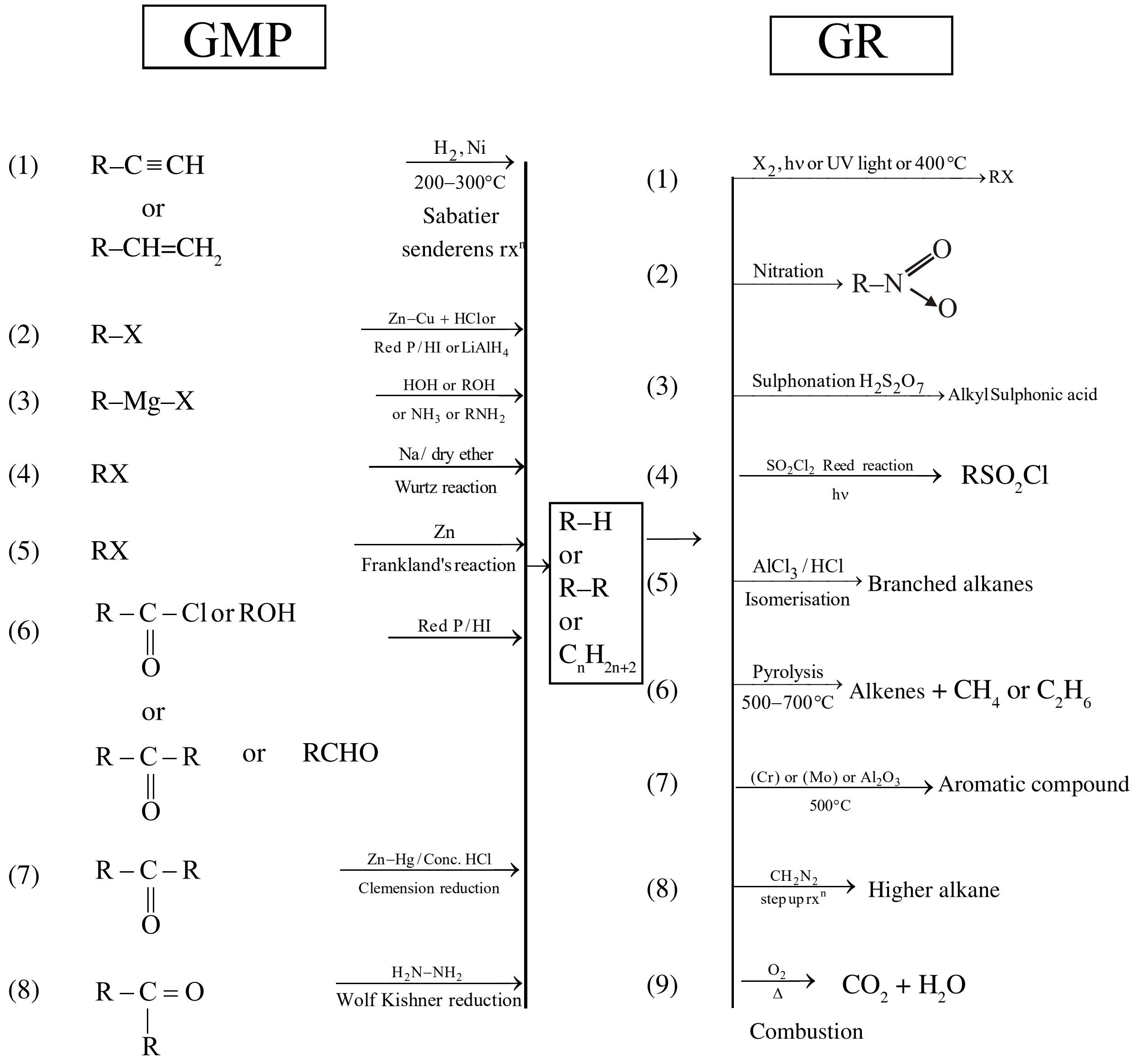
HYDROCARBON

REACTION CHART FOR ALKANES



ALKANES

Introduction of Alkanes

(a) Branched and unbranched aliphatic saturated open chain hydrocarbons are called member of alkanes.

(b) CH_4 is also known as Marsh gas (fire damp).

(c) Calore gas : Mixture of n–butane and isobutane.

(d) LPG (Liquefied petroleum gas) : liquid propane, isobutane.

(e) Natural gas : 80% methane + 10% ethane + 10% propane + small amounts of H_2, N_2, CO_2 etc.

(f) Water gas : $CO + H_2$ (1:1)

(g) Synthesis gas : $CO + 3H_2$(1:3)

General Methods of Preparation

From alkenes and alkynes (Sabatier and Senderens reaction) or (By hydrogenation of alkenes and alkynes) : Alkenes and alkynes on catalytic hydrogenation give alkanes.

$$\underset{\text{Alkene}}{R{-}CH{=}CH{-}R + H_2} \xrightarrow{\text{Catalyst}} \underset{\text{Alkane}}{R{-}CH_2{-}CH_2{-}R}$$

$$\underset{\text{Alkyne}}{R{-}C{\equiv}C{-}R + 2H_2} \xrightarrow{\text{Catalyst}} R{-}CH_2{-}CH_2{-}R$$

Catalyst :

(a) Pd/Pt at ordinary temperature and pressure

(b) Ni, 200–300° C (sabatier)

(c) Raney Nickel at room temp.

(d) Methane can not be prepared by this method

From alkyl Halides (By reduction) :

$$R{-}X \xrightarrow[\text{(Nascent Hydrogen)}]{2H} R{-}H + HX$$

Catalyst :

(i) Zn + HCl

(ii) Zn + CH_3 COOH

(iii) Zn—Cu couple in C_2H_5OH

(iv) Red P + HI

(v) Al – Hg + ethanol

POINTS TO REVISE

- Alkyl halides can also be reduced to alkane by H_2/Pd or $LiAlH_4$ or H_2/Ni.
- Halogen atom of alkyl halide is replaced by hydrogen atom to obtain an alkane.

From alkyl halide (By Wurtz reaction): A solution of alkyl halide in ether on heating with sodium gives alkane.

$$R - X + 2Na + X - R \xrightarrow[\text{ether}]{\text{Dry}} R - R + 2NaX$$

(a) Two moles of alkyl halide are treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

$$2Na + H_2O \longrightarrow 2NaOH + H_2$$

$$\underset{}{CH_3I + NaOH} \longrightarrow \underset{\text{Methanol}}{CH_3OH + NaI}$$

(b) Methane can not be prepared by this method. The alkane produced is higher and symmetrical i.e. it contains double the number of carbon atoms present in the alkyl halide taken.

(c) Two different alkyl halides, on wurtz reaction give all possible alkanes.

(d) The separation of mixture into individual members is not easy because their B.P. are near to each other and thus wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.

From Frankland Reagent:

$$R—X + 2Zn + RX \longrightarrow \underset{\text{Frankland reagent}}{R_2Zn + ZnX_2}$$

$$R_2Zn + R—X \longrightarrow R—R + RZnX$$

From Carboxylic Acid (By decarboxylation) : Sodium salt of saturated monocarboxylic acid on dry distillation with sodalime give alkane.

$$RCOONa + NaOH \xrightarrow[Cao]{\Delta} R—H + Na_2CO_3$$

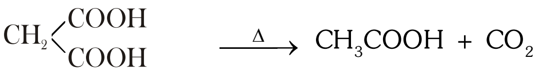
Note :- Sodalime ⇒ NaOH + CaO

POINTS TO REVISE

- The process of elimination of Carbon-di-oxide from Carboxylic acid called decarboxylation.
- The alkane formed by decarboxylation contains one carbon atom less than the original acid.
- Decarboxylation of sodium formate gives H_2

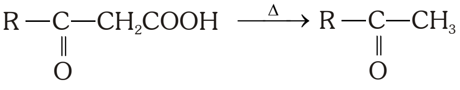
$$\begin{pmatrix} HCOONa + NaOH\,(CaO) \xrightarrow{\Delta} H_2 + Na_2CO_3 \\ CH_3COONa + NaOH + CaO \xrightarrow{\Delta} CH_4 + Na_2CO_3 \end{pmatrix}$$

- If in a compound two carboxylic groups are present and they are attached to same carbon atom then decarboxylation of one of the carboxylic groups takes place simply on heating.



$$CH_2\begin{matrix}\diagup COOH \\ \diagdown COOH\end{matrix} \xrightarrow{\Delta} CH_3COOH + CO_2$$

- $CH_3—CH_2—CH_3$ can be prepared by Butanoic acid and 2–Methyl propanoic acid.
- β-Keto acids are decarboxylated readily simply on heating (soda lime is not required)



$$R—\underset{\underset{O}{\|}}{C}—CH_2COOH \xrightarrow{\Delta} R—\underset{\underset{O}{\|}}{C}—CH_3$$

(6) From carboxylic acid (By Kolbe's electrolysis process) : Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.

$$2RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} \underbrace{R - R + 2CO_2}_{\text{At Anode}} + \underbrace{2NaOH + H_2}_{\text{At Cathode}}$$

$$2C_2H_5 - COONa \xrightarrow[2H_2O]{\text{electro.}} C_2H_5 - C_2H_5 + 2CO_2 + 2NaOH + H_2$$

POINTS TO REVISE

- Electrolysis of an acid salt gives symmetrical alkane, However in case of a mixture of Carboxylic acid salts, all probable alkanes are formed.

$$R'COOK + R''COOK \xrightarrow{\text{Electrolysis}} (R'—R'' + R'—R' + R''—R'') + 2CO_2 + H_2 + 2NaOH$$

- At anode alkane and CO_2 gas is formed while at cathode NaOH and H_2 gas is formed.
- The concentration of NaOH in solution is increased with time so pH of solution is also increased.

From alkanol, alkanals, Alkanone and alkanoic acid (By reduction) :

The reduction of either of the above compound in presence of red P and HI gives corresponding alkane.

$$R—OH + 2HI \xrightarrow[150^\circ C]{\text{Red P}} R—H + H_2O + I_2$$

$$R—CHO + 4HI \xrightarrow[150^\circ C]{\text{Red P}} RCH_3 + H_2O + 2I_2$$

$$R—CO—R + 4HI \xrightarrow[150^\circ C]{\text{Red P}} R—CH_2—R + H_2O + 2I_2$$

$$RCOOH + 6HI \xrightarrow[150^\circ C]{\text{Red P}} R—CH_3 + H_2O + 3I_2$$

In the above reaction I_2 is formed which may react with alkane to form alkyl halide. So red P is added in the reaction to remove I_2 formed in the reaction.

$$R—CH_3 + I_2 \rightleftharpoons R—CH_2—I + HI$$

$$2P + 3I_2 \longrightarrow 2PI_3$$

From alkanones (By Clemmensen's method) : Carbonyl compound may also be reduced with Zinc amalgam and concentrated HCl (Zn–Hg/HCl), this reaction is called Clemmensen reduction.

$$R—CO—R' + 4H \xrightarrow[\text{con.HCl}]{\text{Zn–Hg}} R—CH_2—R' + H_2O$$

From alkanals and alkanones (By Wolf Kishner reaction) :

$$>C=O \xrightarrow[(2)\,OH^-/\text{heat}]{(1)\,NH_2NH_2} >CH_2$$

From G.R. :

(a) **Formation of alkanes with same number of C atoms :** Grignard reagent reacts with the compounds having active hydrogen to form alkane.

$$\begin{aligned} R-Mg-X + H-O-H &\longrightarrow R-H + Mg(OH)X \\ + R-O-H &\longrightarrow R-H + Mg(OR)X \\ + R-NH-H &\longrightarrow R-H + Mg(NHR)X \end{aligned}$$

This reaction is used to determine the number of active H-atoms in the compound this is known as Zerewitnoff's method.

(b) **G.R. react with alkyl halide to give higher alkanes :**

$$RMgX + R'-X \longrightarrow R-R' + MgX_2$$

Corey-House Synthesis : This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type R—R'

$$R-X \xrightarrow[\substack{(ii)\,CuX \\ (iii)\,R'-X}]{(i)\,Li} R-R' + RCu + LiX$$

Note: In Corey-house reaction symmetrical and unsymmetrical alkane both can be formed.

From metal carbide (By hydrolysis) :

Only CH_4 can be obtained by the hydrolysis of Be or Al carbides

$$Al_4C_3 + 12H_2O \xrightarrow{\Delta} 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \xrightarrow{\Delta} 2Be(OH)_2 + CH_4$$

Physical & Chemical Properties of alkane

Physical properties

(i) **Solubility** : Alkanes being non polar and thus insoluble in water but soluble in nonpolar solvents

Ex. C_6H_6, CCl_4 ,ether etc.

(ii) **Boiling point** - $\propto$ molecular weight (for n-alkanes)

$$\because \boxed{\text{Vander Waals force of attraction} \propto \text{molecular weight} \propto \text{surface area of molecule.}}$$

i.e. boiling point Pentane < hexane < heptane

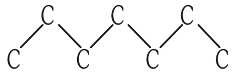
Also boiling point $\propto \dfrac{1}{\text{number of side chain}}$

because the shape approaches to spherical which results in decrease in van der Waal's forces (as surface area decreases)

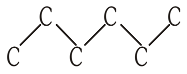
Thus boiling point n–Pentane > Isopentane > neopentane

(iii) **Melting Point :** M.P. of alkanes do not show regular trend. Alkanes with even number of carbon atoms have higher M.P. than their adjacents alkanes of odd number of carbon atoms.

The abnormal trend in M.P. is due to the fact that alkanes with odd carbon atoms have their end carbon atom on the same side of the molecule and in even carbon atom alkane the end Carbon atom on opposite side. Thus alkanes with even carbon atoms are packed closely in crystal lattice to permit greater intermolecular attractions.



<



Odd number of carbon

Even number of carbon

Chemical Properties

Oxidation :

(a) **Complete oxidation or combustion :** Alkanes burn readily with non-luminous flame in presence of air or oxygen to give CO_2 and water with evolution of heat. Therefore, alkanes are used as fuels.

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)\ H_2O + Q;\ (\Delta H = -ve)$$

(b) **Incomplete oxidation :** In limited supply of air, alkane gives carbon black and CO.

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

C–black (used in printing ink)

(c) **Catalytic oxidation :**

(i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.

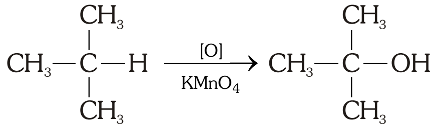
$$2CH_4 + O_2 \xrightarrow[\text{High P and T}]{\text{Red hot Cu or Fe tube}} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow[230^0C,100atm]{Mo_2O_3} HCHO + H_2O$$

(ii) Alkanes on oxidation in presence of maganese acetate give fatty acids.

$$CH_3(CH_2)_nCH_3 \xrightarrow[\text{high Temp}]{(CH_3COO)_2Mn} CH_3(CH_2)_nCOOH$$

(iii) Tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-H \xrightarrow[KMnO_4]{[O]} CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-OH$$

Substitution Reactions : Substitution reaction in alkanes shows free radical mechanism.

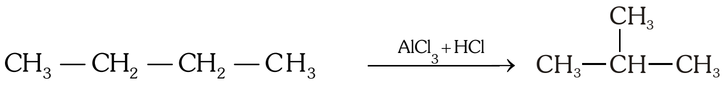
$$CH_4 + Cl_2 \xrightarrow{h\nu} CH_3\text{–}Cl + HCl \text{ (mono-substitution product)}$$

$$CH_4 + \underset{\text{excess}}{Cl_2} \xrightarrow{h\nu} CH_3\text{–}Cl \text{ (major)}$$

$$\underset{\text{excess}}{CH_4} + Cl_2 \xrightarrow{h\nu} CCl_4$$

$$CH_3CH_2CH_3 + Br_2 \xrightarrow{h\nu} CH_3\text{–}CHBr\text{–}CH_3 + CH_3\text{–}CH_2\text{–}CH_2\text{–}Br$$

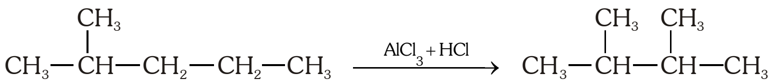
Isomerization: Unbranched chain alkanes on heating with $AlCl_3$ + HCl / 200⁰C are converted in to branched chain alkanes



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3+HCl} CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_3$$

n-butane Isobutane

Branched chain alkanes converted to more branched alkane.



$$CH_3-\overset{\overset{\large CH_3}{|}}{C}H-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3+HCl} CH_3-\overset{\overset{\large CH_3}{|}}{C}H-\overset{\overset{\large CH_3}{|}}{C}H-CH_3$$

Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

Pyrolysis or Cracking or thermal decomposition : When alkanes are heated to 500-700⁰C they are decomposed in to lower hydrocarbon. This decomposition is called pyrolysis.

Ex. $CH_4 \xrightarrow{1000^\circ C} C + H_2$

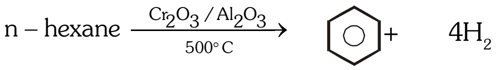
$$CH_3-CH_3 \xrightarrow[\text{absence of air}]{500^\circ C} CH_2=CH_2+H_2$$

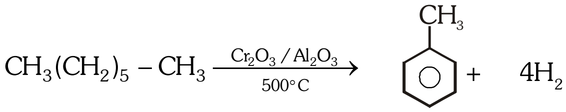
$$CH_3CH_2CH_3 \longrightarrow \begin{cases} CH_2=CH_2+CH_4 \\ CH_3-CH=CH_2+H_2 \end{cases}$$

n-Butane $\xrightarrow{\text{Cracking}}$ 1-Butene + 2–Butene + Ethane + Ethene + Propene + CH_4 + H_2

Aromatization:

Unbranched higher alkanes (from 6 to 10 carbon atoms) when heated in presence of oxides of Cr, Mo, V on Al_2O_3 support at 500⁰ C aromatic hydrocarbons are formed.





n-heptane Toluene

PETROLEUM

Flash Point : Flash point of an oil is that minimum temperature at which the oil gives so much vapour that it starts burning in the presence of air when it comes in contact with a spark. Flash point depends on local temperature of countries.

Flash point of kerosene in **India ⇒ 44⁰C, in France ⇒ 35⁰C, in England ⇒ 23⁰C**

Knocking : Preignition of the fuel-air mixture in the cylinder ahead of the flame causes knocking. knocking reduces efficiency of the engine and also damages the cylinder and piston of the engine.

Octane Number (Quality of Gasoline) : Octane no. is a scale which is used to determine the quality of a fuel in an internal engine. Two pure hydrocarbons are selected as standard.

(i) n - heptane – straight chain hydrocarbon knocks very badly have octane no. zero

(ii) Iso-octane – branched hydrocarbon, good antiknocking properties, have octane no. 100.

Octane no. of a fuel : The percentage of iso-octane by volume in a mixture of iso-octane and n-heptane which has the same antiknocking properties as the fuel under examination.

For example – Let knocking of a fuel is same as a mixture of 70% iso-octane and 30% n-heptane, then its octane no. is 70.

Order of quality of Gasoline or petrol : (i) Length of chain ↑ , the octane no. ↓

(ii) branches ↑ octane no. ↑

Straight chain alkane < branched chain alkane < olefins < cycloalkane < aromatic compound

Octane number can be increased by : (i) Cracking (ii) Isomerization (iii) Aromatization

Antiknocking agents – (Gasoline additives) : Quality of a fuel is increased by :

(i) By using fuel of higher octane no.

(ii) By addition of certain compounds to the gasoline which reduce knocking. These are called antiknocking agents.

Ex. Tetraethyl lead (TEL) – $Pb(C_2H_5)_4$

Tetra methyl lead – $Pb(CH_3)_4$

In cylinder of engine $Pb(C_2H_5)_4$ decomposes in ethyl radicals which combine with the radicals produced due to irregular combustion and this prevents knocking.

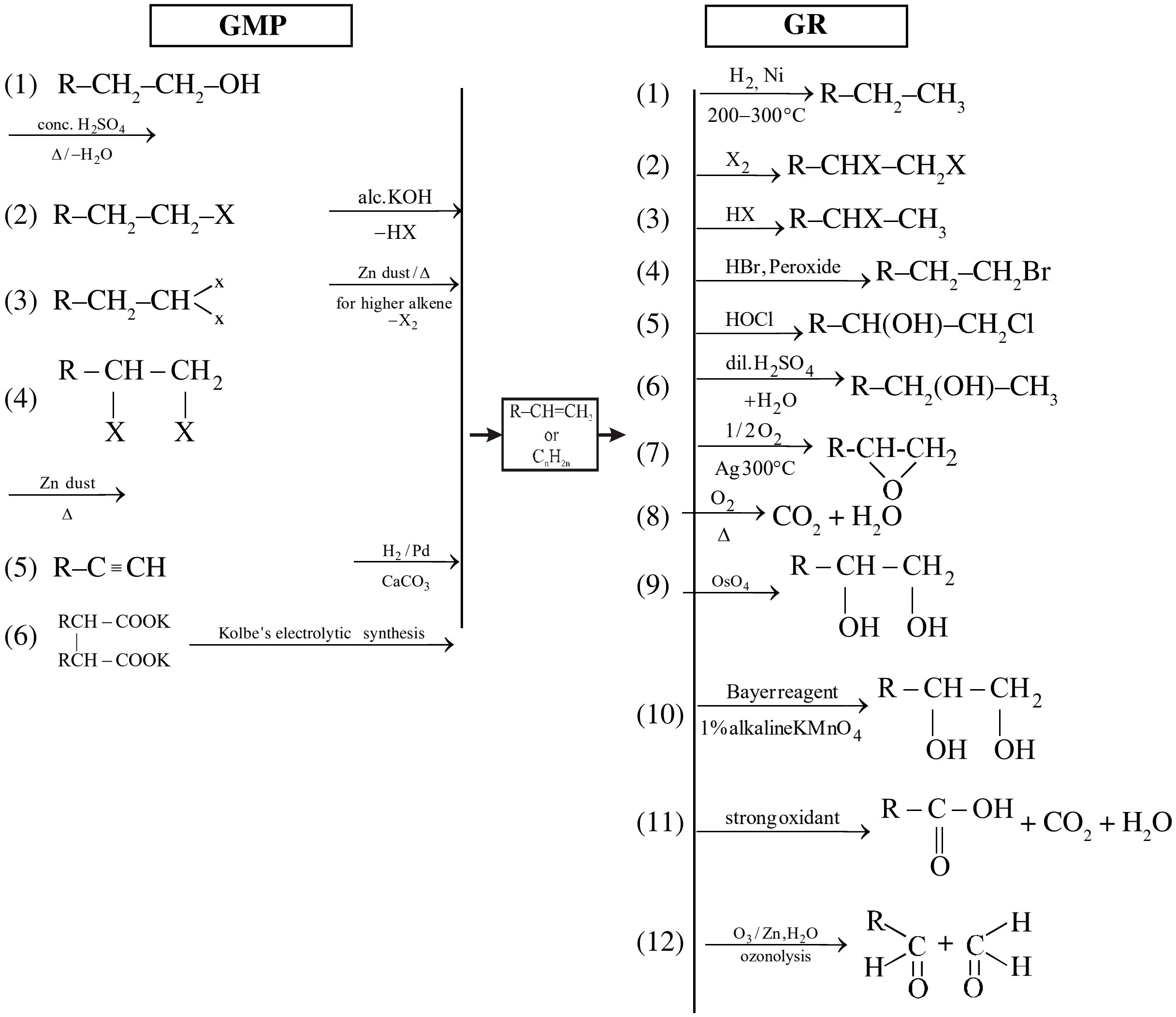
$$Pb(C_2H_5)_4 \xrightarrow{\text{heat}} Pb + 4CH_3\dot{C}H_2$$

but combustion of TEL with petrol gives Litharge (PbO) which deposited in cylinder walls and piston has jammed. So Ethylene dibromide is added with petrol.

$$Br—CH_2—CH_2—Br \longrightarrow CH_2{=}CH_2 + Br_2$$

$$Pb + Br_2 \longrightarrow PbBr_2\uparrow \text{ (Volatile)}$$

REACTION CHART FOR ALKENES



GMP

(1) $R{-}CH_2{-}CH_2{-}OH \xrightarrow[\Delta/-H_2O]{\text{conc. } H_2SO_4}$

(2) $R{-}CH_2{-}CH_2{-}X \xrightarrow[-HX]{\text{alc.KOH}}$

(3) $R{-}CH_2{-}CH{<}\begin{matrix}X\\X\end{matrix} \xrightarrow[\text{for higher alkene } -X_2]{\text{Zn dust}/\Delta}$

(4) $\underset{X}{\underset{|}{R-CH}}-\underset{X}{\underset{|}{CH_2}} \xrightarrow[\Delta]{\text{Zn dust}}$

(5) $R{-}C{\equiv}CH \xrightarrow[CaCO_3]{H_2/Pd}$

(6) $\begin{matrix}RCH-COOK\\|\\RCH-COOK\end{matrix} \xrightarrow{\text{Kolbe's electrolytic synthesis}}$

$\boxed{\begin{matrix}R{-}CH{=}CH_2\\ \text{or}\\ C_nH_{2n}\end{matrix}}$

GR

(1) $\xrightarrow[200-300°C]{H_2,\ Ni} R{-}CH_2{-}CH_3$

(2) $\xrightarrow{X_2} R{-}CHX{-}CH_2X$

(3) $\xrightarrow{HX} R{-}CHX{-}CH_3$

(4) $\xrightarrow{\text{HBr, Peroxide}} R{-}CH_2{-}CH_2Br$

(5) $\xrightarrow{HOCl} R{-}CH(OH){-}CH_2Cl$

(6) $\xrightarrow[+H_2O]{\text{dil.} H_2SO_4} R{-}CH_2(OH){-}CH_3$

(7) $\xrightarrow[\text{Ag } 300°C]{1/2\,O_2} \underset{\diagdown\ O\ \diagup}{R\text{-}CH\text{-}CH_2}$

(8) $\xrightarrow[\Delta]{O_2} CO_2 + H_2O$

(9) $\xrightarrow{OsO_4} \underset{OH}{\underset{|}{R-CH}}-\underset{OH}{\underset{|}{CH_2}}$

(10) $\xrightarrow[1\%\ \text{alkaline}\ KMnO_4]{\text{Bayer reagent}} \underset{OH}{\underset{|}{R-CH}}-\underset{OH}{\underset{|}{CH_2}}$

(11) $\xrightarrow{\text{strong oxidant}} R-\underset{O}{\underset{\|}{C}}-OH + CO_2 + H_2O$

(12) $\xrightarrow[\text{ozonolysis}]{O_3/Zn,H_2O} \begin{matrix}R\\H\end{matrix}{>}\underset{O}{\underset{\|}{C}} + \underset{O}{\underset{\|}{C}}{<}\begin{matrix}H\\H\end{matrix}$

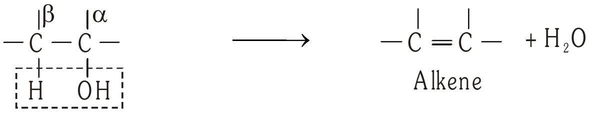
Introduction of Alkenes

Alkene are also called olefins (oil forming) since the first member ethylene (C_2H_4) was found to form an only liquid on reaction with chlorine.

$$CH_2{=}CH_2 + Cl_2 \longrightarrow Cl{-}CH_2{-}CH_2{-}Cl$$

General Methods of Preparation

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**.



$$\underset{\boxed{H\quad OH}}{-\overset{\beta}{C}-\overset{\alpha}{C}-} \longrightarrow \underset{\text{Alkene}}{-C{=}C-} + H_2O$$

Alcohol

The dehydration can be carried with $\mathbf{Al_2O_3}$ or with **mineral acid** upon heating.

(a) Dehydration with $\mathbf{Al_2O_3}$: Ethene is prepared by heating ethanol with Al_2O_3 at 620 K.

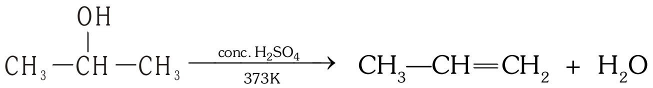
$$CH_3{-}CH_2{-}OH \xrightarrow[620K]{Al_2O_3} CH_2{=}CH_2 + H_2O$$

Ethanol Ethene

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

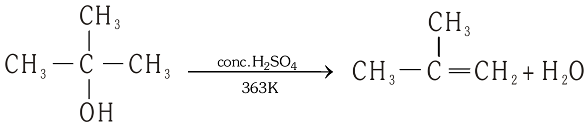
$$CH_3{-}CH_2{-}OH \xrightarrow[440K]{conc.\ H_2SO_4} CH_2{=}CH_2 + H_2O$$

Ethanol Ethene



$$CH_3-\overset{\overset{OH}{|}}{C}H-CH_3 \xrightarrow[373K]{conc.\ H_2SO_4} CH_3{-}CH{=}CH_2 + H_2O$$

Propan–2–ol Propene



$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow[363K]{conc.H_2SO_4} CH_3-\overset{\overset{CH_3}{|}}{C}{=}CH_2 + H_2O$$

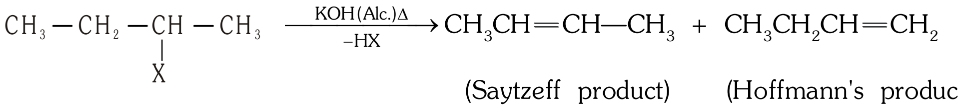
2–Methylpropan–2–ol 2–Methylpropene

From the above reactions, it is clear that the order of acidic dehydration in different alcohols is $\boxed{\text{Tertiary > Secondary > Primary}}$

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

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

Ex.



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

(Saytzeff product) (Hoffmann's product)

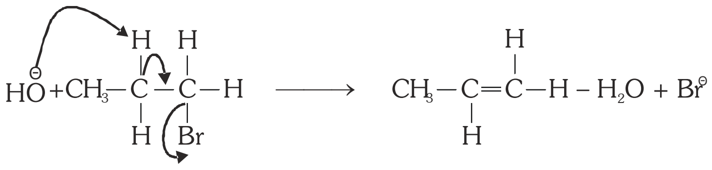
The ease of dehydrohalogenation show the order

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)

Ex.

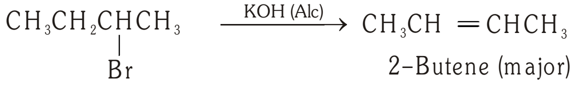


$$\boxed{\text{Rate of reaction} \propto [CH_3CH_2CH_2Br]\ [\overset{\ominus}{O}H]}$$

Ex. $CH_3CH_2CH_2CH_2Br \xrightarrow{KOH\,(Alc)} CH_3CH_2CH{=}CH_2$

1–Butene

Ex.

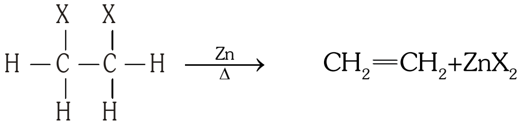


$CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow{KOH\,(Alc)} CH_3CH=CHCH_3$

2–Butene (major)

From Alkyl dihalide (By dehalogenation of Vicinal or Gem dihalide) : Removal of X_2 from a substrate by Zn dust or Zn—Cu in alcoholic Solution..

(a) From **Vicinal dihalide :** same number carbon alkene is obtained.



$H-\underset{H}{\overset{X}{C}}-\underset{H}{\overset{X}{C}}-H \xrightarrow[\Delta]{Zn} CH_2{=}CH_2{+}ZnX_2$

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

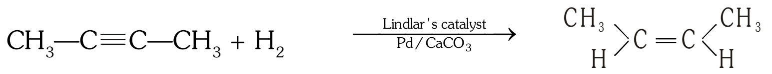
$CH_3CH\boxed{X_2 + 2Zn + X_2}CHCH_3 \xrightarrow{\Delta} CH_3—CH{=}CH—CH_3 + ZnX_2$

By the controlled hydrogenation of alkynes :

Alkynes can be converted into alkenes as a result of **controlled reduction** in two ways:

(a) **By the use of Lindlar's catalyst :** Lindlar's catalyst is a mixture of palladium catalyst deposited over barium sulphate or calcium carbonate. The catalytic mixture is slightly poisoned by quinoline or sulphur and allows the reduction or hydrogenation of alkyne with hydrogen only upto the alkene stage. The major product is cis-Alkene.

Ex.



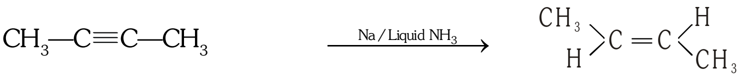
$CH_3—C{\equiv}C—CH_3 + H_2 \xrightarrow[Pd/CaCO_3]{Lindlar's\ catalyst}$ cis-$CH_3CH{=}CHCH_3$

But–2–yne cis–but–2–ene

In place of Lindlar's catalyst Nickel-boride (Ni–B also called P-2 catalyst) can also be used.

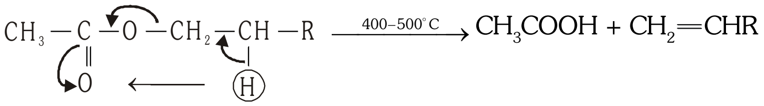
(b) **By the action of sodium in liquid ammonia :** This is known as **Birch reduction** and the major product is a **trans alkene** i.e., the two hydrogen atoms get attached on the opposite side of the double bond.

For example,



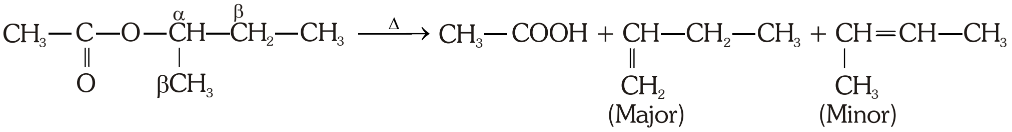
But–2–yne trans–but–2–ene

By Pyrolysis of ester :



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

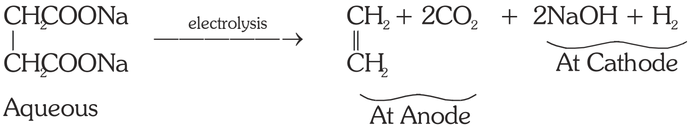
Ex.



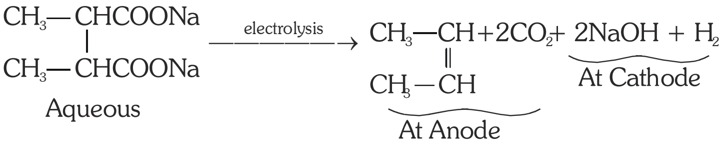
$$CH_3-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{\beta CH_3}{|}}{\overset{\alpha}{C}H}-\overset{\beta}{C}H_2-CH_3 \xrightarrow{\Delta} CH_3-COOH+\underset{\underset{\underset{(Major)}{CH_2}}{\|}}{C}H-CH_2-CH_3+\underset{\underset{\underset{(Minor)}{CH_3}}{|}}{C}H=CH-CH_3$$

In the reaction to form an alkene a β-hydrogen from alkyl ester is attracted by oxygen atom of keto group.

By Kolbe's method: Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.



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



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

PHYSICAL & CHEMICAL PROPERTIES OF ALKENES

Physical Properties

(1) All are colourless and have no characteristic odour. Ethene has pleasant smell.

(2) Lower members (C_2 to C_4) gaseous medium (C_5 to C_{17}) liquid and higher members are solid.

(3) The B.P., M.P. and specific gravity show a regular increase with increase in molecular weight

(4) The increase in branching in carbon chain decreases the B.P. among isomeric alkenes.

(5) The B.P. and M.P. 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.

(6) Insoluble in water because they can not form H-bond with water molecule, they dissolve freely in organic solvent like benzene, $CHCl_3$, CCl_4 etc.

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 -

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

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 hinderance (ii) Hyperconjugation

Alkenes give the following type of reactions :

(A) Addition reaction. (B) Oxidation reaction. (C) Substitution reaction.

(D) Polymerization Reaction. (E) Isomerisation

(A) Addition Reaction :

[A$_1$] Free Radical Addition

(1) Addition of H_2 :

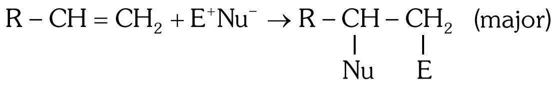
$$R{-}CH{=}CH_2 + H_2 \xrightarrow{\text{Ni,Pt or Pd}} R{-}CH_2{-}CH_3 + \text{ Heat of Hydrogenation.}$$

(a) Reaction is exothermic, Heat released in reaction 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.

[A$_2$] Electrophlic Addition Reactions:



$$R-CH=CH_2 + E^+Nu^- \rightarrow R-\underset{Nu}{\underset{|}{CH}}-\underset{E}{\underset{|}{CH_2}} \text{ (major)}$$

Reagent	E^+	Nu^-
HX	H^+	X^-
X_2	X^+	X^-
I–Cl	I^+	Cl^-
dil. H_2SO_4	H^+	OH^-
Con. H_2SO_4	H^+	HSO_4^-
NOCl	$^+N{=}O$	Cl^-
HOCl	Cl^+	OH^-

(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) Combustion:

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

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

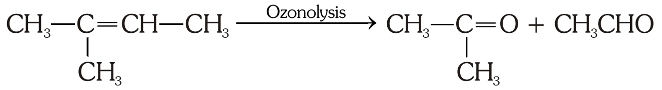
(2) Ozonolysis : (A test for unsaturation in molecule)

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

(ii) Ozonides are explosive compound.

(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.

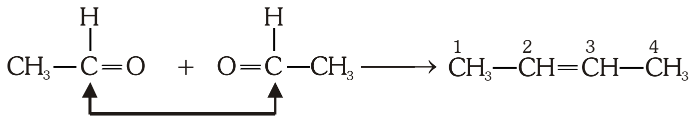
Ex.



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

(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.

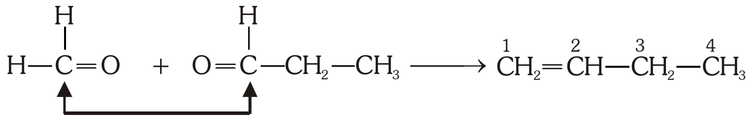
Ex.



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

Ethanal But-2-ene

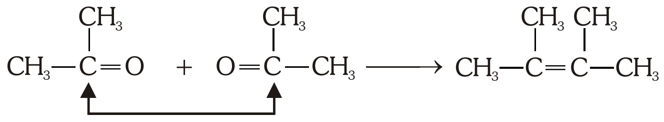
Ex.



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

Methanal Propanal But-1-ene

Ex.

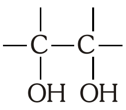


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=O + O=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3 \longrightarrow CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=\overset{\displaystyle CH_3}{\overset{|}{C}}-CH_3$$

Propanone 2,3–Dimethyl but–2–ene

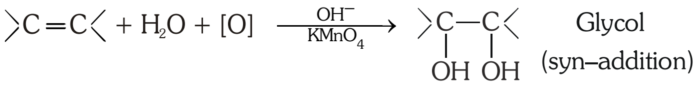
It may be noted that reaction with bromine water or Baeyer's reagent detects the presence of double bond (or unsaturation) in an alkene while ozonolysis helps in locating the position of the double bond.

Hydroxylation : Oxidation of carbon-carbon double bond to



$-\underset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}-\underset{\displaystyle OH}{\underset{|}{\overset{|}{C}}}-$ is known as hydroxylation.

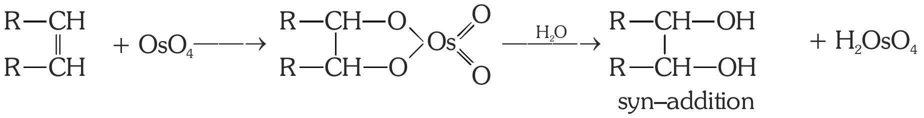
(a) Oxidation by Baeyer's reagent (A test for unsaturation) **:** Alkenes on passing through dilute alkaline 1% cold $KMnO_4$ (i.e., Baeyer's reagent) decolourise the pink colour of $KMnO_4$ and gives brown ppt of MnO_2. The reaction involves syn addition.



$$>C=C< + H_2O + [O] \xrightarrow[KMnO_4]{OH^-} >\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}<$$

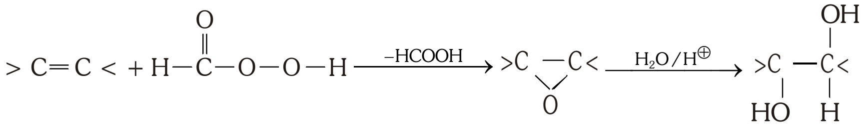
Glycol
(syn–addition)

(b) By OsO_4 :



syn–addition

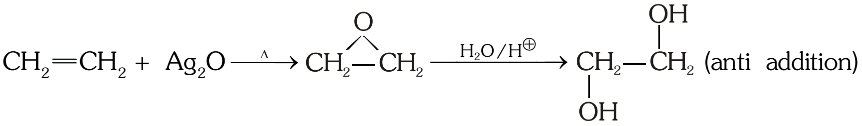
(c) By peracid :



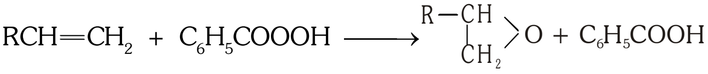
(Anti-addition)(glycol)

(d) By Ag_2O/Δ :

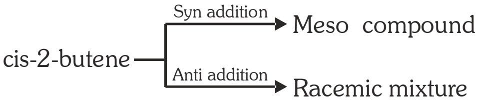
(a) Alkenes reacts with oxygen in the presence of Ag catalyst at 250°–400° C to form epoxide.

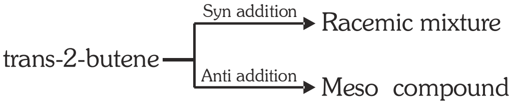


(anti addition)



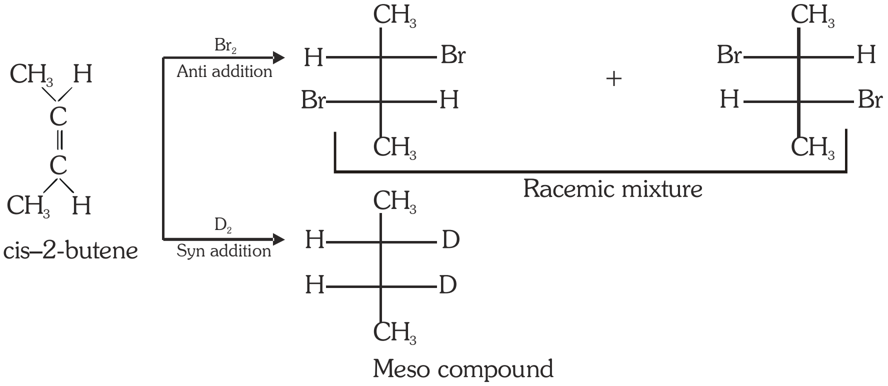
Epoxide



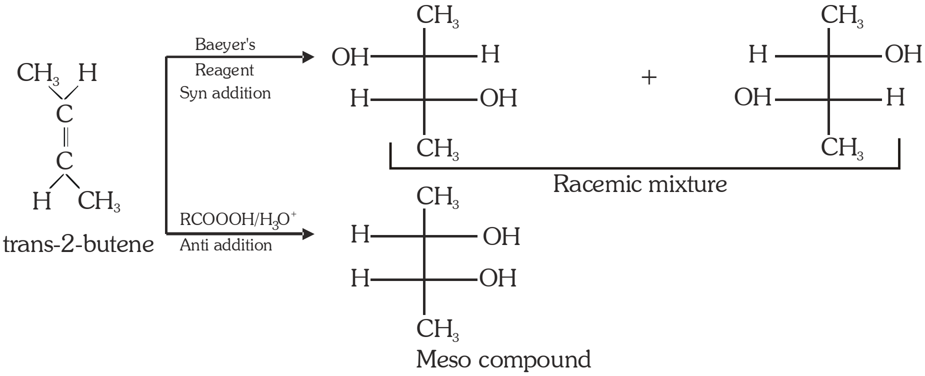


$$\boxed{\begin{array}{l}\text{Syn addition on alkene} \longrightarrow H_2, \text{Baeyer's reagent}, OsO_4/H_2O \\ \text{Anti addition on alkene} \longrightarrow X_2, HOX, RCOOOH/H_3O^{\oplus}, Ag_2O/H_3O^{+}\end{array}}$$

Ex.. (i)



(ii)

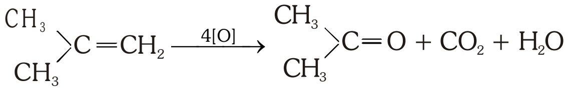


Oxidation by strong oxidising agent (Oxidative cleavage): The alkenes themselves are readily oxidised to acid or ketone by means of acid permagnate. If HCOOH is formed, it further oxidized to CO_2 and H_2O. Keep it in mind that no further oxidation of ketones will takes place.

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

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

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



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

(C) Substitution Reaction (Allylic Substitution):

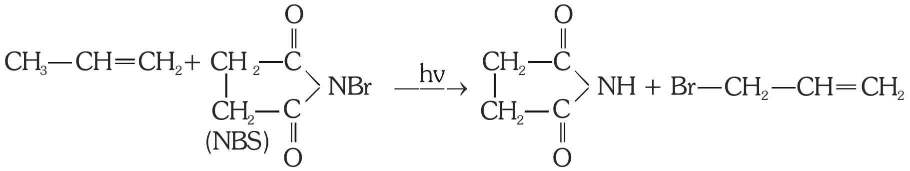
When alkenes are treated with low concentration of Cl_2 or Br_2 at high temperature or with NBS/hν one of their allylic hydrogen is replaced by halogen atom. Allylic position is the carbon adjacent to one of the unsaturated carbon atoms. It is free radical substitution.

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

Allyl chloride

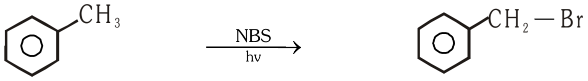
(3-Chloro-1-propene)

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

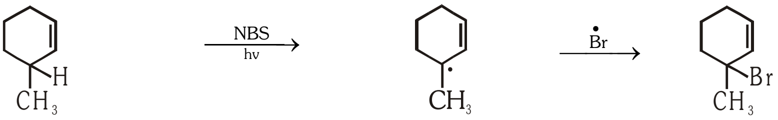


Substitution reaction is not given by ethene.

Ex. (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.

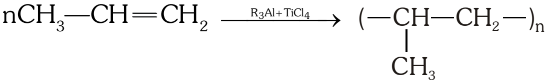
(iv) The presence of oxygen initiates free radical mechanism.

(v) Addition polymerization can also be carried out by ionic mechanism by using Ziegler - Natta Catalysts ($R_3Al+TiCl_4$)

Ex. $nCH_2{=}CH_2 \longrightarrow (\text{—}CH_2\text{—}CH_2\text{—})n$

ethene Poly ethene

used in the manufacture of insulating Coating, sheeting and moulded products.

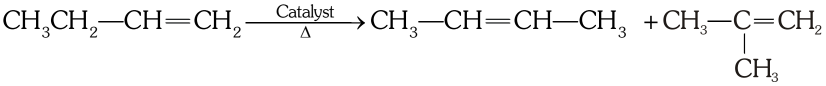


$$nCH_3\text{—}CH{=}CH_2 \xrightarrow{R_3Al+TiCl_4} (\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}H}\text{—}CH_2\text{—})_n$$

Polypropene or Koylene (Plastic)

(E) Isomerisation :

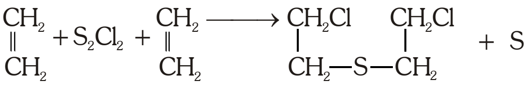
Alkene on heating to 500° to 700 °C or on heating in presence of catalyst [$AlCl_3$ or $Al_2(SO_4)_3$] undergo isomerisation.



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

1–Butene 2–Butene Isobutylene

Uses:
(1) In plastic formation.
(2) In oxy ethylene welding
(3) As food preservatives and ripening fruits.
(4) As general anaesthetic (C_2H_4 with 10% O_2)
(5) In preparation of mustard gas

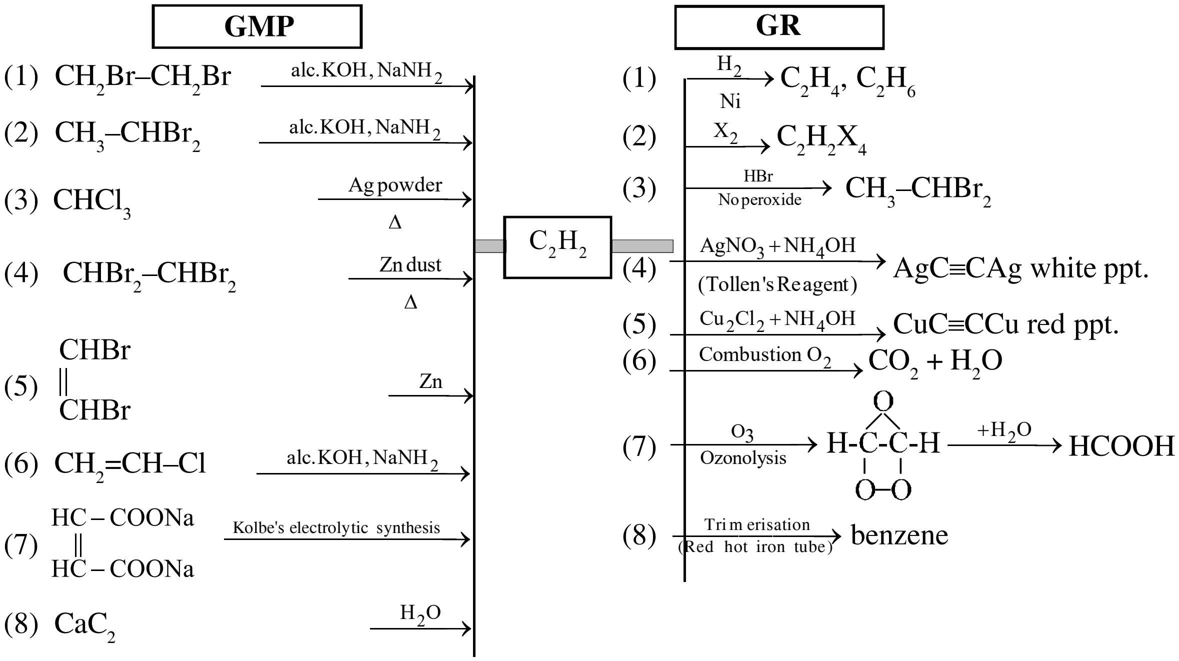


$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + S_2Cl_2 + \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \longrightarrow \begin{matrix}CH_2Cl & & CH_2Cl\\ | & & |\\ CH_2 & \text{—}S\text{—} & CH_2\end{matrix} + S$$

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

(mustard gas)

REACTION CHART FOR ALKYNES



C_2H_2

GMP

(1) $CH_2Br–CH_2Br \xrightarrow{\text{alc.KOH, NaNH}_2}$

(2) $CH_3–CHBr_2 \xrightarrow{\text{alc.KOH, NaNH}_2}$

(3) $CHCl_3 \xrightarrow[\Delta]{\text{Ag powder}}$

(4) $CHBr_2–CHBr_2 \xrightarrow[\Delta]{\text{Zn dust}}$

(5) $\begin{matrix} CHBr \\ \| \\ CHBr \end{matrix} \xrightarrow{\text{Zn}}$

(6) $CH_2{=}CH–Cl \xrightarrow{\text{alc.KOH, NaNH}_2}$

(7) $\begin{matrix} HC-COONa \\ \| \\ HC-COONa \end{matrix} \xrightarrow{\text{Kolbe's electrolytic synthesis}}$

(8) $CaC_2 \xrightarrow{H_2O}$

GR

(1) $\xrightarrow[\text{Ni}]{H_2} C_2H_4, C_2H_6$

(2) $\xrightarrow{X_2} C_2H_2X_4$

(3) $\xrightarrow[\text{No peroxide}]{\text{HBr}} CH_3–CHBr_2$

(4) $\xrightarrow[\text{(Tollen's Reagent)}]{AgNO_3 + NH_4OH} AgC{\equiv}CAg$ white ppt.

(5) $\xrightarrow{Cu_2Cl_2 + NH_4OH} CuC{\equiv}CCu$ red ppt.

(6) $\xrightarrow{\text{Combustion } O_2} CO_2 + H_2O$

(7) $\xrightarrow[\text{Ozonolysis}]{O_3} \underset{\text{O–O}}{\overset{\text{O}}{\text{H-C-C-H}}} \xrightarrow{+H_2O} HCOOH$

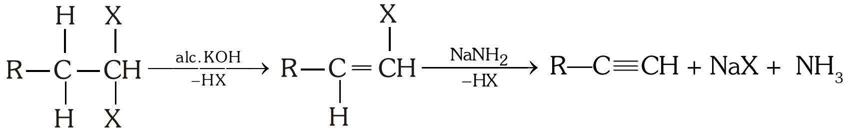
(8) $\xrightarrow[\text{(Red hot iron tube)}]{\text{Trimerisation}}$ benzene

Introduction of Alkynes

Alkynes are unsaturated hydrocarbons and characterised by the presence of a triple bond between the two carbon atoms ($C\equiv C$). The carbon-carbon triple bond is also called acetylenic bond. It consists of a strong σ and two weak π bonds. Alkynes are isomers of alkadienes and cycloalkenes.

General Methods of Preparation

From Gem dihalides (by dehydrohalogenation) : Dehydrohalogenation agents are : $NaNH_2$ (Sodamide) or Alc. KOH or ROH + RONa.

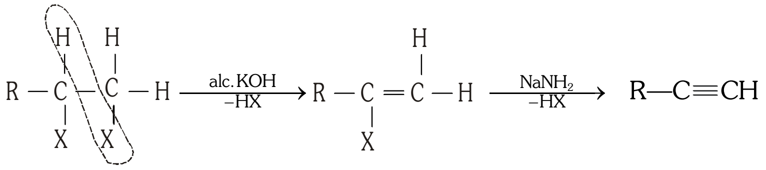


$$R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}H \xrightarrow[-HX]{alc.KOH} R-\underset{H}{C}=\overset{X}{C}H \xrightarrow[-HX]{NaNH_2} R-C\equiv CH + NaX + NH_3$$

(Stable by resonance)

(Vinyl halide)

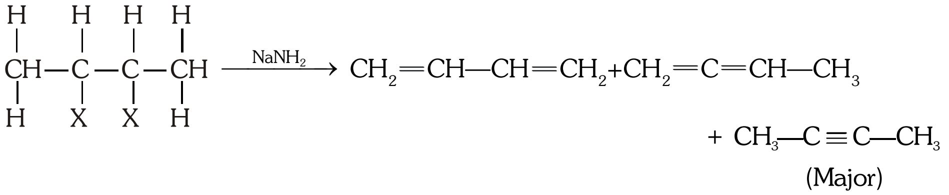
From Vicinal dihalides (by dehydrohalogenation) :



$$R-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-H \xrightarrow[-HX]{alc.KOH} R-\underset{X}{C}=\overset{H}{C}-H \xrightarrow[-HX]{NaNH_2} R-C\equiv CH$$

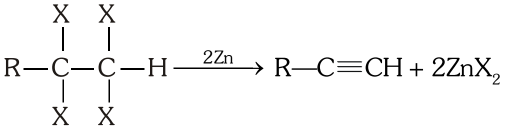
(a) Elimination of Vic. dihalides gives also alkadiene (1, 2 and 1, 3 alkadienes) but the major product is alkyne.

Ex.



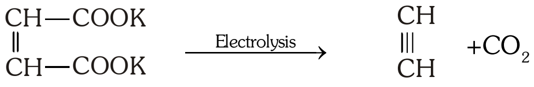
$$\underset{H}{\overset{H}{C}}H-\underset{X}{\overset{H}{C}}-\underset{X}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}H \xrightarrow{NaNH_2} CH_2=CH-CH=CH_2+CH_2=C=CH-CH_3 + \underset{(Major)}{CH_3-C\equiv C-CH_3}$$

Dehalogenation of tetrahalo alkane : By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H \xrightarrow{2Zn} R-C\equiv CH + 2ZnX_2$$

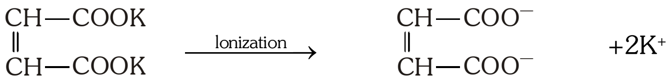
From Kolbe's electrolysis : By the electrolysis of aqueous Solution. of sodium or potassium fumarate or maleate, acetylene is formed at anode.



$$\begin{matrix}CH-COOK\\ \|\\ CH-COOK\end{matrix} \xrightarrow{Electrolysis} \begin{matrix}CH\\ |||\\ CH\end{matrix} + CO_2$$

(Aqueous)

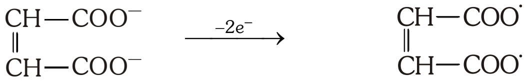
Mechanism :



$$\begin{matrix}CH-COOK\\ \|\\ CH-COOK\end{matrix} \xrightarrow{Ionization} \begin{matrix}CH-COO^-\\ \|\\ CH-COO^-\end{matrix} +2K^+$$

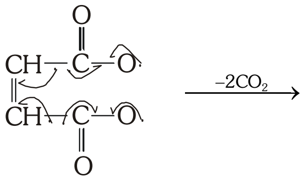
(Aqueous)

at anode (Alkyne and CO_2 gas is formed)

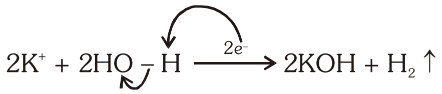


$$\begin{matrix} CH-COO^- \\ \| \\ CH-COO^- \end{matrix} \xrightarrow{-2e^-} \begin{matrix} CH-COO^{\cdot} \\ \| \\ CH-COO^{\cdot} \end{matrix}$$

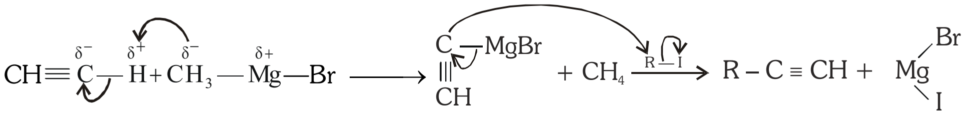
(Oxygen free radical)

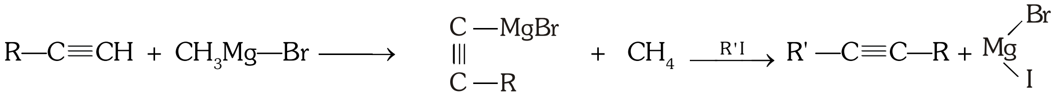


at cathode (KOH and H_2 gas is formed)



Preparation of higher alkynes by Grignard reagent : By this method lower alkyne is converted in to higher alkyne





Preparation of Ethyne or Acetylene:

(a) From Metal carbide [Laboratory method] : Acetylene is prepared in the laboratory by the action of water on calcium carbide.

$$CaC_2 + 2H_2O \longrightarrow CH{\equiv}CH + Ca(OH)_2$$

$$[Ca^{+2} + \overset{\ominus}{C}{\equiv}\overset{\ominus}{C} + 2H^+ + 2OH^- \longrightarrow CH{\equiv}CH + Ca(OH)_2]$$

(b) From haloform [CHI_3, $CHCl_3$] : Pure acetylene is obtained when iodoform or chloroform is heated with Silver powder

$$CHI_3 + 6Ag + I_3CH \xrightarrow{\Delta} CH{\equiv}CH + 6AgI$$

Physical & Chemical Properties of Alkynes

Physical Properties

(i) First three members [C_2 to C_4] are gases, from C_5 to C_{12} are liquid and after that they are solid.

(ii) Alkynes are slightly soluble in H_2O but soluble in CCl_4, benzene, acetone and alcohol.

(iii) B.P., M.P. and densities of alkynes are comparatively more than alkenes and alkanes due to more polarisation.

$$\boxed{\text{B.P.} \propto \text{mol.wt.} \propto \frac{1}{\text{number of side chains}}}$$

Chemical Properties

The chemical properties of alkynes are due to two factors

(a) Presence of π electrons : Due to presence of loosely bonded π electrons, alkynes like alkenes, undergo easily electrophilic addition reaction.

Carbon-carbon triple bond is less reactive than the carbon-carbon double bond towards electrophilic addition reactions.

In addition to electrophilic additions, alkynes also undergo nucleophilic addition with nucleophiles

(b) Presence of acidic hydrogen atom : The hydrogen atom attached to the triple bonded carbon can be removed by a strong base and hence acetylene and 1-alkynes are considered as weak acids.

Explanation : The amounts of s-character in various types of C—H bonds is as-

$\equiv$C—H	$=$C—H	—C—H
50%	33%	25%

Since s electrons are closer to the nucleus than the p electrons, the electrons present in a bond having more s-character will be closer to nucleus. Due to high s-character of the C—H bond in alkyne (s$=$50%) the electrons constituting this bond are more strongly held by the carbon nucleus, with the result the H present on $\equiv$ C–H can be easily removed as proton.

POINTS TO REVISE

- The acidic nature of the three types of –C–H bonds as

$$\underset{sp}{\equiv C\text{—}H} > \underset{sp^2}{=C\text{—}H} > \underset{sp^3}{\text{—}C\text{—}H}$$

- Relative acidic order $H_2O > ROH > HC \equiv CH > HNH_2 > CH_2 = CH_2 > CH_3 - CH_3$

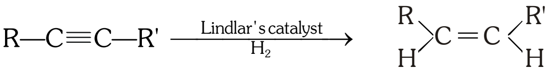
---

(1) Addition reaction

(a) Addition of hydrogen : Alkynes reacts with hydrogen in presence of a catalyst.In presence of Pt., Pd or Ni alkynes give alkanes with H_2

$$R\text{—}C\equiv CH \xrightarrow[300°C]{Ni, H_2} R\text{—}CH=CH_2 \xrightarrow[300°C]{Ni, H_2} R\text{—}CH_2\text{—}CH_3$$

In presence of Lindlar's catalyst [$Pd / CaCO_3 +$ quinoline or Nickle boride] alkynes give cis – alkene

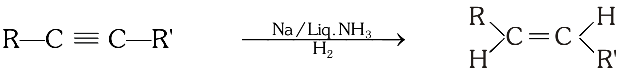


$$R\text{—}C\equiv C\text{—}R' \xrightarrow[H_2]{\text{Lindlar's catalyst}} \begin{matrix} R \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} R' \\ H \end{matrix}$$

(Stereo specific reaction)

cis - alkene

In presence of Na/NH_3 alkynes give trans-alkene. **(Birch Reduction)**



$$R\text{—}C \equiv C\text{—}R' \xrightarrow[H_2]{Na / Liq. NH_3} \begin{matrix} R \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} H \\ R' \end{matrix}$$

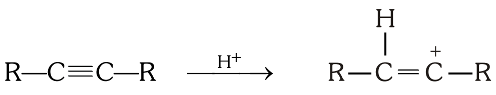
(Stereo specific reaction)

trans-alkene

(b) Electrophilic addition : Addition reactions where the addition is initiated by electrophile (positive group). The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in C$\equiv$C, the π electrons are tightly held by carbon nuclei and so they are less easily available for reaction with electrophiles.

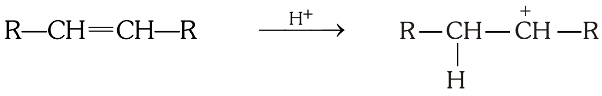
Another reasons is : The intermediates when an electrophile attack on alkene and alkynes are :

(i)



$$R\text{—}C\equiv C\text{—}R \xrightarrow{H^+} R\text{—}\overset{\overset{\displaystyle H}{|}}{C}=\overset{+}{C}\text{—}R$$

(ii)



$$R\text{—}CH=CH\text{—}R \xrightarrow{H^+} R\text{—}\underset{\underset{\displaystyle H}{|}}{CH}\text{—}\overset{+}{CH}\text{—}R$$

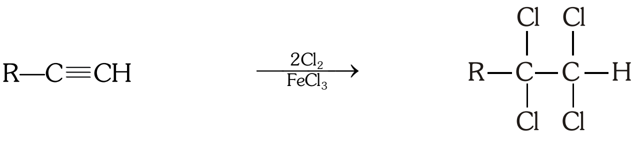
Stability of intermediates :

$\text{R—CH}=\overset{\oplus}{\text{C}}\text{—R}$ < $\text{R—CH}_2\text{—}\overset{\oplus}{\text{C}}\text{H—R}$

(+) ve on more EN atoms is less stable — more stable

So we can say that alkenes are more reactive towards electrophilic addition reaction.

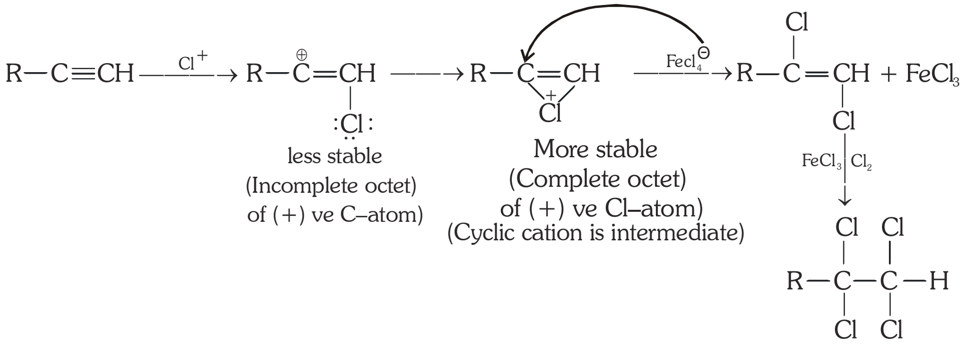
(i) Addition of Halogens : Alkynes react with Cl_2 or Br_2 in dark in presence of metal halide and form di and tetra halo derivatives.



$$\text{R—C}\equiv\text{CH} \xrightarrow[\text{FeCl}_3]{2\text{Cl}_2} \text{R—CCl}_2\text{—CCl}_2\text{—H}$$

Mechanism :

$$Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$$



less stable (Incomplete octet) of (+) ve C–atom)

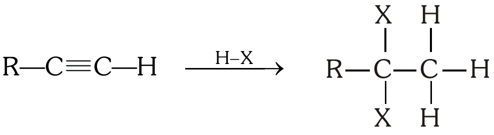
More stable (Complete octet) of (+) ve Cl–atom) (Cyclic cation is intermediate)

(Product)

(Tetrachloride)

(ii) Addition of halogen acids (H – X) : Addition according to Markovnikov's Rule.

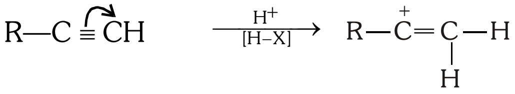
Reactivity order of H – X : $\boxed{HI > HBr > HCl > HF}$



$$\text{R—C}\equiv\text{C—H} \xrightarrow{\text{H–X}} \text{R—CX}_2\text{—CH}_2\text{—H}$$

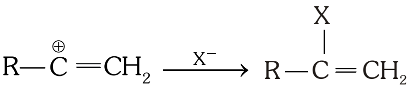
(Gem dihalides major product)

Mechanism :



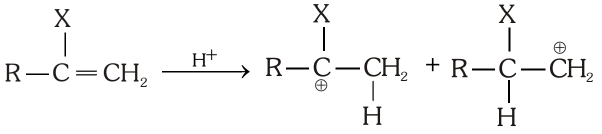
$$\text{R—C}\equiv\text{CH} \xrightarrow[\text{[H–X]}]{\text{H}^+} \text{R—}\overset{+}{\text{C}}\text{=}\underset{\text{H}}{\text{C}}\text{—H}$$

(Intermediate is carbocation)



$$\text{R—}\overset{\oplus}{\text{C}}\text{=CH}_2 \xrightarrow{\text{X}^-} \text{R—}\overset{\text{X}}{\text{C}}\text{=CH}_2$$

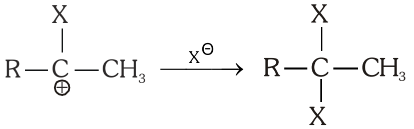
Further



$$R-\overset{X}{\overset{|}{C}}=CH_2 \xrightarrow{H^+} R-\overset{X}{\overset{|}{\underset{\oplus}{C}}}-\underset{H}{\underset{|}{CH_2}} + R-\overset{X}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{\oplus}{C}H_2$$

(more stable due to +M of X) (only –I of X)

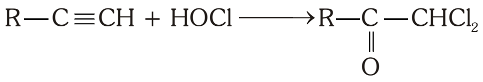
so



$$R-\overset{X}{\overset{|}{\underset{\oplus}{C}}}-CH_3 \xrightarrow{X^{\ominus}} R-\overset{X}{\overset{|}{\underset{X}{\underset{|}{C}}}}-CH_3$$

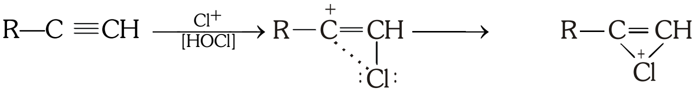
(Major Product)

(iii) Addition of HOX : Alkynes react with hypohalous acids according to Markovnikov's rule and form gem diol, which are unstable, lose a molecule of water and form dihalo aldehyde or dihalo ketones.



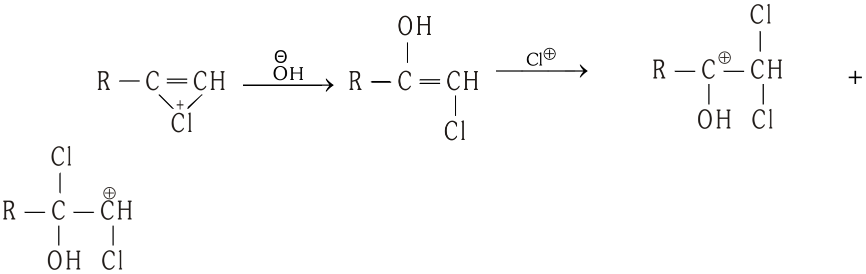
$$R-C\equiv CH + HOCl \longrightarrow R-\underset{O}{\underset{\|}{C}}-CHCl_2$$

Mechanism :



$$R-C\equiv CH \xrightarrow[\text{[HOCl]}]{Cl^+} R-\overset{+}{C}=\underset{:\ddot{Cl}:}{\underset{|}{CH}} \longrightarrow R-C=CH \ (\text{bridged } \overset{+}{Cl})$$

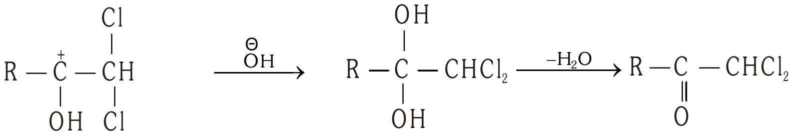
(Cyclic cation)



$$R-C=CH \ (\overset{+}{Cl}) \xrightarrow{\overset{\ominus}{O}H} R-\overset{OH}{\overset{|}{C}}=\underset{Cl}{\underset{|}{CH}} \xrightarrow{Cl^{\oplus}} R-\underset{OH}{\underset{|}{C^{\oplus}}}-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{CH}}}} + R-\overset{Cl}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\overset{\oplus}{\underset{Cl}{\underset{|}{CH}}}$$

(more stable due to +M of OH group) (less + M of Cl - Atom)

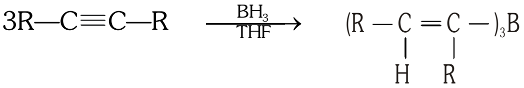
so



$$R-\underset{OH}{\underset{|}{\overset{+}{C}}}-\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{CH}}}} \xrightarrow{\overset{\ominus}{O}H} R-\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CHCl_2 \xrightarrow{-H_2O} R-\underset{O}{\underset{\|}{C}}-CHCl_2$$

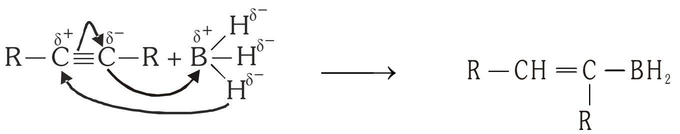
(Unstable) (Dichloro ketones)

(iv) Addition of BH_3 / THF or B_2H_6 (Hydroboration) : THF - Tetrahydrofuran is used as solvent.

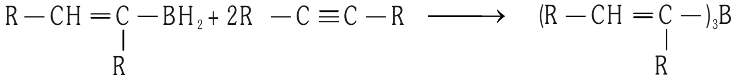


$$3R-C\equiv C-R \xrightarrow[THF]{BH_3} (R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-)_3B$$

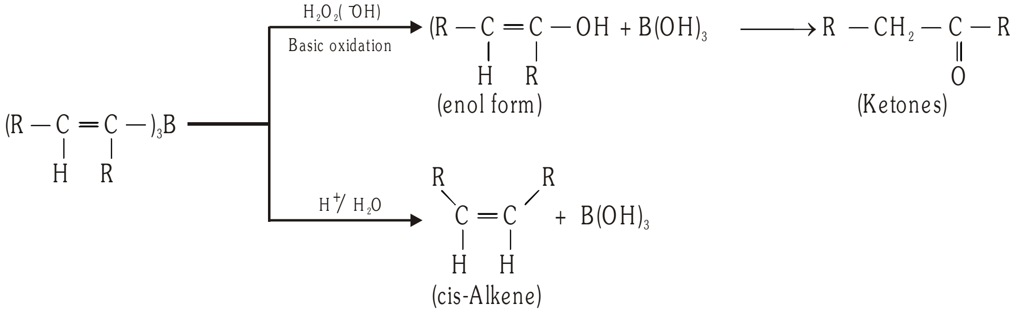
Since BH_3 is not available as monomer so a solvent THF is used for the stability of BH_3.



$$R-\overset{\delta+}{C}\equiv\overset{\delta-}{C}-R+\overset{\delta+}{B}H_3^{\delta-}\longrightarrow R-CH=\underset{R}{\underset{|}{C}}-BH_2$$



$$R-CH=\underset{R}{\underset{|}{C}}-BH_2+2R-C\equiv C-R\longrightarrow (R-CH=\underset{R}{\underset{|}{C}}-)_3B$$

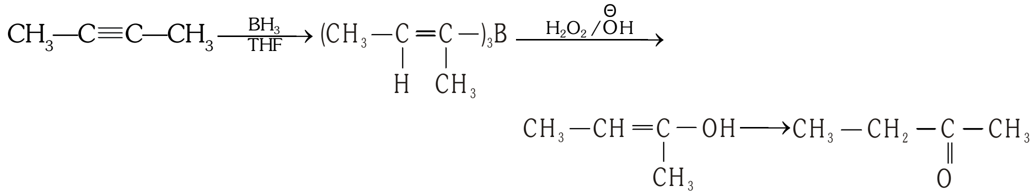


$$(R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-)_3B\xrightarrow[\text{Basic oxidation}]{H_2O_2(\overset{-}{O}H)}(R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-OH+B(OH)_3\longrightarrow R-CH_2-\underset{O}{\underset{\|}{C}}-R$$

(enol form) (Ketones)

$$(R-\underset{H}{\underset{|}{C}}=\underset{R}{\underset{|}{C}}-)_3B\xrightarrow{H^+/H_2O}\underset{H}{\underset{|}{\overset{R}{C}}}=\underset{H}{\underset{|}{\overset{R}{C}}}+B(OH)_3$$

(cis-Alkene)

Ex. 

$$CH_3-C\equiv C-CH_3\xrightarrow[THF]{BH_3}(CH_3-\underset{H}{\underset{|}{C}}=\underset{CH_3}{\underset{|}{C}}-)_3B\xrightarrow{H_2O_2/\overset{\ominus}{O}H}$$

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

(enol form less stable) (keto form more stable)

Oxidation Reactions

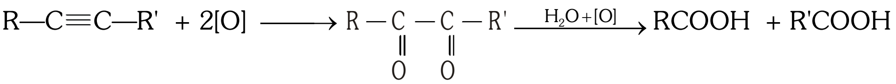
(a) Combustion :

$$C_nH_{2n-2}+\frac{3n-1}{2}O_2\longrightarrow nCO_2+(n-1)H_2O+\text{Heat}$$

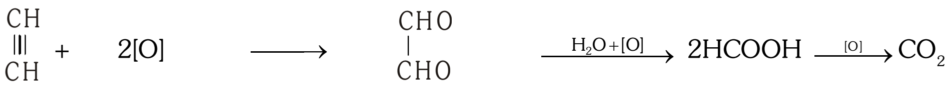
$$2HC\equiv CH+5O_2\longrightarrow 4CO_2+2H_2O+312\text{ K.cal}$$

The combustion of acetylene is used for welding and cutting of metals in which oxy-acetylene flame having high temp (3000^{0}C) is produced.

(b) Oxidation with acidic $KMnO_4$: In presence of acidic $KMnO_4$, alkynes are oxidised to monocarboxylic acids.

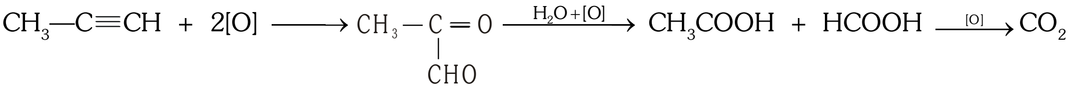


$$R-C\equiv C-R'+2[O]\longrightarrow R-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-R'\xrightarrow{H_2O+[O]}RCOOH+R'COOH$$



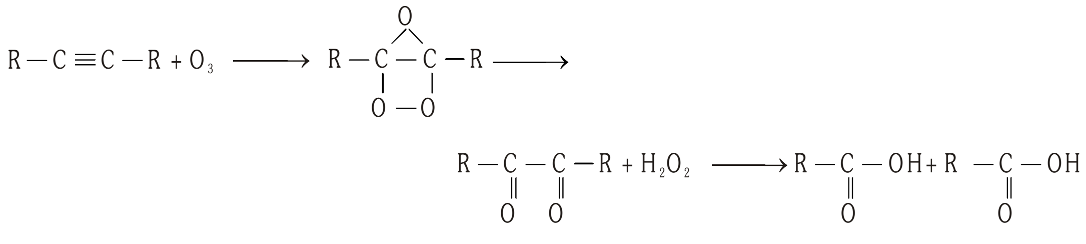
$$\underset{CH}{\underset{|||}{CH}}+2[O]\longrightarrow\underset{CHO}{\underset{|}{CHO}}\xrightarrow{H_2O+[O]}2HCOOH\xrightarrow{[O]}CO_2$$

glyoxal



$$CH_3-C\equiv CH+2[O]\longrightarrow CH_3-\underset{CHO}{\underset{|}{C}}=O\xrightarrow{H_2O+[O]}CH_3COOH+HCOOH\xrightarrow{[O]}CO_2$$

(c) Oxidation with ozone (O_3) : In the ozonolysis both sp-C-atoms are converted into $-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-$group.



$$R-C\equiv C-R+O_3 \longrightarrow R-\underset{O-O}{\overset{O}{C-C}}-R \longrightarrow$$

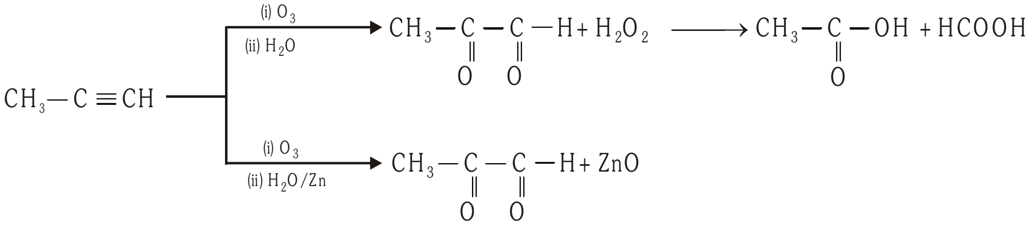
$$R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R+H_2O_2 \longrightarrow R-\underset{\underset{O}{\|}}{C}-OH+R-\underset{\underset{O}{\|}}{C}-OH$$

Ozonide (Addition of ozone) (Acids)

In this reaction H_2O_2 is oxidant which oxidise $R-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-R$ into acids.

But if we use some amount of Zn as reductant with H_2O then it reduce H_2O_2 so oxidation does not take place $H_2O_2 + Zn \longrightarrow ZnO + H_2O$

Ex.



$$CH_3-C\equiv CH \xrightarrow[\text{(ii) } H_2O]{\text{(i) } O_3} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H+H_2O_2 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-OH+HCOOH$$

$$CH_3-C\equiv CH \xrightarrow[\text{(ii) } H_2O/Zn]{\text{(i) } O_3} CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H+ZnO$$

Substitution Reaction : (Formation of metallic derivatives)

Only 1-alkynes give substitution reaction and show acidic characters $\equiv \overset{\delta^-}{C}-\overset{+\delta}{H}$

Acetylene is dibasic acid where as propyne is monobasic means acetylene can give two H^+ where as propyne can give one H^+.

(a) Formation of sodium acetylides : Acetylene and 1-alkynes react with sodamide to form acetylides

$$H-C\equiv C-H \xrightarrow{NaNH_2} NaC\equiv C-H \xrightarrow{NaNH_2} NaC\equiv CNa$$

Mono sodium acetylide Disodium acetylide

(b) Formation of copper and silver acetylides : Copper and silver acetylides are obtained by passing 1-alkynes in the ammonical Solution. of cuprous chloride and silver nitrate (Tollen's reagent) respectively.

$$R-C\equiv C-H + Cu_2Cl_2 + NH_4OH \longrightarrow R-C\equiv CCu + NH_4Cl + H_2O$$

ammonical cuprous-chloride copper acetylide [Red ppt.]

$$R-C\equiv C-H + AgNO_3 + NH_4OH \longrightarrow R-C\equiv CAg + NH_4NO_3 + H_2O$$

Tollen's reagent White ppt.

These reactions are used for detecting the presence of acetylenic hydrogen. These are test to distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

Isomerisation: When alkyne-1 is heated with alc. KOH alkyne-2 is obtained.

$$CH_3—CH_2—C\equiv CH \xrightarrow[\Delta]{\text{alc. KOH}} CH_3—C\equiv C—CH_3$$

1–Butyne 2–Butyne

When alkyne -2 is heated with $NaNH_2$ alkyne -1 is obtained

$$CH_3—C\equiv C—CH_3 \xrightarrow[\Delta]{NaNH_2} CH_3—CH_2—C\equiv CH$$

2–Butyne 1–Butyne

Polymerisation :

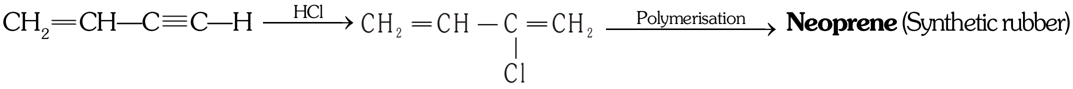
(a) Linear polymerisation :

Dimerisation : When two molecules of acetylene passed through a Solution. of Cu_2Cl_2 and NH_4Cl a vinyl acetylene is obtained.

$$2HC\equiv C—H \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2=CH—C\equiv C—H$$

mono vinyl acetylene (butenyne)

When vinyl acetylene react with HCl then chloroprene is obtained.



$$CH_2=CH—C\equiv C—H \xrightarrow{HCl} CH_2=CH-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2 \xrightarrow{\text{Polymerisation}} \textbf{Neoprene}\text{ (Synthetic rubber)}$$

2- chloro-1,3-butadiene

[chloroprene]

Trimerisation : 3 molecules of acetylene.

$$3CH\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2=CH—C\equiv C—CH=CH_2$$

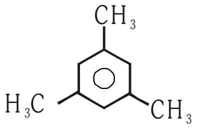
Divinyl acetylene

(b) Cyclic polymerisation : When alkyne is passed through red hot metallic tube, cyclic polymerisation takes place with the formation of aromatic compound

$$3CH\equiv CH \xrightarrow[\text{iron tube}]{\text{Red hot}}$$

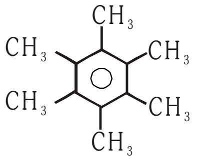
Benzene

$$3\ CH_3—C\equiv CH \xrightarrow[\text{iron tube}]{\text{Red hot}}$$



Mesitylene

$$3\ CH_3—C\equiv C—CH_3 \xrightarrow[\text{iron tube}]{\text{Red hot}}$$



Hexa methyl benzene

Uses of Acetylene

(i) Oxyacetylene flame used in welding and cutting

(ii) Acetylene is used as an illuminant

(iii) Acetylene is used for artificial ripening of fruits

(iv) Used for manufacture of acetaldehyde, acetic acid, ethyl alcohol, westron, westrosol, PVC, PVA, Chloroprene, butadiene, Lewisite etc.

(v) It is used as a general anaesthetic.

Test for alkynes :

(i) Decolourization of Br_2 in CCl_4 Solution..

(ii) Decolourisation of 1% alkaline $KMnO_4$ Solution..

(iii) 1- alkynes give white ppt. with ammonical $AgNO_3$ and red ppt with ammonical cuprous chloride Solution..

Note : (i) and (ii) tests are used for determination of unsaturation (i.e, presence of double or triple bond in any compound). (iii) Test is used for distinguish between alkenes and 1-alkynes or 1-alkyne and 2-alkyne.

Separation of ethane, ethene and ethyne :