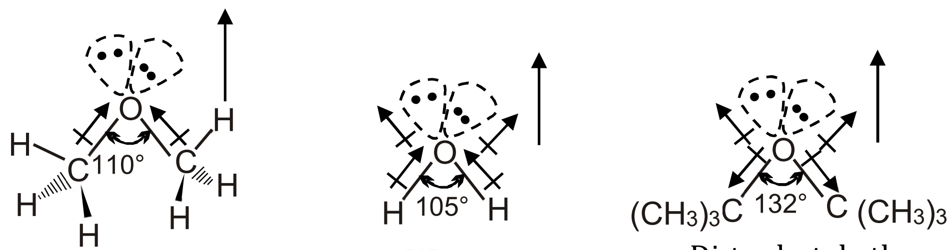
ALCOHOLS, PHENOLS AND ETHERS
ETHERS

ETHER

Similar to water, ethers exhibit a bent structure characterized by an sp^3 hybridized oxygen atom, resulting in an almost tetrahedral bond angle.



Dimethyl ether Water Di-ter.butyl ether

The bonding in ethers can be elucidated by drawing comparisons with water and alcohol. Van der Waals strain interactions between alkyl groups contribute to the oxygen bond angle being more expansive in ethers than in alcohols and greater in alcohols than in water. An illustrative case is di-tert-butyl ether, in which steric hindrance between the tert-butyl groups results in a significant augmentation of the C – O – C bond angle.

R—O—R (Dialkyl ether), alkoxy alkane. It's General formula is $C_nH_{2n+2}O$.

CH_3—O—CH_2CH_3 (Methoxy ethane) or ethyl methyl ether or 2–oxa butane Ether is monoalkyl derivative of R–OH and dialkyl derivative of H_2O

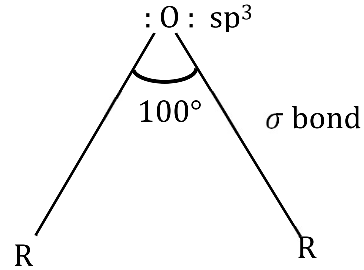
$$\text{R — OH} \xrightarrow[+R]{-H} \text{R — O — R} \xleftarrow[+2R]{-2} \text{H — O — H}$$

Classification: They may be classified as

(a) Simple or symmetrical ether. e.g., R–O–R

(b) Mixed or unsymmetrical ether e.g., R–O–R'

STRUCTURE



The bent shape of the ether molecule is a consequence of the repulsion between the lone pair of electrons on the oxygen atom and the bonded electrons. This leads to a bond angle of 110 degrees, which is larger than the bond angle in water (105 degrees) due to the presence of bulky alkyl groups that cause repulsion. The bent structure gives ethers a dipole moment, making them polar molecules.

GENERAL METHODS OF PREPARATION

(A) From alkyl halides

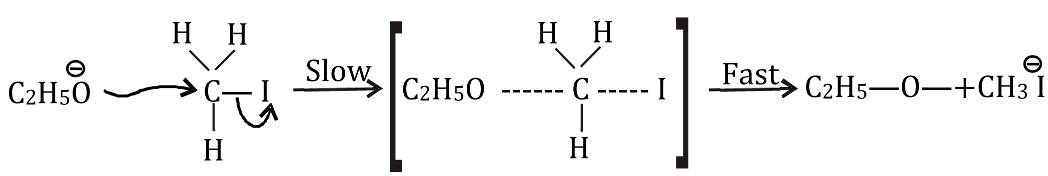
(i) By Williamson's synthesis

$R — X + Na — O — R \longrightarrow R — O — R + NaX$ [S_N2 Reaction]

Ex. $CH_3 — I + C_2H_5\,O^- Na^+ \longrightarrow CH_3 — CH_2O — CH_3 + NaI$

MECHANISM: [S_N2 Reaction]

$$C_2H_5\overset{\ominus}{O}\,Na^{\oplus} \rightleftharpoons C_2H_5\overset{\ominus}{O} + Na^{\oplus}$$

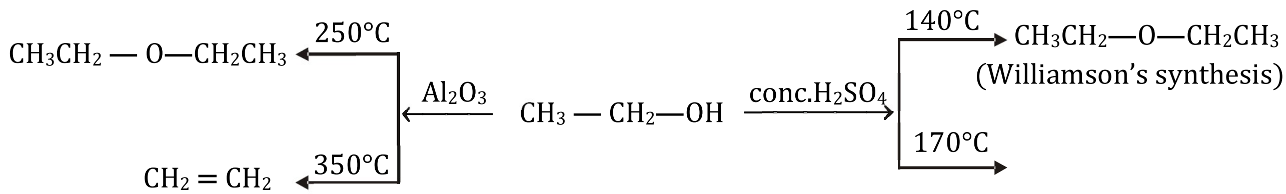


(ii) Reaction with Dry Ag2O

$$2RX + Ag_2O \xrightarrow{\Delta} R—O—R + 2AgX$$

(B) **From R–OH**

(i) **By dehydration:** $R - OH \xrightarrow[\Delta]{\text{conc. } H_2SO_4} ?$



(ii) **Reaction with CH_2N_2** (diazomethane)

$$R - OH + CH_2 - N_2 \xrightarrow[BF_4]{\Delta} R - O - CH_2 - H + N_2$$

PHYSICAL PROPERTIES

(i) CH_3OCH_3, $CH_3OCH_2CH_3$ are gases and higher are volatile liquids.

(ii) Ether are less polar [μ=1.18D].

(iii) Ethers are less soluble in H_2O.

(iv) Ethers have less BP then corresponding alcohol.

Ex. Ethers are less soluble in H_2O. Why?

Sol. **Reason:** Due to less polar, it forms weaker H–Bonding with H_2O.

Ex. Ethers have less BP than corresponding alcohol. Why?

Sol. **Reason:** No H–Bonding in ether molecules.

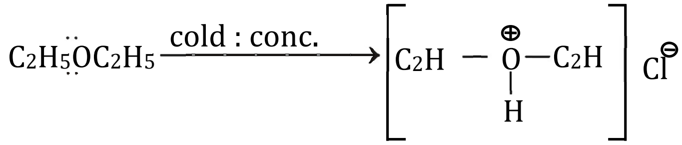
CHEMICAL PROPERTIES

Ethers exhibit lower polarity, resulting in reduced reactivity and a lack of reaction with active metals like sodium (Na) and potassium (K), cold diluted acids, as well as oxidizing and reducing agents.

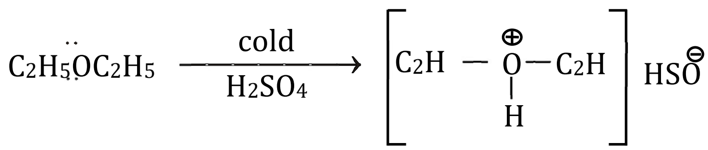
Reason: They do not have any active functional group.

1. **Basic nature:** Due to presence of λ. p on oxygen atom ether behaves as Lewis's base

   Ethers react with cold conc. acid and form oxonium ion



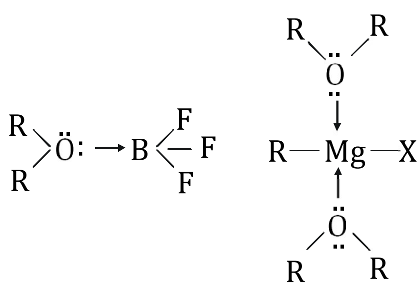
Ex. (diethyl oxonium chloride)



Ex. (diethyl oxonium hydrogen sulphate)

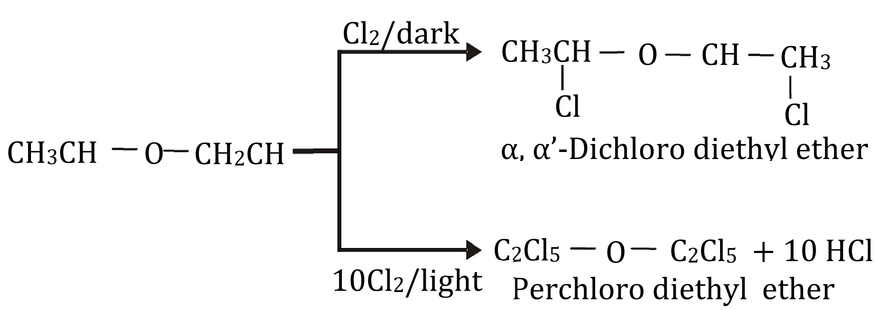
Ether form dative bond with Lewis's acids like BF_3, $AlCl_3$, RMgX etc.

Ex.



[Ether is used as solvent] for Grignard reagent.

2. **Halogenation**



3. **Formation of peroxides:** Ethers can combine with atmospheric oxygen or ozonized oxygen, and this phenomenon can be elucidated by a free radical mechanism, as free radicals are the intermediates in this process.

$$\underset{\text{(Non polar)}}{C_2H_5—O—C_2H_5} \xrightarrow[\text{Long sunlight or UV}]{O_2\text{(nonpolar)}} CH_3CH_2—O—\underset{\underset{O—O—H}{|}}{CHCH_3}$$

$$C_2H_5\ddot{\underset{..}{O}}C_2H_5 + \ddot{\underset{..}{O}} \longrightarrow C_2H_5\ddot{\underset{..}{O}}C_2H_5 \text{ Or } (C_2H_5)_2O \longrightarrow O$$

$$\downarrow$$

$$:\ddot{\underset{..}{O}}:$$

$$CH_3CH_2—O—CH_2— \xrightarrow[\text{Long contact}]{Q_2} CH_3—CH_2\ O— \xrightarrow{Q_2} Ph$$

$$CH_3—CH_2—O—\underset{\underset{O—O—H}{|}}{CH}—Ph$$

stable by resonance

Peroxides are unstable and explosives.

Test for peroxides

$$\text{ether (peroxide)} \xrightarrow{FeSO_4/KCN} \text{Red colour}$$

$$\text{ether (peroxide)} + Fe^{+2} \longrightarrow Fe^{+3} \xrightarrow{CNS} \underset{\text{(Red)}}{Fe(CNS)_3}$$

4. **Reaction with hot dil. H_2SO_4:** $R—O—R \xrightarrow[H_2SO_2]{\text{hot dil.}} 2R—OH$

5. **Reaction with hot conc. H_2SO_4:** $R—O—R \xrightarrow{\text{hot conc. } H_2SO_4} 2RHSO_4$

$CH_3—CH_2—O—CH_2—CH_3$ with H_2SO_4:

- cold dil. → No Reaction
- cold conc. → Oxonium salt
- hot dil. → Ethyl alcohol
- hot conc. → Ethyl hydrogen sulphate

6. **Reaction with PCl_5:** $ROR + PCl_5 \xrightarrow{\text{heat}} 2RCl + POCl_3$

7. **Reaction with BCl_3:** $3ROR + BCl_3 \longrightarrow 3RCl + (RO)_3B$

8. **Reaction with RCOCl:** $ROR + RCOCl \xrightarrow[ZnCl_2\text{ heat}]{AlCl_3} RCOOR + RCl$

9. **Reaction with CO:** $ROR + CO \xrightarrow[150^\circ C]{\frac{BF_3}{HgO} 500\ atm} RCOOR$

10. **Reaction with C_2H_5Na:**

$$\underset{\underset{H}{|}}{CH_2}-CH_2-O-CH_2\underset{\underset{H}{|}}{CH_2}+\overset{\ominus}{C_2H_5} \longrightarrow CH_3CH_2OH + CH_2CH_2 + C_2H_6$$

Stronger base

11. **Dehydration:** $CH_3CH_2-O-CH_2CH_3 \xrightarrow{Al_2O_3} 2CH_2 = H_2O$

12. **Reduction:** $CH_3CH_2OCH_2CH_3 \xrightarrow[heat]{Red\ P+HI} 2CH_3CH_3$

13. **Oxidation:**

$$CH_3CH_2-O-CH_2CH \xrightarrow{H^-/K_2Cr_2O_7} 2CH_3CH_2OH \xrightarrow{[O]} 2CH_3CHO \xrightarrow{[O]} 2CH_3COOH$$

14. **Combustion:** $C_2H_5OC_2H_5 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$

(explosive mixture)

15. **Reaction with HX:** Reactivity of HX

$$HI > HBr > HCI$$

(A) **REACTION WITH COLD CONC. HX:** Ethers exhibit different reactions when they come into contact with various concentrated halogen acids. When reacted with cold and concentrated hydrochloric acid (HCl), which is considered less reactive, ethers can form compounds known as oxonium salts. These reactions involve the ether molecule undergoing protonation and forming a positively charged oxygen atom in the resulting oxonium ion.

On the other hand, when ethers are treated with cold and concentrated hydroiodic acid (HI) and hydrobromic acid (HBr), which are more reactive than HCl, they undergo a distinct reaction. In this case, the C-O bond within the ether molecule is cleaved, resulting in the formation of two new compounds, typically an alkyl halide and an alcohol.

So, depending on the specific halogen acid used, ethers can either form oxonium salts with HCl or undergo C-O bond cleavage when exposed to the more reactive HI and

HBr. This reactivity difference is primarily attributed to the varying strengths of the halogen acids involved.