Hydrocarbon

ALKANE

(i) Branched and unbranched aliphatic saturated hydro carbons are called member of alkane. The structural formula of alkane have only single bonds or all bonds in alkane is only σ bonds.

(ii) Alkanes does not reacts with chemical reagants such as dil. and conc. HCl, dil. & conc. H_2SO_4, dil. & conc. HNO_3, Caustic soda, acidic & basic $K_2Cr_2O_7$, $KMnO_4$ etc. That is why alkanes are called paraffins. (Parum=little, affins = reactivity).

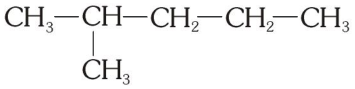
Property	**Characteristics of alkane**
General formula	C_nH_{2n+2}
C—C Bond energy	82.67 kcal/mole
C—H Bond energy	98.67 kcal/mole
Bond angle	$109^\circ.28'$
C—C Bond length	1.54 A°
C—H Bond length	1.112 A°
Hybridisation on C	sp^3
shape	Tetrahedral

Solved Examples

Ex. 1 Draw the all possible isomers of C_6H_{14} and assign relations between them.

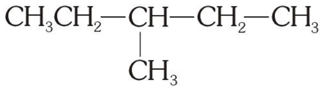
(a) $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$

n–Hexane

(b) 

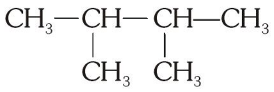
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3$

Isohexane (2-methyl pentane)

(c) 

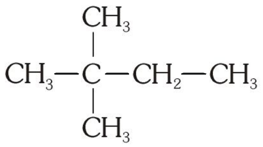
$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$

3–Methyl pentane

(d) 

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$

2,3–Dimethyl butane

(e) 

$CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_2-CH_3$

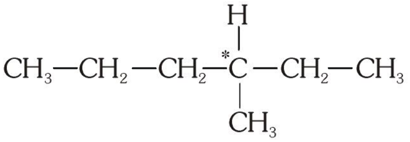
Neohexane (2,2-Dimethyl butane)

- a, b and d - Chain isomers
- b and c - Position isomers
- a, c, e - Chain isomers
- d and e - Position isomers
- a, c, d - Chain isomers

Ex. 2 Draw the structure of optically active alkane which have minimum carbon atom.

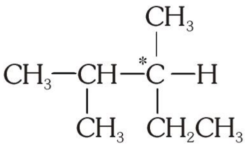
C_7H_{16}

or



$CH_3-CH_2-CH_2-\overset{*}{C}H(CH_3)-CH_2-CH_3$

or



$CH_3-CH(CH_3)-\overset{*}{C}H(CH_3)-CH_2CH_3$

Note: Alkane generally shows chain and position isomerism (for more details refer isomerism in study material provided to you.)

Composition :

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

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

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

(d) Kerosene oil : Mixture of alkanes having C_{12} to C_{16}.

(e) Gasoline : (Petrol): Mixture of alkanes having C_6 to C_8.

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

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

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

$$CH_4 + H_2O \longrightarrow \underbrace{CO + 3H_2}_{\text{Synthesis gas}}$$

General Methods of preparation

1. From alkenes and alkynes (Sabatier and Sandrens reaction) or (By hydrogenation of alkenes and alkynes) : Alkenes and alkynes on catalytic hydrogenation gives 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 temp. and pressure

(b) Ni, 200–300° C (sabatier)

(c) Raney Nicker at room temp.

(d) Raney nickel is obtained by boiling Ni/Al with NaOH. Al dissolved & Ni obtained in finally divided state.

(e) Methane can not be prepared by this method (From unsaturated hydrocarbon).

2. From alkyl Halides (By reduction) :

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

Catalyst :

(i) Zn + HCl

(ii) Zn + CH_3 COOH

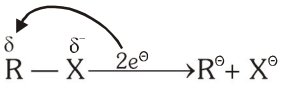
(iii) Zn—Cu couple in C_2H_5OH

(iv) Red P + HI

(v) Al + Hg + ethanol

Mechanism :

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



$$\overset{\delta}{R} — \overset{\delta^-}{X} \xrightarrow{2e^{\ominus}} R^{\ominus} + X^{\ominus}$$

$$R^- + H^+Cl^- \longrightarrow \underset{\text{Product}}{R—H} + Cl^{\ominus}$$

$$Zn^{+2} + 2Cl^- \longrightarrow ZnCl_2.$$

(a) Alkyl halides can also be reduced to alkane by H_2/Pd or $LiAlH_4$ or H_2/Ni.

(b) Reduction is due to the electron transfer from the metal to the substrate (R- X)

(c) If any alkyl halide is asked, the H-atom of any carbon atom of given alkane is removed by halogen atom.

3. 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 treated with Na in presence of dry ether. If ether is wet then we obtain alcohol.

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

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

(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 raction give all possible alkanes.

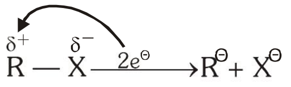
(d) The seperation of mixture in to individual members is not easy because their B.P. are near to each other and thus wurtz reaction is not suitable for the synthesis of alkanes containing odd number of carbon atom.

(e) This reaction generally fails with tertiary alkyl halide.

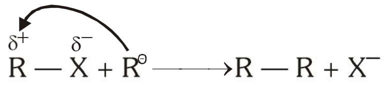
Mechanism : Two mechanism have been proposed for this reaction.

(a) Ionic Mechanism:

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



$$\overset{\delta+}{R} - \overset{\delta-}{X} \xrightarrow{2e^{\ominus}} R^{\ominus} + X^{\ominus}$$



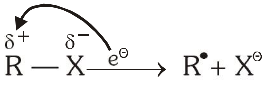
$$\overset{\delta+}{R} - \overset{\delta-}{X} + R^{\ominus} \longrightarrow \underset{\text{Product}}{R - R} + X^{-}$$

$$2Na^{\oplus} + 2X^{\ominus} \longrightarrow 2NaX$$

Ex. $2C_2H_5—I + 2Na \longrightarrow \underset{\text{n–butane}}{C_2H_5—C_2H_5} + 2NaI$

(b) Free radical mechanism :

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

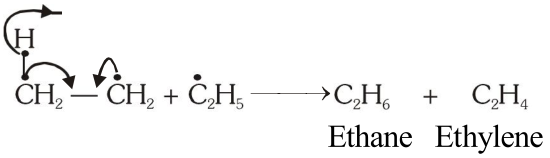


$$\overset{\delta+}{R} - \overset{\delta-}{X} \xrightarrow{e^{\ominus}} R^{\bullet} + X^{\ominus}$$

$$R^{\bullet} + R^{\bullet} \longrightarrow \underset{\text{Product}}{R - R}$$

$$Na^{\oplus} + X^{\ominus} \longrightarrow NaX$$

Free radicals also undergo Disproportionation i.e. one radical gains hydrogen at the expense of the other which loss hydrogen.



$$\overset{H}{CH_2} — \dot{C}H_2 + \dot{C}_2H_5 \longrightarrow \underset{\text{Ethane}}{C_2H_6} + \underset{\text{Ethylene}}{C_2H_4}$$

This explains the presence of ethylene and ethane in the butane obtained by Wurtz reaction.

Solved Examples

Ex. 3 If two moles of Isopropyl chloride reacts with Na in presence of dry ether. Which alkane is obtained.

Sol. 2, 3-Dimethyl butane.

Ex. 4 If isopropyl chloride and ethyl chloride both react with Na in presence of dry ether which alkanes are obtained.

Sol. n-Butane, 2-Methyl butane and 2, 3-Dimethyl butane.

Ex. 5 Which of the following compound can not obtained from wurtz reaction.

(1) ethane (2) butane (3) isobutane (4) hexane

[Hint : In wurtz reaction unsymmetrical alkane can not be obtained.**]**

Sol. (3)

Ex. 6 When ethyl chloride and n-propyl chloride undergoes wurtz reaction which is not obtained.

(1) n–butane (2) n–pentane

(3) n–hexane (4) isobutane

Sol. (4) $C_2H_5—Cl + C_3H_7Cl \xrightarrow[\text{dry ether}]{\text{Na}} C_2H_5—C_2H_5 + C_3H_7—C_3H_7 + C_2H_5—C_3H_7$

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(4) From Frankland Reagent: If Zn is used in place of Na, the reaction is named as Frankland reaction.

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

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

(5) From Carboxylic Acid (By decarboxylation) : Saturated monocarboxylic acid salt of sodium or potassium on dry distillation with soda lime give alkane.

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

Soda Lime

(a) The process of elimination of Carbon-di-oxide from Carboxylic acid called decarboxylation.

(b) Replacement of -COOH by hydrogen is known as decarboxylation.

The alkane formed always contains one carbon atom less than the original acid.

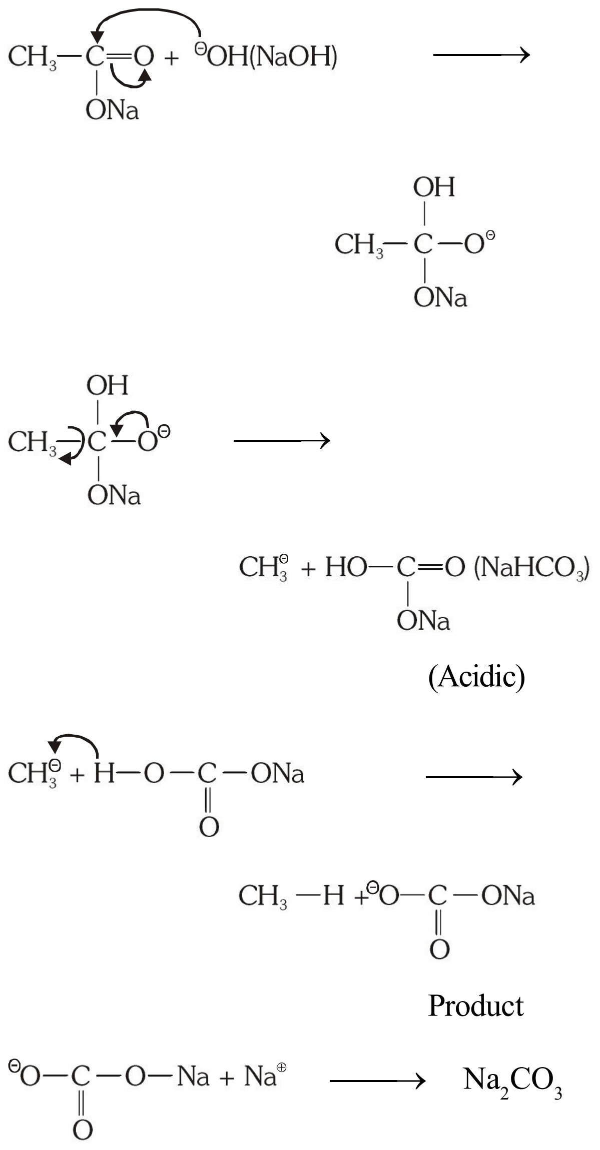
(c) This reaction is employed for stepping down a homologous series.

(d) Soda lime is prepared by soaking quick lime CaO with NaOH solution and then drying the products.

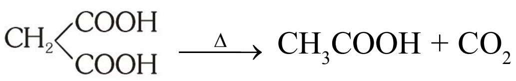
(e) Decarboxylation of sodium formate gives H_2

$$\left(\begin{array}{l} HCOONa + NaOH\ (CaO) \xrightarrow{\Delta} H_2 + Na_2CO_3 \\ CH_3COONa + NaOH + CaO \xrightarrow{\Delta} CH_4 + Na_2CO_3 \end{array}\right)$$

Mechanisim : Decarboxylation proceeds via. the formation of carbanion intermediate as follows.



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



$$CH_2(COOH)_2 \xrightarrow{\Delta} CH_3COOH + CO_2$$

(b) CH_4 can be prepared by CH_3COOH.

(c) C_2H_6 can be prepared by CH_3CH_2COOH.

(d) $CH_3—CH_2—CH_3$ can be prepared by Butanoic acid and 2–Methyl propanoic acid.

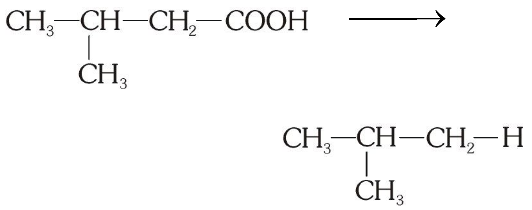
Solved Examples

Ex. 7 How many acids can be taken to obtain isobutane from decarboxylation ?

(1) 4 (2) 3 (3) 2 (4) 5

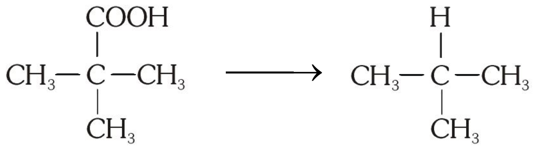
Sol. (3) To obtain isobutane the acids are

(i)



$$CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—COOH \longrightarrow CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—H$$

(ii)



$$CH_3—\underset{CH_3}{\underset{|}{\overset{COOH}{\overset{|}{C}}}}—CH_3 \longrightarrow CH_3—\underset{CH_3}{\underset{|}{\overset{H}{\overset{|}{C}}}}—CH_3$$

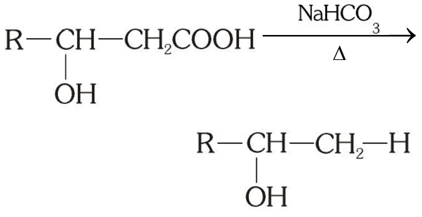
So two acids can be taken.

$\boxed{\text{Reactivity of acid } \alpha \text{ stability of carbanion}}$

Presence of electron attracting group (–I) in the hydrocarbon part of the fatty acid increases the decarboxylation.

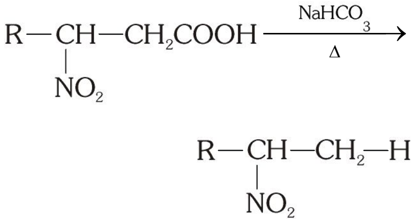
If – I is more effective group then weak base may be taken.

Ex. (1)



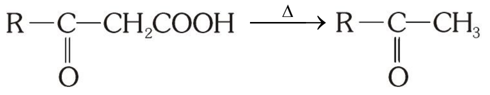
$$R—\underset{OH}{\underset{|}{CH}}—CH_2COOH \xrightarrow[\Delta]{NaHCO_3} R—\underset{OH}{\underset{|}{CH}}—CH_2—H$$

(2)



$$R—\underset{NO_2}{\underset{|}{CH}}—CH_2COOH \xrightarrow[\Delta]{NaHCO_3} R—\underset{NO_2}{\underset{|}{CH}}—CH_2—H$$

(3) β-Keto acids are decarboxylated readily simply on heating (soda lime is not required)



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

Ex. 8 Give reactivity order for decarboxylation ?

$CH_3—CH_2—COOH$

I

$CH_2CH—COOH$

II

$CH \equiv C —COOH$

III

(1) I > II > III (2) III > II > I

(3) III > I > II (4) None is correct

Sol. (2) In decarboxylation intermediates are,

$CH_3 — CH_2^{\ominus}$ $CH_2{=}CH^{\ominus}$ $CH{\equiv}C^{\ominus}$

I II III

The stability order of carbanion – III > II > I

So reactivity order for acid is – III > II > I

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(6) From carboxylic acid (By Kolbe's process) :

Alkanes are formed on electrolysis of concentrated aqueous solution of sodium or potassium salt of saturated monocarboxylic acids.

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

Electrolysis of Sodium propionate solution give n-butane, ethylene, ethane and ethyl propionate as follows-

$$2C_2H_5 — COONa \xrightarrow{\text{electro.}} C_2H_5 — C_2H_5 + 2CO_2 + 2NaOH + H_2$$

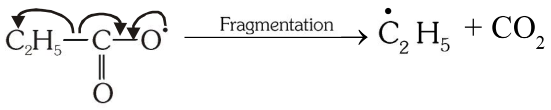
Mechanism :

$$C_2H_5—COONa \xrightarrow[H_2O]{\text{electro.}} C_2H_5 —COO^{\ominus} + \overset{\oplus}{Na}$$

(Ionization)

At Anode :

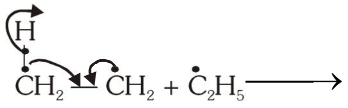
$$C_2H_5—COO^{\ominus} \xrightarrow{-e^{\ominus}} C_2H_5—COO^{\bullet}$$



$$C_2H_5-\underset{\underset{O}{\|}}{C}-\dot{O} \xrightarrow{\text{Fragmentation}} \dot{C}_2H_5 + CO_2$$

$$\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow C_2H_5-C_2H_5$$

Product



$$\dot{C}H_2-CH_2(H) + \dot{C}_2H_5 \longrightarrow$$

$$CH_3-CH_2-H + CH_2=CH_2$$

(minor products)

An ester is also formed.

$$C_2H_5-CO\dot{O} + \dot{C}_2H_5 \longrightarrow$$

$$C_2H_5-COOC_2H_5$$

(minor products)

At cathode : $Na^{\oplus} + e^{\ominus} \longrightarrow Na$

$$Na + H_2O \longrightarrow NaOH + \tfrac{1}{2}H_2$$

(a) Methane can not be prepared by this method.

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

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

(c) Presence of alkyl groups in α - position decrease the yield of alkanes.

(d) True aromatic acids do not undergo Kolbe's electrolytic reaction.

(e) Free radical mechanism has been suggested for Kolbe reaction.

(f) At anode alkane (major) and CO_2 gas is formed while at cathode NaOH and H_2 gas is formed.

(g) The concentration of NaOH in solution is increased with time so pH of solution is also increased.

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

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

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

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

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

$$RCOOH + 6HI \xrightarrow[150^\circ C]{Red\ P} R-CH_2-R + H_2O + 3I_2$$

In the above reaction I_2 is formed which acts as reducing agent and may reduce alkane and form alkyl halide. So red P is added in the reaction to remove I_2 formed in the reaction.

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

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

(7) From alkanones (By Clemmensen's method) :

Carbonyl compound (Preferably ketones) may also be reduced with Zinc amalgam and concentrated HCl (Zn—Hg/HCl), this reaction is called Clemmensen reduction.

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

CH_4, CH_3-CH_3, isobutane and neopentane are not obtained from Ketones because these alkane do not contain $>CH_2$ group.

(8) From alkanals and alkanones (By Wolf Kishner reaction) :

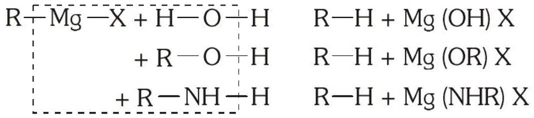
$$>C=O + NH_2NH_2 \longrightarrow$$

$$>C=N.NH_2 \xrightarrow[180^\circ C]{C_2H_5OH/Na} >CH_2 + N_2$$

Hydrazene Hydrazone

(9) From G.R. :

(a) **Formation of alkanes with same number of C atoms :** With same number of C-atoms as G.R. react with compound containing active hydrogen alkanes is obtained.



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

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 :**

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

Solved Examples

Ex.7 Which of the following does not give alkane with R—Mg—X.

(1) Ph—OH (2) Cl—NH_2

(3) CH_3COOH (4) HCl

[Hint : Except Cl—NH_2 all have active hydrogen, but Cl—NH_2 when reacts with R—Mg—X the oduct is R—NH_2.**]**

Sol. (2)

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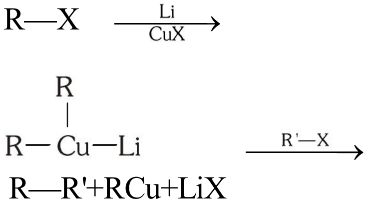
(10) Corey-House Synthesis : This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type R—R'



$$R-X \xrightarrow[CuX]{Li} R_2CuLi \xrightarrow{R'-X} R-R' + RCu + LiX$$

Lithium dialkyl copper

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

Solved Examples

Ex. 8 Which of the following reaction can not be used to obtained propane .

(1) Wurtz reaction

(2) Corey-house reaction

(3) Decarboxylation of acid salt

(4) All of them

[Hint: Wurtz reaction is used for symmetrical alkanes.**]**

Sol. (1)

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(11) 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 properties :

(i) C_1 to C_4 gases, Neopentane also gas but n-pentane and isopentane are low B.P. liquids.

(ii) Next members C_5 to C_{17} are Colourless liquids and above C_{17} are Waxy solids.

(iii) **Density** : The density of alkanes increases with increase in molecular weight and becomes constant at 0.8 g/mL. Thus all alkanes are lighter than water.

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

Ex. C_6H_6, CCl_4 ,ether etc.

- The solubility of alkanes decreases with increase in molecular weight
- Liquid alkanes are themselves good non-polar solvents.

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

$$\because \boxed{\begin{array}{r} \text{Vanderwaals force of attraction} \propto \text{molecular weight} \\ \propto \text{surface area of molecule.} \end{array}}$$

i.e. boiling point Pentane < hexane < heptane

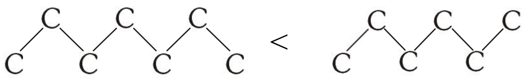
$$\text{Also boiling point} \propto \frac{1}{\text{number of side chain}}$$

because the shape approaches to spherical which results in decrease in Vanderwaals forces (as surface area decreases)

Thus boiling point n–Pentane > Isopentane > neopentane

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

Solved Examples

Ex.9 Alkanes are inert is nature, why ?

Sol. Alkanes are quite inert substances with highly stable nature. Their inactiveness has been explained as:

(i) Alkanes have all the C—C and C—H bonds being stronger σ bonds and are not influenced by acid, oxidants under ordinary conditions.

(ii) The C—C bond is completely non polar and C—H is weak polar. Thus polar species i.e. electrophiles or nucleophiles are unable to attack these bonds under ordinary conditions.

Chemical Properties :

(1) Oxidation :

(a) **Complete oxidation or combustion :** 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 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)

(c) **Catalytic oxidation :**

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

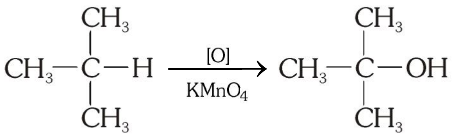
$$2CH_4 + O_2 \xrightarrow[\text{High P and T}]{\text{Red hot Cu or Fe tube}} 2CH_3OH$$

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

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

$$CH_3(CH_2)_nCH_3 \xrightarrow[\text{high Temp}]{(CH_3COO)_2\,Mn} CH_3(CH_2)_nCOOH$$

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



$$(CH_3)_3C{-}H \xrightarrow[KMnO_4]{[O]} (CH_3)_3C{-}OH$$

Solved Examples

Ex.10 How many litre of Oxygen required for complete conbustion of 6.0 g ethane at NTP ?

Sol. $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$

60 g ethane required O_2 (at NTP) = 7 × 22.4 litre

1 g ethane required O_2 (at NTP) = $\frac{7\times22.4}{2\times30}$ litre

6 g ethane required O_2 (at NTP)

$= \frac{7\times22.4}{2\times30}\times6 = 15.68$ litre

---

(2) Substitution Reactions : Substitution reaction in alkanes shows free radical mechanism.

They give following substitution reaction.

(a) Halogenation : Replacement of H-atom by halogen atom

$$R{-}H + X_2 \longrightarrow R{-}X + HX$$

Halogenation is made on exposure to (halogen + alkane) mixture to UV or at elevated temp.

The reactivity order for halogens shows the order.

$$\boxed{F_2 > Cl_2 > Br_2 > I_2}$$

Reactivity order of hydrogen atom in alkane is

$$\boxed{\text{Tertiary C – H > Sec. C – H > primary C – H}}$$

(i) **Fluorination :** reacts explosively even in dark. Fluorination can be achieved without violence when alkane is treated with F_2 diluted with an inert gas (like N_2)

By the action of HgF_2 on bromo or iodo derivatives.

$$C_2H_5I + HgF_2 \longrightarrow C_2H_5F + HgI_2$$

(ii) **Chlorination :**

It takes place in the following conditions -

(i) At 300° C in darkness.

(ii) At 100° C in presence of organic peroxides.

(iii) At 150° C in the presence of Tetraethyllead.

(iv) In the presence of diffused sunlight.or UV radiation.

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

The monochloro derivative of alkane is obtained by taking alkane in large excess.

When chlorine is in excess, a mixture of mono, di, tri, tetra and perchloro derivatives is obtained.

$$\boxed{\text{At 12 noon explosively } CH_4 + Cl_2 \longrightarrow C + HCl}$$

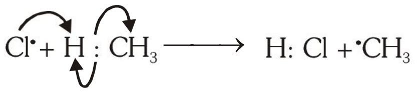
Mechanism for

$$CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$$

Step I **Chain initiation step :**

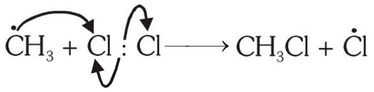
$$Cl:Cl \xrightarrow[\text{or } \Delta]{UV} Cl^\bullet + Cl^\bullet$$

Step II **Chain propagation step :**



$$Cl^\bullet + H:CH_3 \longrightarrow H:Cl + {}^\bullet CH_3$$

Methane Methyl radical



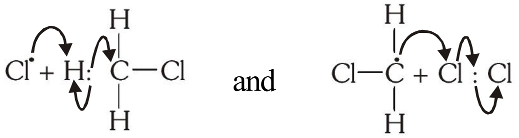
$$\dot{C}H_3 + Cl:Cl \longrightarrow CH_3Cl + \dot{C}l$$

Step III **Chain termination step :**

$$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2,\ CH_3^\bullet + {}^\bullet Cl \longrightarrow CH_3Cl,$$

$$CH_3^\bullet + {}^\bullet CH_3 \longrightarrow CH_3CH_3$$

A ${}^\bullet Cl$ can also attack CH_3Cl to form chloromethyl ($\dot{C}H_2Cl$) free radical. This free radical participates further in the chain reaction to yield methylene chloride (dichloromethane).



Similarly, chloroform and CCl_4 are obtained by further chain reaction.

(iii) **Bromination** : Br_2 reacts with alkanes in a similar manner but less vigorously.

(iv) **Iodination :** Iodine reacts with alkanes reversibly. HI formed as the by product is a powerful reducing agent and is capable of reducing the CH_3I to CH_4.

Iodination may be carried out in the presence of an oxidising agent such as HIO_3, HIO_4, HNO_3, HgO etc. Which destroy HI,

$$CH_4 + I_2 \rightleftharpoons CH_3I + HI$$

$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$

Iodination is very slow because energy of activation of the reaction is very large

$$CH_4 + I^\bullet \longrightarrow HI + \dot{C}H_3$$

(i) Halogenation is inhibited in presence of oxygen because oxygen reacts with alkyl free radicals to form less reactive peroxy alkyl radical $R{-}O{-}O^\bullet$ which can not propagate the chain.

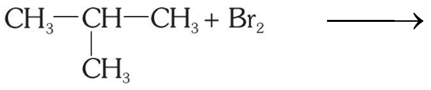
(ii) Reactivity ratio of H atom for Chlorination (1° : 2° : 3° H) 1 : 3.8 : 5

Reactivity ratio of H atom for bromination (1 : 82 : 1600)

Solved Examples

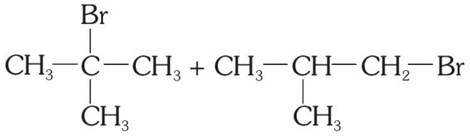
Ex.11 What is the percentage of products obtained from monobromination of isobutane ?

Sol.



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 + Br_2 \longrightarrow$

(I)



$CH_3-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 + CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Br$

(II)

$$\frac{\text{Product (I)}}{\text{Product (II)}} = \frac{\text{No. of primary H}}{\text{No. of tertiary H}} \times$$

$$\frac{\text{reactivity of primary H}}{\text{reactivity of tertiary H}} = \frac{9}{1}\times\frac{1}{1600}=\frac{9}{1600}$$

$$\%\text{ of product (I)} = \frac{9}{1600+9}\times 100 = 0.56\%$$

$$\%\text{ of product (II)} = \frac{1600}{1600+9}\times 100 = 99.44\%$$

(b) Nitration : (Vapour phase nitration) This involves the substitution of a hydrogen atom of alkane with -NO_2 group.

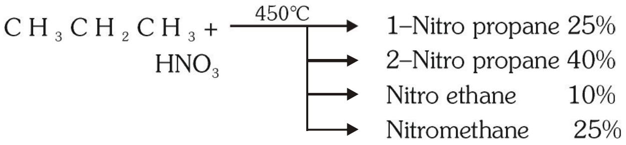
At ordinary temperature, alkanes do not react with HNO_3. But reacts with vapours of Conc. HNO_3 at 450° C.

$$R - H + HO - NO_2 \xrightarrow{400\text{–}500^0 C} R - NO_2 + H_2O$$

Since the reaction is carried at high temp. the C—C bonds of alkanes break during the reaction and a mixture of nitroalkanes is formed.

Ex. $CH_3—CH_3 +$

$$HNO_3 \xrightarrow{450^0 C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$$



$CH_3CH_2CH_3 + HNO_3 \xrightarrow{450°C}$
1–Nitro propane 25%
2–Nitro propane 40%
Nitro ethane 10%
Nitromethane 25%

Mechanism : (Free Radical substitution)

Step – I

$$HO - NO_2 \xrightarrow{\Delta} \dot{O}H + \dot{N}O_2$$

$$R - H + \dot{O}H \longrightarrow \dot{R} + H_2O$$

Step – II

$$\dot{R} + HO - NO_2 \longrightarrow R - NO_2 + \dot{O}H$$

(Product)

Step – III

$$\dot{R} + \dot{N}O_2 \longrightarrow R - NO_2$$

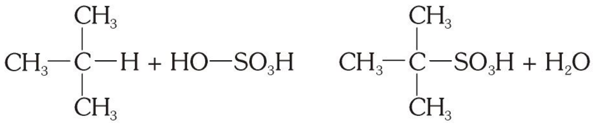
$$\dot{R} + \dot{O}H \longrightarrow R - OH \quad \text{(minor)}$$

$$\dot{O}H + \dot{N}O_2 \longrightarrow HONO_2$$

(c) Sulphonation : Replacement of H atom of alkane by –SO_3H is known sulphonation.

Alkane react with fuming H_2SO_4 or oleum ($H_2S_2O_7$). The branched lower alkanes and higher alkanes react to give alkane sulphonic acid.

Ex.



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-H + HO-SO_3H \quad CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-SO_3H + H_2O$

2–Methyl propane

The reactivity order for sulphonation is tert. H > Sec. H > prim. H

Mechanism : (Free Radical substitution)

$$HOSO_3H \xrightarrow{400^0 C} HO^\bullet + \dot{S}O_3H$$

$$C_6H_{13}H + \dot{O}H \longrightarrow \dot{C}_6H_{13} + H_2O$$

$$\dot{C}_6H_{13} + \dot{S}O_3H \longrightarrow C_6H_{13}SO_3H$$

Lower members such as propane, butane, pentane etc. react with SO_3 in vapour phase to form sulphonic acids.

$$C_3H_8 + SO_3 \longrightarrow C_3H_7 - SO_3H$$

(d) Chlorosulphonation (Reed reaction) : Reaction with a mixture of SO_2 and Cl_2 at ordinary temp. in the presence of UV light is called chlorosulphonation.

$$C_3H_8 + SO_2 + Cl_2 \xrightarrow{UV} C_3H_7SO_2Cl + HCl$$

Propane sulphonyl Chloride

Further hydrolysis of alkane sulphonyl chloride gives alkane sulphonic acid.

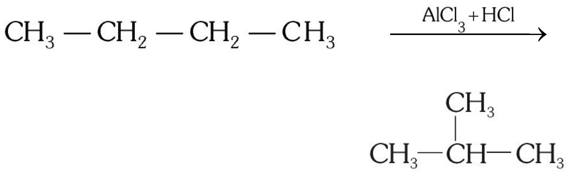
$$C_3H_7SO_2Cl \xrightarrow{H_2O} C_3H_7SO_3H + HCl$$

propane sulphonic acid

$$C_3H_7SO_3H + NaCl \longrightarrow C_3H_7SO_3 - Na + HCl$$

Sodium salt of sulphonic acid (used as detergent)

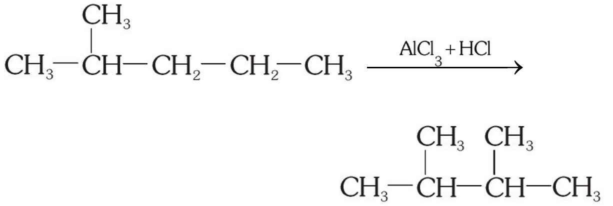
(3) **Isomerization:** Unbranched chain alkanes on heating with $AlCl_3 + HCl / 200^0C$ are converted in to branched chain alkanes



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

n-butane Isobutane

Branched chain alkanes converted to more branched alkane.



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

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

(4) **Pyrolysis or Cracking or thermal decomposition** When alkanes are heated to 500-700^{0}C they are decomposed in to lower hydrocarbon. This decomposition is called pyrolysis. In petroleum industry it is also termed as cracking.Cracking is used for the manufacture of petrol, petrol gas/oil gas etc.

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

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

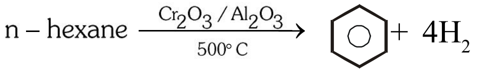
$$CH_3CH_2CH_3 \longrightarrow \begin{cases} CH_2{=}CH_2 + CH_4 \\ CH_3-CH{=}CH_2 + H_2 \end{cases}$$

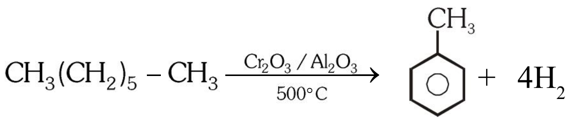
n-Butane $\xrightarrow{\text{Cracking}}$ 1-Butene + 2–Butene + Ethane + Ethene + Propene + CH_4+ H_2

The mechanism of pyrolysis occurs via free radicals.

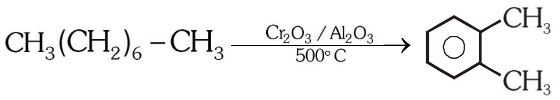
(5) **Hydroforming or dehydrogenation or cyclisation or catalytic reforming or aromatization :**

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 500^0 C aromatic hydrocarbons are formed.





n-heptane Toluene



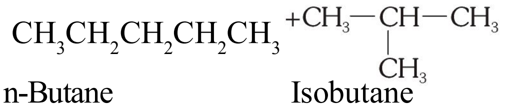
n-octane o-xylene

It provides an excellent method of passing from aliphatic to aromatic series.

(6) **Insertion of CH_2 group.**

$$\text{Alkane} + :CH_2 \longrightarrow \text{All isomers of higher number.}$$

$$CH_3CH_2CH_3 + :CH_2 \longrightarrow$$



$$CH_3CH_2CH_2CH_2CH_3 + CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_3$$

n-Butane Isobutane

Carbene (:CH_2) obtained from Ketene ($CH_2 = C = O$) or diazomethane (CH_2N_2)

(7) **Chlorinolysis** :

$$CH_3-CH_2-CH_3+Cl_2\xrightarrow[\text{Pressure}]{300-400^0C}\underset{(s)}{C_2Cl_6}+\underset{(\ell)}{CCl_4}+\underset{(g)}{HCl}$$

IMPORTANT TIPS

1. $CH_4+O_3\xrightarrow{350^\circ C}HCHO+H_2O+2O_2$

2. $\underset{\text{Steam}}{CH_4+H_2O}\xrightarrow[Ni]{1000^\circ C}\underset{\text{Synthesis gas}}{CO+3H_2}$

3. $CH_4\xrightarrow[Ni]{1000^\circ C}C+2H_2$

   (Carbon black used in prep. of printing ink.)

4. $CH_4+N_2\xrightarrow{\text{Electric arc}}2HCN+3H_2$

5. $CH_4+NH_3\xrightarrow[Al_2O_3]{1000^0C}HCN+3H_2$

6. $CO+H_2\xrightarrow[200^\circ-300^\circ c]{Ni}CH_4+H_2O$

7. $CO_2+H_2\xrightarrow[200^\circ-300^\circ c]{Ni}CH_4+2H_2O$

} These are also known as **Sabatier and Sandrens reaction.**

Solved Examples

Ex.12 8 c.c. of gaseous hydrocarbon requires 40 c.c. of O_2 for complete combustion. Identify hydrocarbon.

Sol. Volume of hydrocarbon = 8 c.c. ; Volume of O_2 = 40 c.c.

Formula No. 1, $\frac{8}{40}=\frac{2}{3n+1}$ (For alkane)

$\frac{1}{5}=\frac{2}{3n+1}$ or $3n+1=10$ or

$3n=10-1=9$, $n=3$

The value of n comes in whole number from 1st formula it means hydrocarbon is Alkane and it is of 3C atom.

$\therefore$ Hydrocarbon is C_3H_8 (Propane)

Ex. 13 10 mL of a mixture of CH_4 and C_3H_8 requires 41 mL of oxygen for complete combustion. What is the volume of CH_4 and C_3H_8 in the mixture.

Sol. Suppose the volume of CH_4 in $(CH_4+C_3H_8)$ mix = x c.c.

= Volume of C_3H_8 will be = 10 – x c.c.

For CH_4

$CH_4+2O_2\rightarrow CO_2+2H_2O$

$\because$ 1 Vol. of CH_4 requires 2 vol. of O_2 for complete combustion

$\therefore$ x c.c. of CH_4, 2x c.c. of O_2

For C_3H_8

$C_3H_8+5O_2\rightarrow 3CO_2+4H_2O$

$\because$ 1 volume of C_3H_8 requires 5 ml of O_2 for complete combustion

$\therefore$ (10 – x) c.c. of C_3H_8 requires 5(10 – x) c.c. of O_2

Total Volume of O_2 = 2x + 5 (10 – x) it is equivalent to 41

(according to question)

$\because$ $2x+5(10-x)=41$

$\therefore$ $x=3$ c.c.

Volume of CH_4 is 3 c.c. and

volume of C_3H_8 is 7 c.c.

Ex. 14 The density of one hydrocarbon at N.T.P. is 1.964 g/litre. Identify the hydrocarbon.

Sol. Molecular weight of Hydrocarbon

= density of 1 lit. x 22.4 = 1.964 x 22.4 = 44

So Molecular weight of hydrocarbon = 44

So the hydrocarbon is C_3H_8 (Propane).

ALKENE

Alkene are also called olefins as they forms oily compounds on reaction with halogens (oleum, oil + fines, forming).

Firstly, Ethylene reacts with Cl_2, gives oily liquid ethylene dichloride. That is why ethylene called as olefiant gas. (Olefiant gas, oleum, oil + fiant, make)

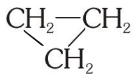
$$CH_2{=}CH_2 + Cl_2 \longrightarrow Cl{-}CH_2{-}CH_2{-}Cl$$

Property of alkene	**Characteristics**
General formula	C_nH_{2n}
C—C Bond energy	142 Kcal/mole
C—H Bond energy	98.67 kcal/mole
Bond angle 109°.28	Trigonal planar
Characteristic reaction	Electrophilic addition reactions
C—C Bond length	1.34 A°
C—H Bond length	1.10 A°
Hybridisation on C	sp^2
%C : %H	85.71 : 14.29
Empirical formula	CH_2

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

Solved Examples

Ex. 15 What is relation between $CH_3CH{=}CH_2$,



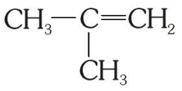
?

Sol. Ring chain isomerism

Ex.16 (a) $CH_3CH_2CH{=}CH_2$

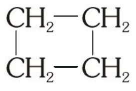
(b) $CH_3{-}CH{=}CH{-}CH_3$

(c)



$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2$

(d)



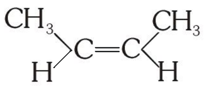
Define relations between a,b,c,d ?

Sol. a and b – Position isomerism

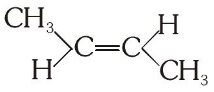
a and c – Chain isomerism

a and d – Ring chain isomerism

b also show Geometrical isomerism



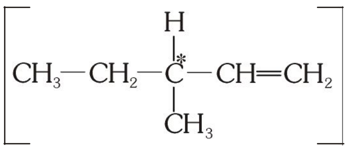
cis–2–butene



trans–2–butene

Ex.16 How many minimum carbon atom persent in optically active alkene?

Ans. 6C,

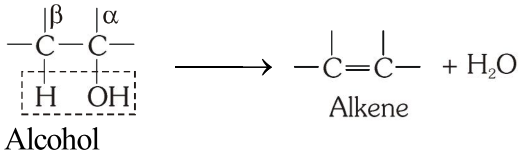


$$CH_3{-}CH_2{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{\overset{*}{C}}}}}{-}CH{=}CH_2$$

3–Methyl–1–Pentene

General Methods of Preparation :

(1) From Alcohols : Alkenes can be prepared from monohydric alcohols or alkanols by the loss of H_2O and the reaction is known as **dehydration reaction**. For the dehydration, the presence of a β-hydrogen in alcohol is necessary.



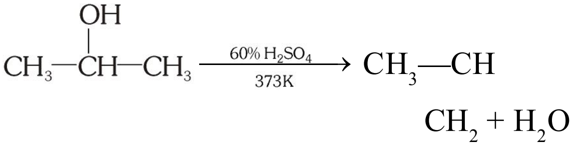
The dehydration can be carried with $\mathbf{Al_2O_3}$ or with **mineral acid** upon heating.

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

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

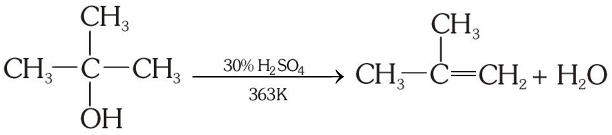
(b) Dehydration with mineral acid : Alcohols upon heating with conc. H_2SO_4 form alkenes and the reaction is called **acidic dehydration.**

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



$$CH_3-\overset{OH}{\overset{|}{C}H}-CH_3 \xrightarrow[373K]{60\%\ H_2SO_4} CH_3-CH \quad CH_2 + H_2O$$

Propan–2–ol Propene



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[363K]{30\%\ H_2SO_4} CH_3-\overset{CH_3}{C}=CH_2 + H_2O$$

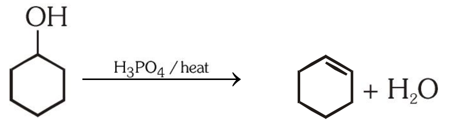
2–Methylpropan–2–ol 2–Methylpropene

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

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

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

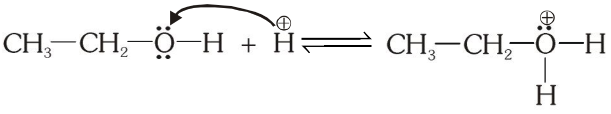
Ex.



Cyclohexanol Cyclohexene

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

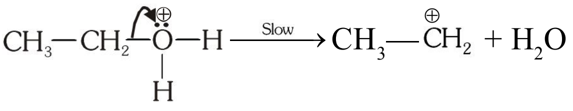
Step I : Alcohol being a Lewis base accepts a proton (H^+) from the acid in a reversible step as follows:



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

Ethanol (From acid) Protonated ethanol

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



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

Ethyl carbocation

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

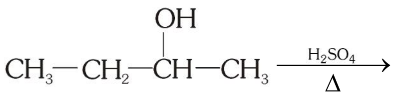
Step III : Carbocation is unstable in nature and loses a H^+ and changes into ethene in a fast step as follows:

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

Ethene

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

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



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

2–butanol

$CH_3-CH\ CH-\ CH_3+CH_3-CH_2-CH=CH_2$

main product 1–butene

2–butene 80% 20%

$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\Delta]{H_2SO_4}$

1–butanol

$CH_3-CH=CH-CH_3 + CH_3CH_2CH=CH_2$

2–butene80% 1–butene 20%

Main product

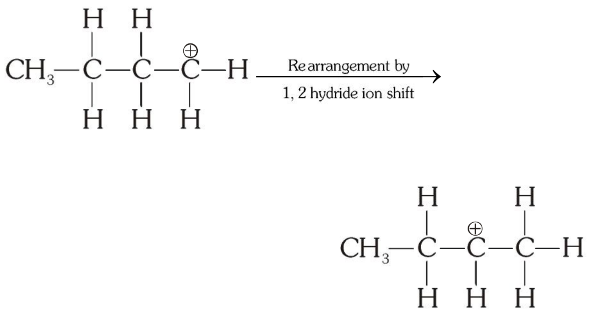
Mechanism : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

$$CH_3CH_2CH_2-CH_2-\ddot{\underset{..}{O}}-H+\overset{\oplus}{H} \longrightarrow$$

$$CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2$$

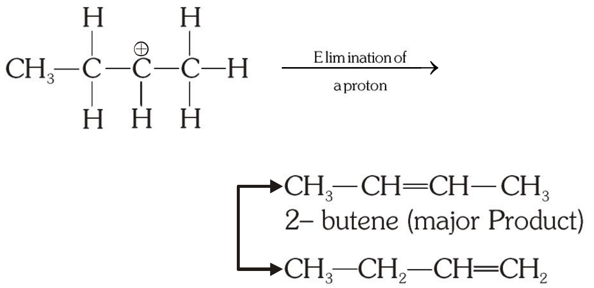
$$CH_3CH_2CH_2CH_2\overset{\oplus}{O}H_2 \longrightarrow CH_3CH_2CH_2-\overset{\oplus}{C}H_2+H_2O$$

Primary Carbonium ion



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

1^0 Carbonium 2^0 Carbonium more stable



$$CH_3-\overset{\oplus}{C}H-CH_3 \xrightarrow[\text{a proton}]{\text{Elimination of}}$$

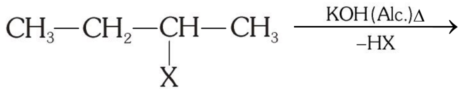
$CH_3-CH=CH-CH_3$
2– butene (major Product)
$CH_3-CH_2-CH=CH_2$

butene (minor product)
(Saytzeff rule)

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

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

Ex.



$$CH_3-CH_2-\underset{X}{CH}-CH_3 \xrightarrow[-HX]{KOH(Alc.)\Delta}$$

$$CH_3CH=CH-CH_3 + CH_3CH_2CH=CH_2$$

(Saytzeff rule)

The ease of dehydrohalogenation show the order

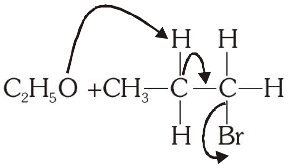
For alkyl group

tertiary	>	secondary	>	primary

For halogen in halide

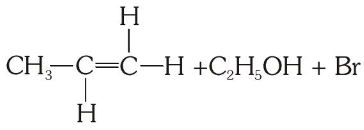
Iodide	>	Bromide	>	Chloride	>	flouride

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)



$$C_2H_5O + CH_3-CH_2-CH_2-Br$$

Ex.



$$CH_3-\underset{H}{C}=\overset{H}{C}-H + C_2H_5OH + Br$$

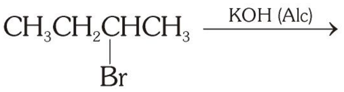
Rate of reaction	∝	$[CH_3CH_2CH_2Br]\ [C_2H_5\overset{\ominus}{O}]$

Ex.

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

1–Butene

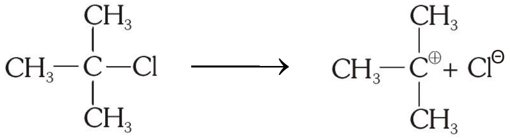
Ex.



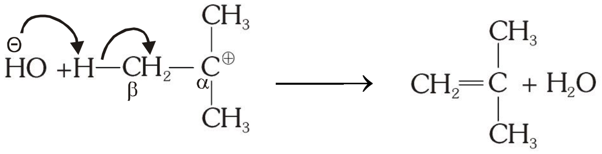
$$CH_3CH_2\underset{Br}{C}HCH_3 \xrightarrow{KOH\ (Alc)}$$

$CH_3CH=CHCH_3$
2–Butene (major)

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

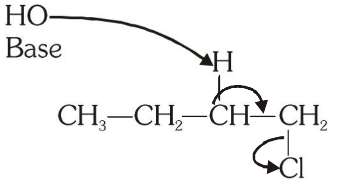


$$(CH_3)_3C-Cl \longrightarrow (CH_3)_3C^{\oplus} + Cl^{\ominus}$$



$$\overset{\ominus}{H}O + H-CH_2-\overset{\oplus}{C}(CH_3)_2 \longrightarrow CH_2=C(CH_3)_2 + H_2O$$

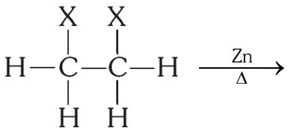
E_2 mechanism : Those alkyl halides which do not give Stable Carbonium ion on ionization show E_2 elimination.



$$CH_3-CH_2-CH=CH_2 + H_2O + Cl$$

(3) **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, 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

$$CH_3CH\ \boxed{X_2\ \ + 2Zn + X_2}\ CHCH_3 \longrightarrow$$

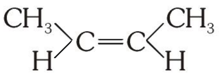
$$CH_3—CH{=}CH—CH_3 + ZnX_2$$

(4) **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 next step in the reaction i.e., hydrogenation of alkene to alkane is not possible since the catalyst is no longer in a position to catalyse the reaction. The addition of hydrogen to the alkyne molecule occurs from the same side of the double bond. It is, therefore, **cis addition** in nature. This reaction is stereospecific reaction.

Ex. $CH_3—C{\equiv}C—CH_3 + H_2 \xrightarrow{\text{Lindlar's catalyst}}$



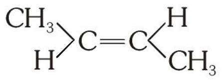
But–2–yne cis–but–2–ene

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 product is a **trans alkene** i.e., the two hydrogen atoms get attached on the opposite side of the double bond.

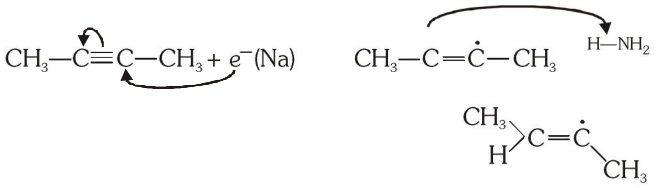
For example,

$CH_3—C{\equiv}C—CH_3 \xrightarrow{Na / Liquid\ NH_3}$



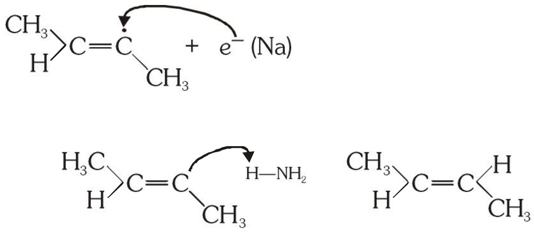
But–2–yne trans–but–2–ene

Mechanism : The mechanism of Birch reduction is called **ion-electron** mechanism and proceeds in two steps. In the first step, alkyne takes up an electron from sodium atom to form **ion-radical** which accepts a H^+ ion from ammonia molecule to form a free radical.



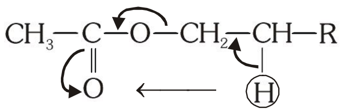
But–2–yne Ion–radical Free radical

The free radical again accepts one electron from the metal atom followed by H^+ ion from ammonia to form the desired product.



anion trans–2–Butene

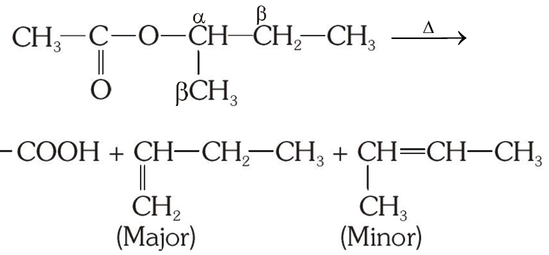
(5) **By Pyrolysis of ester :**



$\xrightarrow{400–500^\circ C} CH_3COOH + CH_2{=}CHR$

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

Ex.



$$CH_3-\underset{\underset{O}{\|}}{C}-O-\overset{\alpha}{\underset{\underset{\beta CH_3}{|}}{C}H}-\overset{\beta}{C}H_2-CH_3 \xrightarrow{\Delta}$$

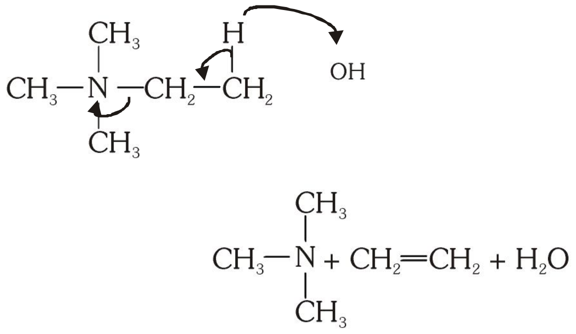
$$CH_3-COOH+\underset{(Major)}{\underset{\underset{CH_2}{\|}}{CH}-CH_2-CH_3}+\underset{(Minor)}{CH=CH-\underset{\underset{CH_3}{|}}{CH_3}}$$

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

(a) By this reaction methane cann't be obtained.

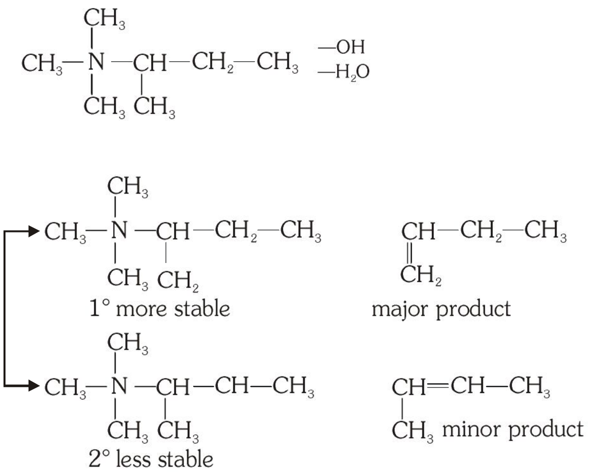
(b) In this reaction intermediate is transition state and major product is determined by crowding alkyl groups.

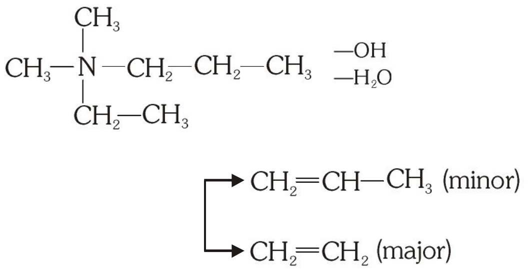
(6) By Pyrolysis of tetra alkyl ammonium ion :



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}+CH_2{=}CH_2+H_2O$$

Ex.





Ex.

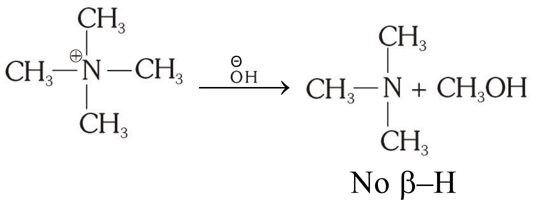
$$CH_3-\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}-CH_2-CH_2-CH_3 \xrightarrow[-H_2O]{-OH} \begin{cases} CH_2{=}CH-CH_3\ (minor) \\ CH_2{=}CH_2\ (major)\end{cases}$$

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

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

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

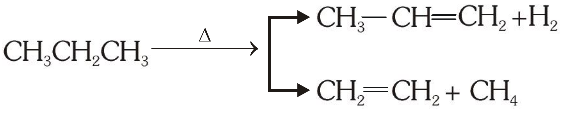
(d) By this reaction methane can not be prepared.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{\overset{\oplus}{N}}}-CH_3 \xrightarrow{\overset{\ominus}{O}H} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}}+CH_3OH$$

No β–H

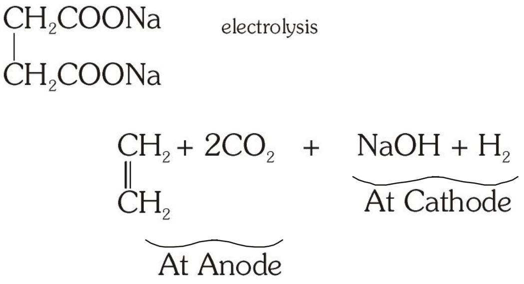
(7) By Pyrolysis of alkane :



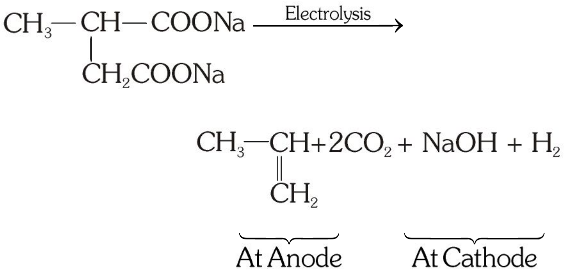
$$CH_3CH_2CH_3 \xrightarrow{\Delta} \begin{cases} CH_3-CH{=}CH_2+H_2 \\ CH_2{=}CH_2+CH_4 \end{cases}$$

(8) By Kolbe's method:

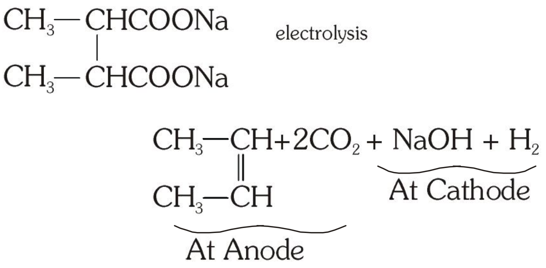
Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.



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

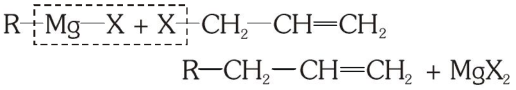


$$CH_3-\underset{\underset{CH_2COONa}{|}}{CH}-COONa \xrightarrow{Electrolysis} \underbrace{CH_3-\underset{\underset{CH_2}{\|}}{CH}+2CO_2}_{At\ Anode}+\underbrace{NaOH+H_2}_{At\ Cathode}$$



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

(9) From Grignard reagent: This reaction is used to obtained higher alkenes and it is nucleophilic substitution (NSR).

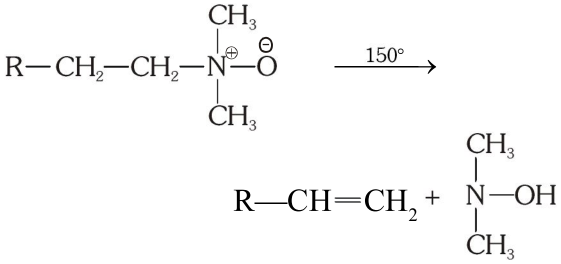


$$R-\boxed{Mg-X + X}-CH_2-CH=CH_2 \quad R-CH_2-CH=CH_2 + MgX_2$$

Ex. $CH_3-CH_2-MgCl + Cl-CH_2-CH=CH_2$ $\longrightarrow CH_3-CH_2-CH_2-CH=CH_2$

(10) Pyrolysis of Tri alkyl amine Oxide :

(Cope Reaction)



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

Alkene

Solved Examples

Ex.17 $CH_3-Mg-Cl + Cl-CH=CH_2 \longrightarrow$ Product

Sol. In vinyl chloride there is partial double bond in between – C – Cl so no substitution take place.

Physical Properties :

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

(2) Lower members (C_2 to C_4) are gases, middle one (C_5 to C_{17}) are liquids, higher are solids.

(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 -

$CH_2=CH_2$ > $R-CH=CH_2$ >
$R_2C=CH_2$ ≈ $RCH=CHR$
> $R_2C=CHR$ > $R_2C=CR_2$
(Trans < Cis)

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

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

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 :

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

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

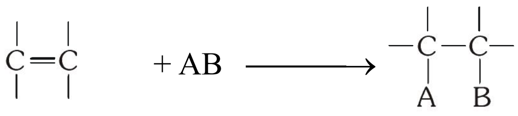
(b)

$$\boxed{\begin{aligned}\text{Stability of alkene} &\propto \frac{1}{\text{heat of hydrogenation}}\\ &\propto \frac{1}{\text{reactivity of alkene with } H_2}\end{aligned}}$$

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

[A_2] ELECTROPHILIC ADDITION REACTIONS

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

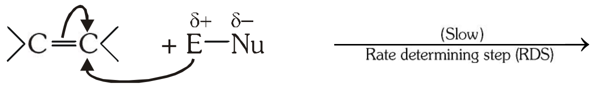


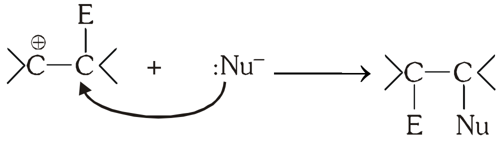
$$>C=C< + AB \longrightarrow -\underset{A}{C}-\underset{B}{C}-$$

Alkene Attacking molecule Addition product

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

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

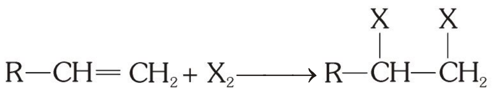




Addition product

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

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



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

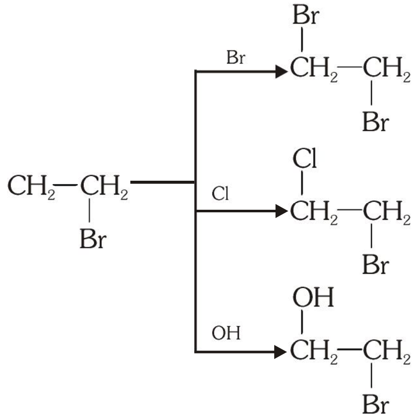
(Vicinal halides)

Solved Examples

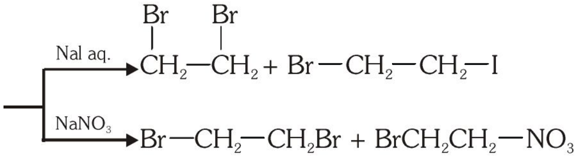
Ex.18 $\underset{\text{Ethylene}}{CH_2=CH_2} + Br_2 \xrightarrow{aq.NaCl}$ Products,

what are the products?

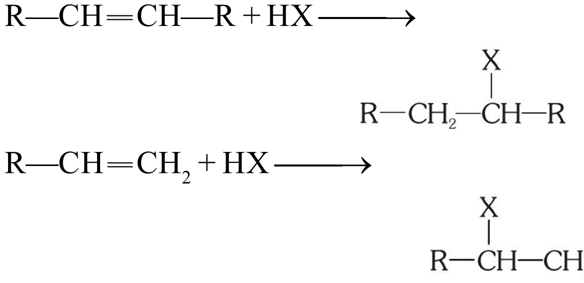
Sol. $CH_2=CH_2 + Br_2$



Similarly $CH_2=CH_2 + Br_2$



(2) Addition of halogen acid :



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

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

Note:

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

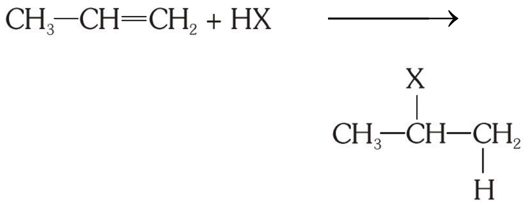
(ii) Their addition is an example of electrophilic addition.

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

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

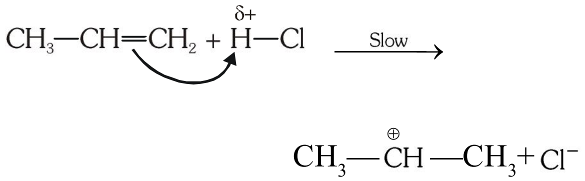
MARKOWNIKOFF'S RULE STATES :

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



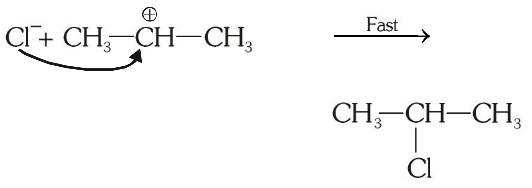
$$CH_3-CH=CH_2 + HX \longrightarrow CH_3-\overset{X}{CH}-\underset{H}{CH_2}$$

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



$$CH_3-CH=CH_2 + \overset{\delta+}{H}-Cl \xrightarrow{Slow} CH_3-\overset{\oplus}{CH}-CH_3 + Cl^-$$

Secondary carbocation



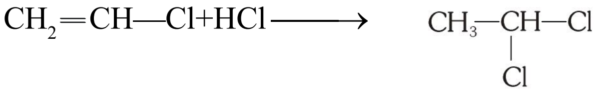
$$Cl^- + CH_3-\overset{\oplus}{CH}-CH_3 \xrightarrow{Fast} CH_3-\underset{Cl}{CH}-CH_3$$

2–Chloropropane

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

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

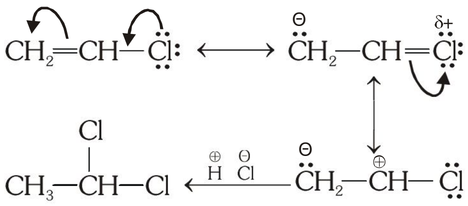
(b) Second Rule : In the addition of HX to vinyl halide and analogous compounds, the halogen attaches itself to the carbon atom, on which the halogen atom is already present.



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

Ethylidene chloride

Mechanism :



$$CH_2=CH-\ddot{\underset{..}{Cl}}: \longleftrightarrow \overset{\ominus}{\ddot{C}H_2}-CH=\overset{\delta+}{\ddot{\underset{..}{Cl}}}:$$

$$CH_3-\overset{Cl}{CH}-Cl \xleftarrow{\overset{\oplus}{H}\ \overset{\ominus}{Cl}} \overset{\ominus}{\ddot{C}H_2}-\overset{\oplus}{CH}-\underset{..}{\ddot{Cl}}$$

In vinyl chloride two effects operate simultaneously in opposite direction-

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

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

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

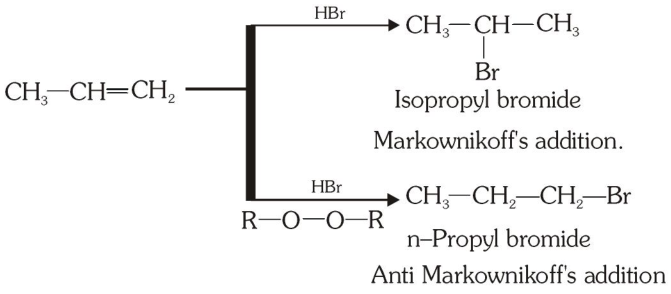
All polar reagents of the general structure $\overset{\oplus}{Y}\ \overset{\ominus}{Z}$ (such as $\overset{\oplus}{H}-\overset{\ominus}{X}$, $\overset{\oplus}{H}-\overset{\ominus}{OH}$ $\overset{\oplus}{H}-\overset{\ominus}{SO_3H}$, $\overset{\oplus}{X}\ \overset{\ominus}{OH}$) add on unsymmetrical unsaturated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

ANTI MARKONIFF'S RULE OR PEROXIDE EFFECT OR KHARASCH RULE

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

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

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



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

$$CH_3-CH=CH_2 \xrightarrow[R-O-O-R]{HBr} CH_3-CH_2-CH_2-Br$$

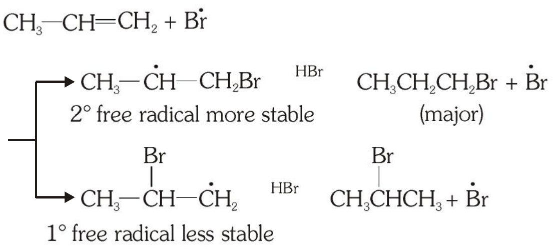
Mechanism :

(i) Chain initiation -

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

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

(ii) Chain propagation



(iii) Chain termination :

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

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

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

Solved Examples

Ex. 19 Why HCl and HI do not give antimarkownikoff products in the presence of peroxides.?

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

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

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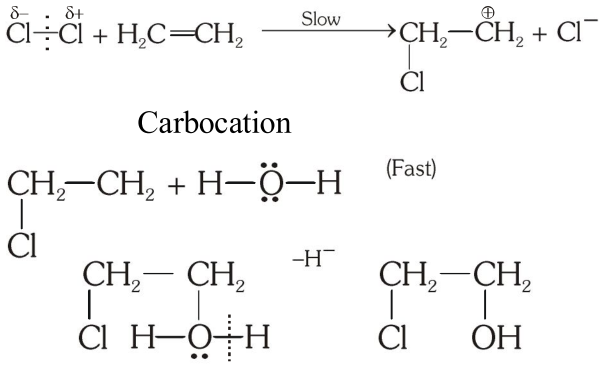
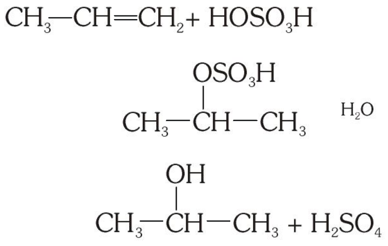
(3) Addition of Hypohalous acid (or X_2/H_2O, or HOX) : It is a electrophilic addition and follows Markownikoff's rule.



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

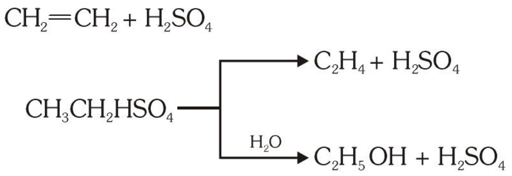
Reactivity order is **HOCl > HOBr > HOI**

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



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

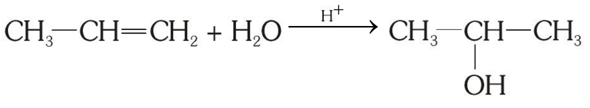
Isopropyl alcohol



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

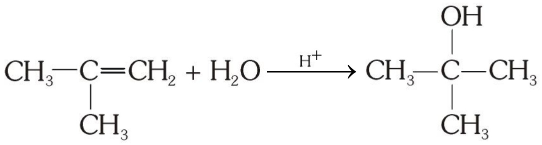
(5) Addition of water (Hydration of alkenes) : Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as the **hydration reaction** . Intermediate in this reaction is carbo cation, so rearrangement will take place.

(i)



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

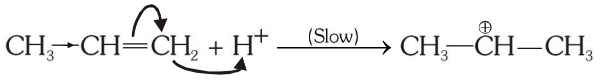
Propene   Propan-2-ol



(ii) $$CH_3—\underset{CH_3}{\underset{|}{C}}=CH_2 + H_2O \xrightarrow{H^+} CH_3—\overset{OH}{\underset{CH_3}{C}}—CH_3$$

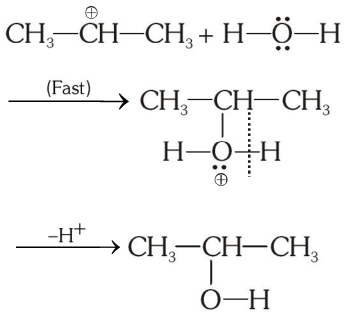
2–Methylpropene   72-Methylpropan-2-ol

Mechanism :



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

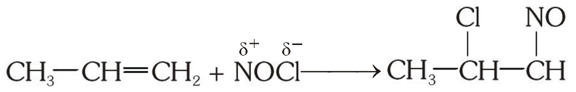
Carbocation (2°)



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

Propan-2-ol

(6) Addition of NOCl (Tilden reagant) :

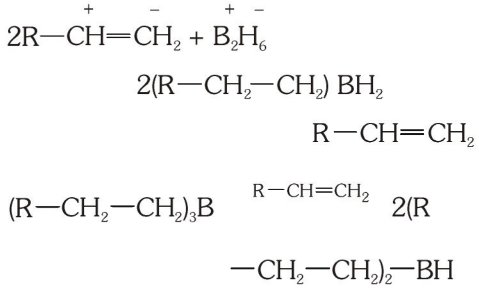


$$CH_3-CH=CH_2 + \overset{\delta+}{N}O\overset{\delta-}{Cl} \longrightarrow CH_3-\underset{}{\overset{Cl}{C}H}-\overset{NO}{C}H$$

Propylene nitrosochloride

(7) Hydroboration : It obeys markoni'koff's rule.Diborane readily reacts with alkenes giving trialkyl

boranes. The reaction is called hydroboration.



$$2R-\overset{+}{C}H=\overset{-}{C}H_2 + \overset{+}{B}_2\overset{-}{H}_6$$

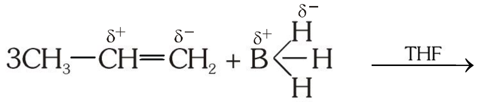
$$2(R-CH_2-CH_2)\,BH_2$$

$$R-CH=CH_2$$

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

Trialkylborane

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

Ex. 

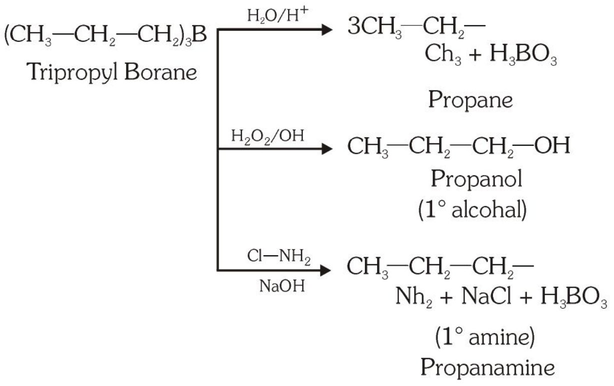
$$3CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 + \overset{\delta+}{B}\begin{smallmatrix}\overset{\delta-}{H}\\ -H\\ H\end{smallmatrix} \xrightarrow{THF}$$

$(CH_3-CH_2-CH_2)_3B$

BHR$_2$ also can be taken.

Ex. $CH_3-\overset{\delta+}{C}H=\overset{\delta-}{C}H_2 + BHR_2 \longrightarrow$

$CH_3-CH_2-CH_2-BR_2$



$$(CH_3-CH_2-CH_2)_3B \xrightarrow{H_2O/H^+} 3CH_3-CH_2-Ch_3 + H_3BO_3$$

Tripropyl Borane

Propane

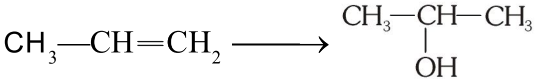
$$\xrightarrow{H_2O_2/OH} CH_3-CH_2-CH_2-OH$$

Propanol (1° alcohal)

$$\xrightarrow[NaOH]{Cl-NH_2} CH_3-CH_2-CH_2-Nh_2 + NaCl + H_3BO_3$$

(1° amine) Propanamine

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

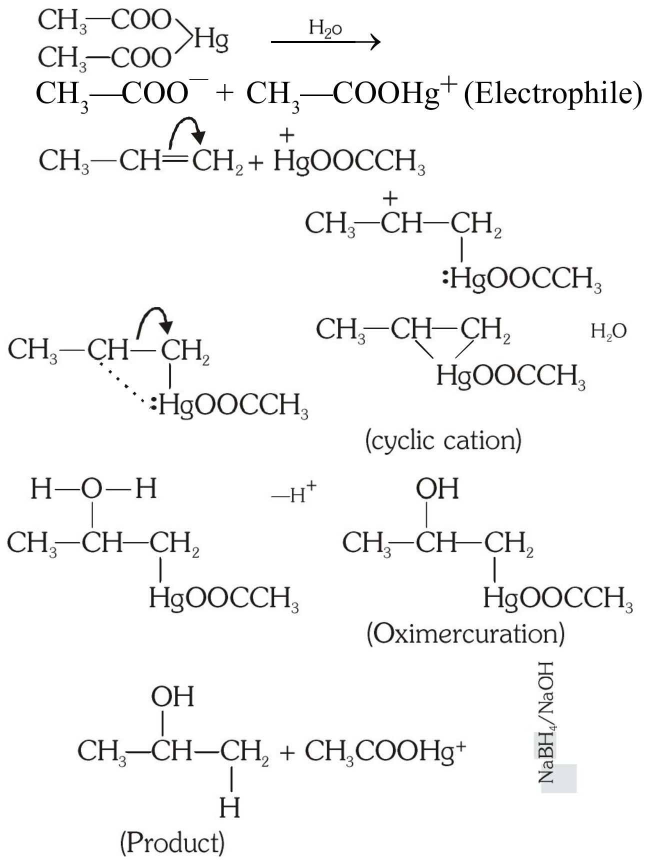


$$CH_3-CH=CH_2 \longrightarrow CH_3-\underset{OH}{CH}-CH_3$$

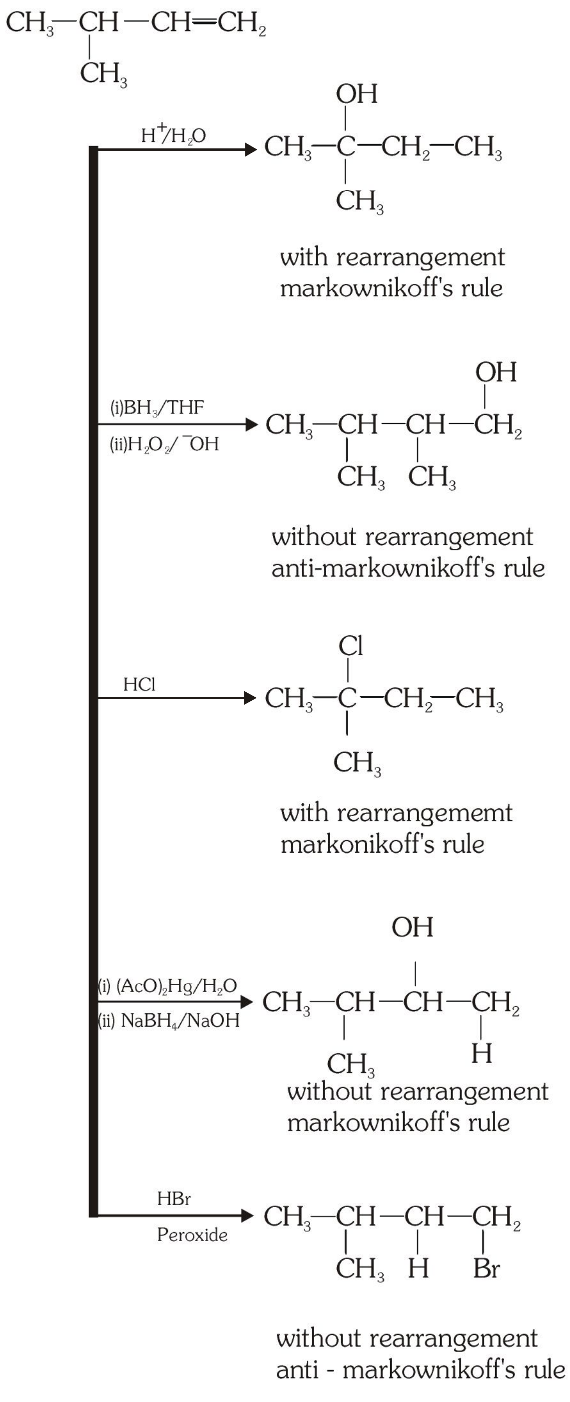
(i) $(AcO)_2$ Hg/H_2O (Mercuric acetate) or $(CH_3COO)_2$ Hg/H_2O

(ii) $NaBH_4$/NaOH

Mechanism :



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



(9) Addition with $(CH_3CO)_2O$, $CH_3COC\ell$, $(CH_3)_3CC\ell$ and $CH_3OCH_2C\ell$:

Alkenes condense with acetic anhydride in presence a catalyst e.g. $ZnCl_2$ to form unsaturate ketones. Reaction is also called acetylation.Acid chloride, alkyl chlorides and α-halogenated ethers also combine with alkenes in presence of $AlCl_3$.

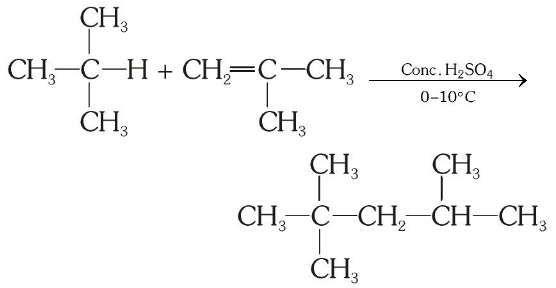
$$CH_2{=}CH_2 + (CH_3CO)_2O \xrightarrow{ZnCl_2} CH_2{=}CHCOCH_3 + CH_3COOH$$

$$CH_3COCl + CH_2{=}CH_2 \xrightarrow{AlCl_3} CH_3COCH_2CH_2Cl$$

$$(CH_3)_3CCl + CH_2{=}CH_2 \xrightarrow{AlCl_3} (CH_3)_3CCH_2CH_2Cl$$

$$(CH_3)OCH_2Cl + CH_2{=}CH_2 \longrightarrow CH_3OCH_2CH_2CH_2Cl$$

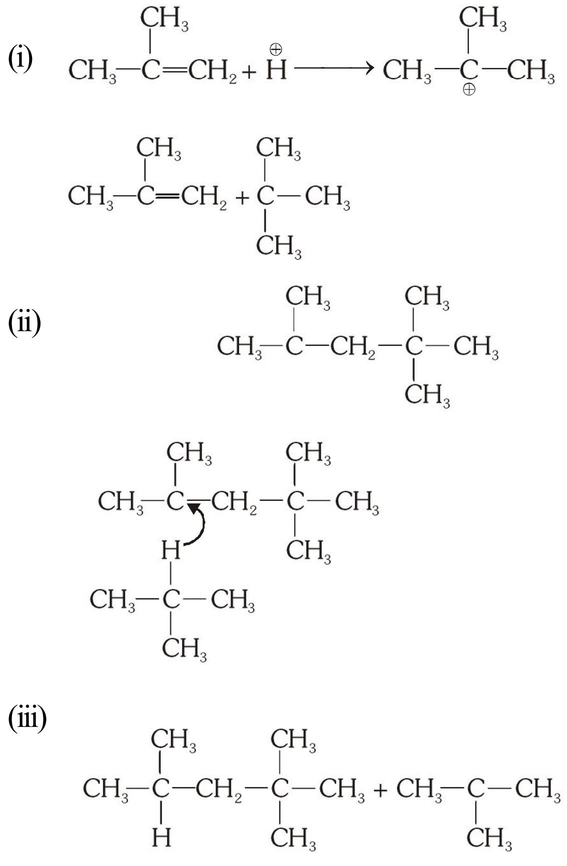
(10) Addition of alkanes (alkylation) : The addition of an alkane to an alkene results in the formation of higher alkane.



$$(CH_3)_3CH + CH_2{=}C(CH_3)CH_3 \xrightarrow[0-10°C]{Conc.\,H_2SO_4} (CH_3)_3CCH_2CH(CH_3)CH_3$$

Isooctane (an important aviation fuel) (Octane No.=100)

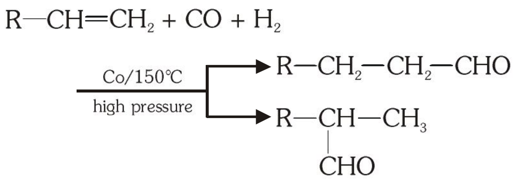
Mechanism :



The carbonium ion formed in step (II) then abstract a hydride ion $\overset{\ominus}{H}$: from isobutane to give isooctane.The carbonium ion formed in the last step propagates the chain reaction.

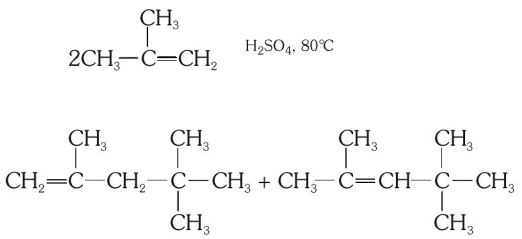
(11) Hydroformylation or Oxo reaction : Alkenes react with Carbon monoxide and hydrogen at 100 – 150°C temperature and high pressure (200 atm) in the presence of Cobalt catalyst to produce an aldehyde.It does not follows markonikoff's rule.

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



$$R{-}CH{=}CH_2 + CO + H_2 \xrightarrow[\text{high pressure}]{Co/150^\circ C} \begin{cases} R{-}CH_2{-}CH_2{-}CHO \\ R{-}\underset{\underset{CHO}{|}}{CH}{-}CH_3 \end{cases}$$

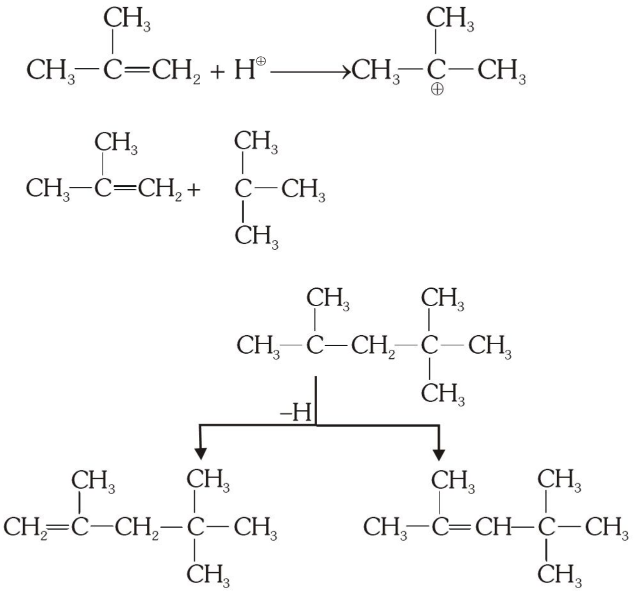
(12) Alkenylation (Addition of alkene) In presence of H_2SO_4 or H_3PO_4 at 80°C dimerisation of isobutylene take place gives two isomer of octene.



$$2CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 \xrightarrow{H_2SO_4,\ 80^\circ C}$$

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

Mechanism :



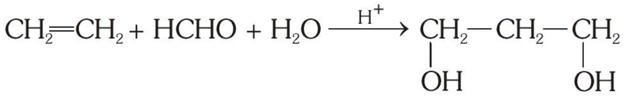
$$CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2 + H^{\oplus} \longrightarrow CH_3{-}\underset{\oplus}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3$$

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

$$CH_3{-}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \xrightarrow{-H}$$

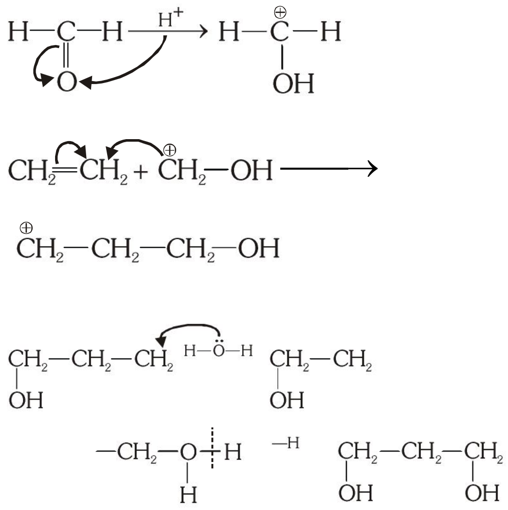
$$CH_2{=}\overset{\overset{CH_3}{|}}{C}{-}CH_2{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3 \qquad CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_3$$

(13) Addition of HCHO : In the presence of mineral acid HCHO is added to alkene molecule to obtain diol.



$$CH_2{=}CH_2 + HCHO + H_2O \xrightarrow{H^+} \underset{\underset{OH}{|}}{CH_2}{-}CH_2{-}\underset{\underset{OH}{|}}{CH_2}$$

Mechanism:



$$H{-}\underset{\underset{O}{\|}}{C}{-}H \xrightarrow{H^+} H{-}\underset{\underset{OH}{|}}{\overset{\oplus}{C}}{-}H$$

$$CH_2{=}CH_2 + \overset{\oplus}{C}H_2{-}OH \longrightarrow$$

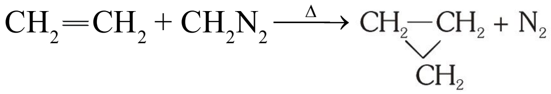
$$\overset{\oplus}{C}H_2{-}CH_2{-}CH_2{-}OH$$

$$\underset{\underset{OH}{|}}{CH_2}{-}CH_2{-}CH_2 \quad H{-}\ddot{O}{-}H \quad \underset{\underset{OH}{|}}{CH_2}{-}CH_2$$

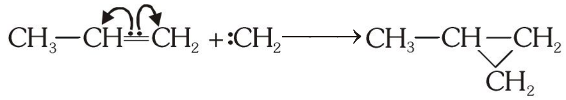
$$-CH_2{-}\underset{\underset{H}{|}}{O}{-}H \quad \xrightarrow{-H} \quad \underset{\underset{OH}{|}}{CH_2}{-}CH_2{-}\underset{\underset{OH}{|}}{CH_2}$$

(14) Addition of Carbene : The addition of carbene to alkene is always carried by diazomethane CH_2N_2

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

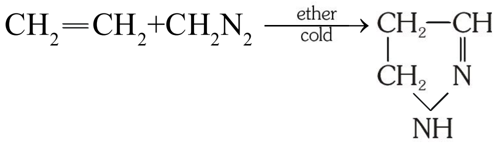


$$CH_2{=}CH_2 + CH_2N_2 \xrightarrow{\Delta} CH_2{-}CH_2\ (\text{ring with } CH_2) + N_2$$



$$CH_3{-}CH{=}CH_2 + :CH_2 \longrightarrow CH_3{-}CH{-}CH_2\ (\text{ring with } CH_2)$$

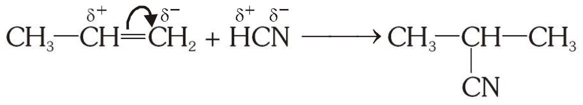
Since : CH_2 is an electrophile (neutral) and there is more electron density on double bond so first attack of :CH_2 will be at double bond.



$$CH_2{=}CH_2 + CH_2N_2 \xrightarrow[\text{cold}]{\text{ether}}$$

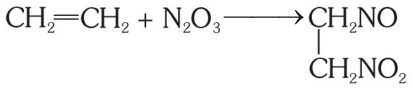
pyrazoline

(15) Addition of HCN:



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

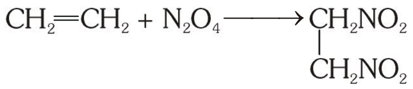
(16) Addition of N_2O_3:



$$CH_2=CH_2+N_2O_3\longrightarrow \underset{\displaystyle CH_2NO_2}{\underset{|}{CH_2NO}}$$

ethylene nitrosite

(17) Addition of N_2O_4:



$$CH_2=CH_2+N_2O_4\longrightarrow \underset{\displaystyle CH_2NO_2}{\underset{|}{CH_2NO_2}}$$

ethylene nitrosate

(B) OXIDATION REACTION :

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

(1) alkene on combustion gives CO_2 and H_2O

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

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

Solved Examples

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

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

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

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

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

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

Ex. 21 How many mole of oxygen is required for complete combustion of 1 mole of Alkene.

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

keeping in mind, the above equation.

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

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

= 1.5n mole of O_2 **Ans.**

Ex.22 30 mL mixture of ethylene and Butylene is burnt in presence of oxygen then 150 mL of oxygen is required, what is the volume of Ethylene & Butylene in mixture.

Sol. Let the volume of C_2H_4 = x mL

So volume of Butylene = (30–x) mL

For C_2H_4

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

from equation

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

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

For C_4H_8

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

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

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

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

x = 10

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

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

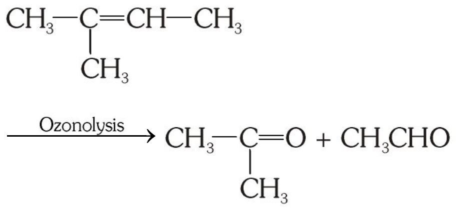
(2) Ozonolysis : (A test for unsaturation in molecule)

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

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

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

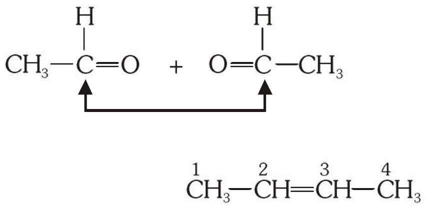
Ex.



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

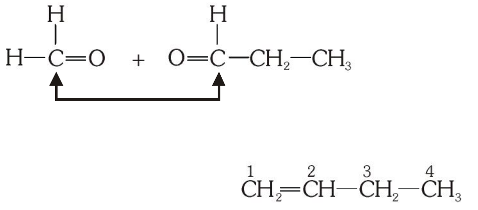
(iv) Ozonolysis of alkenes helps in locating the position of double bond in an alkene. It can be achieved by joining together the carbon atoms of the two carbonyl compounds formed as the products of ozonolysis with double bond.

Ex.



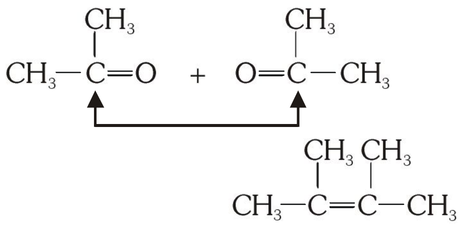
Ethanal But-2-ene

Ex.



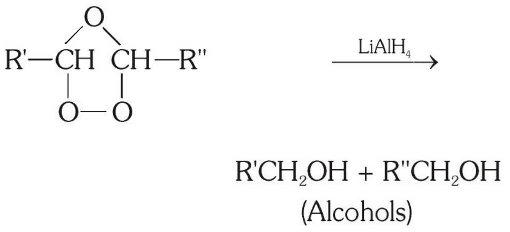
Methanal Propanal But-1-ene

Ex.



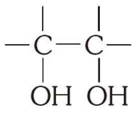
Propanone 2,3–Dimethyl but–2–ene

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

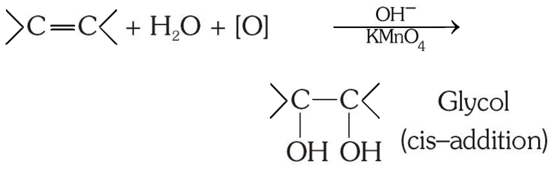


$R'CH_2OH + R''CH_2OH$

(Alcohols)

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

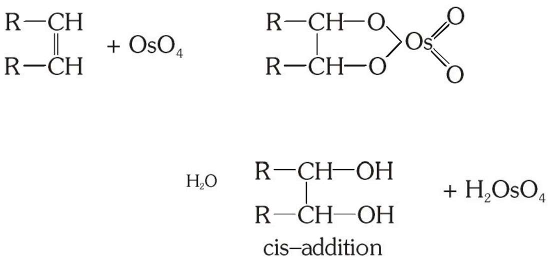
(a) Oxidation by Baeyer's reagent (A test for unsaturation) **:** Alkenes on passing through dilute alkaline 1% cold $KMnO_4$ (i.e., Baeyer's reagent) decolourise the pink colour of $KMnO_4$ and gives brown ppt MnO_2 and glycol.



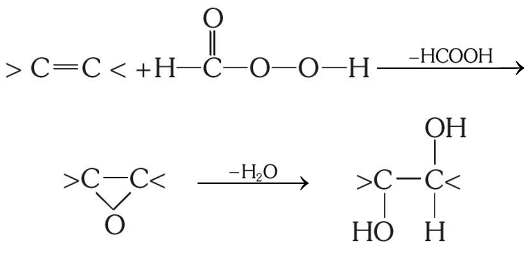
$$>C=C< + H_2O + [O] \xrightarrow[KMnO_4]{OH^-} >\underset{OH}{\underset{|}{C}}-\underset{OH}{\underset{|}{C}}<$$

Glycol (cis–addition)

(b) By OsO_4 :



(c) By peracid :

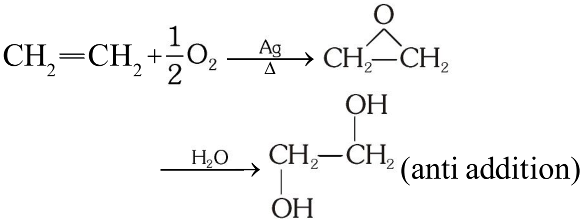


$$>C=C< + H-\overset{O}{\overset{\|}{C}}-O-O-H \xrightarrow{-HCOOH}$$

trans glycol

(4) Epoxidation :

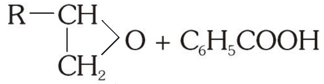
(a) Alkenes reacts with oxygen in the presence of Ag catalyst at 250°–400° C to form epoxide.



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

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

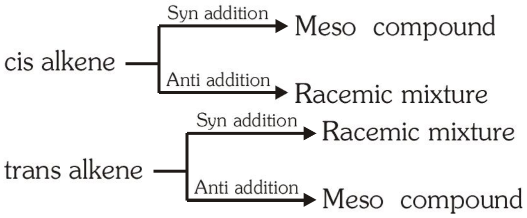
$RCH{=}CH_2 + C_6H_5COOOH \longrightarrow$



$R{-}CH{-}CH_2{>}O + C_6H_5COOH$

Epoxide

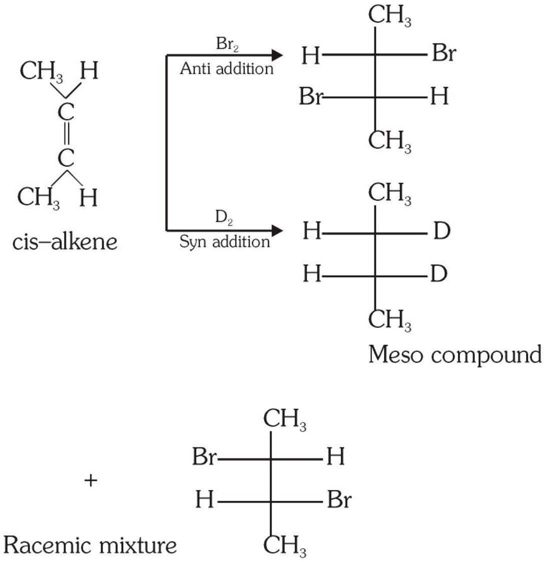
Emmons have found that perbenzoic oxy trifluoroacetic acid (CF_3COO_2H) is a very good reagent for epoxidation and hydroxylation.



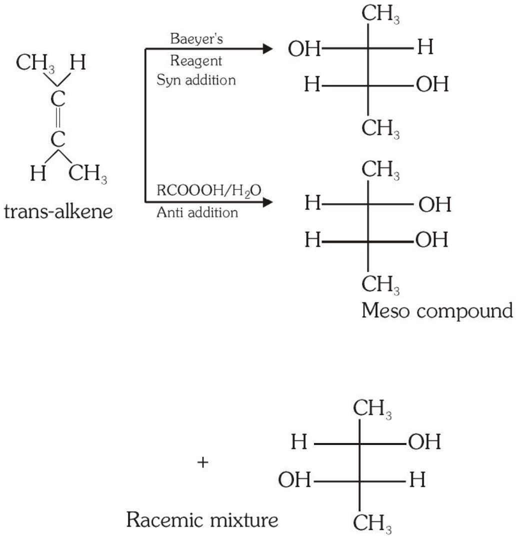
Syn addition on alkene $\longrightarrow$ H_2, O_2, Baeyer's reagent, OSO_4 / H_2O

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

Ex.. (i)



(ii)



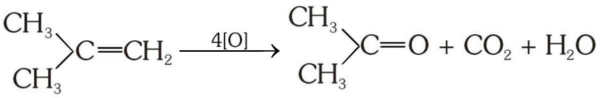
(5) **Oxidation by strong oxidising agent (Oxidative cleavage):** The alkenes themselves are readily oxidised to acid or ketone by means of acid permagnate or acid dichromate. If HCOOH is formed, it further oxidized to CO_2 and H_2O. Keep it in mind that no further oxidation of ketones will takes place.

$$CH_2{=}CH_2 + 4[O] \longrightarrow$$

$$2HCOOH \xrightarrow{2[O]} 2CO_2 + H_2O$$

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

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



$$(CH_3)_2C{=}CH_2 \xrightarrow{4[O]} (CH_3)_2C{=}O + CO_2 + H_2O$$

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

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

(C) SUBSTITUTION REACTION

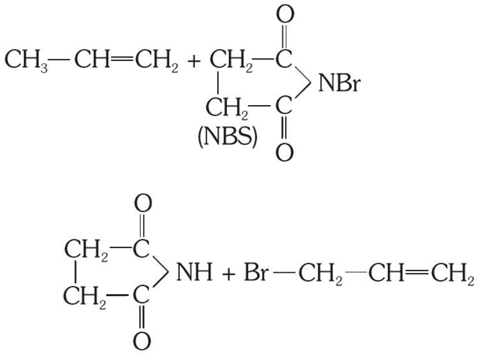
(allylic substitution)

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

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

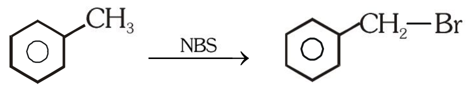
Allyl chloride (3-Chloro-1-propene)

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

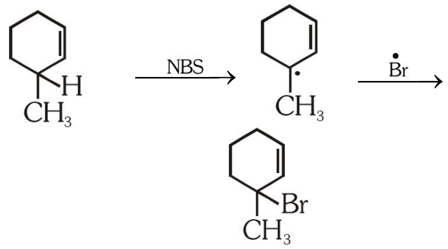


Substitution reaction is not given by ethene.

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.

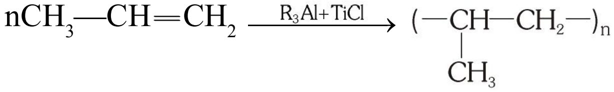
(iv) The presence of oxygen initiates free radical mechanism.

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

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

ethene Poly ethene

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

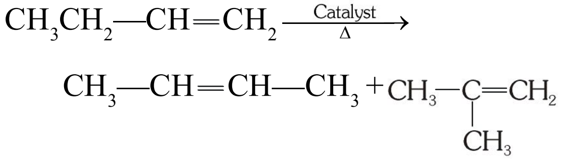


$$nCH_3—CH=CH_2 \xrightarrow{R_3Al+TiCl} (—\underset{\displaystyle CH_3}{\underset{|}{C}H}—CH_2—)_n$$

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.



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

1–Butene 2–Butene Isobutylene

USES :

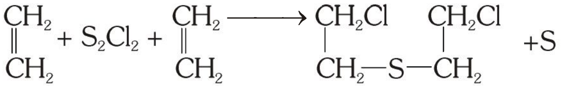
(1) In plastic formation.

(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



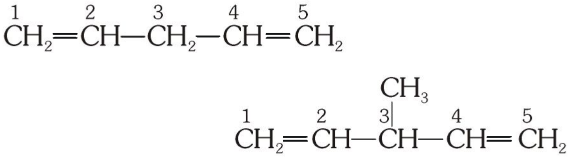
$$\begin{matrix}CH_2\\ \| \\ CH_2\end{matrix} + S_2Cl_2 + \begin{matrix}CH_2\\ \| \\ CH_2\end{matrix} \longrightarrow \begin{matrix}CH_2Cl & & CH_2Cl\\ | & & | \\ CH_2 & —S— & CH_2\end{matrix} + S$$

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

DIENES

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

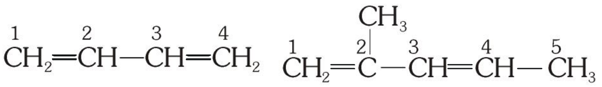
Isolated dienes or non conjugated dienes : In an isolated diene, the two double bonds are separated by more than one single bond. For example,



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

Penta–1,4–diene 3–Methylpenta–1, 4–diene

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



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

Buta-1,3-diene 2-Methylpenta-1,3-diene

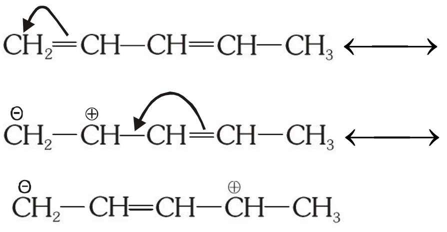
Commulate dienes : In this case, the two double bonds in the molecules are present at adjacent positions. For example,

$$\overset{1}{C}H_2{=}\overset{2}{C}{=}\overset{3}{C}H_2 \qquad \overset{1}{C}H_2{=}\overset{2}{C}{=}\overset{3}{C}H{-}\overset{4}{C}H_3$$

Propa-1,2–diene Buta–1, 2–diene

Comparison of relative stabilities of isolated and conjugated dienes :

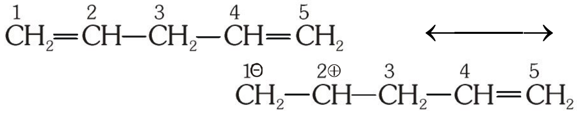
Resonance Theory : The relative stabilities of the two types dienes can also be justifid on the basis of the theory of resonance. Penta-1,3-diene (conjugated diene) is a hybrid of the following contributing structures.



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

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

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



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

(I) (II)

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

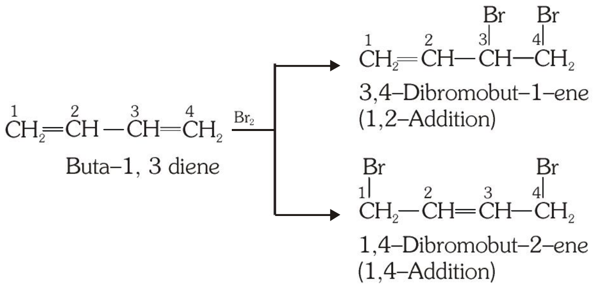
Properties of Conjugated Dienes :

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

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

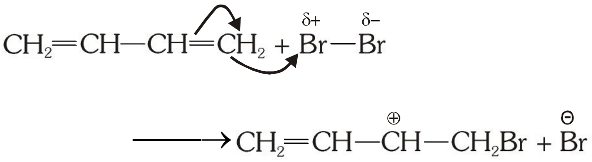
(A) Electrophilic Addition Reactions : The electrophilic addition is illustrated by the attack of halogen and halogen acid on buta–1,3–diene, a conjugated diene.

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



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

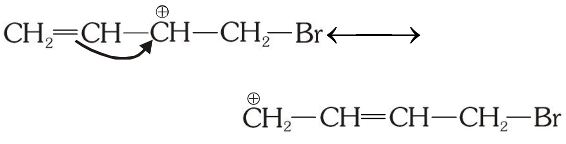
Mechanism : The addition is electrophilic in nature and the halogen molecule (bromine) provides the electrophilie for the attack.



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

Buta-1, 3-diene Carbocation (2°)

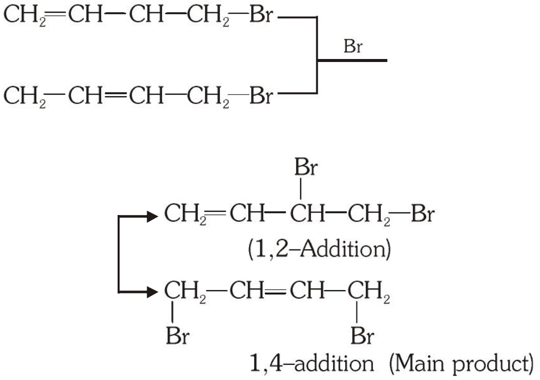
The 2° carbocation get stablised by resonance as follows –



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

I II

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



$$\left.\begin{array}{l} CH_2{=}CH{-}\overset{\oplus}{C}H{-}CH_2{-}Br \\ \overset{\oplus}{C}H_2{-}CH{=}CH{-}CH_2{-}Br \end{array}\right] \xrightarrow{Br^-} \begin{array}{l} CH_2{=}CH{-}CH(Br){-}CH_2{-}Br \\ CH_2(Br){-}CH{=}CH{-}CH_2(Br) \end{array}$$

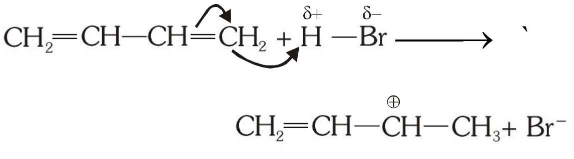
(1,2–Addition)

1,4–addition (Main product)

(b) Addition of H – X :

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

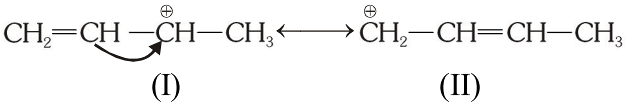
Mechanism : The addition is electrophilic in nature as H^+ ion is the electrophile.



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

Carbocation (2°)

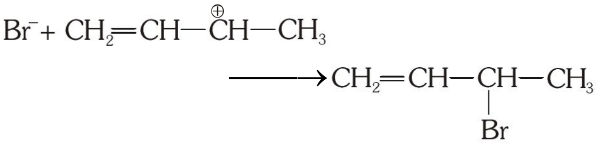
The carbocation gets resonance stabilised as follows



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

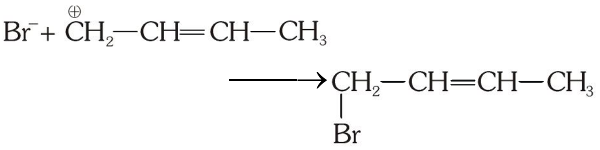
(I) (II)

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



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

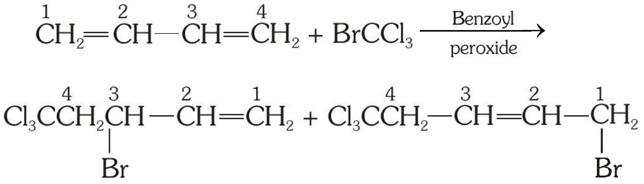
1,2–Addition product



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

1,4–Addition product

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



$$\overset{1}{C}H_2{=}\overset{2}{C}H{-}\overset{3}{C}H{=}\overset{4}{C}H_2 + BrCCl_3 \xrightarrow[\text{peroxide}]{\text{Benzoyl}} Cl_3\overset{4}{C}\overset{3}{C}H_2\underset{Br}{\overset{2}{C}H}{-}\overset{1}{C}H{=}CH_2 + Cl_3\overset{4}{C}\overset{3}{C}H_2{-}\overset{2}{C}H{=}CH{-}\underset{Br}{\overset{1}{C}H_2}$$

Buta–1,3–diene Bromotri- chloromethane

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

Step I : Generation of free radical

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

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

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

Trichloromethyl free radical

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

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

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

Free radical (secondary)

The free radical gets resonance stabilised

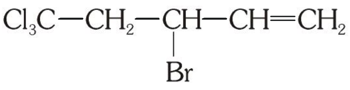
$$Cl_3C{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \longleftrightarrow$$

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

Step III. Change of free radical into addition product

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

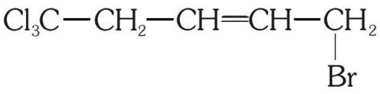
$$BrCCl_3 + Cl_3C{-}CH_2{-}\dot{C}H{-}CH{=}CH_2 \longrightarrow$$



$$Cl_3C{-}CH_2{-}\underset{\underset{Br}{|}}{CH}{-}CH{=}CH_2$$

(1,2-Addition product)

$$BrCCl_3 + Cl_3C{-}CH_2{-}CH{=}CH{-}\dot{C}H_2$$



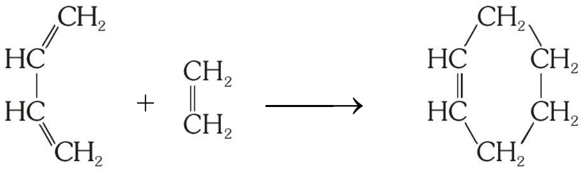
$$Cl_3C{-}CH_2{-}CH{=}CH{-}\underset{\underset{Br}{|}}{CH_2}$$

(1,4–Addition product)

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

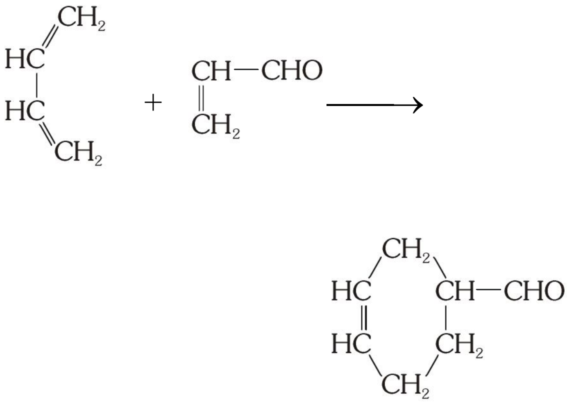
Cyclo-addition reactions are one of the most important reactions of conjugated dienes. Cyclo-addition involves the combination between a conjugated diene (4π-electron system) and a compound containing a double bond (2π-electron system) called **dienophile** which means a diene loving or attracting molecule.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

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



Buta–1,3–diene Ethene

Cyclohexene **(Diel Alder adduct)**



Buta–1,3–diene Propenal (Acrolein)

3-cyclohexene carbaldehyde

Volume of hydrocarbon will be given and volume of O_2 for complete combustion will also be given. What is hydrocarbon is to be asked ?

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

Formula No. 1 $\dfrac{\text{Volume of H.C.}}{\text{Volume of } O_2} = \dfrac{2}{3n+1}$

(for Alkane)

Formula No. 2 $\dfrac{\text{Volume of H.C.}}{\text{Volume of } O_2} = \dfrac{2}{3n}$

(for Alkene)

Formula No. 3 $\dfrac{\text{Volume of H.C.}}{\text{Volume of } O_2} = \dfrac{2}{3n-1}$

(for Alkyne)

Solved Examples

Ex. 23 How much propanol is required for dehydration to get 2.24 litre of Propene at N.T.P. if yield is 100%.

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

Molecular weight of propanol = 60

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

$\because$ 22.4 litre of C_3H_6 can be get from dehydration of 60 g of propanol.

$\therefore$ 1 litre of propene can be get from dehydration

of $\frac{60}{22.4}$ g of propanol

$\therefore$ 2.24 litre of propene can be get from dehydration

of $\frac{60}{22.4}$x2.24 g of propano

= 6 g

ALKYNES

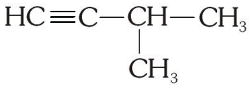
Alkynes are unsaturated hydrocarbons and characterised by the presence of a triple bond between the two carbon atoms (C≡C). The triple bond is also called acetylinic bond. It consists of a strong σ and two weak π bonds. Alkynes are isomers of alkadienes and cycloalkenes .

Property	**Characteristics of alkynes**
General formula	C_nH_{2n-2}
C—C Bond energy	198 K cal/mole
Hybridisation on C	sp
Bond angle	180^0
C—C Bond length	1.20 A^0
C—H Bond length	1.08 A^0
shape	linear

Solved Examples

Ex.24 The minimum number of carbon atoms present in alkyne which contains one side chain , are

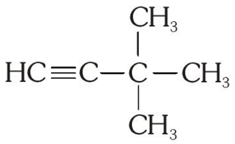
Sol. 5C,



$$HC\equiv C-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

Ex.25 The minimum number of carbon atoms present in alkyne which contains two side chain , are

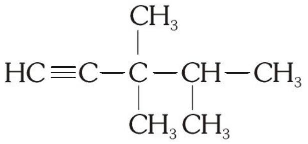
Sol. 6C,



$$HC\equiv C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

Ex26 The minimum number of carbon atoms present in alkyne which contains three side chain , are

Sol. 8C,

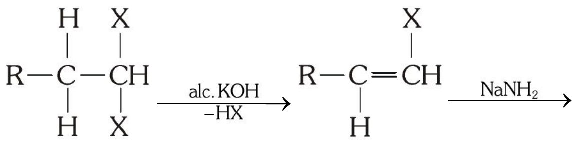


$$HC\equiv C-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

General Methods of Preparation :

1. From Gem dihalides (by dehydrohalogenation)

Dehydrohalogenation agents are : $NaNH_2$ (Sodamide) or Alc. KOH or ROH + RONa.



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

$R—C\equiv CH + NaX + NH_3$

(Stable by resonance)

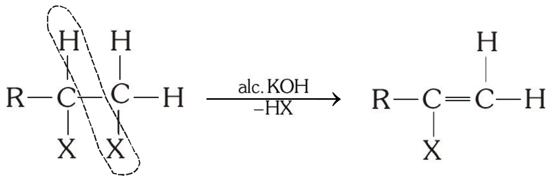
(Vinyl halide)

(a) Due to stability of vinyl halide by resonance there is partial double bond in which elimination does not take place by alc. KOH so stronger base $NaNH_2$ is used.

(b) Basic strength : $\overset{\ominus}{N}H_2$ is stronger base then $RO^{\ominus}$

(c) Trans elimination takes place in forming of alkynes.

2. From Vicinal dihalides
(by dehydrohalogenation)

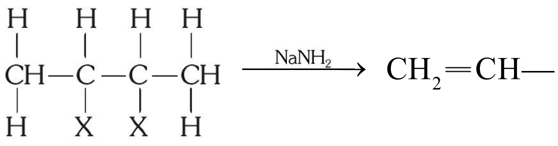


$$R-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle X}{\underset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle X}{\underset{|}{C}}}}-H\xrightarrow[-HX]{alc.\,KOH}R-\underset{\displaystyle X}{\underset{|}{C}}=\overset{\displaystyle H}{\overset{|}{C}}-H$$

$$\xrightarrow[-HX]{NaNH_2} R—C\equiv CH$$

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

Ex.



$$\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle H}{\underset{|}{CH}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle X}{\underset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle X}{\underset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle H}{\underset{|}{CH}}}}\xrightarrow{NaNH_2}CH_2=CH—$$

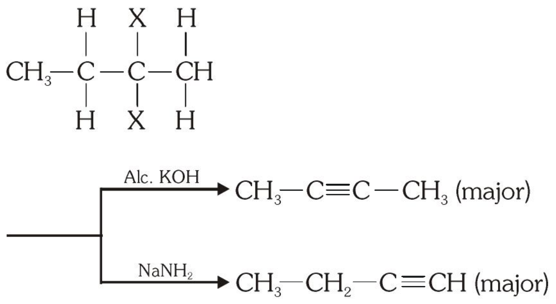
$CH=CH_2 + CH_2=C=CH—CH_3 +$

$CH_3—C\equiv C—CH_3$

(Major)

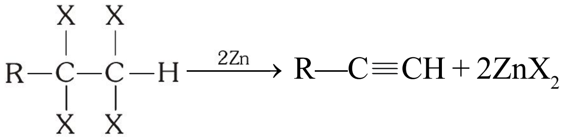
(b) Non terminal gem dihalide gives 2-Alkyne in presence of alc. KOH while gives 1-alkyne in presence of $NaNH_2$.

Ex.



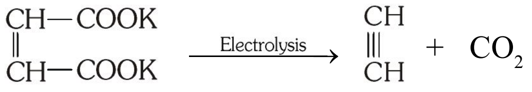
$$CH_3-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-\underset{H}{\overset{H}{C}}H \begin{cases} \xrightarrow{\text{Alc. KOH}} CH_3-C\equiv C-CH_3 \text{ (major)} \\ \xrightarrow{NaNH_2} CH_3-CH_2-C\equiv CH \text{ (major)} \end{cases}$$

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



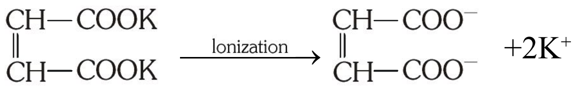
$$R-\underset{X}{\overset{X}{C}}-\underset{X}{\overset{X}{C}}-H \xrightarrow{2Zn} R-C\equiv CH + 2ZnX_2$$

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



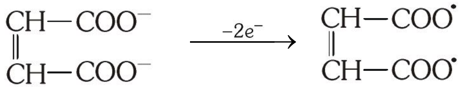
$$\begin{array}{l} CH-COOK \\ \| \\ CH-COOK \end{array} \xrightarrow{\text{Electrolysis}} \begin{array}{c} CH \\ ||| \\ CH \end{array} + CO_2$$

Mechanism :



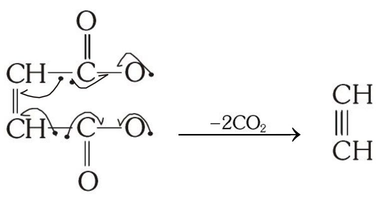
$$\begin{array}{l} CH-COOK \\ \| \\ CH-COOK \end{array} \xrightarrow{\text{Ionization}} \begin{array}{l} CH-COO^- \\ \| \\ CH-COO^- \end{array} +2K^+$$

at anode (Alkyl and CO_2 gas is formed)



$$\begin{array}{l} CH-COO^- \\ \| \\ CH-COO^- \end{array} \xrightarrow{-2e^-} \begin{array}{l} CH-COO^{\bullet} \\ \| \\ CH-COO^{\bullet} \end{array}$$

(Oxygen free radical)



$$\begin{array}{l} CH-\overset{O}{\overset{\|}{C}}-O^{\bullet} \\ \| \\ CH-\underset{O}{\underset{\|}{C}}-O^{\bullet} \end{array} \xrightarrow{-2CO_2} \begin{array}{c} CH \\ ||| \\ CH \end{array}$$

at cathode (KOH and H_2 gas is formed)

$2K^+ + 2e^- \longrightarrow 2K$

$2K + 2H_2O \longrightarrow 2KOH + H_2\uparrow$

Solved Examples

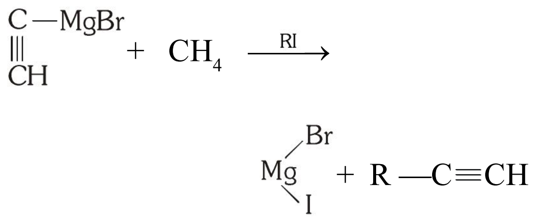
Ex.27 Is PH of solution changed in Kolbe's electrolysis.

Sol. The concentration of NaOH solution increased so pH of solution is increased with time.

---

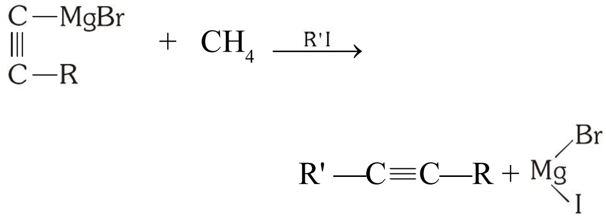
5. **Preparation of higher alkynes by Grignard reagent :** By this method lower alkyne is converted in to higher alkyne

$$CH\equiv \overset{\delta-}{C}-\overset{\delta+}{H}+\overset{\delta-}{CH_3}-\overset{\delta+}{Mg}-Br \longrightarrow$$



$$\begin{array}{l} C-MgBr \\ ||| \\ CH \end{array} + CH_4 \xrightarrow{RI} Mg\begin{array}{l} Br \\ I \end{array} + R-C\equiv CH$$

$$R-C\equiv CH + CH_3Mg-Br \longrightarrow$$



$$\begin{array}{l} C-MgBr \\ ||| \\ C-R \end{array} + CH_4 \xrightarrow{R'I} R'-C\equiv C-R + Mg\begin{array}{l} Br \\ I \end{array}$$

6 **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) **Manufacture :** Acetylene is manufactured by heating methane or natural gas at 1500⁰C in an electric arc

$$2CH_4 \xrightarrow{\text{Electric arc}} CH\equiv CH + 3H_2$$

(c) **Berthelot's process :** Acetylene is synthesized by striking an electric arc between carbon electrodes in presence of hydrogen.

$$2C + H_2 \xrightarrow{1200^\circ C} CH\equiv CH$$

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

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

(e) Partial oxidation of methane : A recent method for manufacturing of acetylene is the controlled partial oxidation of methane at high temperature.

$$4CH_4 + 3O_2 \xrightarrow{1500°C} 2CH{\equiv}CH + 6H_2O$$

Physical Properties :

(i) First three members [C_2 to C_4] are gases, from C_5 to C_{11} 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 additons, alkynes also undergo nucleophilic addition with nucleophiles

(b) Presence of acidic hydrogen atom : The hydrogen atom attached to the triple bonded carbon can be easily 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-

≡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 more 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 ═ CH can be easily removed as proton

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

≡C—H	>	=C—H	>	—C—H
sp		sp^2		sp^3

Relative acidic order

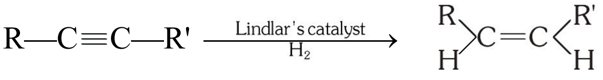
H_2O > ROH > $HC{\equiv}CH$ > HNH_2 > $CH_2{=}CH_2$ > $CH_3{-}CH_3$

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

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

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



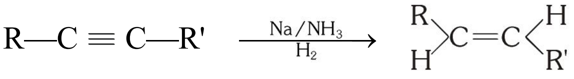
$$R{-}C{\equiv}C{-}R' \xrightarrow[H_2]{\text{Lindlar's catalyst}} \overset{R}{\underset{H}{>}}C{=}C\overset{R'}{\underset{H}{<}}$$

cis - alkene

(Stereo specific reaction)

In presence of Na/NH_3 alkynes give trans-alkene.

(Birch Recuction)



$$R{-}C \equiv C{-}R' \xrightarrow[H_2]{Na/NH_3} \overset{R}{\underset{H}{>}}C{=}C\overset{H}{\underset{R'}{<}}$$

trans-alkene

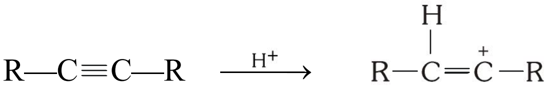
(Stereo specific reaction)

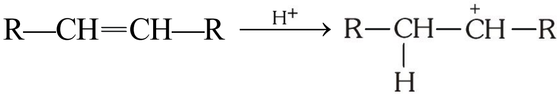
(b) Electrophilic addition : Addition reactions where the addition is initiated by electrophile (positive group). The characteristic reaction of alkynes is electrophilic addition but the reactivity of alkynes towards electrophilic addition is less than alkenes because in C≡C, the π electrons are tightly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

Reactivity order of hydrocarbons for electrophilic addition

$\boxed{\text{Alkenes > Alkynes > Alkanes}}$.

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

(i) 
$R-C\equiv C-R \xrightarrow{H^+} R-\overset{H}{\overset{|}{C}}=\overset{+}{C}-R$

(ii) 
$R-CH=CH-R \xrightarrow{H^+} R-\underset{H}{\underset{|}{CH}}-\overset{+}{CH}-R$

Stability of intermediates :

$R-CH=\overset{\oplus}{C}-R \quad < \quad R-CH_2-\overset{\oplus}{CH}-R$

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

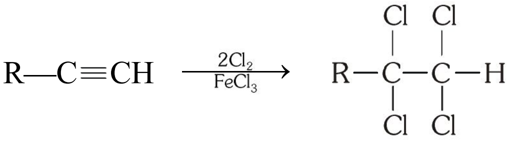
So we can say that alkenes are more reactive towards electrophilic addition reaction.

(1) Addition of Halogens :

Reactivity order of Halogens

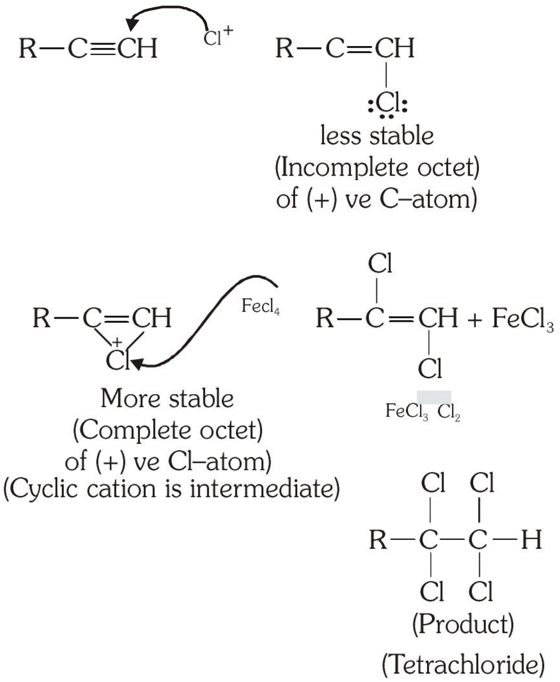
$Cl_2 > Br_2 > I_2$

Alkynes react with Cl_2 or Br_2 in dark in presence of metal halide and form di and tetra halo derrivatives.


$R-C\equiv CH \xrightarrow[FeCl_3]{2Cl_2} R-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-H$

Mechanism :

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



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

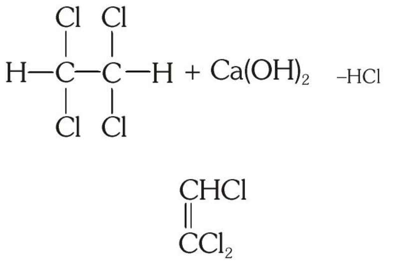
More stable (Complete octet) of (+) ve Cl–atom) (Cyclic cation is intermediate)

(Product)

(Tetrachloride)

Acetylene tetrachloride is also called as westron.

When westron is treated with $Ca(OH)_2$ then we get westrosol

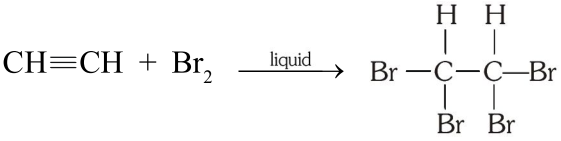

$H-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-H + Ca(OH)_2 \xrightarrow{-HCl} \begin{matrix} CHCl \\ \| \\ CCl_2 \end{matrix}$

Westrosol or triclene

Both westron and westrosol are used as solvents in cloth industries

Reaction with dilute Br_2 or bromine water:

$CH\equiv CH + Br_2 \xrightarrow{H_2O} Br-CH=CH-Br$


$CH\equiv CH + Br_2 \xrightarrow{\text{liquid}} Br-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-\underset{Br}{\underset{|}{\overset{H}{\overset{|}{C}}}}-Br$

Reaction with Iodine :

$CH{\equiv}CH + I_2 \xrightarrow{\text{ethanol}} CHI{=}CHI$

(addition reaction)

$CH{\equiv}CH + I_2 \xrightarrow{NH_3} I{-}C{\equiv}C{-}I + NH_4I$

Di iodoacetylene

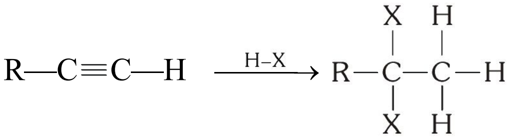
(substitution reaction)

(2) Addition of halogen acids (H – X) :

Addition according to Markowni-Koff's Rule.

Reactivity order of H – X :

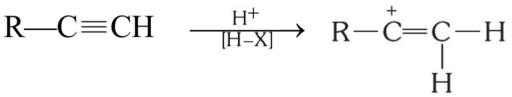
HI	>	HBr	>	HCl	>	HF



$$R{-}C{\equiv}C{-}H \xrightarrow{H-X} R{-}\underset{X}{\overset{X}{C}}{-}\underset{H}{\overset{H}{C}}{-}H$$

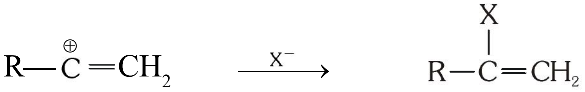
(Gem dihalides major product)

Mechanism :



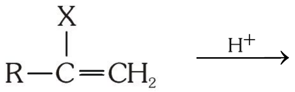
$$R{-}C{\equiv}CH \xrightarrow[\text{[H–X]}]{H^+} R{-}\overset{+}{C}{=}\underset{H}{C}{-}H$$

(Intermediate is carbocation)

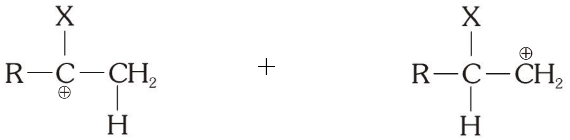


$$R{-}\overset{\oplus}{C}{=}CH_2 \xrightarrow{X^-} R{-}\overset{X}{C}{=}CH_2$$

Further



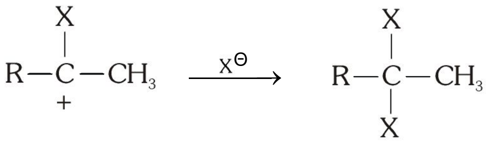
$$R{-}\overset{X}{C}{=}CH_2 \xrightarrow{H^+}$$



$$R{-}\underset{\oplus}{\overset{X}{C}}{-}\underset{H}{CH_2} \quad + \quad R{-}\underset{H}{\overset{X}{C}}{-}\overset{\oplus}{CH_2}$$

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

so



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

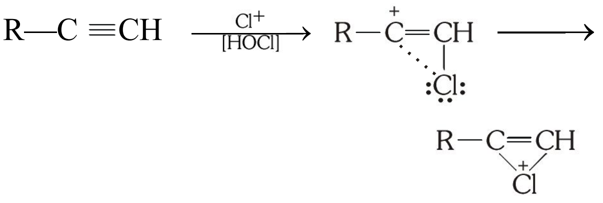
(Major Product)

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

Reactivity order	HOCl	>	HOBr	>	HOI

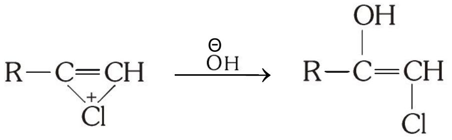
$$R{-}C{\equiv}CH + HOCl \longrightarrow R{-}\underset{O}{\underset{\|}{C}}{-}CHCl_2$$

Mechanism :



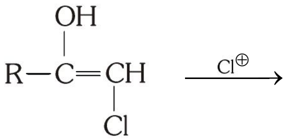
$$R{-}C{\equiv}CH \xrightarrow[\text{[HOCl]}]{Cl^+} R{-}\overset{+}{C}{=}\underset{:\ddot{Cl}:}{CH} \longrightarrow R{-}C{=}CH \ (\overset{+}{Cl}\text{ bridged})$$

(Cyclic cation)

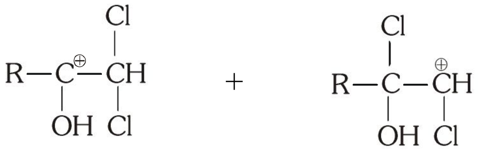


$$R{-}C{=}CH\ (\overset{+}{Cl}\text{ bridged}) \xrightarrow{\overset{\ominus}{O}H} R{-}\overset{OH}{C}{=}\underset{Cl}{CH}$$

Further



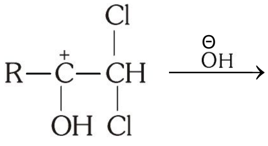
$$R{-}\overset{OH}{C}{=}\underset{Cl}{CH} \xrightarrow{Cl^{\oplus}}$$



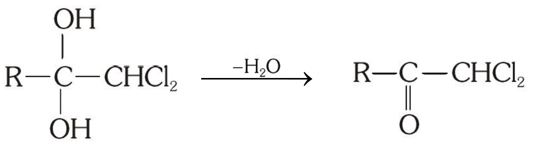
$$R{-}\underset{OH}{\overset{\oplus}{C}}{-}\underset{Cl}{\overset{Cl}{CH}} \quad + \quad R{-}\underset{OH}{\overset{Cl}{C}}{-}\underset{Cl}{\overset{\oplus}{CH}}$$

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

so



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

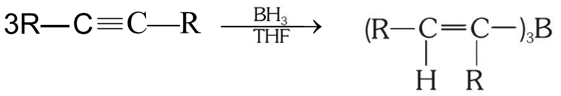


$$R{-}\underset{OH}{\overset{OH}{C}}{-}CHCl_2 \xrightarrow{-H_2O} R{-}\underset{O}{\underset{\|}{C}}{-}CHCl_2$$

(Unstable) (Dichloro ketones)

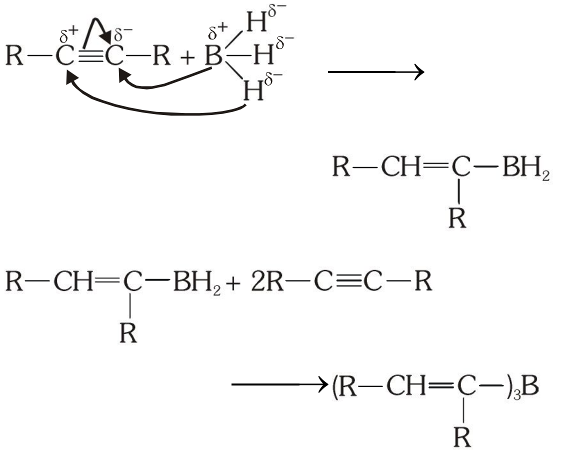
(4) Addition of BH_3 / THF or B_2H_6

(Hydroboration) : THF - Tetrahydrofurane is used as solvent.



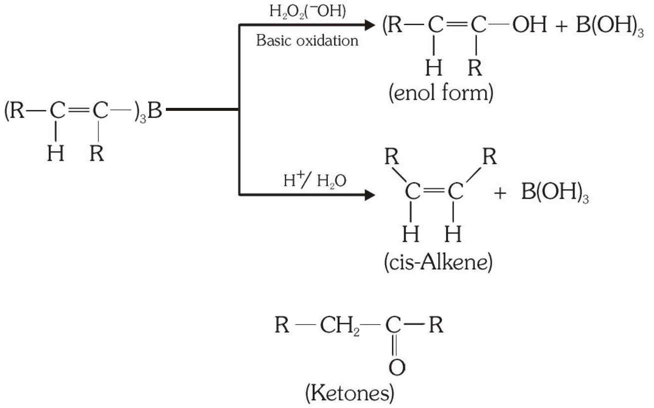
$$3R—C\equiv C—R \xrightarrow[THF]{BH_3} (R—\underset{H}{C}=\underset{R}{C}—)_3B$$

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

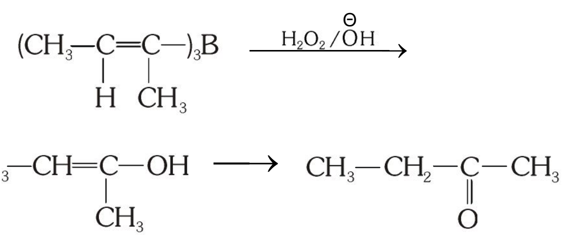


$$R—CH=\underset{R}{C}—BH_2$$

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



Ex. $CH_3—C\equiv C—CH_3 \xrightarrow[THF]{BH_3}$



$$(CH_3—\underset{H}{C}=\underset{CH_3}{C}—)_3B \xrightarrow{H_2O_2/\overset{\ominus}{O}H}$$

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

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

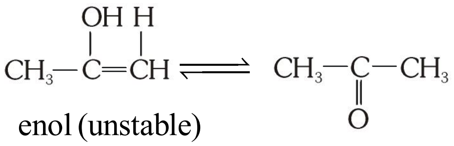
(c) Nucleophilic addition reaction : In these reactions some heavy metal cation like Hg^{+2}, Pb^{+2}, Ba^{+2} are used. These cation attracts the π^- e^- of alkynes and decrease the e^- density and hence a nucleophile can attack an alkynes.

(1) Addition of dil. H_2SO_4 (Hydration) : The addition of water takes place in the presence of Hg^{+2} and H_2SO_4 [1% $HgSO_4$+40% H_2SO_4]. In this reaction carbonyl compounds are obtained .

$$CH\equiv CH + H—OH \longrightarrow$$

$$\underset{\text{enol unstable}}{CH_2=CH—OH} \rightleftharpoons CH_3—CHO$$

$$CH_3—C\equiv CH + H—OH \longrightarrow$$

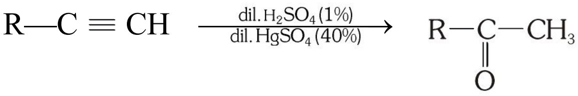


$$CH_3—\overset{OH}{C}=\overset{H}{CH} \rightleftharpoons CH_3—\underset{\|O}{C}—CH_3$$

enol (unstable)

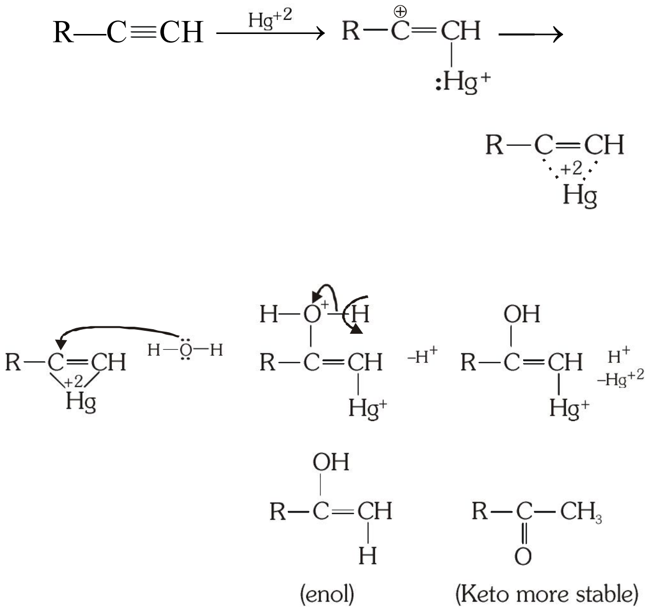
A structure in which –OH group is attached to double bond carbon is called as enol (ene + – ol).

This reaction is used for preparation of aldehyde and ketone.

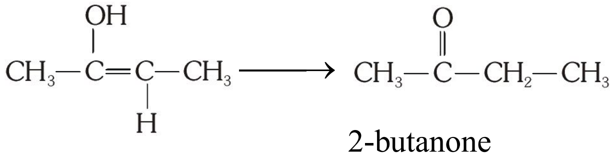


$$R—C\equiv CH \xrightarrow[\text{dil. }HgSO_4(40\%)]{\text{dil. }H_2SO_4(1\%)} R—\underset{\|O}{C}—CH_3$$

Mechanism :



Ex. $CH_3—C\equiv C—CH_3 \xrightarrow[Hg^{+2}]{H^+/H_2O}$



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

2-butanone

(2) Addition of HCN : The addition of HCN in presence of barium cyanide to form vinyl cyanide.

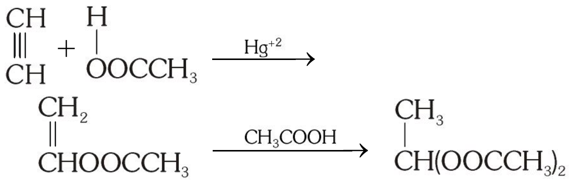
$CH\equiv CH + HCN \xrightarrow{Ba(CN)_2} CH_2{=}CHCN$

The vinyl cyanide is used for making polymers such as orlon and Buna-N rubber.

$$CH_2{=}CHCN \xrightarrow{\text{Polymerisation}} (-CH_2-\underset{\underset{CN}{|}}{CH}-)_n$$

Orlon

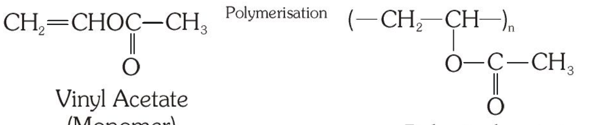
(3) Addition of acetic acid : Acetate acetylene combines with acetic acid in presence of murcuricsulphate. It first forms vinyl acetate and then ethylidene acetate.



$$\begin{matrix}CH\\|||\\CH\end{matrix} + \begin{matrix}H\\|\\OOCCH_3\end{matrix} \xrightarrow{Hg^{+2}}$$

$$\begin{matrix}CH_2\\\|\\CHOOCCH_3\end{matrix} \xrightarrow{CH_3COOH} \begin{matrix}CH_3\\|\\CH(OOCCH_3)_2\end{matrix}$$

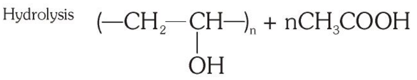
vinyl acetate　　Ethylidene acetate



$$CH_2{=}CHO\underset{\underset{O}{\|}}{C}-CH_3 \xrightarrow{\text{Polymerisation}} (-CH_2-\underset{\underset{O-\underset{\underset{O}{\|}}{C}-CH_3}{|}}{CH}-)_n$$

Vinyl Acetate
(Monomer)

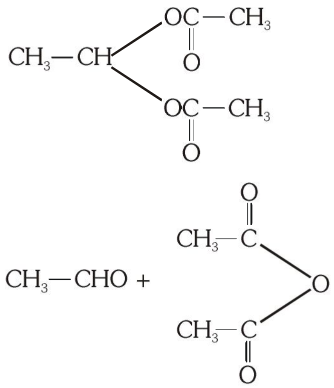
Poly vinyl acetate
(Polymer : adhesive compound)



$$\xrightarrow{\text{Hydrolysis}} (-CH_2-\underset{\underset{OH}{|}}{CH}-)_n + nCH_3COOH$$

Poly vinyl alcohol

When ethylidene acetate is heated it give acetaldehyde and acetic anhydride

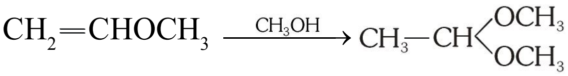


$$CH_3-CH\begin{matrix}\diagup OC-CH_3 \\ \quad\ \|\\ \quad\ O\\ \diagdown OC-CH_3\\ \quad\ \|\\ \quad\ O\end{matrix}$$

$$CH_3-CHO + \begin{matrix} CH_3-\overset{\overset{O}{\|}}{C}\diagdown\\ \qquad\quad O\\ CH_3-\underset{\underset{O}{\|}}{C}\diagup\end{matrix}$$

(4) Addition of alcohols : In presence of BF_3 and HgO alkynes react with alcohols and form acetal and ketal

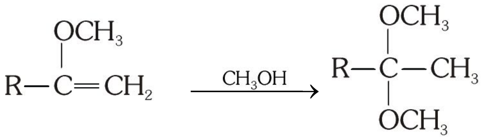
$CH\equiv CH + CH_3OH \xrightarrow[HgO]{BF_3}$



$$CH_2{=}CHOCH_3 \xrightarrow{CH_3OH} CH_3-CH\begin{matrix}\diagup OCH_3\\ \diagdown OCH_3\end{matrix}$$

Methylal (acetal)

$R—C\equiv CH + CH_3—OH \xrightarrow[HgO]{BF_3}$

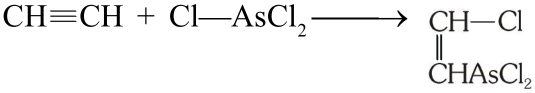


$$R-\overset{\overset{OCH_3}{|}}{C}=CH_2 \xrightarrow{CH_3OH} R-\overset{\overset{OCH_3}{|}}{\underset{\underset{OCH_3}{|}}{C}}-CH_3$$

Ketal

Acetylene forms acetal while other alkynes form ketal.

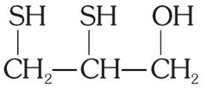
(d) Addition of $AsCl_3$: In presence of $AlCl_3$ or $HgCl_2$ acetylene combines with $AsCl_3$ to yield Lewisite gas. It is four times poisonous than mustard gas.



$$CH\equiv CH + Cl—AsCl_2 \longrightarrow \begin{matrix}CH—Cl\\\|\\CHAsCl_2\end{matrix}$$

2-Chlorovinyl dichloro arsine (Lewisite gas)

The action of Lewsite may be checked by its antidote BAL (British Anti Lewisite). BAL combines with the Lewisite to form a cyclic non toxic compound.



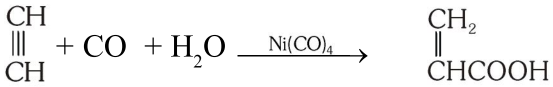
$$\underset{}{\overset{\overset{SH}{|}}{CH_2}}-\overset{\overset{SH}{|}}{CH}-\overset{\overset{OH}{|}}{CH_2}$$

2, 3–Dimercapto–1–propanol [BAL]

(e) Carbonylation : Reaction of alkynes with CO in presence of $Ni(CO)_4$

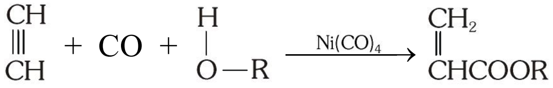
Alkyne + CO + $H_2O \xrightarrow{Ni(CO)_4}$ Olefinic acid

Alkyne + CO + R–OH $\xrightarrow{Ni(CO)_4}$ Olefinic ester



$$\begin{matrix}CH\\|||\\CH\end{matrix} + CO + H_2O \xrightarrow{Ni(CO)_4} \begin{matrix}CH_2\\\|\\CHCOOH\end{matrix}$$

Acrylic acid



$$\begin{matrix}CH\\|||\\CH\end{matrix} + CO + \begin{matrix}H\\|\\O-R\end{matrix} \xrightarrow{Ni(CO)_4} \begin{matrix}CH_2\\\|\\CHCOOR\end{matrix}$$

Alkyl acrylate

2 OXIDATION REACTIONS :

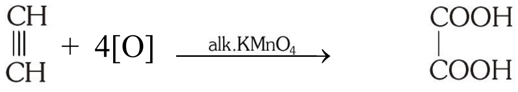
(a) Combustion :

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

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

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

(b) Oxidation with alkaline $KMnO_4$: Oxidation with alkaline $KMnO_4$ gives carboxylic acids.



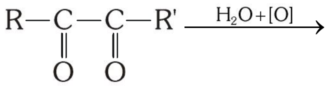
$$CH\equiv CH + 4[O] \xrightarrow{alk.KMnO_4} COOH{-}COOH$$

Acetylene Oxalic acid

$$CH_3{-}C\equiv CH + 4[O] \xrightarrow{alk.KMnO_4} CH_3{-}COOH + HCOOH$$

(c) Oxidation with acidic $KMnO_4$ or $K_2Cr_2O_7$: In presence of acidic $KMnO_4$ or acidic $K_2Cr_2O_7$. Alkynes are oxidised to monocarboxylic acids.

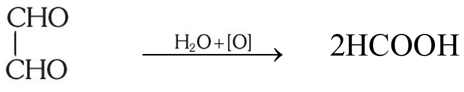
$$R{-}C\equiv C{-}R' + 2[O] \longrightarrow$$



$$R{-}\underset{\|}{\overset{}{C}}{-}C{-}R' \quad (R{-}CO{-}CO{-}R') \xrightarrow{H_2O+[O]}$$

RCOOH + R'COOH

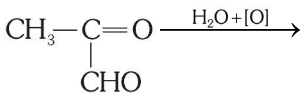
$$CH\equiv CH + 2[O] \longrightarrow$$



$$CHO{-}CHO \xrightarrow{H_2O+[O]} 2HCOOH$$

glyoxal

$$CH_3{-}C\equiv CH + 2[O] \longrightarrow$$



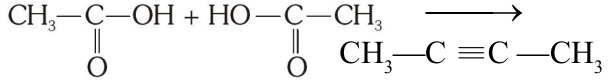
$$CH_3{-}C(=O){-}CHO \xrightarrow{H_2O+[O]}$$

$$CH_3COOH + HCOOH$$

Solved Examples

Ex.28 An alkyne on oxidation with acidic $KMnO_4$, only acetic acid is obtained what is given alkynes ?

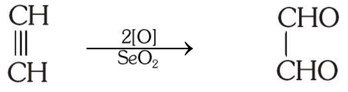
Sol. In Oxidation of alkynes two moles of mono carboxylic acids are obtained.



$$CH_3{-}\underset{\underset{O}{\|}}{C}{-}OH + HO{-}\underset{\underset{O}{\|}}{C}{-}CH_3 \longrightarrow CH_3{-}C\equiv C{-}CH_3$$

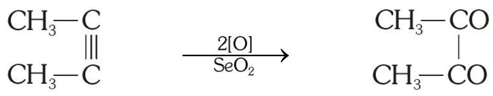
2–Butyne

(d) Oxidation with selenium dioxide : Selenium dioxide oxidises alkynes to the dicarbonyl compounds.



$$CH\equiv CH \xrightarrow[SeO_2]{2[O]} CHO{-}CHO$$

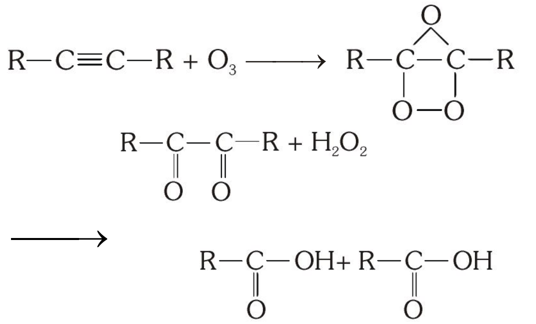
Glyoxal



$$CH_3{-}C\equiv C{-}CH_3 \xrightarrow[SeO_2]{2[O]} CH_3{-}CO{-}CO{-}CH_3$$

2–Butyne Butane - 2, 3 -dione

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



$$R{-}C\equiv C{-}R + O_3 \longrightarrow R{-}\underset{\underset{O-O}{|\quad |}}{C{-}C}{-}R \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}R + H_2O_2 \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}OH + R{-}\underset{\underset{O}{\|}}{C}{-}OH$$

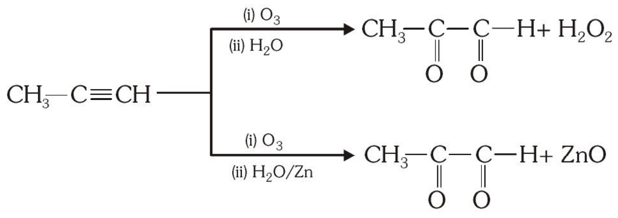
Ozonide (Addition of ozone) (Acids)

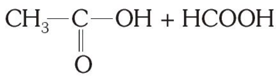
In this reaction H_2O_2 is oxidant which oxidise $R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}R$ into acids.

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.





$CH_3-\underset{\underset{O}{\|}}{C}-OH + HCOOH$

3 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

Dry alkynides are generally unstable and explosive. These are easily converted in to original alkynes when heated with dilute acids.

$NaC\equiv CNa + 2HNO_3 \longrightarrow HC\equiv CH + 2NaNO_3$

This reaction can be used for the purification, seperation and identification of 1-alkynes.

(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) respectivley.

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

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 for distinguish alkenes and alkynes or 1-alkynes and 2-alkynes.

4. ISOMERISATION:

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

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

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

5. POLYMERISATION :

(a) Linear polymerisation :

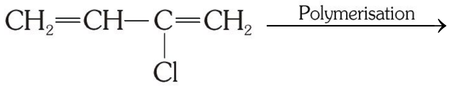
Dimerisation : When two molecules of acetylene passed through a solution of Cu_2Cl_2 and NH_4Cl a vinyl acetylene is obtained.

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

mono vinyl acetylene

When vinyl acetylene react with HCl then chloroprene is obtained.

$CH_2=CH-C\equiv C-H \xrightarrow{HCl}$



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

Neoprene (Synthetic rubber)

2- chloro-1,3-butadiene

[chloroprene]

Trimerisation : 3 molecules of acetylene.

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

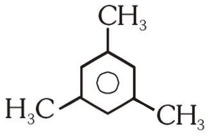
Divinyl acetylene

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

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

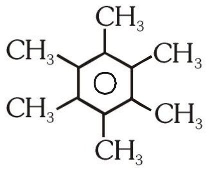
Benzene

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



Mesitylene

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



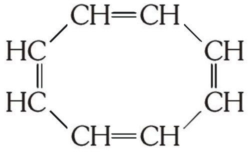
Hexa methyl benzene

$3\ HC\equiv CH \xrightarrow[(C_6H_5)_3P]{Ni(CO)_4}$

(triphenyl–1–phosphene)

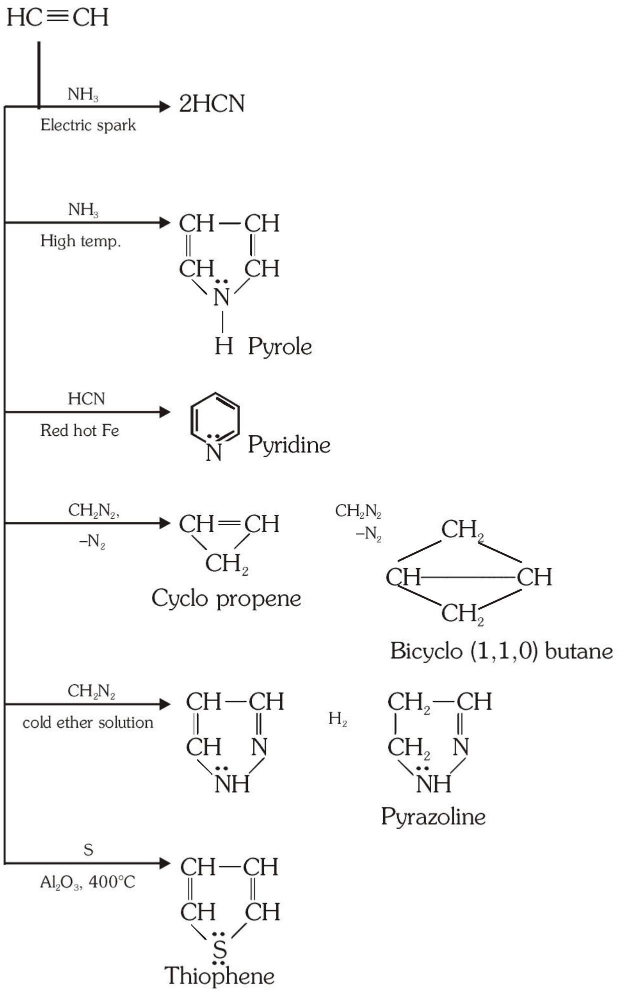
benzene (90% yield)

$4CH\equiv CH \xrightarrow{Ni(CN)_2}$



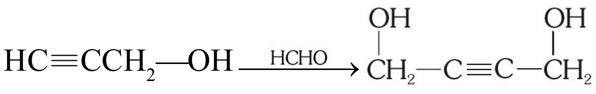
1,3,5,7–cyclooctatetraene

Other reactions of acetylene :



(vi) Reaction with HCHO : This reaction is called ethynylation.

$CH\equiv CH + HCHO \xrightarrow{Cu}$



$$HC\equiv CCH_2—OH \xrightarrow{HCHO} \overset{OH}{\overset{|}{CH_2}}—C\equiv C—\overset{OH}{\overset{|}{CH_2}}$$

propargyl alcohol

(vii) Reaction with NaOCl : (Substitution reaction)

$H — C\equiv C—H + NaOCl \xrightarrow[\text{absence of air and light}]{0°C}$

$H—C\equiv C—Cl + NaOH$

$H—C\equiv C—Cl + NaOCl \xrightarrow[\text{absence of air and light}]{0°C}$

$Cl—C\equiv C—Cl + NaOH$

Dichloro acetylene

USES OF ACETYLENE :

(i) Oxyacetylene flame used in welding and cutting

(ii) Acetylene is used as an illuminant

(iii) Acetylene is used for artificial ripenning 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.

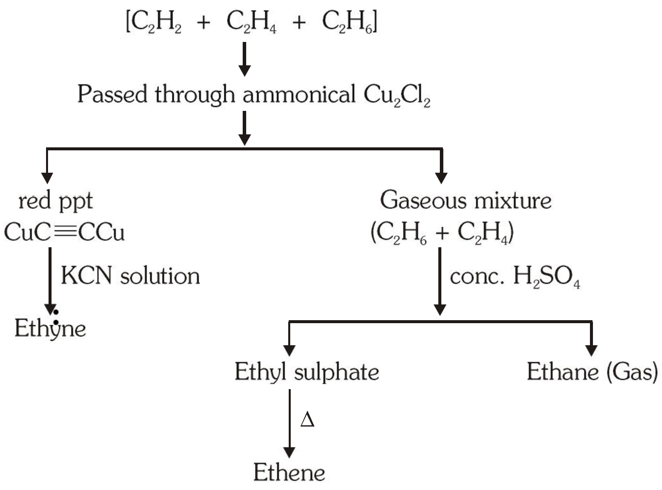
(iii) 1- alkynes give white ppt. with ammonical $AgNO_3$ and red ppt with ammonical cuprous chloride solution.

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.

Seperation of ethane, ethene and ethyne



AROMATIC HYDROCARBONS (Arenes)

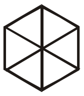
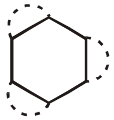
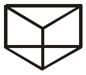
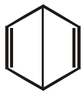
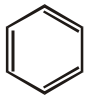
Special points about Arenes :

- Arenes are cyclic, planar and follow Huckel's rule.
- There should be cyclic resonance in Arenes.
- General formula of Arenes are C_nH_{2n-6y} where n = Number of carbons
  y = Number of rings
- Characteristic reaction of arenes is Electrophilic substitution reaction (ESR).
- Arenes are cyclic unsaturated compounds but do not give test of unsaturaion with Br_2/CCl_4 or alk. $KMnO_4$.
- Main source of Arenes is coaltar.
- They have higher precentage of carbon so burn with smoky flame.

Special points about Benzene : [Ph–H or C_6H_6]

- Benzene was discovered by **Faraday** from whale oil.
- Benzene was prepared by **Hoffman** from coaltar.
- Benzene has cyclic, planar and hexagonal structure.
- All carbons are sp^2 hybridised and bond angle is 120°
- Number of bond angle of 120° = 3 × 6 = 18
- Number of σ bonds = 12 and number of π bonds = 3
- C—C [bond length] = 1.39Å and C—H [bond length] = 1.09Å
- Resonance energy = 36.6 Kcal.
- Heat of hydrogenation = 49.8 Kcal.

Defferent structure of benzene :

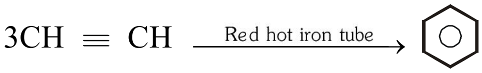
S.No.	Name of structure	Structure	Given by
(i)	Diagonal structure		Clause
(ii)	Centric structure		Baeyer and Armstrong
(iii)	Partial bond structure		Thiels
(iv)	Prismitic structure		Ladenberg
(v)	Parallel bond structure		Dewar
(vi)	Alternate bond structure		Kekule

General methods of preparation :

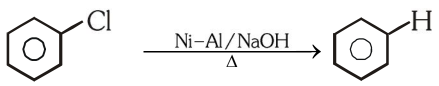
(i) From alkanes (By cyclisation or Aromatisation) Hydroforming or catalytic reforming

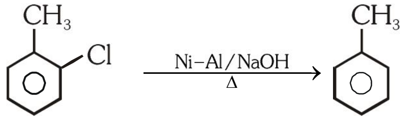
$$n-\text{Hexane} \xrightarrow[600°C]{Cr_2O_3/Al_2O_3} \text{Benzene} + 4H_2$$

(ii) From alkyne (By cyclic polymerisation) When acetylene is passed through red hot metallic tube cyclic polymerisation takes place and benzene is formed.

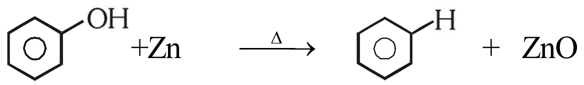


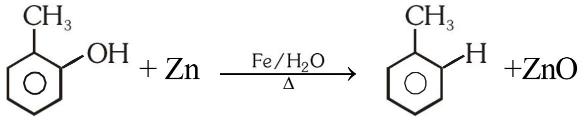
(iii) From Haloarenes (By reduction) :



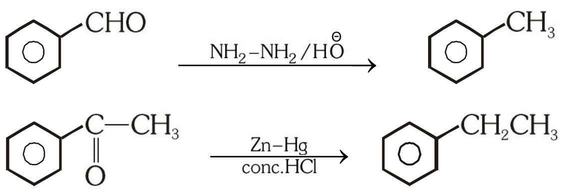


(iv) From Phenolic compounds (By deoxygenation)

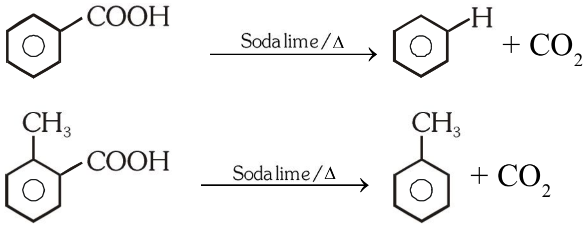




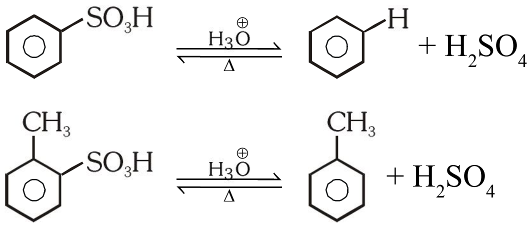
(v) From carbonyl compounds (By reduction) :



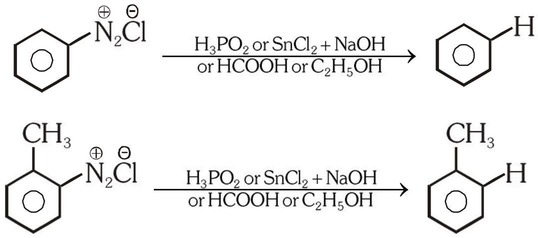
(vi) From carboxylic acids (By decarboxylation) :



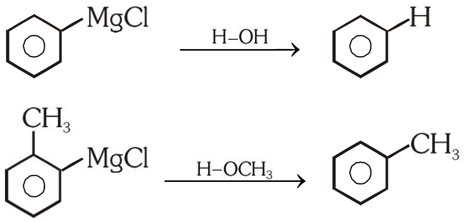
(vii) From sulphonic acids (By hydrolysis) :



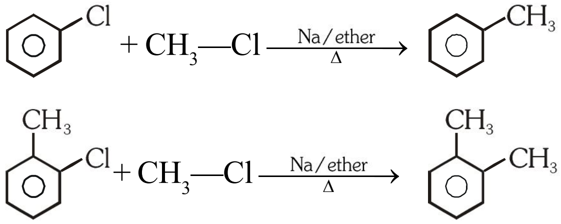
(viii) By diazonium salts :



(ix) By Grignard reagent :



(x) By Wurtz fittig reaction :



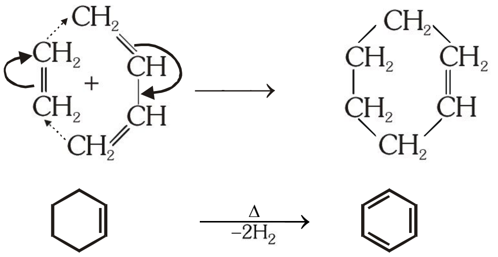
(xi) From petroleum :

Petroleum $\xrightarrow{\text{high temp.}}$

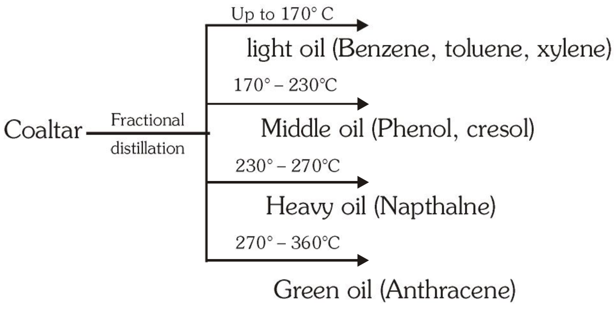
Mixture of lower $\xrightarrow[\text{required hydrocarbons}]{\text{Seperate}}$

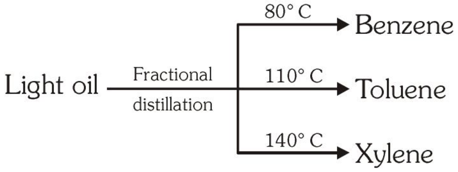
$$CH_2{=}CH_2 + CH_2{=}CH—CH{=}CH_2$$

hydrocarbons



(xii) From coaltar :





Physical properties :

(i) Benzene is colourless liquid [B.P. is 80°C]

(ii) Benzene is insoluble in H_2O and density less than H_2O

(iii) Benzene is used as a solvent and it is soluble in organic solvents.

(iv) It is highly inflammable and burns with smoky flame.

Chemical properties :

Benzene show following types of reaction –

(A) Addition reactions

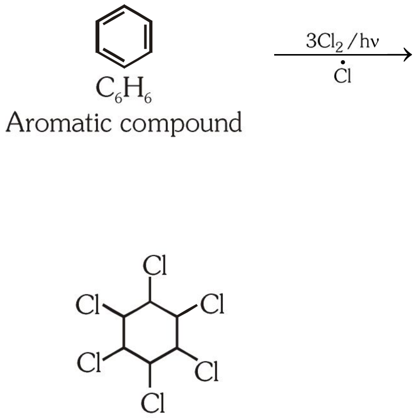
(B) Electrophilic substitution reactions

(C) Oxidation reactions

(D) Extra special reactions

(A) Addition reaction :

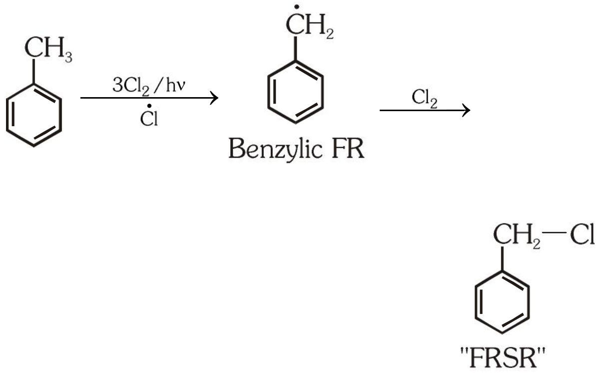
(i) Addition of X_2



C_6H_6
Aromatic compound

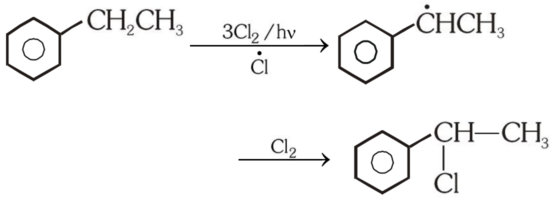
Alicyclic compound ($C_6H_6Cl_6$)
Benzene hexachloride
BHC or 666 or
Gammexane or lindane
*BHC is used as powerful insecticide

Formation of BHC from C_6H_6 is an example of free radical addition reaction.



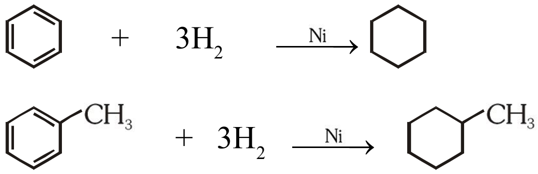
Benzylic FR

"FRSR"

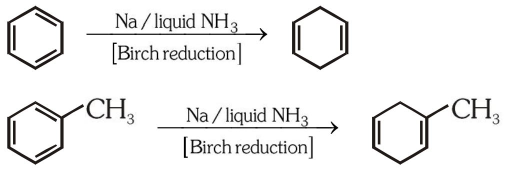


(ii) Addition of H_2 :

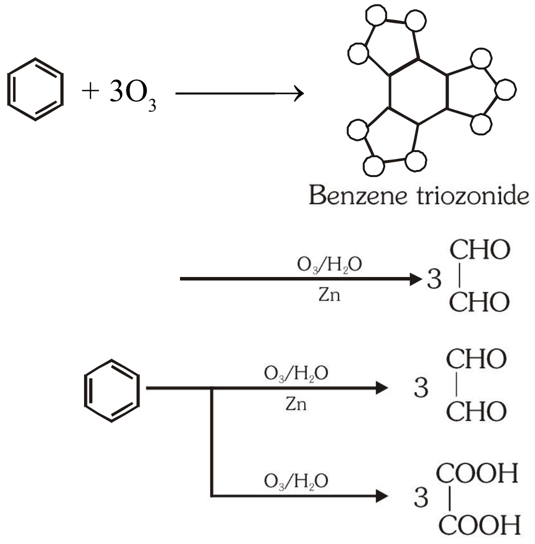
(a) Complete hydrogenation :



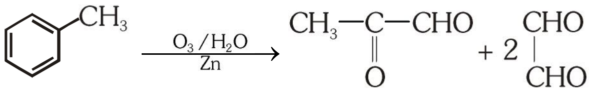
(b) Partial hydrogenation :



(iii) Addition of O_3 :



Benzene triozonide

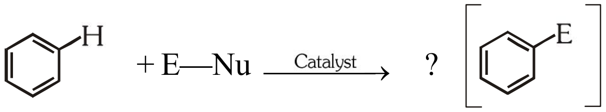


Addition of 3 mole Cl_2 or 3 mole H_2 or 3 mole O_3 on benzene show presence of 3 double bonds in benzene.

Benzene does not give addition reaction with Br_2/CCl_4 or alkaline $KMnO_4$

(B) Electrophilic substitution reaction [ESR] :

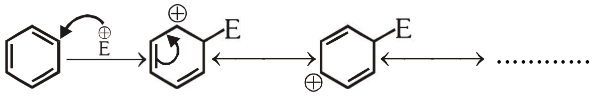
Characteristic reaction of arenes is ESR



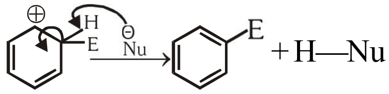
Mechanism :

Formation of $\overset{\oplus}{E}$ $E - Nu \xrightarrow{\text{Catalyst}} \overset{\oplus}{E} + \overset{\ominus}{Nu}$

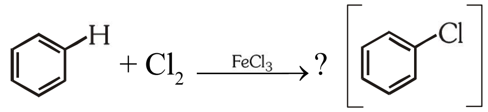
Attack of $\overset{\oplus}{E}$



Abstraction of $\overset{\oplus}{H}$



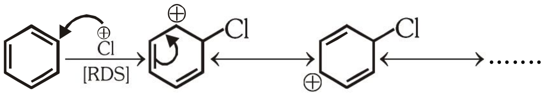
(i) Halogenation :



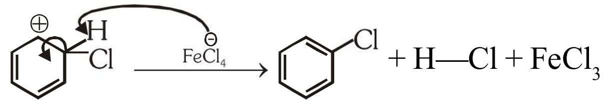
Mechanism :

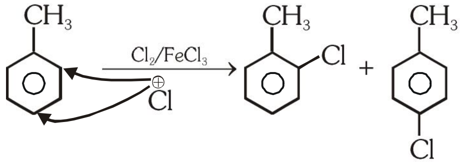
Formation of $\overset{\oplus}{E}$ $Cl-Cl + FeCl_3 \longrightarrow \overset{\oplus}{Cl} + Fe\overset{\ominus}{Cl_4}$

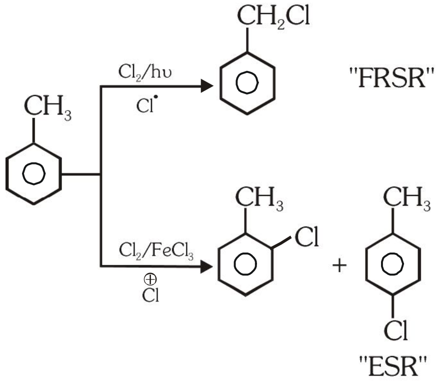
Attack of $\overset{\oplus}{E}$



Abstraction of $\overset{\oplus}{H}$

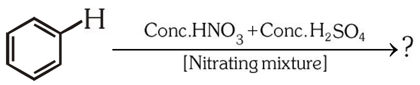


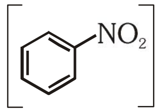




Note: CH_3 group in toluene is o/p directing and activating group.

(ii) Nitration :

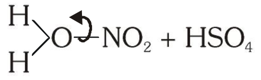




Formation of $\overset{\oplus}{E}$

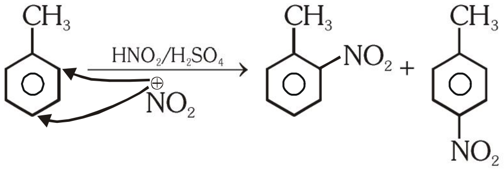
$H\ddot{\underset{\cdot\cdot}{O}}_2-NO_2 \quad + H-HSO_4$

(Bronsted base) (Bronsted acid)



$H_2O + NO_2$

[Attacking species]

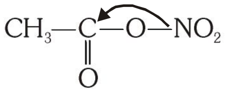


Following reagents can be used in nitration

F. H_2SO_4 + F. HNO_3

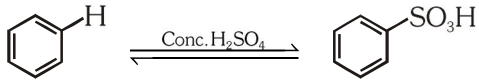
$\overset{\oplus}{N}O_2\overset{\ominus}{B}F_4$

$\overset{\oplus}{N}O_2\overset{\ominus}{C}lO_4$



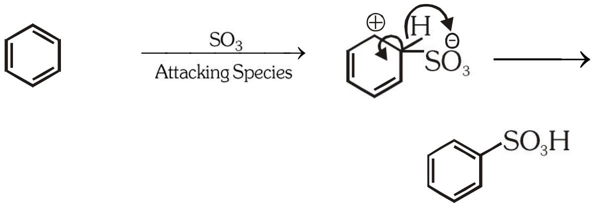
$CH_3-\underset{\underset{O}{\|}}{C}-O-NO_2$ [Acetyl nitrate]

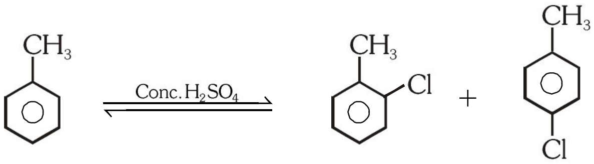
(iii) Sulphonation :



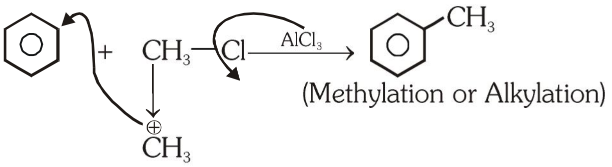
Mechanism :

$$2H_2SO_4 \rightleftharpoons SO_3 + H\overset{\ominus}{S}O_4 + H_3\overset{\oplus}{O}$$

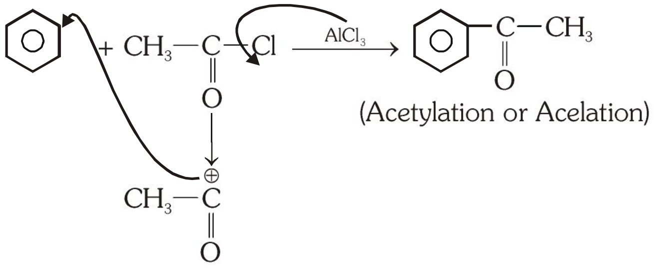




(iv) Friedel crafts reaction [FCR] : Alkylation or acylation of arenes in presence of lewis acid [$FeCl_3$, $AlCl_3$ or $ZnCl_2$...] is called as FCR. CS_2 or nitrobezene is used as solvent in FCR.

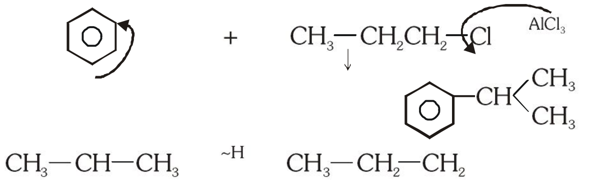


(Methylation or Alkylation)

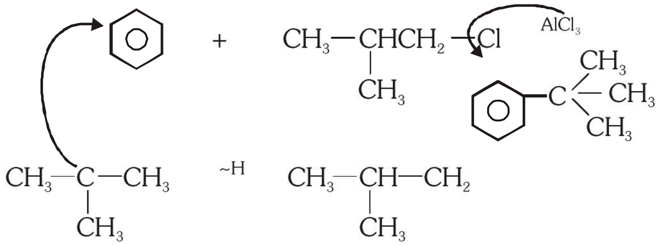


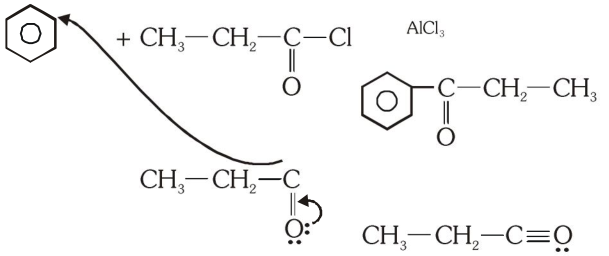
(Acetylation or Acelation)

Intermediate carbocation is formed in FCR so rearrangement may be possible.

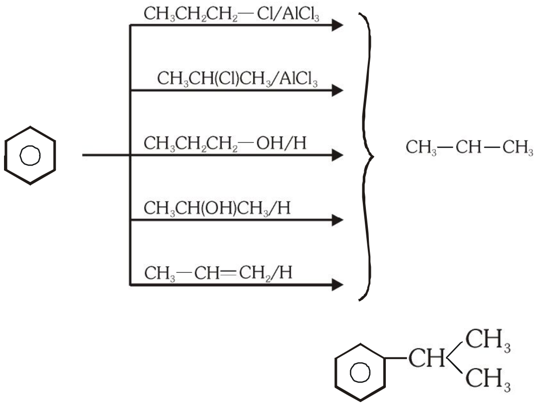


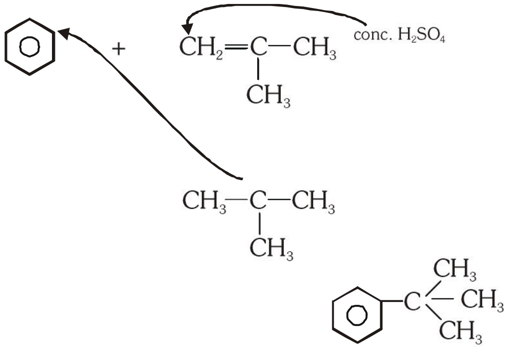
Isobropyl benzene (Cumene)

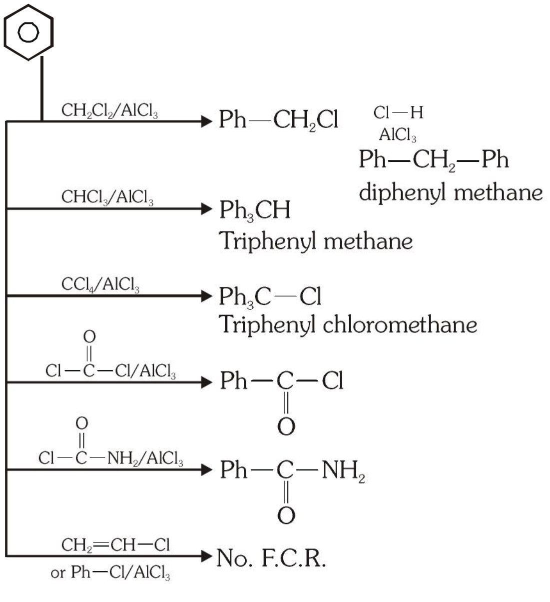




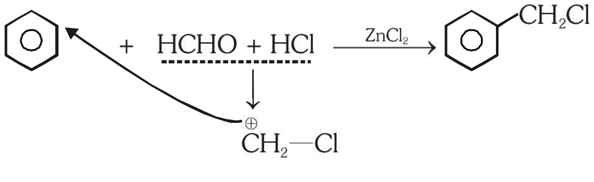
Complete octet RS



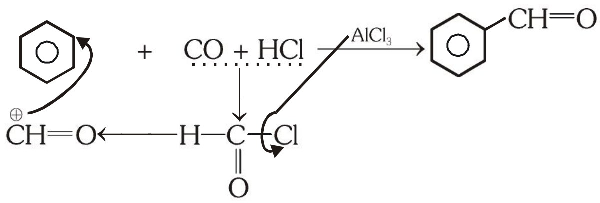




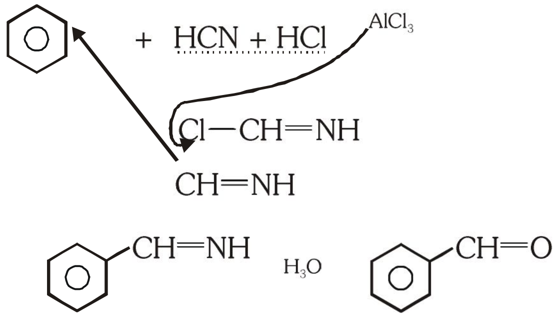
(v) Chloromethylation :



(vi) Gatterman's Kosch Reaction :



(vii) Gatterman's Aldehyde synthesis :



The important electrophiles used in the aromatic substitution are the following -

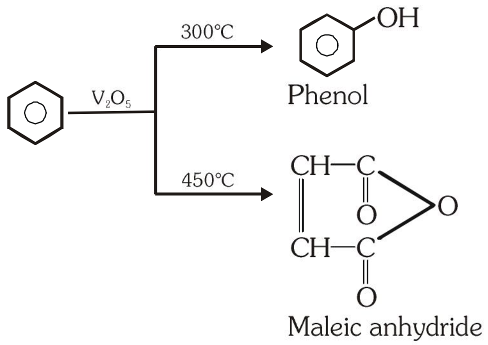
Electrophilic	Source	Name of substitution reaction
Cl^+ (Chloronium)	$Cl_2 + AlCl_3$ or $FeCl_3$	Chlorination
Br^+ (Bromonium)	$Br_2 + AlBr_3$ or $FeBr_3$	Bromination
NO_2^+ (Nitronium)	$HNO_3 + H_2SO_4$	Nitration
SO_3 (Sulphertrioxide)	conc. H_2SO_4, fuming sulphuric acid	Sulphonation
R^+ (Alkyl carbonium)	$RX + AlX_3$ (X= Cl or Br) $ROH + H^+$	Friedel crafts (Alkylation)
$R-\overset{\oplus}{C}=O$ (Acyl carbonium)	$ROCl + AlCl_3$	Friedel crafts (Acylation)

(C) Oxidation reactions :

(i) Combustion :

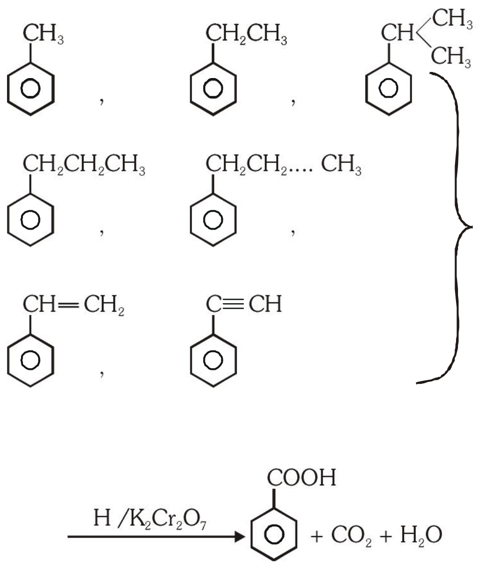
$$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O$$

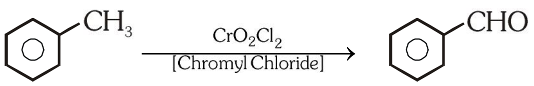
(ii) Catalytic Oxidation :



(iii) Side chain Oxidation :

Atleast one benzylic –H containing alkyl benzene gives benzoic acid in presence of strong oxidising agent.



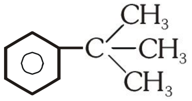


[Etard reaction]

Solved Examples

Ex.29 t–butyl benzene does not gave benzoic acid in presence of $H^{\oplus}/K_2Cr_2O_7$

Sol. t–butyl benzene does not cantain benzylic–H



[Absence of benzylic –H]

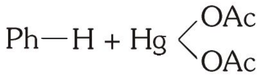
(D) Extra special reactions :

(i) Pyrolysis :

$$2Ph—H \xrightarrow{\text{Red hot Fe tube}} Ph—Ph + H_2$$

(Biphenyl)

(ii) Mercuration :



$$Ph—H + Hg\begin{matrix} OAc \\ OAc \end{matrix}$$

Ph—HgOAc + Ac—OH
Phenyl mercuric acetate

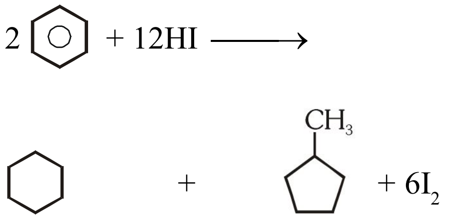
(iii) Formation of sandwitch or π–complex compound :

$$2C_6H_6 \xrightarrow[AlCl_3]{CrCl_3} (C_6H_6)_2$$

$$\overset{\oplus}{Cr}\, AlCl_4^{\ominus} \xrightarrow{\text{Reduction}} (C_6H_6)Cr$$

Bis benzene chromium

(iv) Reduction with HI –



Cyclohexane Methyl cyclo pentane