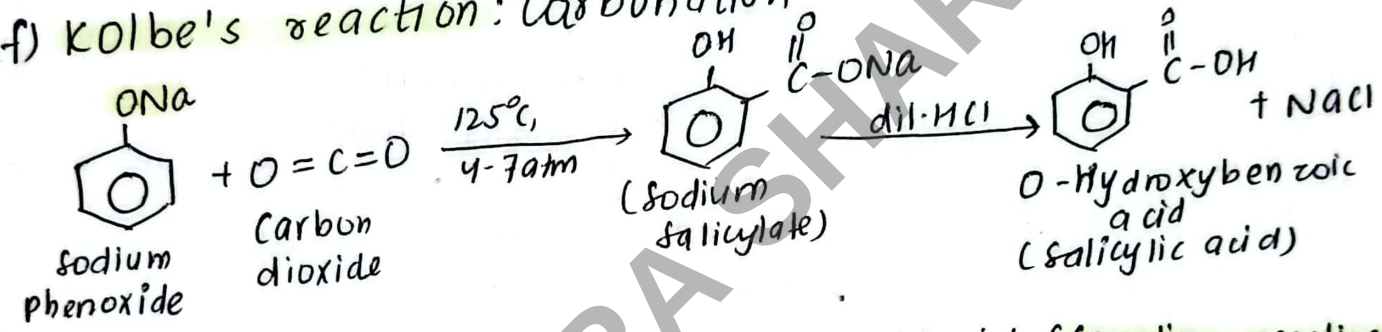
d) Friedel craft Alkylation and Acylation



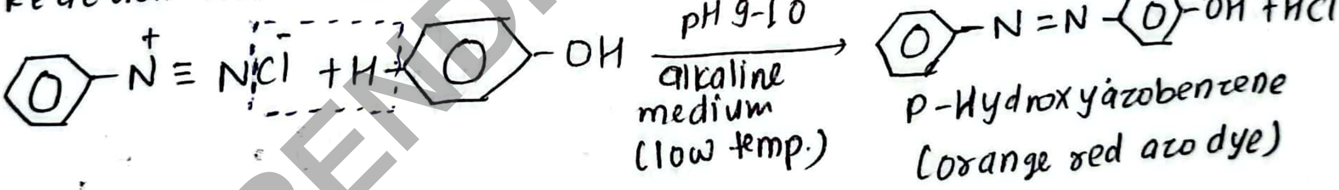
(e) Reimann-Tiemann reaction (Formation of hydroxy benzaldehyde)



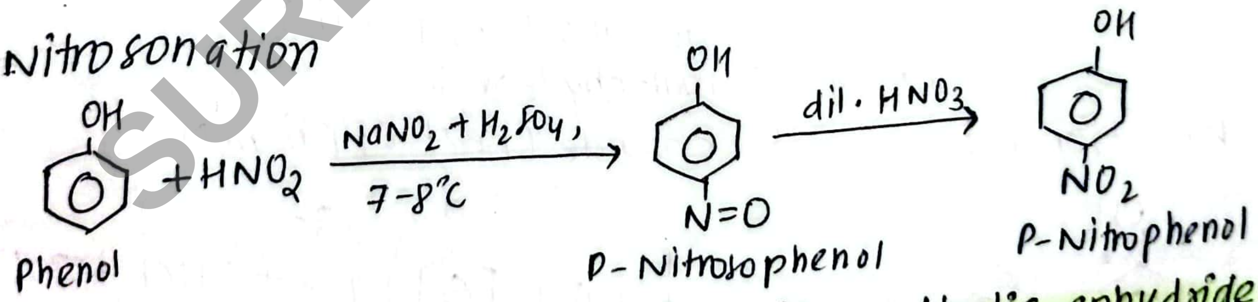
(f) Kolbe's reaction: Carbonation



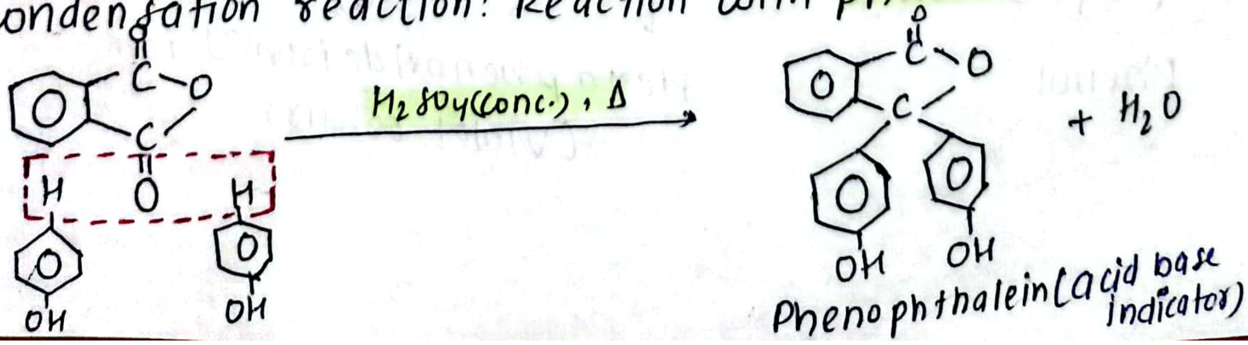
(g) Reaction with benzenediazonium chloride (Coupling reaction)



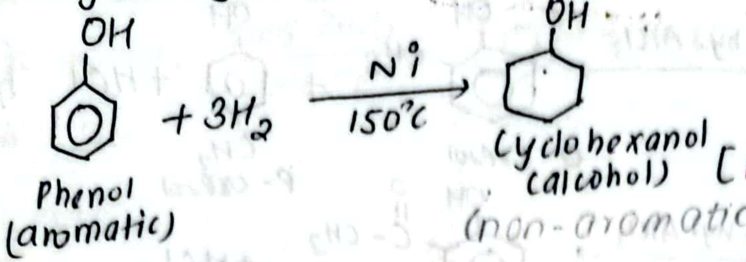
(h) Nitrosonation



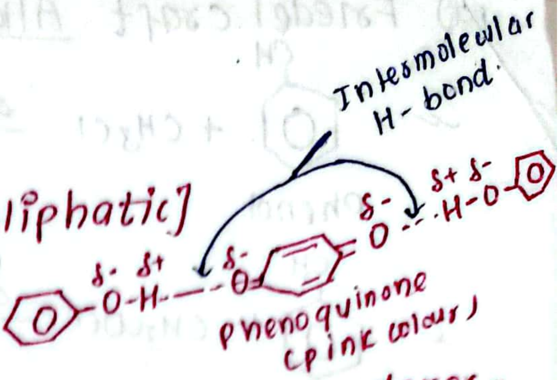
i) Condensation reaction: Reaction with phthalic anhydride



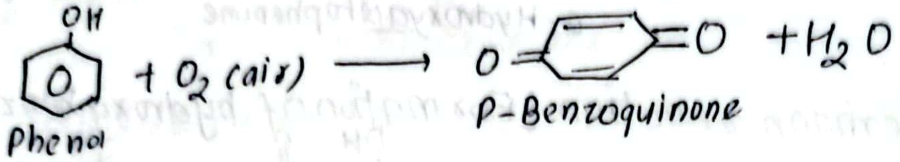
8. Catalytic hydrogenation



[Aliphatic]

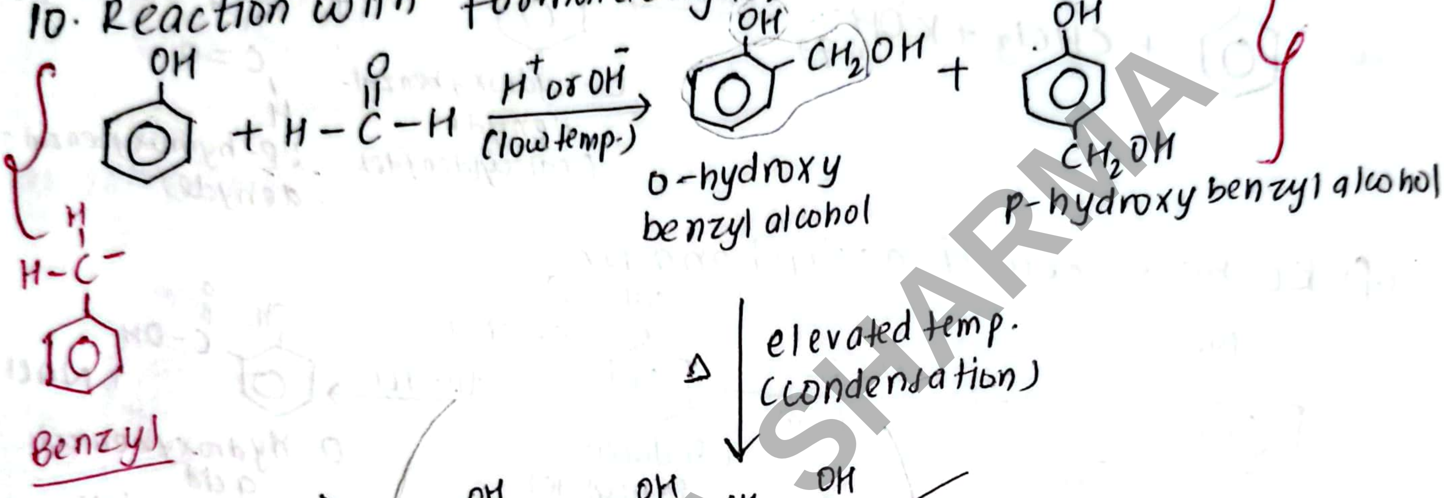


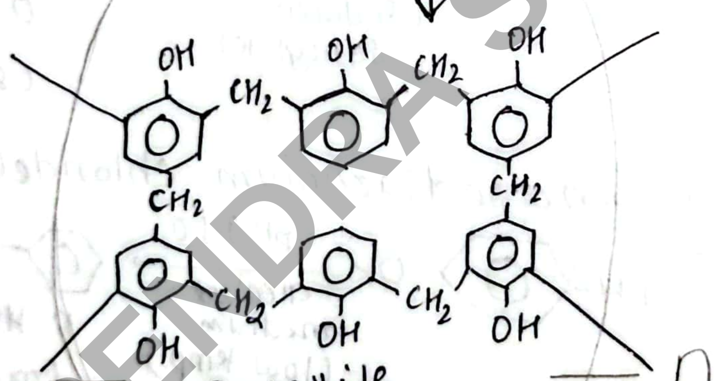
9. Air oxidation



Lederer-Manasse reaction.

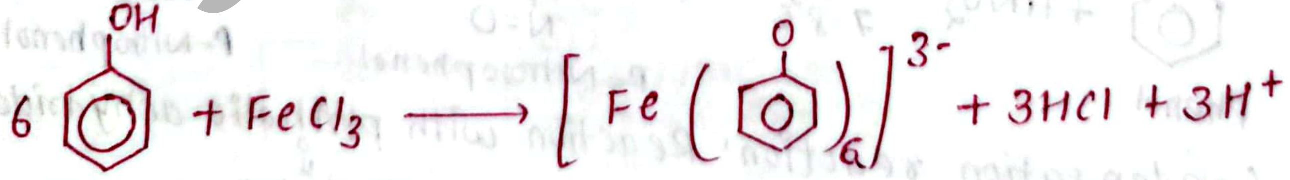
10. Reaction with formaldehyde:





Bakelite
(Thermosetting plastic)
Phenol-formaldehyde resin

11. Reaction with ferric chloride (Test of phenol)



Phenol

Hexaphenoxide iron(III) ion
(Violet colour)

Ethers

- anhydride of alcohols: $R-O-H + H-O-R \longrightarrow R-O-R + H_2O$
- alkoxy derivative of alkane: $R-H \xrightarrow[+OR]{-H} R-OR$

$R-O-R' \Rightarrow R=R' \rightarrow$ symmetrical ether (simple) ; $R \neq R' \rightarrow$ unsymmetrical (mixed) ethers

General methods of preparation:-

1. From alkyl halides

(a) Williamson's systhesis

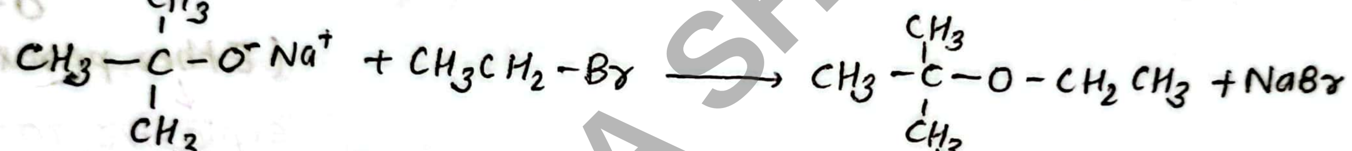
$$\overset{\delta+}{R}-\overset{\delta-}{X} + R'O^-Na^+ \longrightarrow R-O-R' + NaX$$

sodium alkoxide (or potassium)

(OR^- → acts as nucleophile)

- Both simple as well as mixed ethers can be obtained.
- Secondary and tertiary alkyl halides are not used, rather we use secondary and tertiary alkoxide.

→ undergo elimination rxn to give alkene as alkoxide ions act as strong base as well



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^-Na^+ + CH_3CH_2-Br \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_2CH_3 + NaBr$$

Sodium tert-butoxide (nucleophile) — tert-butyl ethyl ether

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + CH_3CH_2O^-Na^+ \longrightarrow CH_3-\overset{CH_3}{C}=CH_2 + CH_3CH_2OH + NaBr$$

(base)

(b) By the action of dry silver oxide:

$$2R-X + Ag_2O \longrightarrow R-O-R + 2AgX$$

- Suitable for preparation of simple ethers.

(2) From alcohols

$$2R-OH \xrightarrow[Al_2O_3,\ 250^\circ C]{conc.\ H_2SO_4, \Delta,\ 140^\circ C} R-OR + H_2O$$

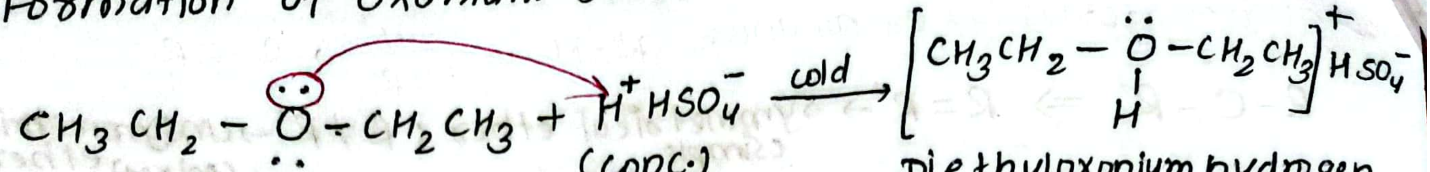
$R-OH + H-OR$
↓
$R-O-R + H_2O$
↓
By intermolecular dehydration

Physical properties:-

Chemical properties → ethers relatively less reactive class ↳ so, used as solvents in laboratori

A. Reactions involving ethereal oxygen:-

1. Formation of Oxonium salt:

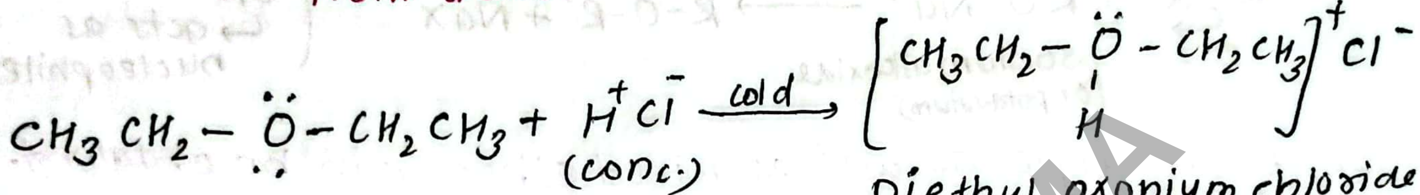


$$CH_3CH_2-\ddot{O}-CH_2CH_3 + \overset{+}{H}\overset{-}{HSO_4} \xrightarrow{cold} \left[CH_3CH_2-\underset{H}{\ddot{O}}-CH_2CH_3\right]^{+} HSO_4^{-}$$

(conc.)

Diethyloxonium hydrogen sulphate (oxonium salt)
↓
Stable at low temp.

* Due to lone pair of electron on oxygen atom, ether behaves as Bronsted-Lowry base and accepts H^+ from acids.



$$CH_3CH_2-\ddot{O}-CH_2CH_3 + \overset{+}{H}\overset{-}{Cl} \xrightarrow{cold} \left[CH_3CH_2-\underset{H}{\ddot{O}}-CH_2CH_3\right]^{+} Cl^{-}$$

(conc.)

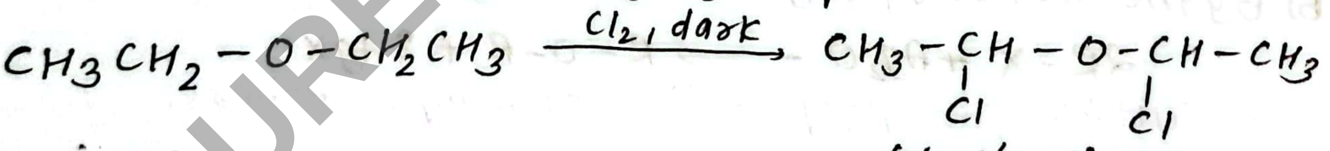
Diethyl oxonium chloride (oxonium salt)

(2) Reaction with air

$$CH_3CH_2-O-CH_2CH_3 + O_2\,(Air) \xrightarrow{light} CH_3CH_2-O-\underset{O-OH}{CH}-CH_3$$

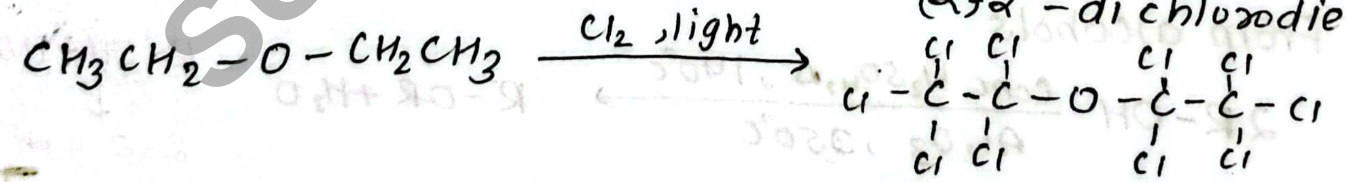
(Ether peroxide)
↓
explosive and unstable
(so care should be taken during distillation of old sample of ethers)
↳ may contain ether peroxide

B. Reactions involving alkyl group



$$CH_3CH_2-O-CH_2CH_3 \xrightarrow{Cl_2,\ dark} CH_3-\underset{Cl}{CH}-O-\underset{Cl}{CH}-CH_3$$

(α, α'-dichlorodiethyl)



$$CH_3CH_2-O-CH_2CH_3 \xrightarrow{Cl_2,\ light} Cl-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-O-\underset{Cl}{\overset{Cl}{C}}-\underset{Cl}{\overset{Cl}{C}}-Cl$$

(Perchlorodiethyl ether)

C. Reactions involving cleavage of C-O bond.

1. Reactions with HBr and HI.

In cold $R-O-R + HI \xrightarrow{cold} R-OH + RI$

* When unsymmetrical ether is treated with conc. HI, the cleavage takes place such that oxygen atom remains attached with larger alkyl group.

For 3° alkyl group, bond breakage takes place such that oxygen remains attached to smaller alkyl group.

3° haloalkane more feasible → high stability of 3° carbocation

In hot and excess HI

$$R-O-R + HI \longrightarrow R-OH + RI$$

$$R-OH + HI \longrightarrow RI + H_2O$$

$$R-O-R + 2HI \xrightarrow{\Delta} 2RI + H_2O$$

(2) Reaction with sulphuric acid (dilute)

$$R-O-R + H_2O \xrightarrow{\text{Dilute } H_2SO_4} 2ROH \text{ (hydrolysis)}$$

$$R-O-R + \text{conc.} H_2SO_4 \xrightarrow[\text{warm}]{} \underset{\text{alcohol}}{ROH} + \underset{\text{alkyl hydrogen sulphate}}{RHSO_4}$$

(3) Reaction with phosphorus pentachloride

$$R-O-R + PCl_5 \xrightarrow{\Delta} 2RCl + POCl_3$$

Laboratory preparation of Diethyl Ether

Principle: Step 1: $\underset{\text{Ethanol}}{C_2H_5-OH} + \underset{\text{conc.}}{H-OSO_3H} \xrightarrow{100^\circ C} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5-OSO_3H} + H_2O$

Step 2: $C_2H_5-OSO_3H + H-O-C_2H_5 \xrightarrow{140^\circ C} C_2H_5-O-C_2H_5 + H_2SO_4$

Overall: $\underset{\text{(excess)}}{2CH_3CH_2OH} + \text{conc.} H_2SO_4 \xrightarrow[\Delta]{140^\circ C} C_2H_5-O-C_2H_5 + H_2O$

But: $CH_3CH_2OH + \text{conc.} H_2SO_4 \xrightarrow[\Delta]{170^\circ C} \underset{\text{Ethene}}{CH_2=CH_2} + H_2O$

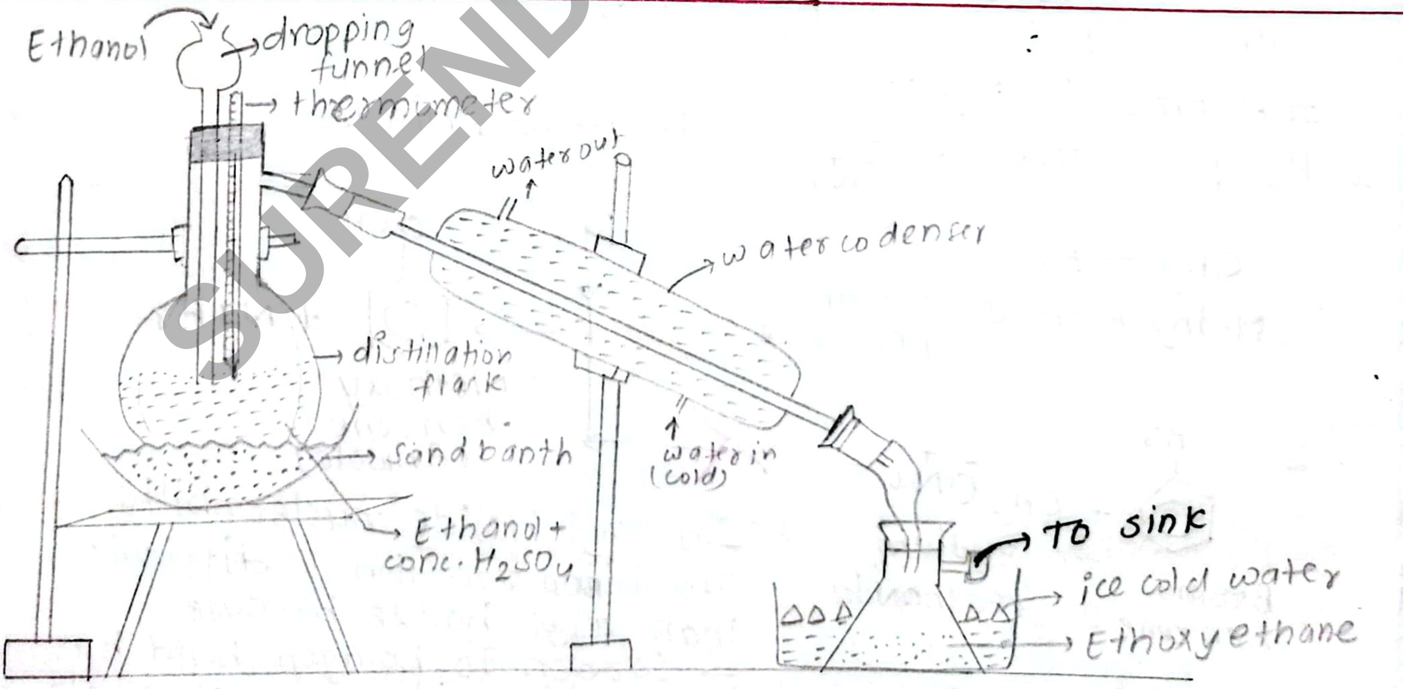


Fig:- Laboratory preparation of ethoxyethane

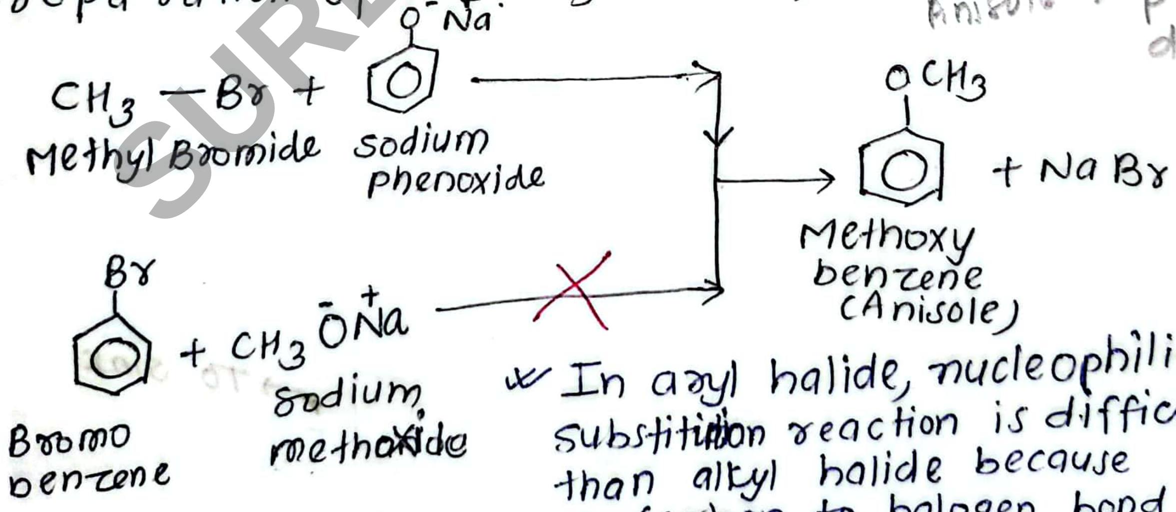
✓ Procedure:-
About 100ml of ethyl alcohol is taken in a distillation flask in which dropping funnel, thermometer, water condenser and receiver. The rubber tube is attached to the side tube of receiver to carry away any uncondensed vapour of ether. The whole apparatus is made air tight as ether is highly inflammable. About 100 ml of concentrated sulphuric acid is added from dropping funnel and heated to about 140°C on sand bath. Ether so formed distills off and is collected in ice cooled receiver. As ether starts distilling a continuous stream of fresh alcohol is added from the dropping funnel at rate of the formation of ether. In this process, ether can be obtained continuously, hence this process is called Williamson's continuous etherification

✓ Purification:-
(i) Ether is treated with dilute NaOH in a separating funnel, which dissolves SO_2, CO_2 and other acidic impurities.
(ii) Ether is washed with water → to remove water soluble impurities
(iii) It is treated with 50% $CaCl_2$ → to remove alcohol forming alcoholates.
(iv) It is dried over anhydrous $CaCl_2$.
(v) Finally, ether is redistilled at about 34 to 40°C to get it in pure and dry state.

Aromatic Ethers

✓ Preparation of Methoxybenzene/Anisole

Anisole → ortho para director



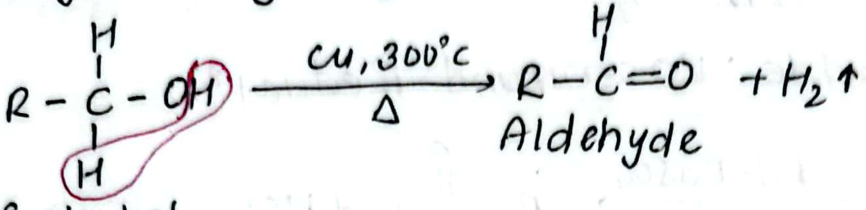
✓ In aryl halide, nucleophilic substitution reaction is difficult than alkyl halide because
→ Carbon to halogen bond has partial double bond character due to resonance effect.
✓ C−X bond is less polar due to hybridization effect.

Aldehydes [$R-\overset{O}{\overset{\|}{C}}-H$] & Ketones [$R-\overset{O}{\overset{\|}{C}}-R$]

General methods of preparation:-

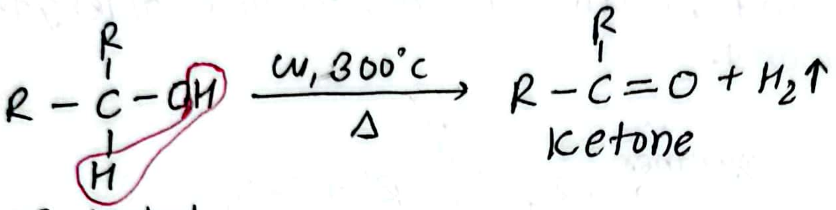
(1) From alcohols

(i) catalytic dehydrogenation of vapour alcohols.



$$R-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH \xrightarrow[\Delta]{Cu,\,300^\circ C} R-\overset{H}{\overset{|}{C}}=O + H_2\uparrow$$

1° alcohol



$$R-\overset{R}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH \xrightarrow[\Delta]{Cu,\,300^\circ C} R-\overset{R}{\overset{|}{C}}=O + H_2\uparrow$$

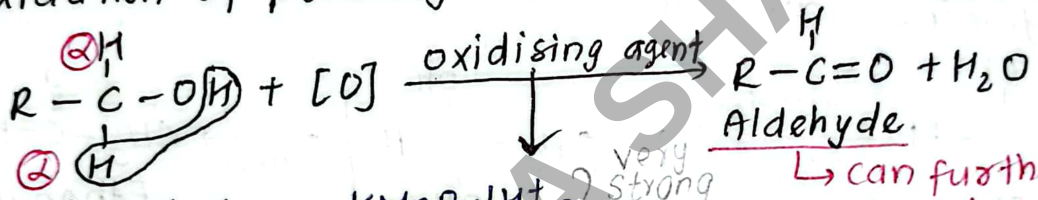
2° alcohol

(ii) By oxidation of alcohols : loss of one or more α-Hydrogen

one → aldehyde

more → usually two ↳ carboxylic acid

(a) Oxidation of primary alcohol



$$R-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH + [O] \xrightarrow{\text{oxidising agent}} R-\overset{H}{\overset{|}{C}}=O + H_2O$$

1° alcohol

[loss of one α-H]

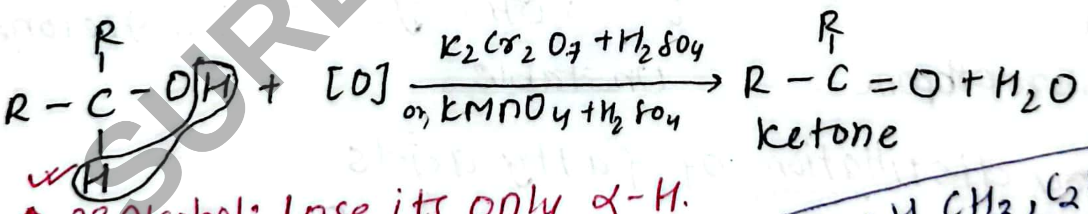
↳ can further oxidise to give carboxylic acid.

$KMnO_4/H^+$, $K_2Cr_2O_7/H^+$, } very strong oxidizing agent

$CrO_3/Pyridine$, PCC, Collin's reagent in CH_2Cl_2

↳ Prevents further oxidation of aldehydes to carboxylic acids.

(b) Oxidation of secondary alcohol :



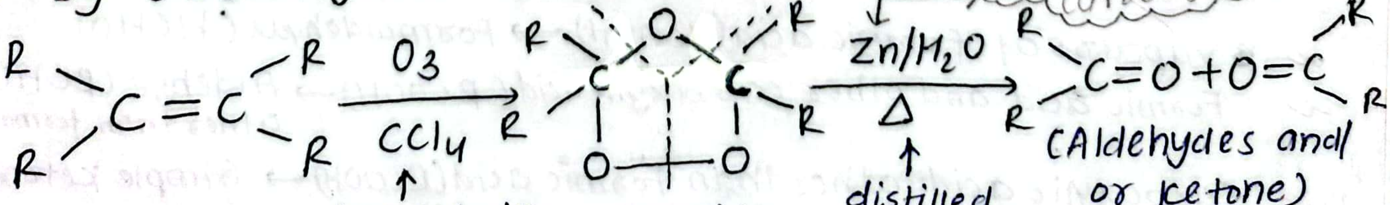
$$R-\overset{R}{\overset{|}{\underset{H}{\underset{|}{C}}}}-OH + [O] \xrightarrow[\text{or, } KMnO_4 + H_2SO_4]{K_2Cr_2O_7 + H_2SO_4} R-\overset{R}{\overset{|}{C}}=O + H_2O$$

2° Alcohol: Lose its only α-H.

$R \rightarrow H, CH_3, C_2H_5 \cdots$

2. By ozonolysis of Alkenes

Prevents oxidation of aldehyde & ketone to carboxylic acid



Alkene

↑ treated with ozone in presence of CCl_4 as solvent

ozonide

↑ distilled with water in presence of zinc

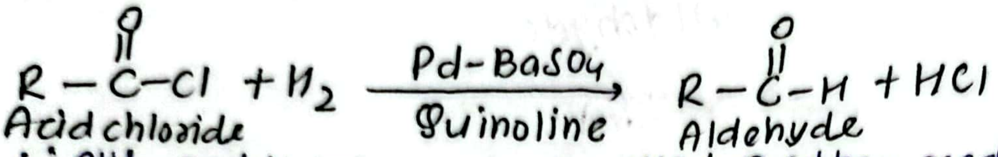
(Aldehydes and/or ketone) + H_2O_2

$H_2O_2 + Zn \rightarrow ZnO + H_2O$

- Ozonolysis occurs in two steps: (a) Formation of ozonide + (b) decomposition of ozonide
- Unbranched alkenes give aldehydes only
- Zinc: absorbs H_2O_2 which would otherwise oxidises aldehydes to carboxylic acids.

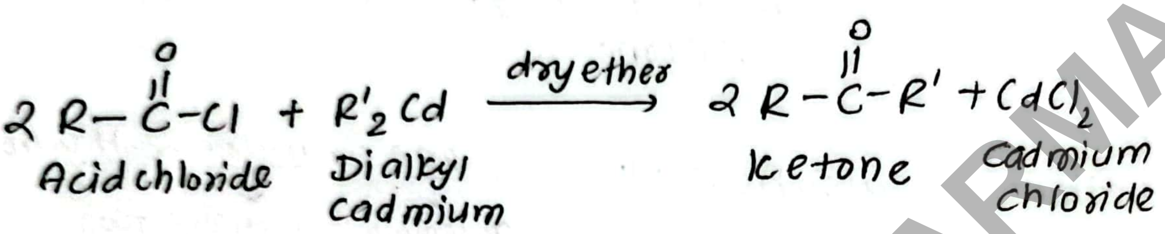
$$Zn + H_2O_2 \longrightarrow Zn(OH)_2$$

(3) From Acid chloride : Rosenmund Reduction



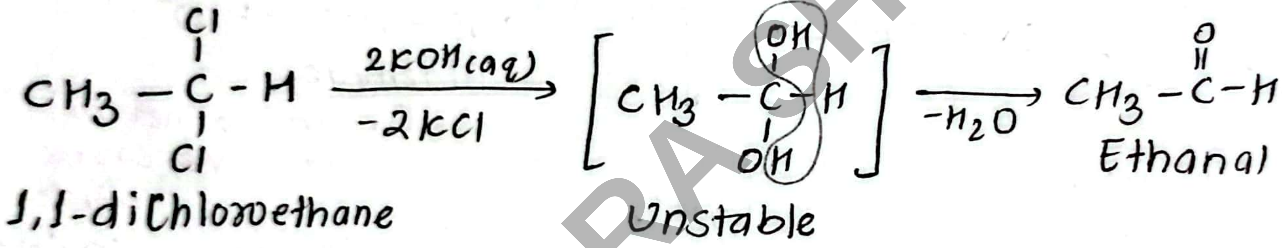
$$\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow[\text{Quinoline}]{Pd-BaSO_4} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + HCl$$

- $LiAlH_4$ and H_2/Ni can't be used as they reduce aldehyde further into 1° alcohol.

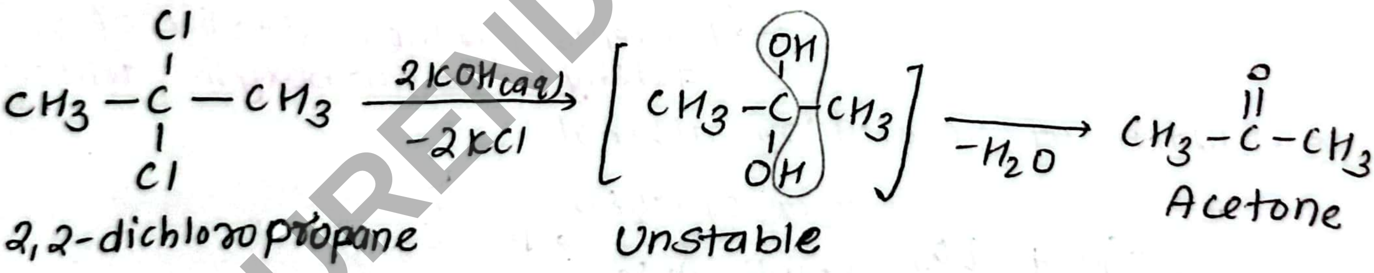


$$2\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + \underset{\text{Dialkyl cadmium}}{R'_2Cd} \xrightarrow{\text{dry ether}} 2\underset{\text{Ketone}}{R-\overset{O}{\overset{\|}{C}}-R'} + \underset{\text{Cadmium chloride}}{CdCl_2}$$

(4) From geminal dihalides

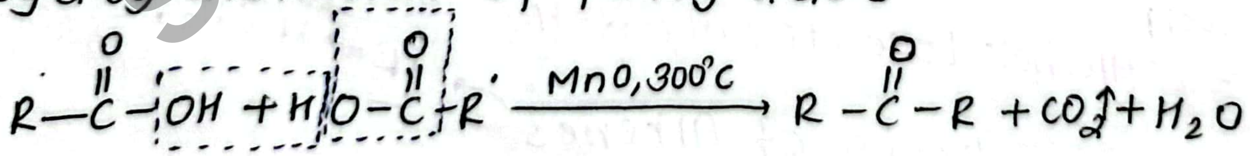


$$\underset{\text{1,1-dichloroethane}}{CH_3-\overset{Cl}{\underset{Cl}{C}}-H} \xrightarrow[-2KCl]{2KOH(aq)} \underset{\text{Unstable}}{\left[CH_3-\overset{OH}{\underset{OH}{C}}-H\right]} \xrightarrow{-H_2O} \underset{\text{Ethanal}}{CH_3-\overset{O}{\overset{\|}{C}}-H}$$



$$\underset{\text{2,2-dichloropropane}}{CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3} \xrightarrow[-2KCl]{2KOH(aq)} \underset{\text{Unstable}}{\left[CH_3-\overset{OH}{\underset{OH}{C}}-CH_3\right]} \xrightarrow{-H_2O} \underset{\text{Acetone}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$

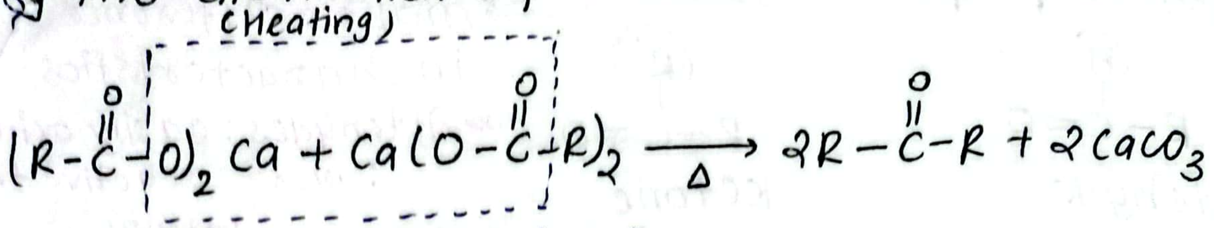
(5) By dry distillation of fatty acids



$$R-\overset{O}{\overset{\|}{C}}-OH + H-O-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{MnO, 300^\circ C} R-\overset{O}{\overset{\|}{C}}-R + CO_2\uparrow + H_2O$$

- Vapours of formic acid (HCOOH) ⟶ Formaldehyde (HCHO)
- Formic acid and other carboxylic acid (RCOOH) ⟶ Aldehye (RCHO) other than formaldehyde
- Carboxylic acid other than Formic acid (RCOOH) ⟶ Simple ketones (R–CO–R)

by the distillation of calcium salts of Fatty acids



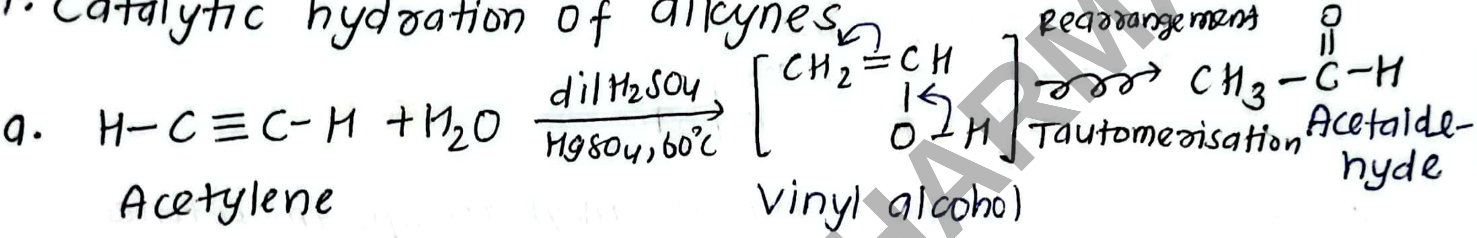
(Heating)

$$(R-\overset{O}{\overset{\|}{C}}-O)_2Ca + Ca(O-\overset{O}{\overset{\|}{C}}-R)_2 \xrightarrow[\Delta]{} 2R-\overset{O}{\overset{\|}{C}}-R + 2CaCO_3$$

calcium salt of carboxylic acid

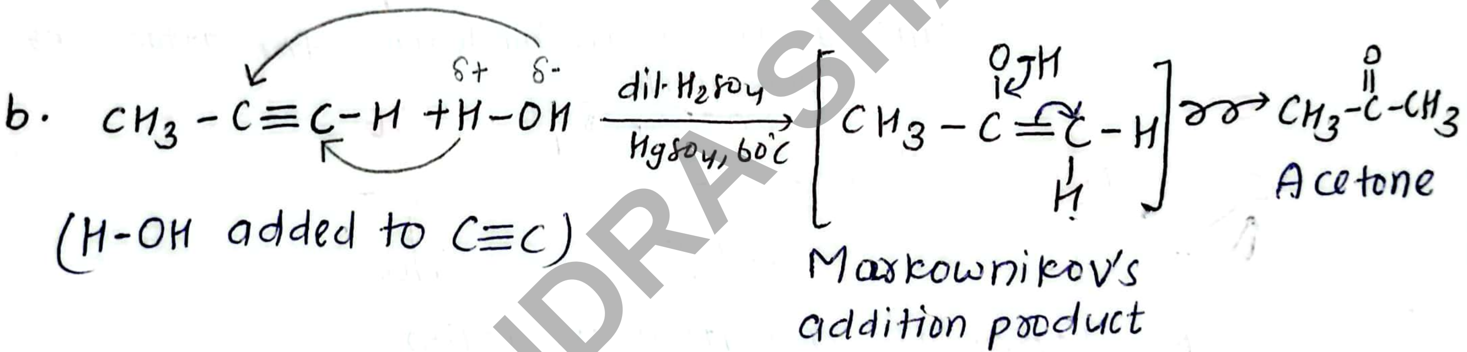
- Calcium formate [Calcium salt of Formic acid] $\{(HCOO)_2Ca\} \rightarrow$ Formaldehyde
- Mixture of calcium formate and calcium salt of other acids $[(HCOO)_2Ca]$ $[(RCOO)_2Ca] \rightarrow$ Aldehyde
- Calcium carboxylate $[(RCOO)_2Ca] \rightarrow$ Simple ketone
  other than calcium formate

7. Catalytic hydration of alkynes



$$\text{a. } H-C\equiv C-H + H_2O \xrightarrow[HgSO_4,\,60^\circ C]{dil\,H_2SO_4} \left[\begin{matrix} CH_2=CH \\ \quad\quad | \\ \quad\quad O-H \end{matrix}\right] \xrightarrow[\text{Tautomerisation}]{\text{Rearrangement}} CH_3-\overset{O}{\overset{\|}{C}}-H$$

Acetylene — Vinyl alcohol — Acetaldehyde



$$\text{b. } CH_3-C\equiv C-H + \overset{\delta+}{H}-\overset{\delta-}{OH} \xrightarrow[HgSO_4,\,60^\circ C]{dil\,H_2SO_4} \left[CH_3-\overset{OH}{\overset{|}{C}}=\underset{H}{\underset{|}{C}}-H\right] \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

(H-OH added to C≡C)

Markownikov's addition product

Acetone

Chemical properties

$R-\overset{\text{(H)}}{C}=O$ $R-\overset{\text{(R')}}{C}=O$

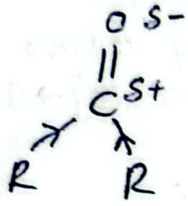
Aldehyde Ketone

→ makes difference in characteristics

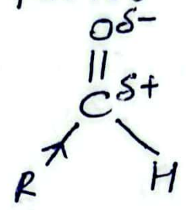
* Aldehydes : easily oxidised : more reactive than ketones ↓ oxidised with difficulty

* Both has carbonyl group ($>C=O$)

↳ Reasons: ① Electronic factor

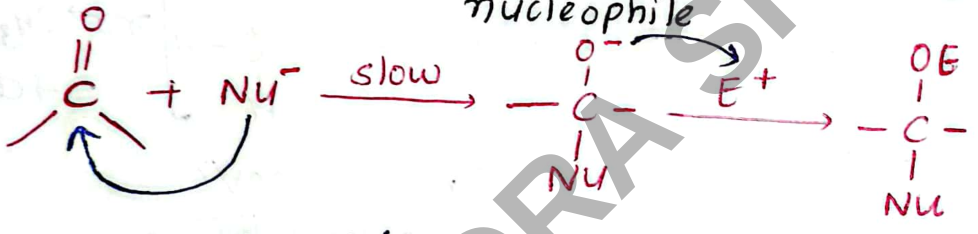


Ketones: [Carbonyl carbon attached with two bulky alkyl groups)
↓
it makes carbonyl less electropositive and make carbonyl group less reactive for nucleophilic attack.



Aldehydes: [Carbonyl carbon attached with only one alkyl group(e⁻ releasing groups)

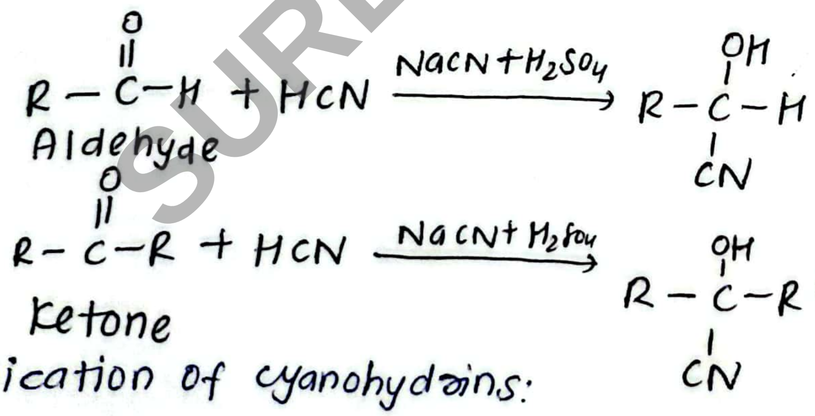
② Steric factor: two bulky alkyl groups in ketones cause much steric hinderence for attack by nucleophile



Nucleophilic addition reaction.

A. Nucleophilic addition reactions :

1. Addition of HCN (hydrogen cyanide) [$NaCN + H_2SO_4$
↳ $HCN + NaHSO_4$]



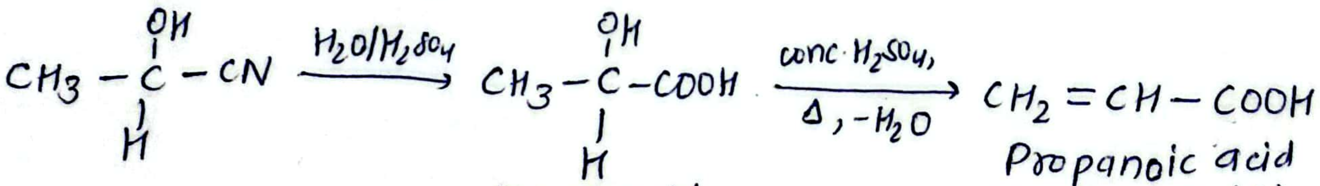
$$R-\overset{O}{\overset{\|}{C}}-H + HCN \xrightarrow{NaCN + H_2SO_4} R-\underset{CN}{\overset{OH}{C}}-H$$

Aldehyde Aldehyde cyanohydrin

$$R-\overset{O}{\overset{\|}{C}}-R + HCN \xrightarrow{NaCN + H_2SO_4} R-\underset{CN}{\overset{OH}{C}}-R$$

Ketone (ketone cyanohydrin)

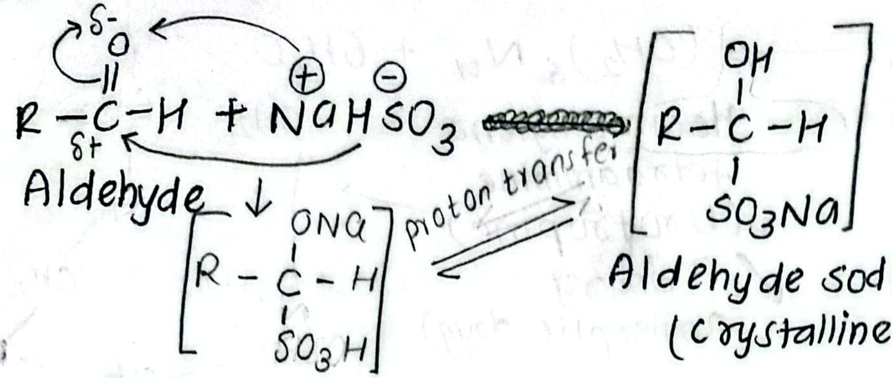
Application of cyanohydrins:



$$CH_3-\underset{H}{\overset{OH}{C}}-CN \xrightarrow{H_2O/H_2SO_4} CH_3-\underset{H}{\overset{OH}{C}}-COOH \xrightarrow[\Delta, -H_2O]{conc. H_2SO_4} CH_2=CH-COOH$$

Lactic acid Propanoic acid (Acrylic acid)

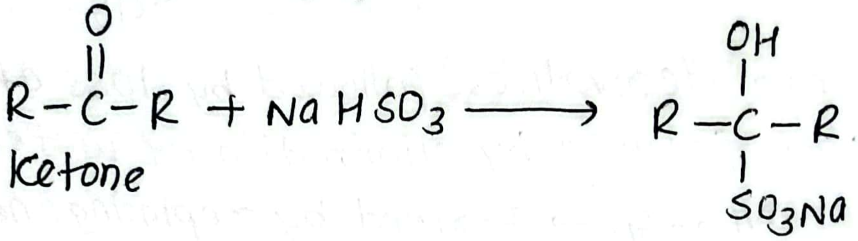
ddition of $NaHSO_3$ (Sodium bisulphite) [Test of Aldehydes and ketones]
↳ crystalline ppt.



$$R-\overset{O}{\overset{\|}{C}}-H + NaHSO_3 \rightleftharpoons \left[R-\overset{ONa}{\underset{SO_3H}{C}}-H\right] \xrightarrow{\text{proton transfer}} \left[R-\overset{OH}{\underset{SO_3Na}{C}}-H\right]$$

$[(RCHO)NaHSO_3]$

Aldehyde sodium bisulphite
(crystalline ppt.)

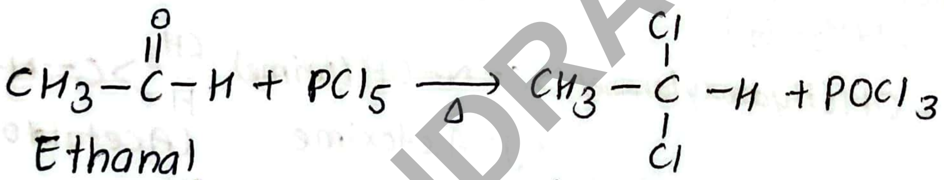


$$R-\overset{O}{\overset{\|}{C}}-R + NaHSO_3 \longrightarrow R-\overset{OH}{\underset{SO_3Na}{C}}-R$$

Ketone sodium bisulphite
(crystalline ppt.)

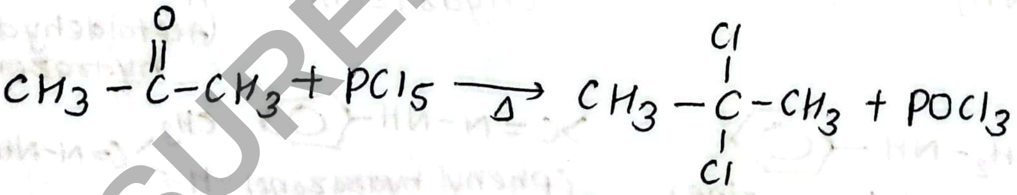
3. Addition of Grignard reagents: Grignard synthesis of alcohols
↳ Preparation of alcohol

4. Reaction of phosphorus pentachloride (PCl_5):
Formation of geminal dihalides $[-\overset{O}{\overset{\|}{C}}- \rightarrow -\overset{Cl}{\underset{Cl}{C}}-]$



$$CH_3-\overset{O}{\overset{\|}{C}}-H + PCl_5 \xrightarrow{\Delta} CH_3-\overset{Cl}{\underset{Cl}{C}}-H + POCl_3$$

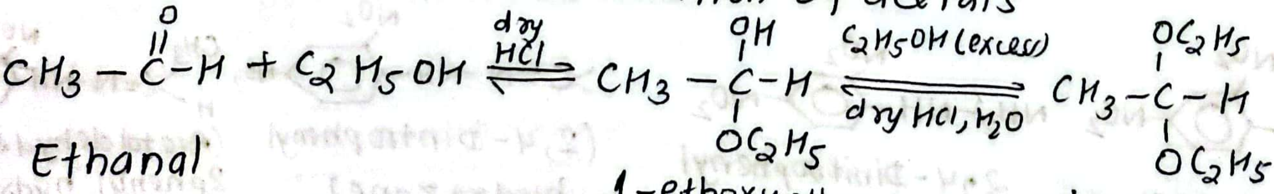
1,1-dichloroethane



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + PCl_5 \xrightarrow{\Delta} CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3 + POCl_3$$

2,2-dichloropropane

5. Addition of alcohols: Formation of acetals



$$CH_3-\overset{O}{\overset{\|}{C}}-H + C_2H_5OH \underset{}{\overset{\text{dry HCl}}{\rightleftharpoons}} CH_3-\overset{OH}{\underset{OC_2H_5}{C}}-H \underset{\text{dry HCl},\ H_2O}{\overset{C_2H_5OH\ (\text{excess})}{\rightleftharpoons}} CH_3-\overset{OC_2H_5}{\underset{OC_2H_5}{C}}-H$$

1-ethoxyethanol
(Hemi-acetal)

1,1-diethoxy ethane
(acetal)

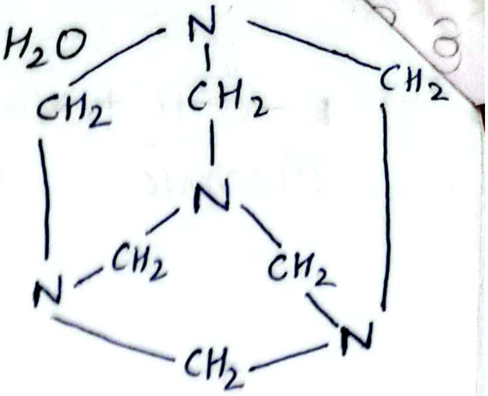
(Aliphatic ketones do not form acetals)

6. Addition of ammonia

$6\,HCHO + 4NH_3 \longrightarrow (CH_2)_6N_4 + 6H_2O$

Formaldehyde

Hexamethylene tetraammine (Urotropine) (Urinary antiseptic drug)



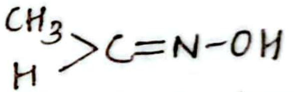
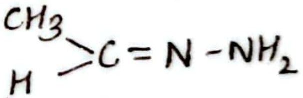
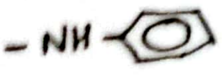
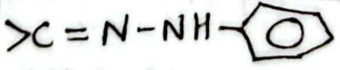
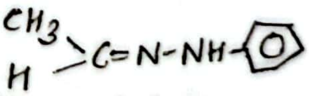
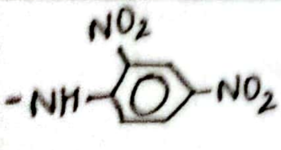
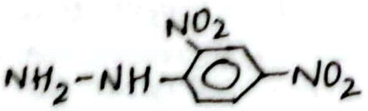
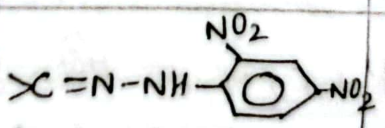
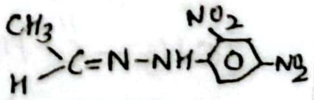
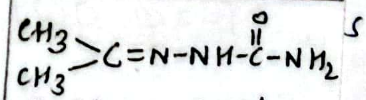
7. Addition of ammonia derivatives followed by loss of water (Nucleophilic addition followed by elimination of water)

- Ammonia derivatives (NH_2-G) → Formed by replacing one H-atom by a group G from NH_3

$>C=\boxed{O + H_2}N-G \xrightarrow{-H_2O} >C=N-G$

Imine

Imine ↓ Organic compound containing carbon nitrogen (C=N) double bond

G	Ammonia derivatives (NH_2-G)	The Product	Example
$-OH$	NH_2-OH (Hydroxylamine)	$>C=N-OH$ (oxime) eg: Acetoxime	 $CH_3(H)C=N-OH$ (Acetaldoxime)
$-NH_2$	NH_2-NH_2 (Hydrazine)	$>C=N-NH_2$ (Hydrazone)	 $CH_3(H)C=N-NH_2$ (Acetaldehyde hydrazone)
	 (Phenyl hydrazine)	 (Phenyl hydrazone)	 (Acetaldehyde phenylhydrazone)
	 2,4-Dinitrophenyl hydrazine (2,4-DNP)	 (2,4-Dinitrophenyl hydrazone) (Yellow ppt)	 (Acetaldehyde 2,4-dinitrophenyl hydrazone) (Yellow ppt.)
$-NHCONH_2$	$NH_2-NHCONH_2$ (Semicarbazide)	$>C=N-NHCONH_2$ (Semicarbazone) [crystalline ppt]	 $(CH_3)_2C=N-NH-CO-NH_2$ Acetone semicarbazone (crystalline ppt.)

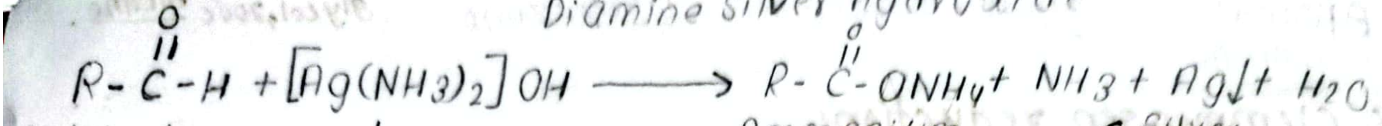
ehydes & ketones

CH2

idation of aldehyde & ketone

Tollens test → Only gives by both aliphatic and aromatic aldehyde (not responded by ketone)

Tollens reagent → $[Ag(NH_3)_2]OH$
Diamine silver hydroxide



$$R-\overset{O}{\overset{\|}{C}}-H + [Ag(NH_3)_2]OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONH_4 + NH_3 + Ag\downarrow + H_2O$$

Aldehyde ↓ mild oxidizing agent; Ammonium alkanoate; ↙ Silver mirror

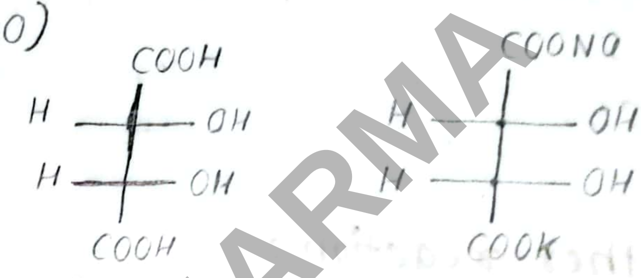
Silver mirror test: the metallic silver appears in the form of mirror deposited around the inner wall of test tube

(b) Fehlings Test

Fehlings reagent → Fehlings sol^n A + Fehlings sol^n B

Fehlings sol^n A: Aqueous $CuSO_4$ ($CuSO_4 \cdot 5H_2O$) (Blue color)

Fehlings sol^n B: (Sodium potassium tartarate)



Tartaric acid; Sodium potassium tartarate (Colourless)

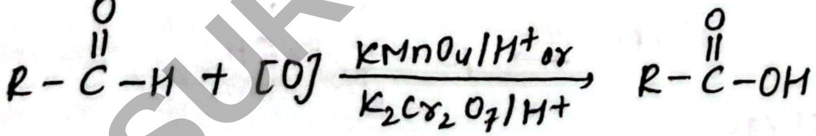
Fehlings sol^n → $[Cu^{++} + OH^-]$ → deep blue colour

$$R-\overset{O}{\overset{\|}{C}}-H + [\overset{+2}{Cu} + OH^{-1}] \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + \overset{+1}{Cu_2O}\downarrow + H_2O$$

Carboxylic acid; Brick ppt

Note - Only given by aliphatic aldehydes

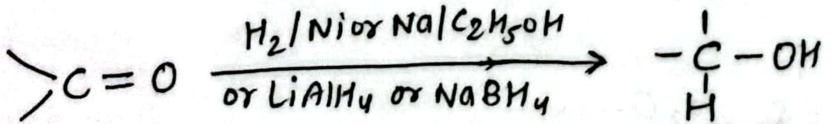
(c) Oxidation using acidified $KMnO_4$ or acidified $K_2Cr_2O_7$:



$$R-\overset{O}{\overset{\|}{C}}-H + [O] \xrightarrow[K_2Cr_2O_7/H^+]{KMnO_4/H^+ \text{ or}} R-\overset{O}{\overset{\|}{C}}-OH$$

C. Reduction of aldehydes and ketones

1. Reduction to alcohols

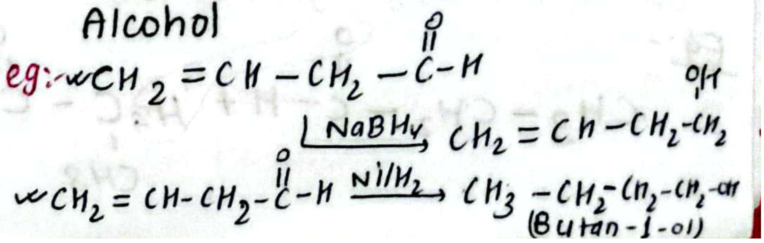


$$>C=O \xrightarrow[\text{or } LiAlH_4 \text{ or } NaBH_4]{H_2/Ni \text{ or } Na/C_2H_5OH} -\underset{H}{\underset{|}{\overset{|}{C}}}-OH$$

Aldehyde or ketone → Alcohol

Aldehyde ↓ 1°alcohol

Ketone ↓ 2°alcohol



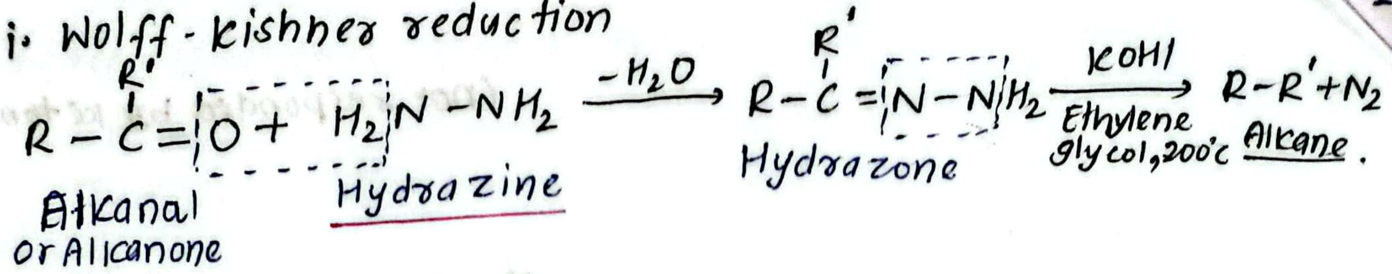
eg:- $CH_2=CH-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{NaBH_4} CH_2=CH-CH_2-CH_2-OH$

$CH_2=CH-CH_2-\overset{O}{\overset{\|}{C}}-H \xrightarrow{Ni/H_2} CH_3-CH_2-CH_2-CH_2-OH$ (Butan-1-ol)

NaBH4 is selective reducing agent → only reduces carbonyl group but not C=C

2. Reduction to alkanes (hydrocarbons)

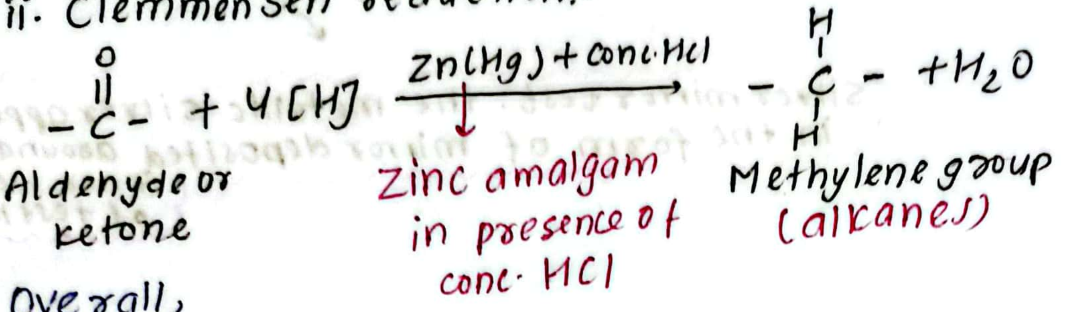
i. Wolff-kishner reduction



$$R-\overset{R'}{C}=O + H_2N-NH_2 \xrightarrow{-H_2O} R-\overset{R'}{C}=N-NH_2 \xrightarrow[\text{Ethylene glycol, 200°c}]{KOH} R-R' + N_2$$

Alkanal or Alkanone — Hydrazine — Hydrazone — Alkane.

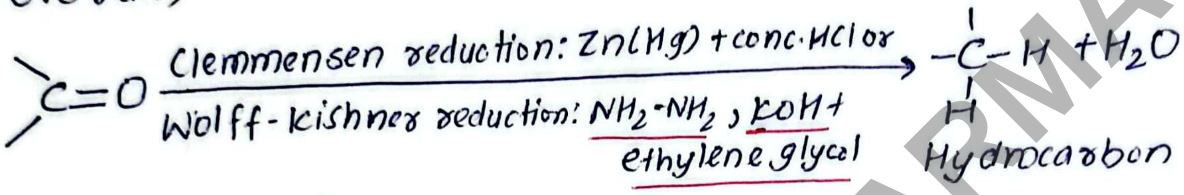
ii. Clemmensen reduction:-



$$-\overset{O}{\overset{\|}{C}}- + 4[H] \xrightarrow{Zn(Hg) + conc.HCl} -\overset{H}{\underset{H}{C}}- + H_2O$$

Aldehyde or ketone — Zinc amalgam in presence of conc. HCl — Methylene group (alkanes)

Overall,

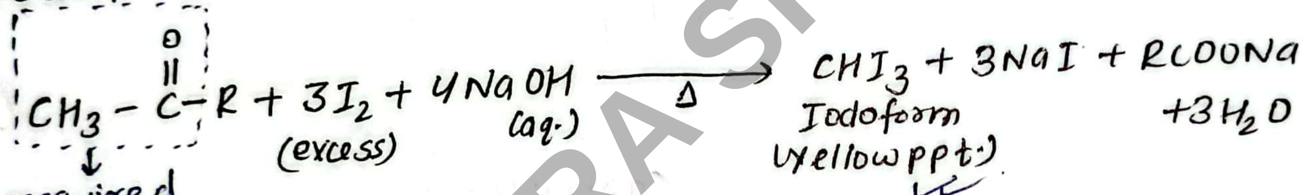


$$>C=O \xrightarrow[\text{Wolff-kishner reduction: } NH_2-NH_2\text{, KOH + ethylene glycol}]{\text{Clemmensen reduction: Zn(Hg) + conc. HCl or}} -\underset{H}{\overset{|}{C}}-H + H_2O$$

Hydrocarbon

D. Other reactions

1. Iodoform test → For Aldehydes or ketones having $CH_3-\overset{O}{\overset{\|}{C}}-$ structure

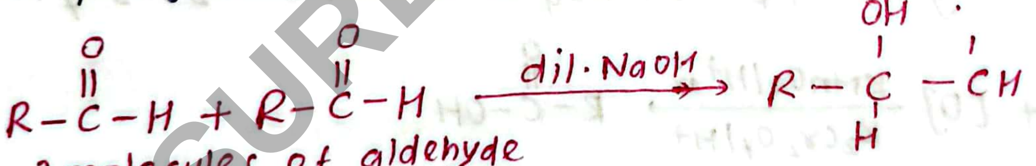


$$CH_3-\overset{O}{\overset{\|}{C}}-R + 3I_2 + 4NaOH \xrightarrow{\Delta} CHI_3 + 3NaI + RCOONa + 3H_2O$$

(excess) (aq.) — Iodoform (yellow ppt.)

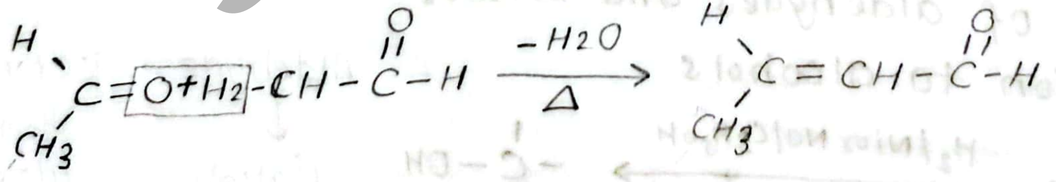
required for giving +ve iodoform test

2. Aldol condensation: Aldehyde and ketone having at least one α-hydrogen condenses with each other to produce the β-hydroxy aldehyde or ketones.



$$R-\overset{O}{\overset{\|}{C}}-H + R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{dil.NaOH} R-\overset{OH}{\underset{H}{C}}-CH$$

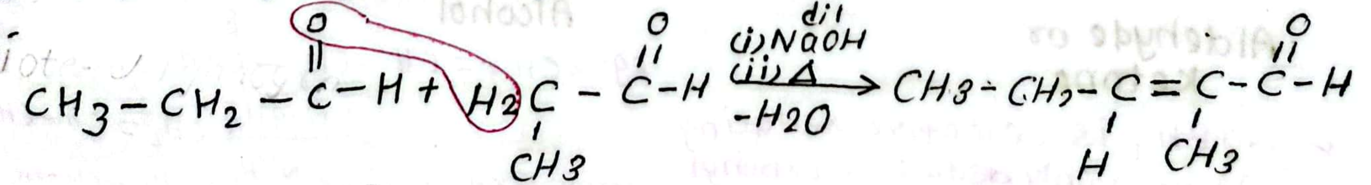
2 molecules of aldehyde



$$\overset{H}{\underset{CH_3}{>}}C=O + H_2-CH-\overset{O}{\overset{\|}{C}}-H \xrightarrow[\Delta]{-H_2O} \overset{H}{\underset{CH_3}{>}}C=CH-\overset{O}{\overset{\|}{C}}-H$$

✓ α-H always gives H_2O.

Eg:



$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + H_2\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-H \xrightarrow[-H_2O]{(i)\ dil.\ NaOH,\ (ii)\ \Delta} CH_3-CH_2-\underset{H}{C}=\underset{CH_3}{C}-\overset{O}{\overset{\|}{C}}-H$$

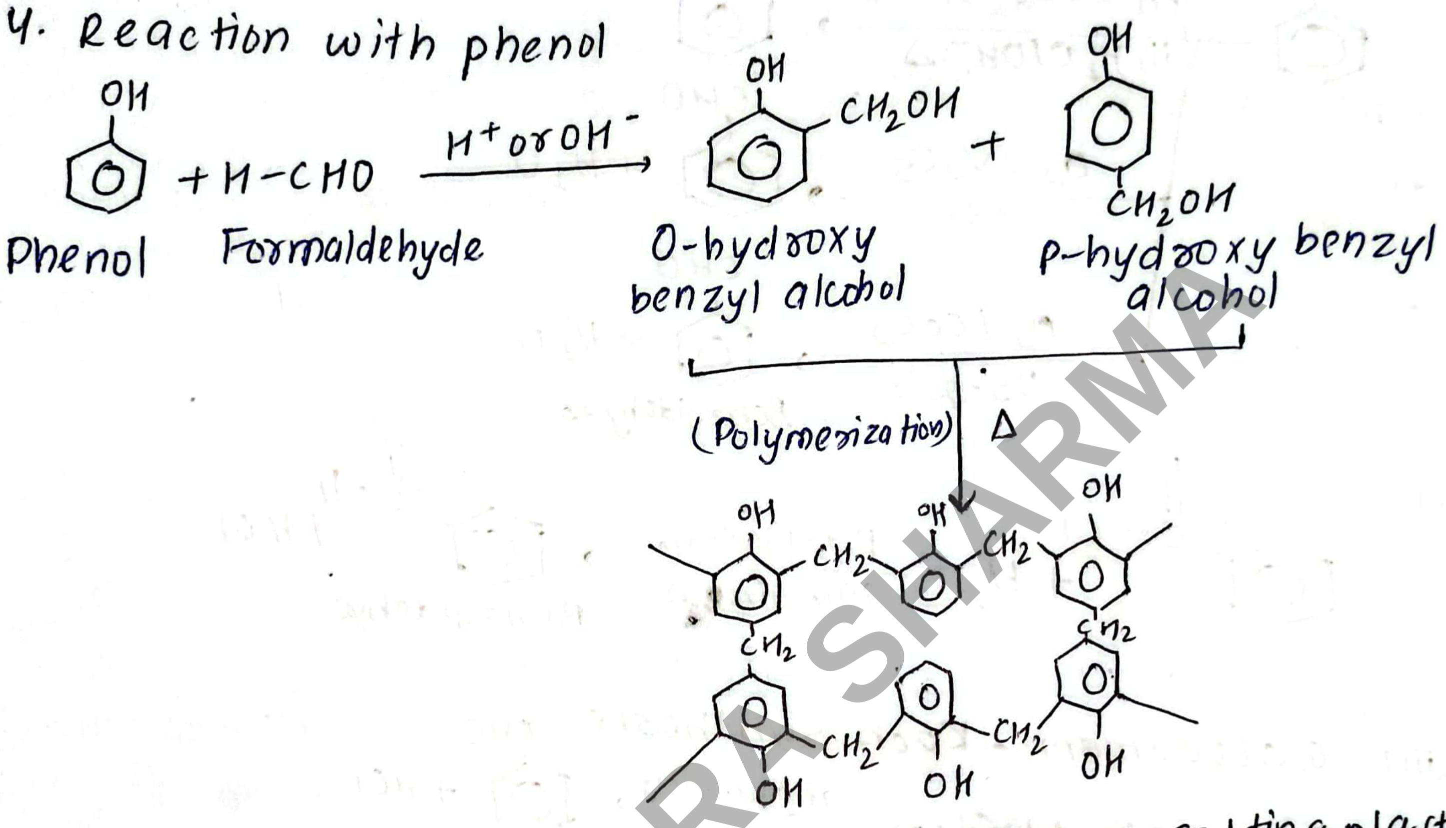
nnizzaro reaction:-

ldehydes that do not have α-hydrogen undergo disproportio-ation i.e. self oxidation-reduction on treatment with concentrated alkali solution.

$$H-CHO + H-CHO \xrightarrow[\Delta]{conc.NaOH} CH_3OH + HCOONa$$

2 moles of methanal methanol Sodium methanoate (Sodium formate)

4. Reaction with phenol

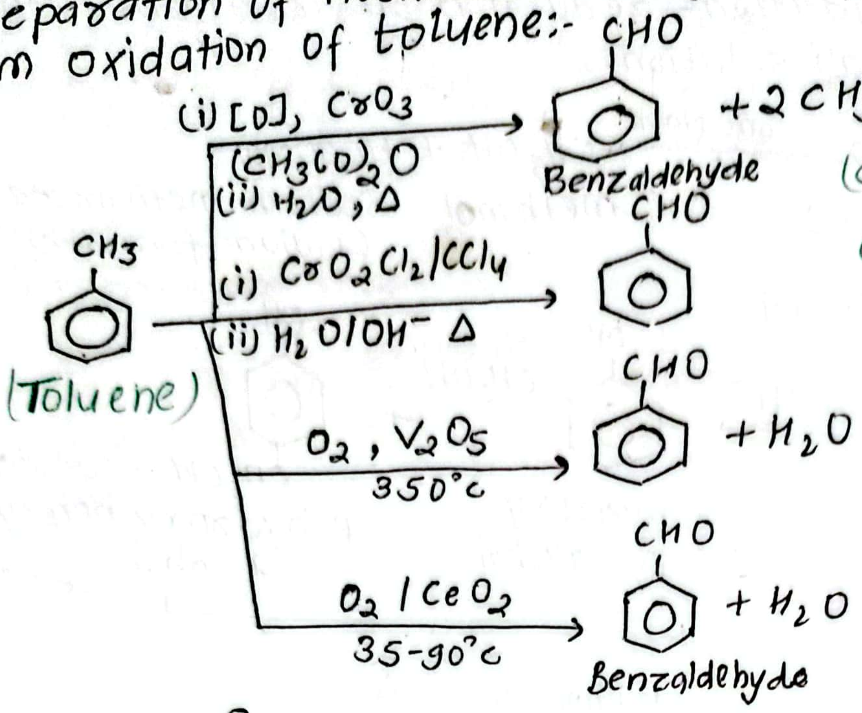


Bakellite (Thermosetting plastic)

#Aromatic Aldehydes and Ketones:-

Preparation of Aromatic Aldehyde (Benzaldehyde)

(i) From oxidation of toluene:-



CrO_3 ↳ chromic anhydride

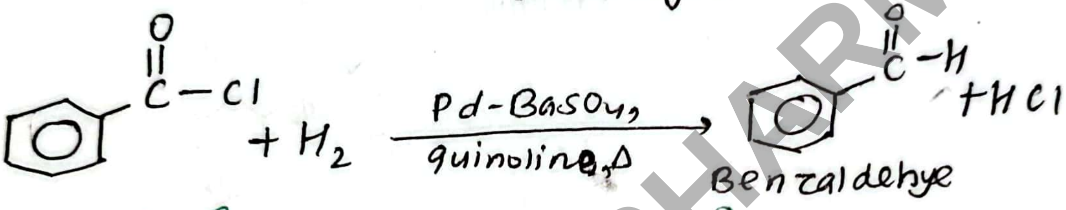
$(CH_3CO)_2O$ → acetic anhydride

CrO_2Cl_2 → chromyl chloride

V_2O_5 → vanadium pentoxide

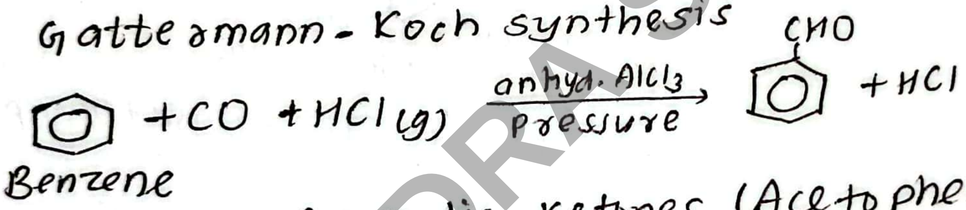
CeO_2 → cerium oxide
↳ for selective oxidation of toluene

(ii)



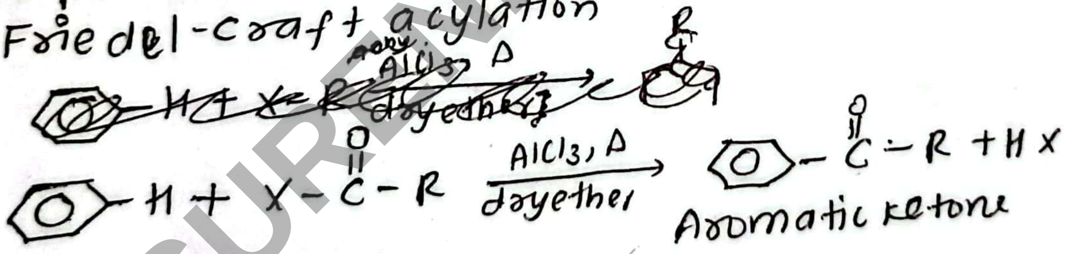
* Rosenmund's Reduction

(iii) Gattermann-Koch synthesis



Preparation of Aromatic ketones (Acetophenone)

* Friedel-craft acylation



$R \rightarrow CH_3 \Rightarrow$ Acetophenone.

R→  ⇒ Benzophenone
(Diphenyl ketone)

Surendra sharma

Carboxylic acid (Alkanoic acid)

↓

have $-COOH$ (carboxyl) functional group

* open chain aliphatic monocarboxylic acid → fatty acids

General methods of Preparation of Monocarboxylic acids:-

1. From primary alcohols and aldehydes (By oxidation):-

Oxidising agents → $Na_2Cr_2O_7/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$, $KMnO_4/H_2SO_4$

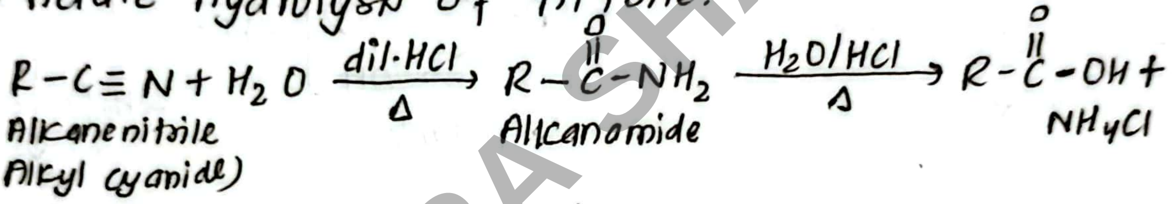
$$\underset{1^\circ \text{ Alcohol}}{RCH_2OH} + [O] \xrightarrow[-H_2O]{K_2Cr_2O_{7(aq)}/H^+,\Delta} \underset{\text{Aldehyde}}{RCHO} \xrightarrow[\Delta]{[O],\ K_2Cr_2O_{7(aq)}/H^+} \underset{\text{Carboxylic acid (Same no. of C)}}{RCOOH}$$

2. From nitriles (By hydrolysis): Nitrile synthesis

$$R-C\equiv N + H_2O \xrightarrow[\text{(acid)}]{H^+} R-COOH + NH_4^+ \quad \text{(acidic hydrolysis)}$$

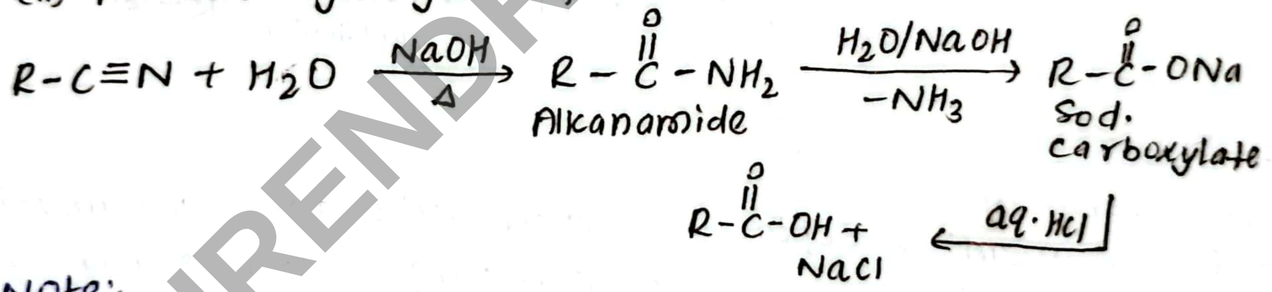
$$R-C\equiv N + H_2O \xrightarrow[\text{(Base)}]{OH^-} R-COO^- + NH_3 \quad \text{(Basic hydrolysis)}$$

(i) Acidic hydrolysis of nitrile:



$$\underset{\text{Alkanenitrile (Alkyl cyanide)}}{R-C\equiv N} + H_2O \xrightarrow[\Delta]{dil \cdot HCl} \underset{\text{Alkanamide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[\Delta]{H_2O/HCl} R-\overset{O}{\overset{\|}{C}}-OH + NH_4Cl$$

(ii) Alkaline hydrolysis of nitrile:-

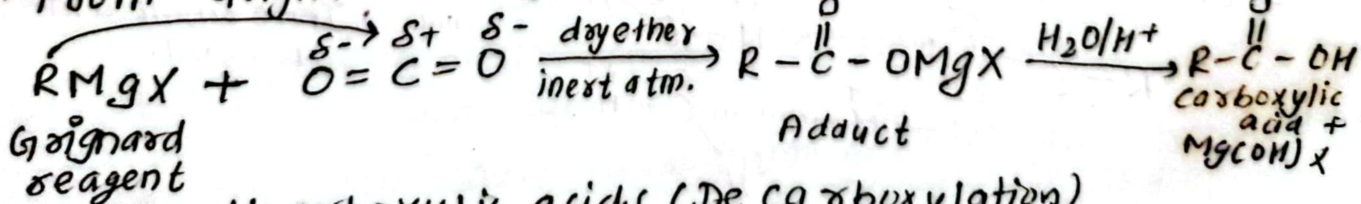


$$R-C\equiv N + H_2O \xrightarrow[\Delta]{NaOH} \underset{\text{Alkanamide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow[-NH_3]{H_2O/NaOH} \underset{\text{Sod. carboxylate}}{R-\overset{O}{\overset{\|}{C}}-ONa}$$

$$\underset{\text{aq}\cdot HCl}{\downarrow} \quad R-\overset{O}{\overset{\|}{C}}-OH + NaCl$$

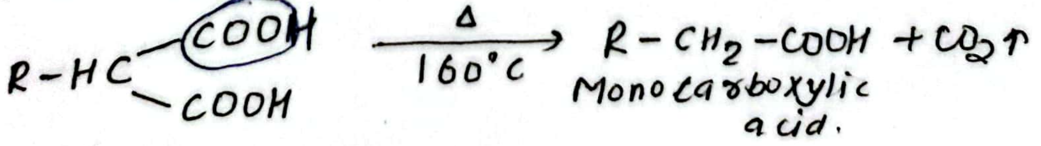
Note:-
Nitrile synthesis helps in increasing the length of a carbon chain than that of the parent alkyl halide.

3. From Grignard reagent (Carbonation):



$$\underset{\text{Grignard reagent}}{RMgX} + \overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O} \xrightarrow[\text{inert atm.}]{\text{dry ether}} \underset{\text{Adduct}}{R-\overset{O}{\overset{\|}{C}}-OMgX} \xrightarrow{H_2O/H^+} \underset{\text{Carboxylic acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + Mg(OH)X$$

4. From dicarboxylic acids (Decarboxylation)



$$R-HC\begin{matrix} COOH \\ COOH \end{matrix} \xrightarrow[160^\circ C]{\Delta} \underset{\text{Monocarboxylic acid}}{R-CH_2-COOH} + CO_2\uparrow$$

Eg:- $\begin{matrix}COOH\\ |\\ COOH\end{matrix} \xrightarrow[160°C]{\Delta} \underset{\text{Formic acid}}{HCOOH} + CO_2 \uparrow$

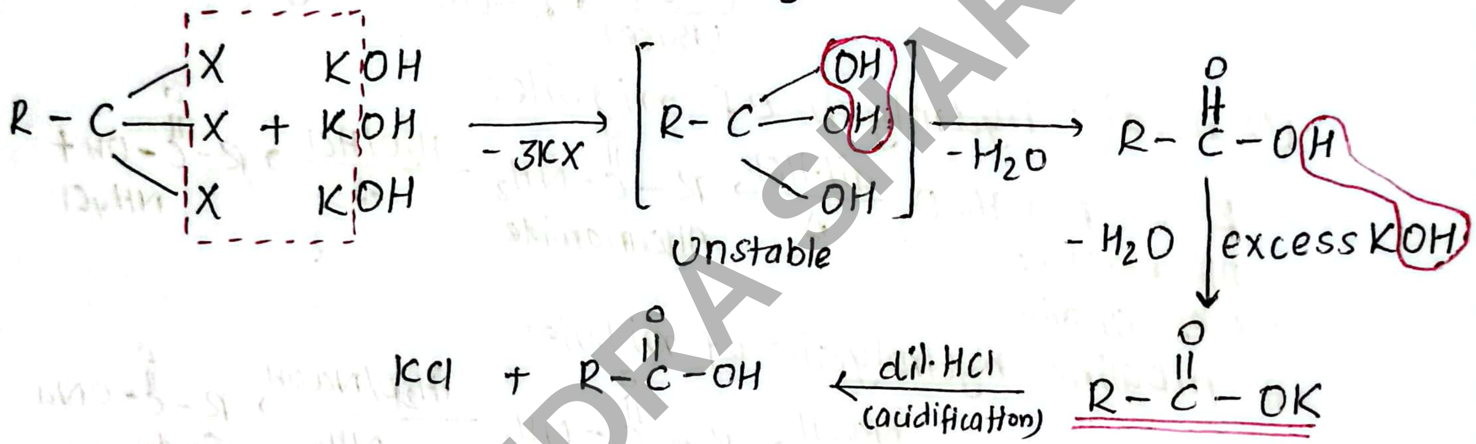
✓ Dicarboxylic acids with one or without intervening carbon atom b/w two -COOH groups on simple heating produce monocarboxylic acid with elimination of CO_2.

5. From sodium alkoxide (alkali alcoholates):-

$$\underset{\substack{\text{sodium alkoxide}\\ \text{(alkali alcoholate)}}}{RONa} + \underset{\substack{\text{(pure}\\ \text{dry)}}}{CO} \xrightarrow[\Delta]{\text{Pressure}} \underset{\text{Sod. carboxylate}}{RCOONa} \xrightarrow[\text{(acidification)}]{aq.\,HCl} \underset{\text{Carboxylic acid}}{RCOOH} + NaCl$$

6. From trihaloalkanes:

Hydrolysis of trihaloalkanes containing three halogen atoms at the same carbon atom with hot and aqueous solution of caustic alkali (NaOH or KOH) followed by acidification.

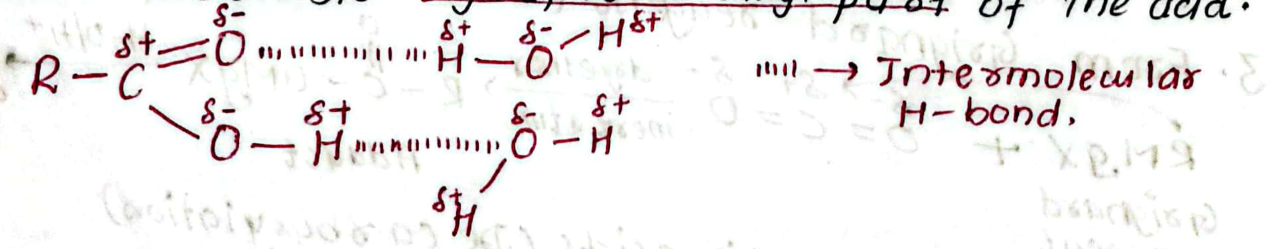


Physical properties:-

1. Solubility:

→ Lower members (C_1 to C_4) of carboxylic acids are miscible with water due to formation of effective intermolecular hydrogen bonding b/w carboxylic acid and water.

→ Whereas ~~solubi~~ higher members are insoluble in water due to water insoluble hydrophobic alkyl part of the acid.

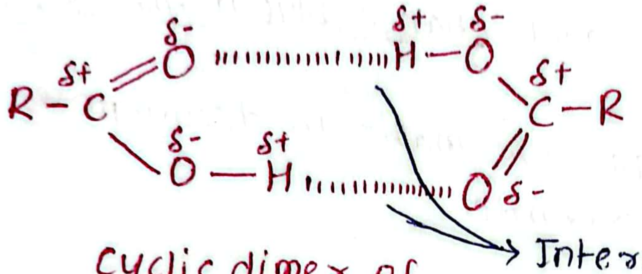


Boiling Point:-

→ BP of lower members of carboxylic acids are higher than that of alcohols of comparable molecular masses. It is because a pair of carboxylic acid molecules are held together by two intermolecular hydrogen bonds.

→ These two carboxylic acids exist as cyclic dimers.

→ O-H bond in carboxylic acid is more polar than that of alcohol, due to electron withdrawing effect of carbonyl group ($>C=O$) in carboxylic acid.



Cyclic dimer of carboxylic acids

→ Intermolecular H-bonding b/w a pair of acid (stronger than alcohols)

Intermolecular H-bonding b/w a pair of alcohols.

Chemical properties of Monocarboxylic acids:-

A. Reaction due to H-atom of the -COOH group: Acidic Nature

→ Carboxylic acid → most acidic of all organic compounds.

$$\underset{}{RCOOH} + H_2O \xrightleftharpoons{\text{ionization}} \underset{\text{carboxylate ion}}{RCOO^-} + \underset{\text{Hydronium ion}}{H_3O^+}$$

Hydronium ion → responsible for acidic behaviour

1. Litmus test :- Turns blue litmus red : due to presence of H_3O^+ in aq. solution

2. Reaction with active metals (Na, K, Zn, Mg, etc): ~~R~~ liberates H_2 gas.

$$\underset{\text{Carboxylic acid}}{2RCOOH} + 2Na \longrightarrow \underset{\text{Sod. carboxylate}}{2RCOONa} + H_2\uparrow$$

3. Reaction with metal oxides:- Gives corresponding salts of carboxylic acid (carboxylate) and water.

$$2RCOOH + \underset{\text{sod. oxide}}{Na_2O} \longrightarrow 2RCOONa + H_2O$$

4. Reaction with caustic alkali (NaOH or KOH): Gives corresponding carboxylate salt and water.

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

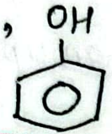
5. Reaction with metal carbonates and bicarbonates (Test of carboxylic acids)

→ Gives brisk effervescence of carbondioxide gas

$$2RCOOH + \underline{Na_2CO_3} \longrightarrow 2RCOONa + CO_2\uparrow + H_2O$$

$$RCOOH + \underset{\text{Sod. bicarbonate}}{NaHCO_3} \longrightarrow RCOONa + CO_2\uparrow + H_2O$$

But,



$+ NaHCO_3/Na_2CO_3 \longrightarrow$ NO Reaction

Phenol

✲ Though phenol & carboxylic acid (only o.c.) change blue litmus red

Phenols are weak acid as it is unable to decompose sodium carbonate or bicarbonate.

6. Reaction with ammonia:

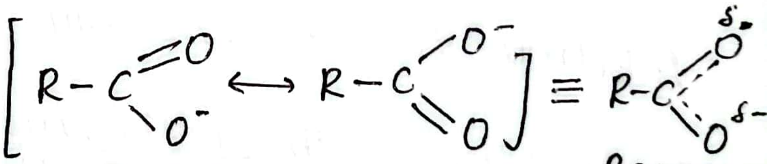
$$RCOOH + NH_3 \longrightarrow \underset{\text{(Ammonium carboxylate)}}{RCOONH_4} \xrightarrow[\text{(on heating)}]{\Delta} \underset{\text{(Amide)}}{RCONH_2} + H_2O$$

Acidic nature of carboxylic acid:-

In aqueous solution there exists a measurable equilibrium b/w acid and H_3O^+

$$\underset{\text{Carboxylic acid}}{RCOOH} + H_2O \rightleftharpoons \underset{\text{carboxylate ion}}{RCOO^-} + \underset{\text{Hydronium ion}}{H_3O^+}$$

→ Carboxylate ion (conjugate base of carboxylic acid) is stabilized by resonance, its corresponding acid (carboxylic acid) is fairly acidic



Resonance structure of carboxylate ion

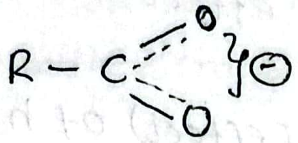
Resonance hybrid

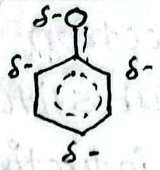
→ Conjugate base of strong acid is relatively stable

→ $$\underset{\text{Alcohol}}{R-\ddot{O}-H} \rightleftharpoons \underset{\text{Alkoxide ion (highly unstable)}}{R-\ddot{O}^-} + H^+$$

Though both carboxylic acid and alcohol both contain -OH group, alcohol is far less acidic than carboxylic acid due to absence of resonance in alkoxide ion.

→





Resonance hybrid (Phenoxide)

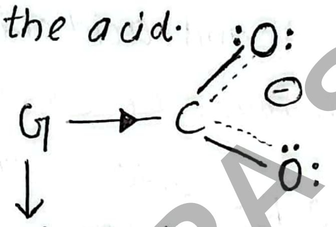
→ Carboxylic acids are stronger acids than phenols because, resonance hybrid of carboxylate is more stable than phenoxide ion. The negative charge is identically distributed over two oxygen atoms in carboxylate ion, while negative charge is present in oxygen and in carbon (electropositive element) in phenoxide ion making it less stable.

→ Thus, carboxylic acids ionize to the greater extent and behaves as strong acids than phenols.

Effect of substituent(s) on Acidity of Carboxylic Acids

(a) Effect of electron donating substituents:-

↳ Any factor that destabalizes the carboxylate ion decreases the acidity of the acid.



electron donating (releasing) substituent

G = **D**onates electron → **D**establises the anion by intensifying negative charge

↓

Decreases the acidic nature of the acid

Alkyl groups

*electron donating effect:

$H- < CH_3- < CH_3CH_2- < CH_3CH_2CH_2-$

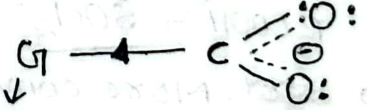
C no. increases

electron donating effect increases

Acidic nature decreases

(b) Effect of electron withdrawing substituents.

→ Any factor that stabilises the carboxylate ion increases the acidity of the acid.

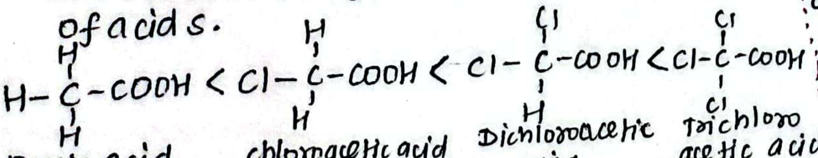


withdraws electron

↳ stablises the anion by dispersing negative charge on carboxylate ion and hence increases acidic nature of corresponding carboxylic acid.

Case I Number of substituents

More the no. of e⁻ withdrawing substituents, higher the acidic nature of acids.



$H_3C-COOH < ClCH_2-COOH < Cl_2CH-COOH < Cl_3C-COOH$

Acetic acid, chloroacetic acid, Dichloroacetic acid, Trichloro acetic acid

→ Cl- withdraws electron due to −I effect.

Case-II : Nature of substituents:-

Electron withdrawing inductive effect (−I effect) of halogen

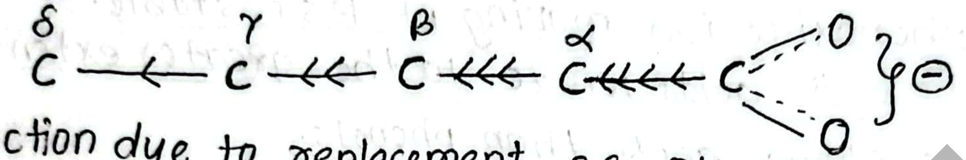
↳ F > Cl > Br > I

$F \leftarrow CH_2COOH > Cl \leftarrow CH_2COOH > Br \leftarrow CH_2COOH > I \leftarrow CH_2COOH$

⟶ Acidic nature decreases ⟶

Case III: Position or location of substituencts.

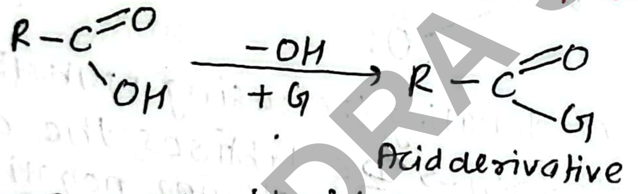
Electron withdrawing inductive effect (−I effect) decreases rapidly with distance from the carboxyl group.



B. Reaction due to replacement of −OH part of −COOH group:-

→ −OH part replaced by electron rich species like −Cl, −OR', $-NH_2$ and −OCOR' to yield Acidchloride [R−COCl], ester [R−COOR'], acid amide [$R-CONH_2$] and acid anhydride [R−COOCOR']

↙ Functional derivatives of carboxylic acid:



$$R-C(=O)OH \xrightarrow[+G]{-OH} \underset{\text{Acid derivative}}{R-C(=O)G}$$

G = Cl (SOCl$_2$)
= OR' ($SOCl_2 \rightarrow R'OH$)
= NH_2 ($NH_3 \rightarrow \Delta$]
= OCOR' [P_2O_5 or C. H_2SO_4]

1. Formation of acid chlorides:-

✓ $\underset{\text{Carboxylic acid}}{3RCOOH} + \underset{\text{Phosphorus trichloride}}{PCl_3} \xrightarrow{50^\circ C} \underset{\text{Acid chloride}}{3RCOCl} + \underset{\text{Phosphorus acid}}{H_3PO_3}$

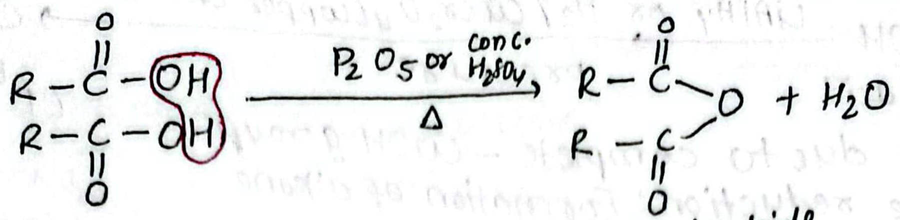
✓ $RCOOH + PCl_5 \xrightarrow{100^\circ C} RCOCl + \underset{\text{Phosphorus oxychloride}}{POCl_3} + HCl$

✓ $RCOOH + SOCl_2 \xrightarrow{\text{Pyridine, reflux}} RCOCl + SO_2\uparrow + HCl\uparrow$

↳ ~~Best~~ More conviniently used since products formed besides acid chlorides are gases (HCl & SO_2), and can be easily separated from chlorides.

alogen

Formation of acid anhydrides: Dehydration of carboxylic acid with strong dehydrating agent like P_2O_5 or conc. H_2SO_4

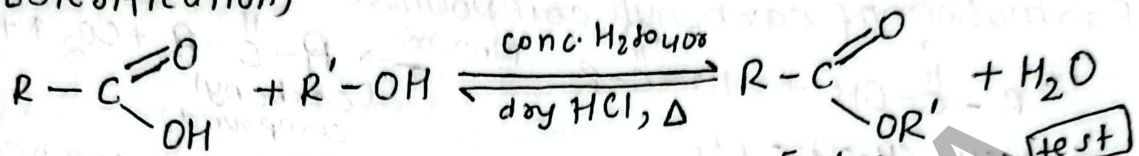


$$\begin{matrix} R-\overset{O}{\overset{\|}{C}}-OH \\ R-\underset{O}{\underset{\|}{C}}-OH \end{matrix} \xrightarrow[\Delta]{P_2O_5 \text{ or conc. } H_2SO_4} (RCO)_2O + H_2O$$

Acid anhydride
(Alkanoic anhydride)

3. Formation of ester:

i. Direct method:
(Esterification)



$$R-C{\overset{O}{\diagup\!\!\diagup}}\diagdown_{OH} + R'-OH \underset{\text{dry } HCl, \Delta}{\overset{\text{conc. } H_2SO_4 \text{ or}}{\rightleftharpoons}} R-C{\overset{O}{\diagup\!\!\diagup}}\diagdown_{OR'} + H_2O$$

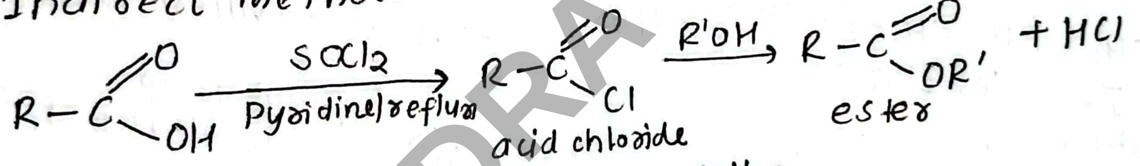
Carboxylic acid Alcohol Ester → $\boxed{\text{test}}$
(Fruity smell)

- -OH group from acid and H-atom from alcohol are eliminated as water
- Rxn is reversible → so there is low yield of product

Reactivity of alcohol : $CH_3OH > 1° > 2° > 3°$

Reactivity of acid : $HCOOH > CH_3COOH > RCH_2COOH > R_2CHCOOH > R_3CCOOH$

(ii) Indirect method



$$RCOOH \xrightarrow[\text{Pyridine/reflux}]{SOCl_2} RCOCl \xrightarrow{R'OH} RCOOR' + HCl$$

acid chloride ester

- irreversible: so rxn go on completion.

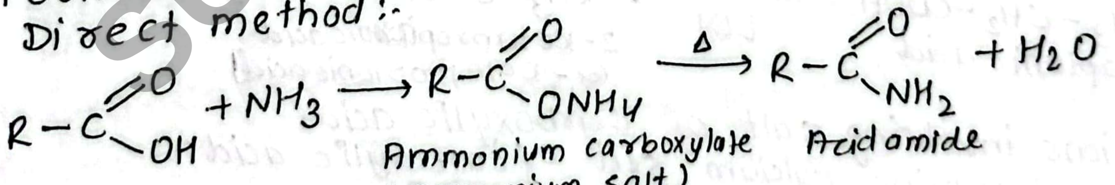
(iii) Diazomethane method:

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

Diazomethane methylesters

4. Formation of amide:

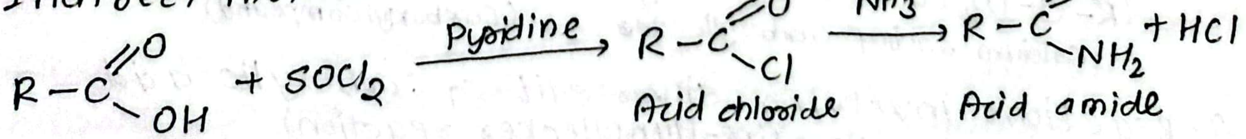
(i) Direct method:-



$$RCOOH + NH_3 \longrightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

Ammonium carboxylate (ammonium salt) Acid amide

(ii) Indirect method:-



$$RCOOH + SOCl_2 \xrightarrow{\text{Pyridine}} RCOCl \xrightarrow{NH_3} RCONH_2 + HCl$$

Acid chloride Acid amide

C. Reaction due to >C=O part of –COOH group:-

Partial reduction: Formation of alcohols: → can't use $NaBH_4$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[\text{pressure}]{LiAlH_4 \text{ or } H_2/CuCr_2O_4 \text{ (Copper chromite}} \underset{\substack{\text{Ethanol} \\ (1^\circ \text{ alcohol})}}{CH_3CH_2OH}$$

D. Reaction due to complete –COOH group:

1. complete reduction: Formation of alkane

$$\underline{RCOOH} + 6HI \xrightarrow[200^\circ C]{\text{red } P} \underset{\text{alkane}}{R\underline{CH_3}} + H_2O + 3I_2$$

(prolonged reduction in sealed tube)

2. Formation of carbonyl compounds:

✓ $$R-\overset{O}{\overset{\|}{C}}-OH + HO-\overset{O}{\overset{\|}{C}}-R \xrightarrow{MnO, 300^\circ C} \underset{\text{(carbonyl compound)}}{R-\overset{O}{\overset{\|}{C}}-R} + CO_2\uparrow + H_2O$$

R → H, CH_3, CH_3CH_2-, etc

✓ For different R variety of carbonyl compound can be formed.

E. Reaction due to alkyl (R-) group of carboxylic acid:-

1. α-Halogenation of aliphatic acid [Hell-Volhard-Zelinsky reaction (HVZ)]

$$\text{Carboxylic acid having } \alpha\text{-hydrogen atom} \xrightarrow[\text{red } P_4,\ -HBr]{\text{Halogens } (Cl_2 \text{ or } Br_2)/} \alpha\text{-halo carboxylic acid}$$

eg:-

$$\underset{\text{Isovaleric acid}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-OH} \xrightarrow[-HBr]{\text{red } P_4/Br_2} \underset{\alpha\text{-Bromo isovaleric acid}}{CH_3-\overset{CH_3}{\overset{|}{C}H}-\overset{Br}{\overset{|}{C}H}-\overset{O}{\overset{\|}{C}}-OH}$$

2. Oxidation

a. β-oxidation

$$\underset{\text{(Butyric acid)}}{CH_3-CH_2-CH_2-COOH} \xrightarrow[[O]]{H_2O_2} \underset{(\beta\text{-Hydroxybutyric acid})}{CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-COOH} + H_2O$$

← alkyl group oxidized at β-position.

b. Selective oxidation [(SeO_2), alkyl group is oxidized at α-position to form α-keto acid]

$$\underset{\text{Propionic acid}}{CH_3-CH_2-COOH} \xrightarrow[[O]]{SeO_2} \underset{\substack{\text{2-Ketopropanoic acid} \\ (\alpha\text{-Keto propionic acid})}}{CH_3-\overset{O}{\overset{\|}{C}}-COOH} + H_2O$$

✓ F. Reactions involving salt of carboxylic acids

1. Reaction involving calcium salt of carboxylic acid:

$$\underset{\text{Calcium salts of carboxylic acids}}{(R-\overset{O}{\overset{\|}{C}}-O)_2Ca + Ca(O-\overset{O}{\overset{\|}{C}}-R')_2} \xrightarrow{\Delta} \underset{\text{(Carbonyl compound)}}{2R-\overset{O}{\overset{\|}{C}}-R'} + 2CaCO_3$$

✓ 2. Reactions involving silver salt of carboxylic acid (Hunsdiecker or Borodine-Hunsdiecker reaction)

→ $$RCOOAg + \underline{Cl_2/Br_2} \xrightarrow{CCl_4 \text{ (solvent)}} \underset{RBr}{RCl}/ + CO_2\uparrow + AgCl/$$

CH_2OH

dalime decarboxylation:-

$$R\text{-}COONa + NaOH \xrightarrow{CaO,\ \Delta} R\text{-}H + Na_2CO_3$$

↳ alkane have 1-C less than acid. (used in dec. carbon chain in organic conversion)

4. Kolbe's electrolytic decarboxylation

$$\underset{\text{or } (RCOOK)}{RCOONa_{(aq.)}} \longrightarrow RCOO^- + Na^+$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At anode, $2RCOO^- \longrightarrow \underset{\text{Alkane (higher)}}{R\text{-}R} + 2CO_2 + 2e^-$

At cathode,
$H^+ + e^- \longrightarrow H$
$H + H \longrightarrow H_2$

5. Reactions involving ammonium salt of carboxylic acid:

(a)
$$\underset{\text{Ammonium carboxylate}}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}ONH_4} \xrightarrow{\Delta} \underset{\text{(Amide)}}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2} + H_2O$$
→ Heated alone

(b)
$$\underset{\text{Ammonium carboxylate}}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}ONH_4} \xrightarrow{P_2O_5,\ \Delta} \underset{\text{Nitrile}}{R\text{-}C\equiv N} + 2H_2O$$
→ Heated in presence of P_2O_5

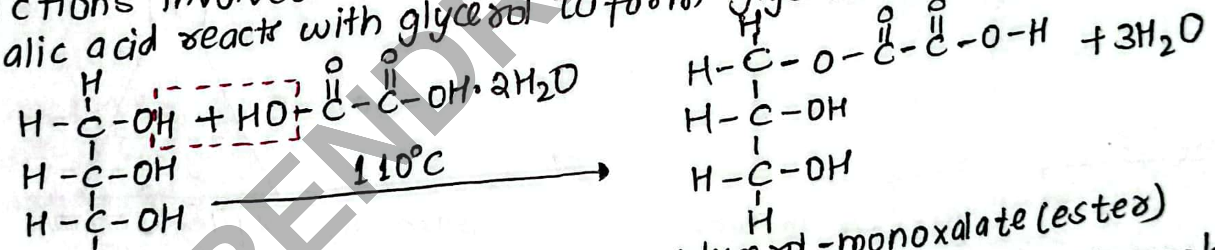
Laboratory preparation of Formic acid

Principle:-

$$\underset{\text{(crystalline oxalic acid)}}{\begin{matrix}COOH\\|\\COOH\end{matrix}\cdot 2H_2O} \xrightarrow[110°C]{\text{Anhydrous Glycerol}} \underset{\text{(Formic acid)}}{HCOOH} + CO_2 + 2H_2O$$

Reactions involved:

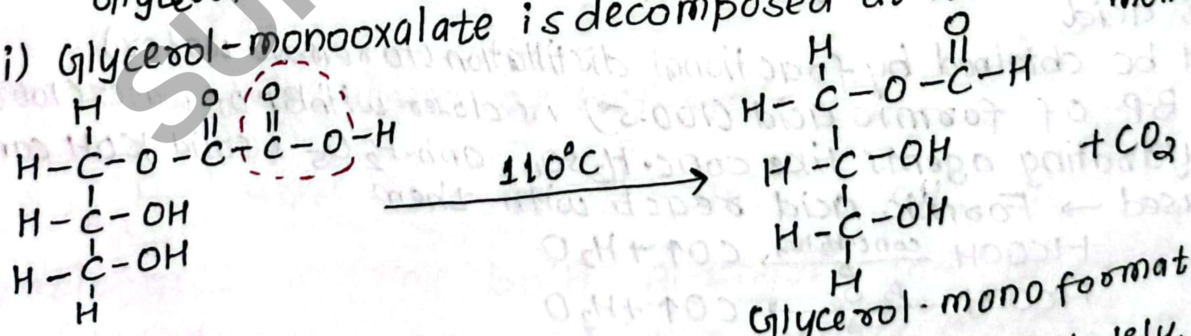
(i) Oxalic acid reacts with glycerol to form glycerol-monooxalate



Glycerol

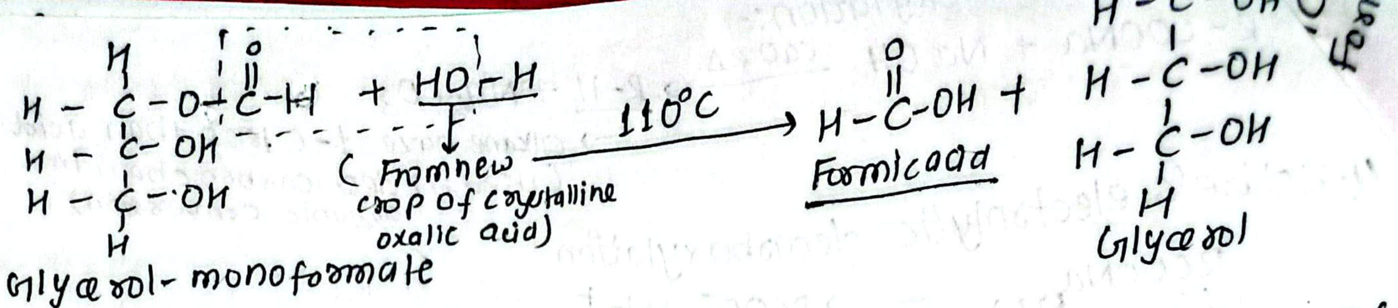
Glycerol-monoxalate (ester)

(ii) Glycerol-monooxalate is decomposed at 110°C into glycerol-monoformate.



Glycerol-monoformate (ester)

(iii) When the effervescence of CO_2 ceases completely, further amount of crystalline oxalic acid $[(COOH)_2 \cdot 2H_2O]$ is added when glycerol-monoformate is hydrolyzed with water of crystallization of crystalline oxalic acid into formic acid.



Procedure:-

40g. crys. Oxalic acid + 50g anh. glycerol ⟶ Δ110°C → Effervescence of CO_2 ceases

↓

Flask is cooled → Fresh bath of oxalic acid crystals (40g) → Δ110°C → Thus formed Formic acid is collected in a receiver as aqueous formic acid.

#

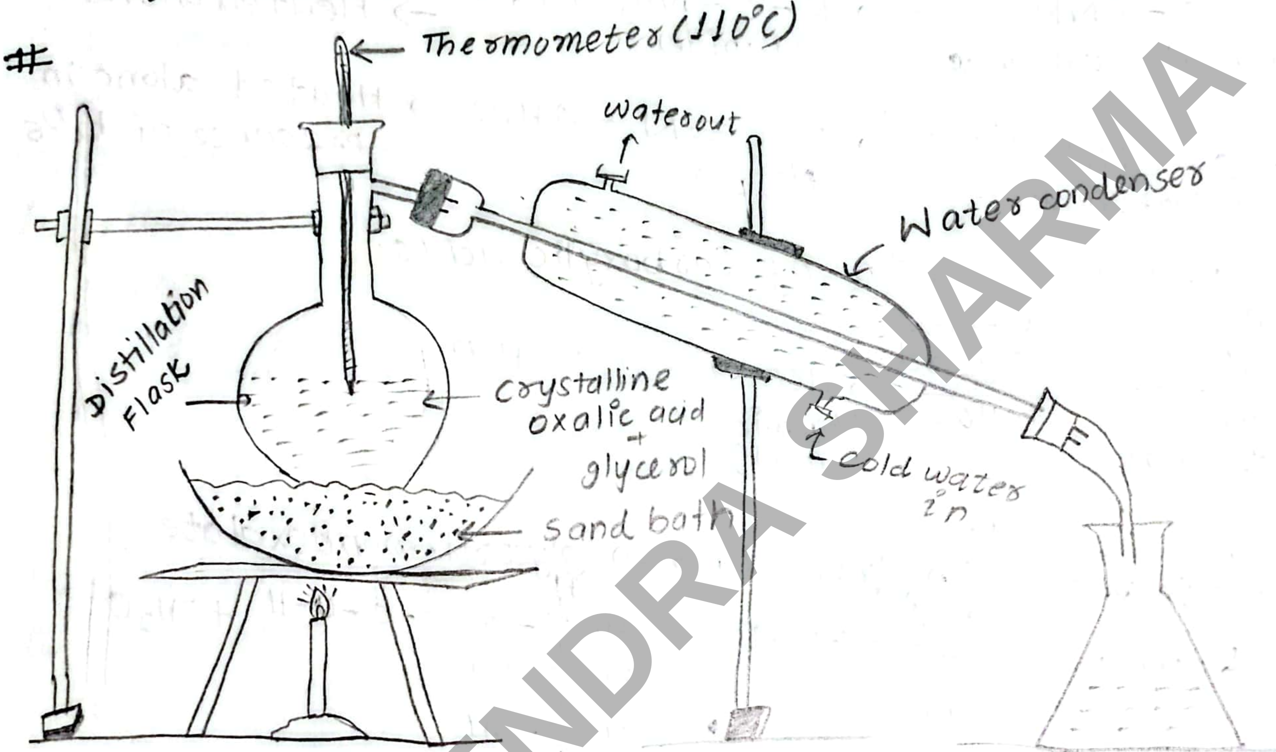


Fig: Laboratory preparation of aqueous Formic acid

Preparation of anhydrous formic acid from aqueous formic acid

(i) Cannot be obtained by fractional distillation (to remove water)
↳ B.P. of formic acid (100.5°) is closer with BP of water (100°C)

(ii) Dehydrating agents like conc. H_2SO_4, anh. P_2O_5 & solid KOH can't be used → Formic acid react with them

$$HCOOH \xrightarrow[\Delta]{conc.\ H_2SO_4} CO\uparrow + H_2O$$

$$HCOOH \xrightarrow[\Delta]{P_2O_5} CO\uparrow + H_2O$$

$$HCOOH + KOH \longrightarrow HCOOK + H_2O$$

So, chemical method of separation is applied.
↳ carried out by using water condenser as separating device.

$COOH_{(aq)} + PbCO_{3(aq)} \xrightarrow{\text{Neutralization}} (HCOO)_2Pb_{(aq)} + CO_2\uparrow + H_2O$

Formic acid　　Lead carbonate　　　　Lead formate

↳ neutralized till completion of effervescence of CO_2 gas

$(HCOO)_2Pb_{(aq)} \xrightarrow{\text{crystallization}} (HCOO)_2Pb$ (crystals)

Lead formate solution

↳ are taken in inner tube of water condenser

→ water condenser : apparatus fitted as shown in fig

→ steam is passed through outer jacket & H_2S passed under pressure from upper end.

→ Anhydrous formic acid formed is collected in a receiver ; ppt. of PbS remain in condenser due to wool plug

→ An. formic acid may contain dissolved H_2S : removed by redistilling an. formic acid with fresh lead formate crystals.

$(HCOO)_2Pb_{(s)} + H_2S_{(g)} \xrightarrow{100^\circ C} 2HCOOH_{(l)} + PbS_{(s)}\downarrow$

Anhydrous formic acid　　Lead sulphide (black ppt.)

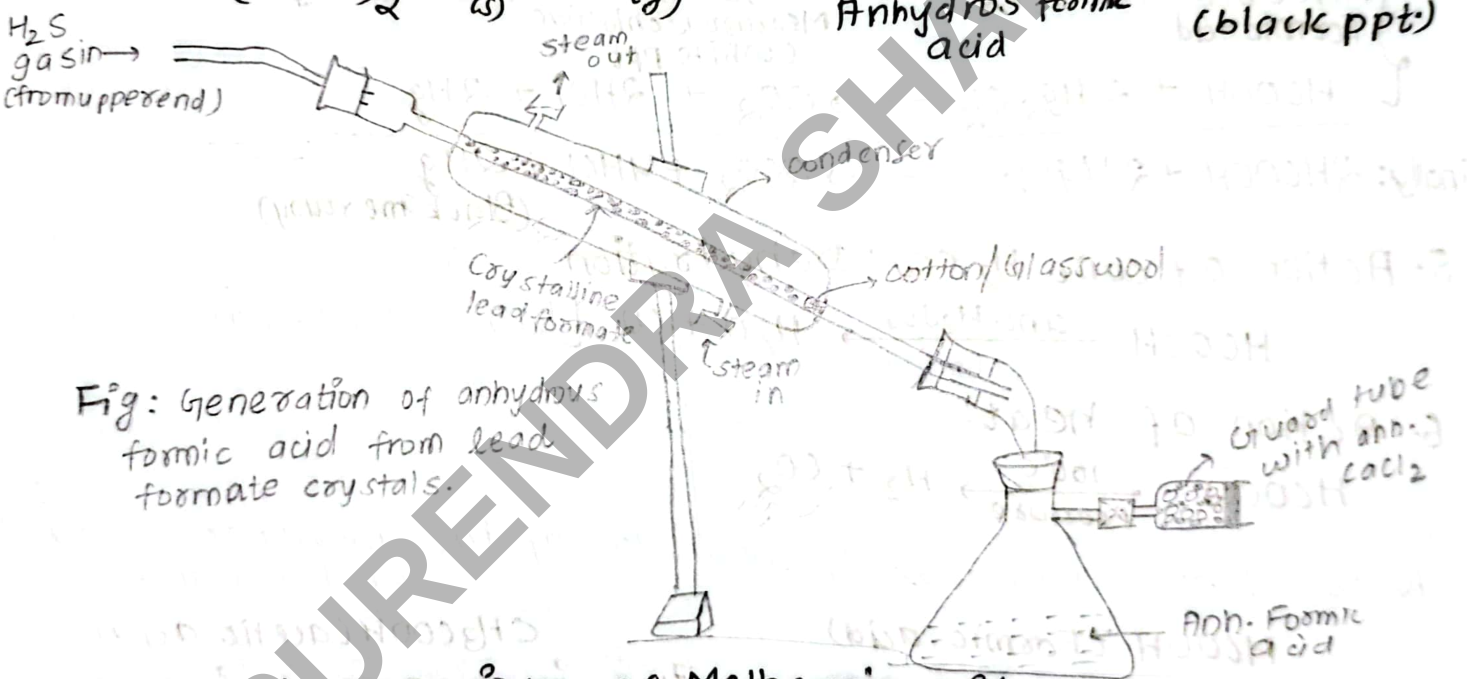
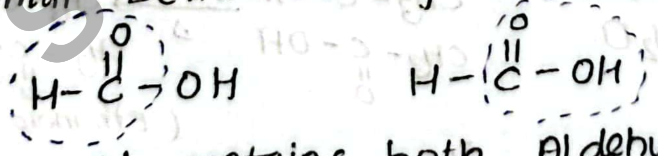


Fig: Generation of anhydrous formic acid from lead formate crystals.

Abnormal behaviour of Methanoic acid



$H-\overset{O}{\overset{\|}{C}}-OH$　　$H-\overset{O}{\overset{\|}{C}}-OH$

Formic acid contains both Aldehyde and carboxyl group

So it behaves as an acid as well as aldehyde

Compairision of properties of Formic acid with acetic acid:-

⟶

1. Tollen's test(Silver mirror test)

$$\underset{\substack{\text{Formic acid}\\ \downarrow \\ \text{oxidized to } CO_2}}{HCOOH} + \underset{\substack{\text{Tollen's reagent}\\ \downarrow \\ \text{reduced to silver}}}{2[Ag(NH_3)_2]OH} \xrightarrow[\text{(in water bath)}]{\text{warm}} \underset{\text{Silver mirror}}{2Ag\downarrow} + CO_2\uparrow + 2H_2O + 4NH_3$$

(deposited on the inner wall of test tube.

2. Fehling's test:

$$\underset{\substack{\text{Formic acid}\\ \downarrow \\ \text{Oxidised to } CO_2}}{HCOOH} + \underset{\substack{\text{Fehling's solution}\\ \downarrow \\ \text{reduced to } Cu_2O}}{[2Cu^{++} + 4OH^-]} \xrightarrow[\text{(in water bath)}]{\text{warm}} \underset{\text{(red ppt.)}}{Cu_2O\downarrow} + CO_2\uparrow + 3H_2O$$

3. Reaction with acidified $KMnO_4$:- (Permanganate test)

$$\underset{\text{Formic acid}}{5HCOOH} + \underset{\substack{\text{Pot. Permanganate}\\ \text{(Pink colour)}}}{2KMnO_4} + 3H_2SO_4 \xrightarrow{\text{warm}} K_2SO_4 + 2MnSO_4 + 5CO_2 + 8H_2O$$

→ pink colour of $KMnO_4$ is discharged.

4. Reaction with mercuric chloride:

$$\underset{\text{Formic acid}}{HCOOH} + 2HgCl_2 \longrightarrow \underset{\substack{\text{Mercurous chloride}\\ \text{(white ppt)}}}{Hg_2Cl_2\downarrow} + CO_2 + 2HCl$$

$$HCOOH + 2Hg_2Cl_2 \longrightarrow CO_2 + 2HCl + 2Hg$$

Finally: $2HCOOH + 2HgCl_2 \longrightarrow 2CO_2 + 4HCl + \underset{\text{(Black mercury)}}{2Hg}$

5. Action of conc. H_2SO_4: Dehydration

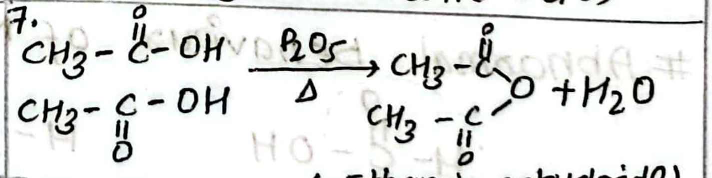
$$HCOOH \xrightarrow[\text{(dehydrated)}]{\text{conc. } H_2SO_4} H_2O + CO$$

[Lab. prep. of carbon monoxide

6. Action of heat:

$$HCOOH \xrightarrow[\text{pressure}]{160^\circ C} H_2 + CO_2$$

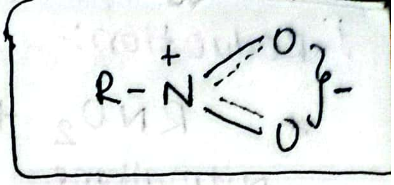
Note: Acetic acid doesn't show any of the above tests, action and reaction.

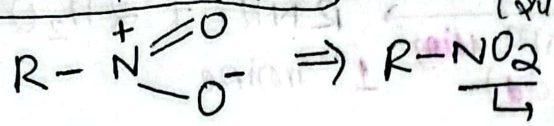
	HCOOH (Formic acid)	CH_3COOH (acetic acid)
7.	Action with P_2O_5: $HCOOH \xrightarrow[\Delta]{P_2O_5} CO + H_2O$	7.  (Ethanoic anhydride)
8.	Reaction with PCl_5: $HCOOH + PCl_5 \rightarrow HCOCl + POCl_3 + HCl$ ↳ Methanoyl chloride decomposes to CO & HCl $HCOCl \rightarrow CO + HCl$ overall: $HCOOH + PCl_5 \rightarrow 2HCl + CO + POCl_3$	8. $CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$ $CH_3COOH \xrightarrow[SOCl_2]{PCl_5, PCl_3} CH_3COCl$ (acetyl chloride.
9.	Sodalime decarboxylation: Gives H_2 gas $HCOOH + NaOH \xrightarrow[\Delta]{CaO} H_2 + Na_2CO_3$	9. : Gives methane $CH_3COOH + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$

colorless liquid with pleasant odour & sparingly soluble in water. ←

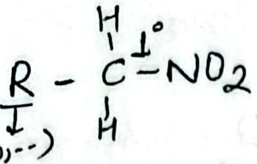
Nitro compounds

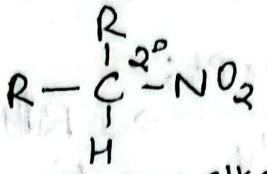
(Surendra Sharma)

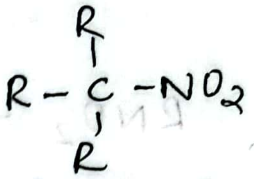




→ $R-\overset{+}{N}(=O)-O^-$ ⇒ $R-NO_2$
↳ Nitro group

→ 
(CH_3, --)
Primary nitroalkane


2° nitroalkane


3° nitroalkane

MOP :

① From alkyl halides

$$CH_3CH_2Br + AgNO_2 \xrightarrow{\Delta} CH_3CH_2-\overset{+}{N}(=O)-\overset{-}{O} + AgBr$$

(1° alkyl halides specially R-Br and R-I)
[aq. ethanolic solⁿ of silver nitrite]
Nitroethane

But,

$$CH_3CH_2Br + KNO_2 \xrightarrow{\Delta} CH_3CH_2-O-N=O + KBr$$

Bromoethane [Pot. nitrite] → Ethyl nitrite [Alkyl nitrite]

② From alkanes:- (Substitution Rxn)

$$CH_4 \xrightarrow{HNO_3,\ 400°C} CH_3NO_2$$

[Alkane] Fuming. vapour phase nitration
[Mixture of all possible nitro alkanes by carbon chain fission rxn of alkanes]

eg:

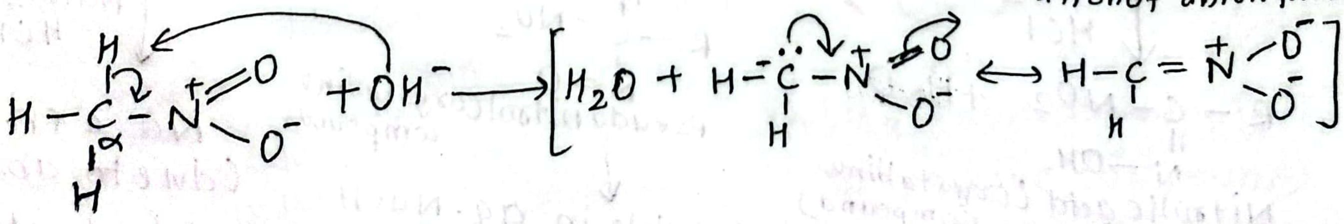
$$CH_3CH_2CH_3 \xrightarrow{HNO_3,\ 400°C} CH_3CH_2CH_2NO_2 + CH_3-\underset{NO_2}{\underset{|}{CH}}-CH_3 + CH_3CH_2NO_2 + CH_3NO_2$$

1-Nitropropane   2-nitropropane   Nitroethane

③ # Chemical properties:-

1° & 2° NO_2 compound having α-H are acidic so they react with $NaOH_{(aq.)}$ to form salt

↳ due to (i) −I effect of $-NO_2$
(ii) resonance stabilization of anion formed.

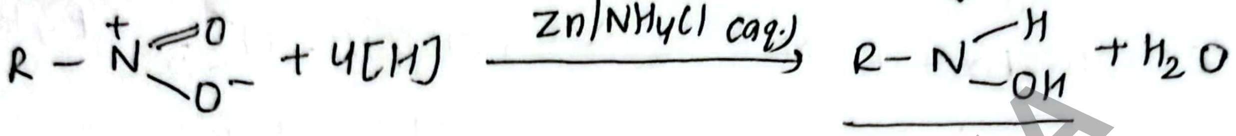


1. Reduction:-

$$* \quad \underset{\text{Nitroalkane}}{RNO_2} + 6[H] \xrightarrow[\text{(acidic sol}^n\text{ using metal \& acid)}]{Sn/HCl\ ;\ Fe/HCl\ ;\ Zn/HCl} \underset{1^\circ\text{ amine}}{RNH_2} + 2H_2O$$

$$* \quad \underset{\text{Nitroalkane}}{RNO_2} \xrightarrow[LiAlH_4]{3H_2/Ni\text{ or }Pt;} \underset{1^\circ\text{ amine}}{RNH_2} + 2H_2O$$

* Nitroalkanes can be reduced in neutral sol^n using Zn-dust in aq. ammonium chloride into N-alkylhydroxylamine.



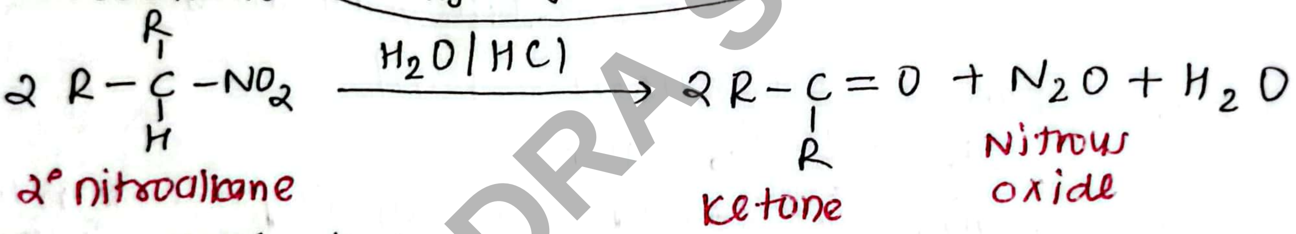
$$R-\overset{+}{N}{\overset{=O}{\underset{-O^-}{}}} + 4[H] \xrightarrow{Zn/NH_4Cl\ (aq.)} R-N{\overset{-H}{\underset{-OH}{}}} + H_2O$$

② Hydrolysis.

ⓐ 1° nitroalkane

$$\underset{(1^\circ\text{ nitroalkane})}{RCH_2NO_2} + H_2O \xrightarrow[\Delta]{aq.HCl\text{ or }85\%\ H_2SO_4} \underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Hydroxylamine.}}{NH_2OH}$$

ⓑ 2° nitroalkane hydrolysed to



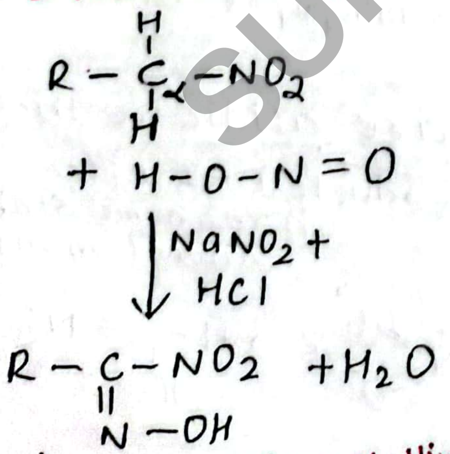
$$2\ \underset{2^\circ\text{ nitroalkane}}{R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}-NO_2} \xrightarrow{H_2O/HCl} 2\ \underset{\text{Ketone}}{R-\underset{\underset{R}{|}}{C}=O} + \underset{\text{Nitrous oxide}}{N_2O} + H_2O$$

ⓒ 3° → no hydrolysis.

③ Rxn with nitrous acid. (Distinguish 1°, 2°, 3° nitroalkanes as Hoffmann's method)

HNO_2

ⓐ 1° Nitroalkanes



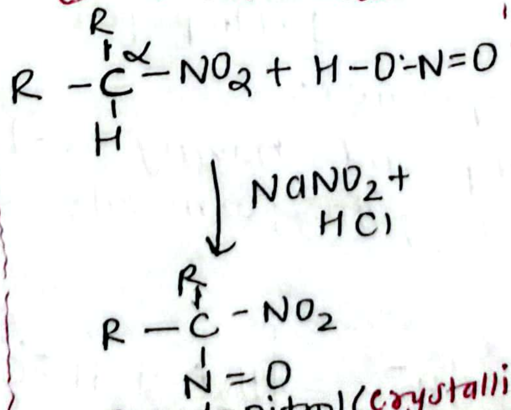
$$R-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{}_{\alpha}-NO_2 + H-O-N=O \xrightarrow{NaNO_2 + HCl} R-\underset{\underset{N-OH}{||}}{C}-NO_2 + H_2O$$

Nitrolic acid (crystalline compound)

↓

Soluble in aq. NaOH to give red sol^n

ⓑ 2° Nitroalkanes



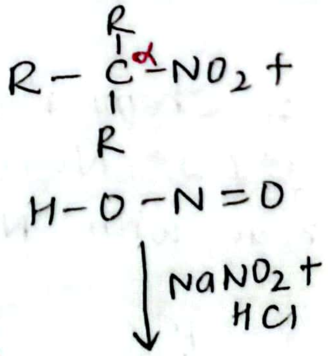
$$R-\overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}}{}^{\alpha}-NO_2 + H-O-N=O \xrightarrow{NaNO_2 + HCl} R-\overset{\overset{R}{|}}{\underset{\underset{N=O}{|}}{C}}-NO_2$$

Pseudonitrol (crystalline compound)

↓

Soluble in aq. NaOH to give blue sol^n

ⓒ 3° nitroalkanes

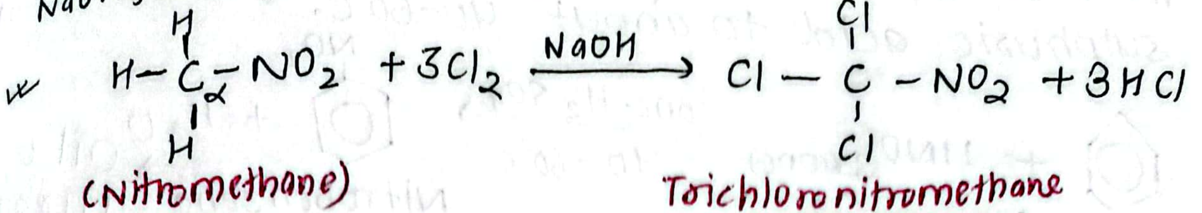


$$R-\overset{\overset{R}{|}}{\underset{\underset{R}{|}}{C}}{}^{\alpha}-NO_2 + H-O-N=O \xrightarrow{NaNO_2 + HCl} \text{No rxn}$$

No rxn (due to absence of α-Hydrogen atom)

1. Halogenation:-

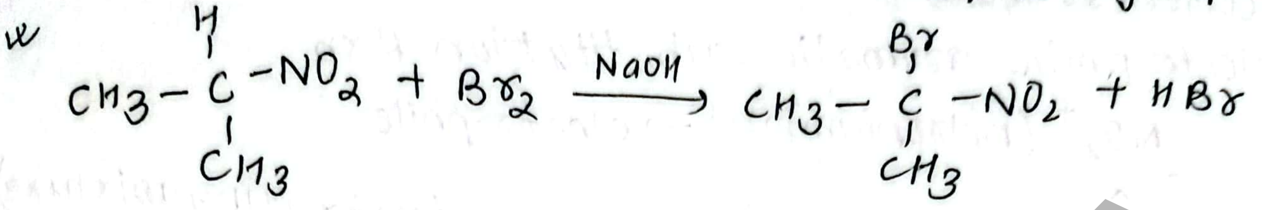
→ 1° and 2° nitroalkanes when treated with Cl_2 or Br_2 in presence of NaOH, undergo α-halogenation.



$$H-\overset{H}{\underset{H}{C_\alpha}}-NO_2 + 3Cl_2 \xrightarrow{NaOH} Cl-\overset{Cl}{\underset{Cl}{C}}-NO_2 + 3HCl$$

(Nitromethane)

Trichloronitromethane
(Chloropicrin)
↳ tear gas/insecticide.



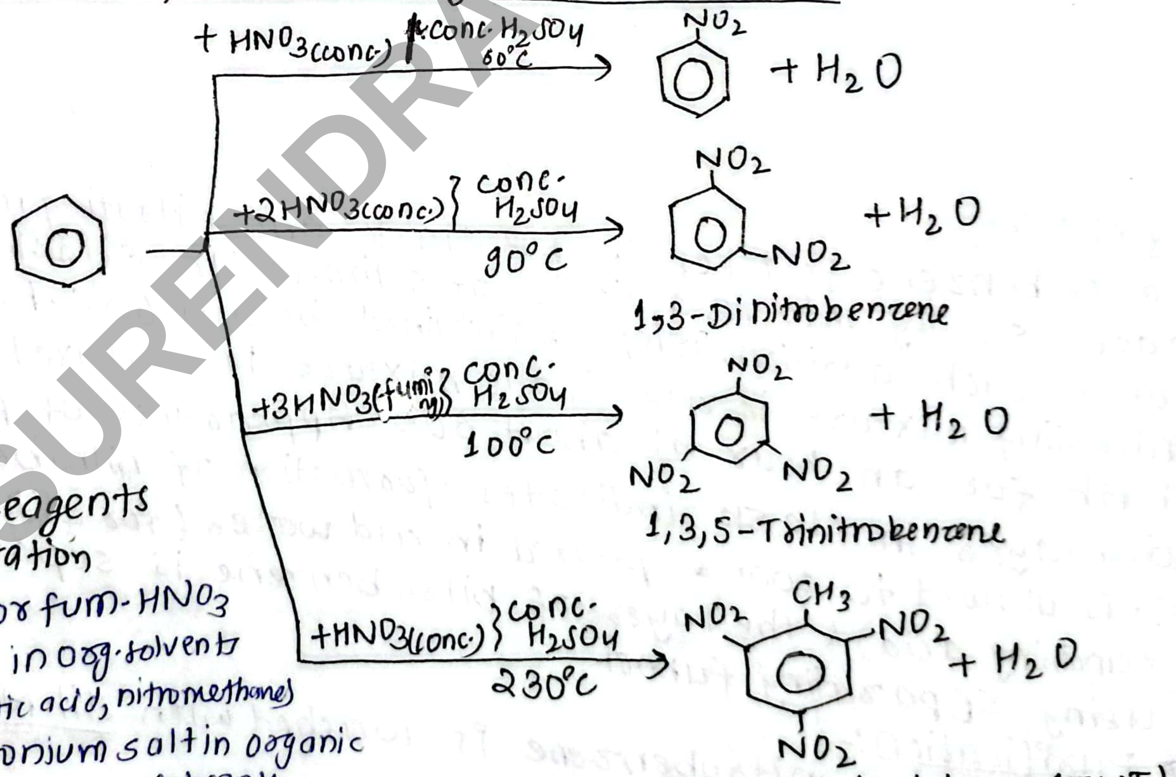
$$CH_3-\overset{H}{\underset{CH_3}{C}}-NO_2 + Br_2 \xrightarrow{NaOH} CH_3-\overset{Br}{\underset{CH_3}{C}}-NO_2 + HBr$$

Aromatic Nitro compounds:- → denser than water

Nitrobenzene

MOP

By nitration of aromatic hydrocarbons (arenes)



1,3-Dinitrobenzene

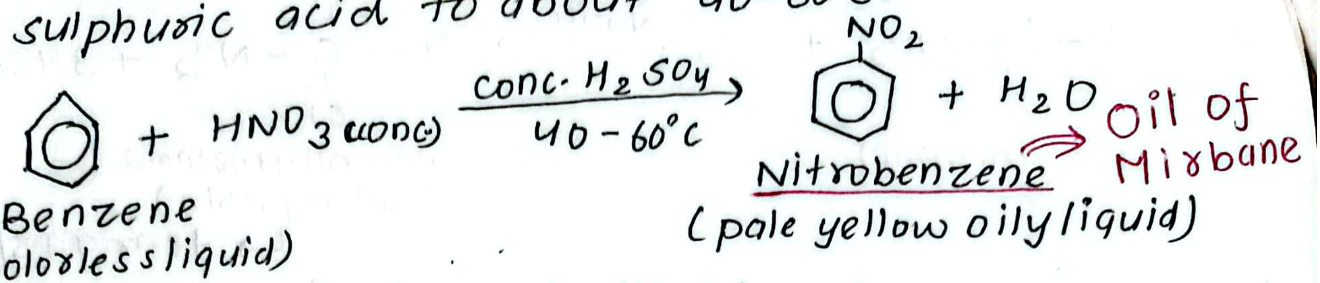
1,3,5-Trinitrobenzene

2,4,6-Trinitrotoluene (TNT)
(Explosive compound)

Other Reagents for nitration
(i) conc. or fum. HNO_3
(ii) HNO_3 in org. solvents (acetic acid, nitromethane)
(iii) Nitronium salt in organic solvents.
(iv) Acyl nitrates
(v) N_2O_5 in CCl_4, N_2O_4

#Laboratory preparation of Nitrobenzene :-

Theory: Nitrobenzene is prepared by refluxing benzene with a mixture of concentrated nitric acid and concentrated sulphuric acid to about 40-60°C.



→ electrophilic aromatic substitution Rxn

NO_2^+ (nitronium ion) → electrophile

↑ conc. HNO_3 & conc. H_2SO_4 (nitrating mixture)
60ml 60ml

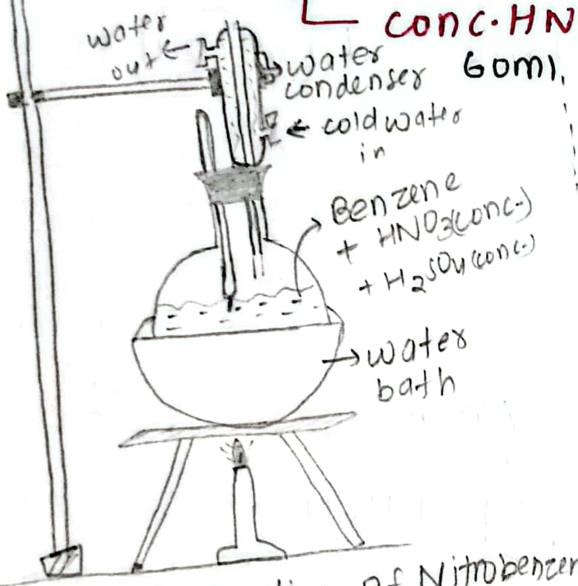


Fig: Lab prepration of Nitrobenzene (reflux)

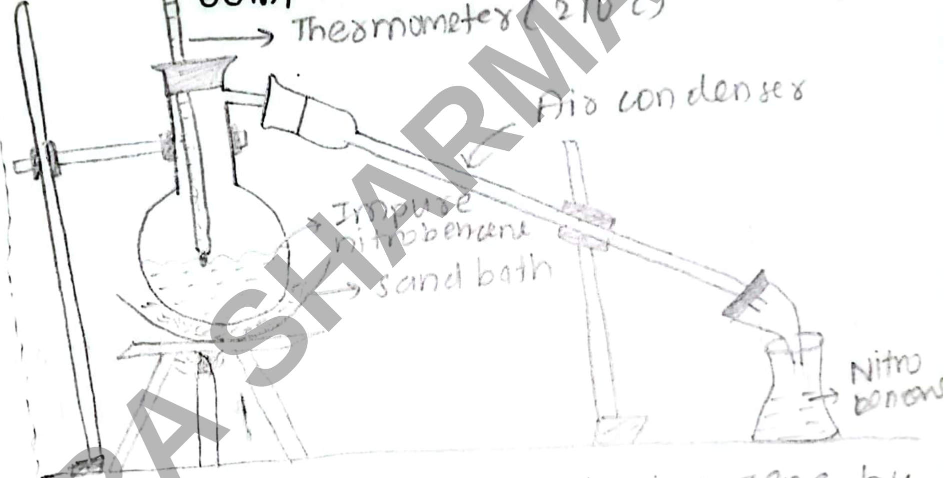


Fig: Purification of Nitrobenzene by Distillation.

→ **Procedure:-**

50ml of benzene is taken in RB flask and nitrating mixture is added slowly into it, a little at a time, with shaking & cooling after each addition. Temp. maintained below 60°C. After, whole nitrating mixture is added, the mixture is refluxed on water bath for an hour at about 60°C. Appearance of pale yellow oily layer in flask indicates formation of nitrobenzene. It is allowed to cool & poured in cold water (for dilution of remaining acid) & the layer of nitrobenzene is separated using separating funnel.

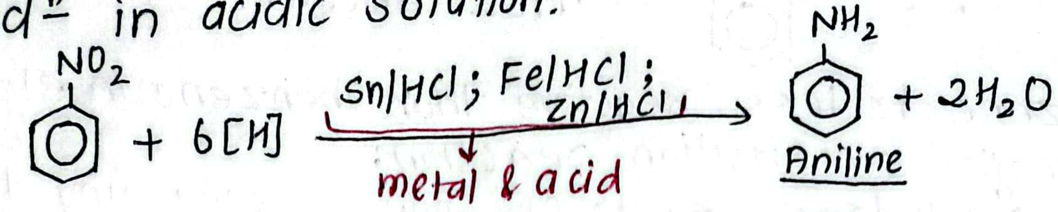
→ **Purification:-**

(i) Thus obtained nitrobenzene is washed with dil. Na_2CO_3 to remove acidic impurities.
(ii) Then washed with water several times to remove salts.
(iii) Dried with anhydrous $CaCl_2$.
(iv) Finally, distilled to about 210-215°C using air condenser to get pure nitrobenzene.

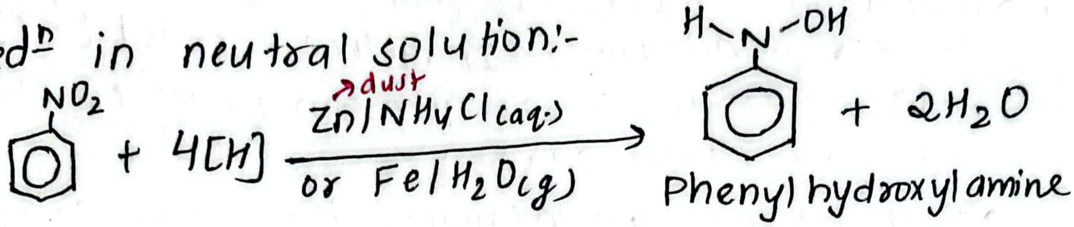
Chemical properties of Nitrobenzene:-

p. Reaction due to $-NO_2$: Reduction

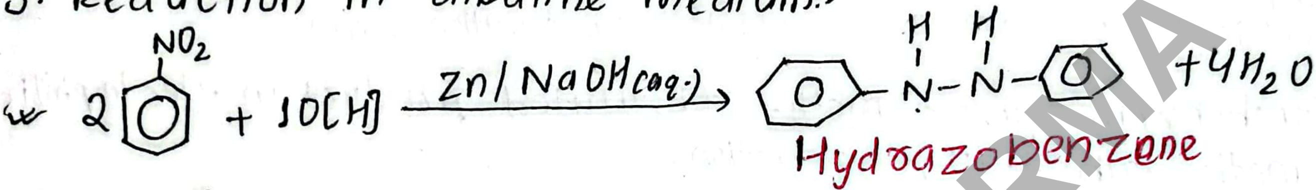
1. Red^n in acidic solution:

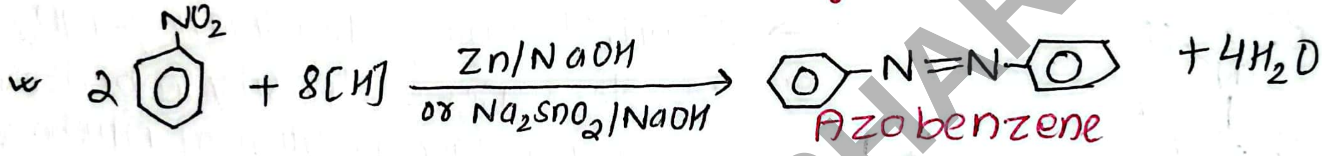


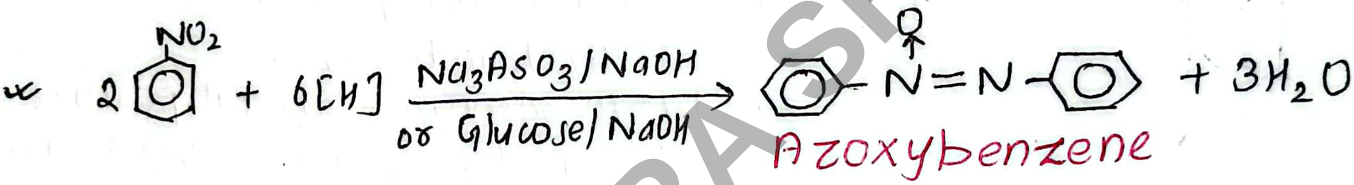
2. Red^n in neutral solution:-



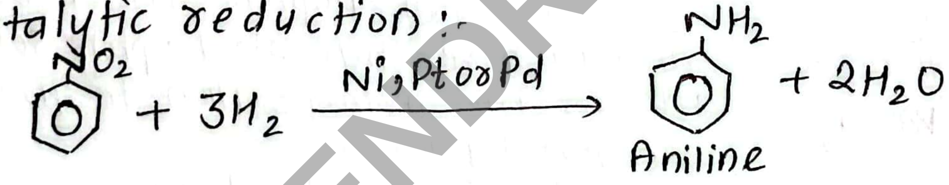
3. Reduction in alkaline medium:-



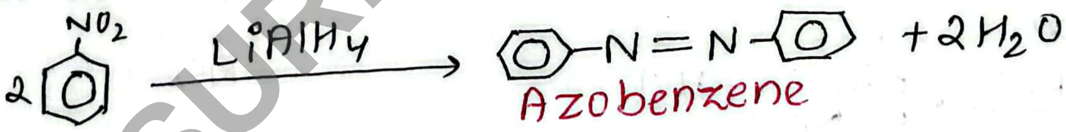




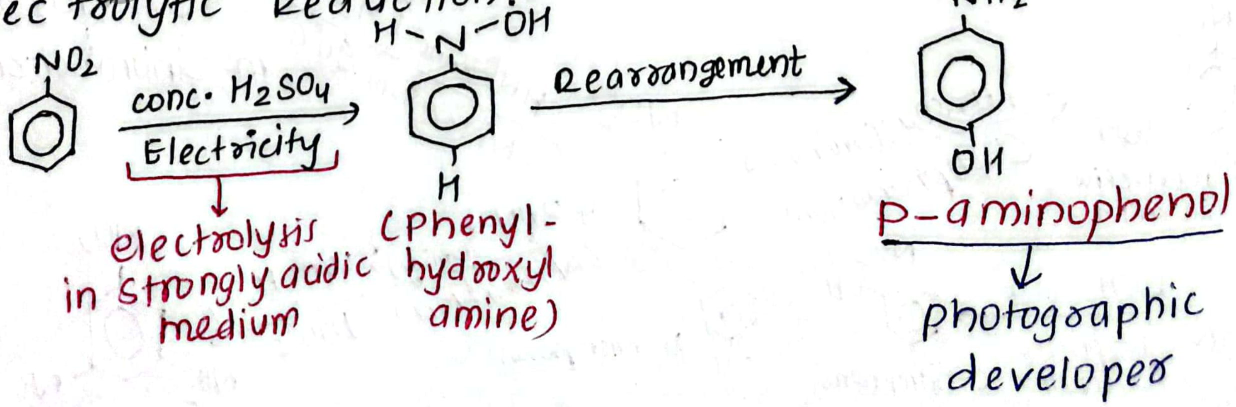
4. Catalytic reduction:



5. Reduction with $LiAlH_4$:



6. Electrolytic Reduction:-



B. Reaction due to benzene ring: Electrophilic aromati substitution reaction.

→ Deactivating group

→ Meta director

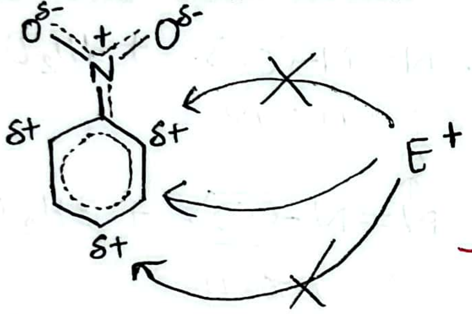
* Nitrobenzene is less reactive than benzene in electrophilic aromatic subsitution reaction:

(i) withdraws electrons from benzene ring due to e⁻ withdrawing Inductive effect (−I) of $-NO_2$ group since nitrogen is more electronegative than carbon

(ii) decreases e⁻ density in benzene ring of nitrobenzene as compared to that of benzene.

(iii) deactivating group (makes benzene ring less reactive than benzene in electrophilic aromatic substitution rxn.)

* Nitrobenzene gives meta- substituted product in electrophilic aromatic substitution reaction.



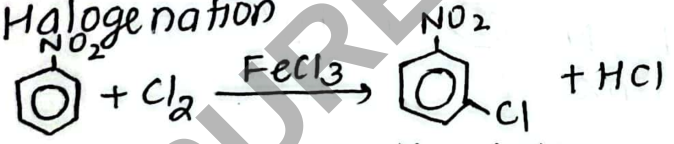
→ e⁻ withdrawing deactivating $-NO_2$ group decreases e⁻ density in benzene ring making each position of nitrobenzen less reactive than benzene.

→ But, due to resonance, partial positive charge (δ+) is developed in ortho- & para- positions, so electrophilic attack becomes difficult here. Thus, electrophile selectively attacks the meta position to give meta substituted products.

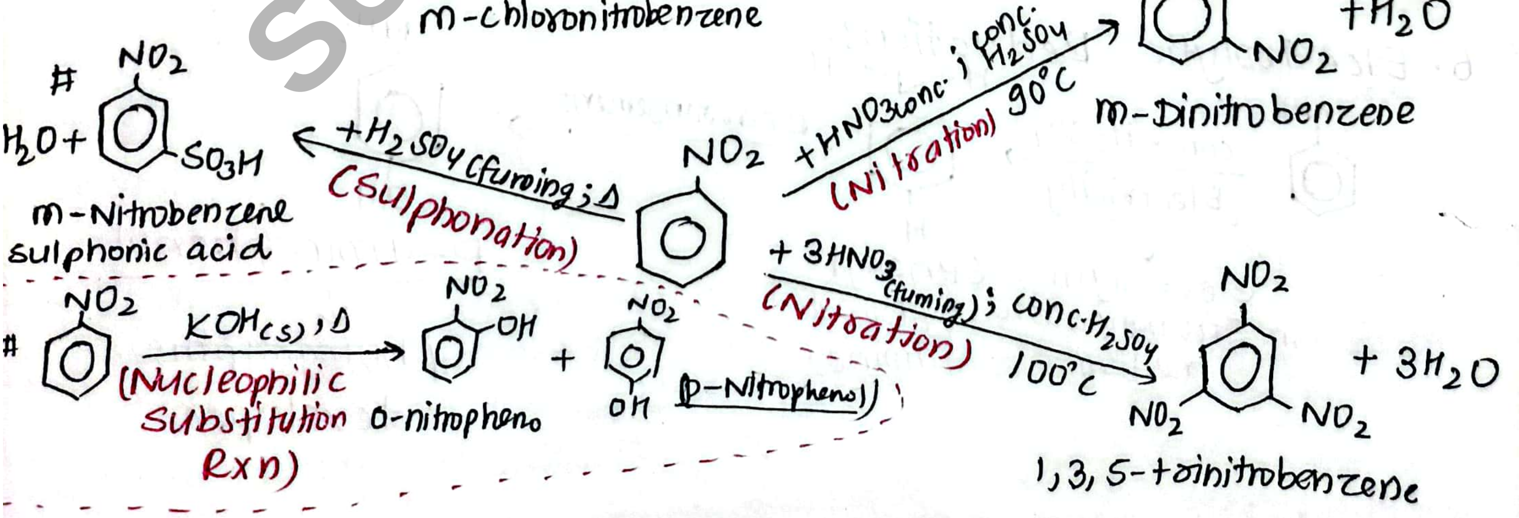
→ So, $-NO_2$ is meta director.

→ Nitrobenzene doesn't give Friedel-Crafts reaction, due to strongly deactivating effect of $-NO_2$.

1. Halogenation



m-chloronitrobenzene



m-Nitrobenzene sulphonic acid

m-Dinitrobenzene

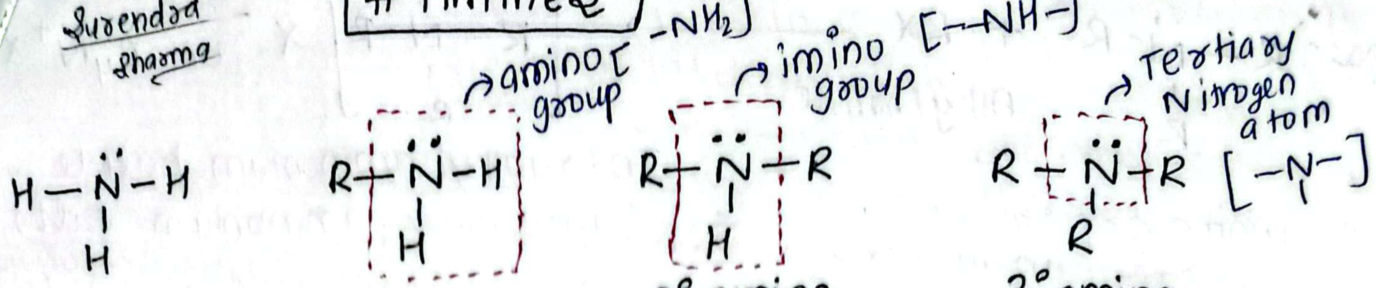
1, 3, 5-trinitrobenzene

o-nitropheno

(p-Nitrophenol)

Surendra Sharma

Amines



Ammonia 1° amine 2° amine 3° amine

where, R = Alkyl or Aryl group

Basic nature - Reacts with acid to form ammonium salts-

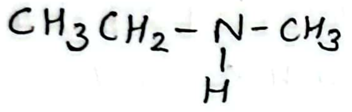
Discovery: By Wurtz by boiling alkyl isocyanates with alkali.

$$RNCO + 2KOH \xrightarrow{Boil} RNH_2 + K_2CO_3$$

IUPAC : Amino- .... / ....-amine

If alkyl group is present in Nitrogen as substituent, it is indicated by writing N- before the substituent.

eg:-



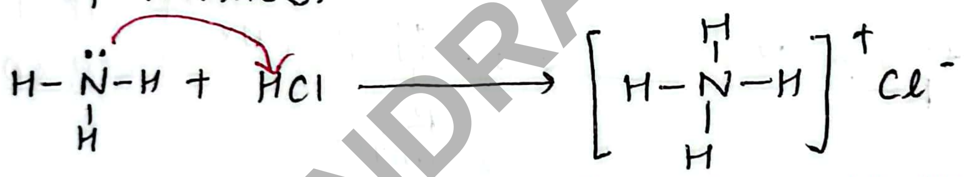
$CH_3CH_2-\underset{H}{\underset{|}{N}}-CH_3$

N-Methylaminoethane

$CH_3-\underset{CH_3}{\underset{|}{N}}-CH_3$

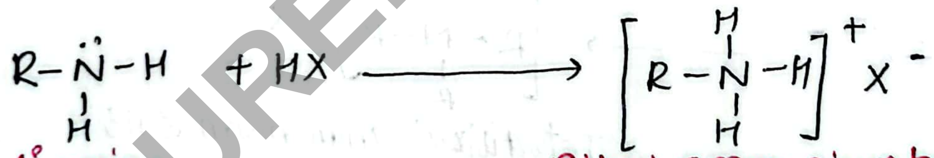
N,N-Dimethylaminomethane

Salts of Amines:



$$H-\underset{H}{\underset{|}{\ddot{N}}}-H + HCl \longrightarrow \left[H-\underset{H}{\overset{H}{N}}-H\right]^+ Cl^-$$

Ammonium chloride

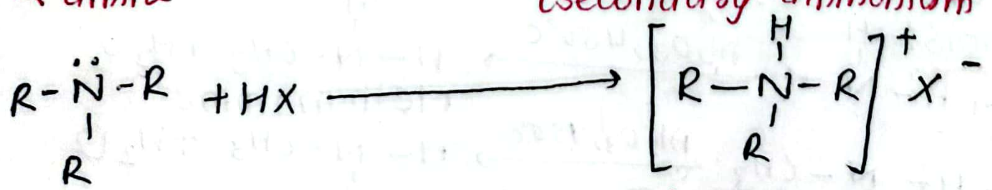


$$R-\underset{H}{\underset{|}{\ddot{N}}}-H + HX \longrightarrow \left[R-\underset{H}{\overset{H}{N}}-H\right]^+ X^-$$

1° amine Alkyl ammonium halide

$$R-\underset{H}{\underset{|}{\ddot{N}}}-R + HX \longrightarrow \left[R-\underset{H}{\overset{H}{N}}-R\right]^+ X^-$$

2° amine Dialkyl ammonium halide (Secondary ammonium salt)



$$R-\underset{R}{\underset{|}{\ddot{N}}}-R + HX \longrightarrow \left[R-\underset{R}{\overset{H}{N}}-R\right]^+ X^-$$

3° amine Trialkyl ammonium halide

① - Amine
↓
- ammonium
And
- aniline
↓
- anilinium
\+
② anion (i.e. halide)
⇓
Salt

$$R-\ddot{N}(R)-R + RX \longrightarrow [R-N(R)(R)-R]^+X^-$$

or, R_4N^+, pre From

Alkyl halide

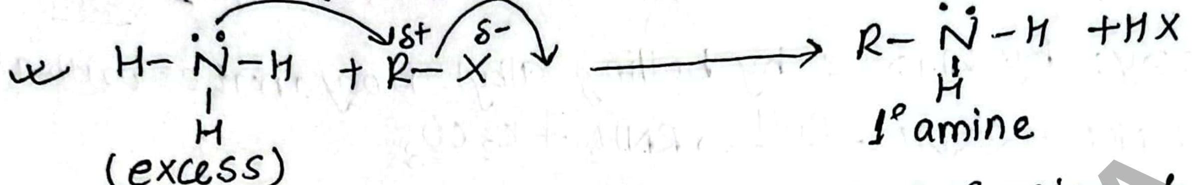
Tetraalkyl ammonium halide

white crystalline & soluble in water ← [(Quaternary ammonium salt)

Methods of preparation:-

* For mixture of amines:-

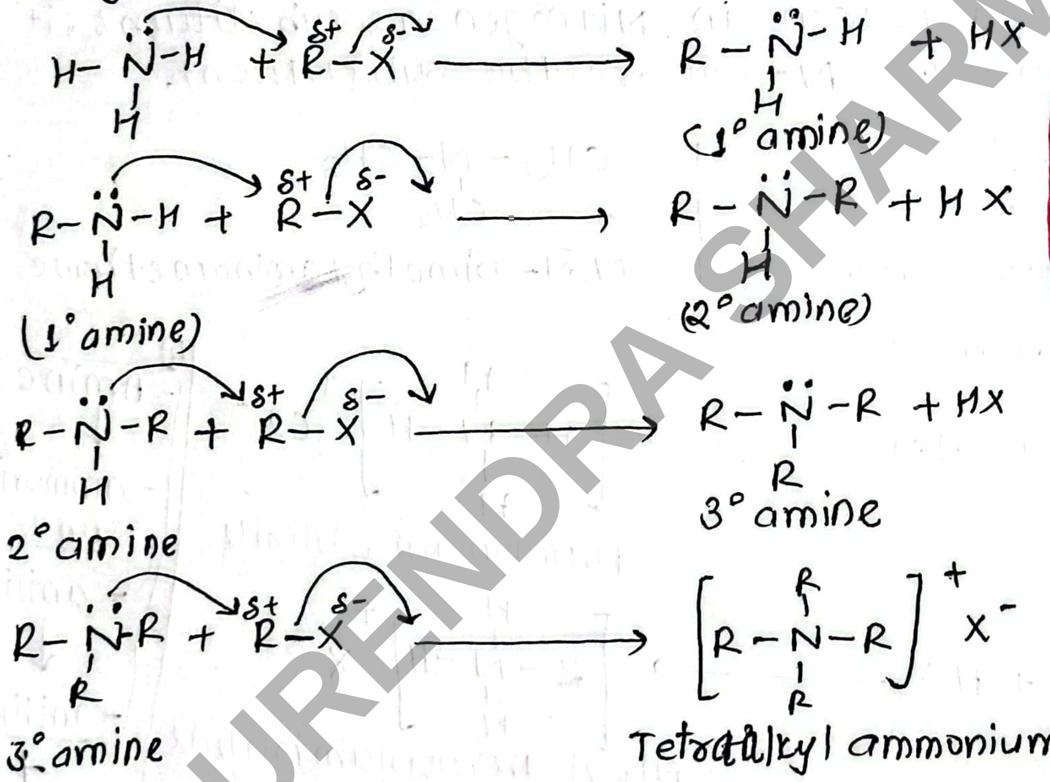
1. From alkyl halides (Hofmann's ammonolysis of alkyl halides):



$$H-\ddot{N}(H)-H + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow R-\ddot{N}(H)-H + HX$$

(excess) 1° amine

Alkyl halide - excess : mixture of 1°, 2°, 3° amines & 4° ammom salt.



$$H-\ddot{N}(H)-H + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow R-\ddot{N}(H)-H + HX$$

(1° amine)

$$R-\ddot{N}(H)-H + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow R-\ddot{N}(H)-R + HX$$

(1° amine) (2° amine)

$$R-\ddot{N}(H)-R + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow R-\ddot{N}(R)-R + HX$$

2° amine 3° amine

$$R-\ddot{N}(R)-R + \overset{\delta+}{R}-\overset{\delta-}{X} \longrightarrow [R-N(R)(R)-R]^+X^-$$

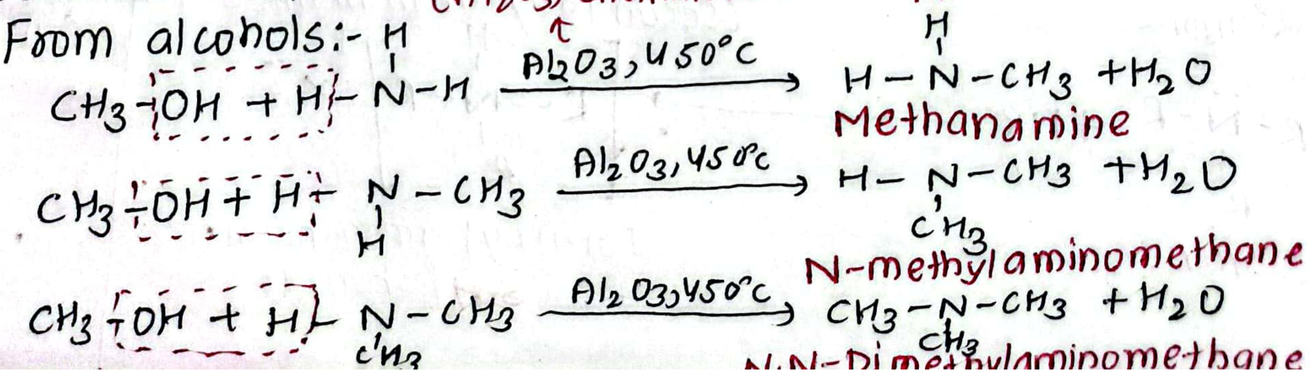
3° amine Tetraalkyl ammonium salt.

NH_3, 1°, 2° amine acts as nucleophile in this nucleophilic substitution Rxn.

This method is not suitable for prepn of arylamines since aryl halides are less reactive towards nucleophilic substitutn rxn.

2. From alcohols:-

(Al_2O_3) alumina or copper chromite



$$CH_3-OH + H-N(H)-H \xrightarrow{Al_2O_3,\ 450°C} H-N(H)-CH_3 + H_2O$$

Methanamine

$$CH_3-OH + H-N(H)-CH_3 \xrightarrow{Al_2O_3,\ 450°C} H-N(CH_3)-CH_3 + H_2O$$

N-methylaminomethane

$$CH_3-OH + H-N(CH_3)-CH_3 \xrightarrow{Al_2O_3,\ 450°C} CH_3-N(CH_3)-CH_3 + H_2O$$

N,N-Dimethylaminomethane

Preparation of Primary amines:-

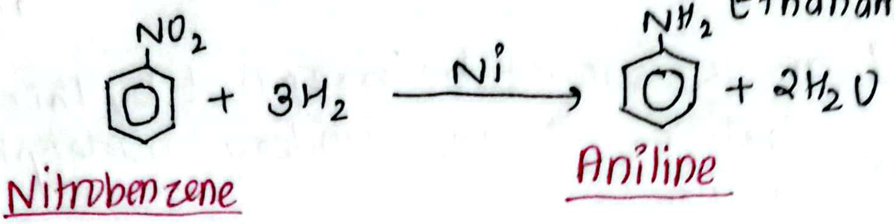
From nitro compounds.

$$R-\boxed{NO_2} \xrightarrow[\text{or } Fe/HCl]{H_2/Ni \text{ or } Pt \text{ or } Sn/HCl} R-\boxed{NH_2}$$

1° amine

eg: $CH_3CH_2NO_2 + 6[H] \xrightarrow{Sn/HCl} CH_3CH_2-NH_2 + 2H_2O$

Ethanamine



Nitrobenzene

Aniline

2. From nitriles

Mendius Rxn.

$$R\boxed{CN} \xrightarrow[Na/C_2H_5OH]{H_2/Ni,\ LiAlH_4} R-\boxed{CH_2NH_2}$$

1° amine

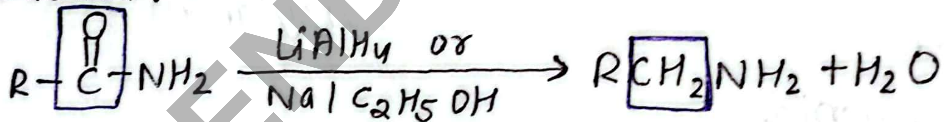
- This method is useful in increasing carbon chain length by one carbon atom.

eg: $CH_3CH_2OH \xrightarrow{PBr_3} CH_3CH_2Br \xrightarrow{alc.KCN} CH_3CH_2CN \xrightarrow{H_2/Ni} CH_3CH_2CH_2N$

Ethanol, Bromoethane, Propane nitrile, 1-Aminopropane

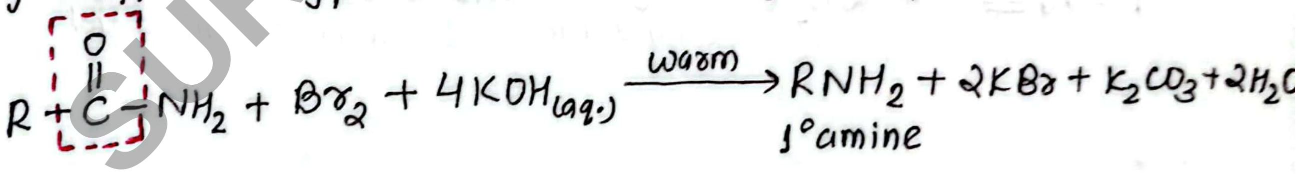
3. From amides:

ⓐ By reduction:



$$R-\boxed{\overset{O}{\overset{\|}{C}}}-NH_2 \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} R\boxed{CH_2}NH_2 + H_2O$$

ⓑ By Hoffmann hypobromite rearrangement/ Hofmann degradation

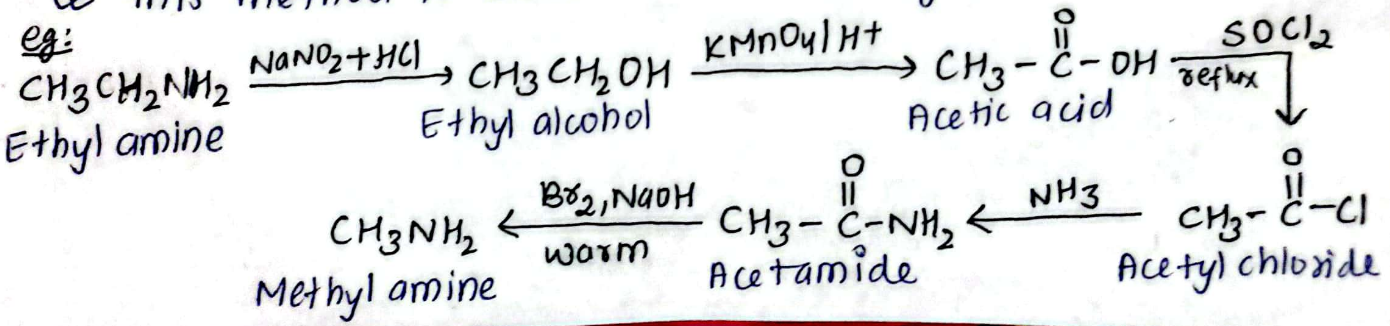


$$R-\boxed{\overset{O}{\overset{\|}{C}}}-NH_2 + Br_2 + 4KOH_{(aq.)} \xrightarrow{warm} RNH_2 + 2KBr + K_2CO_3 + 2H_2O$$

1° amine

- Decarbonylation Rxn.
- This method is utilized in descending the series by 1-C.

eg:

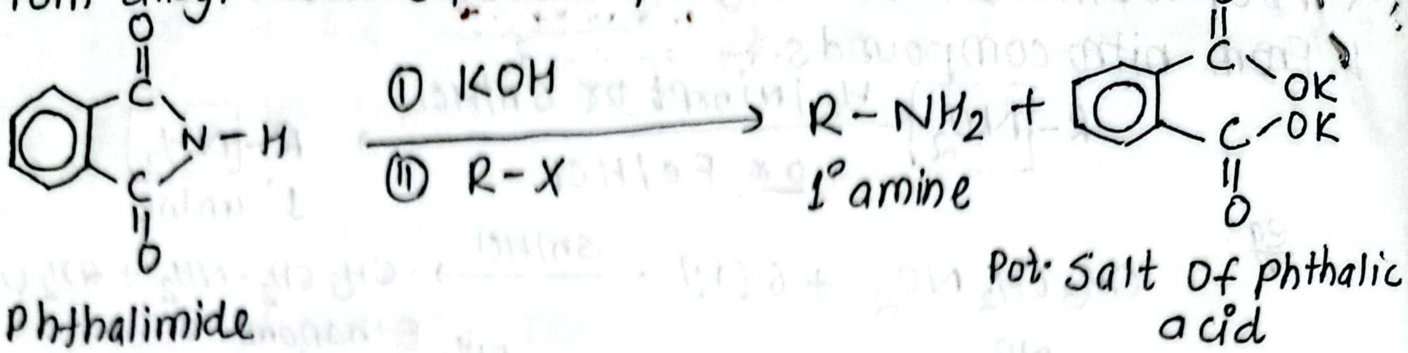


$$CH_3CH_2NH_2 \xrightarrow{NaNO_2+HCl} CH_3CH_2OH \xrightarrow{KMnO_4/H^+} CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[reflux]{SOCl_2} CH_3-\overset{O}{\overset{\|}{C}}-Cl$$

$$CH_3NH_2 \xleftarrow[warm]{Br_2,NaOH} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xleftarrow{NH_3} CH_3-\overset{O}{\overset{\|}{C}}-Cl$$

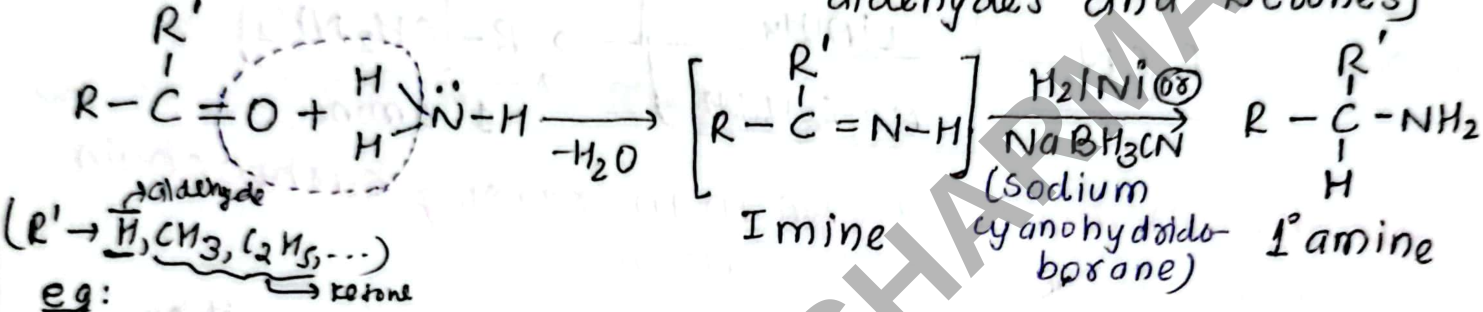
Ethyl amine, Ethyl alcohol, Acetic acid, Acetyl chloride, Acetamide, Methyl amine

4. From alkyl halide (Gabriel phthalimide synthesis)



→ Aromatic 1° amine cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution easily.

5. From aldehydes and ketones (Reductive ammination of aldehydes and ketones)



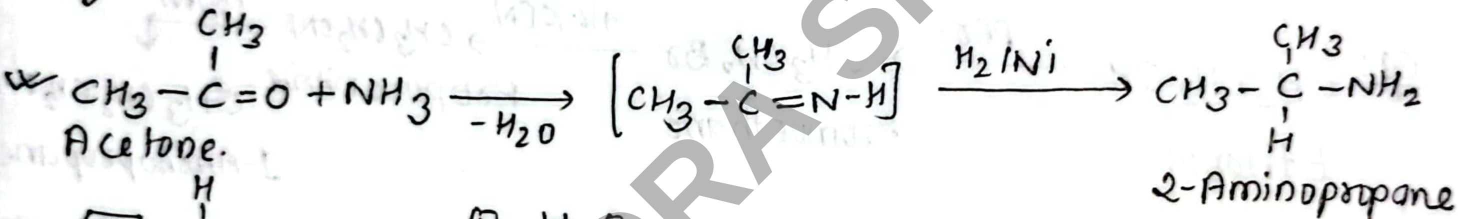
$$R-\overset{\overset{R'}{|}}{C}=O + H_2\ddot{N}-H \xrightarrow[-H_2O]{} \left[R-\overset{\overset{R'}{|}}{C}=N-H\right] \xrightarrow[\substack{NaBH_3CN \\ \text{(Sodium cyanohydrido-borane)}}]{H_2/Ni \text{ (or)}} R-\underset{\underset{H}{|}}{\overset{\overset{R'}{|}}{C}}-NH_2$$

Imine

1° amine

$(R' \rightarrow \underbrace{H}_{\text{aldehyde}}, \underbrace{CH_3, C_2H_5, \ldots}_{\text{ketone}})$

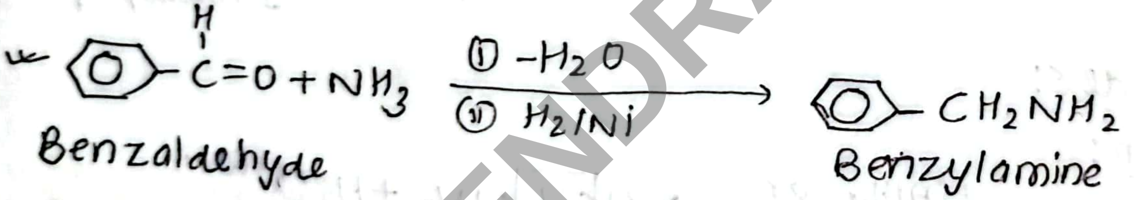
eg:



$$CH_3-\overset{\overset{CH_3}{|}}{C}=O + NH_3 \xrightarrow[-H_2O]{} \left[CH_3-\overset{\overset{CH_3}{|}}{C}=N-H\right] \xrightarrow{H_2/Ni} CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH_2$$

Acetone.

2-Aminopropane



Benzaldehyde

Benzylamine

6. From isocyanides

$$R-N\equiv C + 2H_2O \xrightarrow{H_2O/H^+} R-NH_2 + HCOOH$$

dilute acids.

1° amine

Formic acid