

Alcohols and Phenols and ethers

11.2.2 Nomenclature of alcohols

- In common system, alcohols are named as *alkyl alcohols*.
- According to IUPAC system, alcohols are called '*alkanols*', by replacing '-e' of alkane by '-ol'.

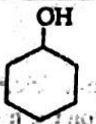

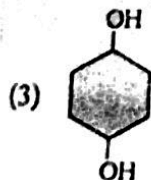
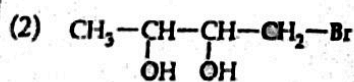
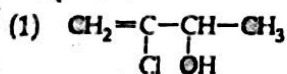
Compound	Common name	IUPAC name
CH ₃ -OH	methyl alcohol	Methanol
CH ₃ -CH ₂ -CH ₂ -OH	<i>n</i> -Propyl alcohol	Propan-1-ol
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{OH} \end{array}$	isopropyl alcohol	Propan-2-ol
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{OH} \end{array}$	<i>sec</i> -Butyl alcohol	Butan-2-ol
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$	isobutyl alcohol	2-Methylpropan-1-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{OH} \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl alcohol	2-Methylpropan-2-ol
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$	neopentyl alcohol	2,2-Dimethylpropan-1-ol
		Cyclohexanol
		3-Methylcyclopentanol

Illustration: Give the IUPAC names of the following compounds:



Soln.: (1) 3-chlorobut-3-en-2-ol

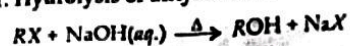
(2) 4-bromobutane-2,3-diol

(3) Cyclohexane-1,4-diol

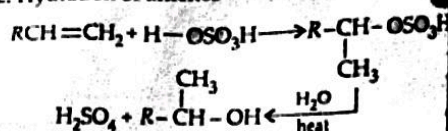
11.2.3 Preparation of alcohols

General methods of preparation

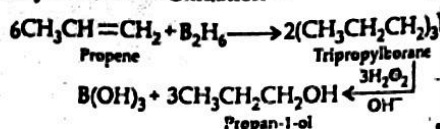
1. Hydrolysis of alkyl halides



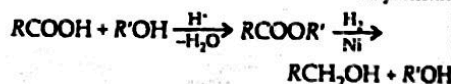
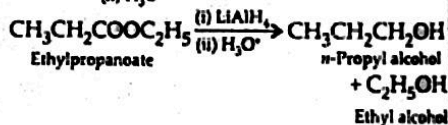
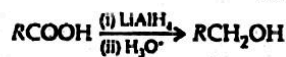
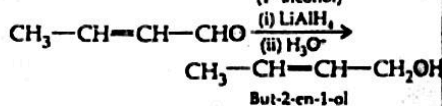
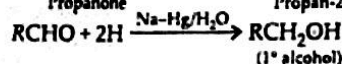
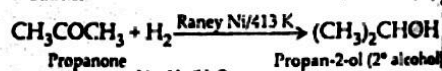
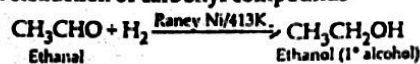
2. Hydration of alkenes



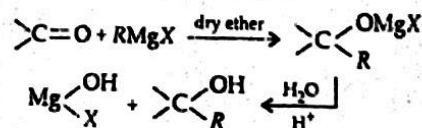
3. Hydroboration-Oxidation



4. Reduction of carbonyl compounds

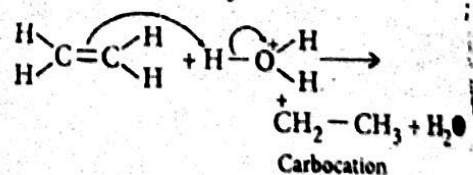
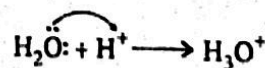


5. Addition of Grignard reagent

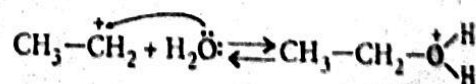


Mechanism of hydration:

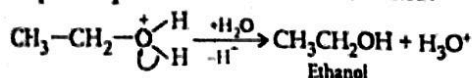
Step 1: Generation of carbocation:



Step 2: Nucleophilic attack of water on carbocation:

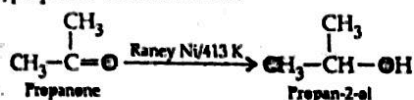


- Step 3: Deprotonation to form an alcohol:

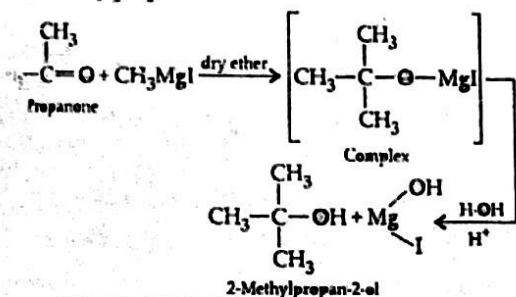


Question: How is propanone converted into Propan-2-ol (ii) 2-Methylpropan-2-ol?

Ans.: (i) Propan-2-ol: When propanone is hydrogenated at 313 K in the presence of catalyst such as finely divided Ni, propan-2-ol is obtained.

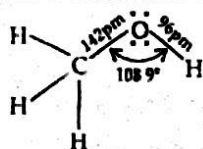


(ii) 2-Methylpropan-2-ol: When propanone is treated with methyl magnesium iodide in the presence of dry ether, a complex is formed, which on acid hydrolysis gives 2-methylpropan-2-ol.



12.4 Structure of alcohols

- In alcohols $R\text{-OH}$, the O atom of hydroxyl group is attached to C atom by a sigma (σ) bond formed by the overlapping of sp^3 hybridised orbital of C atom with sp^3 hybridised orbital of O atom.
- O atom of the hydroxyl group has two bond pairs and two lone pairs of electrons. The C—O—H bonds are not linear and the bond angle is 108.9° , slightly less than the tetrahedral angle ($109^\circ 28'$) due to the repulsion between two lone pairs of electrons of O atom.



12.5 Physical properties of alcohols

Physical state: Lower alcohols are colourless liquids with characteristic smell while higher alcohols are colourless, odourless waxy solids.

Solubility: Solubility of alcohols in water is due to their ability to form hydrogen bonds with water molecules.

- The solubility decreases with increase in size of an alkyl group.
- For isomeric alcohols, solubility increases with increase in branching: $1^\circ < 2^\circ < 3^\circ$

- Boiling points:** The boiling points of alcohols increase with increase in the number of carbon atoms as van der Waals' forces increase.

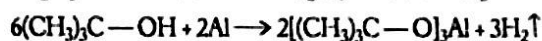
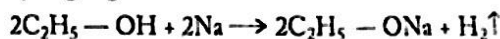
- In alcohols, the boiling points decrease with increase of branching in carbon chain due to decrease in van der Waals' forces with decrease in surface area. $1^\circ > 2^\circ > 3^\circ$

11.2.6 Reactions of alcohols

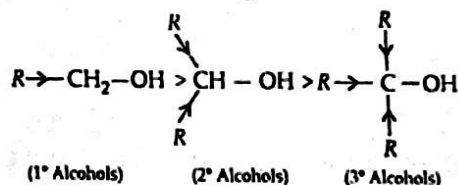
- Alcohols are neutral to litmus. In fact, alcohols are Bronsted acids *i.e.*, they donate proton of —OH group to stronger bases. Alcohols also behave as Lewis bases by donating lone pair of electrons present on oxygen. The C—O and O—H bonds in alcohols are polar hence, alcohols are quite reactive.

Action of metals

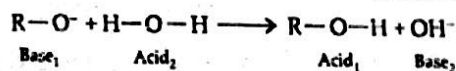
- Alcohols react with active metals like sodium, potassium, aluminium to give corresponding alkoxides liberating hydrogen gas.



- These reactions explain acidic nature of alcohols. The acidic character of alcohols is due to the polar nature of O—H bond. Alkyl group is electron releasing group and increases electron density on oxygen which results in decrease in polarity of O—H bond. As number of alkyl groups increases, acidic strength of alcohols decreases.



- Consider the reaction of water with alkoxides.



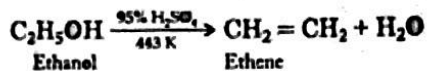
- From the above reaction, it is noted that the water is better proton donor than alcohol and alkoxide ion is better proton acceptor than hydroxide ion. Thus alcohols are weaker acids than water and alkoxide ions are stronger bases than hydroxide ions.

Illustration: *t*-Butyl alcohol reacts less rapidly with metallic sodium than the primary alcohol. Explain.

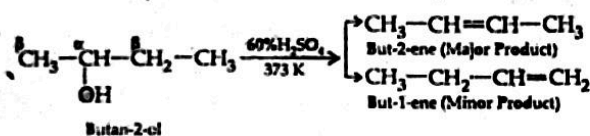
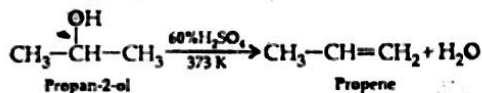
Soln.: The +I effect of three methyl groups on central carbon atom of *t*-butyl alcohol makes it partially negative with the result that it pushes the electron pair of C—O—H bond towards H-atom and thus, H atom is not replaced easily.

• Dehydration of alcohols :

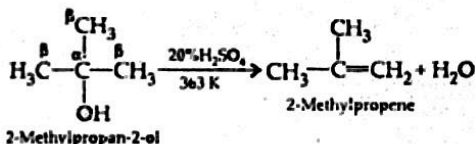
- ▶ A primary alcohol is dehydrated by heating with 95% H₂SO₄ at 443 K.



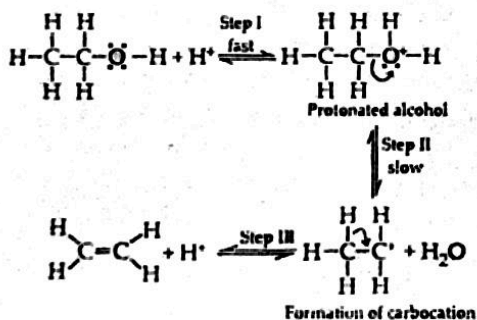
- ▶ A secondary alcohol is dehydrated by heating with 60% H₂SO₄ at 373 K.



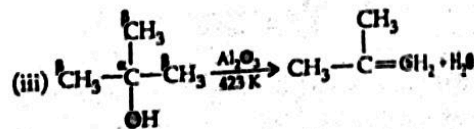
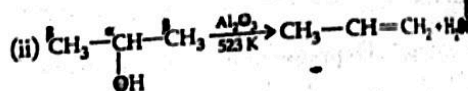
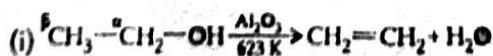
- ▶ A tertiary alcohol is easily dehydrated by heating with 20% H₂SO₄ at 363 K.



• Mechanism of dehydration :

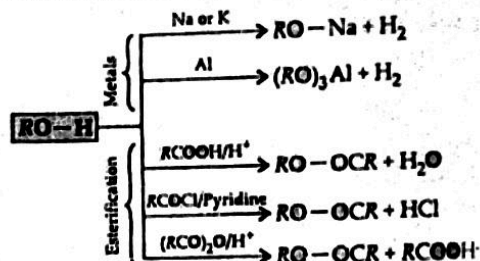


- ▶ Ease of dehydration of alcohols follow the order of stability of carbocations (as they are formed as intermediates) :
3° alcohols > 2° alcohols > 1° alcohols
- ▶ Dehydration of alcohol always occurs in accordance with the Saytzeff rule i.e., the more substituted alkene is the major product.
- ▶ Dehydration of alcohols often give alkenes derived from rearranged carbocations.
- ▶ Alternatively, an alcohol can be dehydrated by passing vapours of alcohols over heated alumina (Al₂O₃). Temperature required for the dehydration reaction decreases from primary to tertiary i.e., tertiary alcohols are most easily dehydrated.

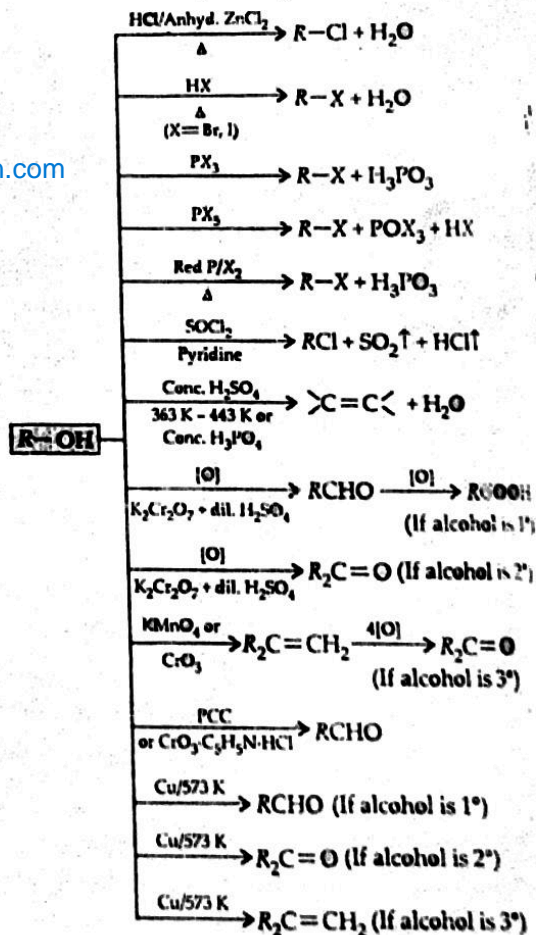


Chemical reactions

• Reactions involving cleavage of O-H bond



• Reactions involving cleavage of C-O bond



Distinction

- Lucas test : Lucas reagent is a solution of conc. HCl with anhyd. ZnCl₂. With Lucas reagent,
 - ▶ Primary alcohols - No cloudiness

- Secondary alcohols – Cloudiness in 5 minutes
- Tertiary alcohols – Cloudiness immediately

12.7 Uses of alcohols

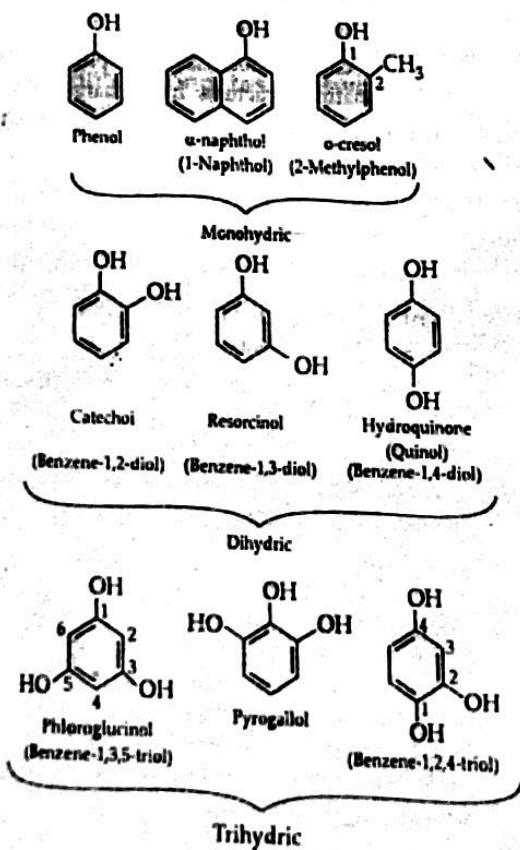
- Methyl alcohol is used as an industrial solvent for oils, fats, gums, celluloid etc.
- It is used for dry cleaning and for preparation of perfumes and varnishes, and also as an antifreeze agent for automobile radiators in cold countries.
- Ethyl alcohol is used as a solvent for dyes, oils, perfumes, cosmetics and drugs.
- A mixture of 10 – 20% ethyl alcohol with petrol is used as motor fuel.
- Ethyl alcohol is used to prepare solid fuel which is a dispersion of ethyl alcohol in calcium acetate.

11.3 Phenols

- Phenols are the compounds in which hydroxy (-OH) group is directly linked to aromatic ring having formula C_6H_5OH .

11.3.1 Classification and nomenclature of phenols

- Like alcohols, phenols are also classified as monohydric, dihydric and trihydric phenols.



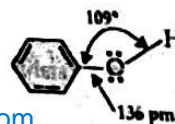
Nomenclature

- The simplest hydroxy derivative of benzene is phenol also called *carbolic acid*. It is its common name and also an accepted IUPAC name.
- As structure of phenol involves a benzene ring, in its substituted compounds, the terms *ortho* for (1,2-disubstituted), *meta* for (1,3-disubstituted) and *para* for (1,4-disubstituted) are used in the common names.
- The numbering of the ring starts with —OH substituted carbon while the other carbon atoms are indicated by lowest number in the IUPAC system.

Compound	Common name	IUPAC name
	o-Cresol	2-Methylphenol
	o-Aminophenol	2-Aminophenol

11.3.2 Structure of functional group

- In phenols, the —OH group is attached to sp^2 hybridised C-atom of an aromatic ring.
 - ▶ The C—O bond length (136 pm) in phenol is slightly less than the C—O bond length in alcohol due to partial double bond character of C—O bond and sp^2 hybridised state of C atom to which O atom is attached.



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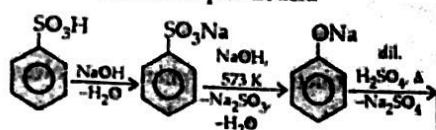
Illustration: Why is the C—O bond length in phenol shorter than in alcohol?

Soln.: In phenol carbon atom uses sp^2 hybrid orbital to form C—O bond whereas in alcohol carbon uses sp^3 hybrid orbital. sp^2 has greater s character hence bond is shorter.

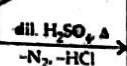
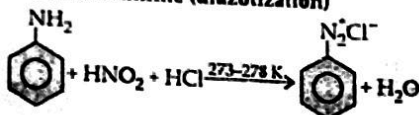
11.3.3 Preparation of phenol

General methods of preparation

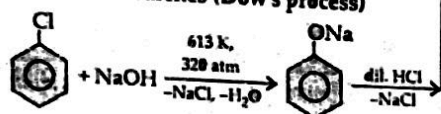
1. From benzenesulphonic acid



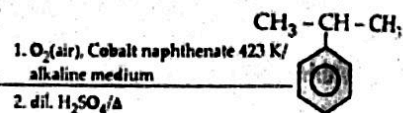
2. From aniline (diazotization)



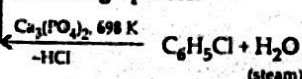
3. From haloarenes (Dow's process)



4. From cumene



5. Raschig's process



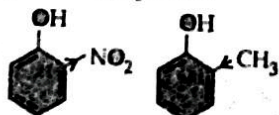
11.3.4 Physical properties of phenol

- State and smell : Pure phenol is colourless crystalline solid.
- Phenol has characteristic smell known as phenolic or carbolic odour.
- Phenol has melting point 315 K and boiling point 455 K. The high boiling point of phenol is due to intermolecular hydrogen bonding.
- Phenol is sparingly soluble in water but completely soluble in alcohol, ether etc.
- Acidity : Phenol is a weak acid, weaker than even carbonic acid. Phenol turns pink on exposure to air and light due to formation of mixtures of quinones.

Illustration : *o*-Nitrophenol is more acidic than *o*-cresol. Explain why?

Soln.: (1) In *o*-nitrophenol, nitro group (NO_2) is an electron withdrawing group which enhances the acidic strength ($-I$ effect). The $\text{O}-\text{H}$ bond is under strain and release of proton (H^+), becomes easier. Further *o*-nitrophenoxide ion is more stabilised due to resonance.

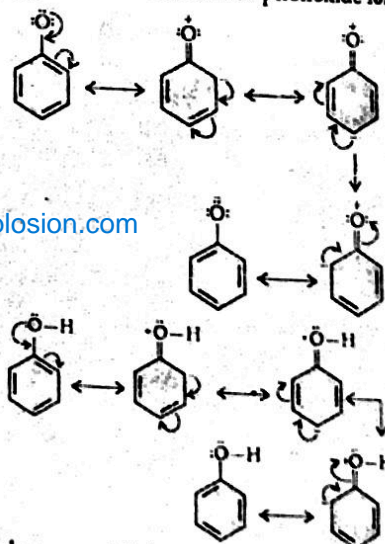
(2) The methyl group in *o*-cresol is an electron releasing group which decreases the acidic strength ($+I$ effect). The electron density on the ring as well as on the $\text{O}-\text{H}$ bond increases. This makes the release of H^+ ion difficult. In other words, *o*-cresols have less tendency to form stable phenoxide ion by releasing a proton.



Hence, *o*-nitrophenol is more acidic than *o*-cresol.

11.3.5 Reactions of phenol

- **Acidic nature :** Phenols are more acidic than alcohols as the hydroxyl group in phenol is directly attached to highly electronegative sp^2 hybridised C atom of benzene ring which decreases the electron density on O atom.
 - ▶ This increases the polarity of $\text{O}-\text{H}$ bond and results in an increase in ionisation of phenols.
 - ▶ Moreover, in phenoxide ion, the charge is delocalised which makes phenoxide ion more stable thus favours the ionisation of phenol.
 - ▶ There is charge delocalisation in phenol also, but its resonating structures have charge separation making phenol less stable than phenoxide ion.



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- ▶ An electron withdrawing group, increases the acidic strength of phenol in substituted phenol while an electron releasing group decreases the acidic strength of phenol.

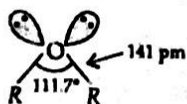
11.4.3 Nomenclature

- 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.
- According to IUPAC system of nomenclature, ethers are regarded as hydrocarbon derivatives in which a hydrogen atom is replaced by an -OR or -OAr group, where R and Ar represent alkyl and aryl groups, respectively.
 - The larger R group is chosen as the parent hydrocarbon.

Chemical structure	Common name	IUPAC name
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3$	Methyl n-propyl ether	1-Methoxypropane
$\text{CH}_3\text{O}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3$	Isopropyl methyl ether	2-Methoxypropane
$\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	3-chloropropyl ethyl ether	3-Chloro-1-ethoxypropane
$\text{C}_6\text{H}_5-\text{O}-\text{CH}_3$	Anisole (Methyl phenyl ether)	Methoxybenzene
$\text{C}_6\text{H}_5-\text{O}-\text{C}_2\text{H}_5$	Phenetole (Ethyl phenyl ether)	Ethoxybenzene
	—	1-Ethoxy-3-ethylcyclohexane

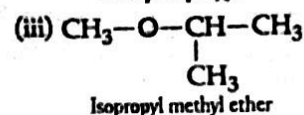
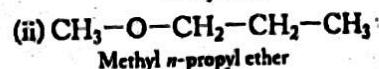
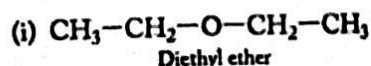
11.4.4 Structure of functional group

- In ethers, the four electron pairs, i.e., the two bond pairs and two lone pairs of electrons on O atom are arranged approximately in a tetrahedral arrangement.
 - The bond angle is slightly greater than the tetrahedral angle due to the repulsive interaction between the two bulky (-R) groups.
 - The C-O bond length (141 pm) is almost the same as in alcohols.

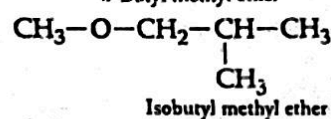
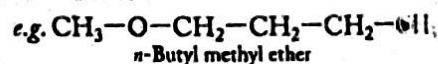
11.4.5 Isomerism futureexplosion.com

- Metamerism:** Ethers having the same molecular formula but different alkyl groups attached on either side of the oxygen atom are called *metamers* of each other.
 - Metamers are either chain isomers or position isomers with same functional group and have different alkyl groups attached to hetero atom; in this case it is oxygen.

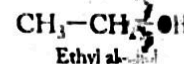
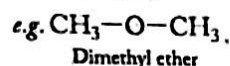
Following metamers can be represented by formula $\text{C}_4\text{H}_{10}\text{O}$.



- Chain isomerism:** The ethers having the same alkyl group on either side of oxygen atom but different arrangements of the carbon chain within the alkyl group are called *chain isomers*.

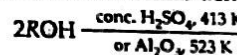


- Functional isomerism:** An ether and an alcohol containing same number of carbon atoms are functional isomers.

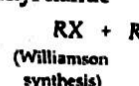


11.4.6 Methods of preparation

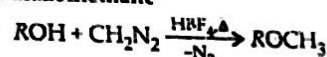
From alcohols (intermolecular dehydration)



From alkyl halide

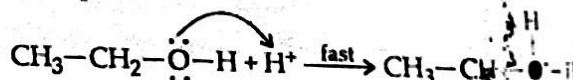


From diazomethane

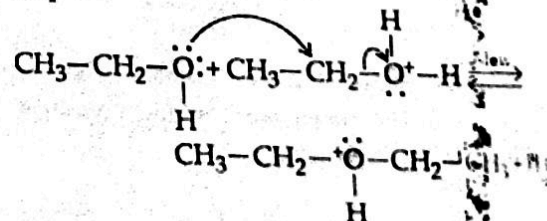


- Dehydration (Formation of ether from alcohol):**

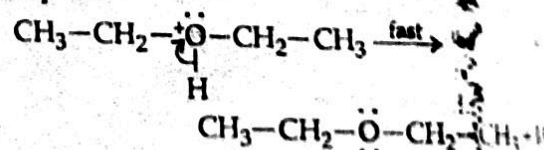
Step-I:



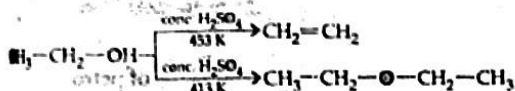
Step-II:



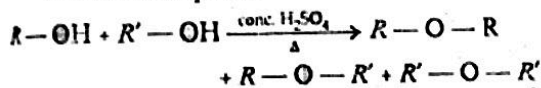
Step-III:



- This is the industrial method used to produce millions of gallons of diethyl ether every year.
- In acidic dehydration of alcohols two reactions compete with each other. As the temperature increases, it becomes more favourable for elimination (453 K and above). Substitution is favoured at 413 K and below.

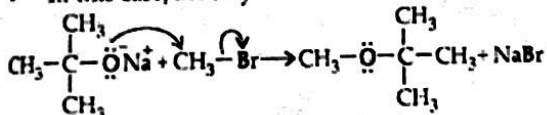


- The method is suitable for the preparation of ethers from primary alcohols only. Dehydration of secondary and tertiary alcohols form alkenes instead of ethers as elimination competes over substitution.
- Simple ethers can be conveniently prepared by this method. Bimolecular dehydration of alcohols is not suitable for preparation of mixed ethers. If a mixture of two different alcohols is used, a mixture of three different ethers is obtained which is difficult to separate.

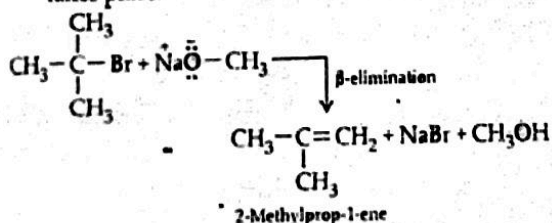


- Dehydration of alcohols for the formation of ethers follows the order, $1^\circ > 2^\circ > 3^\circ$
- Williamson synthesis can be used to prepare ethers containing 2° or 3° alkyl groups through $\text{S}_{\text{N}}2$ mechanism.

- In this case, the alkyl halide must be 1° .



- In the case of 2° and 3° alkyl halides, elimination takes place.



- Williamson synthesis method cannot be used to prepare diaryl ethers.

11.4.7 Physical properties of ethers

- Physical state:** Dimethyl ether and diethyl ether are exceptionally gases at room temperature while all other ethers are colourless liquids with characteristic ethereal smell.
- Polarity:** Due to bent structure, they have net dipole moment and therefore they are polar in nature.
- Boiling points:** Boiling points of ethers are slightly higher than that of alkanes but much lower than that of alcohols

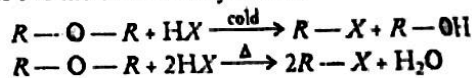
of comparable masses. This is because the dipole-dipole attractive forces in ethers are minor contributors and in alcohols hydrogen bonding is present.

- Solubility:** Ethers are soluble in water to a certain extent due to hydrogen bonding.
 - Solubility decreases with increase of molecular mass.
 - Ethers are fairly soluble in all organic solvents such as alcohol, chloroform, benzene, etc.
- Density:** Ethers are lighter than water.

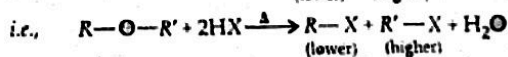
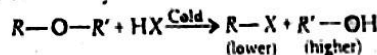
11.4.8 Chemical properties of ethers

Action of hydrogen halides

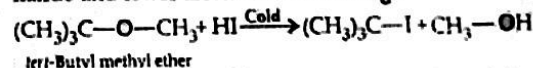
- In cold, a simple ether gives one molecule of alkyl halide and one molecule of an alcohol, while when heated gives two molecules of alkyl halide.



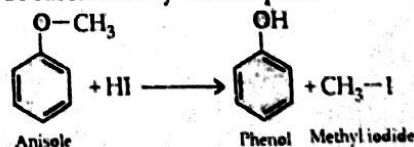
- In cold, a mixed ether gives generally a lower alkyl iodide and a higher alcohol while when heated it gives two different alkyl halides.



- If one of the alkyl groups is tertiary, then tertiary alkyl halide and lower alcohol is formed. e.g.,



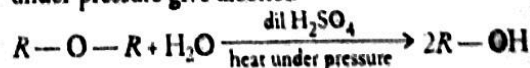
- Alkyl aryl ethers are cleaved at weaker O — R bond to give phenols and alkyl iodide. Ar — O bond is stronger because the carbon atom of phenyl group is sp^2 hybridized and there is partial double bond character. Phenol does not react further with HI because — OH group is attached to sp^2 hybridized carbon atom and cannot be substituted by a nucleophile.



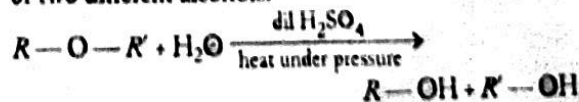
- In case of anisole, the halide formed will be methyl iodide.
- The order of reactivity with halogen acids follows: $\text{HI} > \text{HBr} > \text{HCl}$

Hydrolysis/Action of dilute H_2SO_4

- Simple ethers on heating with dilute sulphuric acid under pressure give alcohol.



- A mixed ether under similar conditions gives mixture of two different alcohols.



Electrophilic substitution reactions

- The alkoxy group ($-\text{OR}$) is *ortho*, *para* directing and activates the aromatic ring towards electrophilic substitution in the same way as phenol.

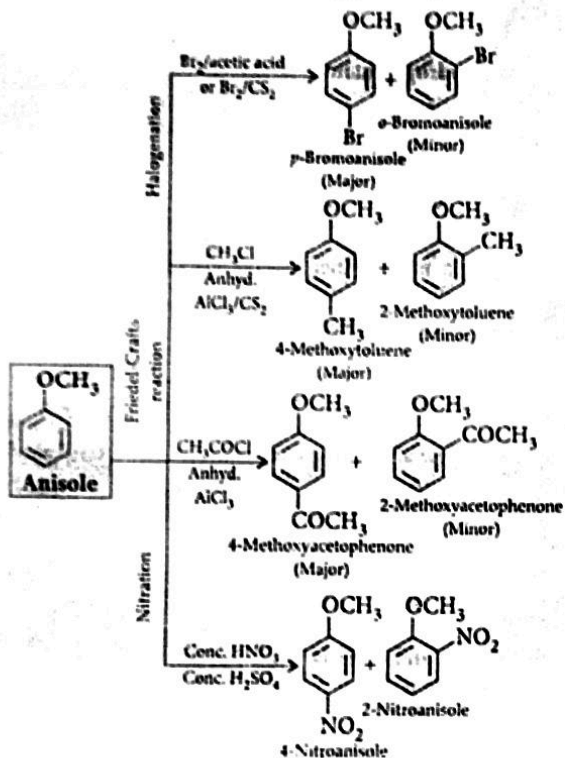
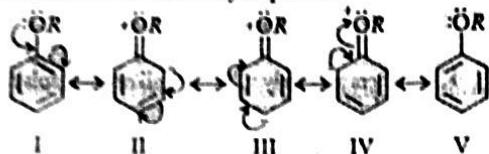
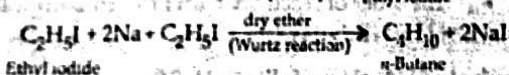
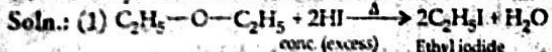


Illustration: How will you effect following two-step conversions?

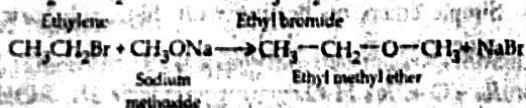
(1) Diethyl ether into *n*-butane

(2) Ethylene into ethyl methyl ether

(3) Dimethyl ether into formic acid



(2) $\text{CH}_2=\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{Br}$



(3) $\text{CH}_3-\text{O}-\text{CH}_3 + \text{H}_2\text{SO}_4 \xrightarrow[\text{(dil)}]{\Delta} 2\text{CH}_3\text{OH}$
Methyl alcohol



11.4.9 Uses of diethyl ether

- Diethyl ether is used as industrial solvent for oils, fuming, resin etc.
- It is used as solvent in the reaction of Grignard reagent.
- It is used as refrigerant.
- A mixture of diethyl ether and ethyl alcohol, known as *Natalite*, is used as fuel (substitute of petrol).

11.4.10 Crown ethers

- The organic compounds with molecules containing large rings of carbon and oxygen atoms are called *crown ethers*.
 - Crown ethers are named as *n*-crown-*m*, where *n* is the total number of carbon and oxygen atoms and *m* is the number of oxygen atoms in the ring.



18 - crown - 6 - ether (o = oxygen atom and ● = -CH₂- group.)

- The cavity inside 18-Crown-6-ether is able to trap K^+ but not Na^+ or Li^+ ion. 15-Crown-5 is able to trap Na^+ ion.
- Crown ethers form strongly bonded complexes with metal ions by coordination through oxygen atom. They also form complexes with ammonium ion (NH_4^+) and alkyl ammonium ion (RNH_3^+).
- The stability of these complexes depends on the size of ion relative to the cavity available in the ring of particular crown ether.
- Crown ethers can be used for increasing solubility of ionic salts in non-polar solvents.
- They also act as catalyst in certain reactions involving organic salts by complexing with positive metal cation and thereby increasing its separation from the organic anion.
- Some of the uses of crown ethers depend on the selectivity for specific size of anions. Thus they can be used to extract specific ions from mixtures and enrich isotope mixtures.
- Crown ethers are also used to remove radioactive elements from radioactive waste. Specialized derivatives of 18 - crown - 6 are used to extract cesium and strontium.