7. ALCOHOLS PHENOLS AND ETHERS

These are compounds containing C – O single bond. The functional group present in Alcohols and phenols is –OH (hydroxyl) group and that present in ethers is –O – group (oxy group). In alcohols, the –OH group is bonded to an alkyl group. So the general formula of alcohols is R-OH. But in phenols, the –OH group is bonded to an aryl group. So the general formula of phenols is Ar-OH.

Classification of Alcohols

1. Depending on the number of–OH groups: Based on this alcohols are classified as monohydric

(contain only one –OH group), dihydric (contain two –OH groups), trihydric (contain three –OH groups) and polyhydric (contain more than two –OH groups). Examples for monohydric alcohols are methanol (CFE-OH), ethanol (CH3-CH2-OH) etc. Example for dihydric alcohol is ethylene glycol (HO-CH2-CH2-OH) and for trihydric alcohol is glycerol (HOCH2-CHOH-CH2OH).

Monohydric alcohols may be further classified according to the hybridisation of the carbon atom to which the hydroxyl group is attached.

i) Compounds containing sp^3 C-OH bond: Here the –OH group is attached to an sp^3 hybridised carbon atom of an alkyl group. They are further classified as follows: Primary, secondary and tertiary alcohols.

Allylic alcohols: In these alcohols, the –OH group is attached to an sp^3 hybridised carbon next to the carbon-carbon double bond. E.g. CH2=CH-CH2-OH (Allyl alcohol)

Benzylic alcohols: In these alcohols, the –OH group is attached to an sp^3 hybridised carbon atom next to an aromatic ring. Allylic and benzylic alcohols may be primary, secondary or tertiary.

ii) Compounds containing sp^2 C -OH bond: These alcohols contain –OH group bonded to a carboncarbon double. These may be vinyl alcohols or phenols. Vinyl alcohols: CHFCH-OH Phenols:

OH

Nomenclature of Alcohols

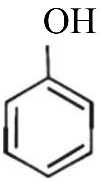
Common Name: By suffixing alcohol to the name of alkyl group (i.e. word root + yl alcohol).

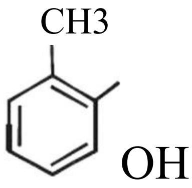
IUPAC Name: By substituting 'e' of alkane with the suffix 'ol' (i.e. alkanol). Some examples:

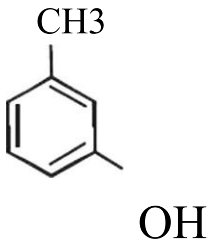
Compound	Common Name	IUPAC name
CH3-OH	Methyl alcohol	Methanol
CH3-CH2-OH	Ethyl alcohol	Ethanol

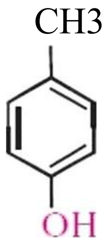
CH3-Cl-b-CH2-OH	n-Propyl alcohol	I-Propanol
CH3-CHOH-CH3	Isopropyl alcohol	2-Propanol
CH3-CH2-CH2-CH2-OH	n-Butyl alcohol	I-Butanol
CH3-CHOH-CH2-CH3	sec-butyl alcohol	2-Butanol
(CH3)2CH-CH2-OH	Isobutyl alcohol	2-Methylpropan-1-ol
(CH3)3C-OH	tert-butyl alcohol	2-Methylpropan-2-ol
(CH3)3C-CH2-OH	Neopentyl alcohol	2,2-Dimethylpropan-1-ol

Nomenclature of Phenols





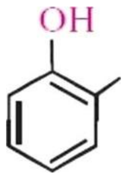


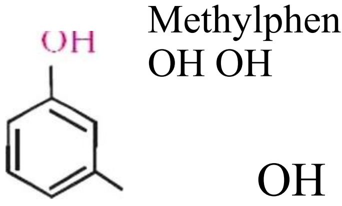


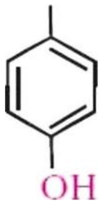
Phenol 0-Cresol In-Cresol p-Cresol

Phenol 2-Methylphenol Methylphenol 3-Methylphenol 4-

OH OH







Catechol Resorcinol Hydroquinone or quinol

Benzene- 1 ,2-diol Benzene- 1 .3-cliol Benzene- 1.4-diol

Preparation of Alcohols

1. From alkenes:

i) By acid catalysed hydration: Alkenes react with water in the presence of acid as catalyst to form alcohols. In the case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markovnikov's rule.

C = C -F H20 C— C

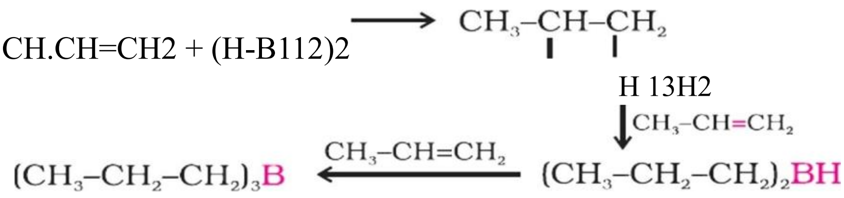
1-1 011

CH.CH-

CH3CH=CH2+ H20 CH3

OH ii) By hydroboration—oxidation reaction: Alkenes add diborane to give trialkyl boranes as addition product. This on oxidation by hydrogen peroxide in the presence of aqueous sodium hydroxide to form alcohols. This reaction is known as hydroboration -oxidation reaction.

The net reaction is the addition of a water molecule to the alkene in a way opposite to the Markovnikov's rule.



CH.CH=CH2 + (H-B112)2

H 13H2

H2013H202, öH

3CH3-CH2-CH2-OH +B(OH

Propan- 1-01

2. <u>From carbonyl compounds</u>

i) Reduction: Carbonyl compounds (aldehydes and ketones) when reduced using lithium aluminium hydride (LiAlH4 or sodium borohydride (NaBH4) or on catalytic hydrogenation (using finely divided metal such as nickel, platinum or palladium), we get alcohols.

Aldehydes give primary alcohols and ketones give secondary alcohols.

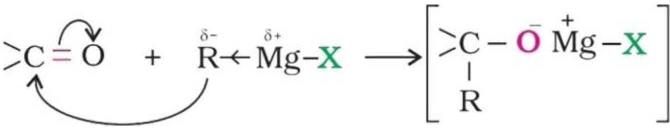
$$\text{R-CHO + [H]} \xrightarrow{\text{LiAlH4}} \text{R\_CH2OH}$$

$$\text{R2CO + [H]} \xrightarrow{\text{LiAlH4}} \text{R2CH-OH}$$

Commercially, acids are reduced to alcohols by converting them to the esters followed by their reduction using hydrogen in the presence of catalyst (catalytic hydrogenation).

R'OH H2

COOH



H20 C- OH +Mg(O

Formaldehyde (methanal) gives primary alcohols, aldehydes other than formaldehyde gives secondary alcohols and ketones give tertiary alcohols.

$$\text{H\_CHO + RMgX} \longrightarrow \text{R-CH -OMgX} \xrightarrow{\text{H20}} \text{R-CH? -OH + MgX(OH)}$$

Formaldehyde adduct 1 ^{0} alcohol

$$\text{R-CHO + RMgX} \longrightarrow \text{RCHOMgX} \xrightarrow{\text{H20}} \text{R2CHOH + MgX(OH)}$$

Aldehyde adduct 2 ^{0} alcohol

H20

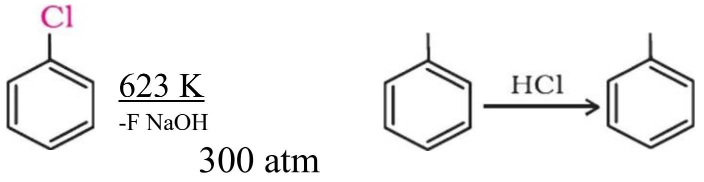
R CO + RMgX→------→R3COMgX   R3C-OH + MgX(OH)

Ketone   adduct   3 ^{0} alcohol

Preparation of Phenols

1. From haloarenes: When chlorobenzene is fused with NaOH at 623K temperature and 320 atmospheric pressure, sodium phenoxide is formed which on acidification, we get phenol.

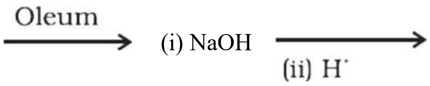
ONa+ OH



Chlorobenzene   Sodium phenoxide   Phenol

2. From benzene sulphonic acid: Benzene on sulphonation with oleum, benzene sulphonic acid is formed which on treating with NaOH followed by acidification, we get phenol.

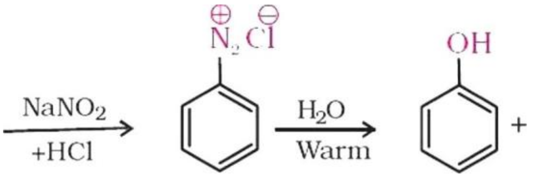
S03H   OH



3. From diazonium salts: When an aromatic primary amine (e.g. aniline) is treated with nitrous acid (prepared by mixing NaN02 & HCI) at 273-278K, a diazonium salt is formed, which on warming with water or treating with dilute acids, we get phenol.

NH2

Z



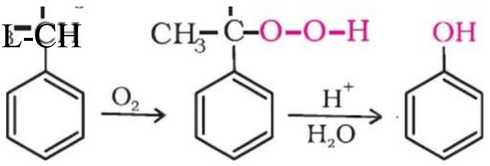
+ HCl

Aniline   Benzene cliazonium chloride

4. From cumene: Cumene is isopropylbenzene (2-phenyl propane). It is oxidised in presence of air, we get cumene hydroperoxide, which on treating with dilute acid, phenol and acetone are formed. This method is used for the manufacture of phenol. fH3

CH3

CFE-CH



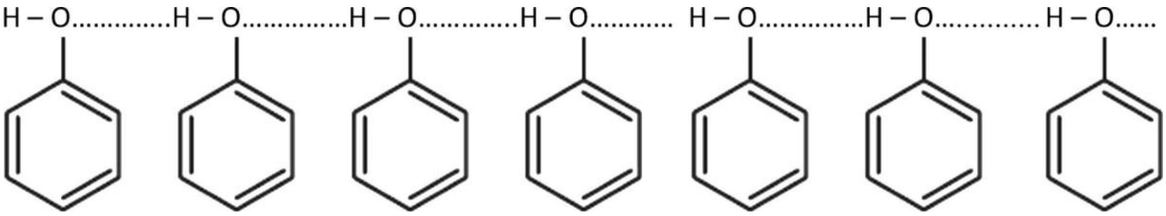
+ CH3COCH3

Cumene   Cumene hydmperoxide

Physical Properties of Alcohols and Phenols

1. Boiling Points: Boiling points of alcohols and phenols are higher than hydrocarbons, ethers, haloalkanes and haloarenes of comparable molecular masses. This is because the -OH group in alcohols and phenols is involved in intermolecular hydrogen bonding.

R- O.....H - O.....H -O..... H- O.....H - H - O.....H - H
- O.....H -O..... H- O.....H - O.....



The boiling points of alcohols and phenols increase with increase in the number of carbon atoms. This is because as the number of carbon atoms increases, the van der Waals forces of attraction increases and hence the boiling point. In alcohols, the boiling points decrease with increase of branching in carbon chain (because of decrease in van der Waals forces with decrease in surface area).

2. Solubility: Alcohols and phenols are soluble in water. But the solubility of alcohols is higher than that of phenols. Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water molecules (inter molecular hydrogen bonding). The solubility decreases with increase in size of alkyl/aryl groups.

Chemical Reactions of Alcohols and Phenols

A) Reactions involving cleavage of O—H bond

1. Acidity of alcohols and phenols:

i) Reaction with metals: Alcohols and phenols react with active metals such as sodium, potassium and aluminium to yield corresponding alkoxides/phenoxides and hydrogen.

$\text{R-OH} + \text{Na} \longrightarrow \text{R-ONa} + \frac{1}{2}\text{H}_2$

(sod. Alkoxide)

$\text{C}_6\text{H}_5\text{-OH} + \text{Na} \longrightarrow \text{C}_6\text{H}_5\text{-ONa} + \frac{1}{2}\text{H}_2$

(sod. Phenoxide)

Phenols also react with aqueous sodium hydroxide to form sodium phenoxides.

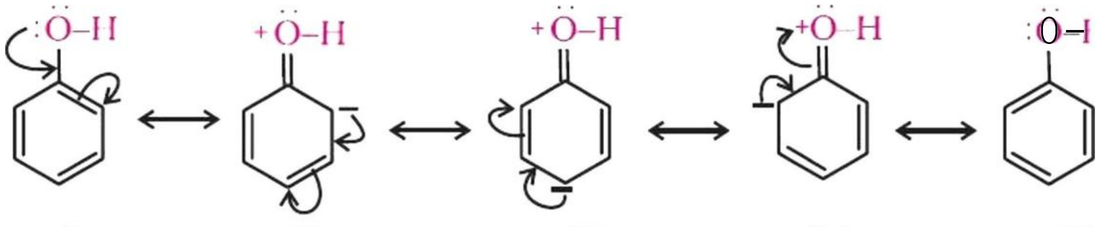
$\text{C}_6\text{H}_5\text{-OH} + \text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{-ONa} + \text{H}_2\text{O}$

The above reactions show that alcohols and phenols are acidic in nature.

ii) Acidity of alcohols: The acidic character of alcohols is due to the polar nature of O—H bond. An electron-releasing group (e.g. alkyl groups like $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ etc.) increases the electron density on oxygen and hence decrease the polarity of O-H bond. This decreases the acid strength. So the acid strength of alcohols decreases in the order:

Primary alcohols > Secondary alcohols > Tertiary alcohols But alcohols are weaker acids than water.

iii) Acidity of phenols: In phenols, the —OH group is directly bonded to an sp ^{2} hybridized carbon atom of the benzene ring. Due to the greater electronegativity of sp ^{2} hybridized carbon (due to greater s-character), the benzene ring acts as an electron withdrawing group. So the lone pair electrons present in oxygen atom of —OH group enters in the benzene ring and the following resonating structures are obtained:



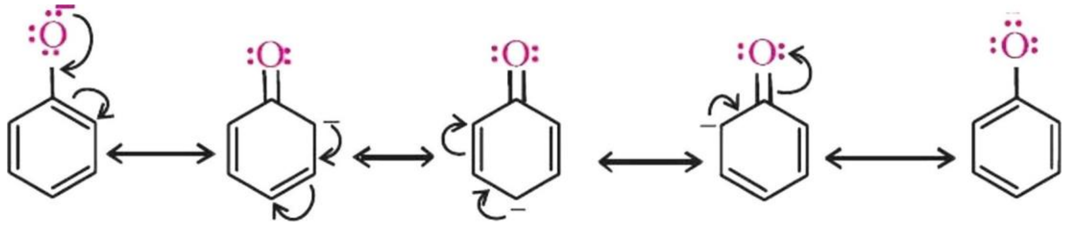
In the resonating structures (Il), (Ill) and (IV), there is a positive charge on the electronegative oxygen atom and hence it attracts the bond pair of electrons in O-H bond. So it is easy to remove the hydrogen atom as H + ion and thus phenol is acidic in nature.

Phenol is more acidic than alcohol. This is due to the following reasons:

1. In alcohol, the O-H group is directly bonded to an sp ^{3} hybridized carbon atom, but in phenol, it is bonded to an sp ^{2} hybridized carbon. Due to the greater s-character and electronegativity of sp2 hybridized carbon, the ease of O-H bond cleavage is greater on phenol and hence it is more acidic than alcohol.
2. The ionization of alcohol and phenol is as follows:

$R-\ddot{\underset{\cdot\cdot}{O}}-H \rightleftharpoons$

The alkoxide ion (R-O-) formed by the ionization of alcohol is not resonance stabilized. So the negative charge is localized on oxygen atom. But the phenoxide ion (C6H5-O-) formed by the ionization of phenol is resonance stabilized as follows.



Due to resonance, the negative charge is delocalized and hence phenoxide ion is more stable which favours the ionization of phenol.

Also phenoxide ion is more stable than phenol, because in phenol, there is a +ve charge on electronegative oxygen atom. So it is less stable and readily lose H+ ion.

The presence of electron withdrawing groups (like nitro group) at ortho and para positions increases the acidic strength of phenol. It is due to the effective delocalisation of negative charge in phenoxide ion. On the other hand, electron releasing groups (like alkyl groups) at these positions decreases the acidic strength of phenol. So cresols are less acidic than phenol.

2. Esterification:

Alcohols and phenols react with carboxylic acids, acid chlorides and acid anhydrides to form esters. The reaction with carboxylic acid and acid anhydride are carried out in the presence of conc. H2S04. The reaction with acid chloride is carried out in the presence of a base (pyridine) so as to neutralise HCI formed during the reaction.

R-OH + R'-COOH R-OCOR' + 1-120
(ester)

C6H5-OH + R'-COOH e— C6H5-OCOR' + 1+20

R-OH + (R'CO)20 R-OCOR' + R'COOH
(acid anhydride)

C6H5-OH + (R'CO)20 C6H5-OCOR' + R'COOH

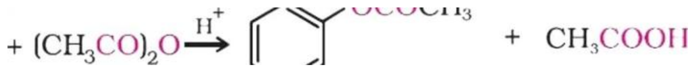
pyridine
R-OH + R'-COCI →------→R-OCOR' + HCI [Schotten-Baumann reaction] (acid chloride)

pyridine
C6H5-OH + R'-COCI 9-----* C6H5-OCOR' + HCI

The introduction of acetyl (CH3CO) group in alcohols or phenols is known as acetylation. Acetylation of salicylic acid produces aspirin, which is used as an analgesic.

COOH COOII

011OCOCH3



Salicylic acid Acetylsalicylic acid
(Aspirin)

B) Reactions involving cleavage of carbon — oxygen (C—O) bond in alcohols

1. Reaction with hydrogen halides: Alcohols react with hydrogen halides in presence of anhydrous zinc chloride (ZnC12) to form alkyl halides.

Anhydrous ZnC12

ROH + HX — -- ·----→ R-X+ H20

The reactivity of primary, secondary and tertiary alcohols with HCI is different and hence this reaction is used for the distinction of the three types of alcohols by a test called Lucas Test.

The difference in reactivity of three classes of alcohols with HCI distinguishes them from one another (Lucas test).

LUCAS TEST:

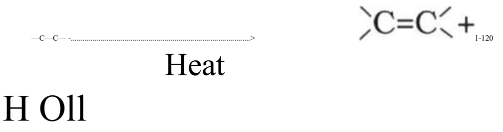
Lucas reagent is a mixture of Conc. HCI and anhydrous ZnC12. Alcohols are soluble in Lucas reagent while their halides are immiscible and produce turbidity in solution.

Tertiary alcohols react with Lucas reagent and form immediate turbidity; secondary alcohols form turbidity within 5 minutes, while primary alcohols do not produce turbidity at room temperature. They give turbidity only on heating.

2. Reaction with phosphorus trihalides (PX3): Alcohols react with phosphorus trihalides to give alkyl halides.

$3R\text{-}OH + PX_3 \rightarrow 3\,R\text{-}X + H_3PO_3$ (X= Cl or Br)

3. Dehydration: Alcohols undergo dehydration (removal of a molecule of water) on treating with a protic acid like concentrated H2S04 or H3P04, or catalysts such as anhydrous zinc chloride or alumina to form alkenes.



The relative ease of dehydration of alcohols follows the order: Tertiary > Secondary > Primary. For example ethanol undergoes dehydration by heating it with concentrated 142504 at 443 K, we get ethene.

$$C_2H_5OH \xrightarrow[443\ K]{H2S04} CH2 = CH2+ 1\text{--}120$$

Secondary and tertiary alcohols are dehydrated under milder conditions.

OH
I
CH3CHCH3 ....> CH3— CH = CH2 +H20 85 % H3P04 440 K

CH3
CFL-C- OH -..................................S +H20 358 K

4. Oxidation:

Alcohols on oxidation give carbonyl compounds (aldehydes and ketones) or carboxylic acids depending on the nature of oxidising agent used. Primary alcohols when oxidized using mild oxidising agent like anhydrous Cr03, we get aldehydes. But with strong oxidising agents like acidified potassium permanganate or potassium dichromate, carboxylic acids are formed.

$$R\text{-}CH20H \xrightarrow{[0]} R\text{-}CHO \xrightarrow{[0]} R\text{-}COOH$$

$$RCH20H \xrightarrow{cr03} *RCHO$$

Primary alcohols are oxidised to aldehydes in good yield by pyridinium chlorochromate (PCC) [a complex of chromium trioxide with pyridine and HCI].

$$CH3 -CH\ CH\_CH20H \xrightarrow{PCC} CH3 - CH = CH\_CHO$$

[crotyl alcohol] [crotanaldehydel

Secondary alcohols are oxidised to ketones by chromic anhydride (Cr03).

$$R2CHOH \xrightarrow{cr03} R2CO$$

With strong oxidising agents, secondary alcohols give carboxylic acids with lesser number of carbon atoms.

$$R2CHOH \xrightarrow{[0]} R2CO \xrightarrow{[0]} R\text{-}COOH$$

Tertiary alcohols do not readily undergo oxidation reaction. But in presence of strong oxidising agents (KMn04) and at high temperature, they first give ketones with lesser number of carbon atoms which on further oxidation give carboxylic acids with still lesser number of carbon atoms.

$$R3C\text{-}0H+ \xrightarrow{[0]} R2C0 \xrightarrow{[0]} R\text{-}COOH$$

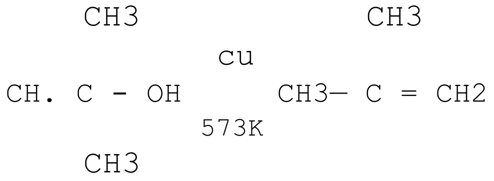
5. Reaction with hot copper catalyst

Primary alcoholic vapours when passed through hot Cu catalyst at 573K, undergo dehydrogenation to form aldehydes, while secondary alcohols undergo dehydrogenation to give ketones.

$$R\_CH20H \xrightarrow{\text{hot cu/573 K}} R\_CHO$$

$$R2CHOH \xrightarrow{\text{hot cu/573 K}} R2CO$$

Tertiary alcohols react with hot Cu catalyst at 573 K, undergo dehydration to give alkenes.



$$CH.\ \underset{CH3}{\overset{CH3}{C}} - OH \xrightarrow[573K]{cu} CH3- \overset{CH3}{C} = CH2$$

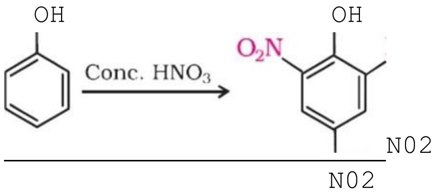
REACTIONS OF PHENOLS

1. Electrophilic Substitution reaction:

In phenol, the —OH group attached to the benzene ring donate electron pairs and hence it activates it towards electrophilic substitution. Also, in the resonating structures of phenol, the electron density is greater on ortho and para positions. So the electrophile enters at these positions.

The common electrophilic aromatic substitution reactions taking place in phenol are:

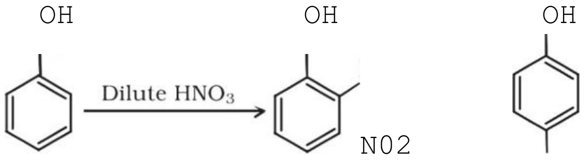
a) Nitration: Phenol reacts with conc. Nitric acid to give an yellow precipitate of 2,4,6trinitrophenol commonly called picric acid.



2, 4, 6-frinitmphenol
(Picric acid)

Picric acid can also be prepared by treating phenol first with concentrated sulphuric acid followed by treating with concentrated nitric acid.

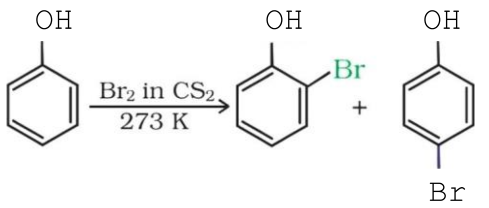
For the preparation of ortho and para nitrophenols, phenol is treated with dil. HN03 at low temperature (298K).



0-Nitrophenol N02 p-Nitrophenol

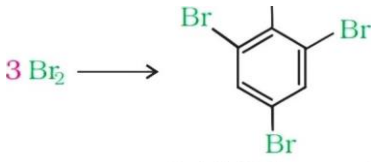
The ortho and para isomers can be separated by steam distillation. o-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while p-nitrophenol is less volatile due to intermolecular hydrogen bonding which causes the association of molecules.

b) Halogenation: When phenol is brominated using Brz in CHC13 or CS2 at low temperature, we get a mixture of ortho and para bromophenols. The reaction takes place in the absence of Lewis acid catalyst (like FeBr3). It is due to the highly activating effect of —OH group attached to the benzene ring.



Minor Major

When phenol is treated with bromine water, we get a white precipitate of 2,4,6-tribromophenol.



2,4,6-Tribromophenol

2. Kolbe's Reaction: Phenol when treated with sodium hydroxide, we get sodium phenoxide which on treating with carbon dioxide followed by acidification, we get orthohydroxybenzoic acid commonly called Salycilic acid. This reaction is called Kolbe's reaction.

OH ONa OH

COOH

NaOH (i) C02

2-Hydroxybenzoic acid
(Salicylic acid)

3. Reimer-Tiemann reaction: Phenol when treated with chloroform in the presence of sodium hydroxide, followed by acidification, we get salicylaldehyde (o-hydroxybenzaldehyde). This reaction is known as Reimer - Tiemann reaction.

OH

NaOH

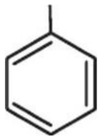
CHO C110

Salicylaldchydc

Intermediate

4. Reaction with zinc dust: Phenol when heated with Zn dust, we get benzene.

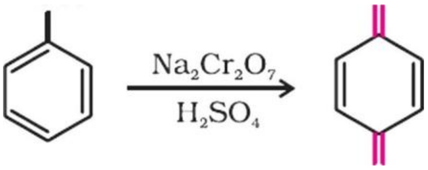
OH



+ ZnO

5. Oxidation: When phenol is oxidised with chromic acid we get a conjugated diketone known as benzoquinone.

OH O



o
benzoquinone

In the presence of air, phenols are slowly oxidised to dark coloured mixtures containing quinones.

Some Commercially Important Alcohols

1. Methanol (CH30H):

Methanol is also known as •wood spirit' since it can be produced by the destructive distillation of wood. It is manufactured by the catalytic hydrogenation of carbon monoxide at about 573-673 K temperature and 200-300 atm pressure and in the presence of ZnO - Cr203 catalyst.

$$CO + 2H_2 \longrightarrow CH_3OH$$

ZnO-Cr203 200-300
atm
573-673 K

It is highly poisonous in nature. It is used as a solvent in paints, varnishes and for making formaldehyde.

2. Ethanol (CH3CH20H):

Ethanol is commonly known as spirit or grain alcohol. It is obtained commercially by the fermentation of sugar. The sugar in molasses, sugarcane or fruits like grapes is converted to glucose and fructose, in the presence of an enzyme, invertase. Glucose and fructose undergo fermentation in the presence of another enzyme, zymase to give ethanol and carbondioxide. Both the enzymes invertase and zymase are produced by yeast.

Invertase
C12H22011 + H_2O →--------+ C6H1206 + C6H1206
Sucrose Glucose Fructose

Zymase
C6H1206→-------* 2C2H50H +2CO_2
Ethanol

Fermentation takes place in anaerobic conditions i.e. in absence of air. If air gets into fermentation mixture, the oxygen of air oxidises ethanol to ethanoic acid (acetic acid), which destroys the taste of alcohol.

The ethanol solution obtained by fermentation contains only 8-10% ethanol and it is called wash. It can be concentrated upto 95.6% by fractional distillation. 95.6% alcohol is called Rectified spirit. It is concentrated to 100% by distilling with small amount of benzene. Ethanol free from water and other impurities (100% pure ethanol) is known as absolute alcohol.

Ethanol is a colourless liquid. It is used as a solvent in paint industry and in the preparation of a number of carbon compounds.

The commercial alcohol is made unfit for drinking by mixing in it some copper sulphate (to give it a colour) and pyridine (a foul smelling liquid). It is known as denaturation of alcohol and the resulting alcohol is known as denatured spirit. If methanol is used for denaturation, it is called methylated spirit. Ethanol can also be manufactured by hydration of ethene.

CHFCH2 + 1--120   CH3-CH2-OH

ETHERS

Nomenclature

Common names of ethers are derived from the names of alkyl/aryl groups written as separate words in alphabetical order and adding the word 'ether' at the end. If both the alkyl groups are the same, the prefix 'di' is added before the alkyl group.

In IUPAC system of nomenclature, ethers are named as 'Alkoxyalkane'. The larger alkyl (R) group is chosen as the parent hydrocarbon. Some examples are:

Compound	Common Name	IUPAC Name
CH30CH3	Dimethyl ether	Methoxymethane
C2H50C2H5	Diethyl ether	Ethoxyethane
CH30CH2CH2CH3	Methyl n-propyl ether	I-Methoxypropane
C6H50CH3	Methylphenyl ether (Anisole)	Methoxybenzene (Anisole)
C6H50CH2CH3	Ethylphenyl ether (Phenetole)	Ethoxybenzene
$C_6H_5O(CH_2)_6$- C1-13	Heptylphenyl ether	I-Phenoxyheptane

If the two alkyl groups on both sides of the —O- group are identical, it is called symmetric ether and if they are different, it is called asymmetric ether.

Preparation of ethers

1. By dehydration of alcohols:

Alcohols undergo dehydration in the presence of protic acids like H2S04 or H3P04 to give ethers based on the reaction conditions.

For example, ethanol when dehydrated with conc. H2S04 at 413 K, we get diethyl ether but at 443 K, we get ethene.

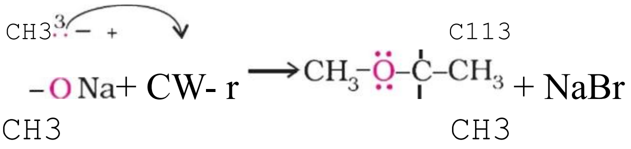
This method is suitable for the preparation of ethers having primary alkyl groups only. In the case of 2^0 and 3^0 alcohols, alkenes are formed as the major product.

2. Williamson's ether synthesis:

Alkyl halide reacts with sodium alkoxide to form ether. This reaction is called Williamson's ether synthesis.

R-X+ R'-ONa +- R-O_R' +NaX

For preparing ethers containing secondary and tertiary alkyl groups, the alkyl halide used should be primary and the alkoxide should be secondary or tertiary.


CH3
C113
–ONa+ CW- r ⟶ CH_3–Ö–C–CH_3 + NaBr
CH3 CH3

If the alkoxide used is primary, dehydrohalogenation occurs and the product formed is an alkene. This is because of the strong basic character of 1^0 alkoxide.

CH3 _

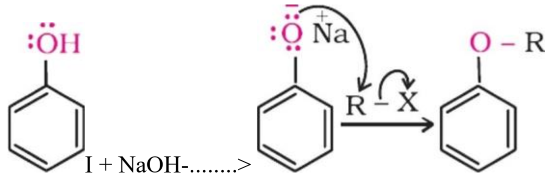
CHg-C-Br + NaÖ-CH3— CH3-C=CH2+NaBr + CH3011

CH3 CH3

2-Methylpropene

The reaction follows SN2 mechanism.

For the preparation of aromatic ethers, one of the reactants should be sodium phenoxide.



Physical Properties

Ethers have lower boiling point than alcohols. This is because in alcohols, there is inter molecular hydrogen bonding, which is absent in ethers. Lower ethers are miscible with water due to the formation of hydrogen bonding with water.

Chemical reactions

1. Reaction with HX:

Ethers on reaction with Hydrogen halide, the C-O bond cleavage occurs and alkyl halides are formed.

R-O-R + I-IX→------→ R_OH + R-X R_OH + IX →------→ R-X+ H20

In the case of ethers containing two different alkyl groups (primary and secondary), the lower alkyl group forms the alkyl halide (1^0 alkyl halide).

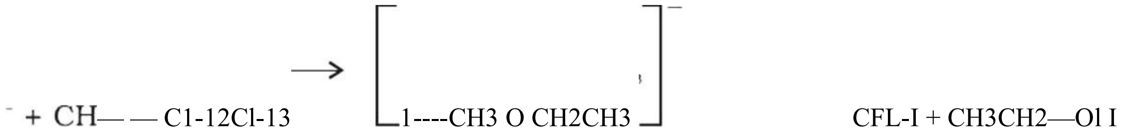
-CH2-CH3 + HI→------→ CH3_1 + CH3-CH2_OH

The order of reactivity of hydrogen halides is as follows: HI > HBr > HCI.

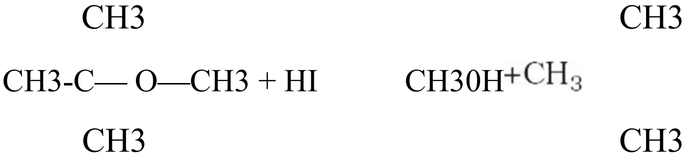
Mechanism:

Step 1: The ether molecule is protonated to form an oxonium ion.

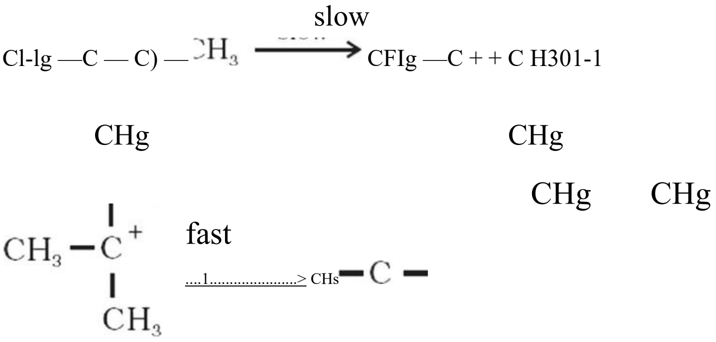
Step 2: The Iodide ion attacks the least substituted carbon of the oxonium ion and displaces an alcohol molecule by SN2 mechanism.



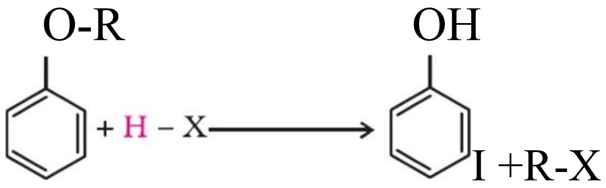
When one of the alkyl group is tertiary, the halide formed is a tertiary halide.



This is because in step 2 of the reaction, the departure of leaving group (HO—CH3) creates a more stable carbocation [(CH3)3C+], and the reaction follows SNI mechanism.

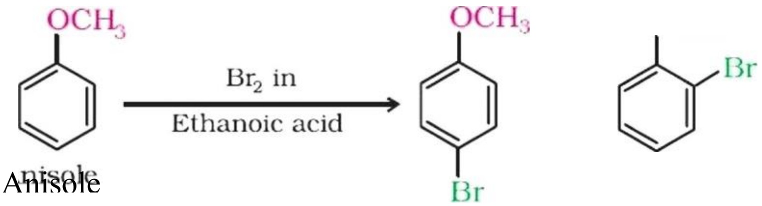


In the reaction of alkyl aryl ethers with RX, one of the products formed is always phenol. Here the O-R bond is weaker than the O—C6H5 bond because the carbon of phenyl group is sp ^{2} hybridised and there is a partial double bond character.



2. Electrophilic substitution Reactions: The alkoxy group (-0R) is ortho, para directing and activates the benzene ring. So the product formed is a mixture of ortho and para isomers.

a) Haloqenation: Anisole on bromination with bromine in ethanoic acid to give a mixture of obromoanisole and p-bromoanisole

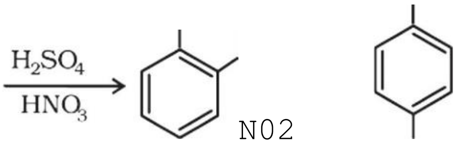


OC113

pBmmoanisole 0-13romoanisole (Major)
(minor)

b) Nitration: Anisole reacts with a mixture of conc. sulphuric acid and conc. nitric acid to give a mixture of ortho and para nitroanisole.

OCH3 OCH3 OCIL



N02

N02

2-Nitroanisole 4-Nitroanisole (Minor)
(Major)

c) Friedel-Crafts reactions:

i) Alkylation: Anisole undergoes Friedel-Crafts alkylation reaction in presence of anhydrous aluminium chloride (a Lewis acid) as catalyst, we get a mixture of ortho and para alkylated anisole.

OCH3

OCH,

OCH3

CH3 I

+CHJCI Anhyd. AIC13

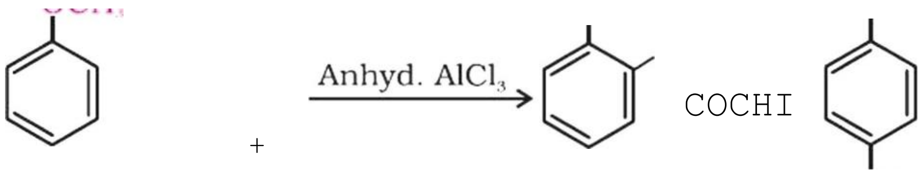
CH3

2-Methoxy-tolucnc (Minor) 4-Methoxy-toluene (Major)

ii)Acylation:

OCII OCIL

OCH,



+

COCHI

CC)CI

cocll.

Ethanoyl chloride 2-Methoxy-acetophenone 4-Methoxy-acetophcnonc

(Minor) (Major)