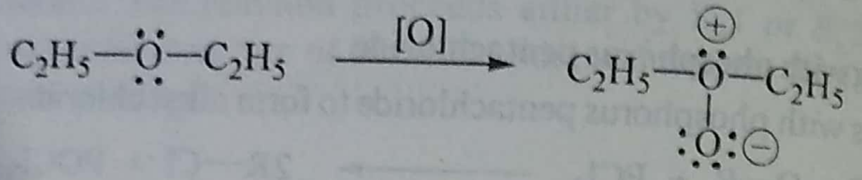
8. Oxidation

(i) Peroxide formation : Ether reacts with oxygen in presence of air to form unstable peroxide. On distillation of ether, this peroxide is left which explodes violently. The presence of peroxide in ether can be detected by the development of red colour when ether is shaken with a solution of ferrous ammonium sulphate and potassium thiocyanate.



$$C_2H_5-\ddot{O}-C_2H_5 \xrightarrow{[O]} C_2H_5-\overset{\oplus}{\ddot{O}}(-\ddot{O}:^{\ominus})-C_2H_5$$

Ferrous is oxidized to ferric which then reacts with $\overset{\ominus}{SCN}$ to give red coloured $Fe(SCN)_3$.

$$Fe^{2+} + \text{ether peroxide} \longrightarrow \text{ether} + Fe^{3+} \xrightarrow{SCN^{\ominus}} \underset{\text{red colour}}{Fe(SCN)_3}$$

(ii) Oxidation with acidic potassium dichromate : Ethers are oxidized with strong oxidizing agents to form aldehydes and acids.

$$C_2H_5-O-C_2H_5 \xrightarrow[H_2SO_4]{K_2Cr_2O_7} 2CH_3CHO \xrightarrow{O} 2CH_3COOH$$

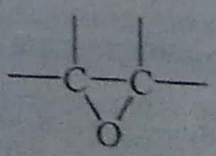
(iii) Combustion : Ethers are volatile and highly inflammable. They burn in air to form carbon dioxide and water.

$$C_2H_5-O-C_2H_5 + 6O_2 \longrightarrow 4CO_2 + 5H_2O$$

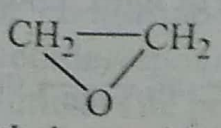
4.2 EPOXIDES

4.2.1 Introduction

Epoxides are three-membered ring ethers. Like cyclopropane the epoxides are highly strained (27k cal/mol strain energy) and exhibit geometrical isomerism. The simplest epoxide is ethylene oxide. The three membered ring imparts unusual properties to epoxides.

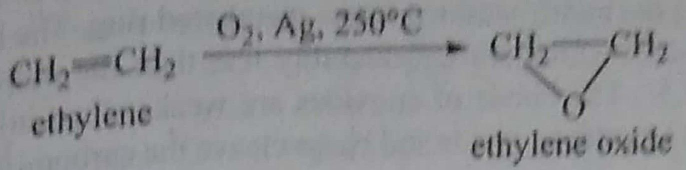


epoxide ring
(oxirane ring)



ethylene oxide
(epoxide)

Ethylene oxide is prepared on an industrial scale by catalytic oxidation of ethylene by air.

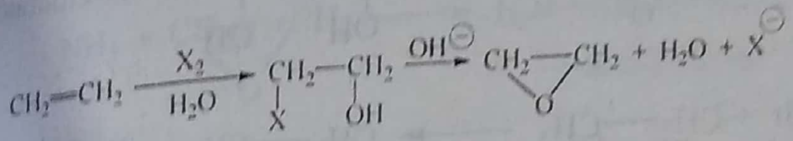


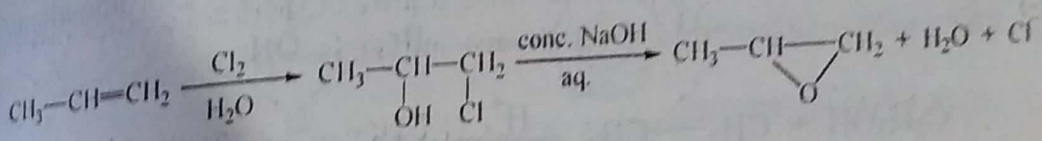
4.2.2 Methods of Preparation

Epoxides can be prepared by the following methods.

1. From halohydrins

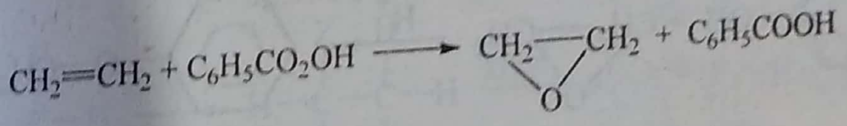
Halohydrins are converted into epoxides by the action of base. Halohydrin is prepared from alkene by addition of halogen and water to the carbon–carbon double bond.

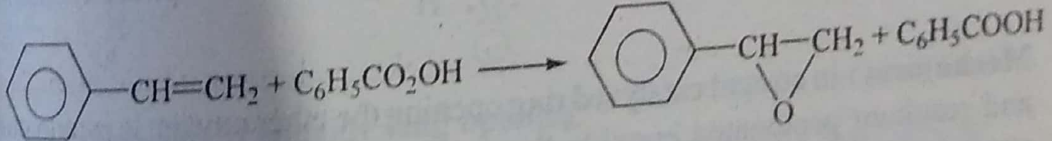


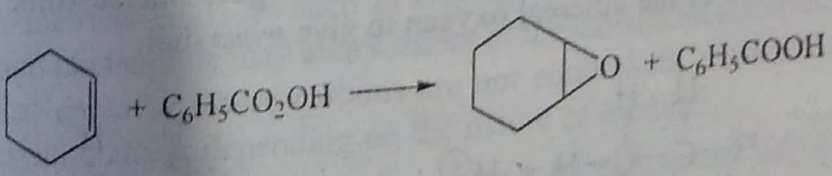


2. By peroxidation of alkenes

Alkenes get oxidized directly to the epoxides by peroxybenzoic acid.





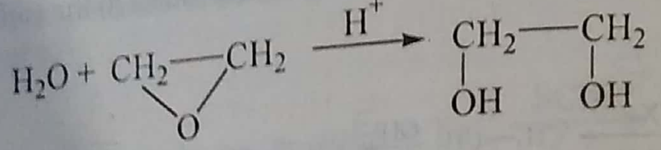


4.2.3 Chemical Reactions

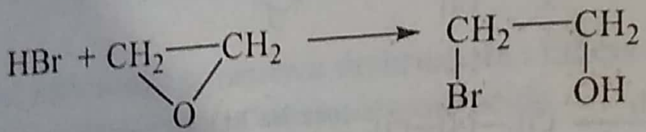
Epoxides are highly reactive compounds. Their reactivity is due to the ease of opening of the highly strained three membered ring. The bond angles of the ring are 60°, which are considerably less than the normal tetrahedral angle of 109.5°. The bonds of epoxides are weaker than in an open chain ether and are less stable. Acids and bases cleave the carbon–oxygen bond of epoxides.

4.2.3.1 Acid-catalyzed ring cleavage

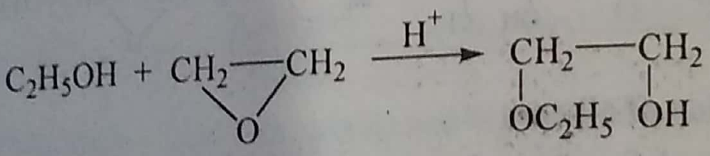
Epoxides undergo acid-catalyzed reactions with extreme ease. Some important reactions are outlined below.



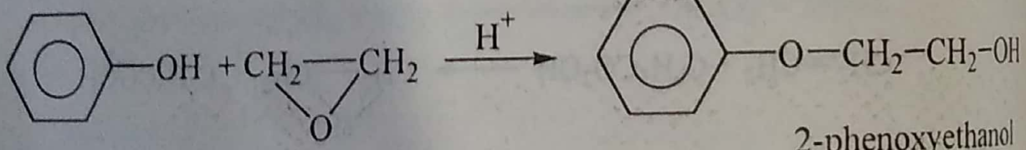
1,2-ethanediol



2-bromoethanol

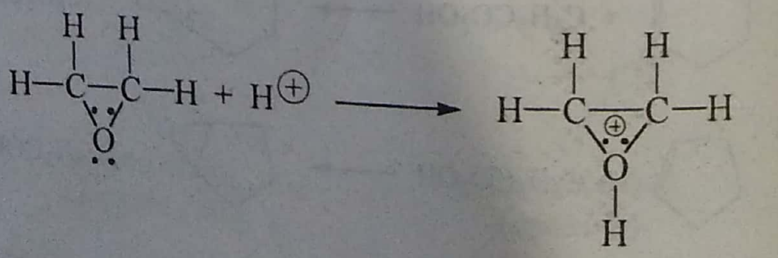


2-ethoxyethanol



2-phenoxyethanol

Mechanism : In an acid catalyzed ring opening the ether oxygen is protonated and resultant protonated epoxide then undergoes nucleophilic attack from opposite side of the ethereal oxygen to give *trans* diol.



protonated epoxide

4.2.3.2 Base-catalyzed ring cleavage

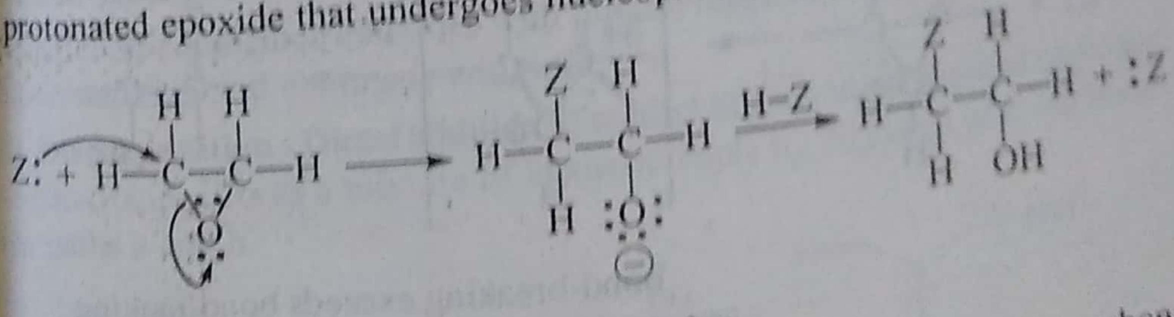
Epoxide ring can also be cleaved by bases.

2-ethoxyethanol

2-aminoethanol

2-phenoxyethanol

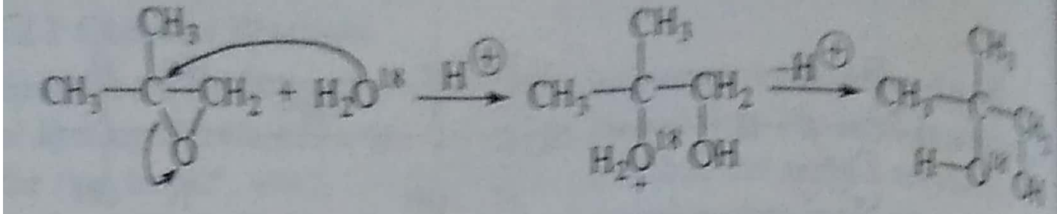
Mechanism : Under alkaline condition it is epoxide itself and not the protonated epoxide that undergoes nucleophile attack.



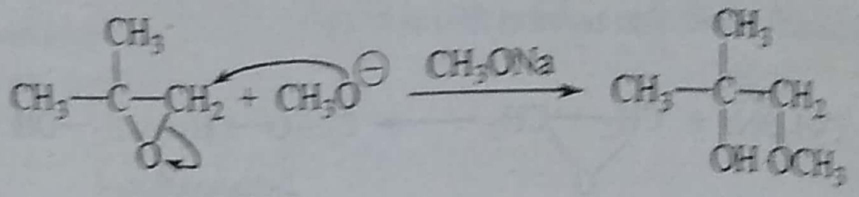
4.2.3.3 Orientation of epoxide ring opening

In case of a symmetrical epoxides such as ethylene oxide, the two carbons are equivalent and nucleophile may attack either of the carbon atoms. But in an unsymmetrical epoxide, where carbons are not equivalent, nucleophile may have preferential attack depending on the nature of medium.

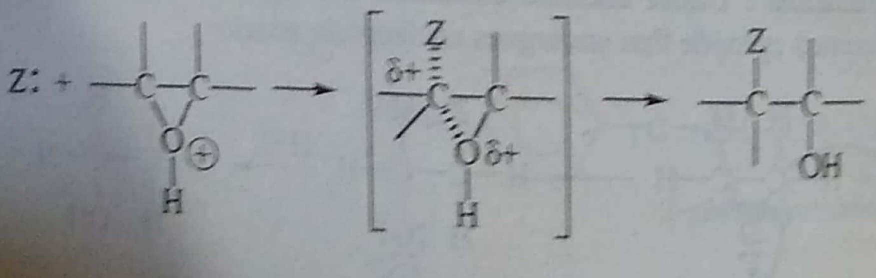
The formation of product depends whether the reaction is acid-catalyzed or base-catalyzed. In acidic medium nucleophile attacks the more substituted carbon. Consider, for example, two reactions of isobutylene oxide :



On contrary in basic medium, nucleophile approaches the less substituted carbon or less sterically hindered portion.



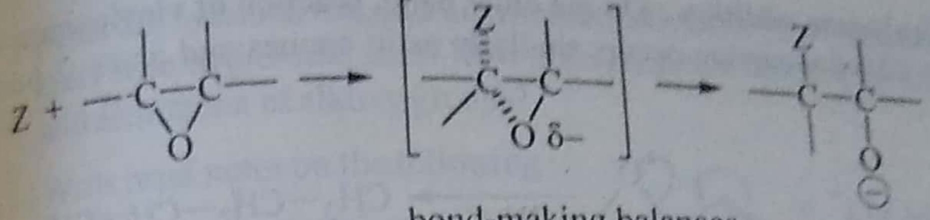
Both reactions are of S_N2 type *i.e.* cleavage of carbon-oxygen bond and attack by nucleophile occurs in a single step. In acid-catalyzed cleavage of an epoxide (Scheme 4.1), the carbon-oxygen bond, already weak because of the angle strain of the three-membered ring, is further weakened by protonation. The leaving group is a very good one, the weakly basic alcoholic hydroxyl. The nucleophile, on the other hand, is poor one (water, alcohol). In the transition state bond breaking has proceeded further than bond-making and carbon has acquired a considerable positive charge.



bond-breaking exceeds bond-making:
positive charge on carbon

Scheme 4.1 : Acid-catalyzed S_N2 cleavage of an epoxide ring

In base-catalyzed cleavage (Scheme 4.2), the leaving group is a poorer one –strongly basic alkoxide oxygen and the nuleophile is a good one (hydroxide, alkoxide). Bond breaking and bond-making are more nearly balanced and reactivity is controlled by steric factors. Attack occurs at the less hindered carbon.

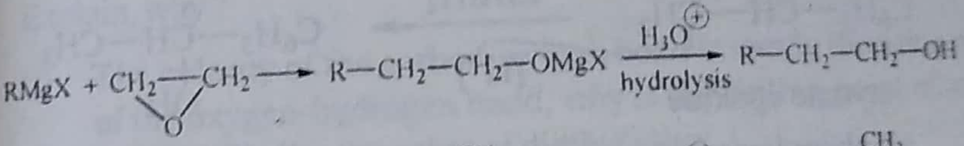


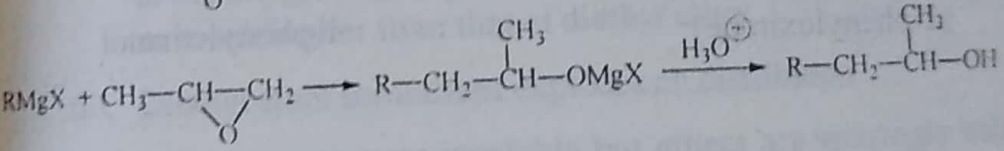
bond-making balances
bond-breaking :
no particular charge on carbon

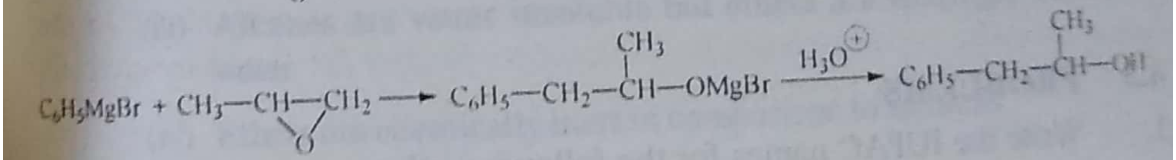
Scheme 4.2 : Base-catalyzed S_N2 cleavage of an epoxide ring

4.2.3.4 Reaction with Grignard reagents

Epoxides react with Grignard reagents to form primary alcohols containing two more carbon atoms than the alkyl or aryl group of Grignard reagent.



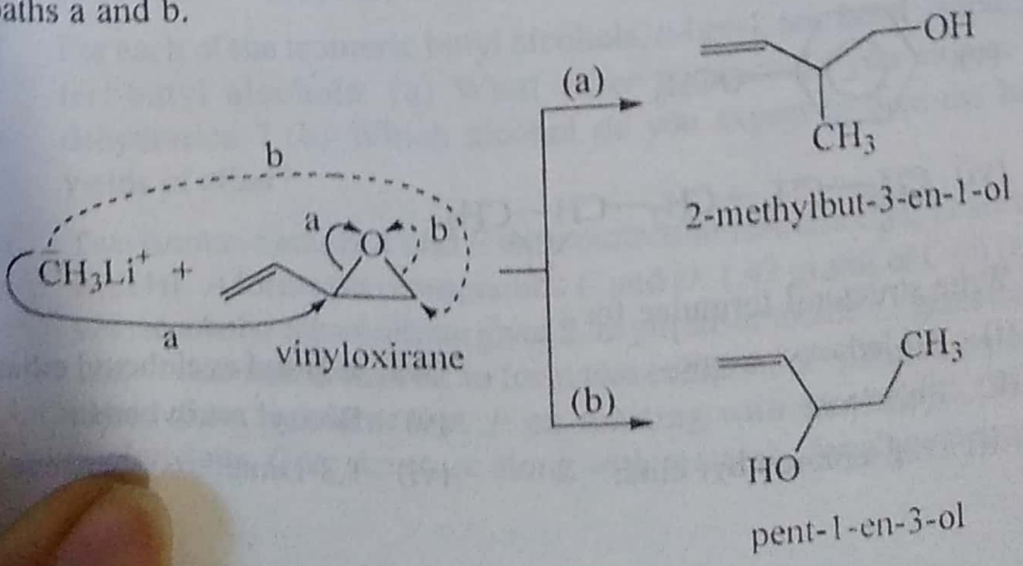




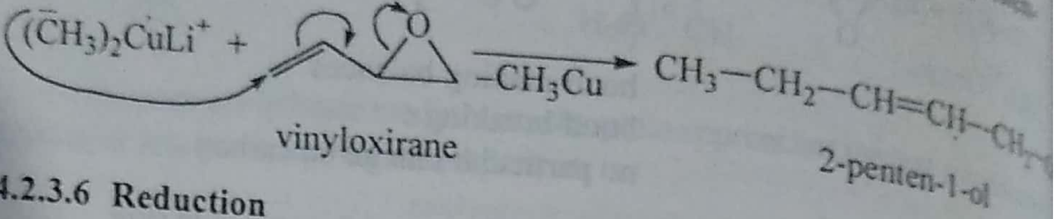
4.2.3.5 Reaction with lithium reagents

Reaction of conjugated epoxides with lithium reagents follows two paths viz. direct addition and conjugate addition.

(i) Direct addition : Direct addition of methyl lithium to conjugated epoxide. vinyloxirane, affords a mixture of isomeric enols by cleavage of C–O bond via paths a and b.

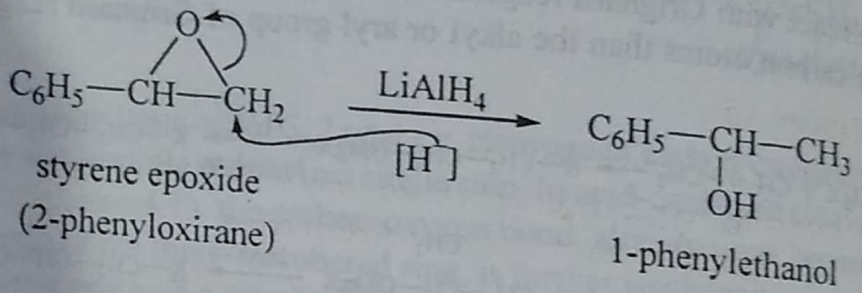


(ii) Conjugate addition : On the other hand, reaction of vinyloxirane wit lithium dimethylcuprate occurs similarly as in enones and gives 2-penten-1-ol.

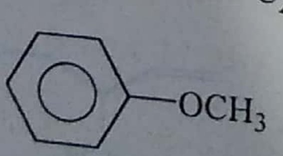


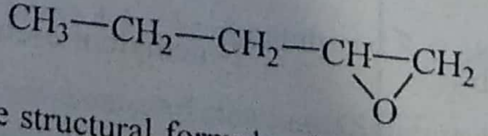
4.2.3.6 Reduction

Reduction of epoxides with $LiAlH_4$ gives corresponding alcohols by cleavage of C-O bond.



4.3 PROBLEMS

1. Write the IUPAC names for the following ethers:
   - (i) $CH_3-O-CH(CH_3)_2$
   - (ii) $(CH_3)_3C-O-CH_2-CH_3$
   - (iii) $(CH_3)_2CH-CH_2-O-CH_2-CH(CH_3)_2$
   - (iv) $p\text{-}BrC_6H_4-O-C_2H_5$
   - (v) 

   - (vi) 
   $CH_3-CH_2-CH_2-\underbrace{CH-CH_2}_{O}$
2. Write structural formulae for :
   - (i) 3-Methoxyhexane
   - (ii) Phenetole
   - (iii) Di-β-chloroethyl ether
   - (iv) *n*-Butyl cyclohexyl ether
   - (v) Benzyl *p*-tolyl ether
   - (vi) 1,3-Dimethoxy benzene