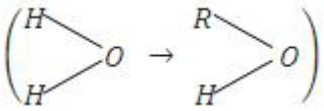
ORGANIC CHEMISTRY

TOPIC: 3

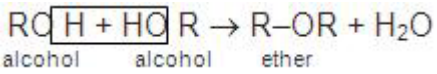
ETHERS

VERY SHORT ANSWER QUESTIONS

1. What are ethers?

(i) Ethers are regarded as dialkyl derivative of water 

or

Anhydride of alcohols 

or alkyl of alcohol (R-OH → R-OR).

(ii) Genera formula of ethers is $C_nH_{2n+2}O$.

(iii) Ethers consist of two alkyl groups attached on oxygen atom. R-O-R.

2. **What are simple ethers?**

Ans: Simple or symmetrical ethers: Both the alkyl groups attached on oxygen atom are same.

e.g. R—O—R or CH_3OCH_3

3. **What are mixed ethers?**

Ans: Mixed or unsymmetrical ethers: Both the alkyl groups attached on oxygen atom are different.

e.g. R—O—R' or $CH_3OC_2H_5$

SHORT ANSWER QUESTIONS

1. **Write the classification of ethers.**

Ans: Ethers are classified as

(a) Simple or symmetrical ethers: Both the alkyl groups attached on oxygen atom are same.

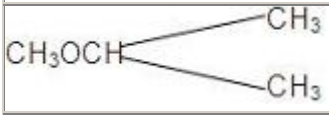
e.g. R—O—R or CH_3OCH_3

(b) Mixed or unsymmetrical ethers: Both the alkyl groups attached on oxygen atom are different.

e.g. R—O—R' or $CH_3OC_2H_5$

2. **Write the nomenclature of ethers.**

Nomenclature: Ethers are supposed to have no functional group and thus IUPAC nomenclature does not provide their suffix name. These are named (in IUPAC) as alkoxy alkane, the smaller alkyl group alongwith oxygen is called alkoxy substituent.

Formula	Trivial Name	IUPAC Name
CH_3OCH_3	dimethyl ether	methoxymethane
$CH_3OCH_2CH_3$	methyl ethyl ether	methoxyethane
$CH_3OCH_2CH_2CH_3$	methyl propyl ether	1-methoxypropane
	methyl isopropyl ether	2-methoxypropane
$CH_3CH_2OCH_2CH_3$	diethyl ether	ethoxyethane

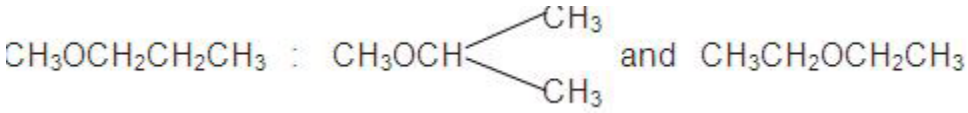
3. **Explain the isomerism in ethers.**

Isomerism

(a) Ethers show functional isomerism with alcohols.

CH_3OCH_3 & CH_3CH_2OH

(b) Ethers with at least four carbon atoms show metamerism due to different alkyl groups attached on bivalent O atom.



3. Explain the structure and chemical nature of ethers.

Ans: Structure : In CH_3OCH_3, the central oxygen atom is sp^3 hybridized with two completely filled sp^3 orbitals having lone pair of electrons and two half filled sp^3 hybridized orbitals. Also carbon atoms are sp^3 hybridized and both the half filled sp^3 orbitals of O atom from strong s (C-O) bonds with half filled sp^3 orbitals of two adjacent carbon atoms of alkyl groups.

The C-O-C bond angle is about 110^oC which is quite closer to 109^o 28' of sp^3 hybridized nature, inspite of the fact that lone pair of electrons must result in contraction in bond angles. This is because of the fact that presence of alkyl groups on O atom counterbalances the repulsion between the lone pair - bond pair electrons and leads to the bond angle nearer to 109^o 28'.

4. **Explain Williamson synthesis.**

Ans: Williamson synthesis: Heating of alkyl halides with sodium or potassium alkoxide give ethers. This is a good method to get better yield of mixed ethers in comparison to above methods. This reaction obeys S_N2 mechanism.

$$R\text{-}ONa + R'I \xrightarrow[\Delta]{ether} R\text{-}OR' + NaI$$

$$R\text{-}ONa + RI \xrightarrow[\Delta]{ether} R\text{-}OR + NaI$$

Note : alkyl halides undergo elimination reaction with sodium alkoxide to produce alkenes

$$(CH_3)_3CCI \xrightarrow{RONa} (CH_3)_2C{=}CH_2 + HCI$$

Therefore to prepare t. alkyl-alkyl ether, one must take an alkyl halide with tertiary alkoxide.

$$CH_3CI + (CH_3)_3CONa \rightarrow (CH_3)_3COCH_3 + NaCI$$

Ethers so obtained are contaminated with traces of water and alcohol. Absolute ethers do not possess traces of water or alcohol and are used in preparation of Grignard reagent. Absolute ethers are obtained by distilling ordinary ether with conc. H_2SO_4 followed by storing over metallic sodium.

LONG ANSWER QUESTIONS

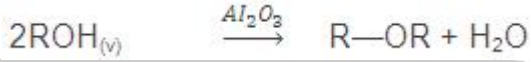
1. **Explain the preparation of Ethers.**

Preparation

(i) By dehydration of alcohols:

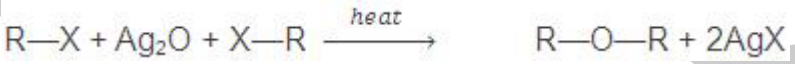
(a) Excess of alcohol on heating with conc. H_2SO_4 to 140°C leads the formation of ethers.

(b) On passing alcohol vapours over heated alumina at 250°C, dehydration of alcohols leads to the formation of ethers.



Note: The secondary and tertiary alcohols on dehydration lead to the formation of alkene as main product.

(ii) By alkyl halides: Alkyl halides on heating with dry Ag_2O (in ether) give ethers.

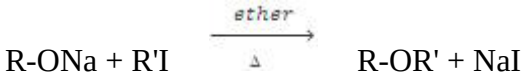


Note: Both methods (i) & (ii) can be used for the preparation of simple ethers. In case of mixed alcohols or mixed halides, the yield is reduced to 1/3rd part producing all possible ethers.

$$R\text{-}OH + HOR' \rightarrow ROR' + R\text{-}OR + R'\text{-}OR'$$

$$R\text{-}X + Ag_2O + R'X \rightarrow ROR' + ROR + R'\text{-}OR'$$

(iii) Williamson synthesis: Heating of alkyl halides with sodium or potassium alkoxide give ethers. This is a good method to get better yield of mixed ethers in comparison to above methods. This reaction obeys S_N2 mechanism.



$$R\text{-}ONa + RI \xrightarrow[\Delta]{ether} R\text{-}OR + NaI$$

Note: alkyl halides undergo elimination reaction with sodium alkoxide to produce alkenes

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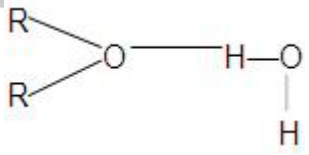
2. **Explain the physical and chemical properties and uses of Ethers.**

Chemical Properties of Ethers

(i) Ethers are colourless, sweet smelling, highly volatile, inflammable liquids

(ii) Ethers are sparingly soluble in water due to H-bonding



(iii) The boiling points of ethers are much lower than corresponding alcohols as they show no hydrogen bonding within themselves like alcohols.

(iv) Vapours of diethyl ether cause unconsciousness on inhaling and thus used as anaesthetic agent.

(v) Ethers having bond angle C-O-C to about 110^o and thus dipole moment of two C-O bond does not cancel out each other. Thus ethers are polar but weak polarity exist (μ for diethyl ether = 1.18 D)

Chemical nature

Ethers are less reactive than compounds containing functional groups. They neither react with active metals, strong bases nor with reducing & oxidizing agents.

The chemical properties of ethers are due to alkyl gp, lone pair of electrons on oxygen atom and cleavage of C-O bond.

1. Reactions due to alkyl group:

(a) Combustion: Ethers are highly inflammable and form explosive mixture with air giving CO_2 and water.

$$C_2H_5O\,C_2H_5 + 6O_2 \rightarrow 4CO_2 + 5H_2O$$

(b) Halogenation: The alkyl group of ether undergoes substitution reaction with chlorine or bromine to give a-halogenated ethers in absence of sunlight. However in presence of sunlight all the hydrogen atoms of ethers are substituted.

$$CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2,dark} CH_3CHClOCHClCH_3$$

α α'-dichloro diethylether

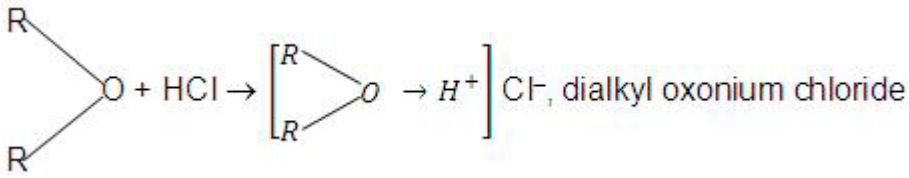
$$CH_3CH_2OCH_2CH_3 \xrightarrow{Cl_2,dark} C_2Cl_2OC_2Cl_5$$

Perchloro diethylether

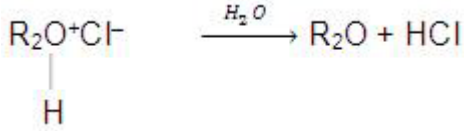
2. Reaction due to ethereal oxygen:

(a) Basic nature:

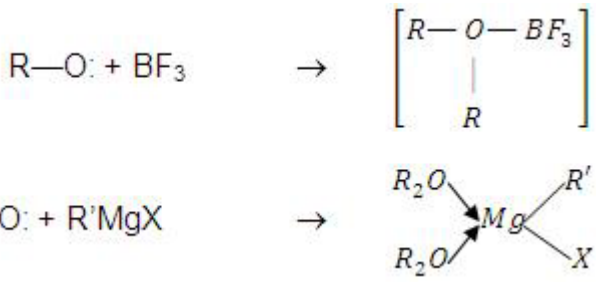
(i) Due to the presence of two lone pair of electrons on oxygen atom, ethers behave as Lewis bases and form salt with strong acids.



(ii) The oxonium salts are soluble in acid solution and regeneration of ether can be made by hydrolysis of these salts.



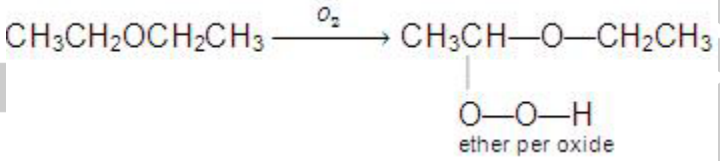
(iii) Ethers also form co-ordination complexes with Lewis acids like BF_3, $AICI_3$, RMgX etc.



Therefore ethers are very good solvent for Grignard reagents.

(b) Formation of per oxides:

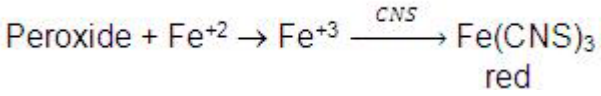
(i) Ethers form peroxide linkage with oxygen if exposed to air or ozonized oxygen in presence of sunlight or ultraviolet light.



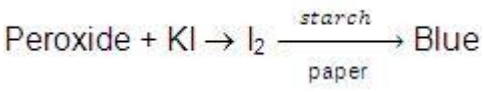
(ii) These per oxides are highly poisonous, oily liquids and decompose violently even at low concentrations. Therefore ethers should not be evaporated to dryness.

(iii) Also the purity of ether should be checked before its use as anesthetic agent. An impure ether (having peroxide linkage)-

(a) Gives red colour when shaken with ferrous ammonium sulphate and potassium thio-cyanate



(b) On mixing with KI solution liberates I_2 which turns starch paper blue.

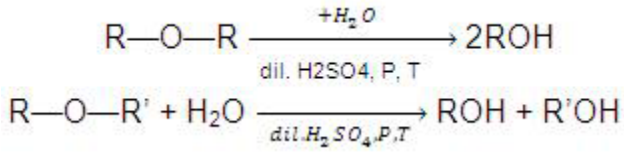


(iv) Ethers are made free from peroxide linkage if they are distilled with conc. H_2SO_4.

(v) Also peroxide formation can be checked if little Cu_2O is added to ether.

3. Reactions involving cleavage of carbon-oxygen bond:

(a) Action of dil. H_2SO_4: Ethers on heating with dilute H_2SO_4 under pressure are hydrolysed to corresponding alcohols.



(b) Action of Conc. H_2SO_4:

Ethers on warming with conc. H_2SO_4 give alkyl hydrogen sulphate.

$R\text{-}OR + H_2SO_4$ conc. $\rightarrow 2R\,HSO_4$

$R\text{-}OR' + H_2SO_4$ conc. $\rightarrow RHSO_4 + R'HSO_4$

(c) Action of HI:

(i) The products formed during action of HI on ethers depend upon temperature

$R\text{-}OR + HI \xrightarrow{cold} R\text{-}OH + RI$

$R\text{-}OR' + HI \xrightarrow{cold} R'\text{-}OH + RI$

Note: In case of mixed ether, halogen atom gets attached to simpler alkyl gp.

$CH_3OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$

(ii) $R\text{-}R + HI \xrightarrow{hot} 2RI + H_2O$

(iii) Similar reactions are observed with HCI, HBr & the reactivity order if HI > HBr > HCI.

(d) Action of PCI_5:

$R\text{-}O\text{-}R + PCI_5 \xrightarrow{\Delta} 2RCI + POCI_3$

(e) Action of Acetyl chloride or Acetic anhydride:

$$R—O—R + CH_3COCl \xrightarrow[AlCl_3]{ZnCl_2\ or} RCl + CH_3COOR$$

$$R—O—R + (CH_3CO)_2O \xrightarrow{AlCl_3} 2CH_3COOR$$

(f) Dehydration:

$$C_2H_5OC_2H_5 \xrightarrow[360^oC]{Al_2O_3} 2CH_2{=}CH_2 + H_2O$$

(g) Action of carbon monoxide:

$$C_2H_5OC_2H_5, + CO \xrightarrow[500\ atm]{BF_3, 150^oC} C_2H_5COOC_2H_5$$

$$ROR + CO \rightarrow RCOOR$$

Uses: Ethers are used as:

(i) General anaesthetic agent

(ii) Refrigerant as produces cooling on evaporation

(iii) Solvent for oils, fats, resins, Grignard reagent etc.

(iv) For providing inert & moisture free medium for reactions e.g. Wurtz reaction.