

ETHER

Preface

Organic compounds in which divalent oxygen atom is attached with two alkyl groups are called ether. It is an easy and simple topic. This topic deals with its general methods of preparation, its various characteristics, physical properties & chemical reactions

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develop better understanding of the chapter and to have better grasping level in the class.

Total number of Questions in Ether are :	
(i) In chapter Examples	4
(iii) Solved Examples	10
Total no. of questions	14

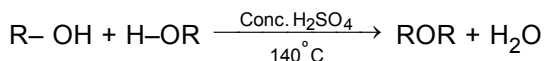
1 GENERAL POINTS ::

- It is dialkyl derivative of water or alkoxy derivative of alkane or monoalkyl derivative of alcohols.
- Their general formula is $C_nH_{2n+2}O$ or $C_nH_{2n+1}O$
- Hybridisation state of oxygen is sp^3 and bond angle is 110° due to counter balance repulsion of alkyl groups.
- If both alkyl groups are similar then these are called as simple ether, if different they are called as mixed ether.
- Carbon oxygen bond length is 1.42 \AA .
- Ether shows chain, position metamerism and functional isomerism. Ethers are functional isomers of alcohols.
- In IUPAC system ethers are called as 'Alkoxy alkane'.

2 METHODS OF PREPARATION ::

2.1 Dehydration of alcohols :

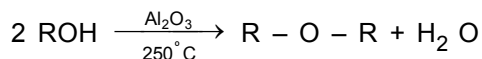
(a) With conc. H_2SO_4 at $140^\circ C$:



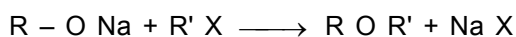
Lower ether are prepared industrially by this method.

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

(b) With Al_2O_3 at $250^\circ C$:



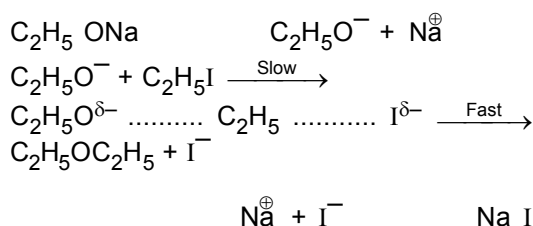
2.2 Williamson synthesis : Heating of alkyl halides with sodium or potassium alkoxides. This is a very good method for the preparation of simple and mixed ethers.



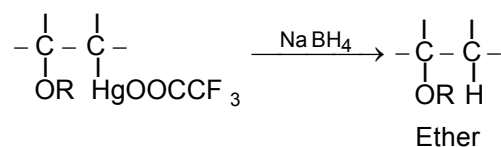
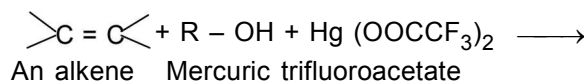
- Order of reactivity of primary halides is : $CH_3X > CH_3CH_2X > CH_3CH_2CH_2X$
- Tendency of alkyl halides to undergo elimination is : $3^\circ > 2^\circ > 1^\circ$

- For better yield, the alkyl halide should be primary and alkoxide should be secondary or tertiary. This method is not applicable to tertiary alkyl halides, because the alkoxide ions being both powerful nucleophiles and bases would bring dehydrohalogenation of the tertiary alkyl halides to form alkenes preferentially.

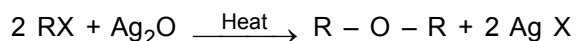
Mechanism : (S_N2)



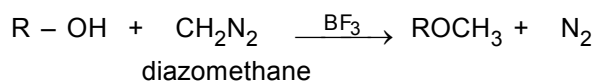
2.3 Alkoxy mercuriation – demercuriation :



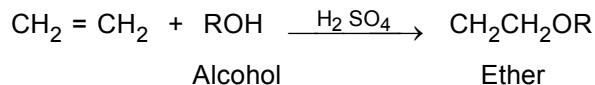
2.4 Heating alkyl halides with silver oxide (dry)



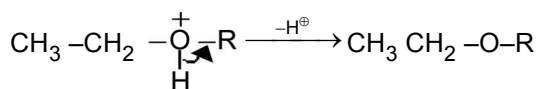
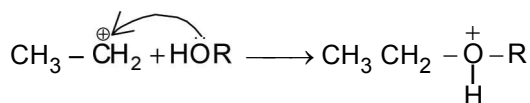
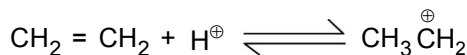
2.5 Action of diazomethane on alcohols : Methyl ethers are formed by this method.



2.6 Addition of alcohols to alkenes :



Mechanism : 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.

Examples based on

Methods of Preparation of Ether

Ex.1 Ethyl iodide reacts with moist Ag_2O to form—
 (A) Ether (B) Alcohol
 (C) Alkene (D) Alkane **Ans.(B)**

Sol. $\text{CH}_3\text{-CH}_2\text{-I} + \text{Ag-O-Ag} + \text{I-CH}_2\text{-CH}_3$
 $\longrightarrow \text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3 + 2\text{AgI}$

Ex.2 Ethyl iodide reacts with sodium ethoxide to form —
 (A) Ethene (B) Ethoxy ethane
 (C) Alcohol (D) None **Ans. (B)**

Sol. Ethers are formed when ethyl iodide reacts with sodium ethoxide .
 $\text{CH}_3\text{-CH}_2\text{-I} + \text{Na-O-CH}_2\text{-CH}_3$
 $\longrightarrow \text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_3 + \text{NaI}$

3 PHYSICAL PROPERTIES

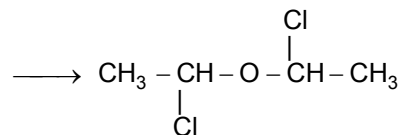
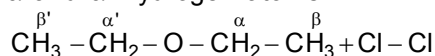
- (a) Ethers are colourless with specific smell liquid. These are highly volatile liquid due to low boiling point.
- (b) These are insoluble in water although they have oxygen atom, but their oxygen atom is neutral due to steric hindrance of both alkyl groups.
- (c) Ether is also called as inert solvent of aliphatic chemistry, due to inertness of oxygen.
- (d) Due to inertness of oxygen, it is best solvent for preparation of highly reactive compounds such as G.R.
- (e) It is used as an anesthetic.
- (f) Boiling point of diethyl ether is 34.5°C .

4. CHEMICAL PROPERTIES

4.1 Halogenation : -

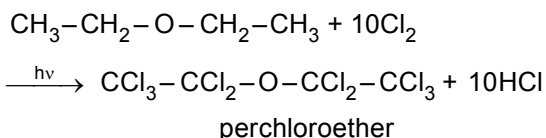
(a) In dark : -

Halogen reacts with ether in dark and substitutes α and α' hydrogen atoms.

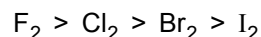


α, α' -dichlorodiethyl ether

(b) In Light : -

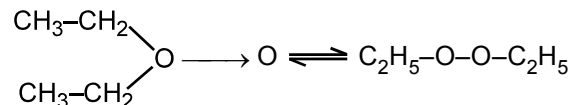
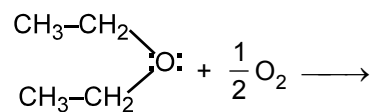


The reactivity order of halogen in halogenation is-

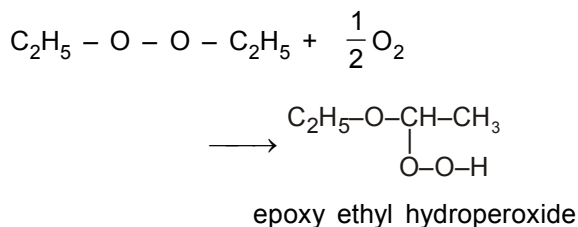


4.2 Oxidation : -

When ether is left open in air, it reacts with atmospheric oxygen and forms peroxide.



When ether is exposed to air for a long time then the above peroxide changes into another peroxide which is called as 'Epoxy ethyl hydroperoxide' and is explosive in nature.

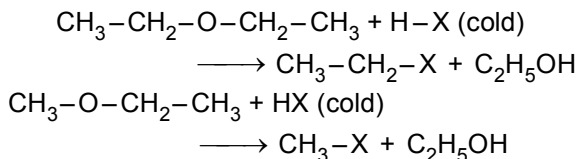


Note :

When ether is oxidised with acidic $\text{K}_2\text{Cr}_2\text{O}_7$ then it forms aldehyde.

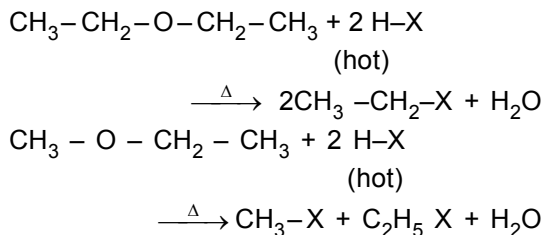
4.3 Reaction with HX : -

(a) If HX is cold : -



Note : If we take unsymmetrical ether with cold H-X then smaller alkyl group forms alkyl halide.

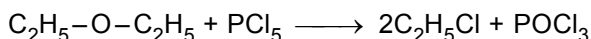
(b) If HX is hot : -



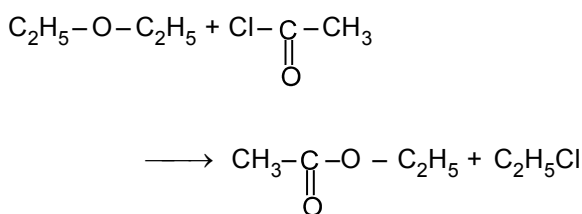
Note :

The above reaction is called '**Ziesel's Method of Alkoxy group estimation**'. If we take unsymmetrical ether with hot H - X then we get two different types of alkyl halide and by the test of both alkyl halide we can confirm alkoxy group of ether.

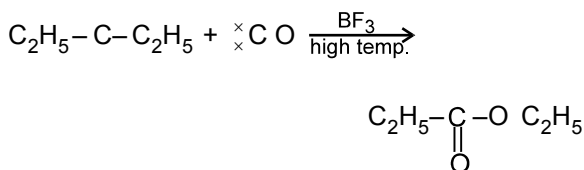
4.4 Reaction with PCl₅ : -



4.5 Reaction with Acetyl Chloride : -

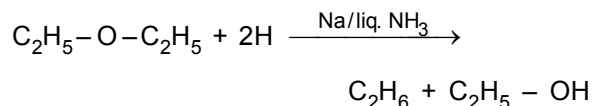


4.6 Reaction with Carbon monoxide :-



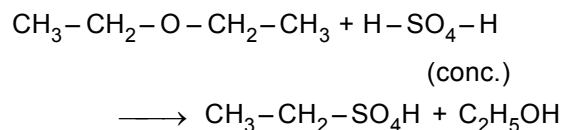
Note : In the case of unsymmetrical ether, CO-group attaches with the bigger alkyl group.

4.7 Reduction :-

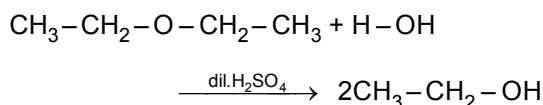


4.8 Reaction with H₂SO₄ :-

(a) With conc. H₂SO₄ :-

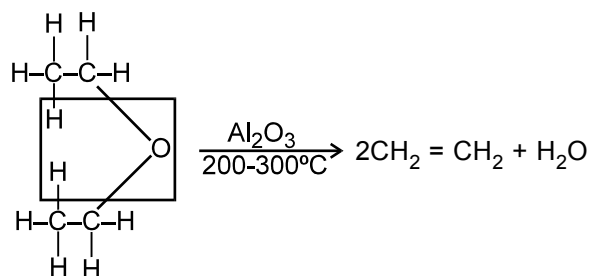


(b) With dil. H₂SO₄ :-



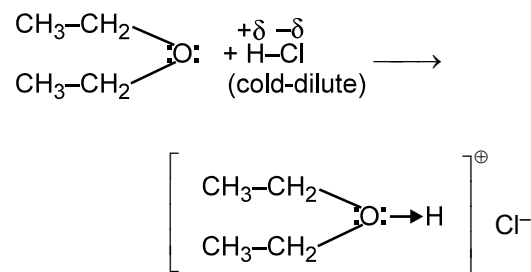
4.9 Dehydration :-

When vapours of ether are passed on heated alumina then by the elimination of water alkene is formed.

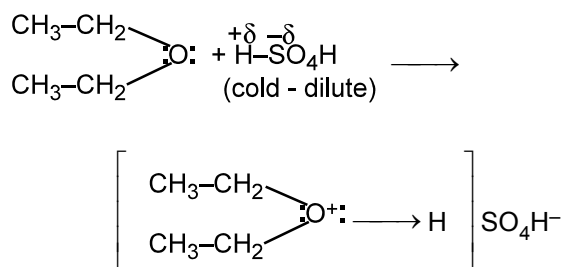


4.10 Preparation of Oxonium Salt :-

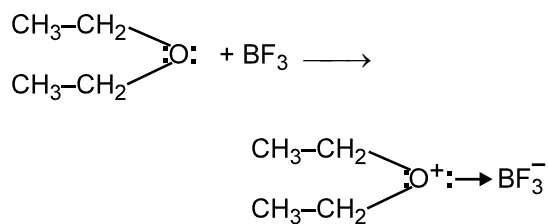
Oxygen of ether has lone pair of electron so it can form salt with mineral acid or lewis acid by forming coordinate bond with it. Such type of salt is called Oxonium Salt.



diethyl oxonium chloride



diethyl oxonium hydrogen sulphate

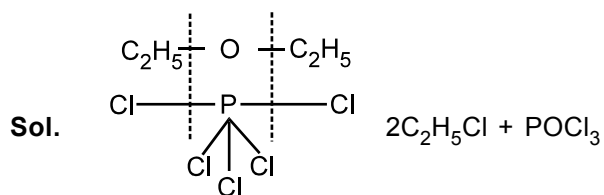


boron trifluoride etherate

Ex.4 Ether reacts with PCl_5 to form –

- (A) Ethyl chloride
- (B) Phosphorous oxy trichloride
- (C) Both (A) & (B)
- (D) None

Ans.(C)



Examples based on **Chemical properties**

Ex.3 Ether reacts with halogen in dark and in light to give –

- (A) Same products
- (B) Different products
- (C) It does not react in light
- (D) It does not react in dark

Ans. (B)

Sol. Ether on halogenation, in dark gives α , α' - dichlorodiethyl ether while in light gives perchloro ether.

SOLVED EXAMPLES

Ex.1 An example of a compound with functional group — O — is -

- (A) Acetic acid (B) Methyl alcohol
(C) Diethyl ether (D) Acetone

(Ans. C)

Sol. Ethers are R — O — R' or R — O — R

Ex.2 An organic compound A reacts with sodium metal and forms B. On heating with conc. H_2SO_4 , A gives diethyl ether. So A and B are -

- (A) C_3H_7OH and CH_3ONa
(B) CH_3OH and CH_3ONa
(C) C_4H_9OH and C_4H_9ONa
(D) C_2H_5OH and C_2H_5ONa

(Ans. D)

Sol. C_2H_5OH (A) reacts with Na to give C_2H_5ONa (B). C_2H_5OH (A) also reacts with conc. H_2SO_4 to form diethyl ether because of dehydration.

Ex.3 In the presence of an acid catalyst, two alcohol molecules will undergo dehydration to give -

- (A) Ester
(B) Anhydride
(C) Ether
(D) Unsaturated hydrocarbon

(Ans. C)

Sol. $ROH + HOR \xrightarrow[-H_2O]{Acid} ROR$

Ex.4 A carbon compound A forms B with sodium metal and again A forms C with PCl_5 , but B and C form diethyl ether. Therefore A, and B and C are -

- (A) C_2H_5OH , C_2H_5ONa , C_2H_5Cl
(B) C_2H_5Cl , C_2H_5ONa , C_2H_5OH
(C) C_2H_5OH , C_2H_6 , $C_2H_5Cl_2$
(D) C_2H_5OH , C_2H_5Cl , C_2H_5ONa

(Ans. A)

Sol. C_2H_5OH (A) + Na \rightarrow C_2H_5ONa (B)
 C_2H_5OH (A) + $PCl_5 \rightarrow C_2H_5Cl$ (C)
 C_2H_5ONa (B) + C_2H_5Cl (C) $\rightarrow C_2H_5OC_2H_5$
+ NaCl

Ex.5 When ethyl iodide is treated with dry silver oxide, it forms -

- (A) Ag (B) $C_2H_5OC_2H_5$
(C) C_2H_5OH (D) $COOH - COOH$

(Ans. B)

Sol. $2C_2H_5I + Ag_2O \rightarrow C_2H_5OC_2H_5 + 2AgI$

Ex.6 C—O—C bond angle in diethyl ether is about-

- (A) 180° (B) 110°
(C) 150° (D) 90°

(Ans. B)

Ex.7 On strong oxidation, diethyl ether gives -

- (A) Ethyl alcohol (B) Acetaldehyde
(C) Acetic acid (D) Methyl alcohol

(Ans. B)

Sol. $CH_3CH_2OCH_2CH_3 \xrightarrow[-H_2O]{[O]} 2CH_3CHO$.

The oxidation may be carried out with $K_2Cr_2O_7$ + conc. H_2SO_4 or alkaline $KMnO_4$ at elevated temperature.

Ex.8 The reaction of $CH_3OC_2H_5$ with HI gives -

- (A) CH_3I (B) C_2H_5OH
(C) $CH_3I + C_2H_5OH$ (D) $C_2H_5I + CH_3OH$

(Ans. C)

Sol. $CH_3OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$. In the case of mixed ethers such as methyl ethyl ether the halogen attaches to a small and less complex group. So the products are CH_3I and C_2H_5OH but not the C_2H_5I and CH_3OH .

Ex.9 The number of methoxy groups in a compound can be determined by treating it with -

- (A) HI and $AgNO_3$
(B) Sodium carbonate
(C) Sodium hydroxide
(D) Acetic acid

(Ans. A)

Sol. $CH_3OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$
 $CH_3I + AgNO_3 \rightarrow AgI + CH_3NO_3$

Ex.10 An ether is heated with phosphorous penta sulphide to give -

- (A) Alkanthiol (B) Dialkyl sulphide
(C) Hydrogen sulphide (D) Thioester

(Ans. B)

