Ethers & Epoxides

$R-O-R'$

* Functional isomers of alcohols.

- Symmetrical Ethers
- Unsymmetrical Ethers

} Depending on R group

Classification:

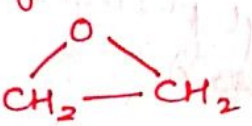
1. **Aliphatic Ethers:** Both R & R' Groups should be aliphatic.
   eg. CH_3-O-CH_3, $C_2H_5-O-C_2H_5$ etc.
2. **Aromatic Ethers:** One of the alkyl groups should be aryl.
   eg. $C_6H_5-O-CH_3$, $C_6H_5-O-C_2H_5$ $C_6H_5-OC_6H_5$

   Further:
   - Phenolic ethers. $C_6H_5-O-CH_3$
   - Diaryl ethers. $C_6H_5-O-C_6H_5$
3. **Cyclic Ethers:** Ethers in which oxygen is present in a ring are called cyclic ether.

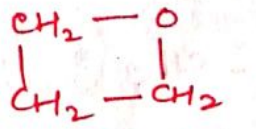
   Further:
   - Simple cyclic Ether → Containing maximum of 3 oxygen atoms in ring
   - Crown ethers :- At least 4-oxygen atoms in ring.

Simple cyclic Ether:

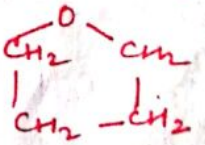
eg.



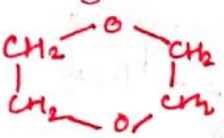
Oxirane. (Ethylene oxide)



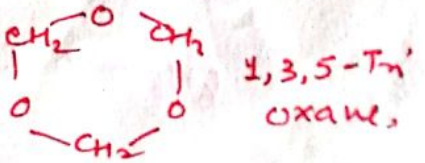
Oxetane



T.H.F



1,4-dioxane.



1,3,5-Trioxane.

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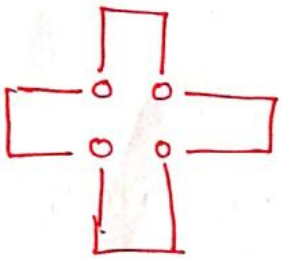
Crown Ethers: ~~eg:~~ Their 3-dimensional shape resembles with the shape of crown.

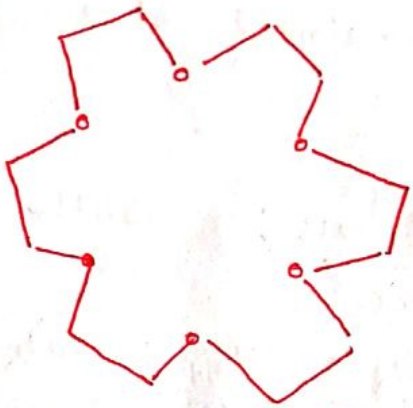
→ named as X crown Y

When X is total number of atoms.

Y is no of oxygen atoms.

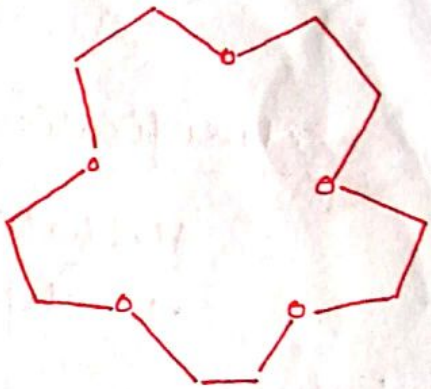


12-Crown-4



~~18 Crown-6~~

18-Crown-6



~~15-Crown-5~~

15 Crown-5

Nomenclature:

1. **Open chain Acyclic Ethers:**

Structure	Common Name	IUPAC. Name
CH_3-O-CH_3	Dimethyl ether or Methyl ether	Methoxy methane
$CH_3-O-C_2H_5$	Ethyl methyl ether	Methoxy ethane
$C_2H_5-O-C_2H_5$	Diethyl ether or Ethyl ether	Ethoxy ethane.
$CH_3-O-CH(CH_3)-CH_3$	Isopropyl methyl ether	2-Methoxy propane
$CH_3-CH(CH_3)-O-CH(CH_3)-CH_3$	Di isopropyl ether	2-propoxy 2-propane.
$C_6H_5-O-CH_3$	Methyl phenyl ether (Anisole)	Methoxy benzene
$C_6H_5-O-C_2H_5$	Ethyle phenyl ether. Phenetole	Ethoxy benzene
$C_6H_5-O-C_6H_5$	~~Phenoxy benzene~~ diphenyle ether	Phenoxybenzene

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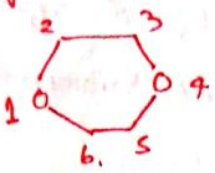
Oxa Names:

Oxacyclopropane

Oxacyclobutane

Oxacyclopentane

oxacyclohexane



~~oxa~~ 1,4-Dioxacyclohexane.

Methods of Formation

A) From Alkyl halides

1) Williamson's Synthesis:

* One of the Best Methods
* Reaction of Alkyl halides with sodium alkoxide.
* Sod. Alkoxide is prepared by r^n of Alcohol + Na.
* It is a nucleophilic substitution reaction

$$2R'-OH + 2Na \longrightarrow 2R'-ONa + H_2\uparrow$$

$$R'-O^{\ominus}Na^{\oplus} + R-X \longrightarrow R'-O-R + NaX$$

Sod. Alkoxide Alkyl halide Ether

* Used for preparation of both symmetrical and unsymmetrical ether's.

Limitation:

* Halogens attached to double bond or aromatic ring cannot be easily displaced by a nucleophilic reagent so aryl halides are not generally used for Williamson's synthesis.
* Reaction is carried out between alkyl halide and sodium phenoxide.

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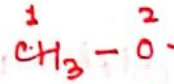
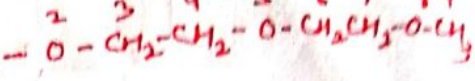
2- Acyclic Polyethers: Long polychain ethers are named as oxa-derivatives of names as alkanes corresponding to the total no of carbon and oxygen atoms present in chain.



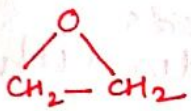
2,5-dioxahexane.



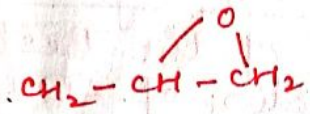
2,5,7-trioxanonane.

3- Cyclic Ethers:

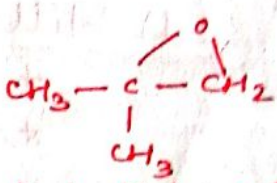
(i) Common Names: In common system three membered cyclic ethers are named as oxides of alkylene from which they are derived.



Epoxide
Ethylene oxide.



Propylene oxide.



Isobutylene oxide.

* Names of some cyclic ethers are based upon the name of their fully hydrogenated products

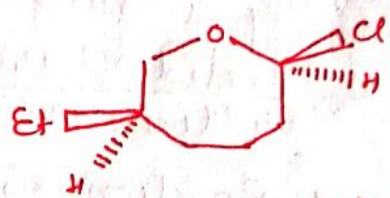
furan → T.H.F.

4-Hpyran or 2-Hpyran → T.H.P. Tetrahydropyran

(ii) IUPAC Names: Different-

n=2 Oxirane. n=3 Oxetane. n=4 Oxolane. n=5 Oxane. n=6 Oxepane.

Trans-2,3-dimethyl oxirane.
or trans dimethyl oxirane



Cis-2-Chloro-6-ethyloxypane.

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B: From Alcohols:

1.- By Dehydration of Alcohols: Either in presence of acid or in presence of ~~heat~~ heated Alumina.

a) Acid Catalysed dehydration:

* Only symmetrical ethers can be prepared.
* In presence of Conc. H_2SO_4 at 140°C

$$R-OH + HO-R \xrightarrow[140^\circ C]{Conc.\ H_2SO_4} R-O-R + H_2O$$

$$2C_2H_5OH \xrightarrow[140^\circ C]{Conc.\ H_2SO_4} C_2H_5-O-C_2H_5 + H_2O$$

* Yield depends upon nature of Alcohol

Primary > Secondry > Teriary
1° > 2° > 3°

* * Dehydration of alcohols is used only for preparing ethers from primary alcohols.
* * This method is not suitable for unsymmetrical ether synthesis. because complex mixture of ethers is always obtained

$$3R-OH + 3HO-R' \xrightarrow[140^\circ C]{Conc.\ H_2SO_4} R-OR + R-OR' + R'-OR + 3H_2O$$

1° Alcohol follows S_N1 mechanism.

2° & 3° Alcohols follow S_N2 mechanism.

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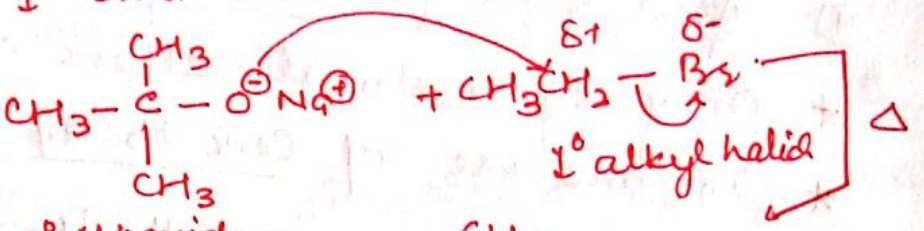
$C_6H_5O^{\ominus}Na^{\oplus} + CH_3CH_2-I \xrightarrow{\Delta} C_6H_5-O-CH_2CH_3 + NaI$

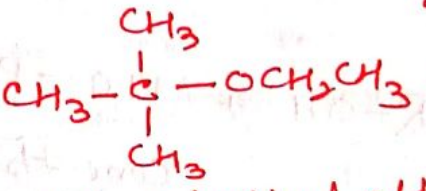
$C_6H_5-Br + CH_3CH_2O^{\ominus}Na^{\oplus} \xrightarrow{\Delta} \times$

* Best yields of unsymmetrical ethers obtained when alkyl halides are 1° and alkoxides are 1°, 2° or 3°.

eg.



3° Alkoxid

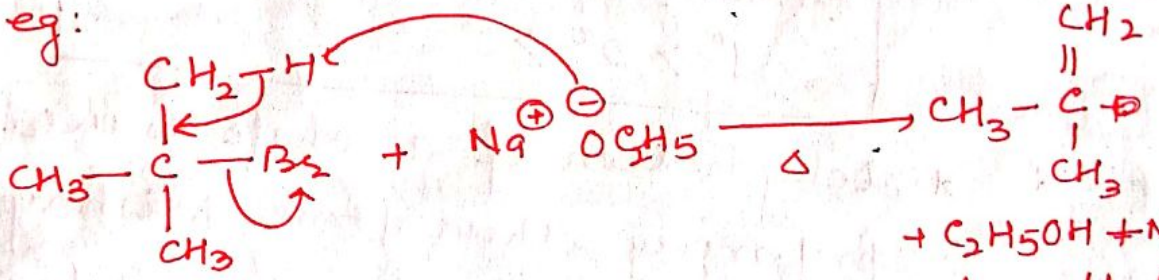


+ NaBr

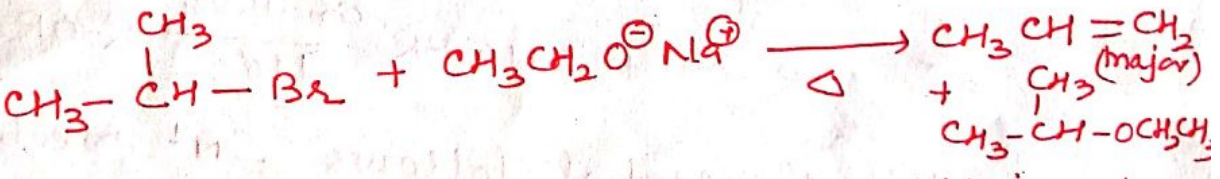
t-butylethyl ether.

* Above ether cannot be prepared by sodium ethoxide with teirtiary butyl chloride or bromide.

eg:



Due to steric hindrance, secondry alkyl halide also prefer to undergo elimination rather than substitution.



79%	21%

2- Reaction of Alkyl halide with dry Ag2O (Anhydrous)

$2CH_3CH_2-Br + Ag_2O \xrightarrow{\Delta} CH_3CH_2-O-CH_2CH_3 + 2AgBr$

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Chemical Properties:

Reactions involving (C-O) bond:

1. With halogen acid:

$$R-O-R + HX \xrightarrow{100^\circ C} R-OH + RX.$$

$$CH_3CH_2-O-CH_2CH_3 + HI \xrightarrow{100^\circ C} CH_3CH_2-I + CH_3CH_2-OH.$$

$$R-OH + HX \text{ (excess)} \xrightarrow{100^\circ C} R-X + H_2O.$$

$$R-O-R + 2HI \xrightarrow{100^\circ C} 2R-I + H_2O$$

* Cyclic ethers are readily cleaved by HBr or HI to yield dihaloalkanes.

T.H.F.

$$+ 2HBr \xrightarrow{100^\circ C} Br-CH_2-CH_2-CH_2-CH_2-Br + H_2O$$

1,4-dibromobutane

* In this case reactivity of Halogen acid. is

$$HI > HBr > HCl.$$

* Cleavage of ethers proceeds through Nucleophilic attack of halide ion on protonated ether molecule.
  - → Greater the nucleophilicity of halide ion. more reactive is the halogen acid.
  - → And. Nucleophilicity of halide ions are

$$I^- > Br^- > Cl^-$$

therefore reactivity = $\boxed{HI > HBr > HCl}$

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