ETHERS AND EPOXIDE

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Ethers - R-O-R linkage

Symmetrical ethers

- R =R′
- *Simple ethers*
  - Dimethyl ether

    Me -O –Me
  - Diethyl ether

    Et - O -Et

Unsymmetrical ethers

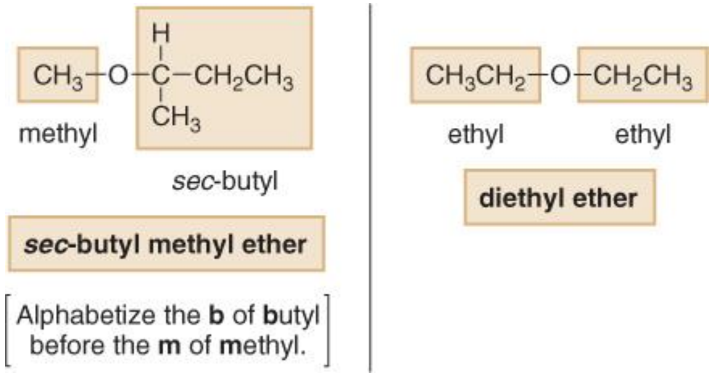
- R ≠ R’
- *Mixed ethers*
  - Ethyl methyl ether

    Me -O –Et
  - Methyl phenyl ether

    Me – O-Ph

Nomenclature

- Simple ethers - assigned common names
  - Name both alkyl groups bonded to the oxygen, arrange these names alphabetically, and add the word ether
  - For symmetrical ethers, name the alkyl group and add the prefix “di-”



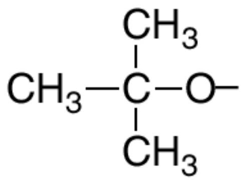
Nomenclature - IUPAC system

- One alkyl group is named as a hydrocarbon chain, the other is named as part of a substituent bonded to that chain:
  - Name the simpler alkyl group as an alkoxy substituent by changing the –yl ending of the alkyl group to –oxy.
  - Name the remaining alkyl group as an alkane, with the alkoxy group as a substituent bonded to this chain

Common alkoxy groups

$CH_3O–$ methoxy

$CH_3CH_2O–$ ethoxy



tert-butoxy

Nomenclature - IUPAC system

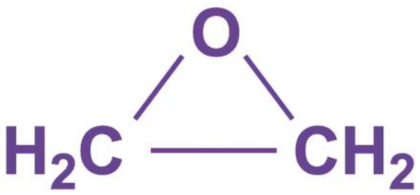
- $CH_3CH_2CH_2OCH_3$
  - 1-methoxypropane
- $CH_3CH(OCH_3)CH_3$
  - 2-methoxypropane
- $CH_3CH(CH_3)OCH_3CH(CH_3)$
  - 2-(2-Propoxy)propane

Polyether

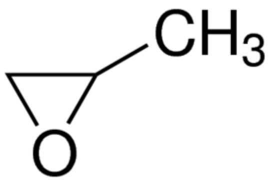
- More than one ether linkage
- Named as Oxa derivative of alkane corresponding to total number of C & O atom present
- CH_3-O-$CH_2CH_2CH_2$-O-CH_3
  - ➢ 1,3-dimethoxypropane or 2,6-Dioxaheptane
- $CH_3OCH_2CH_2CH_3$
  - ➢ 2-oxapentane

Cyclic ether

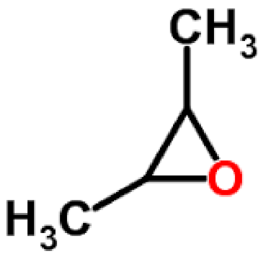
- Epoxides – alkene oxides
- 3 membered cyclic ether



Ethylene oxide
Epoxy ethane
Ethene oxide



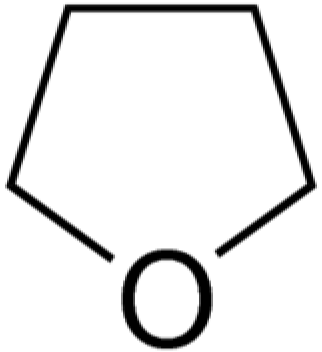
Propyleneoxide
1,2-Epoxypropane
1,2 – Propene Oxide



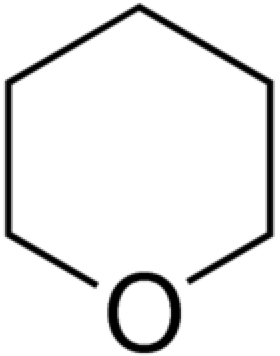
Butyleneoxide
2,3-Epoxybutane
2,3- Butene Oxide

Cyclic ether

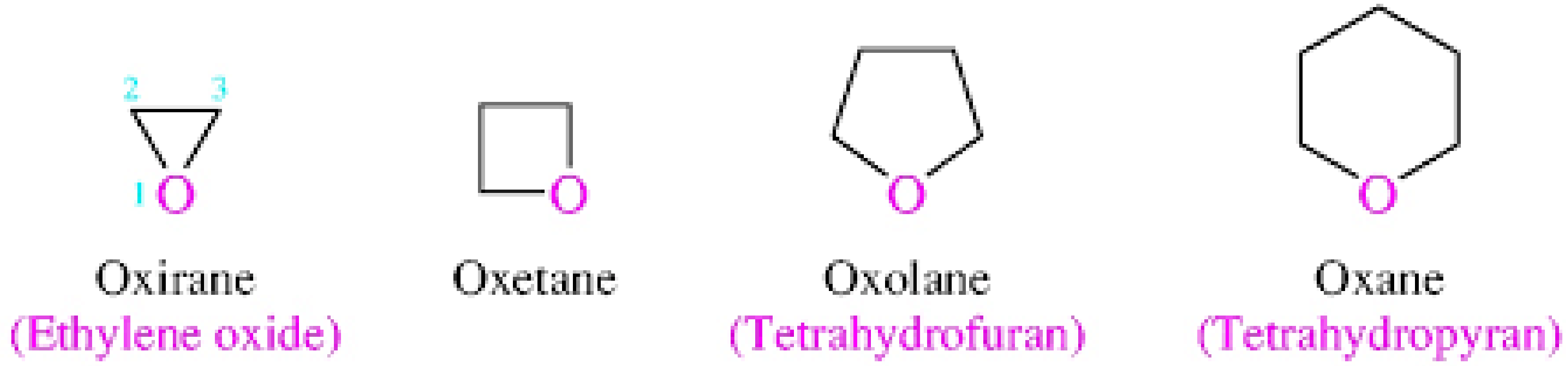
- Tetrahydrofuran



- Tetrahydropyran



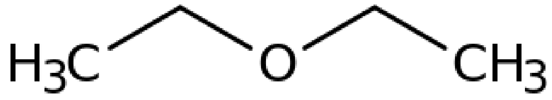
Cyclic ether - IUPAC



Structural isomerism

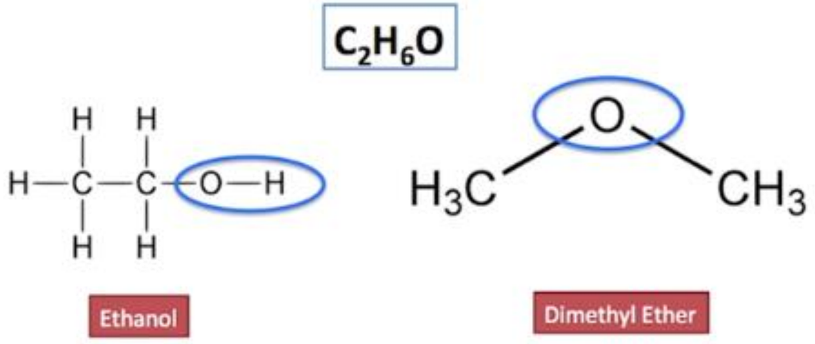
- Exhibits metamerism

Diethyl Ether



Methyl propylether

- Functional group isomers



Preparation

- **Dehydrogenation of alcohol**

- **Industrial synthesis** for diethyl ether:

$$2\ CH_3CH_2\text{-}OH \quad + \quad H_2SO_4 \xrightarrow{140^oC} CH_3CH_2\text{-}O\text{-}CH_2CH_3 \quad + \ H_2O$$

- S_N2 mechanism
- Not generally useful for syntheses of ethers in the lab:

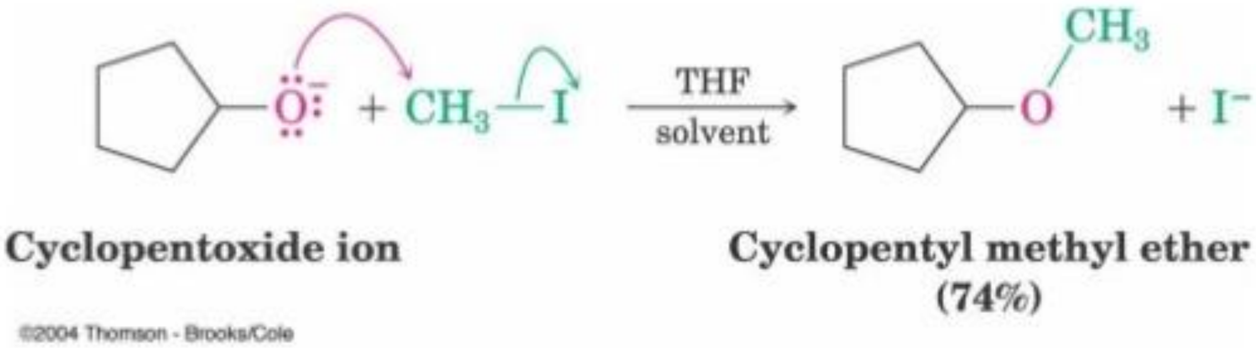
a) Only symmetric ethers can be made this way.

b) Conditions are very compound specific

(at 180^o ethanol would yield ethylene instead of the ether)

Williamson ether synthesis

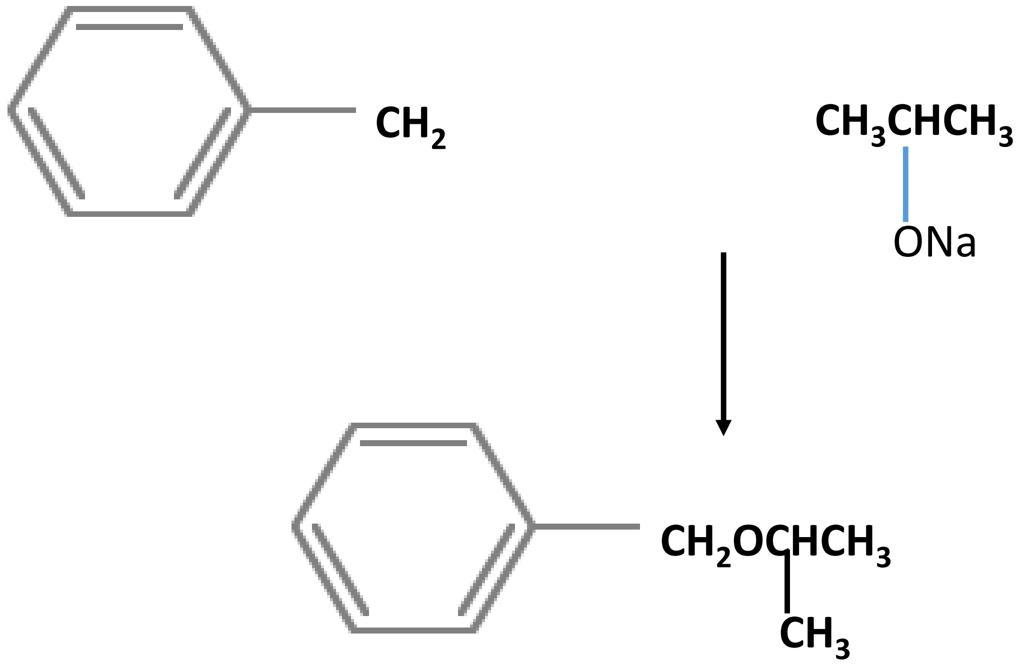
- reaction between a metal alkoxide & alkyl halide
- **$R\text{-}O^{-}Na^{+}$ + $R'\text{-}X$ → $R\text{-}O\text{-}R'$ + NaX**
- $R'\text{-}X$ should be CH_3 or 1°
- S_N2 mechanism



Another Example

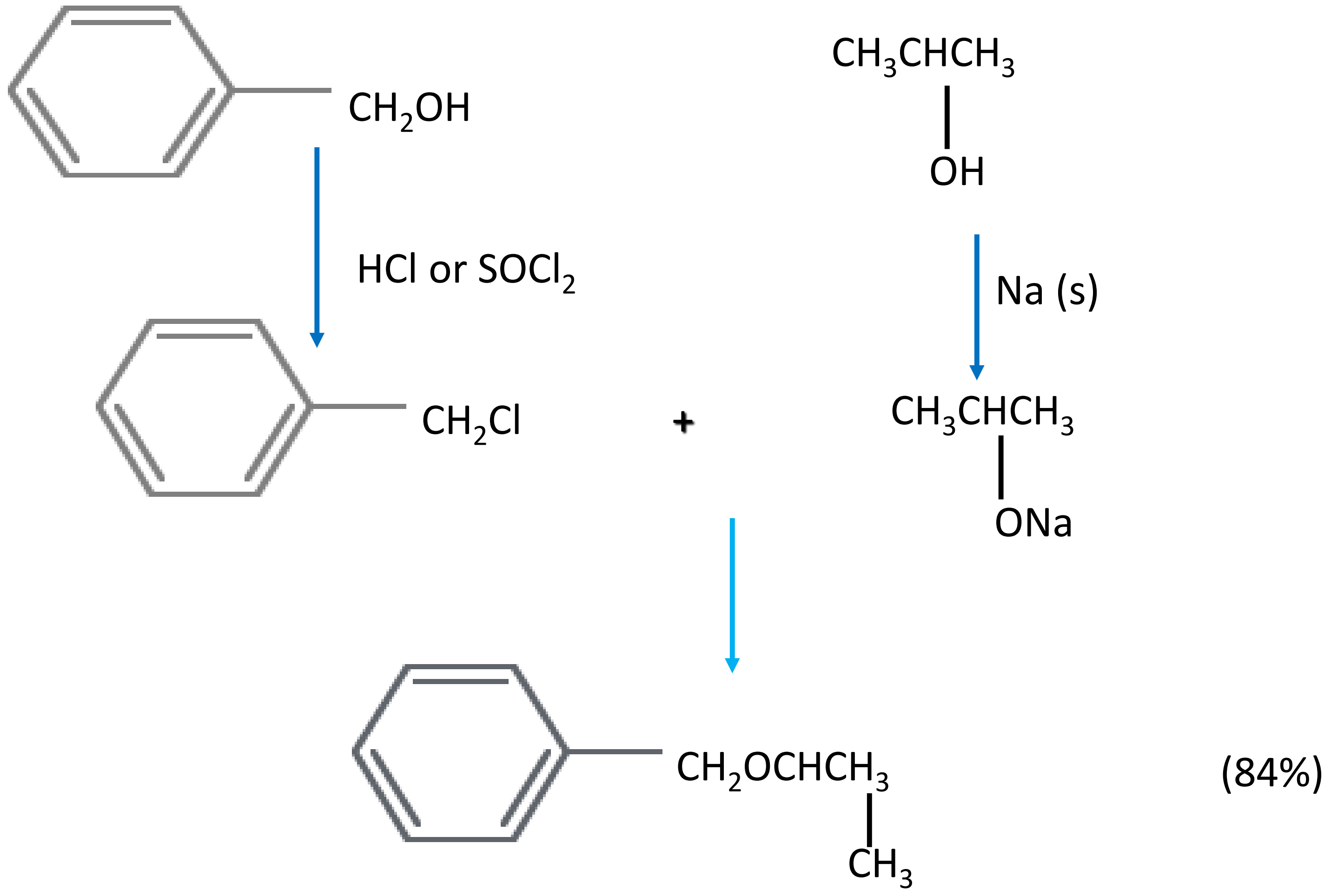
Alkyl halide must be primary

Alkoxide ion can be derived from primary, secondary, or tertiary alcohol



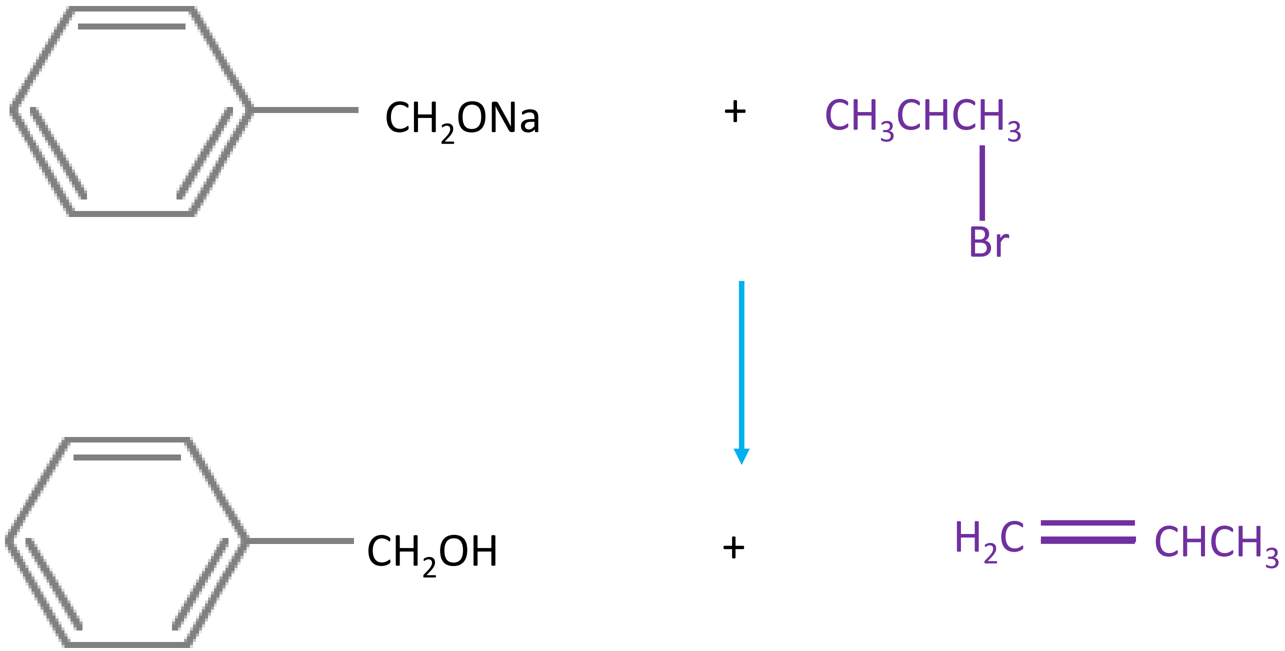
(84%)

1^o Halides & Alkoxides



What if the alkyl halide is not primary?

S_N2 vs E2

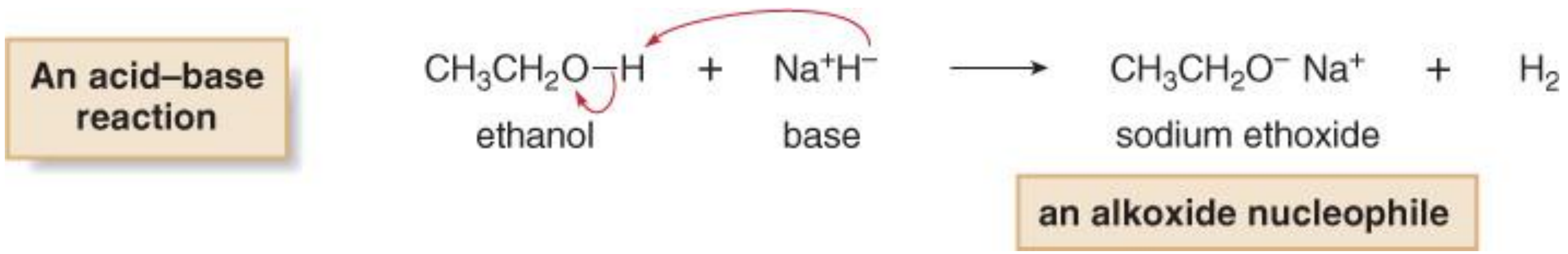


Elimination produces the major product.

Alkoxides

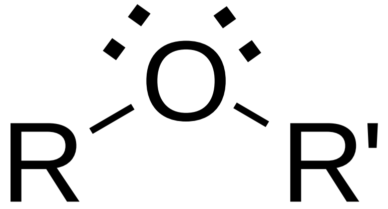
- Alkoxides can be prepared from alcohols by a Brønsted-Lowry acid—base reaction

- For example, sodium ethoxide ($NaOCH_2CH_3$) is prepared by treating ethanol with NaH



- NaH is an especially good base for forming alkoxide - by-product of the reaction, H_2, is a gas that just bubbles out of the reaction mixture

Physical properties:



oxygen is sp^3 hybridized, bond angle ~ 109.5^o

ethers are polar;   no hydrogen bonding

mp/bp moderate

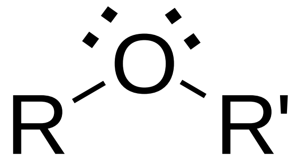
water insoluble

Ethers and epoxides exhibit dipole-dipole interactions because they have a bent structure with two polar bonds

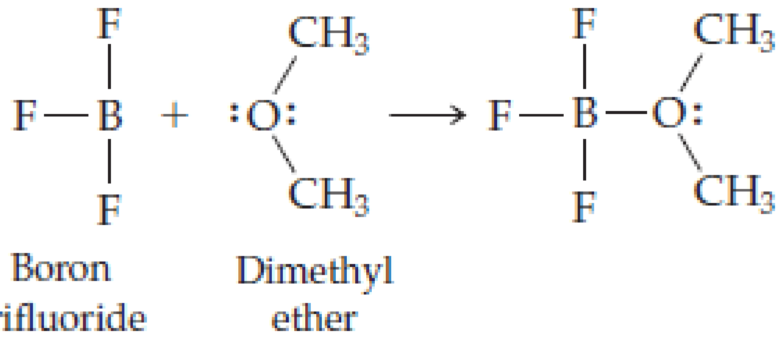
Diethyl ether = very important organic solvent, polar, water insoluble, bp = 35^o.
Very flammable & forms explosive peroxides

Chemical reaction of ethers

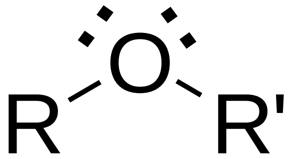
- Two lone pair – Lewis Base



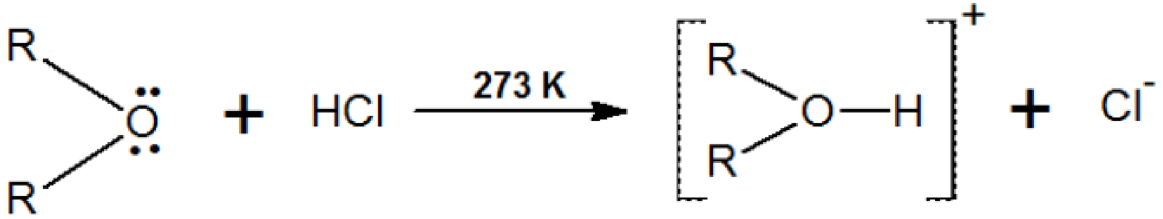
- Basic property –
-
- Forms etherates with Lewis acid such as BF_3



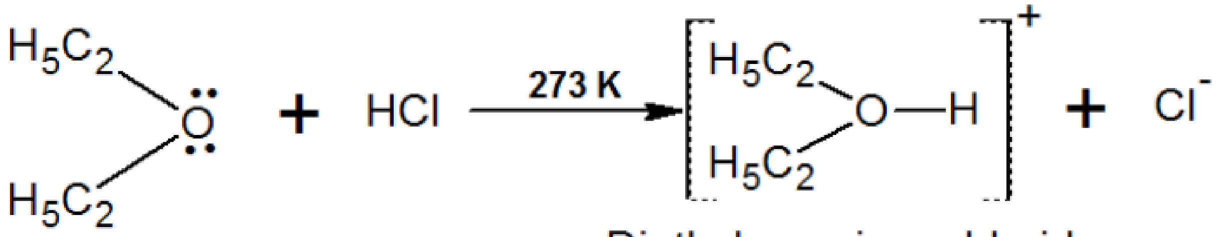
Chemical reaction of ethers



- Basic property –
- Oxonium salt with cold conc. inorganic acid



Dialkyl oxonium chloride



Diethyl oxonium chloride

Chemical reaction of ethers

Acid cleavage

$$R\text{-}O\text{-}R' + \text{(conc) } HX \xrightarrow{\text{heat}} R\text{-}X + R'\text{-}OH$$

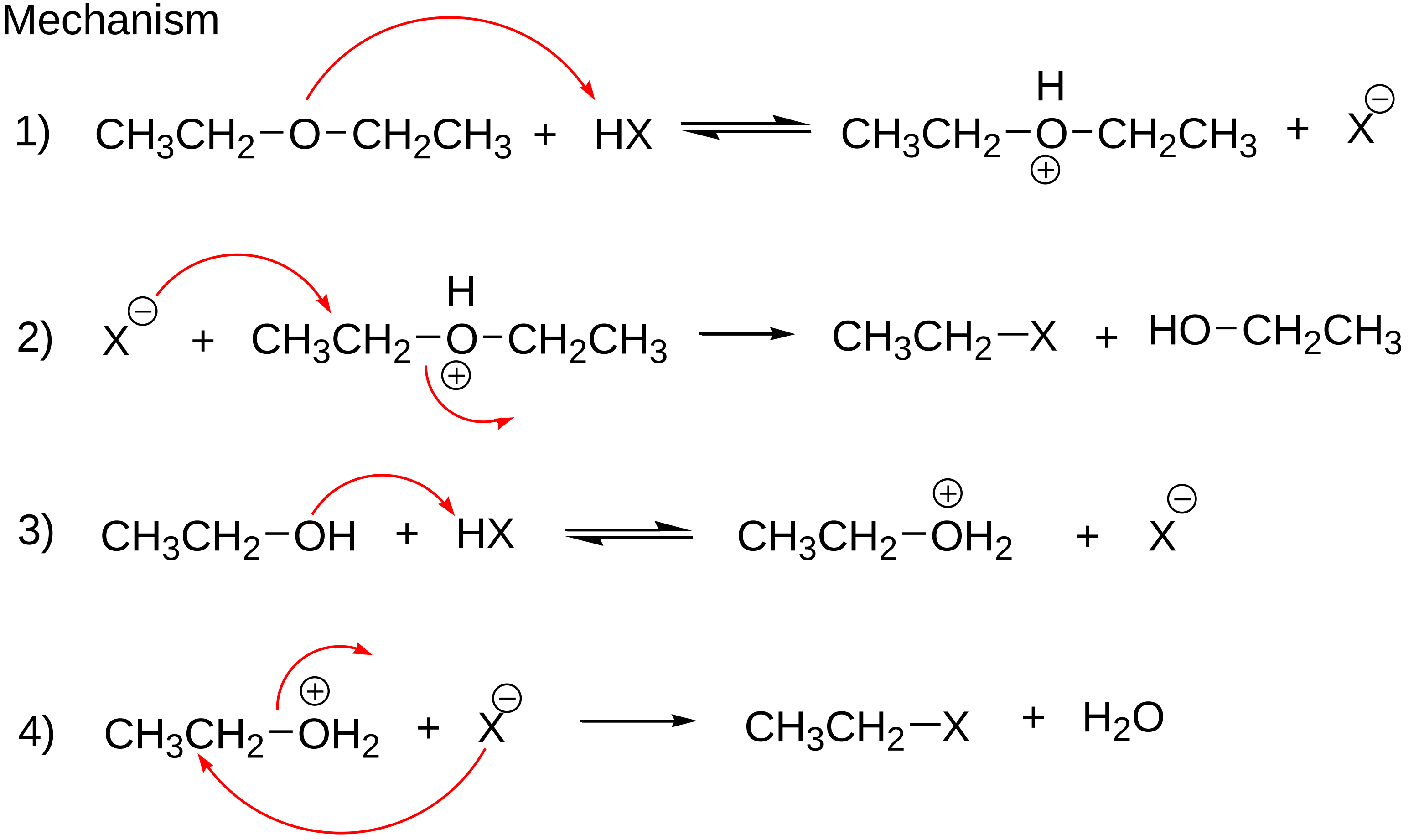
If excess of HX is used, the alcohol formed reacts further to give alkyl halide

$$R\text{-}O\text{-}R' + \text{(conc) } HX \xrightarrow{\text{heat}} R\text{-}X + R'\text{-}X$$

X = Br, I

Acid cleavage

Mechanism



Reactions of unsymmetrical ether

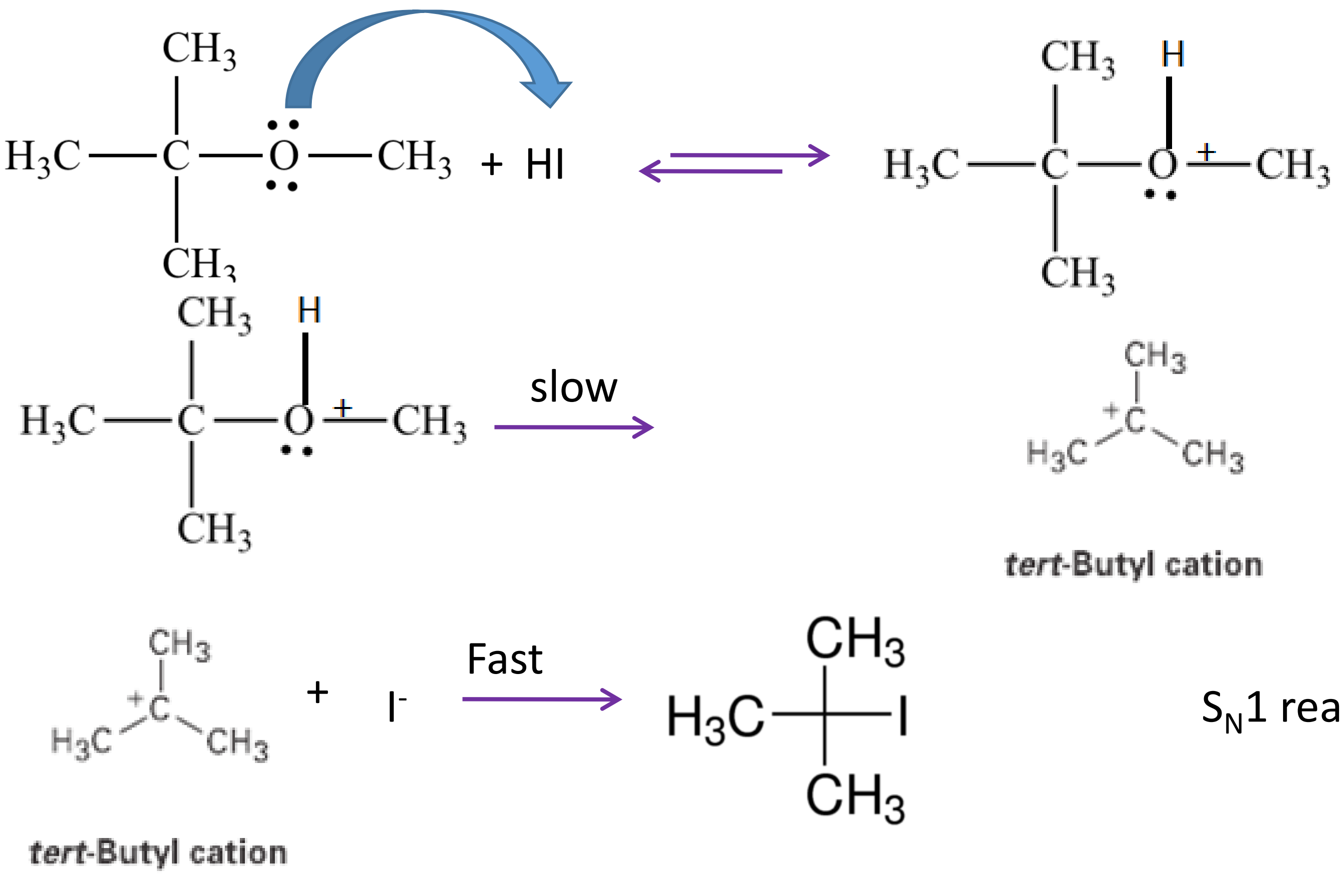
- When alkyl group of an ether is 1^o or 2^o
  - S_N2 mechanism
  - nucleophile I^- attacks the least substituted C of oxocation

$$CH_3\text{-}\ \ddot{O}\text{-}CH_2CH_3 + H\text{-}I \rightleftharpoons CH3\text{-}\ \overset{H}{\underset{+}{O}}\text{-}CH2CH3 + I^-$$

$$I^- + CH_3\text{-}\ \overset{H}{\underset{+}{O}}\text{-}CH_2CH_3 \longrightarrow CH_3I + CH_3\text{-}CH_2\text{-}OH$$

If excess of HI is used , ethanol is converted to ethyl iodide

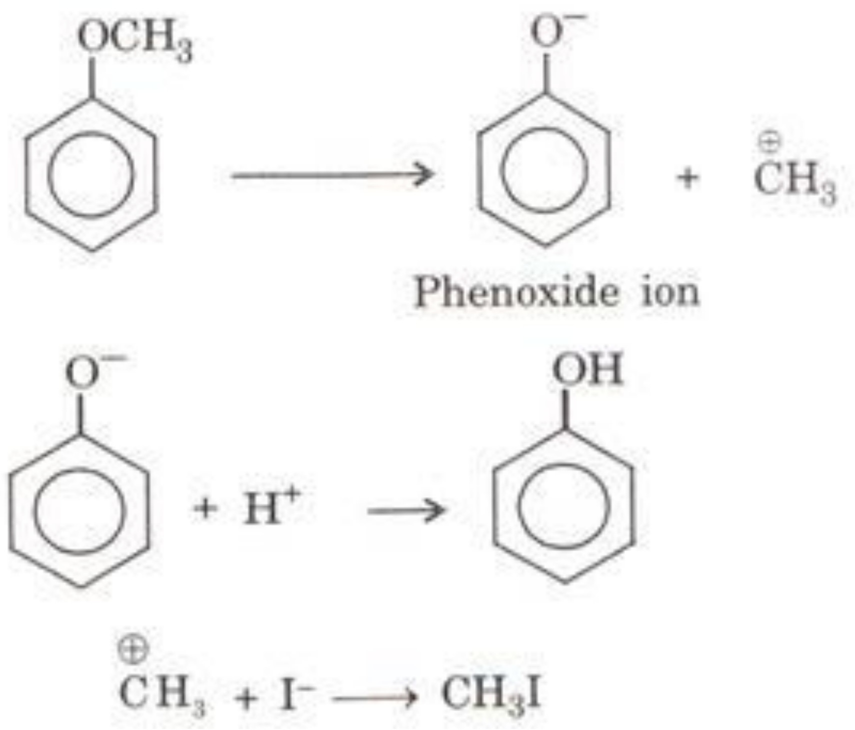
When alkyl group of an ether is 3°



S_N1 reaction

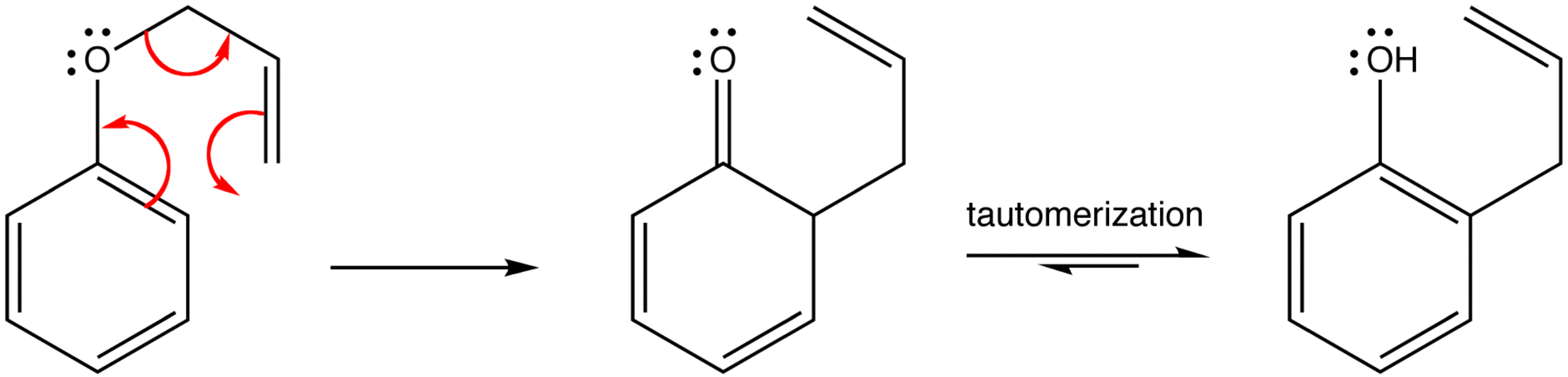
Reaction of aryl ether

- Anisole reacts with HI $CH_3\text{-}O\text{-}CH_3 + HI \longrightarrow CH_3I + C_6H_5OH$



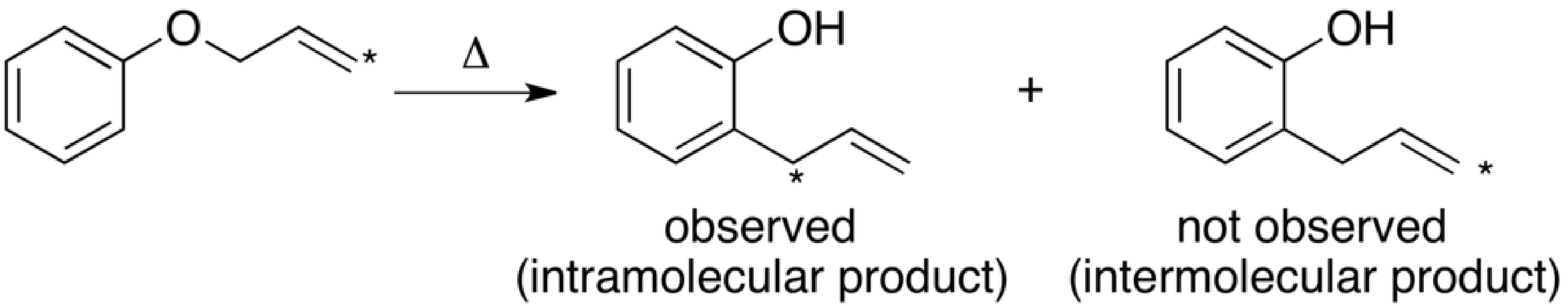
Claisen rearrangement

- [3,3]-sigmatropic rearrangement
- allyl phenyl ether is converted thermally to an unsaturated carbonyl compound followed by rearomatisation



Claisen rearrangement

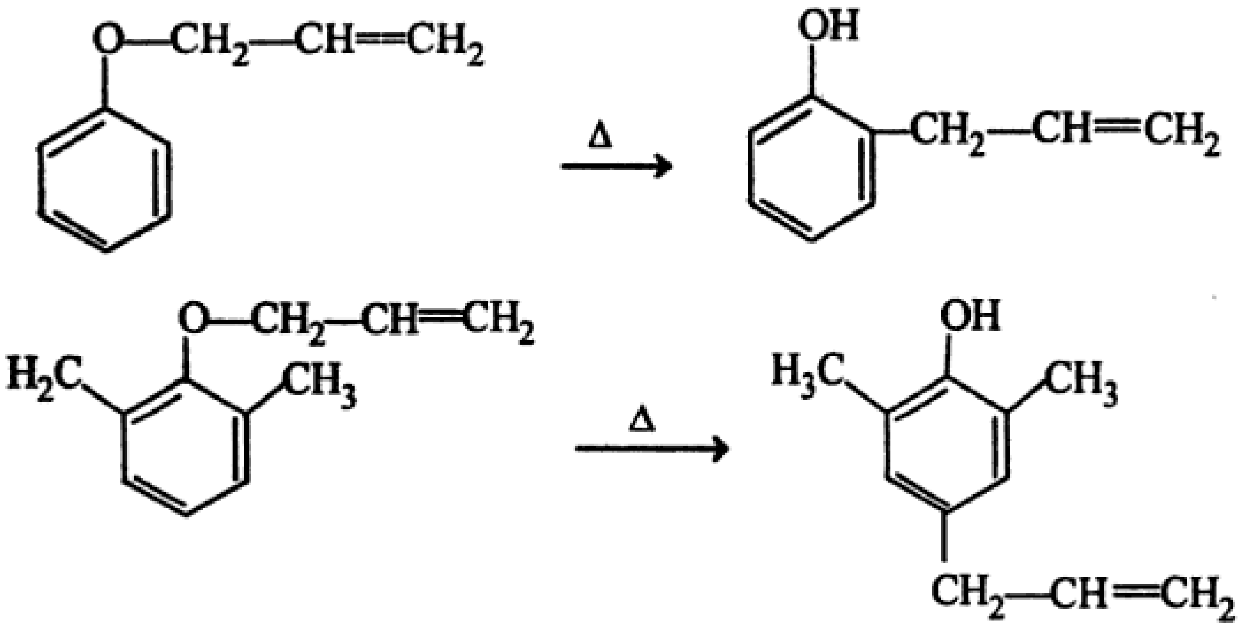
- Allyl group migrates to ortho position
- Inversion of allyl group during rearrangement



- No cross product when reaction carried out with mixture of allyl phenyl ethers – Intramolecular mechanism

Claisen rearrangement

- ortho position is preferred
- If both ortho position occupied – migrate to para position



Zeisel's method -estimation of methoxy group

Reaction B/W ether and Hydroiodic acid used

$$R-OCH_3 + HI \rightarrow R\text{-}OH + H_3C\text{-}I$$

Methoxy liberated is absorbed in alc.Silver nitrate sol^n and silver iodide is ppted.

$$CH_3I + AgNO_3 + H_2O \rightarrow CH_3OH + AgI\downarrow + HNO_3$$

The precipitate of **AgI** is collected washed dried and weighted

One Mole Of Silver Iodide Precipitate Corresponds To Presence Of One Methoxy Group

Zeisel's method

Calculation

Wt of sample taken = w_1 gms

Wt of AgI formed = w_2 gms

From above reaction

1 mole of AgI = one OCH_3 group

234g of AgI = 31g of OCH_3 group

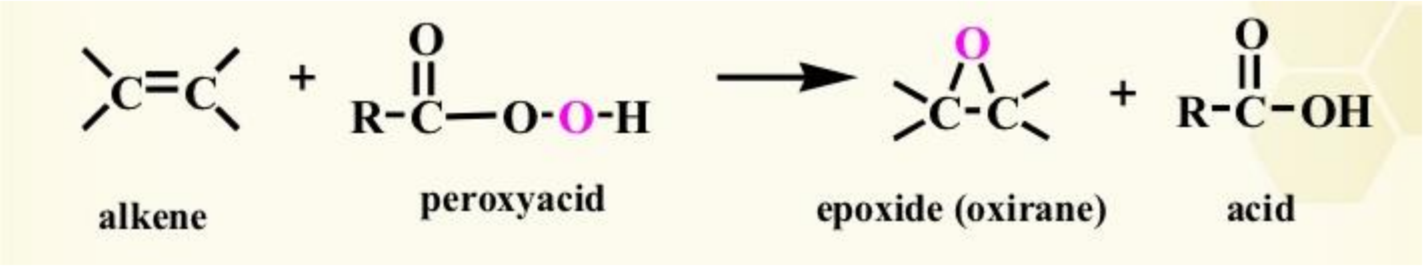
Percentage of methoxy group = $31/234 * w_2/w_1 * 100$

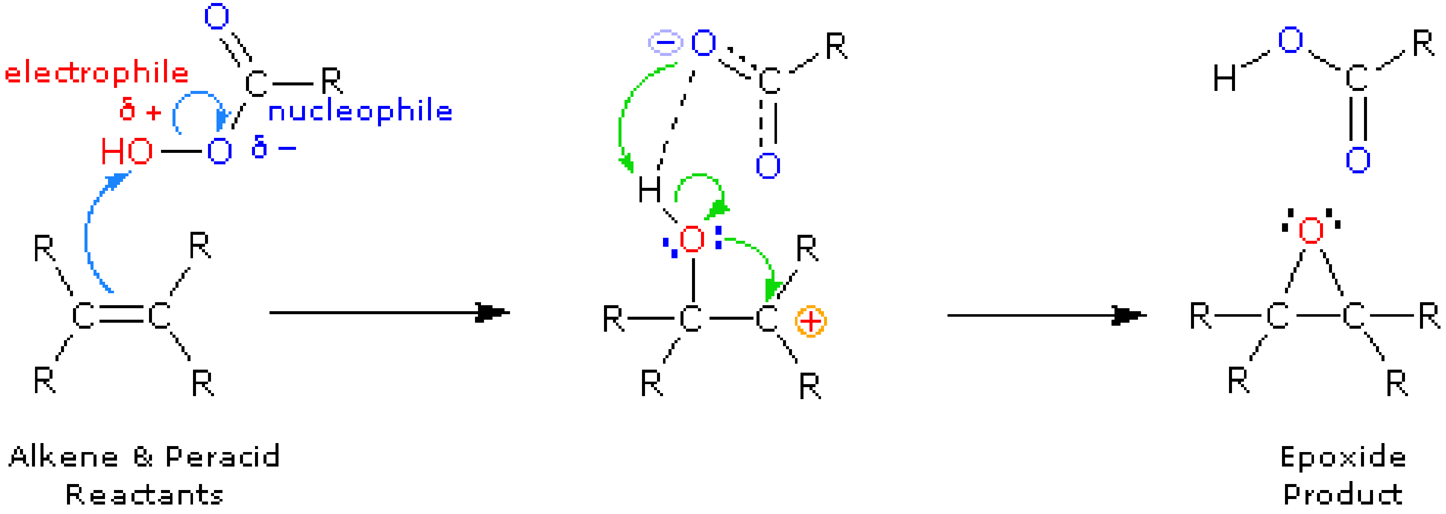
No. of methoxy group in compound = $(w_2 \times M)/(234 \times w_1)$

M= Molecular mass of sample

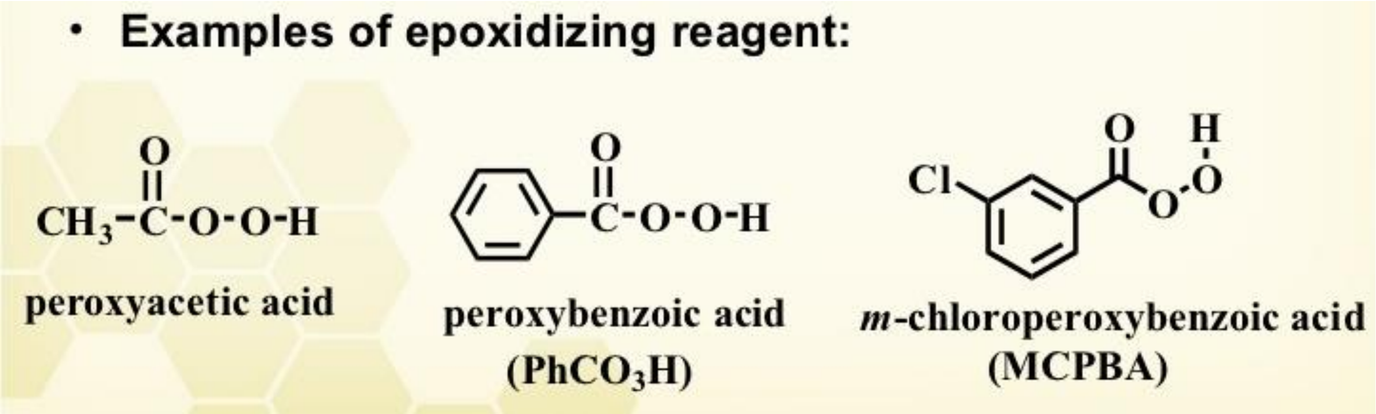
Epoxide - Preperation

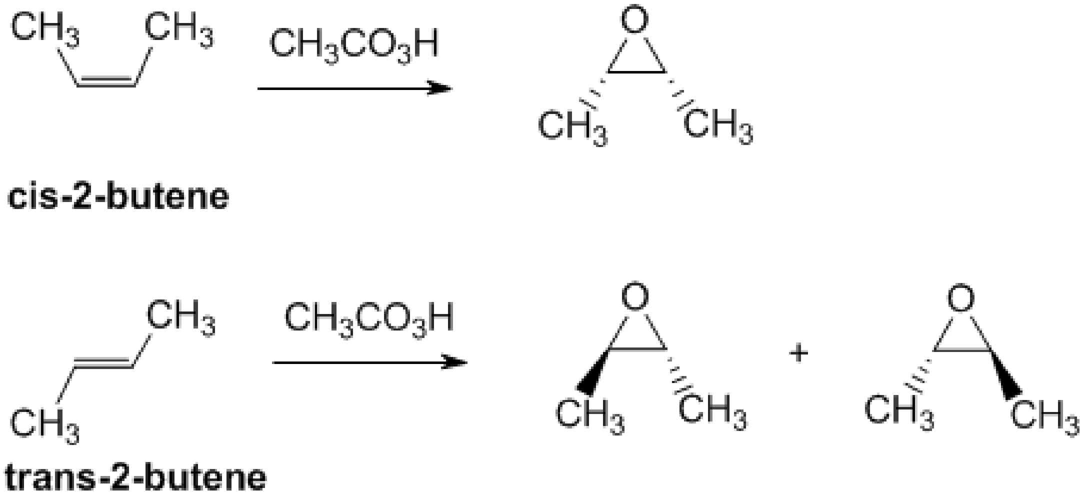
- Epoxidation of alkene
  - Reaction of alkenes with peracid





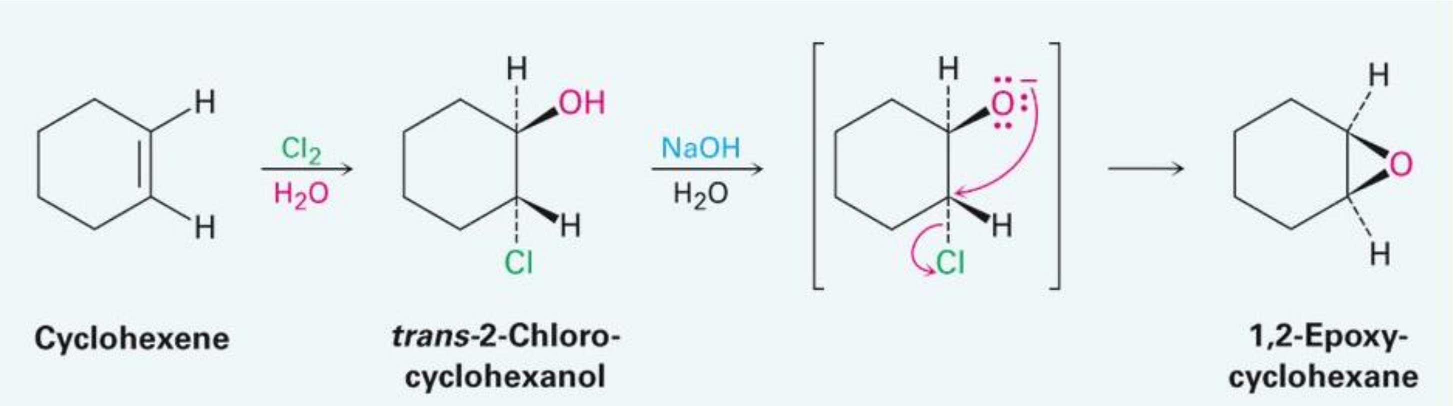
Epoxidation of alkene





Preparation from halohydrin

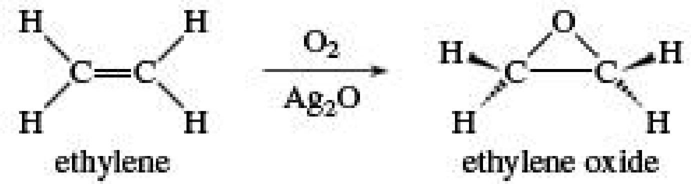
- Addition of HOX to an alkene gives a Halohydrin
- Treatment of a Halohydrin with base gives an epoxide
- Intramolecular Willamson Ether synthesis



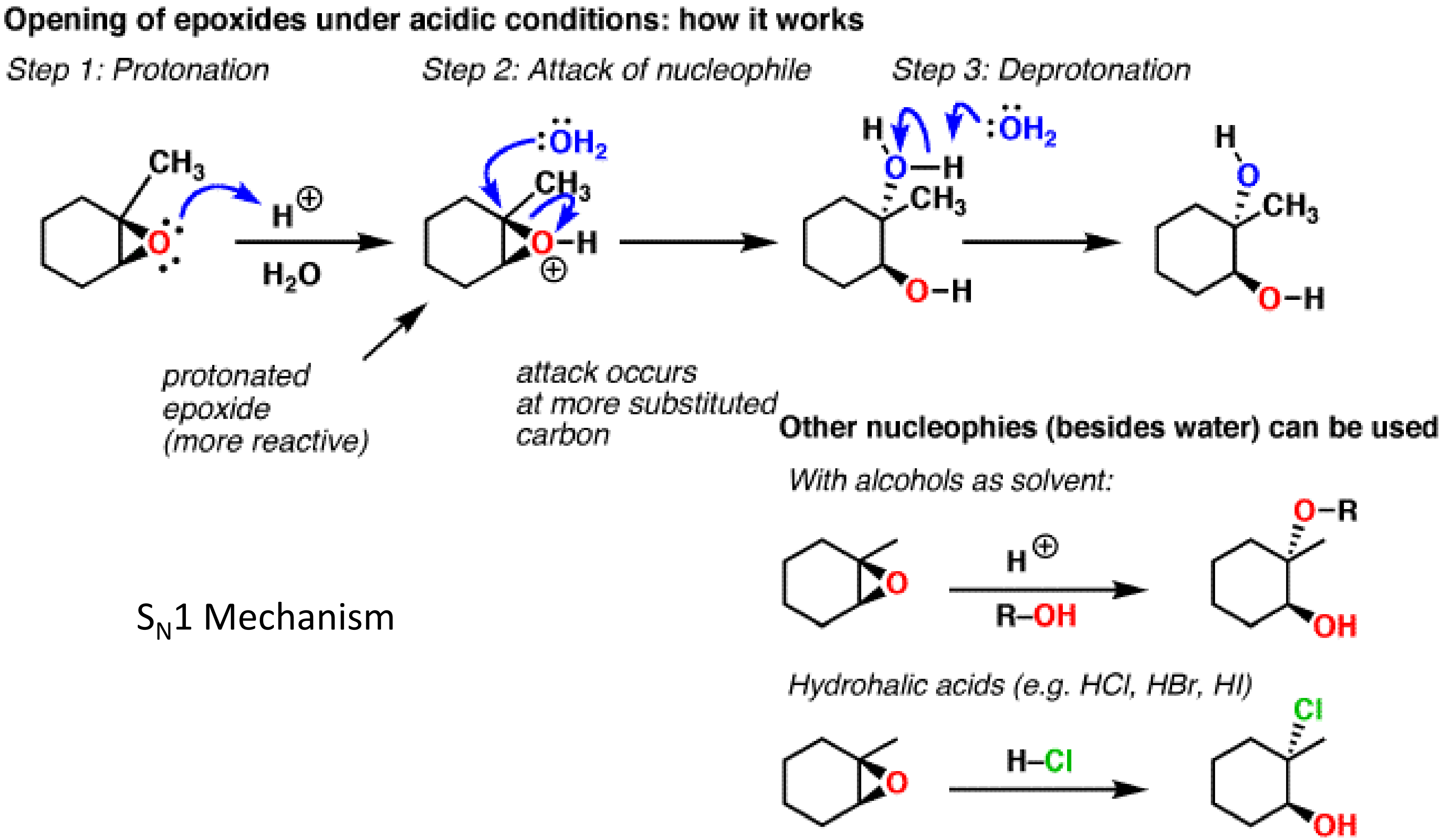
Industrial synthesis of ethylene oxide

- Controlled oxidation (using oxygen or air) of ethylene over a silver catalyst
- Exothermic
- Excessive rise in temperature & over oxidation – complete combustion liberating H_2O & CO_2
- High temperature cause degradation of catalyst

Ag/Al_2O_3 also acts as catalyst

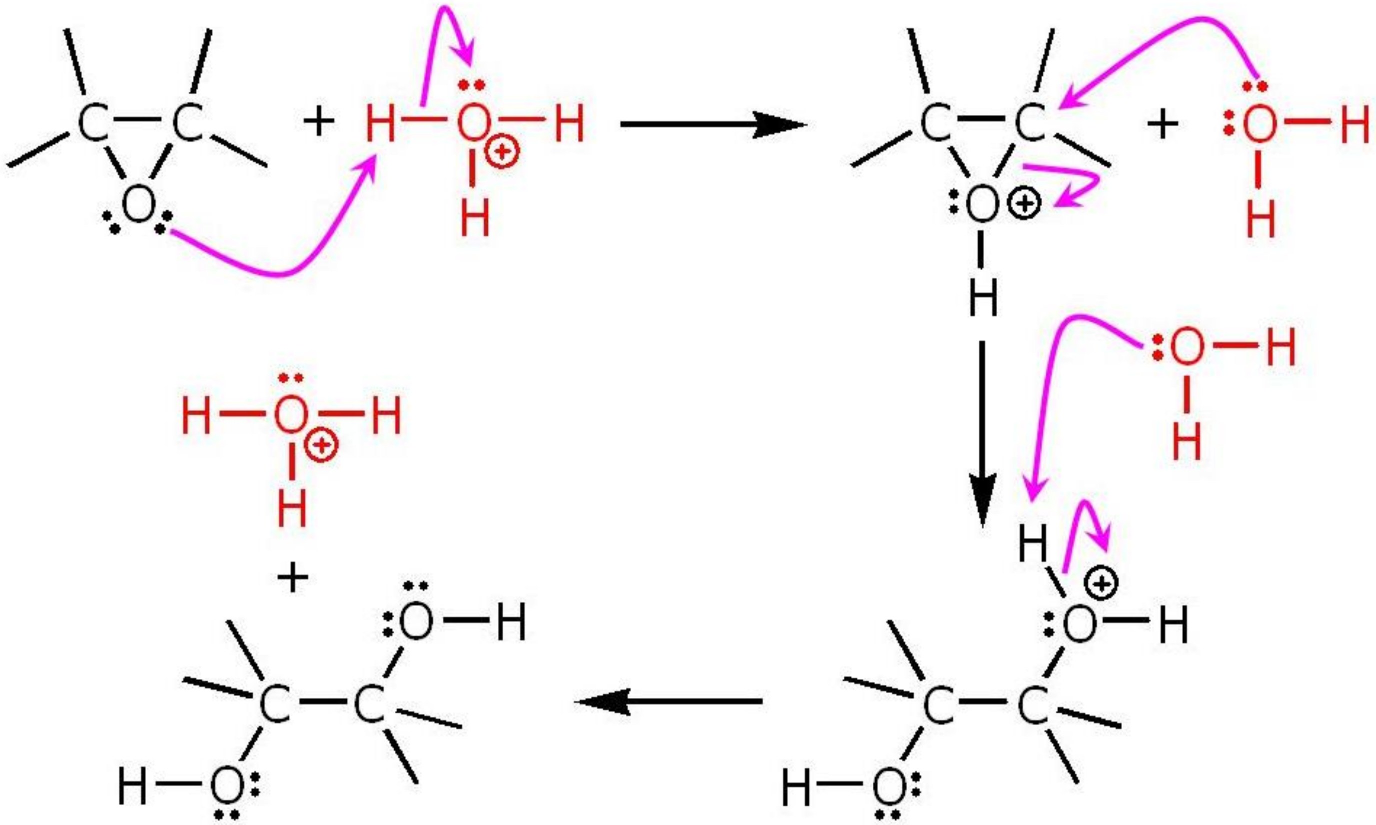


Acid catalyzed ring opening



S_N1 Mechanism

Acid catalyzed ring opening

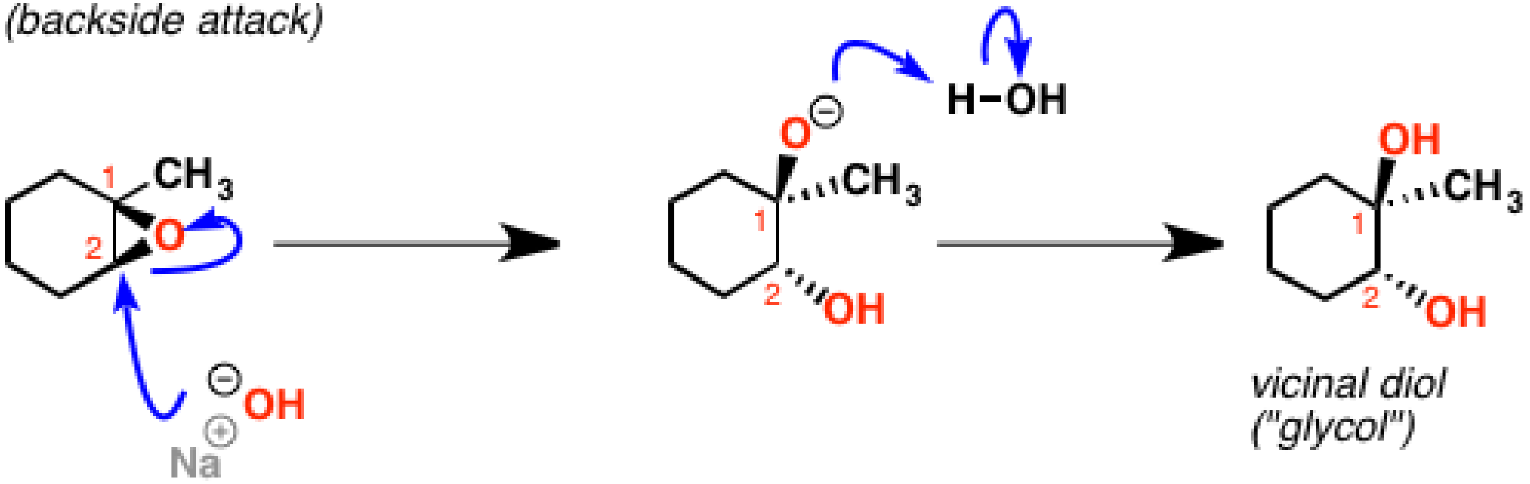


Base catalyzed ring opening

The best explanation for the observed product is that it proceeds through an S_N2 mechanism followed by a protonation (giving the neutral alcohol)

Step 1: S_N2 Reaction (backside attack)

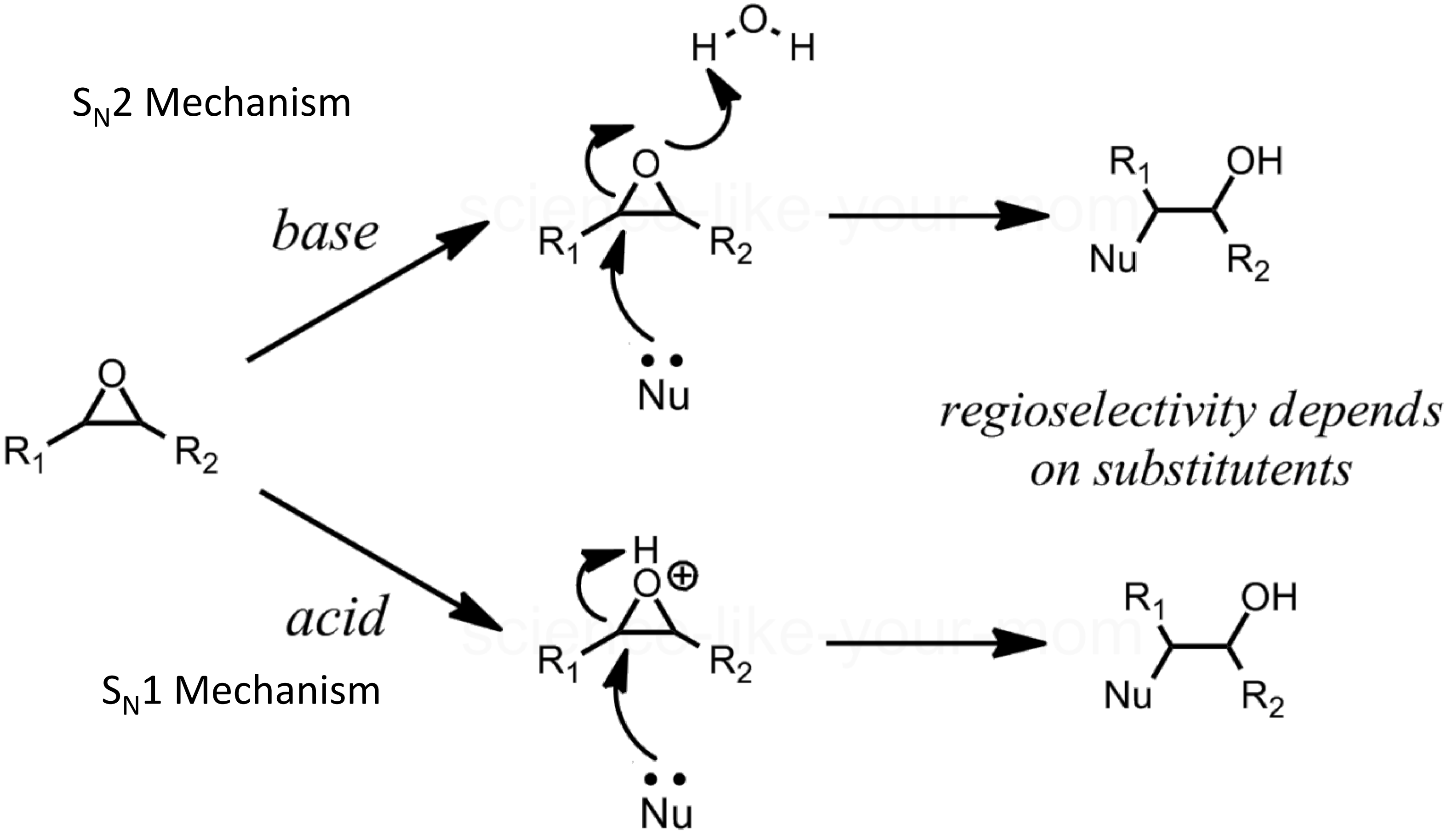
Step 2: Protonation of alkoxide



vicinal diol ("glycol")

Comparison

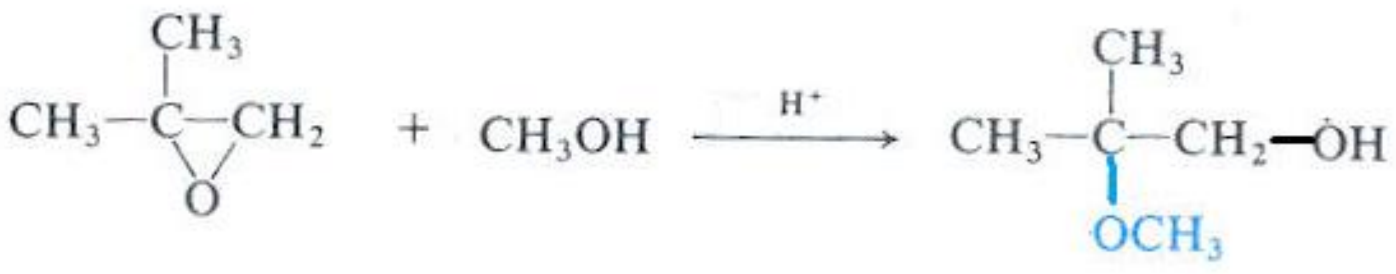
S_N2 Mechanism



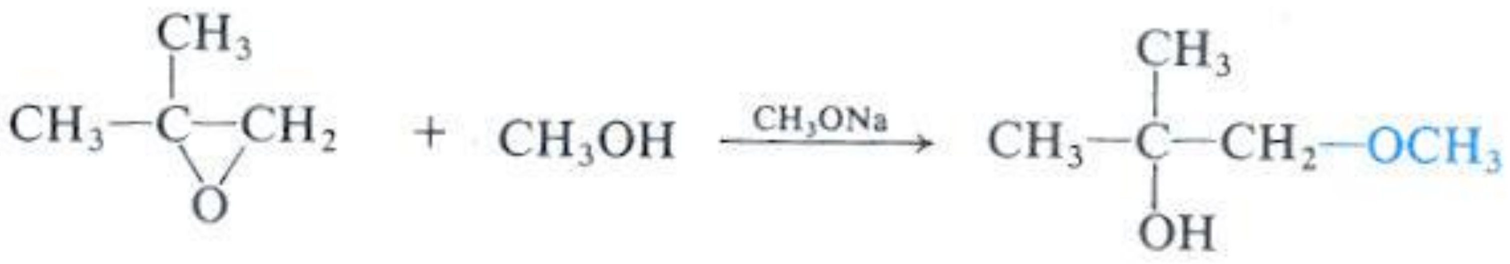
S_N1 Mechanism

Comparison – unsymmetrical epoxide

Acid catalyzed ring opening



Base catalyzed ring opening



Crown Ether

- **Structure**

  cyclic polyethers derived from repeating

  —OCH_2CH_2— units

- **Properties**

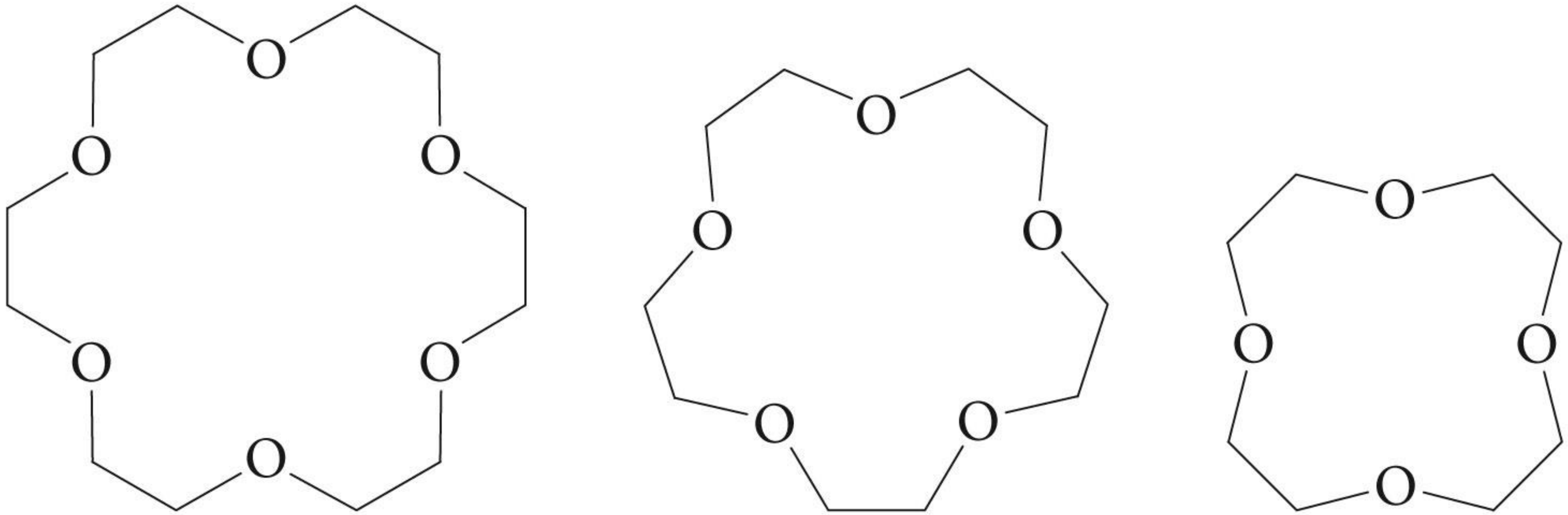
  form stable complexes with metal ions

- **Applications**

  synthetic reactions involving anions

- **Naming**

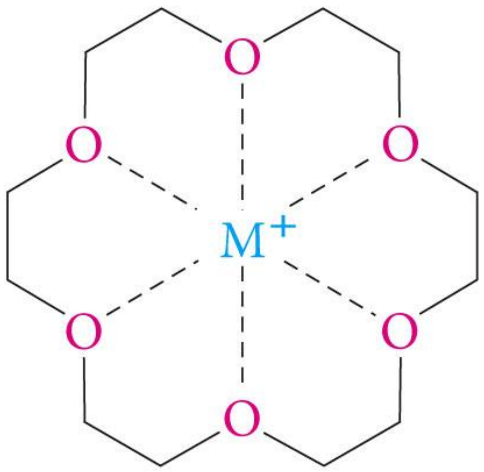
x = total no. of atoms in ring: [x] Crown- no. of oxygen atoms



[18]crown-6 mp 39–40°C
[15]crown-5 (liquid)
[12]crown-4

These compounds are called **Crown ethers** because their molecule have a crown-like shape. The bracket number represents the ring size and the terminal numbers gives the number of oxygen. The oxygen are usually separated by two carbons.

18-Crown-6



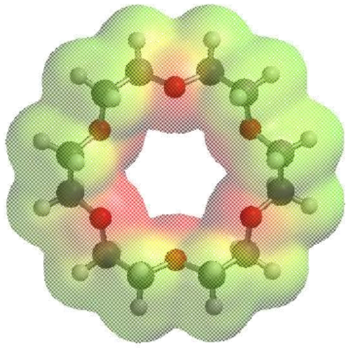
M^+ complexed in [18]crown-6

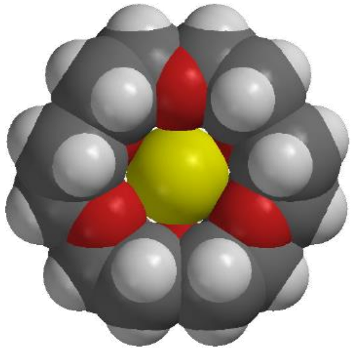
X^-

Cavity diameter		2.6–3.2 Å
Ion diameter	Na^+	1.90 Å
	K^+	2.66 Å
	Cs^+	3.34 Å

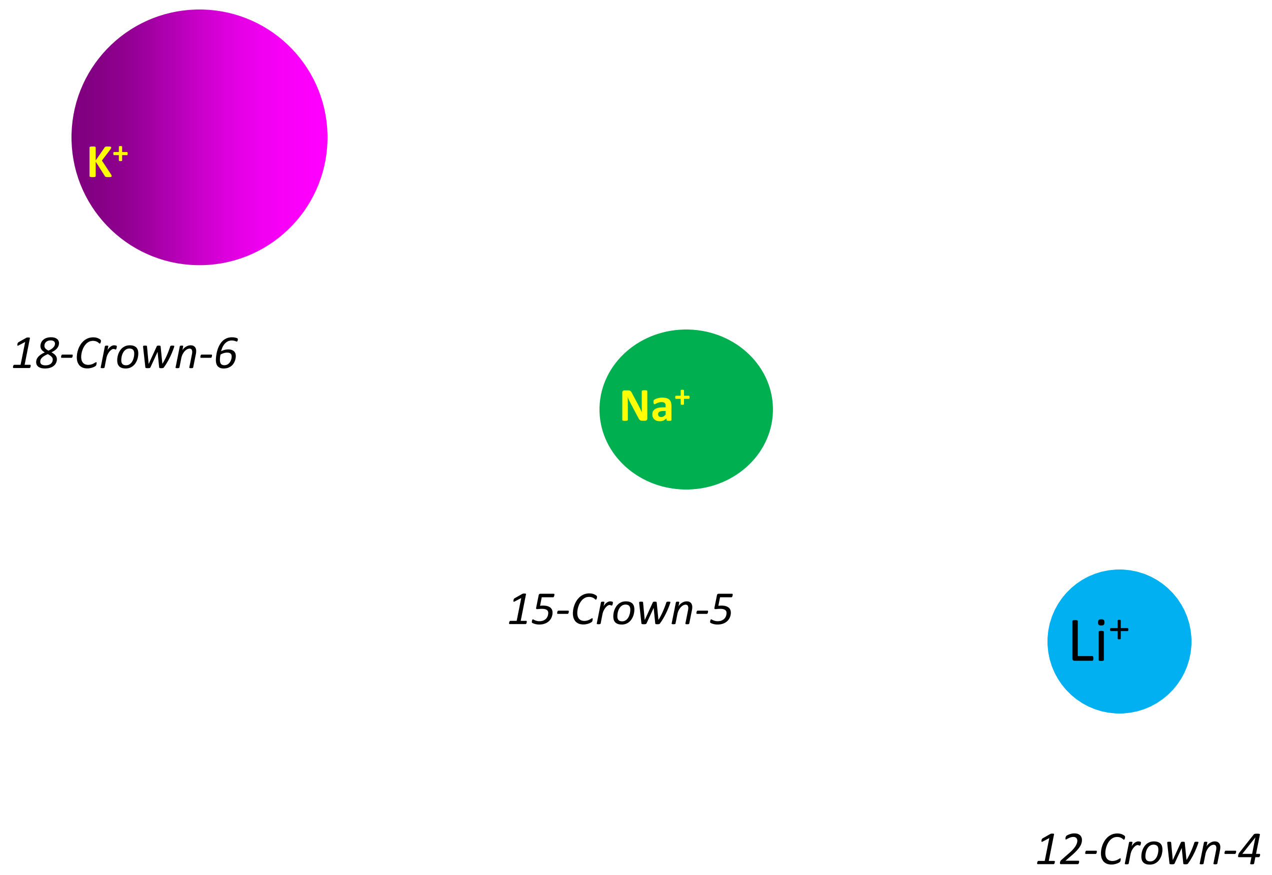
Only this ion achieves a snug fit. (→ K^+)

negative charge concentrated in cavity inside the molecule



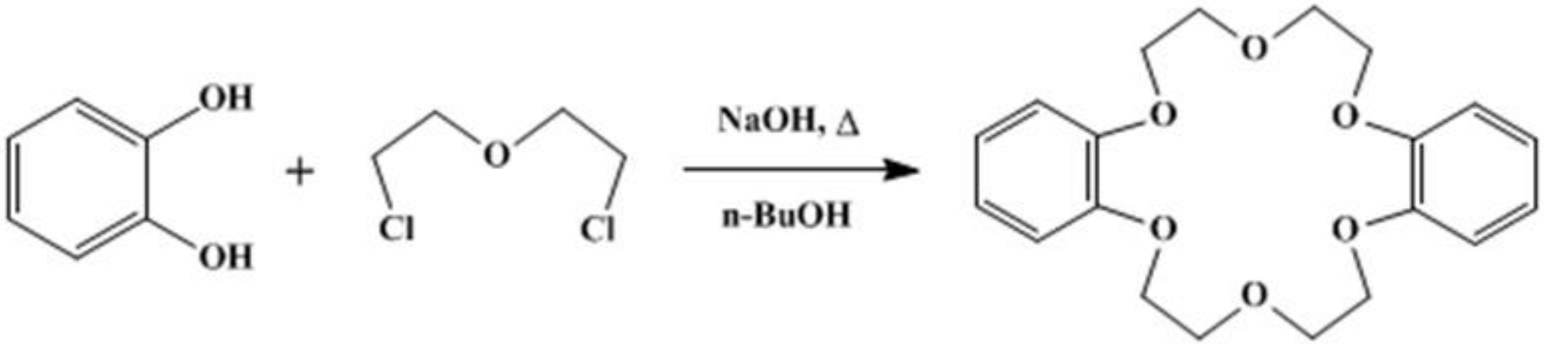


Ion Size & Crown Ether Complexes



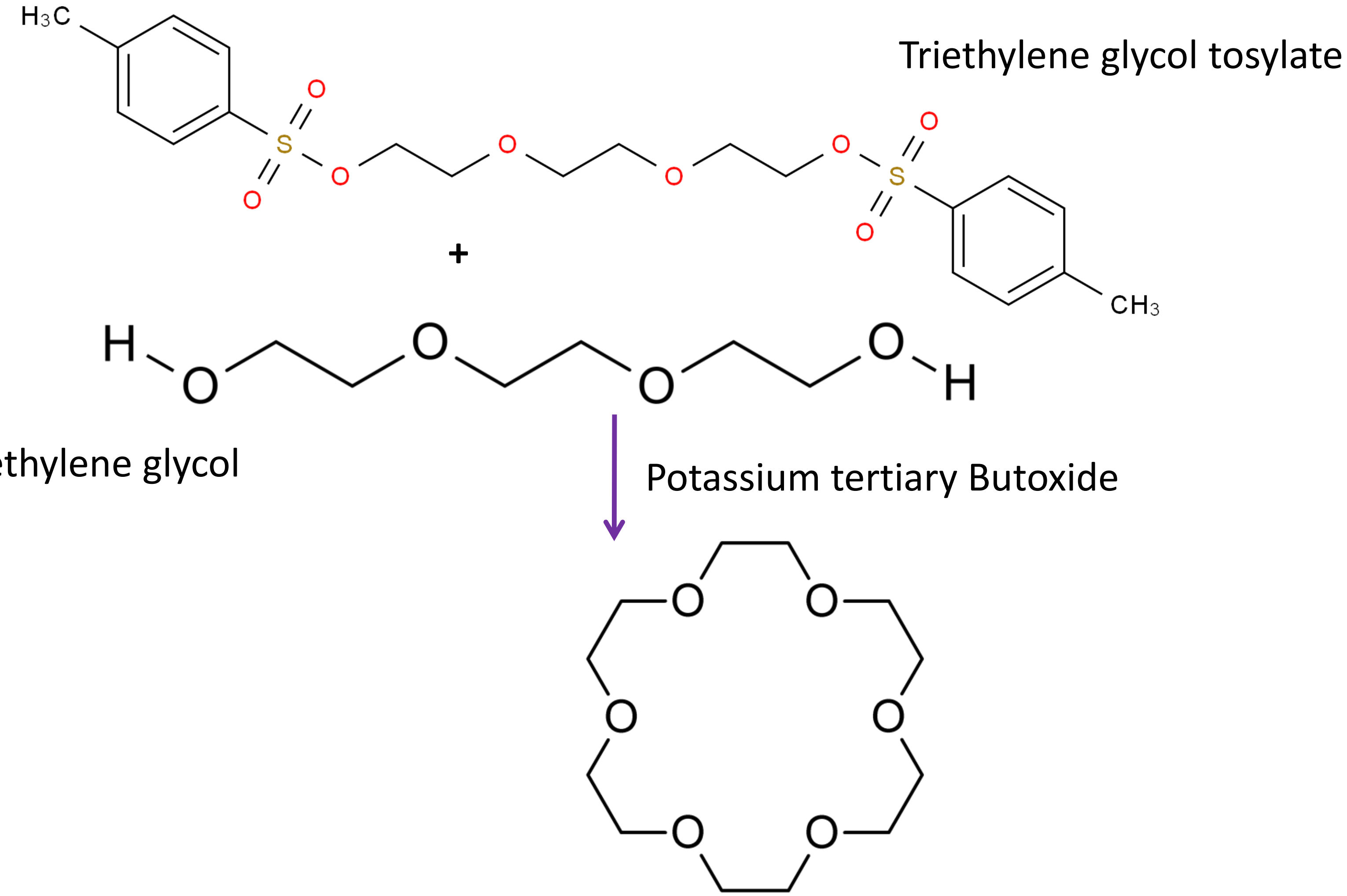
Preparation

- First Synthesis of Ether - Pedersen - 1967



Dibenzo-18-crown-6

Preparation



Application

- Formation of Host Guest complex – inclusion compound
- Phase transfer catalyst – maintains homogeneity between aqueous and organic substrate
- Reaction between aq. $KMnO_4$ & Organic substrate in organic solvent is accelerated by adding crown ether
- Chiral crown ether used for resolution of racemic mixture
- Accelerates nucleophilic substitution and elimination reaction

Reference

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Thank You!