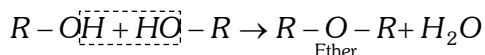


Hydroxy Compounds (Alcohols, Phenols) and Ethers Part 3

Introduction of ether.

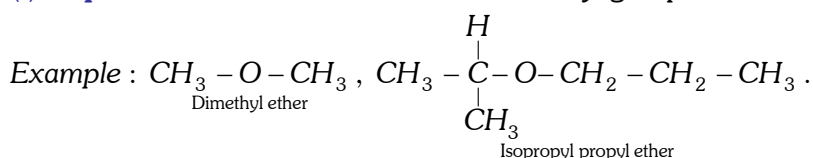
Ethers are anhydride of alcohols, they may be obtained by elimination of a water molecule from two alcohol molecules.



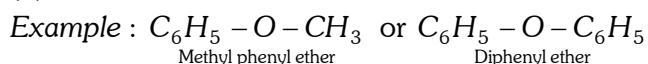
General formula is $C_nH_{2n+2}O$

(1) **Classification** : It may be divided in two category.

(i) **Aliphatic ethers** : Both R of ether are alkyl group.

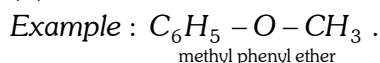


(ii) **Aromatic ethers** : In which either one or both R of ether are aryl groups.

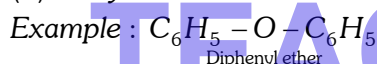


Aromatic ethers are divided in two category.

(a) **Phenolic ethers** : Ethers in which one of the group is aryl and other one is alkyl.

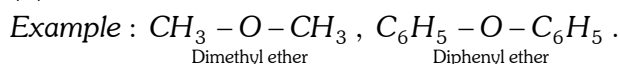


(b) **Diaryl ether** : In which both the groups are aryl group.

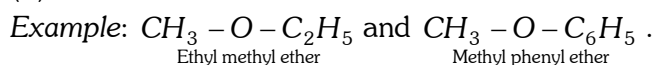


(iii) **Symmetrical and unsymmetrical ethers**,

(a) An ether in which both the R are same known as symmetrical ethers.



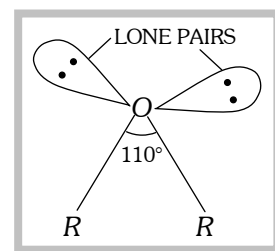
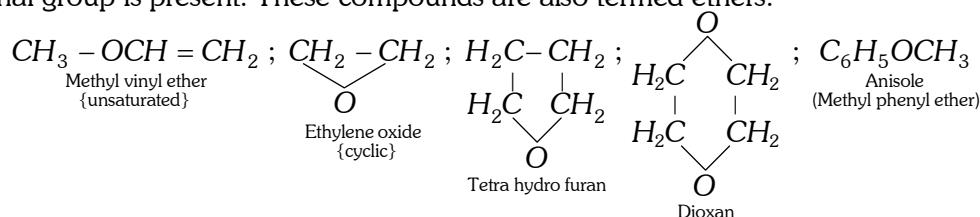
(b) An ether in which the both R are different called unsymmetrical ethers or mixed ethers.



(2) **Structure** : The oxygen atom in ether is sp^3 hybridised. Two of the hybrid orbitals overlap with hybrid

orbital (one each) of two carbon atoms to form sigma bonds. $\text{>C}^{\sigma}-\text{O}^{\sigma}-\text{C}^{\sigma}<$. The bond angle is 110° .

Besides the open chain saturated homologous series, there are numerous organic compounds in which $-O-$ functional group is present. These compounds are also termed ethers.



(3) **Nomenclature** : There are two systems for naming ethers.

(i) **Common names** : When both the alkyl group are same, the prefix *di-* is used. In case of unsymmetrical ethers two alkyl groups are named in alphabetical order.



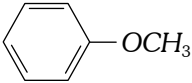
Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

(ii) **IUPAC system** : Ethers are named as **alkoxy alkanes**.

(a) The ethereal oxygen is taken with smaller alkyl group.

Example : CH_3O ; C_2H_5O .
Methoxy Ethoxy group

(b) The R group having the longest carbon chain is chosen as the parent alkane.

Example : $CH_3 - O - C_2H_5$, 
Methoxy ethane Methoxy benzene

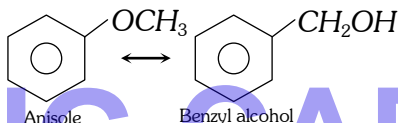
Note : * In case of simple ethers common names are also accepted in IUPAC system.

(4) **Isomerism** : Ether show the following types of isomerism :

(i) **Chain isomerism**

Example : $CH_3 - O - CH_2CH_2CH_2CH_3$, $CH_3 - O - CH_2 - \overset{\overset{CH_3}{|}}{CH} - CH_3$.
1-methoxy butane 1-methoxy-2-methyl propane

(ii) **Functional isomerism**

Example : $CH_3 - O - CH_3 \leftrightarrow CH_3 - CH_2 - OH$, 
Dimethyl ether Ethanol Anisole Benzyl alcohol

(iii) **Metamerism**

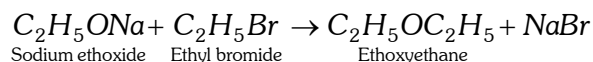
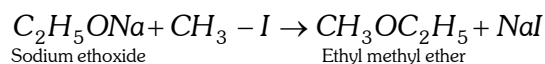
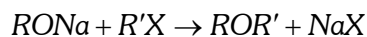
Example : $CH_3CH_2 - O - CH_2CH_3 \leftrightarrow CH_3 - O - CH_2 - CH_2 - CH_3$
Ethoxy ethane Methoxy propane

General methods of preparation of ethers.

(1) **From alkyl halides**

(i) **Williamson's synthesis** : It is the laboratory method for the preparation of ethers.

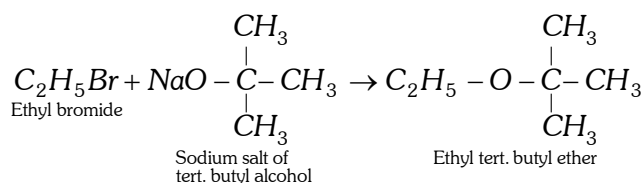
It is a nucleophilic substitution reaction and proceed through SN^2 mechanism.



(a) Order of reactivity of primary halide is $CH_3X > CH_3CH_2X > CH_3CH_2CH_2X$.

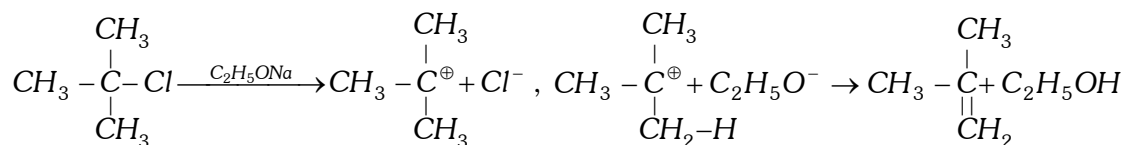
(b) Tendency of alkyl halide to undergo elimination is $3^\circ > 2^\circ > 1^\circ$.

(c) For better yield alkyl halide should be primary and alkoxide should be secondary or tertiary.

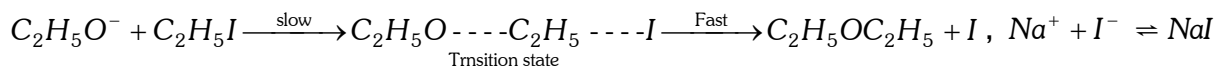


Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

(d) Secondary and tertiary alkyl halides readily undergo E_2 elimination in the presence of a strong base to form alkenes.

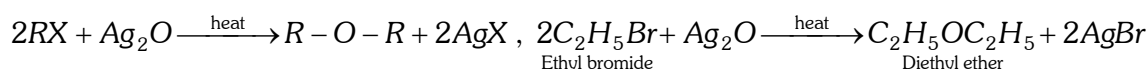


S_N^2 mechanism : $\text{C}_2\text{H}_5\text{ONa} \rightleftharpoons \text{C}_2\text{H}_5\text{O}^- + \text{Na}^+$,



Note : * Aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halide are less reactive toward nucleophilic substitution reaction than alkyl halides.

(ii) **By heating alkyl halide with dry silver oxide**



(2) **From alcohols**

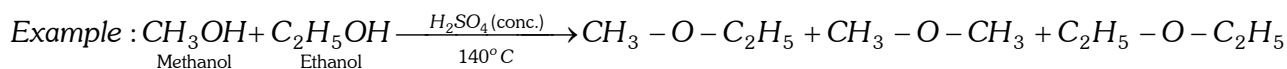
(i) **By dehydration of alcohols**



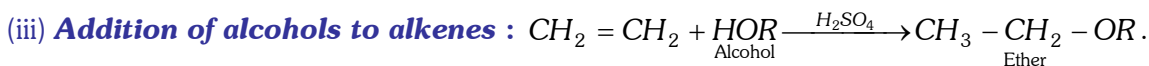
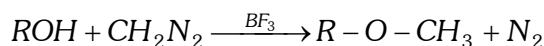
Note : * In this reaction alcohol must be present in excess.

* This reaction is mainly applicable for the dehydration of primary alcohols. Secondary and tertiary alcohols form alkenes mainly.

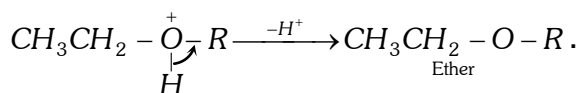
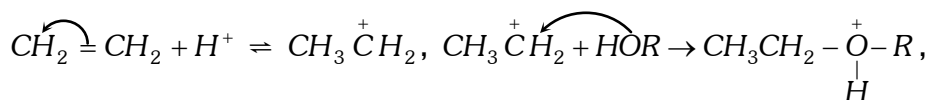
* When this reaction is carried out between different alcohols then there is a mixture of different ethers is obtained.



(ii) **By the action of diazomethane on alcohols :** This reaction is in presence of catalyst, boron trifluoride or HBF_4 .



The intermediate is carbonium ion.

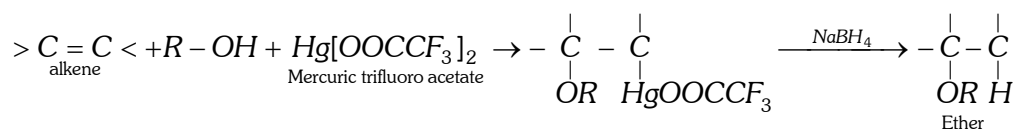


(a) This method is very useful for preparing mixed ethers.

(b) In higher cases, there can be 1, 2-hydride or 1, 2-methyl shift to form more stable carbonium ion.

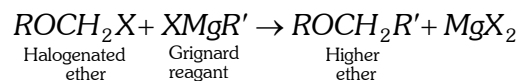
Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

(3) Alkoxy mercuration-demercuration



Note : * This is the best method for the preparation of t-ethers.

(4) Reaction of lower halogenated ether with grignard reagent



- Higher members can be prepared by the action of grignard reagent on lower halogenated ethers.
- Ether form soluble coordinated complexes with grignard reagent.

General properties of ethers.

Physical properties

(1) **Physical state :** Methoxy methane and methoxy ethane are gases while other members are volatile liquid with pleasant smell.

(2) **Dipole moment (D.M.) :** Bond angle of ether is due to sp^3 hybridisation of oxygen atom. Since C – O bond is a polar bond, hence ether possess a net dipole moment, even if they are symmetrical.

D.M. of dimethyl ether is 1.3 D

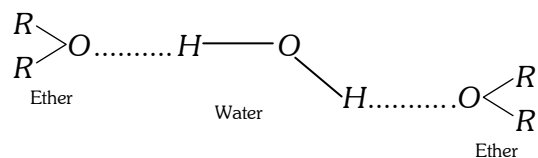
D.M. of di ethyl ether is 1.18 D

Note : * The larger bond angle may be because of greater repulsive interaction between bulkier alkyl groups as compared to smaller H-atoms in water.

(3) **Boiling points :** Boiling points of ethers are much lower than those of isomeric alcohols, but closer to alkanes having comparable mass. This is due to the absence of hydrogen bonding in ethers.

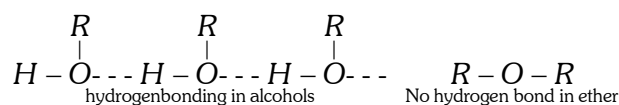
(4) **Solubility :** Solubilities of ethers in water are comparable with those of alcohols.

Example : Di ethyl ether and n-butyl alcohol have approximately the same solubility in water. This is because, ether form hydrogen bond with water much in the same way as alcohol do with water.



Note : * Solubility of ether in water decreases with the size of alkyl groups.

(5) **Hydrogen bonding :** There is no hydrogen directly attach (bonded) to oxygen in ethers, so ethers do not show any intermolecular hydrogen bonding.

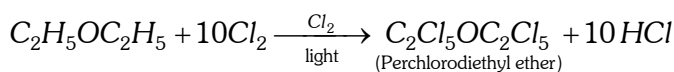
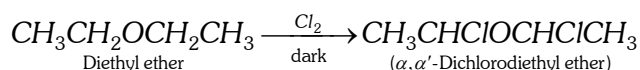


(6) **Density :** Ethers are lighter than water.

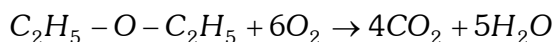
Chemical properties : Ethers are quite stable compounds. These are not easily attacked by alkalies, dilute mineral acids, active metals, reducing agents or oxidising agents under ordinary conditions.

(1) Reaction due to alkyl group

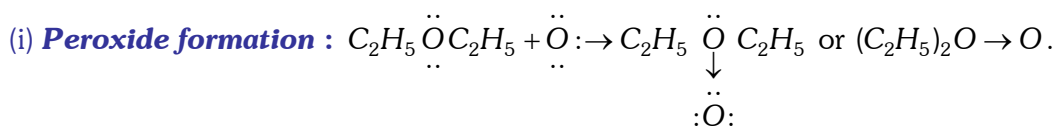
Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3



(ii) **Burning** : Ethers are highly inflammable. They burn like alkanes.



(2) Reaction due to ethereal oxygen



(a) The boiling point of peroxide is higher than that of ether. It is left as residue in the distillation of ether and may cause explosion. Therefore ether may never be evaporated to dryness.

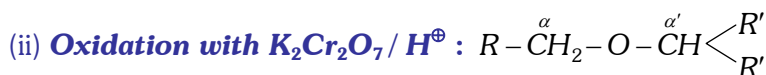
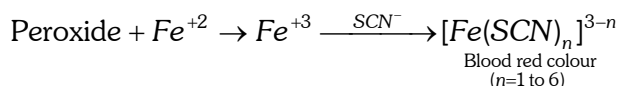
(b) Absolute ether can be prepared by distillation of ordinary ether from conc. H_2SO_4 and subsequent storing over metallic sodium.

Note : * Formation of peroxide can be prevented by adding small amount of Cu_2O to ether.

* With strong oxidising agent like acid, dichromate ethers are oxidised to aldehydes.

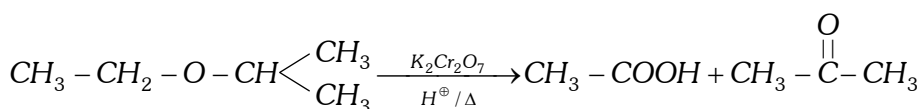
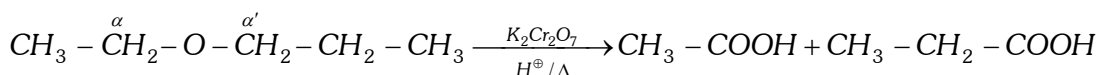


* The presence of peroxide can be indicated by the formation of blood red colour complex in the following reaction.

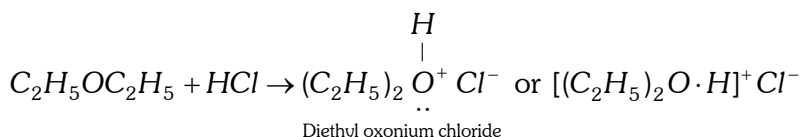


(a) Oxidation of ether can only be possible if any one of the alkyl groups of ether has hydrogen on α -carbon.

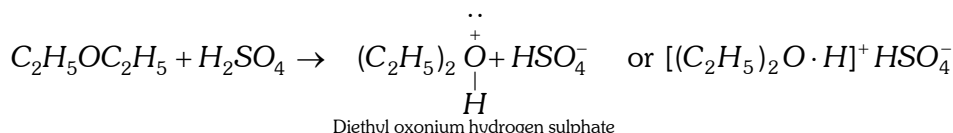
(b) α -carbon having two hydrogens converts in carboxylic group and α -carbon having only one hydrogen converts into keto group.



(iii) **Salt formation** : Due to lone pair of electrons on oxygen atom. Ether behaves as Lewis base and form stable oxonium salt with strong inorganic acids at low temperature.



Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3



The oxonium salts are soluble in acid solution and ethers can be recovered from the oxonium salts by treatment with water.

$$(C_2H_5)_2\overset{\cdot\cdot}{\underset{H}{\text{O}}^+} Cl \xrightarrow{H_2O} (C_2H_5)_2O + HCl$$

Oxonium salt Diethyl ether

Note : ✱ The formation of oxonium salt is similar to the formation of ammonium salts from ammonia and acids.

✱ Ether is removed from alkyl halides by shaking with conc. H_2SO_4 .

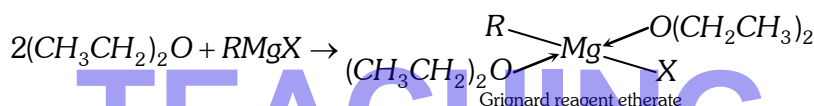
✱ Ethers can be distinguished from alkanes with the help of this reaction.

(iv) **Reaction with Lewis acids :** Being Lewis bases, ethers form complexes with Lewis acids such as BF_3 , $AlCl_3$, $FeCl_3$, etc. These complexes are called **etherates**.

$$\begin{array}{c} CH_3CH_2 \\ \diagdown \\ \text{O} : \\ \diagup \\ CH_3CH_2 \end{array} + BF_3 \rightarrow \begin{array}{c} CH_3CH_2 \\ \diagdown \\ \text{O} \\ \diagup \\ CH_3CH_2 \end{array} \rightarrow BF_3$$

Boron trifluoride etherate (complex)

Similarly, diethyl ether reacts with Grignard reagent forming Grignard reagent etherate.

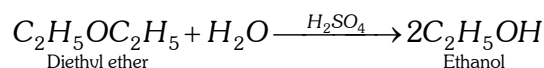


Due to the formation of the etherate, Grignard reagents dissolve in ether. That is why Grignard reagents are usually prepared in ethers. However, they cannot be prepared in benzene, because benzene has no lone pair of electrons and therefore, cannot form complexes with them.

(3) Reaction involving cleavage of carbon-oxygen bond

(i) Hydrolysis

(a) With dil. H_2SO_4 : $ROR + H_2O \xrightarrow{H_2SO_4} 2ROH$



(b) With conc. H_2SO_4 :

$$\begin{array}{c} C_2H_5OC_2H_5 + H_2SO_4 \rightarrow C_2H_5OH + C_2H_5HSO_4 \\ C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O \\ \hline C_2H_5OC_2H_5 + 2H_2SO_4 \rightarrow 2C_2H_5HSO_4 + H_2O \end{array}$$

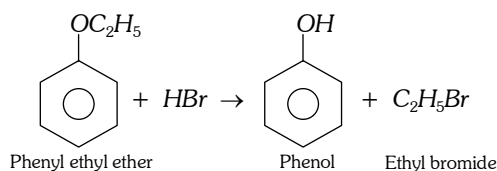
Diethyl ether Ethyl hydrogen sulphate

(ii) Action of hydroiodic acid

(a) **With cold HI :** $C_2H_5OC_2H_5 + HI \xrightarrow{\text{Cold}} C_2H_5I + C_2H_5OH$

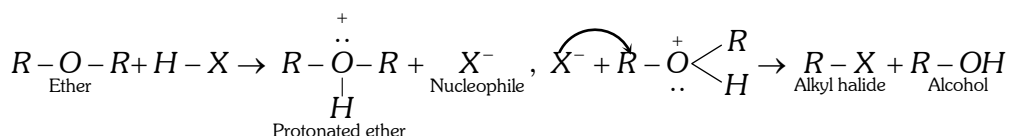
Diethyl ether Ethyl iodide Ethyl alcohol

Note : ✱ Same reaction are observed with HBr and HCl . The order of reactivity of halogen acid $HI > HBr > HCl$.

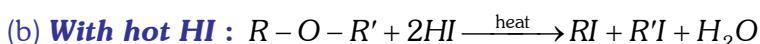


Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

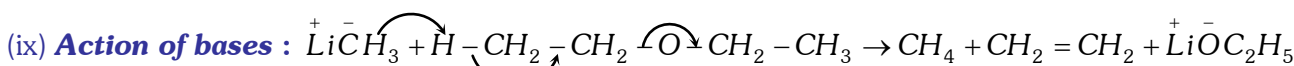
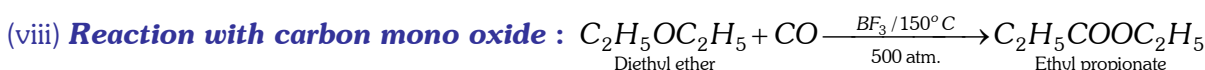
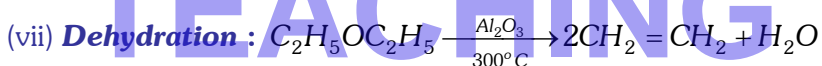
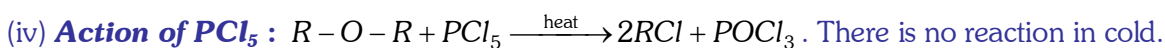
Mechanism of the reaction



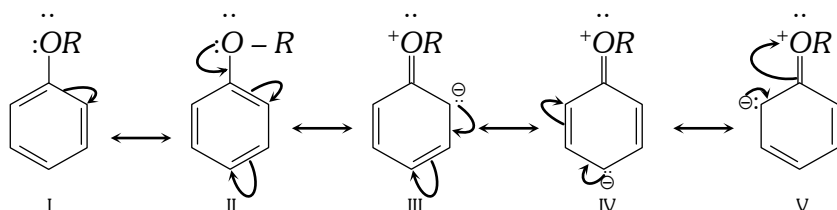
- This can be explained on the basis of steric hinderence.
- The above reaction is a SN' reaction.
- The ether molecule gets protonated by the hydrogen of the acid to form protonated ether and the protonated ether undergoes nucleophilic attack by halide ion $[X^-]$ and form alkyl alcohol and alkyl halide.



Note : * The silver iodide thus form can be detected and estimated. This formed the basis of Zeisel method for the detection and estimation of alkoxy group in a compound.



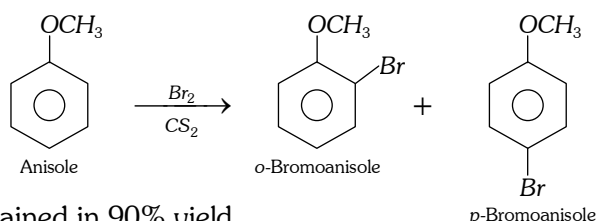
(4) **Ring substitution in aromatic ethers** : Alkoxy group is *ortho* and *para* directing and it directs the incoming groups to *ortho* and *para* position. It activates the aromatic ring towards electrophilic substitution reaction.



III, IV and V show high electron density at *ortho* and *para* position.

(i) **Halogenation** : Phenyl alkyl ethers undergo usual halogenation in benzene ring.

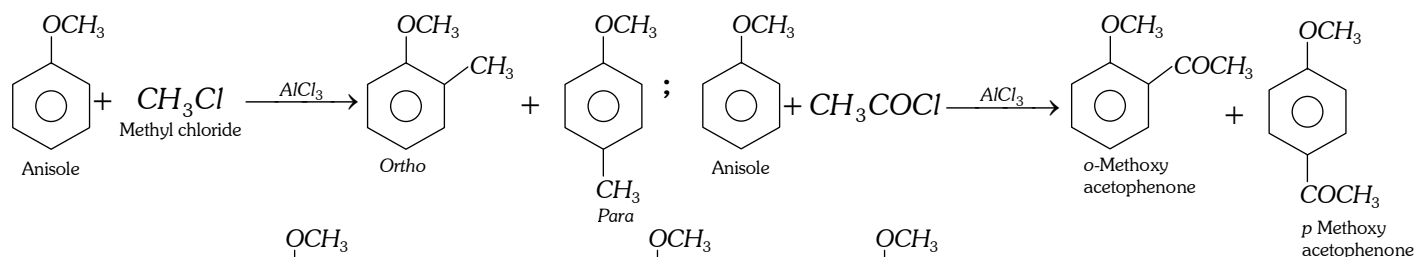
For example, Bromination of anisole gives *ortho* and *para* bromo derivative even in the absence of iron (III) bromide catalyst.



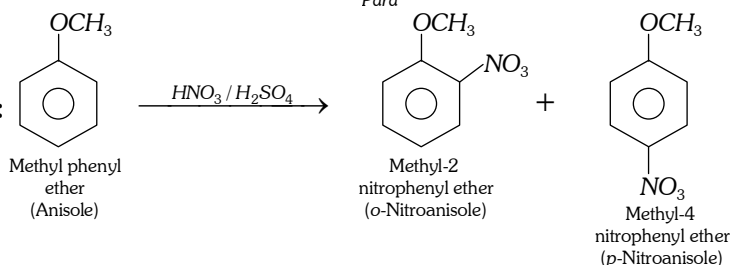
Para isomer is obtained in 90% yield.

Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

(ii) Friedel craft reaction



(iii) Nitration :



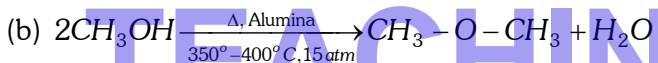
Note : * Ethers are relatively less reactive than phenol towards electrophilic substitution reaction.

Some commercially important compounds of ethers.

(1) **Di methyl ether** : It is the simplest ether.

(i) Preparation

(a) It can be prepared by using any of the general method of preparation.



(c) It can be manufactured by dehydration of methyl alcohol with conc. H_2SO_4 at $140^\circ C$.

(ii) Properties

(a) It is colourless highly inflammable gas having B.P. of $-24.8^\circ C$.

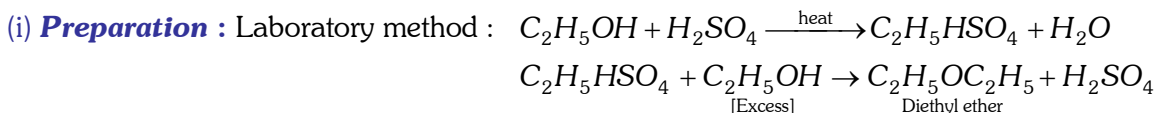
(b) It is soluble in water, alcohols and other organic solvents and gives all the characteristic reactions of ethers.

(iii) Uses

(a) It is used in the form of compressed liquid as a refrigerant, low temperature solvent and propellant for sprays.

(b) It is used for storing food stuffs by freezing on direct contact because it does not leave any undesirable taste or smell.

(2) **Diethyl ether (Sulphuric ether)** : It is the most important member of the ether series and is known as ether. It may also be regarded as an anhydride of C_2H_5OH (ethanol).



It is also known as Williamson's ethereal continuous process.

(ii) Properties

(a) It is a colourless, highly volatile and inflammable liquid having boiling point $34.5^\circ C$.

(b) It has a pleasant smell and burning taste.

(c) It is only slightly soluble in water but readily soluble in organic solvents.

(d) Diethyl ether is itself a very good solvent even for fats and oils.

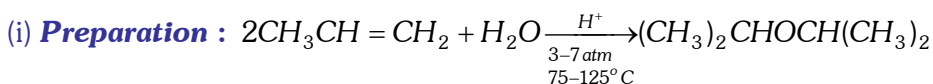
(e) It produces unconsciousness when inhaled.

Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

(iii) Uses

- It is used as a refrigerant.
- It is used as a reaction medium in $LiAlH_4$ reduction and grignard synthesis.
- It is used as an extracting solvent in laboratory.
- Mixture of alcohol and ether is used as petrol substitute under the trade name Natalite.
- It is used in perfumary and in the manufacture of smokeless powder.

(3) Di-isopropyl ether



(ii) **Properties** : It is a colourless liquid with a pear like odour having B.P. $68.5^\circ C$.

(iii) **Uses** : It is used for reducing knocking of petrol.

(4) Divinyl ether



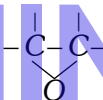
(ii) Properties

(a) It is highly inflammable liquid.

(b) It is colourless and boils at $28.3^\circ C$.

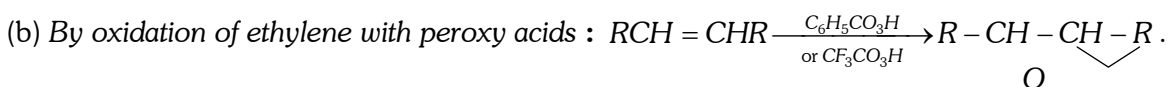
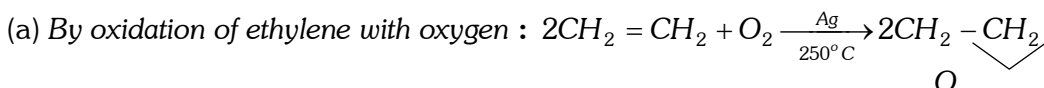
(iii) **Uses** : It is better anaesthetic than di ethyl ether because of its rapid action and rapid recovery from anaesthesia.

(5) Epoxides [oxirane] or cyclic ether

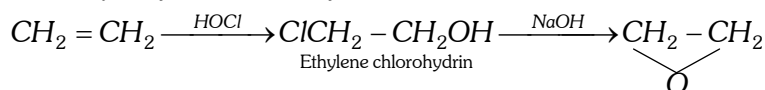


TEACHING CARE

(i) Preparation



(c) By treatment of ethylene chlorohydrin with NaOH



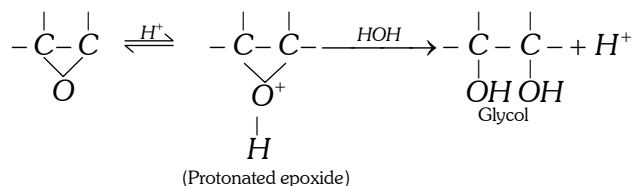
(ii) Properties

(a) It is a poisonous, flammable gas.

(b) Its B.P. is $14^\circ C$.

(c) It is very reactive compound because of its strained configuration.

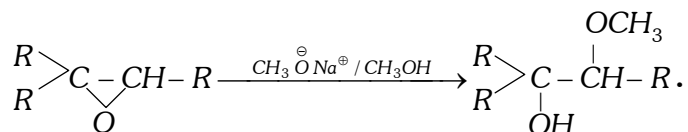
(d) An epoxide is converted into protonated epoxide by acid which can undergo attack by any nucleophilic reagent.



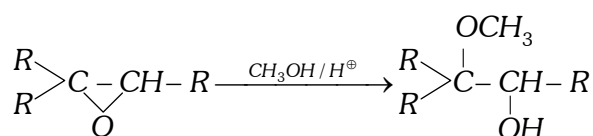
Some of the chemical reactions

Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

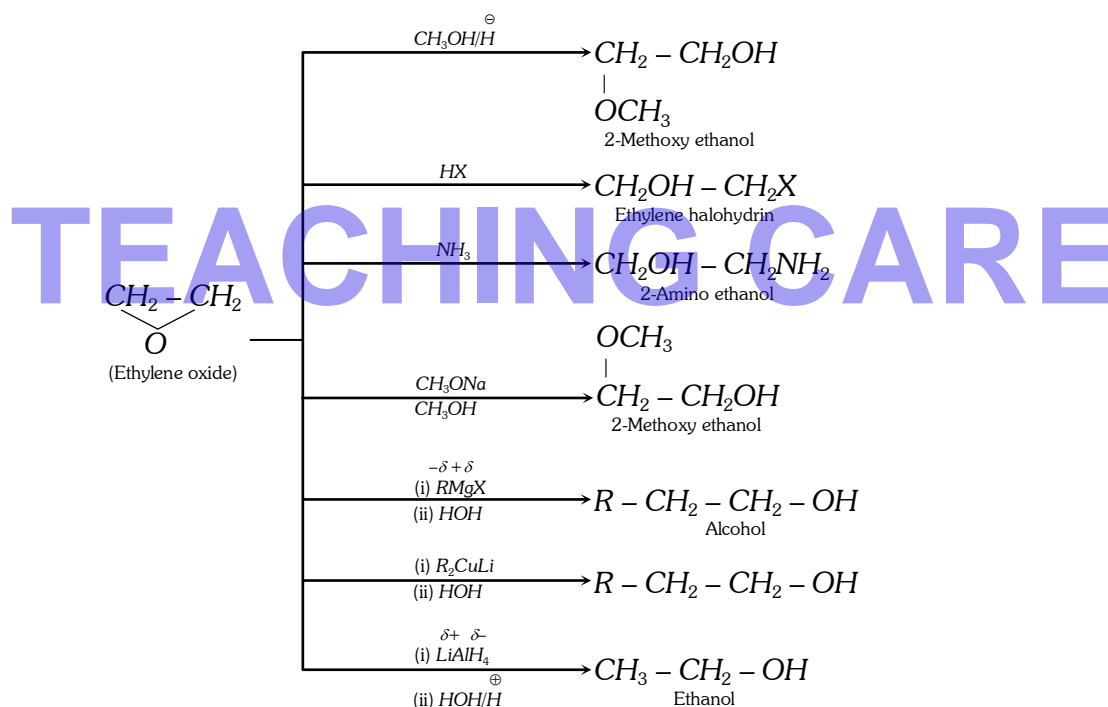
(a) *Case I* : Base catalysed ring opening : In this case nucleophile attack on less hindered carbon of the oxirane ring and reaction is SN^2 mechanism.



(b) *Case II* : Acid catalysed ring opening : Nucleophile attacks on carbon of oxirane ring which is highly substituted. SN^2 reaction is there.



Some reactions of oxirane are given below



Uses

- (a) It is used in the manufacture of ethylene glycol.
- (b) It is used in the manufacture of dacron.
- (c) It is used in the manufacture of solvent ethoxy ethanol used in varnishes and enamels for quick drying.

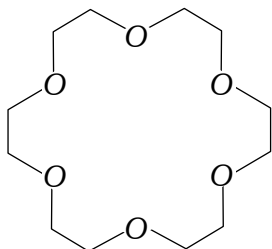
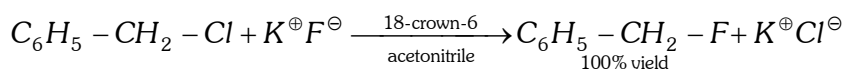
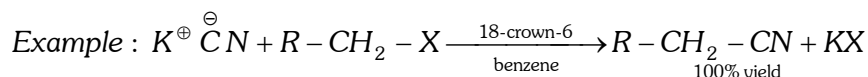
(6) **Crown ethers** : The crown ethers are heterocyclic poly-ethers usually with at least four oxygen atoms. These are called crown ethers because they have crown like shape.

18-crown-6 means compound is eighteen member ring compound out of which $[18 - 6 = 12]$ 12 atoms are carbon [i.e. six ethylene group $-CH_2 - CH_2 -$] and six atoms of oxygen.

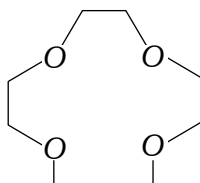
Crown ethers have remarkable affinity for metal ions.

Example : 12-crown-4 has affinity with Li^+ and 18-crown-6 has affinity with K^+ .

Hydroxy Compounds (Alcohals, Phenols) and Ethers Part 3

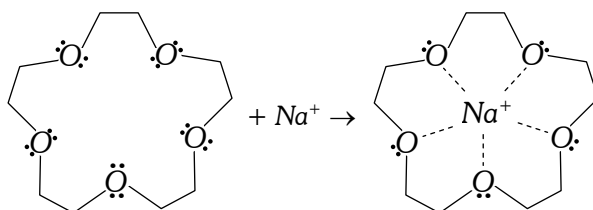


18-crown-6



12-crown-6

A crown ether binds certain metal ions depending on the size of the cavity.



Host

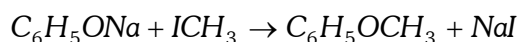
Inclusion compound

In this reaction, the crown ether is the 'host' and the species it binds is the 'guest'. The crown-guest complex is called an **inclusion compound**.

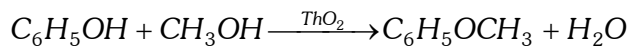
(7) Anisole (Methyl phenyl ether) $C_6H_5OCH_3$ or (methoxy benzene)

(i) Preparation

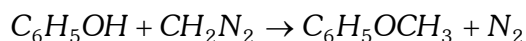
(a) By the action of methyl iodide on sodium phenoxide.



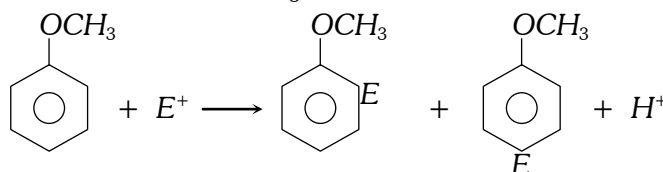
(b) By passing vapours of phenol and methyl alcohol over heated thoria.



(c) By methylation of phenol with diazomethane.



(ii) **Properties** : It is a pleasant smelling liquid. It is used as a solvent in some organic reactions. Anisole undergoes electrophilic substitution reactions. $-OCH_3$ group is *o*- and *p*- directing.



Anisole is decomposed by conc. hydroiodic acid again into phenol.

