

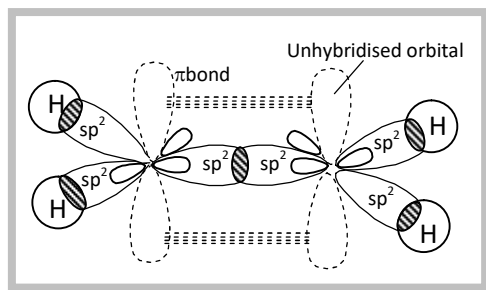
Alkenes.

These are the acyclic hydrocarbon in which carbon-carbon contain double bond. These are also known as olefins, because lower alkene react with halogens to form oily substances. General formula is C_nH_{2n} .

Ex: Ethene C_2H_4 , Propene C_3H_6 , Butene C_4H_8

(1) Structure

- Hybridization of unsaturated 'C' atom is sp^2
- Geometry of unsaturated 'c' atom is trigonal planer
- $C - H$ Bond length is 1.34 \AA
- $C = C$ Bond energy is 143.1 K cal/mol
- $C - H$ Bond length is 1.10 \AA
- $C = C$ Bond energy is 108 Kcal/mol



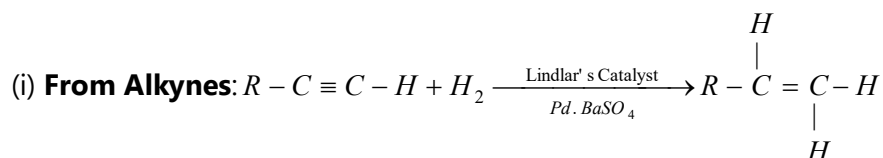
(2) Isomerism

- Chain Isomerism:** $CH_3 - CH_2 - CH = CH_2$ and $(CH_3)_2 - C = CH_2$
- Position Isomerism:** $CH_2 = CH - CH_2 - CH_3$ and $CH_3 - CH = CH - CH_3$
- Functional Isomerism:** [Ring chain] $CH_3 - CH_2 - CH = CH_2$ and $CH_2 - CH_2$
1-butene
Cyclo butene
- Geometrical Isomerism:** $CH_3 - C - H$ and $CH_3 - C - H$
$$\begin{array}{ccc} \text{CH}_3 - \overset{\parallel}{C} - H & & H - \overset{\parallel}{C} - \text{CH}_3 \\ \text{cis-2-butene} & & \text{Trans-2-butene} \end{array}$$
- Optical Isomerism:** $H - C - CH_3$
 CH_2CH_3

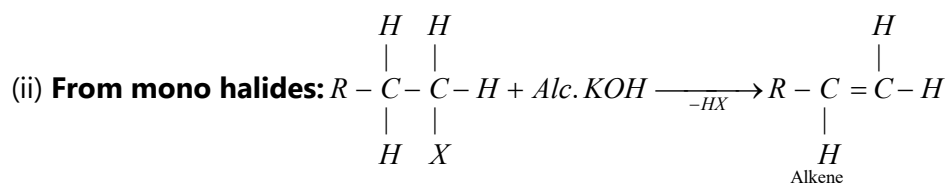
Note: Cumulated polythene having even no. of double bonds. Which has = C $\begin{array}{l} a \\ \diagdown \\ \diagup \\ b \end{array}$ system at the both end can exhibit optical isomerism but cannot exhibit geometrical isomerism.

Cumulated polythene having odd no. of double bonds which have $=C$ system at both end can exhibit geometrical isomerism but cannot exhibit optical isomerism.

(3) Preparation methods



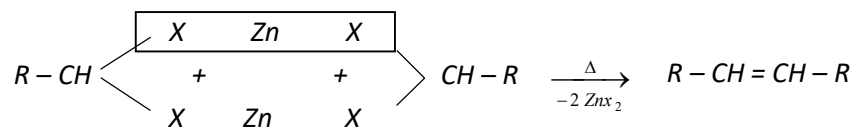
Note: Poison's catalyst such as $BaSO_4, CaCO_3$ are used to stop the reaction after the formation of alkene.



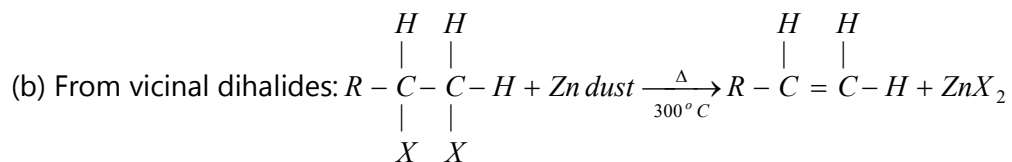
Note: If we use alc. $NaOH$ in place of KOH then trans product is formed in majority because of its stability. According to saytzeff rule.

(iii) From dihalides

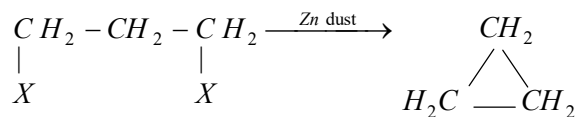
(a) From Gem dihalides

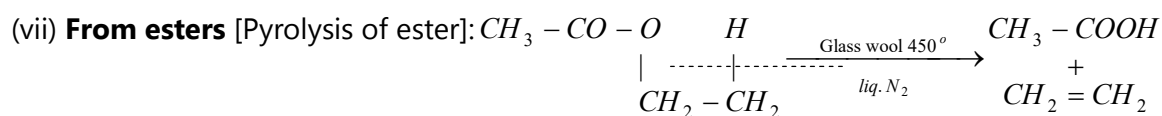
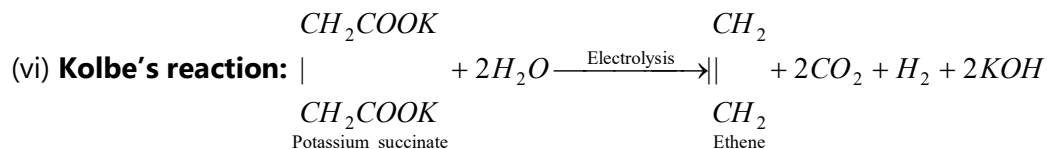
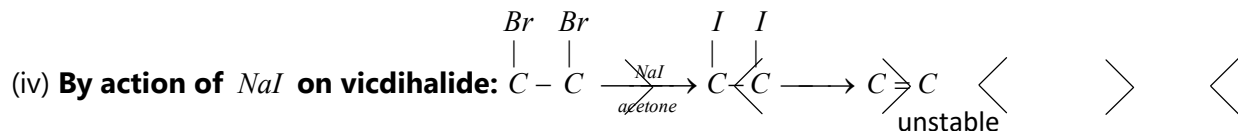


Note: If we take two different types of gemdihalides then we get three different types of alkenes. Above reaction is used in the formation of symmetrical alkenes only.

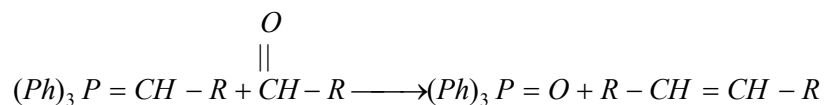
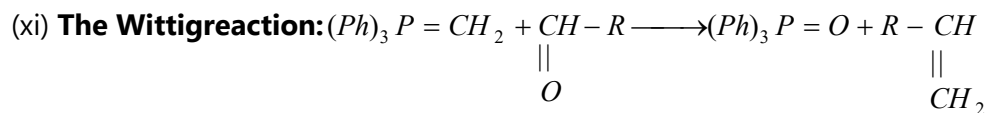
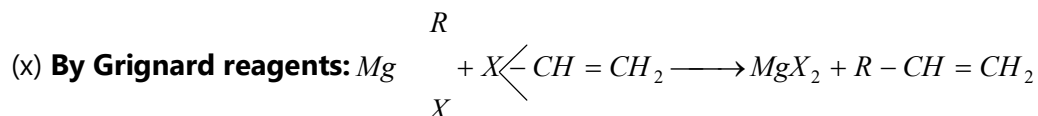
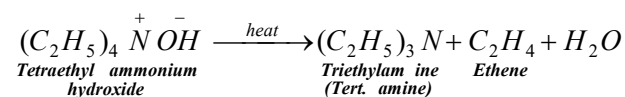


Note: Alkene is not formed from 1, 3 dihalides. Cycloalkanes are formed by dehalogenation of it.

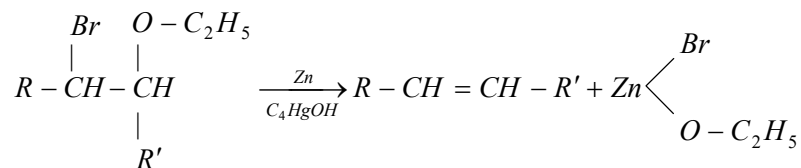




(viii) **Pyrolysis of quaternary ammonium compounds:**



(xii) **From β bromo ether** [Boord synthesis]

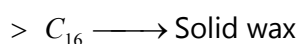
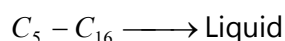
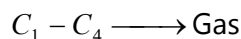


(4) Physical Properties

(i) Alkenes are colorless and odorless.

(ii) These are insoluble in water and soluble in organic solvents.

(iii) Physical state



(iv) B.P. and M.P. decreases with increasing branches in alkene.

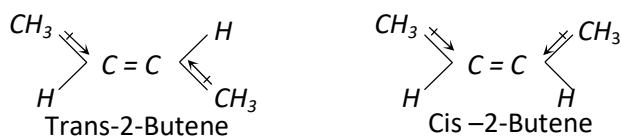
(v) The melting points of cis isomers are lower than trans isomers because cis isomer is less symmetrical than trans. Thus trans packs more tightly in the crystal lattice and hence has a higher melting point.

(vi) The boiling points of cis isomers are higher than trans isomers because cis-alkenes has greater polarity (Dipole moment) than trans one.

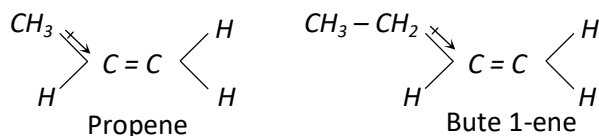
(vii) These are lighter than water.

(viii) **Dipole moment:** Alkenes are weakly polar. The, π -electrons of the double bond. Can be easily polarized. Therefore, their dipole moments are higher than those of alkanes.

The symmetrical trans alkenes are non-polar and hence have zero dipole moments in these alkene the dipole moment of individual bonds are equal in opposite direction. Therefore these get cancelled resulting zero dipole moment for the molecule.

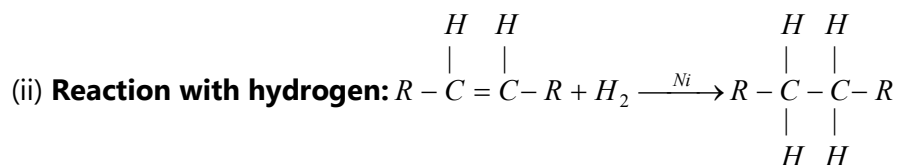
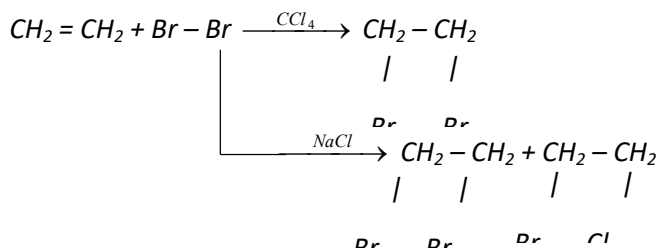


Thus symmetrical and unsymmetrical cis alkene are polar and hence have finite dipole moments

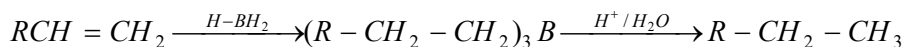


(5) **Chemical properties**

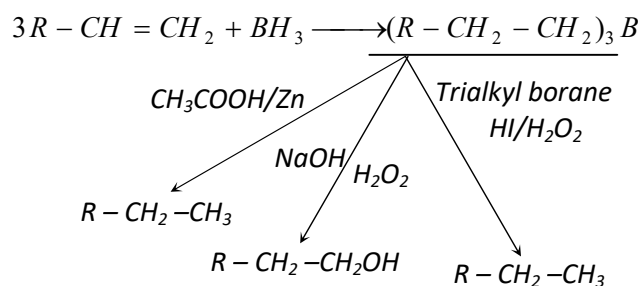
(i) **Francis experiment:** According to Francis electrophile first attacks on olefinic bond.



(iii) **Reduction of alkene via hydroboration:** Alkene can be converted into alkane by protolysis

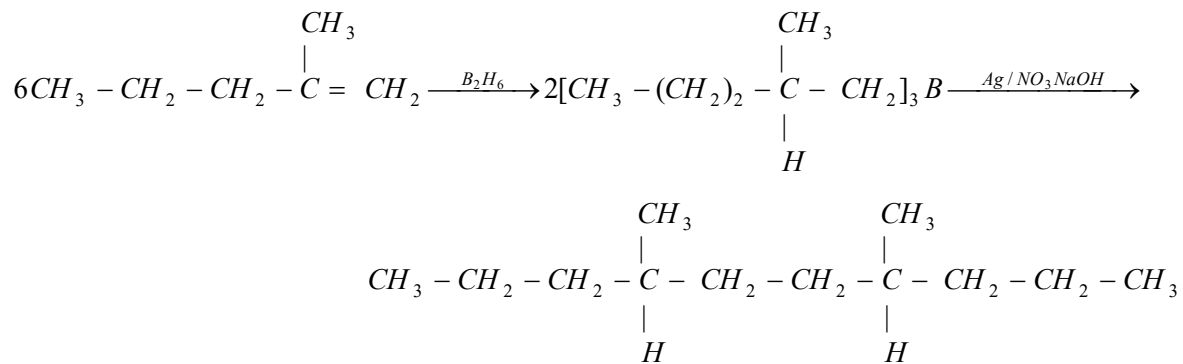


Hydroboration: Alkene give addition reaction with diborane which called hydroboration. In this reaction formed trialkylborane, which is very important and used for synthesis of different organic compound

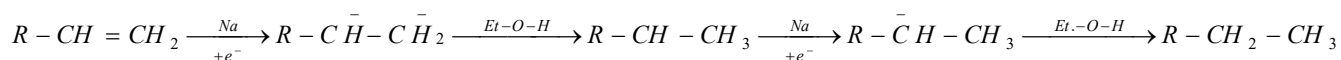


The overall result of the above reaction appears to be antimarkownikoff's addition of water to a double bond.

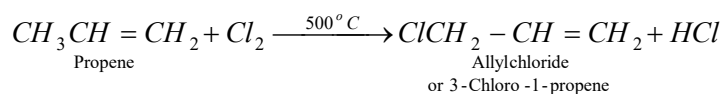
(iv) **By treatment with AgNO₃ + NaOH:** This reaction gives coupling



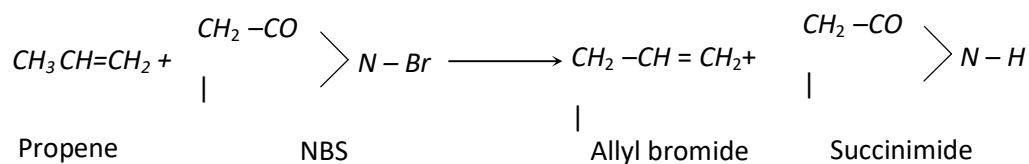
(v) **Birch reduction:** This reaction is believed to proceed via anionic free radical mechanism.



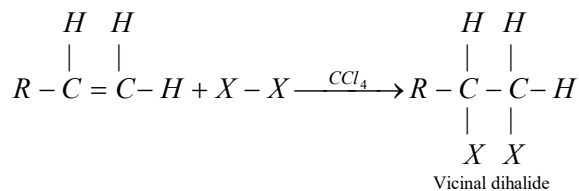
(vi) **Halogenation**



Note: If NBS [N-bromo succinimide] is a reagent used for the specific purpose of brominating alkenes at the allylic position.

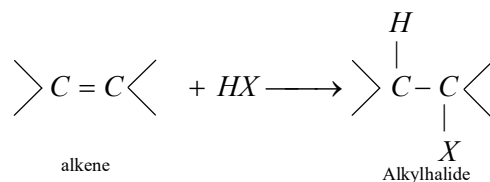


In presence of polar medium alkene form vicinal dihalide with halogen.

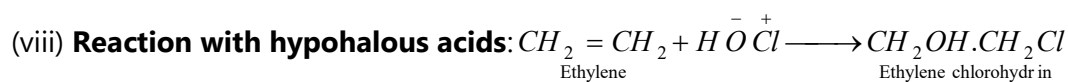
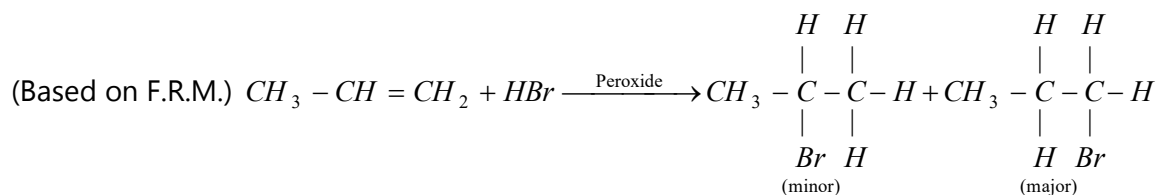
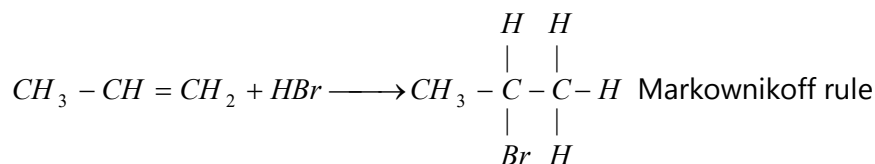


Reactivity of halogen is $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

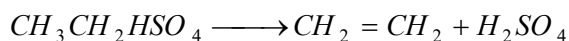
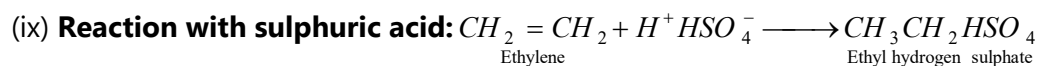
(vii) **Reaction with HX** [Hydrohalogenation]



According to markownikoff's rule and kharasch effect.

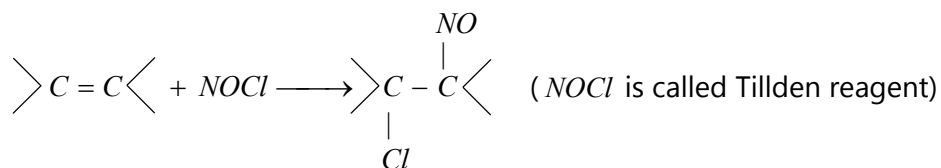


Note: In case of unsymmetrical alkenes markownikoff rule is followed.

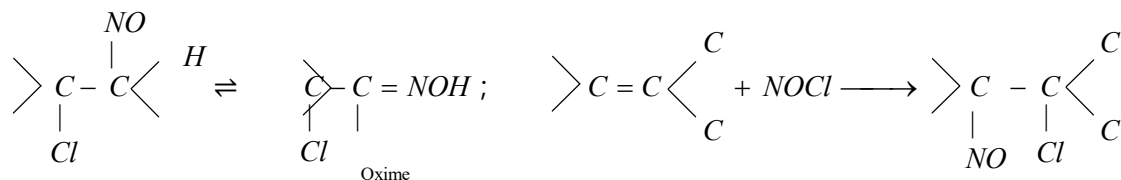


Note: This reaction is used in the separation of alkene from a gaseous mixture of alkanes and alkenes.

(x) **Reaction with nitrosyl chloride**

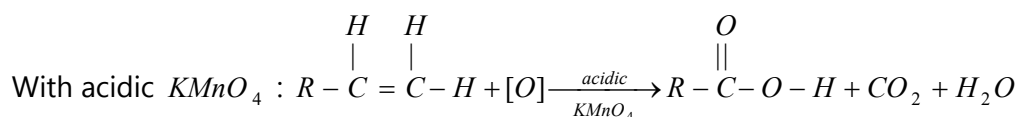
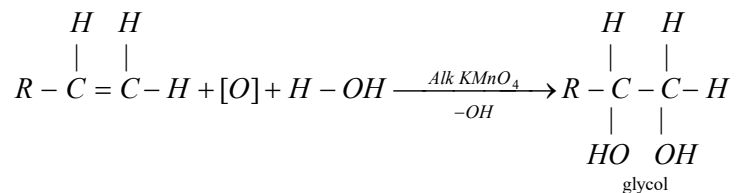


Note: If hydrogen is attached to the carbon atom of product, the product changes to more stable oxime.

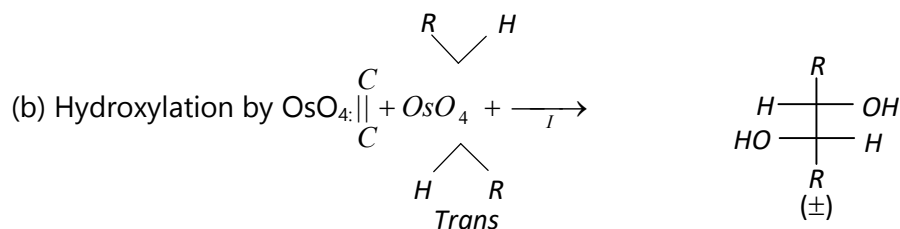
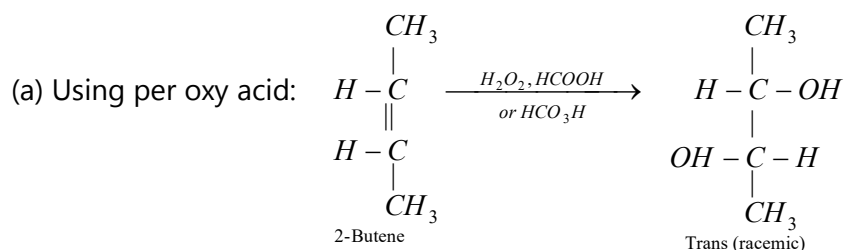


(Blue color)

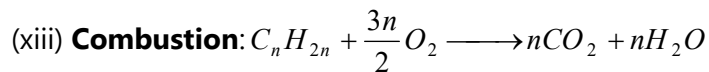
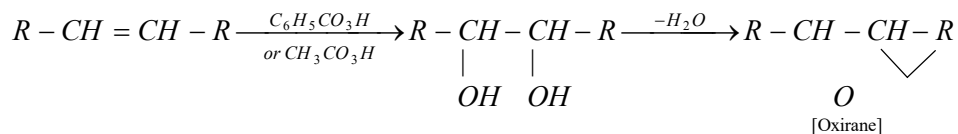
(xi) **Oxidation:** With alkaline $KMnO_4$ [Bayer's reagent]: This reaction is used as a test of unsaturation.



(xii) **Hydroxylation**

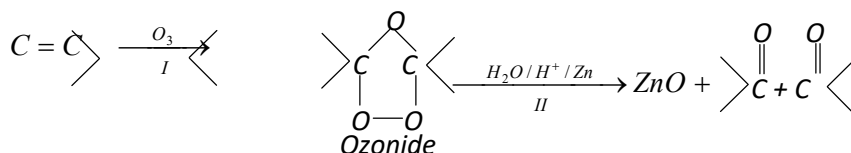


Note: If per benzoic acid or peroxy acetic acid is used then oxirane are formed.



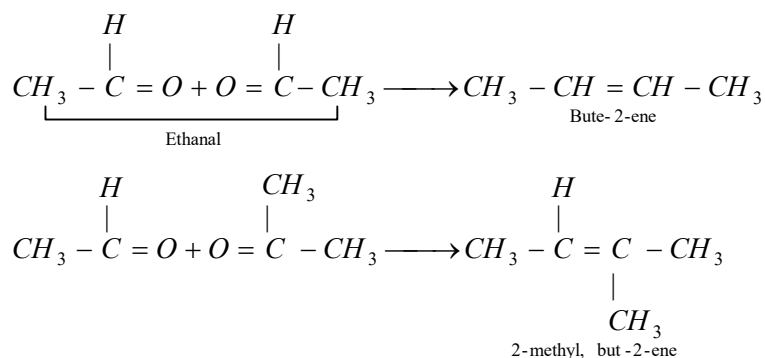
They burn with luminous flame and form explosive mixture with air or oxygen.

(xiv) **Ozonolysis**

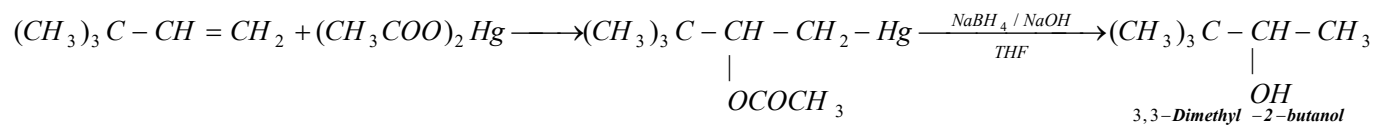


Application of Ozonolysis: This process is quite useful to locate the position of double bond in an alkene molecule. The double bond is obtained by joining the carbon atoms. of the two carbonyl compounds.

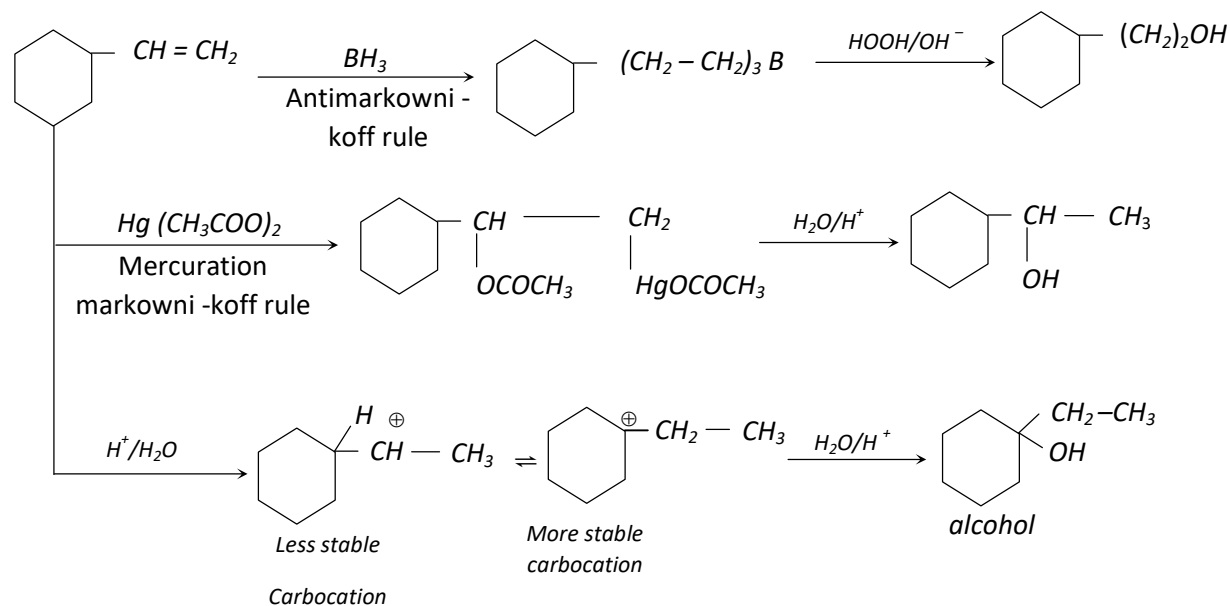
Ex.



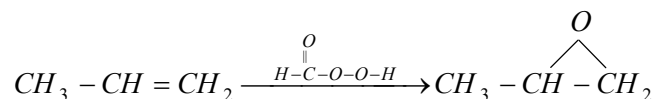
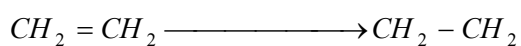
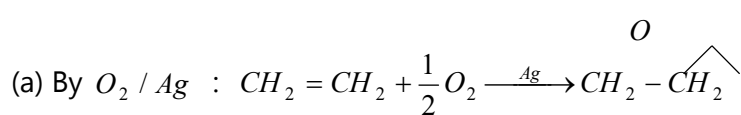
(xv) **Oxy – mercuration demercuration:** With mercuric acetate (in THF), followed by reduction with $\text{NaBH}_4 / \text{NaOH}$ is also an example of hydration of alkene according to markownikoff's rule.



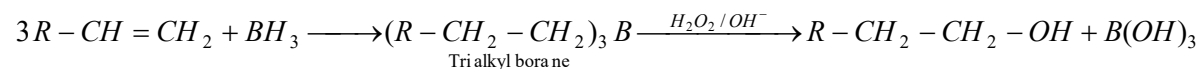
Ex.



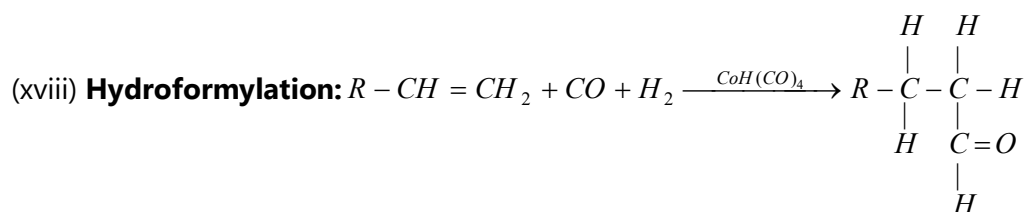
(xvi) **Epoxidation**



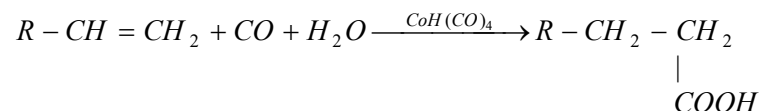
(xvii) **Hydroboration**



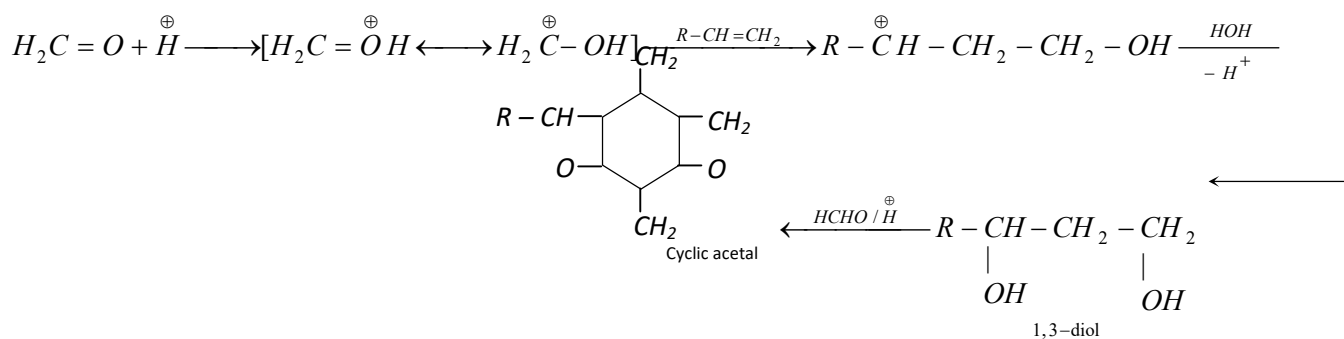
(Anti markownikoff's rule)



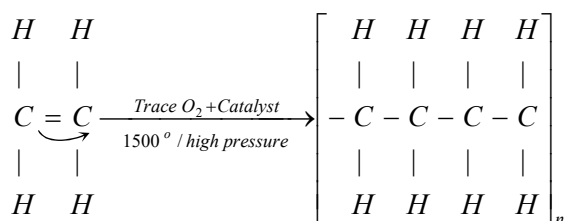
Note: If $CO + H_2O$ is taken then respective acid is formed.



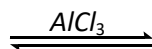
(xix) **Addition of formaldehyde**



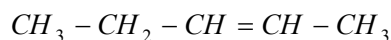
(xx) **Polymerization**



Note: If in polymerization zeigler- natta catalyst $[(R)_3Al + TiCl_4]$ is used then polymerization is known as zeigler-natta polymerization.



(xxi) **Isomerization:** $CH_3 - CH_2 - CH_2 - CH = CH_2$



The mechanism proceeds via carbocation.

(xxii) **Addition of HNO_3 :** $CH_2 = CH_2 + HO - NO_2 \longrightarrow CH_2OH \cdot CH_2NO_2$
Ethene 2-Nitroethanol

(xxiii) **Addition of Acetyl chloride:** $CH_2 = CH_2 + CH_3COCl \longrightarrow CH_2ClCH_2COCH_3$
Ethene 4-Chlorobutane-2-one

(6) **Uses**

(i) For the manufacture of polythene – a plastic material; (ii) For artificial ripening of fruits; (iii) As a general anesthetic; (iv) As a starting material for a large number of compounds such as glycol, ethyl halides, ethyl alcohol, ethylene oxide, etc.; (v) For making poisonous mustard gas (War gas); (vi) For making ethylene-oxygen flame.