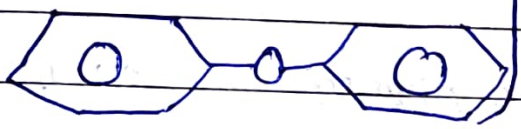
Ether

DATE

Introduction :- Ether are organic compound having the general formula R-O-R' where R & R' may be alkyl or alkyl group If the both groups are identical, the ether is called symmetrical or simple ether and if they are different the ether is called mixed or symmetrical ether.

CH_3-O-CH_3

$C_2H_5-O-C_2H_5$



} Symmetrical or simple ether.

$CH_3-O-C_2H_5$

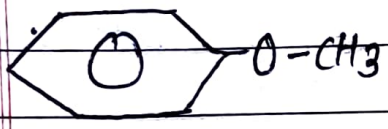
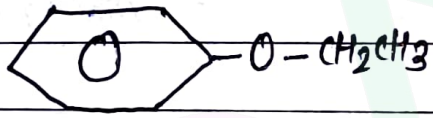
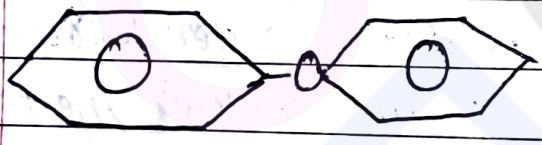
} unsymmetrical or mixed ether

Nomenclature :-

1. Common system :→ In this system ether are named by writing the name of alkyl group in alphabetical order followed by word ether at the end. In case of simple ether the prefix di- added to the name of alkyl or alkyl group.

2. IUPAC System :→ In this system ether are named as ~~ether~~ alkoxy alkane. In case of mixed ether the smaller alkyl group with oxygen is taken as alkyl group and the layer alkyl group determines the parent alkane.

the position of alkoxy group is indicated by serial number of carbon atom to which the alkoxy group is linked

Formula	common name	IUPAC name
CH_3-O-CH_3	Dimethyl ether	Methoxy methane
$CH_3-O-C_2H_5$	Ethyl methyl ether	Methoxy ethane
$C_2H_5-O-C_2H_5$	Diethyl ether	Ethoxy ethane
$CH_3-O-CH_2CH_2CH_3$	Methyl n-propyl ether	1-Methoxy propane
$CH_3-O-CH(CH_3)-CH_3$	Methyl iso-propyl ether	2-Methoxy propane
	Methyl phenyl ether (Anisole)	Methoxy benzene
	Ethyl phenyl ether (phenetole)	Ethoxy benzene
	Di-phenyl ether	phenoxy benzene

Isomerism in Ether →

Aliphatic ether exhibits 3 types of structural isomerism

1. Functional isomerism → Ethers and monohydric alcohols have general formula $C_nH_{2n+2}O$ and are functional isomers. Example:- molecular formula C_2H_6O has two functional isomers.

CH_3-O-CH_3 CH_3CH_2OH

Methoxy methane Ethanol.

Similarly,

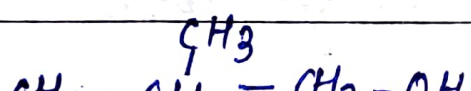
Molecular formula $C_4H_{10}O$ has following function al isomers.

$CH_3-CH_2-O-CH_2-CH_3$

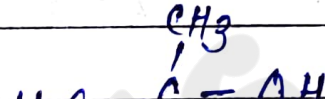
Diethyl ether

$CH_3CH_2CH_2CH_2-OH$

n-butyl alcohol



Iso-butyl alcohol



tert-Butyl alcohol.

Metamerism

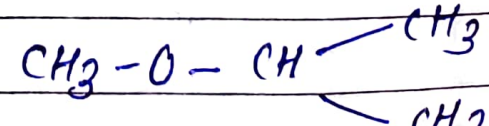
2. ~~Metabolism~~ → The isomerism which arise due to the presence of unequal number of carbon atoms on either side of the ethereal oxygen (-O-). This is called Metamerism. It enables simple ether to isomeric with mixed ether

Simple ether

$CH_3-CH_2-O-CH_2-CH_3$

Mixed ether

$CH_3-O-CH_2-CH_2-CH_3$



Iso-propyl methyl ether.

3. Chain isomerism → The isomerism which arise due to the different arrangement of the carbon chain within the alkyl group on either side of the oxygen atom is called chain isomerism.

Preparation of ether

1. From alcohol → By dehydration of alcohol

a) By using conc. H_2SO_4:-

When excess alcohol is heated with conc. H_2SO_4 at 140°C ether is formed.

General reaction →

$$R-OH + H:OR \xrightarrow[-H_2O]{\text{conc. } H_2SO_4,\ 140^\circ C} R-O-R$$

(Alcohol; ether)

Example:-

$$C_2H_5OH + HOC_2H_5 \xrightarrow[140^\circ C]{\text{conc. } H_2SO_4} C_2H_5-O-C_2H_5 + H_2O$$

$$CH_3-OH + HO-CH_3 \xrightarrow[140^\circ C]{\text{conc. } H_2SO_4} CH_3-O-CH_3 + H_2O.$$

b) Using alumina:-

$$2R-OH \xrightarrow[200^\circ C]{Al_2O_3} R-O-R + H_2O$$

imp

② From alkyl halide :- "Williamson's etherification process".

a) In this method ethers are obtained by heating haloalkanes with sodium or pottasium alkoxide. This reaction involves nucleophic substitution reaction of halogen atom by alkoxide ion.

General reaction :-

$$R\overset{\ominus}{O}:\overset{\oplus}{Na} + X - R \xrightarrow{\Delta} R-O-R' + NaX$$

$R = R'$, $R \neq R'$

Example :-

$$C_2H_5O:Na + Br:C_2H_5 \xrightarrow{\Delta} C_2H_5-O-C_2H_5 + NaBr$$

Uses :- It is used in the preparation of unsymmetrical or mixed ether in symmetrical ether.

In mixed ether the reactant consist of simple alkyl halides and alkoxides with larger alkyl group.

- $C_2H_5\overset{\ominus}{O}\ \overset{\oplus}{Na} + BrCH_3 \xrightarrow{\Delta} C_2H_5-O-CH_3 + NaBr$

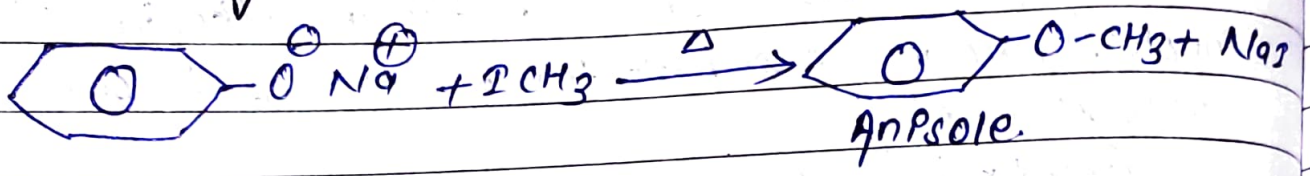
- $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\ominus}{O}\ \overset{\oplus}{Na} + BrCH_2CH_3 \xrightarrow{\Delta} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_2CH_3 + NaBr$

Sod. tert butoxide — Tert-butyl ethyl ether

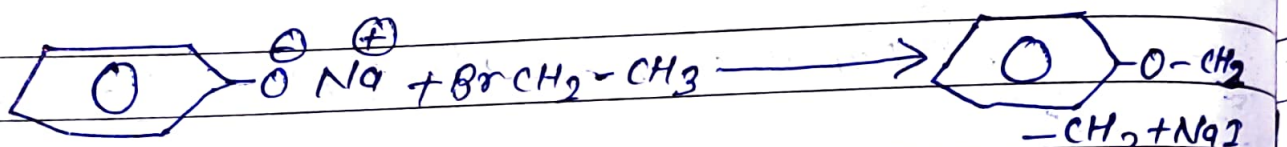
- Tert butyl ethyl ether cannot be obtained by tert-butyl bromide & sodium ethoxide as it give alkene.

$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br + \overset{\oplus}{Na}\ \overset{\ominus}{O}CH_2CH_3 \xrightarrow{\Delta} CH_3-\overset{CH_3}{\underset{CH_2}{C}} + CH_3CH_2OH + NaBr$$

- Alkyl or aryl ether are obtained by heating sodium phenoxide with alkyl halides.



Anisole.



(phenetole)

Note:- Alkyl aryl ether cannot be obtained by taking haloarenes and sodium alkoxide because nucleophilic substitution reaction is difficult in haloarenes due to partial double bond character of carbon halogen bond.

b) By heating alkyl halide with dry silver oxide:-

$$2R-X + Ag_2O \xrightarrow{\Delta} R-O-R + 2AgX$$

e.g.:-

$$2C_2H_5Br + Ag_2O \xrightarrow{\Delta} C_2H_5-O-C_2H_5 + 2AgBr$$

Not in course

Laboratory preparation of ethoxy ethane (diethyl ether) from ethanol:-

Principle:-

It is prepared in lab by heating excess alcohol with conc. H_2SO_4 at 140°C

$$CH_3CH_2OH + H_2SO_4 \xrightarrow{170^\circ C} CH_3CH_2OSO_3H$$

$$CH_3CH_2OSO_3H + HOCH_2CH_3 \xrightarrow[\text{excess}]{140^\circ C} CH_3CH_2-O-CH_2CH_3 + H_2SO_4$$

Diethyl ether.

Date : .

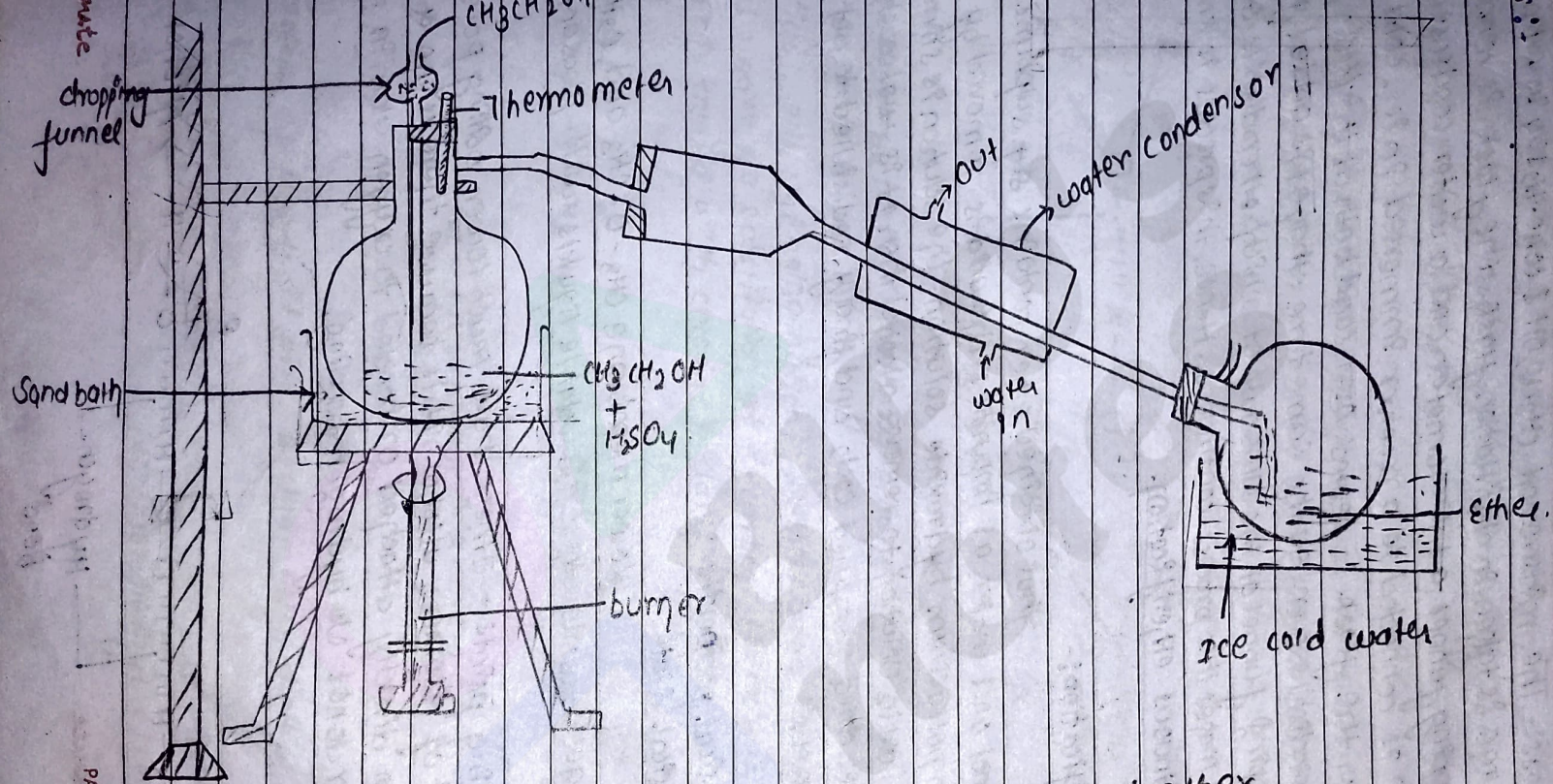


fig:- Lab preparation of diethyl ether.

Process:- The mixture of CH_3CH_2OH & conc. H_2SO_4 in ratio 1:1 by volume is taken in distillation flask. the flask is connected to dropping funnel a thermometer and a water condenser which in turn is connected to a receiver immersed in ice cold water. Now, the flask is heated over sand bath at 140°C, whereby ether distil's over. At the same time ethanol is added from the dropping funnel at the same rate at which ether distil's over. this makes this process continuous. Hence, this process is known as Continuous etherification.

Purification:-

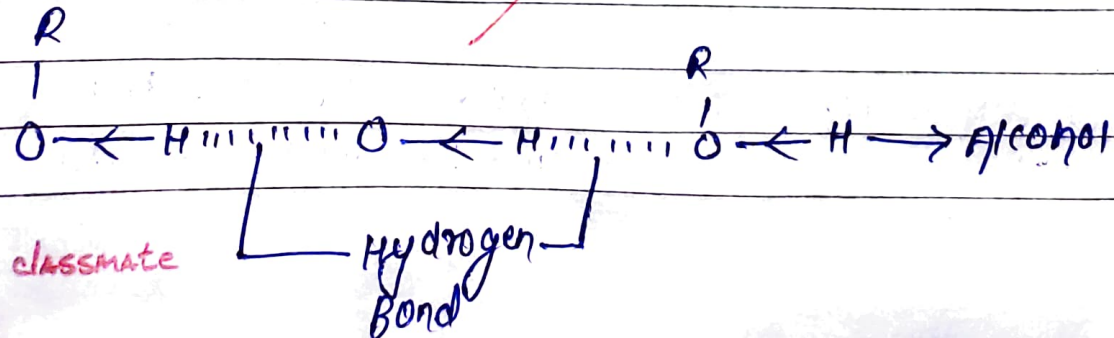
thus obtained ether contains sulphuric acid ethanol and water as impurities. the acid is removed by washing with pottassium hydroxide solution. the solution is shaken with 5% $CaCl_2$ solution to remove alcohol then it is washed with water dried over fused $CaCl_2$ and finally redistilled to get almost pure ether.

physical properties:-

1. physical state:-

Lower membrane CH_3-O-CH_3 and $C_2H_5-O-C_2H_5$ are gases, while ether are volatile liquids with pleasant order.

2. Boiling points:- Ethers have much lower boiling point than that of isomeric alcohol. It is because there is no hydrogen atom directly attached or bonded to oxygen atom in ether. Hence ether do not do hydrogen bonding.

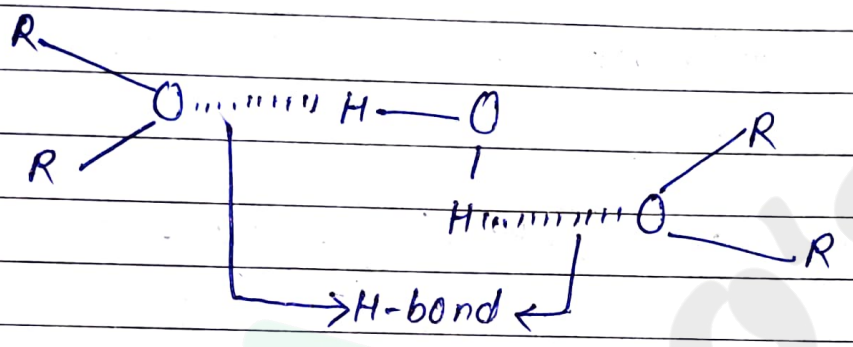


R=CH3 DATE

R-O-R R-O-R → NO- hydrogen bond

→ there is absence of hydrogen bond in dimethyl ether so it has less boiling point then alcohol.

3. Solubility :→ Ethers are slightly soluble in water but readily in organic solvent. the limited solubility in water due to formation of some H-bonding.



Chemical properties of ethoxy ethane →

① Reaction with Cl_2 (halogenation) :→ ethers when treated with halogens under go substitution at α-carbon. For ex:- when diethyl ether is treated with chlorine in dark it gives 1,1 - dichlorodiethyl ether.

$$CH_3-\overset{\alpha'}{CH_2}-O-\overset{\alpha}{CH_2}-CH_3 + Cl_2 \xrightarrow[-HCl]{dark} CH_3-CH_2-O-CH(Cl)-CH_3$$

$$CH_3-CH_2-O-CH(Cl)-CH_3 \xrightarrow[-HCl]{dark} CH_3-C(Cl)_2-O-CH(CH_3)-Cl$$

(1,1 - dichlorodiethyl ether)

- In presence of light, it gives perchloro ethyl diethyl ether.

$$C_2H_5-O-C_2H_5 + 10\,Cl_2 \xrightarrow{light} C_2Cl_5-O-C_2Cl_5 + 10\,HCl$$

(perchlorodiethyl ether).

(2) Reaction with HI → Ether react with conc. halogen acid (HBr and HI) in cold to form alkyl halides and alcohol.

General Reaction:-

$$R-\overset{\ominus}{O}-\overset{\oplus}{R} + \overset{\oplus}{H}\overset{\ominus}{X} \xrightarrow{\text{In cold}} ROH + R-X$$

Example:-

$$C_2H_5-O-C_2H_5 + HI \xrightarrow{\text{cold}} C_2H_5OH + C_2H_5I.$$

→ In case of unsymmetrical ether alkyl halides with smaller alkyl is formed.

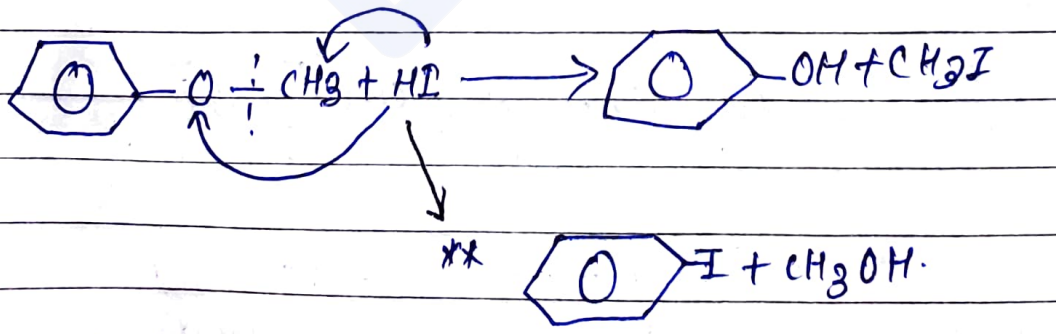
$$C_2H_5-O-CH_3 + HI \xrightarrow{\text{cold}} C_2H_5OH + CH_3I.$$

→ when ether are heated with excess acid then only alkyl halide are formed.

$$C_2H_5-O-C_2H_5 + 2HI \xrightarrow{\Delta} 2C_2H_5I + H_2O.$$
(Excess)

$$CH_3-O-C_2H_5 + 2HI \xrightarrow{\Delta} CH_3I + C_2H_5I + H_2O.$$
(Excess)

** In alkyl aryl ethers the product is phenol and alkyl halides.



During this reaction iodobenzene and methanol are not formed It is due to steric hindrance of large aryl group. The nucleophilic (I^-) attacks the protonated ether from the side of

smaller alkyl group.

(3) Reaction with PCl_5 → ether react with PCl_5 to give alkyl chloride.

G.R →

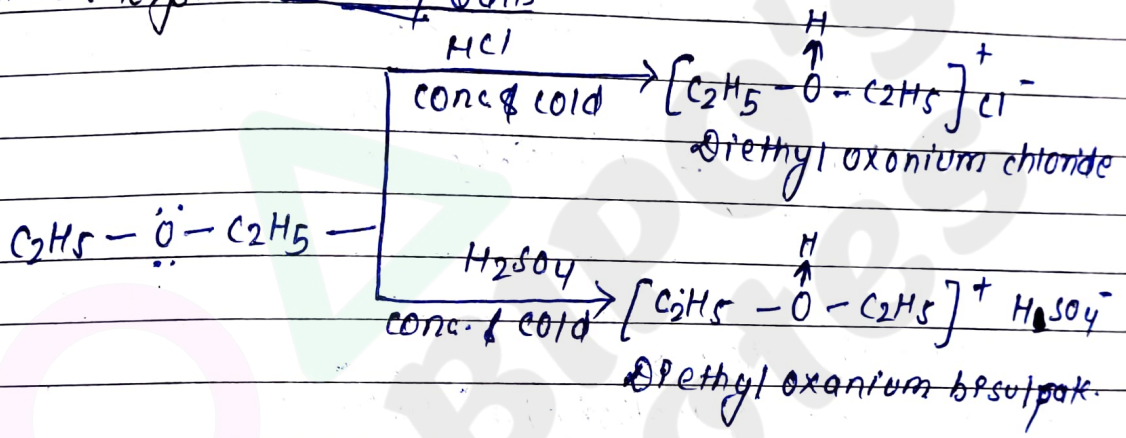
$$R-O-R + PCl_5 \longrightarrow 2R-Cl + POCl_3.$$

Example →

$$C_2H_5-O-C_2H_5 + PCl_5 \longrightarrow 2C_2H_5Cl + POCl_3.$$

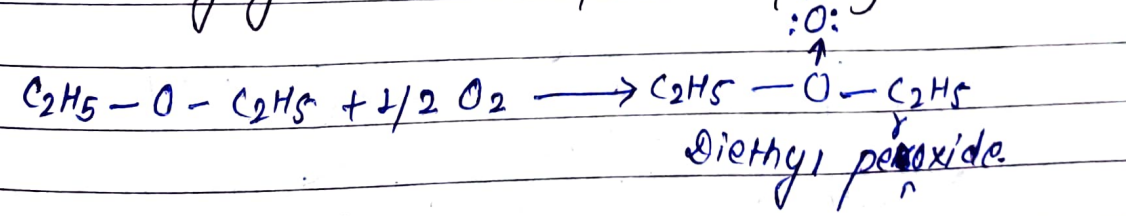
(4) Reaction with conc. HCl & conc. H_2SO_4 →

Ether react with conc & cold mineral acid to forms Oxanium salts.



Oxanium salts are stable at low temperature and high concentration of acid. On dilution they decompose back to give ether/acid.

(5) Reaction with air → Ether react with air to form peroxide which are highly unstable and explode on heating.



Q.N Why old ethers are not distilled?

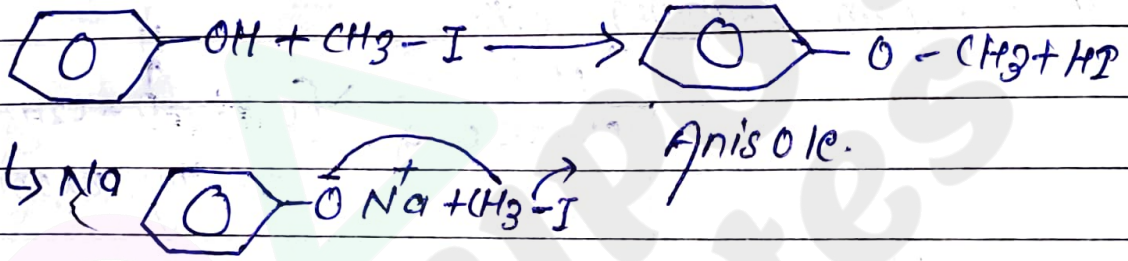
→ Because when it react with air it form high unstable compound i.e peroxide. and exploded on increasing temperature and heating, so old ethers are not distilled.

Uses of ethoxy ethane (diethyl ether) →

1- As solvent for oils, gums, resins, rubber etc.
2. As anaesthetic in surgery.
3. As refrigrants.
4. In the preparation of Grignard's reagent.

NEB 2071, 2072 (c)

(1) How would you obtained anisole from phenol?

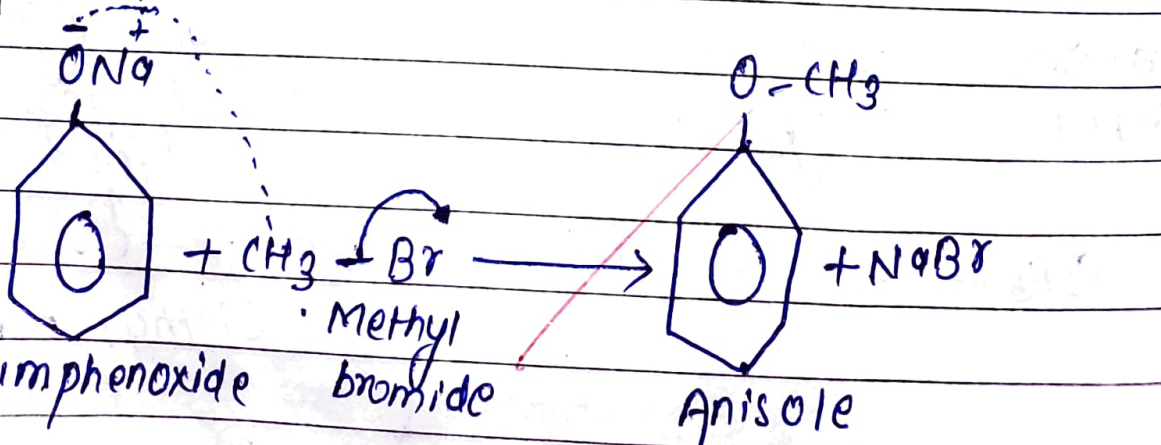


Aromatic ether →

1- preparation of methoxy benzene (anisole)
By Williamson ether synthesis:-

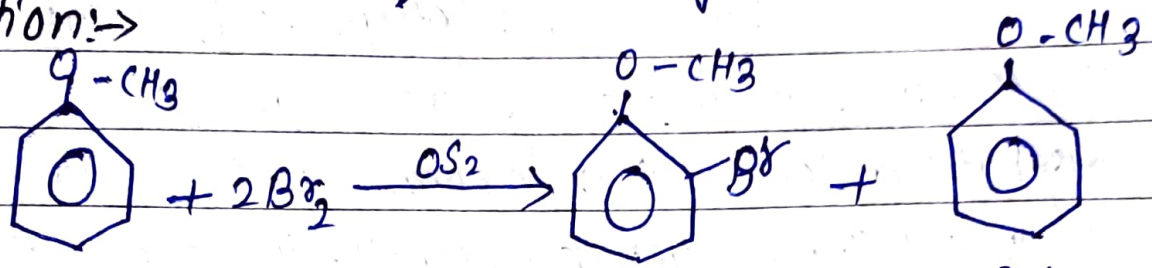
Methoxy ~~anisole~~ benzene (anisole) can be prepared by reacting haloalkane with sodium phenoxide.

Reaction.



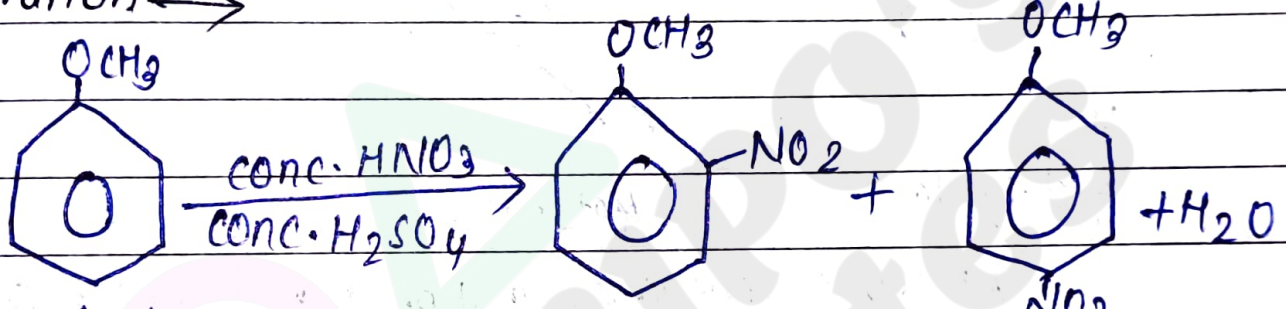
Electrophilic substitution reaction of aromatic ether.

1) Halogenation:→



O-bromoanisole. P-bromo anisole

2) Nitration →

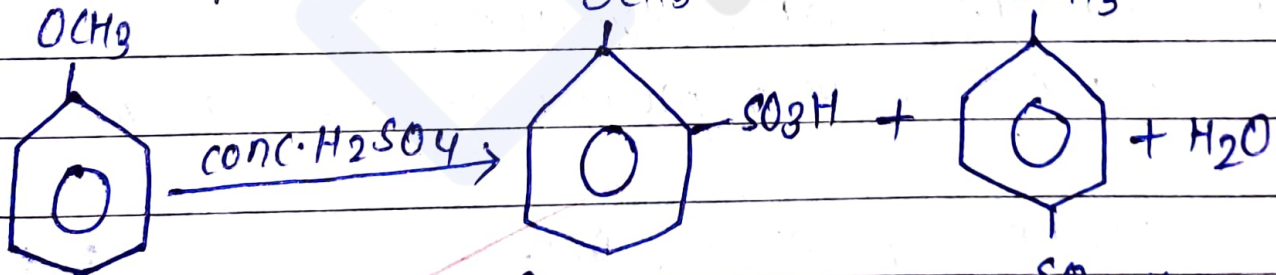


Anisole

O-nitroanisole

P-nitro anisole

3) Solphonation reaction :-



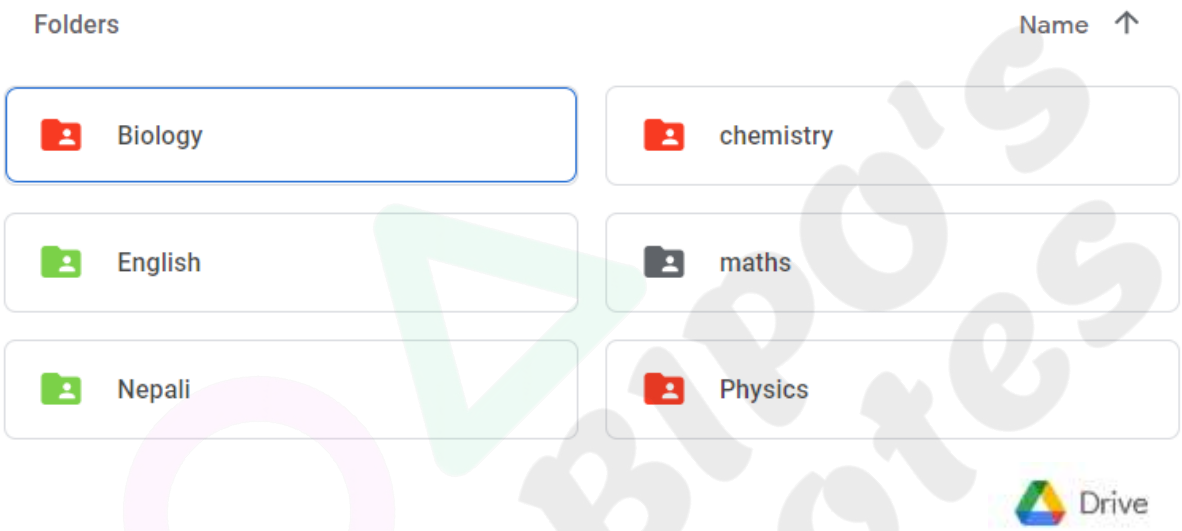
O-methoxy benzene sulphonic acid.

P-methoxy benzene sulphonic acid

Bipin Khatri

(Bipo)

Class 12 complete notes and paper collection.



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