

Ethers are the compound having $-O-$ as the functional group. These are classified as.

- Aliphatic ethers :- in which both R and R' are alkyl group.
 CH_3-O-CH_3 or $CH_3-O-C_2H_5$.

- Aromatic ethers :- in which R is alkyl and R' is aryl group.
or both R and R' are aryl group.

$Ph-O-R_{alkyl}$ or $Ph-O-Ph$.
alkyl aryl ether diaryl ether:
or phenolic ether Diphenyl ether:

- Symmetric or unsymmetric ether.
When both R and R' are same than symmetric and
when R and R' are different than unsymmetric or mixed.

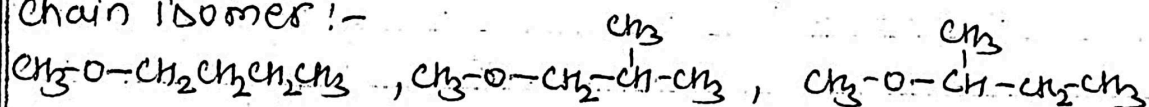
- Nomenclature :-

According to common system, ethers are named according to alkyl group attached to the oxygen atom. The name of the two alkyl or aryl group are written as separate word alphabetically followed by word ether.

According to IUPAC, ethers are named as alkoxy alkanes. The larger group forms parent chain while lower alkyl group is taken with the ethereal oxygen and forms a part of alkoxy group.

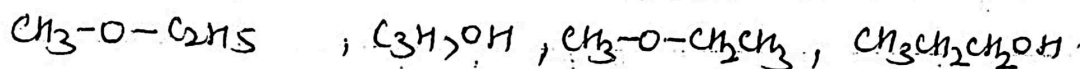
- Isomerism.

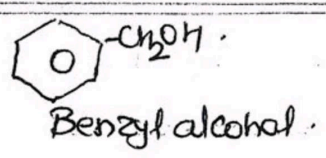
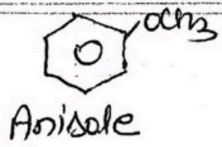
1. Chain isomer :-



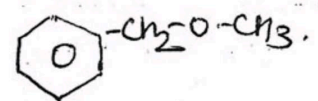
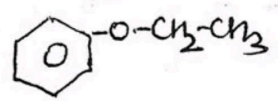
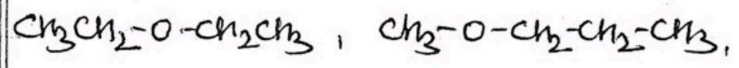
1-methoxybutane, 1-methoxy-2-methylpropane, 2-methoxybutane.

2. Functional Isomer -



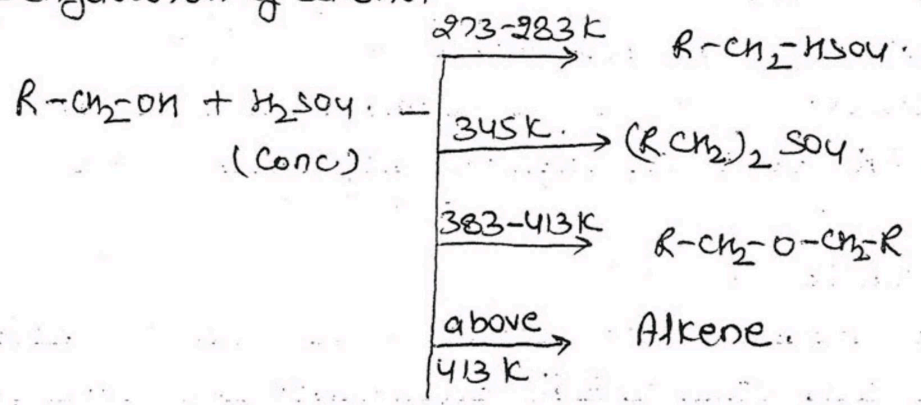


3. Metamerism :-

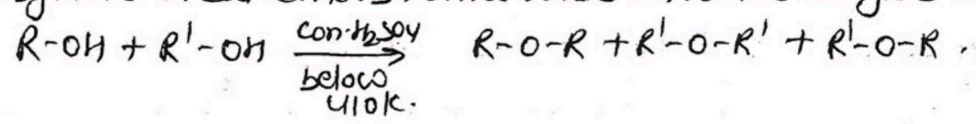


= method of Preparation.

I. Dehydration of alcohol.

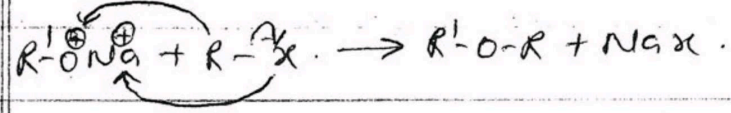
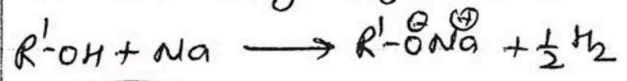


This method is generally not used for the preparation of unsymmetrical ethers. Otherwise mixture may be obtained.



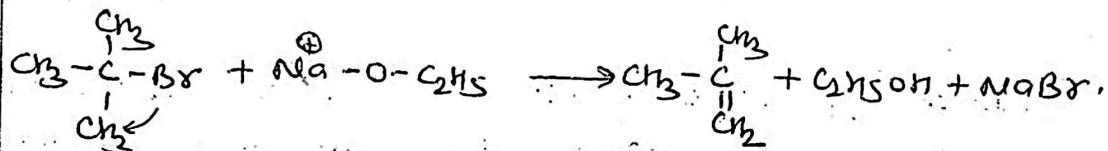
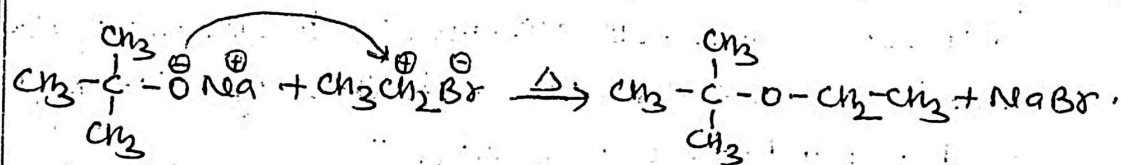
2. From alkyl halide by Williamson's synthesis :-

In laboratory symmetrical and unsymmetrical ethers are prepared by this method. In this method an alkyl halide is treated with sodium alkoxide prepared from sodium and alcohol. The reaction involve (S_N2) attack of an alkoxide ion on primary alkyl halide.



Note: For preparing unsymmetrical ethers, the halide used should be primary because 2° and 3° halide may form alkene as major products due to elimination process.

For 2° and 3° alkyl halide, elimination competes over substitution.

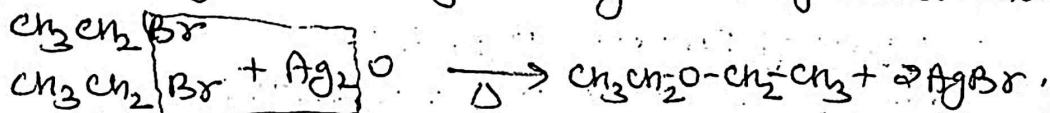


This is because alkoxides are not only nucleophile but strong base also.

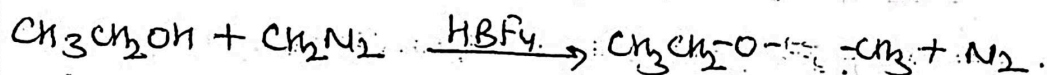
However, aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because aryl halide are less reactive towards nucleophilic substitution reaction than alkyl halide.



3. From alkyl halides by treating with dry silver oxide —



4. By the action of diazomethane on alcohol —



= Physical Properties.

1. Physical state: — Lower members are gases and higher members are low boiling liquids with pleasant smell.

2. Dipole moment — ether have bent or angular structure with sp^3 hybridisation and greater repulsion in two group as compare

to water molecule so ether have net dipole moment and angle greater than $(109^{\circ}28')$ is 111.7°

3. Boiling Points - ethers have low boiling points and lower than that of isomeric alcohols due to absence of Hydrogen bond and have comparable to those of alkanes of same Carbon numbers - but slightly less.

4. Solubility: The solubility of ethers is comparable to those of corresponding alcohols of the same molecular mass but slightly less.

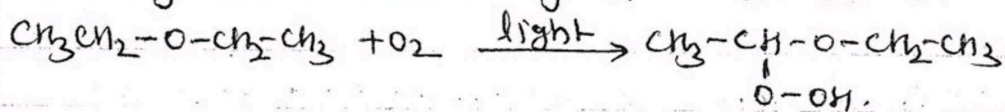
5. Density - All ethers are lighter than water.

= Chemical Properties

Ethers are quite inert and stable compound. They are the least reactive of the functional group. This is because the functional group of ether (-O-) does not contain any active site in their molecule as compared to (-OH) group.

A. Reaction of ethereal oxygen.

1. Action of air (Formation of Peroxide)

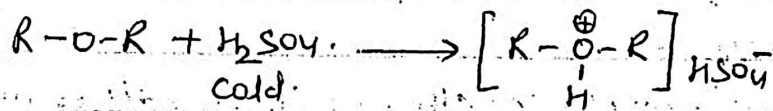


The oxidation occurs at the Carbon atom next to the ethereal oxygen to form hydroperoxide.

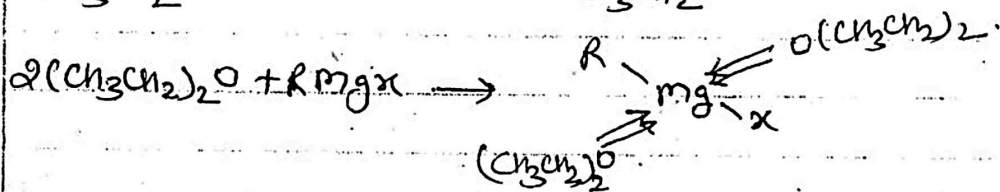
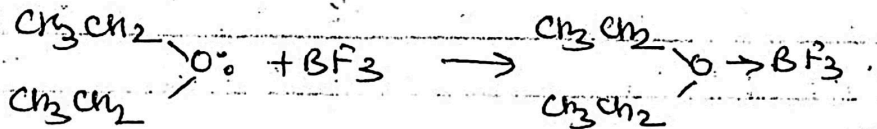
The ether peroxides are reduced to ether and I^- ion is oxidised to I_2 or Fe^{+2} salts are oxidised to Fe^{+3} .

2. Action with Conc. Acids (Formation of oxonium salt)

this test is used to distinguish between ether and alkane because alkane do not react with cold conc. Acids.



3. Reaction with Lewis acids :- Being Lewis base, ethers are form complexes with Lewis acids such as BF_3 , $AlCl_3$, $FeCl_3$ etc. these complexes are called etherates.



Due to the formation of the etherate, Grignard reagent dissolved in ether. So Grignard reagents are usually prepared in ethers. They cannot be prepared in benzene because benzene has no lone pair.

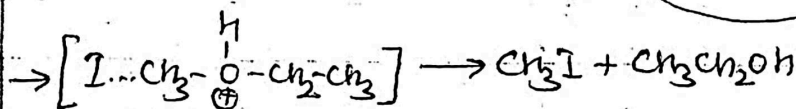
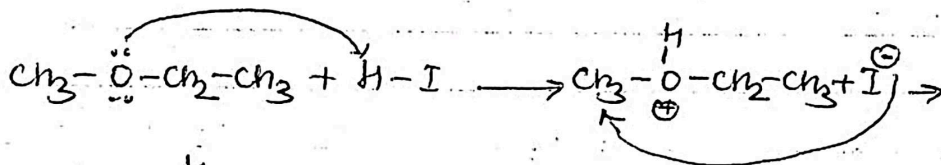
B Reaction Involving C-O bond. -

Carbon-oxygen bond in ethers can be cleaved under drastic condition.

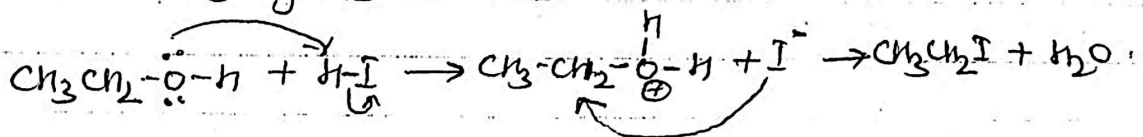
I Cleavage by halogen acids :-



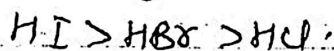
mech.



when excess of HI

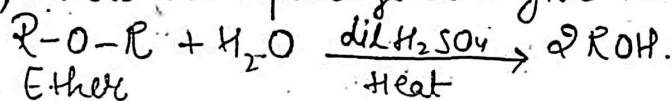


order of reactivity

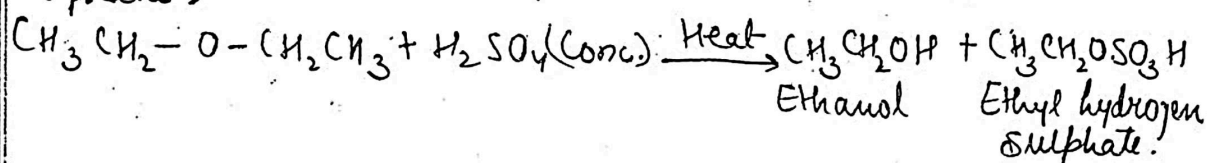


$O-CH_3$ is weaker than the bond between $O-C_6H_5$ because the carbon of phenyl is sp^2 hybridised. Therefore, the attack of halide ion breaks $O-CH_3$ bond to form CH_3-I . It may be noted that phenol does not react further to give halides because the sp^2 hybridised carbon of phenyl does not undergo nucleophilic substitution reactions.

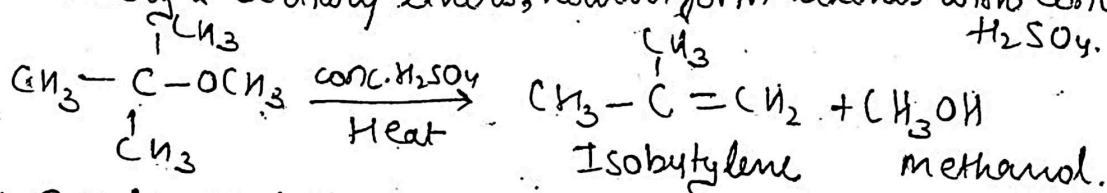
2. Cleavage by Sulphuric Acid:— On heating with dil H_2SO_4 under pressure, ethers are hydrolysed to give alcohols.



If conc. H_2SO_4 is used, ethers form alcohols & ethyl hydrogen sulphates.

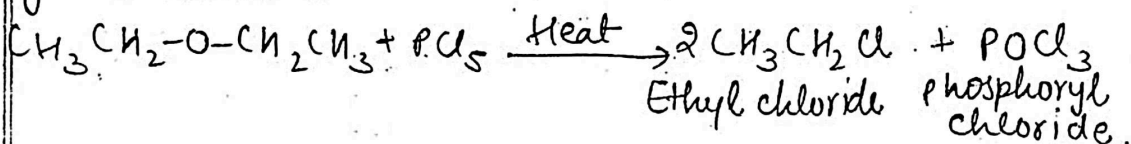


Secondary & tertiary ethers, however form alkenes with conc. H_2SO_4 .

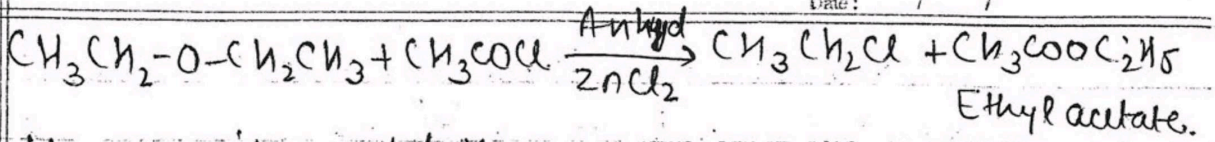


tert-Butyl methyl ether

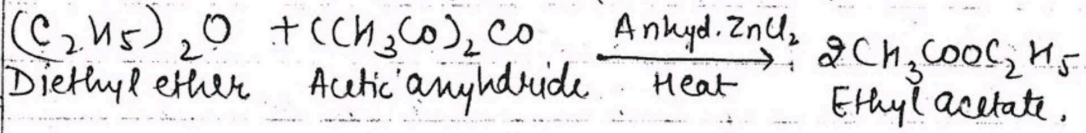
3. Cleavage with phosphorus pentachloride:— Ethers react with PCl_5 on heating to form alkyl chlorides as a result of cleavage of C-O bond.



4. Cleavage by acid chlorides:— Ethers react with acetyl chloride in the presence of anhydrous $ZnCl_2$ to give alkyl halide and esters.

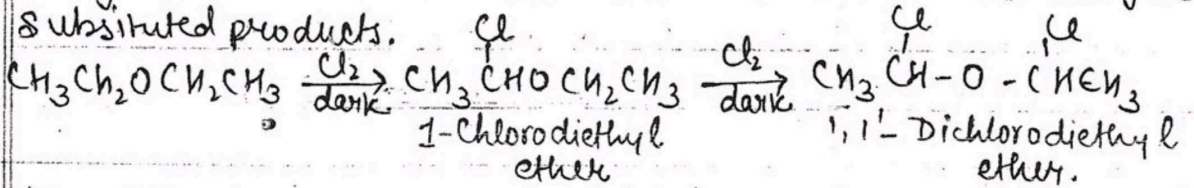


However with anhydrides only esters are formed.

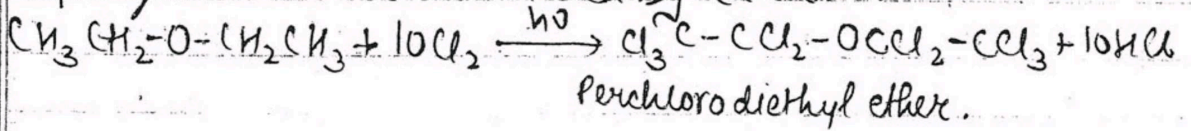


c. Reactions of Alkyl group.

1. Halogenation → Ethers react with Cl or Br in the dark to give substituted products.

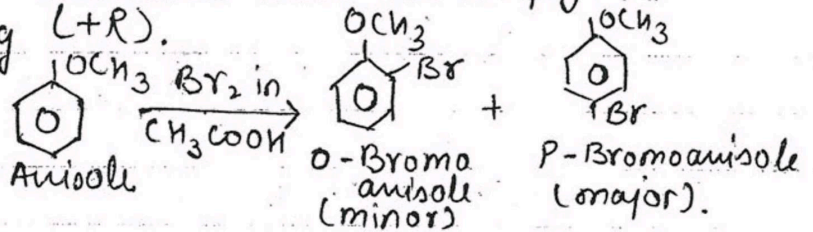


However, in the presence of light & excess of Cl all the hydrogen atoms are substituted by Cl atoms.

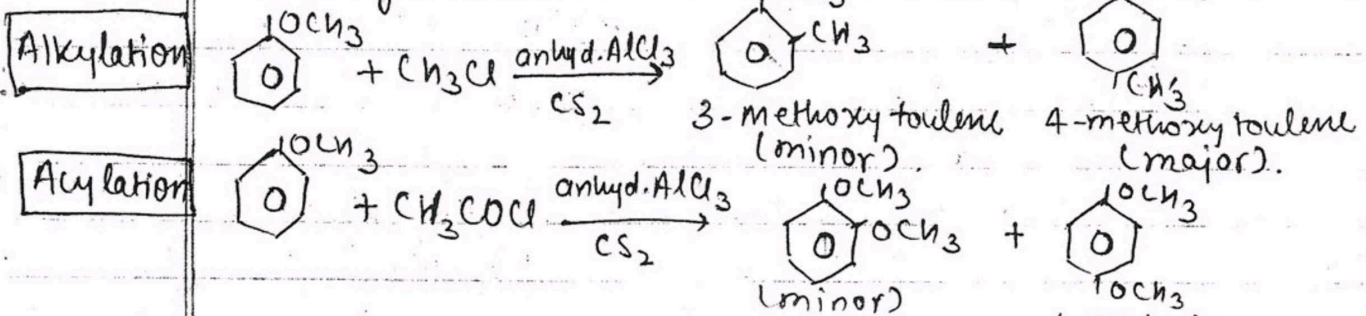


D. Ring Substitution in Aromatic Ethers :- Alkoxy gp. is ortho & para directing (L+R).

1. Halogenation :-



2. Friedel-Craft reaction :-



3. Nitration :-

