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Syllabus Unit-IV Ethers and Epoxides

Ethers: Nomenclature of ethers and their methods of preparation, chemical reactions - Reaction with HI, hot and cold taking symmetric and unsymmetrical ethers.

Crown ethers: Definition, examples, use of crown ethers as phase transfer catalysts. **Epoxides:** Synthesis of 1,2-epoxy ethane and 1,2-epoxycyclopentane, acid catalysed ring opening of 1,2-epoxycyclopentane in aqueous solution.

Ethers

Ethers are compounds in which oxygen is bonded to two alkyl or aryl substituents. They are also regarded as derivatives of water in which both the hydrogen atoms have been replaced by alkyl or aryl groups. Divalent oxygen in ether is known as ethereal oxygen.

If the substituents are identical, the ether is asymmetrical ether (R-O-R). If the substituents are different, the ether is unsymmetrical ether (R-O-R¹).

Nomenclature

1. **The common names**: The name of an ether is given by citing the two groups attached to the ether oxygen in alphabetical order, followed by the word ether.

CH ₃ -O-CH ₃	CH_3 -O- C_2H_5	CH ₃ -OC ₆ H ₅
Diethylether	Ehtylmethylether	Methylphenylether

2. IUPAC names: Ethers are named as alkoxyalkanes, alkoxyalkenes, and alkoxyarenes. Longest chain is parent chain and is the root word.

CH ₃ -O-CH ₃	CH_3 -O- C_2H_5	CH_3 -O- C_6H_5	C_2H_5 -O- C_6H_5
Methoxymethane	Methoxyethane	Methoxybenzene	Ethoxybenzene

3 hours

Methods of Preparation of Ethers:

1. Preparation of Ethers by Dehydration of Alcohols

In the presence of protic acids (like sulphuric acid) alcohols undergo dehydration to produce ethers at 413 K (i. e 140 0 C). This is an ideal method of preparation through primary alcohols.

This method is applicable for symmetrical ethers.

$$2 \text{ R-OH} \xrightarrow{H_2SO_4} \text{ R-O-R} + H_2O$$
Alcohol Ether
$$2 \text{ CH}_3\text{-OH} \xrightarrow{H_2SO_4,140 \text{ }^{\circ}\text{C}} \text{ CH}_3\text{-O-CH}_3 + H_2O$$
Methyl alcohol Dimethyl ether
$$2 \text{ CH}_3\text{CH}_2\text{-OH} \xrightarrow{H_2SO_4,140 \text{ }^{\circ}\text{C}} \text{ CH}_3\text{CH}_2\text{-O-CH}_3\text{CH}_2 + H_2O$$
Ethyl alcohol Diethyl ether

Uni-molecular dehydration may compete:

2. Preparations of Ethers by Williamson Synthesis

Williamson synthesis is versatile method for the preparation of symmetrical and asymmetrical ethers in laboratories. In this method, an alkyl halide is reacted with sodium alkoxide which leads to the formation of ether. The reaction generally follows the ${S_N}^2$ mechanism for primary alcohol.



As we know alkoxides are strong bases and they can react with alkyl halides leading to elimination reactions. Williamson synthesis gives higher yield in the case of primary alkyl halides. In the case of secondary alkyl halides, elimination competes with substitution. Formation of only elimination products is observed in tertiary alkyl halide

Chemical Reactions

Although ethers are relatively inert toward reaction, they usually show good solvent properties for many non polar organic compounds. An acid-catalyzed cleavage occurs when hydriodic acid (HI) reacts with ether. This reaction proceeds via a nucleophilic substitution mechanism.

1. HI under cold condition ethers give alcohol and alkyl halide. In case of mixed ethers higher alkyl group forms alcohol.



2. Under hot condition with excess of HI ethers give alkyl halides. However phenyl ethers always give phenol and alkyl halide as products.

 $C_{2}H_{5} \longrightarrow C_{2}H_{5} + 2 HI \longrightarrow 2C_{2}H_{5} \longrightarrow I + H_{2}O$ Ethyl Iodide $C_{2}H_{5} \longrightarrow CH_{3} + 2 HI \longrightarrow C_{2}H_{5} \longrightarrow I + H_{3}C \longrightarrow I + H_{2}O$ Ethyl methyl ether $Ethyl iodide \qquad Methyl Iodide$ $Methyl Iodide \qquad H_{3}C \longrightarrow I + HO \longrightarrow CH_{3}$ Anisole $Methyl Iodide \qquad Phenol$

Crown ethers

Crown ethers are cyclic compounds that have several ether linkages. These are macrocyclic polyethers .Crown ethers are named as [X]-crown-Y, where X is the total number of atoms in the ring and Y is the number of oxygen atoms in the ring.

Examples:



Crown Ethers as Phase transfer catalyst (PTS):

Phase transfer catalyst is a substance which can transfer a reagent from one phase to other thereby enhancing the rate of reaction.

The ability of crown ethers to form complex with various ions or molecules and ability to transfer ionic reagents from aqueous or solid phase to organic phase, make them as good phase transfer catalyst. Following Features make them good phase transfer catalyst.

- 1. These molecules have a hydrophobic exterior and a hydrophilic interior.
- 2. Cations can get into the central cavity of these compounds and are immobilized due to the negative environment of the heteroatoms.
- 3. The cavity size determines which cations can be encapsulated inside the cavity
- 4. The interactions between the cation and the crown ethers are purely electrostatic, that is through ion dipole attractions.
- 5. Thus each crown ether can selectively capture a cation of a specific size.
- 6. The solvating capacity of crown ethers towards metal ions can be termed as "Host- Guest relationship".

By using Crown ether as PTC yield of the reaction can be enhanced. Ex Crown ether PFDMC (fluorous derivatives of dibenzo-18-crown-6-ether) increases the nucleophilic substitution reaction to 96%.

	KI, 12h		
$C_8H_{17}Br$	>	$C_8H_{17}I$	
l-bromooctane	Crown ether (PFDMC)	1-iodooctane	96% yield

Epoxides

Three-membered cyclic ethers are called as **epoxides**, They are also called as **oxiranes**. **Nomenclature**

Common names: Common names are derived from the name of the alkene from which the epoxide is derived and are named as **alkeneoxide**.

IUPAC names: Simple epoxides are named as derivatives of oxirane or by prefixing **alkane** with epoxy.

Structure	Common Name	IUPAC name
H ₂ C Or CH ₂	Ehyleneoxide	Oxirane Or 1,2-epoxyethane
H ₃ C CH ₃	2-Buteneoxide	2,3-epoxybutane or 2,3-dimethyloxirane
0	Cyclohexeneoxide	1,2- epoxycyclohexane
°	Cyclopenteneoxide	1,2- epoxycyclopentane

Synthesis

I. Synthesis of 1, 2-epoxyethane.

1. Ethylene (H₂C=CH₂) is reacted with oxygen (O₂) at 200–300 °C, in the presence of a silver catalyst supported on alumina.

$$\begin{array}{c} CH_2 = CH_2 + \underbrace{O_2}_{\text{beat}} \xrightarrow{Ag} \underbrace{O_1}_{\text{beat}} \xrightarrow{O_2} CH_2 - CH_2 \\ epoxyethane}_{(ethylene oxide)} \end{array}$$

2. Reacting 1-chloro-2-hydroxyethane with a base like sodium ethoxide.

$$HO-CH_2-CH_2-CI \xrightarrow{base} CH_2-CH_2$$

1-chloro-2-hydroxyethane

II. Synthesis of 1, 2-epoxycyclopentane

By epoxidation of Cyclopentene using peracids like m-chloroperbenzoicacid.



Chemical Reactions

Acid catalysed ring opening of 1, 2-epoxycyclopentane in aqueous solution.

Due to ring strain epoxides are more susceptible to ring opening reaction. In presence of acids like H_2SO_4 they undergo ring opening reaction to give pentane-1, 2-diol. (It is an acid catalysed hydrolysis reaction)



1,2-epoxycyclopentane

Cyclopentane-1,2-diol