## CHAPTER / 17

# Ethers

### *Topics* Covered

- Classification of Ethers
- Nomenclature of Ethers
- Structure of Functional Groups of Ethers
- Preparation of Ethers
- Physical Properties of Ethers
- Chemical Properties
- Reactions Involving Alkyl Group
- Uses of Ethers

The substitution of a hydrogen atom in a hydrocarbon (aliphatic/aromatic) by an alkoxy (O$R$)/aryloxy (OAr) group gives ethers.

e.g.

$$\underset{\text{Alkane}}{R\text{—H}} \xrightarrow[+\text{ O}R]{-\text{H}} \underset{\text{Ether}}{R\text{—O}R}\ ;\ \text{Ar—H} \xrightarrow[+\text{ O}R]{-\text{H}} \underset{\text{Ether}}{\text{Ar—O—}R}$$

$$\underset{\text{Dimethyl ether}}{CH_3\text{—O—}CH_3};\quad \underset{\text{Diethyl ether}}{C_2H_5\text{—O—}C_2H_5};\quad \underset{\text{Methyl phenyl ether}}{C_6H_5\text{—O—}CH_3}$$

## Classification of Ethers

On the basis of type of attached groups, ethers are classified as follows:

(i) **Simple or Symmetrical Ethers** Same alkyl or aryl groups are attached to the oxygen atom.

e.g.

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5},\quad \underset{\text{Dimethyl ether}}{CH_3OCH_3}$$

(ii) **Unsymmetrical Ethers** Different alkyl or aryl groups are attached to the oxygen atom.

e.g.

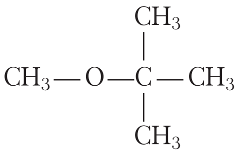
$$\underset{\text{Methyl phenyl ether}}{C_6H_5\text{—O—}CH_3},\quad \underset{\text{Ethyl methyl ether}}{C_2H_5\text{—O—}CH_3}$$

On the basis of symmetry these are further classified into two categories :

(i) **Aliphatic Ethers** Both of the attached groups ($R$ and $R'$) are alkyl groups. They have the general formula, $C_nH_{2n+2}O$.

e.g.

$$\underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3}\ ;$$

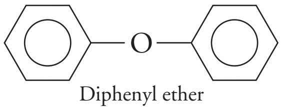


$$CH_3\text{—O—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}\text{—}CH_3$$

Methyl *tert*-butyl ether

(ii) **Aromatic Ethers** Either one or both of the attached groups (*R* and *R′*) is/are aryl groups. Aromatic ethers in which one of the groups is aryl and other is alkyl; is phenolic ether or alkyl aryl ether and if the groups are aryl, they are called diaryl ethers, e.g.

$\underset{\text{Methyl phenyl ether (Phenolic ether)}}{CH_3{-}O{-}C_6H_5}$,

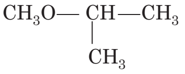
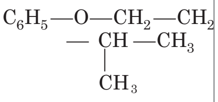
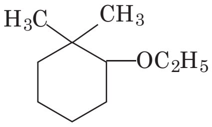

Diphenyl ether
(Diaryl ether)

## Nomenclature of Ethers

They are named as alkoxy alkane. Ethereal oxygen is taken with smaller alkyl group. Larger alkyl group is considered as a part of alkane.

Common names of ethers are derived from the names of alkyl or aryl groups written as a separate word in an alphabetical order and adding the word 'ether'.

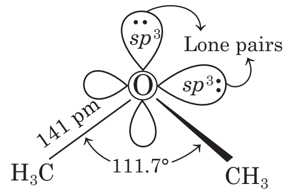
**Common and IUPAC Name of Some Ethers**

| S. N. | Compound | Common name | IUPAC name |
|---|---|---|---|
| 1. | $CH_3OCH_3$ | Dimethyl ether | Methoxymethane |
| 2. | $C_2H_5OC_2H_5$ | Diethyl ether | Ethoxyethane |
| 3. | $CH_3OCH_2CH_2CH_3$ | Methyl *n*-propyl ether | 1-methoxypropane |
| 4. | $C_6H_5OCH_3$ | Methyl *n*-phenyl ether (anisole) | Methoxybenzene |
| 5. | $C_6H_5OCH_2CH_3$ | Ethyl phenyl ether (phenetole) | Ethoxybenzene |
| 6. | $C_6H_5O(CH_2)_6{-}CH_3$ | Heptyl phenyl ether | 1-phenoxyheptane |
| 7. |  $CH_3O{-}\underset{\underset{CH_3}{\vert}}{CH}{-}CH_3$ | Methyl isopropyl ether | 2-methoxypropane |
| 8. |  $C_6H_5{-}O{-}CH_2{-}CH_2{-}\underset{\underset{CH_3}{\vert}}{CH}{-}CH_3$ | Phenyl isopentyl ether | 3-methyl butoxybenzene |
| 9. | $CH_3{-}O{-}CH_2{-}CH_2{-}OCH_3$ | — | 1, 2-dimethoxyethane |
| 10. |  | — | 2-ethoxy-1,1-dimet -hyl cyclohexane |

## Structure of Functional Groups of Ethers

In ethers, the four electron pairs, i.e. the two bond pairs and two lone pairs of electrons on oxygen are arranged in approximate **tetrahedral arrangement**. Bond angle is slightly greater than tetrahedral angle because of the repulsive interaction between two bulky ($-R$) groups.

The C—O bond length (141 pm) is almost the same as that in alcohols.



Structure of methoxymethane

## Preparation of Ethers

Ethers are prepared by the following methods :

### 1. From Alcohols

### (i) By Dehydration of Alcohols

Alcohols undergo dehydration in the presence of protic acids such as $H_2SO_4$, $H_3PO_4$. Formation of the reaction product, alkene or ether depends upon the reaction conditions. e.g. ethanol is dehydrated to ethoxyethane at 413K in the presence of sulphuric acid.

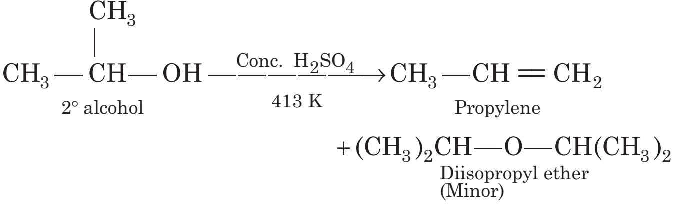
$$\underset{\substack{\text{Ethanol}\\\text{(Excess)}}}{2C_2H_5OH} \xrightarrow[413\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Ethoxyethane}}{C_2H_5{-}O{-}C_2H_5} + H_2O$$

At 443 K, ethene is the main product.

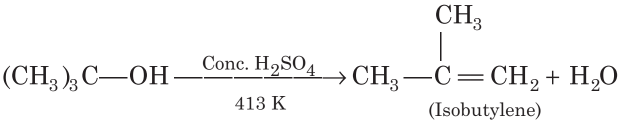
$$CH_3CH_2OH \xrightarrow[443\text{ K}]{H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2} + H_2O$$

### (ii) By Primary Alcohol

To some extent secondary alcohol form ethers on reaction with sulphuric acid at 413 K. Tertiary alcohols almost exclusively yield alkenes.



$$\underset{2^\circ\text{ alcohol}}{CH_3{-}\overset{\overset{CH_3}{\vert}}{CH}{-}OH} \xrightarrow[413\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Propylene}}{CH_3{-}CH{=}CH_2} + \underset{\substack{\text{Diisopropyl ether}\\\text{(Minor)}}}{(CH_3)_2CH{-}O{-}CH(CH_3)_2}$$



$$(CH_3)_3C{-}OH \xrightarrow[413\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{(Isobutylene)}}{CH_3{-}\overset{\overset{CH_3}{\vert}}{C}{=}CH_2} + H_2O$$

### (iii) Catalytic Dehydration

Catalytic dehydration of lower alcohols can also be done by passing the vapours of the alcohol over alumina at 510-530 K.

$$2C_2H_5OH \xrightarrow[510-530\text{ K}]{Al_2O_3} C_2H_5OC_2H_5 + H_2O$$

The order of dehydration of alcohols leading to the formation of ethers follows the order 1° > 2° > 3° alcohols.

### (iv) Reaction of Diazomethane with Alcohols

In the presence of $HBF_4$ as catalyst, alcohols react with diazomethane ($CH_2N_2$) to form methyl ethers in excellent yield.

$$ROH + \underset{\substack{\text{Ethyl}\\\text{ether}}}{CH_2N_2} \xrightarrow{HBF_4} ROCH_3 + \underset{\substack{\text{Leaving}\\\text{group}}}{N_2}$$

## 2. Williamson's Synthesis

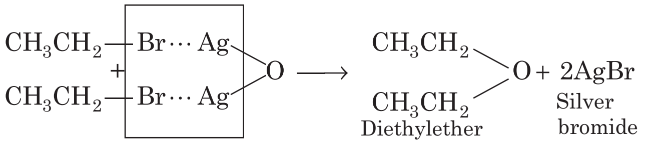
This is one of the best method for the preparation of symmetrical and unsymmetrical ethers. In this method, an alkyl halide is allowed to react with sodium alkoxide.

$$\underset{\text{Alkyl halide}}{R-X} + \underset{\text{Sodium alkoxide}}{R'-\overset{-}{\ddot{O}}\overset{+}{Na}} \longrightarrow \underset{\text{Ether}}{R-\ddot{O}-R'} + \underset{\text{Sodium halide}}{NaX}$$

Ethers containing substituted alkyl groups (secondary or tertiary) may be prepared by this method.

## 3. Reaction of Alkyl Halides with Dry Silver Oxide

Simple ether can be formed by boiling alkyl halide with dry silver oxide.



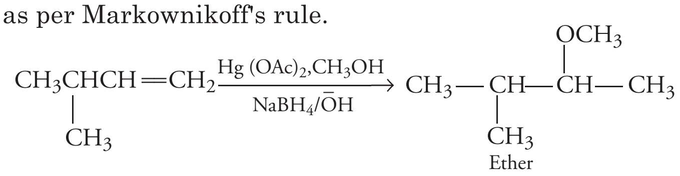
## 4. From Grignard Reagent

It is also repared by Grignard reagent as follows :

$$\underset{\text{Chloromethoxy methane}}{CH_3-O-CH_2Cl} + CH_3MgI \xrightarrow[\text{ether}]{\text{Dry}} \underset{\text{Ethyl methyl ether}}{CH_3-OCH_2CH_3} + \underset{\text{Chloro magnesium iodide}}{Mg(Cl)I}$$

## 5.From Alkenes

In this method, alcohol is added to alkene to form ether as per Markownikoff's rule.



$$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}H}CH{=}CH_2 \xrightarrow[\text{NaBH}_4/\bar{O}H]{\text{Hg (OAc)}_2\text{,CH}_3\text{OH}} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle OCH_3}{\overset{|}{CH}}-CH_3$$

Ether

# Physical Properties of Ethers

(i) **Physical state** Dimethyl ether and ethyl methyl ethers are gases at ordinary temperature, whereas higher ones are liquids with 'ether' smell.

(ii) **Dipolar nature** The C—O bonds in ethers are polar, therefore ethers have a net dipole moment.

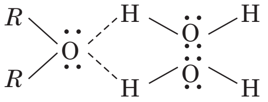
(iii) **Boiling point** Boiling points of ethers are much lower than the boiling points of alcohols. The large difference in boiling points of alcohols and ethers is due to the presence of H-bonding in alcohols. The boiling points of ethers are comparable to alkanes of comparable molecular masses due to their low polarity.

| **Formula** | $CH_3(CH_2)_3CH_3$<br>n-pentane | $C_2H_5-O-C_2H_5$<br>Ethoxyethane | $CH_3(CH_2)_3-OH$<br>Butan-1-ol |
|---|---|---|---|
| **bp/K** | 309.1 | 307.6 | 390 |

(iv) **Solubility** Lower ethers (up to three carbon atoms) are soluble in water and their miscibility with water resembles with those of alcohols of the same molecular mass.

Both ethoxyethane and butan-1-ol are miscible to almost the same extent, i.e. 7.5 and 9 g per 100 mL $H_2O$, respectively, while pentane is essentially immiscible with $H_2O$.

This is due to the fact that just like alcohols, oxygen of ether can also form H-bonds with water molecule.



(v) **Density** All ethers are lighter than water.

# Chemical Properties

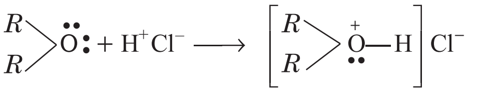
The reactions of ethers are mainly due to lone pair of ethereal O, cleavage of C—O bond and —R group.

## Reactions Due to Ethereal Oxygen

These reactions are mainly due to the lone pair of oxygen. Here ethers behave as bases.

### (i) Action of Concentrated Acids

Such a reaction occurs due to the presence of two lone pairs of electrons over oxygen and oxonium salts are formed.



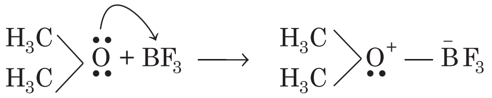
Dialkyl oxonium chloride

These salts are stabilised due to stabilisation by the anion of acids as :

$$(CH_3)_2O + H_2SO_4 \longrightarrow \underset{\text{Diethyl oxonium hydrogen sulphate}}{[(CH_3)_2OH]^+HSO_4^-}$$

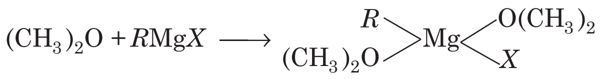
### (ii) Formation of Coordination Complexes

Similarly, ethereal oxygen, being **Lewis base** form coordination complexes, called **etherates**, with Lewis acids such as $BF_3$, $AlCl_3$, $FeCl_3$, Grignard's reagent, etc. as :



Borontrifluoride etherate

Similarly,



Grignard reagent etherate

[Due to this complex formation Grignard reagents dissolve in dry ether.]

## Reactions Involving Cleavage of C—O Bond in Ethers

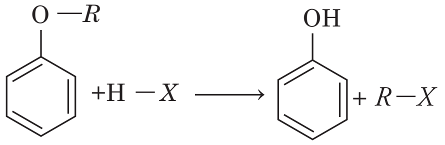
### 1. Action of Halogen Acids

Ethers are less reactive of the functional groups. The cleavage of C — O bond in ethers takes place under drastic conditions with excess of H*X*.

$$\underset{\text{Ether}}{R\text{—O—}R} + HX \xrightarrow{373\text{ K}} \underset{\text{Alcohol}}{R\text{OH}} + \underset{\text{Alkyl halide}}{RX}$$

$$R\text{—OH} + HX \longrightarrow R\text{—}X + H_2O$$

Alkyl aryl ethers are cleaved at alkyl-oxygen bond due to the more stable aryl oxygen bond. The reaction gives phenol and alkyl halide.



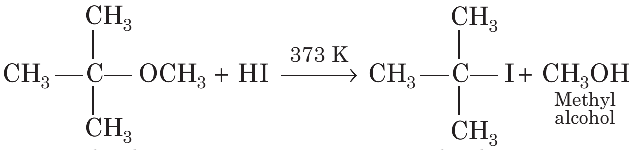
$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + HI \xrightarrow{373\text{ K}} \underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Ethyl iodide}}{C_2H_5I}$$

$$C_2H_5OC_2H_5 + \underset{\text{Excess}}{2HI} \xrightarrow{373\text{ K}} \underset{\text{Ethyl iodide}}{2C_2H_5I} + H_2O$$

The order of reactivity of hydrogen halides is HI > HBr > HCl. The cleavage of ethers takes place with conc. HI or HBr at high temperature.

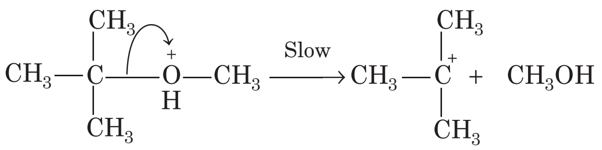
#### (i) Sites of Cleavage

There are different sites of cleavage which are discussed below. If one group is primary alkyl halide, e.g. methyl and other group is tertiary alkyl group, then methanol (major product) and *tert* alkyl halide is obtained.

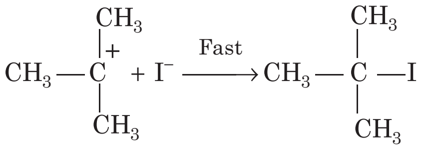


$$\underset{\substack{\text{tert. butyl}\\\text{methyl ether}}}{CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}OCH_3} + HI \xrightarrow{373\text{ K}} \underset{\substack{\text{tert. butyl}\\\text{iodide}}}{CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}I} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

The reaction follows $S_N1$ mechanism.



$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}\underset{H}{\overset{+}{O}}\text{—}CH_3 \xrightarrow{\text{Slow}} CH_3\text{—}\overset{CH_3}{\underset{CH_3}{\overset{+}{C}}} + CH_3OH$$



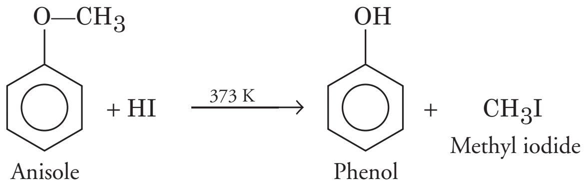
$$CH_3\text{—}\overset{CH_3}{\underset{CH_3}{\overset{+}{C}}} + I^- \xrightarrow{\text{Fast}} CH_3\text{—}\overset{CH_3}{\underset{CH_3}{C}}\text{—}I$$

This is due to the creation of a more stable carbocation, $(CH_3)_3C^+$ with the departure of leaving group, $CH_3$—OH.

#### (ii) Cleavage of Aryl Alkyl Ethers

In case of alkyl aryl ethers such as anisole, methyl phenyl oxonium ion is formed by protonation of ether. The bond between O—$CH_3$ is weaker than the bond between O—$C_6H_5$ because the carbon of phenyl group is $sp^2$-hybridised and there is a partial double bond character.

Thus, the reaction yields phenol and alkyl halide. Phenol does not react further to give halides because $sp^2$-hybridised carbon of phenol cannot undergo nucleophilic substitution reaction required for conversion to halide.

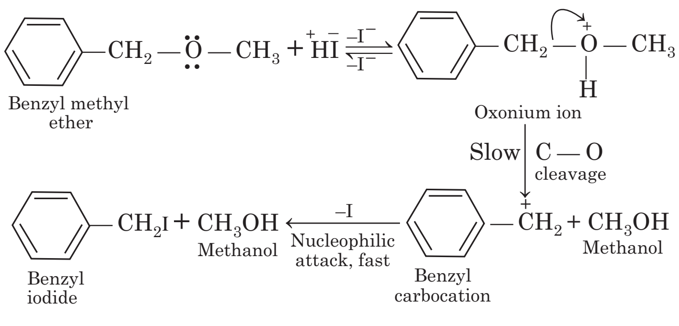


Ethers with two different alkyl groups are also cleaved in the same manner.

If primary and secondary alkyl groups are present, the alkyl halide is always formed from the smaller alkyl group.

#### (iii) Cleavage of Benzyl Alkyl Ethers

In benzyl alkyl ethers, cleavage of C—O bond gives alkyl alcohol and benzyl halide because benzyl carbocation is more stable towards $S_N1$ mechanism.



#### (iv) Cleavage of Diaryl Ethers

Diaryl ethers, like diphenyl ether are not cleaved by HI because the C—O bonds have some double bond character due to resonance between the lone pairs of electron on O-atom and C-atom of aryl groups directly bonded to O-atom.

### 2. Action with Dilute Sulphuric Acid (Hydrolysis)

With dil $H_2SO_4$, under pressure, ethers are hydrolysed to alcohols as shown below:

$$R—O—R + H_2O / H^+ \xrightarrow[\text{Under pressure}]{\text{Dil. } H_2SO_4, \Delta} 2R—OH$$

With conc. $H_2SO_4$, alcohols and alkyl hydrogen sulphates are formed as shown below:

$$\underset{\text{Primary ether}}{R—O—R} + \text{conc. } H_2SO_4 \xrightarrow{\Delta} R—OH + RHSO_4$$

Secondary and tertiary ethers, however form alkenes instead of alcohols.

### 3. Action of Heat (Dehydration)

At 673K, ethers in the presence of $Al_2O_3$ undergo dehydration to form alkenes.

e.g. $$CH_3OCH_3 \xrightarrow[673K]{Al_2O_3} CH_2 = CH_2 + H_2O$$

### 4. Action of Phosphorus Pentachloride

Ethers react with hot phosphorus pentachloride which leads to cleavage at both the oxygen bond forming alkyl chlorides.

$$Cl—PCl_3—Cl + C_2H_5—\overset{+}{O}—C_2H_5 \longrightarrow 2C_2H_5Cl + POCl_3$$

For unsymmetrical ethers,

$$R—O—R' \xrightarrow{PCl_5} RCl + R'Cl + POCl_3$$

By nature of alkyl chloride, we can predict the structure of ether.

### 5. Action with Acid Derivatives

Acid chlorides react with ethers in the presence of anhydrous $ZnCl_2$ or $AlCl_3$ to form alkyl halide and esters as

$$ROR + R'COCl \xrightarrow[\Delta]{AlCl_3 \text{ or Anhy. } ZnCl_2} RCl + R'COOR$$

### 6. Action with Acid Anhydrides

Esters are formed when ethers react with acid anhydrides.

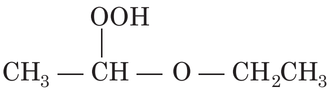
$$R—O—R + (CH_3CO)_2O \xrightarrow[\text{or } ZnCl_2/\Delta]{\text{Anhy. } AlCl_3} 2\ CH_3COOR$$

## Reactions Involving Alkyl Group

### 1. Action of Air and Light

When exposed to air and light for a long time, ethers are oxidised to form hydroperoxides or simply peroxides as

$$CH_3CH_2 — O — CH_2CH_3 \xrightarrow[\text{Light}]{O_2}$$



$$CH_3 — \overset{OOH}{\overset{|}{CH}} — O — CH_2CH_3$$

The reaction occurs by free radical mechanism and oxidation occurs at the C-atom next to ethereal oxygen.

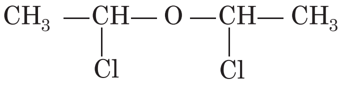
These peroxides are very dangerous compounds as these decompose violently at high temperatures.

### 2. Halogenation

With halogens, ethers give substitution products. The extent of halogenation, however depends upon the reaction conditions.

Diethyl ether reacts in dark to form only mono substituted products of alkyl group, e.g.

$$CH_3 — CH_2 — O — CH_2 — CH_3 \xrightarrow[-2HCl]{Cl_2, \text{ dark}}$$



$$CH_3 — \underset{Cl}{\underset{|}{CH}} — O — \underset{Cl}{\underset{|}{CH}} — CH_3$$

α, α′-dichlorodiethyl ether

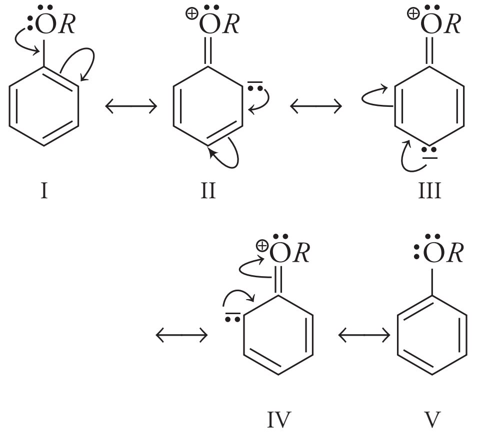
In the presence of light and excess of chlorine, all hydrogen atoms are substituted as :

$$CH_3 — CH_2 — O — CH_2 — CH_3 + \underset{\text{Excess}}{10Cl_2} \xrightarrow{h\nu}$$

$$C_2Cl_5 — O — C_2Cl_5 + 10HCl$$

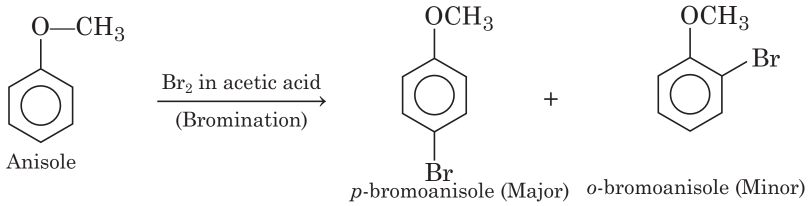
### 3. Electrophilic Substitution

Alkoxy group (—O*R*) is *ortho, para* directing and activates the aromatic ring towards electrophilic substitution. It directs the incoming electrophile at *o* and *p*-positions (because of the negative charges at *o* and *p*-positions indicates more electron density at these positions).



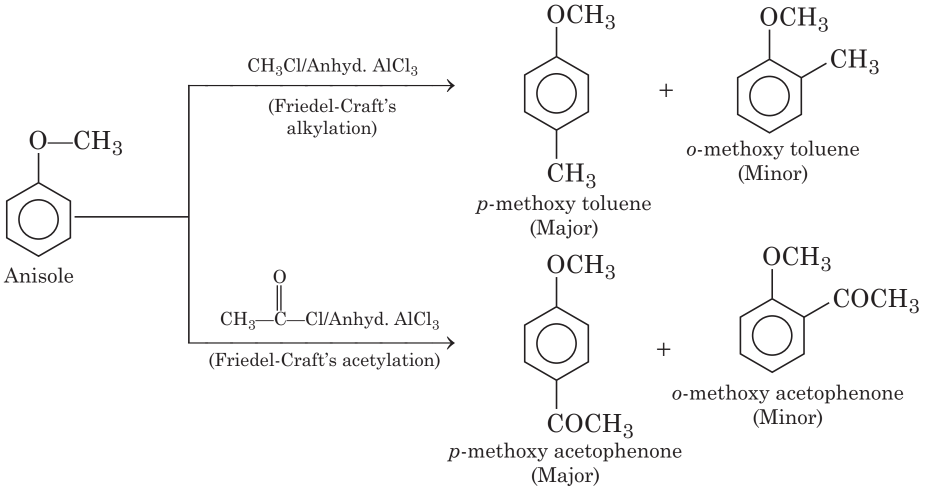
#### (i) Halogenation

Phenylalkyl ethers undergo usual halogenation in the benzene ring, e.g. anisole undergoes bromination with bromine in ethanoic acid even in the absence of iron (III) bromide catalyst. It is due to the activation of benzene ring by the methoxy group. Halide groups are introduced at *o*-and *p*-positions in which the *p*-isomer is obtained in 90% yield.



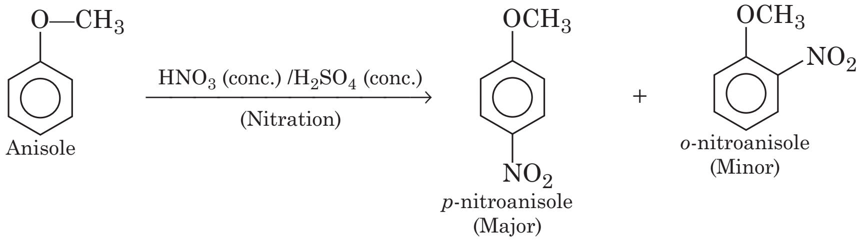
## (ii) Friedel-Craft's Reaction

Anisole undergoes Friedel-Craft's reaction, i.e. the alkyl halide and acyl groups are introduced at *o* and *p*-positions by reaction with alkyl halide and acyl halide in the presence of anhydrous aluminium chloride (a Lewis acid) as catalyst.



## (iii) Nitration

Anisole reacts with a mixture of concentrated sulphuric acid and nitric acid to yield a mixture of *ortho* and *para* nitroanisole.



# Uses of Ethers

Some uses of ethers are:

(i) Dimethyl ether is used as refrigerant and as solvent at low temperatures.
(ii) Used as an industrial solution for oils, resins, gums, etc.
(iii) As an extracting solvent in laboratory and industry because of their almost inert nature and good dissolving power.
(iv) Diphenyl ether is used as heat transfer medium because of its high boiling point.

# PRACTICE QUESTIONS

## Exams', Textbook's Other Imp. Questions

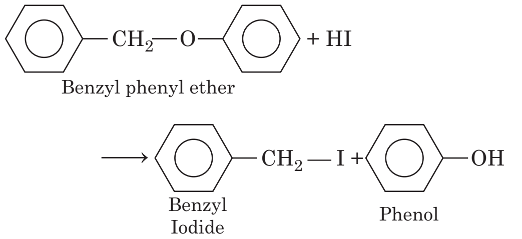
## 1 MARK *Questions*

### Important Questions

**Q.1** The ether $C_6H_5$ —O—$CH_2C_6H_5$ when treated with HI produces. **[Textbook]**

(a) $C_6H_5CH_2I$ (b) $C_6H_5I$
(c) $C_6H_5CH_2OH$ (d) $C_6H_5$—O—$C_6H_5$

***Sol*** (*a*) When benzyl phenyl ether is treated with HI, cleavage of C—O bond takes place and benzyl iodide and phenyl iodide are formed through $S_N1$ mechanism because benzyl carbocation is more stable than phenyl carbocation towards $S_N1$ mechanism.



**Q.2** Which of the following ethers is not cleaved by HI? **[Textbook]**

(a) Methyl phenyl ether (b) Diphenyl ether
(c) Ethyl methyl ether (d) Ethyl phenyl ether

***Sol*** (*b*) Diphenyl ether is not cleaved by HI because the C—O bond has some double bond character due to resonance between the lone pairs of electrons on the O atom and the C-atom of the aryl groups directly linked to the O-atom.

**Q.3** The molecular formula of alkyl ethers is

(a) $C_nH_{2n}O$ (b) $C_nH_{2n+1}$ **[Textbook]**
(c) $C_nH_{2n+2}O$ (d) $C_nH_{2n}O\ C_nH_{2n}$

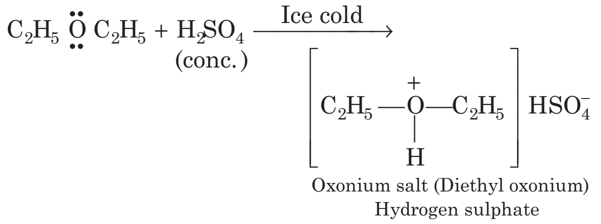
***Sol*** (*c*) The molecular formula of alkyl ethers is $C_nH_{2n+2}O$.

Here, *n* is the number of carbon atoms in ether.

**Q.4** Ethers react with conc. $H_2SO_4$ to form **[Textbook]**

(a) alkyl free radicals
(b) Zwitter ion
(c) oxyanion
(d) oxonium ion

***Sol*** (*d*) Ethers react with cold conc. $H_2SO_4$ to form oxonium salts.



$$C_2H_5\ddot{\underset{\cdot\cdot}{O}}C_2H_5 + \underset{(\text{conc.})}{H_2SO_4} \xrightarrow{\text{Ice cold}} \left[C_2H_5-\underset{\displaystyle H}{\overset{+}{O}}-C_2H_5\right]HSO_4^-$$

Oxonium salt (Diethyl oxonium) Hydrogen sulphate

**Q.5** Ether gives chemical reactions due to **[Textbook]**

(a) C—O bond cleavage
(b) C—H bond cleavage
(c) Lone pair present on oxygen
(d) All of the above

***Sol*** (*d*) Ether gives chemical reaction due to C— O bond cleavage, C—H bond cleavage and lone pair present on oxygen.

**Q.6** Which of the following solvents is used for the preparation of the Grignard reagent? **[Textbook]**

(a) Ethyl alcohol (b) Diethyl ether
(c) Cyclohexanol (d) Benzene

***Sol*** (*b*) Diethyl ether is used as a solvent for the preparation of Grignard reagent.

$$RX + \text{Mg} \xrightarrow{\text{Diethyl ether}} R\text{Mg}X$$

**Q.7** When $(CH_3)_3COCH_3$ is treated with hydroiodic acid, the fragments after the reaction obtained are **[Textbook]**

(a) $(CH_3)_3C—I + HOCH_3$
(b) $(CH_3)_3C—OH + I—CH_3$
(c) $(CH_3)_3CH + CH_3OCH_3 + I_2$
(d) $(CH_3)_3C—OH + CH_4 + I_2$

***Sol*** (*a*) When $(CH_3)_3C—O—CH_3$ is treated with hydroiodic acid, $(CH_3)_3C—I$ and $HOCH_3$ are obtained.

$(CH_3)_3C—O—CH_3 + HI \longrightarrow (CH_3)_3C—I + HOCH_3$

This is because in this reaction, a more stable carbocation is formed and reaction follows $S_N1$ mechanism.

**Q.8** When is $C_6H_5OCH_3$, treated with HI at 373K, the products obtained are **[Textbook]**

(a) $CH_3OH$ and $C_6H_5I$ (b) $CH_3I$ and $C_6H_5OH$
(c) $C_6H_5I$ and $CH_3I$ (d) $C_6H_5OH$ and $CH_3OH$

***Sol*** (*b*) When $C_6H_5$—O—$CH_3$ is treated with HI at 373 K, $CH_3I$ and $C_6H_5OH$ are obtained because methyl phenyl oxonium ion is formed by the protonation of ether.

The bond between O—$CH_3$ is weaker than the bond between O—$C_6H_5$ because the carbon of phenyl group is $sp^2$ hybridised and there is a partial double bond character. Thus, the reaction yields phenol and alkyl halide.

**Q.9** Name one metamer of diethyl ether. **[Textbook]**

***Sol*** Metamer of diethyl ether is 1-methoxypropane.

$H_5C_2OC_2H_5$, $CH_3CH_2CH_2OCH_3$

Diethyl ether 1-methoxypropane

- *True False Type Questions (Q.Nos. 10-13)*

**Q.10** Cleavage of ethyl methyl ether with HI at 373K give methyl iodide and ethanol. **[Textbook]**

***Sol*** True

**Q.11** Phenetole reacts with HI at 373K to give iodobenzene and ethanol. **[Textbook]**

***Sol*** False

**Q.12** Dimethyl ether and ethyl alcohol have the same boiling point as both have same molecular masses. **[Textbook]**

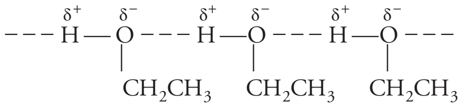
***Sol*** False

**Q.13** *tert*-butyl ether can be prepared by heating sodium ethoxide with *tert*-butyl bromide. **[Textbook]**

***Sol*** False

**Q.14** Give reason for the higher boiling point of ethanol in comparison to methoxymethane. **[Textbook]**

***Sol.*** Ethanol exists as associated molecules because ethanol undergoes intermolecular H-bonding due to the presence of hydrogen attached to the electronegative oxygen atom.



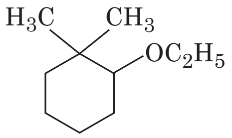
$$---\overset{\delta^+}{H}-\underset{CH_2CH_3}{\overset{\delta^-}{O}}---\overset{\delta^+}{H}-\underset{CH_2CH_3}{\overset{\delta^-}{O}}---\overset{\delta^+}{H}-\underset{CH_2CH_3}{\overset{\delta^-}{O}}---$$

Thus, a larger amount of energy is required to break these H-bonds. Therefore, the boiling point of ethanol is higher than that of methoxymethane which does not form H-bonds.

**Q.15** Give the structure of 1,2-dimethoxymethane and 2-ethoxy 1,1-dimethylcyclohexane. **[Textbook]**

***Sol.*** $CH_3—O—CH_2—O—CH_3$

1,2-dimethoxymethane



2-ethoxy-1, 1-dimethyl cyclohexane

**Q.16** How would you convert ethanol to ethene? **[Textbook]**

***Sol.*** $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[443\text{ K}]{\text{Conc. }H_2SO_4} \underset{\text{Ethene}}{CH_2{=}CH_2} + H_2O$

**Q.17** Give the name of the alkyl halide and sodium alkoxide used to synthesise *tert*-butyl ethyl ether. **[Textbook]**

***Sol.*** Ethyl bromide and sodium *tert*-butoxide.

**Q.18** Why diethyl ether does not react with sodium? **[Textbook]**

***Sol.*** Diethyl ether does not react with sodium because diethyl ether does not contain an active H-attached to oxygen like alcohols and phenols.

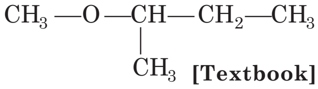
# 2 MARK *Questions*

## Important Questions

**Q.19** Give the IUPAC names of the following :

(i) $CH_3CH_2CH_2OCH_3$ (ii) $CH_3OCH_2CH_2Cl$

(iii) $C_6H_5OC_2H_5$ (iv)



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

**[Textbook]**

***Sol.***

(i) 1-methoxypropane **(1/2)**

(ii) 2-chloro-1-methoxy ethane **(1/2)**

(iii) ethoxy benzene **(1/2)**

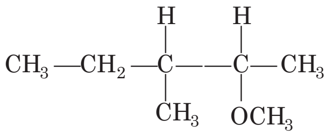
(iv) 2-methoxy butane **(1/2)**

**Q.20** Write the structure of the compounds whose names are as follows **[Textbook]**

(i) 2-ethoxy-3-methyl pentane (ii) 1-ethoxypropane

(iii) 1-phenoxyheptane (iv) anisole and phenetole

***Sol.*** (i)

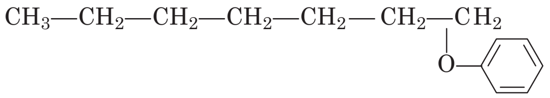


$$CH_3—CH_2—\underset{CH_3}{\underset{|}{\overset{\overset{H}{|}}{C}}}—\underset{OCH_3}{\underset{|}{\overset{\overset{H}{|}}{C}}}—CH_3$$

**(1/2)**

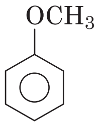
(ii) $C_2H_5OCH_2CH_2CH_3$ **(1/2)**

(iii)

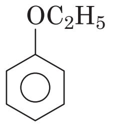


**(1/2)**

(iv)



Anisole



Phenetole **(1/2)**

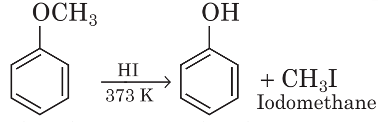
**Q.21** Write the equation of the reaction of hydrogen iodide with **[Textbook]**

(i) 1-propoxypropane (ii) methoxybenzene

***Sol.*** (i) $\underset{\text{1-propoxypropane}}{CH_3CH_2CH_2—O—CH_2CH_2CH_3} \xrightarrow[373\text{ K}]{HI}$

$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2—OH} + \underset{\text{1-iodopropane}}{CH_3CH_2CH_2—I}$ **(1)**

(ii)

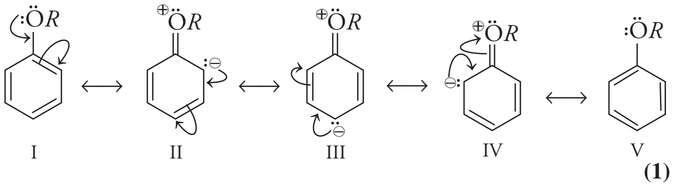


Methoxy benzene Phenol

**(1)**

**Q.22** Explain the fact that in aryl alkyl ethers (i) the alkoxy group activates the benzene ring towards electrophilic substitution and (ii) it directs the incoming substituents to *ortho* and *para*-positions in benzene ring. **[Textbook]**

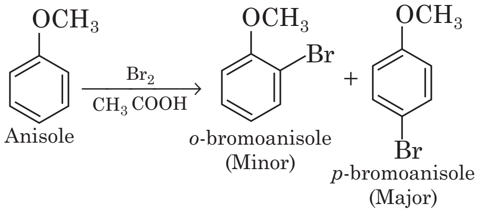
***Sol.*** (i) In aryl alkyl ethers, $+R$-effect of the alkoxy group ($-OR$) increases the electron density in the benzene ring thereby activating the benzene ring towards electrophilic substitution reactions.



I II III IV V

**(1)**

(ii) Electron density is more at *o* and *p*-positions, so *o and p*-products are mainly formed during electrophilic substitution reactions.



**(1)**

# 3 MARK *Questions*

## Exams' Question

**Q.23** What is the Williamson synthesis? **[2018]**

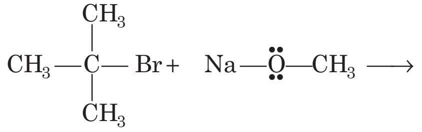
*Or* Give an example for the synthesis of unsymmetrical ether by Williamson's synthesis. **[Textbook]**

***Sol*** Refer to page 250. **(3)**

## Important Questions

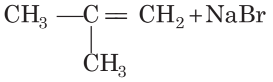
**Q.24** Illustrate with examples the limitations of the Williamson's synthesis for the preparation of certain types of ethers. **[Textbook]**

***Sol.*** (i) Williamson's synthesis is not applicable for tertiary alkyl halides as they yield alkenes instead of ethers. The reaction of $CH_3ONa$ with $(CH_3)_3C{-}Br$ gives exclusively, 2-methyl propene. **(1)**



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-Br + Na-\ddot{\underset{\cdot\cdot}{O}}-CH_3 \longrightarrow$$

*tert*-butyl bromide



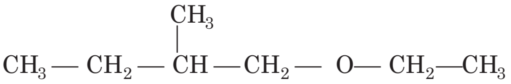
$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2+NaBr$$

2-methyl propene **(1)**

(ii) Aryl and vinyl halides cannot be used as substrates because of their low reactivity in nucleophilic substitution. **(1)**

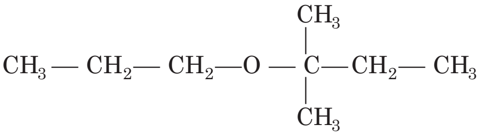
**Q.25** Give the major products that are formed by heating each of the following with HI. **[Textbook]**

(i)



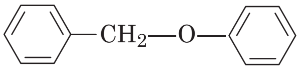
$$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-O-CH_2-CH_3$$

(ii)



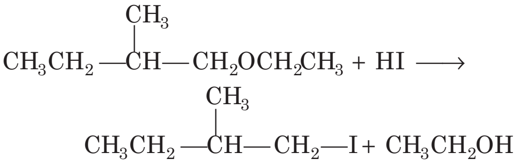
$$CH_3-CH_2-CH_2-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2-CH_3$$

(iii)



***Sol***

(i)

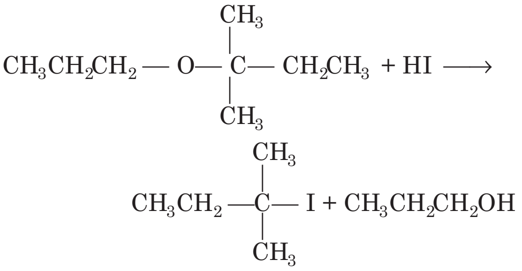


$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2OCH_2CH_3 + HI \longrightarrow$$

$$CH_3CH_2-\overset{CH_3}{\overset{|}{C}H}-CH_2-I + CH_3CH_2OH$$

**(1)**

(ii)

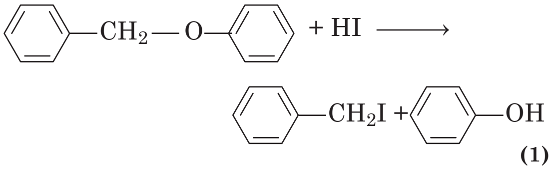


$$CH_3CH_2CH_2-O-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2CH_3 + HI \longrightarrow$$

$$CH_3CH_2-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-I + CH_3CH_2CH_2OH$$

**(1)**

(iii)



**(1)**

# 7 MARK *Questions*

## Exams' Question

**Q.26** Discuss the electrophilic substitution reaction, like halogenation, nitration and Friedel-Crafts reactions of aryl alkyl ethers. **[Textbook]**

***Sol*** See pages 252 and 253. **(7)**

# Chapter Test

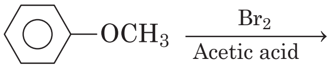
## 1 MARK Questions

**1** Which of the following will exhibit highest boiling point? **[Textbook]**

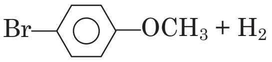
(a) $CH_3CH_2O\ CH_2CH_3$
(b) $CH_3CH_2CH_2CH_2OH$
(c) $CH_3O\ CH_2CH_2CH_3$
(d) $CH_3CH_2CH_2CH_2CH_2OH$

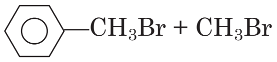
**2** Which of the following cannot be prepared by Williamson synthesis? **[Textbook]**

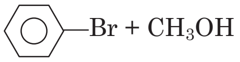
(a) Methoxy benzene (b) Methoxy ethane
(c) Di-*tert*-butyl ether
(d) *tert*-butyl methyl ether

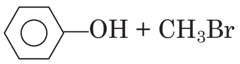
**3** In the reaction, 

the products is/are **[Textbook]**

(a) 

(b) 

(c) 

(d) 

**4** Which of the following pairs will give ether? **[Textbook]**

(a) $C_2H_5ONa$ and $C_2H_5I$ (b) $C_2H_5OH \xrightarrow[373\ K]{H^+}$
(c) $C_2H_5I \xrightarrow{\text{Dry } Ag_2O}$ (d) All of these

[***Ans.*** **1.** (d), **2.** (c), **3.** (a), **4.** (d)]

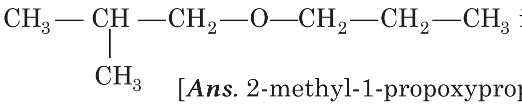
**5** Ethers exhibit functional isomerism with ……… .
[***Ans.*** alcohols]

**6** $C_4H_{10}O$ has ……… metamers, one of them is diethyl ether, while the others are ……… and ……… . [***Ans.*** three, methyl *n*-propyl ether and isopropyl methyl ether]

**7** Williamson's synthesis involves the reactions of an ……… with an ……… .
[***Ans.*** alkoxide, alkyl halide]

**8** Ethers behave as weakly ……… substances due to the presence of two lone pairs of electrons on the oxygen atom. [***Ans.*** basic]

**9** The IUPAC name of


$$\underset{\displaystyle CH_3}{CH_3—\underset{|}{CH}}—CH_2—O—CH_2—CH_2—CH_3$$
is .....

[***Ans.*** 2-methyl-1-propoxypropane]

**10** Which method is used for the estimation of a methoxy group in organic compounds? **[Textbook]**

**11** Which class of ethers are not cleaved by HI? **[Textbook]**

**12** Which product is formed by the Friedel-Crafts reaction of anisole with $CH_3Cl$? **[Textbook]**

## 2 MARK Questions

**13** How will you distinguish $C_2H_5—O—C_2H_5$ and $C_6H_5—O—C_6H_5$ by treating with HI? **[Textbook]**

**14** Why can ethers be cleaved preferentially by hot conc. HI and HBr but not by conc. HCl? **[Textbook]**

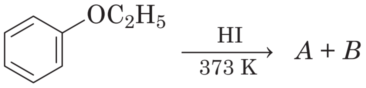
## 3 MARK Questions

**15** Explain, why diphenyl ether is not cleaved by HI. **[Textbook]**

**16** $(CH_3)_3C—O—CH_3 + HI \longrightarrow (CH_3)_3CI + CH_3OH$

Justify the preferential formation of the products. **[Textbook]**

**17** Predict the products *A* and *B*. **[Textbook]**



## 7 MARK Questions

**18** Compound $(A)$, $C_4H_{10}O$, is found to be soluble in sulphuric acid. $(A)$ does not react with metallic sodium or potassium permanganate solution. When $(A)$ is heated with excess of HI, it is convertd to a single alkyl halide. What is the structural formula of $(A)$? **[Textbook]**