HYDROCARBON

1. Structure and Bonding

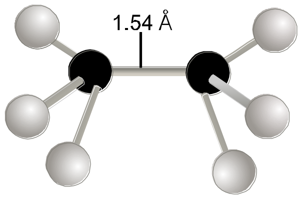
(a) Alkanes are saturated hydrocarbons.

(b) These are represented by general Formula (G.F.) C_nH_{2n+2}

(c) In Ethane C — C bond length is 1.54 Å

(d) The hybridization of (C — C) carbon is sp^3

(e) These are also known as paraffin's.



2. Preparation of alkane

2.1. Wurtz Reaction :

This method is used for preparation of higher alkanes from 1° or 2° alkyl halides. In this method two moles of alkyl halides are treated with 'Na' metal in dry ether.

$$\underset{(1^\circ \text{ or } 2^\circ)}{R\text{ - }X} + 2Na + R\text{ - }X \xrightarrow[\text{ether (dry)}]{Na} R\text{ - }R + 2Na\text{ - }X.$$

Steps involved in wurtz reaction.

$$R\text{ - }X + 2Na \longrightarrow R\text{ - }Na + NaX \qquad \text{..........(i)}$$

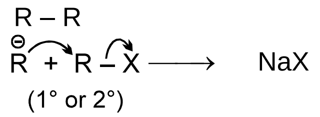
$$R\text{ - }X + R\text{ - }Na \longrightarrow R\text{ - }R + NaX \qquad \text{.........(ii)}$$

Mechanism

(a) Ionic mechanism

$$2Na \longrightarrow 2Na^{\oplus} + 2e^{\ominus};$$

$$\underset{(1^\circ,\ 2^\circ)}{R - X} + 2e^{-} \longrightarrow \overset{\ominus}{R} + \overset{\ominus}{X}$$



$$\overset{\ominus}{R} + \underset{(1^\circ \text{ or } 2^\circ)}{R - X} \longrightarrow R - R + NaX$$

(b) Free Radical Mechanism

$$Na \longrightarrow Na^+ + e^-$$

$$R - X \longrightarrow R^+ + X^-$$

$$R^+ + e^- \longrightarrow R^\cdot$$

$$R^\cdot + R^\cdot \longrightarrow R - R$$

Remark :

(a) With 3° R-X S_N2 and free radical coupling is not possible due to steric hinderence so in that case elimination or disproportionation takes place.

(b) In the ionic mechanism alkyl sodium $(\overset{\ominus}{R}\ \overset{\oplus}{Na})$ is strong base as well as nucleophile which gives S_N2 with R–X.

(c) Ether should be dry if moisture is present then ROH is produced instead of R – R with water .

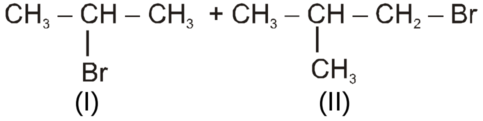
(d) This method is not used for preparation of CH_4.

(e) To get pure alkanes having even number of carbon atoms both alkyl halides must be of same type.

(f) On using two type of alkyl halide we get a mixture of three alkanes because two type of alkyl halides will give us two types of alkyl free radical. Which may combine to each other as well as itself.

$$R\text{ - }X + R'\text{ - }X \xrightarrow[\text{ether (dry)}]{Na} R\text{ - }R' + R'\text{ - }R' + R\text{ - }R + NaX$$

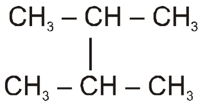
Que. Write the structure of products when structure Ist and IInd undergo Wurtz reaction



$CH_3-\underset{Br}{CH}-CH_3 + CH_3-\underset{CH_3}{CH}-CH_2-Br$

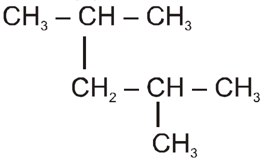
(I) (II)

Ans. (a)



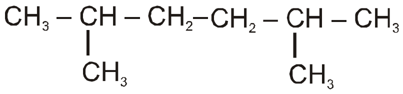
$CH_3-CH(CH_3)-CH(CH_3)-CH_3$

(b)



$CH_3-CH(CH_3)-CH_2-CH(CH_3)-CH_3$

(c)



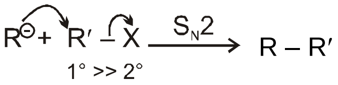
$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-\underset{CH_3}{CH}-CH_3$

2.2. By Corey House alkane synthesis :

It is used for the preparation of pure alkane having odd number of carbon atom.

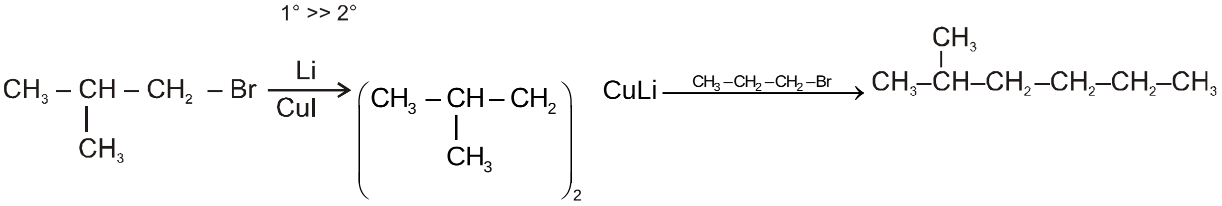
$$\underset{(1°,2°,3°)}{R-X} \xrightarrow{2Li} \overset{\ominus}{R}\,\overset{\oplus}{Li} + LiX \xrightarrow{CuX} \underset{\text{(Gilman's reagent)}}{\overset{R_2CuLi}{\text{Lithiumdialkyl cuprate}}} \xrightarrow[S_N2]{(1^0>2^0)\,R'-X} R-R'$$

Mechanism :

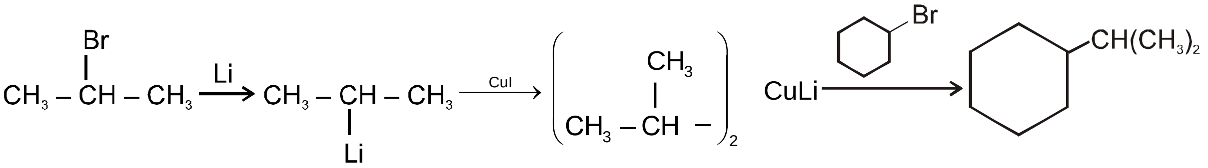


$$R^{\ominus} + \underset{1° >> 2°}{R'-X} \xrightarrow{S_N2} R-R'$$

Ex.



$$CH_3-\underset{CH_3}{CH}-CH_2-Br \xrightarrow[CuI]{Li} \left(CH_3-\underset{CH_3}{CH}-CH_2\right)_2 CuLi \xrightarrow{CH_3-CH_2-CH_2-Br} CH_3-\overset{CH_3}{CH}-CH_2-CH_2-CH_2-CH_3$$



$$CH_3-\overset{Br}{CH}-CH_3 \xrightarrow{Li} CH_3-\underset{Li}{CH}-CH_3 \xrightarrow{CuI} \left(CH_3-\overset{CH_3}{CH}-\right)_2 CuLi \longrightarrow$$

2.3. Reduction of alkyl halides :

(i) By Zn/HCl

$$R-X + Zn/HCl \longrightarrow RH + X^{\ominus}$$

Reaction is proceed as

$Zn \longrightarrow Zn^{2+} + 2e^-$

$R-X \longrightarrow R^+ + X^{\ominus}$

$R^+ + 2e^- \longrightarrow R^{\ominus}$

$R^{\ominus} + HCl \longrightarrow RH + Cl^{\ominus}$

Purest form of methane can be obtained as :

$CH_3I \xrightarrow[\text{Ethanol}]{\text{Zn-Cu(couple)}} CH_4$

$Zn \longrightarrow Zn^{2+} + 2e^-$

$CH_3I \longrightarrow CH_3^+ + I^-$

$CH_3^+ + 2e^- \longrightarrow \overset{\ominus}{C}H_3$

$\overset{\ominus}{C}H_3 + C_2H_5OH \longrightarrow CH_4 + C_2H_5O^{\ominus}$

(ii) Frankland reaction

$$R-X + Zn + R-X \xrightarrow{\text{Ether}} R-R + ZnX_2$$

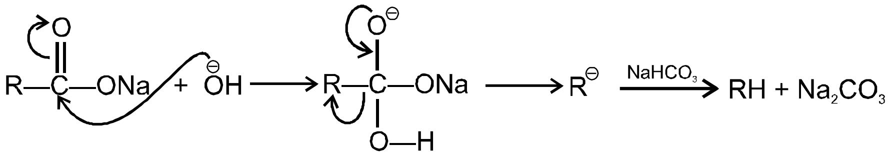
2.4. Preparation of Alkane from acid :

(i) Decarboxylation of sodium salt of acid :

It is removal of CO_2. This reaction is used to desend the series and proceeds via carbanion intermediate.

Reagent → Sodalime [mixture of NaOH + CaO]

$$RCOONa + NaOH \xrightarrow[\Delta]{CaO} RH + Na_2CO_3$$

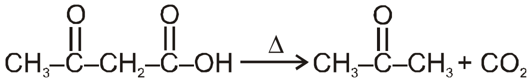


$$R-\overset{O}{\overset{||}{C}}-ONa + \overset{\ominus}{O}H \longrightarrow R-\underset{O-H}{\overset{O^{\ominus}}{\overset{|}{\underset{|}{C}}}}-ONa \longrightarrow R^{\ominus} \xrightarrow{NaHCO_3} RH + Na_2CO_3$$

Note : 1. This method is used to get alkane corresponds to alkyl part of acid.

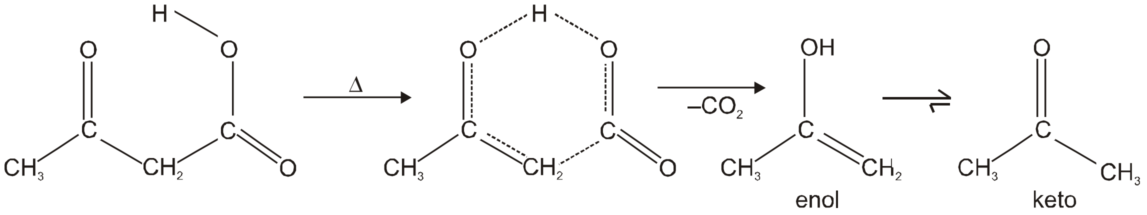
2. That acid will decarboxylate more readily which give more stable carbanion.

3. Among the keto acid, it is **β-keto acid** which undergoes decarboxylation **more readily** because it proceeds via six membered cyclic transition state and syn elimination reaction.



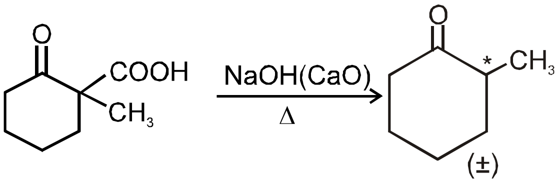
$$CH_3-\overset{O}{\overset{||}{C}}-CH_2-\overset{O}{\overset{||}{C}}-OH \xrightarrow{\Delta} CH_3-\overset{O}{\overset{||}{C}}-CH_3 + CO_2$$

Mechanism



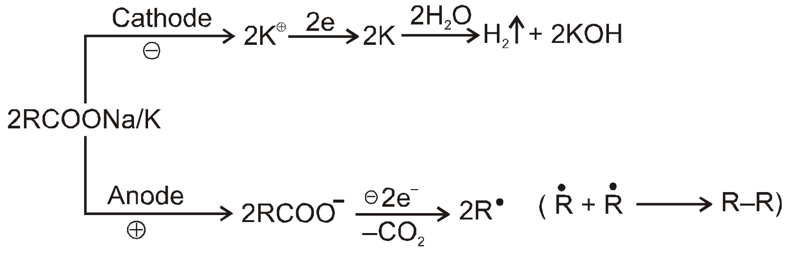
4. During decarboxylation if COOH is present at chiral carbon, then decarboxylation product will be (d + ℓ) mixture.

Ex.



(ii) Kolbe's electrolytic method :

In this method two moles of Na/K - salt of fatty acids is used. During the electrolysis hydrogen gas is liberated at cathode because disharge potential of hydrogen is less than of that metal, while alkane is liberated at anode and this alkane will be dimer of alkyl part of acid.



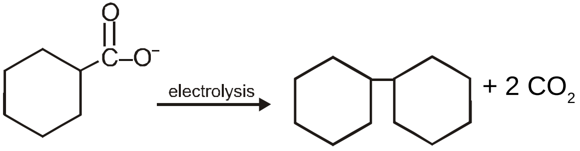
$$\xrightarrow[\ominus]{Cathode} 2K^{\oplus} \xrightarrow{2e} 2K \xrightarrow{2H_2O} H_2\uparrow + 2KOH$$

$$2RCOONa/K$$

$$\xrightarrow[\oplus]{Anode} 2RCOO^{-} \xrightarrow[-CO_2]{\ominus 2e^{-}} 2R^{\bullet} \quad (\dot{R} + \dot{R} \longrightarrow R{-}R)$$

Note : 1. This method is used for the preparation of alkane having even number of carbon atoms. It is not used for methane as well as alkanes having odd number of carbon atom.

Ex-



2. During kolbe's electrolysis pH of electrolyte increases progressively due to increases in concentration of alkali.
3. On using two type of Na/K-salt of fatty acids . We get the mixture of three alkanes. Because two type of salt of fatty acids gives us two types of free radicals which may combine to each other as well as itself.

(iii) Reduction of carboxylic acid :
On passing carboxylic acid in sealed tube containing HI/P at 200°C. We get alkane corresponding to acid.

Ex- $R–COOH + 6HI \xrightarrow[\Delta]{\text{Red P}} R–CH_3 + 2H_2O + 3I_2$

3. Physical properties of alkane

Alkane molecules are held together by weak Vander waal force which depends upon surface area. On increasing molecular mass surface area increases hence Vander waal forces also increased and thus physical properties are increased

$C_1 – C_4 \Rightarrow$ gas
$C_5 – C_{17} \Rightarrow$ liquid
C_{18} ...... $\Rightarrow$ solid

Note : 1. On increasing branching surface area tends to be spherical i.e.Vander waal interaction reduced and hence boiling point decreased.
2. Melting point of alkane having even number of carbon atoms is higher than neighbouring alkanes having odd number of carbon atom. Because in even number of alkanes two ends are facing towards opposite side hence there will be minimum intermolecular repulsion as a result they fit better into crystal lattice.
3. Density of alkane increases with molecular mass and then acquires a constant value 0.8 gm/cc^3. Thus also it is clear that alkane is lighter than water.

4. Chemical reactions of alkane

4.1. Halogenation :

Reagents :- UV light / hν/ high temp (250^0-400^{0}C) / Peroxide + X_2 (Cl_2 + Br_2)

General reaction :-
$R - H + X_2 \xrightarrow{\text{UV light or } 250°–400°} R - X + HX$

Mechanism :- Free radical substitution this reaction is chain reaction which is completed in following three steps.
(i) Chain initiation step : It is homolytic clevage of chlorine molecule to give chlorine free radical .It is an endothermic step .

$$X_2 \xrightarrow[250° - 400°C]{\text{UV or temp.}} 2\dot{X}$$

(ii) Chain propagation step - The step in which reactant and product, both are having free radical . It is longest step .

$\dot{X} + R – H \longrightarrow \dot{R} + HX$; [rds] First propagation step
$\dot{R} + X – X \longrightarrow R – X + \dot{X}$ Secod propagation step

(iii) Chain Termination step - It is the step in which any two free radicals combine to give a product without free radical. It is always exothermic step.

$$\dot{X} + \dot{X} \longrightarrow X_2$$

$$\dot{R} + \dot{R} \longrightarrow R - R$$

$$\dot{R} + \dot{X} \longrightarrow R - X$$

Remark:

(i) Other halogenating reagent is

(a) Chlorination SO_2Cl_2/ Peroxide

(b) Bromination $SO_2\ Br_2$/ Peroxide

Mechanism for (a)

$$RO - OR \longrightarrow 2\ {}^{\bullet}OR$$
$${}^{\bullet}OR + SO_2Cl_2 \longrightarrow ROCl + {}^{\bullet}SO_2Cl$$
$${}^{\bullet}SO_2Cl \longrightarrow {}^{\bullet}Cl + SO_2$$
$$RH + {}^{\bullet}Cl \longrightarrow R^{\bullet} + HCl$$

(ii) Methane reacts with excess of chlorine in diffused sunlight to give the final product as

$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{h\nu} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{h\nu} CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

[carbontetrachloride]

(iii) Reactivity of H = 3°H > 2°H > 1° H

(iv) Reactivity of X_2

Reactivity of X_2 = $F_2 > Cl_2 > Br_2 > I_2$		
1.Direct fluorination of alkane is not possible because it is very explosive. So F_2 is react with alkane in dark and at room temperature	Bromination is similar to chlorination but slower in rate.	1. Iodination is reversible reaction since H–I is formed as a by product, that is strong reducing agent so reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidizing agent like HIO_3, HNO_3 and HgO etc. which destroy HI into I_2. $CH_4 + I_2 \longrightarrow CH_3I + H{-}I$ $HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$
2. Halogen exchange **Reagents** (i) $AgF + H_2O$ (Major) + C_2H_5OH (Minor) **(Swart's Reaction)** Only AgF is soluble among all silver halides in water. $R{-}X \xrightarrow[S_N1]{AgF} R^+ \xrightarrow{F^-} R{-}F + AgX\downarrow$ ppt. (ii) $2C_2H_5Br + HgF_2 \rightarrow 2C_2H_5F + HgBr_2$		2. Halogen exchange Reactions : (Finklstein Reaction) $R{-}X + NaI \xrightarrow[S_N2]{Acetone} R{-}I + NaX\downarrow$ (Cl,Br) (ppt. in acetone) In acetone, NaI is soluble/Ionised but NaCl/NaBr are insoluble. So NaCl/NaBr get precipitate out.

(v) In a chain reaction following reagents are involved :

(a) Initiators : They initiate the chain reaction, Initiators are peroxide (R_2O_2), Perester's etc.

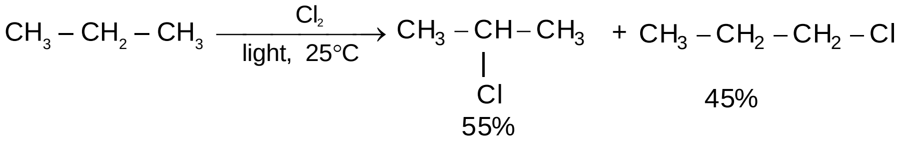
(b) Inhibitors : A substance that slows down or stops the reaction is known as inhibitors

For example O_2 is a good inhibitor.

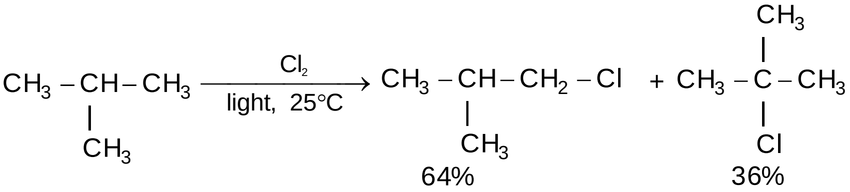
$$\dot{R} + O_2 \longrightarrow R - O - \dot{O} + \dot{R} \longrightarrow R - O - O - R$$

all reactive alkyl free radicals are consumed so reaction stops for a period of time.

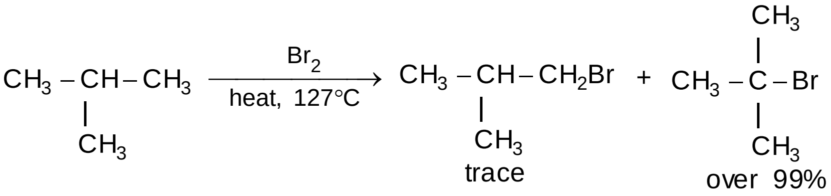
Halogenation of higher alkane :

(a) 

$$CH_3-CH_2-CH_3 \xrightarrow[\text{light, }25^\circ C]{Cl_2} \underset{\underset{55\%}{Cl}}{CH_3-\overset{}{CH}-CH_3} + \underset{45\%}{CH_3-CH_2-CH_2-Cl}$$

(b) 

$$\underset{CH_3}{CH_3-\overset{}{CH}-CH_3} \xrightarrow[\text{light, }25^\circ C]{Cl_2} \underset{\underset{64\%}{CH_3}}{CH_3-CH-CH_2-Cl} + \underset{\underset{36\%}{Cl}}{CH_3-\overset{CH_3}{C}-CH_3}$$

(c) 

$$\underset{CH_3}{CH_3-CH-CH_3} \xrightarrow[\text{heat, }127^\circ C]{Br_2} \underset{\underset{\text{trace}}{CH_3}}{CH_3-CH-CH_2Br} + \underset{\underset{\text{over 99\%}}{CH_3}}{CH_3-\overset{CH_3}{C}-Br}$$

Factors affecting the relative yields :

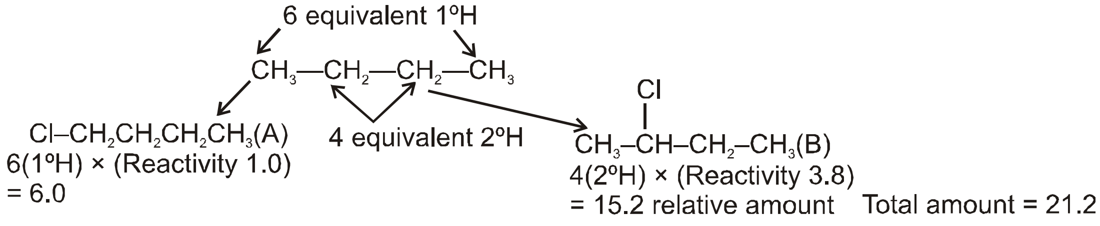
(i) Probability factor : This factor is based on the number of each kind of H atom in the molecule.

(ii) Reactivity of hydrogen : The order of reactivity is 3° > 2° > 1° the relative rate per hydrogen atom is found to be

Primary	Secondary	tertiary	
1 :	3.8 :	5	For chlorination at 25°C
1 :	82 :	1600	For bromination at 127°C

(iii) Reactivity v/s selectivity principle :

The more reactive substance is less selective.

Ex- 

$Cl–CH_2CH_2CH_2CH_3$(A)
6(1°H) × (Reactivity 1.0)
= 6.0

$CH_3–CH(Cl)–CH_2–CH_3$(B)
4(2°H) × (Reactivity 3.8)
= 15.2 relative amount Total amount = 21.2

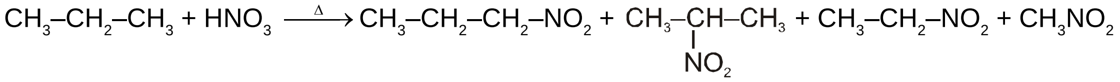
% yield A = $\frac{6}{21.2}$ × 100 = 28.3 % ; % yield B = $\frac{15.2}{21.2}$ × 100 = 71.%

4.2. Nitration of alkane :

It takes place in vapour phase and gives a mixture of nitroderivatives due to cracking.

$$RH + HNO_3 \xrightarrow{400^\circ C} RNO_2 + H_2O$$

$$CH_4 + HNO_3 \xrightarrow{\Delta} CH_3NO_2 + H_2O$$



$$CH_3–CH_2–CH_3 + HNO_3 \xrightarrow{\Delta} CH_3–CH_2–CH_2–NO_2 + CH_3–\underset{NO_2}{CH}–CH_3 + CH_3–CH_2–NO_2 + CH_3NO_2$$

Note : Nitration of propane gives a mixture of four nitroderivatives as it as two types of replaceable H–atom (1° and 2°) and also it undergoes cracking at high temperature.

4.3. Sulphonation of alkane :

Lower alkanes do not undergo sulphonation easily but higher members (from hexane onward) are sulphonated slowly when treated with fuming acid (oleum) at around 400°C

$$RH + H_2SO_4 \xrightarrow[\text{Prolonged heating}]{SO_3} R\text{–}SO_3H + H_2O$$

Note : 1. Lower members like propane, butane and pentane etc. react with SO_3 in vapour phase to give corresponding sulphonic acid.

2. Decreasing order of sulphonation of alkane

3° > 2° > 1° H–atom

3. It s follows free radical mechanism as

$$H_2SO_4 \xrightarrow{\Delta} HO^\bullet + {}^\bullet SO_3H$$

$$RH + {}^\bullet OH \longrightarrow R^\bullet + H_2O$$

$${}^\bullet R + HOSO_3H \longrightarrow R\text{–}SO_3H + {}^\bullet OH$$

4.4. Combustion of Alkane

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \longrightarrow x\,CO_2 + \frac{y}{2} H_2O + \Delta \;; \qquad C_3H_8 + \left(3 + \frac{8}{4}\right) O_2 \longrightarrow 3\,CO_2 + \frac{8}{2} H_2O$$

Hydrocarbon + sufficient supply of $O_2 \Rightarrow CO_2 + H_2O + \Delta$

Hydrocarbon + insufficient supply of $O_2 \Rightarrow CO + H_2O$ or C (black)

Que. How many atoms of oxygen are needed for complete combustion of 2.2 g of propane ?

Ans. $C_3H_8 + 5O_2 \longrightarrow 3\,CO_2 + 4H_2O$

44 gm of C_3H_8 needs = 5 moles of Oxygen = 5 × N_A molecule of Oxygen = 5 × 2 × N_A atom

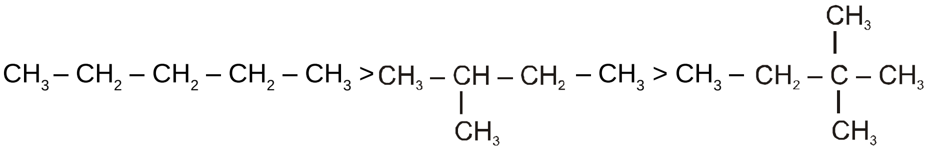
2.2 gm of C_3H_8 needs = $\frac{5 \times 2 \times 2.2 \times N_A}{44}$ = 0.5 × N_A atoms of Oxygen

Note : 1. Heat of combustion α higher homologues

Ex- $C_3H_8 > C_2H_6 > CH_4$

2. Heat of combustion $\propto \frac{1}{\text{Branching of alkane (in isomers)}}$

Ex-

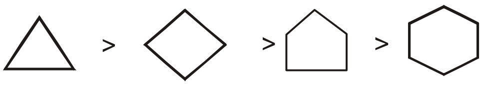


$CH_3 - CH_2 - CH_2 - CH_2 - CH_3 > CH_3 - CH(CH_3) - CH_2 - CH_3 > CH_3 - CH_2 - C(CH_3)_2 - CH_3$

3. Heat of combustion $\propto \frac{1}{\text{size of ring (cycloalkane)}}$

On increasing the size of ring from three to six stability of ring increases and hence heat of combustion (its value) decreases per CH_2 group.

Ex-



4.5. Controlled oxidation :

Alkanes on heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalyst give a variety of oxidation products.

(i) $2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$ (methanol)

(ii) $CH_4 + O_2 \xrightarrow[\Delta]{Mo_2O_3} HCHO + H_2O$

methanal

(iii) $2CH_3CH_3 + 3O_2 \xrightarrow[\Delta]{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$

Ethanoic acid

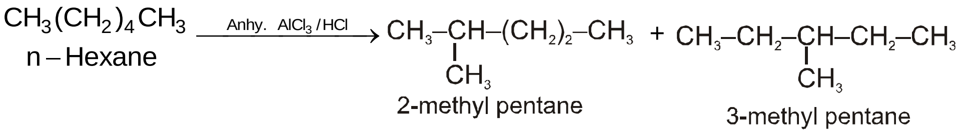
(iv) Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.

$(CH_3)_3CH \xrightarrow[Oxidation]{KMnO_4} (CH_3)_3COH$

2-methylpropan-2-ol

4.6. Isomerization of alkane :

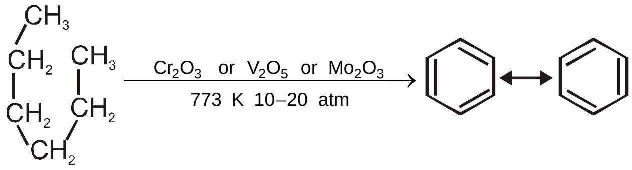
n–Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



$$\underset{n-Hexane}{CH_3(CH_2)_4CH_3} \xrightarrow{Anhy.\ AlCl_3/HCl} \underset{\text{2-methyl pentane}}{CH_3-\underset{CH_3}{\underset{|}{C}}H-(CH_2)_2-CH_3} + \underset{\text{3-methyl pentane}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{C}}H-CH_2-CH_3}$$

4.7. Aromatization of alkane :

n-alkanes having six or more carbon atoms on heating to 773 K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdnum or chromium supported over alumina get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.



Que. Toluene (C_7H_8) is methyl derivative of benzene. Which alkane do you suggest for preparation of toluene ?

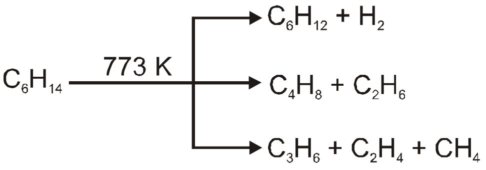
Ans. n – Heptane

4.8. Reaction with steam

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen.

$CH_4 + H_2O \xrightarrow[\Delta]{Ni} CO + 3H_2$

4.9. Cracking of alkane



ALKENE

1. Structure and Bonding :

(A) Alkenes are unsaturated hydrocarbons having at least one double bond. Alkenes are also known as olefins.

(B) These are represented by general Formula C_nH_{2n} (one double bond).

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

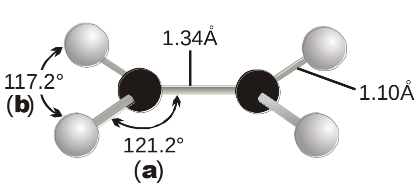
(D) Its bond energy is 146 $kcal.mol^{-1}$

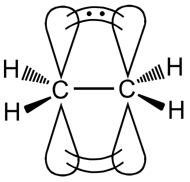
(E) The hybridization of (C = C) carbon is sp^2

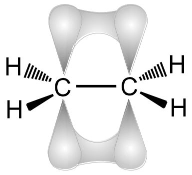
(F) The π e^- cloud is present above and below the plane of σ- bonded skeleton.

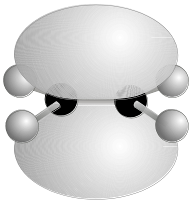
(G) These are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.

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



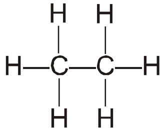
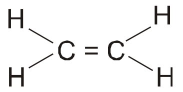






Note : Bond angle a > b since repulsion due to π electrons (double bond - single bond repulsion > single bond - single bond repulsion according to VSEPR theory.

2. Comparative study of alkane, alkene & alkyne :

Hydrocarbon	 (A) Alkane	 (B) Alkene	H — C ≡ C — H (C) Alkyne
(i) C—C Bond distance	1.54 A°	1.34 A°	1.20 A°
(ii) C—H Bond distance	1.09 A°	1.08 A°	1.05 A°
(iii) Hybridisation state	sp^3	sp^2	sp
(iv) Structure	Tetrahedral	Planner	Linear
(v) Electronegativity $sp^3 < sp^2 < sp$	less than sp^2/sp	less than sp more than sp^3	more than sp^2/sp^3
(vi) C—C bond energy	415 kJ	615 kJ	835 kJ
(vii) density	0.5 g/cm^3	0.52 g/cm^3	0.67 g/cm^3
(viii) % s-charactor	25%	33.33 %	50 %

3. Lab Test :

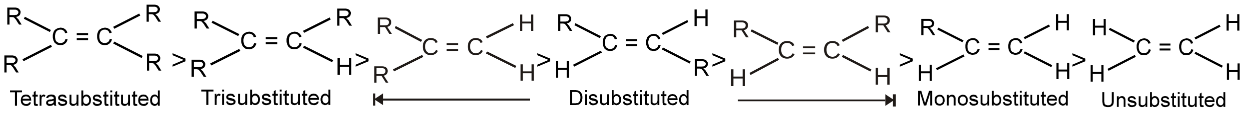
Hydrocarbon	**Alkane**	**Alkene**	**Alkyne (Terminal)**
(i) Br_2/H_2O solution	No effect	Decolorise	Decolorise
(ii) Cold dil. alkaline + $KMnO_4$ Solution	No effect	Brown colour	Brown colour
(iii) Tollen's Reagent	No effect	No effect	White ppt. of silver acetenilied
(iv) Ammonical cuprous chloride solution	No effect	No effect	Red ppt. of cuprous acetenilied

4. Stability of Alkenes :

Overall relative stabilities of Alkenes

The greater the number of attached alkyl groups (i.e., the highly substituted the carbon atoms of the double bond), the greater is the alkene's stability. This order of stabilities can be given in general terms as follows.

Relative stabilities of alkenes



Note- **1.** More and More alkylated double bonded alkene will be more stable.

2. The way of measuring stability of alkene is the determination of heat of hydrogenation. It is applicable only those isomeric alkene which gives same product after hydrogenation.

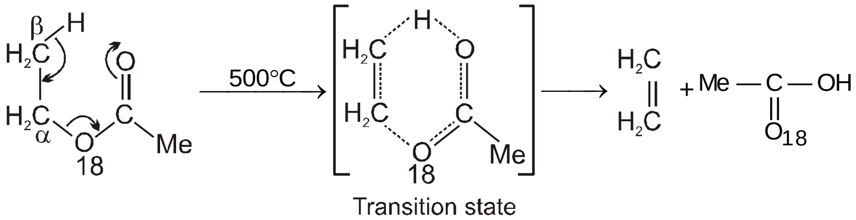
$$\text{Stability} \propto \frac{1}{\text{Heat of Hydrogenation}}$$

i.e. more stable the alkene less will be heat of hydrogenation.

5. Preparation of Alkene :

5.1. Pyrolysis of Ester :

It is the preparation of alkene along with carboxylic acid via formation of six membered cyclic transition state. It is syn elimination and alkene is formed corresponding to alkyl part of alcohol from ester. This addition is also said to be Hoffman elimination.

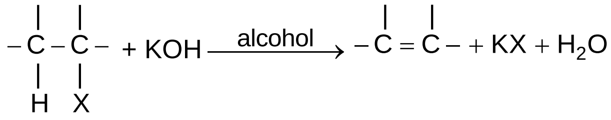


Note : As a direct consequence of cyclic transition state, both the leaving groups namely proton and carboxylate ion are eliminated from the syn position. This is an example of **syn elimination**.

5.2. Dehydro-halogenation of alkyl halide :

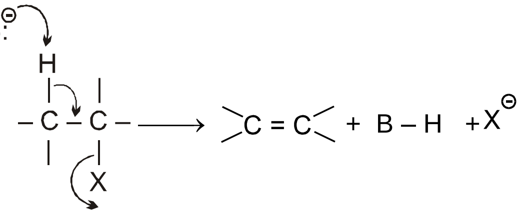
It is removal of H–X from alkyl halide where this reaction is said to be **β-elimination** reaction.

Reagent (i) Hot alcoholic solution of KOH (EtO^- / EtOH) (ii) $NaNH_2$ (iii) $t\text{-}BuO^-$ in t-BuOH



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}- + KOH \xrightarrow{\text{alcohol}} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

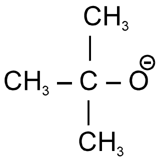
Mechanism



Remark : (i) Here β – H is eliminated by base hence called **β elimination** (follows **Saytzeff rule)**.

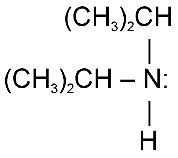
i.e. **(Highly substituted alkene is major product)**. It also involves an anti elimination of HX.

(ii) Bulky bases give hofmann alkenes



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\ominus}{O}$$

t-Butoxide

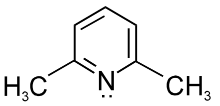


$$(CH_3)_2CH-\underset{\underset{H}{|}}{\overset{\overset{(CH_3)_2CH}{|}}{N}}:$$

Di-isopropylamine

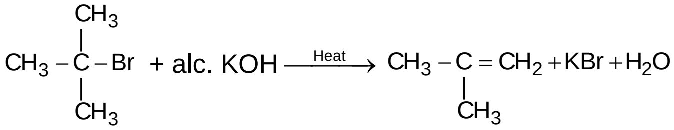
$(CH_3CH_2)_3N$:

Triethylamine



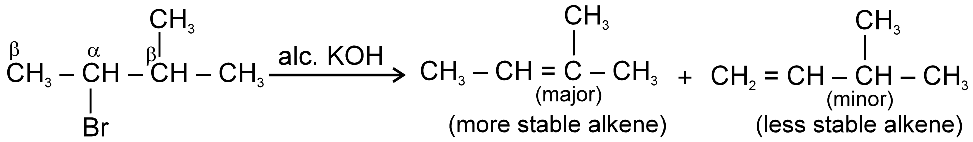
2, 6-dimethyl pyridine

Ex-1.



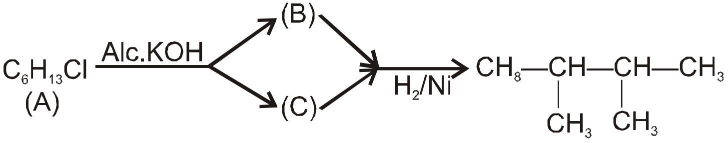
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br+\text{alc. KOH}\xrightarrow{\text{Heat}}CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2+KBr+H_2O$$

Ex-2.



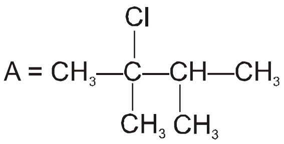
$$\overset{\beta}{CH_3}-\underset{\underset{Br}{|}}{\overset{\alpha}{CH}}-\overset{\overset{CH_3}{\beta|}}{CH}-CH_3\xrightarrow{\text{alc. KOH}}\underset{\substack{\text{(major)}\\ \text{(more stable alkene)}}}{CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_3}+\underset{\substack{\text{(minor)}\\ \text{(less stable alkene)}}}{CH_2=CH-\overset{\overset{CH_3}{|}}{CH}-CH_3}$$

Que. What will be the structure of A in given question ?



$$\underset{(A)}{C_6H_{13}Cl}\xrightarrow{\text{Alc.KOH}}(B)+(C)\xrightarrow[H_2/Ni]{}CH_8-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

Ans.



$$A=CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

5.3. By Dehydration of alcohols

Reagents : (i) H_2SO_4 / 160°C (ii) H_3PO_4 / Δ

$$RCH_2CH_2OH\xrightarrow[\Delta]{P_2O_5\text{ or conc. }H_2SO_4\text{ or }Al_2O_3}R-CH=CH_2+H_2O$$

(iii) P_2O_5 / Δ (iv) Al_2O_3 / 350°C undergo loss of water molecule and form alkenes

5.4. Dehalogenation of dihalo-alkane :

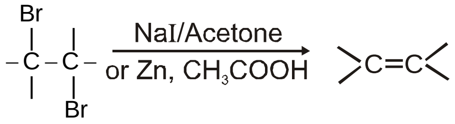
It is removal of X_2 from dihalo alkane.

Reagent: NaI in acetone or zinc in presence of acetic acid or ethanol or Zn/Δ

Dihalides are of two types :

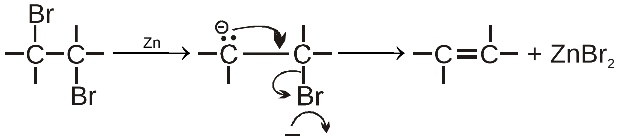
(A) Vicinal dihalide or Alkylene dihalides

General Reaction :



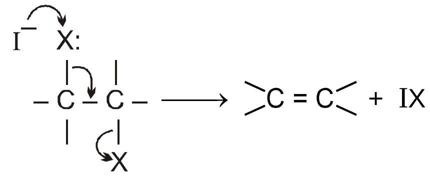
$$-\underset{|}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{|}{C}}-\xrightarrow[\text{or Zn, }CH_3COOH]{\text{NaI/Acetone}}\;>C=C<$$

Mech.



$$-\underset{|}{\overset{\overset{Br}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{|}{C}}-\xrightarrow{Zn}-\underset{|}{\overset{\ominus\,\bullet\bullet}{C}}-\underset{\underset{Br}{|}}{\overset{|}{C}}-\longrightarrow-\underset{|}{C}=\overset{|}{C}-+ZnBr_2$$

Mech. With NaI in acetone :



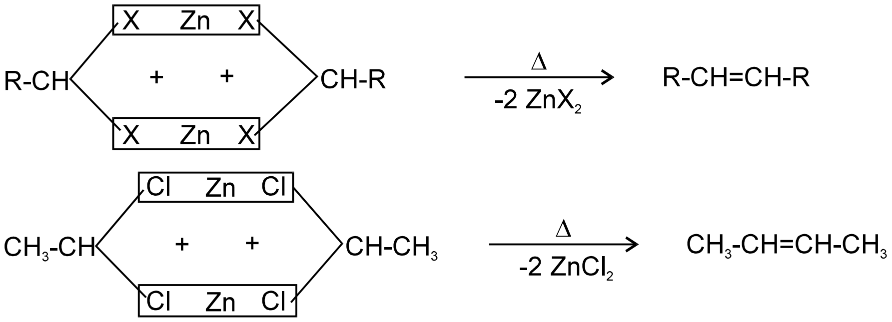
$$-\underset{|}{\overset{\overset{I^-\;X:}{|}}{C}}-\underset{\underset{X}{|}}{\overset{|}{C}}-\longrightarrow\;>C=C<\;+\;IX$$

Remark : Both are E2 elimination and stereospecific antielimination.

(B) Gem-dihalide or Alkylidene halides

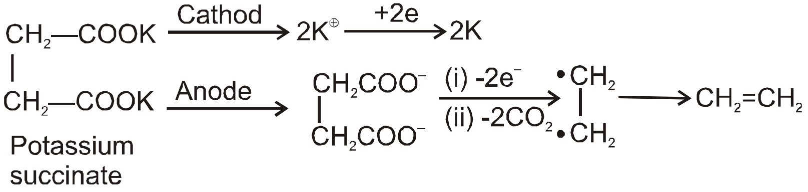
Ex : $CH_3—CHCl_2$ (ethylidene chloride)

When gem dihalide is heated with Zinc dust at 300°C then higher alkenes are formed, which is based on free radical mechanism.



5.5. Electrolysis of Potassium succinate :

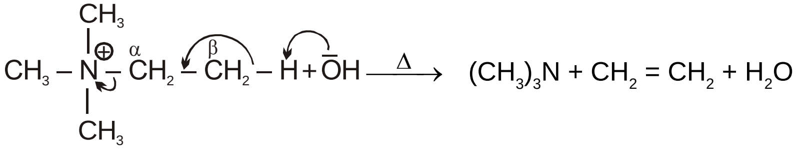
This reaction gives ethylene as follows



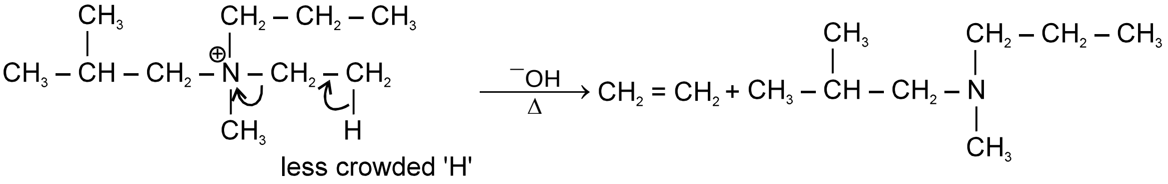
$$\begin{array}{l} CH_2—COOK \xrightarrow{\text{Cathod}} 2K^{\oplus} \xrightarrow{+2e} 2K \\ | \\ CH_2—COOK \xrightarrow{\text{Anode}} \begin{array}{l}CH_2COO^-\\ |\\ CH_2COO^-\end{array} \xrightarrow[(ii)\ -2CO_2]{(i)\ -2e^-} \begin{array}{l}\bullet CH_2\\ |\\ \bullet CH_2\end{array} \longrightarrow CH_2=CH_2 \end{array}$$

Potassium succinate

5.6. By Hofmann Elimination Method



$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{\oplus}{N}}}-\overset{\alpha}{C}H_2-\overset{\beta}{C}H_2-H+\bar{O}H \xrightarrow{\Delta} (CH_3)_3N + CH_2=CH_2+H_2O$$

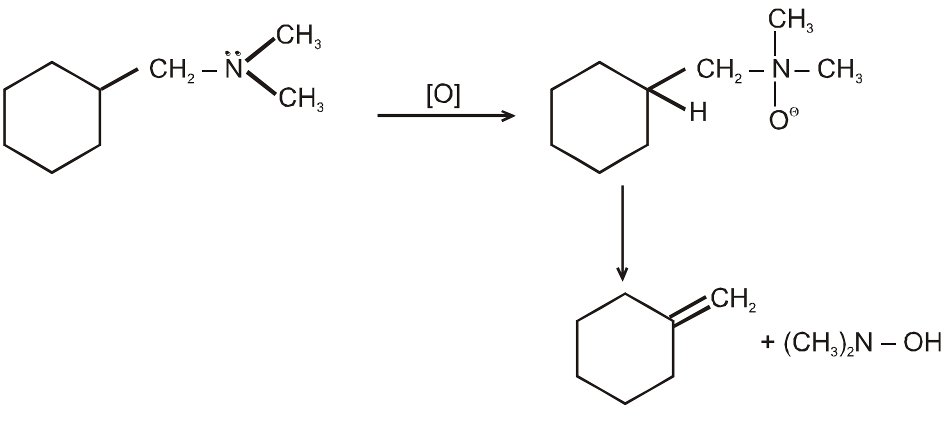


$$CH_3-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{\overset{CH_2-CH_2-CH_3}{\overset{\oplus}{N}}}-CH_2-\underset{H}{CH_2} \xrightarrow[\Delta]{^-OH} CH_2=CH_2+CH_3-\overset{CH_3}{CH}-CH_2-\underset{CH_3}{\overset{CH_2-CH_2-CH_3}{N}}$$

less crowded 'H'

Remark : Less substituted alkenes (Hofmann alkenes) are formed as major product.

5.7. Cope-reaction: Tertiaryamine oxides on heating form alkene, if there is β–hydrogen atom in it.



6. Physical Properites of Alkene

(i) From C_2 – C_4 they are colourless, odourless gases, from C_5 – C_{17} they are colourless liquids, C_{18} onwards alkenes are solids.

(ii) Alkenes are practically insoluble in water because they can not form hydrogen bonds with H_2O molecules. They dissolve freely in organic solvents like benzene, chloroform, CCl_4 petroleum ether., etc.

(iii) The boiling and melting points of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable π bond. alkenes are therefore, lesser volatile than the corresponding alkanes.

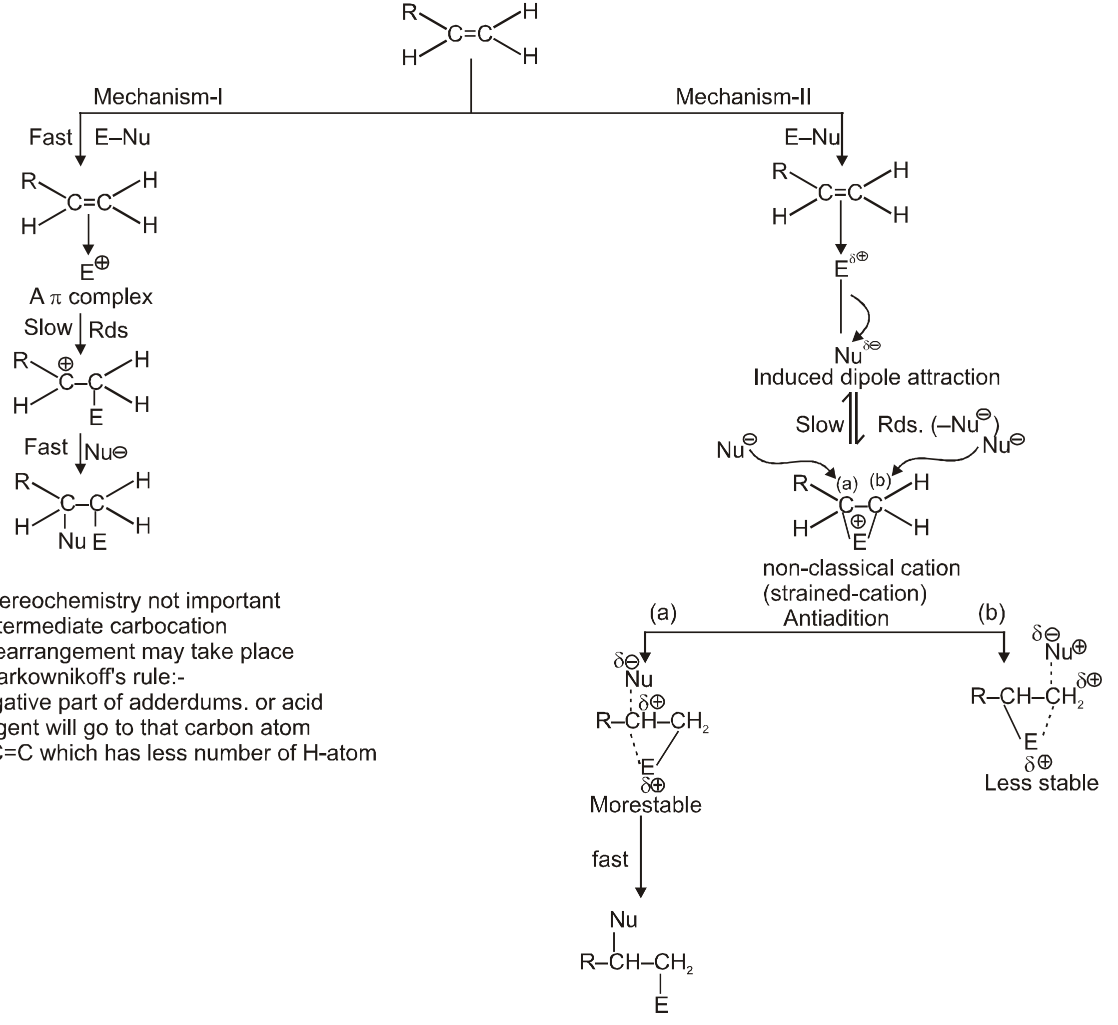
Their boiling points, melting points and specific gravities rise with the increase of molecular weight. The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

MP. and **BP.** $\propto$ mol. wt.

$$\text{B.P} \ \alpha \ \frac{1}{\text{branching in alkenes}}$$

7. Chemical reactions of alkene

Electrophilic addition Reaction :



* Stereochemistry not important
* Intermediate carbocation
* Rearrangement may take place
* Markownikoff's rule:-
Negative part of adderdums. or acid reagent will go to that carbon atom of C=C which has less number of H-atom

*Formation of non classical cation
* Attack of nucleophile on that carbon which have more stable δ⊕ charge
* Anti addition
* Stereospecific
* No carbocation
* No Rearrangement

Example of mechanism-I

(1) Addition of hydrogen halide

(2) Acid-catalysed hydration.

(3) Addition of H_2SO_4.

Example of mechanism-II

(1) Addition of halogen.

(2) Addition of hypohalous. acid.

(3) Oxymercuration-demercuration

(4) Addition of NOCl

Reactivity of an Alkene:

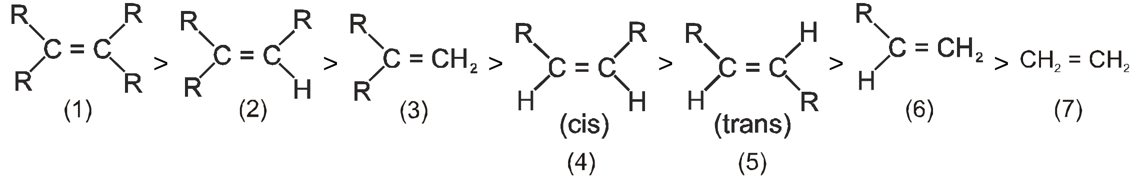
(1) Presence of electron releasing groups (+m, +I) at C = C increases electrophilicity and reactivity.

(2) Presence of ERG stabilises the intermediate carbocation.

(3) More stable , more is reactivity.

Examples of Reactivity Orders :

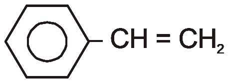
(i)



(ii) $ERG - CH = CH_2 > CH_2 = CH_2 > EWG - CH = CH_2$

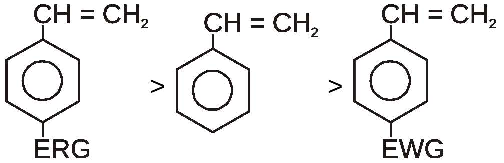
Example :

(a) $\underset{\text{(vinyl ether)}}{CH_3-O-CH=CH_2} > CH_2 = CH_2 > \underset{\text{(acrylonitrile)}}{CH_2=CH-CN}$; (b)

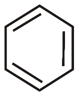


$> CH_2 = CH_2$

(c)



; (d)



$< CH_2 = CH_2$

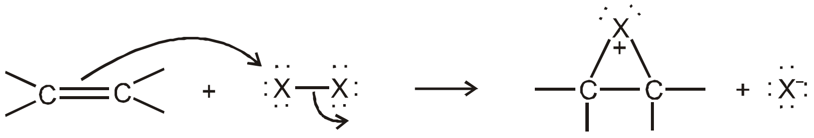
7.1. Additon of halogen (Halogenation) : *“Mechanism-II”*

usually anti addition

($X_2 = Cl_2, Br_2$, but not F_2 and I_2)

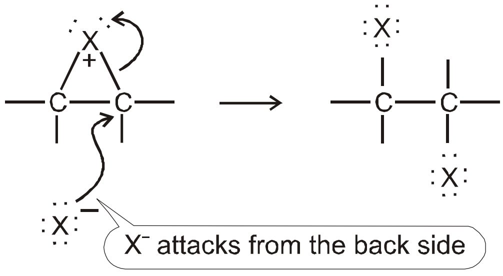
Mechanism

Step 1 :



Halonium ion

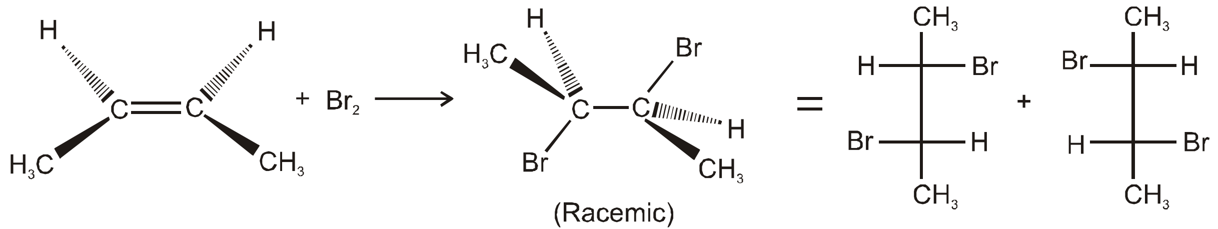
Step 2 :



Remarks : Anti addition
No rearrangement
Markovnikoff's additions

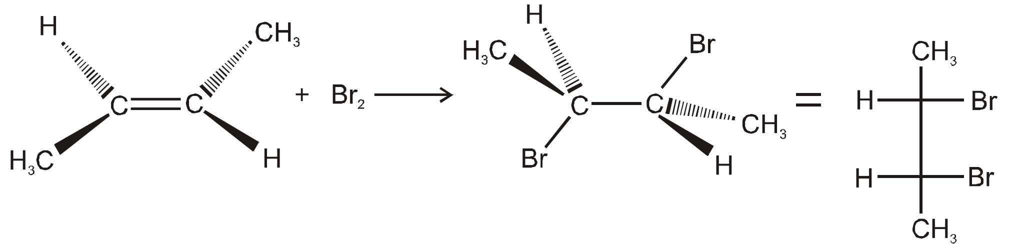
The addition of bromine to cyclopentene is a stereospecific **anti addition.**

Ex.



Cis-2-butene (Racemic) (±)-2,3-dibromobutane

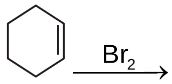
Ex.



Trans-2-butene Meso-2,3-dibromobutane

Que. Predict the product for the following : -

(i)

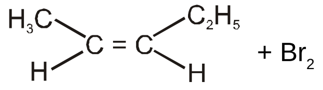


(ii) $CH_3-CH=CH_2 \xrightarrow[CCl_4]{Br_2}$

(iii) $CH_3-CH=CH_2 \xrightarrow{ICl}$

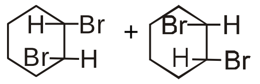
(iv) $CH_3-CH=CH_2 \xrightarrow{BrCl}$

(v)



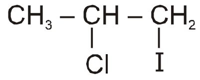
Cis pent-2-ene

Ans. (i)



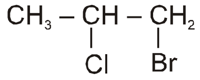
(ii) $CH_3-CHBr-CH_2Br$

(iii)



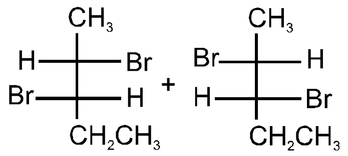
$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{I}{\underset{|}{CH_2}}$

(iv)



$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Br}{\underset{|}{CH_2}}$

(v)

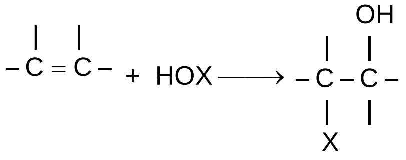


Threo enantiomers

7.2. Addition of HOX : *“Mechanism-II”*

Reagents : (i) $X_2 + H_2O \rightarrow HOX + HX$ or (ii) HOX , H^+

Electrophile : X^+, Halonium ion **;**



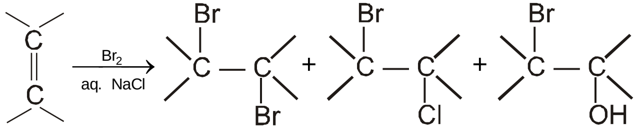
$$-\overset{|}{C}=\overset{|}{C}- + HOX \longrightarrow -\underset{X}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{\overset{OH}{|}}{C}}-$$

Remarks : Anti addition ; No rearrangement ; Markovnikoff's additions

Evidence to support of formation non classical cation :

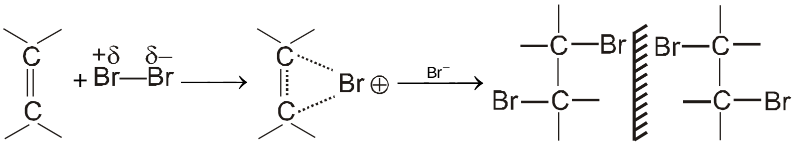
When addition of Br_2 was carried out in the presence of aq. NaCl we get 3-products.

(i) 1,2-dibromoethane (ii) 1-Bromo-2-chloroethane (iii) 2-Bromoethanol



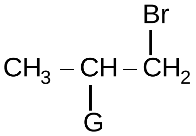
Formation of these three products clearly indicates about intermideate (A) thus addition of bromine water over alkene is electrophilic addition reaction.

Note : This addition always takes place in trans manner because of bulky nature of bromine atom in bromonium, which is a cyclic bridge intermediate. Cyclic bridge intermediate is not classical carbonium ion.



Que. (i) $CH_3–CH=CH_2 \xrightarrow[H^+]{HOCl}$ (ii) $CH_3–CH=CH_2 \xrightarrow[\text{NaCl, KI impurities}]{Br_2/H_2O}$

Ans. (i) $CH_3–CH(OH)–CH_2–Cl$ (ii)

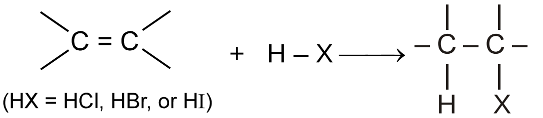


$$CH_3-\underset{G}{CH}-\overset{Br}{CH_2}$$

4 structural products are formed , G=$OH^–$, $Br^–$, $I^–$, $Cl^–$

7.3. Addition of Hydrogen Halides (+ HX) : *"Mechanism-I"*

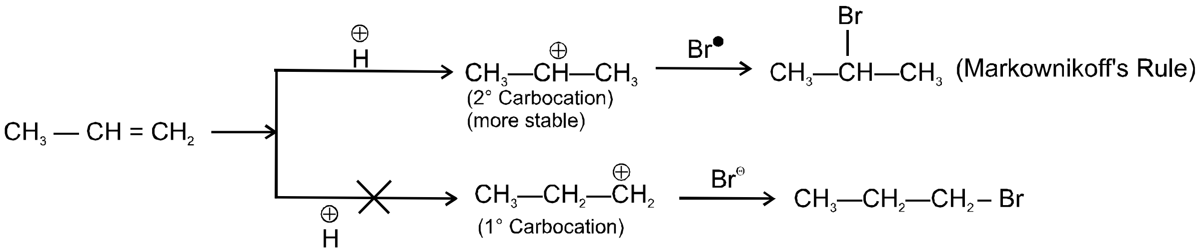
Reagents : HX **;** **Electrophile :** H^+



Remarks : Markovnikoff additon ; Intermediate carbocation ; Rearrangement may take place

Markovnikoff rule : The rule states that negative part of the addendum (adding molecule) or acid reagent gets attached to that carbon atom of unsymmetrical alkene (C=C) which possesses lesser number of hydrogen atom.

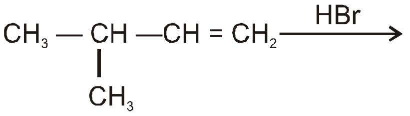
Ex.



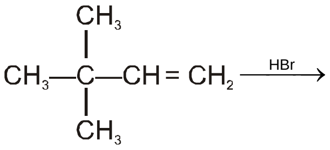
Above reaction is electrophilic addition reaction hence electrophile will go to that carbon atom of C=C which has more no. of H-atoms.

Since 2º carbocation is more stable hence major product is 2-bromopropene.

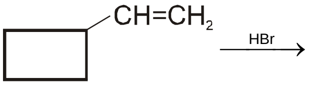
Que. Predict the product for the followings :

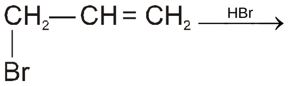
(i) 

$CH_3-\underset{CH_3}{CH}-CH=CH_2 \xrightarrow{HBr}$

(ii) 

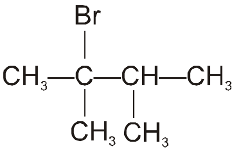
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH_2 \xrightarrow{HBr}$

(iii) 

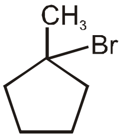
(iv) 

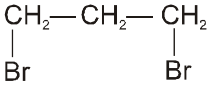
$\underset{Br}{CH_2}-CH=CH_2 \xrightarrow{HBr}$

Ans. (i) $(CH_3)_2C(Br)CH_2CH_3$

(ii) 

$CH_3-\overset{Br}{\underset{CH_3}{C}}-\underset{CH_3}{CH}-CH_3$

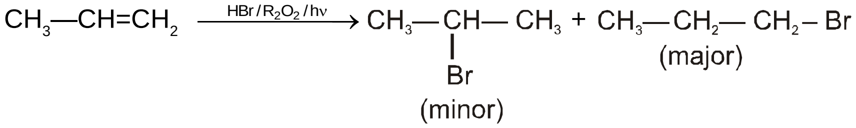
(iii) 

(iv) 

$\underset{Br}{CH_2}-CH_2-\underset{Br}{CH_2}$

7.4. Free Radical Addition of HBr : Kharash Effect or Peroxide Effect :

Reagents : HBr, Peroxide or sunlight



$$CH_3-CH=CH_2 \xrightarrow{HBr/R_2O_2/h\nu} \underset{\text{(minor)}}{CH_3-\underset{Br}{CH}-CH_3} + \underset{\text{(major)}}{CH_3-CH_2-CH_2-Br}$$

Remarks:- Anti Markovnikov's Addition ; Free radical chain reaction ;

Among all the HX peroxide effect observed with only HBr , not with HF, HCl, HI.

Because HF and HCl are held together by strong electrostatic force. So they can never be broken into free radical. HI will give $I^{\bullet}$ but being larger in size $I^{\bullet}$ (inspite of going to C=C) will combined with another $I^{\bullet}$ to give I_2 molecule. Just because of comparable size.

Mechanism : Mechanism of this reaction is completed in following three steps.

(i) Chain initiation step : This reaction is free radical addition reaction in this reaction peroxide undergoes homolytic cleavage to give a free radical from HBr to give $Br^{\bullet}$.

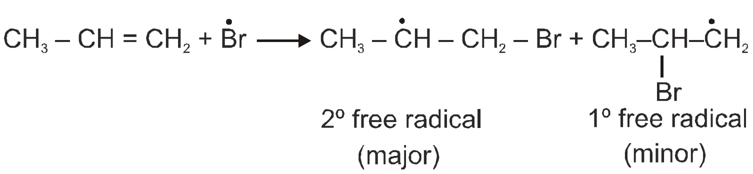
(1) $R-O-O-R \longrightarrow 2R\dot{O}$

(2) $R\dot{O} + HBr \longrightarrow ROH + Br^{\bullet}$

(ii) Chain propagating step : This $Br^{\bullet}$ will go to either carbon of carbon-carbon double bond of propene to give two type of free radicals.

(i) 1º free radical (ii) 2º free radical

Since 2º free radical is more stable then 1º free radical, hence major product is 1-bromopropane.

(3) 

$$CH_3-CH=CH_2+\dot{B}r \longrightarrow \underset{\substack{\text{2º free radical}\\\text{(major)}}}{CH_3-\dot{C}H-CH_2-Br} + \underset{\substack{\text{1º free radical}\\\text{(minor)}}}{CH_3-\underset{Br}{CH}-\dot{C}H_2}$$

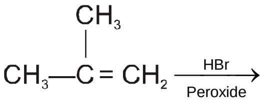
(4) $CH_3-\dot{C}H-CH_2-Br+HBr \longrightarrow CH_3-CH_2-CH_2-Br+\dot{B}r$

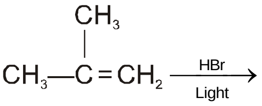
$\dot{B}r$ repeats step (3).

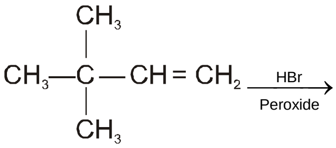
(iii) Chain termination step :

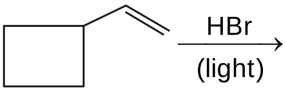
$R-\dot{O}+\dot{O}-R \longrightarrow R-O-O-R$

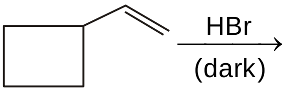
Que. Predict the product for the followings.

(i) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[\text{Peroxide}]{HBr}$

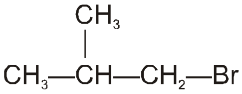
(ii) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 \xrightarrow[\text{Light}]{HBr}$

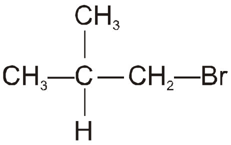
(iii) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr}$

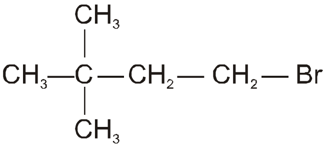
(iv) 

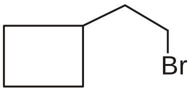
(v) 

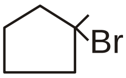
Ans.

(i) 
$CH_3-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_2-Br$

(ii) 
$CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-Br$

(iii) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-CH_2-Br$

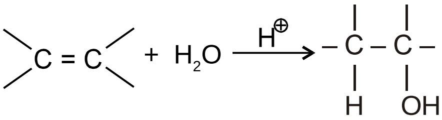
(iv) 

(v) 

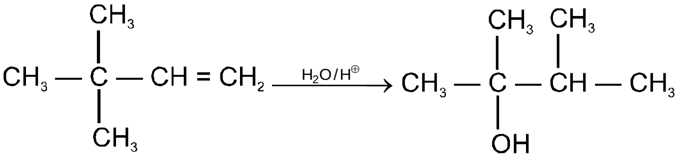
7.5. Addition of H_2O (Hydration Reaction)

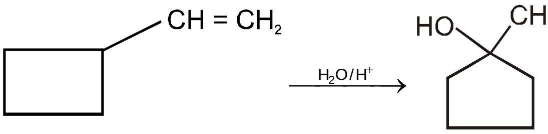
(i) Acid-Catalyzed Hydration of Alkenes : ***"Mechanism-I"***

Reagents : Dilute H_2SO_4 or H_3O^+



Remarks : Markovnikoff additon ; Intermediate carbocation ; Rearrangement may take place

Ex. (a) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH=CH_2 \xrightarrow{H_2O/H^{\oplus}} CH_3-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$

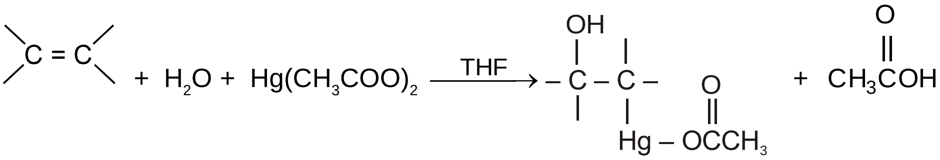
(b) 

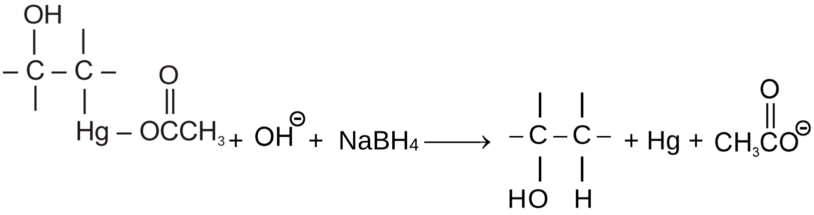
(ii) Oxymercuration-Demercuration : ***"Mechanism-II"***

Reagents : (i) $Hg(OAc)_2$, H_2O (ii) $NaBH_4$

Electrophile :

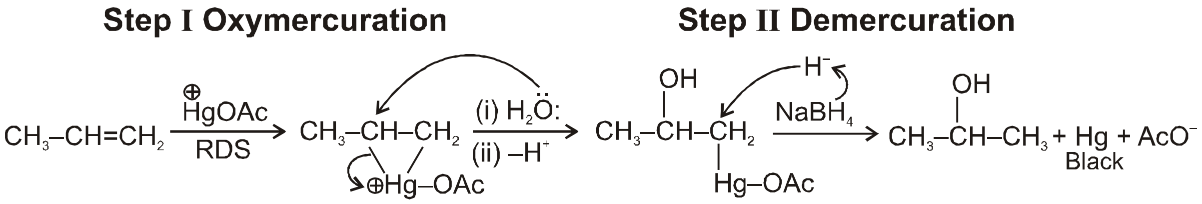
General reaction :





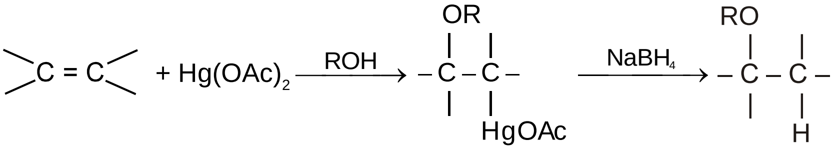
(Demercuration)

Mechanism :



Remarks : No rearrangement ; Markovnikoff's additions

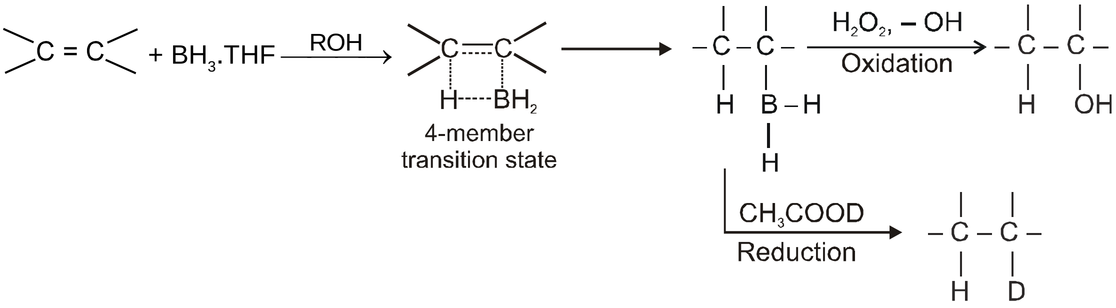
(iii) **Alkoxymercuration - demercuration :** ***"Mechanism-II"***



(iv) **Hydroboration-oxidation : (Syn addition)**

Reagents : BH_3,THF/H_2O_2,^-OH

Mechanism :



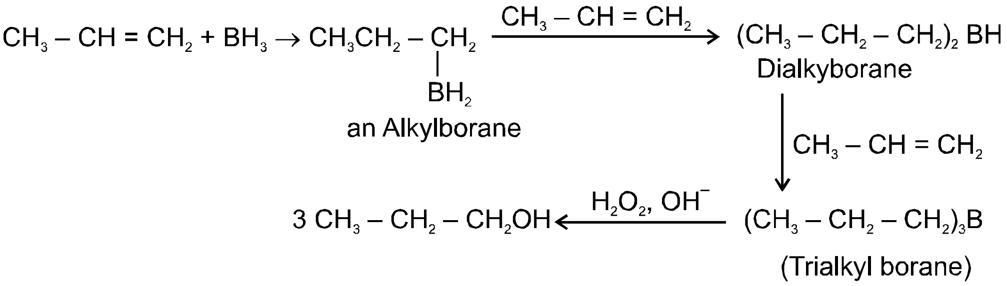
Remarks : Anti Markovnikov's addition.

Stereo specific Syn addition.

Less hindered alkene is more reactive.

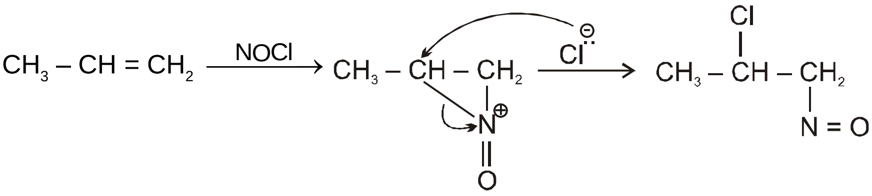
4-membered transition state.

Ex.



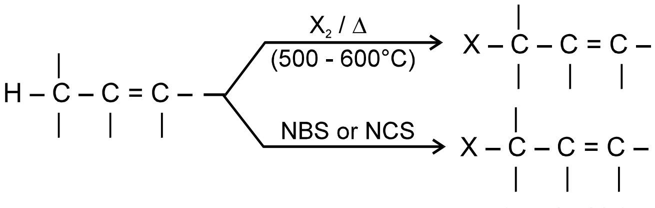
7.6 Other Reactions :

(i) Addition of NOCl :



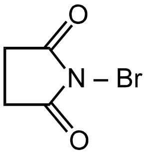
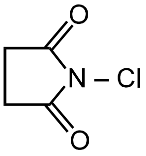
(ii) Allylic substitution Halogenation :

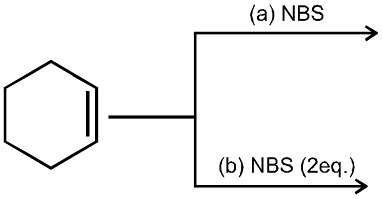
General Reaction

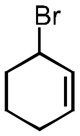
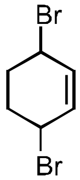


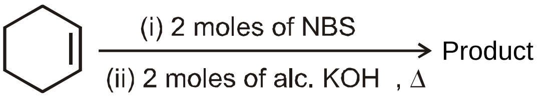
(allyl halide)

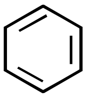
$X_2 = Cl_2, Br_2$

NBS = N-Bromosuccinimide  ; NCS = N-Chlorosuccinimide 

Que. 

Ans. (a)  (b) 

Que. 

Ans. 

(iii) Addition of Carbene :

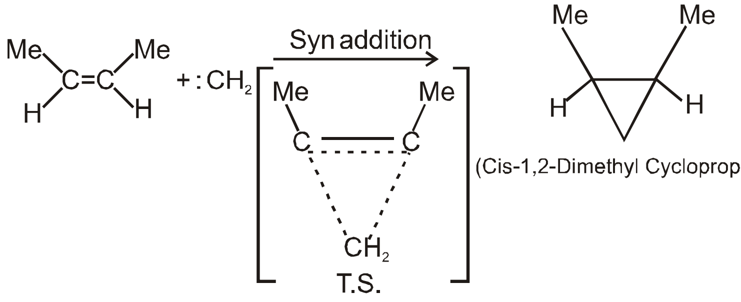
Reagents :

(i) CH_2N_2 , Δ or hν

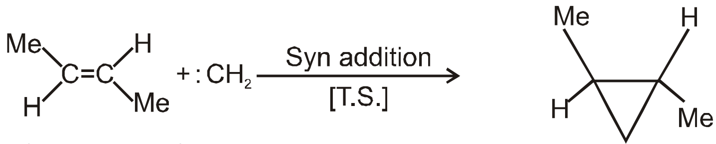
(ii) $CH_2 = C = O$, Δ or hν

(iii) CH_2I_2 + Zn/Cu Couple

(iv) $CHCl_3$ + NaOH

(a) 

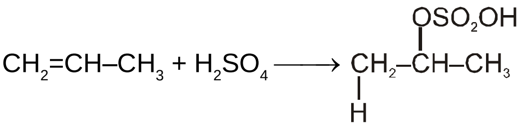
(Cis-1,2-Dimethyl Cyclopropane)

(b) Similarly 

(trans-But-2-ene)

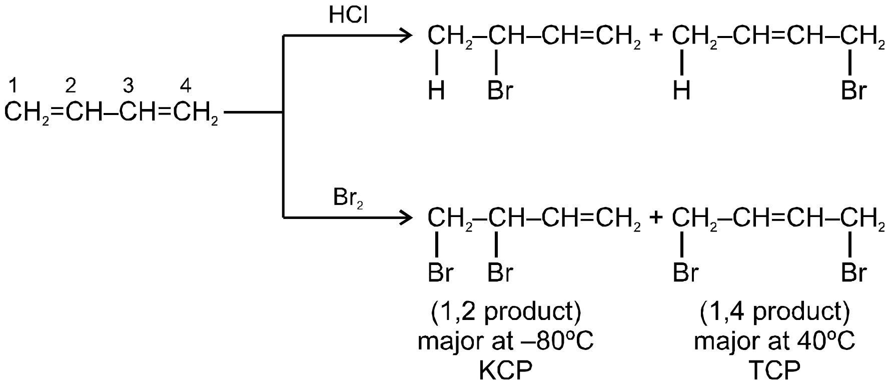
(trans-1,2-Dimethylcyclopropane)

(iv) Addition of H_2SO_4 :



$CH_2{=}CH{-}CH_3 + H_2SO_4 \longrightarrow \underset{\displaystyle H}{\underset{|}{C}}H_2{-}\overset{\displaystyle OSO_2OH}{\overset{|}{C}}H{-}CH_3$ (Isopropyl hydrogen sulphate)

8. Alkadienes :



ALKYNE

1. Introduction

(1) Alkynes are hydrocarbons that contain carbon-carbon triple bond.

(2) Alkynes are also called acetylenes because they are derivatives of acetylene.

(3) The general formula is : C_nH_{2n-2}. (one triple bond)

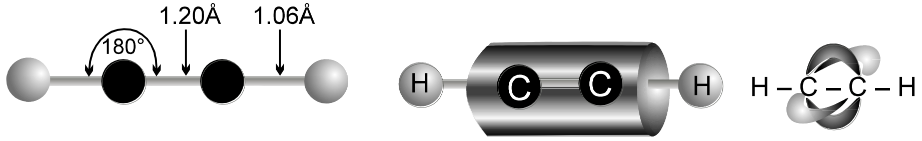
(4) In alkyne $C \equiv C$ bond length is 1.20 Å

(5) Its bond energy is 192 kcal. mol^{-1}

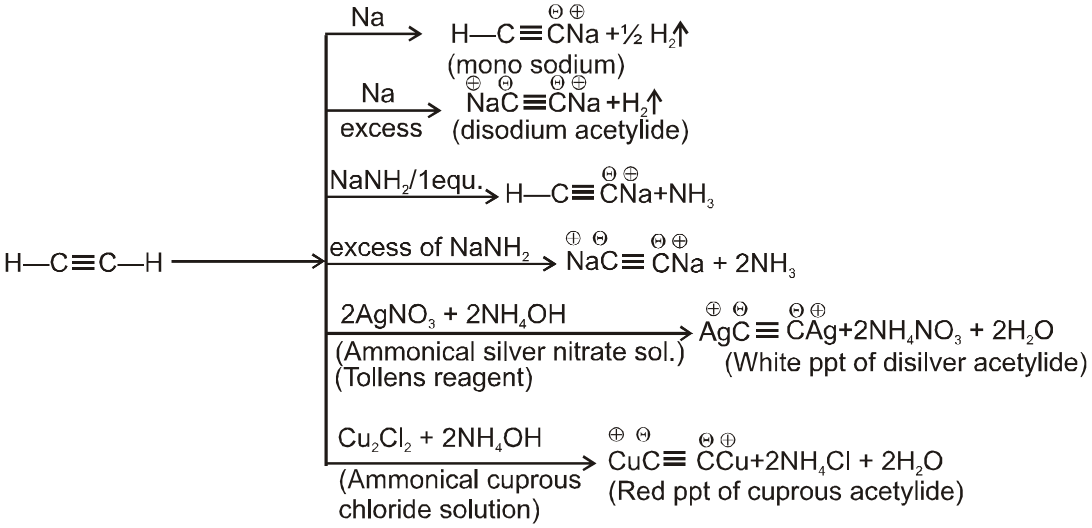
(6) The hybridization of carbon atoms having triple bond ($C \equiv C$) in alkynes is sp

(7) Overlapping of these sp hybrid orbitals with each other and with 1–s of the hydrogen orbitals gives the sigma bond framework which is linear (180°) structure.

(8) Two π bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90°) to each other, forming one π bond with electron density above and below the C–C sigma bond, and the other with electron density in front and in back of the sigma bond. This result in a cylindrical π electron cloud around σ bonded structure



Note : Any type of stereoisomerism does not arise in acetylenic bond due to linearity of $C \equiv C$ bond.

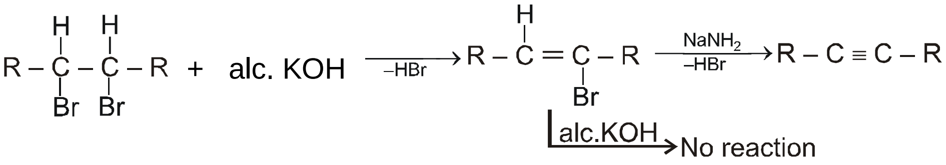


All these reactions are possible with 1-alkyne or acetylene.

2. Methods of preparation :

2.1. By Double Dehydrohalogenation of Gem and Vicinal Dihalide :

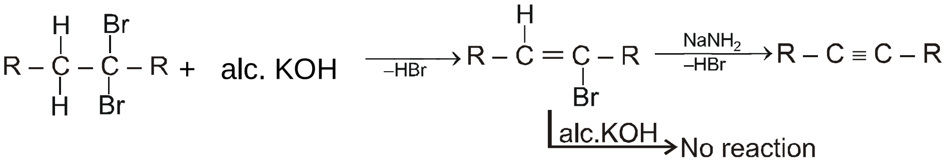
(A) Vicinal Dihalide :



$$R-\overset{H}{\underset{Br}{C}}-\overset{H}{\underset{Br}{C}}-R + \text{alc. KOH} \xrightarrow[-HBr]{} R-\overset{H}{C}=\underset{Br}{C}-R \xrightarrow[-HBr]{NaNH_2} R-C\equiv C-R$$

$NaNH_2$ is more basic than alc. KOH.

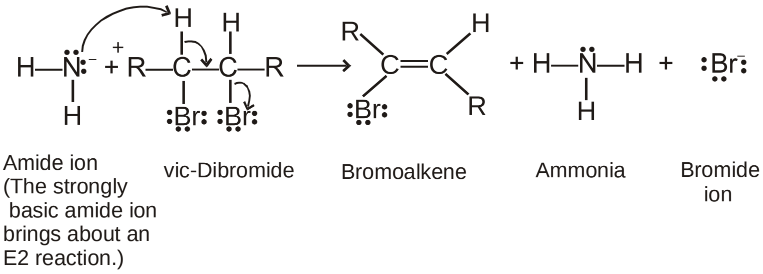
(B) Gem Dihalides :



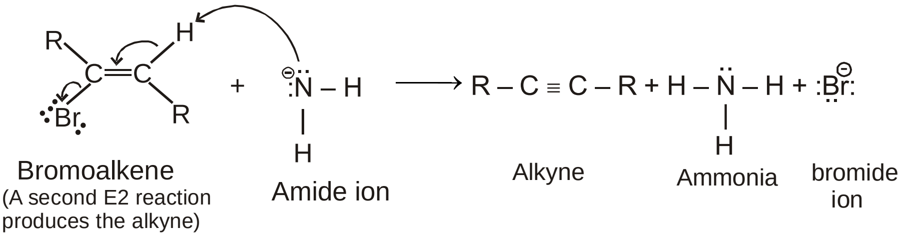
$$R-\overset{H}{\underset{H}{C}}-\overset{Br}{\underset{Br}{C}}-R + \text{alc. KOH} \xrightarrow[-HBr]{} R-\overset{H}{C}=\underset{Br}{C}-R \xrightarrow[-HBr]{NaNH_2} R-C\equiv C-R$$

Mechanism :

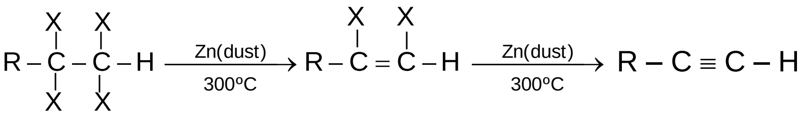
Step 1 :



Step 2 :



2.2. From Tetrahaloalkanes (Dehalogenation) :



$$R-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}-H \xrightarrow[300^{o}C]{Zn(dust)} R-\overset{X}{C}=\overset{X}{C}-H \xrightarrow[300^{o}C]{Zn(dust)} R-C\equiv C-H$$

Note : In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

2.3. Synthesis of Higher Alkynes :

(A) With Na : When acetylene or 1–alkyne react with Na in presence of liq. NH_3 then an intermediate compound sodium acetylide or sodium alkynide is formed which gives higher alkyne with alkyl halide.

$$2\,H-C\equiv C-H+2\,Na\xrightarrow[-H_2]{\text{liq. }NH_3}2H-C\equiv \overset{\ominus\,\oplus}{CNa}\xrightarrow{X-R}H-C\equiv C-R$$

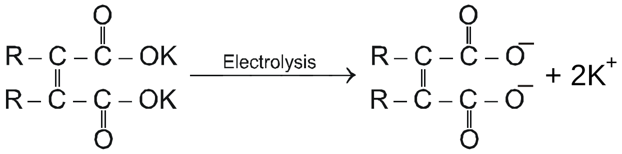
$$2R-C\equiv C-H+2Na\xrightarrow[-H_2]{\text{liq. }NH_3}2R-C\equiv \overset{\ominus\,\oplus}{CNa}\xrightarrow{X-R'}R-C\equiv C-R'$$

(B) With GR : When acetylene or 1–alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.

$$H-C\equiv CH+R-Mg-X\xrightarrow[-RH]{}H-C\equiv C-MgX\xrightarrow[-MgX_2]{XR}H-C\equiv C-R$$

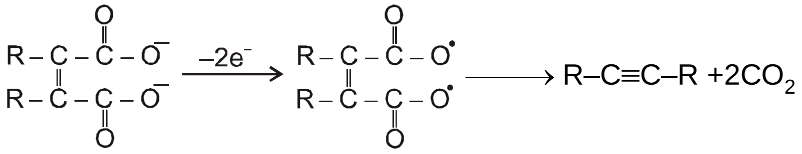
$$R-C\equiv C-H+R-Mg-X\xrightarrow[-RH]{}R-C\equiv C-Mg-X\xrightarrow{R'-X}R-C\equiv C-R'$$

2.4. From Kolbe's Synthesis :



$$\begin{array}{c}R-C-\overset{\overset{O}{\|}}{C}-OK\\ \|\\ R-C-\underset{\underset{O}{\|}}{C}-OK\end{array}\xrightarrow{\text{Electrolysis}}\begin{array}{c}R-C-\overset{\overset{O}{\|}}{C}-O^-\\ \|\\ R-C-\underset{\underset{O}{\|}}{C}-O^-\end{array}+2K^+$$

At Anode :



$$\begin{array}{c}R-C-\overset{\overset{O}{\|}}{C}-O^-\\ \|\\ R-C-\underset{\underset{O}{\|}}{C}-O^-\end{array}\xrightarrow{-2e^-}\begin{array}{c}R-C-\overset{\overset{O}{\|}}{C}-O^\bullet\\ \|\\ R-C-\underset{\underset{O}{\|}}{C}-O^\bullet\end{array}\longrightarrow R–C\equiv C–R+2CO_2$$

Unstable

At Cathode : $2H_2O+2e^{\ominus}\longrightarrow H_2+2OH^{\ominus}$

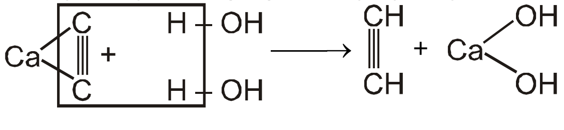
$2OH^-+2K^+\longrightarrow 2KOH$

If R = H, product will be $CH\equiv CH$; If R = CH_3, product will be $CH_3-C\equiv C-CH_3$.

2.5. Preparation of Acetylene :

It is first member of alkyne can be prepared by using any one of the following methods.

(a) In laboratory acetylene if prepared by hydrolysis of calcium carbide.



(b) It can also be prepared from $CHCl_3$ with Ag dust.

$$H-C\boxed{Cl_3+6Ag+Cl_3}-CH\xrightarrow[-6AgCl]{}H-C\equiv C-H$$

(c) $2CHI_3+6Ag\xrightarrow{\Delta}H—C\equiv C—H+6AgI$

Note : Preparation of Higher alkyne from acetylene :

Higher alkyne are prepared from acetylene because of its acidic nature.

(d) $2Mg^{+2}(\overset{-}{C}\equiv C-C^{3-})\xrightarrow{H_3O^+}Mg(OH)_2+CH\equiv C-CH_3$ (Propyne)

3. Physical Properties of Alkyne :

(i) Alkynes are colourless, odourless and tasteless.

(ii) Lower alkynes are partially soluble in H_2O. (It is due to its polarizability)

(iii) Higher alkynes are insoluble in water due to more % of covalent character.

(iv) Completely soluble in organic solvents.

(v) Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.

(vi) Upto C_4 alkynes are gaseous, C_5–C_{11} liquid, C_{12} & above are solids.

(vii) Acetylene & 1-alkyne are acidic in nature. It is due to presence of active H.

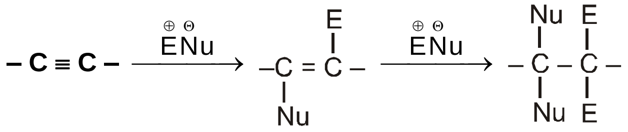
(viii) Order of Solubility, density, B.P., M.P. and Acidic nature : Alkyne > Alkene > Alkane

* All terminal alkynes are acidic in nature.

4. Chemical Properties of Alkyne :

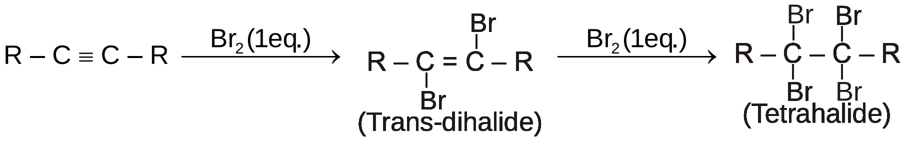
Electrophilic Addition to Alkynes :

General Reaction :



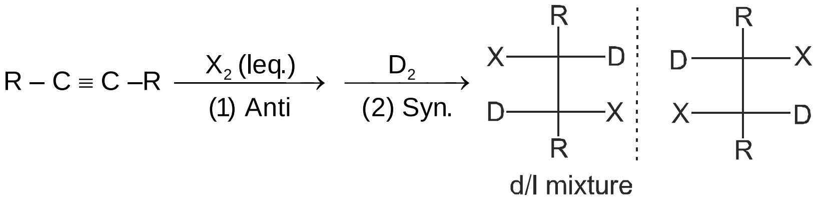
$$-C\equiv C- \xrightarrow{\overset{\oplus\ \ominus}{E\,Nu}} -\underset{Nu}{C}=\overset{E}{C}- \xrightarrow{\overset{\oplus\ \ominus}{E\,Nu}} -\overset{Nu}{\underset{Nu}{C}}-\overset{E}{\underset{E}{C}}-$$

4.1. Halogenation :



$$R-C\equiv C-R \xrightarrow{Br_2(1eq.)} \underset{\text{(Trans-dihalide)}}{R-\underset{Br}{C}=\overset{Br}{C}-R} \xrightarrow{Br_2(1eq.)} \underset{\text{(Tetrahalide)}}{R-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-R}$$

Remark : - Reaction is Anti in both step



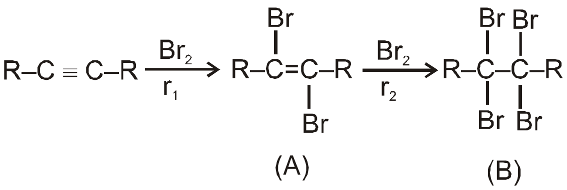
$$R-C\equiv C-R \xrightarrow[\text{(1) Anti}]{X_2\,(1eq.)} \xrightarrow[\text{(2) Syn.}]{D_2}$$

d/l mixture

$$R-C\equiv C-R \xrightarrow[\text{(1) Syn.}]{D_2/Pd/CaCO_3} \xrightarrow[\text{(2) anti}]{Br_2/CCl_4} \text{Same } (d/\ell \text{ mixture})$$

[lindlar, catalyst]

Addition of bromine : Over triple bond finally give tetrabromide product ; which involves formation of dibromo product first.



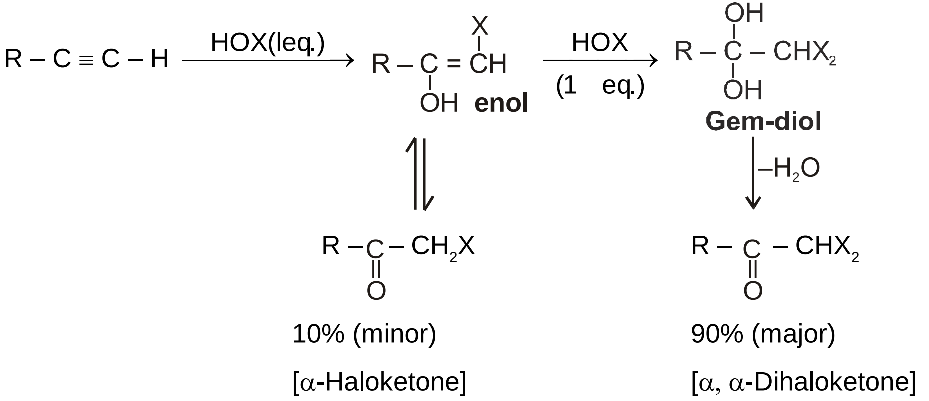
$$R-C\equiv C-R \xrightarrow[r_1]{Br_2} \underset{(A)}{R-\overset{Br}{C}=\underset{Br}{C}-R} \xrightarrow[r_2]{Br_2} \underset{(B)}{R-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-R}$$

Remarks 1. In above reaction $r_2 > r_1$

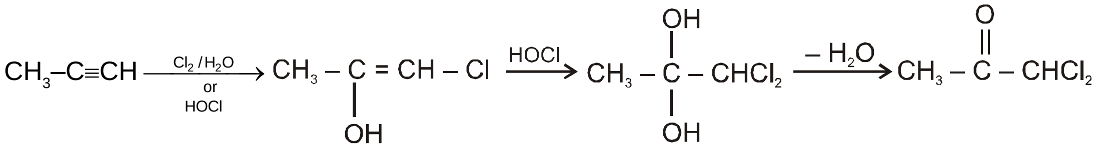
2. Alkyl carbocation is more stable than vinyl carbocation

4.2. Addition of HOX :

Alkynes + HOX ⟶ α, α-dihaloketone + α-haloketone
(90% major) (10% minor)



Ex.

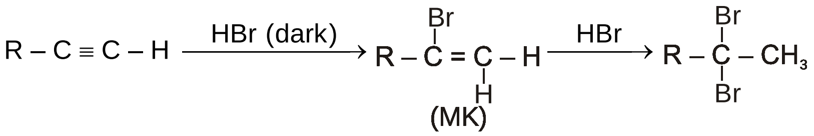


Remarks :

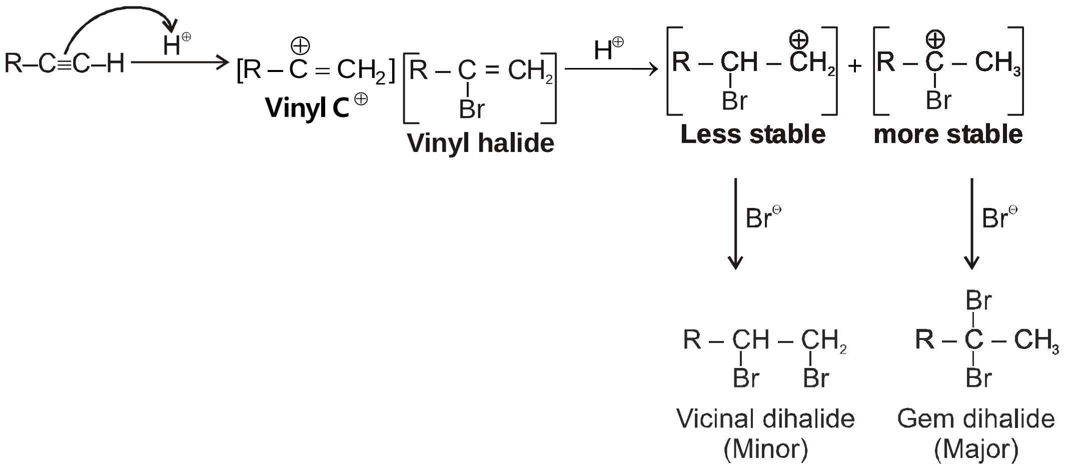
(i) Two molecules of HOX can be added, the end product is α, α-Dihaloketone.

(ii) The intermediate product is an enol which gives a minor product α-haloketone.

4.3. Addition of Hydrogen Halides (+ HX) :



Mechanism :



Remarks :

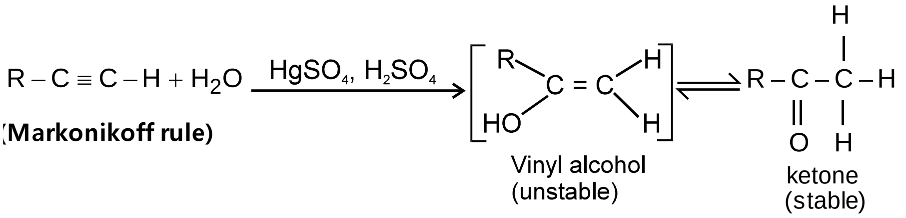
(i) Markovnikov's Addition in both steps.

(ii) If two moles of HX are added the final product is Gemdihalide.

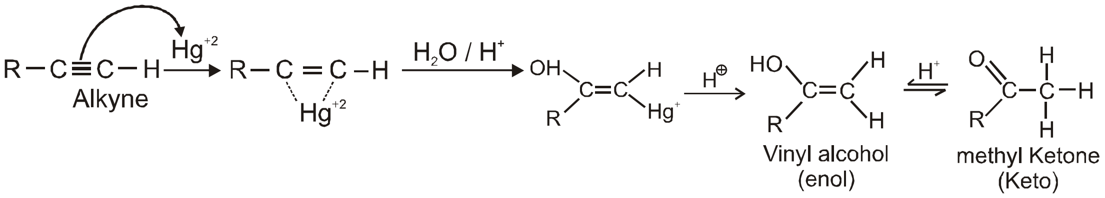
(iii) Electrophilic addition to terminal alkyne is regioselective.

4.4. Addition of H_2O (Hydration Reaction) :

(i) Mercuric ion catalyzed hydration :

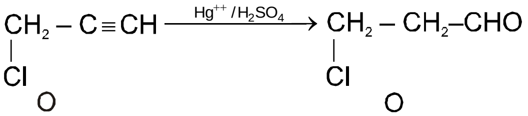


Mech.



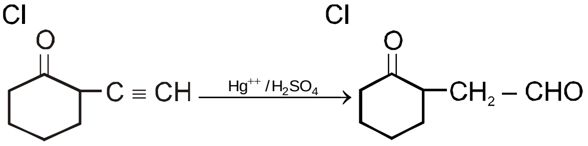
Note: By above reaction it is clear that carbonyl carbon is formed from that carbon of 'C≡C' over which nucleophile water attacks.

Ex. (i)

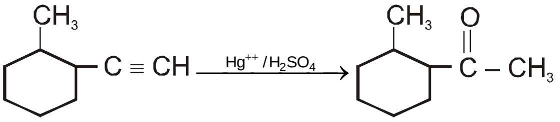


$$\underset{\underset{Cl}{|}}{CH_2}-C\equiv CH \xrightarrow{Hg^{++}/H_2SO_4} \underset{\underset{Cl}{|}}{CH_2}-CH_2\text{–}CHO$$

(ii)



(iii)

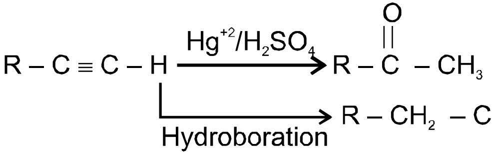


Remarks :
(1) Alkynes add one molecule of water.
(2) The product enol tautomerises to a carbonyl compound (aldehyde or ketone) and further addition does not take place.
(3) The reaction is catalysed by Hg^{+2} ions.
(4) The product is Markownikoff Addition of water.
(5) If hydroboration method is used, then Anti Markownikoff addition of water takes place.

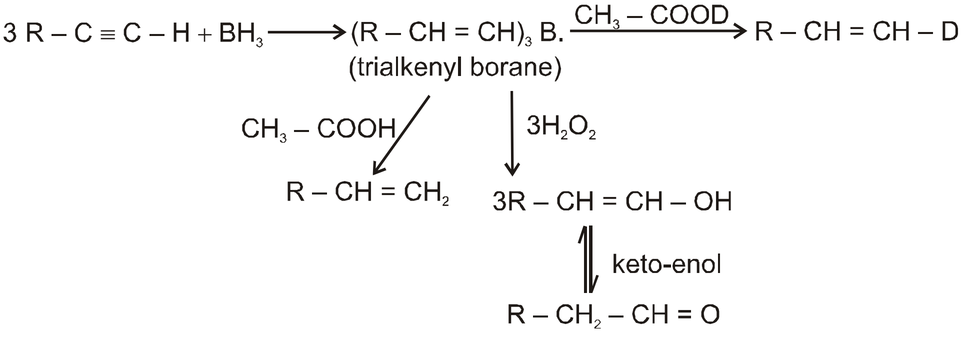
Important:- The product does not appears to be addition product.

(ii) Hydroboration Oxidation of Alkynes :

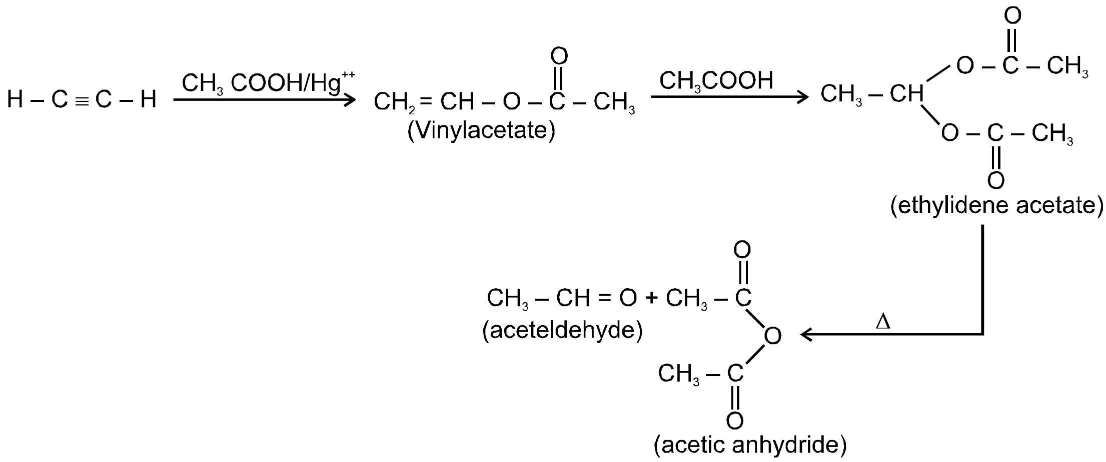
It is used to get aldehyde from terminal alkyne.



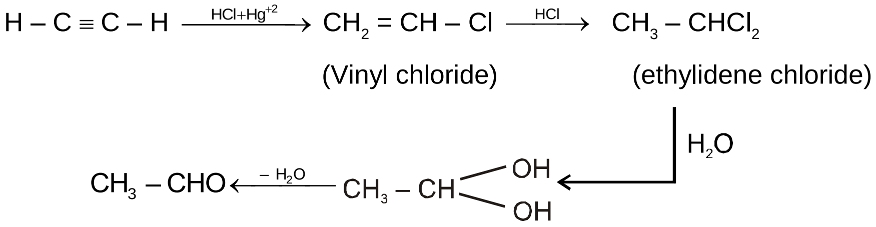
(i)



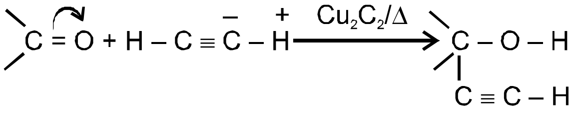
(ii)

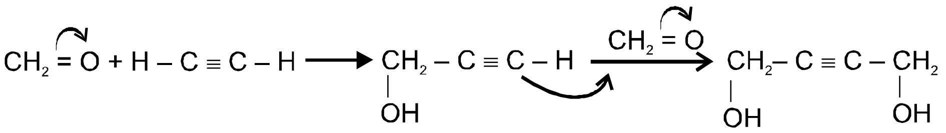


(iii)

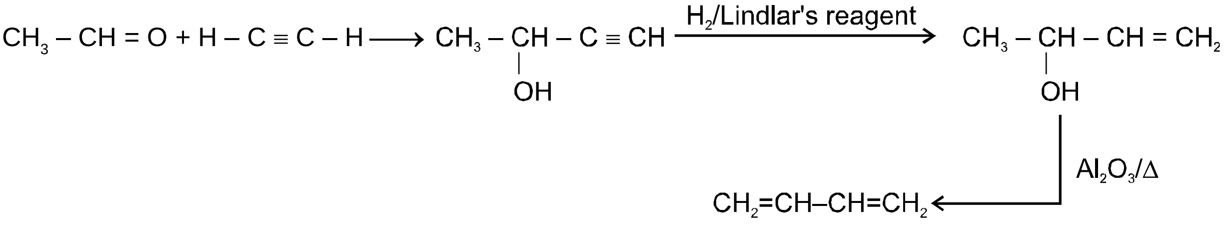


4.5. Nucleophilic addition of 1-alkyne/acetylene over carbonyl compound



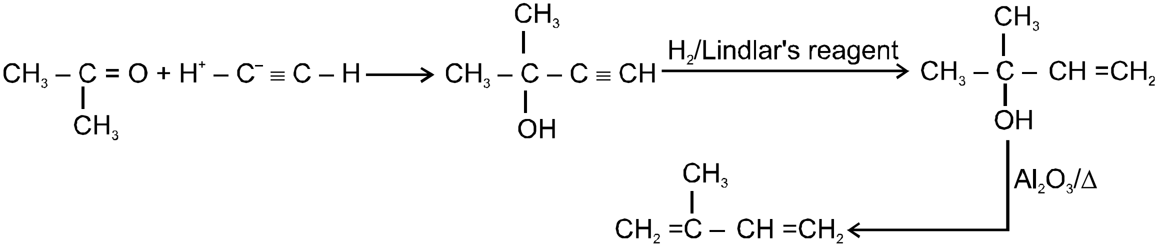


(Dihydroxymethylacetylene)
(But–2–yne–1,4–diol)



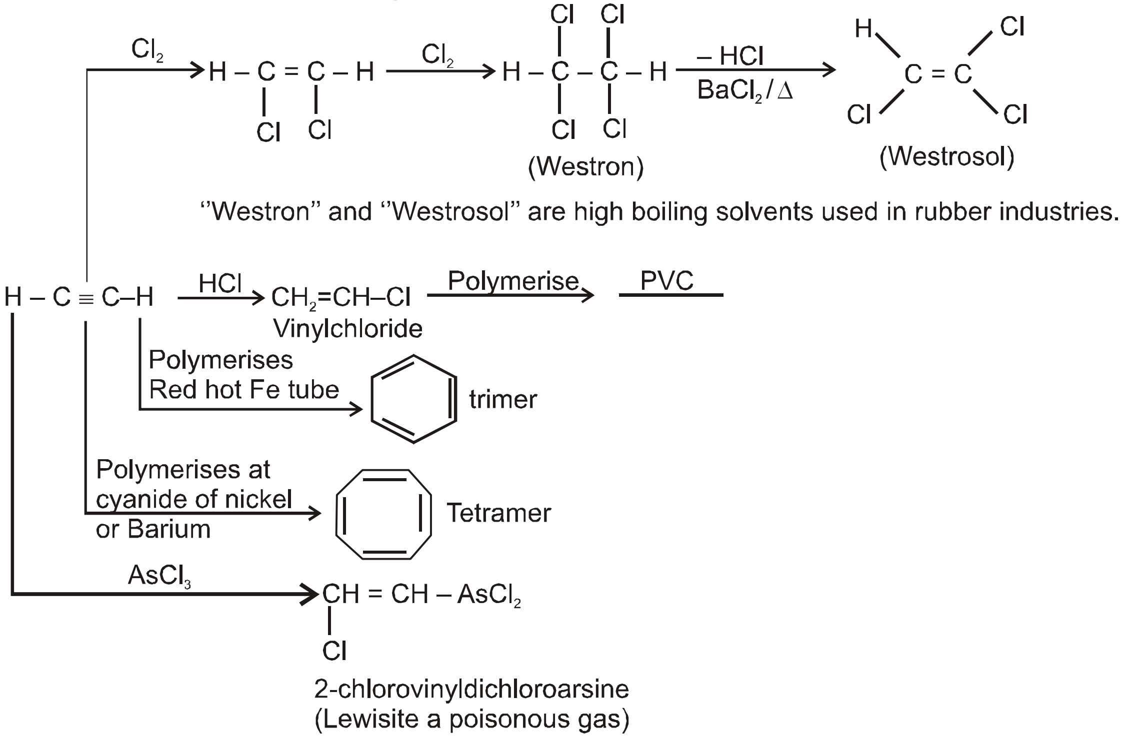
Que. How will you get isoprene from acetone .

Ans.



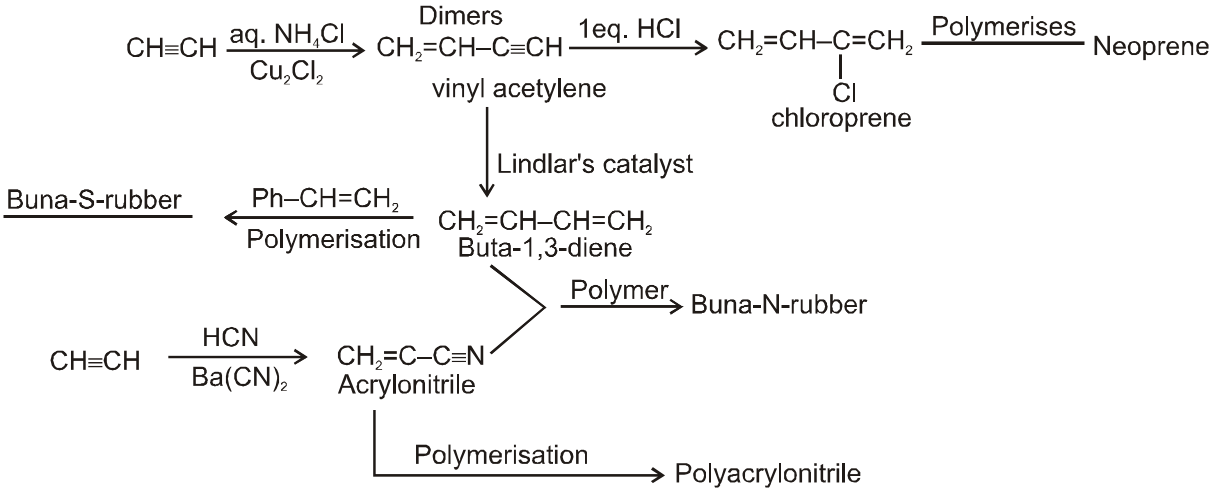
(2-methylbut-1, 3-diene)
(Isoprene) (monomer of natural rubber)

4.6. Other reactions of Alkynes :

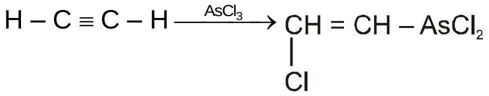


"Westron" and "Westrosol" are high boiling solvents used in rubber industries.

2-chlorovinyldichloroarsine
(Lewisite a poisonous gas)



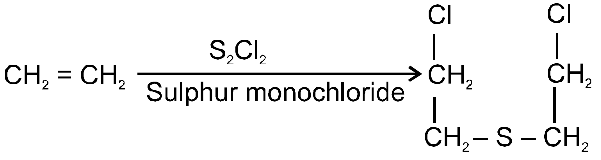
Note* : Neoprene, Polybutadiene, Buna-s and Buna-N are synthetic rubbers.



$$H-C\equiv C-H \xrightarrow{AsCl_3} \underset{\displaystyle Cl}{\underset{|}{C}}H = CH - AsCl_2$$

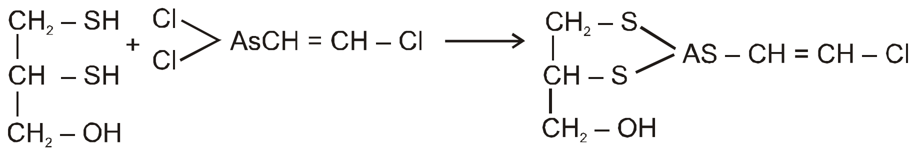
2-chlorovinyldichloroarsine (Lewisite a poisonous gas)

But war gas is musturd gas which is obtained from ethylene as :



$$CH_2 = CH_2 \xrightarrow[\text{Sulphur monochloride}]{S_2Cl_2} \begin{matrix} Cl & & & Cl \\ | & & & | \\ CH_2 & & & CH_2 \\ | & & & | \\ CH_2 & - & S - & CH_2 \end{matrix}$$

BAL (British anti lewisite) is antidose of lewisite which gives non-toxic cyclic products.



(nontoxic cyclic product)

Linear polymerisation of acetylene : -

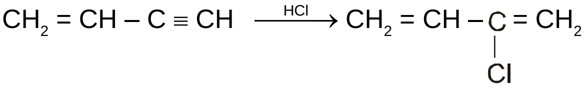
$$H-C\equiv C-H + H-C\equiv C-H \xrightarrow[\Delta]{Cu_2Cl_2/NH_4Cl} CH_2=CH-C\equiv C-H$$

(Vinylacetylene)

$$CH_2=CH-C\equiv C-CH=CH_2 \xleftarrow{H-C\equiv C-H\ +\ Cu_2Cl_2/NH_4Cl}$$

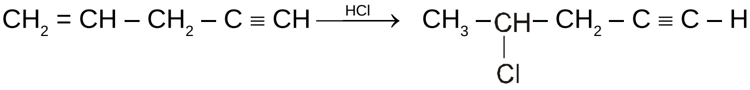
(Divinylacetylene)

Reaction of enyne :-



$$CH_2=CH-C\equiv CH \xrightarrow{HCl} CH_2=CH-\underset{\underset{Cl}{|}}{C}=CH_2$$

(Vinylacetylene)



$$CH_2=CH-CH_2-C\equiv CH \xrightarrow{HCl} CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2-C\equiv C-H$$

(akylacetylene)

Que. Why electrophilic addition reaction is more favorable to double bond as compared to triple bond.

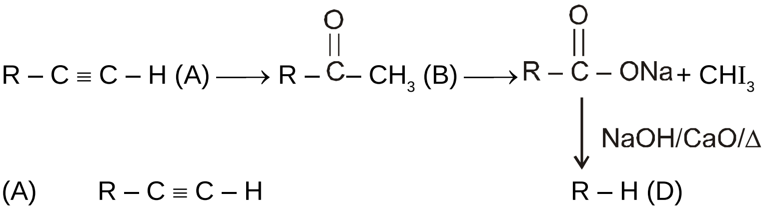
Ans. Though former one is having $2\pi\ e^-$ only and latter one is having $4\pi\ e^-$.

In case of (≡) carbon atom, C-atom is in sp hybridized state which is more electronegative and thus π electron are being held by this more electronegative C–atom i.e. they are not free to be attacked by electrophile.

Que. A give $\longrightarrow$ white ppt with tollen reagent.

$$C_8H_6(A) \xrightarrow{Hg^{++}/H_2SO_4} (B) \xrightarrow{I_2/NaOH} (C) + CHI_3 \xrightarrow{NaOH/(CaO)/\Delta} (D)\ \text{liquid hydro carbon}$$

Ans.



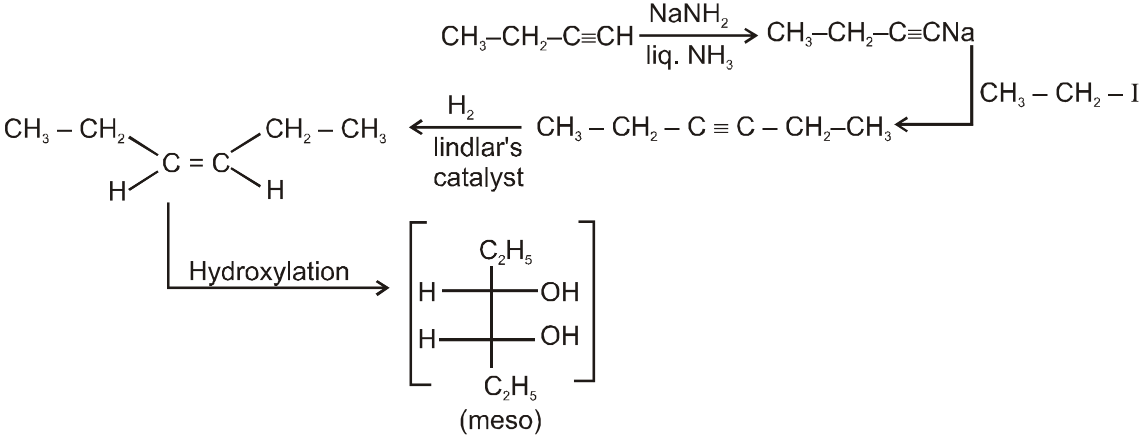
$$R-C\equiv C-H\ (A) \longrightarrow R-\overset{\overset{O}{||}}{C}-CH_3\ (B) \longrightarrow R-\overset{\overset{O}{||}}{C}-ONa + CHI_3 \xrightarrow{NaOH/CaO/\Delta} R-H\ (D)$$

(A) $R-C\equiv C-H$

$R = C_8H_6 - C_2H = C_6H_5$

Que. How will you get meso hexane–3, 4–diol from 1-butyne ?

Ans.



Que. Write apropriate interconversion reaction of the following.

$H-C\equiv C-H \longrightarrow$ (i) meso-2,3-dibromobutane (ii) dl-butane-2, 3- diol

Ans.