ALKENE

❑ Introduction :

Alkenes are hydrocarbons with carbon-carbon double bonds, Alkenes are sometimes called olefins, a term derived from olefiant gas, meaning 'oil forming gas'. Aleknes are among the most important industrial compounds and many alkenes are also found in plants and many alkenes are also found in plants and animals. Ethylene is the largest-volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals. Alkenes polymerises to give many important polymers.

❑ Structure and bonding in Alkenes :

(a) Alkenes are unsaturated hydrocarbons having at least one double bond.

(b) They are represented by general foumula (G.F.) C_nH_{2n} (one double bond)

(c) In Ethene C = C bond length is 1.34 Å

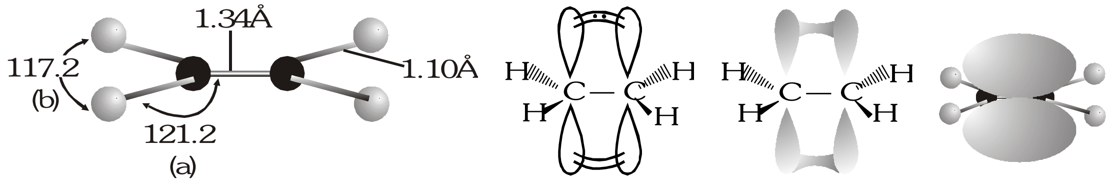
(d) Its bond energy is 146 kcal. mol^{-1}

(e) The hybridization of (C = C) alkenic carbon is sp^2

(f) The π e^- cloud is present above and below the plane of s-bonded skeleton.

(g) They are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.

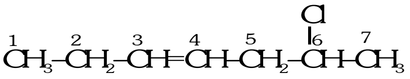
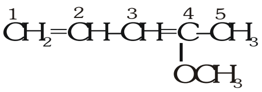
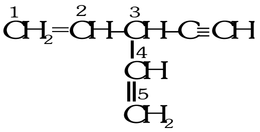
(h) Compounds may exist as conjugated polyenes or as cumulated polyenes or as isolated polyenes

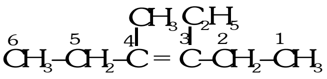
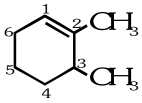
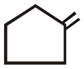
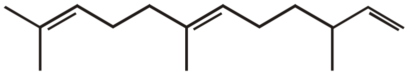


Note : That angle a < b since repulsion due to π electrons (double bond - single bond repulsion > single bond - single bond repulsion according to VSEPR theory.

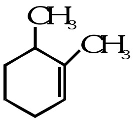
❑ IUPAC Nomenclature of alkenes and alkadienes :

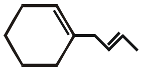
Table - I

S.No.	Compound	Name	Type
1.	$(CH_3)_2C = CH_2$	2–Methylpropene	Alkene
2.	$CH_3–CH=CH–CH_2–CH=CH_2$	Hexa–1, 4–diene	Isolated diene
3.	$CH_2=CH–CH = CH_2$	Buta–1, 3–diene	Conjugated diene
4.	$CH_3–CH=C=CH–CH_3$	Penta–2, 3–diene	Cumulated diene
5.	 $\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_2-\overset{Cl}{\overset{\mid 6}{C}}H-\overset{7}{C}H_3$	6–Chlorohept–3–ene	Alkene
6.	 $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\underset{\underset{OCH_3}{\mid}}{\overset{4}{C}}-\overset{5}{C}H_3$	4–methoxypenta–1, 3–diene	Conjugated diene
7.	 $\overset{1}{C}H_2=\overset{2}{C}H-\underset{\substack{\mid 4\\ CH\\ \| 5\\ CH_2}}{\overset{3}{C}H}-C\equiv CH$	3–Ethynylpenta–1, 4–diene	Isolated diene

S.No.	Compound	Name	Type
8.	 $\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{4}{\overset{CH_3}{C}}=\overset{3}{\overset{C_2H_5}{C}}-\overset{2}{C}H_2-\overset{1}{C}H_3$	3-Ethyl-4-methylhex-3-ene	Alkene
9.		2, 3-Dimethylcyclohex-1-ene	Cycloalkene
10.	$CH_2=C=CH_2$	Propadiene	Cumulated diene
11.	$CH_2=C=O$	Ethenone	Alkene
12.		Methylenecyclopentane	Alkene
13.		Cyclopentylethene	Alkene
14.		3, 7, 11-trimethyldodeca-1, 6, 10-triene	Isolated triene

Ex. Write IUPAC names of :

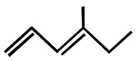
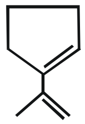
(a) 

(b) 

Sol. (a) 2, 3-Dimethylcyclohexene; (b) 1-(2-butenyl) cyclohex-1-ene

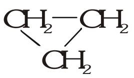
Ex. Give the structure for each of the following

(a) 4-Methyl-1, 3-hexadiene ;(b) 1-Isopropenylcyclopentene

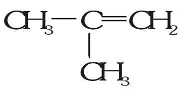
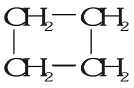
Sol. (a)  ; (b) 

❑ **Isomerism** :

Alkenes show chain, Ring chain or functional, Position, Geometrical isomerism and optical isomerism. For more details refer to isomerism provided to you in study material.

Ex. What is relation between $CH_3CH=CH_2$,  $\underset{CH_2}{CH_2-CH_2}$?

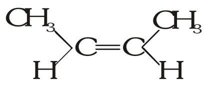
Sol. Ring chain isomerism

Ex. (a) $CH_3CH_2CH=CH_2$ (b) $CH_3-CH=CH-CH_3$ (c)  $CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$ (d)  $\begin{matrix}CH_2-CH_2\\ | \qquad | \\ CH_2-CH_2\end{matrix}$

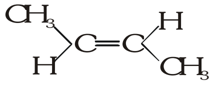
Define relations between a,b,c,d ?

Sol. a and b – Position isomerism ; a and c – Chain isomerism

a and d – Ring chain isomerism ; b also show Geometrical isomerism



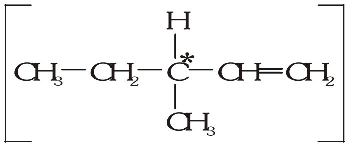
cis–2–butene



trans–2–butene

Ex. How many minimum carbon atom persent in optically active alkene?

Sol. 6C,

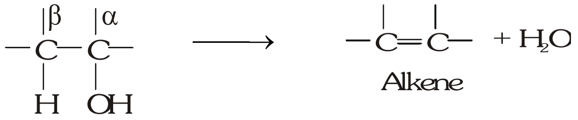


$$\left[CH_3-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{\overset{*}{C}}}-CH=CH_2\right]$$

3–Methyl–1–Pentene

- **Preparation of Alkenes :**

(1) **From Alcohols** : Alkenes can be prepared from monohydric alcohols or alkanols by the loss of H_2O and the reaction is known as **dehydration reaction**.



Alcohol

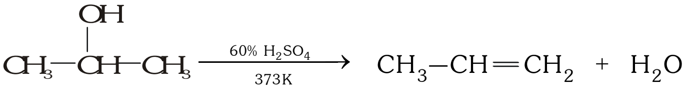
The dehydration can be carried with Al_2O_3 or with **mineral acid** upon heating.

(a) **Dehydration with Al_2O_3** : Ethene is prepared by heating ethanol with Al_2O_3 at 620 K.

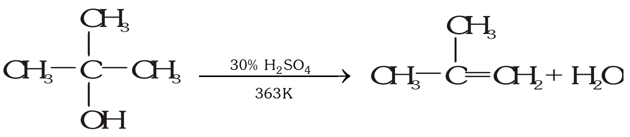
$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[620K]{Al_2O_3} \underset{\text{Ethene}}{CH_2=CH_2}+H_2O$$

(b) **Dehydration with mineral acid** : Alcohols upon heating with conc. H_2SO_4 form alkenes and the reaction is called **acidic dehydration.**

$$\underset{\text{Ethanol}}{CH_3-CH_2-OH} \xrightarrow[440K]{95\%\ H_2SO_4} \underset{\text{Ethene}}{CH_2=CH_2}+H_2O$$



$$\underset{\text{Propan–2–ol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-CH_3} \xrightarrow[373K]{60\%\ H_2SO_4} \underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O$$



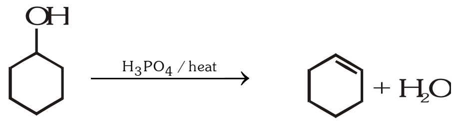
$$\underset{\text{2–Methylpropan–2–ol}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3} \xrightarrow[363K]{30\%\ H_2SO_4} \underset{\text{2–Methylpropene}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH_2} + H_2O$$

From the above reactions, it is clear that the order of acidic dehydration in different alcohols is

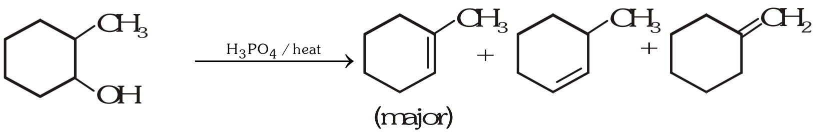
$$\boxed{\text{Tertiary} > \text{Secondary} > \text{Primary}}$$

Cycloalkenes can be prepared in the same way by the dehydration of cycloalkanols.

Example :



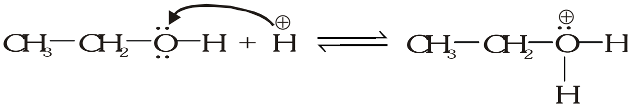
Cyclohexanol Cyclohexene



Regioselectivity of β elimination is governed by Zaitsev's Rule.

Machanism of Reaction: The acidic dehydration of alcohol proceeds through the formation of a carbocation intermediate and is explained as follows :

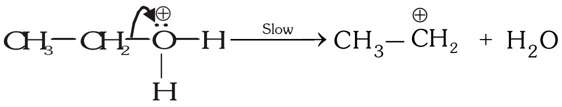
Step I : Alcohol being a Lewis base accepts a proton (H^+) from the acid in a reversible step as follows:



$$CH_3-CH_2-\ddot{\underset{..}{O}}-H + \overset{\oplus}{H} \rightleftharpoons CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\oplus}{\ddot{O}}}-H$$

Ethanol (From acid) Protonated ethano

Step II : Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C – O bond becomes weak and cleaves as follows :



$$CH_3-CH_2-\underset{\underset{H}{|}}{\overset{\oplus}{\ddot{O}}}-H \xrightarrow{\text{Slow}} CH_3-\overset{\oplus}{C}H_2 + H_2O$$

Ethyl carbocation

This is a slow and is regarded as **rate determining step.**

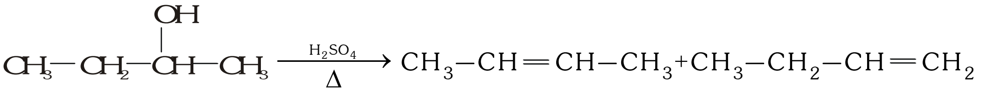
Step III : Carbocation is unstable in nature and loses a H^+ and changes into ethene in a fast step as follows:

$$H-CH_2-\overset{\oplus}{C}H_2 \xrightarrow{\text{Fast}} CH_2=CH_2 + H^+$$

Ethene

Note: Dehydration of secondary and tert alcohol is best carried out by using dil. H_2SO_4. Since alkenes produced from those alcohols have a tendency to form polymers under the influence of concentrated acid.

> **Saytzeff Rule :** When two possible alkenes are obtained by the elimination reaction than that alkene will be in good yield, containing maximum number of alkyl group on double bonded C–atoms



$$CH_3-CH_2-\underset{}{\overset{\overset{OH}{|}}{C}H}-CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3-CH=CH-CH_3 + CH_3-CH_2-CH=CH_2$$

2–butanol main product 1–butene

2–butene 80% 20%

$$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\Delta]{H_2SO_4} CH_3-CH=CH-CH_3 + CH_3CH_2CH=CH_2$$

1-butanol 2-butene80% 1-butene 20%

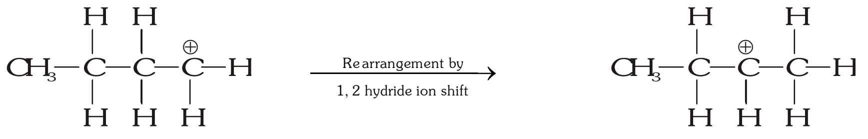
Main product

Mechanism : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

$$CH_3CH_2CH_2-CH_2-\ddot{\underset{\cdot\cdot}{O}}-H + \overset{\oplus}{H} \longrightarrow CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2$$

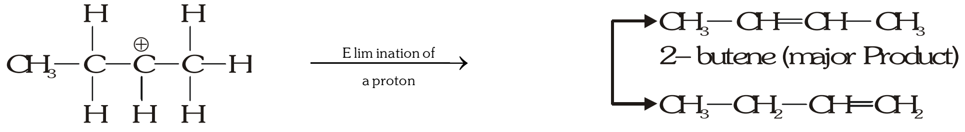
$$CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2 \longrightarrow CH_3CH_2CH_2-\overset{\oplus}{C}H_2 + H_2O$$

Primary Carbonium ion



$$CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2 \xrightarrow[\text{1, 2 hydride ion shift}]{\text{Rearrangement by}} CH_3-CH_2-\overset{\oplus}{C}H-CH_3$$

1^0 Carbonium 2^0 Carbonium more stable



$$CH_3-CH_2-\overset{\oplus}{C}H-CH_3 \xrightarrow[\text{a proton}]{\text{Elimination of}} \begin{cases} CH_3-CH=CH-CH_3 \\ CH_3-CH_2-CH=CH_2 \end{cases}$$

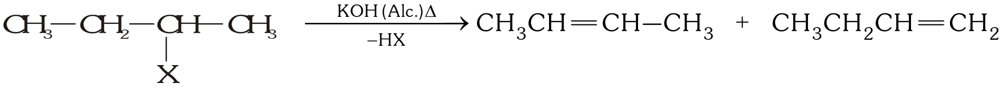
2-butene (major Product)

1-butene (minor product)

(Saytzeff rule)

(2) **From Alkyl halide (By dehydrohalogenation):** Removal of HX from a substrate by alcoholic KOH or $NaNH_2$

$$RCH_2CH_2X \xrightarrow[-HX]{KOH\,(Alc.)\Delta} RCH=CH_2$$

Example : 

$$CH_3-CH_2-\underset{X}{\underset{|}{C}H}-CH_3 \xrightarrow[-HX]{KOH\,(Alc.)\Delta} CH_3CH=CH-CH_3 + CH_3CH_2CH=CH_2$$

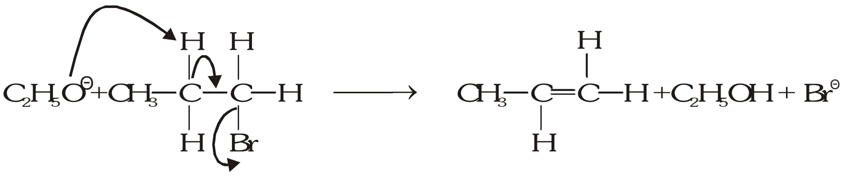
(Saytzeff rule)

The ease of dehydrohalogenation show the order

For alkyl group $\boxed{\text{tertiary} > \text{secondary} > \text{primary}}$

For halogen in halide $\boxed{\text{Iodide} > \text{Bromide} > \text{Chloride} > \text{flouride}}$

It is single step and synchronous process. Removal of proton, the formation of multiple bond between Cα and Cβ and the release of the leaving group X take place simultaneously. (E_2 mechanism)

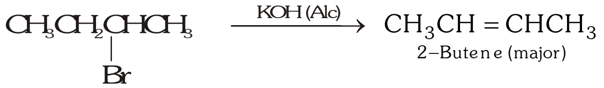
Example : 

$$C_2H_5O^{\ominus} + CH_3-CH_2-CH_2-Br \longrightarrow CH_3-CH=CH-H + C_2H_5OH + Br^{\ominus}$$

$$\boxed{\text{Rate of reaction} \propto [CH_3CH_2CH_2Br]\,[C_2H_5\overset{\ominus}{O}]}$$

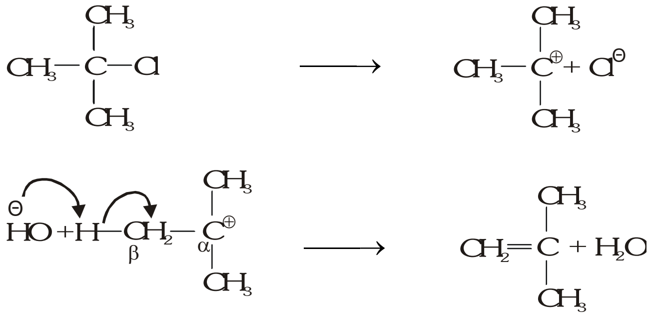
Example : $CH_3CH_2CH_2CH_2Br \xrightarrow{KOH(Alc)} \underset{1\text{–Butene}}{CH_3CH_2CH = CH_2}$

Example :

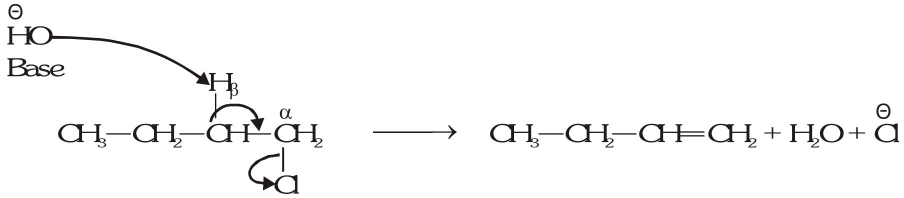


$\underset{\substack{| \\ Br}}{CH_3CH_2CHCH_3} \xrightarrow{KOH(Alc)} \underset{2\text{–Butene (major)}}{CH_3CH = CHCH_3}$

Primary and secondary alkyl halides undergo elimination reaction by E_2 mechanism. E_1 elimination reactions are shown by tertiary alkyl halides which are capable of producing stable (tert) Carbonium ion on show ionization.



E_2 mechanism : Those alkyl halides which do not give Stable Carbonium ion on ionization show E_2 elimination.



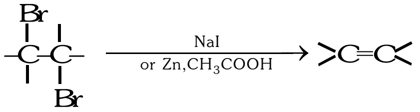
(A) Dehalogenation of vicinal dihalides :

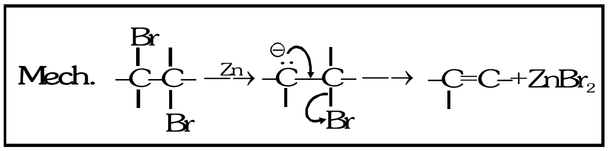
There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vicinal dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.

Dehalogenation of vicinal dihalides can be effected either by NaI in acetone or zinc in presence of acetic acid or ethanol.

◆ **General Reaction**

(i)

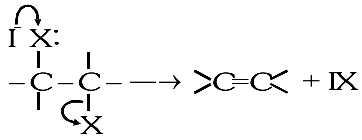




(ii) $CH_3\text{–}CHBr\text{–}CH_2Br \xrightarrow[\left(\substack{CH_3COOH \text{ or} \\ C_2H_5OH \text{ as solvent}}\right)]{\text{Zn dust}} CH_3\text{–}CH\text{=}CH_2$

Mech.

With NaI in acetone :



It involves an **antielimination** of halogen atoms

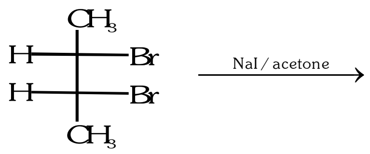
Remarks :

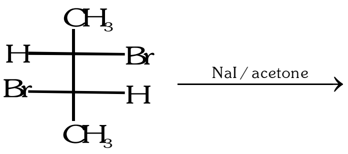
(i) Both are E_2 elimination.

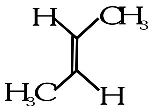
(ii) Both are stereospecific antielimination.

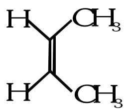
Example : $CH_3-CHBr-CHBr-CH_3 \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3-CH=CH-CH_3$

Ex. Identify the product in the following reactions :

(a)


(b)


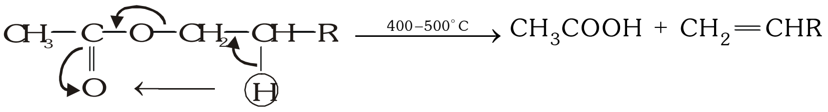
Sol. (a)


; (b)


(B) From **gem dihalide** : Higher alkene obtained

$$CH_3CH\boxed{X_2 \;+ 2Zn + X_2}CHCH_3 \longrightarrow CH_3-CH=CH-CH_3 + ZnX_2$$

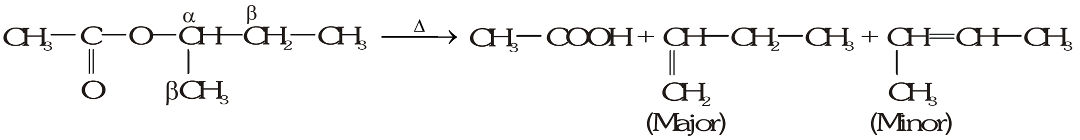
(3) By Pyrolysis of ester :



$$CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-\underset{H}{CH}-R \xrightarrow{400-500^{\circ}C} CH_3COOH + CH_2=CHR$$

Hoffmann's Rule : Less substituted or less stable alkene is major product.

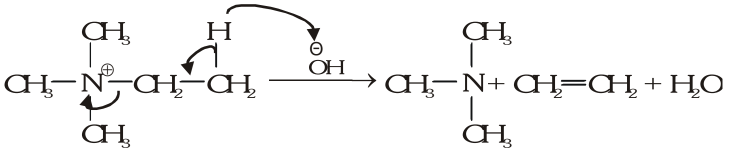
Example :



$$CH_3-\underset{\underset{O}{\|}}{C}-O-\overset{\alpha}{\underset{\beta CH_3}{CH}}-\overset{\beta}{CH_2}-CH_3 \xrightarrow{\Delta} CH_3-COOH + \underset{\underset{\text{(Major)}}{\underset{CH_2}{\|}}}{CH}-CH_2-CH_3 + \underset{\underset{\text{(Minor)}}{CH_3}}{CH}=CH-CH_3$$

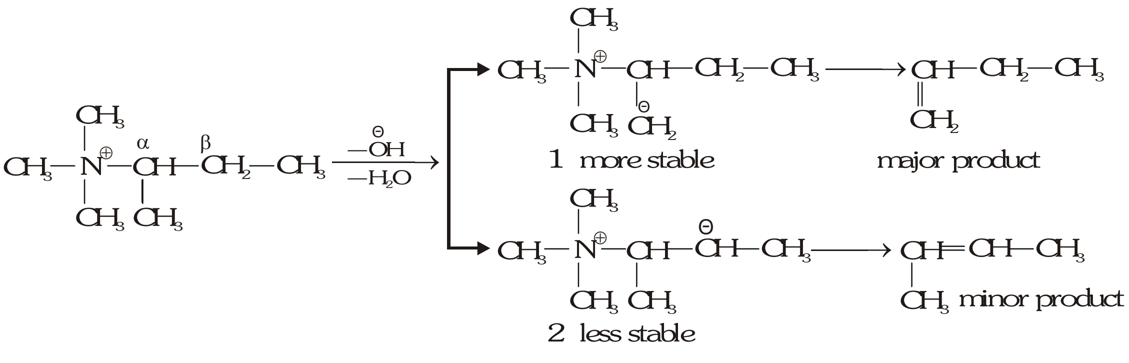
In the reaction to form an alkene a β-hydrogen from alkyl ester is attracted by oxygen atom of keto group & Hoffmann's alkene will be the major product.

(4) By Pyrolysis of tetra alkyl ammonium ion :

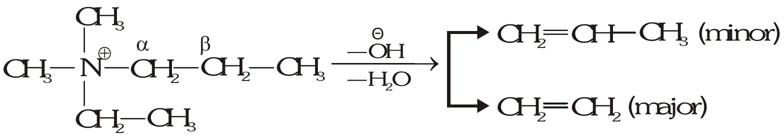


$$CH_3-\overset{CH_3}{\underset{CH_3}{\overset{\oplus}{N}}}-CH_2-\overset{H}{CH_2} \xrightarrow{\overset{\ominus}{O}H} CH_3-\overset{CH_3}{\underset{CH_3}{N}} + CH_2=CH_2 + H_2O$$

Example :



Example :



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_2-CH_3}{|}}{\overset{\oplus}{N}}}-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-CH_3 \xrightarrow[-H_2O]{-\overset{\ominus}{O}H} \begin{cases} CH_2=CH-CH_3 \text{ (minor)} \\ CH_2=CH_2 \text{ (major)} \end{cases}$$

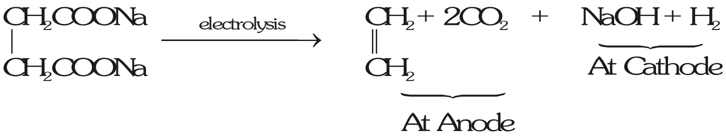
(a) In this reaction β–hydrogen of tetra-alkyl ammonium ion is attracted by a base and alkene is formed.

(b) In this reaction intermediate is carbanion.So yield of product depends on stability of carbanion.

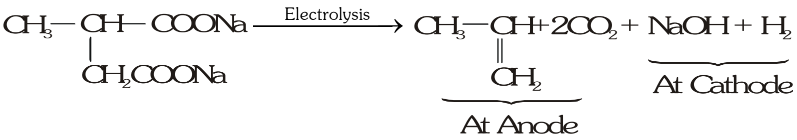
(c) In this reaction Hoffmann's Rule is followed.

(6) By Kolbe's method:

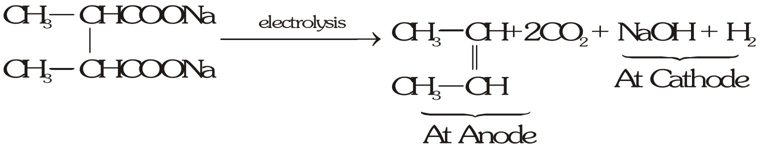
Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.



$$\begin{matrix} CH_2COONa \\ | \\ CH_2COONa \end{matrix} \xrightarrow{\text{electrolysis}} \underbrace{\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + 2CO_2}_{\text{At Anode}} + \underbrace{NaOH + H_2}_{\text{At Cathode}}$$

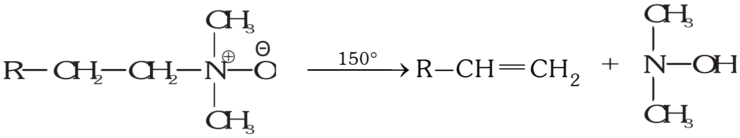


$$CH_3-\underset{\underset{CH_2COONa}{|}}{CH}-COONa \xrightarrow{\text{Electrolysis}} \underbrace{CH_3-\underset{\underset{CH_2}{\|}}{CH}+2CO_2}_{\text{At Anode}} + \underbrace{NaOH + H_2}_{\text{At Cathode}}$$



$$\begin{matrix} CH_3-CHCOONa \\ | \\ CH_3-CHCOONa \end{matrix} \xrightarrow{\text{electrolysis}} \underbrace{CH_3-\underset{\underset{CH_3-CH}{\|}}{CH}+2CO_2}_{\text{At Anode}} + \underbrace{NaOH + H_2}_{\text{At Cathode}}$$

(7) Pyrolysis of Tri alkyl amine Oxide : (Cope Reaction)



$$R-CH_2-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{\overset{\oplus}{N}}}-\overset{\ominus}{O} \xrightarrow{150°} R-CH=CH_2 + \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}}-OH$$

(8) Hydrogenation of alkyne :

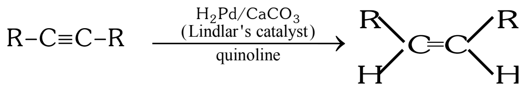
By partial reduction of Alkynes -

(a) **By catalytic Hydrogenation of Alkynes in presence of poisoned catalyst** (A Syn Addition of Hydrogen : Synthesis of cis-Alkenes : This is performed by)

(i) **Lindlar's catalyst** : Metallic palladium deposited on calcium carbonate conditioned with lead acetate and quinoline.

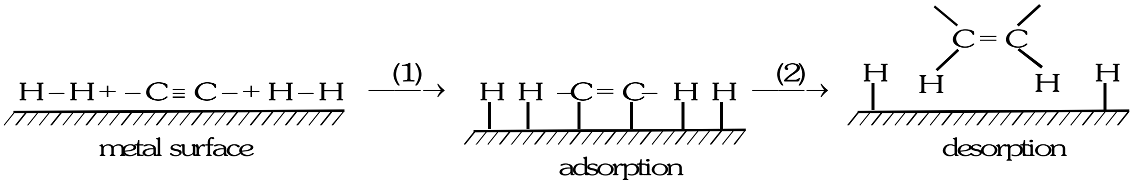
(ii) P-$_2$ catalyst (Ni_2B nickel boride)

General reaction



R–C≡C–R $\xrightarrow[\text{quinoline}]{H_2Pd/CaCO_3 \text{ (Lindlar's catalyst)}}$

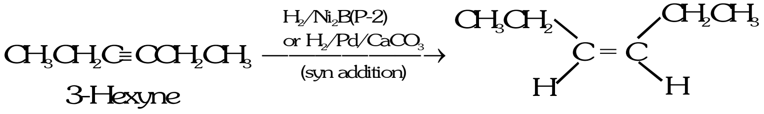
Mechanism of hydrogenation :



Steps : The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

In this state, the reactants lie very close to each other and so the hydrogen atoms start forming bond with carbon. Two hydrogen atoms are added to two triply bonded carbon atoms from the same side of π bond and a **cis or syn addition product** is formed. The product alkene now escapes away from the surface of the catalyst. Quinoline occupies the metal surface inhibiting further reduction to alkanes **Quinoline** therefore is called catalyst poison and such palladium is called dectivated catalyst or poisoned catalyst.

Example :

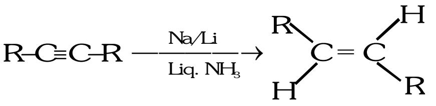


3-Hexyne

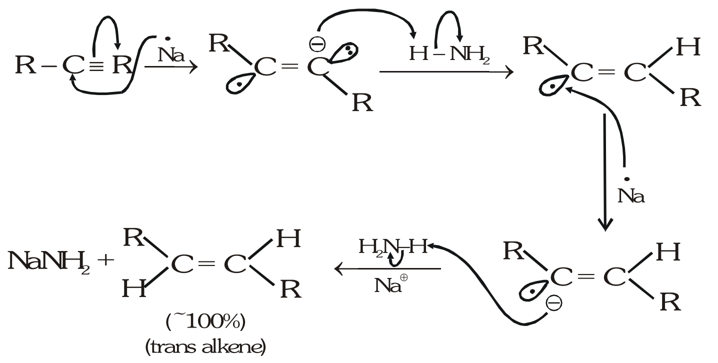
(Z)-3-Hexene
(cis-3-Hexene)
(97%)

(b) **Birch Reduction** : (Anti addition of hydrogen : synthesis of trans-alkenes)

◆ General reaction

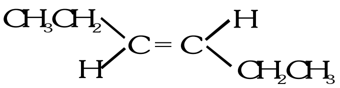


Mechanism : Reagents Na (or Li, K) + liq $NH_3 \longrightarrow Na^+ + e^-$ (sollvated electron)



(~100%)
(trans alkene)

Example : : $CH_3–CH_2–C\equiv C–CH_2–CH_3 \xrightarrow{Na / NH_3(\ell)}$

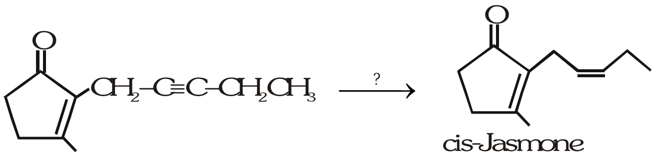


trans
hex-3-ene

Note : This process of reduction is not eligible when terminal alkynes are taken (R–C≡CH) because terminal alkynes form sodium salt with Na metal.

$$CH_3–C\equiv CH + Na/NH_3 \longrightarrow CH_3–C\equiv C–Na^+ + [H]^+$$

Ex. Identify the reagent for following synthesis



(A)

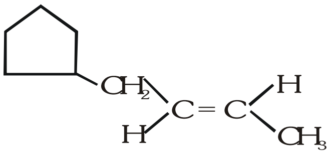
cis-Jasmone

Sol. H_2/Lindlar's catalyst

$$A \xrightarrow[\text{Lindlar's catalyst}]{H_2} \text{cis - Jasmone}$$

Ex. Identify the product in the following reaction :

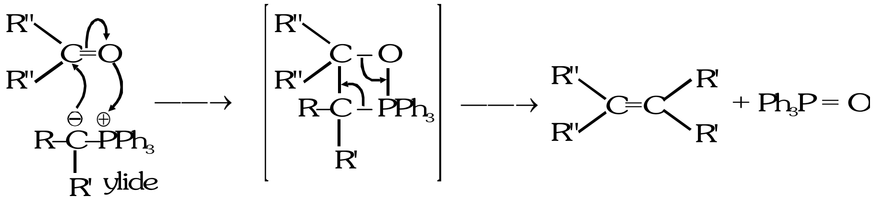
Sol.



(9) Wittig Reaction :

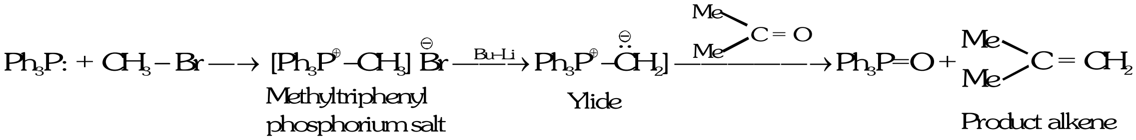
The aldehydes and ketones are converted into alkenes by using a special class of compounds called **phosphorus ylides**, also called Wittig reagents.

The Triphenyl group of phosphorane has a strong tendency to pull oxygen atom of the aldehyde or ketone via a cyclic transition state forming an alkene.



(R, R', R" and R''' may be hydrogen or any alkyl group)

e.g.



$$Ph_3P: + CH_3-Br \longrightarrow [Ph_3\overset{\oplus}{P}-CH_3]\overset{\ominus}{Br} \xrightarrow{BuLi} Ph_3\overset{\oplus}{P}-\overset{\ominus}{\ddot{C}}H_2] \xrightarrow{Me_2C=O} Ph_3P=O + Me_2C=CH_2$$

❑ Physical Properties of Alkenes / Hydrocarbons :

	Physical properties	Homologus series	Isomers
1.	Physical state	C_1 – C_3 gases C_4 – C_{20} liquids > C_20 : solids	
2.	Dipolemoment (μ)		cis > trans
3.	Polarity	–	cis > trans (for C_{ab}=C_{ab} type of alkenes)
4.	Melting point	increases with M.W.	trans > cis (due to more packing capacity
5.	Boiling point	increases with M.W.	cis > trans # branching decreases B.P.  $C-\overset{C}{\overset{\vert}{C}}=C < C-C=C-C$ Polarity increases, boiling point increases
6.	Solubility	Practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc.	cis > trans Polarity increases, solubility in polar solvents increases.
7.	Stability		trans > cis (cis isomers has more Vander Waals repulsion

❑ Chemical Properties :

Alkenes are more reactive than alkane this is because -

(a) The π electrons of double bond are located much far from the carbon nuclei and are thus less firmly bound to them.

(b) π bond is weaker than σ bond and more easily broken.

The reactivity order for alkenes -

$$CH_2{=}CH_2 > R{-}CH{=}CH_2 > R_2C{=}CH_2 \approx \underset{(Trans\ <\ Cis)}{RCH{=}CHR} > R_2C{=}CHR > R_2C{=}CR_2$$

The reactivity order of alkenes has been delt in terms of heat of hydrogenation of alkene, more is the heat of hydrogenation ($\Delta H = -ve$), more is the reactivity, the reactivity of alkene is however also related to

(i) Steric hinderence (ii) Hyperconjugation (iii) Heat of Combustion.

All four butenes may be compared, since all give the same products on combustion viz. $4CO_2+4H_2O$

Alkenes give the following type of reactions :

(a) Addition reaction (b) Oxidation reaction. (c) Substitution reaction.

(d) Polymerization Reaction. (e) Isomerisation

Alkene	Heat of combustion (kJ/mol)	Heat of hydrogenation (kcal/mol)
1-Butene	2719	30.3
Isobutene	2703	27.2
Cis-2-butene	2712	28.6
trans-2-butene	2707	27.6

(A) Addition Reaction :

[A$_1$] free radical addition :

◆ **Addition of H_2 :**

$$R{-}CH{=}CH_2{+}H_2 \xrightarrow{Ni,Pt\ or\ Pd} R{-}CH_2{-}CH_3{+} \quad \text{Heat of Hydrogenation.}$$

Note:(a) Reaction is exothermic, It is called heat of hydrogenation.

(b) $$\boxed{\text{Stability of alkene} \propto \frac{1}{\text{heat of hydrogenation}} \propto \frac{1}{\text{reactivity of alkene with } H_2}}$$

(c) The process is used to obtain vegetable (saturated fats) ghee from hydrogenation of oil.

(B) [A$_2$] Electrophilic addition reactions :

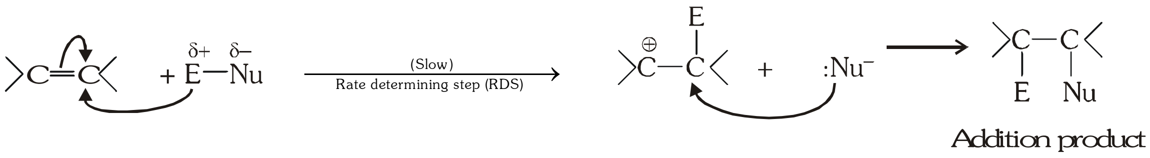
Because of the presence of >C=C< bond in molecules, alkenes generally take part in the **addition reactions.**

$$>C=C< + AB \longrightarrow -\underset{A}{\overset{|}{C}}-\underset{B}{\overset{|}{C}}-$$

Alkene Attacking molecule Addition product

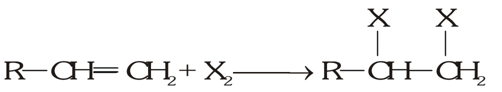
From mechanism point of view, the addition in alkenes is generally **electrophilic in nature** which means that attacking reagent which carries the initial attack is an electrophile (E^+). This is quite expected also as there is high electron density in the double bond. The mechanism proceeds in two steps.

Step I : The π–electron cloud of the double bond causes the polarisation of the attacking molecule (E–Nu) which cleaves to release the electrophile (E^+) for the attack. The double bond simultaneously undergoes electromeric effect and the attack by the electrophile is accomplished in slow step (also called rate determining step) to form a **carbocation** intermediate.



Step II : The nucleophile ($:Nu^-$) released in the slow step combines with the carbocation to give the desired addition product in the fast step.

1. **Addition of Halogen** : It is a electrophilic addition reaction.



$$R-CH=CH_2 + X_2 \longrightarrow R-\underset{X}{\underset{|}{C}H}-\underset{X}{\underset{|}{C}H_2}$$

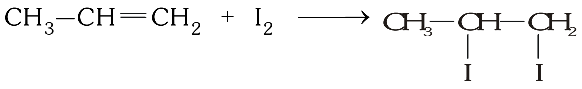
(Vicinal halides)

Note: (a) Reactivity order of halogen is : $Cl_2 > Br_2 > I_2$

(b) Addition of F_2 is exothermic reaction so it is difficult to control.

(c) The addition of Br_2 on alkenes provides a useful test for unsaturation in molecule.The brown colour of the bromine being rapidly discharged. Thus decolarization of 5% Br_2 in CCl_4 by a compound suggest unsaturation in it. Colourless dibromo compound is formed.

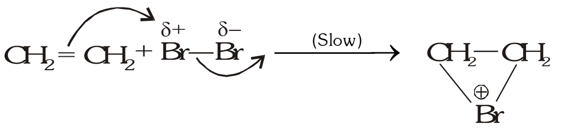
(d) I_2 reacts slowly with alkenes to form Vicinal di-iodides which are unstable and eliminated I_2 molecule very readily to give original alkene due to large size of Iodine they overlap.



$$CH_3-CH=CH_2 + I_2 \longrightarrow CH_3-\underset{I}{\underset{|}{C}H}-\underset{I}{\underset{|}{C}H_2}$$

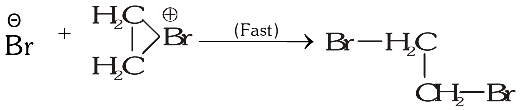
Unstable

◆ **Mechanism** : It is interesting to note that product which is mainly formed as a result of addition is **trans** in nature whereas the cis isomer is obtained in relatively smaller proportions. Since carbocation intermediate is planar (sp^2 hybridised), both cis and trans addition products must be formed almost in equal proportions. The trans product can be justified in case a cyclic ion is formed by the initial electrophile attack.



(Halonium ion)

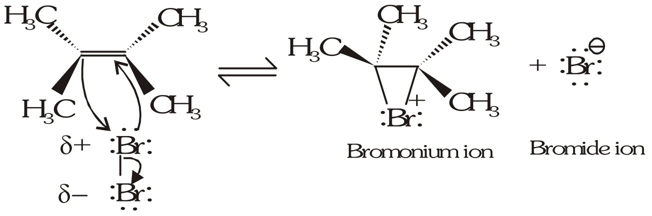
The attack of Br^- ion on the cyclic ion takes place from the side opposite to side where bromine atom is present in order to minimise steric hindrance.



1,2,-Dibromoethane,

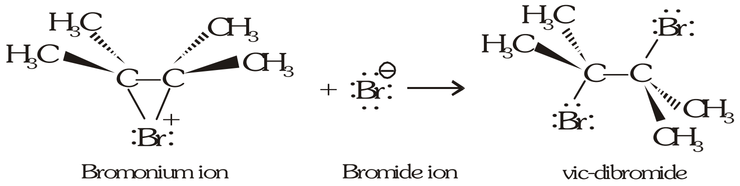
For 2, 3-dimethylbut-2-ene :

Step I :



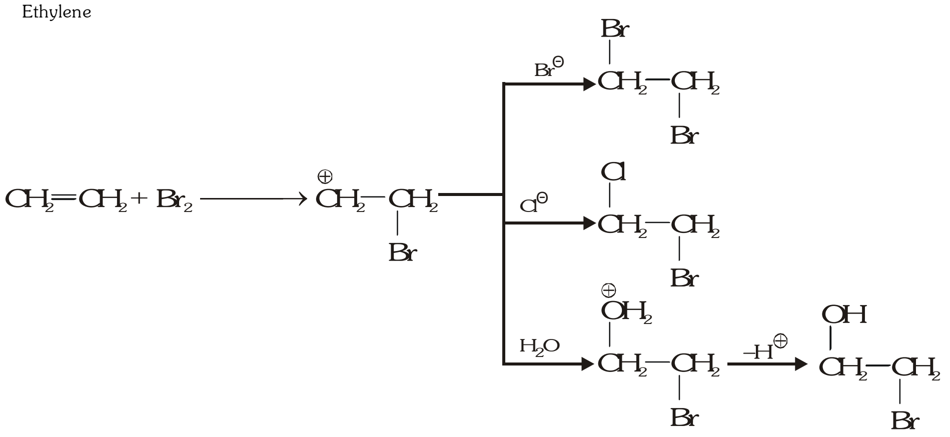
A bromine molecule becomes polarized as it approaches the alkene. The polarized bromine molecule transfers a positive bromine atom (with six electrons in its valance shell) to the alkene resulting in the formaiton of bromonium ion.

Step II :

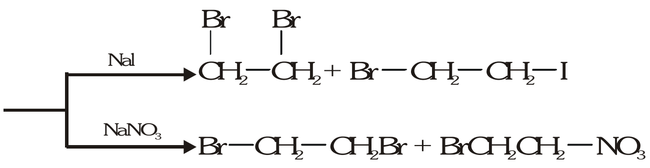


Ex. $\underset{\text{Ethylene}}{CH_2=CH_2} + Br_2 \xrightarrow{\text{aq.NaCl}}$ Products, what are the products?

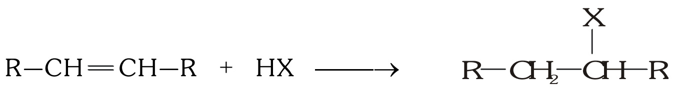
Sol.



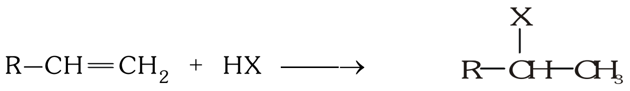
Similarly $CH_2=CH_2 + Br_2$



2. Addition of halogen acid :



$$R-CH=CH-R + HX \longrightarrow R-CH_2-\overset{\overset{\large X}{|}}{C}H-R$$



$$R-CH=CH_2 + HX \longrightarrow R-\overset{\overset{\large X}{|}}{C}H-CH_3$$

Note:(i) The order of reactivity of hydrogen halide is : **HI > HBr > HCl > HF**

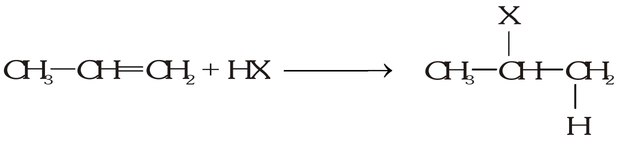
(ii) Their addition is an example of electrophilic addition.

(iii) Addition on alkene proceeds via the formation of more stable carbonium ion.

(iv) Addition of HX on unsymmetrical alkenes ($R-CH=CH_2$) takes place according to Markownikoff's rule.

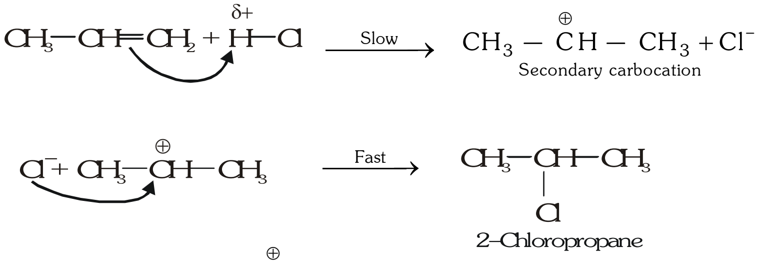
❑ MARKOWNIKOFF'S RULE :

(a) First Rule : When molecule of a HX add up on unsymmetrical unsaturated hydrocarbon, the halogen atom goes to the unsaturated carbon atom bearing lesser number of hydrogen atoms.



$$CH_3-CH=CH_2 + HX \longrightarrow CH_3-\overset{X}{\overset{|}{C}}H-\underset{\underset{H}{|}}{C}H_2$$

Mechanism : It is electrophilic addition and is illustrated by the action of HCl to propene.



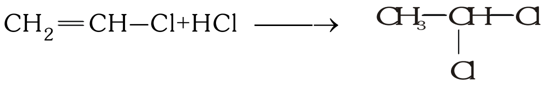
Secondary carbocation

2-Chloropropane

Primary carbocation ($CH_3-CH_2-\overset{\oplus}{C}H_2$) is formed but only in very small proportion since it is less stable than the secondary carbocation. Markownikff's rule can also be stated as :

The electrophilic addition to unsymmetrical alkenes always occurs through the formation of a more stable carbocation intermediate.

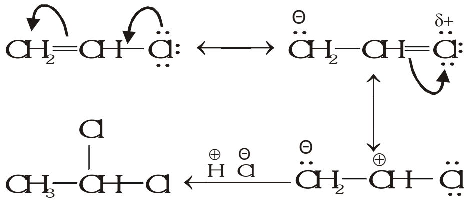
(b) Second Rule : In the addition of HX to vinyl halide and analogous compounds, the halogen attaches itself to the carbon atom, on which the halogen atom is already present.



$$CH_2=CH-Cl+HCl \longrightarrow CH_3-\underset{\underset{Cl}{|}}{C}H-Cl$$

Ethylidene chloride

◆ **Mechanism** :



In vinyl chloride two effects operate simultaneously in opposite direction-

(i) Inductive effect – electron attracting (-I) effect of chlorine.

(ii) Resonance effect – electron pair releasing (+R) effect of chlorine.

The resonance effect is much more than the -I effect of Chlorine at the time of attack.This creates centres of +ve and –ve charges.

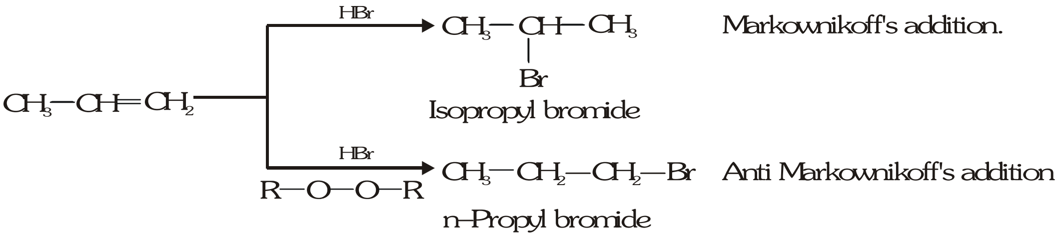
All polar reagents of the general structure $\overset{\oplus}{Y}\overset{\ominus}{Z}$ (such as $\overset{\oplus}{H}-\overset{\ominus}{X}$, $\overset{\oplus}{H}-\overset{\ominus}{OH}$ $\overset{\oplus}{H}-\overset{\ominus}{SO_3H}$, $\overset{\oplus}{X}\overset{\ominus}{OH}$) add on unsymmetrical unsaturated compound in accordance with Markownikoff's rules. Such additions are called normal Markownikoff's rule, where as additions in the opposite manner are reffered to as abnormal or **antimarkownikoff's additions.**

❑ ANTI MARKONIFF'S RULE OR PEROXIDE EFFECT OR KHARASCH RULE :

(i) In the presence of oxygen of peroxides the addition of HBr on unsaturated unsymmetrical compound takes place contrary to Markownikoff's rule. This is called peroxide effect and is due to the difference in the mechanism of the addition.

(ii) In the normal Markownikoff's addition the mechanism is ionic.

(iii) In the presence of peroxide the addition of HBr takes place via free radicals.



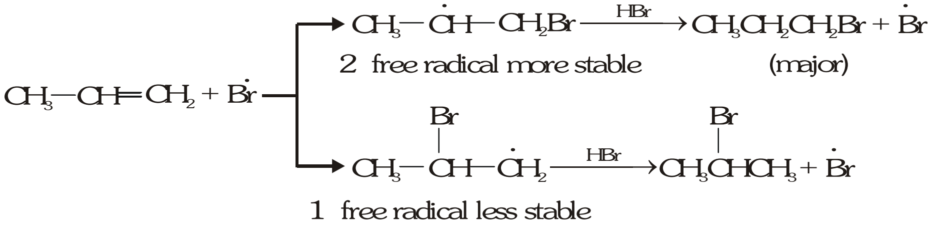
◆ Mechanism :

(i) Chain initiation -

(a) R—O—O—R $\longrightarrow$ $2RO^{\bullet}$

(b) HBr + $RO^{\bullet}$ $\longrightarrow$ ROH + $Br^{\bullet}$

(ii) Chain propagation



(iii) Chain termination :

$R^{\bullet} + {}^{\bullet}R \longrightarrow R-R$

$R^{\bullet} + {}^{\bullet}Br \longrightarrow R-Br$

${}^{\bullet}Br + {}^{\bullet}Br \longrightarrow Br-Br$

Ex. Why HCl and HI do not give antimarkownikoff products in the presence of peroxides.?

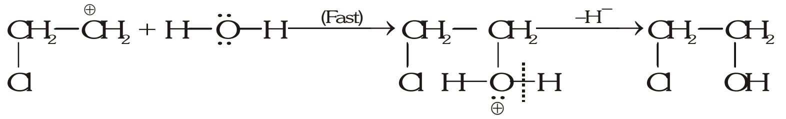
Sol. (a) The H—Cl bond is stronger than H—Br.

(b) The H-I bond is weaker than H—Br bond. It is broken by the alkoxy free radicals obtained from peroxides, but the addition of iodine atom on alkene is endothermic as compared to Br atom therefore iodine atoms so formed combine with each other to yield iodine.

3. **Addition of Hypohalous acid (or X_2/H_2O, or HOX)** : It is a electrophilic addition and follows Markownikoff's rule.

$$\overset{\delta-}{Cl}\vdots\overset{\delta+}{Cl} + H_2C{=}CH_2 \xrightarrow{\text{Slow}} \underset{\underset{Cl}{|}}{CH_2}-\overset{\oplus}{C}H_2 + Cl^-$$

Carbocation



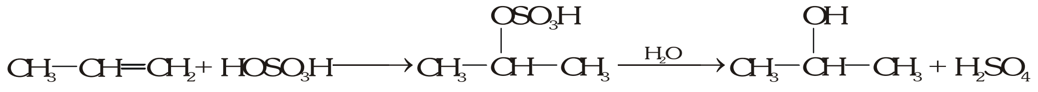
$$\underset{\underset{Cl}{|}}{CH_2}-\overset{\oplus}{C}H_2 + H-\ddot{O}-H \xrightarrow{\text{(Fast)}} \underset{\underset{Cl}{|}}{CH_2}-\underset{\underset{H-\overset{\oplus}{O}-H}{|}}{CH_2} \xrightarrow{-H^-} \underset{\underset{Cl}{|}}{CH_2}-\underset{\underset{OH}{|}}{CH_2}$$

Ethylene chlorohydrin

In the fast step, there is competition between Cl^- ion and H_2O molecule to act as nucleophile but H_2O is a better nucleophile.

$$\boxed{\text{Reactivity order is} \quad HOCl > HOBr > HOI}$$

4. **Addition of H_2SO_4:** Alkene react with conc. H_2SO_4 to produce alkyl hydrogen sulphate. Which gives alcohols on hydrolyses.This reaction used to seprate alkene from a mixture of alkane and alkene.



$$CH_3-CH{=}CH_2 + HOSO_3H \longrightarrow CH_3-\overset{\overset{OSO_3H}{|}}{C}H-CH_3 \xrightarrow{H_2O} CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 + H_2SO_4$$

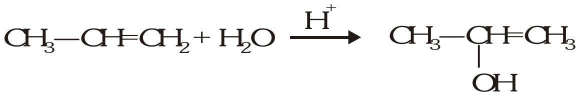
Isopropyl alcohol

$$CH_2{=}CH_2 + H_2SO_4 \longrightarrow CH_3CH_2HSO_4 \begin{cases} \xrightarrow{\Delta} C_2H_4 + H_2SO_4 \\ \xrightarrow{H_2O} C_2H_5OH + H_2SO_4 \end{cases}$$

Ethyl hydrogen sulphate give ethylene when heated 430-440K while ethanol is obtained on boiling it with water.

5. **Addition of water (Hydration of alkenes)** : Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as the **hydration reaction** . Intermediate in this reaction is carbo cation, so rearrangement will take place.

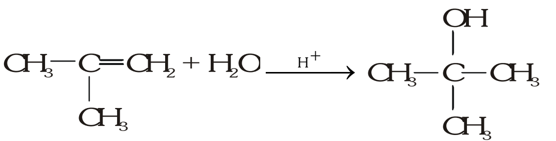
(i)



$$CH_3-CH{=}CH_2 + H_2O \xrightarrow{H^+} CH_3-\underset{\underset{OH}{|}}{C}H{=}CH_3$$

Propene Propan-2-ol

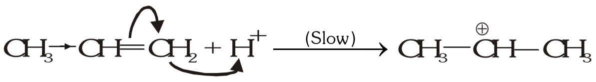
(ii)



$$CH_3-\underset{\underset{CH_3}{|}}{C}{=}CH_2 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

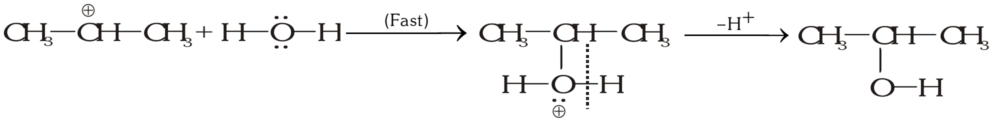
2–Methylpropene 2-Methylpropan-2-ol

◆ **Mechanism** :



$$CH_3\rightarrow CH{=}CH_2 + H^+ \xrightarrow{\text{(Slow)}} CH_3-\overset{\oplus}{C}H-CH_3$$

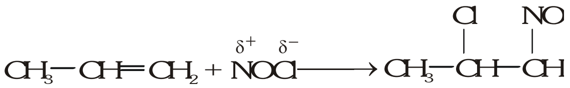
Carbocation (2)



$$CH_3-\overset{\oplus}{C}H-CH_3 + H-\ddot{O}-H \xrightarrow{(Fast)} CH_3-\underset{\underset{\oplus}{H-\ddot{O}-H}}{\underset{|}{C}H}-CH_3 \xrightarrow{-H^+} CH_3-\underset{O-H}{\underset{|}{C}H}-CH_3$$

Propan-2-ol

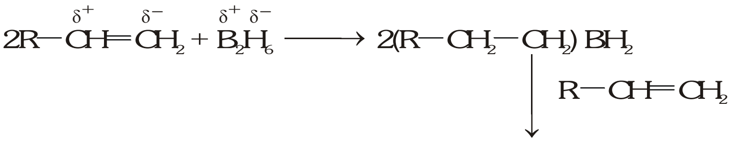
6. **Addition of NOCl (Tilden reagant) :**



$$CH_3-CH=CH_2 + \overset{\delta^+}{N}\overset{\delta^-}{OCl} \longrightarrow CH_3-\overset{Cl}{\overset{|}{C}H}-\overset{NO}{\overset{|}{C}H}$$

Propylene nitrosochloride

7. **Hydroboration** : It obeys markoni'koff's rule.Diborane readily reacts with alkenes giving trialkyl boranes. The reaction is called hydroboration.



$$2R-\overset{\delta^+}{C}H=\overset{\delta^-}{C}H_2 + \overset{\delta^+}{B_2}\overset{\delta^-}{H_6} \longrightarrow 2(R-CH_2-CH_2)BH_2$$

$$2(R-CH_2-CH_2)BH_2 \xrightarrow{R-CH=CH_2} 2(R-CH_2-CH_2)_2-BH$$

$$2(R-CH_2-CH_2)_2-BH \xrightarrow{R-CH=CH_2} (R-CH_2-CH_2)_3B$$

Trialkylborane

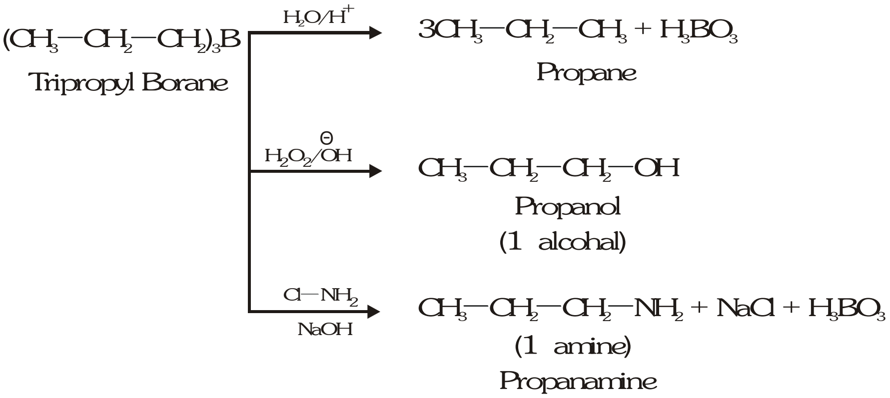
BH_3 does not exist or stable as monomer so a solvent THF (tetra hydro furane) is used.

Example :

$$3CH_3-\overset{\delta^+}{C}H=\overset{\delta^-}{C}H_2 + \overset{\delta^+}{B}H_3^{\delta^-} \xrightarrow{THF} (CH_3-CH_2-CH_2)_3B$$

BHR_2 also can be taken.

Example : $CH_3-\overset{\delta^+}{C}H=\overset{\delta^-}{C}H_2 + BHR_2 \longrightarrow CH_3-CH_2-CH_2-BR_2$

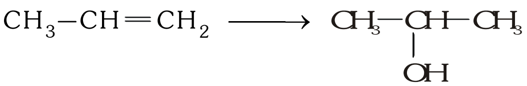


$$(CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O/H^+} 3CH_3-CH_2-CH_3 + H_3BO_3$$

$$(CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O_2/\overset{\ominus}{O}H} CH_3-CH_2-CH_2-OH$$

$$(CH_3-CH_2-CH_2)_3B \xrightarrow[NaOH]{Cl-NH_2} CH_3-CH_2-CH_2-NH_2 + NaCl + H_3BO_3$$

8. **Oxymercuration – demercuration** : Mercuric acetate in tetrahydro furan (THF) is treated with an alkene.The addition product on reduction with sodium Boro hydride in aqueous NaOH solution gives alcohol. It follows the markonikoff's rule.

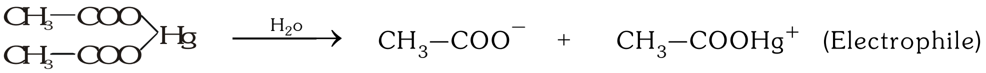


$$CH_3-CH=CH_2 \longrightarrow CH_3-\underset{OH}{\underset{|}{C}H}-CH_3$$

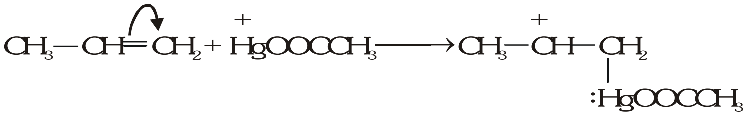
(i) $(AcO)_2$ Hg/H_2O (Mercuric acetate) or $(CH_3COO)_2$ Hg/H_2O

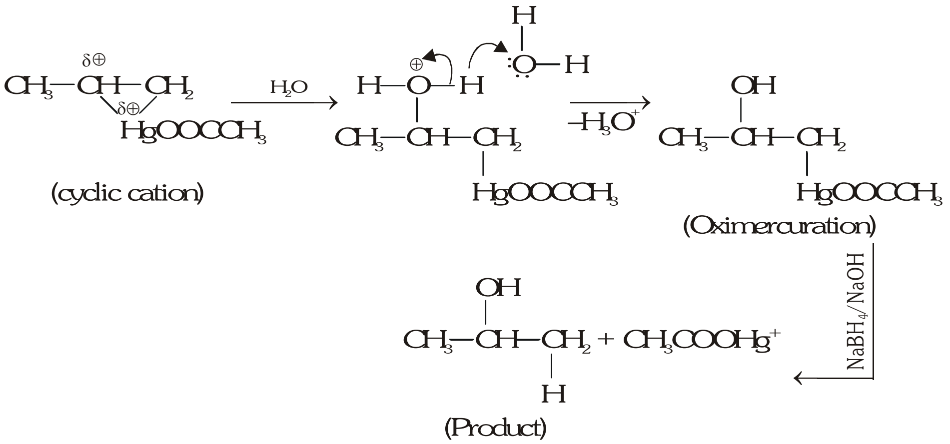
(ii) $NaBH_4/NaOH$

◆◆ **Mechanism** :

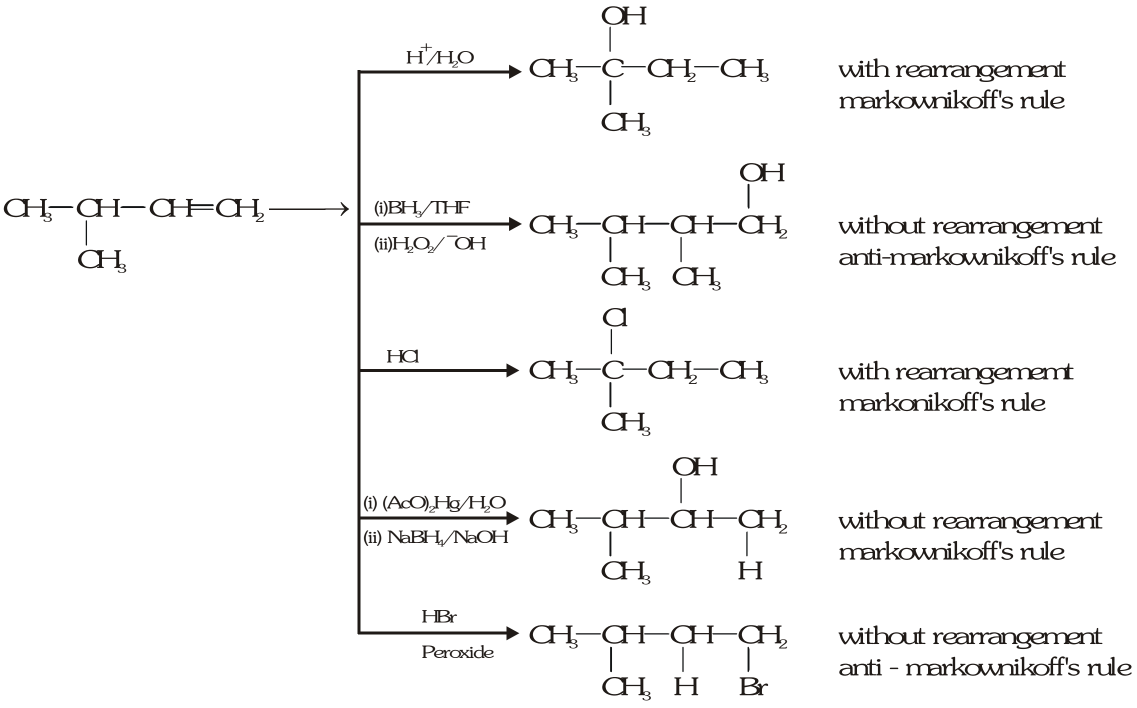


$$(CH_3-COO)_2Hg \xrightarrow{H_2O} CH_3-COO^- + CH_3-COOHg^+ \text{ (Electrophile)}$$



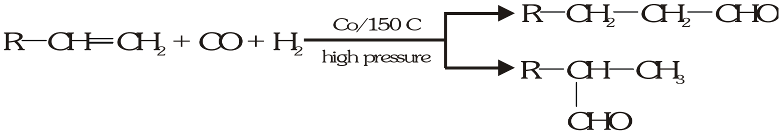


Note : Intermediate is cyclic cation so their is no rearrangement.

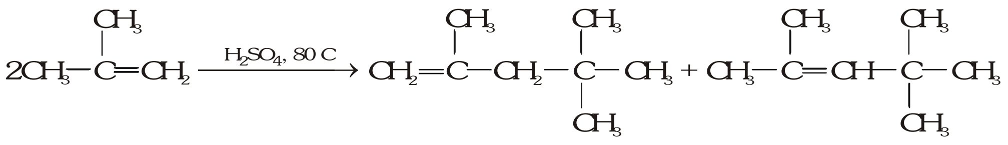


9. **Hydroformylation or Oxo reaction** : Alkenes react with Carbon monoxide and hydrogen at 100 – 150 C temperature and high pressure (200 atm) in the presence of Cobalt catalyst to produce an aldehyde.It does not follows markonikoff's rule.

The net reaction is the addition of a H–atom to one of the Olefinic bond and a formyl (–CHO) group to the other.

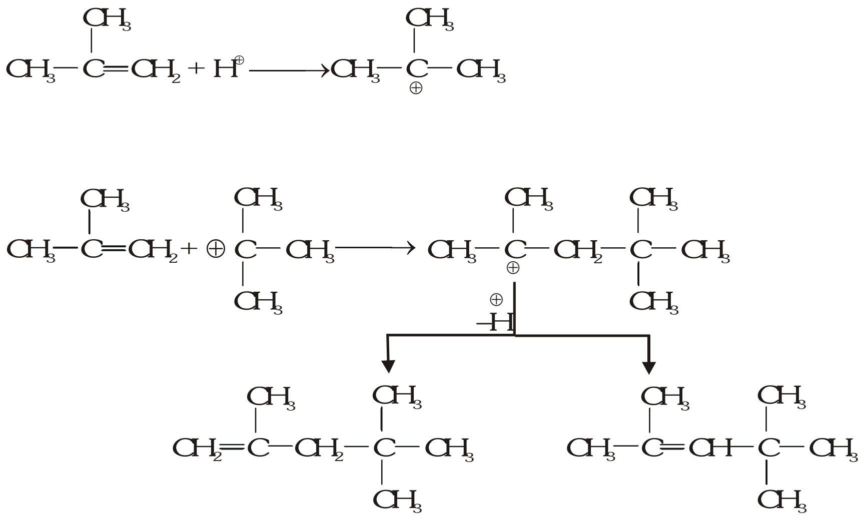


10. Alkenylation (Addition of alkene) In presence of H_2SO_4 or H_3PO_4 at 80 C dimerisation of isobutylene take place gives two isomer of octene.



$$2CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 \xrightarrow{H_2SO_4,\ 80\ C} CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 + CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

Mechanism :



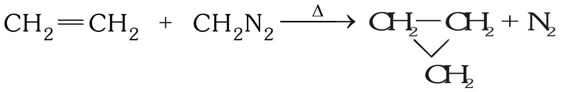
$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + H^{\oplus} \longrightarrow CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_3$$

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + \oplus\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow{-\overset{\oplus}{H}}$$

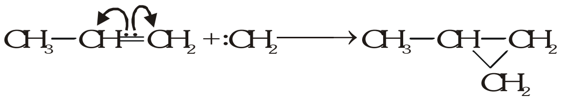
$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \qquad CH_3-\overset{CH_3}{\overset{|}{C}}=CH-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

11. Addition of Carbene : The addition of carbene to alkene is always carried by diazomethane CH_2N_2

Carbene group obtained from diazomethane is added to alkene and give cycloalkanes.



$$CH_2=CH_2 + CH_2N_2 \xrightarrow{\Delta} \underset{CH_2}{CH_2-CH_2} + N_2$$



$$CH_3-CH=CH_2 + :CH_2 \longrightarrow CH_3-\underset{CH_2}{CH-CH_2}$$

Since : CH_2 is an electrophile (neutral) and there is more electron density on double bond so first attack of $:CH_2$ will be at double bond.

12. Addition of HCN:

$$CH_3-\overset{\delta+}{CH}=\overset{\delta-}{CH_2} + \overset{\delta+}{H}\overset{\delta-}{CN} \longrightarrow CH_3-\underset{CN}{\underset{|}{CH}}-CH_3$$

(B) OXIDATION REACTION :

Alkenes are easily oxidised by oxidising agents. Oxidising agents attack on double bond and product formed during oxidation depends on oxidising agents.

(1) alkene on combustion gives CO_2 and H_2O

$$C_nH_{2n} + \frac{3n}{2}O_2 \longrightarrow nCO_2 + nH_2O$$

One mole of alkene requires $\frac{3n}{2}$ moles of O_2 for complete combustion.

Ex : 90 mL of oxygen is required for complete combustion of unsatuarated 20 mL gaseous hydrocarbon, hydrocarbon is ?

Sol. Following two formulae can be used for solution of the above asked question.

$$\frac{\text{Volume of Hydrocarbon}}{\text{Volume of } O_2} = \frac{2}{3n} \qquad \text{(for Alkene)}$$

$$\frac{\text{Volume of Hydrocarbon}}{\text{Volume of } O_2} = \frac{2}{3n-1} \qquad \text{(for Alkyne)}$$

By putting the values in above formulae we can find the hydrocarbon for which n is natural number.

$\frac{20}{90} = \frac{2}{3n}$ n = 3 So hydrocarbon is Propene [C_3H_6].

Ex. How many mole of oxygen is required for complete combustion of 1 mole of Alkene.

Sol. $2C_nH_{2n} + 3nO_2 \longrightarrow 2nCO_2 + 2nH_2O$

keeping in mind, the above equation.

$\because$ for 2 mole of Alkene, 3n mole of O_2 is required for combustion.

$\therefore$ for 1 mole of Alkene, $\frac{3n}{2}$ mole of O_2 is required for combustion.

= 1.5n mole of O_2

Ex. 30 mL mixture of ethylene and Butylene is burnt in presence of oxygen then 150 mL of oxygen is required, what is the volume of Ethylene & Butylene in mixture.

Sol. Let the volume of C_2H_4 = x mL

So volume of Butylene = (30–x) mL

For C_2H_4 $C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

from equation

$\because$ for 1 volume C_2H_4, 3 volume of O_2 is required.

$\because$ for x mL vol. of C_2H_4, 3x ml volume of O_2 is required.

For C_4H_8 $C_4H_8 + 6O_2 \longrightarrow 4CO_2 + 4H_2O$

$\because$ for 1 volume C_4H_8, 6 volume of O_2 is required.

$\because$ for (30–x) mL " " , 6 (30–x) mL of O_2 is required.

Total volume of O_2 = 3x + 6 (30–x) mL = 150 mL(Given)

x = 10

$\because$ Volume of C_2H_4 in mixture is 10 mL

$\because$ Volume of C_2H_4 in mixture is 20 mL

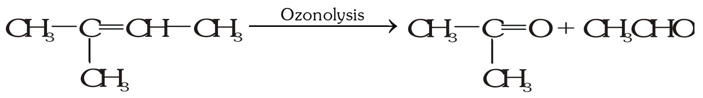
(2) Ozonolysis : (A test for unsaturation in molecule)

(i) The addition of ozone on the double bonds and subsequent a reductive hydrolysis of the ozonide formed is termed as ozonolysis.

(ii) When ozone is passed through an alkene in an inert solvent, it adds across the double bond to form an ozonide. Ozonides are explosive compound they are not isolated.

(iii) On warming with Zn and H_2O, ozonides cleave at the site of the double bond, the products are carbonyl compound (aldehyde or ketone) depending on the nature of the alkene.

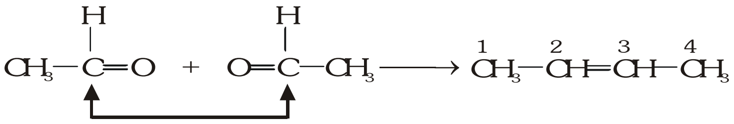
Example :



$$CH_3-\underset{CH_3}{\underset{|}{C}}=CH-CH_3 \xrightarrow{\text{Ozonolysis}} CH_3-\underset{CH_3}{\underset{|}{C}}=O + CH_3CHO$$

(iv) Ozonolysis of alkenes helps in locating the position of double bond in an alkene. It can be achieved by joining together the carbon atoms of the two carbonyl compounds formed as the products of ozonolysis with double bond.

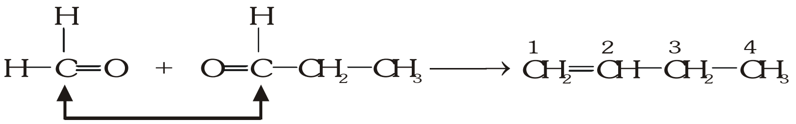
Example :



$$CH_3-\overset{H}{\overset{|}{C}}=O + O=\overset{H}{\overset{|}{C}}-CH_3 \longrightarrow \overset{1}{C}H_3-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_3$$

Ethanal But-2-ene

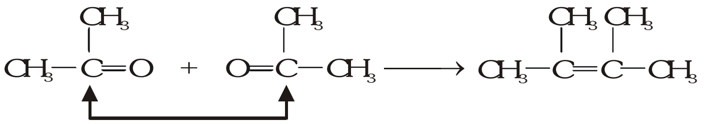
Example :



$$H-\overset{H}{\overset{|}{C}}=O + O=\overset{H}{\overset{|}{C}}-CH_2-CH_3 \longrightarrow \overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_3$$

Methanal Propanal But-1-ene

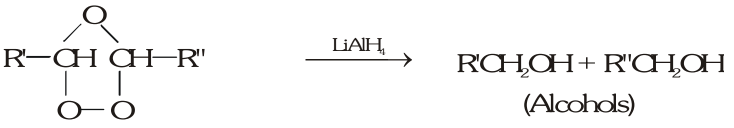
Example :



$$CH_3-\overset{CH_3}{\overset{|}{C}}=O + O=\overset{CH_3}{\overset{|}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH_3$$

Propanone 2,3–Dimethyl but–2–ene

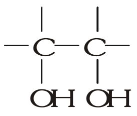
It may be noted that reaction with bromine water or Baeyer's reagent detects the presence of double bond (or unsaturation) in an alkene while ozonolysis helps in locating the position of the double bond. In an reduction of ozonide by $LiAlH_4$ or $NaBH_4$ gives corresponding alcohols.



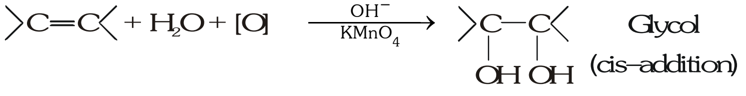
$\xrightarrow{LiAlH_4}$ $R'CH_2OH + R''CH_2OH$

(Alcohols)

(3) **Hydroxylation** : Oxidation of carbon-carbon double bond to $-\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$ is known as hydroxylation.

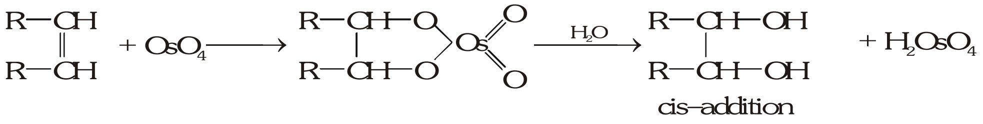


(a) **Oxidation by Baeyer's reagent** (A test for unsaturation) : Alkenes on passing through dilute alkaline 1% cold $KMnO_4$ (i.e., Baeyer's reagent) decolourise the pink colour of $KMnO_4$ and gives brown ppt MnO_2 and glycol.



$$>C=C< + H_2O + [O] \xrightarrow[KMnO_4]{OH^-} >\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}< \quad \text{Glycol (cis–addition)}$$

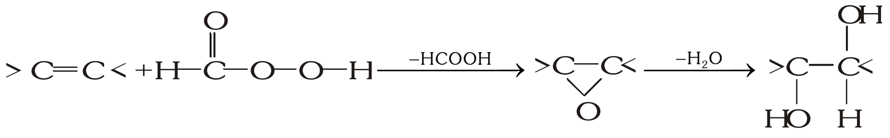
(b) **By OsO_4** :



$\xrightarrow{H_2O}$ $+ H_2OsO_4$

cis–addition

(c) **By peracid** :

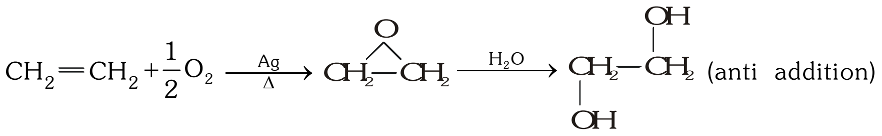


$$>C=C< + H-\overset{O}{\overset{\|}{C}}-O-O-H \xrightarrow{-HCOOH} >C\overset{}{-}C< \text{(epoxide)} \xrightarrow{-H_2O} >\underset{HO}{C}-\overset{OH}{\underset{H}{C}}<$$

trans glycol

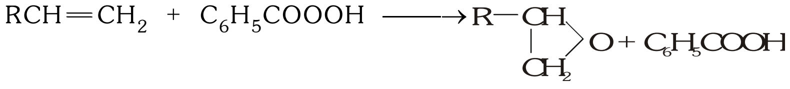
(4) **Epoxidation** :

(a) Alkenes reacts with oxygen in the presence of Ag catalyst at 250 –400 C to form epoxide.



$$CH_2=CH_2+\frac{1}{2}O_2 \xrightarrow[\Delta]{Ag} \overset{O}{CH_2-CH_2} \xrightarrow{H_2O} \underset{OH}{CH_2}-\overset{OH}{CH_2}$$ (anti addition)

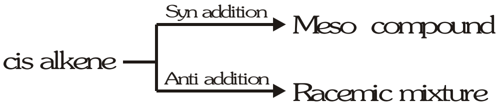
(b) **Prileschiaev reaction:** When an alkene is treated with perbezoic acid an epoxide is formed. Such an epoxidation is known as Prileschiave reactions.

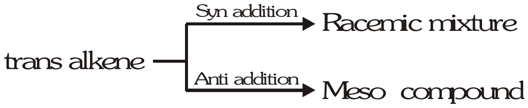


$$RCH=CH_2 + C_6H_5COOOH \longrightarrow R-\underset{CH_2}{CH}\rangle O + C_6H_5COOH$$

Epoxide

Emmons have found that perbenzoic oxy trifluoroacetic acid (CF_3COO_2H) is a very good reagent for epoxidation and hydroxylation.



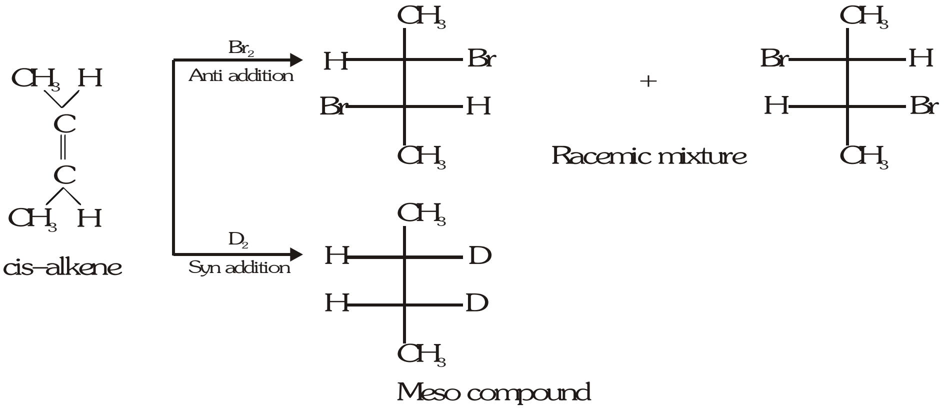


Syn addition on alkene $\longrightarrow H_2, O_2$, Baeyer's reagent, OSO_4 / H_2O

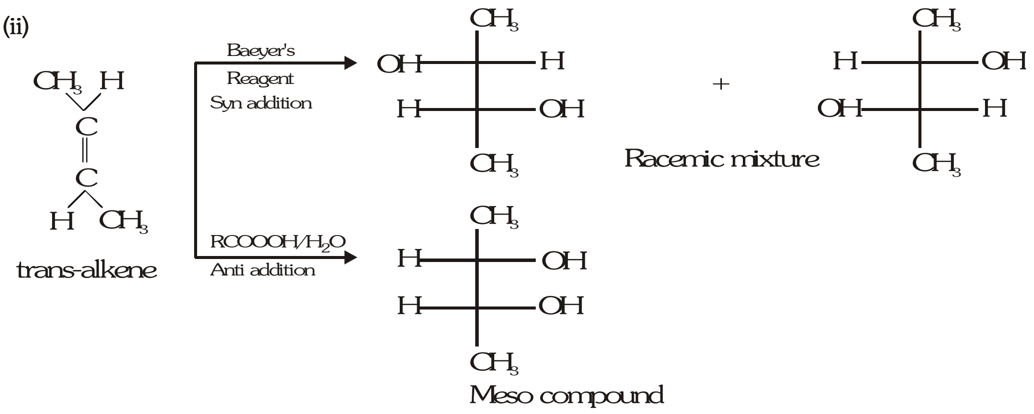
Anti addition on alkene $\longrightarrow X_2$, HOX, $RCOOH / H_2O$, Ag_2O / H_2O

Example :

(i)



(ii)

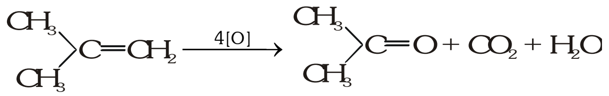


(5) **Oxidation by strong oxidising agent (Oxidative cleavage)** : The alkenes themselves are readily oxidised to acid or ketone by means of acid permagnate or acid dichromate.If HCOOH is formed, it further oxidized to CO_2 and H_2O. Keep it in mind that no further oxidation of ketones will takes place.

$$CH_2{=}CH_2{+}4[O] \longrightarrow 2HCOOH \xrightarrow{2[O]} 2CO_2 + H_2O$$

$$CH_3CH{=}CH_2 \xrightarrow{5[O]} CH_3COOH{+}CO_2{+}H_2O$$

$$CH_3CH{=}CHCH_3 \xrightarrow{4[O]} 2CH_3COOH$$



$$\begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C{=}CH_2 \xrightarrow{4[O]} \begin{matrix}CH_3\\ \\ CH_3\end{matrix}\!\!>C{=}O + CO_2 + H_2O$$

(6) **Oxidation with retention of Carbon-Carbon bond - (Waker process)** :

$$CH_2{=}CH_2{+}H_2O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

(C) SUBSTITUTION REACTION (Allylic substitution) :

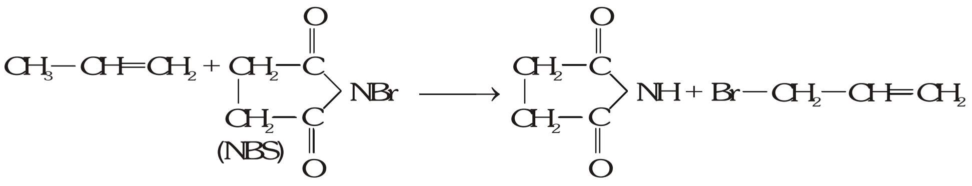
When alkenes are treated with Cl_2 or Br_2 at high temp., one of their allylic hydrogen is replaced by halogen atom. Allylic position is the carbon adjacent to one of the unsaturated carbon atoms.It is free radical substitution.

$$CH_3{-}CH{=}CH_2 + Cl_2 \xrightarrow{500^0\,C} ClCH_2{-}CH{=}CH_2 + HCl$$

Allyl chloride

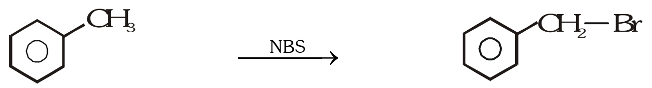
(3-Chloro-1-propene)

N-Bromosuccinimide (NBS) is an important reagent used for allylic bromination and benzlic substitution.

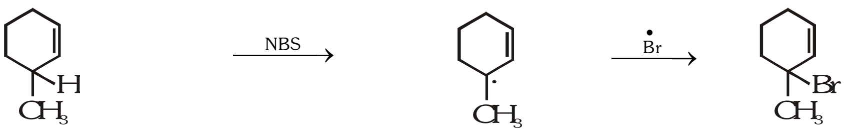


Substitution reaction is not given by ethene.

Example : (i)



(ii)



3 more stable

(D) POLYMERIZATION :

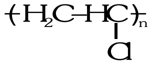
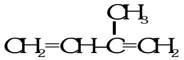
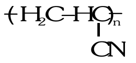
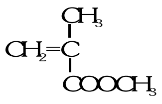
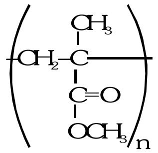
(i) Two or more than two molecules of same compound unit with each other to form a long chain molecule with same empirical formula. This long chain molecule having repeating structural units called polymer, and the starting simple molecule as monomer and process is called addition polymerization.

(ii) Molecular weight of polymer is simple multiple of monomer.

(iii) Polymerization can be carried out by free radical or ionic mechanism.

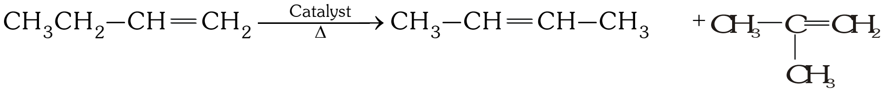
(iv) The presence of oxygen initiates free radical mechanism.

(v) Addition polymerization can also be carried out by ionic mechanism by using Ziegler - Natta Catalysts ($R_3Al+TiZCl_4$)

Name of polymer	Structure of monomer	Structure of Polymer	Properties	Uses Properties
1. Polyvinyl chloride (PVC)	$CH_2=CH-Cl$	 $-(H_2C-\underset{\displaystyle Cl}{\underset{\mid}{HC}})_n-$	Piliable (easily moulded)	Used in handbag, raincoats, vinyl flooring, good electrical insulator for wires
2. Polytetrafluorethylene or Teflon (PTFE)	$F_2C=CF_2$	$-(F_2C-CF_2)_n-$	Flexible and **inert** to solvents, boiling acids,even aquaregia stable upto 598K.	For making non-stick utensils coating
3. Natural rubber	 $CH_2=CH-\overset{\displaystyle CH_3}{\overset{\mid}{C}}=CH_2$ isoprene		Waxy and non-elastic	Used as raw material for making vulcanised rubber which is strong and elastic vulcanised rubber is used in making tyres hose, pipes etc.
4. Orlon	acrylonitrile	 $-(H_2C-\underset{\displaystyle CN}{\underset{\mid}{HC}})_n-$	Fibrous	Used in making Fabrics
5. Poly methyl methacrylate (PMMA)	 $CH_2=\overset{\displaystyle CH_3}{\overset{\mid}{C}}-COOCH_3$ Methyl methacrylate	 $\left(-CH_2-\overset{\displaystyle CH_3}{\overset{\mid}{C}}-\right)_n$ with $-C(=O)-OCH_3$ on C		

(E) ISOMERISATION :

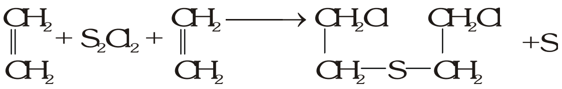
Alkene on heating to 500 to 700 C or on heating in presence of catalyst [$AlCl_3$ or $Al_2(SO_4)_3$] undergo isomerisation.



$$CH_3CH_2-CH=CH_2 \xrightarrow[\Delta]{\text{Catalyst}} CH_3-CH=CH-CH_3 + CH_3-\underset{\displaystyle CH_3}{\underset{\mid}{C}}=CH_2$$

1–Butene 2–Butene Isobutylene

- **Uses :**
  - (a) In plastic formation.
  - (b) In oxy ethylene welding
  - (c) As food preservatives and ripening fruits.
  - (d) As general anaesthetic (C_2H_4 with 10% O_2)
  - (e) In preparation of mustard gas



$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + S_2Cl_2 + \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \longrightarrow \begin{matrix}CH_2Cl & & CH_2Cl\\ | & & |\\ CH_2 & -S- & CH_2\end{matrix} + S$$

2,2' or (β, β') dichloro diethyl-sulphide
(mustard gas)

- **Laboratory test of alkene :**

Functional Group	Reagent	Observation	Reaction	Remarks
$>C=C<$	(1) Bayer's Reagent alk. dil. cold $KMnO_4$	Pink colour disappears	$CH_2=CH_2+H_2O+O \xrightarrow{\text{alk. }KMnO_4} \begin{matrix}CH_2-CH_2\\ \vert \quad\quad \vert\\ OH \quad OH\end{matrix}$	Dihydroxylation
	(2) Br_2/H_2O	Red colour decolourises	$Br_2+CH_2=CH_2 \longrightarrow \begin{matrix}CH_2-CH_2\\ \vert \quad\quad \vert\\ Br \quad Br\end{matrix}$ White ppt.	Dibrominaiton
	(3) O_3 (ozone)	$>C=O$ Compounds	$CH_2=CH_2+O_3 \xrightarrow{Zn/H_2O} 2HCHO$	Ozonolysis

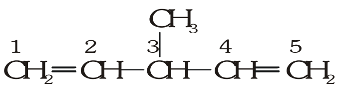
: DIENES :

Dienes are the unsaturated hydrocarbons with carbon-carbon double bonds in their molecules. These are represented by the general formula C_nH_{2n-2} which means that they are isomeric with alkynes (functional isomers). However, their properties are quite different from those of alkynes. Depending upon the relative positions of the two double bond, dienes are classified in three types :

Isolated dienes or non conjugated dienes : In an isolated diene, the two double bonds are separated by more than one single bond. For example,

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H=\overset{5}{C}H_2$

Penta–1,4–diene



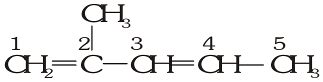
$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{\overset{CH_3}{|}}{\overset{3}{C}H}-\overset{4}{C}H=\overset{5}{C}H_2$$

3–Methylpenta–1, 4–diene

Cunjugated dienes : In a conjugated diene, the two double bonds are present in the conjugated or alternate position and are separated by a single bond.

$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\overset{4}{C}H_2$

Buta-1,3-diene



$$\overset{1}{C}H_2=\overset{\overset{CH_3}{|}}{\overset{2}{C}}-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$$

2-Methylpenta-1,3-diene

Commulate dienes : In this case, the two double bonds in the molecules are present at adjacent positions. For example,

$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H_2$ Propa-1,2-diene

$\overset{1}{C}H_2=\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}H_3$ Buta-1, 2-diene

- **Comparison of relative stabilities of isolated and conjugated dienes :**

Resonance Theory : The relative stabilities of the two types dienes can also be justifid on the basis of the theory of resonance. Penta-1,3-diene (conjugated diene) is a hybrid of the following contributing structures.

$$CH_2=CH-CH=CH-CH_3 \longleftrightarrow \overset{\ominus}{C}H_2-\overset{\oplus}{C}H-CH=CH-CH_3 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH-\overset{\oplus}{C}H-CH_3$$

The delocalisation of π-electron charge because of resonanace decreases the energy of the molecule or increases its stability.

Penta-1, 4-diene (isolated diene) has only two contributing structures.

$$\underset{(I)}{\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H=\overset{5}{C}H_2} \longleftrightarrow \underset{(II)}{\overset{1\ominus}{C}H_2-\overset{2\oplus}{C}H-\overset{3}{C}H_2-\overset{4}{C}H=\overset{5}{C}H_2}$$

Since the carbon atom C_3 is not involved in any resonance, the contributing structures are less in number are compared to the conjugated diene. The isolated diene is, therefore, less stable than a conjugated diene.

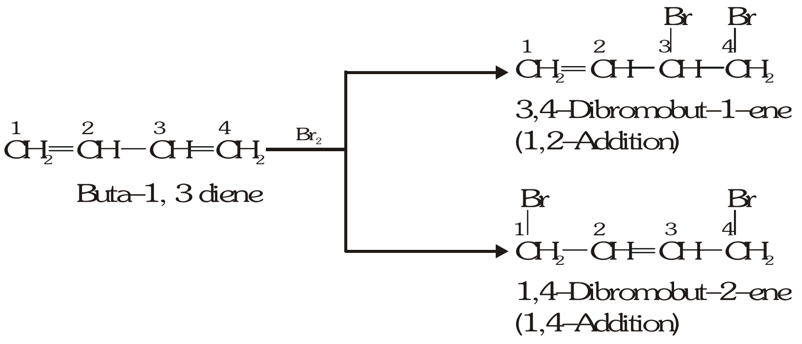
- **Properties of Conjugated Dienes :**

The properties of the isolated dienes are similar to those of simple alkene but those of conjugated dienes are somewhtat modified because of delocalisation of the π-electron charge. However, they also participate in the addition reactions. The important chemical characteristics of the conjugated dienes are briefly discussed.

1. **Addition Reaction** : Conjugated or 1,3-dienes take part in the addition reactions which can proceed by electrophilic as well as free radical mechanism depending upon the nature of the attacking reagent and the reaction conditions.

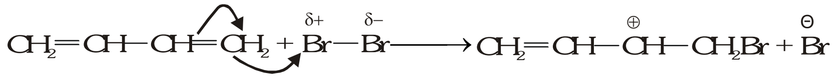
(A) **Electrophilic Addition Reactions** : The electrophilic addition is illustrated by the attack of halogen and halogen acid on buta-1,3-diene, a conjugated diene.

(a) **Addition of halogen** : If one mole of halogen attacks per mole of the diene, two types of addition products are formed. There are 1, 2 and 1, 4 addition products. For example,



1, 2-addition is a normal addition in which one mole of halogen has been added to one of the double bond. But 1, 4-addition is somewhat unexpected.

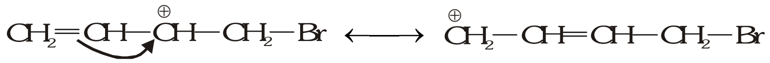
◆ **Mechanism** : The addition is electrophilic in nature and the halogen molecule (bromine) provides the electrophilie for the attack.



$$CH_2{=}CH-CH{=}CH_2 + \overset{\delta+}{Br}-\overset{\delta-}{Br} \longrightarrow CH_2{=}CH-\overset{\oplus}{C}H-CH_2Br + \overset{\ominus}{Br}$$

Buta-1, 3-diene Carbocation (2)

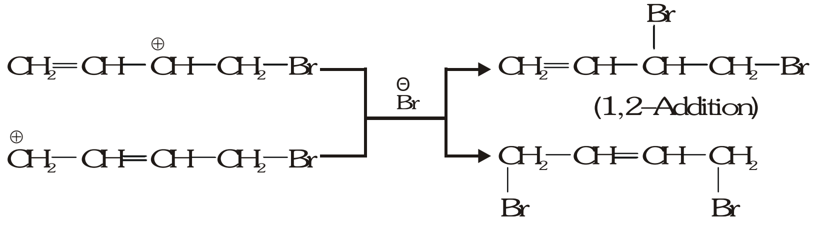
The 2 carbocation get stablised by resonance as follows –



$$CH_2{=}CH-\overset{\oplus}{C}H-CH_2-Br \longleftrightarrow \overset{\oplus}{C}H_2-CH{=}CH-CH_2-Br$$

I II

The attack of $\overset{\ominus}{Br}$ ion on carbocation (I and II)



$$CH_2{=}CH-\overset{\oplus}{C}H-CH_2-Br \xrightarrow{\overset{\ominus}{Br}} CH_2{=}CH-\underset{}{\overset{Br}{\overset{|}{C}H}}-CH_2-Br$$

(1,2–Addition)

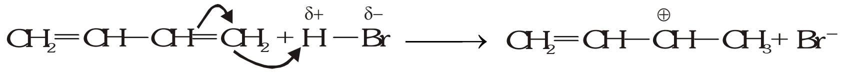
$$\overset{\oplus}{C}H_2-CH{=}CH-CH_2-Br \xrightarrow{\overset{\ominus}{Br}} \underset{\underset{Br}{|}}{CH_2}-CH{=}CH-\underset{\underset{Br}{|}}{CH_2}$$

1,4–addition (Main product)

(b) Addition of H – X :

$$CH_2{=}CH-CH{=}CH_2 \xrightarrow{HBr} ?$$

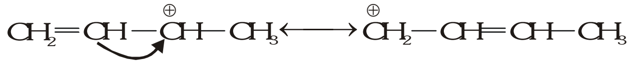
◆ **Mechanism** : The addition is electrophilic in nature as H^+ ion is the electrophile.



$$CH_2{=}CH-CH{=}CH_2 + \overset{\delta+}{H}-\overset{\delta-}{Br} \longrightarrow CH_2{=}CH-\overset{\oplus}{C}H-CH_3 + Br^-$$

Carbocation (2)

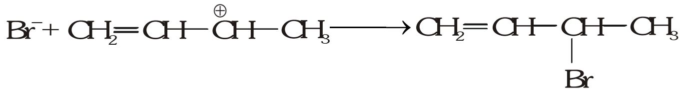
The carbocation gets resonance stabilised as follows :



$$CH_2{=}CH-\overset{\oplus}{C}H-CH_3 \longleftrightarrow \overset{\oplus}{C}H_2-CH{=}CH-CH_3$$

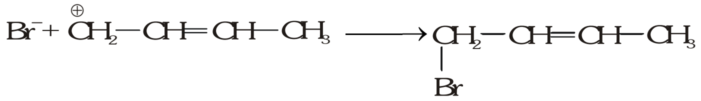
(I) (II)

The attack of Br⁻ ion on the carbocation (I) gives 1,2-addition product whereas the attack on the carbocation (II) yields 1,4-addition product.



$$Br^- + CH_2{=}CH-\overset{\oplus}{C}H-CH_3 \longrightarrow CH_2{=}CH-\underset{\underset{Br}{|}}{CH}-CH_3$$

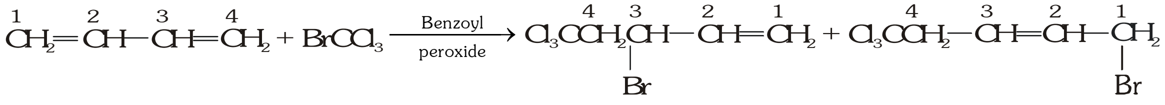
1,2–Addition product



$$Br^- + \overset{\oplus}{C}H_2-CH{=}CH-CH_3 \longrightarrow \underset{\underset{Br}{|}}{CH_2}-CH{=}CH-CH_3$$

1,4–Addition product

(B) **Free Radical Addition Reaction** : The addition to conjugated dienes can also proceed by free radical mechanism provided it is carried in the presence of a suitable reagent which can help in forming a free radical. However, the addition also yields 1,2 and 1,4 addition products. The free radical addition is illustratated by the attack of bromotrichloromethane ($BrCCl_3$) on buta–1,3–diene in the presence of an organic peroxide such as benzoyl peroxide.



$$\overset{1}{C}H_2{=}\overset{2}{C}H-\overset{3}{C}H{=}\overset{4}{C}H_2 + BrCCl_3 \xrightarrow[\text{peroxide}]{\text{Benzoyl}} Cl_3C\overset{4}{C}H_2\underset{\underset{Br}{|}}{\overset{3}{C}H}-\overset{2}{C}H{=}\overset{1}{C}H_2 + Cl_3C\overset{4}{C}H_2-\overset{3}{C}H{=}\overset{2}{C}H-\underset{\underset{Br}{|}}{\overset{1}{C}H_2}$$

Buta–1,3–diene Bromotri-
chloromethane

◆ **Mechanism** : The mechanism of addition is free radical in nature which is initiated by benzoyl free radical. It is explained in the following steps :

Step I Generation of free radical

$$C_6H_5CO{-}O{-}O{-}COC_6H_5 \xrightarrow{\text{Homolysis}} C_6H_5{-}CO{-}\dot{O} + \dot{O}{-}COC_6H_5$$

$$C_6H_5{-}CO{-}\dot{O} \longrightarrow \dot{C}_6H_5 + CO_2$$

$$\dot{C}_6H_5 + BrCCl_3 \longrightarrow C_6H_5{-}Br + \dot{C}Cl_3$$

Trichloromethyl free radical

Step II Attack of free radical on buta-1, 3-diene

$$\dot{C}Cl_3 + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow Cl_3C{-}CH_2{-}\dot{C}H{-}CH{=}CH_2$$

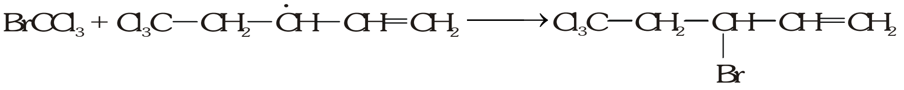
Free radical (secondary)

The free radical gets resonance stabilised

$$Cl_3C{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \longleftrightarrow Cl_3C{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$$

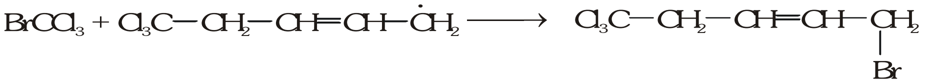
Step III Change of free radical into addition product

The free radicals take up $\dot{Br}$ from the attacking reagent to give the desired addition products. i.e. 1,2 and 1,4 addition products.



$$BrCCl_3 + Cl_3C{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \longrightarrow Cl_3C{-}CH_2{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-}CH{=}CH_2$$

(1,2-Addition product)



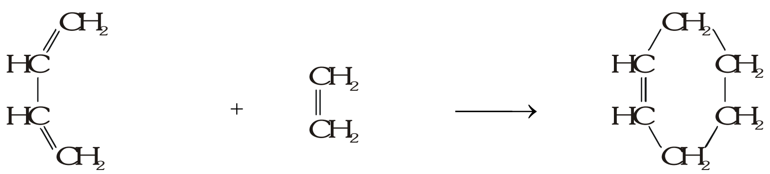
$$BrCCl_3 + Cl_3C{-}CH_2{-}CH{=}CH{-}\dot{C}H_2 \longrightarrow Cl_3C{-}CH_2{-}CH{=}CH{-}\underset{\displaystyle Br}{\underset{|}{C}H_2}$$

(1,4–Addition product)

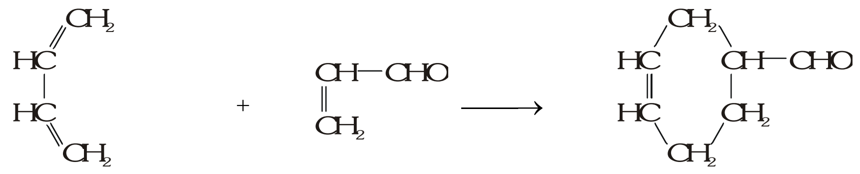
2. **Cyclo-Addition Reaction (Diel Alder Reactions) :**

Cyclo-addition reactions are one of the most important reactions of conjugated dienes. Cyclo-addition involves the combination between a conjugated diene (4π-electron system) and a compound containing a double bond (2π-electron system) called **dienophile** which means a diene loving or attracting molecule. As a result, a six membered ring gets formed and the reaction is therefore known as **cyclo-addition reaction.** It is quite often termed as **(4 +2) cyclo-addition reaction** because four 4π-electron system adds to a two 2π electron system. The reactions of this type are known as : Diel Alder Reaction.

The addition product is called **Diel Alder Adduct.** For example.



Buta–1,3–diene Ethene Cyclohexene **(Diel Alder adduct)**



Buta–1,3–diene Propenal (Acrolein) 3-cyclohexene carbaldehyde

Ex. The density of a hydrocarbon at N.T.P. 2.5 gram/litre. What is hydrocarbon?

Sol. Density of 1 litre hydrocarbon = 2.5 gram/litre

∴ molecular weight of hydrocarbon = 2.5 x 22.4 = 56

After molecular weight , we calculate the molecular formula.

C_nH_{2n+2} = molecular weight (Alkane) or 14n+2 = molecular weight

C_nH_{2n} = molecular weight (alkene) or 14n = molecular weight

C_nH_{2n-2} C_nH_{2n-2} = molecular weight (Alkyne) or 14n–2 = molecular weight

with the help of above three formulae, we can identify the given hydrocarbon

14n = 56 (Alkene) ∵ Hydrocarbon is C_4H_8 (Butene).

n = 4

Volume of hydrocarbon will be given and volume of O_2 for complete combustion will also be given.

What is hydrocarbon is to be asked ?

The above question may be solved with the help of following three formulae.

Formula No. 1 $\frac{\text{Volume of H.C.}}{\text{Volume of } O_2} = \frac{2}{3n+1}$ (for Alkane)

Formula No. 2 $\frac{\text{Volume of H.C.}}{\text{Volume of } O_2} = \frac{2}{3n}$ (for Alkene)

Formula No. 3 $\frac{\text{Volume of H.C.}}{\text{Volume of } O_2} = \frac{2}{3n-1}$ (for Alkyne)

Ex. How much propanol is required for dehydration to get 2.24 litre of Propene at N.T.P. if yield is 100%.

Sol. $C_3H_8O + H_2SO_4 \longrightarrow C_3H_6 + H_2O + H_2SO_4$

Molecular weight of propanol = 60

from the equation given above we can see that from dehydration of 1 mole or 60 gram of propanol we get 1 mole (22.4lit.) of propene as product.

∵ 22.4 litre of C_3H_6 can be get from dehydration of 60 g of propanol.

∴ 1 litre of propene can be get from dehydration of $\frac{60}{22.4}$ g of propanol

∴ 2.24 litre of propene can be get from dehydration of $\frac{60}{22.4}$x2.24 g of propanol

Ans. = 6 g