ORGANIC CHEMISTRY

Topic-1

Halogen compounds

VERY SHORT ANSWER QUESTIONS

1. **How halogen compounds are classified?**

Ans: Compounds derived from hydrocarbons by the replacement of one or more hydrogen atom(s) by the corresponding number of halogen atom(s) are known as halogen derivatives. The halogen derivatives are classified on the basis of nature of hydrocarbon from which they are obtained as

(i) Alkyl halides: Halogen derivative of alkanes

(ii) Alkenyl halides: Halogen derivative of alkenes (Not included in syllabus)

(iii) Alkynyl halides: Halogen derivative of alkynes (Not included in syllabus)

(iv) Aryl halides: Halogen derivative of arenes. (See aromatic part)

2. How Alkyl halides are classified?

Alkyl halides are further classified as

(i) Mono halides: These involve replacement of one H atom by halogen atoms i.e., $C_9H_{2n+1}X$ e.g.

CH_3Cl: methyl chloride or chloromethane

C_2H_5Cl: ethyl chloride or chloroethane

(ii) Di halides: These involve replacement of two H atoms by halogen atoms i.e., $C_8H_{2n}X_2$

CH_2X : methylene halide

$\begin{matrix} CH_2X \\ | \\ CH_2X \end{matrix}$: ethylene dihalide or vicinal dihalides

$\begin{matrix} CH_3 \\ | \\ CHX_2 \end{matrix}$: ethylidene dihalide or geminal dihalides

(iii) Tri halides: These involve replacement of three H atoms by halogen atoms i.e. $C_nH_{2n-1}X_3$ e.g.,

CHX_3: trihalo methane or haloform

(iv) Tetra halide: These involve replacement of four H atoms by halogen atoms i.e. $C_nH_{2n-2}X_4$ e.g., CCI_4.

3. **How mono halides are classified?**

Monohalides or Alkyl halides

(1) General formula $C_nH_{2n+1}X$ e.g., CH_3X, C_2H_5X, ...

(2) Mono halides are further classified as

(A) Primary halides: Halogen atom attached on 1^o carbon or methyl carbon

e.g. CH_3X : halomethane or methyl halide

CH_3CH_2X : haloethane or ethyl halide

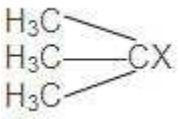
$CH_3CH_2CH_2X$: 1-halopropane or n-propyl halide

(B) Secondary halides: Halogen atoms are attached on 2^o carbon atom

CH_3CHXCH_3 : 2-halopropane or sec. propyl halide or isopropyl halide

$CH_3CHXCH_2CH_3$: 2-halobutane or sec. butyl halide

(C) Tertiary halides : Halogen atoms are attached on 3^o carbon atom



: 2-methyl, 2-halopropane or t.butyl halide

SHORT ANSWER QUESTIONS

1. **Give the methods of preparation of monohalides**

Preparation of Monohalides:

(1) By direct halogenations of alkanes: (See halogenations of alkanes)

$$R\text{-} + X_2 \xrightarrow[\text{or heat}]{\text{U.V light}} R\text{-}X + HX$$

(2) By the addition of HX on alkenes:

$RCH{=}CHR + HX \rightarrow RCH_2\text{-}CHXR$

$CH_2{=}CH_2 + HX \rightarrow CH_3\text{-}CH_3X$

$CH_3CH{=}CH_2 + HX \rightarrow CH_3CHXCH_3$ (Acc. to Markownikoff rule).

(3) By alcohols:

(a) Action of halogen acids:

$$R{-}OH + HCl_g \text{ or } HCl_{conc} \xrightarrow[\text{primary and secondary alcohols}]{ZnCl_2 \text{ is needed for}} RCl + H_2O$$

$$R{-}OH + \underset{48\%}{HBr} \xrightarrow[\text{needed for primary alcohols}]{ZnCl_2 \text{ or } H_2SO_4 \text{ is}} RBr$$

$$R{-}OH + \underset{57\%}{HI} \rightarrow RI$$

The reactivity order for alcohols is: tertiary > secondary > primary alcohol

The reactivity order for halogen acid is: HI > HBr > HCI

Note: Bromides and iodides are also obtained as:

$$ROH + KBr + H_2SO_4 \xrightarrow{\Delta} RBr + KHSO_4 + H_2O$$

$$ROH + KI + H_2SO_4 \xrightarrow{\Delta} RI + KHSO_4 + H_2O$$

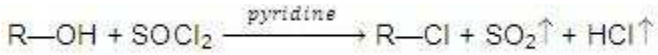
(b) Action of phosphorus halides:

$3ROH + PCI_3 \rightarrow 3RCI + H_3PO_3$

$ROH + PCI_5 \rightarrow RCI + POCI_3 + HCI$

Note: PBr_3 & PI_3 being less stable & thus for bromides & iodines, $P + Br_2$ or $P + I_2$ mixture is used.

(c) Action of thionyl chloride: or Darzen's method



Note: $SOBr_2$ is less stable & SOI_2 does not exist and thus bromides & iodides are prepared by this method.

Explain Borodine-Hunsdicker reaction.

Ans: Borodine-Hunsdicker reaction: Alkyl chlorides and alkyl bromides are obtained by the action of CI_2 or Br_2 in CCI_4 on silver salt of the fatty acids. The reaction proceeds through free radical mechanism.

$RCOOAg + X_2 \rightarrow R\text{-}X + CO_2\ AgX$

(in xylene) (CI2 or Br2)

Note:

1. The yield of alkyl halide is primary > secondary > tertiary

2. Hunsdiecker reaction is used to reduce the length of carbon chain (descent of series).

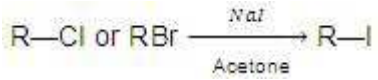
3. Only bromides are obtained in good yield in this reaction. The chlorides can also be obtained by this reaction but the yield is poor. Iodides however cannot be obtained because these form esters with silver salts.

$2RCO_2Ag + I_2 \rightarrow RCO_2R + CO_2 + 2AgI$

This reaction is called Birnbaurn-Simonini reaction.

2. Explain how halide exchange takes place.

Halide exchange: Iodides are usually prepared by this method. The halogen exchange reaction is called Finkelstein reaction.



This method is also used to prepare fluorides.

$2CH_3CI + Hg_2F_2 \rightarrow 2CH_3F + Hg_2CI_2$

3. Explain the physical properties of Alkyl halides.

Physical Properties of Alkyl Halides:

1. Physical state:

(a) CH_3CI, C_2H_5CI, CH_3Br only are gases at room temperature. The alkyl halides up to C_{18} are colourless liquids, while higher are colourless solids.

(b) The b.pt of halides shows following order:

Alkyl iodide > alkyl bromide > alkyl chloride (for a given alkyl group)

Methyl halide < ethyl halide < propyl halide (for a given halide)

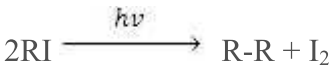
1^o halide > 2^o halide > 3^o halide (for a given halide and alkyl group)

2. Alkyl fluorides & alkyl chlorides are lighter than water, alkyl bromides and alkyl iodides are heavier than water. The density of halides thus follow the order : iodide > bromide > chloride > fluoride.

3. Alkyl halides are soluble in organic solvents but insoluble in water.

4. Alkyl halides burn on Cu wire with green edge flame. This is Beilstein test for halogens. The green or blue colour to flame is due to interaction of halogens with Cu wire.

5. Alkyl iodides are less stable and darken their colour on exposure to light on standing due to adsorption of liberated iodine.



4. Explain the chemical properties of Alkyl halides.

Chemical nature of Alkyl halides:

(a) The alkyl halides are highly reactive due to the high electronegativity difference between carbon & halogen atom which provides polarity in C^{+d} - X^{-d} bond & thus carbon atom of C-X bond is easily attacked by a nucleophile to show nucleophilic substitution.

$R\text{-}X + : N_u \rightarrow R\text{-}N_u + X :$

The nucleophilic substitution may follow S_N1 or S_N2 mechanism. In addition to nucleophilic substitution alkyl halides also show elimination reactions.

(b) Furthermore the reactivity order of alkyl halide is :

R-I > R-Br > R-CI > R-F

The reactivity does not follow the polarity order of bond. On the contrary it has been explained in terms of increasing bond length of C-X bond (maximum in C-I) which gives rise to lower bond energy and thus less stability to C-C bond.

(c) The reactivity order for given alkyl halide also shows the order :

3^o halide > 2^o halide > 1^o halide

This has been explained in terms of +ve inductive effect of alkyl groups which increases the polarity of C-X bond & thereby making it more reactive.

(d) Primary alkyl halides undergo reactions by S_N2 mechanism. The presence of bulky groups in primary halides (in spite of more +ve I.E.) cause steric hindrance & bring them less reactive towards.

S_N2 mechanism $CH_3X > C_2H_5X > C_3H_7X$

5. Explain the chemical properties of Alkyl halides.

Ans: 1. Wurtz reaction:

$$2RX \xrightarrow[\text{dry ether}]{2Na} R\text{—}R + 2NaX$$

$$2RX \xrightarrow[\text{Frankland reaction}]{Zn} R\text{—}R + ZnX_2$$

2. Action of halogen:

$$CH_3X + X_2 \xrightarrow[\text{u.v. light}]{h\nu} CH_2X_2 \xrightarrow{X_2} CHX_3 \xrightarrow{X_2} CX_4$$

Note: C_2Cl_6 (hexachloroethane) is a solid and is known as artificial camphor.

3. Dehydrogalogenation: An α, β-elimination of HX by KOH_{alc}.

$$CH_3CH_2X \xrightarrow[-HX,\ \Delta]{KOH_{alc}\ or\ NaNH_2} CH_2{=}CH_2$$

$$CH_3CHXCHCH_3 \xrightarrow[-HX]{KOH_{alc}} \underset{\text{Minor}}{CH_2{=}CHCH_2CH_3} + \underset{\text{Major}}{CH_3{-}CH{=}CHCH_3}$$

(Acc. to Saytzeff rule)

4. Action of heat: $RCH_2CH_2X \xrightarrow{300^oC} RCH{=}CH_2 + HX$

5. Reduction: $R\text{-}X + 2H \xrightarrow{Reducing\ agent} R\text{-}H + HX$

6. Reactions with metals:

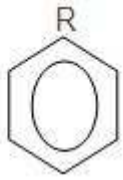
(a) $R{-}X + \underset{\text{(powder)}}{Mg} \xrightarrow{dry\ ether} \underset{\text{Grignard reagent}}{R{-}MgX}$

(b) $2C_2H_5Br + \underset{\text{(powder)}}{2Zn} \xrightarrow[\Delta]{ether} \underset{\text{diethyl zinc}}{(C_2H_5)2Zn} + ZnBr_2$

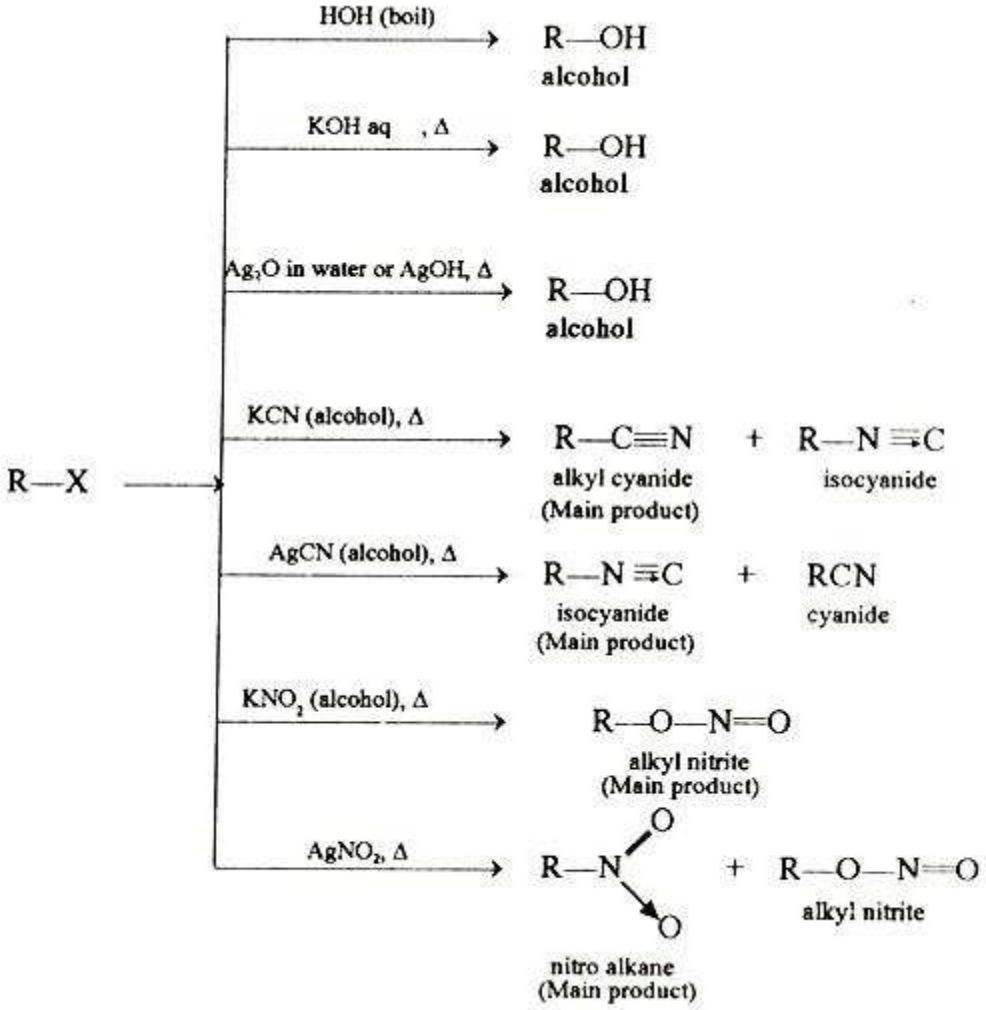
(c) $4C_2H_5Br + \underset{\text{sodium-lead alloy}}{4Pb(Na)} \rightarrow \underset{\substack{\text{tetra ethyl lead}\\ \text{(an antiknock compounds)}}}{(C_2H_5)_4Pb} + 4NaBr + 3Pb$

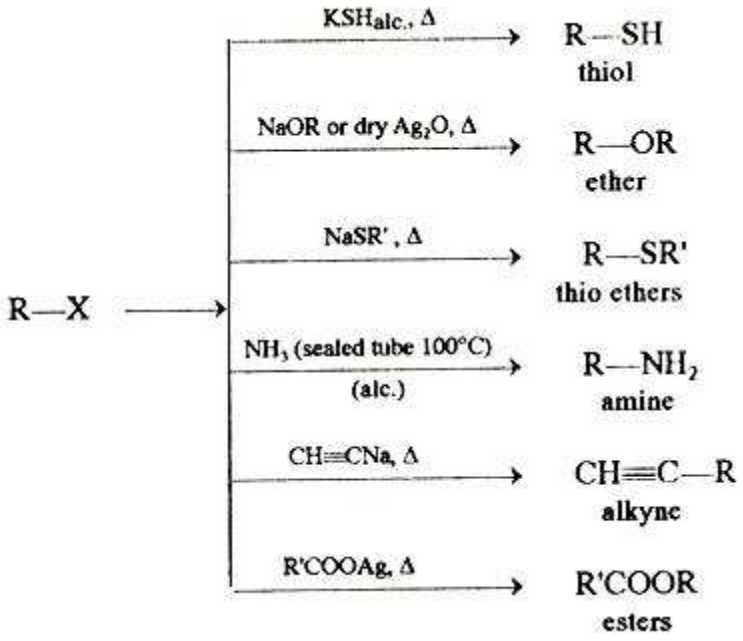
(d) $2C_2H_5Br + \underset{\text{sodium amalgam}}{Hg(Na)} \rightarrow (C_2H_5)_2Hg + NaBr$

7. Friedel-Crafts reaction: Alkyl halides react with benzene in presence of anhydrous $AlCl_3$ to form homologues of C_6H_6.

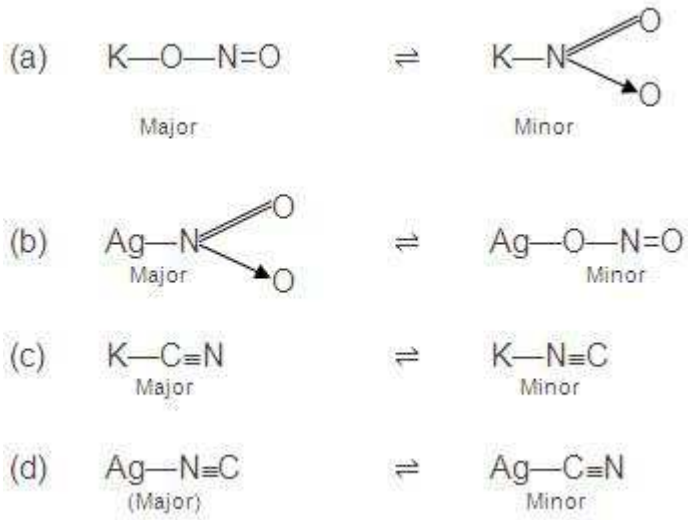
$$C_6H_6 + RCl \xrightarrow{AlCl_3} \text{} + HCl$$

8. Nucleophilic substitution on alkyl halides: Halogen atom of alkyl halides is easily replaced by other nucleophiles to give a large variety of S_N reactions.





Note: The two products formed on reaction of R-X with KNO_2 and $AgNO_2$ as well as with KCN and AgCN are due to tautomerism in these molecules.



Uses:

(i) As alkylating agent i.e. to introduce alkyl gp in a molecule.

(ii) Lower members are used as anaesthetic agent, refrigerant and solvents.

(iii) As synthetic reagent.

6. **Write a Short note on dihalides**

(i) Two H atoms of alkanes are replaced by two halogen atoms to form dihalides.

(ii) General formula $C_nH_{2n}X_2$.

(iii) Dihalides are classified as :

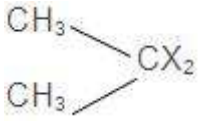
(a) Gem dihalides :

(i) The term gem has derived from geminal meaning for same position.

(ii) The two similar halogen atoms are attached to same carbon atom e.g.

CH_3CHX_2 ethylidene dihalide or 1, 1-dihaloehtane

$CH_3CH_2CHX_2$ propylidene dihalide or 1, 1-dihalopropane



isopropylidene dihalide or 2, 2-dihalopropane

(b) vic dihalides:

(i) The term vic has been derived from vicinal meaning for adjacent carbon atoms.

(ii) The two halogens are attached one each on adjacent carbon atoms e.g.

CH_2XCH_2X ethylene dihalide or 1, 2-dihaloethane

CH_3CHXCH_2X propylene dihalide or 1, 2-diahlopropane

(c) α-ω diahlides:

In these compounds halogen atoms are attached to terminal carbon atoms and are separated by three or more carbon atoms. They are also known as polymethylene halides e.g.

$CH_2X\text{-}CH_2\text{-}CH_2\text{-}CH_2X$ tetra methylene dichloride or 1, 4-dihalobutane

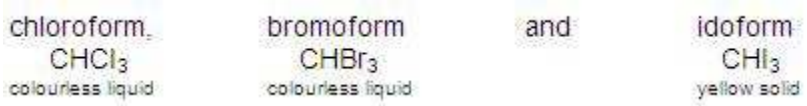
(iv) vic and gem diahalides are position isomers to each other.

7. **Write a note on trihalides?**

The trihalogen derivative of alkanes is prepared by replacement of three hydrogen atoms by three halogen atoms.

(ii) Their general formula is $C_nH_{2n-1}X_3$:

(iii) The trihalogen derivative of methane are also known as haloform



8. **How chloroform is prepared?**

Chloroform ($CHCl_3$) Preparation:

(i) Lab method and Industrial method: By the distillation of ethyl alcohol or acetone with bleaching Powder:

(a) Bleaching powder on hydrolysis gives slaked lime and CI_2 which acts as oxidizing agent as well as chlorinating agent.

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

By ethanol:

$$CI_2 + CH_3CH_2OH \rightarrow CH_3CHO + 2HCl \ (Cl_2 \text{ acts as oxidant})$$

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl \ (CI_2 \text{ acts as substituent})$$

$$2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca \ \text{(hydrolysis)}$$

chloroform Ca formate

By acetone:

$$CH_3COCH_3 + 3CI_2 \rightarrow CCl_3COCH_3 + 3HCI \ (Cl_2 \text{ acts as substituent})$$

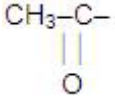
$$2\ CCl_3COCH_3 + Ca(OH)_2 \rightarrow 2\ CHCl_3 + (CH_3COO)_2Ca \ \text{(hydrolysis)}$$

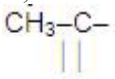
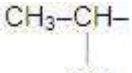
(b) Chloroform is collected with water in lower layer. It is washed with dilute alkali and dried over $CaCl_2$ and then redistilled at 60-65^oC.

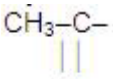
(c) The yield is better if acetone is used.

9. **Explain what is haloform reaction?**

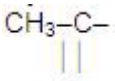
Haloform reaction :

(a) Acetaldehyde and all methyl ketones (2-ones) or carbonyl compounds having  units as well as alcohols [primary (only ethanol) and secondary (only 2-ol) which produce this unit on oxidation by halogen undergo haloform reaction on heating with halogen and NaOH to give haloform.

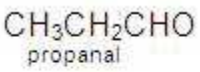
(b) If I_2 + NaOH is used, the haloform reaction yields yellow solid as precipitate confirming the presence of  unit or  in the molecule attached to C or H.

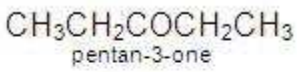
This is known as iodoform test for confirming the presence of acetaldehyde, methyl ketones and alcohols (which produce  unit on oxidation)

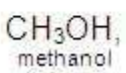
e.g.

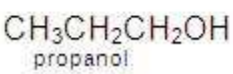
Reactants which give iodoform test because of  unit or producing this unit during oxidation :

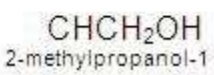


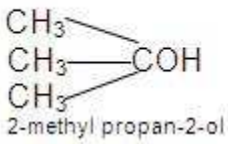












(Since it is not oxidised by I_2)

10. Write the physical properties of trihalides.

<u>Properties of Trihalides:</u>

(i) Pure chloroform and bromoform are colourless liquids, and iodoform is yellow solids.

(ii) All are heavier than water and soluble in organic solvents, but insoluble in water.

(iii) $CHCl_3$ brings temporary unconsciousness when vapours are inhaled for sufficient time and thus used as anaesthetic agent.

(iv) $CHCl_3$ is non inflammable but like other halides its vapours when ignited on Cu wire burn with green edge flame. (Beilstein test).

11. Explain what is Freon?

Freons: The chloro fluoro derivatives of methane and ethane are called freons. Some of the derivatives are: CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichloro difluro methane), HCF_2CHCl_2 (1, 1-dichloro 2, 2-difluoroethane). These are non-inflammable, colourless, non-toxic and low boiling liquids. These are stable upto 550^oC. The most important and useful derivative is CF_2Cl_2 which is commonly known as **Freon** on **Freon-12**.

Freon or freon-12 (CF_2Cl_2) is prepared by treating carbon tetrachloride with antimony trifluoride in the presence of antimony penta chloride (a catalyst).

$$3CCl_4 + 2SbF_3 \xrightarrow[\text{catalyst}]{SbCl_5} 3CCl_2F_2 + 2SbCl_3$$

or by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony penta fluoride.

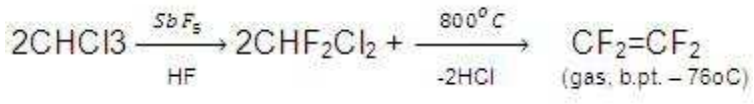
$$CCl_4 + 2HF \xrightarrow{SbF_5} CCl_2F_2 + 2HCl$$

Under normal conditions Freon is a gas. (b.pt. - 29.8^oC). It can easily be liquefied. It is chemically inert and is used in air-conditioning and in domestic refrigerators.

Note: Freon-14 is CF_4, Freon-13 is CF_3Cl, Freon-11 is $CFCl_3$. All these are used as refrigerant.

10. Explain what is Teflon?

Teflon: A plastic like substance produced by the polymerization of tetrafluoroethylene ($CF_2=CF_2$). Tetrafluoroethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.



On polymerization, tetrafluoro ethylene forms a plastic-like material which is called teflon.

$$nCF_2=CF_2 \rightarrow (CF_2\text{-}CF_2)_n$$

tetrafluoro ethylene Teflon

Teflon is chemically inert substances. It is not affected by strong acids and even by boiling aquaregia. It is stable at high temperature and thus, used for electrical insulation and preparation of gasket materials.

12. Expalin what is Westron?

Ans: Acetylene tetrachloride (Westron), $CHCl_2CHCl_2$:

Acetylene tetrachloride is also known as sym. tetrachloroethane. It is prepared by the action of chlorine on acetylene in presence of a catalyst such as ferric chloride, aluminium chloride, iron, quartz or kieselguhr.

$$CH{\equiv}CH + 2Cl_2 \rightarrow CHCl_2CHCl_2$$

In absence of catalyst, the reaction between chlorine and acetylene is highly explosive producing carbon and HCl. The reaction is less violent in presence of catalyst.

It is a heavy, non-inflammable toxic liquid with smell like $CHCl_3$. It is insoluble in water but soluble in organic solvents.

On further chlorination, it forms penta and hexachloroethane. On heating with lime (calcium hydroxide), it is converted to a useful product **westrosol** (CCl_2=CHCl)

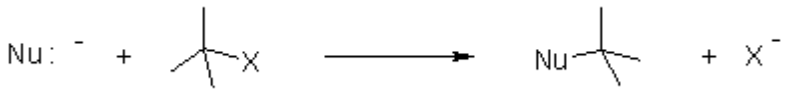
$$2C_2H_2Cl_4 + Ca(OH)_2 \rightarrow 2CHCl_2{=}CCl_2 + CaCl_2 + 2H_2O$$

Both westron and westrosol are used as solvent for oils, fats and varnishes

LONG ANSER QUESTIONS

1. **Explain the mechanisms of nucleophilic substiturion reactions SN^1 and SN^2**

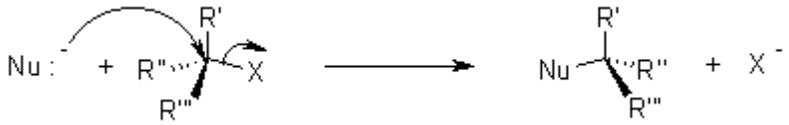
Nucleophilic Substitution (S_N1 and S_N2)



Nucleophilic substitution is the reaction of an electron pair donor (the nucleophile, Nu) with an electron pair acceptor (the electrophile). An sp^3-hybridized electrophile must have a leaving group (X) in order for the reaction to take place.

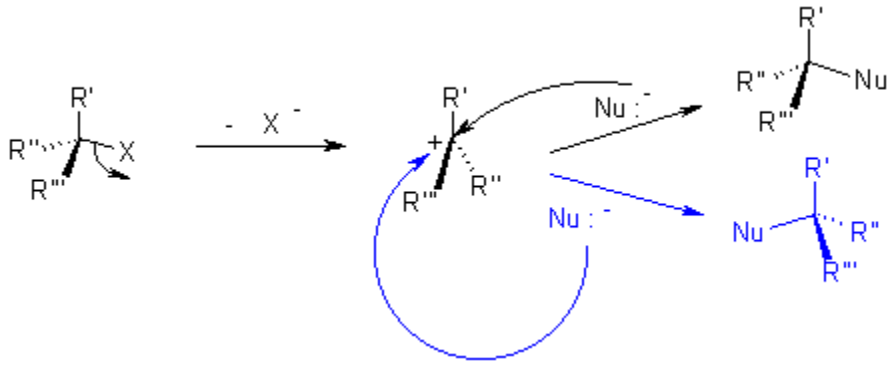
Mechanism of Nucleophilic Substitution

The term S_N2 means that two molecules are involved in the actual transition state:



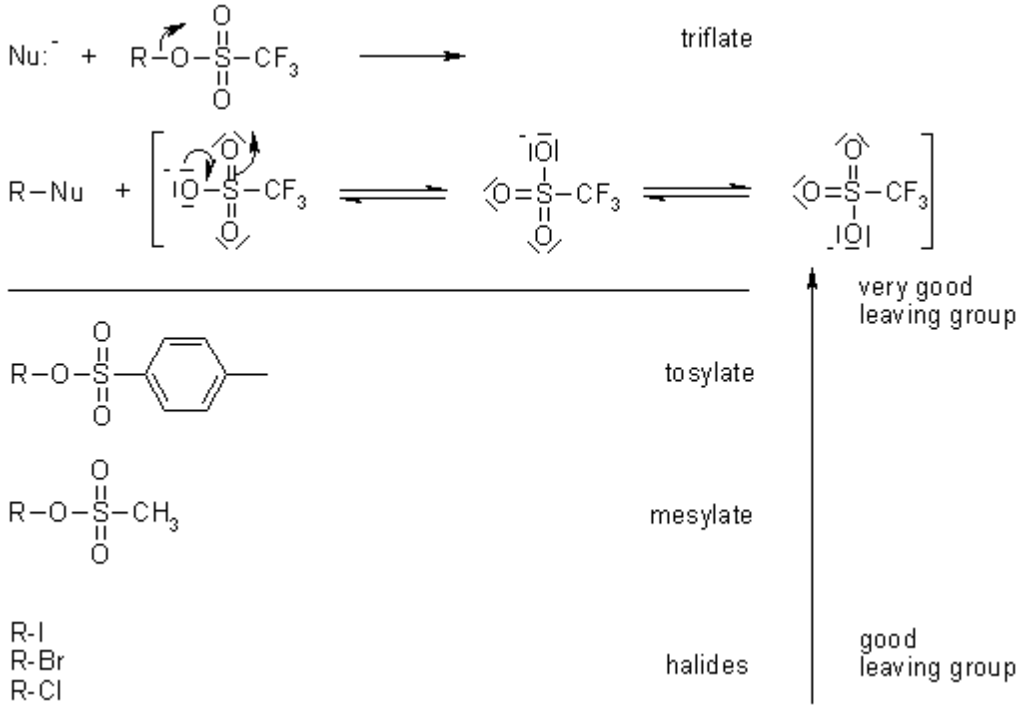
The departure of the leaving group occurs simultaneously with the backside attack by the nucleophile. The S_N2 reaction thus leads to a predictable configuration of the stereocenter - it proceeds with inversion (reversal of the configuration).

In the S_N1 reaction, a planar carbenium ion is formed first, which then reacts further with the nucleophile. Since the nucleophile is free to attack from either side, this reaction is associated with racemization.

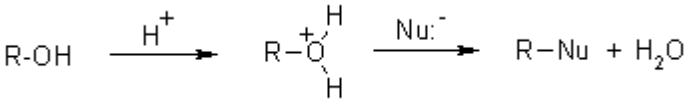


In both reactions, the nucleophile competes with the leaving group. Because of this, one must realize what properties a leaving group should have, and what constitutes a good nucleophile. For this reason, it is worthwhile to know which factors will determine whether a reaction follows an S_N1 or S_N2 pathway.

Very good leaving groups, such as triflate, tosylate and mesylate, stabilize an incipient negative charge. The delocalization of this charge is reflected in the fact that these ions are not considered to be nucleophilic.



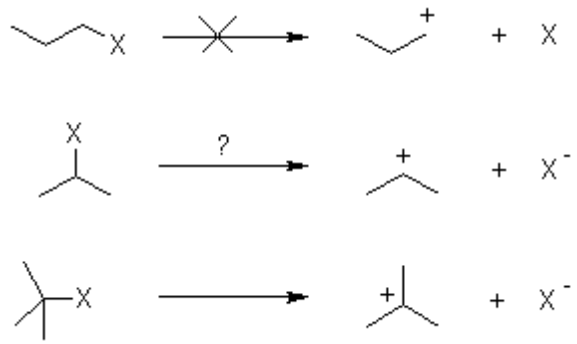
Hydroxide and alkoxide ions are not good leaving groups; however, they can be activated by means of Lewis or Brønsted acids.



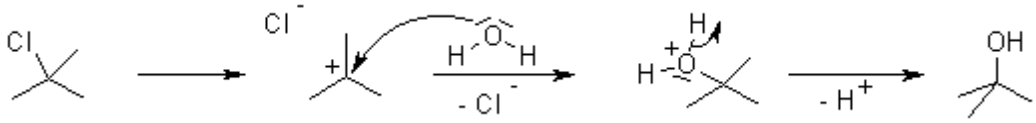
The solvent also plays an important role in determining which pathway the reaction will take, S_N1 versus S_N2. It may safely be assumed that a primary-substituted leaving group will follow an S_N2 pathway in any case, since the formation of the corresponding unstable primary carbenium ion is disfavored. Reaction by the S_N1 pathway is highly probable for compounds with tertiary substitution, since the corresponding tertiary carbenium ion is stabilized through hyperconjugation:

The better the solvent stabilizes the ions, the more probable that the reaction will follow an S_N1 pathway (e.g., in polar protic solvents such as water/acetone). The more highly substituted is the incipient carbenium ion, the more probable that the reaction will follow an S_N1 pathway. The more unreactive the nucleophile, the more probable it becomes that a reaction with secondary and tertiary electrophiles will follow an S_N1 pathway. A weaker nucleophile is not as effective in the backside attack, since this location is sterically shielded, especially in the case of tertiary substrates. Carbenium ions are planar

and therefore less sterically hindered, and are naturally more reactive as electrophiles than the uncharged parent compound.



The hydrolysis of tert-butyl chloride is a typical S_N1 reaction:

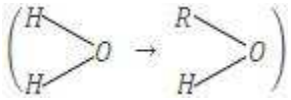


ORGANIC CHEMISTRY

TOPIC: 2 HYDROXY COMPOUNDS, ALCOHOLS AND PHENOLS

VERY SHORT ANSWER QUESTIONS

1. **What are alcohols?**

Alcohols are regarded as mono alkyl derivative of water 

or hydroxyl derivative of hydrocarbons e.g.

$CH_4 \rightarrow CH_3OH$ methyl alcohol (saturated alcohol)

$CH_2{=}CH_2 \rightarrow CH_2{=}CHOH$ vinyl alcohol (unsaturated alcohols)

2. **What are monohydric alcohols?**

Ans: Monohydric alcohols: Containing two OH group e.g. CH_3OH methyl alcohol

3. **What are dihydric alcohols?**

Ans: Dihydric alcohols : Containing two OH group

e.g. CH_2OH

|

CH_2OH

Glycol

4. **What are polyhydric alcohols?**

Ans: Polyhydric alcohols: Containing more than two OH group

e.g. $CH_2OHCHOHCH_2OH$

Glycerol

5. **Why alcohols with two hydroxyl groups present on the same carbon do not exist?**

Ans: If two or more hydroxyl groups attached to same carbon atom, the compound is usually unstable and lose a molecule of water to give a stablecompound and therefore two or more hydroxyl groups must be present on different carbon atoms.

6. What is power alcohol?

Ans: **Power alcohol:**

Rectified spirit + C_6H_6 + Petrol, for generation of power.

7. What is methylated spirit?

Methylated spirit:

(i) Methanol + Pyridine + mineral naptha + Rectified spirit.

(ii) These are added to make sure that it will not be used for beverages. This process is known as denaturation & alcohol is known as denatured spirit.

Type:

(a) Mineralized methylated spirit: 90% Rectified spirit + 10% methanol or pyridine or naphtha

(b) Industrial methylated spirit: 95% Rectified spirit, 5% methanol.

8. What is proof spirit?

Proof spirit:

(i) The % of alcohol is expressed in terms of proof spirit for tax levied on it.

(ii) Proof spirit is ethanol (57.1%) + water

(iii) The weakest possible alcohol % which allows gun powder to catch fire is known as proof spirit.

(iv) 10^o under proof means 100 volume of sample containing as 90 volume of proof spirit.

(v) 10^o over proof means 100 volume of sample containing as 110 volume of proof spirit.

(vi) The determination of strength of alcohol is known as alcoholometry.

(vii) A sample is called over under proof, as it is stronger or weaker than proof spirit.

SHORT ANSWER QUESTIONS

1. **How monohydric alcohols are classified?**

Ans; Monohydric alcohols:

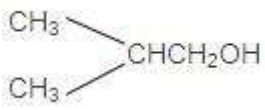
General formula C_nH_{2n+1} OH or $C_nH_{2n+2}O$; usually represented by R-OH where R is alkyl group.

Monohydric alcohols are further classified as

(a) Primary alcohols: -OH group attached on 1^o carbon atom; group : $-CH_2OH$

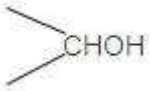
$H\text{-}CH_2OH$, CH_3CH_2OH, $CH_3CH_2CH_2OH$, $CH_3CH_2CH_2OH$

methyl alcohol ethyl alcohol n-propyl alcohol n-butyl alcohol



isobutyl alcohol

(b) Secondary alcohols: -OH group attached on 2^o carbon atom; group:

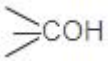


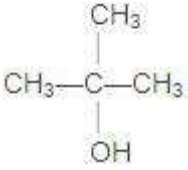
CH_3CHCH_3 $CH_3CH_2CHCH_3$

| |

OH OH

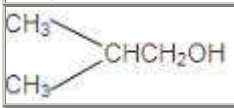
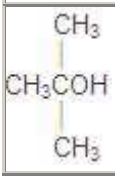
isopropyl alcohol sec. butyl alcohol

(c) Tertiary alcohols: -OH groups attached on 3^o carbon atom; group: 



is tertiary butyl alcohol

2. **Write the nomenclature of alcohols.**

Nomenclature :	**Common name**	**Carbinol name**	**IUPAC name**
CH_3OH	methyl alcohol	carbinol	methanol
CH_3CH_2OH	ethyl alcohol	methyl carbinol	ethanol
$CH_3CH_2CH_2OH$	n-propyl alcohol	ethyl carbinol	propanol-1
$CH_3CHOHCH_3$	isopropyl alcohol	dimethyl carbinol	propanol-2
$CH_3CH_2CH_2CH_2OH$	n-butyl alcohol	propyl carbinol	butanol-1
	isobutyl alcohol	isopropyl carbinol	2-methylpropanol-1
$CH_3CH_2CHOHCH_3$	sec.butyl alcohol	ethylmethylcarbinol	butan-2-ol
	t-butyl alcohol	trimethyl carbinol	2-methylpropan-2-ol

3. **Explain the isomerism in alcohols.**

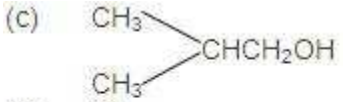
Ans: Isomerism: Molecular formula $C_nH_{2n+2}O$ of alcohols show following types of isomerism.

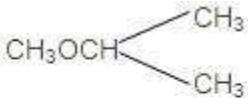
C_3H_8O : $CH_3CH_2CH_2OH$ and $CH_3CHOHCH_3$ are position isomers

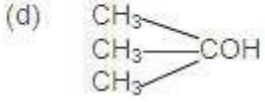
Alcohols **Ethers**

$C_4H_{10}O$: (a) $CH_3CH_2CH_2CH_2OH$ (e) $CH_3CH_2OCH_2CH_3$

(b) $CH_3CH_2CHOHCH_3$ (f) $CH_3OCH_2CH_2CH_3$

(c) 

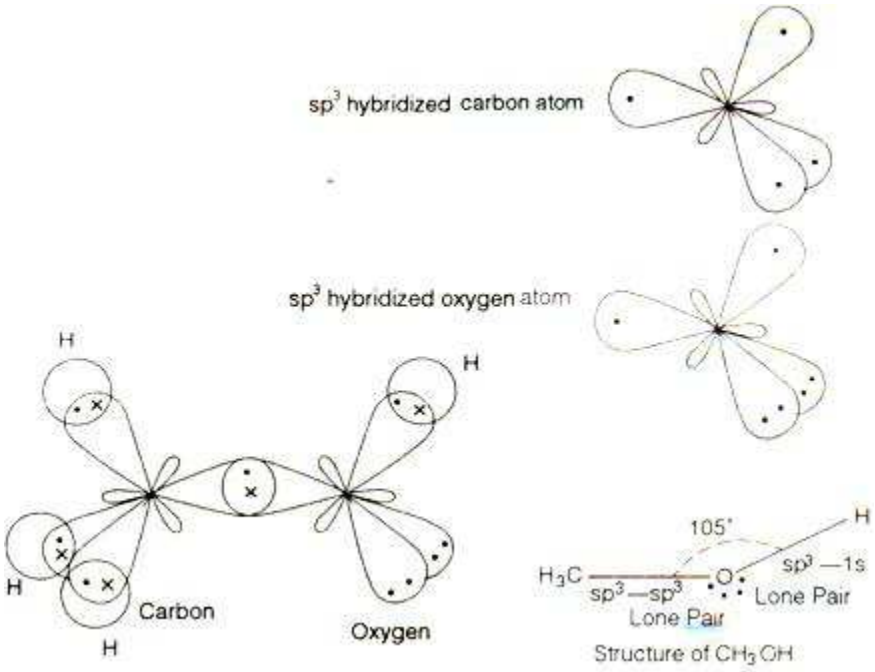
(g) 

(d) 

In all 7 isomers of $C_4H_{10}O$ are noticed among which are **chain isomers (a & c), position isomers (a & b), functional isomers (an alcohol & an ether) as well as metamers (e, f, g).** Also formula (b) **shows optical isomers** for butan-2-ol as it has one asymmetric carbon atom C*.

4. **Explain the structure and chemical behaviour of alcohols.**

Ans: Structure: In alcohols carbon as well as oxygen both show sp^3 hybridization. In carbon all the four sp^3 hybridized orbitals have on electron in each orbital whereas in oxygen two of the four sp^3 hybridized orbitals have one electron & rest two orbitals have on electron pair in each. These two completely filled orbitals in oxygen atom do not take part in bonding and give rise to contraction in bond angles due to lone pair effect and therefore the bond angle C-O-H is 105^o which is lesser than the normal tetrahedral structure.



LONG ANSWER QUESTIONS

1. **Explain the general methods of preparation of alcohols.**

Ans: General methods of preparation of Alcohols

(i) By the hydrolysis of alkyl halides: A nucleophilic substitution.

$$R\text{-}X + KOH_{aq} \rightarrow R\text{-}OH$$

The method is not satisfactory as olefins are also formed as by-products. However better yields is obtained by using moist Ag_2O or aqueous K_2CO_3. Tertiary butyl halides mainly give alkene due to dehydrohalogenation.

(ii) (a) By the hydration of alkenes : An electrophilic addition of H_2O.

$$CH_2=CH_2 + H_2SO_4 \rightarrow CH_3\text{-}CH_2HSO_4 \xrightarrow{H_2O} CH_3CH_2OH$$

$$RCH=CH_2 + H_2SO_4 \rightarrow RCH\text{-}CH_3 \xrightarrow{H_2O} RCHOHCH_3$$

$$\Big|$$

$$HSO_4$$

Except ethyl alcohol no other primary alcohol can be obtained by this method, however hydroboration of terminal alkenes give primary alcohols.

$$6R\text{–}CH=CH_2 + B_2H_6 \rightarrow \underset{\text{tri alkyl borane}}{2(R\text{–}CH_2\text{–}CH_2)_3B} \xrightarrow{H_2O_2} 6RCH_2CH_2OH + 2H_3BO_3$$

(b) By oxymercuration and demercuration of alkanes : Alkenes react with mercuric acetate in presence of H_2O and tetra hydrofuran to give alkyl mercury compounds.

$$RCH=CH_2 \xrightarrow[THF\text{-}H_2O]{Hg(OOCCH_3)_2} \underset{\substack{OH \quad HgOOCCH_3 \\ \text{hydroxyalkyl mercury compound}}}{R\text{—}CH\text{—}CH_2}$$

These mercury compounds on reducing with $NaBH_4$ give alcohols.

$$R\text{—}\underset{OH}{CH}\text{—}\underset{HgOOCCH_3}{CH_2} \rightarrow RCHOHCH_3$$

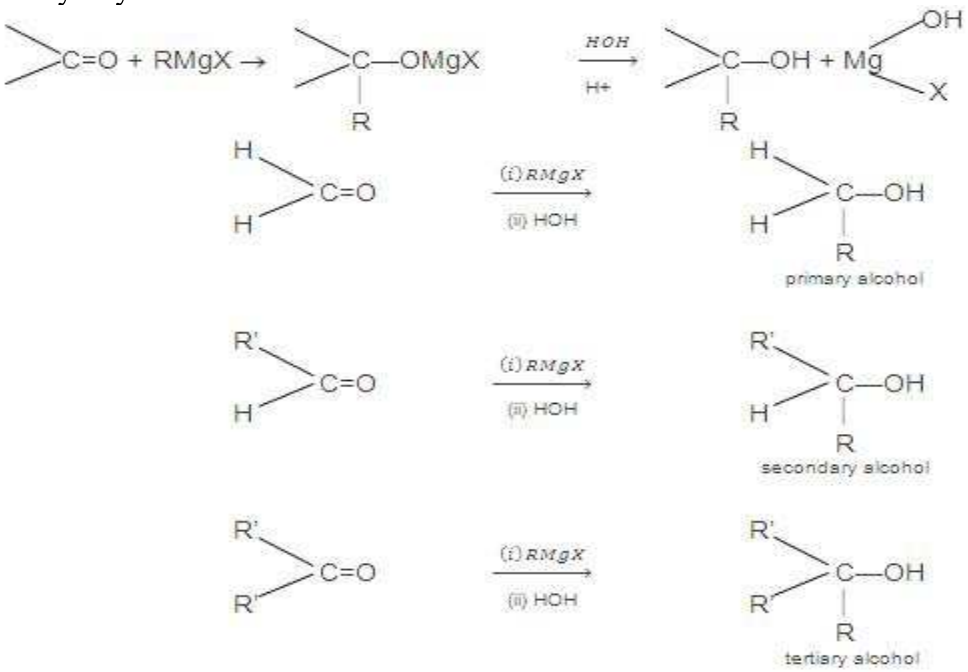
(iii) By the hydrolysis of ethers:

$$R\text{-}O\text{-}R' + HOH \xrightarrow[\text{high P, T}]{dil\ H_2SO_4} R\text{-}OH + R'OH$$

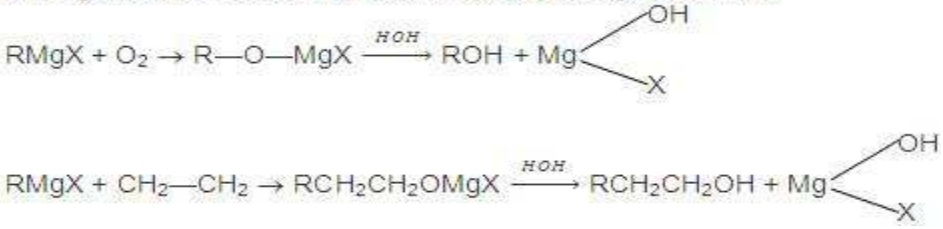
(iv) By the hydrolysis of esters:

$$R\text{—}\underset{\underset{O}{\|}}{C}\text{—}OR' + HOH \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$$

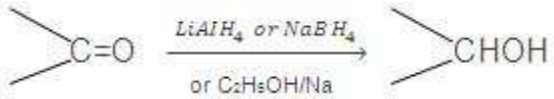
(v) By Grignard reagents: All the three types of monohydric alcohols (primary, secondary and tertiary alcohols) are obtained by the use of Grignard reagents and carbonyl compounds. The addition of RMgX on carbonyl compounds followed with hydrolysis yields alcohols.



Grignard reagents also reacts with O_2 and epoxides to give alcohols.



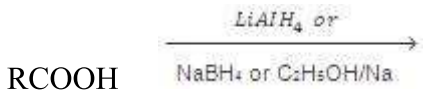
(vi) By the reduction of carbonyl compounds: Reduction of **aldehydes gives primary alcohol and**

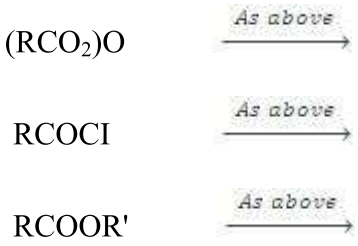


Reduction of ketones gives secondary alcohol.

Note: tertiary alcohols can be obtained by this method.

(vii) By the reduction of acids and their derivatives:





Note: If C_2H_5OH + Na is used as reducing agent, the reduction is known as Bouveault-Blane reaction.

(viii) By the action of nitrous acid on primary amines:

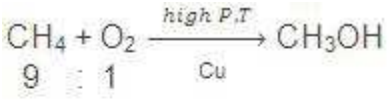
$$R\text{-}NH_2 + HNO_2 \rightarrow R\text{-}OH + N_2 + H_2O$$

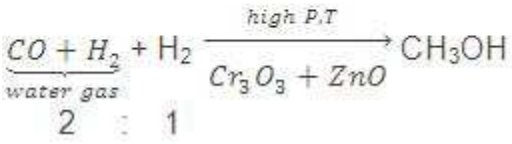
However under similar conditions CH_3NH_2 gives $CH_3\text{-}O\text{-}N{=}O$ or CH_3OCH_3

$$CH_3NH_2 + 2HNO_2 \rightarrow CH_3\text{-}O\text{-}N{=}O + 2H_2O + N_2$$

or $$2CH_3NH_2 + 2HNO_2 \rightarrow CH_3OCH_3 + 2N_2 + 3H_2O$$

(ix) Methanol can also be prepared as





2. **Explain how ethyl alcohol is prepared by fermentation?**

By fermentation:

(i) Fermentation is the slow decomposition of complex organic compounds into simpler organic compounds by the activity of enzymes. Enzymes are complex, nitrogenous (proteins), non living macro molecules of high molecular weight derived from living organisms. These are also known as biological catalysts.

(ii) Fermentation process is generally accompanied with evolution of gases like CO_2 & CH_4 and is exothermic in nature.

(iii) The alcoholic fermentation involves conversion of sugar into ethyl alcohol by yeast.

(iv) The starting material for alcoholic fermentation is starch (potato, rice, barley, maize). The source of starch depends upon its availability in that country. In India, alcoholic fermentation is made by molasses i.e. the dark coloured syrupy liquid left after crystallization of sugar from sugar cane juice. Molasses contains about 50% sugar left after crystallization of sugar from cane juice.

(v) An outline of alcoholic fermentation is given below.

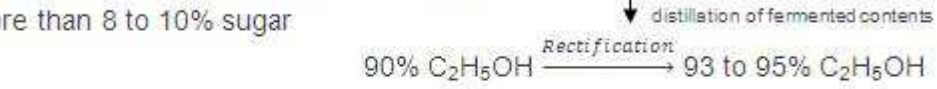
Step I

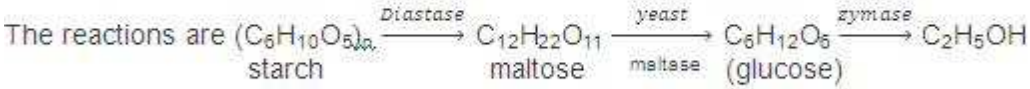
Starchy material, mashed with hot water and Maltose extracted solution is taken

$\xrightarrow[\text{heated with malt at } 50^0C \text{ malt is germinated barley containing diastase enzyme}]{}$

Step II

Maltose obtained from starch or molasses solution diluted to the extent to have not more than 8 to 10% sugar $\xrightarrow[\text{few days at 30oC}]{\text{Add yeast \& keep it for}}$ Fermentation contents







Conditions favorable for fermentation:

1. Optimum temperature range for fermentation s 25-30^oC. At higher temperature enzymes are coagulated.

2. Certain inorganic substances, $(NH_4)_2SO_4$, phosphate etc are added as food for ferment cells.

3. Solution to be fermented should be dilute.

4. Substances like boric acid, mercury slats etc. should not be present as they retard fermentation.

5. Proper aeration should be maintained in fermentation.

Note: The name fermentation has been derived from Latin word ferver meaning to boil, because during fermentation there is lot of frothing due to evolution of CO_2 and this gives the appearance of boiling liquid.

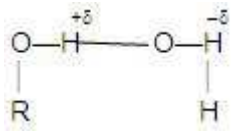
3. **Explain the physical and chemical properties of alcohols.**

Ans: <u>Physical Properties of Alcohols</u>

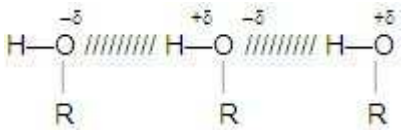
Properties:

(i) Lower alcohols are colourless, volatile, toxic, inflammable liquids with burning taste and spirituous odour. Above C_{12}, alcohols are solid.

(ii) Lower alcohols are soluble in water due to H-bonding, however their solubility decreases with increase in molecular weight of alcohols due to increasing nature of hydrophobic nature (to recedes away from H_2O) of alkyl chain.



(iii) Boiling point of alcohols are much higher than those of corresponding alkanes and thiols due to H-bonding.



However the isomeric alcohols shows the b.pt. order :

primary > secondary > tertiary.

(iv) Alcohols are neutral and do not influence the pH of solution and thus alcohols are weaker acids than water. The basic character: $OC_2H_5 > OH^-$

(v) Lower alcohols form solid derivatives with metallic salt in which alcohol molecule show salvation phenomenon. e.g.

$CaCI_2.4CH_3OH$; $MgCI_2.6CH_3OH$; $CaCI_2.4C_2H_5OH$; $MgCI_2.6C_2H_5OH$

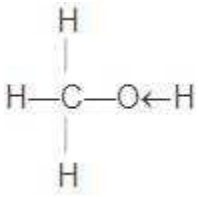
That is why alcohols cannot be dried by anhydrous $CaCl_2$.

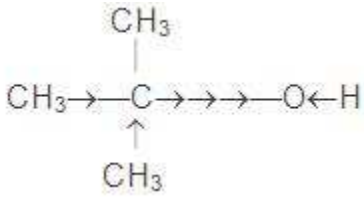
Chemical nature:

(i) Reactions involving H atom of -OH group: All such reactions involving replacement of H atom of -OH group represent Bronsted acid nature of alcohols. The Bronsted acid nature shows the order:

Methyl alcohols > 1^o > 2^o > 3^o alcohol

The tendency to attract electron pair of O-H bond by O atom decreases by the +ve I.E. of CH_3 groups as it intensifies the partial -ve charge on oxygen atom & thus tendency to release H atom decreases in tertiary alcohols.





Following reactions of this category are noticed.

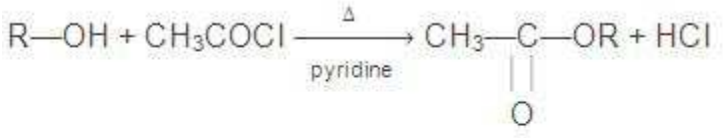
(a) Action of active metals: Strong electropositive metals like Na, K, Ca & Mg react with alcohols forming alkoxides with the liberation of H_2 gas.

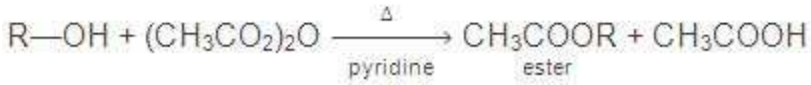
$$R\text{-}OH + Na \rightarrow R\text{-}ONa + 1/2H_2.$$

(b) Action of carboxylic acids or esterification: Alcohols on reacting with anhydrous acids in presence of conc. H_2SO_4 form esters. Concentrated H_2SO_4 acts as catalyst as well as dehydrating agent.

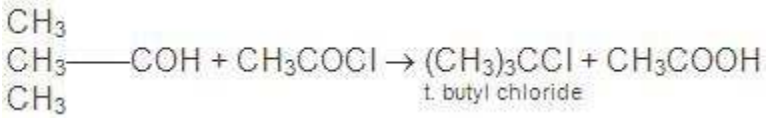
$$R\text{-}OH + HOOCR' \xrightarrow[H_2SO_4]{\Delta} R'COOR + H_2O$$

(c) Action of acetyl chloride and acetic anhydride or acetylation: Replacement of H $(CH_3—\underset{\underset{O}{\|}}{C}—)$ atom by acetyl group. The H atom of alcohol is replaced by acetyl group

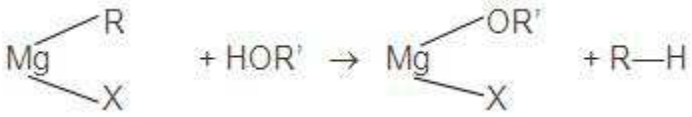




Tertiary alcohols are not acylated, however, they react with acetyl chloride to give alkyl chlorides and in some cases alkenes.



(d) Action of Grignard reagent:



All these reactions show the reactivity order P.A. > S.A. T.Alcohol

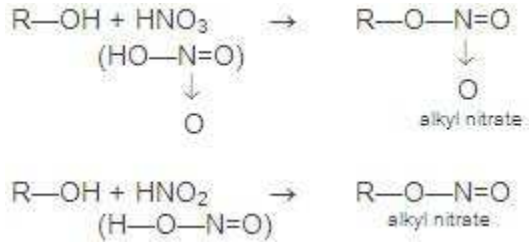
2. Reactions involving replacement of -OH group of alcohols: The -OH group of alcohol has two lone pair of electrons on O atom & thus behaves as Lewis base. The Lewis base nature of alcohols shows the order.

T.A. > S.A. > P. Alcohol

or $3^o > 2^o > 1^o >$ methyl alcohol

K, tertiary alcohols the partial -ve charge on oxygen atom is intensified due to + I.E. of CH_3 groups. This increases the tendency of oxygen atom to donate electron pair or to show cleavage of C-O bond.

(a) Action of inorganic acids: Forms esters with inorganic acids



(b) Action of phosphorus halides:

$$3ROH + PCI_3 \rightarrow 3RCI + H_3PO_3$$

$$ROH + PCI_5 \rightarrow RCI + POCI_3 + HCI$$

Similar reactions are obtained by using $P + Br_2$ and $P + I_2$ for alkyl bromide and iodide preparation because of less stable nature of PBr_3 & PI_3

(c) Action of $SOCI_2$:

$$R\text{-}OH + SOCI_2 \xrightarrow{Pyridine} R\text{-}CI + SO_2 + HCI$$

(d) Action of halogen acids:

$$R—OH + HCl \xrightarrow[\text{secondary alcohols are used}]{ZnCl_2 \text{ or } H_2SO_4 \text{ if}} R—Cl$$

$$R—OH + HBr \xrightarrow[\text{primary alcohols are used}]{ZnCl_2 \text{ or } H_2SO_4 \text{ if}} R—Br$$

$$R—OH + HI \rightarrow R—I$$

The reactivity order for halogen acids is: HI > HBr > HCI

Note:

1. If alcohols are heated with conc. HI and red P, alkanes are formed

$$R\text{-}OH + 2HI \xrightarrow{Phosphorus} R\text{-}H + H_2O + I_2$$

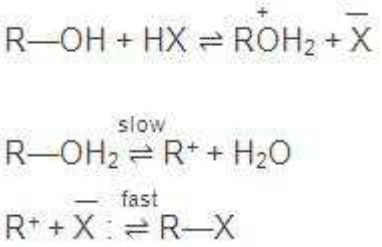
2. For getting bromo and iodo derivatives from alcohols, a mixture of $KBr + H_2SO_4$ and $KI + H_2SO_4$ respectively can be used.

3. Primary alcohols follow S_N2 mechanism during replacement of OH group by halogen atom

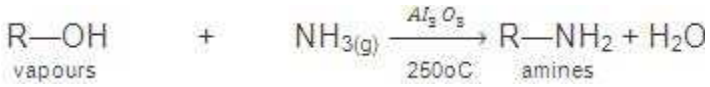
$$R—OH + HX \rightleftharpoons R—\overset{+}{O}H_2 + \overset{-}{X}:$$

$$R—\overset{+}{O}H_2 + \overset{-}{X}: \xrightarrow{Slow} [X \ldots\ldots R—OH_2] \xrightarrow{Fast} X—R + H_2O$$

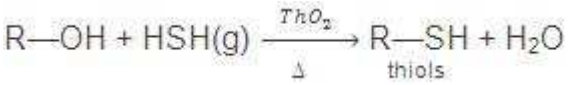
4. Secondary and tertiary alcohols follow S_N1 mechanism during replacement of OH group by halogen atom.



(e) Action of NH_3:



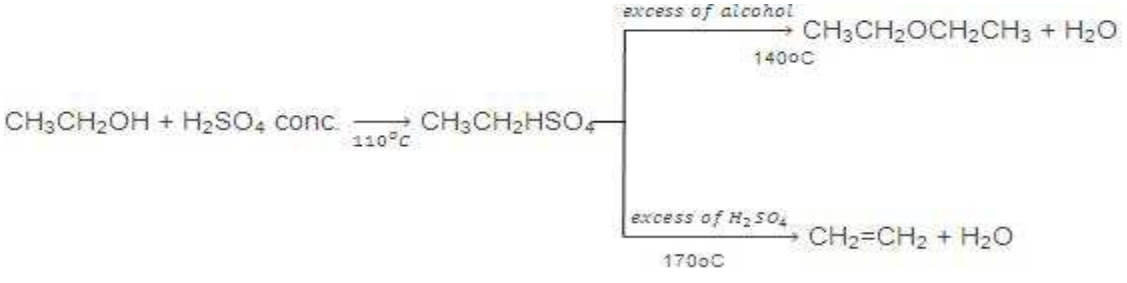
(f) Action of H_2S:

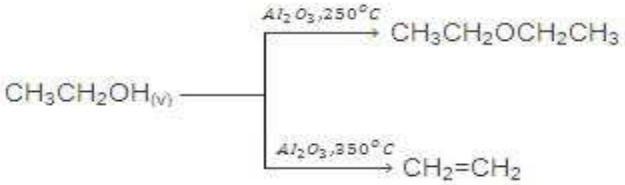


All these reactions (a) to (f) show the reactivity order T.A. > S.A. > P. Alcohol.

3. Reactions involving complete molecule of alcohols:

(a) Dehydration: Dehydration (removal of H_2O) of alcohols yields alkene or ether depending up-on the experimental conditions. The dehydration of alcohol favour the order T.A. > S.A. > P. Alcohol. The action of various dehydrating agents used are given below.

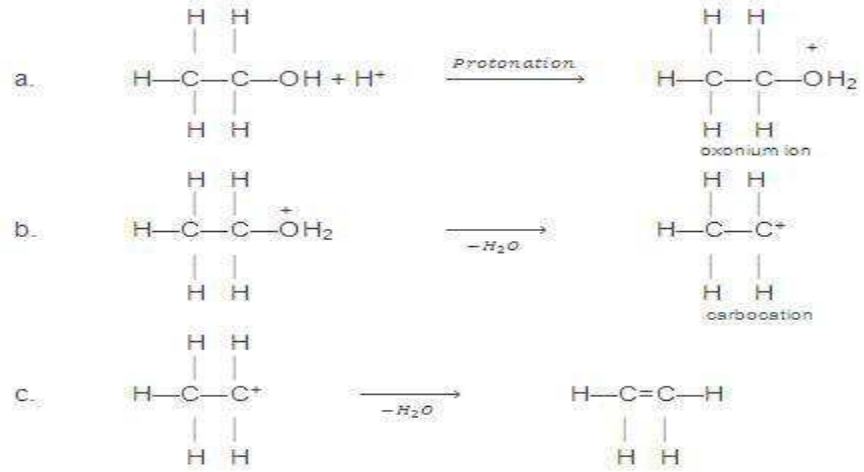




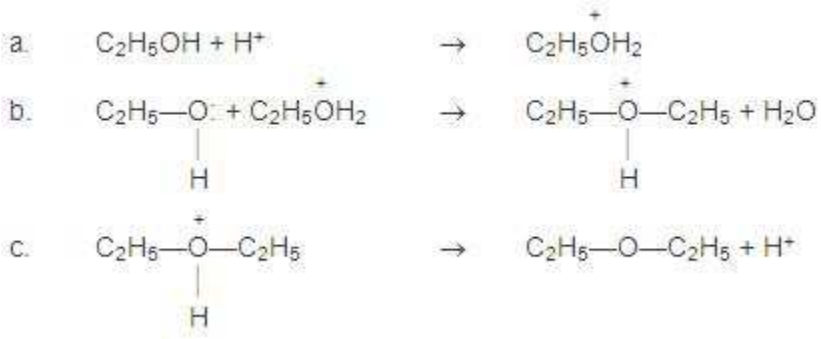
Note:

1. Normally secondary & tertiary alcohols give alkene as main product on dehydration.

2. The mechanism of dehydration of alcohols giving alkene involves protonation of the alcohol followed by loss of a water molecule and a proton.



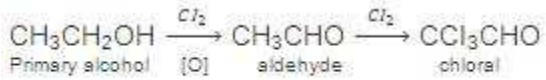
3. The mechanism of dehydration of alcohol giving ether involves protonation of alcohol. An unprotonated molecule of alcohol then combines with the protonated molecule of alcohol losing water molecule. The oxonium ion formed gives ether by a loss of a proton.

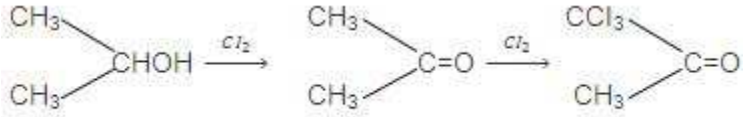


(b) Action of halogens:

(i) Halogens oxidize primary and secondary alcohols to aldehydes and ketones respectively.

(ii) After oxidation, the halogens also show substitution at α-carbon atom of products.

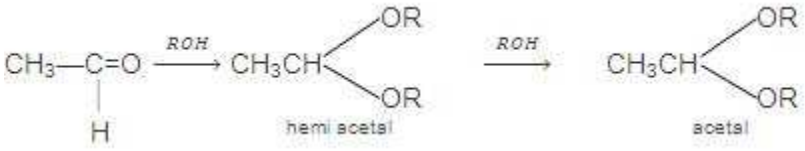




Chemical Nature of Alcohols

Note: Tertiary alcohols are not oxidised by halogens and thus tertiary butyl alcohol does not give iodoform if heated with halogens and alkali.

(c) Acetal formation:



(d) Haloform reaction: Ethyl alcohol and all alkanol-2 (secondary alcohols only) undergo haloform reaction on heating with halogen and alkali. Follow haloform reaction.

Uses:

(i) In beverage industry

(ii) As antiseptic - spirit

(iii) As fuel - spirit lamp

(iv) As solvent for medicines

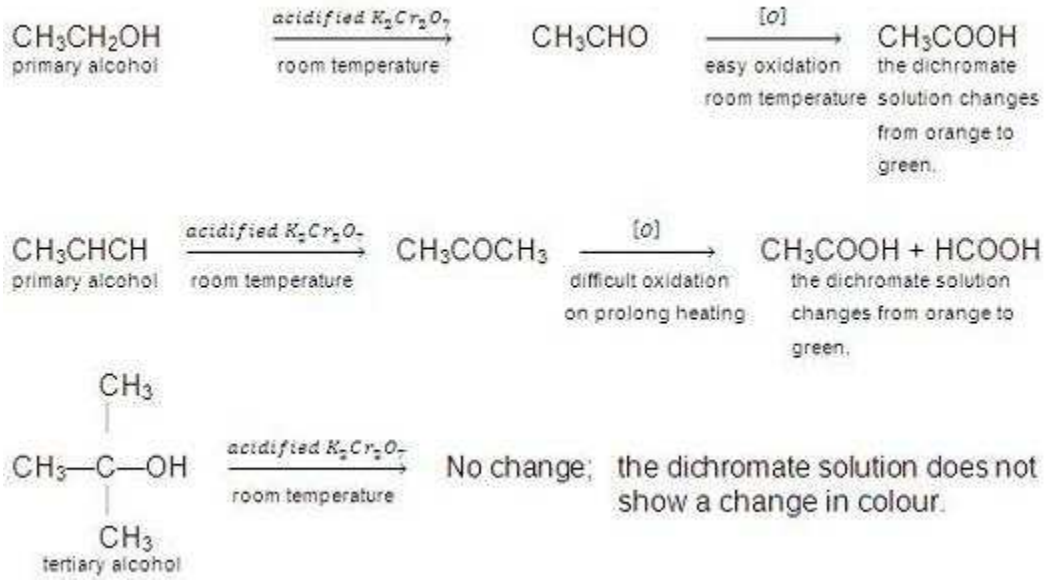
(v) As an antifreeze; glycol and glycerols are used with water to form an antifreeze mixture to cool down the radiators.

4. **How primary, secondary and tertiary alcohols are distinguished?**

Distinction test for primary, secondary and tertiary alcohols

1. By oxidation:

The nature of the oxidation products of alcohols depends upon the nature of alcohol. The oxidizing agent used commonly are acidified $K_2Cr_2O_7$, alkaline or acidified $KMnO_4$ or dilute HNO_3.

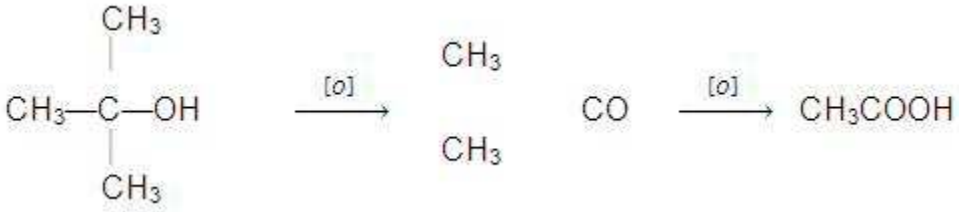


Note:

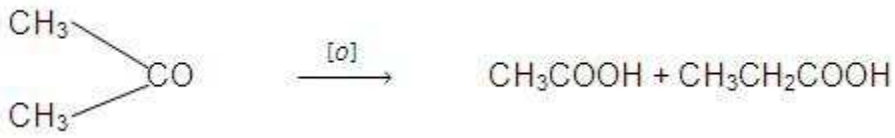
(i) In case of primary alcohol, aldehyde and acid both have same no. of C atoms as parent alcohols have.

(ii) In case of secondary alcohols, ketone has same no. of carbon atoms but acid has lees carbon atom than alcohol and ketone.

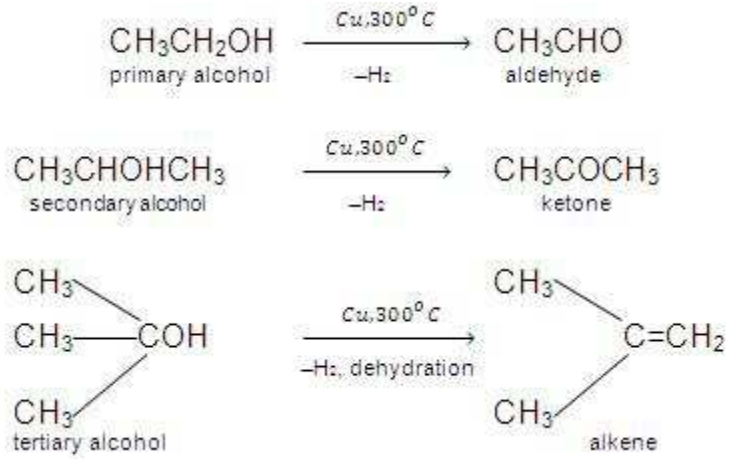
(iii) Tertiary alcohols are not oxidized in neutral or alkaline medium, however under drastic oxidation it gives ketone and acid both having lesser number of carbon atoms that the parent alcohol.



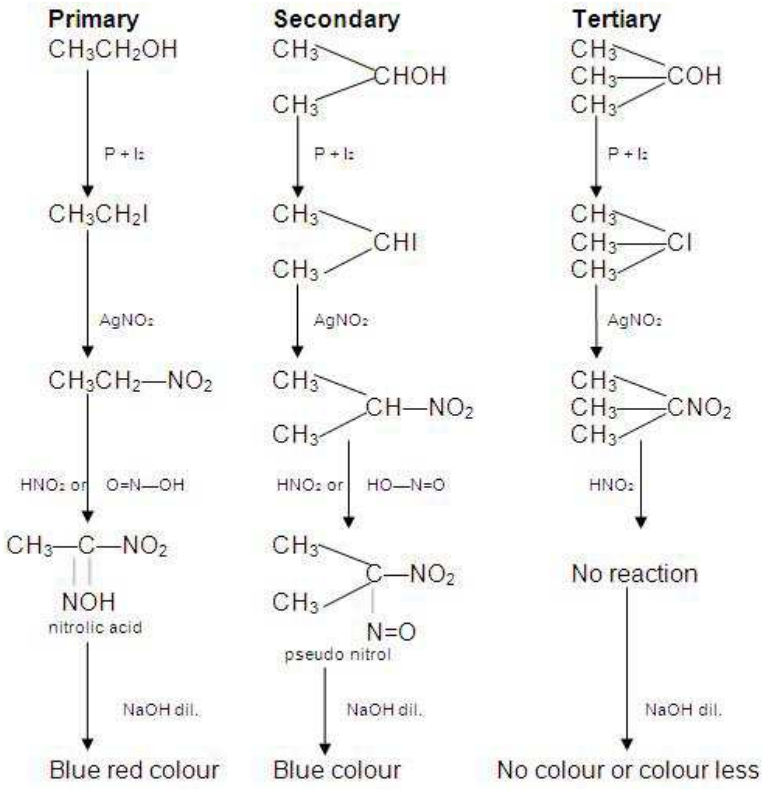
(iv) In case of oxidation of unsymmetrical ketones, the splitting of the ketonic chain takes place according to **Popff's rule,** that the carbonyl group always remains attached to a smaller alkyl group.



2. By catalytic dehydrogenation: The dehydrogenation of alcohol vapours passed over reduced Cu at 300°C gives different products depending upon the nature of alcohols.

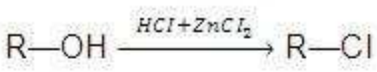


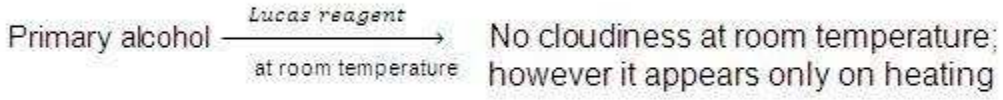
3. By Victor Meyer's test: Alcohols are subjected to a series of operations given below. The final colour of solution indicates the nature of alcohol.

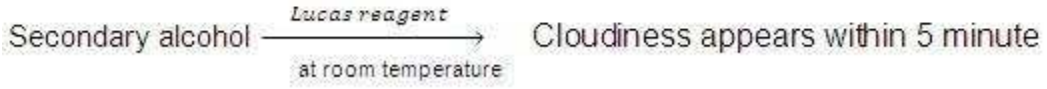


Addition of NaOH simply increases the dissociation of nitrolic acid to increase the concentration of red coloured anions

4. Lucas reagent test: This test is based on the reactivity order of alcohols to replace -OH group by halogen atom i.e. T.A. > S.A. > P.A. The alcohols are allowed to react with Lucas reagent (i.e. conc. HCI and $ZnCI_{2\ anhydrous}$) and following observations are noticed.



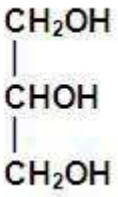




5. **Explain the preparation and properties of Glycerol.**

Ans: **<u>Glycerol or Glycerin</u>**

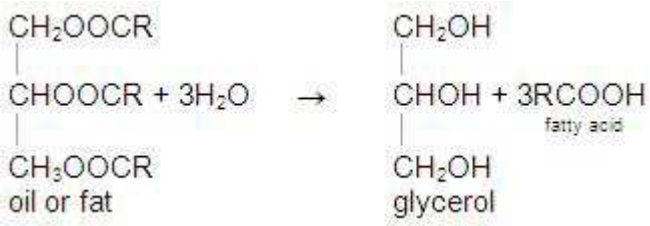
Glycerol or Glycerine



Glycerol is a trihydric alcohol. Its IUPAC name is propane-1, 2, 3-triol and in industry it is known as glycerine.

Manufacture

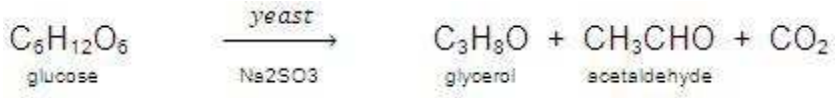
1. From Fats and Oils : On hydrolysis of fats and oils (i.e. glycerides or ester of higher fatty acids) glycerol and fatty acids are formed.



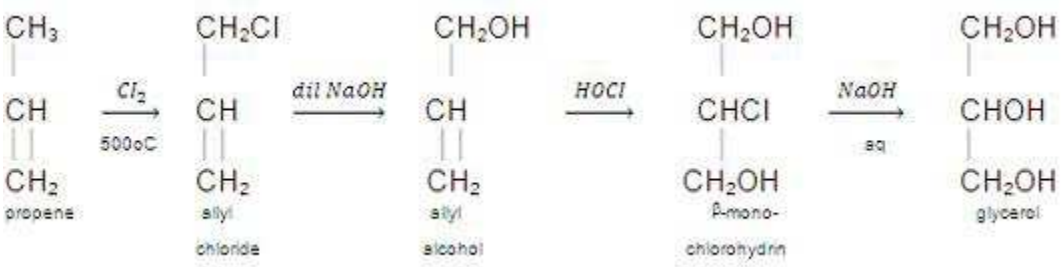
Glycerol is obtained as by-product in soap and candle industry.

2. By Fermentation of sugar:

Alcoholic fermentation of sugar gives 3% glycerol. However, if the fermentation is done in presence of sodium sulphite, the yield can be increased to 25%.



3. Synthesis (From Propene):



Properties

Physical

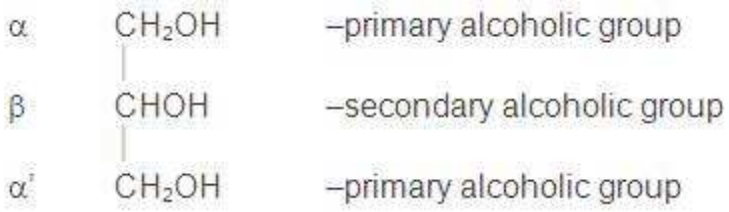
(a) It is a colourless, odourless, viscous and hygroscopic liquid, sweet in taste and non-toxic in nature.

(b) It is soluble in water and ethyl alcohol but insoluble in ether.

(c) The high viscosity and high boiling point of glycerol are due to strong hydrogen bonding.

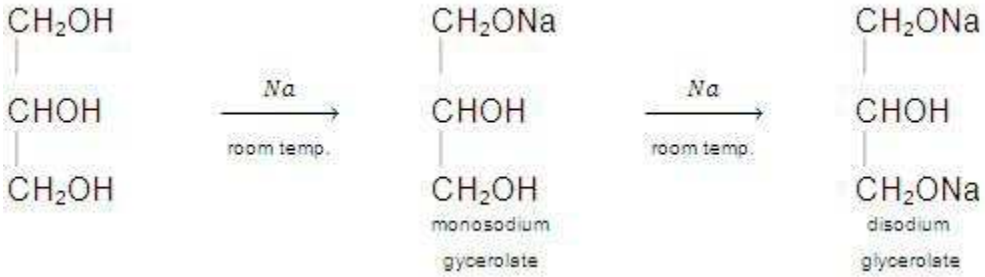
Chemical:

The molecule of glycerol contains two primary -OH groups and one secondary -OH group. The carbon atoms in glycerol are indicated as α,β and α'.

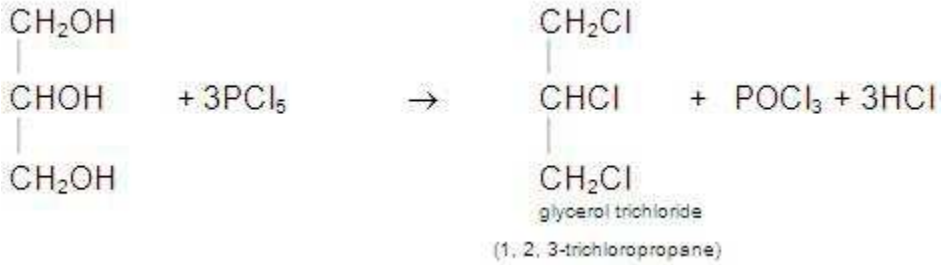


Primary -OH groups are more reactive than secondary -OH group.

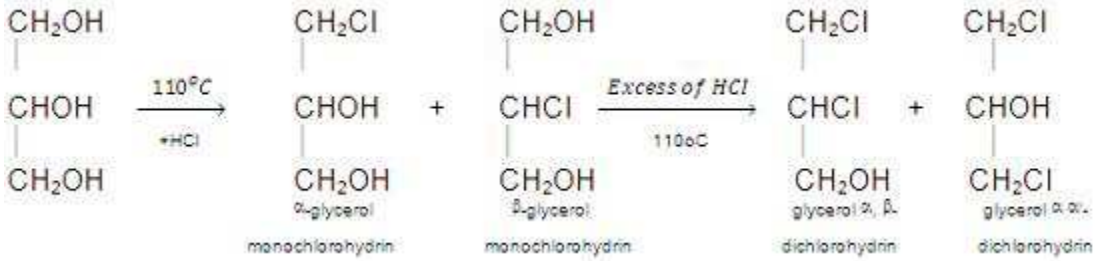
(i) Action of sodium: Only primary alcoholic groups are attacked one by one and secondary alcoholic group is not attacked.



(ii) Action of PCl_5:

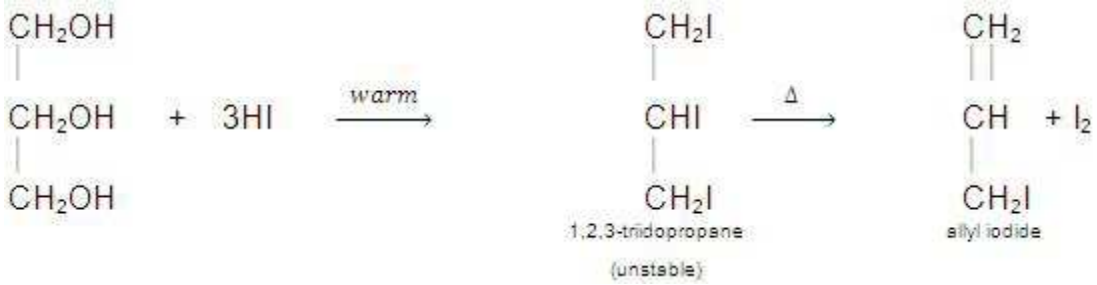


(iii) Action of HCl or HBr:

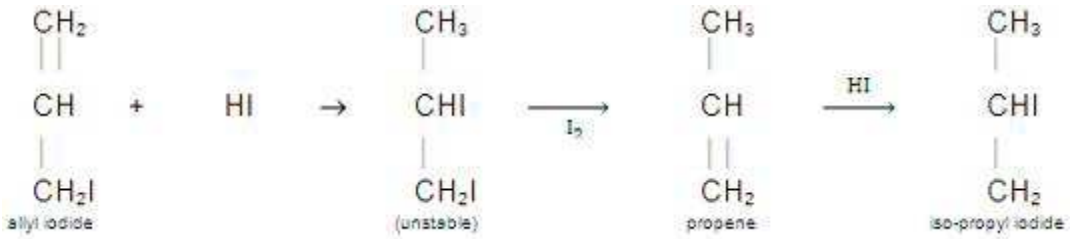


(iv) Action of HI: Glycerol reacts with HI in two ways:

(a) When glycerol is warmed a small amount of hydrogen iodide, allyl iodide is formed.

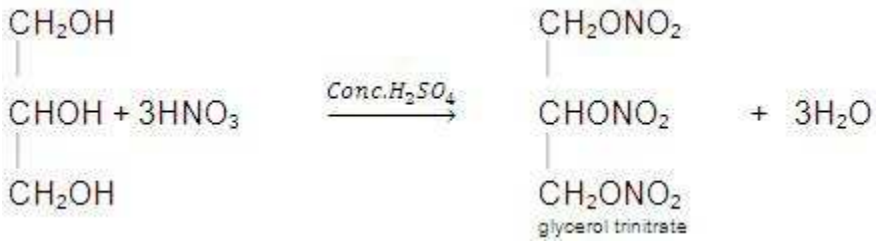


(b) When glycerol is heated with excess of HI, the allyl iodide formed first is reduced to propene. Propene in presence of excess of HI forms iso-propyl iodide.



Note: Same products are obtained when glycerol is treated with phosphorus tri-iodide.

(v) Action of nitric acid:



Glycerol trinitrate is an yellow oily, poisonous liquid and causes headache. It explodes violently when heated rapidly or subjected to sudden shock.

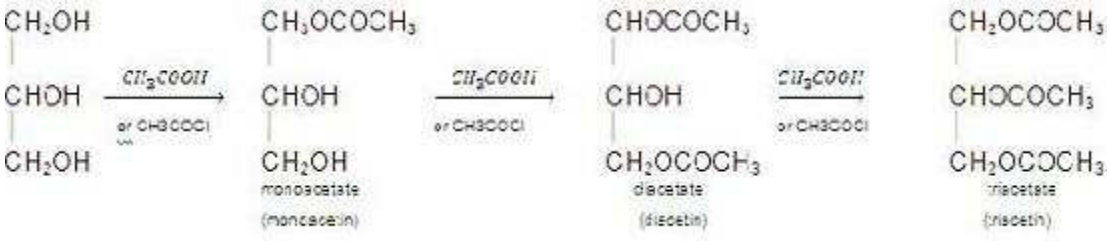
$C_3H_5(ONO_2)_3 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2$

It is a safer explosive when absorbed on kieselguhr and known as dynamite. Some other important explosives prepared from glycerol trinitrate are :

(a) Blasting gelatin: A mixture of glycerol trinitrate an cellulose nitrate (gun cotton).

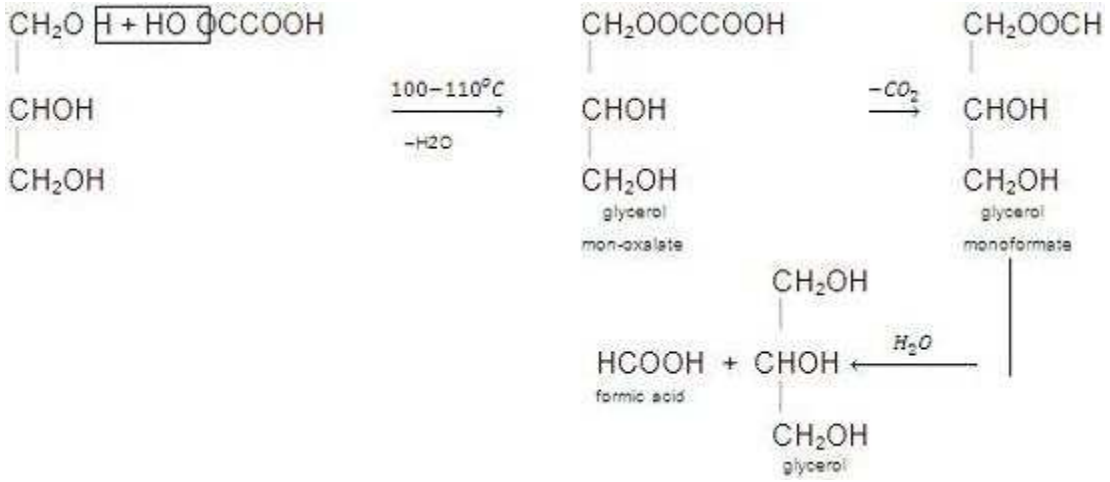
(b) Cordite: It is obtained by mixing glycerol trinitrate with gun cotton and Vaseline. It is smokeless explosive

(vi) Action of CH_3COOH, acetic anhydride or acetyl chloride: Mono, di and trimesters of glycerol are formed.

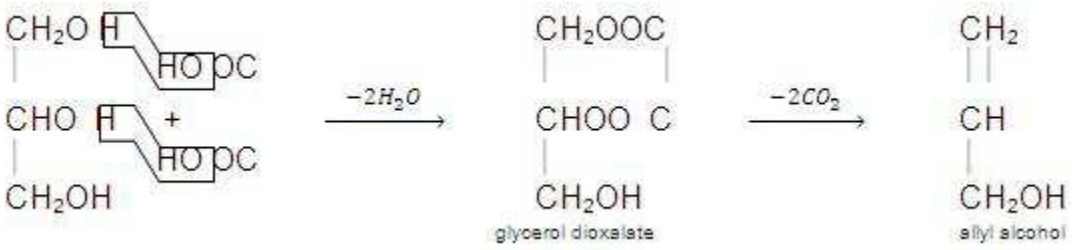


(vii) Action of oxalic acid: Different products are formed under different conditions.

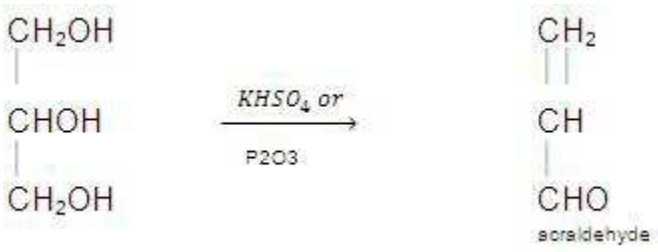
(a) At 110°C and with excess of oxalic acid, formic acid is formed.



(b) At 260°C, allyl alcohol is formed.

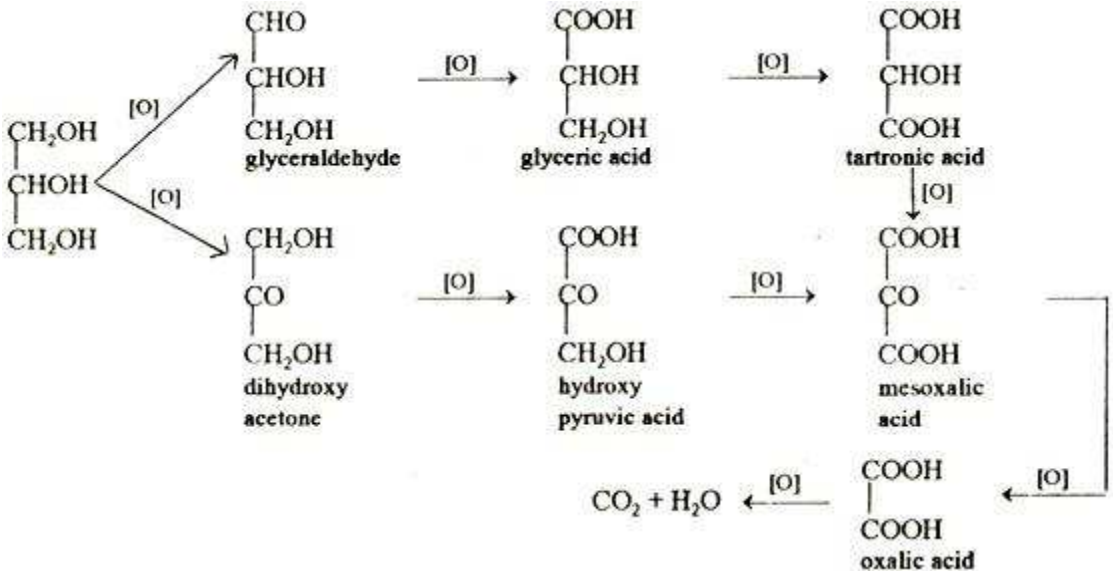


(viii) Dehydration: Glycerol on dehydration by potassium hydrogen sulphate or phosphorus pentaoxide or concentrated sulphuric acid gives acrolein or acraldehyde which has a characteristic bad odour.



This reaction can be used as a test of glycerol.

(ix) Oxidation: Glycerol gives different oxidation products depending on the nature of oxidizing agent.



Oxidation of Glycerol with.....

(a) Dilute HNO_3 gives mainly glyceric acid.

(b) Conc. HNO_3 gives glyceric acid and tartronic acid.

(c) Bismuth nitrate gives mainly mesoxalic acid.

(d) Fenton's reagent ($H_2O_2 + F_2SO_4$) or NaOBr or Br_2-water in presence of Na_2CO_3 gives glyceraldehydes and dihydroxy acetone.

(e) Solid $KMnO_4$, gives oxalic acid and carbon dioxide. The reaction is violent and explosion occurs.

Uses

(a) As a sweetening agent in confectionary, beverages and medicines due to nontoxic nature.

(b) As antifreeze in automobile radiators.

(c) In the manufacture of plastics & synthetic fibres.

(d) In the manufacture of explosives like dynamite and cordite.

(e) As a lubricant in watches.

(f) In the preparation of good quality of soaps, hand lotions, vanishing creams, shaving creams and tooth pastes.

(g) In the manufacture of various organic compounds like, formic acid, allyl alcohol, acrolein, etc.

(h) As a preservative.

(i) In the preparation of non-drying inks, printing inks and stamp pad inks.

6. **Explain the preparation and properties of Phenol.**

PHENOL

Phenols are molecules that have a hydroxyl group attached to the carbon atom of an

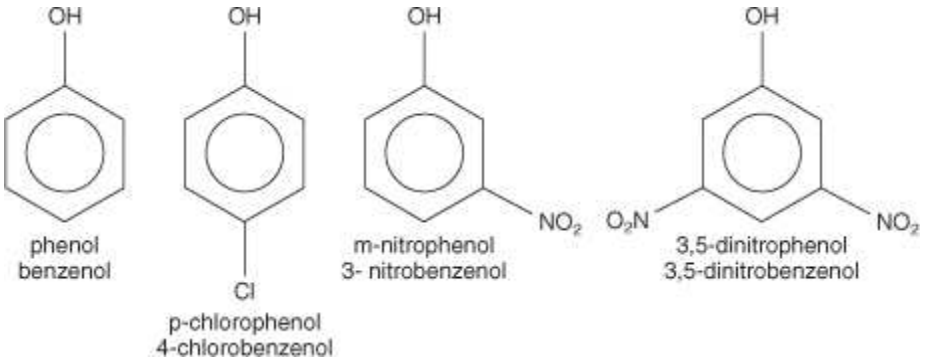
aromatic ring.

Nomenclature:

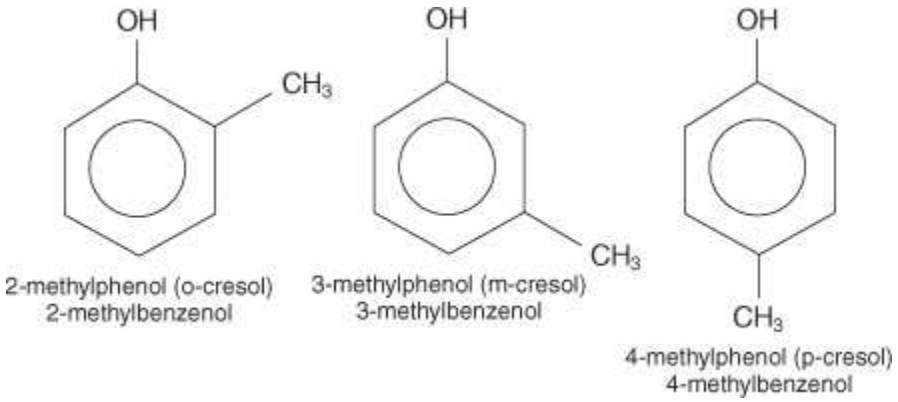
By definition, phenol is hydroxybenzene. Phenol is a common name for the compound. Its IUPAC name would be benzenol, derived in the same manner as the IUPAC names for aliphatic alcohols.

When a phenol molecule is substituted with additional groups, either the ortho, meta, para system or the numbering system can be employed. In either case, if the parent molecule is referred to as a *phenol*, the nomenclature being used is the common system.

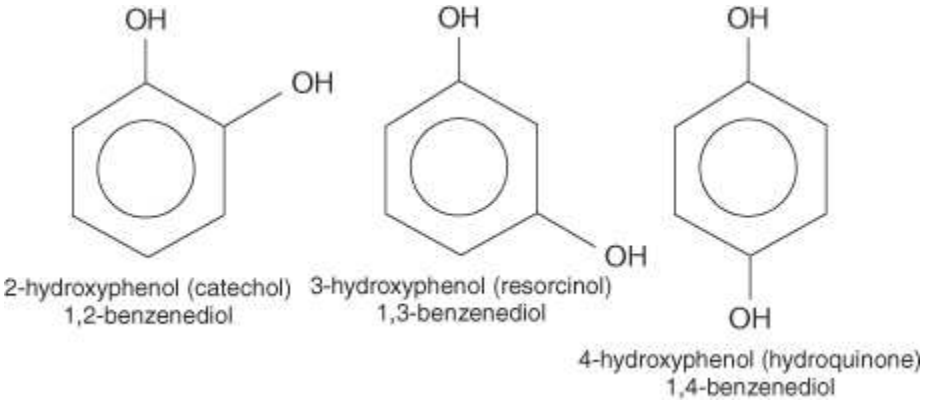
In IUPAC nomenclature, the parent molecule is called benzenol, and substituents are always numbered with the OH group being given the understood first position. For the compounds below, the first name listed is the common name and the second is the IUPAC name.



Certain phenols are referred to by common names. For example, methyl phenols are called *cresols*. In the illustrations below, the first name under each compound is its common name, and the bottom name is its IUPAC name.



Similarly, hydroxyphenols have common names, which are listed first under each of the following illustrations, while the IUPAC names are listed last.

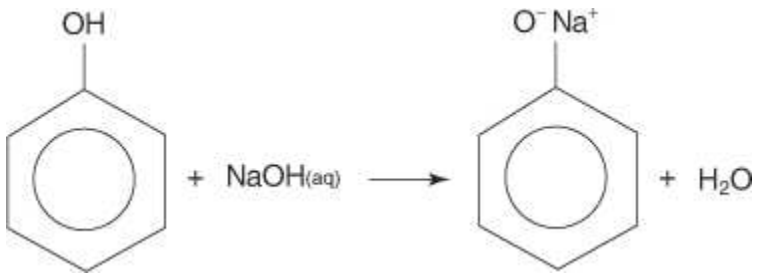


Physical properties

1. Low molecular weight phenols are normally liquids or low melting solids.
2. Due to hydrogen bonding, most low molecular weight phenols are water-soluble.
3. Phenols tend to have higher boiling points than alcohols of similar molecular weight because they have stronger intermolecular hydrogen bonding.

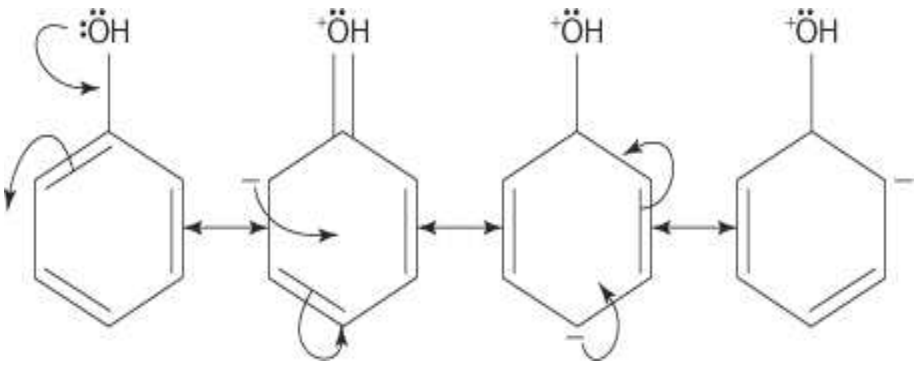
Acidity

Phenols show appreciable acidity (p $K_a = 8^{-10}$). For example, phenol reacts with aqueous NaOH as follows.



This is a typical neutralization reaction.

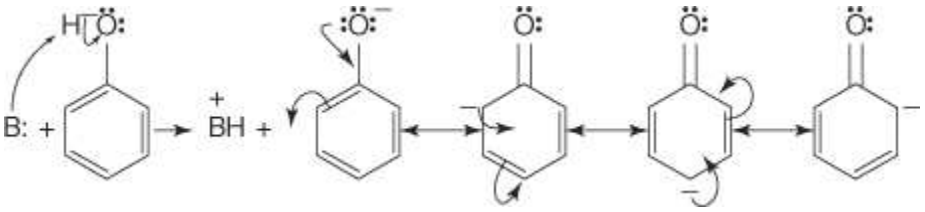
Because of their high acidity, phenols are often called **carbolic acids.** The phenol molecule is highly acidic because it has a partial positive charge on the oxygen atom due to resonance, and the anion that is formed by loss of a hydrogen ion is also resonance stabilized.



Resonance structures of phenol

Notice that three of the four contributing structures possess a positive charge on the oxygen atom of the molecule. Thus, the true hybrid structure must possess a partial positive charge. Because oxygen is an electronegative element, the electrons in the oxygen-hydrogen bond orbital are attracted to the oxygen atom, resulting in partially positive hydrogen.

Loss of a hydrogen ion to a base creates a phenoxide ion that is resonance stabilized.



Notice that upon removal of the hydroxy hydrogen by a base, the phenoxide anion results. This anion is resonance stabilized by delocalization of an electron pair throughout the molecule, as shown by the contributing structures.

Synthesis of Phenols

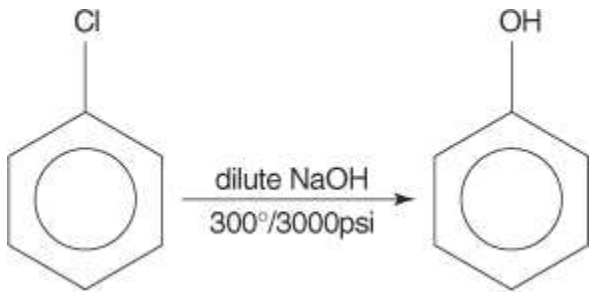
You can prepare phenols in large quantities by the pyrolysis of the sodium salt of benzene sulfonic acid, by the Dow process, and by the air oxidation of cumene. Each of these processes is described below. You can also prepare small amounts of phenol by the peroxide oxidation of phenylboronic acid and the hydrolysis of diazonium salts.

1. Pyrolysis of sodium benzene sulfonate

In this process, benzene sulfonic acid is reacted with aqueous sodium hydroxide. The resulting salt is mixed with solid sodium hydroxide and fused at a high temperature. The product of this reaction is sodium phenoxide, which is acidified with aqueous acid to yield phenol.

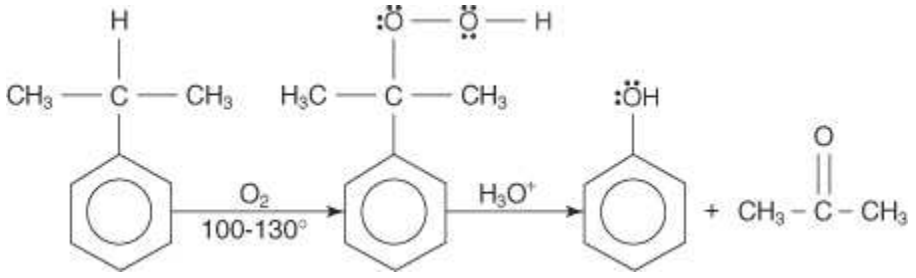
2. Dow process

In the Dow process, chlorobenzene is reacted with dilute sodium hydroxide at 300°C and 3000 psi pressure. The following figure illustrates the Dow process.



3. Air oxidation of cumene:

The air oxidation of cumene (isopropyl benzene) leads to the production of both phenol and acetone, as shown in the following figure. The mechanisms for the formation and degradation of cumene hydroperoxide require closer looks, which are provided following the figure.



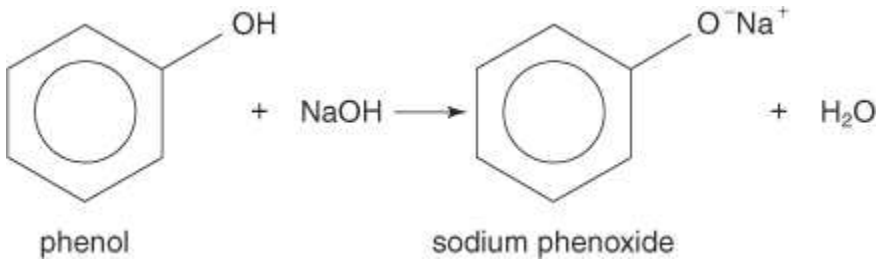
Chemical properties:

I. Reactions of Phenolic Hydrogen:

Phenols are acidic because of the ease with which the oxygen atom will release the hydrogen bonded to it. This section describes typical reactions that occur as a result of the acidity of phenols.

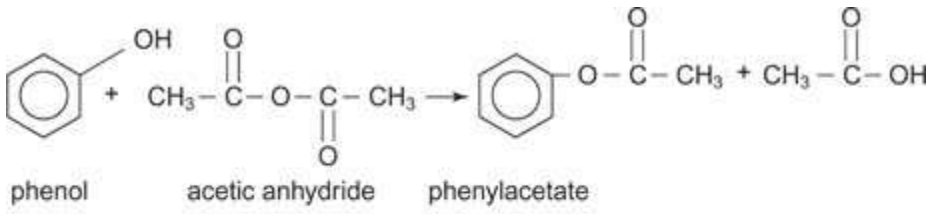
1. Reactions with bases:

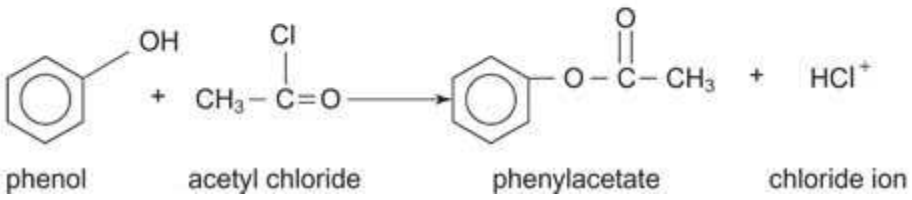
Because phenol is acidic, it reacts with bases to form salts.



2. Esterification of phenol:

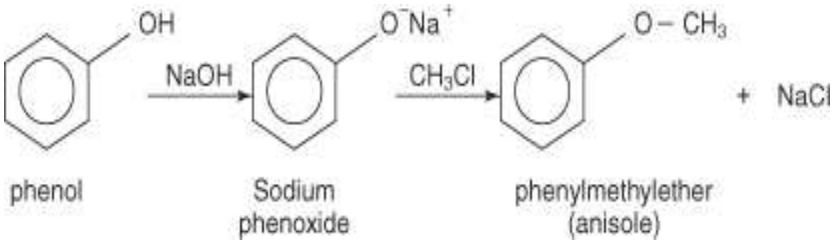
Phenols form esters with acid anhydrides and acid chlorides.





3. Williamson ether synthesis:

Ethers are produced from phenol by the Williamson method via an S_N mechanism.

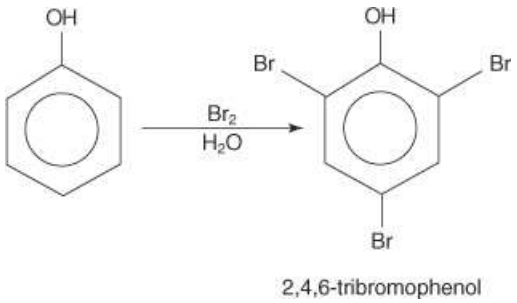


II. <u>Reactions of Phenolic Benzene Rings</u>:

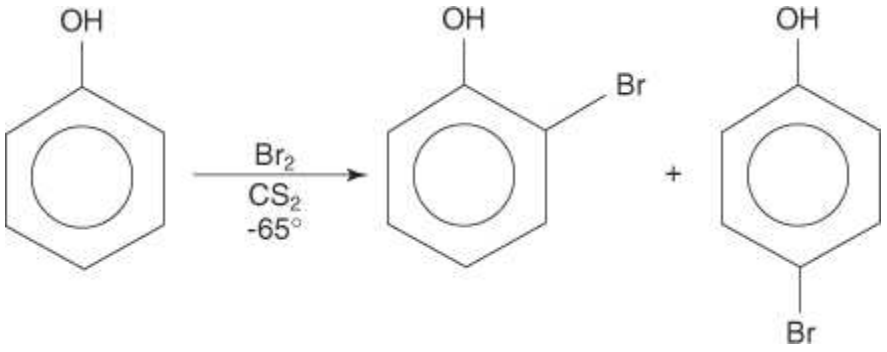
The hydroxy group in a phenol molecule exhibits a strong activating effect on the benzene ring because it provides a ready source of electron density for the ring. This directing influence is so strong that you can often accomplish substitutions on phenols without the use of a catalyst.

1. **Halogenation:**

Phenols react with halogens to yield mono-, di-, or tri-substituted products, depending on reaction conditions. For example, an aqueous bromine solution brominates all ortho and para positions on the ring.

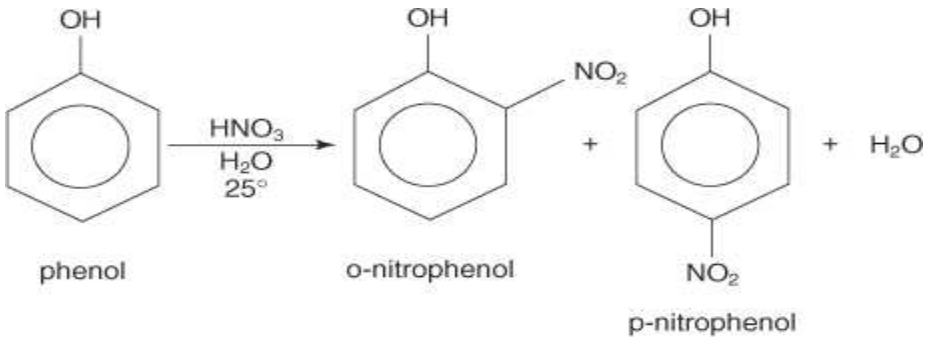


Likewise, you can accomplish monobromination by running the reaction at extremely low temperatures in carbon disulfide solvent.



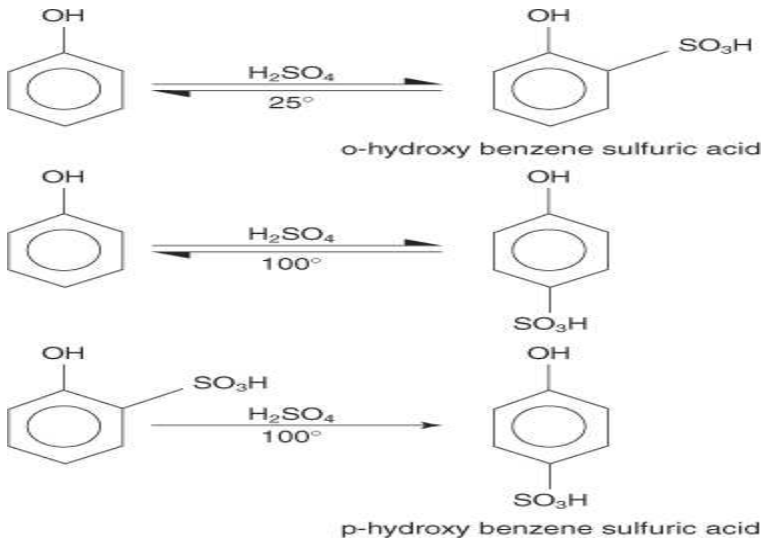
2. Nitration:

Phenol, when treated with dilute nitric acid at room temperature, forms ortho- and para-nitrophenol.



3. Sulfonation:

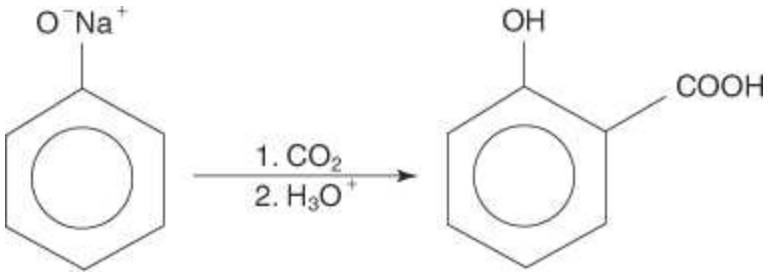
The reaction of phenol with concentrated sulfuric acid is thermodynamically controlled. At 25°C, the ortho product predominates while at 100°C, the para product is the major product.



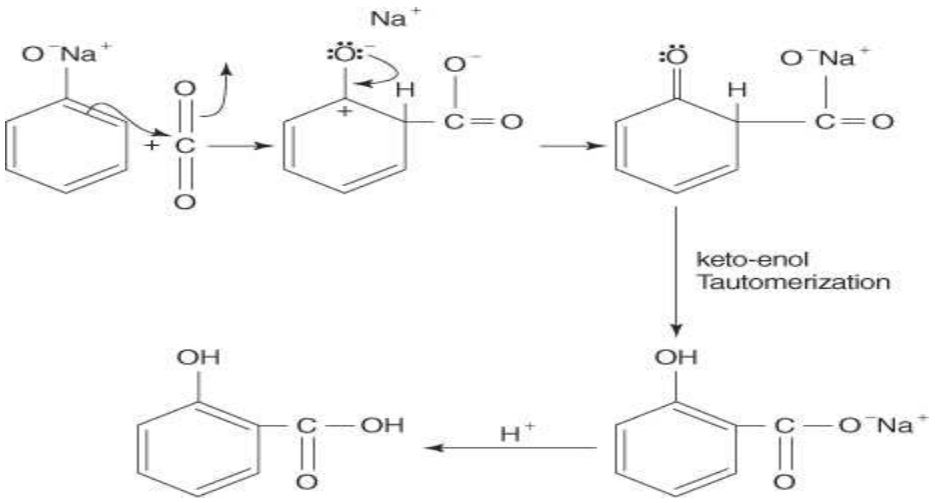
Notice that at both 25° and 100°, initially an equilibrium is established. However, at the higher temperature, the equilibrium is destroyed and the more thermodynamically stable product is produced exclusively.

4. Kolbe reaction:

The reaction of a phenoxide ion with carbon dioxide to produce a carboxylate salt is called the Kolbe reaction.



The Kolbe Reaction progresses via a carbanion intermediate.



In this reaction, the electron deficient carbon atom in carbon dioxide is attracted to the electron rich π system of the phenol. The resulting compound undergoes keto-enol tautomerization to create the product.

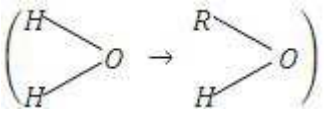
ORGANIC CHEMISTRY

TOPIC: 3

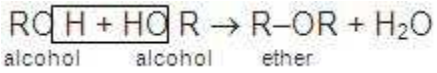
ETHERS

VERY SHORT ANSWER QUESTIONS

1. What are ethers?

(i) Ethers are regarded as dialkyl derivative of water 

or

Anhydride of alcohols 

or alkyl of alcohol (R-OH → R-OR).

(ii) Genera formula of ethers is $C_nH_{2n+2}O$.

(iii) Ethers consist of two alkyl groups attached on oxygen atom. R-O-R.

2. **What are simple ethers?**

Ans: Simple or symmetrical ethers: Both the alkyl groups attached on oxygen atom are same.

e.g. R—O—R or CH_3OCH_3

3. **What are mixed ethers?**

Ans: Mixed or unsymmetrical ethers: Both the alkyl groups attached on oxygen atom are different.

e.g. R—O—R' or $CH_3OC_2H_5$

SHORT ANSWER QUESTIONS

1. **Write the classification of ethers.**

Ans: Ethers are classified as

(a) Simple or symmetrical ethers: Both the alkyl groups attached on oxygen atom are same.

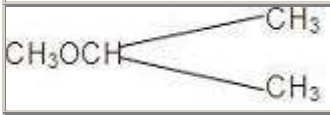
e.g. R—O—R or CH_3OCH_3

(b) Mixed or unsymmetrical ethers: Both the alkyl groups attached on oxygen atom are different.

e.g. R—O—R' or $CH_3OC_2H_5$

2. **Write the nomenclature of ethers.**

Nomenclature: Ethers are supposed to have no functional group and thus IUPAC nomenclature does not provide their suffix name. These are named (in IUPAC) as alkoxy alkane, the smaller alkyl group alongwith oxygen is called alkoxy substituent.

Formula	Trivial Name	IUPAC Name
CH_3OCH_3	dimethyl ether	methoxymethane
$CH_3OCH_2CH_3$	methyl ethyl ether	methoxyethane
$CH_3OCH_2CH_2CH_3$	methyl propyl ether	1-methoxypropane
	methyl isopropyl ether	2-methoxypropane
$CH_3CH_2OCH_2CH_3$	diethyl ether	ethoxyethane

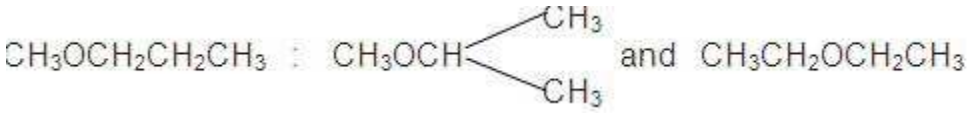
3. **Explain the isomerism in ethers.**

Isomerism

(a) Ethers show functional isomerism with alcohols.

CH_3OCH_3 & CH_3CH_2OH

(b) Ethers with at least four carbon atoms show metamerism due to different alkyl groups attached on bivalent O atom.



3. Explain the structure and chemical nature of ethers.

Ans: Structure : In CH_3OCH_3, the central oxygen atom is sp^3 hybridized with two completely filled sp^3 orbitals having lone pair of electrons and two half filled sp^3 hybridized orbitals. Also carbon atoms are sp^3 hybridized and both the half filled sp^3 orbitals of O atom from strong s (C-O) bonds with half filled sp^3 orbitals of two adjacent carbon atoms of alkyl groups.

The C-O-C bond angle is about 110^oC which is quite closer to 109^o 28' of sp^3 hybridized nature, inspite of the fact that lone pair of electrons must result in contraction in bond angles. This is because of the fact that presence of alkyl groups on O atom counterbalances the repulsion between the lone pair - bond pair electrons and leads to the bond angle nearer to 109^o 28'.

4. **Explain Williamson synthesis.**

Ans: Williamson synthesis: Heating of alkyl halides with sodium or potassium alkoxide give ethers. This is a good method to get better yield of mixed ethers in comparison to above methods. This reaction obeys S_N2 mechanism.

$$R\text{-}ONa + R'I \xrightarrow[\Delta]{ether} R\text{-}OR' + NaI$$

$$R\text{-}ONa + RI \xrightarrow[\Delta]{ether} R\text{-}OR + NaI$$

Note : alkyl halides undergo elimination reaction with sodium alkoxide to produce alkenes

$$(CH_3)_3CCI \xrightarrow{RONa} (CH_3)_2C{=}CH_2 + HCI$$

Therefore to prepare t. alkyl-alkyl ether, one must take an alkyl halide with tertiary alkoxide.

$$CH_3CI + (CH_3)_3CONa \rightarrow (CH_3)_3COCH_3 + NaCI$$

Ethers so obtained are contaminated with traces of water and alcohol. Absolute ethers do not possess traces of water or alcohol and are used in preparation of Grignard reagent. Absolute ethers are obtained by distilling ordinary ether with conc. H_2SO_4 followed by storing over metallic sodium.

LONG ANSWER QUESTIONS

1. **Explain the preparation of Ethers.**

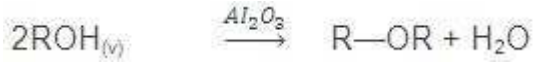
Preparation

(i) By dehydration of alcohols:

(a) Excess of alcohol on heating with conc. H_2SO_4 to 140°C leads the formation of ethers.

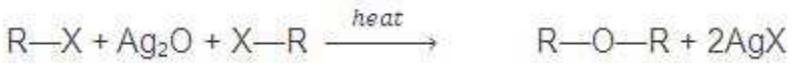


(b) On passing alcohol vapours over heated alumina at 250°C, dehydration of alcohols leads to the formation of ethers.



Note: The secondary and tertiary alcohols on dehydration lead to the formation of alkene as main product.

(ii) By alkyl halides: Alkyl halides on heating with dry Ag_2O (in ether) give ethers.

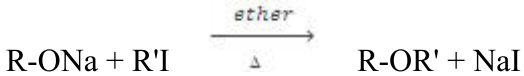


Note: Both methods (i) & (ii) can be used for the preparation of simple ethers. In case of mixed alcohols or mixed halides, the yield is reduced to 1/3rd part producing all possible ethers.

$$R\text{-}OH + HOR' \rightarrow ROR' + R\text{-}OR + R'\text{-}OR'$$

$$R\text{-}X + Ag_2O + R'X \rightarrow ROR' + ROR + R'\text{-}OR'$$

(iii) Williamson synthesis: Heating of alkyl halides with sodium or potassium alkoxide give ethers. This is a good method to get better yield of mixed ethers in comparison to above methods. This reaction obeys S_N2 mechanism.



$$R\text{-}ONa + RI \xrightarrow[\Delta]{ether} R\text{-}OR + NaI$$

Note: alkyl halides undergo elimination reaction with sodium alkoxide to produce alkenes

$$(CH_3)_3CCI \xrightarrow{RONa} (CH_3)_2C{=}CH_2 + HCI$$

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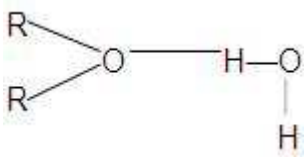
Ethers so obtained are contaminated with traces of water and alcohol. Absolute ethers do not possess traces of water or alcohol and are used in preparation of Grignard reagent. Absolute ethers are obtained by distilling ordinary ether with conc. H_2SO_4 followed by storing over metallic sodium.

2. **Explain the physical and chemical properties and uses of Ethers.**

<u>Chemical Properties of Ethers</u>

(i) Ethers are colourless, sweet smelling, highly volatile, inflammable liquids

(ii) Ethers are sparingly soluble in water due to H-bonding



(iii) The boiling points of ethers are much lower than corresponding alcohols as they show no hydrogen bonding within themselves like alcohols.

(iv) Vapours of diethyl ether cause unconsciousness on inhaling and thus used as anaesthetic agent.

(v) Ethers having bond angle C-O-C to about 110^o and thus dipole moment of two C-O bond does not cancel out each other. Thus ethers are polar but weak polarity exist (μ for diethyl ether = 1.18 D)

Chemical nature

Ethers are less reactive than compounds containing functional groups. They neither react with active metals, strong bases nor with reducing & oxidizing agents.

The chemical properties of ethers are due to alkyl gp, lone pair of electrons on oxygen atom and cleavage of C-O bond.

1. Reactions due to alkyl group:

(a) Combustion: Ethers are highly inflammable and form explosive mixture with air giving CO_2 and water.

$$C_2H_5O\,C_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

(b) Halogenation: The alkyl group of ether undergoes substitution reaction with chlorine or bromine to give a-halogenated ethers in absence of sunlight. However in presence of sunlight all the hydrogen atoms of ethers are substituted.

$$CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2,dark} CH_3CHClOCHClCH_3$$

α α'-dichloro diethylether

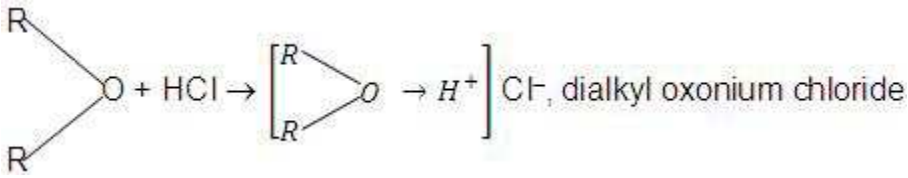
$$CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2,dark} C_2Cl_2OC_2Cl_5$$

Perchloro diethylether

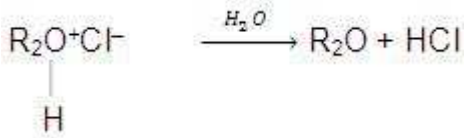
2. Reaction due to ethereal oxygen:

(a) Basic nature:

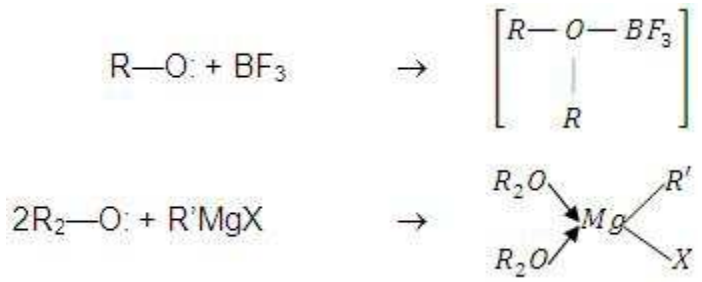
(i) Due to the presence of two lone pair of electrons on oxygen atom, ethers behave as Lewis bases and form salt with strong acids.



(ii) The oxonium salts are soluble in acid solution and regeneration of ether can be made by hydrolysis of these salts.



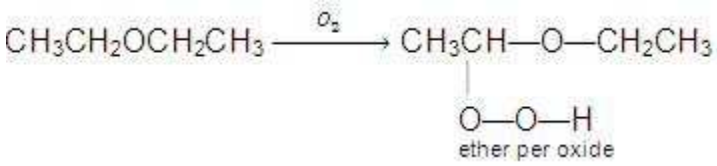
(iii) Ethers also form co-ordination complexes with Lewis acids like BF_3, $AICI_3$, RMgX etc.



Therefore ethers are very good solvent for Grignard reagents.

(b) Formation of per oxides:

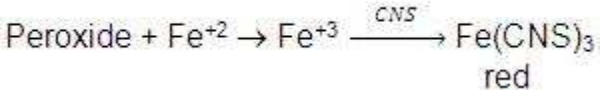
(i) Ethers form peroxide linkage with oxygen if exposed to air or ozonized oxygen in presence of sunlight or ultraviolet light.



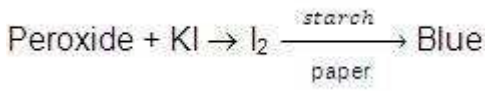
(ii) These per oxides are highly poisonous, oily liquids and decompose violently even at low concentrations. Therefore ethers should not be evaporated to dryness.

(iii) Also the purity of ether should be checked before its use as anesthetic agent. An impure ether (having peroxide linkage)-

(a) Gives red colour when shaken with ferrous ammonium sulphate and potassium thio-cyanate



(b) On mixing with KI solution liberates I_2 which turns starch paper blue.

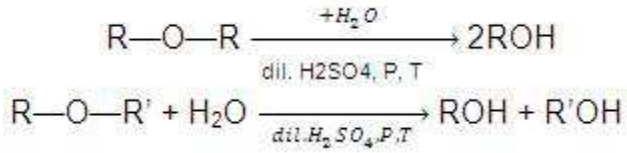


(iv) Ethers are made free from peroxide linkage if they are distilled with conc. H_2SO_4.

(v) Also peroxide formation can be checked if little Cu_2O is added to ether.

3. Reactions involving cleavage of carbon-oxygen bond:

(a) Action of dil. H_2SO_4: Ethers on heating with dilute H_2SO_4 under pressure are hydrolysed to corresponding alcohols.



(b) Action of Conc. H_2SO_4:

Ethers on warming with conc. H_2SO_4 give alkyl hydrogen sulphate.

$R\text{-}OR + H_2SO_4$ conc. $\rightarrow 2R\ HSO_4$

$R\text{-}OR' + H_2SO_4$ conc. $\rightarrow RHSO_4 + R'HSO_4$

(c) Action of HI:

(i) The products formed during action of HI on ethers depend upon temperature

$$R\text{-}OR + HI \xrightarrow{cold} R\text{-}OH + RI$$

$$R\text{-}OR' + HI \xrightarrow{cold} R'\text{-}OH + RI$$

Note: In case of mixed ether, halogen atom gets attached to simpler alkyl gp.

$CH_3OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$

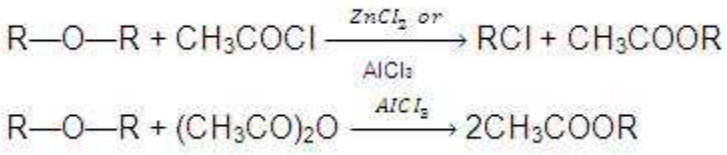
(ii) $R\text{-}R + HI \xrightarrow{hot} 2RI + H_2O$

(iii) Similar reactions are observed with HCI, HBr & the reactivity order if HI > HBr > HCI.

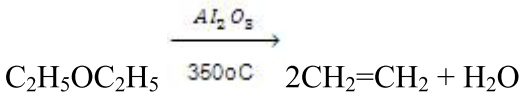
(d) Action of PCI_5:

$$R\text{-}O\text{-}R + PCI_5 \xrightarrow{\Delta} 2RCI + POCI_3$$

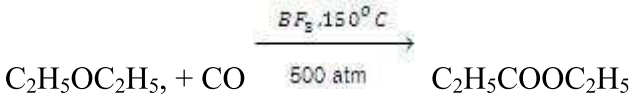
(e) Action of Acetyl chloride or Acetic anhydride:



(f) Dehydration:



(g) Action of carbon monoxide:



$$ROR + CO \rightarrow RCOOR$$

Uses: Ethers are used as:

(i) General anaesthetic agent

(ii) Refrigerant as produces cooling on evaporation

(iii) Solvent for oils, fats, resins, Grignard reagent etc.

(iv) For providing inert & moisture free medium for reactions e.g. Wurtz reaction.

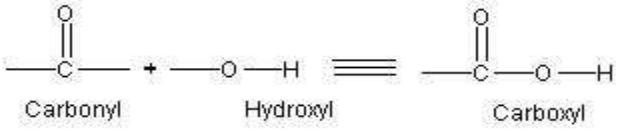
ORGANIC CHEMISTRY

TOPIC: 4 CARBOXYLIC ACIDS

VERY SHORT ANSWER QUESTIONS

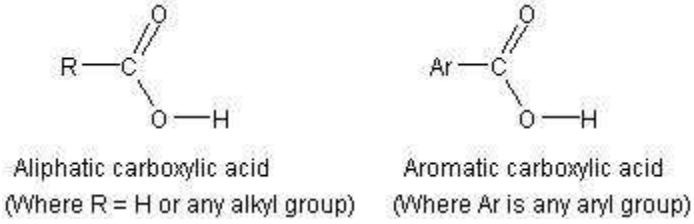
1. **Define carboxylic acid.**

Ans: Carboxylic acids are characterized by the presence of carboxyl group. The –COOH group which itself is made up of a carbonyl group (C=O) and a hydroxyl group (¾OH) is called carboxyl group (carb from carbonyl and oxyl from hydroxyl)



2. What are different types of carboxylic acids?

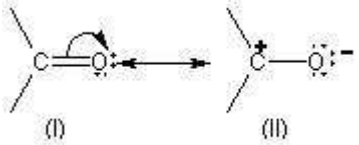
Ans: Carboxylic acids may be aliphatic or aromatic



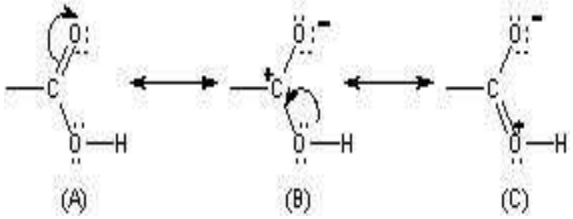
3. **Explain the structure of carboxylic acid.**

Ans: Comparison of resonating structures of carboxylic group and carbonyl group **.**

Carbonyl group has two resonance structures (I and II)



However, for a carboxyl group, three resonance structures (A, B and C) can be written.



In both structures (A) and (C), the C – atom and the two O – atoms have eight electrons in their respective valence shells while in structure (B), C – atom has only six electrons. Therefore, structure (B) is less stable than structure (C), in other words the two important resonance structures of carboxyl group are structures (A) and (C). In both these structures, carboxyl carbon is electrically neutral. However in case of aldehydes and ketones, only one structure i.e. I is electrically neutral. As a result, the carboxyl carbon of the resonance hybrid is less positive and hence less electrophilic than the carbonyl carbon of aldehydes and ketones. However, it may be noted that like carbonyl group, carboxyl group is also polar due to resonance structures (B) and (C).

SHORT ANSWER QUESTIONS

1. **Explain the nomenclature of carboxylic acids.**

Ans: **NOMENCLATURE:** The aliphatic carboxylic acids are commonly known by their initial names, which have been derived from the source of the particular acid.

Examples:

- HCOOH Formic acid [Latin: Fermica = ant]
- CH_3COOH Acetic acid [Latin: acetum = Vinegar]
- $CH_3–CH_2–COOH$ Propionic acid [Greek: Proton = First; Pion = Fat]
- $CH_3(CH_2)_2COOH$ Butyric acid [Latin: Butyrum = Butter]
- $CH_3(CH_2)_3COOH$ Valeric acid
- $CH_3(CH_2)_{14}COOH$ Palmitic acid
- $CH_3(CH_2)_{16}COOH$ Stearic acid

Alternative system of nomenclature is naming the acids as the derivatives of acetic acids. The only exception being formic acid.

Example:

$CH_3 – CH_2 – COOH$ Methyl acetic acid

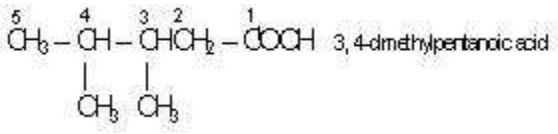
$(CH_3)_3C – COOH$ Trimethyl acetic acid

According to the IUPAC system of nomenclature, the suffix of the monocarboxylic acid is ‘oic acid’, which is added to the name of the alkane corresponding to the longest carbon chain containing the carboxyl group, e.g.

HCOOH methanoic acid

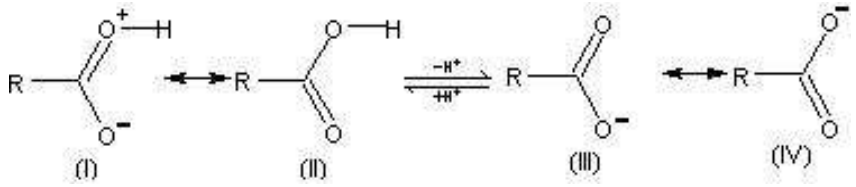
$CH_3 – CH_2 – CH_2 – COOH$ butanoic acid

The positions of side-chains (or substituents) are indicated by numbers, the numbering to be started from the side of the carboxyl group.



2. **Explain the acidity of carboxylic acids**.

Ans: **Acidity of Carboxylic Acids**: The acidity of a carboxylic acid is due to the resonance stabilization of its anion.



Because of the resonance, both the carbon oxygen bond in the carboxylate anion have identical bond length. In the carboxylic acid, these bond lengths are no longer identical.

The acidity of carboxylic acid depends very much on the substituent attached to –COOH group. Since acidity is due to the resonance stabilization of anion, substituent causing stabilization of anion increases acidity whereas substituent causing destabilization of anion decrease acidity. For example, electron withdrawing group disperses the negative charge of the anion and hence makes it more stable causing increase in the acidity of the corresponding acid; on the other hand, electron-releasing group increases the negative charge on the anion and hence makes it less stable causing the decrease in the acidity. In the light of this, the following are the orders of a few substituted carboxylic acids.

LONG ANSWER QUESTIONS

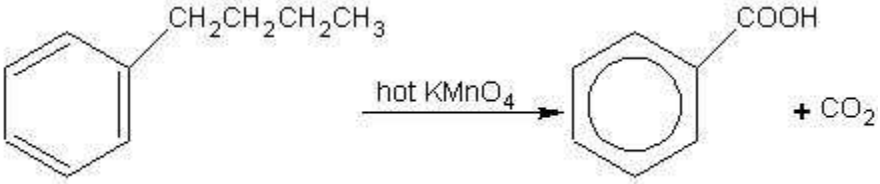
1. **Explain the general methods of preparation of Carboxylic acids.**

Ans: GENERAL METHODS OF PREPARATION

1. Oxidation of alcohols, aldehydes and ketones

2. Oxidation of alkyl benzenes: Although benzene and alkane are quite unreative towards the usual oxidizing agents ($KMnO_4$, $K_2Cr_2O_7$ etc). The benzene ring renders an aliphatic side chain quite susceptible to oxidation. The side chain is oxidised down to the ring and only a carboxyl group (¾COOH) remains to indicate the position of the original side chain. Potassium permanganate is generally used for this purpose, although

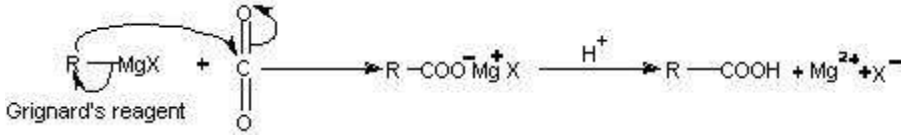
potassium dichromate or dilute nitric acid can also be used. (Oxidation of a side chain is more difficult, however, than oxidation of an alkene and requires prolonged treatment with hot $KMnO_4$)



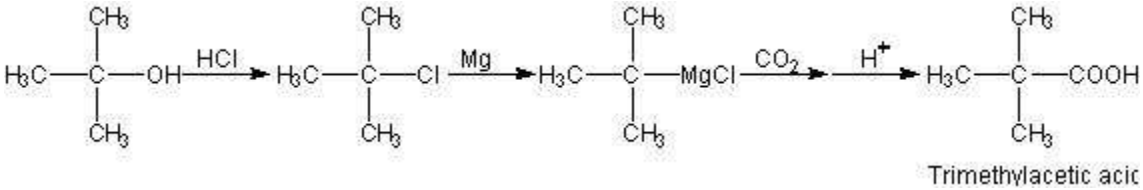
This reaction is used for two purposes (a) synthesis of carboxylic acids and (b) identification of alkyl benzenes.

3. Carbonation of Grignard reagents: The Grignard synthesis of a carboxylic acid is carried out by bubbling gaseous CO_2 into the ether solution of the Grignard reagent or by pouring the Grignard reagent on crushed dry ice (solid CO_2). In the latter method dry ice serves not only as reagent but also as cooling agent.

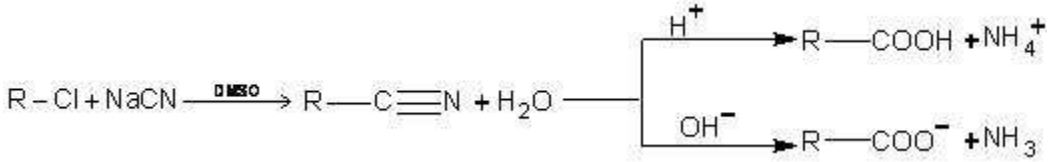
The Grignard reagent adds to the carbon – oxygen double bond of CO_2 just as in the reaction with aldehydes and keotnes. The product is the magnesium salt of the carboxylic acid, from which the free acid is liberated by treatment with mineral acid.



The Grignard's reagent can be prepared from primary, secondary, tertiary or aromatic halides. The method is limited only by the presence of other reactive group in the molecule. The following synthesis illustrates the application of this method.



Hydrolysis of nitriles: Aliphatic nitriles are prepared by treatment of alkyl halides with sodium cyanide in a solvent that will dissolve both reactants. In dimethyl sulfoxide (DMSO), reaction occurs rapidly and exothermically at room temperature. The resulting nitrile is then hydrolysed to the acid by boiling with aqueous alkali or acid.

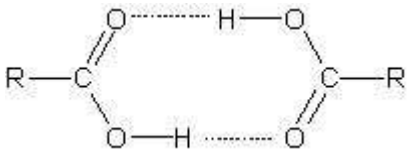


2. **Explain the physical and chemical properties of carboxylic acids.**

I. PHYSICAL PROPERTIES: Some important physical properties of carboxylic acids are given below,

1. Solubility: As the size of the alkyl group increases, the solubility of the acid decreases and polarity is reduced.

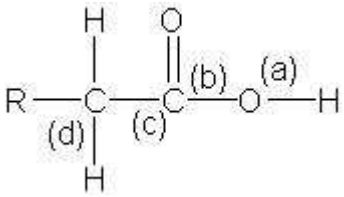
2. Boiling points: Due to intramolecular hydrogen bonding dimerization of acid takes place and boiling point of carboxylic acid is higher than expected.



3. Melting points: The melting points of aliphatic carboxylic acids do not show a regular pattern. The first ten members show a alteration effect, i.e. the melting point of an acid containing even number of carbon atoms is higher than the next lower and next higher homologues containing odd number of carbon atoms.

II **CHEMICAL REACTIONS**

The characteristic chemical behavior of carboxylic acids is, of course, determined by their functional group, carboxyl, –COOH. This group is made up of a carbonyl group (C = O) and a hydroxyl group (–OH). As we shall see, it is the –OH that actually undergoes nearly every reaction. Loss of H^+, or replacement by another group but it does so in a way that is possible only because of the effect of the C = O.



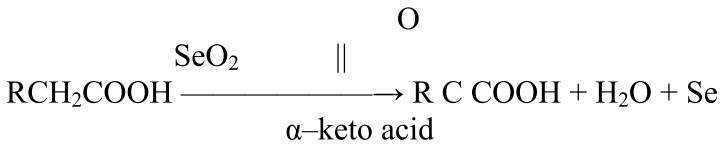
Carboxylic acids can also show various types of reactions.

(i) Removal of H^+ (due to cleavage of O — H bond) by reaction with a base (at 'a' above)
(ii) C — O bond breaks at b (by PCl_5, PCl_3, $SOCl_2$, NH_3/Δ)
(iii) Nucleophilic attack at point (c) in carboxyl carbon (Ester formation)
Reaction in which OH is replaced by — NH_2, Cl is S_N type

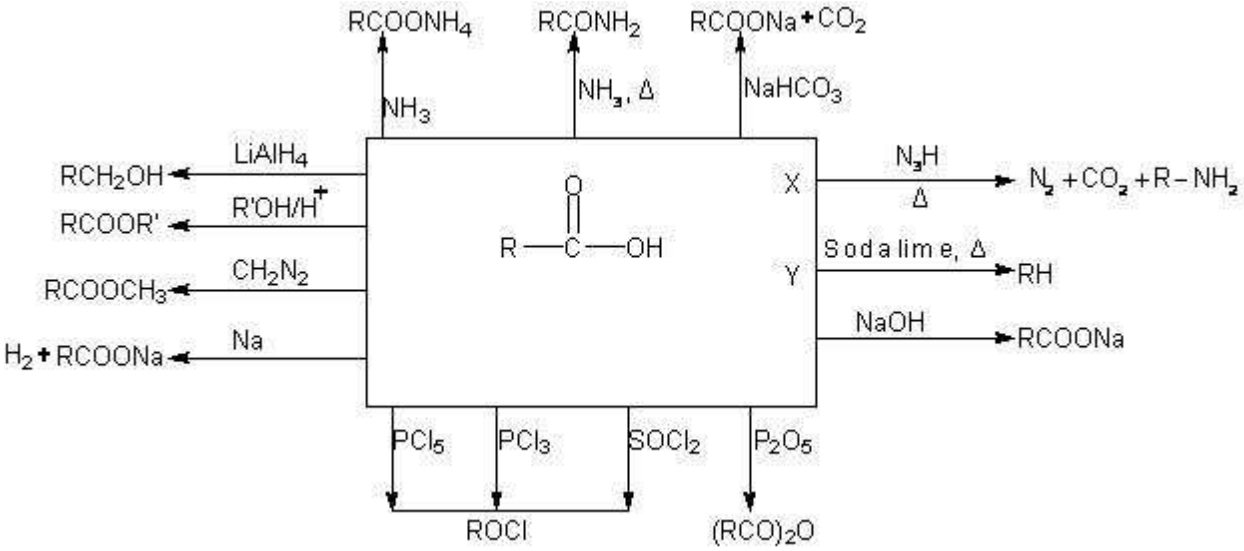


(iv) Halogenation at α–C by P/Br_2 at point d (Hell – Volhard Zelinsky reaction)

(v) Oxidation of α - methylene group by SeO_2

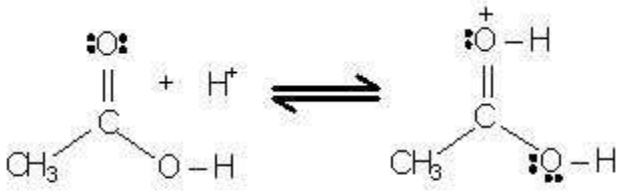


Some reactions are summarized below:

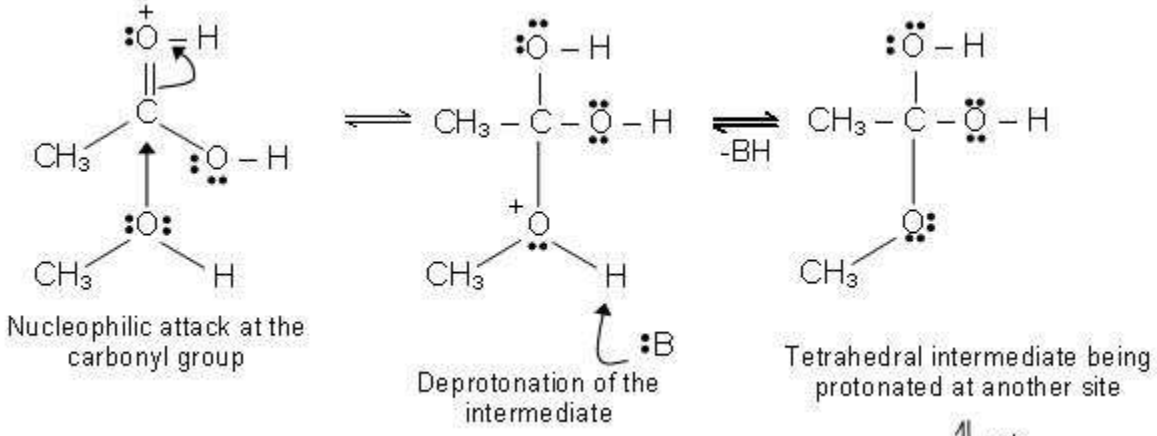


3. **Explain the mechanism of esterification reactions of Carboxylic acids.**

Ans: **The Mechanism of the Esterification Reaction:** The step in the mechanism for the formation of an ester from an acid and an alcohol are the reverse of the steps for the acid-catalyzed hydrolysis of an ester, the reaction can go in either direction depending on the conditions used. A carboxylic acid does not react with an alcohol unless a strong acid is used as a catalyst; protonation makes the carbonyl group more electrophilic and enables it to react with the alcohol, which is a weak nucleophile.



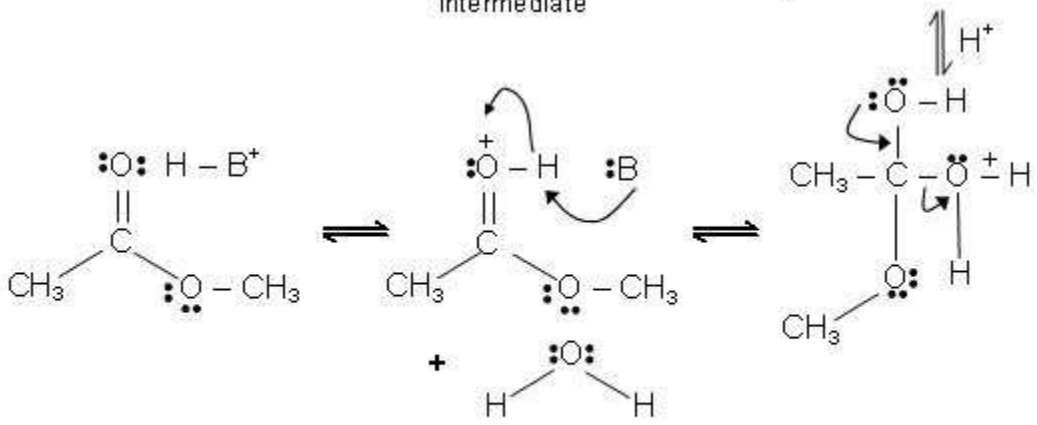
Protonation of the carbonyl group



Nucleophilic attack at the carbonyl group

Deprotonation of the intermediate

Tetrahedral intermediate being protonated at another site



Deprotonation of the carbonyl group

The initial step in both reactions involves nucleophilic addition at the carbonyl carbon atom. It is after the initial nucleophilic attack has taken place that the two reactions differ. The tetrahedral intermediate formed from an aldehyde or ketone usually accepts a proton to form a stable addition product. By contrast, the intermediate formed from an acyl compound usually eliminates a leaving group: this elimination leads to regeneration of the carbon oxygen double bond and to a substitution product. The overall process in the case of acyl substitution occurs, therefore, by a nucleophilic addition–elimination mechanism. Acyl compounds react as they do so because they all have good leaving groups attached to the carbonyl carbon atom.

4. **Explain the preparation and properties of acetic acid.**

Ans: <u>Introduction to dilute Acetic acid:</u>

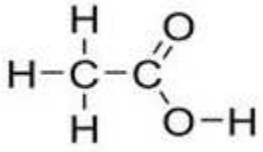
Acetic acid is an organic acid. It is also named as ethanoic acid. Acetic acid means acetic acid which is dilute in concentration.

The molecular formula of acetic acid is CH_3COOH. It is also written as CH_3CO_2H.

The empirical formula of dilute acetic acid is CH_2O, because the dilute acetic acid contains 2 carbon atoms, 2 oxygen atoms and 4 hydrogen atoms.

The molecular mass of dilute acetic acid is 60.05g. Dilute acetic acid is a simplest weak carboxylic acid which partially dissociates in aqueous solution.

The structural formula of dilute acetic acid is as shown below.



HOAc is the abbreviation of dilute acetic acid; where Ac is the acetyl group i.e. CH_3CO_2.

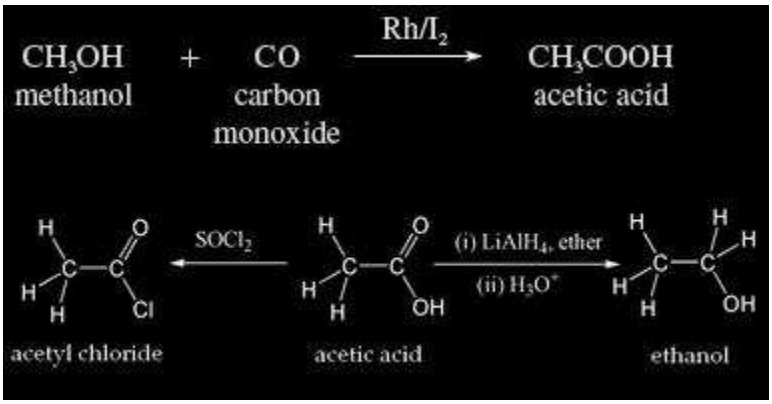
I. Method of Preparation of Acetic acid.

Acetic acid is prepared from

1. **Methyl cyanide:** When methyl cyanide is boiled with dilute hydrochloric acid, it undergoes hydrolysis to give acetic acid and ammonium chloride. The reaction is as follows **$CH_3CN + 2H_2O + HCl$ ===> CH3COOH + NH4Cl**

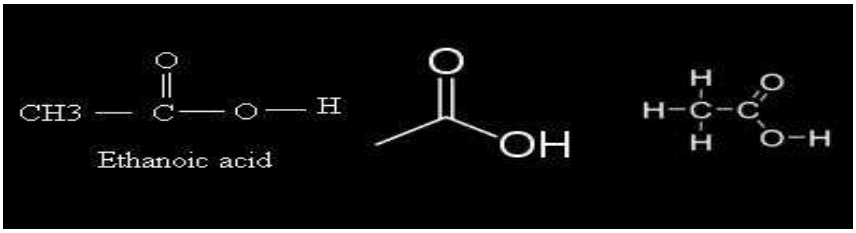
2. **Acetaldehyde:** Acetaldehyde undergoes oxidation at 60^0C in presence of Manganese acetate, which prevents the formation of peracetic acid which is an explosive. **$CH_3CHO + O_2$ ===> $2CH_3COOH$**

3. Acetic acid is prepared by oxidation of acetaldehyde, by oxidation of ethanol as well as by oxidation of butane and butene... Acetic acid can be also be prepared by the oxidation of primary alcohols with alkaline potassium per manganate solution or potassium dichromate. Acetic acid is corrosive to metals. It can be obtained by acetyl chloride and used to prepare ethanol.

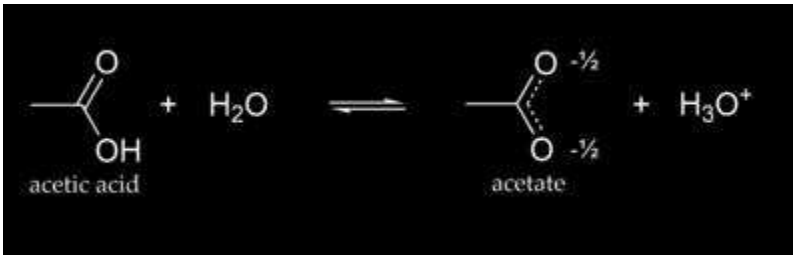


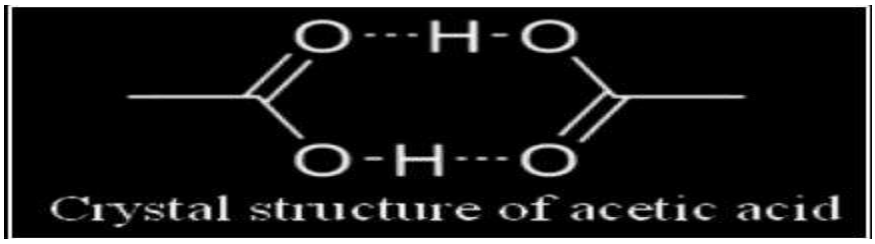
II. Structure of Acetic Acid

Ethanoic acid is also known as acetic acid in the second member of carboxylic acid. It has molecular formula of $C_2H_4O_2$. Its formula is **CH_3COOH.**



Acetic acid can lose its hydrogen atom as an H^+ ions. This property gives acidic character to acetic acid. It is a weak, monoprotic acid in aqueous solution,





The molecules of acetic acids are paired up into dimers joined with hydrogen bonds

III. Properties of Acetic Acid:

1. Physical properties of acetic acid:

- Acetic acid is vinegar; it has a sour taste and a pungent smell.
- Acetic acid is highly corrosive in nature, so it has to be handled with care.
- Acetic acid is hygroscopic in nature.
- The melting point and the boiling point of acetic acid are 16.5^0C and 118.1^0C.
- Acetic acid is miscible in water, i.e. it has solubility in aqueous solution.
- The pH and pK_a value of acetic acid is 2.4 and 4.76 at 25^0C respectively.

2. Chemical properties of acetic acid:

a) Acetic acid reacts with ethyl alcohol in presence of concentrated sulphuric acid, which acts as dehydrating agent to give ethyl acetate which is an ester and the reaction is called esterification reaction.

$$\mathbf{CH_3COOH + C_2H_5OH \ ===> \ CH_3COOC_2H_5 + H_2O}$$

b) When two molecules of acetic acid undergo condensation, it gives acetic anhydride

$$\mathbf{CH_3COOH + CH_3COOH \ ===> \ CH_3CO\text{-}O\text{-}COCH_3 + H_2O}$$

c) Acetic acid reacts with sodium hydroxide and gives sodium acetate; it is an example for acid-base reaction. It is also called as neutralization reaction.

$$\mathbf{CH_3COOH + NaOH \ ===> \ CH_3COONa + H_2O}$$

IV. Applications of Acetic Acid:

- Acetic acid is used as anti-scaling agent.
- Dilute acetic acid is used in clinical laboratory.
- Some salts of acetic acid like silver and copper acetate is used as pesticide and fungicide respectively. Palladium acetate is used as catalyst in coupling reactions in organic chemistry. Similarly some salts of acetic acid are used in textile industry, dyes, etc..,
- Acetic acid has wild applications in polymer field.

ORGANIC CHEMISTRY

Topic-5

Amines – Classification and separation

VERY SHORT ANSWER QUESTIONS

1. What are amines?

Ans: **Amines** are aliphatic and aromatic derivatives of ammonia. Amines, like ammonia, are weak bases ($K_b = 10^{-4}$ to 10^{-6}). This basicity is due to the unshared electron pair on the nitrogen atom.

2. What are primary amines?

Ans: Those amine compounds that have only one group attached to the nitrogen atom are primary amines.

Ex: $CH_3 – NH_2$ (Methyl Amine)

3. **What are secondary amines?**

Ans: Those amine compounds that have two groups attached to the nitrogen atom are secondary amines.

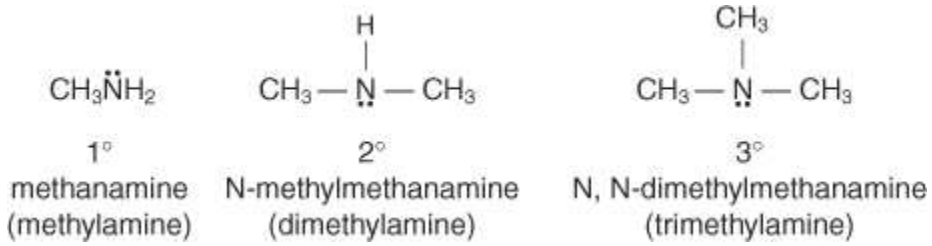
4. What are tertiary amines?

Ans: Those amine compounds that have three groups attached to the nitrogen atom are tertiary amines.

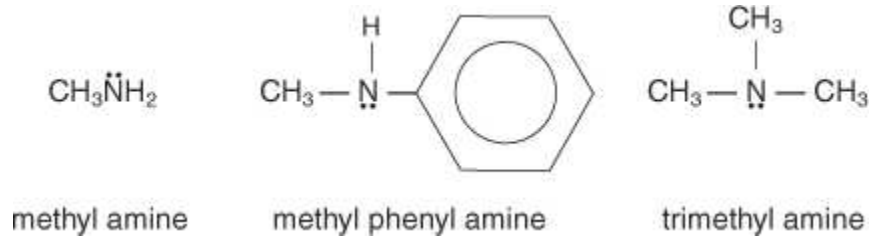
SHORT ANSWER QUESTIONS

1. **Explain the classification of Amines.**

Ans: Classification of amines: Amines are classified as primary, secondary, or tertiary based upon the number of carbon-containing groups that are attached to the nitrogen atom. Those amine compounds that have only one group attached to the nitrogen atom are primary, while those with two or three groups attached to the nitrogen atom are secondary and tertiary, respectively.



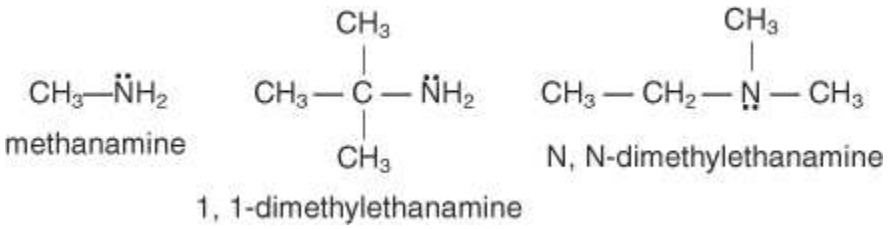
In the common system, you name amines by naming the group or groups attached to the nitrogen atom and adding the word amine.



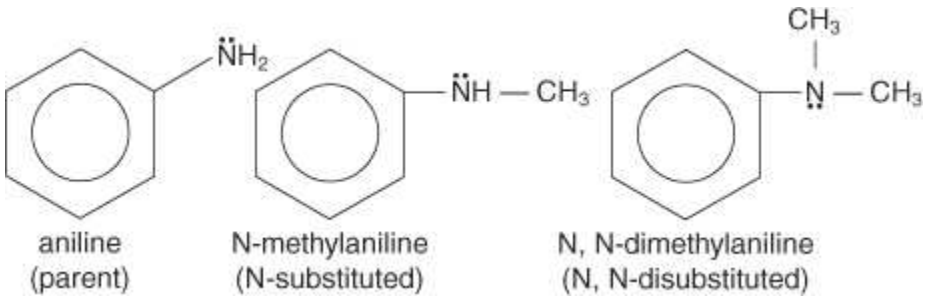
2. **Explain the nomenclature of Amines.**

Ans: In the IUPAC System, apply the following rules to name amines:

1. Pick out the longest continuous chain of carbon atoms. The parent name comes from the alkane of the same number of carbons.
2. Change the -e of the alkane to "amine."
3. Locate and name any substituents, keeping in mind that the chain is numbered away from the amine group. Substituents, which are attached to the nitrogen atom instead of the carbon of the chain, are designated by a capital N.



Aromatic amines belong to specific families, which act as parent molecules. For example, an amino group (—NH_2) attached to benzene produces the parent compound aniline.



3. Explain the basicity of amines.

Ans: Basicity of amines : Amines are basic because they possess a pair of unshared electrons, which they can share with other atoms. These unshared electrons create an electron density around the nitrogen atom. The greater the electron density, the more basic the molecule. Groups that donate or supply electrons will increase the basicity of amines while groups that decrease the electron density around the nitrogen decrease the basicity of the molecule. For alkyl halides in the gas phase, the order of base strength is given below:

$(CH_3)_3 N > (CH_3)_2NH > CH_3NH_2 > NH_3$

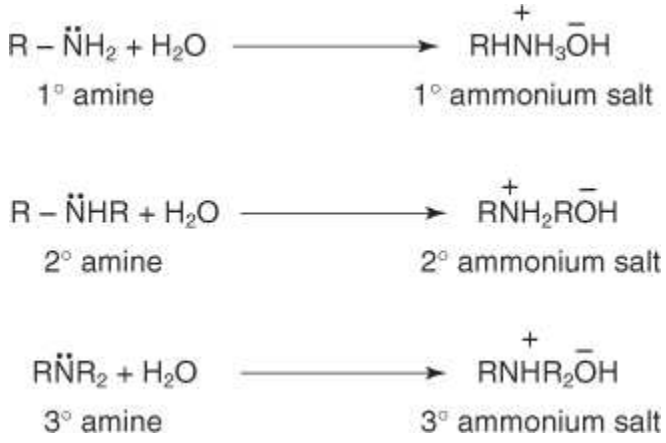
most basic — least basic

However, in aqueous solutions, the order of basicity changes.

$(CH_3)_2 NH > CH_3NH_2 > (CH_3)_3N > NH_3$

most basic — least basic

The differences in the basicity order in the gas phase and aqueous solutions are the result of solvation effects. Amines in water solution exist as ammonium ions.



In water, the ammonium salts of primary and secondary amines undergo solvation effects (due to hydrogen bonding) to a much greater degree than ammonium salts of tertiary amines. These solvation effects increase the electron density on the amine nitrogen to a greater degree than the inductive effect of alkyl groups.

Arylamines are weaker bases than cyclohexylamines because of resonance. Aniline, a typical arylamine, exhibits the resonance structures shown in Figure 1 .

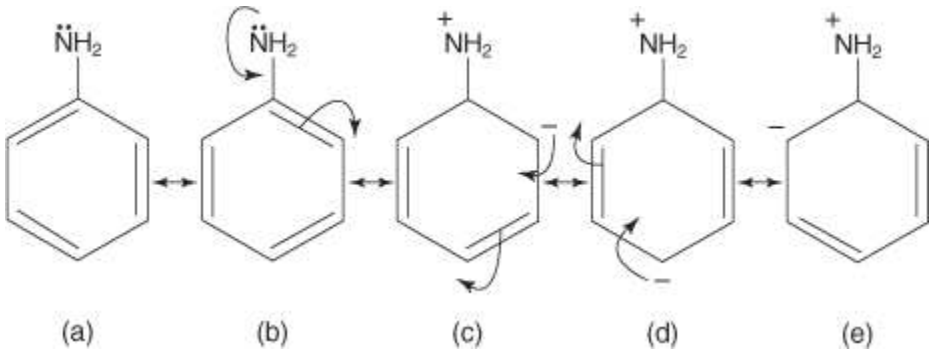


Figure 1

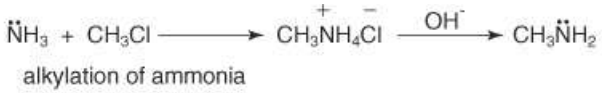
As structures b through e in Figure 1 show, delocalization of the unshared electron pair occurs throughout the ring, making these electrons less available for reaction. As a result of this electron delocalization, the molecule becomes less basic.

LONG ANSWER QUESTIONS

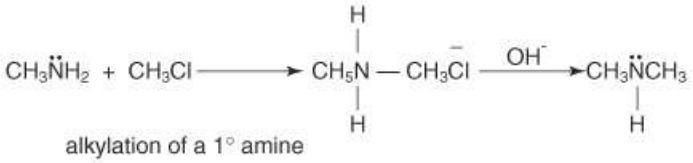
1. **Explain the methods of preparation of amines.**

Ans: Preparation of Amines: The alkylation of ammonia, Gabriel synthesis, reduction of nitriles, reduction of amides, reduction of nitrocompounds, and reductive amination of aldehydes and ketones are methods commonly used for preparing amines.

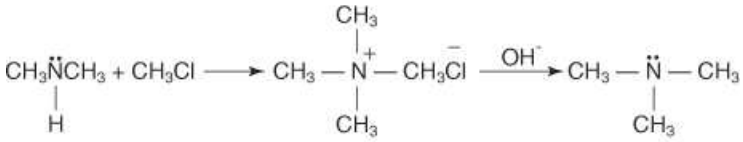
a) Alkylation of ammonia: The reaction of ammonia with an alkyl halide leads to the formation of a primary amine. The primary amine that is formed can also react with the alkyl halide, which leads to a disubstituted amine that can further react to form a trisubstituted amine. Therefore, the alkylation of ammonia leads to a mixture of products.



alkylation of ammonia



alkylation of a 1° amine



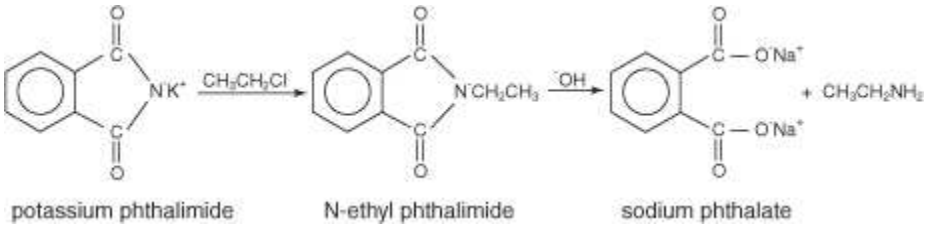
alkylation of a 2° amine

b) Reduction of alkylazides: You can best prepare a primary amine from its alkylazide by reduction or by the **Gabriel synthesis.**

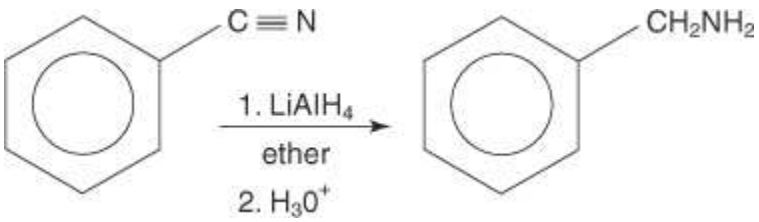


Ethyl Azide

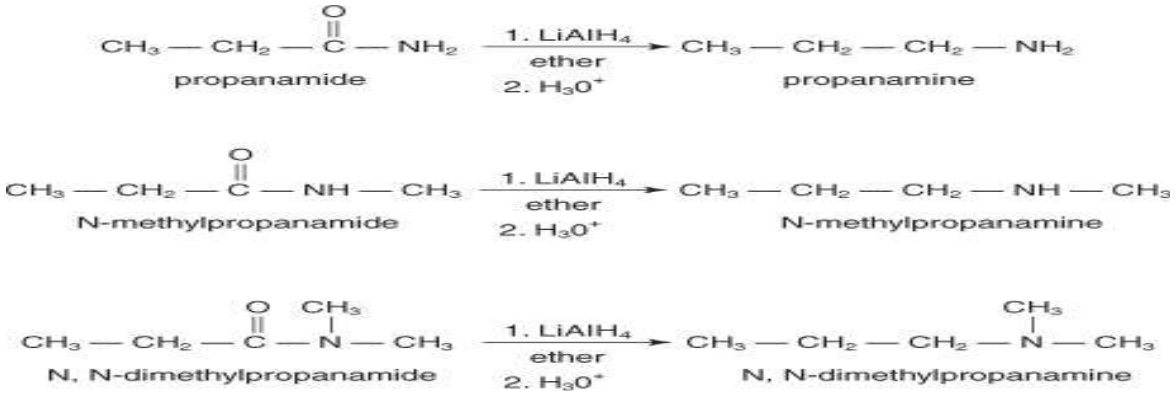
In the **Gabriel synthesis**, potassium phthalimide is reacted with an alkyl halide to produce an N-alkyl phthalimide. This N-alkyl phthalimide can be hydrolyzed by aqueous acids or bases into the primary amine.



c) Reduction of nitriles : Nitriles can be reduced by lithium aluminum hydride ($LiAlH_4$) to primary amines.

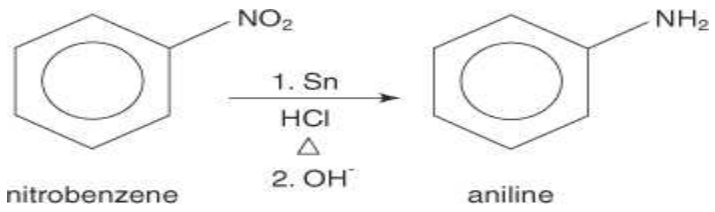


d) Reduction of amides: Amides yield primary amines on reduction by lithium aluminum hydride, while N-substituted and N, N-disubstituted amides produce secondary and tertiary amines, respectively.



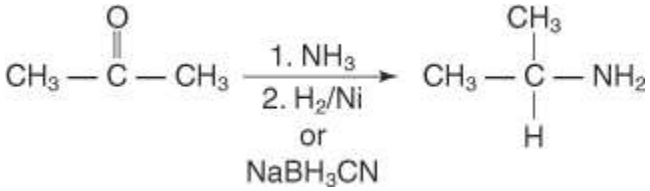
Because amides are easily prepared, their reduction is a preferred method for making all classes of amines.

e) Reduction of nitrocompounds: Aromatic amines are normally prepared by reduction of the corresponding aromatic nitro compound.

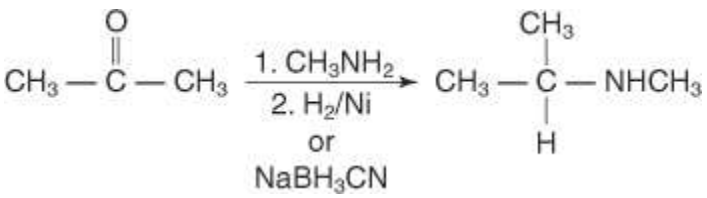


f) Reductive amination of aldehydes and ketones: Aldehydes or ketones can be reduced by catalytic or chemical reductions in the presence of ammonia or primary or secondary amines, producing primary, secondary, or tertiary amines.

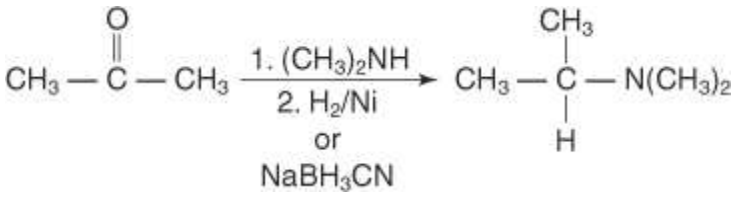
The reaction of a ketone with ammonia, followed by catalytic reduction or reduction by sodium cyanoborohydride, produces a 1° amine.



N-substituted amines are produced by reaction of ketones with primary amines, followed by reduction.



N, N-disubstituted amines can be produced by reaction of 2° amines with ketones followed by reduction.



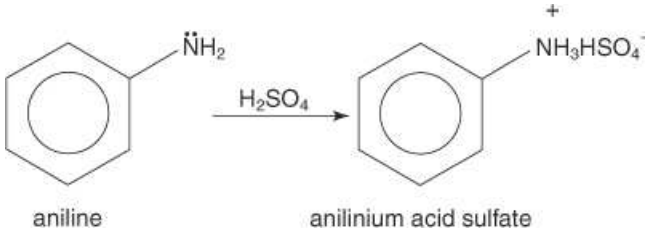
2. **Explain the physical and chemical properties of amines.**

I. Physical properties of amines: some of the physical properties of amines are as follows.

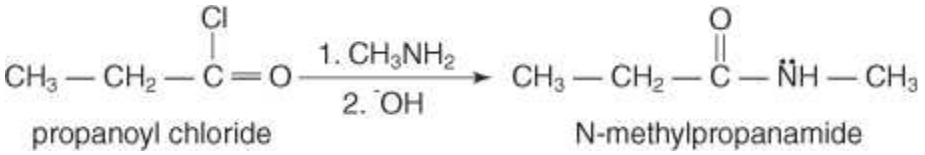
- The lower aliphatic amines are gases with fishy odour.
- Primary amines with three or more carbon atoms are liquid and still higher ones are solid.
- Aniline and other arylamines are usually colourless but get coloured on storage due to atmospheric oxidation.
- Higher amines are essentially insoluble in water.
- Amines are soluble in organic solvents like alcohols, ether benzene.

II. Chemical properties of Amines: Due to the unshared electron pair, amines can act as both bases and nucleophiles.

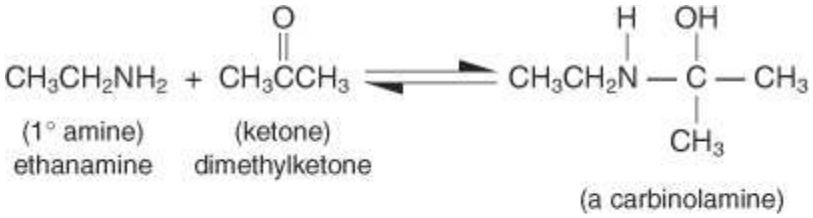
a) Reaction with acids: When reacted with acids, amines donate electrons to form ammonium salts.

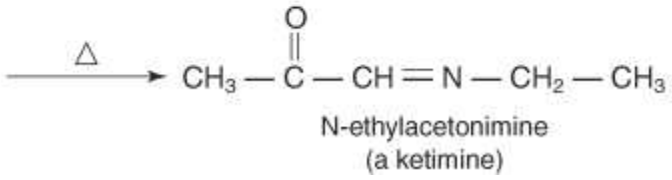


b) Reaction with acid halides: Acid halides react with amines to form substituted amides.

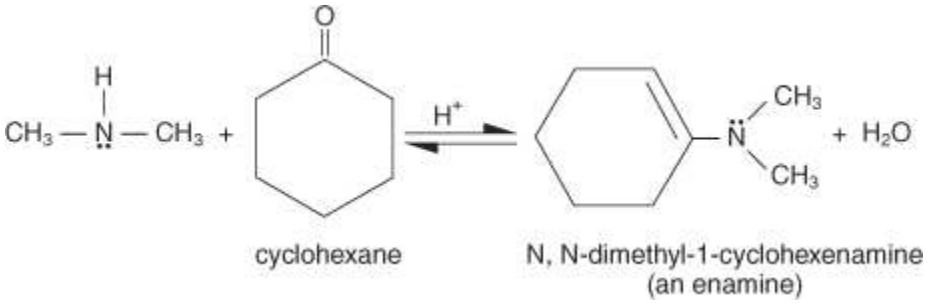


c) Reaction with aldehydes and ketones: Aldehydes and ketones react with primary amines to give a reaction product (a carbinolamine) that dehydrates to yield aldimines and ketimines (Schiff bases).

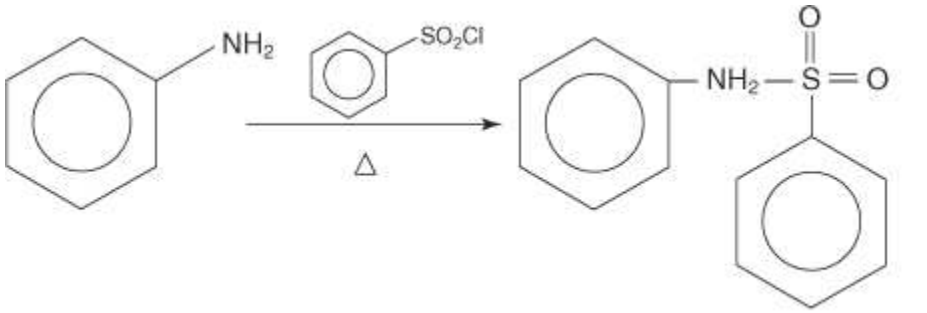




If you react secondary amines with aldehydes or ketones, enamines form.

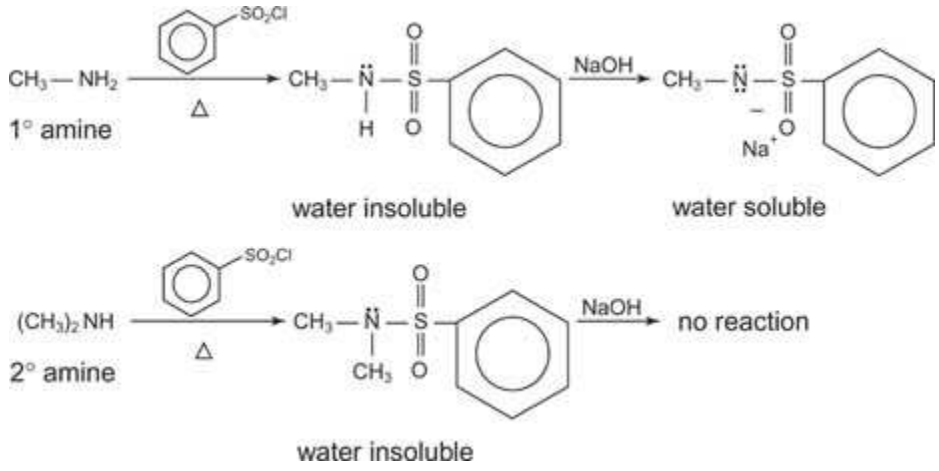


d) Reaction with sulfonyl chlorides: Amines react with sulfonyl chlorides to produce sulfonamides. A typical example is the reaction of benzene sulfonyl chloride with aniline.

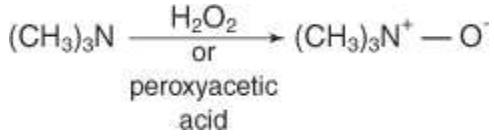


N-phenylbenzenesulfonamide

e) The Hinsberg test: The Hinsberg test, which can distinguish primary, secondary, and tertiary amines, is based upon sulfonamide formation. In the Hinsberg test, an amine is reacted with benzene sulfonyl chloride. If a product forms, the amine is either a primary or secondary amine, because tertiary amines do not form stable sulfonamides. If the sulfonamide that forms dissolves in aqueous sodium hydroxide solution, it is a primary amine. If the sulfonamide is insoluble in aqueous sodium hydroxide, it is a secondary amine. The sulfonamide of a primary amine is soluble in an aqueous base because it still possesses an acidic hydrogen on the nitrogen, which can be lost to form a sodium salt.



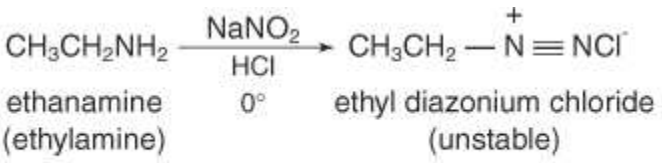
f) Oxidation: Although you can oxidize all amines, only tertiary amines give easily isolated products. The oxidation of a tertiary amine leads to the formation of an amine oxide.

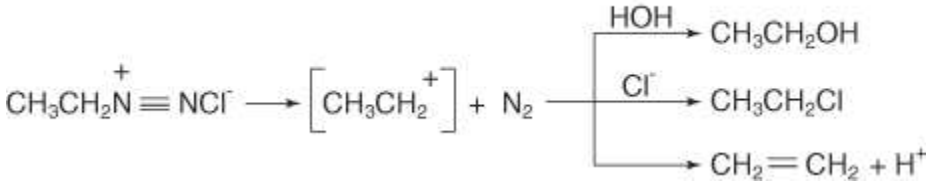


Arylamines tend to be easily oxidized, with oxidation occurring on the amine group as well as in the ring.

g) Reaction with nitrous acid: Nitrous acid is unstable and must be prepared in the reaction solution by mixing sodium nitrite with acid.

Primary amines react with nitrous acid to yield a diazonium salt, which is highly unstable and degrades into a carbocation that is capable of reaction with any nucleophile in solution. Therefore, reacting primary amines with nitrous acid leads to a mixture of alcohol, alkenes, and alkyl halides.

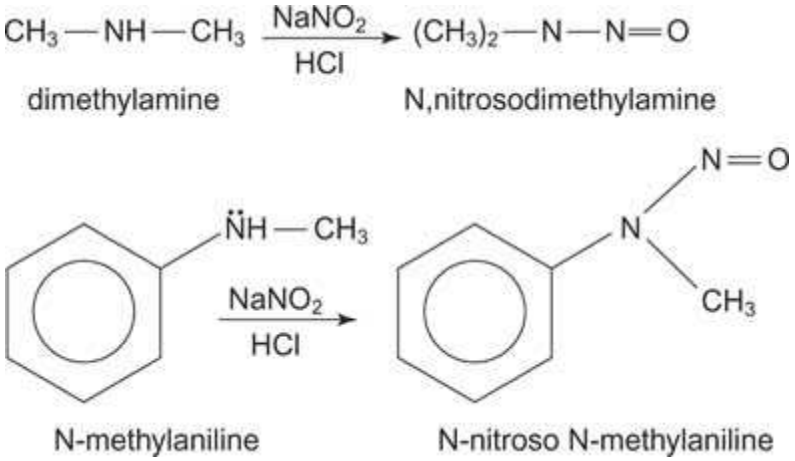




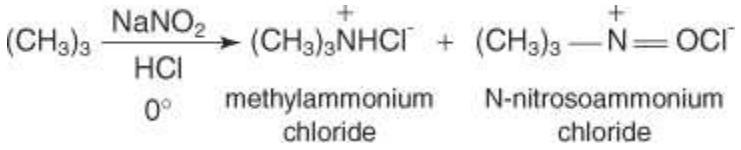
Primary aromatic amines form stable diazonium salts at zero degrees.



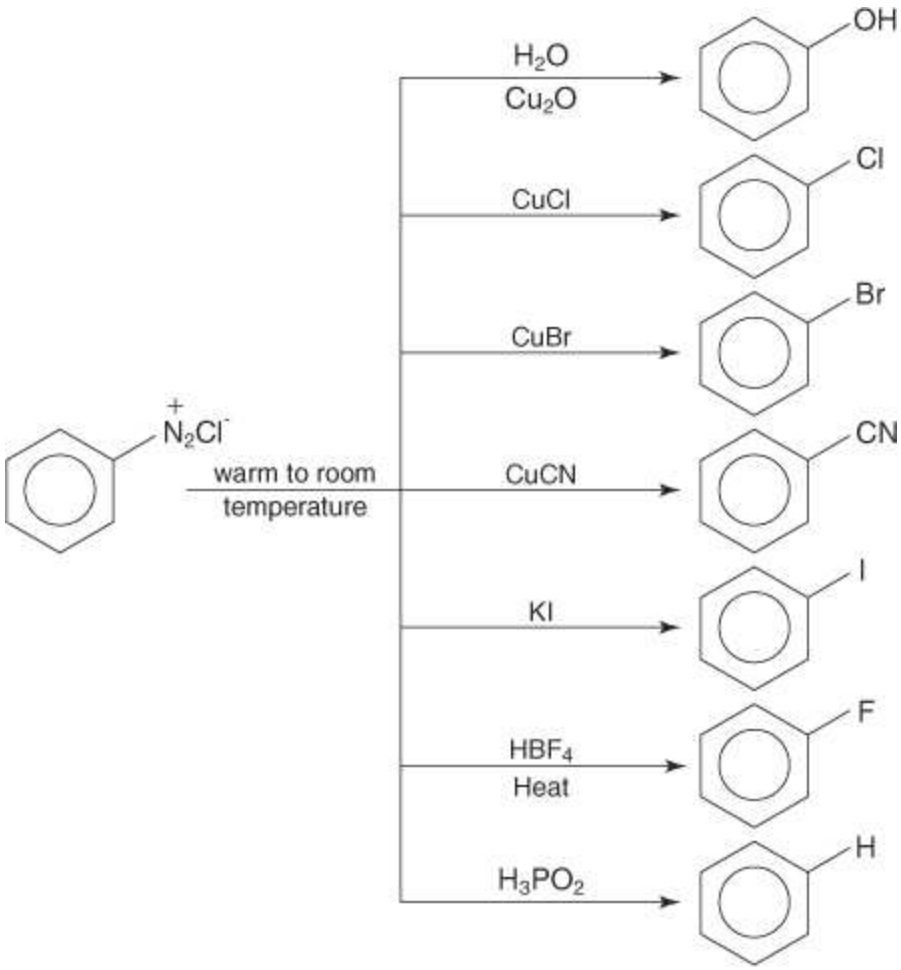
Secondary aliphatic and aromatic amines form nitrosamine with nitrous acid.



Tertiary amines react with nitrous acid to form N-nitrosoammonium compounds.



h) Reactions of aromatic diazonium salts: Diazonium salts of aromatic amines are very useful as intermediates to other compounds. Because aromatic diazonium salts are only stable at very low temperatures (zero degrees and below), warming these salts initiates decomposition into highly reactive cations. These cations can react with any anion present in solution to form a variety of compounds. Figure illustrates the diversity of the reactions.



III. Uses of Amines

1) Dyes

Aromatic amines are mainly used as a starting material for the production of azo dyes. It reacts with nitric (III) acid to form diazonium salt, which goes through coupling reaction to form azo compound. As azo-compounds are highly coloured, they are used broadly in dyeing industries, like: Methyl orange, Direct brown 138, Sunset yellow FCF and Ponceau.

2) Drugs

Many drugs are designed for mimicing or to interfere with the action of natural amine neurotransmitters, can be exemplified by the amine drugs:

Chlorpheniramine is an antihistamine which helps to relieve allergic disorders caused due to cold, hay fever, itchy skin, insect bites and stings.

Chlorpromazine is a tranquillizer which sedates without inducing sleep. It is used to relieve anxiety, excitement, restlessness and sometimes even mental disorder.

Ephedrine and Phenylephrine in form of amine hydrochlorides,are used as decongestants.

Amphetamine, Methamphetamine, and Methcathinone are amines which are listed as controlled substances by the DEA (diethanolamine).

Amitriptyline, Imipramine, Lofepramine and Clomipramine are tricyclic anti-depressants and tertiary amines.

Nortriptyline, Desipramine, and Amoxapine are tricyclic anti-depressants and secondary amines.

3. Industrial uses

Aqueous monoethanolamine (MEA), diglycolamine (DGA), diethanolamine (DEA), diisopropanolamine (DIPA) and methyldiethanolamine (MDEA) are used broadly in industries for removing carbon dioxide (CO2) and hydrogen sulfide (H2S) from natural gas streams and also from refinery process streams. They may also be helpful in removing CO2 from combustion gases / flue gases and may have got potential for abatement of greenhouse gases.

3. How primary, secondry and tertiary amines can be separated?

Ans: Separation of 1^o, 2^o and 3^o amines

- The mixture of amines is reacted with benzene sulphonyl chloride. The product mixture obtained is treated with aqueous HCl and filtered.
- The filtrate contains tertiary amine as its hydrochloride which can be isolated as amine with addition of base.
- The acid insoluble residue contains the 2^o and 1^o amine. This residue is treated with aq KOH solution and filtered.
- The secondary amine sulphonamide is insoluble in alkali so it is obtained as a residue. It is hydrolysed to get secondary amine.
- The filtrate on acidification gives the sulphonamide of the primary amine which is isolated after hydrolysis.

ORGANIC CHEMISTRY

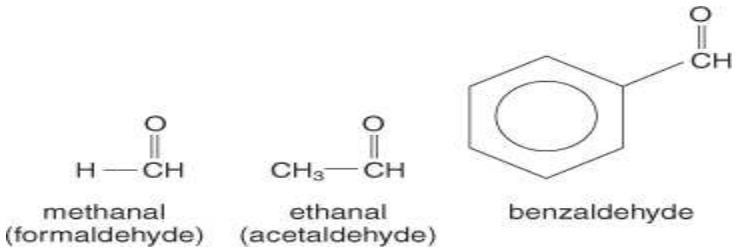
TOPIC: 6

Carbonyl compounds, Acetaldehyde and Acetone

VERY SHORT ANSWER QUESTIONS

1. **What are aldehydes?**

Ans: Aldehydes: All aldehydes, except for formaldehyde, have a carbonyl group (C=O) attached to a hydrogen on one side and an alkyl or aryl group on the other side. Formaldehyde, the simplest aldehyde, has hydrogen on both sides of the carbonyl group.



2. **What are physical properties of aldehydes?**

Ans: Physical properties:

Both aldehydes and ketones, have higher boiling points than hydrocarbons of similar chain lengths due to a greater degree of polarity and greater dipole-dipole interaction between molecules.

Carbonyl groups cannot form strong intermolecular hydrogen bonds, so both aldehydes and ketones generally boil at lower temperatures than their alcohol analogues.

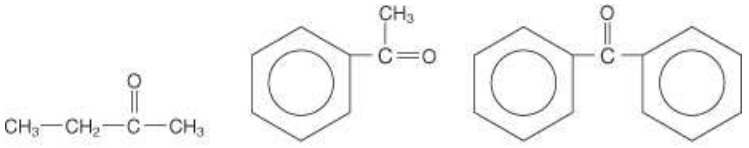
However, aldehydes and ketones of low molecular weight do form strong hydrogen bonds with water, leading to good solubility.

3. **Explain the structure of carbonyl group**

Ans: Structure of the carbonyl group: In aldehydes and ketones, the carbonyl group, with its attached hydrogen atom, alkyl group, or aryl group, lies in a plane with all bond angles close to 120°. The bond length of the carbon-oxygen double bond is significantly shorter than the average bond length of a carbon-oxygen single bond in alcohols or ethers. This factor makes the carbonyl group polar. Both aldehydes and ketones have dipole moments that are substantially greater than those of analogues with carbon-carbon double bonds. For example, 1-butene shows a dipole moment of 0.3 debye units (0.3 D), while propanol has a dipole moment of 2.5 D.

4. **What are ketones?**

Ans: Ketones: Ketones are compounds in which an oxygen atom is bonded to a carbon atom, which is itself bonded to two or more carbon atoms.

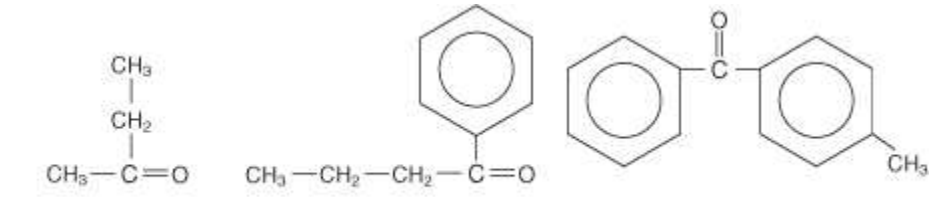


2-butanone (methyl ethyl ketone) | 1-phenylethanone (methyl phenyl ketone) | diphenyl methanone (diphenyl ketone)

SHORT ANSWER QUESTIONS

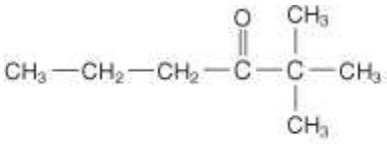
1. Explain the IUPAC naming of Ketones.

Ans: Like aldehydes, ketones can be named using either the common system or the IUPAC system. In the common system, ketones names are created by naming the groups attached to the carbonyl carbon and then adding the word *ketone*. Following are several examples:

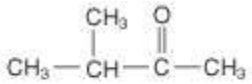


ethyl methyl ketone | phenyl propyl ketone | phenyl p-tolyl ketone

The five IUPAC rules for aldehydes also apply to ketones, with one exception: After dropping the -e ending of the alkane name, you add -one for ketones (rather than -al, which designates aldehydes).

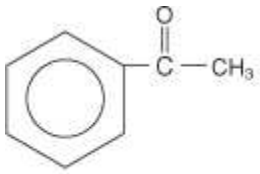


2,2-dimethyl-3-hexanone

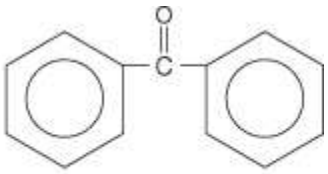


3-methyl-2-butanone

In the IUPAC system, aromatic ketones are considered benzenesubstituted aliphatic ketones.

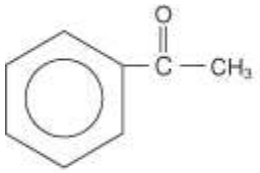


1-phenylethanone

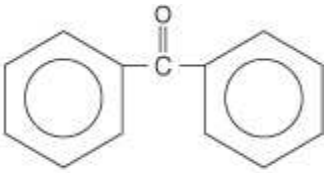


diphenyl methanone

Many aromatic compounds retain their common names in the IUPAC system. Following are two such examples:



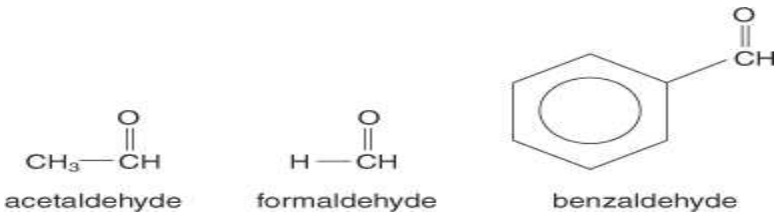
acetophenone



benzophenone

2. What is the nomenclature of aldehydes?

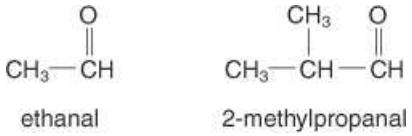
Nomenclature: Aldehydes are named using either the common system or the IUPAC system. Aldehyde common names are derived from the common names of the corresponding carboxylic acid. For example:



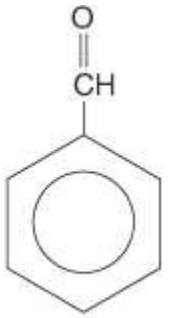
The IUPAC system employs a series of rules to formulate compound names. The following rules explain how to name aliphatic aldehydes:

1. Pick out the longest continuous chain of carbon atoms that contains the carbonyl group.
2. The parent name comes from the alkane name of the same number of carbons.
3. Drop the -e ending of the alkane name and add -al.
4. Number the chain so that the carbonyl carbon has the lower possible number.
5. Locate and name substituents.

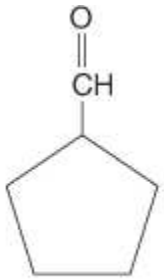
The following examples illustrate IUPAC naming:



In the IUPAC system, cyclic, aliphatic, and aromatic aldehydes are named by adding the word carbaldehyde to the name of the ring system.



benzenecarbaldehyde



cyclopentanecarbaldehyde

Most chemists use the name benzaldehyde instead of benzenecarbaldehyde. Many texts and articles also use this alternate name.

LONG ANSWER QUESTIONS

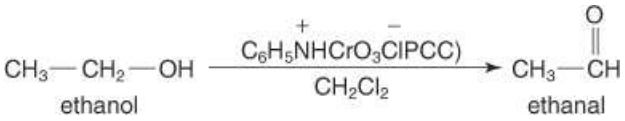
1. Explain the methods of preparation of Aldehydes.

Synthesis of Aldehydes

Aldehydes can be prepared via a number of pathways. Some of the common methods are explained here.

a) The oxidation of primary alcohols

Primary alcohols can be oxidized by mild oxidizing agents, such as pyridinium chlorochromate (PCC), to yield aldehydes.

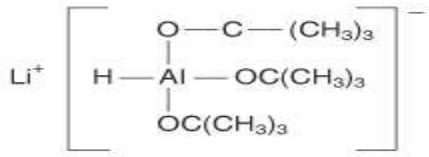


The use of strong oxidizing agents would lead to the fully-oxidized product (carboxylic acid).

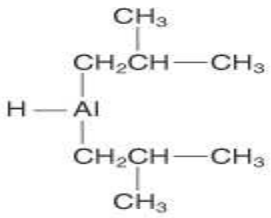
b) The reduction of acyl chlorides, esters, and nitriles

Reduction by mild reducing agents converts acyl chlorides, esters, and nitrites into aldehydes. The reducing agents of choice are usually lithium tri-tert-butoxy aluminum hydride (LATB—H) and diisobutylaluminum hydride (DIBAL—H). Following are the structures for these compounds:

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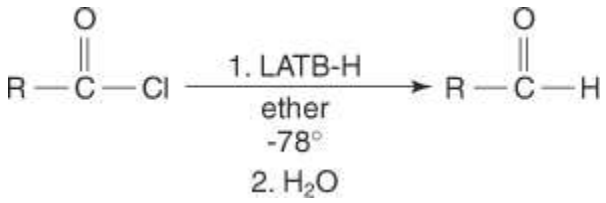
lithium tri-tert-butoxyaluminum hydride
(LATB-H)



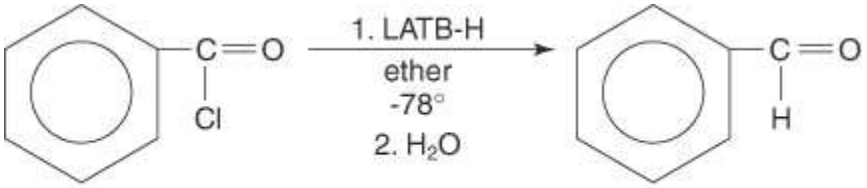
diisobutylaluminum hydride
(DIBAL-H)

c) Acyl chloride reduction

Acyl chlorides can be reduced by reacting them with lithium tri-tert-butoxyaluminum hydride at −78°C.



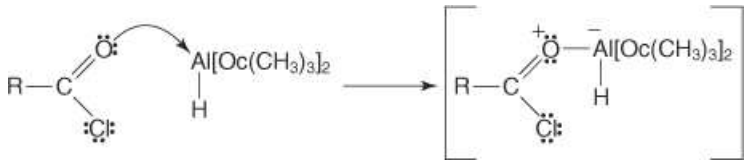
Following is a typical reduction of an aromatic compound employing this reagent.



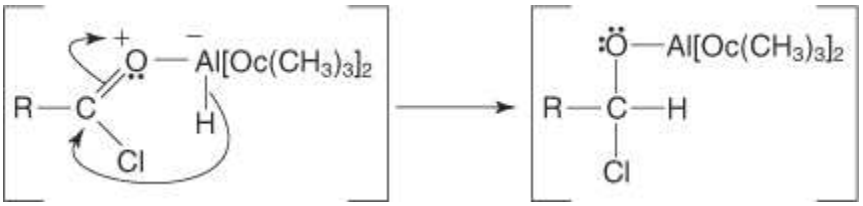
benzoyl chloride benzaldehyde

The mechanism for acid chloride reduction proceeds via a hydride-ion transfer from the reducing agent to the acid chloride. The following steps summarize this mechanism.

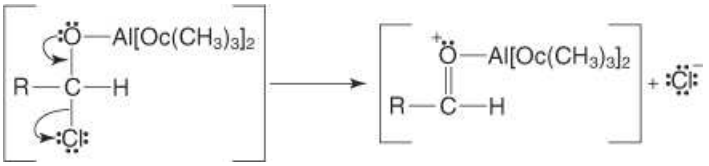
1. An acid-base reaction occurs between an electron pair on the oxygen of the carbonyl group and the aluminum atom of the LATB—H.



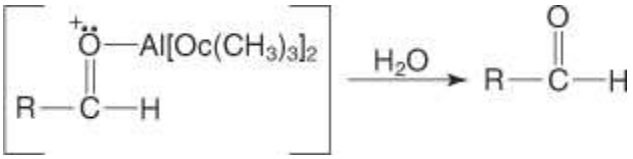
2. A hydride ion is transferred to the carbonyl carbon with a corresponding movement of the π electrons of the carbonyl group to the carbonyl oxygen.



3. A chloride ion is liberated with anchimeric assistance from an electron pair on the carbonyl oxygen.

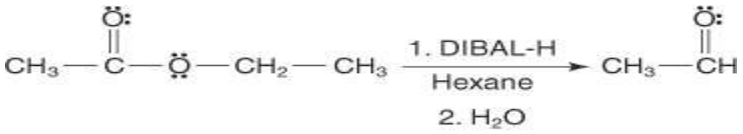


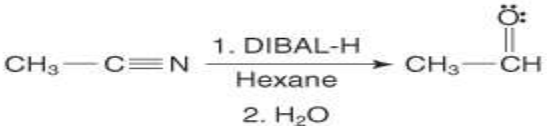
4. The aluminum complex is hydrolyzed by the addition of water to form the aldehyde.



d) Ester and nitrile reduction:

You can use di isobutylaluminum hydride to reduce both esters and nitriles to aldehydes. Typical examples are the reduction of ethyl ethanoate (ethyl acetate) and ethanenitrile (acetonitrile) to ethanal (acetaldehyde).

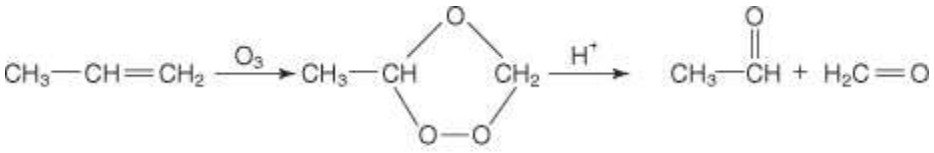




The mechanism for both of these reactions is very similar to the mechanism for the reduction of acyl chlorides by LATB—H. The first step is an acid-base reaction between an unshared electron pair on oxygen or nitrogen with the aluminum atom of the DIBAL—H. The second step is the transfer of a hydride ion from the DIBAL—H to the carbon atom of the carbonyl or nitrile group. The last step is the hydrolysis of the aluminum complex to form the aldehyde.

e) Ozonolysis of alkenes

Alkenes in which the carbon(s) of the double bond possess one or more hydrogen atoms react with ozone (O_3) to generate aldehydes. The reaction of propene with ozone to form acetaldehyde and formaldehyde illustrates this method of preparation.



an ozonide

f) Hydroboration of terminal alkynes:

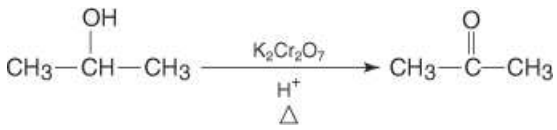
Terminal alkynes react rapidly with borane to produce an intermediate compound that is easily oxidized to an aldehyde. For example, you can produce pentenal by reacting pentyne with borane and oxidizing the resulting intermediate with aqueous hydrogen peroxide.

2. **Explain the methods of preparation of ketones.**

Ans: Synthesis of Ketones : Like aldehydes, ketones can be prepared in a number of ways. The following sections detail some of the more common preparation methods: the oxidation of secondary alcohols, the hydration of alkynes, the ozonolysis of alkenes, Friedel-Crafts acylation, the use of lithium dialkylcuprates, and the use of a Grignard reagent.

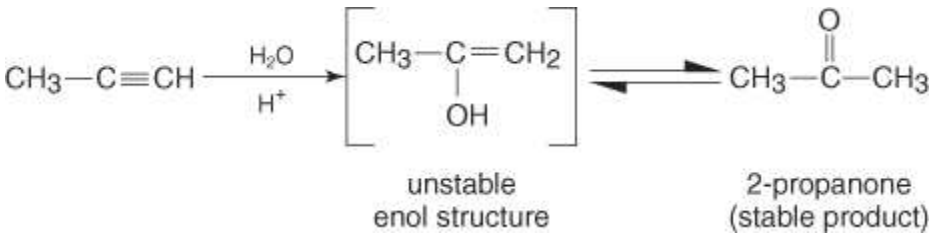
a) Oxidation of secondary alcohols:

The oxidation of secondary alcohols to ketones may be carried out using strong oxidizing agents, because further oxidation of a ketone occurs with great difficulty. Normal oxidizing agents include potassium dichromate ($K_2Cr_2O_7$) and chromic acid (H_2CrO_4). The conversion of 2-propanol to 2-propanone illustrates the oxidation of a secondary alcohol.



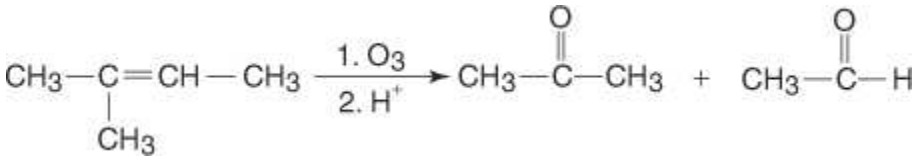
b) Hydration of alkynes:

The addition of water to an alkyne leads to the formation of an unstable vinyl alcohol. These unstable materials undergo keto-enol tautomerization to form ketones. The hydration of propyne forms 2-propanone, as the following figure illustrates.



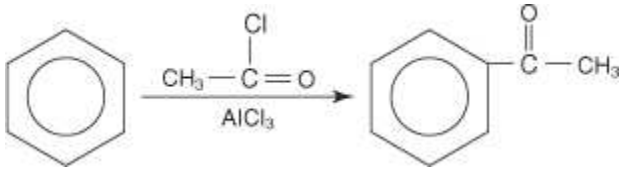
c) Ozonolysis of alkenes

When one or both alkene carbons contain two alkyl groups, ozonolysis generates one or two ketones. The ozonolysis of 1,2-dimethyl propene produces both 2-propanone (a ketone) and ethanal (an aldehyde).



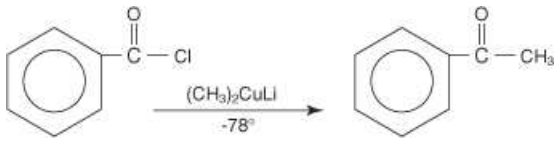
d) Friedel-Crafts acylation

Friedel-Crafts acylations are used to prepare aromatic ketones. The preparation of acetophenone from benzene and acetyl chloride is a typical Friedel-Crafts acylation.



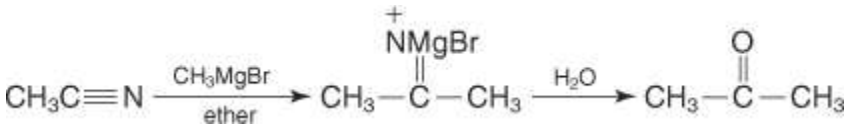
e) Lithium dialkylcuprates

The addition of a lithium dialkylcuprate (Gilman reagent) to an acyl chloride at low temperatures produces a ketone. This method produces a good yield of acetophenone.



f) Grignard reagents

Hydrolysis of the salt formed by reacting a Grignard reagent with a nitrile produces good ketone yields. For example, you can prepare acetone by reacting the Grignard reagent methyl magnesium bromide (CH_3MgBr) with methyl nitrile ($CH_3C\quad N$).



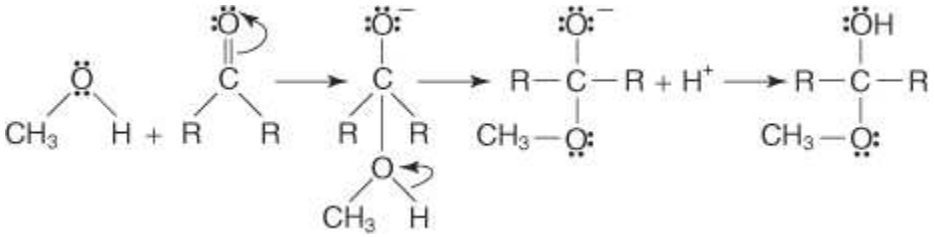
3. Explain the reactions of aldehydes and ketones.

Ans: Reactions of Aldehydes and Ketones:

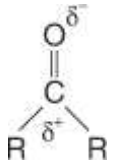
Aldehydes and ketones undergo a variety of reactions that lead to many different products. The most common reactions are nucleophilic addition reactions, which lead to the formation of alcohols, alkenes, diols, cyanohydrins (RCH(OH)C N), and imines R_2C NR), to mention a few representative examples.

a) Reactions of carbonyl groups:

The main reactions of the carbonyl group are nucleophilic additions to the carbon-oxygen double bond. As shown below, this addition consists of adding a nucleophile and a hydrogen across the carbon-oxygen double bond.



Due to differences in electronegativities, the carbonyl group is polarized. The carbon atom has a partial positive charge, and the oxygen atom has a partially negative charge.



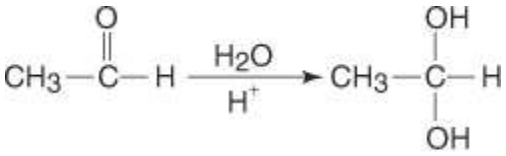
Aldehydes are usually more reactive toward nucleophilic substitutions than ketones because of both steric and electronic effects. In aldehydes, the relatively small hydrogen

atom is attached to one side of the carbonyl group, while a larger R group is affixed to the other side. In ketones, however, R groups are attached to both sides of the carbonyl group. Thus, steric hindrance is less in aldehydes than in ketones.

Electronically, aldehydes have only one R group to supply electrons toward the partially positive carbonyl carbon, while ketones have two electron-supplying groups attached to the carbonyl carbon. The greater amount of electrons being supplied to the carbonyl carbon, the less the partial positive charge on this atom and the weaker it will become as a nucleus.

b) Addition of water:

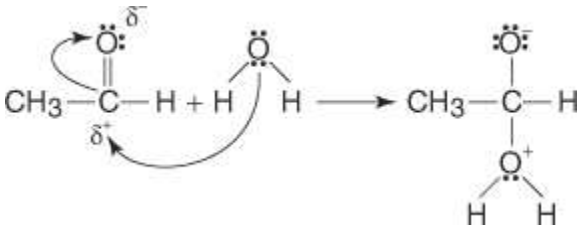
The addition of water to an aldehyde results in the formation of a hydrate.



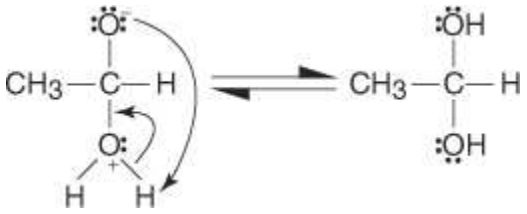
hydrate

The formation of a hydrate proceeds via a nucleophilic addition mechanism.

1. Water, acting as a nucleophile, is attracted to the partially positive carbon of the carbonyl group, generating an oxonium ion.

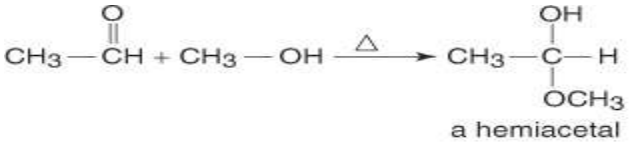


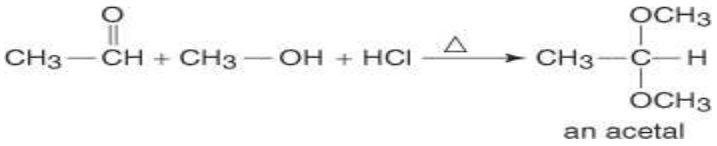
2. The oxonium ion liberates a hydrogen ion that is picked up by the oxygen anion in an acid-base reaction.



Small amounts of acids and bases catalyze this reaction. This occurs because the addition of acid causes a protonation of the oxygen of the carbonyl group, leading to the formation of a full positive charge on the carbonyl carbon, making the carbon a good nucleus. Adding hydroxyl ions changes the nucleophile from water (a weak nucleophile) to a hydroxide ion (a strong nucleophile). Ketones usually do not form stable hydrates.

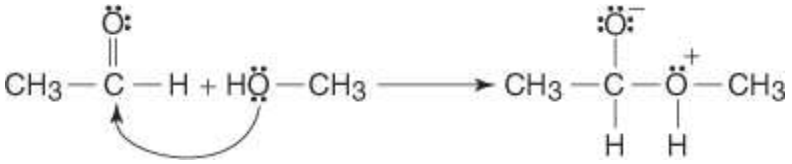
c) Addition of alcohol: Reactions of aldehydes with alcohols produce either **hemiacetals** (a functional group consisting of one —OH group and one —OR group bonded to the same carbon) or **acetals** (a functional group consisting of two —OR groups bonded to the same carbon), depending upon conditions. Mixing the two reactants together produces the hemiacetal. Mixing the two reactants with hydrochloric acid produces an acetal. For example, the reaction of methanol with ethanal produces the following results:



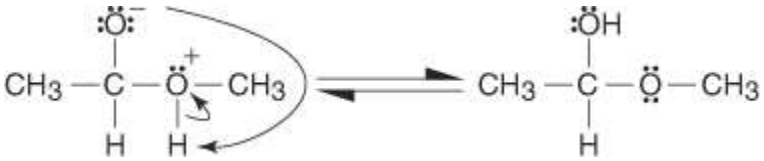


A nucleophilic substitution of an OH group for the double bond of the carbonyl group forms the hemiacetal through the following mechanism:

1. An unshared electron pair on the alcohol's oxygen atom attacks the carbonyl group.

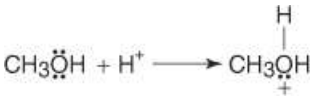


2. The loss of a hydrogen ion to the oxygen anion stabilizes the oxonium ion formed in Step 1.

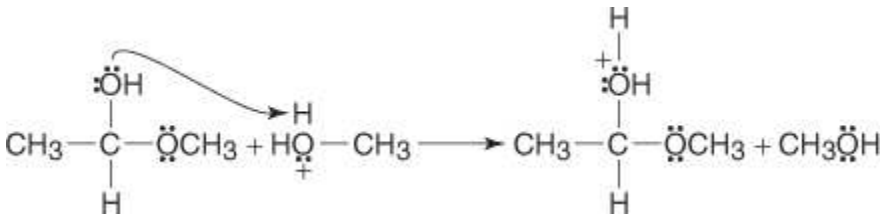


The addition of acid to the hemiacetal creates an acetal through the following mechanism:

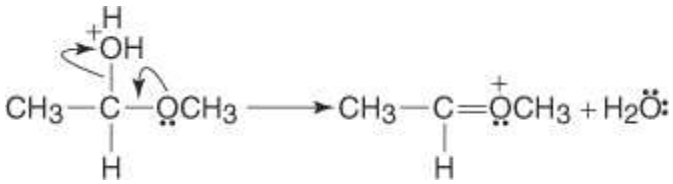
1. The proton produced by the dissociation of hydrochloric acid protonates the alcohol molecule in an acid-base reaction.



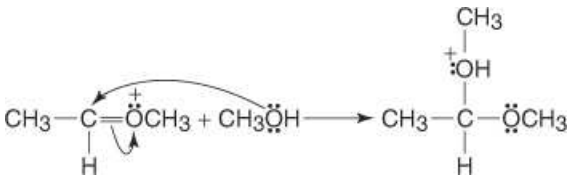
2. An unshared electron pair from the hydroxyl oxygen of the hemiacetal removes a proton from the protonated alcohol.



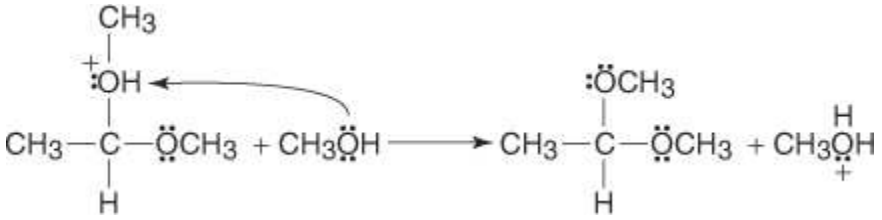
3. The oxonium ion is lost from the hemiacetal as a molecule of water.



4. A second molecule of alcohol attacks the carbonyl carbon that is forming the protonated acetal.

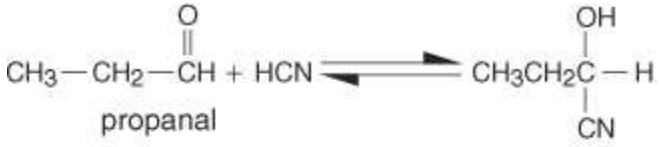


5. The oxonium ion loses a proton to an alcohol molecule, liberating the acetal.



d) Addition of hydrogen cyanide:

The addition of hydrogen cyanide to a carbonyl group of an aldehyde or most ketones produces a cyanohydrin. Sterically hindered ketones, however, don't undergo this reaction.

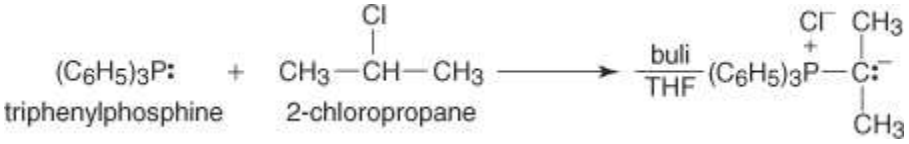




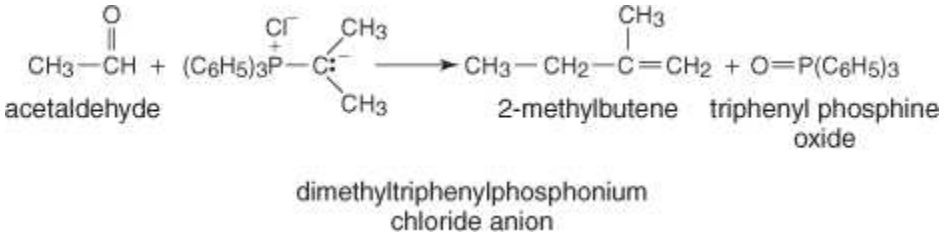
The mechanism for the addition of hydrogen cyanide is a straightforward nucleophilic addition across the carbonyl carbony oxygen bond.

e) Addition of Ylides (the Wittig reaction):

The reaction of aldehydes or ketones with phosphorus ylides produces alkenes of unambiguous double-bond locations. Phosphorous ylides are prepared by reacting a phosphine with an alkyl halide, followed by treatment with a base. Ylides have positive and negative charges on adjacent atoms.

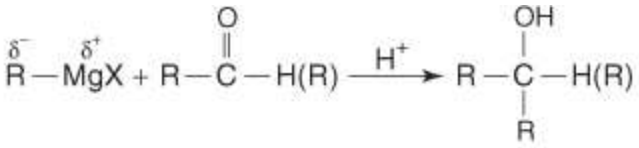


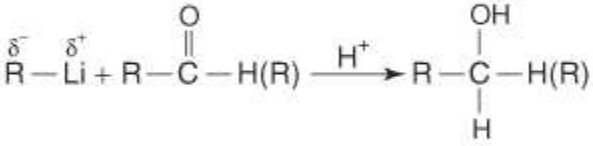
The following illustration shows the preparation of 2-methylbutene by a Wittig reaction.

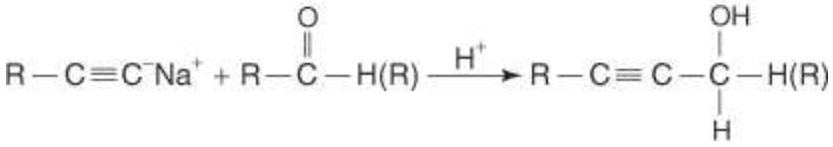


f) Addition of organometallic reagents

Grignard reagents, organolithium compounds, and sodium alkynides react with formaldehyde to produce primary alcohols, all other aldehydes to produce secondary alcohols, and ketones to produce tertiary alcohols.







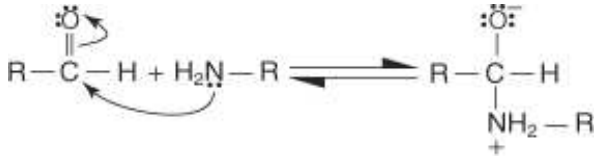
g) Addition of ammonia derivatives:

Aldehydes and ketones react with primary amines to form a class of compounds called imines.

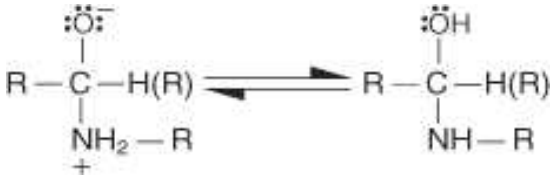


The mechanism for imine formation proceeds through the following steps:

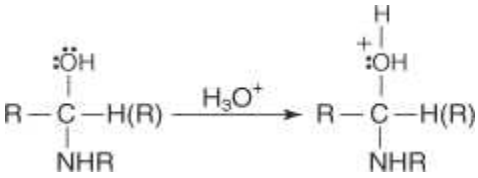
1. An unshared pair of electrons on the nitrogen of the amine is attracted to the partial-positive carbon of the carbonyl group.



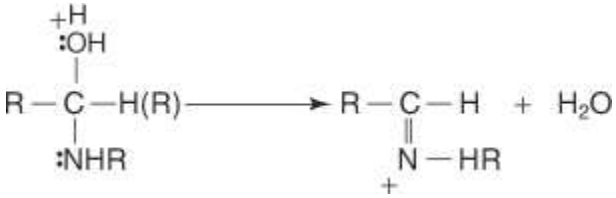
2. A proton is transferred from the nitrogen to the oxygen anion.



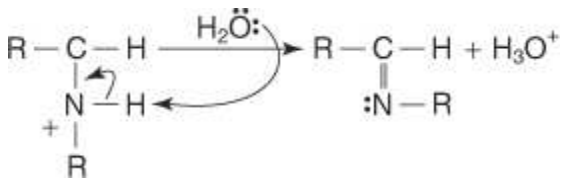
3. The hydroxy group is protonated to yield an oxonium ion, which easily liberates a water molecule.



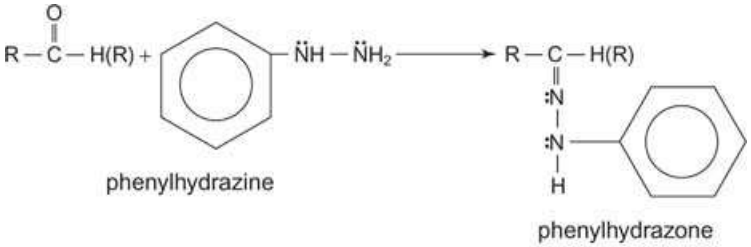
4. An unshared pair of electrons on the nitrogen migrate toward the positive oxygen, causing the loss of a water molecule.

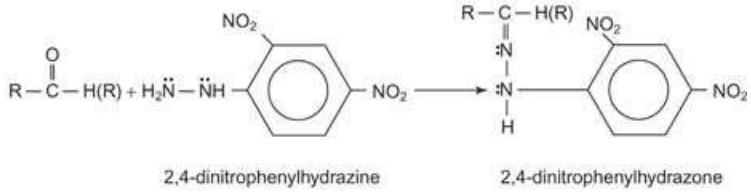


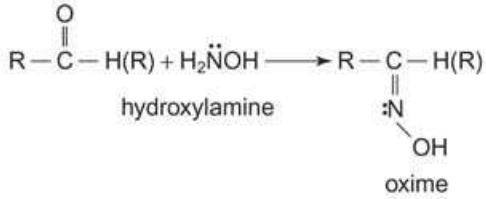
5. A proton from the positively charged nitrogen is transferred to water, leading to the imine's formation.

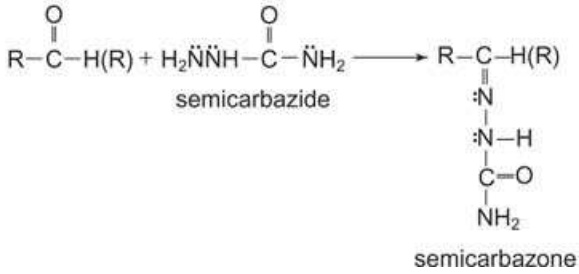


Imines of aldehydes are relatively stable while those of ketones are unstable. Derivatives of imines that form stable compounds with aldehydes and ketones include phenylhydrazine, 2, 4-dinitrophenylhydrazine, hydroxylamine, and semicarbazide.





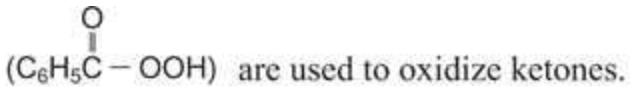


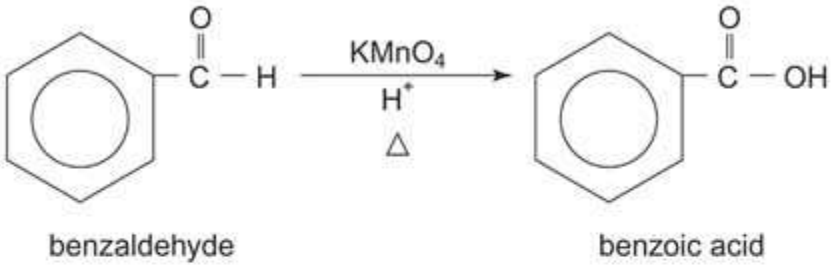


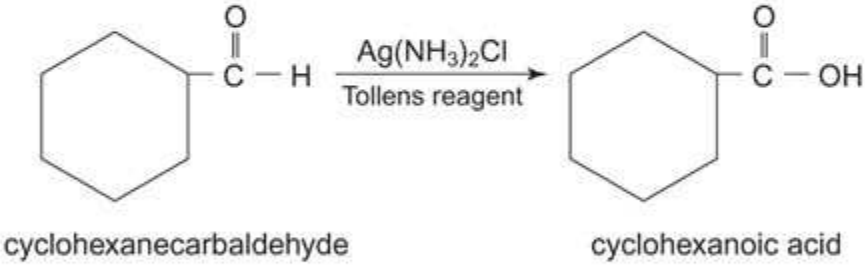
Oximes, 2, 4-dinitrophenylhydrazones, and semicarbazones are often used in qualitative organic chemistry as derivatives for aldehydes and ketones.

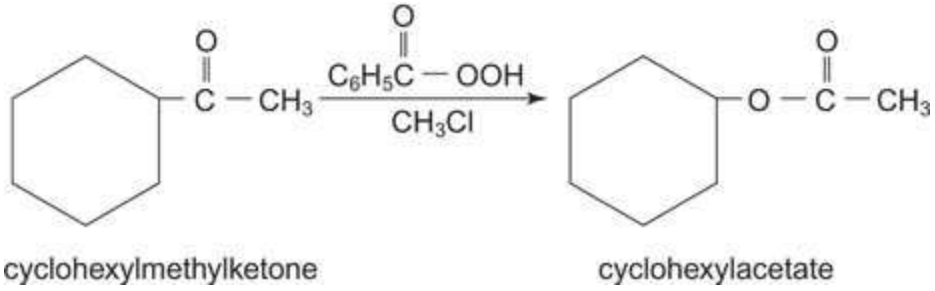
h) Oxidations of aldehydes and ketones :

Aldehydes can be oxidized to carboxylic acid with both mild and strong oxidizing agents. However, ketones can be oxidized to various types of compounds only by using extremely strong oxidizing agents. Typical oxidizing agents for aldehydes include either potassium permanganate ($KMnO_4$) or potassium dichromate ($K_2Cr_2O_7$) in acid solution and Tollens reagent. Peroxy acids, such as peroxybenzoic acid:

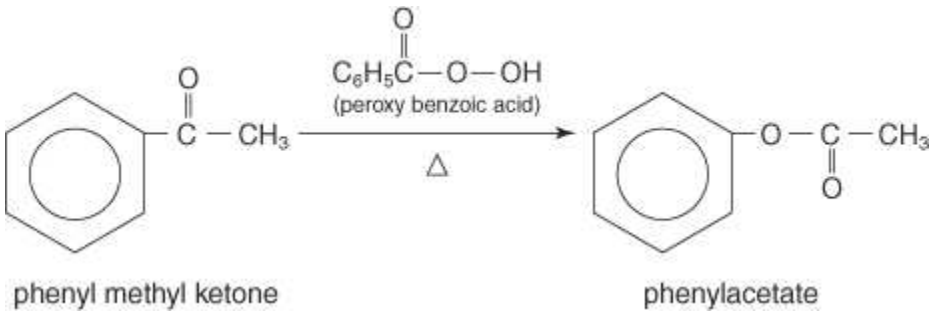




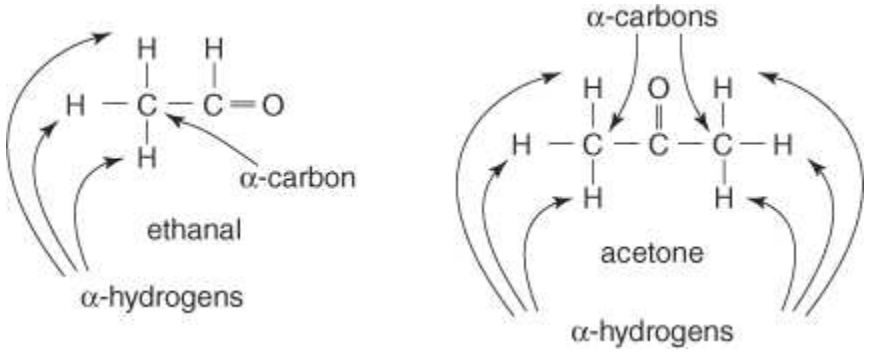




i) Baeyer-Villiger oxidation is a ketone oxidation, and it requires the extremely strong oxidizing agent peroxybenzoic acid. For example, peroxybenzoic acid oxidizes phenyl methyl ketone to phenyl acetate (an ester).

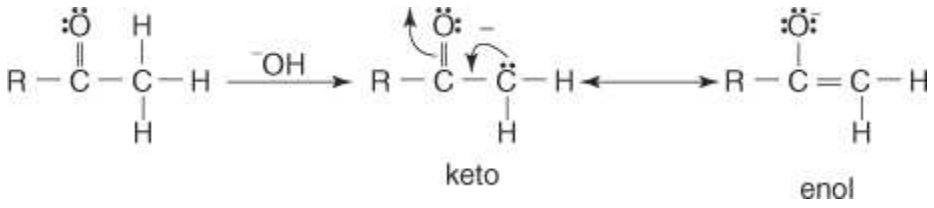


j) Aldol reactions : In addition to nucleophilic additions, aldehydes and ketones show an unusual acidity of hydrogen atoms attached to carbons alpha (adjacent) to the carbonyl group. These hydrogens are referred to as α hydrogens, and the carbon to which they are bonded is an α carbon. In ethanal, there is one α carbon and three α hydrogens, while in acetone there are two α carbons and six α hydrogens.



Although weakly acidic (K_a 10^{-19} to 10^{-20}), α hydrogens can react with strong bases to form anions. The unusual acidity of α hydrogens can be explained by both the electron withdrawing ability of the carbony group and resonance in the anion that forms. The electron withdrawing ability of a carbonyl group is caused by the group's dipole nature, which results from the differences in electronegativity between carbon and oxygen.

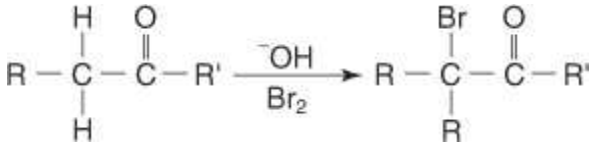
The anion formed by the loss of α hydrogen can be resonance stabilized because of the mobility of the π electrons that are on the adjacent carbonyl group.



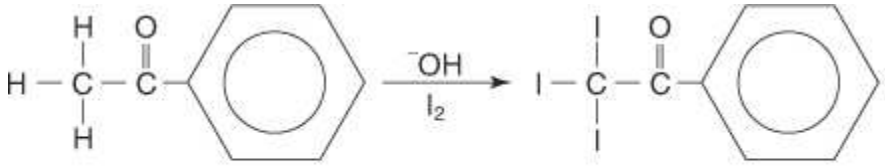
The resonance, which stabilizes the anion, creates two resonance structures — an enol and a keto form. In most cases, the keto form is more stable.

k) Halogenation of ketones

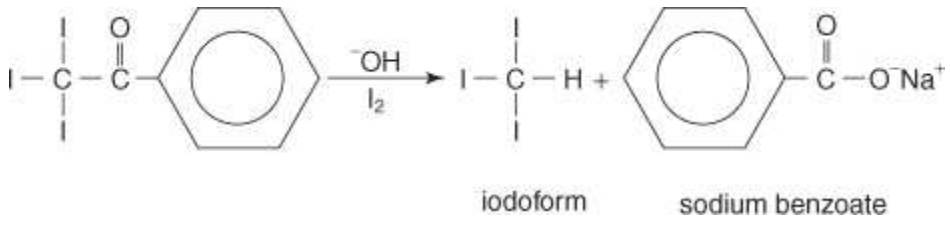
In the presence of a base, ketones with α hydrogens react to form α haloketones.



Likewise, when methyl ketones react with iodine in the presence of a base, complete halogenation occurs.



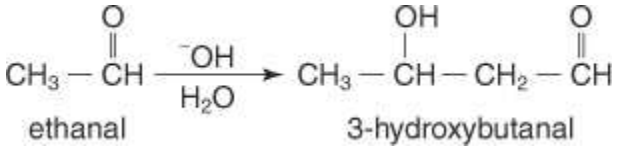
The generation of sodium hypoiodate in solution from the reaction of iodine with sodium hydroxide leads to the formation of iodoform and sodium benzoate, as shown here.



Because iodoform is a pale yellow solid, this reaction is often run as a test for methyl ketones and is called the **iodoform test**.

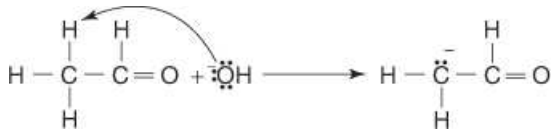
l) Aldol condensation:

Aldehydes that have α hydrogens react with themselves when mixed with a dilute aqueous acid or base. The resulting compounds, β-hydroxy aldehydes, are referred to as **aldol compounds** because they possess both an aldehyde and alcohol functional group.

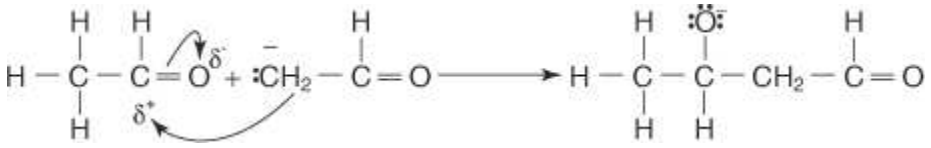


The aldol condensation proceeds via a carbanion intermediate. The mechanism of base-catalyzed aldol condensation follows these steps:

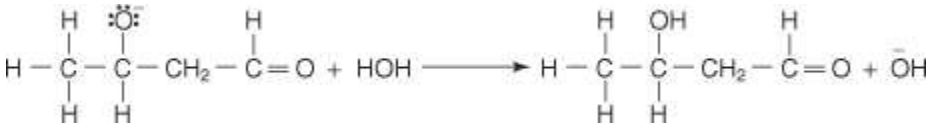
1. The base removes an α hydrogen.



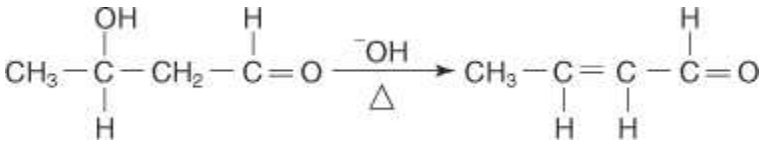
2. The carbanion undergoes nucleophilic addition with the carbonyl group of a second molecule of ethanal, which leads to formation of the condensation product.



3. A reaction with water protonates the alkoxide ion.

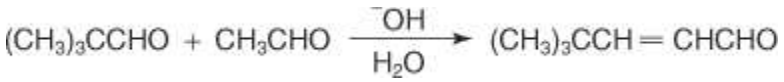


If the aldol is heated in basic solution, the molecule can be dehydrated to form an α β-unsaturated aldehyde.



m) Cross-aldol condensation:

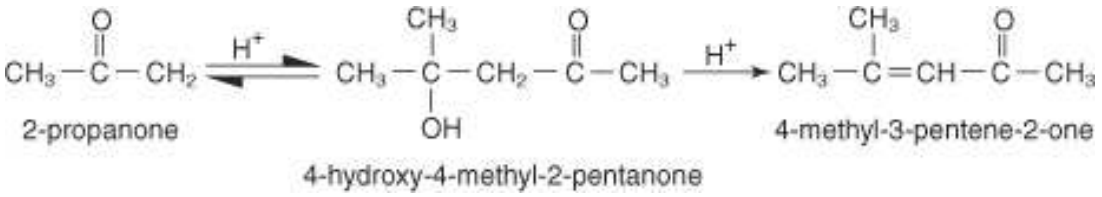
An aldol condensation between two different aldehydes produces a cross-aldol condensation. If both aldehydes possess α hydrogens, a series of products will form. To be useful, a cross-aldol must be run between an aldehyde possessing an α hydrogen and a second aldehyde that does not have α hydrogens.



n) Ketonic aldol condensation:

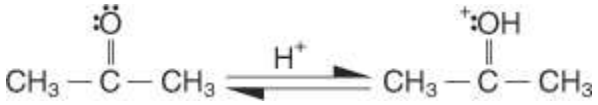
Ketones are less reactive towards aldol condensations than alde-hydes. With acid catalysts, however, small amounts of aldol product can be formed. But the Aldol product

that forms will rapidly dehydrate to form a resonance-stabilized product. This dehydration step drives the reaction to completion.

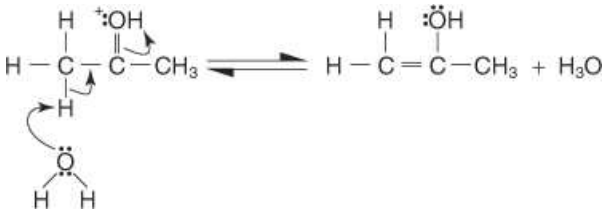


The acid-catalyzed aldol condensation includes two key steps: the conversion of the ketone into its enolic form, and the attack on a protonated carbonyl group by the enol. The mechanism proceeds as follows:

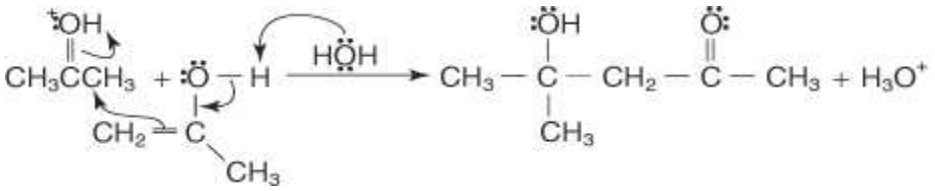
1. The oxygen of the carbonyl group is protonated.



2. A water molecule acting as a base removes an acidic α hydrogen, which leads to an enol.

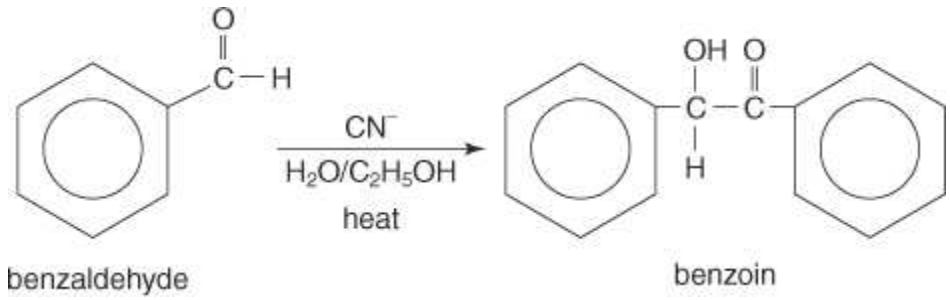


3. The enol attacks a protonated carbonyl group of a second ketone molecule.



o) The benzoin condensation:

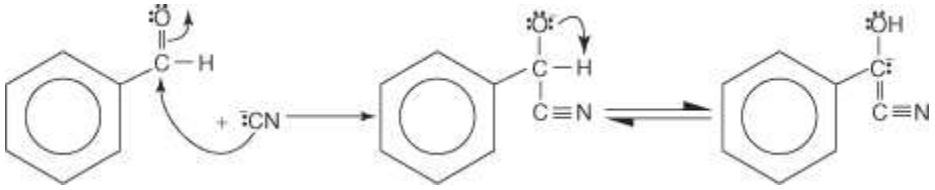
Aromatic aldehydes form a condensation product when heated with a cyanide ion dissolved in an alcohol-water solution. This condensation leads to the formation of α hydroxy ketones.



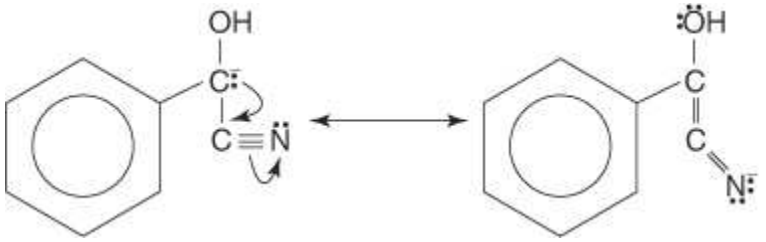
The cyanide ion is the only known catalyst for this condensation, because the cyanide ion has unique properties. For example, cyanide ions are relatively strong nucleophiles, as well as good leaving groups. Likewise, when a cyanide ion bonds to the carbonyl group of the aldehyde, the intermediate formed is stabilized by resonance between the molecule and the cyanide ion. The following mechanism illustrates these points.

The benzoin condensation reaction proceeds via a nucleophilic substitution followed by a rearrangement reaction.

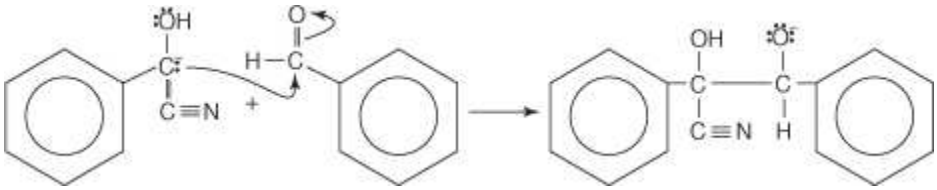
1. The cyanide ion is attracted to the carbon atom of the carbonyl group.



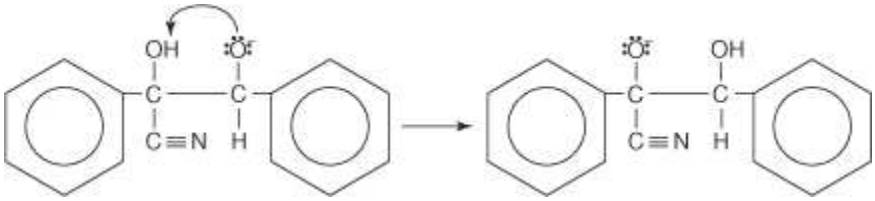
2. The carbanion is resonance-stabilized.



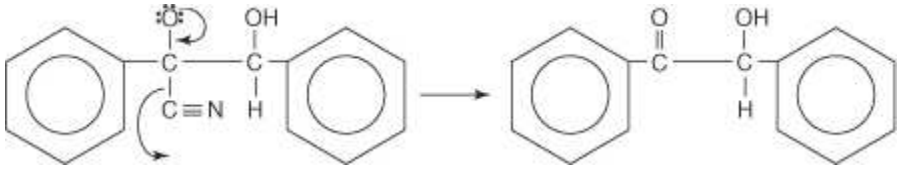
3. The carbanion attacks a second molecule of benzaldehyde.



4. The alkoxide ion removes a proton from the hydroxide group.



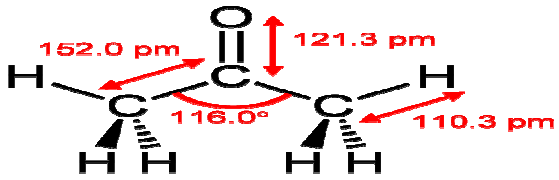
5. A pair of electrons on the alkoxide ion is attracted to the carbon bonded to the cyanide group, which then leaves to generate the product.



4. Explain the preparation and properties of acetone.

Ans: Acetone is the organic compound with the formula $(CH_3)_2CO$. This colorless, mobile, flammable liquid is the simplest example of the ketones**.** Acetone is miscible

with water and serves as an important solvent in its own right, typically as the solvent of choice for cleaning purposes in the laboratory.



I . Methods of preparation:

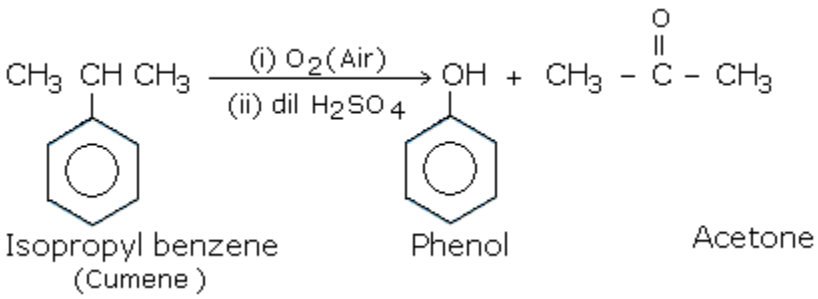
a) By Dry Distillation of Calcium Acetate: It can also be prepared by dry distillation of calcium acetate.

$$\underset{\text{calcium acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{Dry distillation}} CaCO_3 + \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

b) By Wacker Process: Acetone can also be prepared from propene by Wacker Process. In this process a gaseous mixture of propene and air is passed through a solution of copper (II) chloride and palladium (II) chloride between 293k to 333k**.**

$$\underset{\text{Propene}}{CH_3CH=CH_2} + O_2 \xrightarrow{CuCl_2, PdCl_2} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3}$$

c) Acetone is also formed as by-product during the manufacture of phenol from cumene.



II. Properties of Acetone

a) Physical Properties

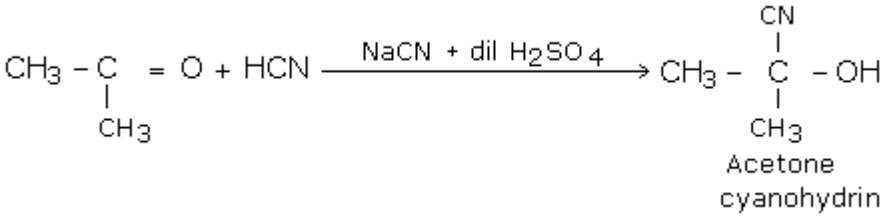
- Acetone is a colourless, inflammable, volatile liquid with characteristic sweetish smell. Its boiling point is 56^oC.

- It is miscible with water, alcohol and ether in all proportions.
- It specific gravity is 0.792 at 293k

b) Chemical Properties

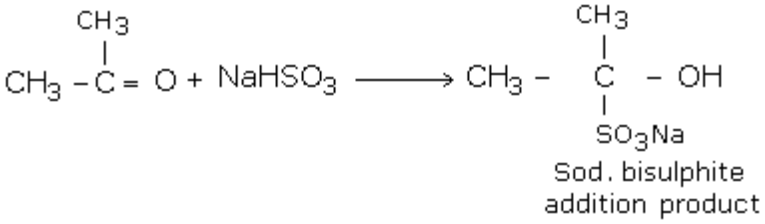
1) Addition of Hydrogen Cyanide:

When acetone is treated with sodium cyanide and dilutes sulphuric acid, a cyanohydrin is formed due to addition of hydrogen cyanide to the carbonyl group.



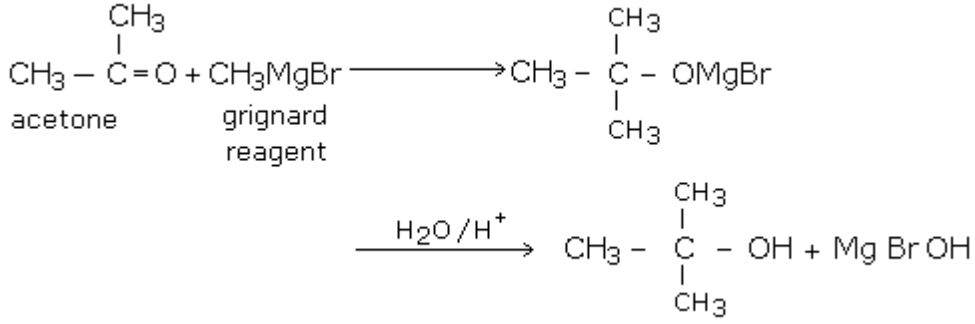
2) Addition of Sodium bisulphate

When acetone is treated with a saturated solution of sodium bisulphate, a crystalline addition product is formed.



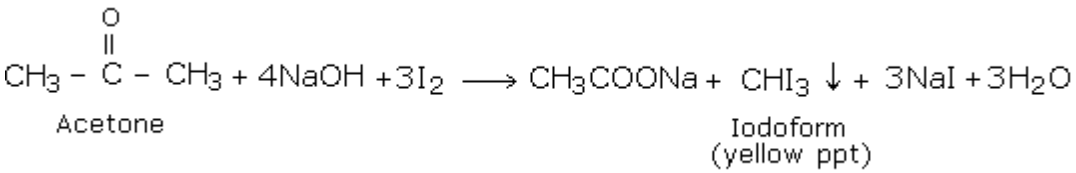
3) Addition of Grignard Reagents

Grignard reagents on reaction with acetone, followed by hydrolysis yield alcohols



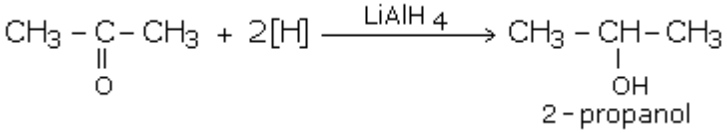
4) Haloform Reaction:

Acetone on reaction with iodine in the presence of sodium hydroxide, yields yellow crystalline precipitate of iodoform

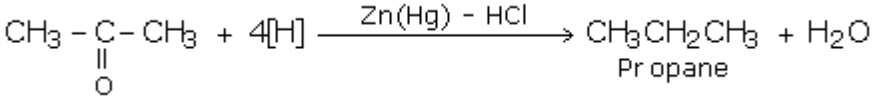


5) Reduction

Acetone can be reduced to 2-propanol by reaction with lithium aluminum hydride.



Acetone can be reduced to propane by reaction with zinc-amalgam and hydrochloric acid.



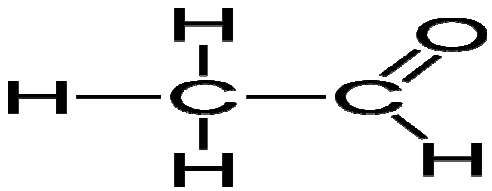
This reaction is known as **Clemmensen reduction**.

III. <u>Uses of Acetone</u>

- It is used as solvent in paints, varnishes and lacquers
- It is used as delusterant (removes the lustre from a textile) for cellulose acetate fibres
- It is used in the preparation of cordite (smokeless gun powder) and plexiglass (unbreakable glass)
- It is used for specification testing of vulcanised rubber products
- It is used as nail polish remover
- It is used to clean and dry parts of precision equipment

5. Explain the preparation and properties of acetaldehyde.

Ans: **Acetaldehyde** (systematically **ethanal**) is an organic chemical compound with the formula CH_3CHO or MeCHO. It is one of the most important aldehydes, occurring widely in nature and being produced on a large scale industrially. Acetaldehyde occurs naturally in coffee, bread, and ripe fruit, and is produced by plants as part of their normal metabolism. It is also produced by oxidation of ethanol and is popularly believed to be a cause of hangovers.



I.. Method of preparation:

Ethanal is manufactured by passing a mixture of ethene and oxygen under pressure into an aqueous solution of palladium chloride and cupric chloride catalysts.

$$CH_2 = CH_2 + H_2O + \frac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO + H_2O$$

This method called the Wacker's process has almost replaced the earlier method involving hydration of ethyne.

II. Physical Properties

(i) Acetaldehyde is a colorless volatile liquid. It boils at 21°*C*.

(ii) It has a characteristic pungent smell.

(iii) It is soluble in water, chloroform, ethyl alcohol and ether. Its aqueous solution has a pleasant odour. In water, it is hydrated to a considerable extent to form ethylidene diol.

$$CH_3CHO + H_2O \longrightarrow CH_3CH(OH)_2$$

III. Uses:

Acetaldehyde is used:

(i) In the preparation of acetic acid, acetic anhydride, ethyl acetate, chloral, 1,3-butadiene (used in rubbers), dyes and drugs.

(ii) As an antiseptic inhalant in nose troubles.

(iii) In the preparation of paraldehyde (hypnotic and sporofic) and metaldehyde (solid fuel).

(iv) In the preparation of acetaldehyde ammonia (a rubber accelerator).

ORGANIC CHEMISTRY

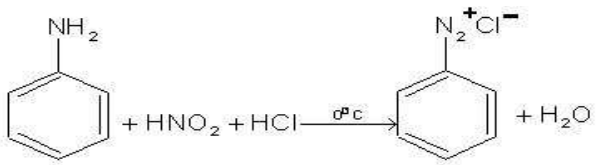
TOPIC: 7

Diazonium salts – Preparation, synthetic applications and uses.

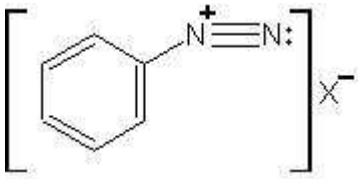
DIAZONIUM SALT:

I. Preparation of Diazonium salt:

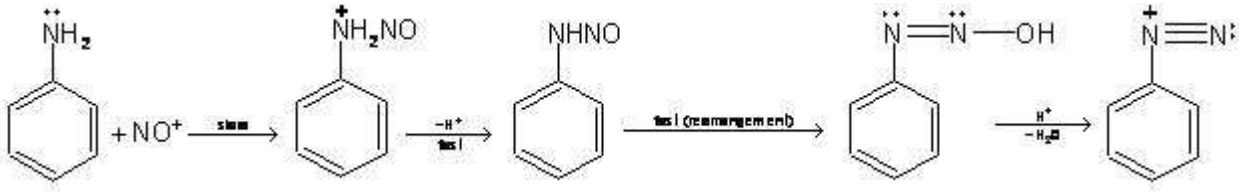
When primary aromatic amine is treated with nitrous acid in a cool solution, product is unstable compound, known as diazonium salt.



This reaction is known as diazotisation. Diazonium salts have the structure



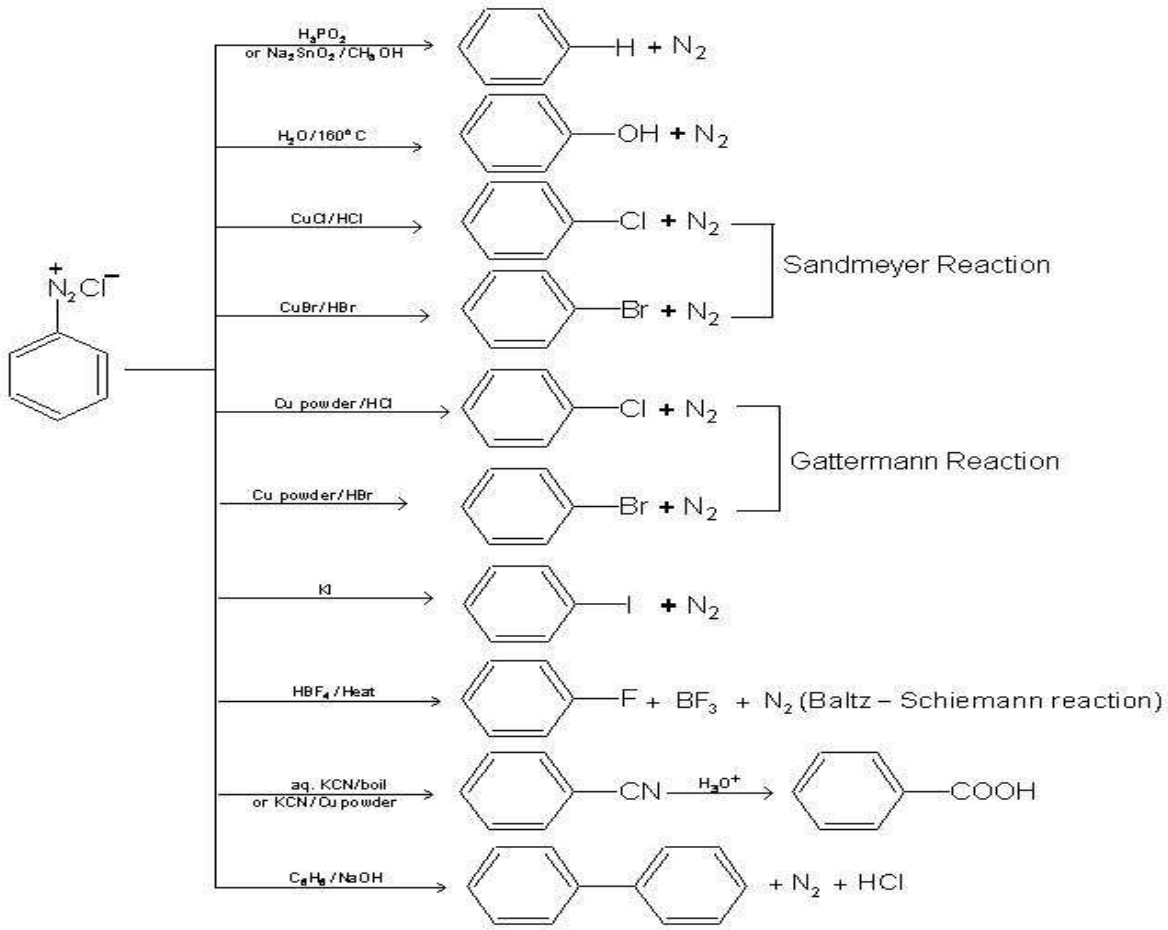
Mechanism of diazotisation:



II. Reactions of diazonium salts:

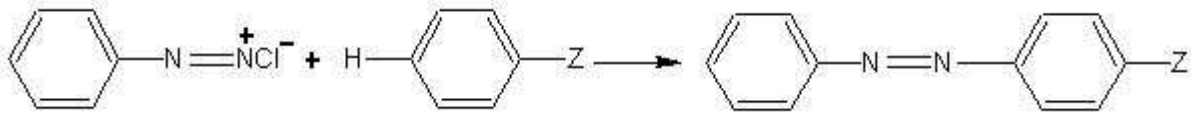
These salts give substitution reactions and coupling reactions as follows:

1. Substitution reactions:

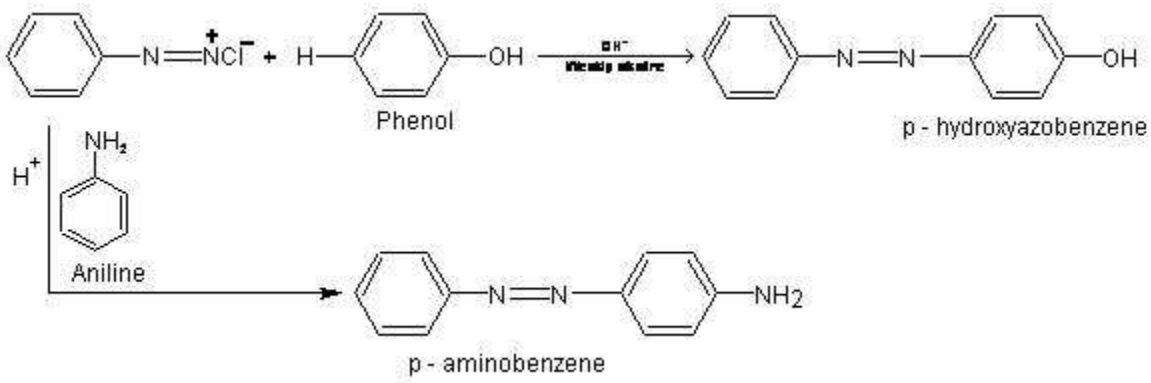


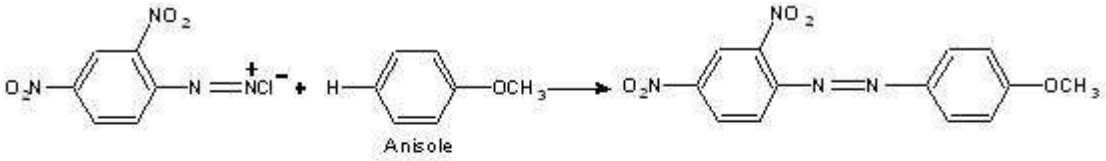
2. COUPLING REACTIONS:

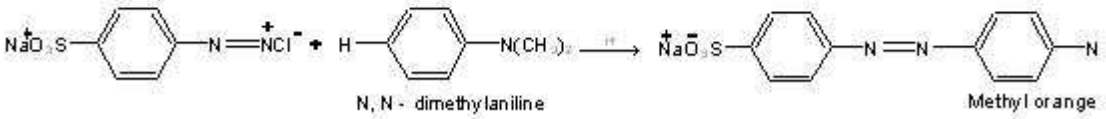
Coupling reactions are electrophilic substitution reactions. Some examples are as follows:
General reaction



Examples:


Phenol
p - hydroxyazobenzene
Aniline
p - aminobenzene


Anisole


N, N - dimethylaniline
Methyl orange

ORGANIC CHEMISTRY

Topic-8

HALOGEN COMPOUNDS

LONG ANSWER QUESTIONS

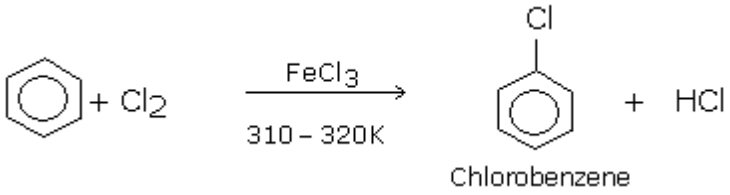
1. Explain the method of preparation of Chlorobenzene.

Preparation of Chlorobenzene:

1. Direct Chlorination of aromatic ring:

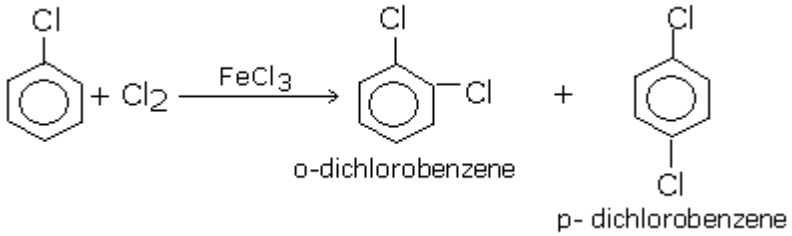
Direct chlorination of benzene or other aromatic hydrocarbon gives chloroarenes. This reaction is carried out in the presence of Lewis acids such as ferric or aluminium halides ($FeCl_3$, $FeBr_3$, $AlCl_3$) in the dark, at ordinary temperatures (310-320 K).

The Lewis acid acts as a catalyst or a halogen carrier, as its function is to carry the chlorine to the aromatic hydrocarbon. In actual practice, iron filings in the presence of chlorine commonly used. The chlorine reacts with iron filings to form corresponding Lewis acids.

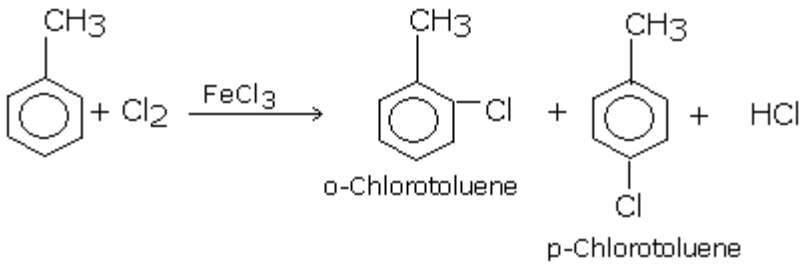


Halogenation of arenes is an electrophilic substitution reaction. The function of the halogen carrier is to generate 'electrophile' which attacks the benzene ring to form the product.

With excess halogen, the second halogen also gets introduced in the ring at ortho and para positions with respect to the first halogen because halogens are ortho and para directing groups.

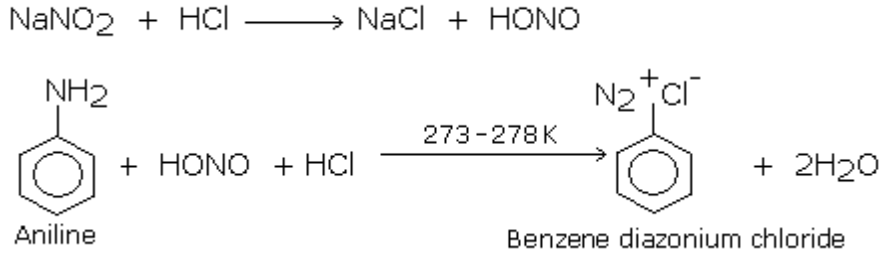


Similarly, chlorination of toluene gives a mixture of ortho and para chlorotoluene because $-CH_3$ group in toluene is ortho and para directing.



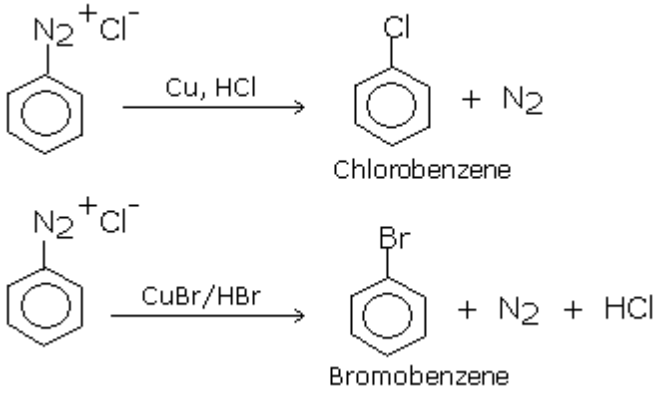
2. Sandmeyer's reaction:

This reaction consists of treating freshly prepared diazonium salt solution with cuprous chloride or cuprous bromide dissolved in corresponding halogen acids. Chloro and bromoarenes are formed. Diazonium salts required for this purpose are prepared by treating ice-cold solution of aniline in excess of dilute HCl with an aqueous solution of sodium nitrite at low temperature (0-5^{o}C). This reaction is known as diazotization reaction.



The benzene diazonium salt is used for preparing aryl halides as:

The Sandmeyer reaction has been modified to 'Gattermann reaction'. Copper powder is used in the presence of corresponding halogen acid (HCl or HBr) in place of cuprous halide (CuCl, CuBr).



2.Explain the Properties of Chlorobenzene.

I. Physical properties of Chlorobenzene:

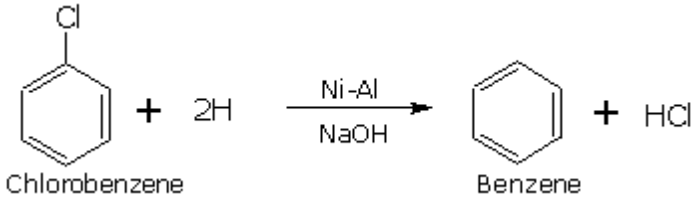
- It is a liquid at room temperature
- It is heavier than water.
- It is insoluble in water but soluble in organic solvents.
- Its boiling point is more than benzene

.

II. Chemical properties:

a) Reduction of chlorobenzene

With $LiAlH_4$ or nickel aluminium alloy (Ni-Al), haloarenes undergo reduction to hydrocarbons in the presence of an alkali. The reduction is brought about by nascent hydrogen.



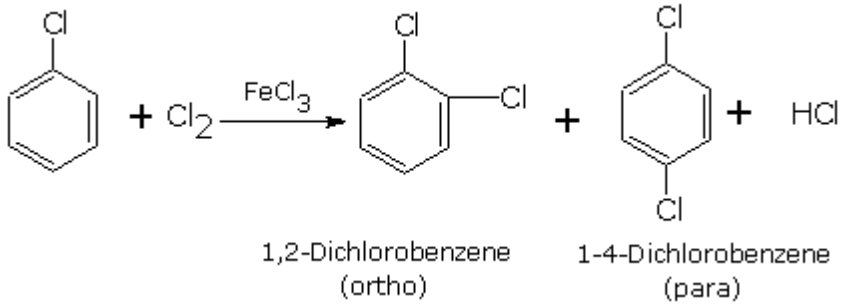
b) Electrophilic substitution reactions:

a) Chlorinatin of Chlorobenzene:

- Clorobenzene undergo electrophilic substitution reactions slowly as compared to benzene. hloro group is ortho and para directing (para-product usually predominates over the ortho product).

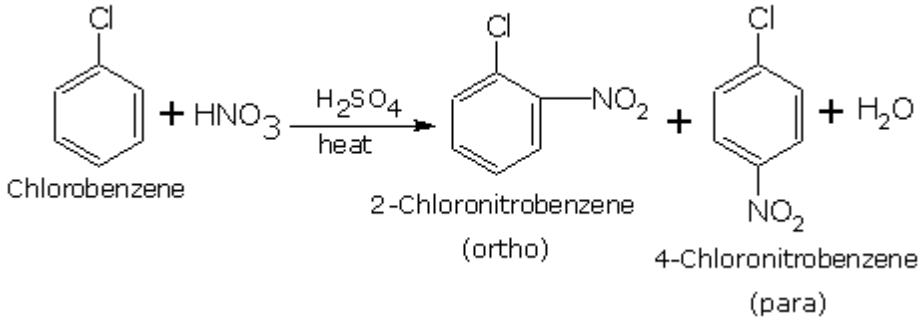
Halogenation

Haloarenes react with halogens in the presence of ferric salt as catalyst to give ortho para isomers.



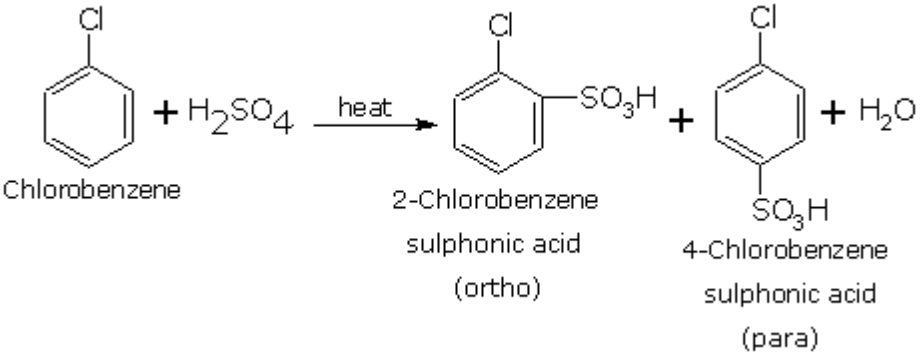
b) Nitration

Haloarenes with concentrated HNO_3 in the presence of concentrated H_2SO_4.



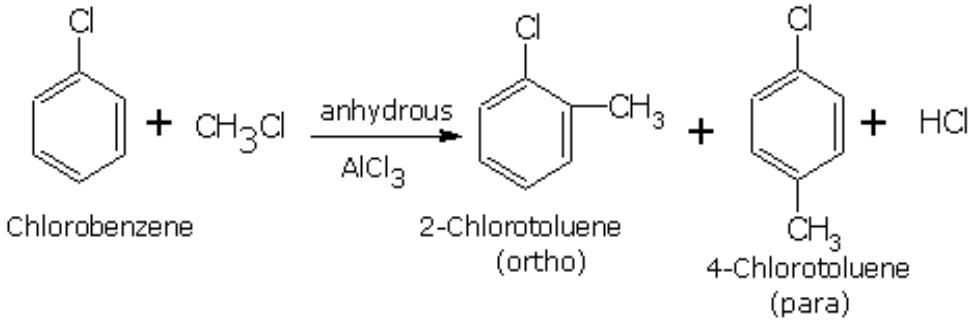
c) Sulphonation

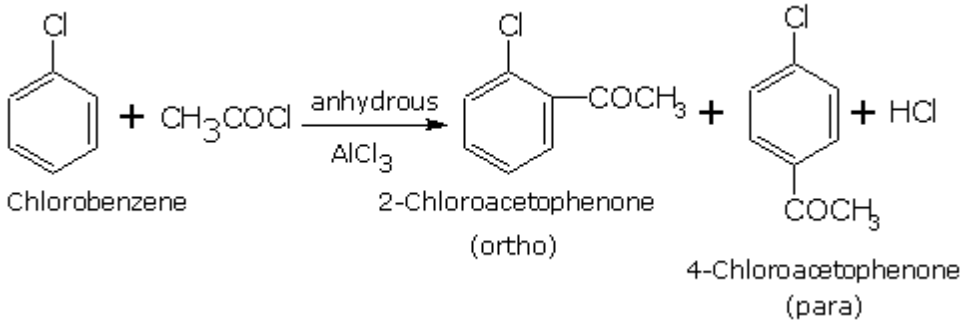
Sulphonation occurs when haloarene is treated with concentrated H_2SO_4.



d) Alkylation and acylation

The alkylation and acylation reaction, known as **'Friedel-Craft reaction'**, is carried by treating haloarene with alkyl chloride or acyl chloride in the presence of a catalyst like anhydrous aluminium chloride. For example,



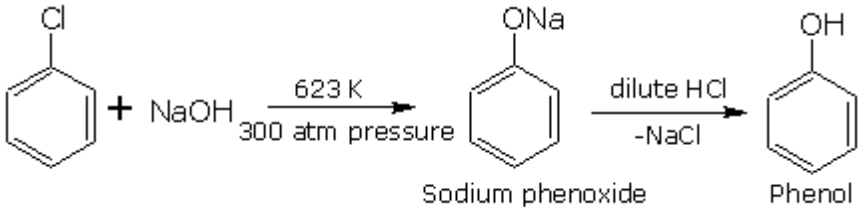


c) Action with Na, Mg and chloral

Haloarenes are chemically less reactive than haloalkanes. They can undergo the following reactions:

Replacement by hydroxy group (formation of phenol)

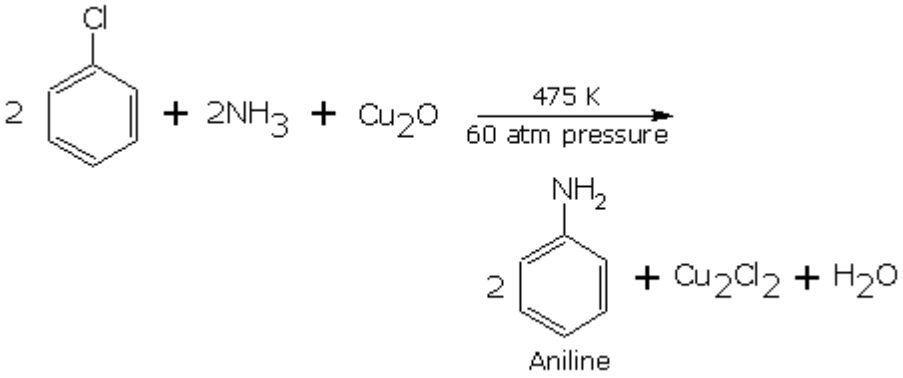
When aryl halides are heated at 623 K and under pressure (300 atm), with aqueous solution of sodium hydroxide, the halogen atom is replaced by hydroxyl group forming phenol. Firstly sodium phenoxide is formed, which on acidification gives phenol.



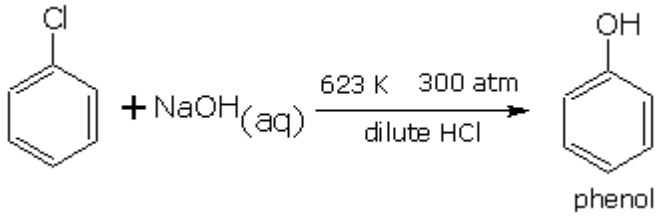
This reaction forms the basis for the manufacture of phenol by Dow's process.

Substitution by amino group (formation of aniline)

The halogen atom is replaced by amino group when aryl halides are heated with aqueous ammonia in the presence of cuprous oxide (catalyst) at 475 K and under a pressure of 60 atm.,



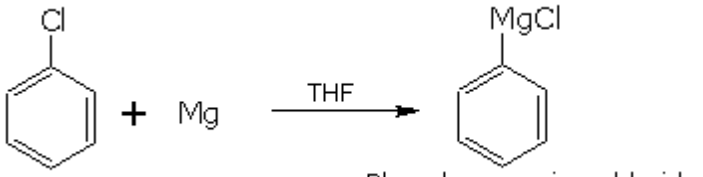
d) Reaction with NaOH: When reacted with NaOH, chloro benzene converts to Phenol



e) **Reaction of magnesium**

Aryl bromides and iodides react with magnesium in dry ether to form Grignard reagent.

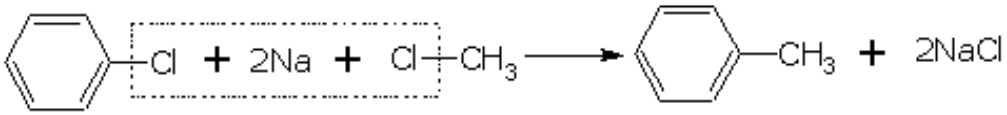
Chlorobenzene reacts with magnesium in the presence of tetrahydrofuran (THF) solvent.



Phenyl magnesium chloride

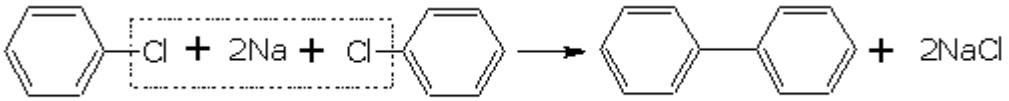
f) **Reaction with sodium**

Aryl halide undergo 'Wurtz Fitting reaction' when heated with alkyl halide in the presence of sodium in anhydrous ether. Halogen atom is replaced by alkyl group.



Toluene

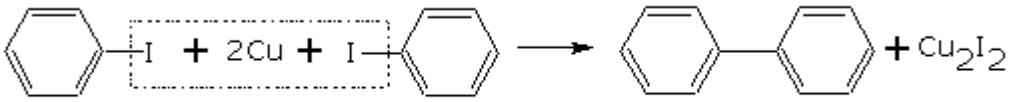
However, when haloarenes react with sodium in the presence of ether, diphenyl is formed. This reaction is called 'Fitting reaction'.



Diphenyl

g) **Reaction with copper powder**

Iodobenzene gives diphenyl when heated with copper powder in a sealed tube. This reaction is called 'Ullmann reaction'.



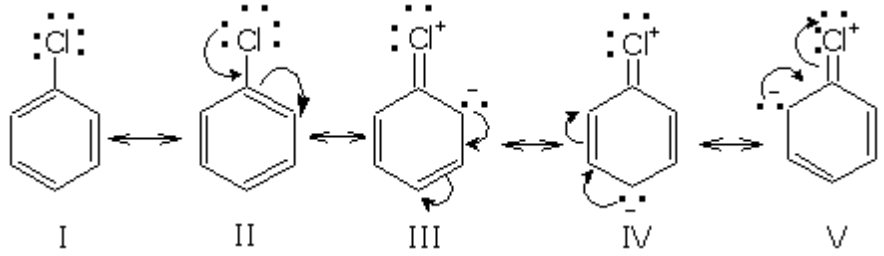
Dinhenyl

SHORT ANSWER QUESTIONS

1. **Explain the resonance in Chlorobenzene.**

Resonance in chlorobenzene:

There is delocalisation of electrons in haloarenes due to resonance. For example, chlorobenzene is considered to be a resonance hybrid of the following structures:

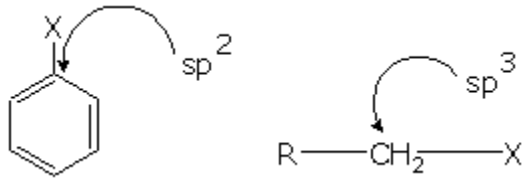


The contribution of structures III, IV and V imparts a partial double bond character to the carbon-chlorine bond. The shortening of bond length imparts stability to aryl halides and as a result, the bond cleavage becomes rather difficult. The aryl halides are, therefore, less reactive than alkyl halides.

2.Explain the hybridization state of chlorobenzene.

Hybridization states of carbon atom

The carbon atom of the C-X bond in haloalkanes, is sp^3 hybridised while in haloarenes the carbon atom is sp^2 hybridized. The sp^2 hybridized carbon atom with a greater's' character is more electronegative. It can hold the electron pair of the bond more tightly than the sp^3 hybridized carbon atom in alkyl halides. This has fewer tendencies to release electrons to the halogen. As a result, the bond cleavage in aryl halides is somewhat more difficult than in alkyl halides.



3. Explain the polarity in Chlorobenzene.

Polarity of carbon-halogen bond: The sp^2 hybridized carbon atom in the C-X bond in haloarene molecule is more electronegative than the sp^3 hybrid carbon atom in alkyl halide. This carbon has fewer tendencies to release electrons to the chlorine atom and so the C-Cl bond in aryl halides is less polar than in alkyl halides. This is supported by the fact that the dipole moment of chlorobenzene is 1.73 D while the dipole moment of chloroethane is 2.05 D. Lesser the polarity of C-Cl bond, lesser is the reactivity. Thus, haloarenes are less reactive towards the substitution reactions than haloalkanes. However, under drastic conditions, aryl halides undergo substitution reactions.

ORGANIC CHEMISTRY

Topic-9

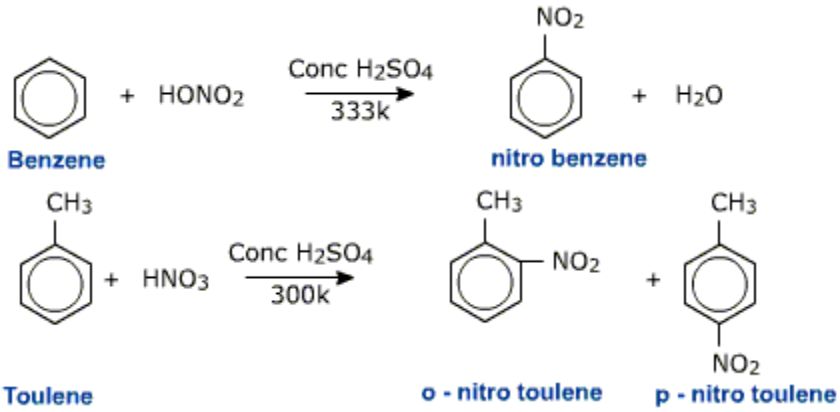
NITROBENZENE

LONG ANSWER QUESTIONS

1. **Explain the methods of preparation of Nitrobenzene.**

Laboratory preparation of nitrobenzene

Aromatic compounds can be directly nitrated using a mixture of concentrated nitric acid and sulphuric acid.



This reaction is an example of electrophilic substitution of benzene. The electrophile is a nitronium (NO_2^+) ion.

The nitronium ion attacks to the benzene ring resulting in the formation of a carbocation. Electron releasing substituents like $-CH_3$, $-OCH_3$, -OH, $-NH_2$ etc activate the ring and stabilize the carbocation while electron withdrawing groups like $-NO_2$, -CN, $-SO_3H$, -X activate the carbocation.

The nitrating mixture of conc. H_2SO_4 and conc. HNO_3 con nitrate even deactivated compounds like nitrobenzene under refluxing conditions to get m-dinitrobenzene. For nitration of activated aromatic systems like phenol and then ether derivatives, even milder conditions can be used.

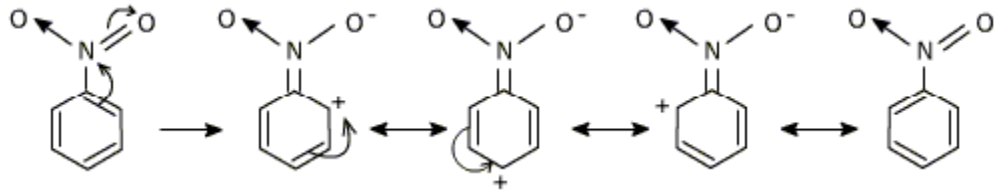
2.Explain the physical and chemical properties of Nitrobenzene.

I. Physical properties of Nitrobenzene:

- Nitrobenzene is a colourless to pale yellow oily liquid that presents a fire hazard.
- Its odour resembles that of bitter almonds or "shoe polish," with odour.
- It is insoluble in water and soluble in organic solvents.

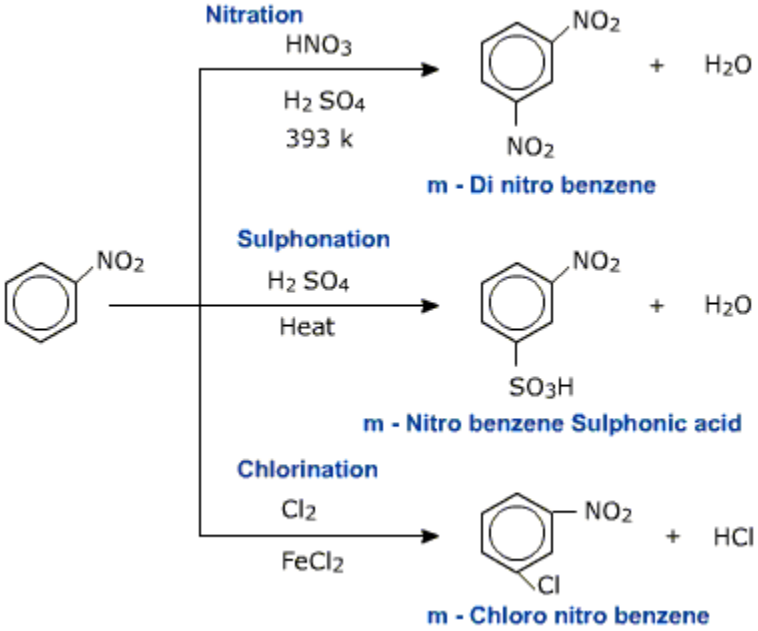
II. Chemical properties of aromatic nitrocompounds

The nitro group strongly deactivates the benzene ring towards electrophilic substitution. Nitro group is electron withdrawing group and thus causes electron deficiency at ortho and para positrons as is clear from the resonating structures of nitro benzene.



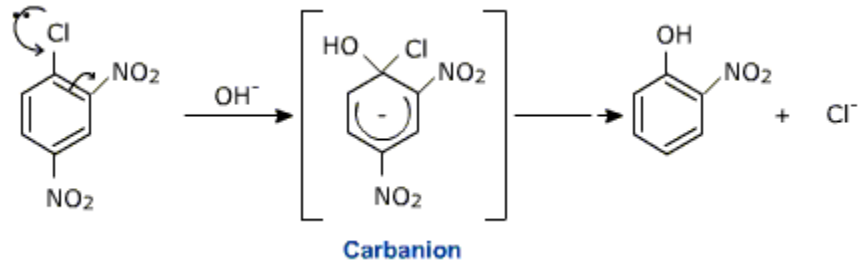
Since the meta positron is relatively rich in electron density compared to ortho and para positrons electrophilic attack is more likely to occur at meta position. Thus the -NO_2 group is meta directing as far as electrophilic ring substitution is concerned.

A) Electrophilic substitution reaction



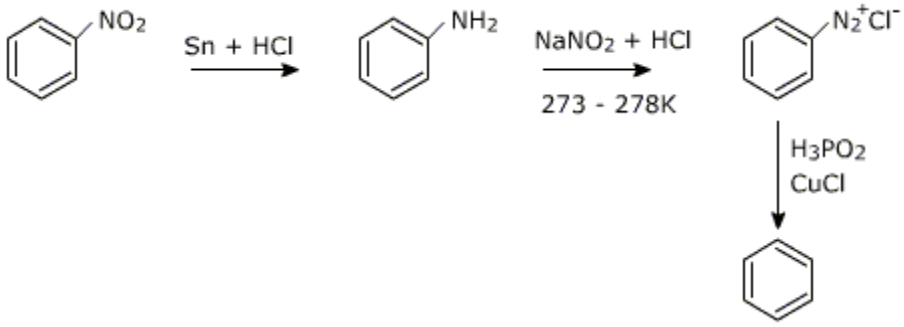
b) Influence on the reaction of other functional group

The presence of nitro group facilitates nucleophilic substitution of otherwise unreactive aromatic halides by stabilizing the intermediate carbanion.



c) Reduction of nitrobenzene

The nitro group can be removed from an aromatic ring via the following steps:
i) Reduction of nitro group to amine
ii) Diazotization of amine with HNO_2
iii) Reductive removal of the diazonium group using sodium borohydride or hypophosphorus acid/ Cu^{+}mixture.



3. **Explain the uses and safety precautions of Nitrobenzene**

1 <u>Uses of nitrobenzene</u>

- .Approximately 95% of nitrobenzene is consumed in the production of aniline

- More specialized applications include the use of nitrobenzene as a precursor to rubber chemicals, pesticides, dyes, explosives, and pharmaceuticals.
- Nitrobenzene is also used in shoe and floor polishes, leather dressings, paint solvents, and other materials to mask unpleasant odors.
- Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps.
- A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol (also known as acetaminophen) (Mannsville 1991)
- Nitrobenzene is also used in Kerr cells, as it has an unusually large Kerr constant.
- Aside from its conversion to aniline, nitrobenzene is readily converted to related derivatives such as azobenzene, nitrosobenzene, and phenyl hydroxylamine. The nitro- group is deactivating, thus substitution tends to occur at the *meta*-position.

2. **<u>Safety</u>**

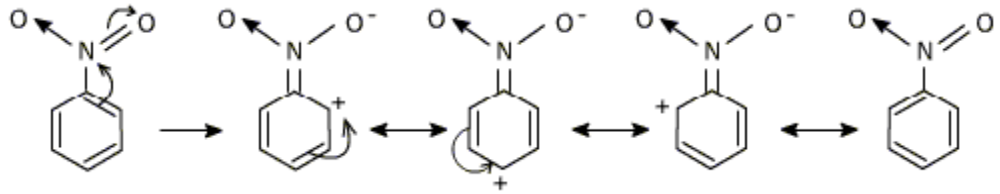
- Nitrobenzene is highly toxic (TLV 5 mg/m^3) and readily absorbed through the skin.

- Although nitrobenzene is not currently known to be a carcinogen, prolonged exposure may cause serious damage to the central nervous system, impair vision, cause liver or kidney damage, anemia and lung irritation.
- Inhalation of fumes may induce headache, nausea, fatigue, dizziness, cyanosis, weakness in the arms and legs, and in rare cases may be fatal.
- The oil is readily absorbed through the skin and may increase heart rate, cause convulsions or rarely death.
- Ingestion may similarly cause headaches, dizziness, nausea, vomiting and gastrointestinal irritation.

SHORT ANSWER QUESTIONS

1. Explain the structure of nitrobenzene.

The nitro group strongly deactivates the benzene ring towards electrophilic substitution. Nitro group is electron withdrawing group and thus causes electron deficiency at ortho and para positrons as is clear from the resonating structures of nitro benzene.



Since the meta positron is relatively rich in electron density compared to ortho and para positrons electrophilic attack is more likely to occur at meta position. Thus the $-NO_2$ group is meta directing as far as electrophilic ring substitution is concerned.

2. Give uses of nirobenzene.

- More specialized applications include the use of nitrobenzene as a precursor to rubber chemicals, pesticides, dyes, explosives, and pharmaceuticals.
- Nitrobenzene is also used in shoe and floor polishes, leather dressings, paint solvents, and other materials to mask unpleasant odors.
- Redistilled, as oil of mirbane, nitrobenzene has been used as an inexpensive perfume for soaps.
- A significant merchant market for nitrobenzene is its use in the production of the analgesic paracetamol (also known as acetaminophen) (Mannsville 1991)

ORGANIC CHEMISTRY

Topic-10

PHENOL

LONG ANSWER QUESTIONS

1. Explain the methods of preparation of phenol.

Introduction of phenols: A phenol contains -OH group(s) directly attached to an aryl carbon atom(s). The simplest phenol is hydroxybenzene also called phenol with formula C_6H_5OH. Simple phenol is an antiseptic. A phenolic compound hexachlorophene is a constituent of several mouthwashes, deodorant soaps and medicinal skin cleansers.

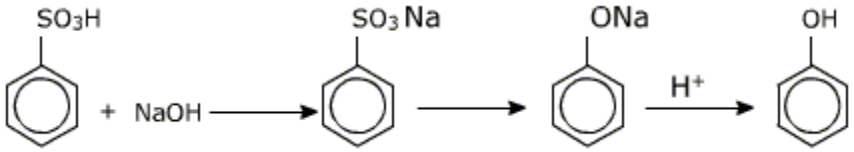
It must be noted that the aromatic compounds in which -OH group is not directly attached to benzene ring are not phenols but are called aromatic alcohols. These may be regarded as aryl derivatives of aliphatic alcohols.

Preparation of phenol

In the early nineteenth century, phenol was selected from coal tar by destructive distillation. Now phenol is commercially produced synthetically. The laboratory methods of preparation of phenols are:

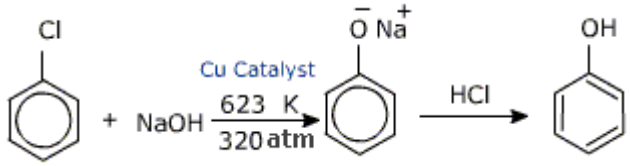
i) From aryl sulphonic acids

An aryl sulphonic acid yields the corresponding phenol on heating it with molten sodium hydroxide at 570 - 620 K. The sodium salt is obtained which is hydrolysed with acid to obtain free phenol.



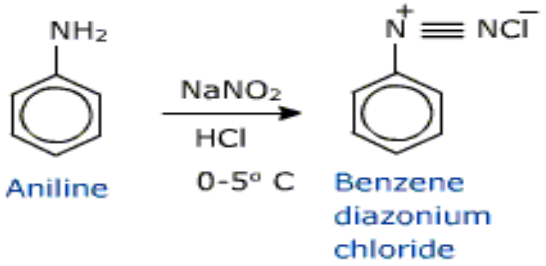
ii) From haloarenes

Chlorobenzene (an haloarene) is hydrolysed by treating it with 10% NaOH at 623 K and 320 atmospheric pressure in presence of Cu catalyst. Phenol is obtained by acidification of sodium phenoxide.

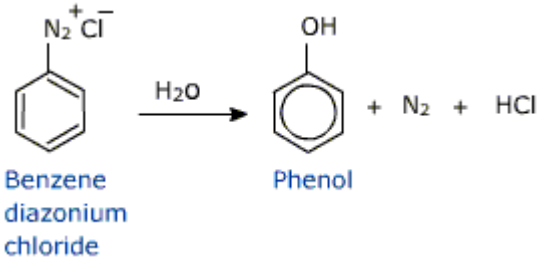


iii) Hydrolysis of diazonium salts

A diazonium salt is formed by treating an aromatic primary amine with nitrous acid (obtained from a mixture of $NaNO_2$ and HCl) at low temperature of 273 K to 278 K.



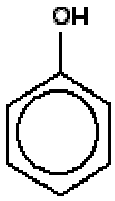
Diazonium salts are hydrolysed to phenols treating with dilute acids.



2. Explain the physical properties, structure and acidic nature of Phenol.

a) **<u>The structure of phenol</u>**

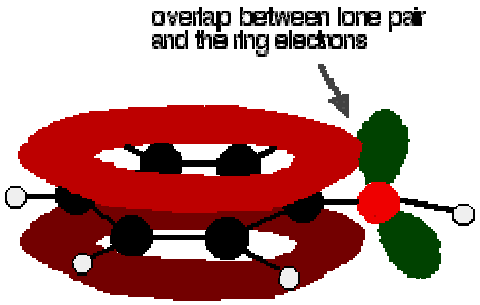
The simplest way to draw the structure of phenol is:



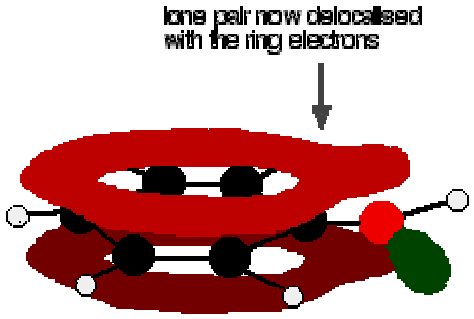
. . . But to understand phenol properly, you need to dig a bit deeper than this.

There is an interaction between the delocalised electrons in the benzene ring and one of the lone pairs on the oxygen atom. This has an important effect on both the properties of the ring and of the -OH group.

One of the lone pairs on the oxygen overlaps with the delocalised ring electron system . . .



. . . giving a structure rather like this:



The donation of the oxygen's lone pair into the ring system increases the electron density around the ring. That makes the ring much more reactive than it is in benzene itself. That is explored in another page in this phenol section.

It also helps to make the -OH group's hydrogen a lot more acidic than it is in alcohols. That will also be explored elsewhere in this section.

b) Physical properties:

1. Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discoloured.

2. Melting and boiling points: It is useful to compare phenol's melting and boiling points with those of methylbenzene (toluene). Both molecules contain the same number of electrons and are a very similar shape. That means that the intermolecular attractions due to Van der Waals dispersion forces are going to be very similar.

	melting point (°C)	**boiling point (°C)**
C_6H_5OH	40 - 43	182
$C_6H_5CH_3$	-95.0	111

The reason for the higher values for phenol is in part due to permanent dipole-dipole attractions due to the electronegativity of the oxygen - but is mainly due to hydrogen bonding.

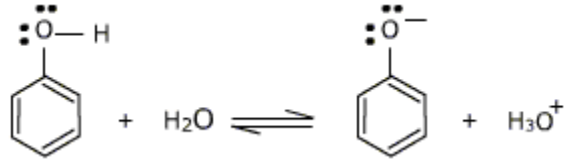
Hydrogen bonds can form between a lone pair on an oxygen on one molecule and the hydrogen on the -OH group of one of its neighbours.

3. Solubility in water

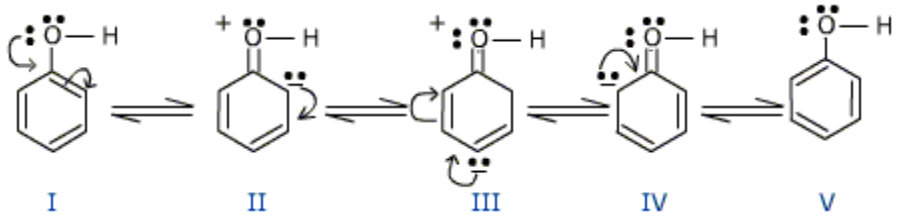
Phenol is moderately soluble in water - about 8 g of phenol will dissolve in 100 g of water. If you try to dissolve more than this, you get two layers of liquid. The top layer is a solution of phenol in water, and the bottom one a solution of water in phenol. The solubility behaviour of phenol and water is complicated. Phenol is somewhat soluble in water because of its ability to form hydrogen bonds with the water.

c) Acidic nature of phenol

Phenols turn blue litmus red and react with metals liberating hydrogen. However they do not react with carbonates or bicarbonates.
Phenols behave as acids because of the presence of polar O-H group in them. They ionise in aqueous solutions to give H^+ ions.



Phenols as well as phenoxide ion both are resonance stabilised. The various contributing structures of phenol and phenoxide ion are given below:



3. **Explain the chemical properties of phenol.**

I. Action with PCl5, PX3, NH3, Zn, Na benzene diazonium chloride and phthalic anhydride

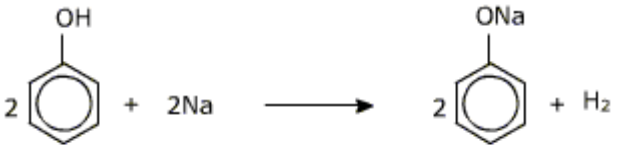
In alcohols and phenols, -OH group is the functional group. Thus the chemical properties of alcohols generally involve the reactions of -OH group. They can undergo substitution as well as elimination reaction.

Reactions of alcohols are classified into three types.

1) Reactions involving cleavage of -OH bond.

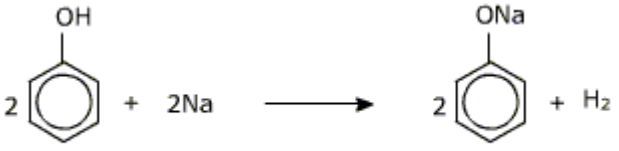
Reaction with metals

Phenols react with metals such as sodium, potassium and aluminium to yield corresponding alkoxides and hydrogen.



Phenol Sodium phenoxide

In addition to this, phenols react with aqueous sodium hydroxide to form sodium phenoxides.



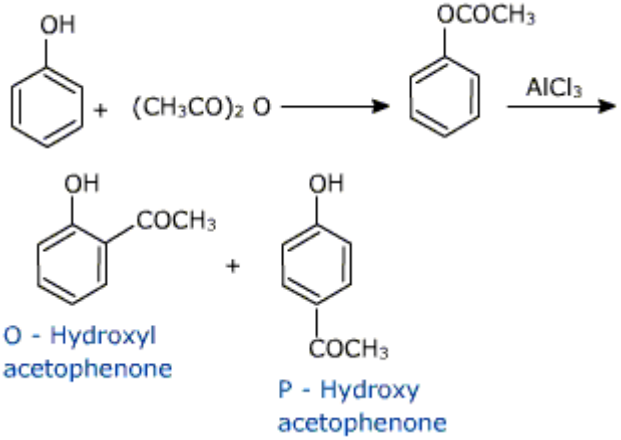
Phenol Sodium phenoxide

The above reactions show that phenols are acidic in nature. In fact, phenols are Bronsted acids i.e., they can donate a proton to a strong base (B:).

II. Acylation reaction, Kolbe's reaction, Reimer Tiemann's reaction

Acylation

Esters of phenols yields phenolic ketones on treatment with anhydrous aluminium chloride.



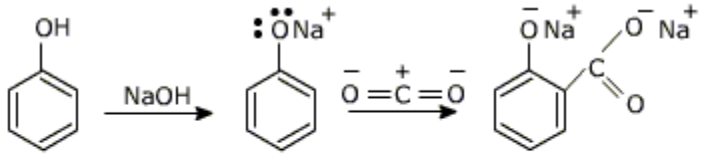
O - Hydroxyl acetophenone

P - Hydroxy acetophenone

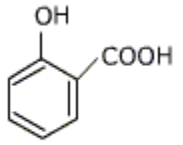
Phenyl ethanoate yields ortho and para hydroxy acetophenones. It involves migration of an acyl groyp from phenolic oxygen to ortho and para positions of the aromatic ring.

Kolbe's reaction

On reaction sodium salt of phenol with carbon dioxide gas, ortho hydroxy benzoic acid is formed as the main product. The temperature is 400 K and a pressure of 4-7 atm is required. Sodium salicylateis formed which an acidification yields salicylic acid (ortho hydroxy benzoic acid).



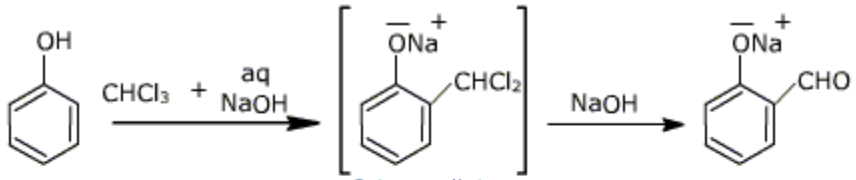
Sodium salicylate



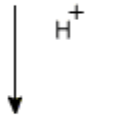
2- Hydroxy benzoic acid
(Salicylic acid)

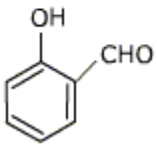
Reimer Tiemann's reaction

On treating phenol with chloroform in presence of sodium hydroxide at 340 K, a - CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemenn reaction. This results in the formation of O - hydroxybenzaldehyde (salicylaldehyde) and para-hydroxybenzaldehyde, the ortho isomer being the major product.



Intermediate compound

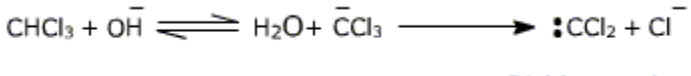




Salicylaldehyde

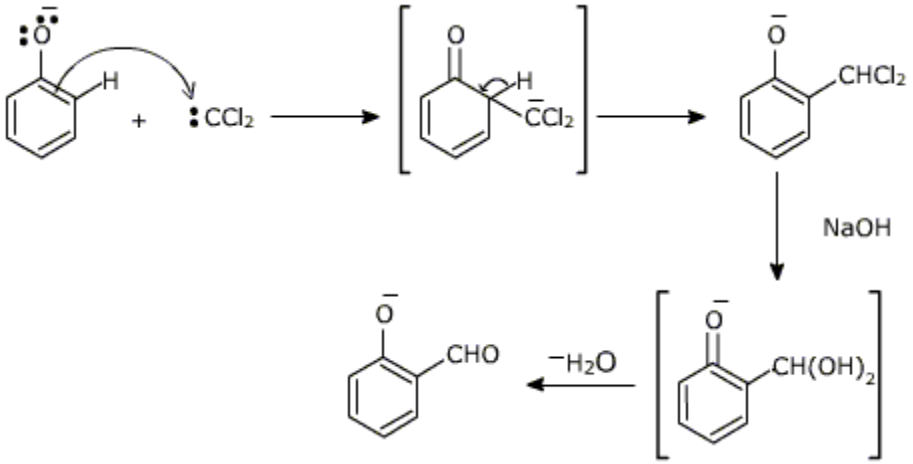
The intermediate substituted benzal chloride is hydrolysed in presence of alkali to produce salicylaldehyde.

Reimer Tiemenn reaction is an electrophilic substitution reaction. The first step is generation of electrophile.



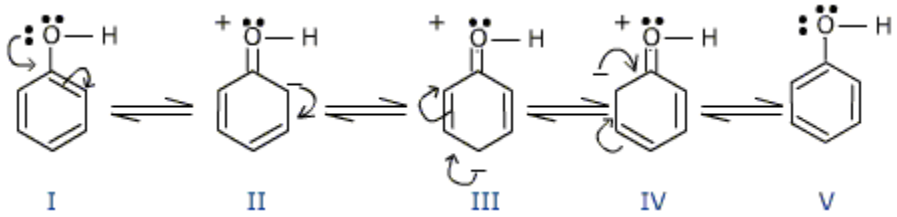
Dichloro carbene
(electrophile)

Dichlorocarbene contains a sextet of electrons and thus is a strong electrophile.



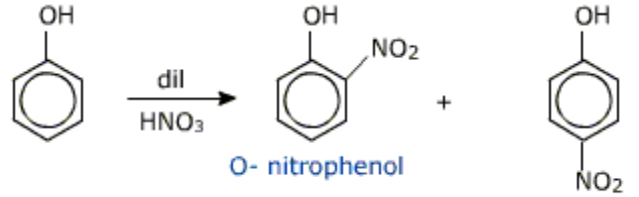
III. Electrophilic substitution of phenol

The -OH group attached to the benzene ring in phenol activates, it towards electrophilic substitution. It directs the incoming group to ortho and para positions in the ring as these positions become electron rich due to electronic effect (also mesomeric effect) caused by -OH group.

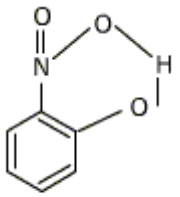


Common electrophilic aromatic substitution reactions taking place in phenol are as follow:

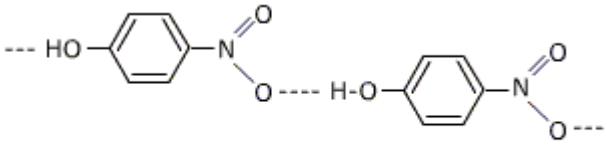
(i) <u>Nitration</u> - with dilute nitric acid at low temperature (298 K), phenol yields a mixture of ortho and para nitro phenols.



The ortho and para isomers can be separated by steam distillation O-Nitro phenol is steam volatile due to intra molecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding, which causes association of molecules.

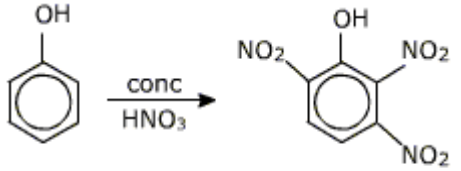


Intra molecular hydrogen bonding in O-nitro phenol



P- Nitrophenol with inter molecular hydrogen bonding

With concentrated nitric acid, phenol is converted to 2,4,6 trinitrophenol. This reaction involves nitration accompanied by oxidation of Phenol.



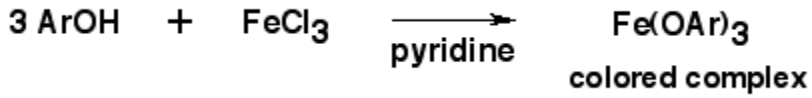
2,4,6 Trinitrophenol (Picric acid)

Industrially, picric acid is prepared by treating phenol first with conc.H_2SO_4 which converts it to phenol 2, 4 disulphonic acid. This yields picric acid on treatment with conc. HNO_3.

4. Explain the tests and uses of phenol.

a) Laboratory test of phenol

Phenol



Standard Phenol

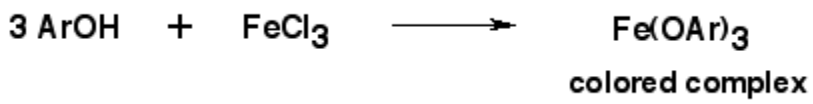
Procedure (for water-soluble phenols)
The iron (III) chloride test for phenols is not completely reliable for acidic phenols, but can be administered by dissolving 15 mg of the unknown compound in 0.5 mL of water or water-alcohol mixture and add 1 to 2 drops of 1% aqueous iron (III) chloride solution.

Positive Test
A red, blue, green, or purple color is a positive test.

Cleaning up
Since the quantity of material is extremely small, the test solution can be diluted with water and flushed down the drain.

Iron(III) Chloride - Pyridine Test for Water-Insoluble Phenols

Phenol



b) Uses of phenol

- The main use of phenol is as a feedstock for phenolic resins, bisphenol A and caprolactam (an intermediate in the production of nylon-6).

- It is used in the manufacture of many products including insulation materials, adhesives, lacquers, paint, rubber, ink, dyes, illuminating gases, perfumes, soaps and toys.

- Also used in embalming and research laboratories.

- It is a product of the decomposition of organic materials, liquid manure, and the atmospheric degradation of benzene.
- It is found in some commercial disinfectants, antiseptics, lotions and ointments.

- Phenol is active against a wide range of microorganisms, and there are some medical
- and pharmaceutical applications including topical anesthetic and ear drops, sclerosing agent.

- It is also used in the treatment of ingrown nails in the "nail matrix phenolization method".

- Another medical application of phenol is its use as a neurolytic agent, applied in order to relieve spasms and chronic pain.

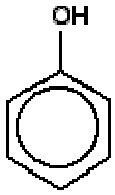
- It is used in dermatology for chemical face peeling

SHORT ANSWER QUESTIONS

1. Explain the structure of phenol.

The structure of phenol

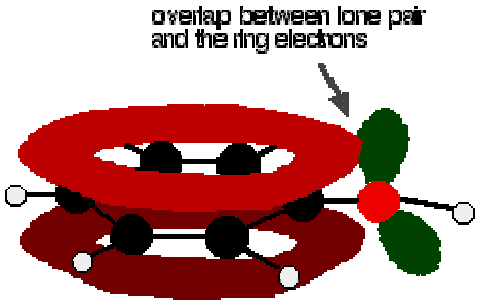
The simplest way to draw the structure of phenol is:



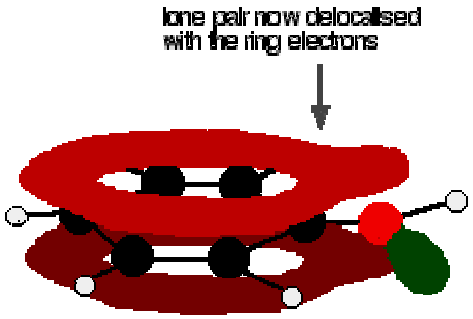
. . . but to understand phenol properly, you need to dig a bit deeper than this.

There is an interaction between the delocalised electrons in the benzene ring and one of the lone pairs on the oxygen atom. This has an important effect on both the properties of the ring and of the -OH group.

One of the lone pairs on the oxygen overlaps with the delocalised ring electron system . . .



. . . giving a structure rather like this:



The donation of the oxygen's lone pair into the ring system increases the electron density around the ring. That makes the ring much more reactive than it is in benzene itself. That is explored in another page in this phenol section.

2. Explain the physical properties of phenol.

Physical properties

1. Pure phenol is a white crystalline solid, smelling of disinfectant. It has to be handled with great care because it causes immediate white blistering to the skin. The crystals are often rather wet and discoloured.

2. Melting and boiling points

It is useful to compare phenol's melting and boiling points with those of methylbenzene (toluene). Both molecules contain the same number of electrons and are a very similar shape. That means that the intermolecular attractions due to van der Waals dispersion forces are going to be very similar.

	melting point (°C)	**boiling point (°C)**
C_6H_5OH	40 - 43	182
$C_6H_5CH_3$	-95.0	111

The reason for the higher values for phenol is in part due to permanent dipole-dipole attractions due to the electronegativity of the oxygen - but is mainly due to hydrogen bonding.

Hydrogen bonds can form between a lone pair on an oxygen on one molecule and the hydrogen on the -OH group of one of its neighbours.

3. Solubility in water

Phenol is moderately soluble in water - about 8 g of phenol will dissolve in 100 g of water.

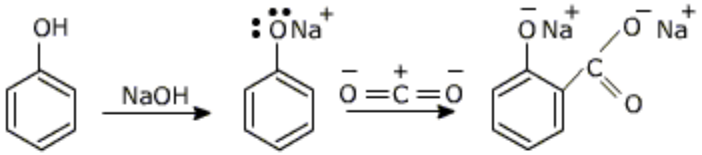
If you try to dissolve more than this, you get two layers of *liquid*. The top layer is a solution of phenol in water, and the bottom one a solution of water in phenol. The solubility behaviour of phenol and water is complicated.

Phenol is somewhat soluble in water because of its ability to form hydrogen bonds with the water.

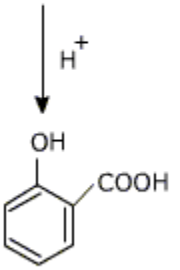
3. **Explain Kolbe' reaction**

Kolbe's reaction

On reaction sodium salt of phenol with carbon dioxide gas, ortho hydroxy benzoic acid is formed as the main product. The temperature is 400 K and a pressure of 4-7 atm is required. Sodium salicylates formed which an acidification yields salicylic acid (ortho hydroxy benzoic acid).



Sodium salicylate

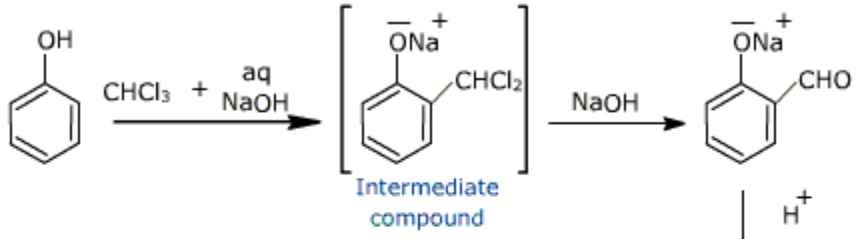


2- Hydroxy benzoic acid
(Salicylic acid)

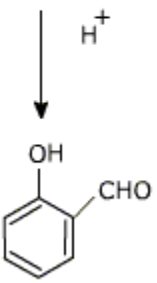
4. Explain Reimer Tiemann's reaction

Reimer Tiemann's reaction

On treating phenol with chloroform in presence of sodium hydroxide at 340 K, a - CHO group is introduced at ortho position of benzene ring. This reaction is known as Reimer - Tiemenn reaction. This results in the formation of O - hydroxybenzaldehyde (salicylaldehyde) and para-hydroxybenzaldehyde, the ortho isomer being the major product.



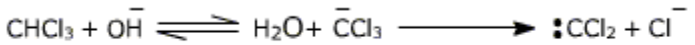
Intermediate compound



Salicylaldehyde

The intermediate substituted benzal chloride is hydrolysed in presence of alkali to produce salicyl aldehyde.

Reimer Tiemenn reaction is an electrophilic substitution reaction. The first step is generation of electrophile.



Dichloro carbene
(electrophile)

Dichlorocarbene contains a sextet of electrons and thus is a strong electrophile.

