

ALCOHOL, PHYNOL, ETHER

INTRODUCTION

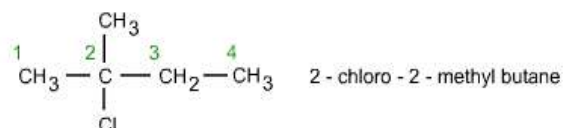
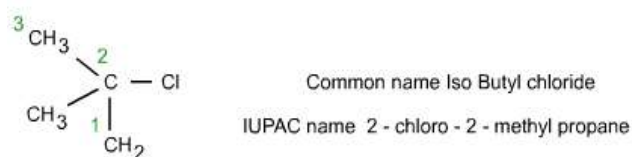
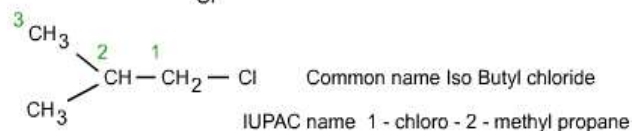
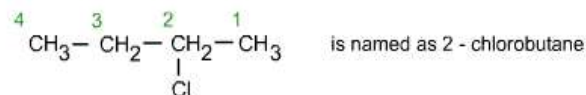
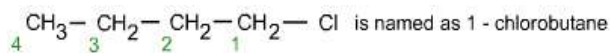
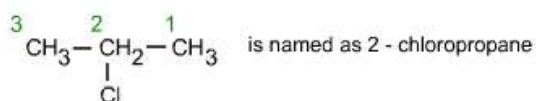
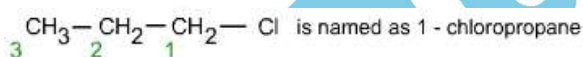
The replacement of hydrogen atom in saturated aliphatic hydrocarbons and arenes by a halogen atom (F, Cl, Br, I) gives haloalkanes and haloarenes respectively.

Haloalkanes are known as alkyl- halides and haloarenes are called aryl halides. The hydroxy derivatives of aliphatic-hydrocarbon are known as alcohols and hydroxy derivatives of aromatic hydrocarbons are called as phenols.

Nomenclature

Haloalkanes

In IUPAC system, haloalkanes are considered as derivative of corresponding alkanes and are named as haloalkanes. Some IUPAC names are as under
 $\text{CH}_3 - \text{Cl}$ is named as chloromethane
 $\text{CH}_3 - \text{CH}_2 - \text{Cl}$ is named as chloroethane



Some common names and IUPAC names of a few dihalides are given below

Formula	Common name	IUPAC name
CH_2Cl_2	Methylene chloride	Dichloromethane
$\text{CH}_3\text{CH}_2\text{Cl}_2$	Ethylidene chloride	1, 1 - Dichloroethane
CH_2CH_2 $\text{Cl} \quad \text{Cl}$	Ethylene dichloride	1, 2 - Dichloroethane

HALOARENES

The prefixes like chloro, bromo etc are added before the name of aromatic hydrocarbons.

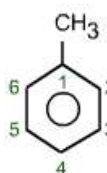


Chloro benzene

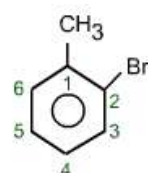
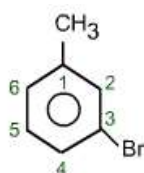
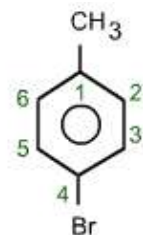
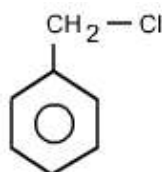


Bromo benzene

In a benzene ring the relative positions of functional groups are 1,2; 1,3 and 1,4 indicated by prefix ortho (o), meta (m) and para (p) respectively.



Toluene

2 Bromo toluene
or
o - Bromo toluene3 Bromo toluene
or
m - Bromo toluene4 Bromo toluene
or
p - Bromo toluene

Phenyl chloromethane

Nomenclature of alcohols

Alcohols are named by replacing 'e' in the name of parent alkane by ol. The position of carbon atom attached to -OH group is specified by a number and its number should be least.

Alcohols with one hydroxy group are known as monohydric alcohols similarly having two-OH groups are called diols or glycols. Alcohols having three -OH groups are called triols. Names of some alcohols are given below.

Structure	Common name	IUPAC name
$\text{CH}_3 - \text{CH}_2 - \text{OH}$	Ethyl alcohol	Ethanol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	n propyl alcohol	1 propanol
$\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$	n butyl alcohol	1 - butanol
$\text{CH}_3 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2 - \text{CH}_3$	sec butyl alcohol	2 - butanol
$\text{CH}_3 - \underset{\text{CH}_3}{\underset{\text{OH}}{\text{C}}} - \text{CH}_2 - \text{CH}_3$	tert butyl alcohol	2 - methyl - 2 - propanol
$\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{OH}$	iso butyl alcohol	2 - methyl - 1 - propanol
$\text{CH}_2 - \text{OH}$ $\text{CH}_2 - \text{OH}$	Ethylene glycol	1,2 - ethane diol
$\text{CH}_2 - \underset{\text{OH}}{\text{CH}} - \text{CH}_2$ $\text{OH} \quad \text{OH} \quad \text{OH}$	Glycerine or Glycerol	1,2,3 - propane triol

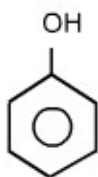
If a organic compound contains four or more than four hydroxy groups (-OH) they are called polyhydric alcohols. Alcohols which contain only one hydroxy group are monohydric alcohols, classified as Primary, Secondary and Tertiary alcohols depending upon whether -OH group is attached to which carbon atom.

$\text{CH}_3 - \text{CH}_2 - \text{OH}$ ethyl alcohol is a primary alcohol (1°)

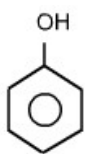
$\text{CH}_3 - \underset{\text{H}}{\underset{\text{OH}}{\text{C}}} - \text{CH}_3$ iso propyl alcohol is a secondary alcohol (2°)

$\text{CH}_3 - \underset{\text{OH}}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$ tert butyl alcohol is a tertiary alcohol (3°)

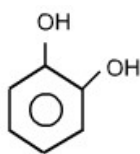
Naming of Phenols When -OH group is attached to benzene nucleus it is called phenol.



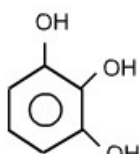
If benzene ring contains one- OH group it is called monohydric phenol. If benzene ring contains two- OH group it is called dihydric phenol and with three -OH groups it is called trihydric phenol.



Hydroxy benzene
or
(Phenol)

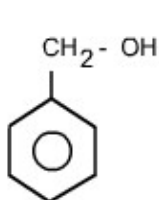


1,2 - Dihydroxy
benzene
or (Catechol)

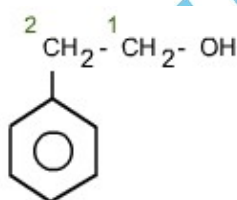


1,2,3 - Trihydroxy
benzene
or (Pyrogallol)

We have to remember that if -OH group is not attached to benzene ring then it is not phenol but then they are called aromatic alcohols. Some aromatic alcohols are as under.



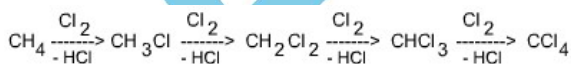
Phenyl methanol



2 - phenyl ethanol

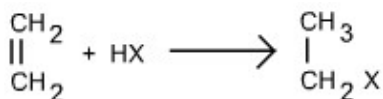
Haloalkanes Preparation

• **From hydrocarbons** Halogens (Cl_2 , Br_2 , I_2) react with alkanes in the presence of UV light and form haloalkane

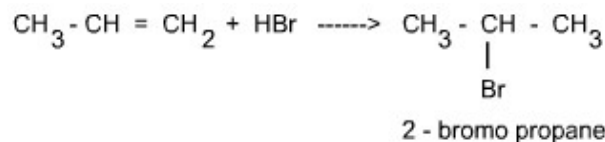


Methane gives a mixture of four products. By fractional distillation we can get pure component.

• **From alkenes** Haloalkenes can be prepared by the addition of halogen acids (HCl , HBr , HI)

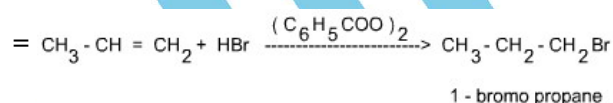


Addition of halogen acid takes place in accordance with Markownikoff's rule (electronegative group will go to that carbon atom which is having least hydrogen) For example



2 - bromo propane

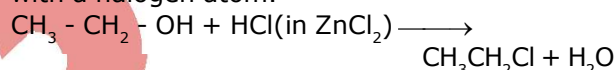
However in the presence of peroxides such as Benzoyl peroxide ($\text{C}_6\text{H}_5 - \text{COO} - \text{OOC} - \text{C}_6\text{H}_5$), the addition of HBr to unsymmetrical olefins (alkenes, alkynes) takes place just opposite to Markownikoff's rule



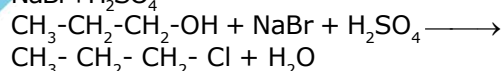
1 - bromo propane

The above effect is due to presence of peroxide therefore it is called peroxide effect or Kharasch effect.

• **From alcohols** We can get haloalkanes from alcohols due to substitution of the hydroxyl group with a halogen atom.



Here anhydrous ZnCl_2 is dehydrating agent which will absorb the water molecules. Haloalkanes can also be obtained by treating the alcohols with $\text{NaBr} + \text{H}_2\text{SO}_4$



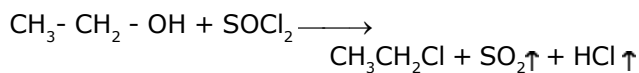
1 Propanol + NaHSO_4 Reactivity of halogen acids towards alcohols is as $\text{HI} > \text{HBr} > \text{HCl}$ HI is more reactive because we will get more and more H^+ **Reactivity of alcohols towards halogen acid is as under** Tertiary alcohol > Secondary alcohol > Primary alcohol Haloalkenes are also obtained by the reaction of alcohols with PCl_3 or P

(a) $3 \text{CH}_3 - \text{CH}_2 - \text{OH} + \text{PCl}_3 \longrightarrow 3 \text{CH}_3 - \text{CH}_2 - \text{Cl} + \text{H}_3\text{PO}_3$

(b) $3 \text{CH}_3 - \text{CH}_2 - \text{OH} + \text{PCl}_5 \longrightarrow 3 \text{CH}_3 - \text{CH}_2 - \text{Cl} + \text{POCl}_3 + \text{HCl}$ ($\text{P}_4 + \text{I}_2$)

(c) $3 \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{OH} + \text{PI}_3 \longrightarrow 3 \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{I} + \text{H}_3\text{PO}_3$

In the above reaction red phosphorous (P_4) reacts with Iodine to give PI_3 $\text{P}_4 + 6\text{I}_2 \longrightarrow 4\text{PI}_3$ By Darzen's procedure we can get pure haloalkanes. In this method alcohols are refluxed with thionyl chloride (SOCl_2) in the presence of a small amount of pyridine

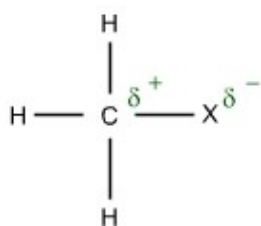


Thionyl chloride is preferred because in this process the side products are gases and can be easily expelled during distillation and we will get chloroalkanes in pure state.

PROPERTIES OF HALOALKANES

- Physical** Melting point and boiling point of haloalkanes are in the order of $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$. It is due to higher molecular mass of Iodoalkanes and also magnitude of vander waal's forces of attraction which is highest. Haloalkanes are polar in nature but they are insoluble in water because they are not able to form hydrogen bonds. They are soluble in organic solvents. Alkyl fluorides and chlorides are lighter than water but alkyl bromides and iodides are generally heavier. Order of increasing densities are as under Fluorides < Chlorides < Bromide < Iodide

- Chemical** Haloalkanes are polar in nature

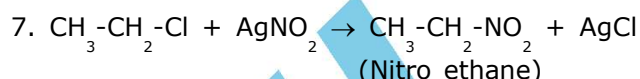
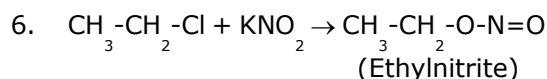
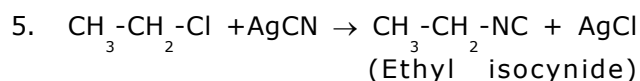
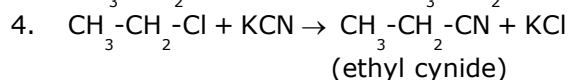
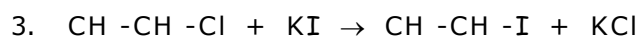


As X is more electronegative, it will attract the bonded electrons toward it self and X will get a slightly negative charge. Carbon which is bonded with X will get a slightly positive charge (δ^+). Presence of partial positive charge (δ^+) on the carbon atom makes it susceptible to attack by electron rich group called nucleophiles. When a nucleophil stronger than the halide ion approaches the positively charged carbon atom of an alkyl halide, the halogen atom along with its bonding electron pair gets displaced and a new bond with the carbon and the nucleophile is formed. **These reactions are called nucleophilic substitution reactions.**



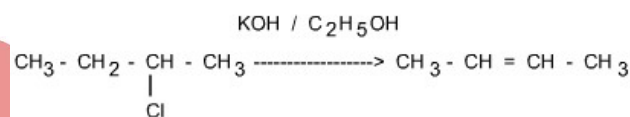
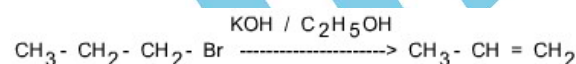
Examples of nucleophilic substitution reaction

- $\text{CH}_3 - \text{CH}_2 - \text{Cl} + \text{NaOH (aqueous)} \rightarrow \text{CH}_3 - \text{CH}_2 - \text{OH} + \text{NaCl (alcohol)}$
- $\text{CH}_3 - \text{CH}_2 - \text{Cl} + \text{NaOCH}_3 \rightarrow \text{CH}_3 - \text{CH}_2 - \text{O-CH}_3 + \text{NaCl (ether)}$



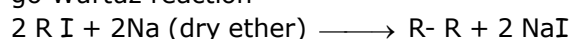
Elimination reaction of haloalkanes

Haloalkanes undergo elimination reactions on treatment with an alcoholic solution of KOH. Some examples are as under

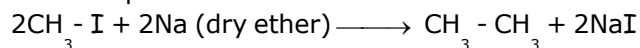


Here from 2-chlorobutane we get 2-butene which is having two alkyl groups ($-\text{CH}_3$) and it is more stable compound. These reactions are known as **Dehydrohalogenation**. **Reaction with metals** Haloalkanes form alkylmagnesium halides (Grignard reagents) when it is treated with Mg in dry ether as solvent.

$\text{R-X} + \text{Mg} \longrightarrow \text{R-Mg-X}$
Grignard reagents are highly reactive compounds, they are used for the preparation of a number of other carbon compounds such as alcohols, aldehydes, ketones and carboxylic acids. Haloalkanes on treatment with sodium metal undergo Wurtz-Fittig reaction

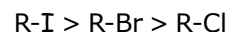


For example



Order of reactivity of haloalkanes

Iodoalkanes are more reactive than bromoalkanes because bond dissociation energy of C-I is less than C-Br due to bigger size I. So order of reactivity is as under

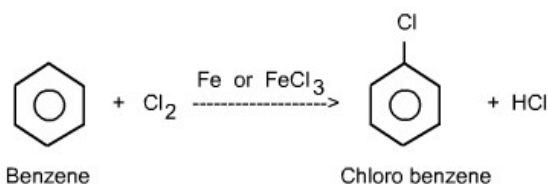


PREPARATION OF HALOALKANES

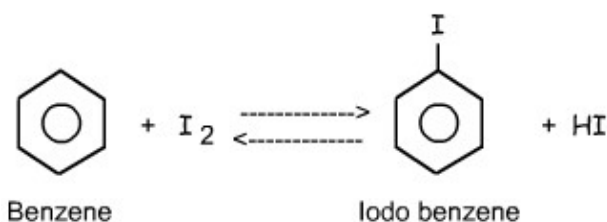
Haloalkanes are prepared from alcohol but haloalkanes are not prepared by phenols. It is not easy to replace OH group by Cl group.

Some methods are as under for the preparation of haloalkanes.

Halogenation of Benzene

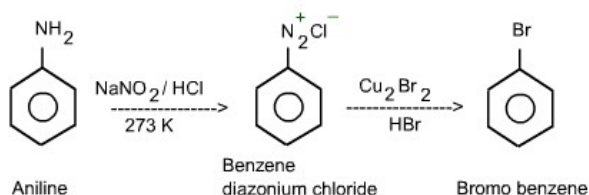
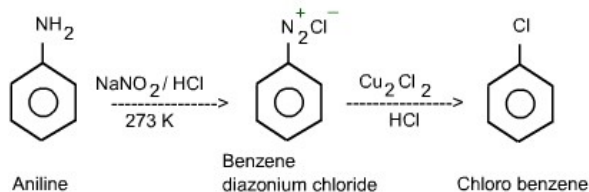


Bromobenzene can also be prepared by above method. For the preparation of Iodobenzene, Iodination is carried out in the presence of an oxidising agent like HIO_3 or HNO_3 .

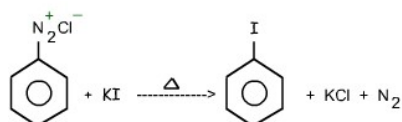


here HI will react with the oxidising agent
 $5\text{HI} + \text{HIO}_3 \longrightarrow 3\text{H}_2\text{O} + 3\text{I}_2$

From Diazonium salt



The above reaction is called Sandmeyer's reaction. Iodo benzene can be prepared by treating the benzene diazonium chloride with KI (aqueous)



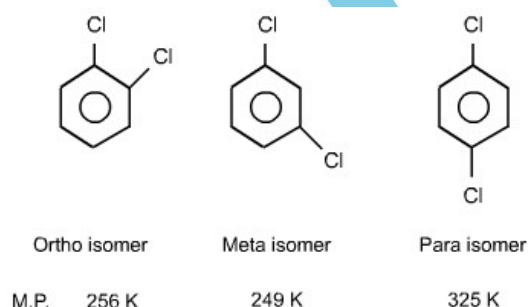
Fluoro arenes are prepared as under



PROPERTIES OF HALOARENES

• Physical

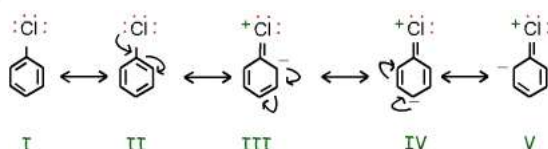
The boiling points of monohalogen derivatives of benzene follow the order as Iodobenzene > Bromobenzene > Chlorobenzene. The boiling point of Isomeric dihalobenzenes are nearly the same but the melting points of these compounds show a considerable variation. Para isomers generally have 70 to 100 degrees higher melting point than the ortho and meta isomers



The higher melting point of para isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice. Haloarenes are insoluble in water, acids or bases but soluble in organic solvents. Haloarenes are heavier than water.

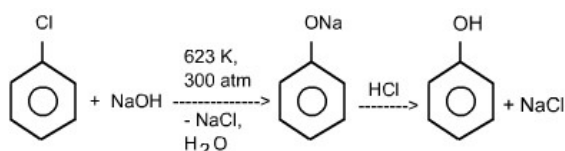
• Chemical

Haloarenes (halobenzene) are less reactive due to their resonance stabilisation. Resonating structure is as under.

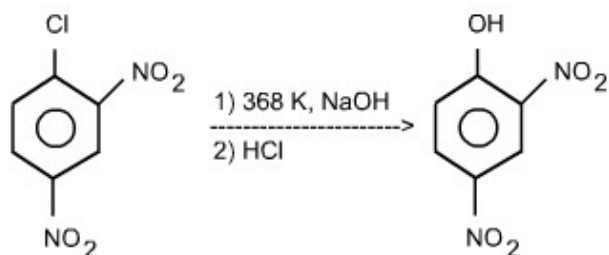


Structure III, IV, V show that C-Cl bond has double bond character. As a result of this the C-X bond in chlorobenzene is shorter and stronger as compared to chloroalkanes. Thus cleavage of C-Cl bond in chlorobenzene is difficult some chemical reactions are as under

Replacement by - OH group

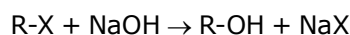


The reactivity of the haloarenes towards nucleophilic substitution reaction increases if some electrons withdrawing group such as $-\text{NO}_2$, $-\text{CN}$, $-\text{COOH}$ group is attached to the ring.

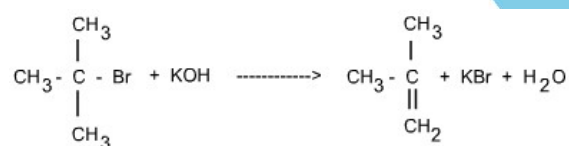
For example**Alcohols and phenols****Methods of preparation of alcohols**

Some methods are as follows

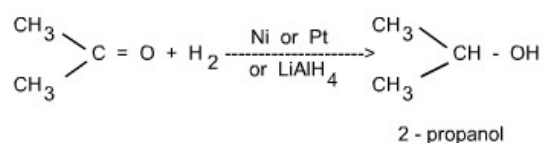
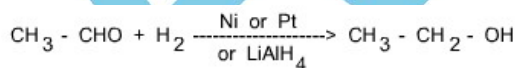
From haloalkanes Haloalkanes are hydrolysed to alcohols by treatment with aqueous NaOH.



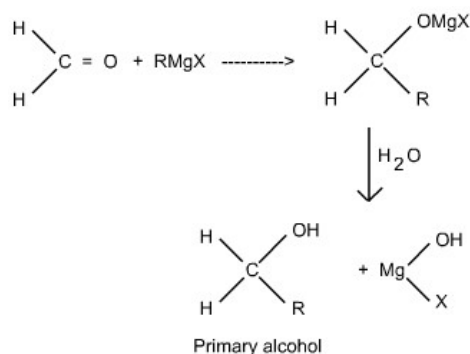
Primary haloalkanes give a good yield of alcohols while tertiary haloalkanes are converted mainly into alkenes due to dehydrohalogenation.

**From aldehydes**

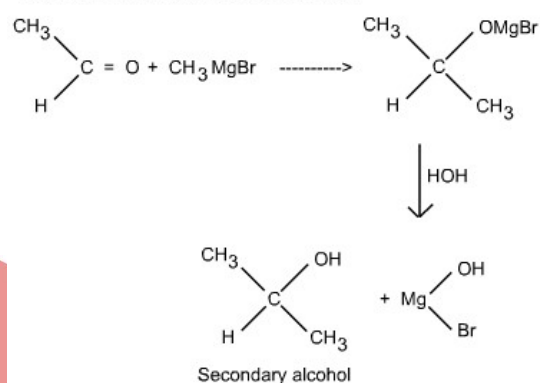
Aldehyde on reduction gives primary alcohol and ketone gives secondary alcohol. The reducing agents used are LiAlH_4 , NaBH_4 , Na/C H OH or H_2 with Ni or Pt or Pd as a catalyst

**Use of grignard's reagent**

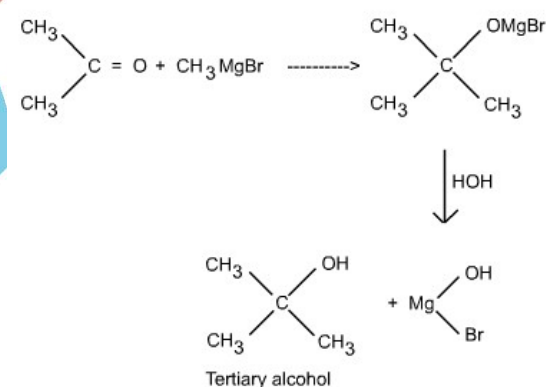
This method can be used for the preparation of all the three types of alcohols. The reaction of RMgX with formaldehyde (HCHO) give a primary alcohols



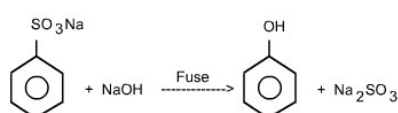
Any aldehyde will give secondary alcohol



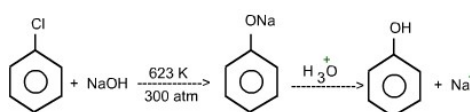
Ketone will give tertiary alcohol

**Methods of preparation of phenols****From sulphonic acid salt**

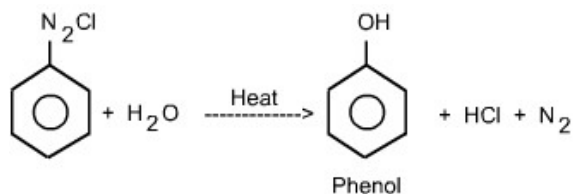
Phenols are prepared by the fusion of sodium sulphonates with NaOH



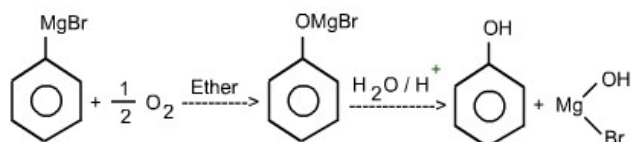
From haloarenes also we get phenols

**From diazonium salts**

In the lab phenols are prepared by the hydrolysis of diazonium salt with water or dilute acid.



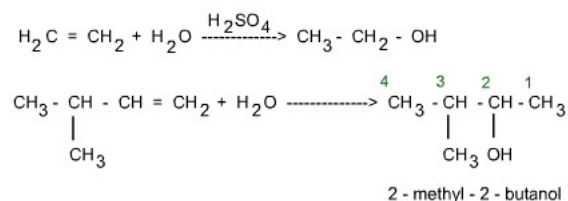
From grignard reagent



Industrial preparation of alcohols

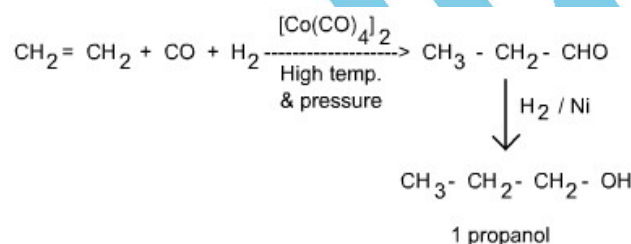
By the hydration of alkenes

Alkenes are converted to alcohols by the addition of water in the presence of H_2SO_4 .



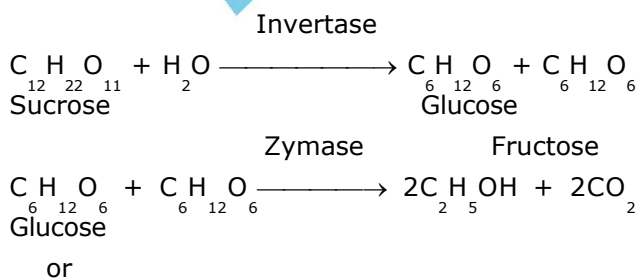
By Oxo process

Alkenes react with $\text{CO} + \text{H}_2$ in the presence of $[\text{Co}(\text{CO})_4]_2$ as a catalyst and at high temperature and pressure to give aldehydes. Catalytic hydrogenation of aldehydes gives primary alcohols.



By the fermentation of carbohydrates

Fermentation of sugar present in molasses, grapes or beet give ethylalcohol

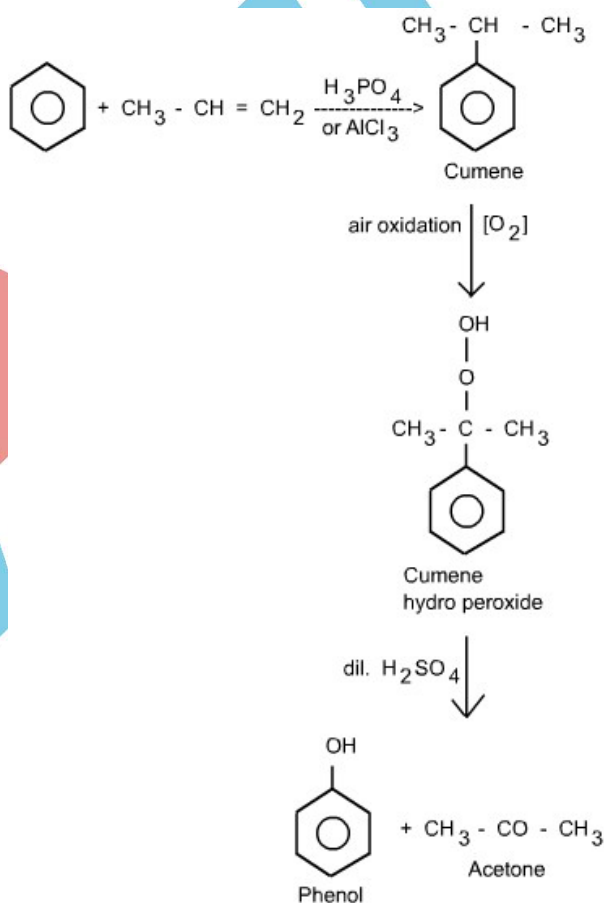


Fructose

The process of breaking down large molecules into simple ones in the presence of enzymes is known as fermentation. It is old process for the preparation of ethyl alcohol.

Industrial preparation of phenols

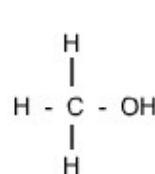
The starting material for the preparation of phenol is cumene. Cumene is prepared by Friedel-Craft alkylation of benzene with propene. Cumene is oxidised by air to cumene hydroperoxide which on treatment with dil H_2SO_4 gives phenol and acetone.



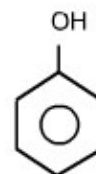
Properties of alcohol and phenol

Structure

Simple structure of alcohol methyl alcohol and phenol are given below :

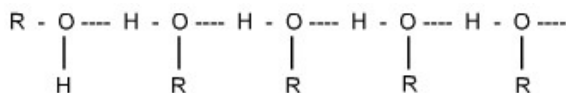


Methanol



Phenol

As oxygen is more electronegative than carbon and hydrogen therefore C-O and O-H bonds in alcohols and phenols are polar bonds and hence both alcohols and phenols possess a net dipole moment. Due to polar nature, alcohols and phenols are capable of forming hydrogen bonds.



Physical properties of alcohol

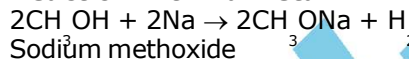
The lower member of alcohols are colourless volatile liquids. Higher alcohols are odourless and tasteless. Higher alcohols having 12 or more carbon atoms are colourless waxy solids. Lower members of alcohols are soluble in water due to formation of hydrogen bond. With water higher members are insoluble in water due to increase in the size of alkyl group. Boiling point of alcohols are much higher than alkanes, haloalkanes or ethers of comparable molecular masses. This is due to intermolecular hydrogen bonds which exists in the alcohol molecules.

Physical properties of phenols

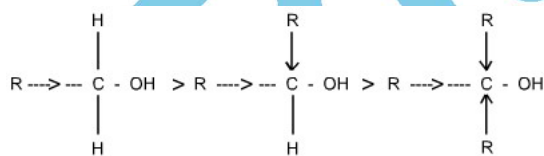
Phenols are colourless crystallite solids or liquids. Phenols are sparingly soluble in water because of the larger hydrocarbon part of the molecule. Phenols have higher boiling points than arenes because of hydrogen bonding.

Chemical properties of alcohol

Reaction with Na metal



Sodium methoxide
The above reaction shows the acidic nature of alcohols. Primary alcohols are more acidic than secondary alcohol is more acidic than tertiary alcohols.

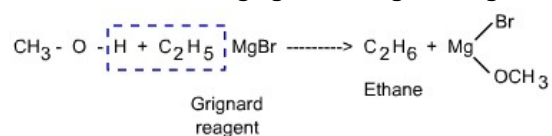


Primary alcohol Secondary alcohol Tertiary alcohol

-----> Acidic character decreases ----->

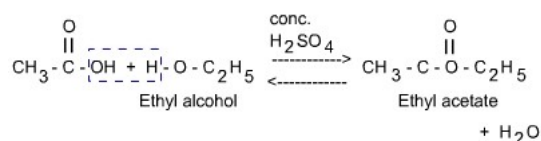
Reaction with grignard reagent

Alcohol react with grignard reagent to give alkane.



Reaction with carboxylic acid

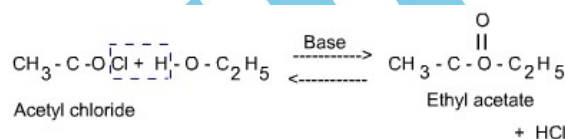
Alcohol reacts with monocarboxylic acids in the presence of conc H_2SO_4 to form esters.



The above reaction is called esterification

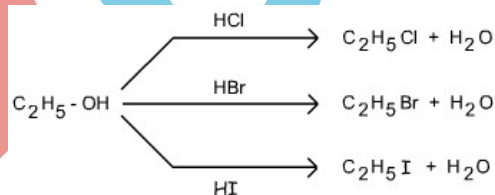
Reaction with acid chloride

Alcohol when treated with acid chloride in the presence of bases like pyridine form esters. This reaction is called acylation.

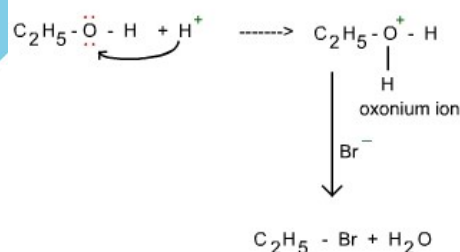


Reaction with hydrogen halides (HCl, HBr, HI)

Alcohols react with hydrogen halides and form alkyl halides.



Mechanism of reaction is as under

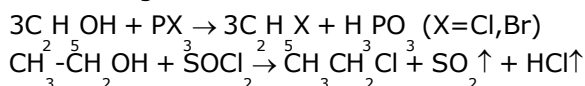


In the above reaction H^+ ion has attached on oxygen of ethyl alcohol which is having two lone pair of electron and acting as a base. The order of reactivity of hydrogen halides are as under **HI > HBr > HCl**

The order of reactivity of alcohols are as under

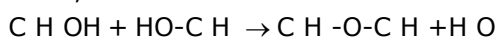
Tertiary alcohol > Secondary alcohol > Primary alcohol

Reaction with phosphorous trihalide and thionyl chloride Alcohols are converted to alkyl halide with PX_3 thionyl chloride reacts with alcohol to give chloroalkenes.

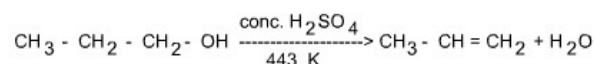
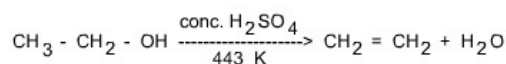


Reaction with H₂SO₄

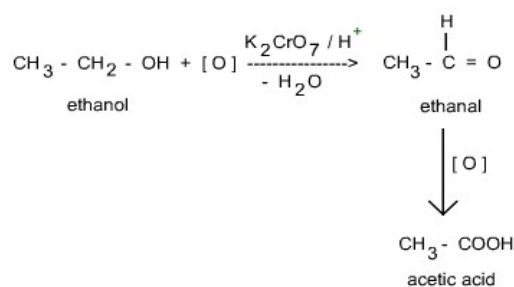
When excess of alcohol is treated with H₂SO₄ at 413K, ether is obtained.



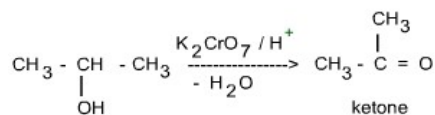
When alcohol is treated with H₂SO₄ at 443K alkene is obtained.

**Oxidation of alcohol**

Alcohols under go oxidation with oxidising agents like chromium trioxide (CrO₃), KMnO₄, K₂Cr₂O₇, HNO₃. Primary alcohol give aldehyde which on further oxidation gives an acid.

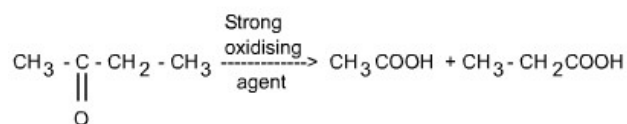
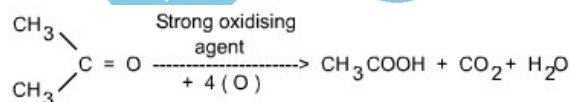


Secondary alcohol gives ketones on oxidation. Ketones do not readily undergo further oxidation.

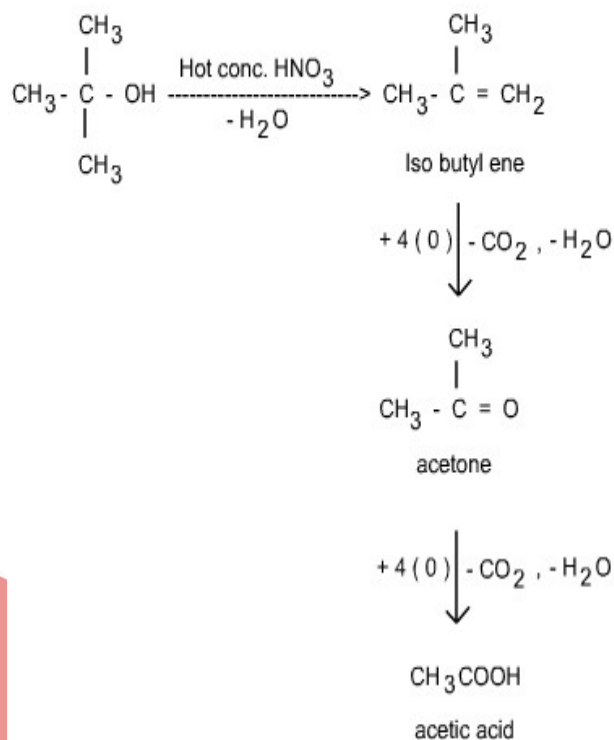


secondary alcohol

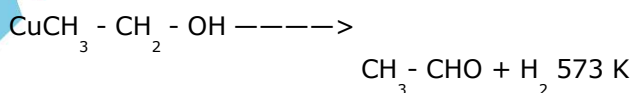
Ketones with strong oxidising agent oxidised to a mixture of carboxylic acid with lesser numbers of carbon atoms than the starting alcohol.



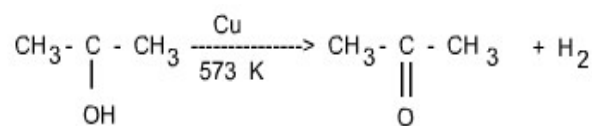
Tertiary alcohols are not oxidised with mild oxidising agents. When oxidation is carried out under acidic conditions, tertiary alcohols first undergo dehydration to form alkene. The alkene formed is then oxidised to ketone which is finally oxidised to carboxylic acid with lesser number of carbon atoms than the starting alcohol.



Dehydrogenation Alcohols are oxidised by passing alcohol vapours over heated copper at 573K



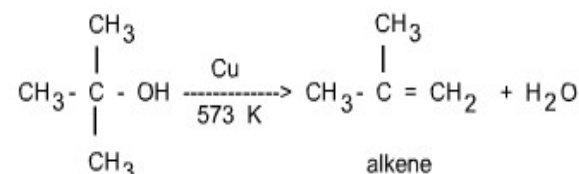
Primary alcohol aldehyde



Secondary alcohol

Ketone

Tertiary alcohols are resistant to oxidation but they get dehydrated to form an alkene.

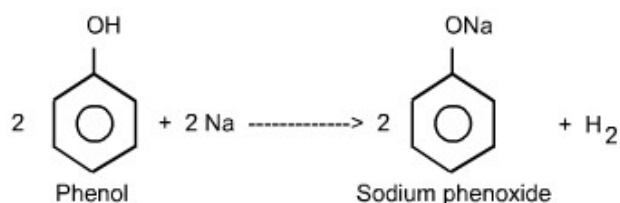


Tertiary alcohol

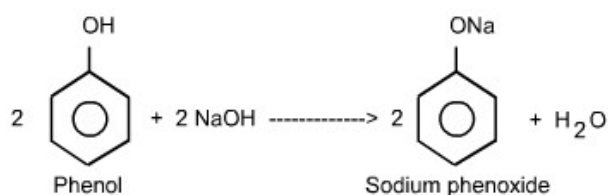
alkene

Chemical properties of phenols

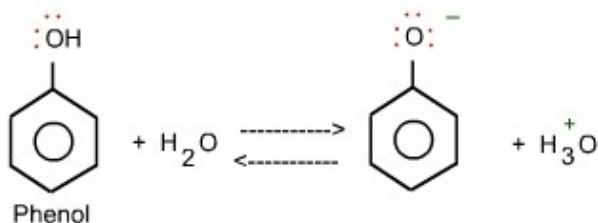
Reaction with metals Phenols react with Na or K to form salt and hydrogen gas is liberated

**Reaction with alkalis**

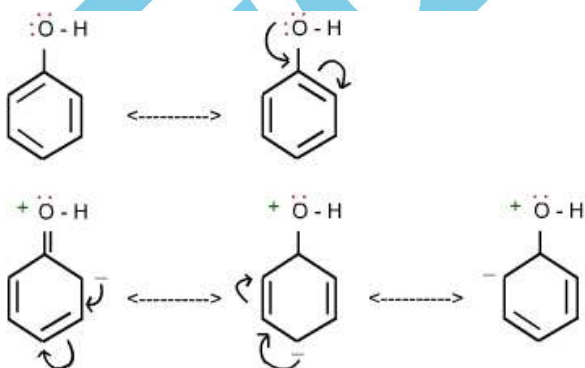
Phenols are soluble in solutions of alkalis (NaOH or KOH).

**Phenol behave as acid**

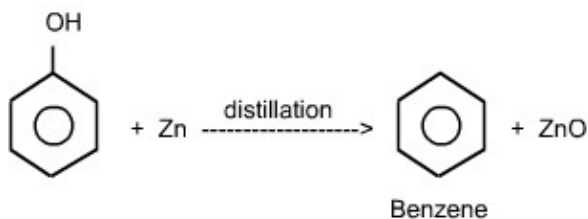
Because of the presence of polar O-H group in them, they ionise in aqueous solution to give H^+ ions.



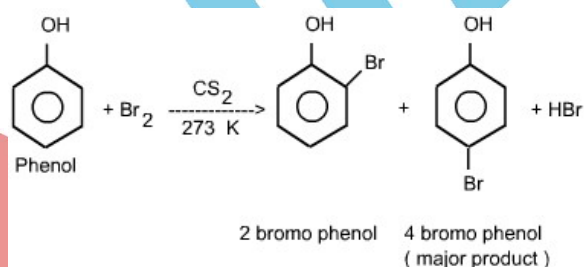
Resonating structure of phenols is as under



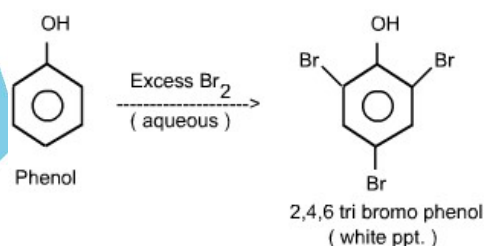
Due to above resonating structure, H will go out taking a positive charge and this is the reason that phenol is acidic in nature.

Reaction with Zn dust

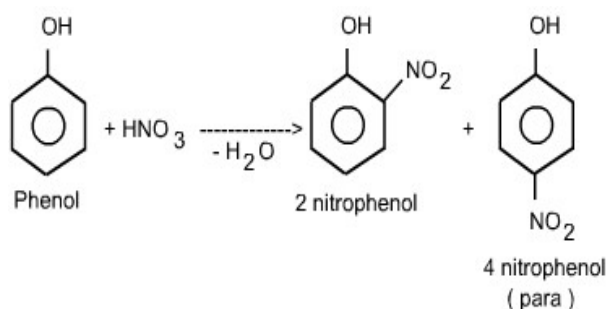
Reaction with bromine Phenol react with Bromine in the presence of less polar solvent such as CS_2 or CCl_4 at low temperature and give monobromophenol.



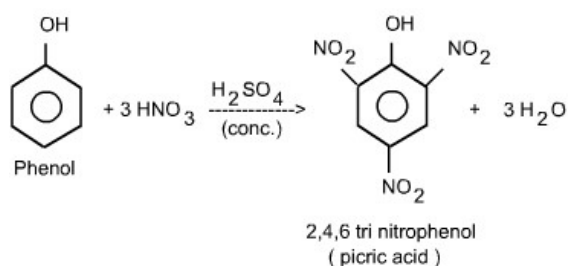
Phenol give 2,4,6 tri bromo phenol when treated with bromine water

**Nitration**

Phenol react with dilute HNO_3 at low temperature (293K) to give a mixture of ortho and para nitrophenol.

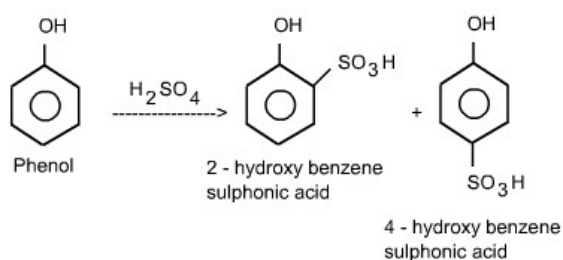


With conc HNO_3 and in the presence of H_2SO_4 phenol gives 2,4,6, trinitrophenol.(picric acid)



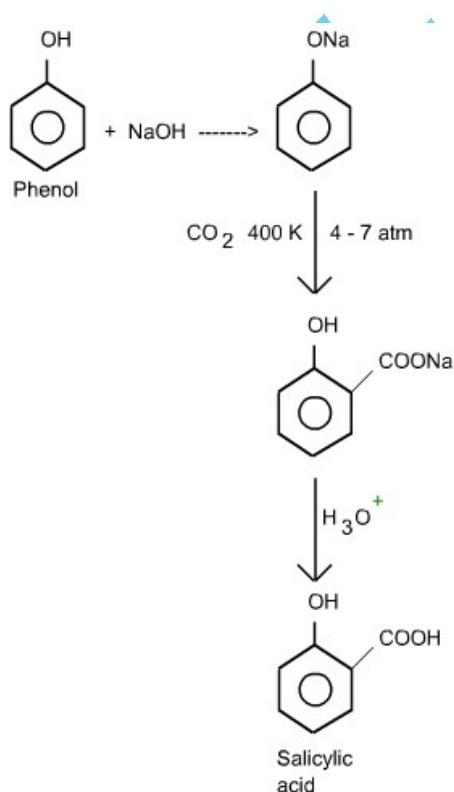
Sulphonation

Phenols are sulphonated with conc H_2SO_4

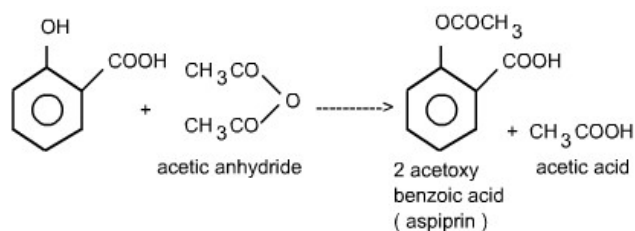


Kolbe's reactions

When sodium phenoxide is heated with CO_2 at 400K and at 4-7 atmospheric pressure, sodium salicylate is formed. This on acidification yields salicylic acid.

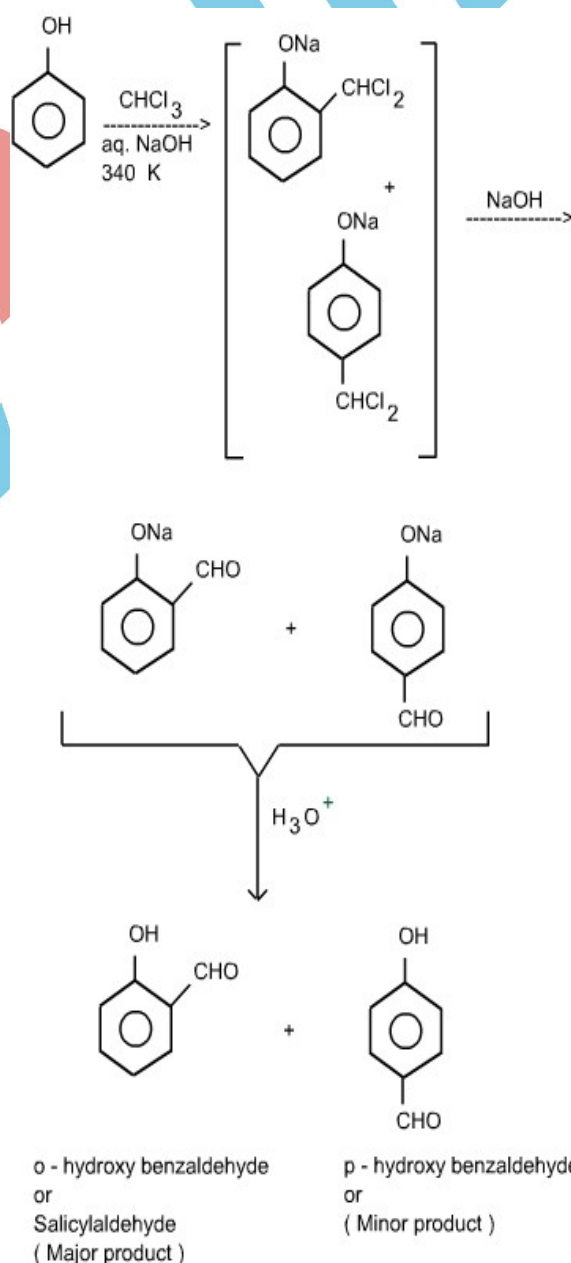


Salicylic acid is the starting material for the manufacture of 2 acetoxybenzoic acid (aspirin).

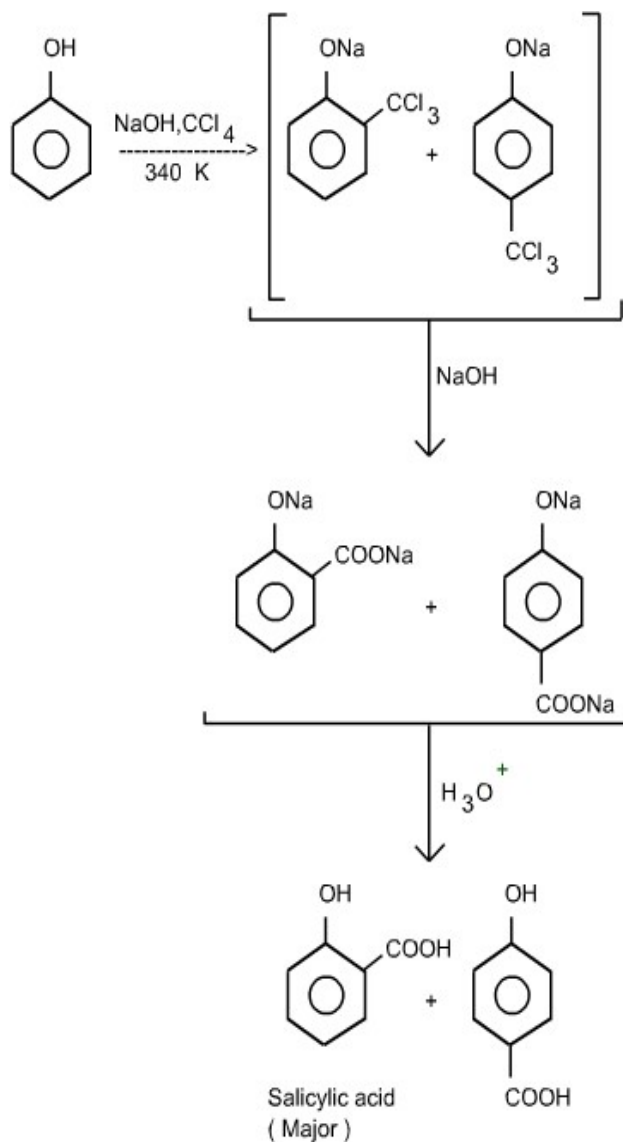


Reimer-Tiemann reaction

Treatment of phenol with chloroform in the presence of aqueous alkali at 340 K result in the formation of o-Hydroxy benzaldehyde and p hydroxy benzaldehyde



If in the above reaction CCl_4 is used in place of chloroform (CHCl_3), Salicylic acid is obtained as the major product.³



Correlation of physical propertie

Haloalkanes In general they are colourless, sweetsmelling liquids. Lower members like CH_3Cl , CH_2Br , CH_3Br , CH_3I are colourless gases while members having very-high molecular masses are solid. Haloalkanes are polar in nature but they are insoluble in water because they are not able to form hydrogen bonds with water. They are soluble in organic solvents. Haloalkanes have higher boiling points than the corresponding hydrocarbons. This is due to the fact that unlike hydrocarbons haloalkanes are polar in nature and there are strong dipole-dipole interactions between the molecules.]

Haloarenes

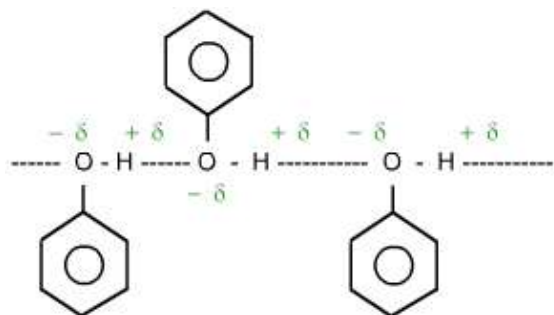
Are generally colour less liquid or crystalline solids. They are also insoluble in water like haloalkanes. They are heavier than water. The melting and boiling points of aryl halides are nearly the same as those of alkyl halides containing the same number of carbon atoms, Haloarenes are chemically less reactive than haloalkanes.

Alcohol

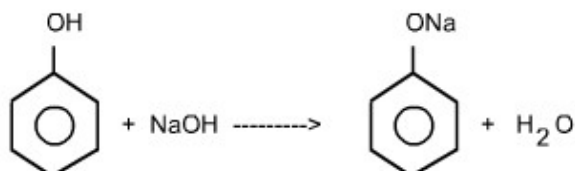
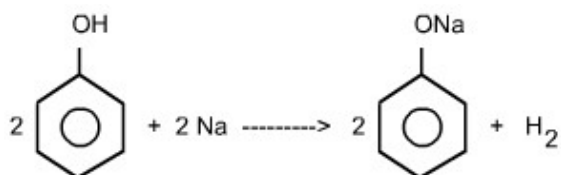
Lower members are colourless liquid. Higher members (more than 12 carbon atoms) are colourless, odourless wax like solids. Alcohols exist as associated molecules having intermolecular hydrogens bonds. They have higher boiling points as compared to other organic compounds of similar molecular masses such as hydrocarbons ethers, haloalkanes and it is due to presence of hydrogen bonds in alcohol. Lower members are soluble in water because they form hydrogen bonds with water however as the size of alcohol molecule increases the alkyl group becomes more and more important as compared to OH group and this prevents the alcohol from mixing with water.

Phenols

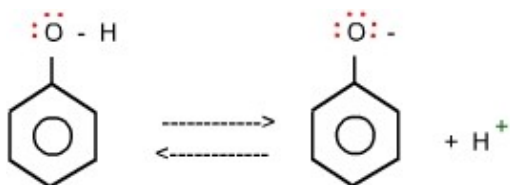
Are colourless crystalline solid or liquids. Unlike alcohols, phenols are very less soluble in water. The non-polar aryl group is very large in size and it almost completely mask the polar character of the OH group however, phenols are soluble in alcohols ethers and also in NaOH. Boiling point of phenols are higher than the boiling points of the aromatic hydrocarbons of comparable molecular masses. It is due to presence of intermolecular hydrogen bonds in phenols.



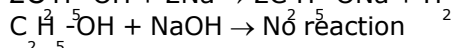
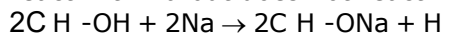
Phenols are acidic in nature. They turn blue litmus red and react with alkali metal and alkalies to form their salts.



However phenol is weaker acid than carboxylic acid. Therefore like carboxylic acid it does not react with Na_2CO_3 and NaHCO_3 .



Phenols are more acidic than alcohols. Alcohols react with Na but does not react with NaOH



Preparation, properties and uses of chloroform(CHCl_3)

Preparation

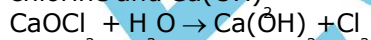
It is prepared by the following methods

Laboratory method

It is prepared in the lab by the reaction of ethyl alcohol or propanone and bleaching power.

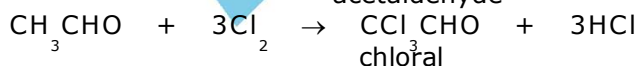
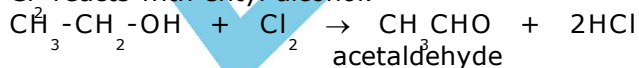
• From ethanol

First bleaching powder react with water to give chlorine and Ca(OH)_2

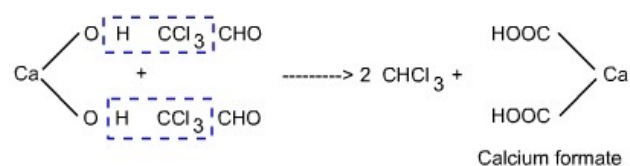


Bleaching powder

Cl_2 reacts with ethyl alcohol.

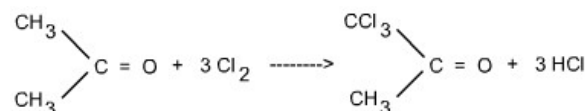
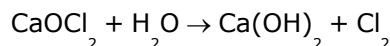


Chloral reacts with lime to give chloroform.

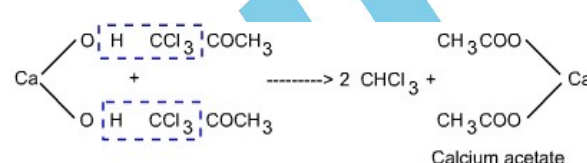


• From propanol

reaction occurs as follows



Trichloro propanone react with lime to form CHCl_3



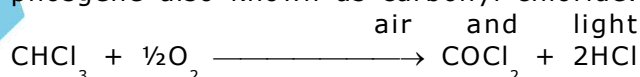
Physical properties of chloroform

Chloroform is sweet smelling colourless liquid. Its bp is 334K and freezing point is 210K. It is sparingly soluble in water but readily soluble in organic solvent such as ethanol and ether. It is good solvent for oils and waxes. It is used as an anaesthetic.

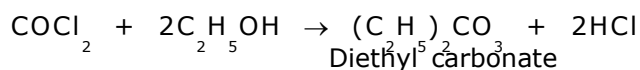
Chemical properties of chloroform

• Chloroform is slowly oxidised by air

In the presence of light to a poisonous gas phosgene also known as carbonyl chloride.

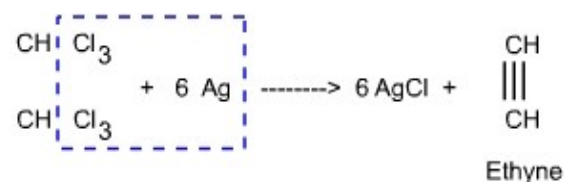


To check the oxidation it is stored in coloured bottles completely filled so the air is kept out. A small amount of ethyl alcohol is added to the bottle. This alcohol reacts with phosgene that may be formed during storage. Ethanol converts the toxic phosgene to harmless diethyl carbonate.



• Reaction with silver powder

On warming with Ag powder chloroform is converted into acetylene



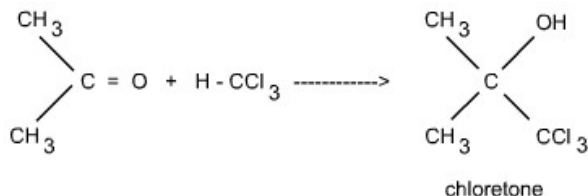
• Nitration

Chloroform reacts with conc. HNO_3 to form nitro chloroform or chloropicrin.



• Condensation with acetone

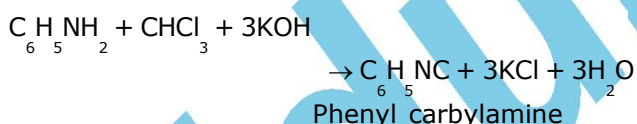
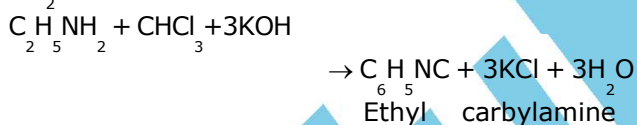
It forms chloretone in the presence of KOH



Chloretone is used as a sleep producing (Hypnotic) drug.

• Carbylamine reaction

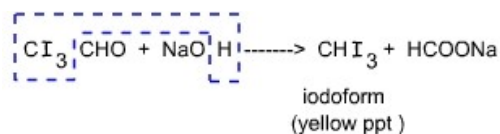
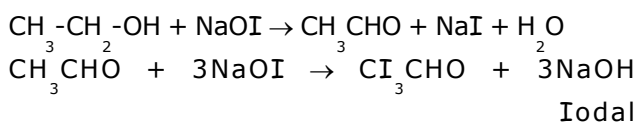
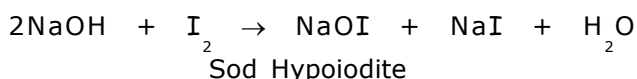
It reacts with primary amine (both aliphatic and aromatic) and alcoholic potash to give isocyanide compound which is commonly known as carbylamine. It has a unpleasant smell and is used to detect NH_2 group.



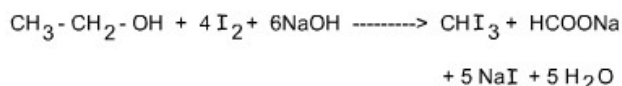
Uses Used in medicine, lab reagent, anaesthetic. It is used in preparation of chloropicrin, chloretone.

Iodoform(CHI_3) or Tridomethane

Preparation In the lab it is prepared by the action of iodine on ethyl alcohol or acetone in the presence of alkali.

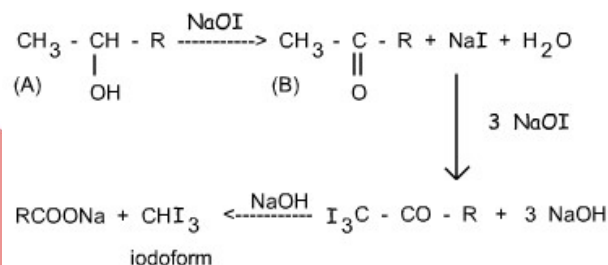


The complete reaction may be written as



In place of NaOH, Na_2CO_3 can also be used.

Compounds which are having structure like (A) and (B) in the following reaction give positive iodoform test.



Physical properties of Iodoform

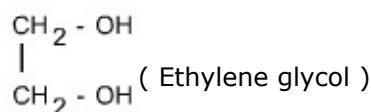
It is a yellow coloured solid having mp 382K. It is insoluble in water but dissolves in organic solvent.

Chemical properties of Iodoform

Chemical reactions of Iodoform are similar to chloroform.

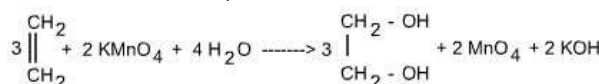
Uses of Iodoform

- It is used in antiseptic
 - It is used to manufacture pharmaceuticals.
- Ethane diol

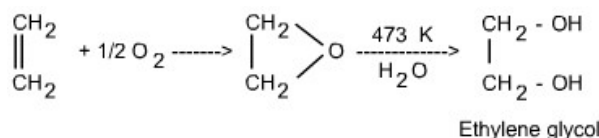


Preparation

- In lab, it is prepared by the action of alkaline solution of KMnO_4 on ethene.



- Commercially it is prepared by the oxidation of ethene to epoxy-ethane and then epoxy ethane is hydrolysed by steam at 473K.

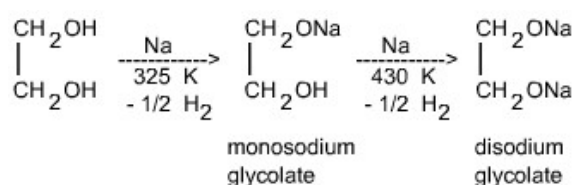


Physical properties of ethylene glycol

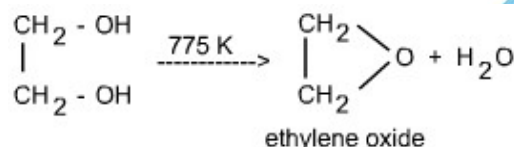
- Ethylene glycol is a colourless syrupy liquid with sweet taste.
- Its mp is 261.5K and b.p is 470K.
- It is miscible with water in all proportions. It forms low freezing mixtures with water and is therefore used as antifreeze.

Chemical properties of ethylene glycol

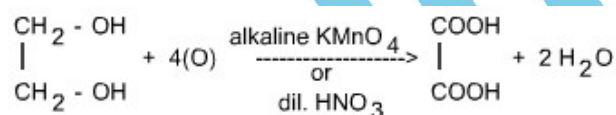
- It contains two primary -OH groups hence it shows the general chemical properties of primary alcohols.



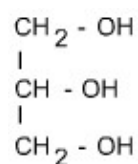
- When heated at about 775K it forms ethylene oxide



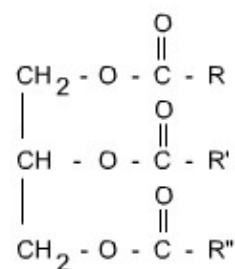
- Ethylene glycol on oxidation with dil HNO_3 or alkaline KMnO_4 it gives oxalic acid

**Uses**

- It is used in the manufacture of terylene
- It is used in organic synthesis.
- It is used as a solvent and preservative
- It is used as an anti-freeze for car radiators.

Glycerol or 1,2,3 Propane triol

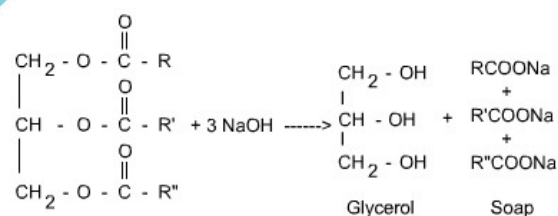
Glycerol occurs in nature in oils and fats. Oils and fats are triester of glycerol with higher fatty acids. These triesters are called glycerides. Thus oils and fats are glycerides. The higher fatty acid may be palmitic and $\text{C}_{15}\text{H}_{31}\text{COOH}$ or stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$) a glyceride may be represented by general formula as



In a glyceride R, R', R'' may be same or different alkyl groups.

Preparation**By Hydrolysis of oils and fats**

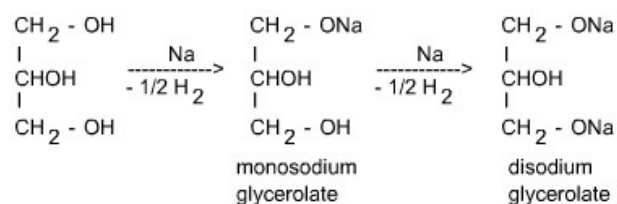
Oils and fats on hydrolysis with alkalies give glycerol and sodium salt of higher fatty acids (soap). The alkaline hydrolysis of oils and fats is called saponification.

**Physical properties of Propane triol or Glycerol**

- Glycerol is colourless odourless syrupy liquid.
- It has sweet taste.
- It is soluble in water in all proportions.
- Glycerol is hygroscopic in nature and absorbs moisture from air.
- Glycerol is non toxic in nature.

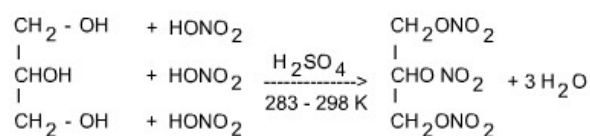
Chemical properties of Propane triol or Glycerol

- Reaction with Na metal.**



- Nitration.**

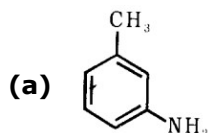
Glycerol reacts with cone HNO_3 in the presence of cone H_2SO_4 at 283-298 K to form glycerol trimate.

**Uses of Propane triol or Glycerol**

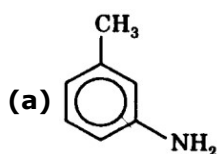
- It is used in the preparation of nitro glycerine which is used to make an explosive (dynamite).
- Used as a preservative and sweetening agent for foods.
- Used in the manufacture of cosmetics and transparent soaps.
- As a lubricant for watches and clocks.
- It is used to prepare organic compaounds such as allyl alcohol, formic acid etc.

SOLVED PROBLEMS

Q.1 Give the common and IUPAC names the following compounds:

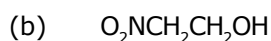


Ans. Common name IUPAC name



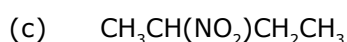
– m – Toluidine;

3 – Methyl aniline



– β – Nitroethylalcohol;

2 – Nitroethanol



– m – Nitrobutane;

2 – Nitrobutane

Q.2 Write structures for the following compounds:

(a) TNT (b) Picric acid

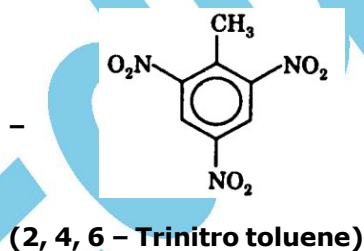
(c) p – nitrotoluene

(d) Azoxybenzene

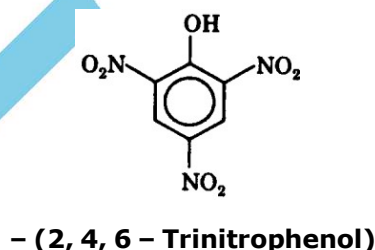
(e) Benzene diazonium chloride

(e) Sulphanilic acid

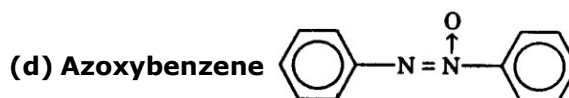
Ans. (a) T. N. T. –



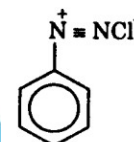
(b) Picric acid



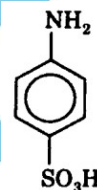
(c) p – nitrotoluene



(e) Benzenediazonium chloride –



(f) Sulphanilic acid

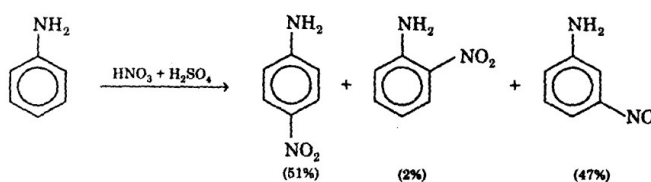


Q.3 Why do nitro compounds have higher boiling points than the hydrocarbons having almost same molecular mass?

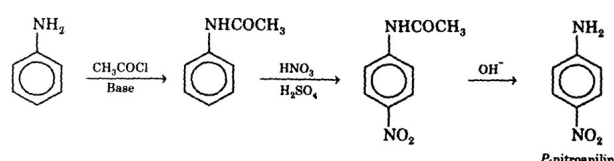
Ans. The higher boiling points of nitro compounds as compared to hydrocarbon having almost same molecular mass is due to the fact that nitro compounds have large dipole moments and thus they have high polarity.

Q.4 How do you prepare p – nitroaniline from aniline?

Ans. p – Nitroaniline can be prepared by nitration of aniline.

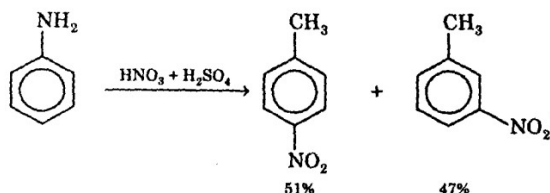


For facilitating nitration, aromatic amines are converted to amide which after nitration are hydrolyzed back to amino group.



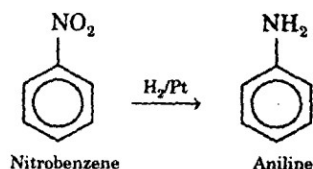
Q.5 Explain what happens when aniline reacts with a mixture of sulphuric acid and nitric acid?

Ans. A mixture of conc. H_2SO_4 and conc. HNO_3 acts as a nitrating agent and nitroaniline is formed.



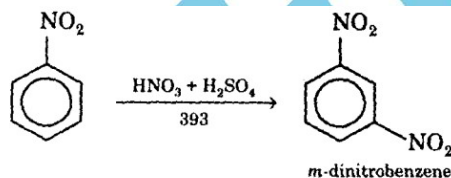
Q.6 How is nitrobenzene converted to aniline under neutral conditions?

Ans. By catalytic hydrogenation



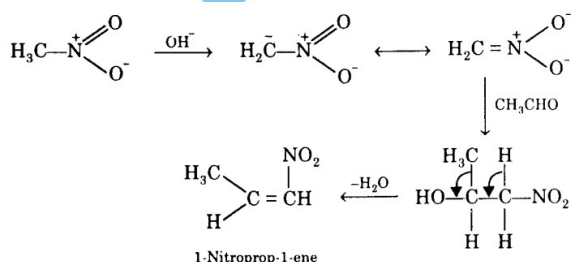
Q.7 Explain why does nitrobenzene on nitration with nitric acid and sulphuric acid form only m - dinitrobenzene?

Ans. The $-\text{NO}_2$ group strongly deactivates the benzene ring towards electrophilic substitution and thus we get m - dinitrobenzene as the only product.



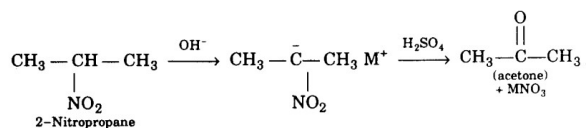
Q.8 How will you prepare convert 1 - nitropropene - 1 from acetaldehyde?

Ans. Nitromethane in alkaline medium reacts with acetaldehyde (CH_3CHO) to give 1 - Nitroprop-1-ene.



Q.9 How can you convert 2 - nitropropane to acetone?

Ans.



Q.10 Explain why is nucleophilic substitution of p - nitrochlorobenzene easier than that of chlorobenzene?

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

Q.11 Write structures for the following compounds:

- (a) Butyronitrile
- (b) Phenylacetone nitrile
- (c) Propylcarbylamine.

Ans. (a) Butyronitrile - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$
 (b) Phenylacetone nitrile - $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$
 (c) Propylcarbylamine - $\text{CH}_3\text{CH}_2\text{N} \Rightarrow \text{C}$.

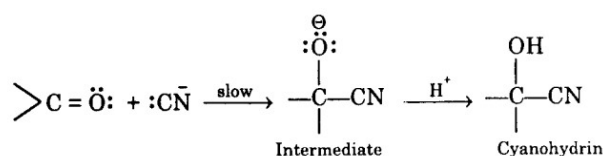
Q.12 Why is acetonitrile preferred a solvent for running organic reactions?

Ans. Acetonitrile is preferred as solvent because it is not reactive in mild acidic or basic conditions. It is highly polar and so it can dissolve a number of reactants. It has moderate b.p. and so it can be easily removed. It is miscible with water and many organic solvents.

Q.13 Explain the role of mineral acid in the reaction of a carbonyl compound with aq. KCN.

Ans. The reaction is supposed to proceed by the nucleophilic attack of $:\text{CN}^-$ ion.

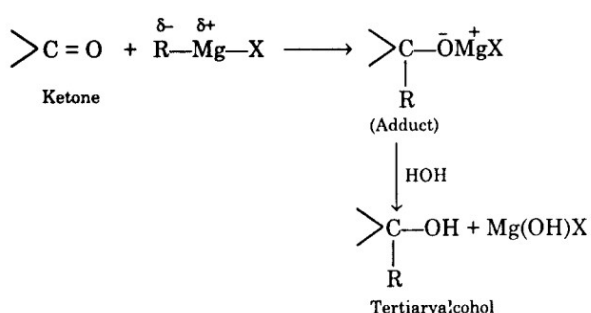
The mineral acid is added to generate HCN in situ. (i.e. $\text{KCN} + \text{HCl} \rightarrow \text{HCN} + \text{KCl}$)



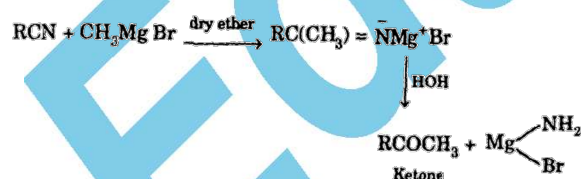
Q.14 How is it that a ketone reacts with Grignard reagent to form a tertiary alcohol but in the reaction of a nitrile with Grignard reagent, a ketone is formed?

Ans. In Grignard's reagents (RMgX) the $\text{C} \leftarrow \text{Mg}$ bond is highly polar and carbon is electronegative relative to electropositive magnesium.

Tertiary Alcohols are produced by the reaction of Grignards reagents with Ketones.

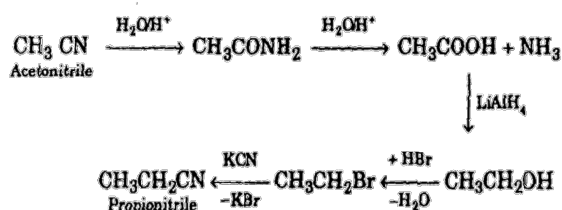


In reaction of Nitrile with Grignard's reagent, the initially formed imine derivative is hydrolyzed to form a ketone. This is reaction offer a new route to obtain ketones as esters always react further with Grignards reagent to form tertiary alcohols.



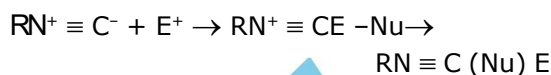
Q.15 How will you convert acetone nitrile to propionitrile?

Ans.



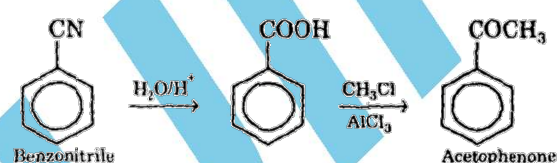
Q.16 How does an isocyanide react with an electrophile and a nucleophile at the same isocyanide carbon? Give an example.

Ans. In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.



Q.17 How will you convert benzonitrile to acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$)?

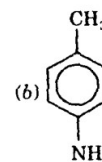
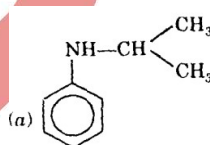
Ans.



Q.18 Draw structures for the following compounds.

(a) N-isopropylaniline (b) p-toluidine (c) t-butylamine.

Ans.



Q.19 Arrange following sets in order of their basic strength:

(a) Ethylamine, Ammonia and Triethylamine

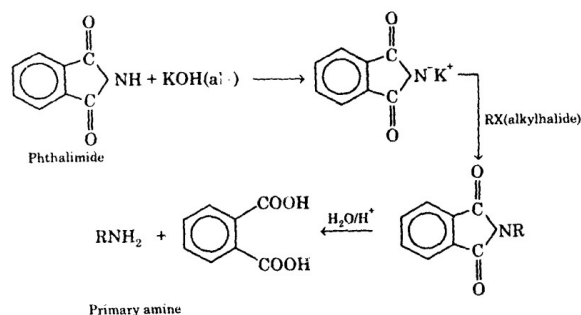
(b) Aniline, p-nitroaniline, p-toluidine.

Ans. (a) Ammonia < Triethylamine < Ethylamine

(b) p-Toluidine > p-nitroaniline > aniline.

Q.20 How will you prepare a pure sample of a primary amine from a primary alkyl halide?

Ans. By Gabriel Synthesis



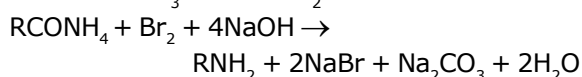
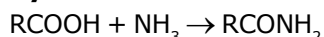
Q.21 How will you convert an alkyl halide into a primary amine having one more carbon than the alkyl halide used?

Ans. By Action With Alc. KCN

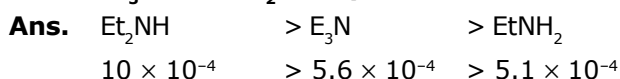


Q.22 How can a carboxylic acid be converted to an amine having one carbon atom less than the carboxylic acid used?

Ans. By Hofmann Bromadide Reaciton



Q.23 Explain the observed K_b order : $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$, in aqueous solution.



The K_b value of $\text{Et}_2\text{NH} > \text{Et}_3\text{N}$ and Et_2NH_2 .

It is because, in solution ammonium cations are stabilized not only by electron releasing effect of the alkyl groups but also by solvation through their hydrogen bond donation to the solvent. It is evident that due to the number of hydrogen atoms present on the nitrogen and thereby similar number of hydrogen bonds, the stability of aliphatic ammonium cations and also the basic strength will be in the order primary > secondary > tertiary amine which is opposite to the electron releasing effect based basic strength (i.e. tertiary > secondary > primary). There could also be some steric repulsion to H – bonding in cations derived from tertiary amines. Due to a combination of all these effects (i.e., electron releasing, H – bonding, steric) the stability of carbonium cation in solution and thereby the resulting basic strength order of aliphatic amines is **secondary > tertiary > primary.**

It explains the observed K_b values.

Q.24 What will be the basic strength order of EtNH_2 , Et_2NH , Et_3N in gas phase? Explain.

Ans. In gas phase the trend is as expected i.e., tertiary amine > secondary amine > primary amine > ammonia.

It is because, the solvent effect is missing in gas phase.

Q.25 Why are amines less acidic than comparable alcohols?

Ans. Alcohols have higher b.p. than aliphatic amines because there is stronger intermolecular hydrogen bonding in alcohols than in aliphatic amines due to more electronegativity of oxygen than nitrogen.

Q.26 Why are primary amines higher boiling than tertiary amines?

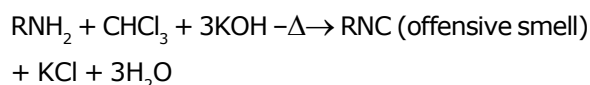
Ans. Primary amines form hydrogen bonding (intermolecular) where as tertiary amines have no hydrogen bonding. Because of this, the b.p. of primary amines is higher as compared to that of tertiary amines.

Q.27 Why are aromatic weaker bases than aliphatic amines?

Ans. Alkyl amines are stronger bases than NH_3 and aryl amines because alkyl groups are electron donating and so they provide greater electron availability on nitrogen where as the aromatic ring (in aryl amines) is electron withdrawing and so it reduces the electron density on nitrogen.

Q.28 How can you find out whether a given amine is a primary amine? Write the chemical reaction involved in the test you perform.

Ans. By Carbylamine Reaction. Primary amines when heated with chloroform and KOH and alkyl isocyanide (RNC) is formed which has a very unpleasant smell



Q.29 How can you separate a mixture of primary, secondary and tertiary amines? Write chemical reactions involved in the process.

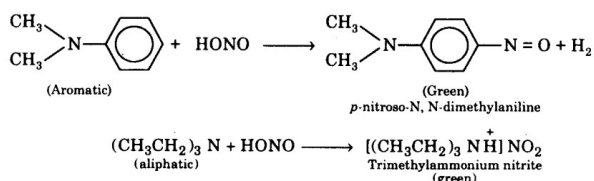
Ans. For this the mixture of amines is treated with benzene sulphonyl chloride and the product mixture obtained is treated with HCl and filtered. The filtrate contains tertiary amine as its hydrochloride and is isolated by addition of a base (KOH).

The residue is treated with aq KOH solution and filtered. The filtrate when acidified gives sulphonamide of primary amine and it can be isolated after hydrolysis.

The residue (sulphonamide insoluble in alkali) is hydrolyzed to get secondary amine.

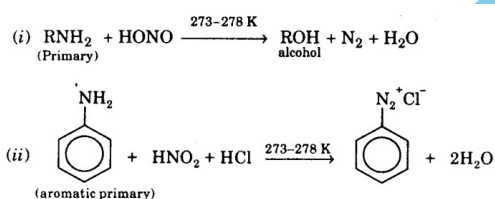
Q.30 How do aromatic and aliphatic tertiary amines react with nitrous acid?

Ans.

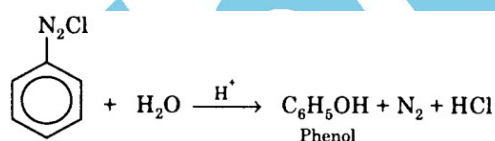


Q.31 How do aliphatic primary and secondary amines react with nitrous acid?

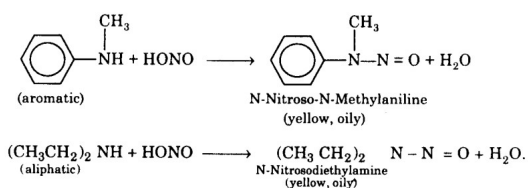
Ans.



If however, the temperature rises above 273 K, the initially formed diazonium salt decomposes to form phenol.



Secondary amines (both aliphatic and aromatic) react with HONO to give N-nitrosoamines, which being insoluble in dilute mineral acids separate out as yellow oily compounds



Q.32 Explain how does the presence or absence of hydrogen on N of amines affect the modes of their reactions with nitrous acid?

Ans. When 'N' is attached with 2 hydrogen atoms (i.e., a primary amine) then on reaction with HONO we get an alcohol and nitrogen gas.

If 'N' is attached with 1 hydrogen atom (i.e., a secondary amine), then on reaction with HONO we get an oily compound (i.e., Nitrosoamine).

If 'N' is not attached with hydrogen (i.e., a tertiary amine) then protonation will occur to form a salt soluble in water.

Q.33 How will you prepare ethyl amine from acetaldehyde?

Ans. CH_3CHO (Acetaldehyde) $\xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} + \text{NH}_3 \xrightarrow{-\text{Al}_2\text{O}_3 / \text{heat}} \text{CH}_3\text{CH}_2\text{NH}_2$
(Ethylamine) + H_2O

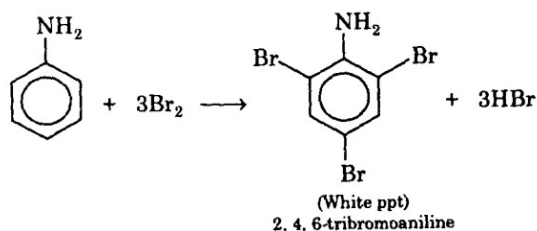
Q.34 Amino group is o, p – directing for aromatic electrophilic substitution. Why does aniline on nitration gives a substantial amount of m – nitroaniline?

Ans. It is due to protonation of aniline to form $\text{C}_6\text{H}_5\text{NH}_3^+$ which is meta – directing and deactivating.

Q.35 Why does bromination of aniline, even under very mild conditions give 2, 3, 5 – tribromoaniline instantaneously?

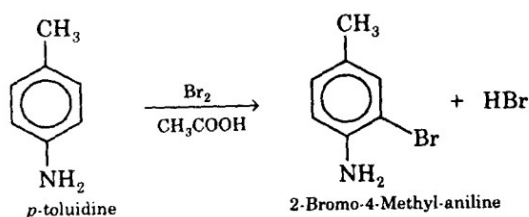
Ans. Yes aniline gets brominated instantaneously even in the absence of a catalyst and even under mild conditions. It is because $-\text{NH}_2$ group is electron releasing and so it increases reactivity towards electrophilic substitutions. Because of this aniline when reacted with bromine gives 2, 4, 6 – tribromoaniline (i.e., all

the three o-, p-positions get brominated).



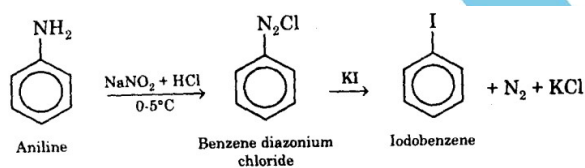
Q.36 How can you convert p-toluidine to 2-bromo-4-methylaniline?

Ans.

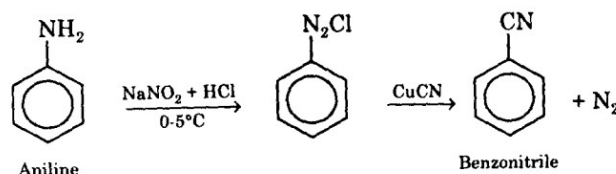


Q.37 How can you convert aniline to iodobenzene?

Ans.



Q.38 How can you get benzonitrile from aniline?
Ans.



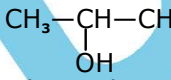



Q.39 Why is an amide more acidic than an amine?

Ans. In amide $\text{—}\overset{\text{O}}{\parallel}{\text{C}}\text{—}$ group is attached to NH_2 which is electron withdrawing group and so the acidic character of amide increases whereas in amine there is alkyl group which is electron releasing and makes it more basic or less acidic.

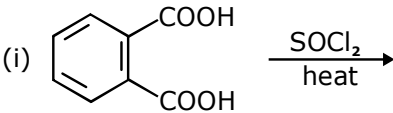
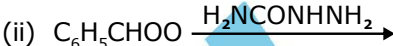

EXERCISE-I

UNSOLVED PROBLEMS

- Q.1 Write the structure of allyl alcohol. Also give its IUPAC name.
- Q.2 Write the structure of phenetole and give its IUPAC name.
- Q.3 Write the structure of anisole and give its IUPAC name.
- Q.4 Draw the structure of sec-butyl alcohol and give its IUPAC name.
- Q.5 Write the structure of tert-butyl alcohol and give its IUPAC name.
- Q.6 Write the structure of isopropyl alcohol and give its IUPAC name.
- Q.7 What happens when acetyl chloride reacts with phenol? Write the chemical equation.
- Q.8 How will you convert benzene diazonium chloride into phenol?
- Q.9 Convert propanoic acid to propanol
- Q.10 Complete the reaction :
- $$\text{C}_2\text{H}_5\text{OH} \xrightarrow[633 \text{ K}]{\text{Al}_2\text{O}_3} ? + ?$$
- Q.11 How will you convert methanol into ethanol?
- Q.12 Arrange the following set of compounds in order of their increasing boiling points : Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.
- Q.13 Arrange the following compounds in increasing order their acid strength : Propane-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.
- Q.14 Arrange the following alcohols in order of increasing reactivity towards Lucas reagent : 2-butanol, 1-butanol, 2-methyl-2-propanol.
- Q.15 Alcohols react with halogen acids of phosphorus halides to form haloalkanes but phenol does not form halobenzenes. Explain
- Q.16 Given mechanism of preparation of ethoxyethane from ethanol.
- Q.17 Which is a stronger acid — phenol or cresol? Explain.
- Q.18 Give chemical tests to distinguish between compounds in each of the following pairs.
- (i) Phenol and benzyl alcohol
- (ii) Butan-2-ol and 2-Methylpropan-2-ol.
- Q.19 (a) Give chemical tests of distinguish between following pairs of compounds.
- (i)  and 
- (ii)  and 
- (b) Why is phenol more acidic than ethanol?
- Q.20 Describe the mechanism of formation of diethyl ether from ethanol in the presence of concentrated sulphuric acid.
- Q.21 A unique method of addition of water to alkenes in a way opposite to the Markownikov's rule was developed by H.C. Brown in 1959. In this method, alcohol is obtained in excellent yield. Name the method. How can you use this method to obtain propan-1-ol from propane in excellent yield?
- Q.22 Give the major products that are formed by heating each of the following ethers with HI.
- Q.23 Give the structures and IUPAC names of the products expected from the following reactions
- (a) Catalytic reduction of butanal.
- (b) Hydration of propane in the presence of dilute sulphuric acid.
- (c) Reaction of propene with methyl magnesium bromide followed by hydrolysis.
- Q.24 Write the structures of the major products expected from the following reactions :
- (a) Mononitration of 3-methylphenol
- (b) Dinitration of 3-methylphenol.
- (c) Mononitration of phenylmethanoate.

EXERCISE-II

BOARD PROBLEMS

- Q.1 Explain why phenols do not undergo substitution of the —OH group like alcohols ?
- Q.2 Ortho-nitrophenol is more acidic than ortho-methoxyphenol. Why ?
- Q.3 Name the reagents which are used in the following conversions :
 (i) A primary alcohol to an aldehyde
 (ii) Butan -2-one to butan -2-ol
 (iii) Phenol to 2, 4, 6-tribromophenol.
- Q.4 Alcohols react both as nucleophiles as well as electrophiles. Write one reaction of each type and describe its mechanism.
- Q.5 How would you carry out the following conversions ?
 (i) Ethyl magnesium chloride to propan -1-ol
 (ii) Benzyl chloride to benzyl alcohol
- Q.6 Explain the mechanism of the following reactions
 (i) Addition of Grignard's reagent to the carbonyl group of a compound forming an adduct followed by hydrolysis.
 (ii) Acid catalyzed dehydration of an alcohol forming an alkene.
 (iii) Acid catalyzed hydration of an alkene forming an alcohol.
- Q.7 Explain the following observations :
 (i) The boiling point of ethanol is higher than that of methoxymethane.
 (ii) Phenol is more acidic than ethanol.
 (iii) o-and p-nitrophenols are more acidic than phenol.
- Q.8 How would you obtain
 (i) picric acid (2, 4, 6-trinitrophenol) from phenol,
 (ii) 2-Methylpropene from 2 Methylpropanol ?
- Q.9 How would you obtain the following :
 (i) Benzoquinone from phenol
 (ii) 2-Methylpropan-2-ol from methylmagnesium bromide
 (iii) Propan-2-ol from propane
- Q.10 (a) Give chemical tests to distinguish between the following :
 (i) Benzoic acid and ethyl benzoate
 (ii) Benzaldehyde and acetophenone
- (b) Complete each synthesis by giving missing reagents or products in the following
- (i) 
- (ii) 
- (iii) 
- Q.11 (a) Illustrate the following name reactions :
 (i) Cannizzaro's treaction
 (ii) Clemmensen readuction
 (b) How would you obtain the following :
 (i) But -2-enal from ethanal
 (ii) Butanoic acid from butanol
 (iii) Benzoic acid form ethylbenzene
- Q.12 How many the following conversions be carried out :
 (i) Propene to propan-2-ol
 (ii) Anisole to phenol
 (Write the reaction only)
- Q.13 Why is the reactivity of al lte three classes of alcohols with conc. HCl and ZnCl₂ (Lucas reagent) different ?
- Q.14 Give chemical tests to distinguish between compound in each of the following pairs :
 (i) Phenol and benzyl alcohol
 (ii) Butan -2-ol and 2 Methylpropan-2-ol
- Q.15 You are given benzene, conc. H₂SO₄ and NaOH. Write the equations for the preparation of phenol using these reagents.
- Q.16 Explain the mechanism of the following reaction

$$\text{CH}_3 - \text{CH}_2 - \text{OH} \xrightarrow[443\text{K}]{\text{H}^+} \text{CH}_2 = \text{CH}_2 + \text{H}_2\text{O}$$
- Q.17 Write the equations involved in the following reactions :
 (i) Reimer – Tiemann reaction
 (ii) Willamson's ether synthesis