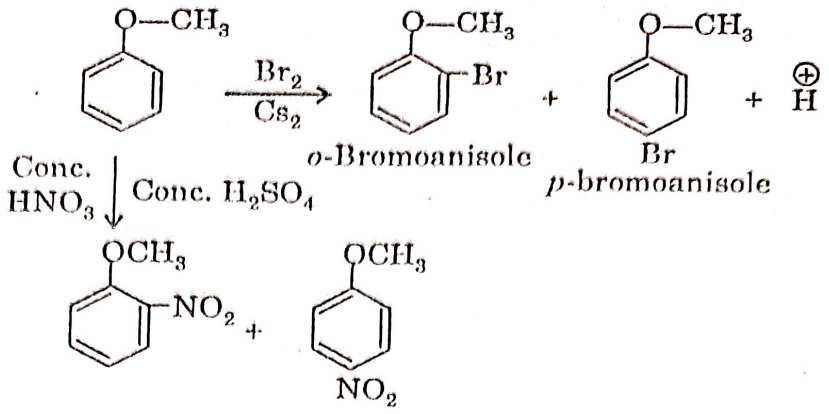
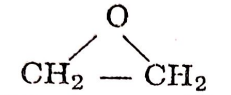
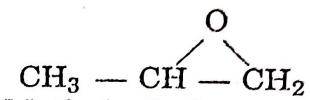


EPOXIDES

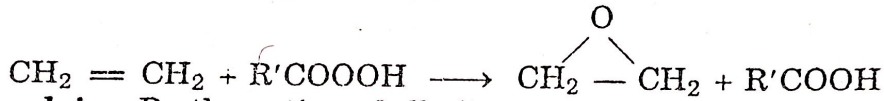
The three membered cyclic esters are called epoxides. These compounds are very important in synthetic organic chemistry. The common name of an expoxide uses the common name of alkene followed by oxide.


Ethylene oxide

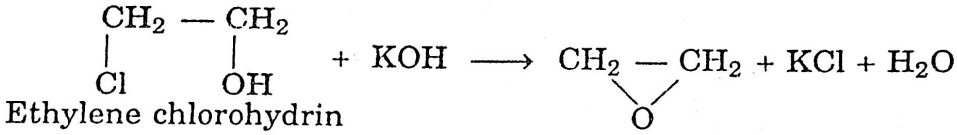

Methyl ethylene oxide

Preparation

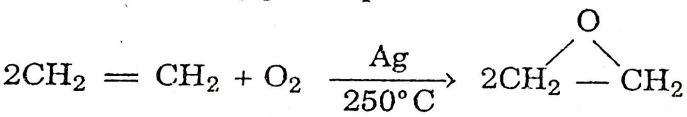
(1) By the action of peracids on a alkenes :



(2) From halohydrin : By the action of alkali.


Ethylene chlorohydrin

(3) Ethylene on oxidation with oxygen in presence of silver catalyst gives ethylene oxide.

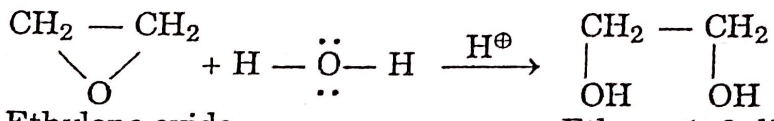


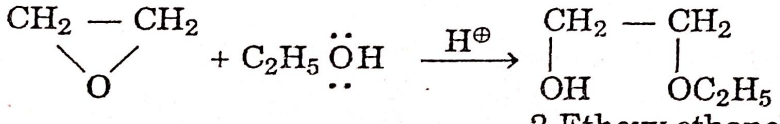
Properties

The three membered ring epoxides have great angular strain since its bond angles are about 60° which are much smaller than the tetrahedral carbon angle of 109.5° or the divalent angle of 110° of ether. The bonds in epoxides are, therefore, much weaker than in ordinary ether and they tend to open up rapidly and they show high reactivity.

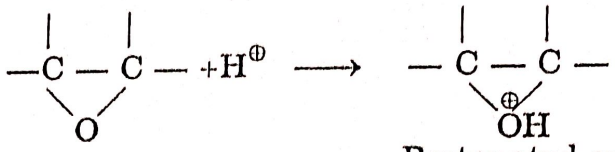
The nucleophilic substitution reactions of epoxides are their characteristic reactions and take place in alkaline or acidic medium. The ring undergoes cleavage as below :

(1) Acid catalysed cleavage : Epoxides on treatment with a nucleophilic reagent like $H-\ddot{O}-H$, $R-\ddot{O}-H$ or $:\overset{\ominus}{Br}$ in the presence of an acid undergo cleavage, *e.g.*,


Ethylene oxide — Ethane-1, 2-diol


2-Ethoxy ethanol

Mechanism : The epoxide is first protonated by the action of acid.

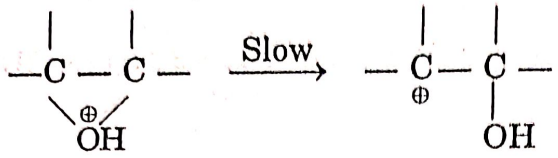


Protonated epoxide

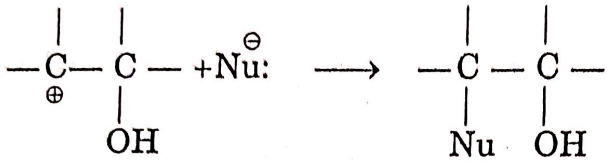
The protonated epoxide then undergoes nucleophilic attack by S_N^1 or S_N^2 mechanism.

S_N^1 mechanism :

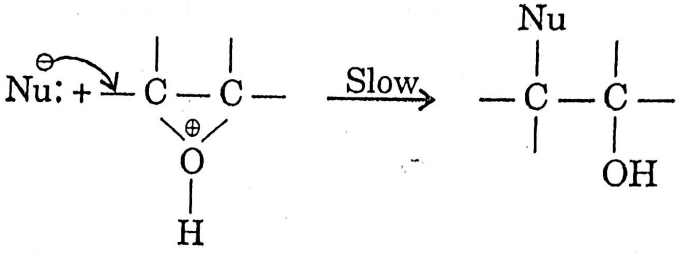
(i)

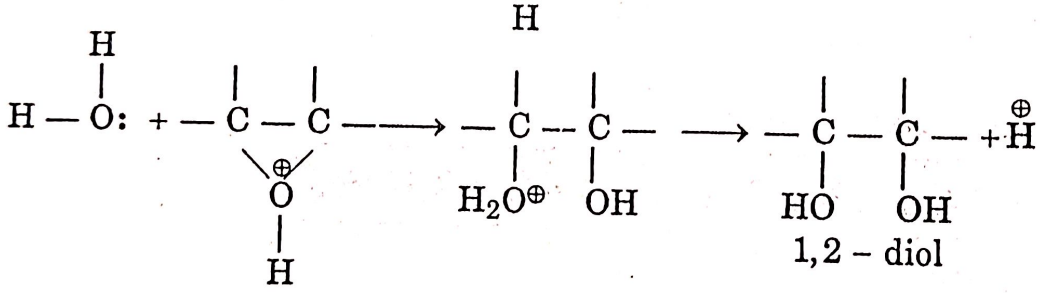


(ii)

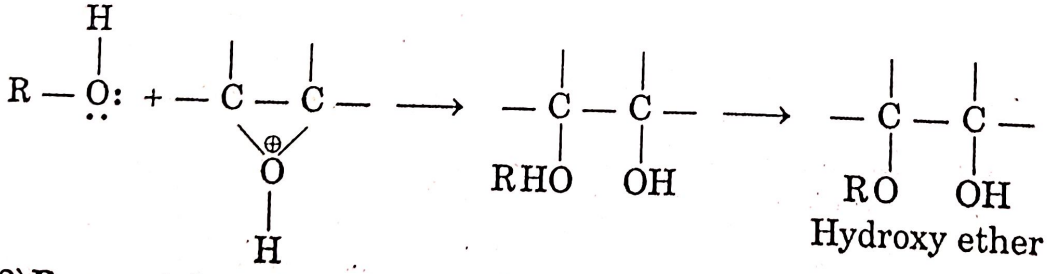


S_N^2 mechanism :



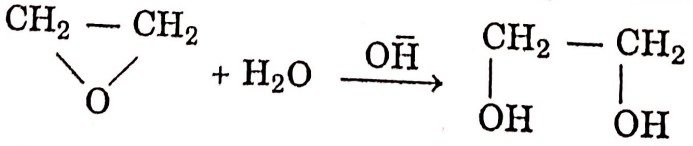


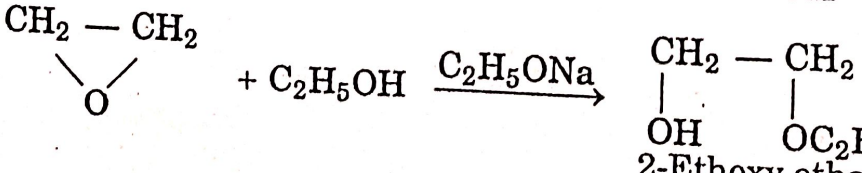
1,2 – diol



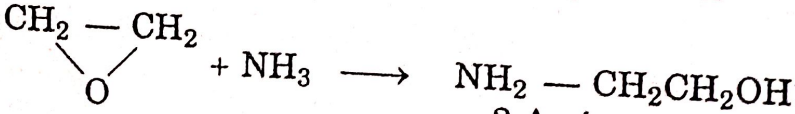
Hydroxy ether

(2) **Base catalysed cleavage :** When an epoxide is treated with strong nucleophilic reagents (*e.g.* NaOH, C_2H_5ONa, NH_3, $R-NH_2$ etc.). The epoxide undergoes cleavage.



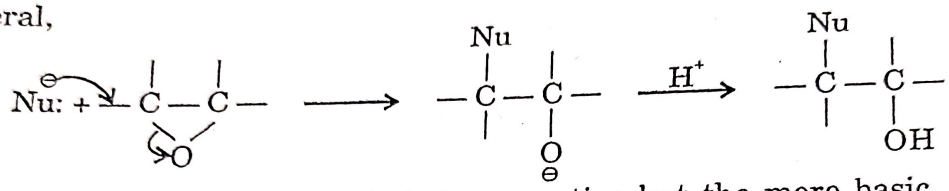


2-Ethoxy ethanol



2-Amino ethanol

In general,



Here, the non-protonated epoxide is less reactive but the more basic, more strongly nucleophilic reagent compensates its lower reactivity.

(3) **Reaction with Grignard reagent :** Primary alcohol is obtained.

$$CH_3MgI + CH_2 - CH_2 \longrightarrow CH_3CH_2CH_2OMgI \xrightarrow[H_2O]{H^{\oplus}} CH_3CH_2CH_2OH + Mg(OH)I$$

(4) **Reaction with carblithium compound :**

$$R - Li + CH_2 - CH_2 \longrightarrow R - CH_2CH_2OLi \xrightarrow[H_2O]{H^{\oplus}} R - CH_2CH_2OH + LiOH$$

(5) ***Action of heat :*** Ethylene oxide gives acetaldehyde.

$$CH_2 - CH_2 \xrightarrow{Heat} CH_3CHO$$

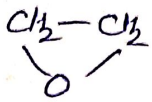
(6) **Reduction with lithium aluminium hydride :**

$$CH_2 - CH_2 \xrightarrow[[H]]{LiAlH_4} CH_3CH_2OH$$

Uses

Epoxides are used in organic synthesis.

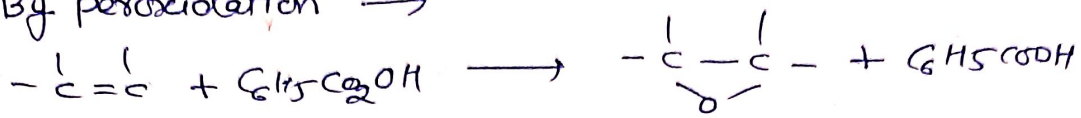
Epoxide

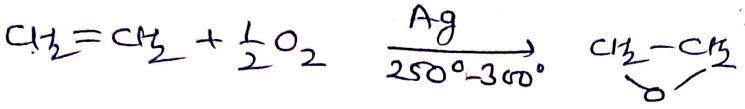
 Ethylene oxide or epoxyethane.

- It is a cyclic ether.
- It is isomer of CH_3CHO.
- IUPAC name Epoxyethane or oxirane.

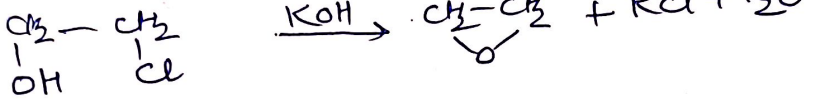
Preparation :→

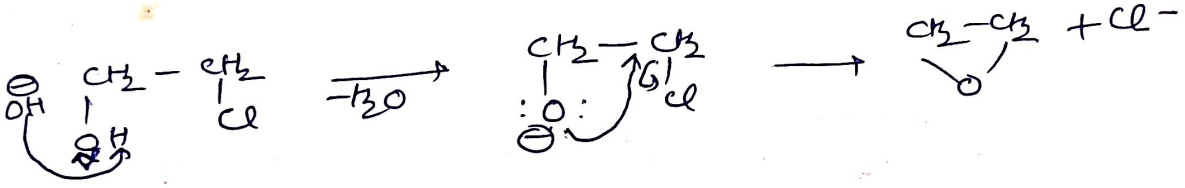
(i) By peroxidation →



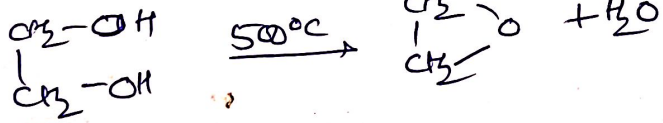


(ii) By ethylene chlorohydrin →

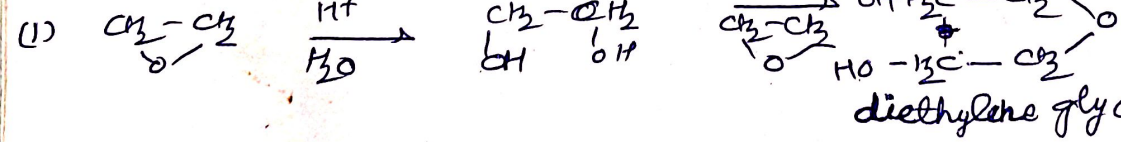


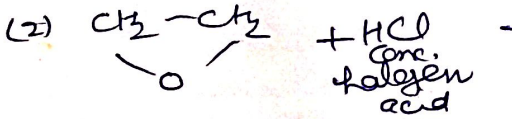


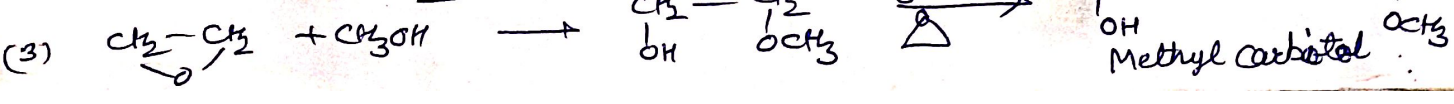
(iii) From ethylene glycol



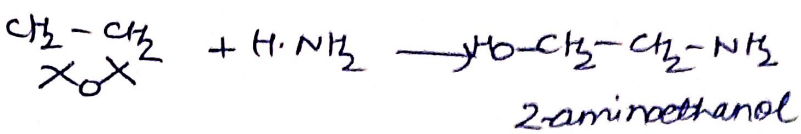
Physical properties:– 1. Colourless gas (12.5°C B.P.)
2. Ether like smell
3. It is reactive due to strain. due to strain ring is open gives the addition rxn.

(1) 
diethylene glycol

(2) 

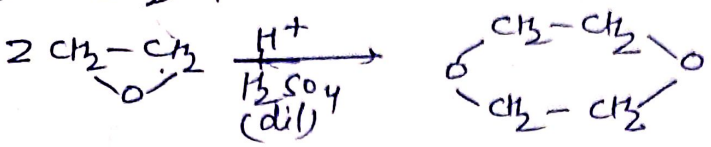
(3) 
Methyl carbitol

(4) Reacⁿ. with NH_3 :→



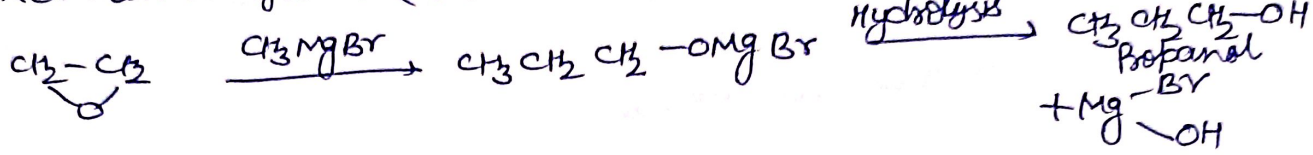
2-aminoethanol

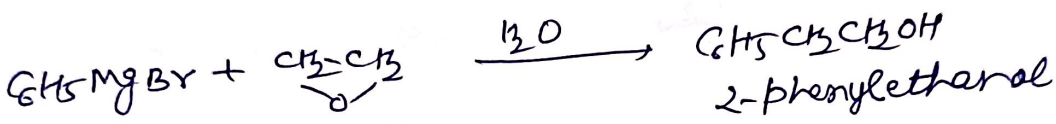
(5) dil H_2SO_4 :→



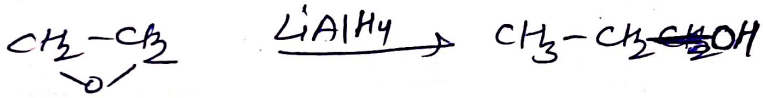
1,4-dioxane.

(6) Reaⁿ. with RMgX → (G.R.)

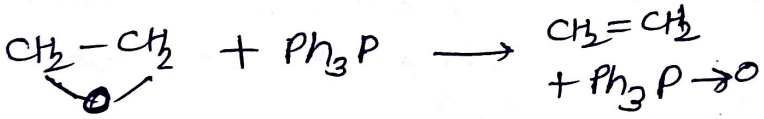




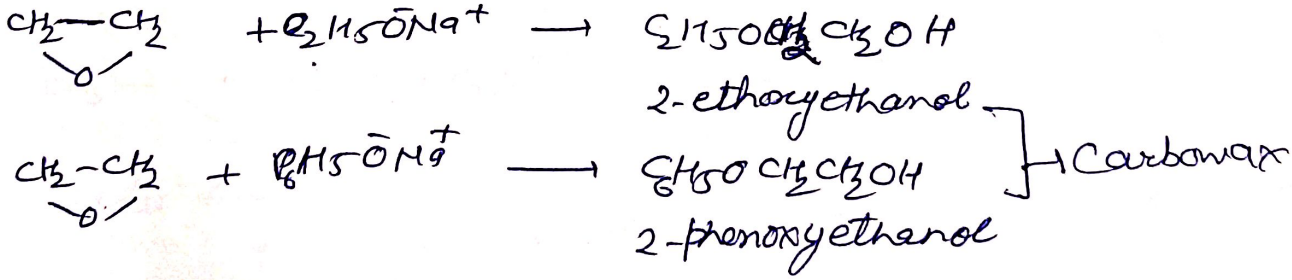
(7) Reduction :-



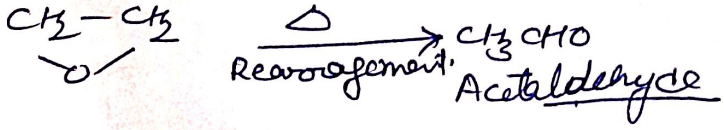
(8) Reaⁿ with Ph_3P : → Reduction by triphenylphosphine



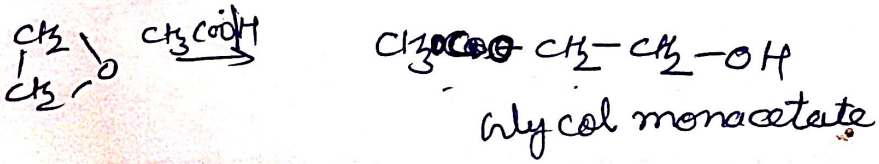
(9) Rxⁿ Base :→



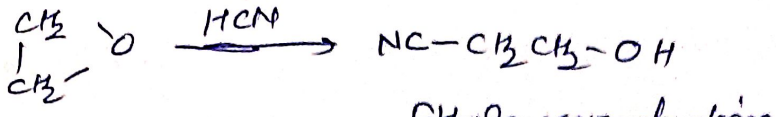
(10) On heat :-



(11) Rxⁿ with acetic acid :→

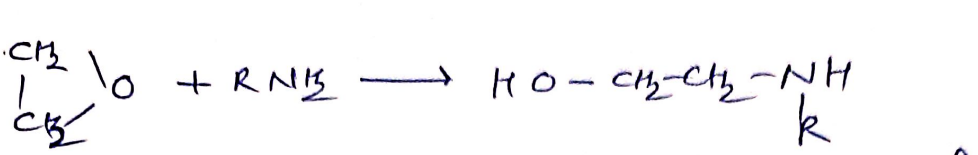


(12) Reaction with HCN :—

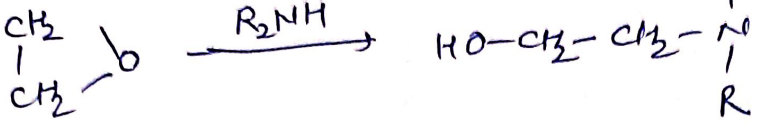


Ethylenecyanohydrin

(13)

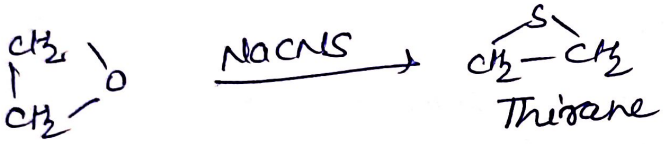


2-(N-alkyl)-aminoethanol



2-(N,N-dialkyl)-aminoethanol

(14) Rxn with NaCNS (Sodiumthiocyanate)



Thirane

Mechanism of Epoxide ring opening :→

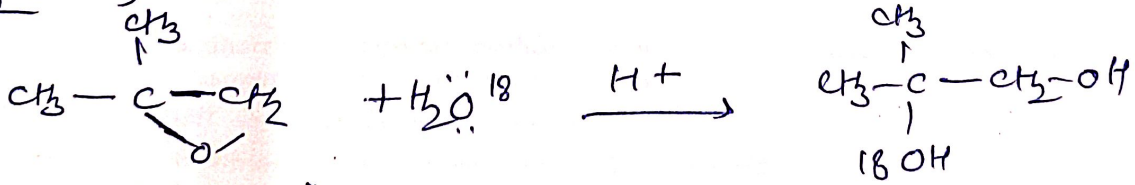
$Nu^{\ominus}$ द्वारा attack किसी भी C– पर हो सकता है।

Symmetric epoxide → दोनों C-पर समान रूप से attack हो सकता है।

Asymmetric epoxide → Medium of reaction.

Acidic catalysed & Base catalysed.

Example :→



Isobutylene oxide

Acidic medium में → $Nu^{\ominus}$ का आक्रमण अधिक प्रतिस्थापी-C पर होता है

Basic medium → $Nu^{\ominus}$ का attack कम प्रतिस्थापी C-पर होता है।