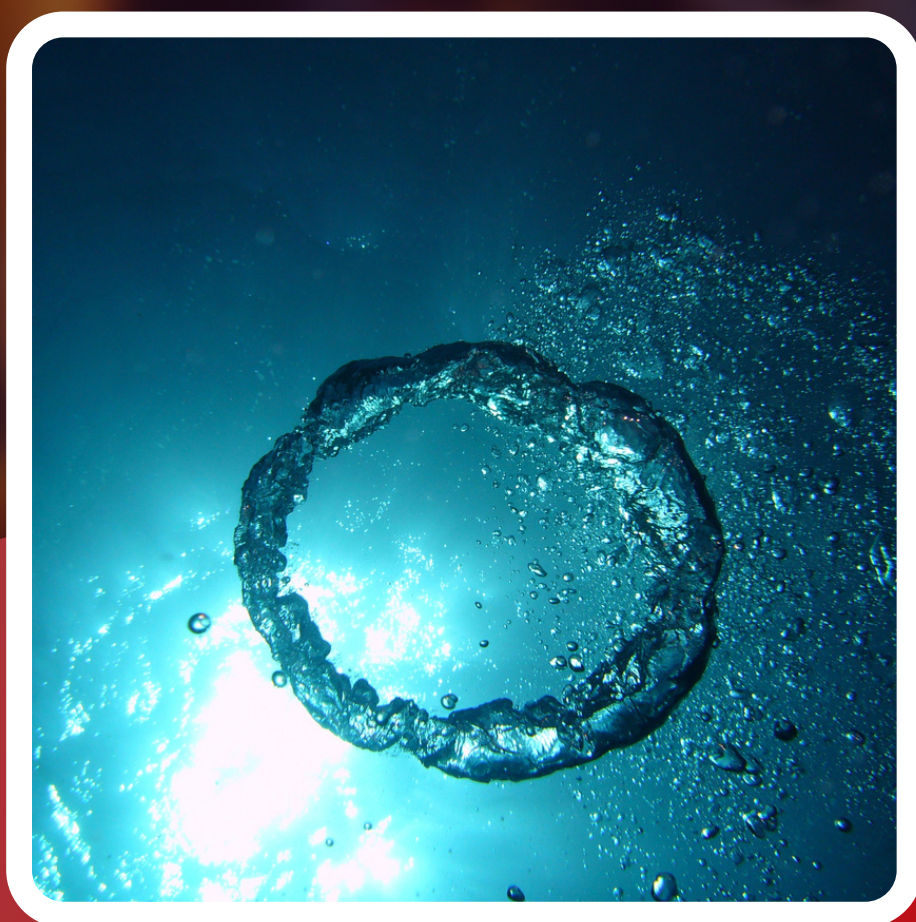


ORGANIC CHEMISTRY

ENTHUSIAST | LEADER | ACHIEVER



STUDY MATERIAL

Oxygen Containing Compounds

ENGLISH MEDIUM

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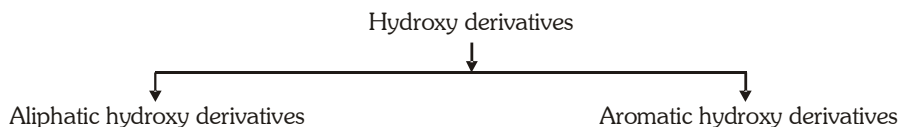
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OXYGEN CONTAINING COMPOUND

1.0 HYDROXY DERIVATIVES



1.1 Aliphatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp^3 'C' (Alcoholic compounds).

1.2 Aromatic Hydroxy Derivatives

Hydroxy derivatives in which —OH is directly attached to sp^2 'C' or benzene ring (Phenolic compounds).

Aliphatic hydroxy derivatives :

(a) Classification according to number of —OH groups :

(i) Monohydric	[one —OH]	→	CH_3CH_2-OH
(ii) Dihydric	[two —OH]	→	$\begin{array}{cc} CH_2 & - & CH_2 \\ & & \\ OH & & OH \end{array}$
(iii) Trihydric	[three —OH]	→	$\begin{array}{ccccc} CH_2 & - & CH & - & CH_2 \\ & & & & \\ OH & & OH & & OH \end{array}$
(iv) Polyhydric	[n —OH]	→	$\begin{array}{ccccccc} CH_2 & - & CH & - & CH & - & CH & - & CH & - & CH_2 \\ & & & & & & & & & & \\ OH & & OH & & OH & & OH & & OH & & OH \end{array}$

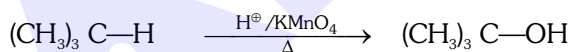
(b) Classification according to nature of carbon :

(i) p or 1° - alcohol	→	CH_3CH_2-OH
(ii) s or 2° - alcohol	→	$(CH_3)_2CH-OH$
(iii) t or 3° - alcohol	→	$(CH_3)_3C-OH$

2.0 MONOHYDRIC ALCOHOL

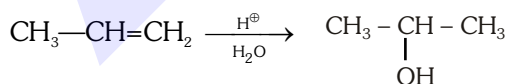
2.1 General Methods of Preparation

(i) From alkanes (By oxidation):

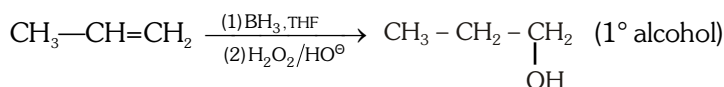


(ii) From alkenes :

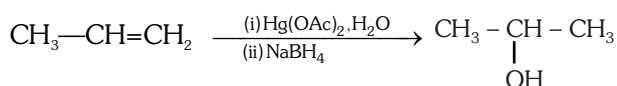
(a) By hydration :

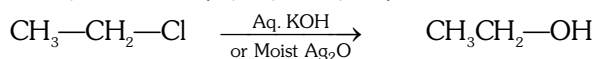
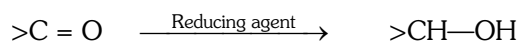


(b) By hydroboration oxidation :

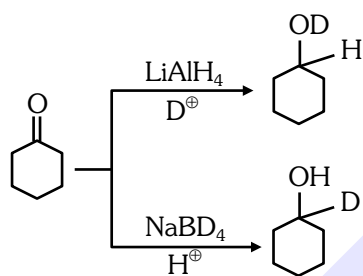
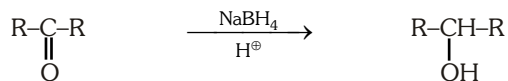
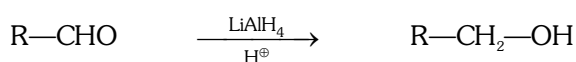


(c) By oxymercuration demercuration :

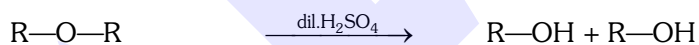
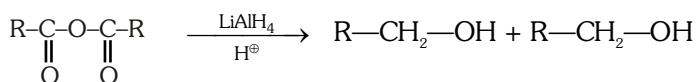
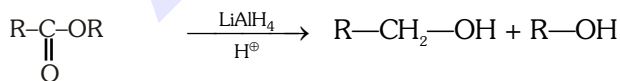
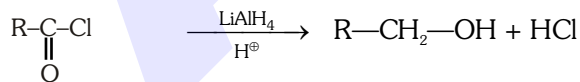
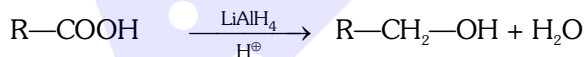
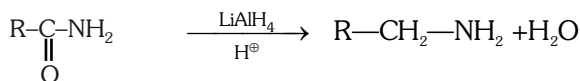


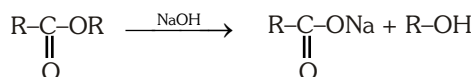
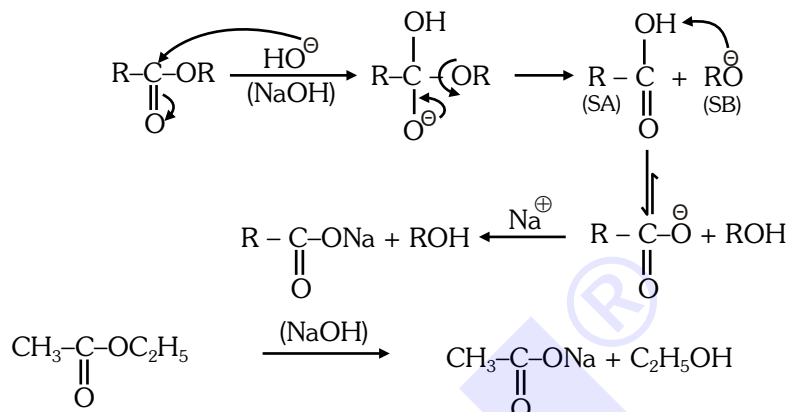
(iii) From alkyl halides (By hydrolysis) :

(iv) From carbonyl compounds (By reduction) :

GOLDEN KEY POINTS

Reducing agents may be,

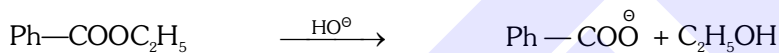
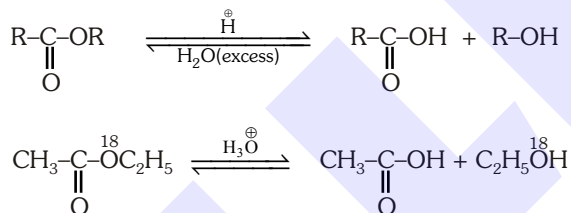
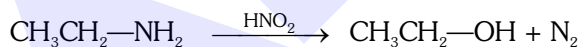
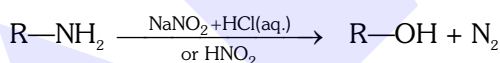
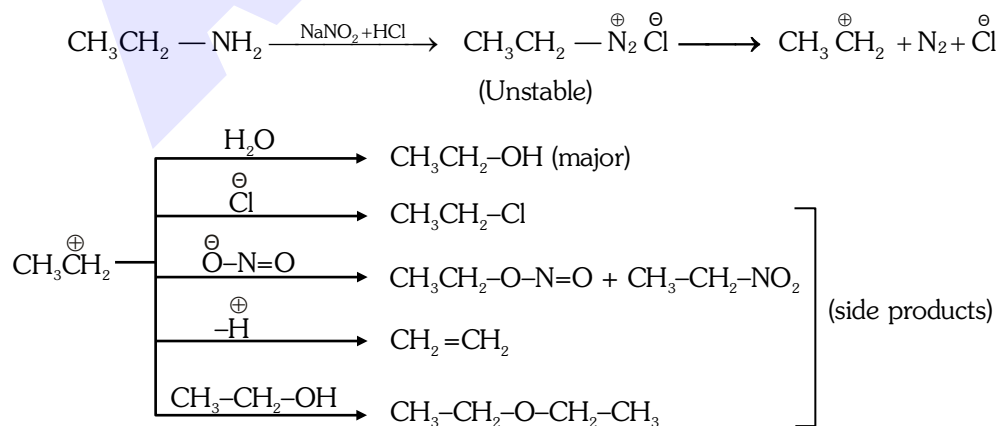


Crotonaldehyde

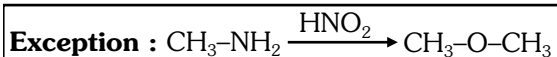
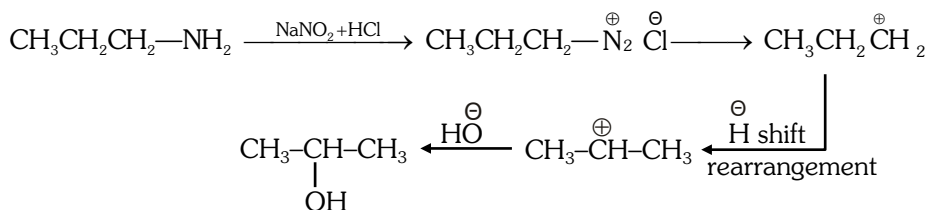
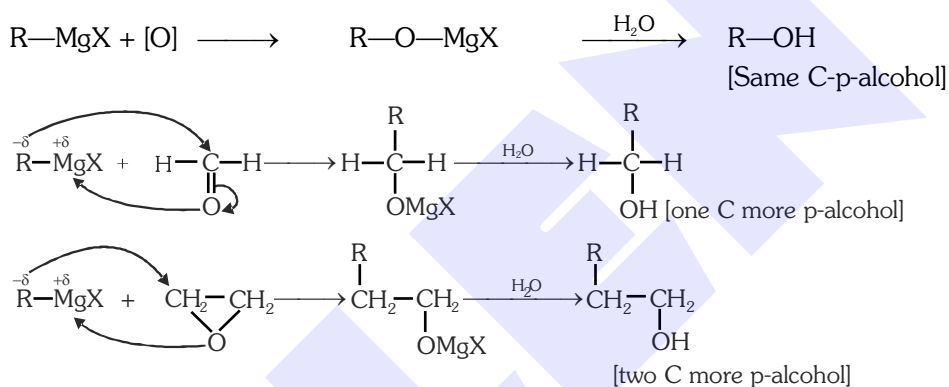
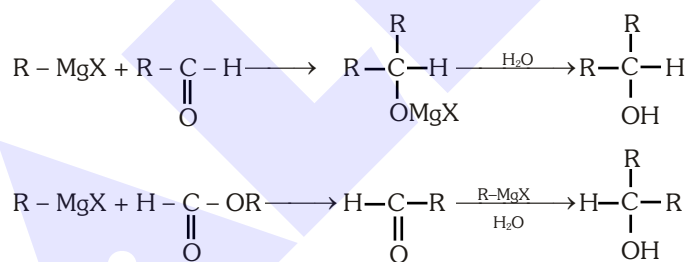
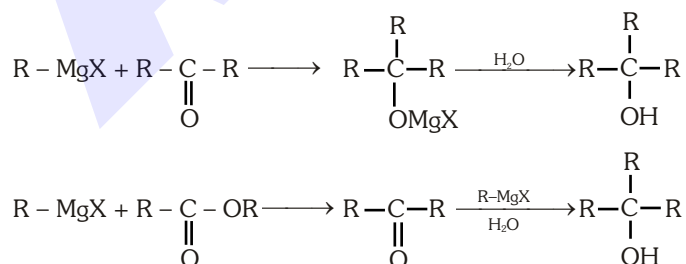
(v) From ethers :

(vi) From acid and derivatives (By reduction) :

Note : Amide on reduction gives amine not alcohol.


(vii) From esters (By hydrolysis) :**(a) By alkaline hydrolysis :****Mechanism :**

Hydrolysis is Nucleophilic substitution reaction (NSR) and Order of reaction is 2. Alkaline hydrolysis is also called as saponification

**(b) By acidic hydrolysis :****(viii) From p-amines :****Mechanism :**

Intermediate is carbocation so rearrangement may be possible.

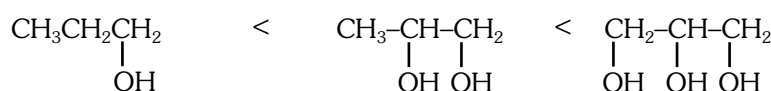
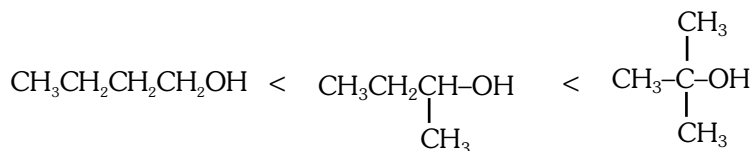
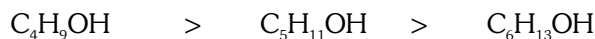
Illustrations
Illustration 1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{—NH}_2 \xrightarrow{\text{NaNO}_2 + \text{HCl}} ?$
Solution.
Mechanism :

(ix) From Grignard reagent :
(a) p-alcohol :

(b) s-alcohol :

(c) t-alcohol :

Physical properties :

- (i) C_1 to C_{11} are colourless liquids and higher alcohols are solids.
- (ii) Density of monohydric alcohol is less than H_2O .
- (iii) Density \propto mol. wt. (for monohydric alcohol).

- (iv) **Solubility** : C_1 to C_3 and t-butyl alcohol is completely soluble in H_2O due to H-bonding.

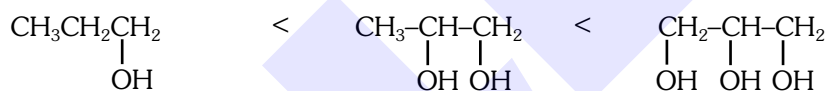
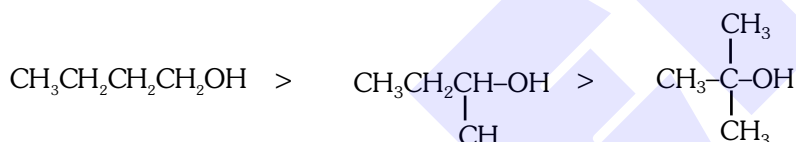
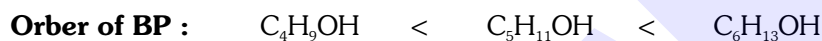
$$\text{solubility} \propto \frac{\text{No. of side chains}}{\text{molecular weight}}$$

Order of solubility :



[Number of OH increases, H-bonding increases]

- (v) **Boiling points** : $BP \propto \frac{\text{molecular weight}}{\text{No. of side chains}}$



[Number of OH increases, H-bonding increases]

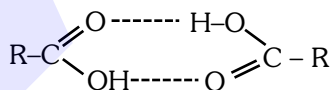
Illustrations

Illustration 2. Boiling point of alcohol is more than corresponding ether. Why ?

Solution. H-bonding in alcohol.

Illustration 3. Boiling point of alcohol is less than corresponding carboxylic acid. Why ?

Solution. Dimer formation in carboxylic acid.

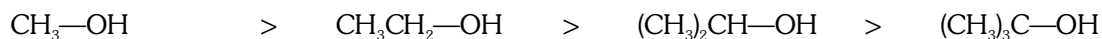


2.3 Chemical Properties

Monohydric alcohol shows following reactions

- (A) Reaction involving cleavage of $O \div H$
- (B) Reaction involving cleavage of $C \div OH$
- (C) Reaction involving complete molecule of alcohol

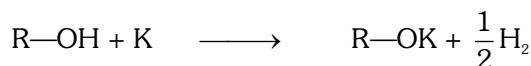
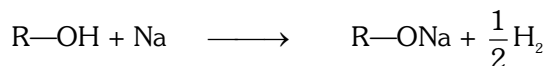
(A) Reaction involving cleavage of $O-H$: Reactivity order (Acidic nature) is



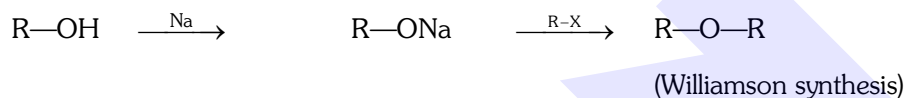
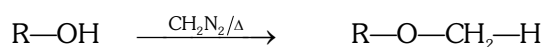
(i) Acidic nature :



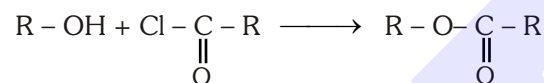
Alcohols are less acidic than H_2O and neutral for litmus paper and give H_2 with active metals (Na, K)



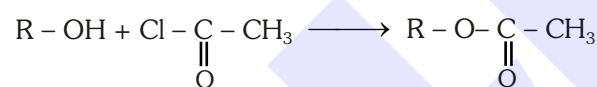
(ii) Alkylation:



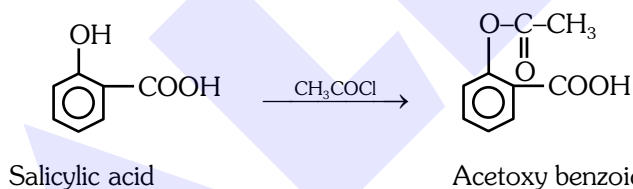
(iii) Acylation :



(Acylation)



(Acetylation)

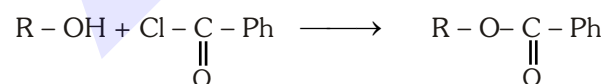


Acetoxy benzoic acid

Acetyl salicylic acid

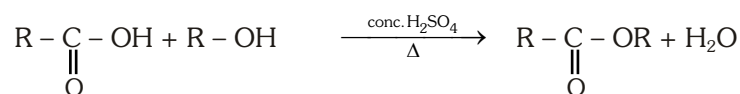
Aspirin [Used as analgesic and antipyretic]

(iv) Benzoylation : (Schotten Baumann's Reaction) :

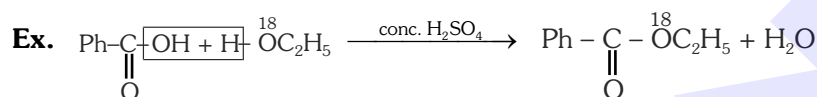
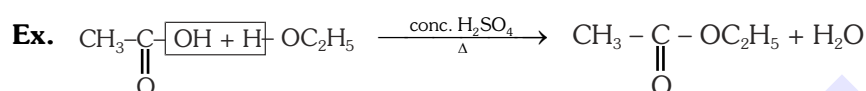
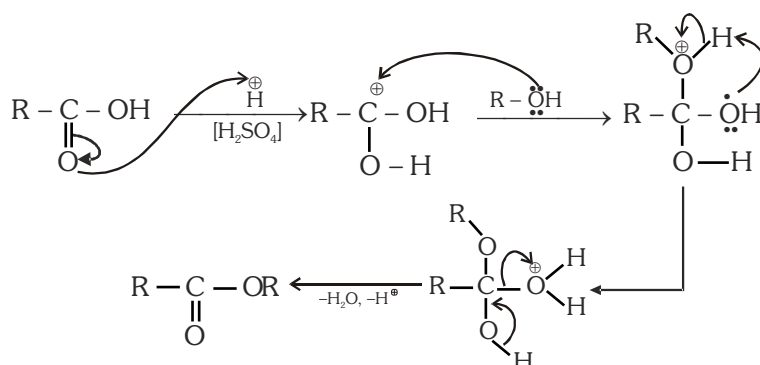


(Benzoylation)

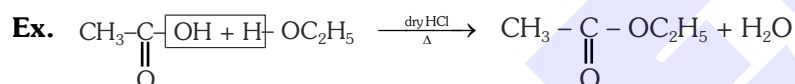
(v) Esterification :



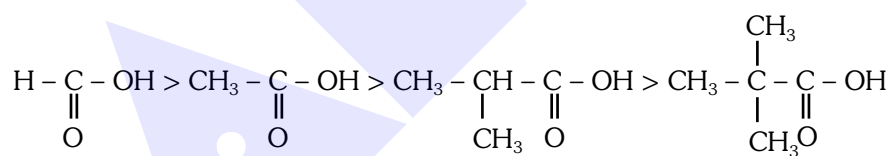
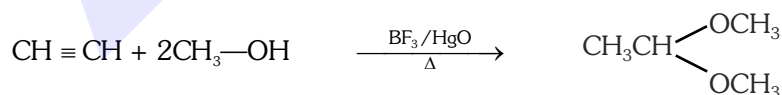
Conc. H_2SO_4 is used as catalyst and dehydrating agent.

Mechanism :

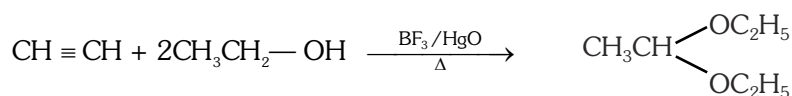
Dry HCl can also be used as dehydrating agent.

**GOLDEN KEY POINTS**

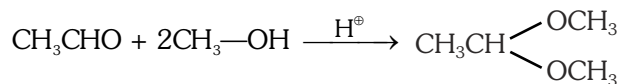
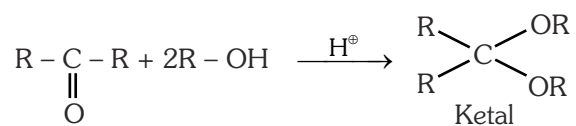
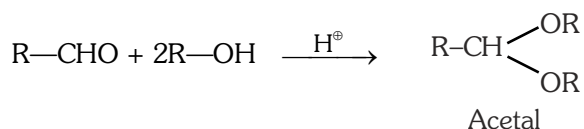
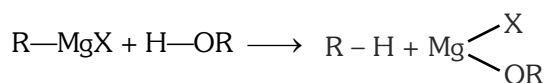
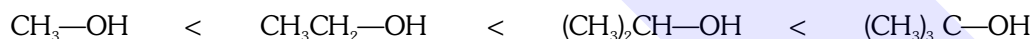
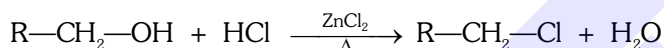
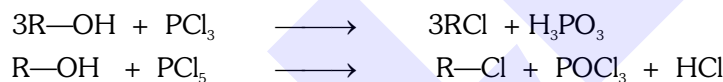
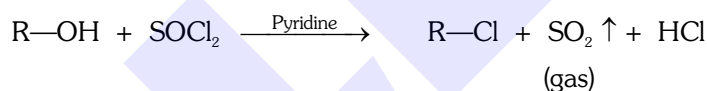
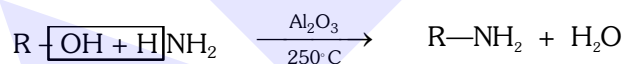
- Reactivity for esterification $\propto \frac{1}{\text{Steric hindrance}}$.
- Reactivity of $R-OH$ [If acid is same] : $CH_3-OH > 1^\circ > 2^\circ > 3^\circ$ alcohol
- Reactivity of $RCOOH$ [If alcohol is same] :

**(vi) Reaction with CHCH :**

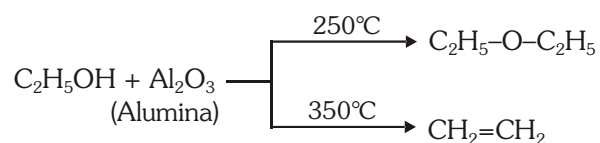
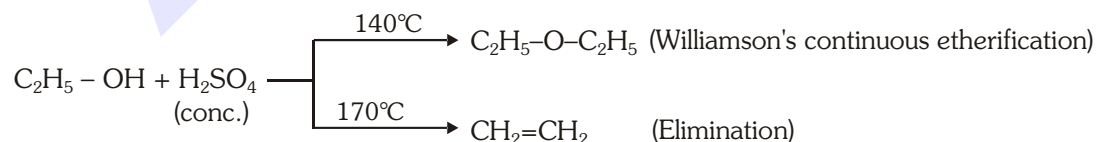
Methylal

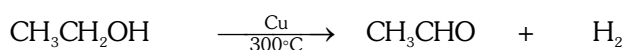


Ethylal

(vii) Reaction with carbonyl compounds :

(viii) Reaction with Grignard reagent :

(B) Reaction involving cleavage of $C-\overset{|}{\text{O}}H$: Reactivity order or basic nature is

(i) Reaction with halogen acid :

 Reactivity order of the acids is $HI > HBr > HCl$
(ii) Reaction with phosphorous halides :

(iii) Reaction with thionyl chloride ($SOCl_2$) :

(iv) Reaction with NH_3 : Alumina (Al_2O_3) is used as dehydrating agent.

(C) Reaction involving complete molecule of alcohol :
(i) Dehydration : Removal of H_2O

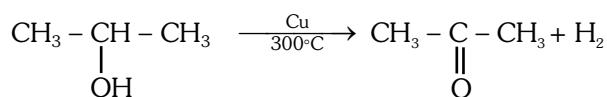
- (a) Intermolecularly removal of H_2O [formation of ether]
- (b) Intramolecularly removal of H_2O [formation of alkene]


 Ease of dehydration follows the order : $3^\circ ROH > 2^\circ ROH > 1^\circ ROH$

(ii) Catalytic Dehydrogenation :

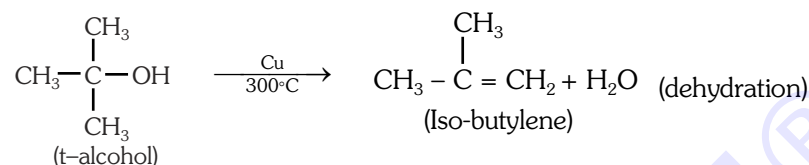
(p- alcohol)

(Acetaldehyde)



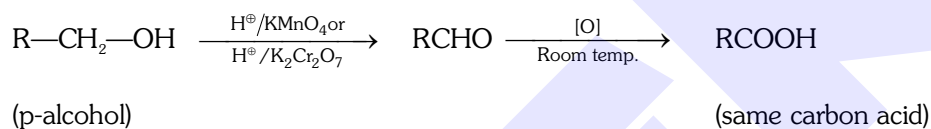
(s- alcohol)

(acetone)



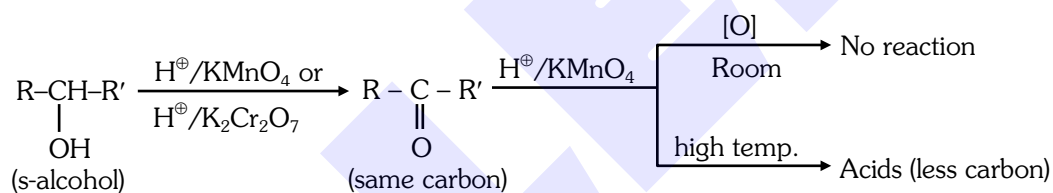
(t-alcohol)

(Iso-butylene)

(iii) Oxidation :

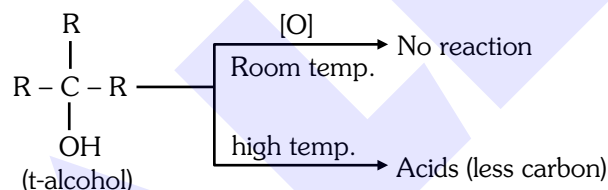
(p-alcohol)

(same carbon acid)

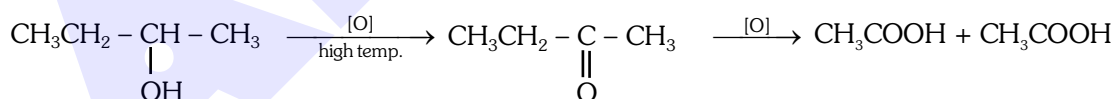


(s-alcohol)

(same carbon)



(t-alcohol)



Carbonyl group goes with smaller alkyl group [Popoff's rule suggested for oxidation of unsymmetrical ketones]

(iv) Distinction between 1°, 2° and 3° alcohols :

(a) Lucas test : A mixture of HCl(conc.) and anhydrous ZnCl_2 is called Lucas reagent.

p-alcohol $\xrightarrow{\text{ZnCl}_2 + \text{HCl}}$ No turbidity at room temp. [On heating within 30 minutes.]

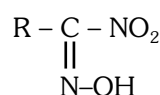
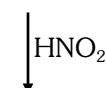
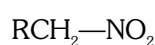
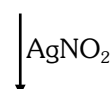
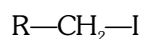
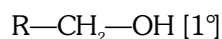
s-alcohol $\xrightarrow{\text{ZnCl}_2 + \text{HCl}}$ Turbidity appears within 5 minutes.

t-alcohol $\xrightarrow{\text{ZnCl}_2 + \text{HCl}}$ Turbidity appears within 2-3 sec.

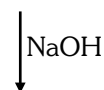
(b) Victor - Meyer test :

 p-alcohol \longrightarrow Red colour

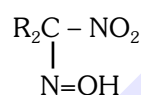
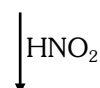
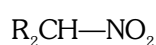
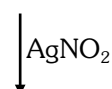
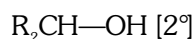
 s-alcohol \longrightarrow Blue colour

 t-alcohol \longrightarrow No colour


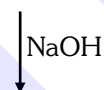
Nitrolic acid (blue)



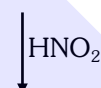
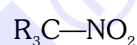
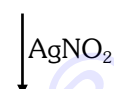
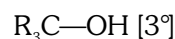
Sodium nitrolate (Red)



Pseudonitrol (blue)

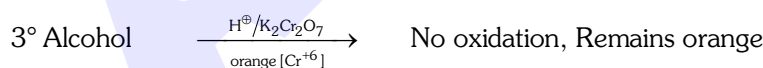
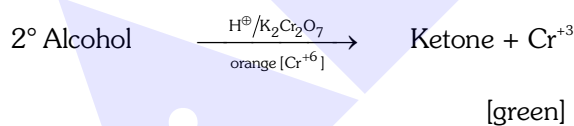
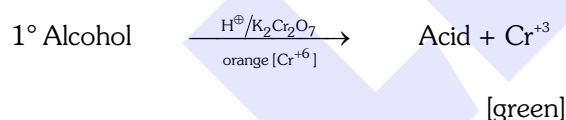


No reaction (Remains blue)

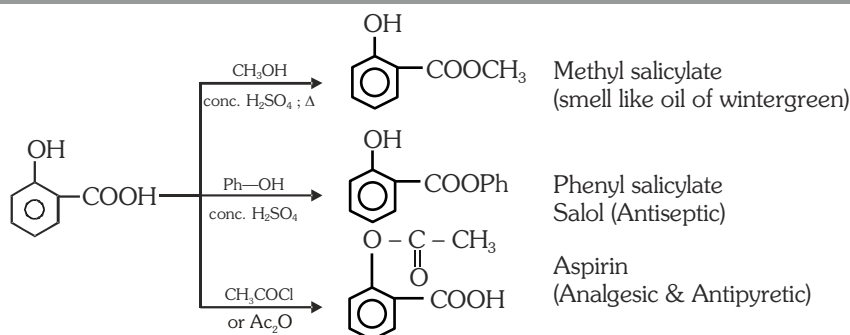


No reaction

Colourless

(C) Dichromate test :

(v) Distinction between CH_3-OH and C_2H_5OH

	CH_3OH	CH_3CH_2OH
B.P.	65°C	78°C
$I_2 + NaOH$	No ppt	Yellow ppt of CHI_3
$Cu/300^\circ C$	Smell of formalin $[HCHO]$	No smell
Salicylic acid	Smell like oil of wintergreen	No smell


BEGINNER'S BOX-1

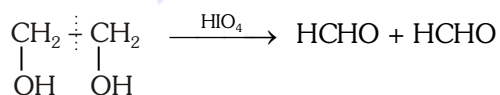
- Which of the following reactions of alkanols does not involve C–O bond breaking
 - (1) $\text{CH}_3\text{CH}_2\text{OH} + \text{SOCl}_2$
 - (2) $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{PBr}_3$
 - (3) $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH}$
 - (4) $\text{ROH} + \text{HX}$
- Which of the following alkanols is most soluble in water
 - (1) 1-Butanol
 - (2) 2-Butanol
 - (3) Isobutyl alcohol
 - (4) t-Butyl alcohol
- $\text{CH}_3\text{CH}_2\text{CH}_2\text{-OH} \xrightarrow{\text{PCl}_3} \text{A} \xrightarrow{\text{Alc. KOH}} \text{B} \xrightarrow{\text{H}_3\text{O}^+} \text{C}$
 Find product 'C' is
 - (1) $\text{CH}_3\text{CH}=\text{CH}_2$
 - (2) $\text{CH}_3\text{-}\underset{\text{OH}}{\text{CH}}\text{-CH}_3$
 - (3) $\text{CH}_3\text{-}\underset{\text{Cl}}{\text{CH}}\text{-CH}_3$
 - (4) $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Cl}$

Important facts about alcohols

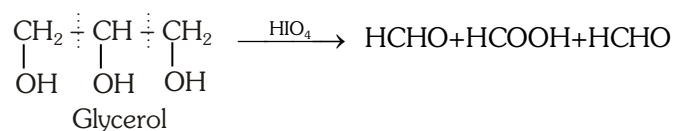
- Toxicity [ethyl alcohol < Iso propyl alcohol < methyl alcohol]
- Absolute alcohol : Ethyl alcohol - 99.5%-100%
- Power alcohol : Rectified spirit + C_6H_6 + Petrol for generation of power
- Methylated spirit : Methanol + Pyridine + mineral naptha + rectified spirit.
- 70% CH_3OH is known as wood spirit.
- 90% $\text{C}_2\text{H}_5\text{OH}$ is known as Raw spirit.
- $\text{C}_2\text{H}_5\text{OH}$ is technically called WASH.
- Rectified spirit contains 95.5% alcohol and 4.5% H_2O .

GOLDEN KEY POINTS

Oxidation by HIO_4 [per iodic acid] or $(\text{CH}_3\text{COO})_4\text{Pb}$ [lead tetraacetate] :

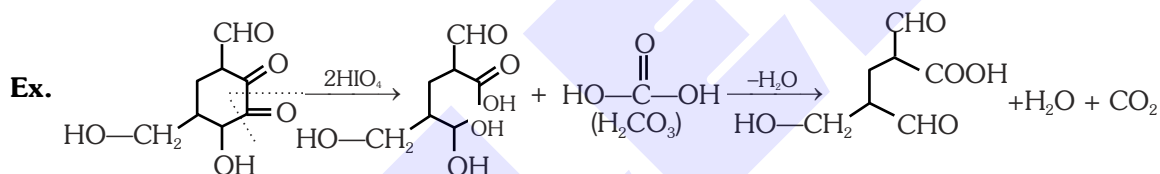
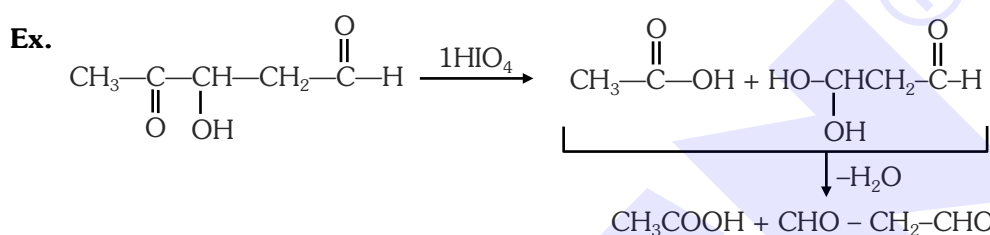
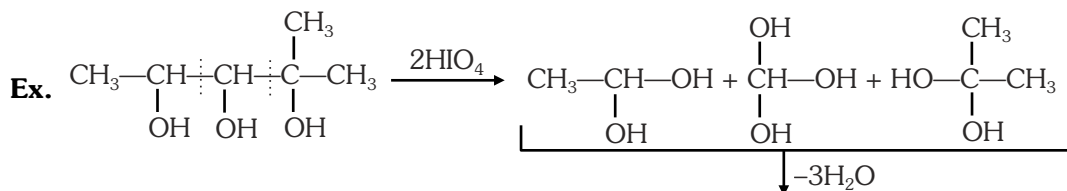


(Ethylene glycol)

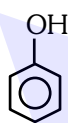


Condition for oxidation by HIO_4 or $(\text{CH}_3\text{COO})_4\text{Pb}$

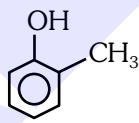
- (i) At least 2 —OH or 2 $>\text{C=O}$ or 1 —OH and 1 $>\text{C=O}$ should be at vicinal carbons.
- (ii) One HIO_4 breaks one C—C bond and adds one —OH to each carbon.


4.0 AROMATIC HYDROXY DERIVATIVES

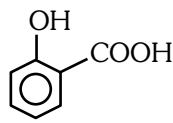
Phenolic compounds : Compounds in which —OH group is directly attached to sp^2c [Benzene ring]



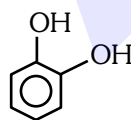
Phenol



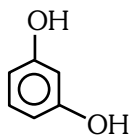
o-Cresol



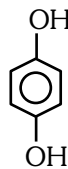
Salicylic acid



Catechol



Resorcinol



Quinol

All phenolic compounds give colour with neutral FeCl_3 .

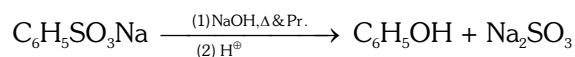


PHENOL (C₆H₅OH)

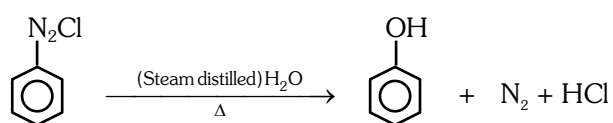
Phenol is also known as carboic acid. In phenol —OH group is attached with sp² hybridised carbon.

4.1 General Methods of Preparation

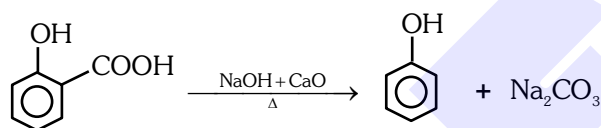
- (1) From benzene sulphonic acid :** When sodium salt of benzene sulphonic acid is fused with NaOH phenol is obtained.



- (2) From benzene diazonium chloride :** When benzene diazonium chloride solution is warmed with water, phenol is obtained with evolution of nitrogen.

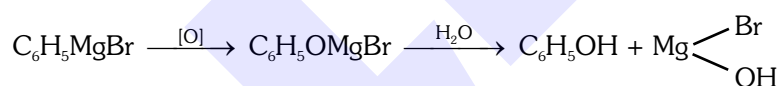


- (3) By distilling a phenolic acid with sodalime (decarboxylation):**

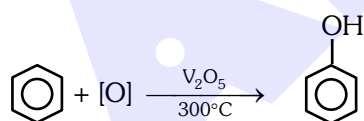


Salicylic acid

- (4) From Grignard reagent :** The Grignard reagent on reaction with oxygen and subsequent hydrolysis yields phenol.



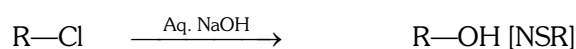
- (5) From benzene :**



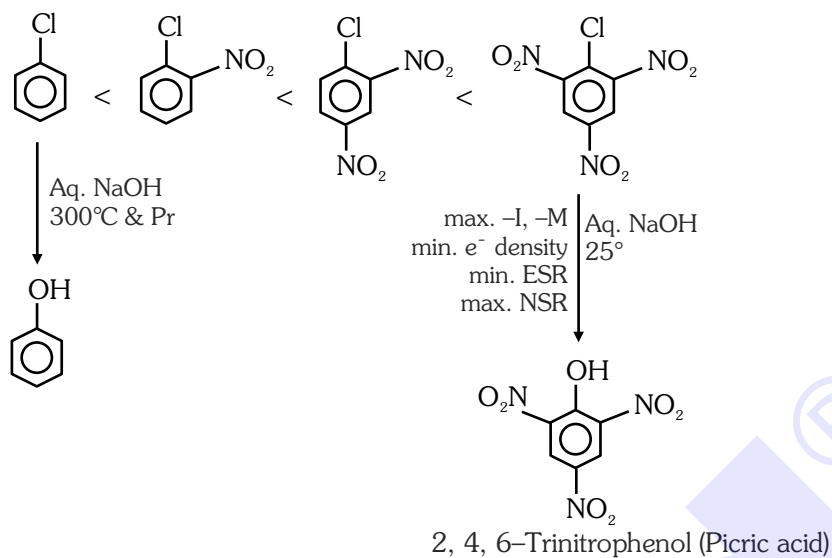
- (6) From chloro benzene :**



Stable by resonance



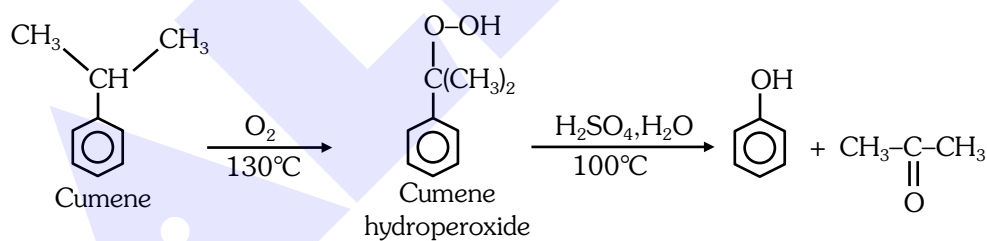
Order for NSR :



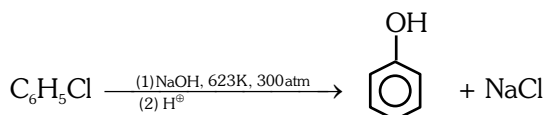
(7) Industrial preparation of phenol : Phenol can be prepared commercially by :

- (a) Cumene
- (b) Dow's process

(a) From cumene (Isopropyl benzene) : Cumene is oxidised with oxygen into cumene hydroperoxide in presence of a catalyst. This is decomposed by dil. H_2SO_4 into phenol and acetone.

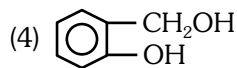
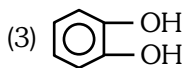
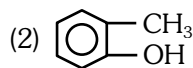
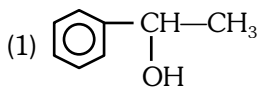


(b) Dow process : This process involves alkaline hydrolysis of chloro benzene-(obtained by above process) followed by acidification.



BEGINNER'S BOX-2

1. Which of the following compounds does not show phenolic properties :-



2. The number of dihydric phenols possible with the molecular formula $C_6H_6O_2$ is :-

(1) 2

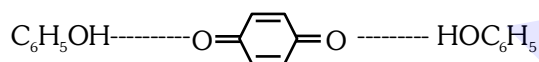
(2) 3

(3) 4

(4) 5

4.2 Physical Properties

- (i) Phenol is a colourless, crystalline solid.
- (ii) It attains pink colour on exposure to air and light. (slow oxidation)



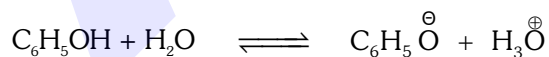
Phenoquinone (pink colour)

- (iii) It is poisonous in nature but acts as antiseptic and disinfectant.
- (iv) Phenol is slightly soluble in water, readily soluble in organic solvents.
- (v) Solubility of phenol in water is much lower than alcohols because of larger hydrocarbon part in the molecule.
- (vi) Due to intermolecular H-Bonding, phenol has relatively high boiling point than the corresponding hydrocarbons, aryl halides.

4.3 Chemical Properties

(A) Reactions due to -OH group :

- (i) **Acidic Nature** : Phenol is a weak acid. The acidic nature of phenol is due to the formation of stable phenoxide ion in solution. The phenoxide ion is stable due to resonance. The negative charge is spread through out the benzene ring which is stabilising factor in the phenoxide ion. Electron withdrawing groups ($-NO_2$, $-Cl$) increase the acidity of phenol while electron releasing groups ($-CH_3$ etc.) decrease the acidity of phenol.

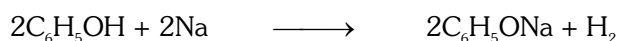


Phenol is stronger acid than alcohols but weaker than the carboxylic acids and even carbonic acid.

GOLDEN KEY POINTS

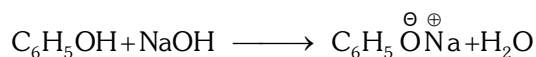
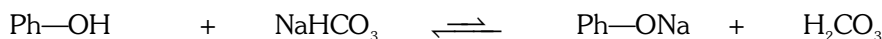
- The acidic nature of phenol is observed as the following:

- (i) Phenol changes blue litmus to red.
- (ii) Highly electro positive metals react with phenol.



Pre-Medical

(iii) Phenol reacts with strong alkalies to form phenoxides.

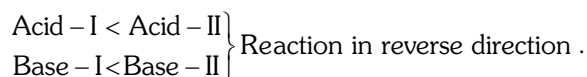
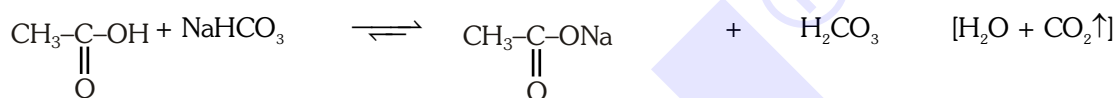

 (iv) However phenol does not decompose Na_2CO_3 or NaHCO_3 because phenol is weaker acid than carbonic acid.


Acid-I

Base-I

Base-II

Acid-II

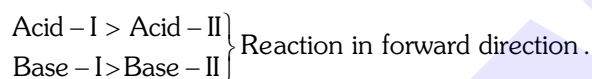

Note : Acetic acid reacts with NaHCO_3 and gives effervescence of CO_2 .


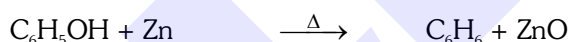
Acid-I

Base-I

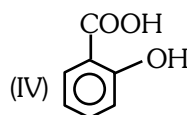
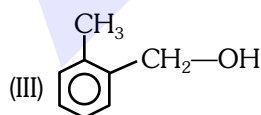
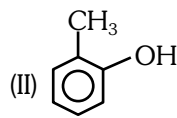
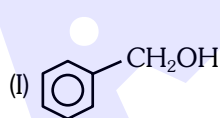
Base-II

Acid-II


(ii) Reaction with PCl_5 : Phenol reacts with PCl_5 to form chloro benzene. POCl_3 formed as biproduct reacts with phenol to form triphenyl phosphate.

(iii) Reaction with Zn dust: When phenol is distilled with zinc dust benzene is obtained.


Illustrations

Illustration 4. In which of the following compound deoxygenation is possible when heated with Zn


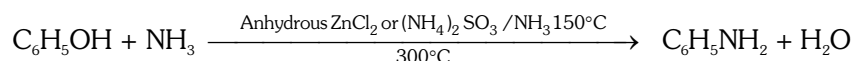
(1) I, II, III

(2) I, III, IV

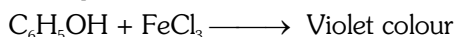
(3) II, IV

(4) II, III

Solution
Ans.(3) Observed in phenolic compound.

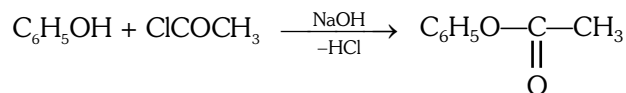
(iv) Reaction with NH_3 : Phenol reacts with NH_3 in presence of anhydrous ZnCl_2 to form aniline.


- (v) **Reaction with FeCl_3 :** Phenol gives violet colouration with FeCl_3 solution (neutral) due to formation of a complex.

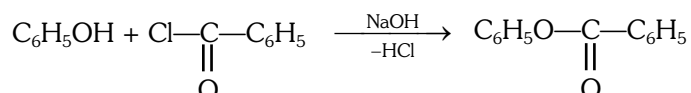


This reaction is used to differentiate phenol from alcohols.

- (vi) **Acetylation :** Phenol reacts with acid chlorides or acid anhydrides in alkali solution to form phenyl esters.

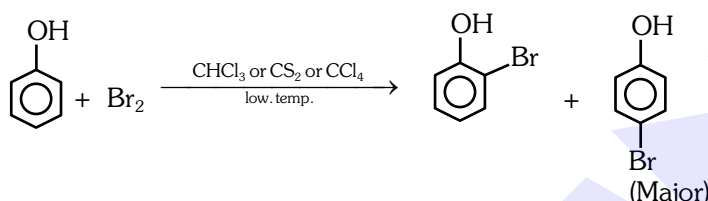


- (vii) **Benzoylation (Schotten-Baumann reaction)**

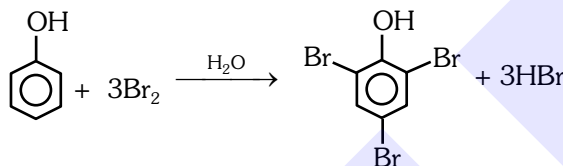


- (B) **Reaction of Benzene Ring :** The $-\text{OH}$ group is ortho and para directing. It activates the benzene ring.

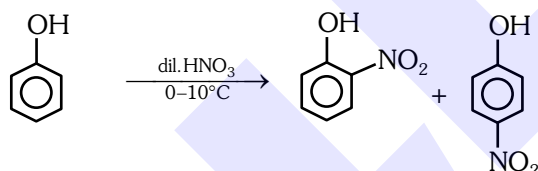
- (i) **Halogenation :** Phenol reacts with bromine in CCl_4 to form mixture of o- and p-bromo phenol.



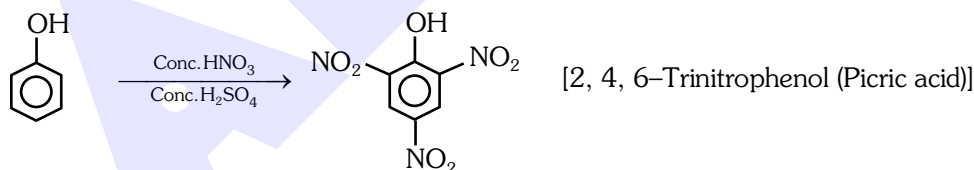
Phenol reacts with bromine water to form a white ppt. of 2,4,6-tribromo phenol. (Test for phenol)



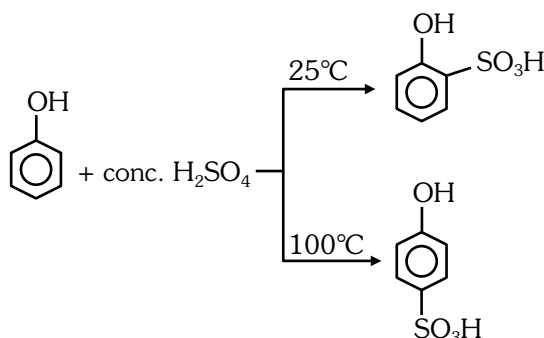
- (ii) **Nitration :** Phenol reacts with dil. HNO_3 at $0^\circ\text{--}10^\circ\text{C}$ to form o- and p- nitro phenols.

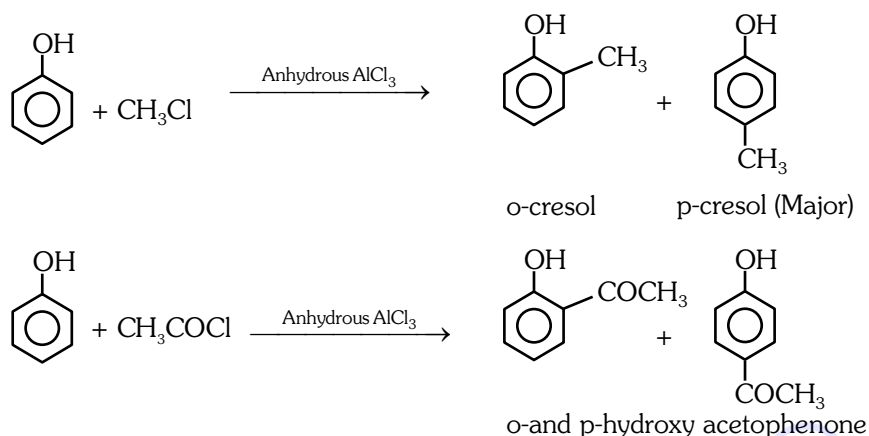


When phenol is treated with nitrating mixture than it forms 2,4,6- trinitro phenol (picric acid) but it is not good method to form picric acid because nitric acid oxidise phenol into p-Benzoquinone

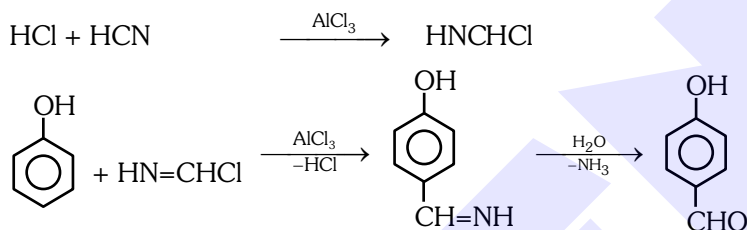


- (iii) **Sulphonation:** Phenol reacts with fuming H_2SO_4 to form o- and p-hydroxy benzene sulphonic acid at different temperatures.

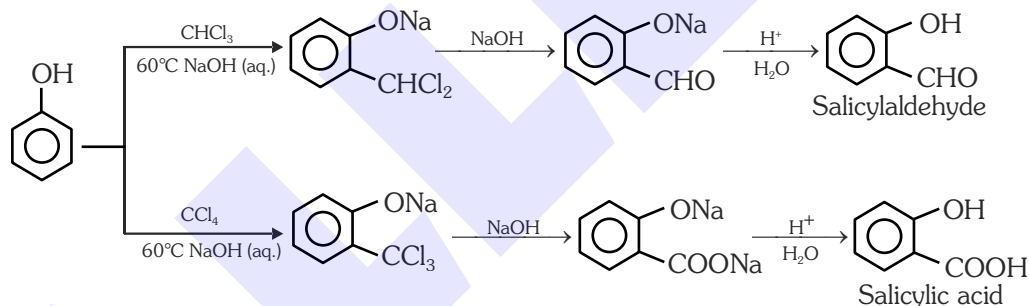


(iv) Friedel - Craft 's reaction:


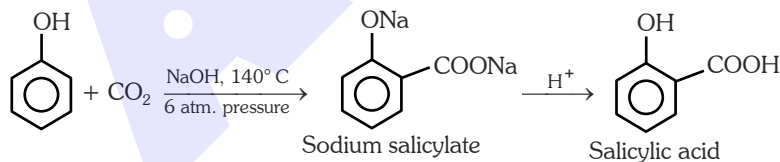
(v) Gattermann aldehyde synthesis : When phenol is treated with liquid HCN and HCl gas in presence of anhydrous AlCl_3 it yields mainly p- hydroxy benzaldehyde (formylation)



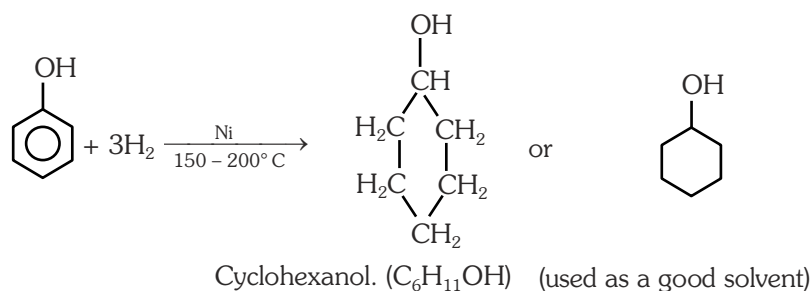
(vi) Reimer-Tiemann reaction : Phenol on refluxing with chloroform and NaOH (aqueous) followed by acid hydrolysis yields o-hydroxy benzaldehyde. When CCl_4 is used salicylic acid is formed.



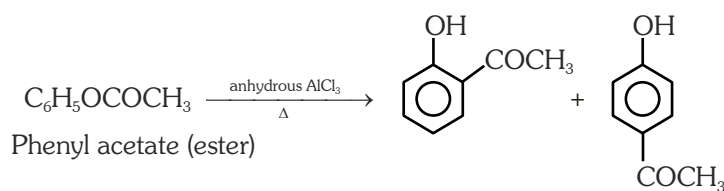
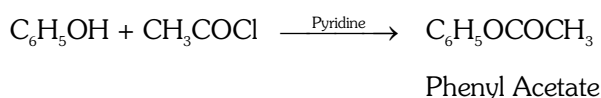
(vii) Kolbe's Schmidt reaction : It involves the reaction of $\text{C}_6\text{H}_5\text{OH}$ with CO_2 and NaOH at 140°C followed by acidification to form salicylic acid.



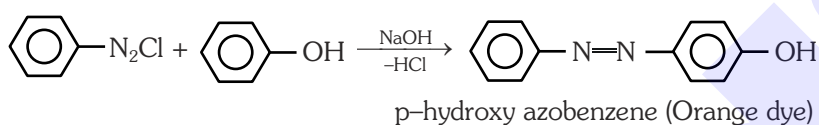
(viii) Hydrogenation: Phenol when hydrogenated in presence of Ni at $150\text{-}200^\circ\text{C}$ forms cyclohexanol.



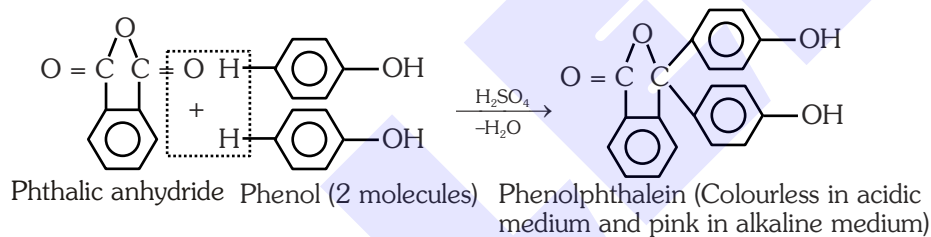
(ix) Fries rearrangement reaction:



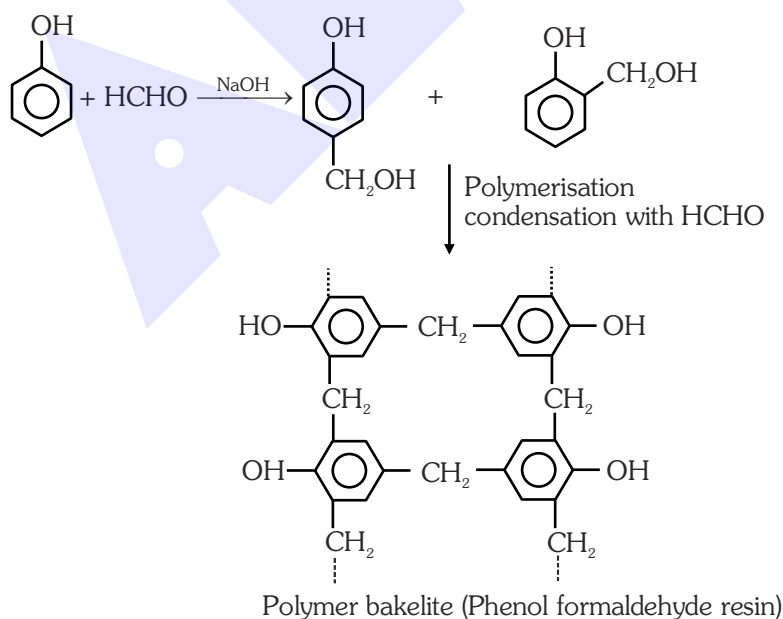
(x) Coupling reactions: Phenol couples with benzene diazonium chloride in presence of an alkaline solution to form a dye (p- hydroxy azobenzene) orange dye.

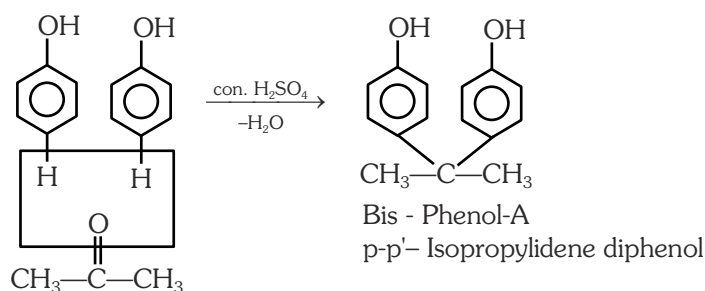
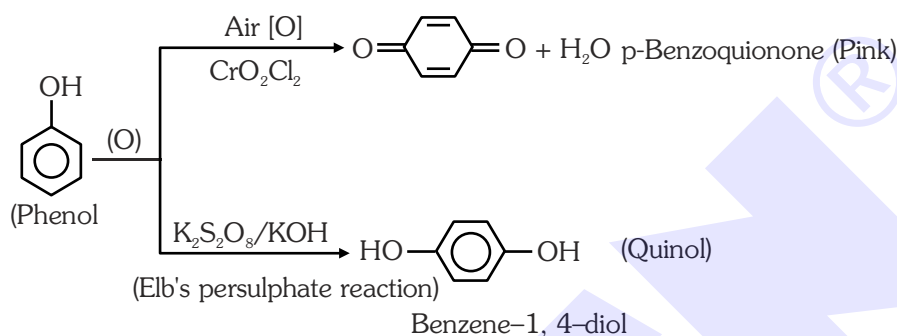


Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form a dye (phenolphthalein) used as an indicator.



(xi) Lederer Manasse (Condensation with formaldehyde) : Phenol condenses with HCHO (excess) in presence of NaOH or weak acid (H^+) to form a polymer known as bakelite (resin).



(xii) Reaction with acetone: (Condensation with acetone)

(xiii) Oxidation:

BEGINNER'S BOX-3

1. Reimer-Tiemann formylation reaction involves addition of :-

- | | |
|--------------------------------------|--|
| (1) Chloroform on phenoxide ion | (2) Trichloromethyl carbanion on phenoxide ion |
| (3) Dichlorocarbene on phenoxide ion | (4) Hydroxide ion on phenol |

2. Phenol reacts with benzenediazonium chloride solution to form a compound of the structure :-

- | | |
|-----|-----|
| (1) | (2) |
| (3) | (4) |

 3. Phenol $\xrightarrow[\text{conc. H}_2\text{SO}_4]{\text{NaNO}_2}$ Green colour $\xrightarrow{\text{H}_2\text{O}}$ red colour $\xrightarrow{\text{NaOH}}$ Blue colour

This reaction is associated with the name of :-

- | | | | |
|----------------|-------------|----------------|--------------------|
| (1) Gattermann | (2) Hofmann | (3) Liebermann | (4) Reimer-Tiemann |
|----------------|-------------|----------------|--------------------|

Test of Phenol :

- Phenol turns blue litmus to red.
- Aqueous solution of phenol gives a violet colour with a drop of ferric chloride.
- Phenol gives Liebermann's nitroso test.
- Aqueous solution of phenol gives a white ppt. of 2,4,6-tribromophenol with bromine water.
- Phenol combines with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which gives pink colour with alkali.

Differences between phenol and alcohol (C₂H₅OH) :

- (1) Phenol is more acidic than aliphatic alcohol due to resonance in phenoxide ion.
- (2) Phenol gives violet colour with FeCl₃ while aliphatic alcohol does not give.
- (3) Phenol gives triphenyl phosphate with PCl₅ while aliphatic alcohol does not.
- (4) Phenol on oxidation gives quinone while alcohol gives aldehyde or ketone and acids.

Uses of Phenol :

Phenol is used :

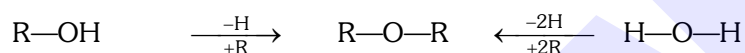
- (1) As an antiseptic in soaps and lotions. "Dettol" (mixture of chloroxylenol and terpineol)
- (2) In manufacture of azodyes, phenolphthalein, picric acid (explosive), cyclohexanol (Solvent for rubber), plastics (bakelite) etc.
- (3) In manufacture of drugs like aspirin, salol, phenacetin etc.
- (4) As preservative for ink.

5.0 ETHER

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is C_nH_{2n+2}O.

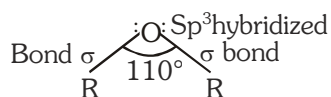
CH₃—O—CH₂CH₃ (Methoxy ethane) or Ethyl methyl ether

Ether is monoalkyl derivative of R—OH and dialkyl derivative of H₂O



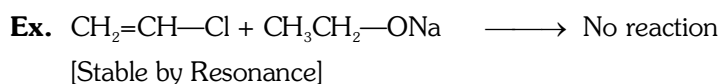
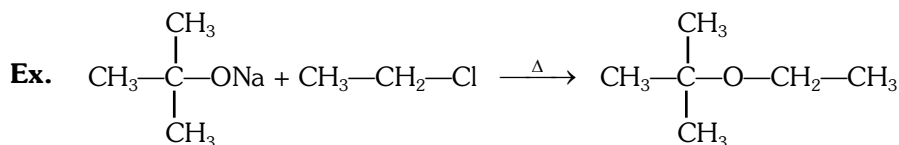
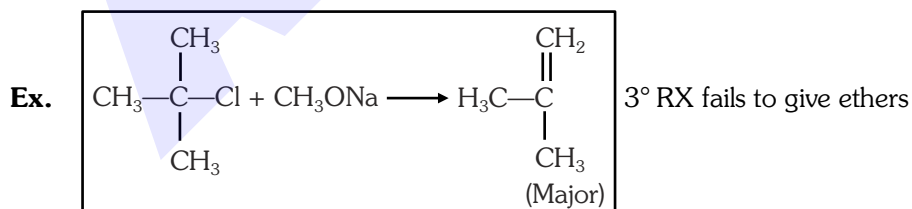
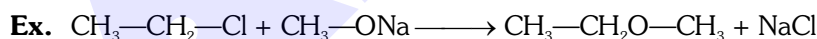
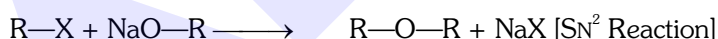
Classification : They may be classified as :

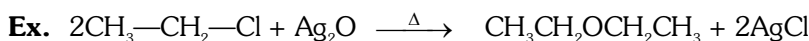
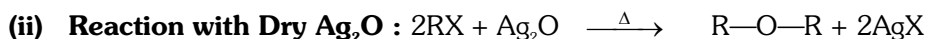
- (a) Simple or symmetrical ether. e.g. R—O—R
- (b) Mixed or unsymmetrical ether e.g. R—O—R'

Structure :

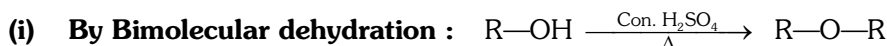
The molecule of ether is bent due to presence of lone pair.

The bond angle is 110°. It is greater than that of water (105°) due to the repulsion between bulkier alkyl groups. Due to bent structure, it possess dipole moment and hence are polar molecules.

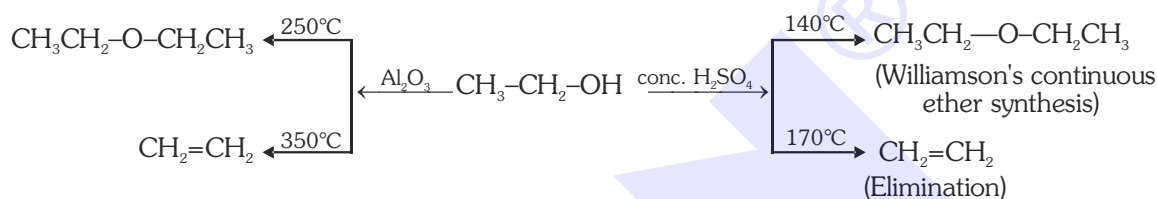
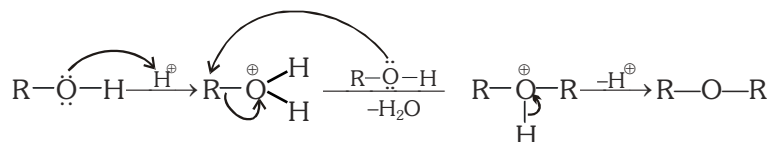
5.1 General Methods of Preparation**(a) From alkyl halides :****(i) By Williamson's synthesis :**



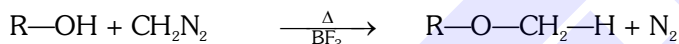
(b) From R-OH:



Mechanism :



(ii) **Reaction with CH_2N_2 (diazomethane) :**



5.2 Physical Properties

- CH_3OCH_3 , $\text{CH}_3\text{OCH}_2\text{CH}_3$ are gases and higher ethers are volatile liquids.
- Ethers are less polar.
- Ethers are less soluble in H_2O .
- Ethers have less BP than corresponding alcohol.

Illustrations

Illustration 5. Ethers are less soluble in H_2O . Why ?

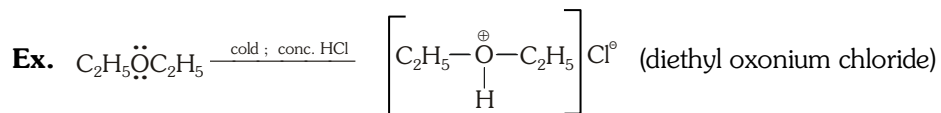
Solution. Due to less polarity, it forms weaker H-Bonding with H_2O .

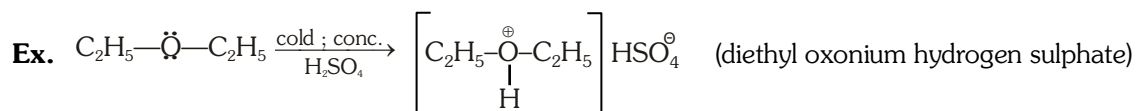
5.3 Chemical properties

Ethers are less polar so less reactive and do not react with active metals [Na, K], cold dil. acid, oxidising and reducing agent. They do not have any active functional group.

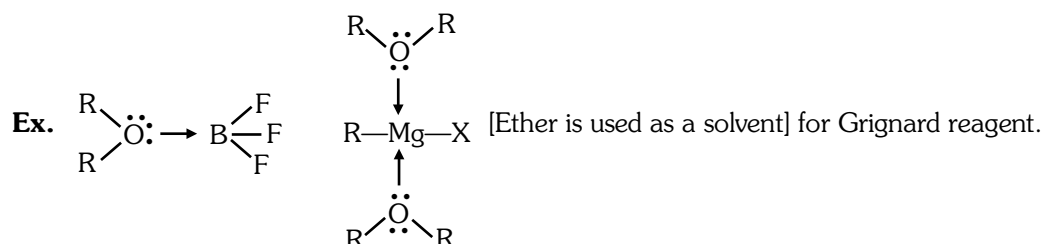
(1) Basic nature : Due to presence of $\ell.p$ on oxygen atom ether behave as lewis base

Ethers react with cold conc. acid and form oxonium salts.

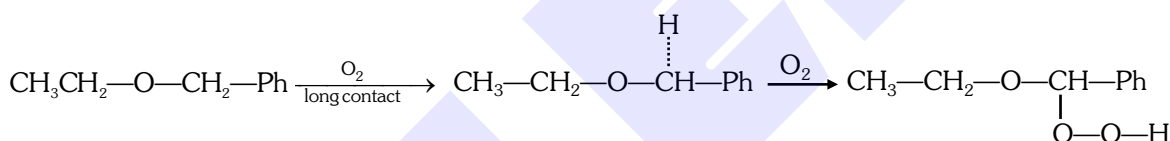
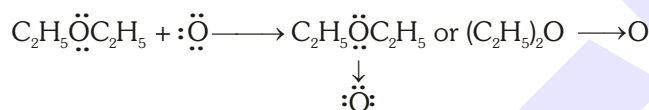
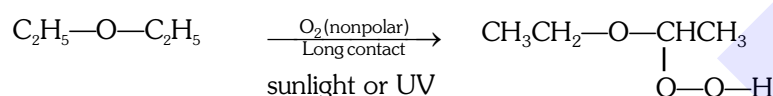




Ethers form dative bond with Lewis acids like BF_3 , AlCl_3 , RMgX etc.



(2) Formation of peroxides : Ether add up atmospheric oxygen or ozonised oxygen. It is explained by Free radical mechanism as intermediate is free radical.



Peroxides are unstable and explosives.

GOLDEN KEY POINTS

Test for peroxides

Ether (peroxide) $\xrightarrow{\text{FeSO}_4/\text{KCNS}}$ Red colour

Ether (peroxides) + $\text{Fe}^{+2} \longrightarrow \text{Fe}^{+3} \xrightarrow{\text{CNS}^-} \text{Fe}(\text{CNS})_3$ (Red)

(3) Reaction with PCl_5 : $\text{ROR} + \text{PCl}_5 \xrightarrow{\text{heat}} 2\text{RCl} + \text{POCl}_3$

(4) Reduction : $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \xrightarrow[\text{heat}]{\text{Red P + HI}} 2\text{CH}_3\text{CH}_3$

(5) Reaction with HX : $\text{R-O-R}' + \text{HI} \longrightarrow \text{R-OH} + \text{R}'\text{-I}$

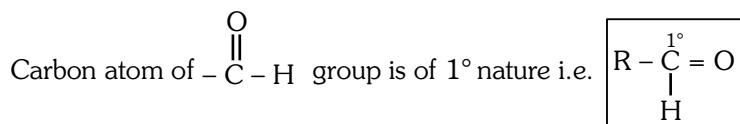
Uses of ether :

- General anaesthetic agent.
- Solvent for oil, fats, resins, Grignard reagent.
- For providing inert & moist free medium to organic reaction e.g. Wurtz reactions.
- In perfumery.
- Di-isopropyl ether \longrightarrow In petrol as an antiknock compound.
- Mixture of alcohol and ether is used as a substitute of petrol. Trade name "**Natalite**"

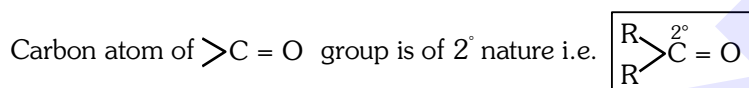
6.0 CARBONYL COMPOUNDS

Organic Compounds having $>C=O$ group are called carbonyl compounds and $>C=O$ group is known as carbonyl group. Its general formula is $C_n H_{2n} O$ ($n = 1, 2, 3, \dots$) Carbonyl compounds are grouped into two categories.

(a) Aldehydes : Aldehyde group is $-\overset{\overset{O}{\parallel}}{C}-H$ (also known as formyl group). It is a monovalent group



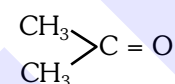
(b) Ketones : The carbonyl group $>C=O$ is a Ketonic group when its both the valencies are satisfied by alkyl group. It is a bivalent group.



Ketones are further classified as :

- Simple or Symmetrical ketones :** Having two similar alkyl groups. $\boxed{R_2\overset{\overset{\parallel}{O}}{C}}$
- Mixed or unsymmetrical ketones :** Having two different alkyl groups. $\boxed{R\overset{\overset{\parallel}{O}}{C}R'}$

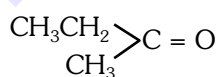
Ex. (Ketones) : **Symmetrical**



(Acetone or Dimethyl ketone)

Propanone

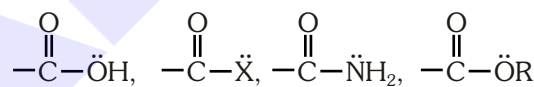
Unsymmetrical



(Ethyl methyl ketone)

Butanone

Sp. Point :



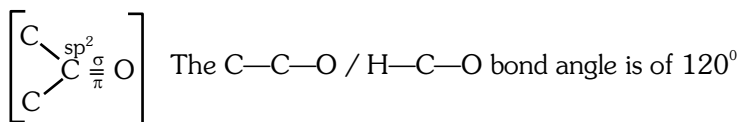
In all the compounds given above, lone pair of electrons and double bond are in conjugate system.

$\left(\begin{array}{c} \overset{\overset{O}{\parallel}}{C} \\ \diagup \\ -C-\ddot{Z} \end{array} \right)$ so resonance occurs. These compounds have $-\overset{\overset{O}{\parallel}}{C}-$ group still they are not carbonyl compounds

because these compounds have characteristic reactions different from carbonyl compounds.

Structure : In $>C=O$ compounds C-atom is sp^2 hybridised which forms two σ bonds and one π bond.

The unhybridised atomic orbital of C-atom and the parallel 2p orbital of oxygen forms the π bond in $>C=O$ group



Due to electro-negativity difference in C & O atoms, the $>\text{C}=\text{O}$ group is polar.

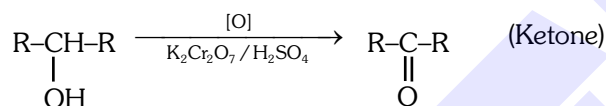
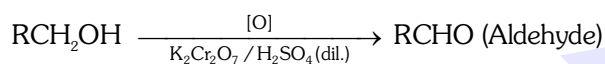
$>\overset{\delta+}{\text{C}}=\overset{\delta-}{\text{O}}$ Hence aldehydes and Ketones possess considerable dipole moment.

6.1 General Methods of Preparation

(A) For both Aldehydes and Ketones

(1) By Oxidation of Alcohols :

(a) **By $\text{K}_2\text{Cr}_2\text{O}_7 / \text{H}_2\text{SO}_4$:** Oxidation of primary alcohols gives aldehyde and oxidation of secondary alcohols gives Ketones.



Aldehydes are quite susceptible to further oxidation to acids -



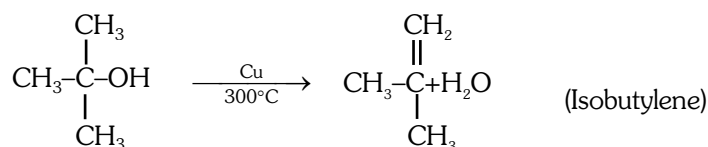
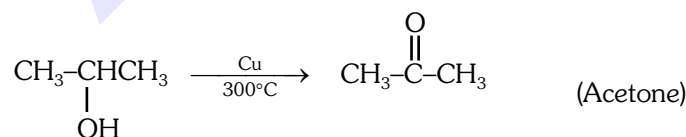
Thus oxidation of primary alcohols is made at the temperature much above the boiling point of aldehyde and thus aldehydes are vapourised out and prevented from being oxidised.

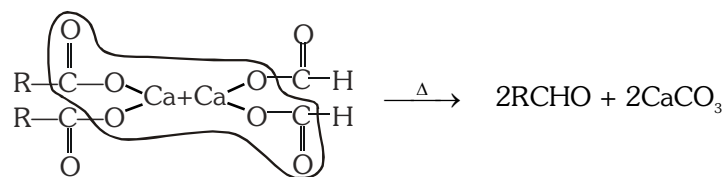
(b) **Mild Oxidising Agent :** 1° alcohols will get oxidised with CrO_3 / Pyridine, (**collin's reagent**) or P.C.C (Pyridinium chloro chromate $\text{CrO}_3 + \text{C}_5\text{H}_5\text{N} + \text{HCl}$) to aldehyde and 2° alcohols to ketone.



By this reaction, **good yield of aldehyde** is possible.

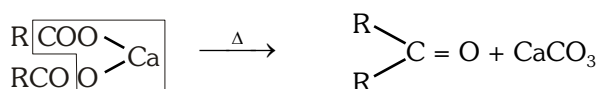
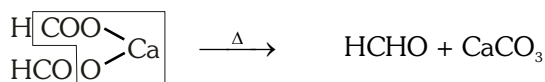
(2) Dehydrogenation of alcohols :



(3) By dry distillation of Ca-salts of carboxylic acid :


Calcium alkanoate

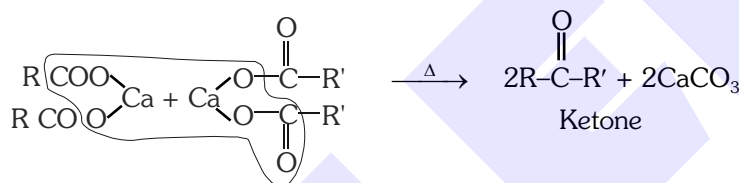
Calcium formate

 ($\text{R}-\text{C}-\text{R}$ and HCHO are also formed)
 \parallel
 O


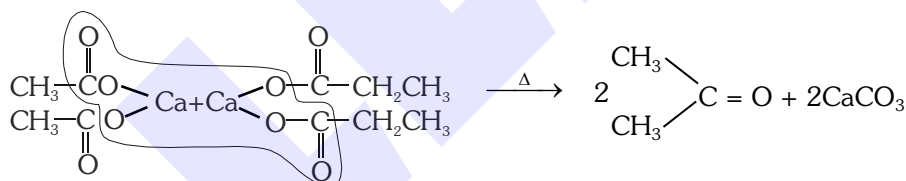
Calcium-alkanoate

Ketone

Calcium salts of acids other than formic acid on heating together give unsymmetrical ketone



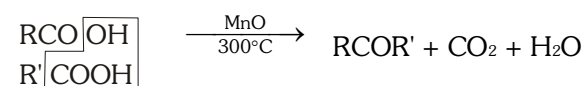
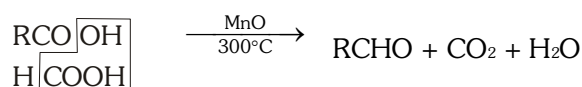
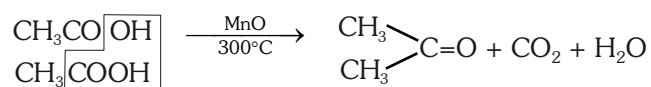
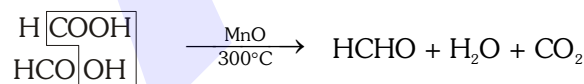
To prepare ethyl methyl ketone Calcium acetate and Calcium propionate are used :



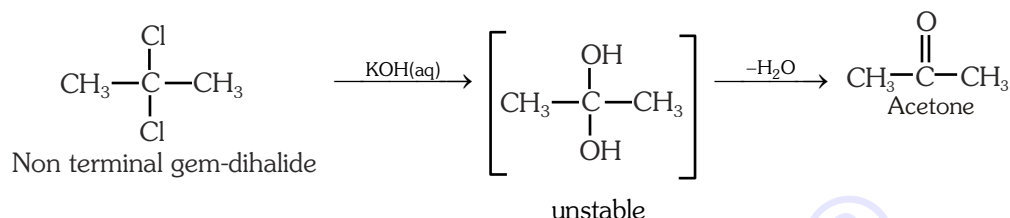
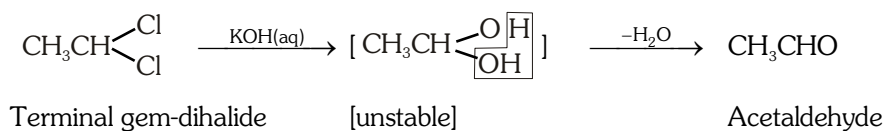
Calcium Acetate Calcium propionate

Ethyl methyl ketone

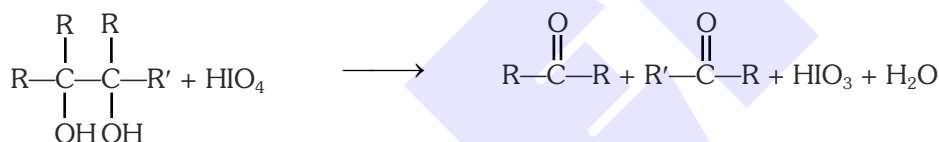
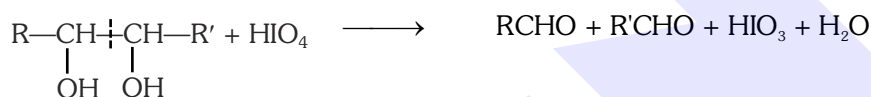
(4) By Thermal decomposition of carboxylic acids : Vapour of carboxylic acids when passed over

 $\text{MnO}/300^\circ\text{C}$ give carbonyl compounds


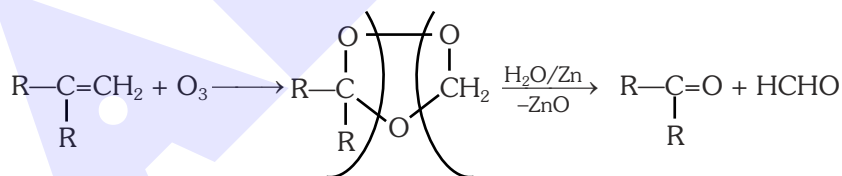
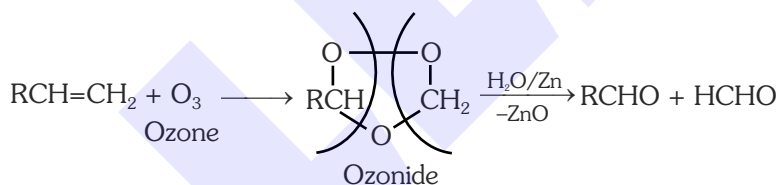
- (5) By Hydrolysis of gem dihalides :** Terminal gem-dihalides on hydrolysis give aldehydes while the non-terminal gem-dihalides give ketones.



- (6) By Oxidation of diols :** With periodic acid (HIO_4) or lead tetra acetate $(\text{CH}_3\text{COO})_4\text{Pb}$ vicinal diols get oxidised to form carbonyl compounds



- (7) By Ozonolysis of alkenes :** This reaction is used to determine the position of double bond in alkene. Zn is used to decompose H_2O_2 formed during hydrolysis.

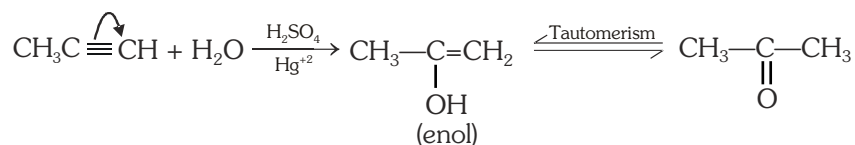


- (8) From Alkyne :**

- (a) Hydration :** With dil H_2SO_4 & 1% HgSO_4 at $60-80^\circ\text{C}$.

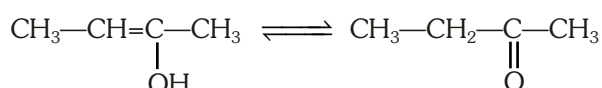
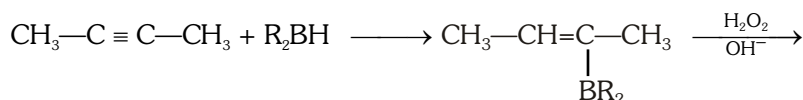
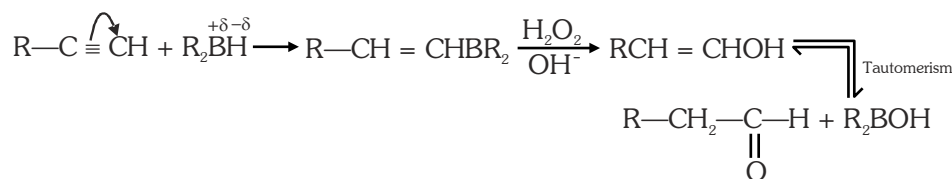


Other alkynes mainly give ketone :



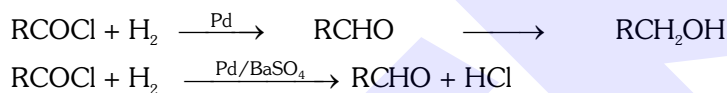
(b) Hydroboration : Reaction with B_2H_6 or R_2BH give alkenyl dialkyl borane.

1-alkyne gives \longrightarrow aldehyde
other alkynes \longrightarrow ketone

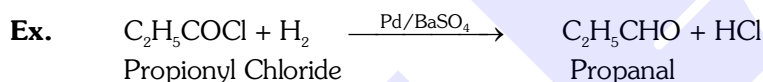


(B) For Aldehydes only

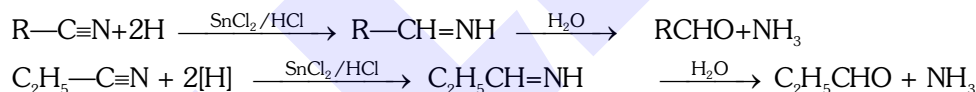
(1) Rosenmund's reduction :



$BaSO_4$ controls the further reduction of aldehyde to alcohols. Formaldehyde can not be prepared by this method.

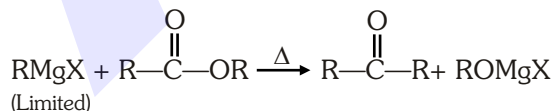
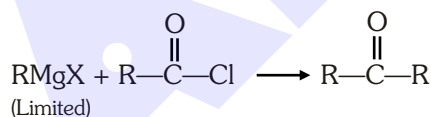
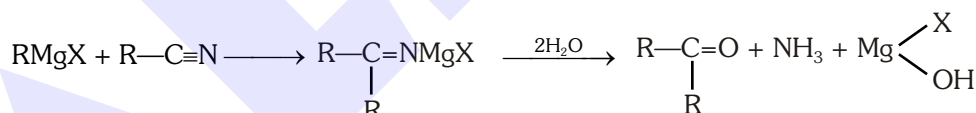


(2) Stephen's reduction :

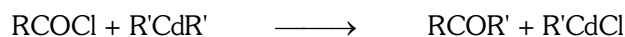


(C) For Ketones only

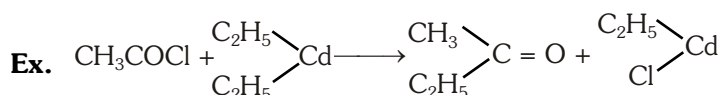
(1) From Grignard's reagent :



(2) From dialkyl Cadmium : $R'CdR'$ (dialkyl Cadmium) is an organometallic compound.



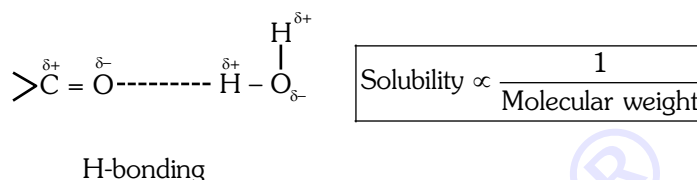
This reaction is superior than Grignard Reaction because the ketones formed, further reacts with Grignard reagent to form 3° alcohols.



6.2 Physical Properties

State : Only formaldehyde is gas, all other carbonyl compounds upto C_{11} are liquids and C_{12} & onwards solid.

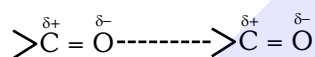
Solubility : C_1 to C_3 (formaldehyde, acetaldehyde and propionaldehyde) and acetone are freely soluble in water due to polarity of $>\overset{\delta+}{C}=\overset{\delta-}{O}$ bond and can form H—bond with water molecule. C_5 onwards are insoluble in water.



Boiling point : $\text{Boiling point} \propto \text{Molecular weight}$

Boiling point order is - **Alcohol > Ketone > Aldehydes > Alkane** (of comparable molecular mass)

This is because in alcohols intermolecular H-bonding is present but in carbonyl compounds H-bonding doesn't exist, instead dipole-dipole & vander waal force of attraction is present. Alkanes are non polar.



Density : Density of carbonyl compounds is lower than water.

BEGINNER'S BOX-4

- Acids do not give the characteristic reactions of $C=O$ group because of :-
 - (1) Dimerisation
 - (2) Resonance
 - (3) Cyclic structures
 - (4) Attached alkyl radical
- The vapour density of a compound is 44. Its molecular formula will be -
 - (1) C_2H_5O
 - (2) $C_3H_6O_2$
 - (3) $C_4H_{10}O$
 - (4) $C_5H_{12}O$
- 23 gm of sodium of reaction with methyl alcohol gives :
 - (1) Half mole of H_2
 - (2) One mole of H_2
 - (3) One mole of O_2
 - (4) none

6.3 Chemical Properties

Carbonyl compounds undergo following reactions :

6.3.1 Nucleophilic addition reactions (Already discussed in Reaction Mechanism Part-2)

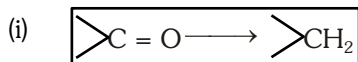
6.3.2 Other reactions

6.3.3 Reactions of only aldehyde

6.3.4 Reactions of only ketones

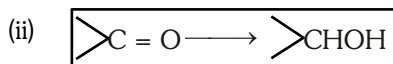
6.3.2 Other reactions

(a) Reduction : The nature of product depends upon the reducing agent used.



Reducing agents are

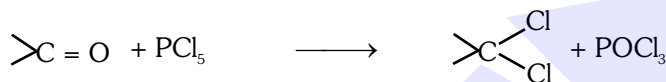
- Red P/HI at 150°C
- Zn-Hg/HCl [Clemmensen's reduction]
- (i) N_2H_4 (ii) OH^- / Δ [Wolff Kishner reduction]



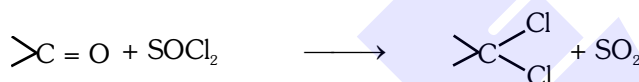
Reducing agents are

- Metal + H_2
- LiAlH_4
- NaBH_4
- $\text{Na} + \text{C}_2\text{H}_5\text{OH}$

(b) Reaction with PCl_5 & SOCl_2 :

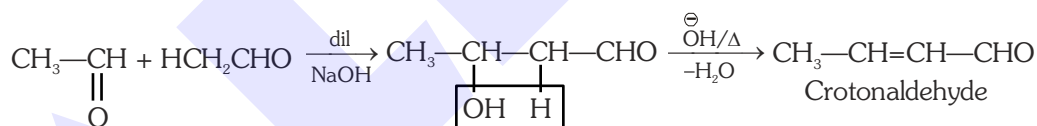


Phosphorus penta chloride



Thionyl chloride

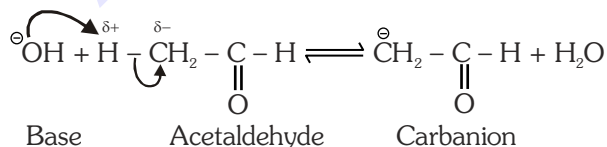
(c) Aldol Condensation : Carbonyl compounds which contain α -H atoms undergo condensation with dil. NaOH to give aldol. Aldol contains both alcoholic and carbonyl group, which on heating in alkaline medium gets converted into α, β -unsaturated carbonyl compound.



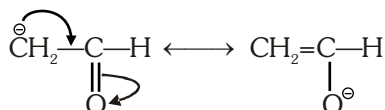
Mechanism of aldol condensation : It takes place in the following two stages :

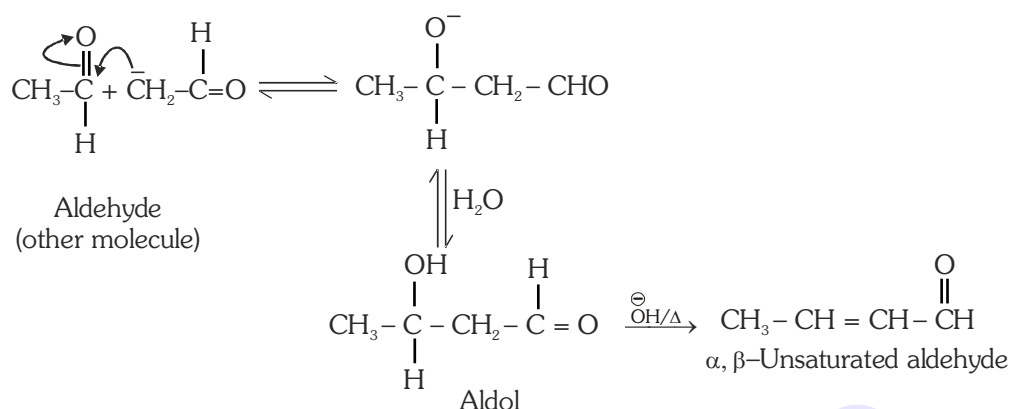
- Formation of Carbanion
- Combination of carbanion with other carbonyl molecule.

(i) Formation of Carbanion : α -H atom of $\text{>C} = \text{O}$ group are quite acidic which can be removed easily as proton, by a base



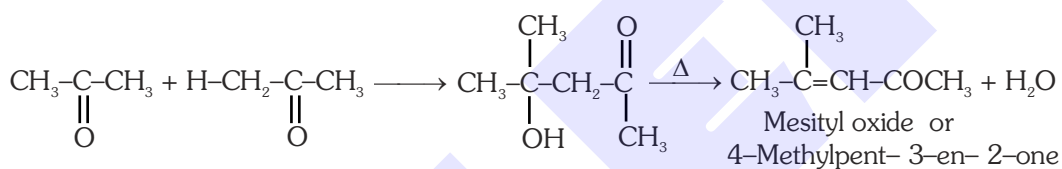
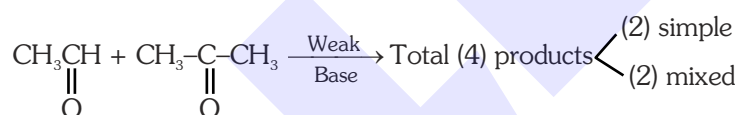
Carbanion thus formed is stable because of resonance -



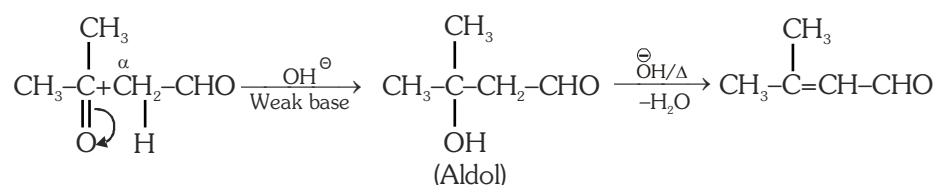
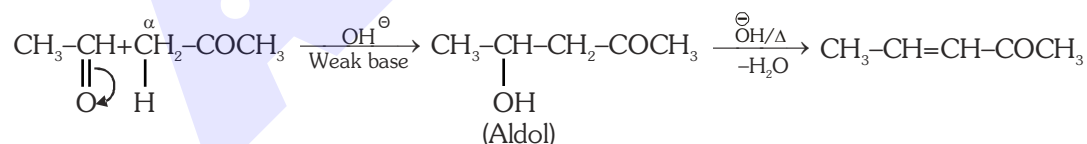
(ii) Combination of carbanion with other carbonyl molecule :

Identical carbonyl compounds \longrightarrow Simple or self aldol condensation.

Different carbonyl compounds \longrightarrow Mixed or crossed aldol condensation.

Simple or Self condensation :**Mixed or Crossed aldol Condensation :**

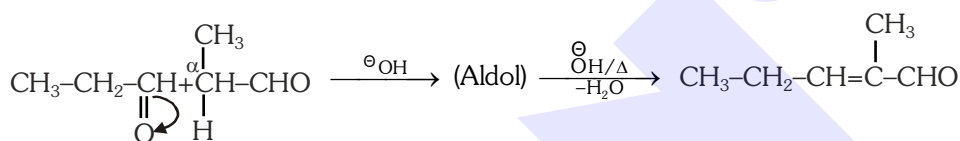
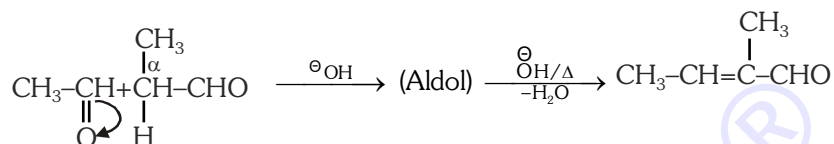
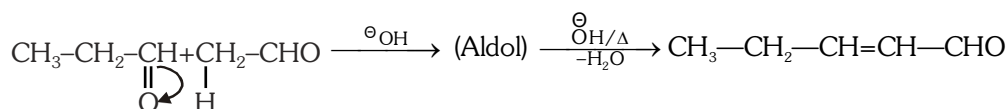
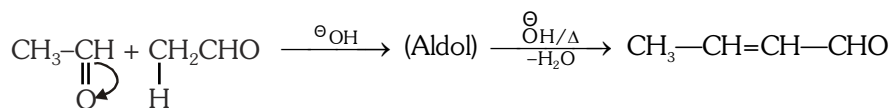
Mixed aldol condensation products of the above reaction are :



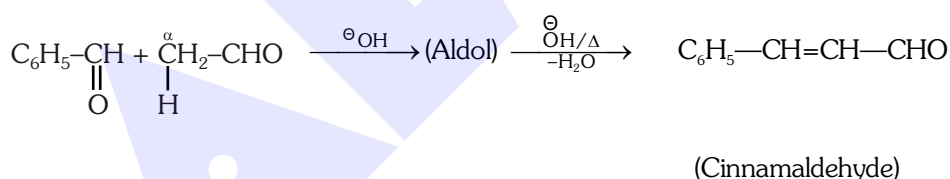
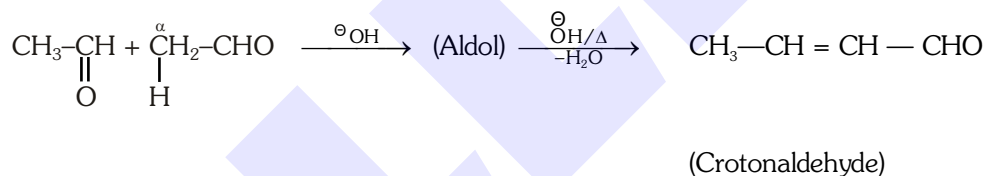
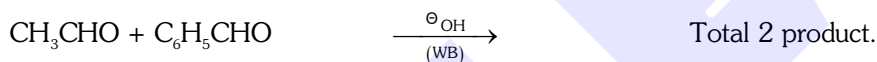
Illustrations

Illustration 6. $\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{CHO}$ Total 4 products. Write structure of products ?

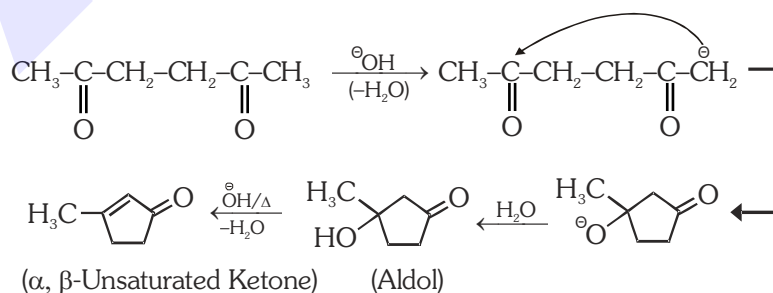
Solution.


GOLDEN KEY POINTS

- If in crossed aldol condensation reaction, only one carbonyl compound have α -H then total two products are formed.



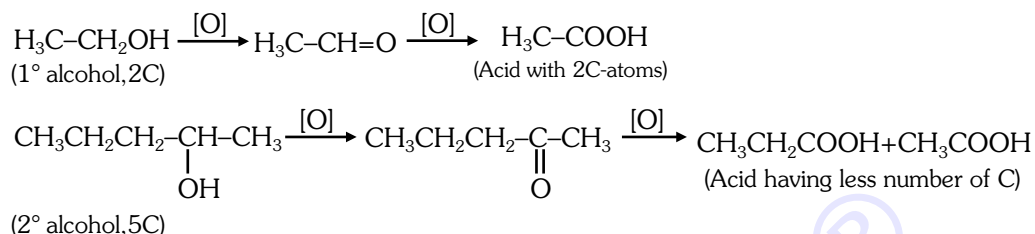
- Intramolecular** aldol condensation :



Here one more product having 3 membered ring is also possible, but 5 membered ring is more stable than 3 membered ring so above product is formed as a major product.

(d) Oxidation reactions : Oxidation reactions :

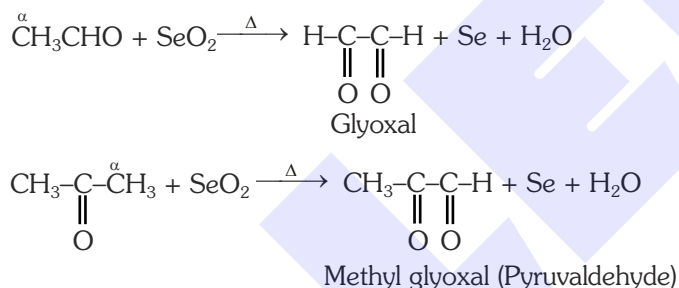
- (i) By $K_2Cr_2O_7/H_2SO_4$:** On oxidation with $K_2Cr_2O_7/H_2SO_4$ 1° alc. gives aldehyde, which on further oxidation gives acid with same number of carbons. If 2° alcohol is oxidised at elevated temperature using $KMnO_4/H^+$, it gets oxidised to give acids with less number of C-atom.



- (ii) SeO_2 (Selenium dioxide) :** Ketones or aldehydes on oxidation with SeO_2 give dicarbonyl compounds.

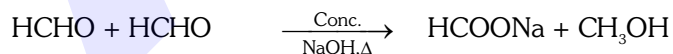
This reaction is possible only in compounds containing $\alpha\text{-CH}_2\text{-}$ unit.

HCHO doesn't show this reaction.

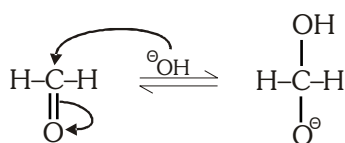
**6.3.3 Reactions of only aldehydes :**

- (a) Cannizaro's reaction :** Those aldehydes which do not contain $\alpha\text{-H}$ atom give this reaction, with conc. NaOH or KOH ; Products are Salt of carboxylic acid + alcohol

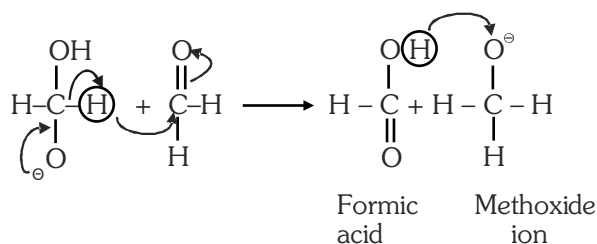
In this reaction one molecule of carbonyl compounds is oxidised to acid, while other is reduced to alcohol, such type of reactions are called redox reaction.

**Mechanism involved in cannizaro's reaction :**

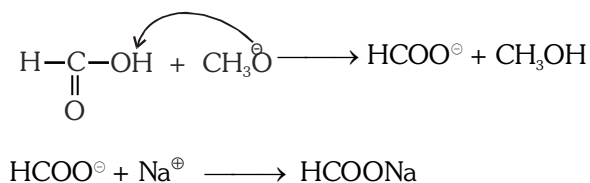
- (a) Rapid reversible addition of OH^- to one molecule of HCHO .



- (b) Transfer of hydride ion H^- to second molecule of HCHO



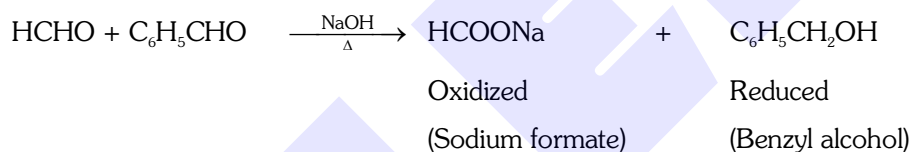
- (c) Proton exchange



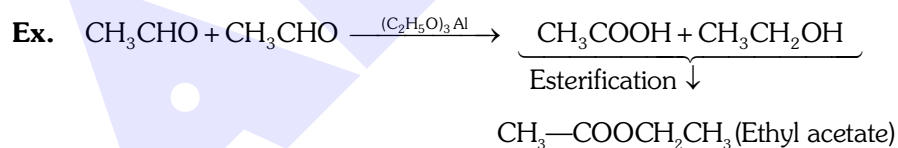
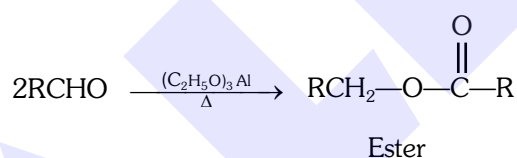
When molecules are same \longrightarrow Simple cannizaro reaction (disproportionation reaction)

Two different molecules \longrightarrow Mixed cannizaro reaction (Redox reaction)

In mixed or crossed cannizaro reaction more reactive aldehyde is oxidised and less reactive aldehyde is reduced.

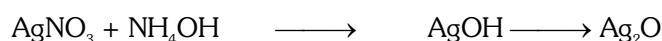
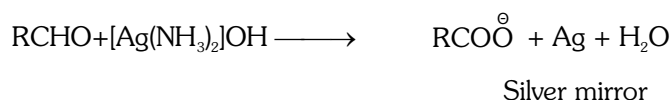
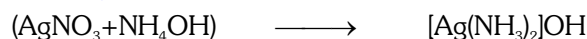


- (b) **Tischenko reaction** : It is a modified cannizaro reaction. All aldehydes undergo this reaction in presence of $(\text{C}_2\text{H}_5\text{O})_3\text{Al}$, to form ester.



- (c) **Reducing character** : Aldehydes are easily oxidised so they are strong reducing agents.

- (i) **Tollen's reagent** : It oxidises aldehydes. Tollen's reagent is ammoniacal silver nitrate solution

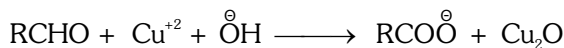


(ii) **Fehling's solution** : It is a mixture of aqueous CuSO_4 , NaOH and sodium potassium tartarate.

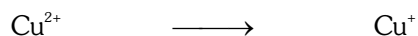
Fehling solution A- (aq.) solution of CuSO_4

Fehling solution B- Roschelle salt (Sodium potassium tartarate + NaOH)

Fehling solution A + Fehlings solution B (Dark blue colour of cupric tartarate)



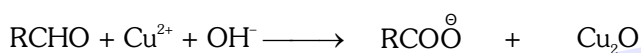
(Cuprous oxide-Red ppt.)



(Cupric - Blue)

(Cuprous - Red ppt.)

(iii) **Benedict's solution** : It is a mixture of CuSO_4 + sodium citrate + NaOH . It provides Cu^{+2} . It is reduced by aldehyde to give red ppt of cuprous oxide.



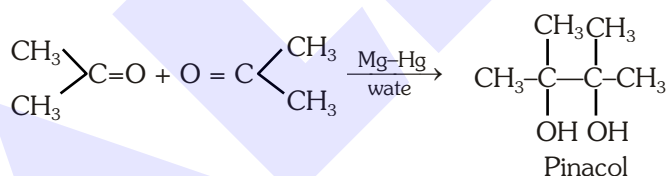
(Cuprous oxide-Red ppt.)

(iv) **Schiff's reagent** : Dilute solution of p-rosaniline hydrochloride or magenta dye, is a pink coloured dye and is known as schiff' dye.

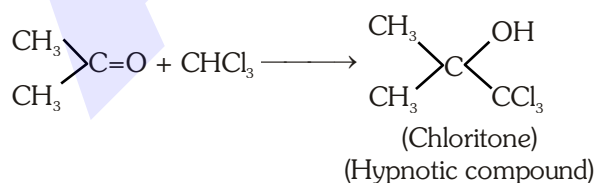
Its pink colour is discharged by passing SO_2 gas and the colourless solution obtained is called schiff's reagent, Aldehyde reacts with this reagent to restore the pink colour.

6.3.4 Reaction of Only Ketones

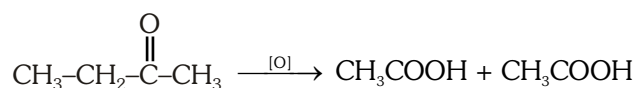
(1) **Reduction** : Acetone is reduced by magnesium amalgam and water to give pinacol.



(2) **Reaction with chloroform** :

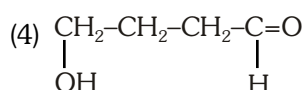
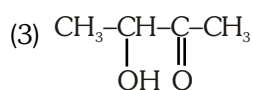
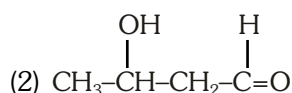
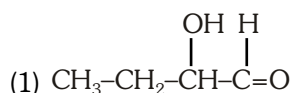


(3) **Oxidation reaction** : According to popoff's rule $\text{>C}=\text{O}$ group stays with smaller alkyl group.



BEGINNER'S BOX-5

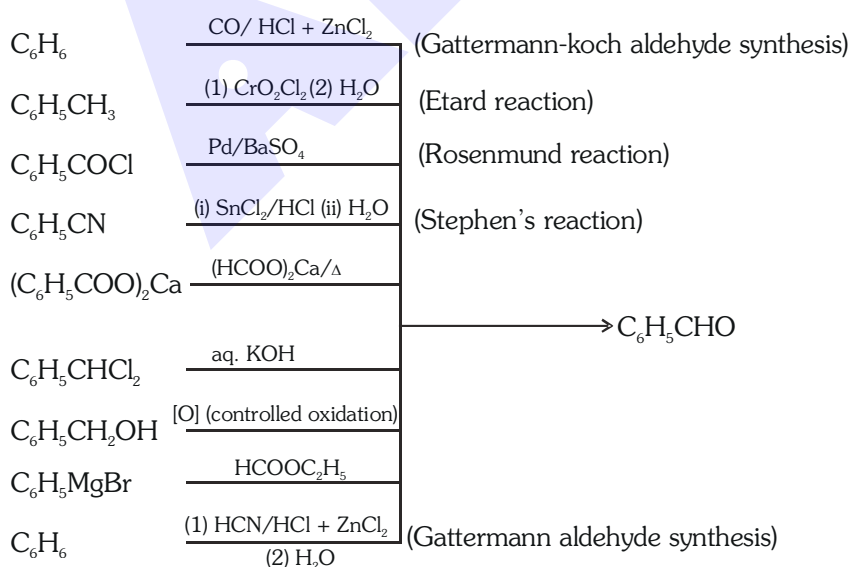
- 1.** The compounds capable in reaction with Tollen's reagent is (are):
(1) Formaldehyde (2) Formic acid (3) Acetaldehyde (4) All the above
- 2.** Acetaldehyde reacts with NaOH to form :-



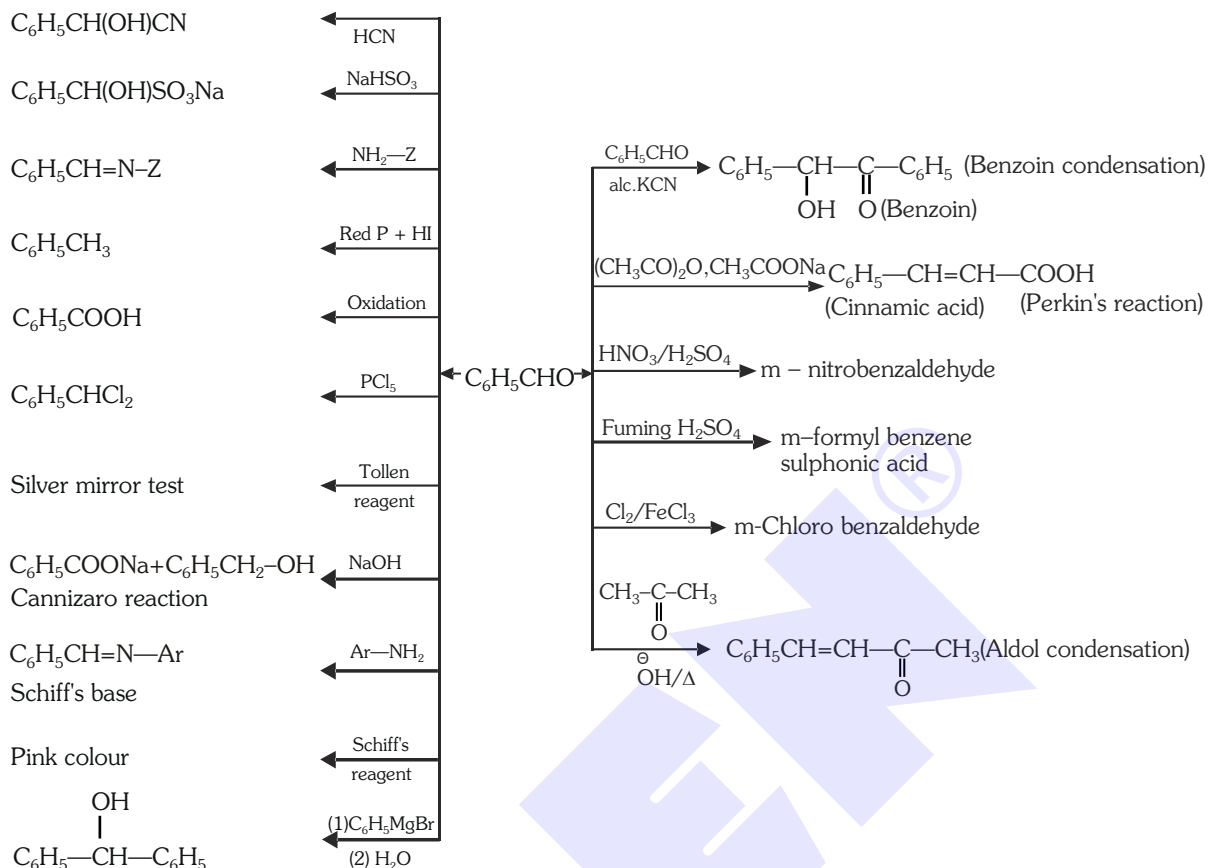
- 3.** Fehling's solution is a :-
- (1) Solution of magenta dye bleached by SO_2
 - (2) Ammonical solution of AgNO_3
 - (3) Mixture of a solution of CuSO_4 and a solution of caustic soda and sodium potassium tartarate
 - (4) Alcoholic solution of 2,4-dinitrophenylhydrazine

7.0 BENZALDEHYDE (C₆H₅CHO) [OIL OF BITTER ALMONDS (COMPONENT OF BITTER ALMOND)]

7.1 General Methods of Preparation



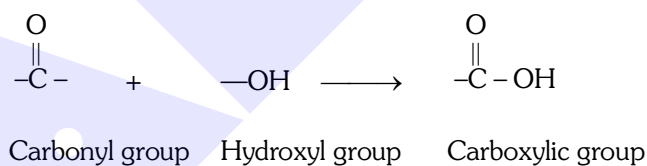
7.2 Chemical Properties



8.0 CARBOXYLIC ACID

Organic compounds having $-COOH$ group are called Carboxylic acids. This functional group is composed of

Carbonyl ($\overset{O}{\parallel}C-$) and hydroxyl ($-OH$) group.



The properties of the carboxylic group are not simply the combined properties of these two groups, but it has its own distinctive properties. The acidic nature of carboxylic acids is due to the presence of replaceable H-atom in the Carboxylic group. The general formula is $C_nH_{2n}O_2$.

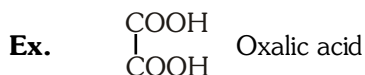
Classification :

Monocarboxylic acid (RCOOH) : Having one carboxylic group, also called monobasic acid.

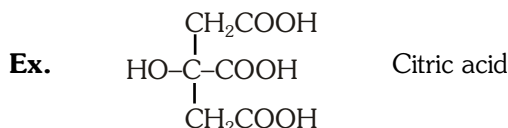
General formula - $C_nH_{2n}O_2$ ($n = 1, 2, 3, \dots$). Higher mono carboxylic acids are called **fatty acids**.

Ex. CH_3COOH acetic acid

Dicarboxylic acid : Having two carboxylic groups, also called dibasic acid.



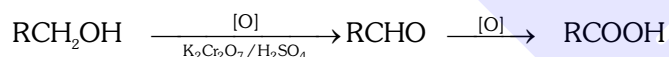
Tricarboxylic acid : Having three carboxylic groups also called tribasic acid.



Structure : The carbon atom of $-\text{COOH}$ group is sp^2 hybridised, this C-atom is in centre and thus bond angle around C-atom is 120° .

8.1 General Methods of Preparation

8.1.1 By Oxidation of alcohols & carbonyl compounds : Oxidation is carried out by acidified $\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4 .



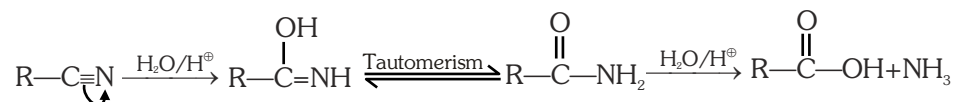
Acids are third oxidation products of alkane.



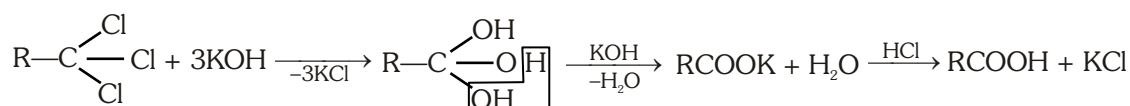
GOLDEN KEY POINTS

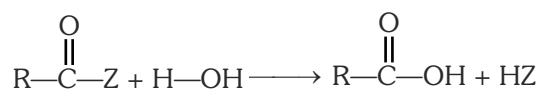
- Aldehyde on oxidation give acids having same no. of C-atoms.
- Ketones on oxidation give acids having less no. of C-atoms.
- Oxidation of Ketones occurs on prolonged treatment with strong oxidising agent.

8.1.2 By hydrolysis of alkane nitriles or cyanides : Complete hydrolysis takes place in acidic medium (dil. HCl). In alkaline medium there is partial hydrolysis.

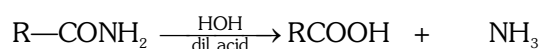
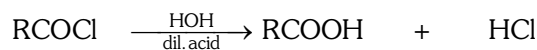
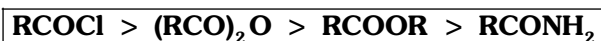
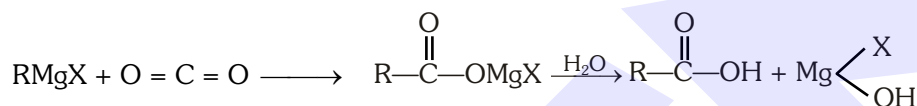


8.1.3 By alkaline hydrolysis of 1, 1, 1-trihaloalkane :



8.1.4 By hydrolysis of acid derivatives :


Reactivity order of acid derivatives :


8.1.5 From Grignard's reagent :


Carbon dioxide

 Solid CO_2 (dry ice) is used

8.2 Physical Properties

 Carboxylic acids from C_1 — C_4 are completely soluble in water.

$$\text{Solubility} \propto \frac{1}{\text{molecular weight}}$$

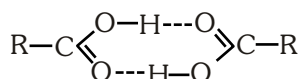
Solubility is due to intermolecular H - bonding with water molecules.

Boiling point : $\text{B. P. \& M. P.} \propto \text{Molecular weight,}$

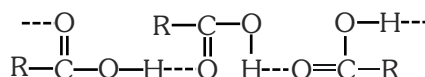
Acids > alcohol

This is because in acids two oxygen atoms take part in H - bonding (while in alcohol only one O - atom takes part).

In vapour or soluble state lower acids occur in the form of dimers.



But in liquid state it exists in polymer form.

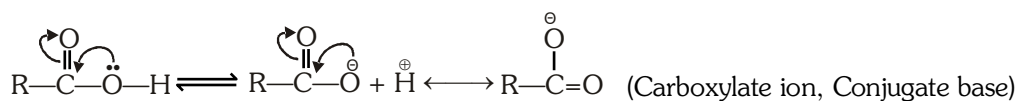


Melting point : Acids having even number of C-atoms have higher melting point as compared to having odd number of C - atoms. The carboxyl group and terminal methyl group in even member acids lie on opposite side to provide more close packing in crystal lattice which results in high melting point.

8.3 Chemical Properties

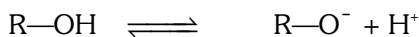
8.3.1 Reaction due to - H atom of - COOH group

(a) Acidic character :



Carboxylate ion is stabilised by resonance so carboxylic acids show considerable acidic character.

In case of alcohol alkoxide ion is not stabilised so they are neutral.



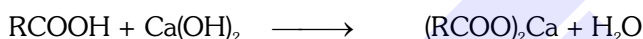
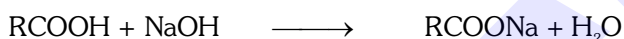
alkoxide ion

(a) Carboxylic acids turn blue litmus to red.

(b) Addition of carboxylic acid to NaHCO_3 in water gives out effervescence of CO_2 .



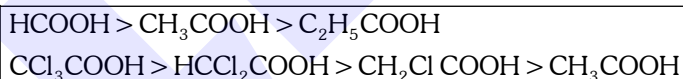
(c) Form salts with alkalies.



(d) Action of metals.

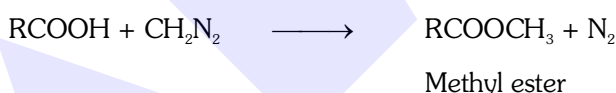


The acidic character order is :



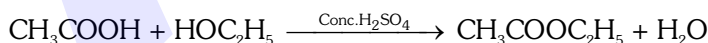
Acidic character may be explained on the basis of I effect and resonance.

(b) Reaction with CH_2N_2 : Methyl ester can be prepared by this method.

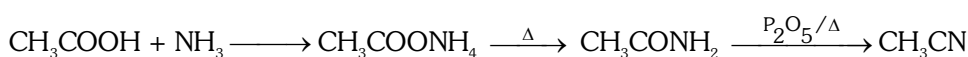


8.3.2 Reaction due to - OH group

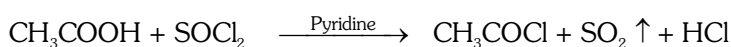
(a) Esterification :



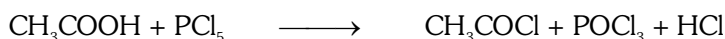
(b) Reaction with NH_3 :

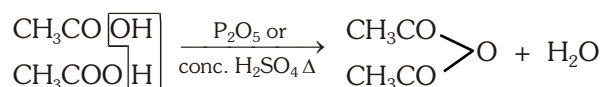


(c) Reaction with thionyl chloride :

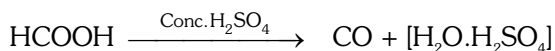
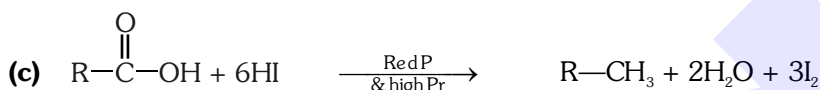
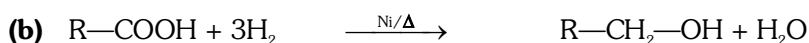
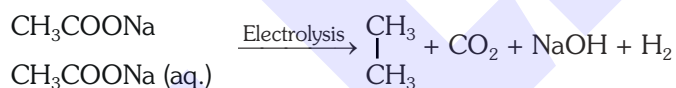
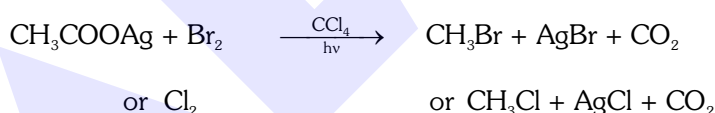
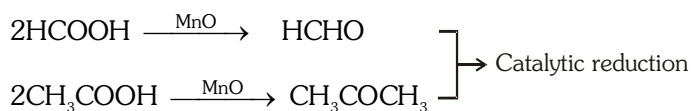
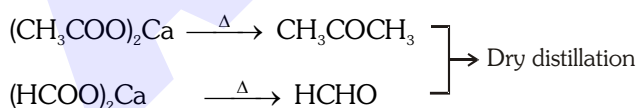
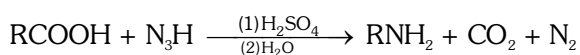


(d) Reaction with PCl_5 :



(e) Reaction with P₂O₅ (dehydrating agent) :

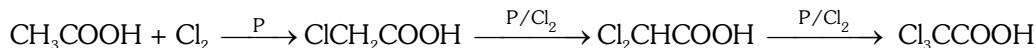
HCOOH is dehydrated by Conc. H₂SO₄

**8.3.3 Reaction due to $\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}- \end{array}$ group of COOH :****8.3.4 Reaction due to —COOH group :****(a) Decarboxylation :****(b) Kolbe's electrolysis :****(c) Hunsdiecker reaction :****(d) Formation of carbonyl compounds :****(e) Schmidt reaction :** The amine formed has one C - atom less than the reactant acid.

Hydrazoic acid

8.3.5 Reaction due to alkyl (R) group :

(a) Halogenation [HVZ reaction] : [Hell volhard Zelinsky reaction] : In this reaction α - H atoms are replaced by halogen atoms.


GOLDEN KEY POINTS
Test for HCOOH and CH₃COOH

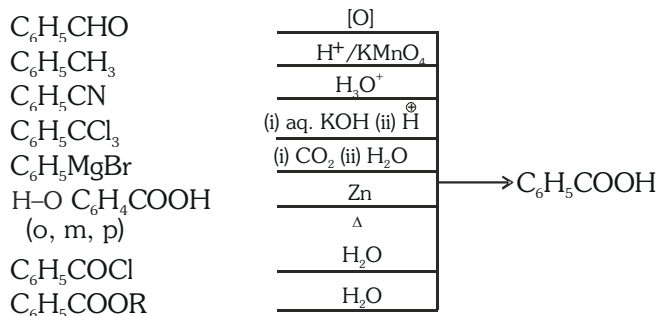
Test	HCOOH	CH ₃ COOH
1. Reducing character		
Reducing agents		
Tollen reagent	Silver mirror	×
Fehling solution	Cu ₂ O red ppt.	×
K ₂ Cr ₂ O ₇	Cr ⁺³ (green)	×
2. Decarboxylation.	Na ₂ CO ₃ + H ₂	CH ₄

Uses of Formic Acid :

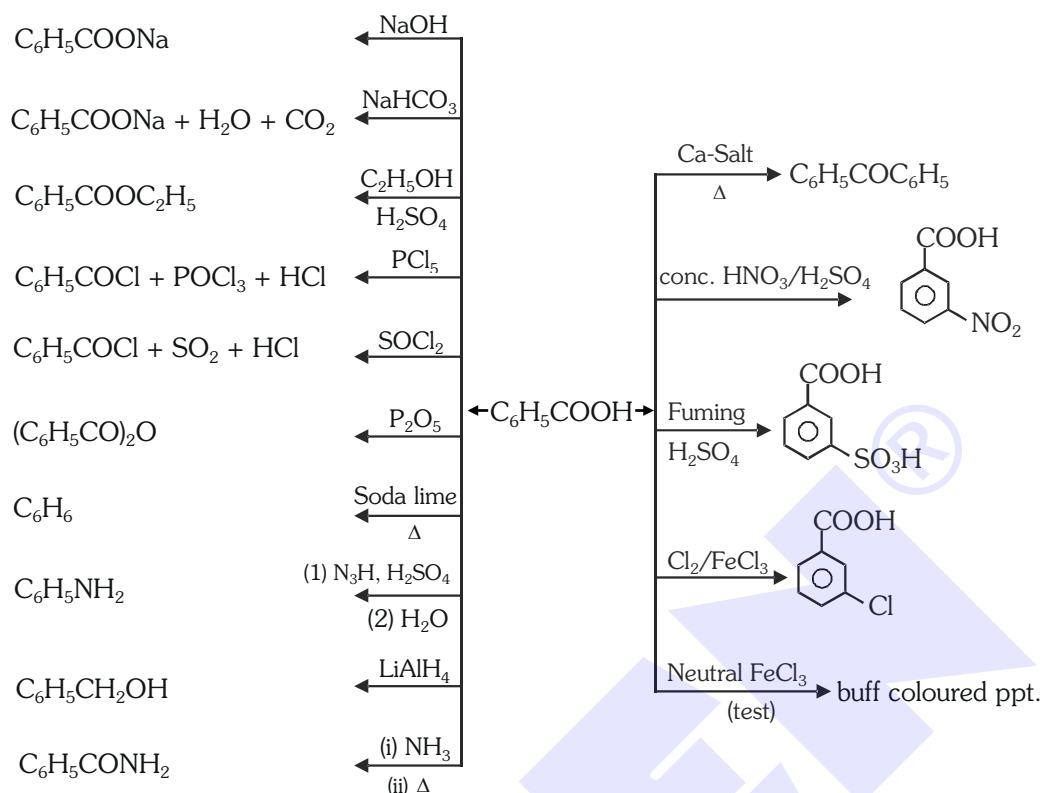
- As an antiseptic
- For preservation of fruits.
- For leather tanning.
- In dying wool and cotton fabrics.

Uses of Acetic Acid :

- Vinegar (6 - 10% solution) used as **table acid** and manufacture of pickles.
- For manufacture of rubber from latex and casein from milk CH₃COOH is used as coagulant.
- As a solvent and laboratory reagent.

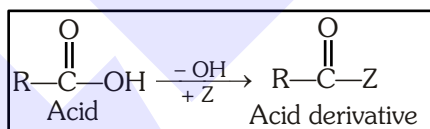
9.0 BENZOIC ACID (C₆H₅COOH)
9.1 General Method of Preparation :


9.2 Chemical properties



10.0 ACID DERIVATIVES

Replacement of $-OH$ group from a carboxylic group ($-COOH$) by a nucleophile like Cl^- , CH_3COO^- , $C_2H_5O^-$, NH_2^- , forms acid derivatives.

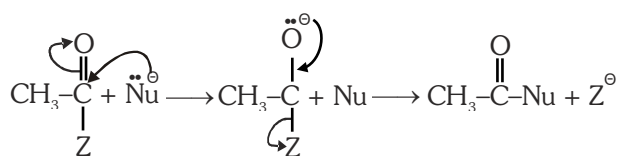


$R-\overset{O}{\parallel}C-$ is Acyl group and Z is nucleophile Cl^\ominus , CH_3COO^\ominus , $C_2H_5O^\ominus$, NH_2^\ominus

Ex. $CH_3-\overset{O}{\parallel}C-$ Acetyl group

Characteristic reaction for acid derivatives is nucleophilic substitution reaction :

Mechanism :

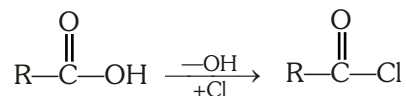


In this reaction Z is leaving group. Weak bases are good leaving groups.

Reactivity order : $CH_3COCl > CH_3COOCOCH_3 > CH_3COOC_2H_5 > CH_3CONH_2$

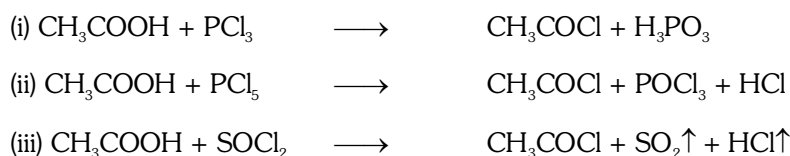
10.1 Acetyl Chloride

Replacement of —OH group from a —COOH group by Cl— atom gives acid chloride.

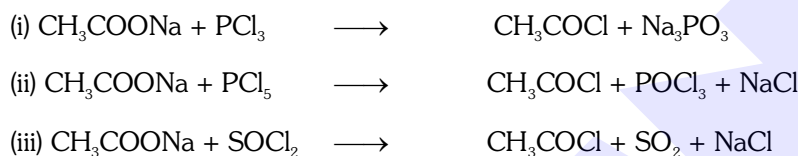


10.1.1 General Method of Preparation :

(a) By heating CH_3COOH with PCl_3 , PCl_5 & SOCl_2 :



(b) By heating the salt of acids with PCl_3 , PCl_5 or SOCl_2 :



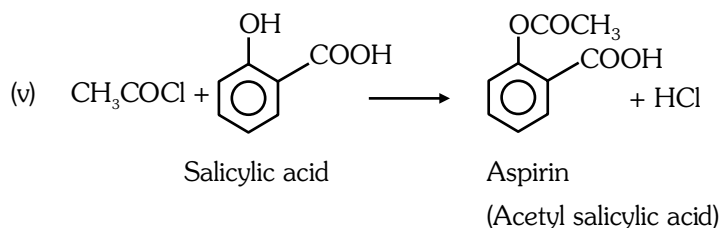
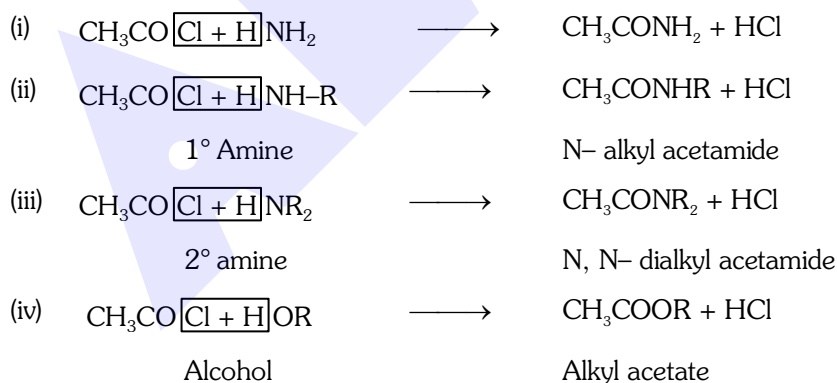
10.1.2 Physical properties :

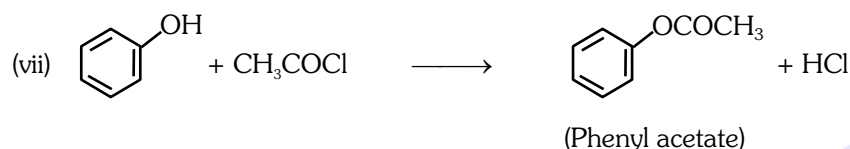
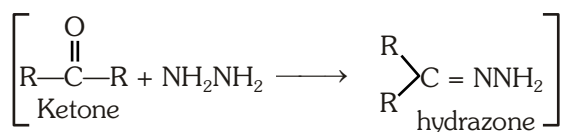
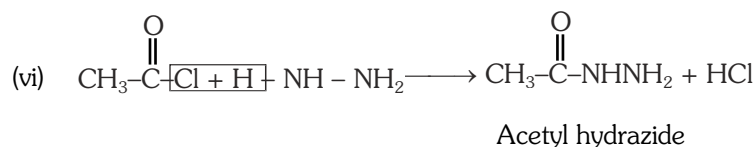
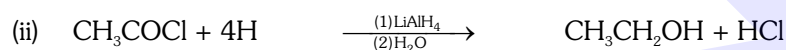
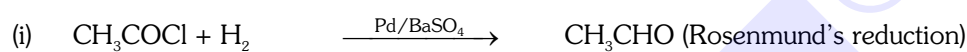
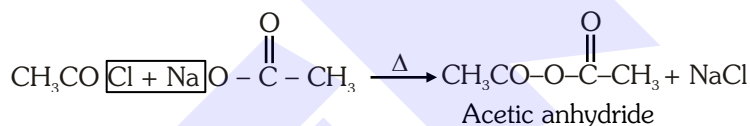
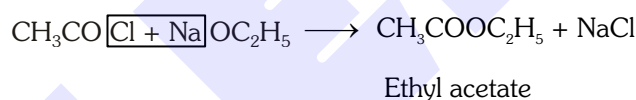
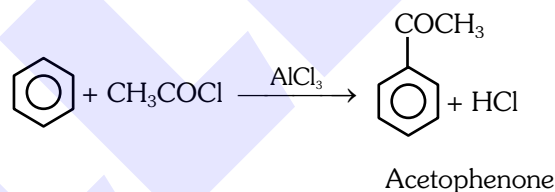
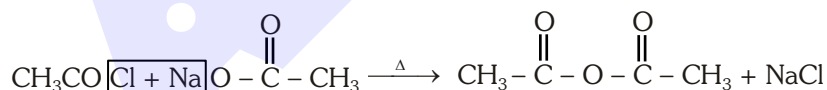
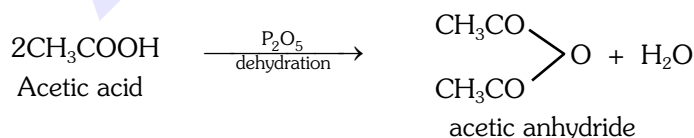
- (i) Pungent smelling liquid.
- (ii) Boiling point 52°C .
- (iii) Soluble in organic solvent, slowly soluble in water.
- (iv) It produces fumes in moist air due to the formation of HCl.

10.1.3 Chemical properties :

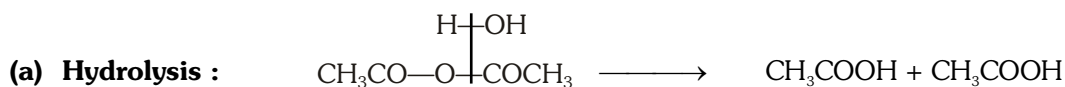
(a) Hydrolysis : $\text{CH}_3\text{CO}[\text{Cl} + \text{H}]\text{OH} \longrightarrow \text{CH}_3\text{COOH} + \text{HCl}$

(b) Reaction with active H - containing compounds (Acetylation) :

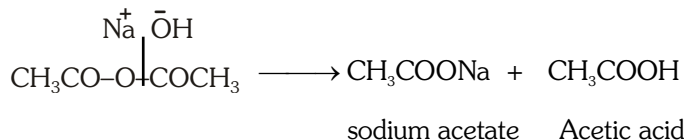


**(c) Reduction :****(d) With Sodium acetate :****(e) With Sodium ethoxide :****(f) Friedel crafts reaction :****10.2 Acetic Anhydride (Ethanoic Anhydride)****10.2.1 General Method of Preparation :****(a) By heating acetyl Chloride with anhydrous sodium acetate [Lab. Method] :****(b) By Dehydration of acetic acid :****10.2.2 Physical Properties :**

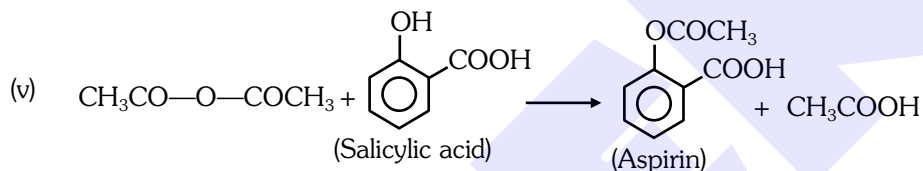
- (i) It is pungent smelling liquid.
- (ii) Sparingly soluble in water, soluble in ether & alcohol.
- (iii) Boiling point 139°C.

10.2.3 Chemical Properties :


Hydrolysis order : **Alkaline > Acidic > neutral**



(b) **Reaction with active H - containing compounds (Acetylation) :**



(c) **Reduction :** With LiAlH_4 in ether gives ethyl alcohol



(d) **Reaction with PCl_5 & SOCl_2 :**



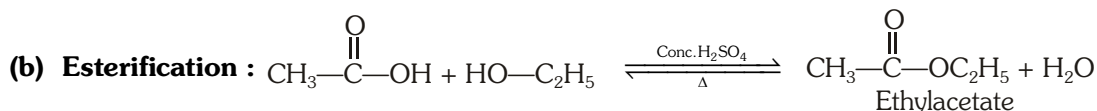
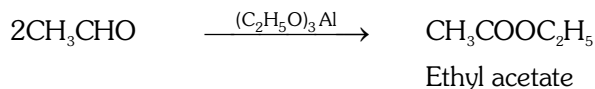
Phosphorous Oxychloride


10.2.4 Uses

- As an acetylating agent
- In the manufacture of cellulose acetate, aspirin, phenacetin, acetamide, & acetophenone etc.
- For detection and estimation of hydroxyl and amino group.

10.3 Ethyl acetate
10.3.1 General Method of Preparation :

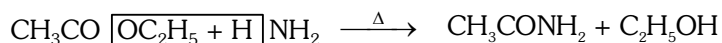
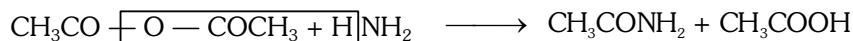
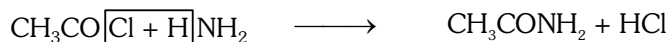
(a) **Tischenko reaction :** By treating acetaldehyde with aluminium ethoxide. (Modified cannizaro reaction)



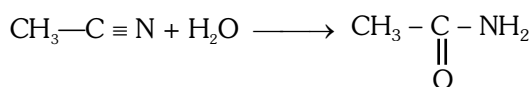
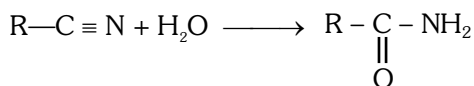
10.4 Acetamide

10.4.1 General Method of Preparation :

(a) Ammonolysis of acid derivatives :

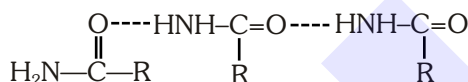


(b) Hydrolysis of alkyl cyanides : By the partial hydrolysis of alkyl cyanides.



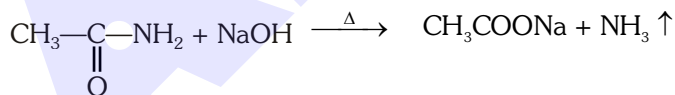
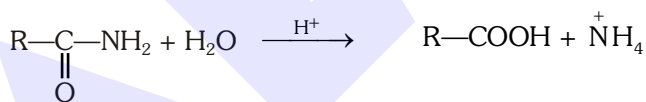
10.4.2 Physical Properties :

- (i) Acetamide is white crystalline solid.
- (ii) Pure acetamide is odourless.
- (iii) Impure acetamide - Smell like mouse.
- (iv) Lower amides are soluble in water, due to H-bonding.
- (v) Their higher M. P. and B. P. are due to intermolecular H- bonding.

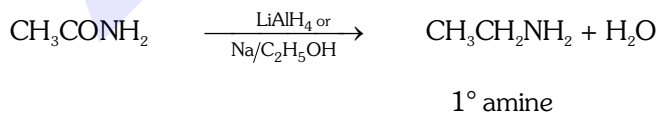


10.4.3 Chemical Properties :

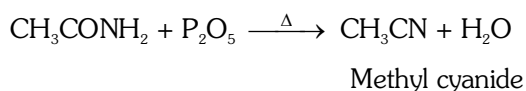
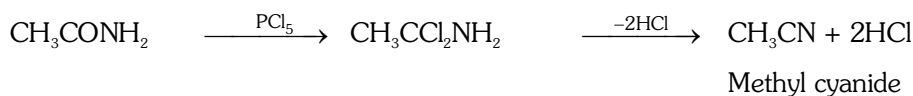
(a) Hydrolysis : Amides are hydrolysed rapidly in acidic medium. In alkaline medium hydrolysis is carried out in temperature condition.

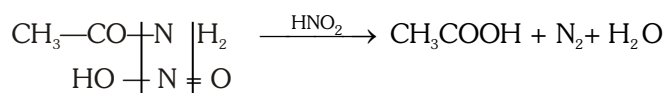
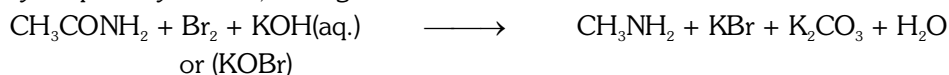
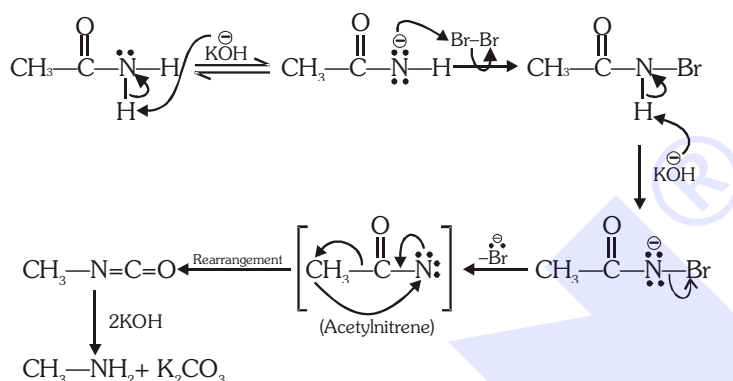


(b) Reduction to primary amines : Amine contains same number of carbon atoms.



(c) Dehydration with PCl₅, SOCl₂ or P₂O₅ :



(d) Reaction with nitrous acid :**(e) Hoffmann's bromamide degradation reaction :** Amides on reaction with bromine, and NaOH or KOH yield primary amines, having one C-atom less than the amides.**Mechanism :**

ANSWER'S KEY

BEGINNER'S BOX-1	Que.	1	2	3							
	Ans.	3	4	2							
BEGINNER'S BOX-2	Que.	1	2								
	Ans.	1	2								
BEGINNER'S BOX-3	Que.	1	2	3							
	Ans.	3	2	3							
BEGINNER'S BOX-4	Que.	1	2	3							
	Ans.	2	4	1							
BEGINNER'S BOX-5	Que.	1	2	3							
	Ans.	4	2	3							
BEGINNER'S BOX-6	Que.	1	2	3	4						
	Ans.	2	1	3	1						