05 Hydrocarbons

ALKANE

Introduction:

(i) Branched and unbranched aliphatic saturated hydrocarbons 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 reagents 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	Property	Characteristics of alkane
General formula	C_nH_{2n+2}	C—C Bond length	1.54 A°
C—C Bond energy	82.67 kcal/mole	C—H Bond length	1.112 A°
C—H Bond energy	98.67 kcal/mole	Hybridisation on C	sp^3
Bond angle	109°.28′	Shape	Tetrahedral

General Methods of Preparations:

1. From alkenes and alkynes (Sabatier and Senderens 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 Nickel at room temp.

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

(e) Methane cannot 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_3COOH (iii) Zn—Cu couple in C_2H_5OH

(iv) Red P + HI (v) Al + Hg + ethanol

Mechanism : $Zn \longrightarrow Zn^{2\oplus} + 2e^{\ominus}$ $\quad R—X \xrightarrow{2e^{\ominus}} R^{\ominus} + X^{\ominus}$

$R^{\ominus} + H^{\oplus}Cl^{\ominus} \longrightarrow R—H + Cl^{\ominus}$ $\quad Zn^{2\oplus} + 2Cl^{\ominus} \longrightarrow ZnCl_2$

Product

Key points:

(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.

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

$CH_3I + NaOH \longrightarrow CH_3OH + NaI$

Methanol

(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, through Wurtz reaction give all possible alkanes.

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

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

Mechanism : Two mechanism have been proposed for this reaction.

(a) Ionic Mechanism:

$2Na \longrightarrow 2Na^{\oplus} + 2e^{\ominus}$ $\quad R—X \xrightarrow{2e^{\ominus}} R^{\ominus} + X^{\ominus}$

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

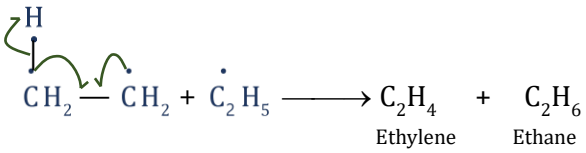
Product

Example : $2C_2H_5—I + 2Na \longrightarrow C_2H_5—C_2H_5 + 2NaI$

n–butane

(b) Free radical mechanism :

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



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

Illustration 1:

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

Solution:

2, 3-Dimethyl butane.

Illustration 2:

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

Solution:

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

Illustration 3:

Which of the following compound cannot obtained from Wurtz reaction.

(A) ethane (B) butane (C) isobutane (D) hexane

Ans. (C)

Solution:

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

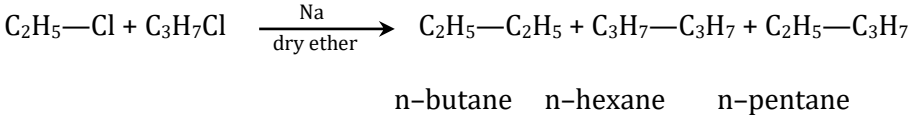
Illustration 4:

When ethyl chloride and n-propyl chloride undergoes Wurtz reaction which is not obtained.

(A) n–butane (B) n–pentane (C) n–hexane (D) isobutane

Ans. (D)

Solution:



4. Corey-House Synthesis :

This method is suitable for the preparation of unsymmetrical alkanes i.e. those of type R—R'

(i) $RX + 2Li \longrightarrow RLi + LiX$

(ii) $2RLi + CuX \longrightarrow R_2CuLi + LiX$

(iii) $R_2CuLi + R'X \longrightarrow R—R' + RCu + LiX$

Note :

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

5. From Frankland Reagent:

If Zn is used in place of Na, the reaction is named as Frankland reaction.

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

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

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

$$\underset{\text{Soda lime}}{RCOONa + NaOH} \xrightarrow[CaO]{\Delta} R—H + Na_2CO_3$$

Key points :

(a) The process of elimination of Carbon dioxide from Carboxylic acid called decarboxylation.

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

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

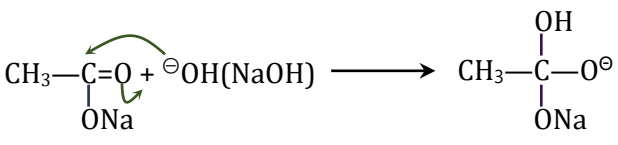
(d) This reaction is employed for stepping down a homologous series.

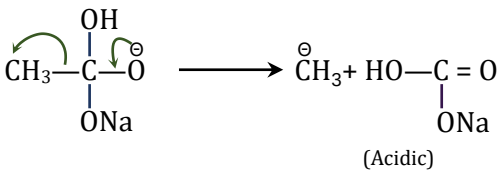
(e) Soda lime is prepared by soaking quick lime CaO with NaOH solution and then drying the products.

(f) Decarboxylation of sodium formate gives H_2

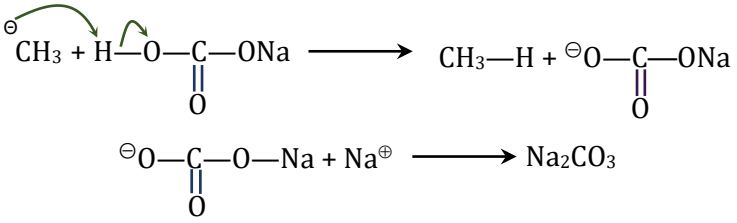
$$\begin{pmatrix} HCOONa + NaOH\ (CaO) \xrightarrow{\Delta} H_2 + Na_2CO_3 \\ CH_3COONa + NaOH\ (CaO) \xrightarrow{\Delta} CH_4 + Na_2CO_3 \end{pmatrix}$$

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



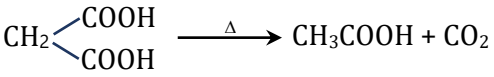


(Acidic)



Key points :

(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.



(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.

Illustration 5:

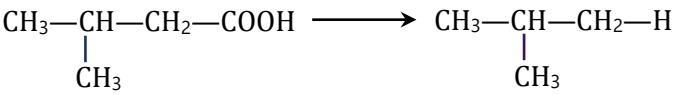
How many acids can be taken to obtain isobutane from decarboxylation?

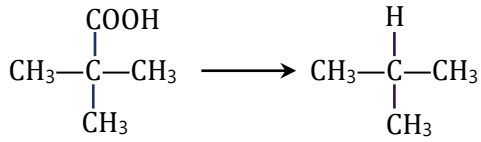
(A) 4 (B) 3 (C) 2 (D) 5

Ans. (C)

Solution:

To obtain isobutane the acids are

(i) 

(ii) 

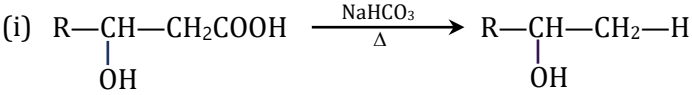
So, two acids can be taken.

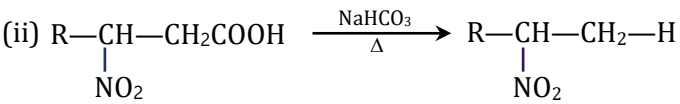
Reactivity of acid $\propto$ stability of carbanion

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.

Example :

(i) 

(ii) 

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

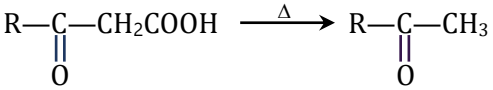


Illustration 6:

Give reactivity order for decarboxylation ?

$CH_3—CH_2—COOH$ $CH_2=CH—COOH$ $CH\equiv C—COOH$

I II III

(A) I > II > III (B) III > II > I (C) III > I > II (D) None is correct

Ans. (B)

Solution:

In decarboxylation intermediates are,

$CH_3—\overset{\ominus}{C}H_2$ $CH_2=\overset{\ominus}{C}H$ $CH\equiv\overset{\ominus}{C}$

I II III

The stability order of carbanion – III > II > I

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

7. 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-

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

$$C_2H_5—COONa \xrightarrow[\substack{H_2O\\(\text{Ionization})}]{\text{electrolysis}} C_2H_5—\overset{\ominus}{C}OO + \overset{\oplus}{Na}$$

Mechanism :

At Anode : $C_2H_5—\overset{\ominus}{C}OO \xrightarrow{-e^{\ominus}} C_2H_5—\dot{C}OO$

$$C_2H_5—\overset{\displaystyle O}{\overset{\|}{C}}—\dot{O} \xrightarrow{\text{Fragmentation}} \dot{C}_2H_5 + CO_2$$

(a) Combination $\dot{C}_2H_5 + \dot{C}_2H_5 \longrightarrow \underset{\text{(Product)}}{C_2H_5—C_2H_5}$

(b) Disproportionation $CH_2(H)—\dot{C}H_2 + \dot{C}_2H_5 \longrightarrow CH_3—CH_2—H + CH_2CH_2$ (Minor product)

(c) An ester is also formed $C_2H_5—\dot{C}OO + \dot{C}_2H_5 \longrightarrow \underset{\text{(minor Product)}}{C_2H_5—COOC_2H_5}$

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

$Na + H_2O \longrightarrow NaOH + 1/2H_2$

Key points :

(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 electrolysis 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.

8. 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.

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

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

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

$$RCOOH + 6HI \xrightarrow[150°C]{\text{Red P}} R—CH_2—H + H_2O + 3I_2$$

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.

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

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

9. 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.

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

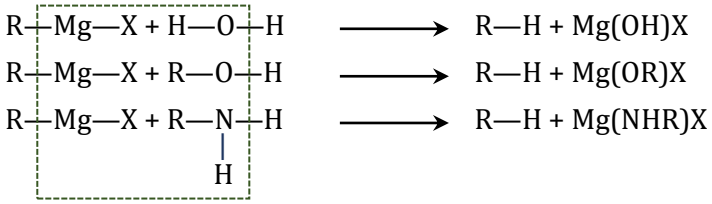
CH_4, $CH_3—CH_3$, isobutane and neopentane are not obtained from Ketones because these alkane do not contain $\diagdown CH_2 \diagup$ group.

10. From alkanals and alkanones (By Wolf Kishner reaction) :

$$\diagdown C = O + NH_2NH_2 \longrightarrow \underset{\text{Hydrazine}}{} \quad \diagdown C = N–NH_2 \xrightarrow[180^{\circ}]{C_2H_5OH/Na} \diagdown CH_2 + N_2$$

11. From Grignard Reagent (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.



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

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

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

Illustration 7:

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

(A) Ph—OH (B) Cl—NH_2 (C) CH_3COOH (D) HCl

Ans. (B)

Solution:

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

12. 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

Example : 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)

$\because$ Vanderwaals force of attraction $\propto$ molecular weight $\propto$ surface area of molecule.

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 Vander Waals 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.

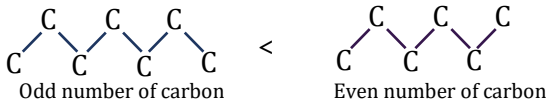


Illustration 8:

Alkanes are inert in nature, why ?

Solution:

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.

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

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

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

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

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

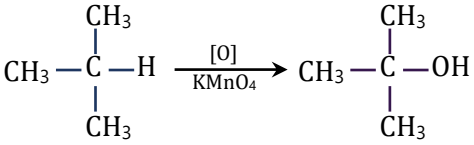


Illustration 9:

How many litre of Oxygen required for complete combustion of 6.0 g ethane at NTP ?

Solution:

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

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 hen 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 :

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

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.

$$\boxed{CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl}$$

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

Step-I **Chain initiation step :** $Cl - Cl \xrightarrow[or\,\Delta]{UV} \dot{Cl} + \dot{Cl}$

Step-II **Chain propagation step :** $\dot{Cl} + H\text{—}CH_3 \longrightarrow H\text{—}Cl + \dot{C}H_3$

Methane — Methyl

$$\dot{C}H_3 + Cl\text{—}Cl \longrightarrow CH_3Cl + \dot{Cl}$$

Step-III **Chain termination step :** $\dot{Cl} + \dot{Cl} \longrightarrow Cl_2$, $\dot{C}H_3 + \dot{Cl} \longrightarrow CH_3Cl$,

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3CH_3$$

A $\dot{Cl}$ 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).

$$\dot{Cl} + H\text{—}\underset{H}{\overset{H}{C}}\text{—}Cl \longrightarrow HCl + \dot{C}H_2Cl$$

$$Cl_2 + \dot{C}H_2Cl \longrightarrow CH_2Cl_2 + \dot{Cl}$$

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

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

Key point :

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 cannot propagate the chain.

Reactivity selectivity Principle :

(i) Probability factor : The factor is based on the number of each kind of H atom in the molecule. For example, is $CH_3\text{—}CH_2\text{—}CH_2\text{—}CH_3$ there are six equivalent 1° H's and four equivalent 2° H's.

The probability of abstracting 1° H's to 2° H's is 6 to 4. i.e., 3 to 2.

(ii) Reactivity of halogen free radical : the more reactive chlorine free radical is less selective and more influenced by the probability factor. On the other hand, the less reactive Br radical is more selective and less influenced by the probability factor (Reactivity selectivity principle).

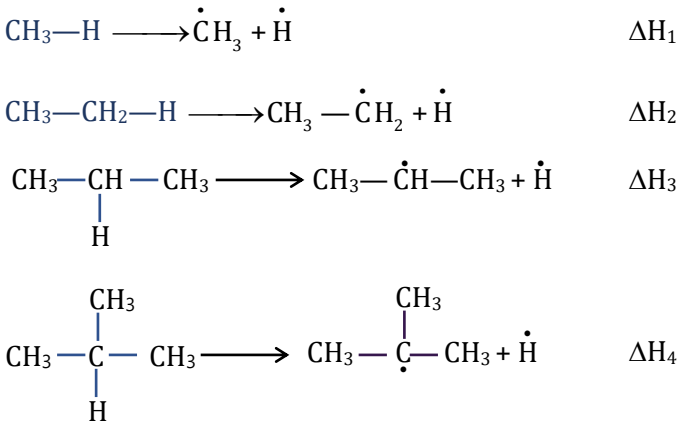
(iii)Reactivity of alkanes (ease of abstraction of 'H' atoms) : Since the rate determining step in halogenations is abstraction of hydrogen by a halogen atom be the formation of alkyl radical, halogenation of alkanes follows order of stability of free radical is 3° > 2° > 1° > CH_3.

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)

The above order of stability of radicals is due to the ease of their formation from the corresponding alkane which in turn is due to difference in the value of ΔH.



Reactivity of any H-atom ∝ number of H atoms of that kind × reactivity of that H.

Thus, the amount of energy required to form the various classes of radicals decreases in the order CH_3 > 1° > 2° > 3° ($\Delta H_1 > \Delta H_2 > \Delta H_3 > \Delta H_4$). Therefore, it is easiest to form 3° radical and it is most difficult to form CH_3. We can also interpret this in an alternative way the case of abstraction of H atoms from hydrocarbon follows the sequence 3° > 2° > 1° > CH_4 which should also be the case of formation of free radicals.

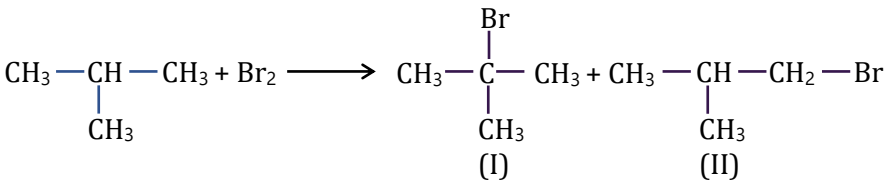
The above order of stability is in accordance with the stability of free radicals on the basis of delocalization of odd electron. Order of stability of free radical is :

Allyl > benzyl > 3° > 2° > 1° > methyl > vinyl.

Illustration 10:

What is the percentage of products obtained from monobromination of isobutane ?

Solution:



$$\frac{\text{Product (I)}}{\text{Product (II)}} = \frac{\text{No. of primary H}}{\text{No. of tertiary H}} \times \frac{\text{reactivity of primary H}}{\text{reactivity of tertiary H}} = \frac{9}{1} \times \frac{1}{1600} = \frac{9}{1600}$$

% of product (I) = $\frac{9}{1600+9}\times100=0.56\%$

% of product (II) = $\frac{1600}{1600+9}\times100=99.44\%$

(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.

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

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.

Example : $CH_3-CH_3 + HNO_3 \xrightarrow{450^\circ C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$

$CH_3CH_2CH_3 + HNO_3 \xrightarrow{450^\circ C}$

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

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

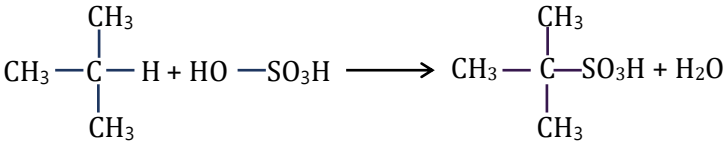
$\dot{O}H + \dot{N}O_2 \longrightarrow HONO_2$

(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.

Example :



2–Methylpropane 2–methylpropane–2–sulphonic acid

The reactivity order for sulphonation is Tert. H > Sec. H > Prim. H

Mechanism : (Free Radical substitution)

$$HOSO_3H \xrightarrow{400^\circ C} H\dot{O} + \dot{S}O_3H$$

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

$$\dot{R} + \dot{S}O_3H \longrightarrow RSO_3H$$

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

$$C_3H_7SO_3H + NaCl \longrightarrow C_3H_7SO_3Na + HCl$$

Sodium salt of sulphonic acid
(used as detergent)

3. Isomerisation :

Unbranched chain alkanes on heating with $AlCl_3$ + HCl / 200°C are converted into branched chain alkanes

$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{\text{Anhyd.}AlCl_3\ /\ HCl} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

n-butane Isobutane

Branched chain alkanes converted to more branched alkane.

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_3 \xrightarrow{\text{Anhyd.}AlCl_3\ /\ HCl} CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$$

$$CH_3(CH_2)_4CH_3 \xrightarrow{\text{Anhy.}AlCl_3/HCl} CH_3\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2)_2-CH_3 + CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

n-Hexane

2-Methylpentane 3-Methylpentane

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°C they are decomposed into 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.

Example :

$$CH_4 \xrightarrow{1000°C} C + H_2$$

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

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

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

$$C_6H_{14} \xrightarrow{773K} \begin{cases} C_6H_{12} + H_2 \\ C_4H_8 + C_2H_6 \\ C_3H_6 + C_2H_4 + CH_4 \end{cases}$$

dodecane, a constituent of kerosene oil on heating to 973K in the presence of platinum, palladium or nickel gives a mixture of heptane and pentene.

$$\underset{\text{Dodecane}}{C_{12}H_{26}} \xrightarrow[973K]{Pt/Pd/Ni} \underset{\text{Heptane}}{C_7H_{16}} + \underset{\text{Pentene}}{C_5H_{10}} + \text{Other products}$$

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.

$$\text{n - hexane} \xrightarrow[500°C]{Cr_2O_3/Al_2O_3} \text{C}_6\text{H}_6 + 4H_2$$

$$CH_3(CH_2)_5 - CH_3 \xrightarrow[500°C]{Cr_2O_3/Al_2O_3} \text{C}_6\text{H}_5\text{CH}_3 + 4H_2$$

n-heptane Toluene

$$CH_3(CH_2)_6 - CH_3 \xrightarrow[500°C]{Cr_2O_3/Al_2O_3} \text{C}_6\text{H}_4(\text{CH}_3)_2 + 4H_2$$

n-octane o-xylene

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

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

6. Reaction with steam :

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen. This method is used for industrial preparation of dihydrogen gas

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

SOLVED EXAMPLES

Illustration 11:

Which of the following reactions can be employed for getting unsymmetrical alkanes in good yield ?

(A) Wurtz reaction (B) Corey–House reaction

(C) Both (D) None of these

Ans. (B)

Solution:

Wurtz reaction is suitable for symmetrical (even) alkanes

Illustration 12:

Sodium propionate on decarboxylation with sodalime gives

(A) Propane (B) Ethane (C) Butane (D) Pentane

Ans.(B)

Solution:

Decarboxylation with soda lime results in the formation of alkane with one carbon less than the starting compounds.

Illustration 13:

Which of the following alkanes cannot be produced by Kolbe electrolysis of sodium or potassium salts of carboxylic acids ?

(A) Methane (B) Ethane (C) Butane (D) Hexane

Ans.(A)

Solution:

In Kolbe electrolysis, the alkane is formed by union of two alkyl groups. The alkane formed has, thus, two or more carbon atoms.

Illustration 14:

The homolytic fission of hydrocarbon results in the formation of -

(A) Free radicals (B) Carbocations (C) Carbanions (D) Carbenes.

Ans.(A)

Solution:

Homolytic fission results in the formation of free radicals.

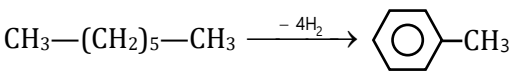
Illustration 15:

n-Heptane when heated to a temperature of about 800 K under high pressure in the presence of Cr_2O_3/Al_2O_3 catalyst gives -

(A) 1-heptene (B) 2-Methylhexane (C) Toluene (D) Xylene.

Ans.(C)

Solution:



Toluene

Illustration 16:

The reaction conditions leading to the best yield of C_2H_5Cl are -

(A) C_2H_6 (excess) + $Cl_2 \xrightarrow{\text{UV light}}$ (B) $C_2H_6 + Cl_2 \xrightarrow[\text{room temperature}]{\text{Dark}}$

(C) $C_2H_6 + Cl_2$ (excess) $\xrightarrow{\text{UV light}}$ (D) $C_2H_6 + Cl_2 \xrightarrow{\text{UV light}}$

Ans.(A)

Solution:

C_2H_6 should be used in excess, otherwise polychlorination will take place

Illustration 17:

Number of structural isomer which can be theoretically obtained on monochlorination of 2-methylbutane is-

(A) 6 (B) 2 (C) 3 (D) 4

Ans.(D)

Solution:

(A) $CH_2(Cl)-CH(CH_3)-CH_2-CH_3$ (B) $CH_3-C(Cl)(CH_3)-CH_2-CH_3$

(C) $CH_3-CH(CH_3)-CH(Cl)-CH_3$ (D) $CH_3-CH(CH_3)-CH_2-CH_2(Cl)$

Illustration 18:

Complete oxidation of ethane yields -

(A) Ethanol (B) Ethanoic acid (C) Ethanal (D) CO_2 and H_2O

Ans.(D)

Solution:

$2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$

Illustration 19:

In iso-pentane, the H atom that can be most easily substituted by free radical mechanism is on : -

$\overset{1}{CH_3}-\overset{2}{CH}(CH_3)-\overset{3}{CH_2}-\overset{4}{CH_3}$

(A) C–1 (B) C–2 (C) C–3 (D) C–4

Ans.(B)

Solution:

Ease of substitution of various types of H atoms is 3° > 2° > 1°.

Illustration 20:

8 cc of gaseous hydrocarbon requires 40 cc of O_2 for complete combustion. Identify hydrocarbon.

Solution:

Volume of hydrocarbon = 8 cc ; Volume of O_2 = 40 cc

$$\frac{\text{Moles of H.C.}}{\text{Moles of } O_2} = \frac{1}{\left(\frac{3n+1}{2}\right)}$$

$$\frac{8}{40} = \frac{2}{3n+1} \text{ (For alkane)}$$

$$\frac{1}{5} = \frac{2}{3n+1} \text{ or } 3n + 1 = 10 \quad \text{or} \quad 3n = 10 - 1 = 9, n = 3$$

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)

Illustration 21:

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.

Solution:

Suppose the volume of CH_4 in (CH_4 + C_3H_8) mix = x cc

= Volume of C_3H_8 will be = (10 – x) cc

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 cc of CH_4, 2x cc 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) cc of C_3H_8 requires 5(10 – x) cc 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 cc

Volume of CH_4 is 3 cc and volume of C_3H_8 is 7 cc

Illustration 22:

If 5 g C_2H_5I reacts with Na (Metallic) in presence of ether, and the yield is 60% then how many grams of n-butane will you get.

Solution:

$$2C_2H_5I + 2Na \longrightarrow C_4H_{10} + 2NaI$$

Molecular weight of C_2H_5I = 24 + 5 + 127 = 156

Molecular weight of C_4H_{10} = 48 + 10 = 58

Two molecule of C_2H_5I are taking part in above reaction.

$\therefore$ We get 58 g of C_4H_{10} from 2 x 156 g of C_2H_5I

$\therefore$ We get $\frac{58}{2\times156}$ g C_4H_{10} from 1 g of C_2H_5I

$\therefore$ We get $\frac{58\times5}{2\times156}$ g C_4H_{10} from 5 g of C_2H_5I

yield is 60%

So the quantity of C_4H_{10} will be $\frac{58\times5}{2\times156}\times\frac{60}{100}$ g = 0.55 g

Illustration 23:

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

Solution:

Molecular weight of Hydrocarbon = density of 1 lit. × 22.4 = 1.964 × 22.4 = 44

So Molecular weight of hydrocarbon = 44

So, the hydrocarbon is C_3H_8 (Propane).

ALKENE :

Introduction :

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

Structure and bonding in Alkenes :

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

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

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

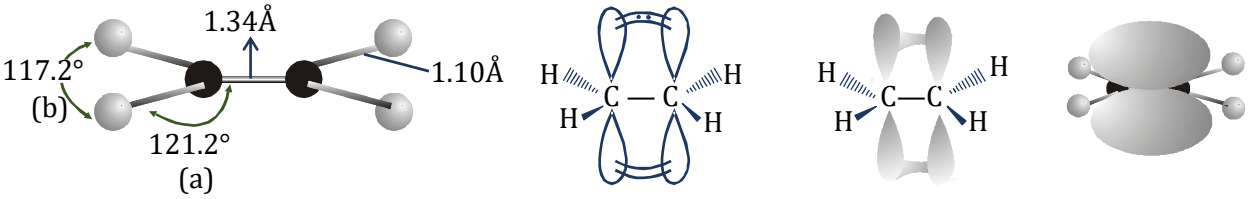
(d) Its bond energy is 146 kcal. mol^{-1}

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

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

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

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

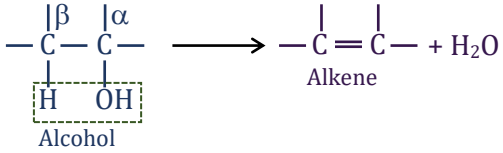


Note :

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

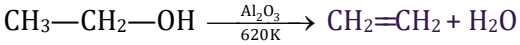
General Methods of Preparations :

(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.



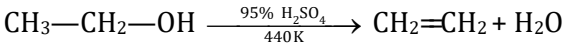
The dehydration can be carried with **Al_2O_3** or with **mineral acid** upon heating.

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

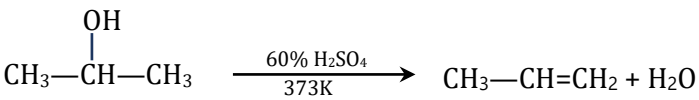


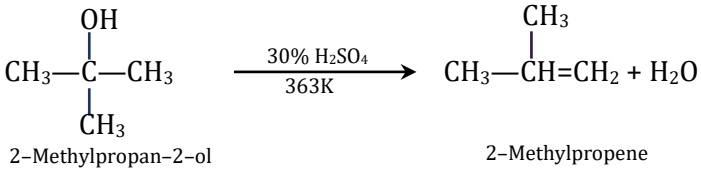
Ethanol Ethene

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



Ethanol Ethene



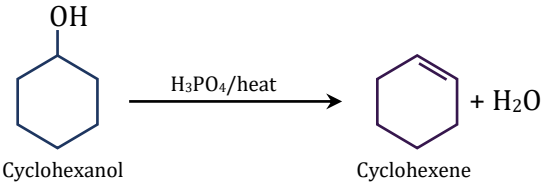


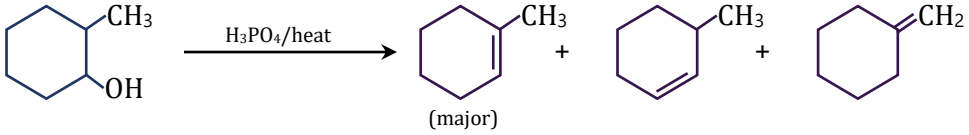
From the above reactions, it is clear that the order of acidic dehydration in different alcohols is

Tertiary > Secondary > Praimary

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

Example :

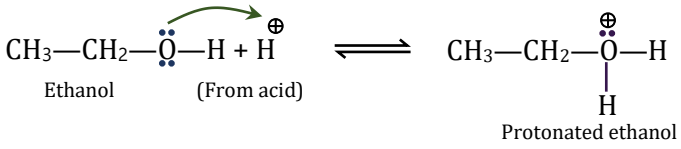




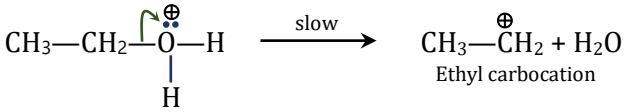
Regioselectivity of β elimination is governed by Zaitsev's Rule.

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

Step I : Alcohol being a Lewis base accepts a proton ($H^{\oplus}$) from the acid in a reversible step as follows

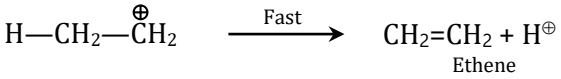


Step II : Due to presence of positive charge on electronegative oxygen, its electron accepting tendency increases. As a result C – O bond becomes weak and cleaves as follows :



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

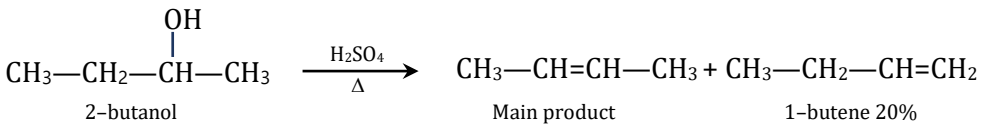
Step III : Carbocation is unstable in nature and loses $H^{\oplus}$ and changes into ethene in a fast step as follows:

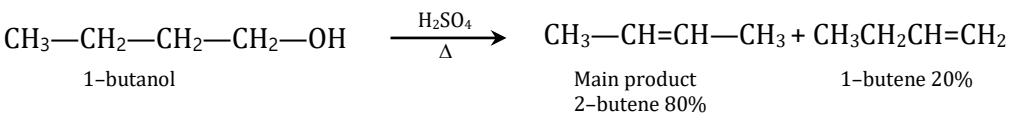


Note :

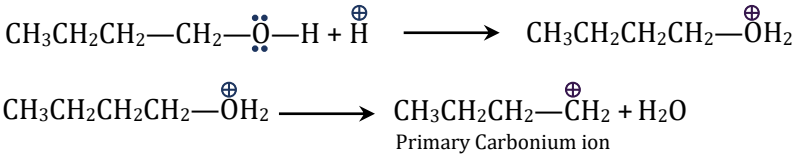
Dehydration of secondary and tertiary alcohol is best carried out by using dil. H_2SO_4. Since alkenes produced from those alcohols have a tendency to form polymers under the influence of concentrated acid.

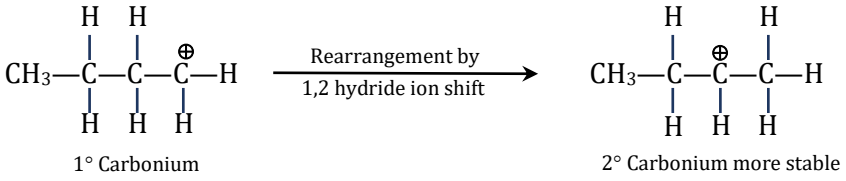
Saytzeff Rule : When two possible alkenes are obtained by the elimination reaction than that alkene will be in good yield, containing maximum number of alkyl group on double bonded C–atoms

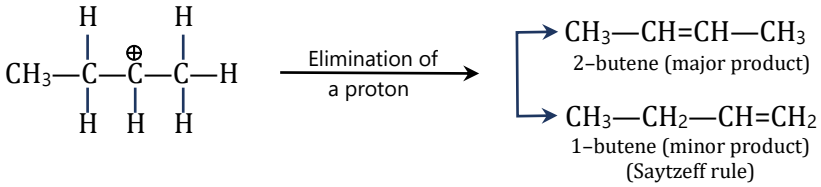




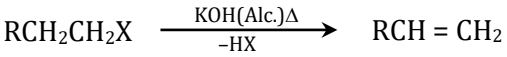
Mechanism : Acid catalyzed dehydration of alkanols proceeds via the formation of more stable carbonium ion.

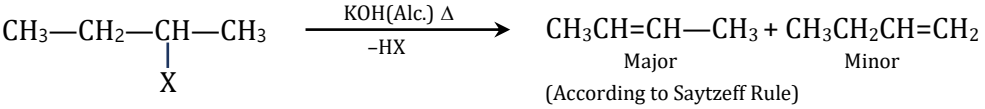






(2) From Alkyl halide (By dehydrohalogenation): Removal of HX from a substrate by alcoholic KOH or $NaNH_2$



Example : 

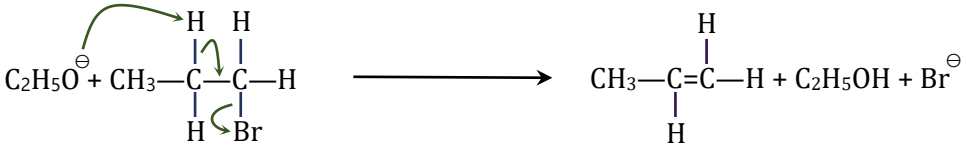
The ease of dehydrohalogenation show the order

For alkyl group | tertiary > secondary > primary |

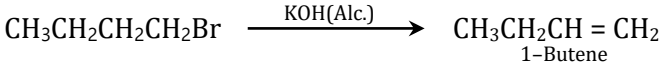
For halogen in halide | Iodide > Bromide > Chloride > flouride |

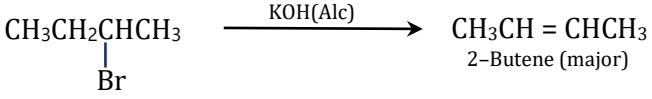
It is single step and synchronous process. Removal of proton, the formation of multiple bond between Cα and Cβ and the release of the leaving group X take place simultaneously.

(E2 mechanism).

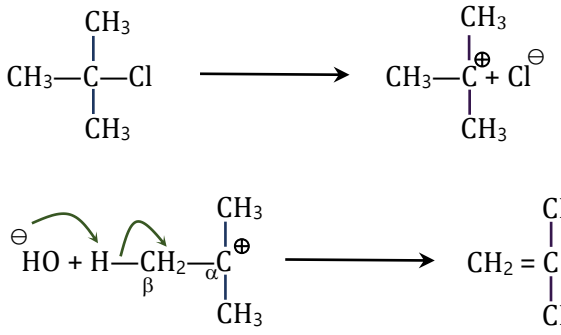
Example : 

Rate of reaction ∝ $[CH_3CH_2CH_2Br]\,[C_2H_5O^{\ominus}]$

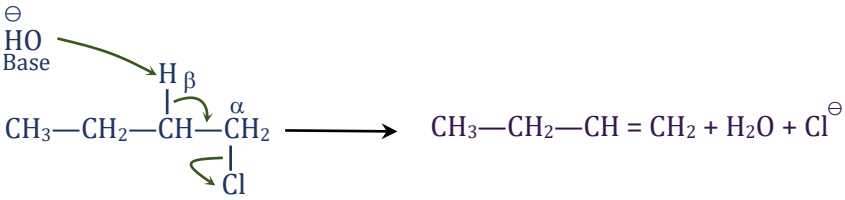
Example : 

Example : 

Primary and secondary alkyl halides undergo elimination reaction by E2 mechanism. E1 elimination reactions are shown by tertiary alkyl halides which are capable of producing stable (tert) Carbonium ion on show ionization.



E2 mechanism : Those alkyl halides which do not give Stable Carbonium ion on ionization show E2 elimination.

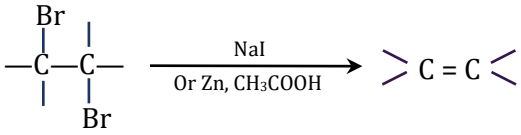


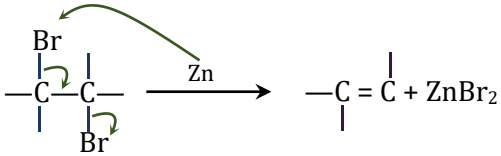
(A) Dehalogenation of vicinal dihalides :

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

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

General Reaction

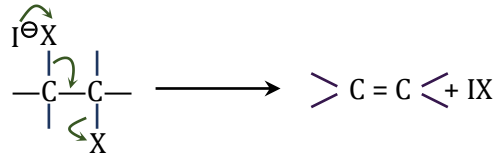
(i) 

Mech. 

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

Mech.

With NaI in acetone :



It involves antielimination of halogen atoms

Remarks :

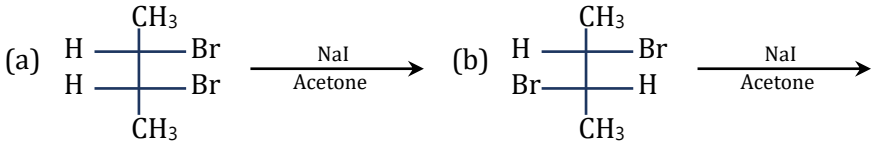
(i) Both are E2 elimination.

(ii) Both are stereospecific antielimination.

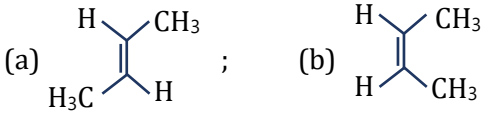
Example : $CH_3—CHBr—CHBr—CH_3 \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3—CH=CH—CH_3$

Illustration 24:

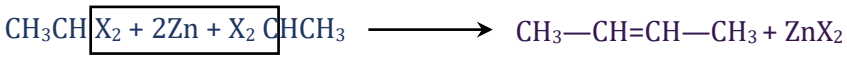
Identify the product in the following reactions :



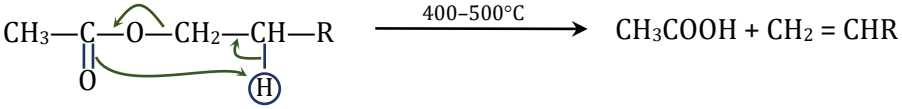
Solution:



(B) From gem dihalide : Higher alkene obtained

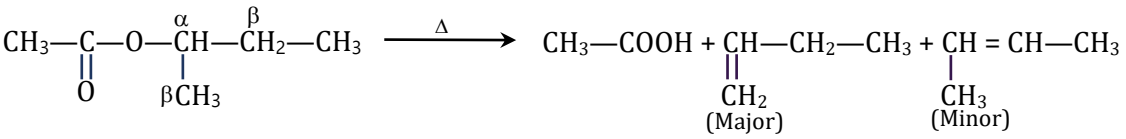


(3) By Pyrolysis of ester :



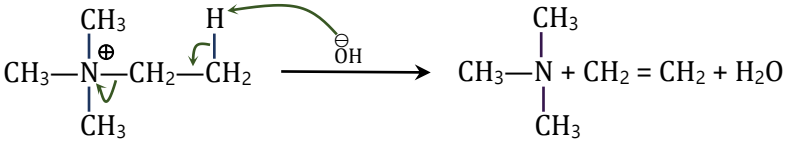
Hoffmann's Rule : Less substituted or less stable alkene is major product.

Example:

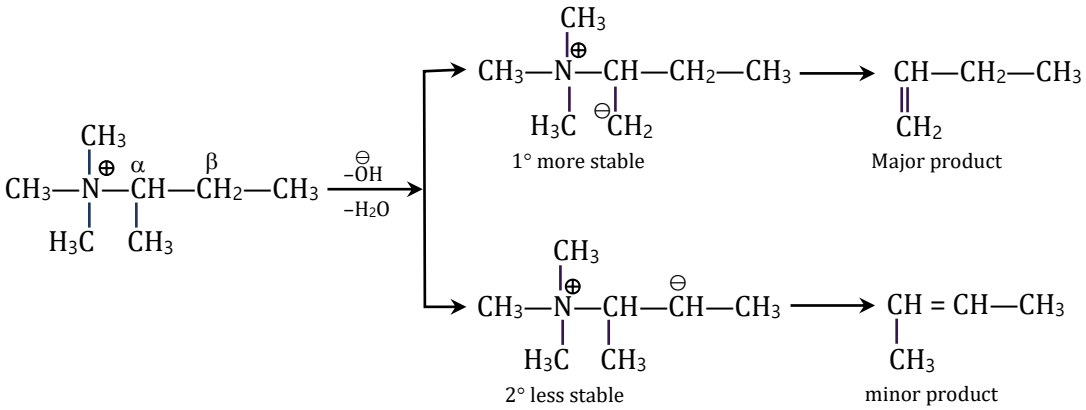


In the reaction to form an alkene a β-hydrogen from alkyl ester is attracted by oxygen atom of keto group & Hoffmann's alkene will be the major product.

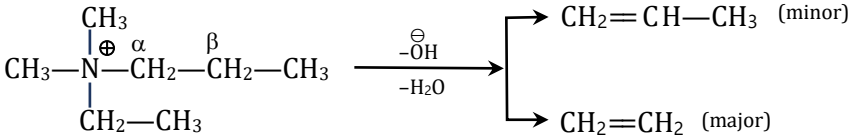
(4) By Pyrolysis of tetra alkyl ammonium ion :



Example :



Example :



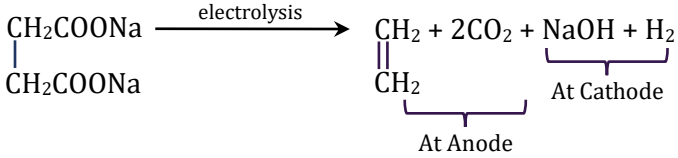
(a) In this reaction β–hydrogen of tetra-alkyl ammonium ion is attracted by a base and alkene is formed.

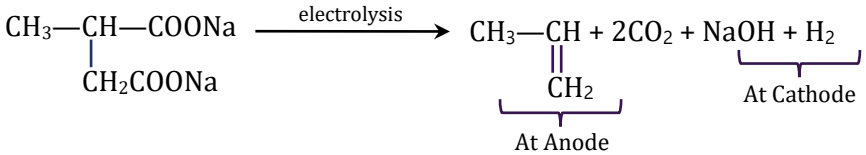
(b) In this reaction intermediate is carbanion. So yield of product depends on stability of carbanion.

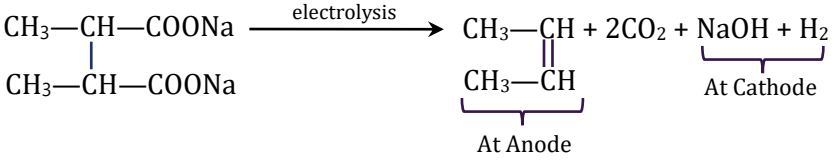
(c) In this reaction Hoffmann's Rule is followed.

(5) By Kolbe's method :

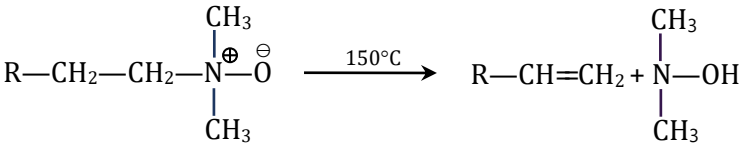
Electrolysis of potassium or sodium salt of saturated dicarboxylic acid gives alkene.



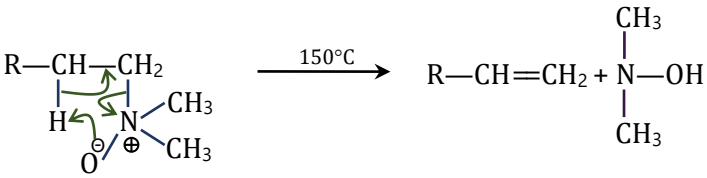




(6) Pyrolysis of Trialkyl amine Oxide : (Cope Reaction)



Mechanism :



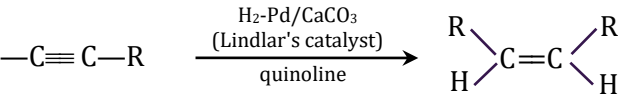
(8) Hydrogenation of alkyne :

By partial reduction of Alkynes -

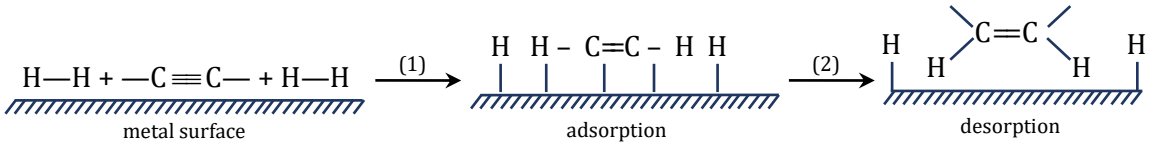
(a) By catalytic Hydrogenation of Alkynes in presence of poisoned catalyst (A Syn Addition of Hydrogen : Synthesis of cis-Alkenes : This is performed by)

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

(ii) P–2 catalyst (Ni_2B nickel boride)

General reaction 

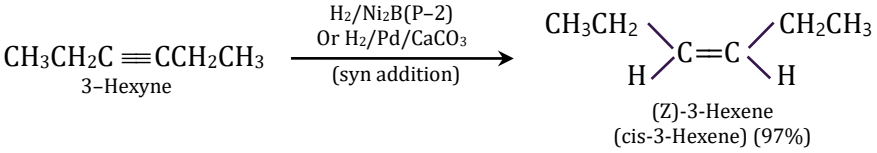
Mechanism of hydrogenation :



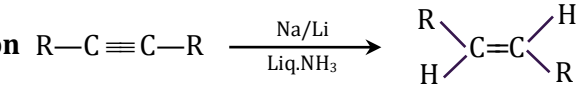
Steps : The reactant alkyne molecules and hydrogen molecules get adsorbed at the surface of metal catalyst. It is chemical adsorption (chemisorption).

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

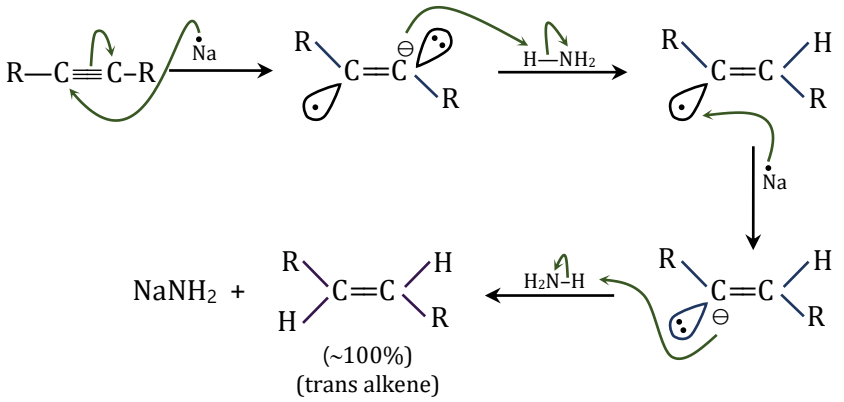
Example :

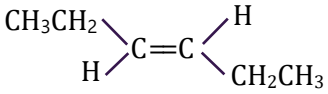


(b) Birch Reduction : (Anti addition of hydrogen : synthesis of trans-alkenes)

General reaction 

Mechanism : Reagents Na (or Li, K) + liq. NH_3 ⟶ $Na^{\oplus} + e^{\ominus}$ (solvated electron)



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

trans hex–3–ene

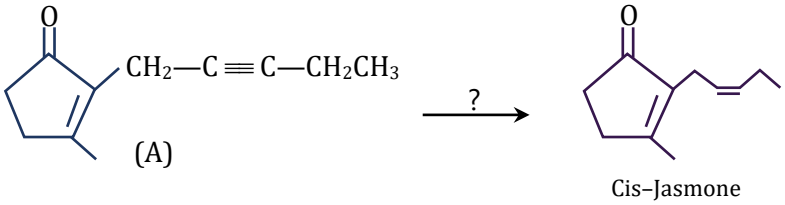
Note :

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

$$CH_3—C\equiv CH + Na/NH_3 \longrightarrow CH_3—C\equiv C^{\ominus}Na^{\oplus} + [H]^{\oplus}$$

Illustration 25:

Identify the reagent for following synthesis



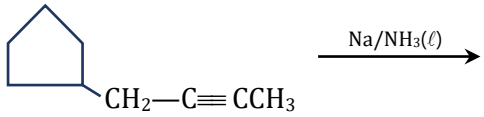
Solution:

H_2/Lindlar's catalyst

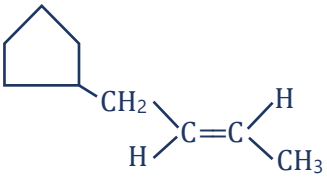
$$A \xrightarrow[\text{Lindlar's catalyst}]{H_2} \text{Cis—Jasmone}$$

Illustration 26:

Identify the product in the following reaction :

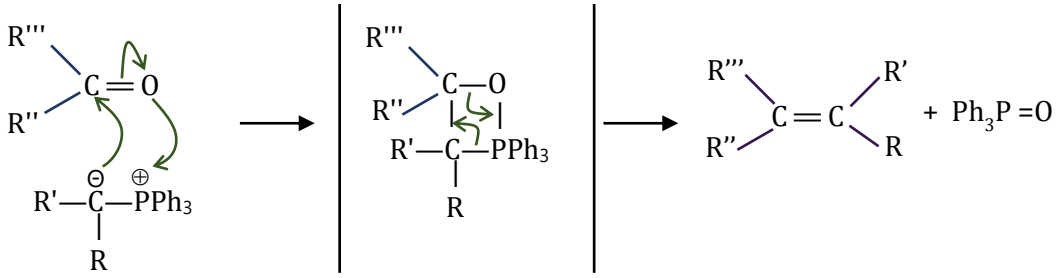


Solution:



(9) Wittig Reaction :

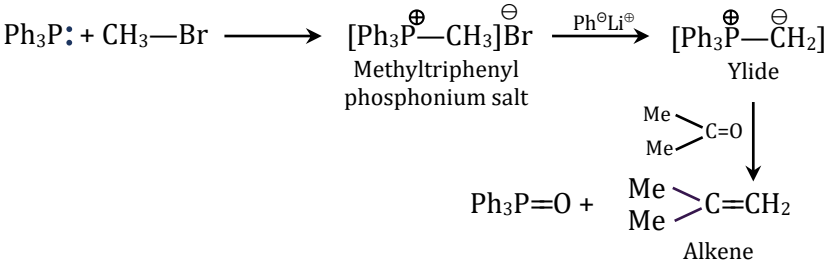
The aldehydes and ketones are converted into alkenes by using a special class of compounds called **phosphorus ylides**, also called Wittig reagents.



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

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

e.g.



Physical Properties of Alkenes :

S. No.	Physical properties	Homologus series	Isomers
1.	Physical state	$C_1 - C_3$ gases $C_4 - C_{20}$ liquids $> C_{20}$: solids	
2.	Dipole moment (μ)		cis > trans
3.	Polarity	–	cis > trans (for $C_{ab}=C_{ab}$ type of alkenes)
4.	Melting point	increases with M.W.	trans > cis (due to more packing capacity)
5.	Boiling point	increases with M.W.	cis > trans # branching decreases B.P. C | C—C=C < C—C=C—C Polarity increases, boiling point increases
6.	Solubility	Practically insoluble in water but fairly soluble in nonpolar solvents like benzene petroleum ether, etc.	cis > trans Polarity increases, solubility in polar solvents increases.
7.	Stability		trans > cis (cis isomers has more Vander Waals repulsion)

Chemical Properties :

Alkenes are more reactive than alkane this is because -

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

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

The reactivity order for alkenes -

$CH_2=CH_2 > R—CH=CH_2 > R_2C=CH_2 \approx RCH=CHR > R_2C=CHR > R_2C=CR_2$

(Trans < Cis)

The reactivity order of alkenes has been derived in terms of heat of hydrogenation of alkene, more is the heat of hydrogenation (ΔH = –ve), more is the reactivity, the reactivity of alkene is however also related to

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

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

Alkenes give the following type of reactions :

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

(d) Polymerization Reaction. (e) Isomerisation

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

(A) Addition Reaction :

free radical addition :

Addition of H_2 :

$$R—CH=CH_2 + H_2 \xrightarrow{\text{Ni, Pt or Pd}} R—CH_2—CH_3 + \text{heat of hydrogenation}$$

Note :

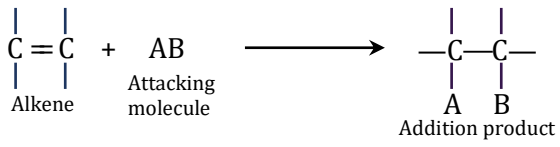
(a) Reaction is exothermic, It is called heat of hydrogenation.

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

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

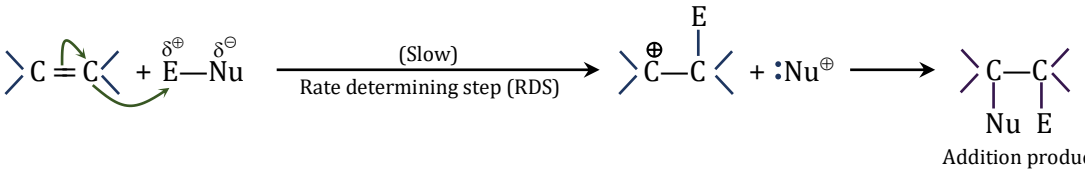
(B) Electrophilic addition reactions :

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



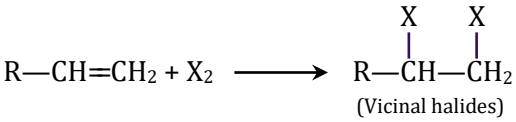
From mechanism point of view, the addition in alkenes is generally **electrophilic in nature** which means that attacking reagent which carries the initial attack is an electrophile ($E^{\oplus}$). This is quite expected also as there is high electron density in the double bond. The mechanism proceeds 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 ($E^{\oplus}$) for the attack. The double bond simultaneously undergoes electrometric effect and the attack by the electrophile is accomplished in slow step (also called rate determining step) to form a **carbocation** intermediate.



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

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



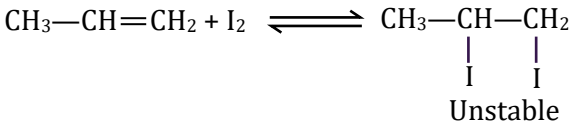
Note :

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

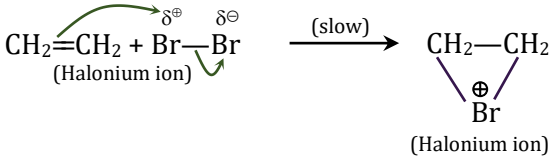
(b) Addition of F_2 is exothermic reaction so it is difficult to control.

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

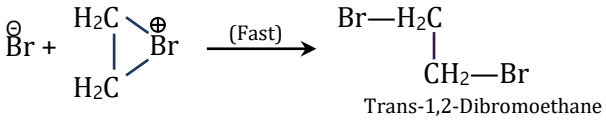
(d) I_2 reacts slowly with alkenes to form vicinal di-iodides which are unstable and eliminated I_2 molecule very readily to give original alkene due to large size of Iodine they overlap.



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

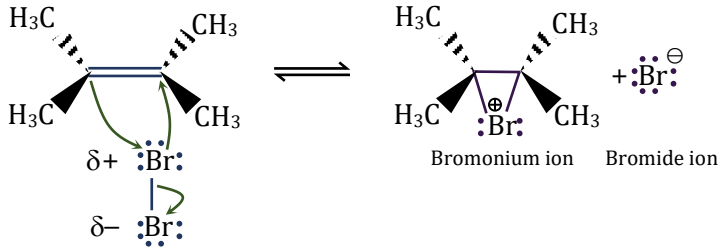


The attack of Br^- ion on the cyclic ion takes place from the side opposite to side where bromine atom is present in order to minimize steric hindrance.



For 2, 3-dimethylbut-2-ene :

Step I :



A bromine molecule becomes polarized due to π electrons of alkene. Dut to polarisation formation cyclic bromonium ion takes place.

Step II :

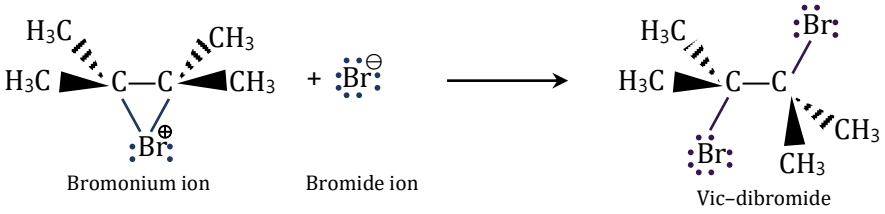
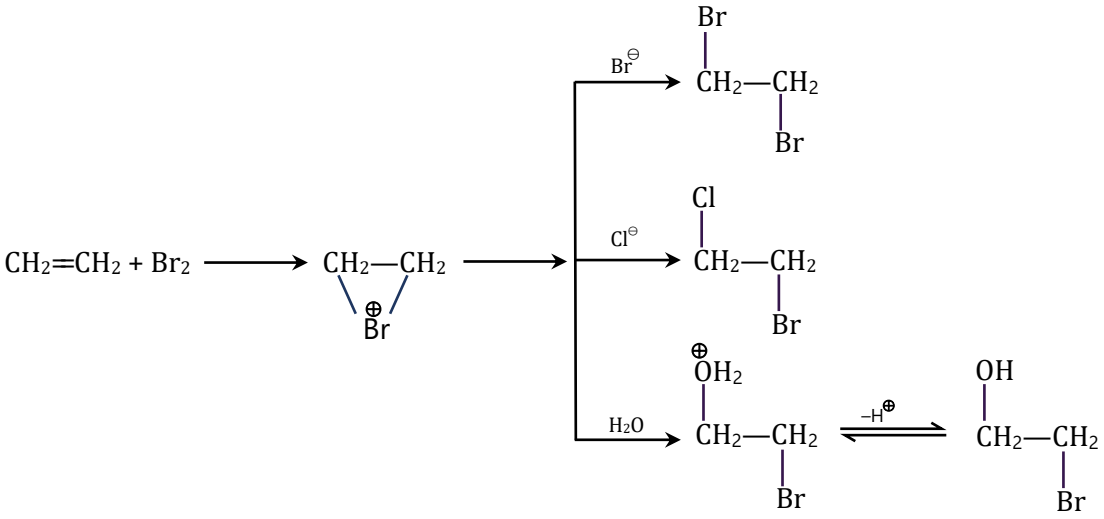


Illustration 27:

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

Ethylene

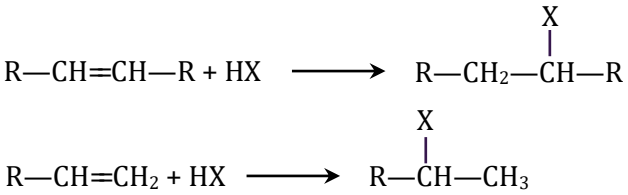
Solution:



Similarly, $CH_2{=}CH_2 + Br_2 \longrightarrow$ $\xrightarrow{NaI\ (aq.)}$ $CH_2(Br)-CH_2(Br) + Br-CH_2-CH_2-I$

$\xrightarrow{NaNO_3}$ $Br-CH_2-CH_2Br + BrCH_2CH_2-NO_3$

2. Addition of halogen acid :



Note :

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

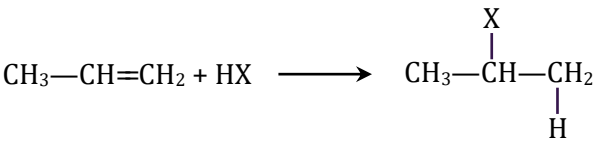
(ii) Their addition is an example of electrophilic addition.

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

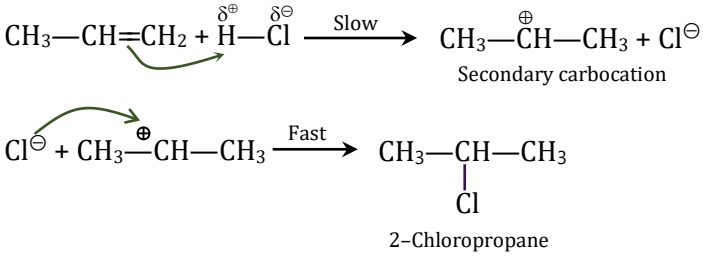
(iv) Addition of HX on unsymmetrical alkenes ($R-CH=CH_2$) takes place according to Markovnikov rule.

MARKOVNIKOV RULE :

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



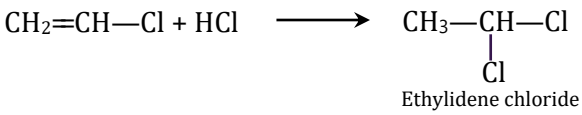
Mechanism : It is electrophilic addition and is illustrated by the action of HCl to propene.



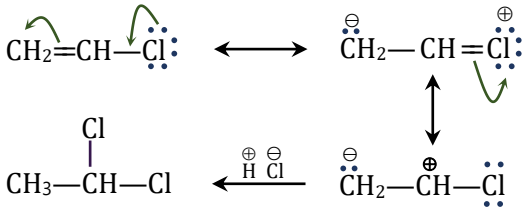
Primary carbocation ($CH_3-CH_2-\overset{\oplus}{C}H_2$) is formed but only in very small proportion since it is less stable than the secondary carbocation. Markovnikov rule can also be stated as :

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.



Mechanism :



In vinyl chloride two effects operate simultaneously in opposite direction-

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

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

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

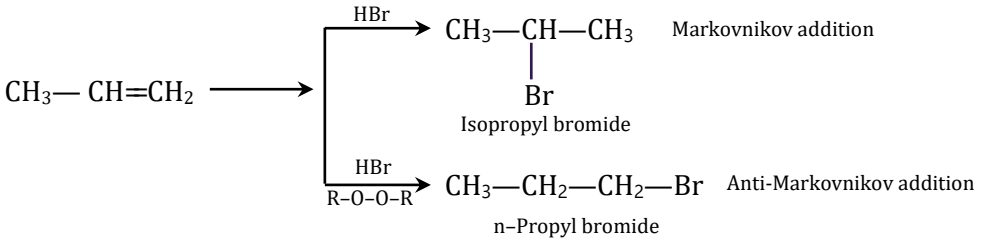
All polar reagents of the general structure $\overset{\oplus}{Y}\overset{\ominus}{Z}$ (such as $\overset{\oplus}{H}—\overset{\ominus}{X}$, $\overset{\oplus}{H}—\overset{\ominus}{O}H$, $\overset{\oplus}{H}—\overset{\ominus}{S}O_3H$, $\overset{\oplus}{X}\overset{\ominus}{O}H$) add on unsymmetrical unsaturated compound in accordance with Markovnikov rules. Such additions are called normal Markovnikov rule, whereas additions in the opposite manner are referred to as abnormal or **Anti Markovnikov additions.**

Anti markovnikov's rule or peroxide effect or kharasch effect :

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

(ii) In the normal Markovnikov addition, the mechanism is ionic.

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



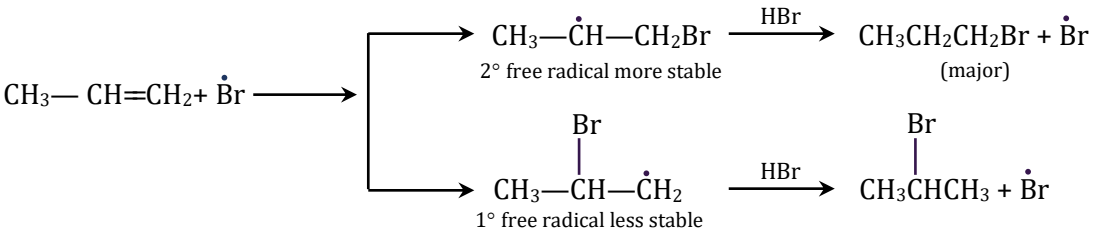
Mechanism :

(i) Chain initiation :

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

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

(ii) Chain propagation :



(iii) Chain termination :

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

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

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

Illustration 28:

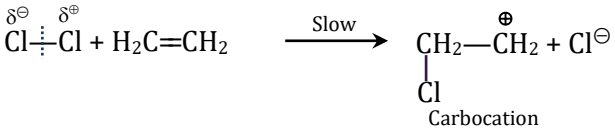
Why HCl and HI do not give Anti-Markovnikov products in the presence of peroxides.?

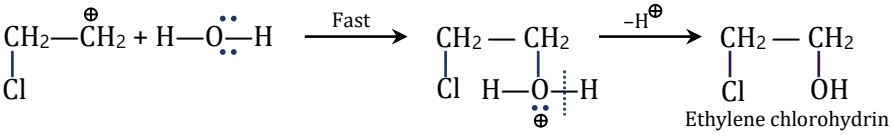
Solution:

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

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

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

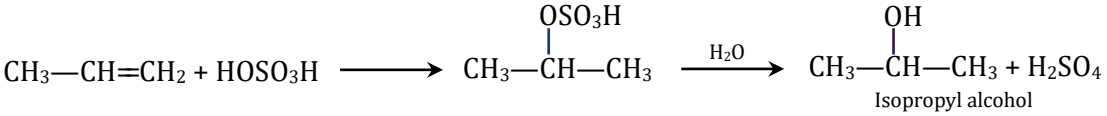


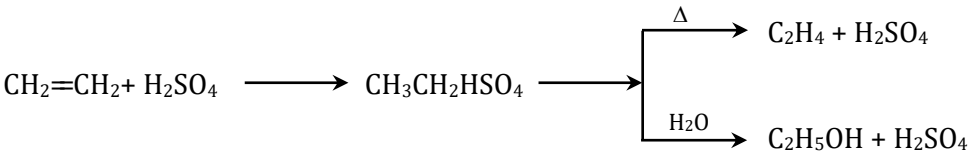


In the fast step, there is competition between $Cl^{\ominus}$ ion and H_2O molecule to act as nucleophile but H_2O is a better nucleophile.

Reactivity order is	HOCl > HOBr > HOI

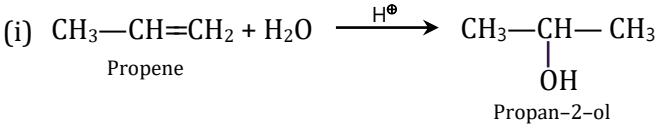
4. **Addition of H_2SO_4:** Alkene react with conc. H_2SO_4 to produce alkyl hydrogen sulphate. Which gives alcohols on hydrolysis. This reaction used to separate alkene from a mixture of alkane and alkene.

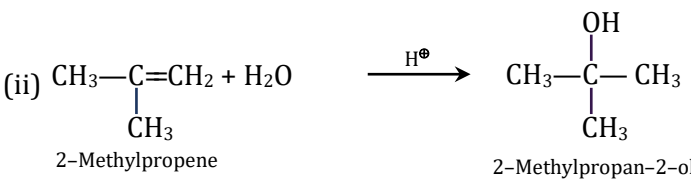




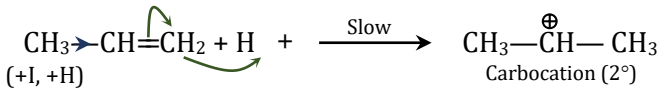
Ethyl hydrogen sulphate give ethylene when heated 430-440K while ethanol is obtained on boiling it with water.

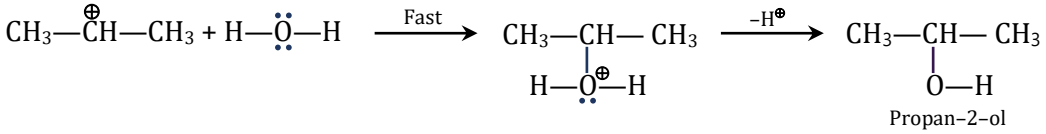
5. **Addition of water (Hydration of alkenes) :** Propene and higher alkenes react with water in the presence of acid to form alcohol. This reaction is known as the **hydration reaction**. Intermediate in this reaction is carbocation, so rearrangement will take place.





Mechanism :

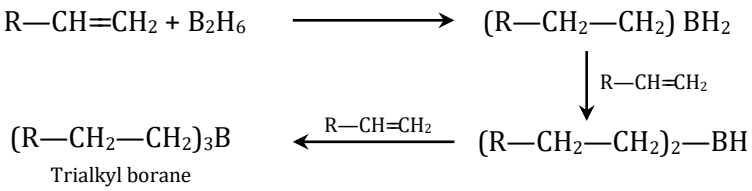




6. Addition of NOCl (Tilden reagant) : $CH_3—CH=CH_2 + \overset{\delta\oplus}{N}O\overset{\delta\ominus}{Cl} \longrightarrow$ $CH_3—\underset{Cl}{CH}—\underset{NO}{CH_2}$

Propylene nitroso chloride

7. Hydroboration : It obeys Markovnikov rule. Diborane readily reacts with alkenes giving trialkyl boranes. The reaction is called hydroboration.

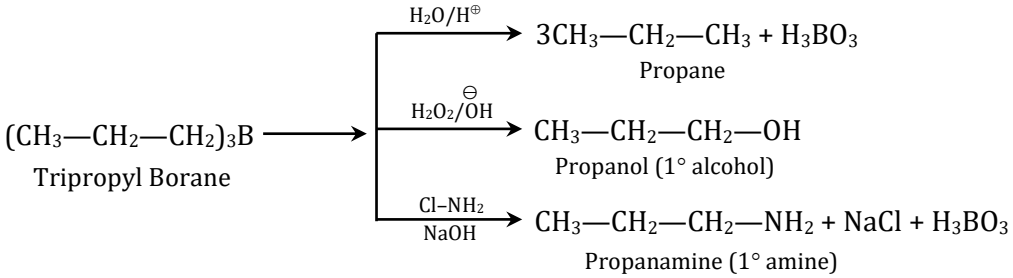


BH_3 does not exist or stable as monomer so a solvent THF (tetrahydrofuran) is used.

Example : $3CH_3—CH=CH_2 + B\begin{matrix}H\\ \\H\end{matrix}\!\!\begin{matrix}\diagup\\ \\\diagdown\end{matrix}\!\!H \xrightarrow{THF} (CH_3—CH_2—CH_2)_3B$

BHR_2 also can be taken.

Example : $CH_3—CH=CH_2 + BHR_2 \longrightarrow CH_3—CH_2—CH_2—BR_2$



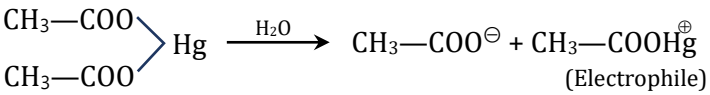
8. Oxymercuration–demercuration : Mercuric acetate in tetrahydro furan (THF) is treated with an alkene. The addition product on reduction with sodium borohydride in aqueous NaOH solution gives alcohol. It follows the markovnikov rule.

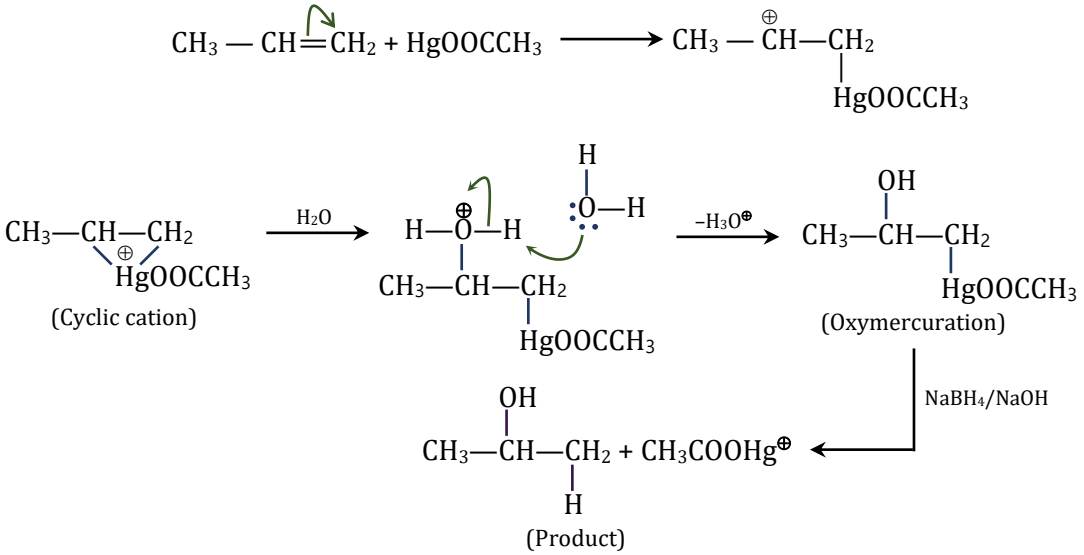
$$CH_3—CH=CH_2 \longrightarrow CH_3—\underset{OH}{CH}—CH_3$$

(i) $(AcO)_2Hg/H_2O$ (Mercuric acetate) or $(CH_3COO)_2Hg/H_2O$

(ii) $NaBH_4/NaOH$

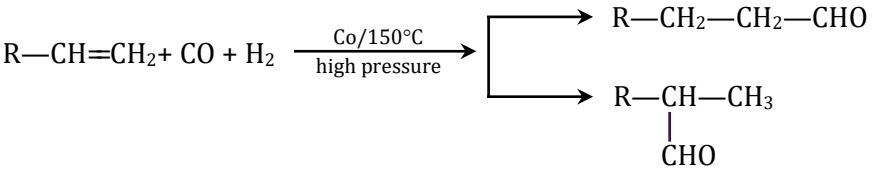
Mechanism :





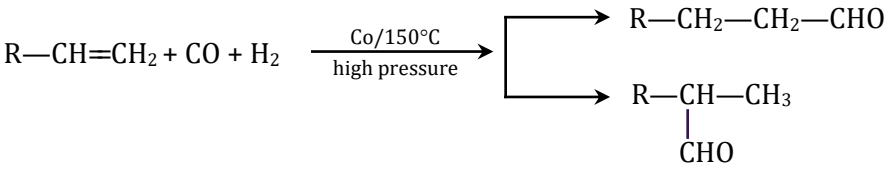
Note :

Intermediate is cyclic cation so their is no rearrangement.

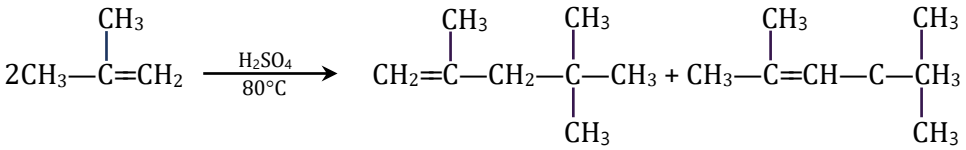


9. **Hydroformylation or Oxo reaction:** Alkenes react with Carbon monoxide and hydrogen at 100 – 150°C temperature and high pressure (200 atm) in the presence of Cobalt catalyst to produce an aldehyde. It does not follows Markovnikov rule.

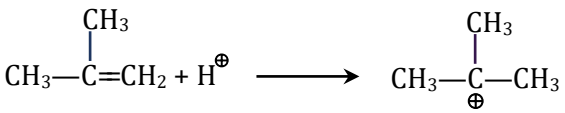
   The net reaction is the addition of a H–atom to one of the Olefinic bond and a formyl (–CHO) group to the other.

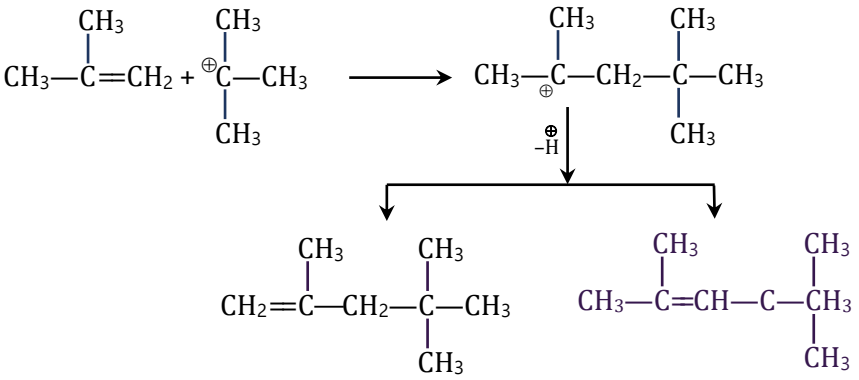


10. **Alkenylation (Addition of alkene):** In presence of H_2SO_4 or H_3PO_4 at 80°C dimerisation of isobutylene take place gives two isomer of octene.

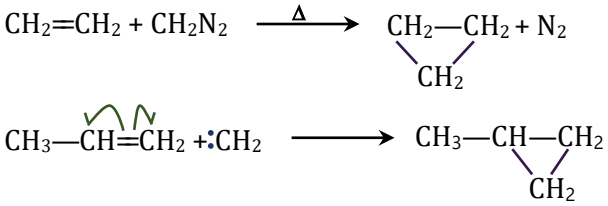


Mechanism :



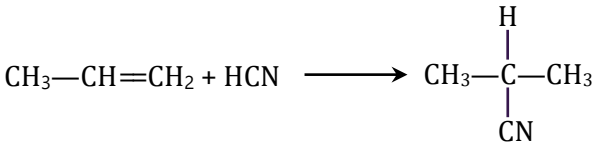


11. Addition of Carbene : The addition of carbene to alkene is always carried by diazomethane CH_2N_2 Carbene group obtained from diazomethane is added to alkene and give cycloalkanes.



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

12. Addition of HCN:



(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.

Illustration 29:

90 mL of oxygen is required for complete combustion of unsaturated 20 mL gaseous hydrocarbon, hydrocarbon is ?

Solution:

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

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

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

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

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

Illustration 30:

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

Solution:

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

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

Illustration 31:

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.

Solution:

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 "volume C_4H_8", 6 (30–x) ml of O_2 is required.

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

x = 10

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

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

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

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

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

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

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

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

Example : $\overset{1}{CH_3}-\overset{2}{CH}=\overset{3}{CH}-\overset{4}{CH_3}$ (But–2–ene) $\xrightarrow{\text{Ozonolysis}}$ $CH_3-\underset{\text{Ethanal}}{\underset{|}{\overset{H}{C}}=O} + O=\underset{\text{Ethanal}}{\underset{|}{\overset{H}{C}}}-CH_3$

Example : $\overset{1}{CH_2}=\overset{2}{CH}-\overset{3}{CH_2}-\overset{4}{CH_3}$ (But–1–ene) $\xrightarrow{\text{Ozonolysis}}$ $\underset{\text{Methanal}}{\underset{|}{\overset{H}{C}}=O} + O=\underset{\text{Propanal}}{\underset{|}{\overset{H}{C}}}-CH_2-CH_3$

Example : $CH_3-\underset{\text{2,3–Dimethyl but–2–ene}}{\underset{|}{\overset{H_3C}{C}}=\underset{|}{\overset{CH_3}{C}}-CH_3}$ $\xrightarrow{\text{Ozonolysis}}$ $CH_3-\underset{\text{Propanone}}{\underset{|}{\overset{CH_3}{C}}=O} + O=\underset{\text{Propanone}}{\underset{|}{\overset{CH_3}{C}}}-CH_3$

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.

$R'-\underset{O-O}{\overset{O}{CH\ CH}}-R'' \xrightarrow{LiAlH_4} R'CH_2OH + R''CH_2OH$ (Alcohols)

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

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

$\rangle C=C\langle + H_2O + [O] \xrightarrow[KMnO_4]{OH^{\ominus}} \underset{OH\ OH}{\rangle C-C\langle}$ Glycol (cis–addition)

(b) By OsO_4 :

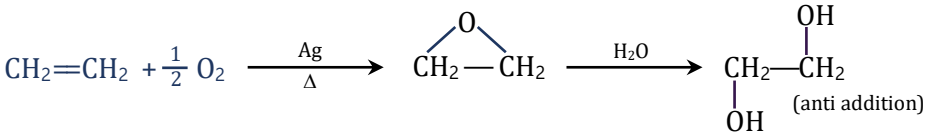
$\underset{R-CH}{\overset{R-CH}{\|}} + OsO_4 \longrightarrow \underset{R-CH-O}{\overset{R-CH-O}{|}}Os\overset{O}{\underset{O}{\|}} \xrightarrow{H_2O} \underset{R-CH-OH}{\overset{R-CH-OH}{|}} + H_2OSO_4$ (cis–addition)

(c) By peracid :

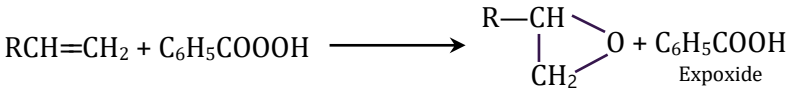
$\rangle C=C\langle + H-\overset{O}{\overset{\|}{C}}-O-O-H \xrightarrow{-HCOOH} \rangle C-C\langle \xrightarrow{-H_2O} \underset{OH\ H}{\rangle C-C\langle}$ Trans glycol

(4) Epoxidation :

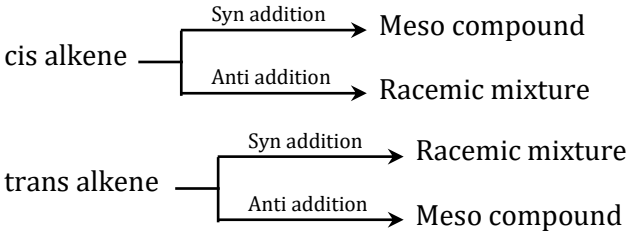
(a) Alkenes reacts with oxygen in the presence of Ag catalyst at 250°–400° C to form epoxide.



(b) When an alkene is treated with perbezoic acid an epoxide is formed.



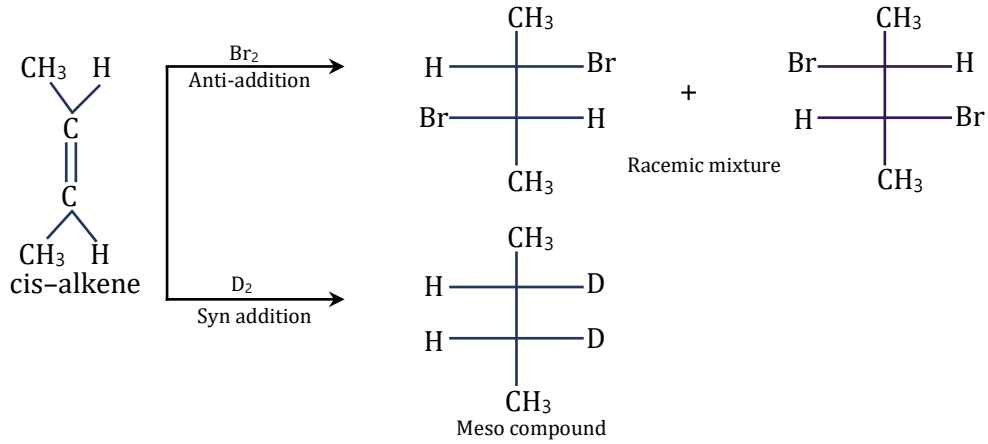
Emmons have found that perbenzoic oxy trifluoroacetic acid (CF_3COOH) is a very good reagent for epoxidation and hydroxylation.



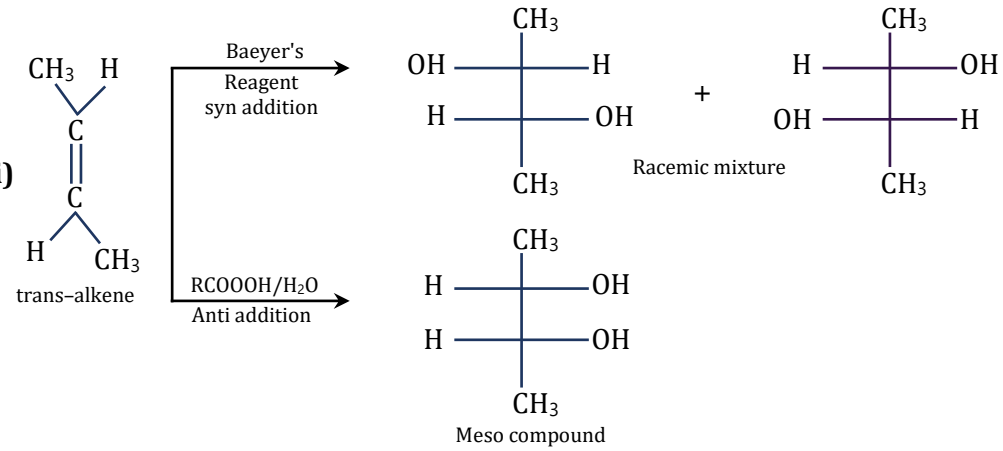
Syn addition on alkene $\longrightarrow H_2O_2$, Baeyer's reagent, OsO_4 / H_2O
Anti addition on alkene $\longrightarrow X_2$, HOX, RCOOH / H_2O, Ag_2O / H_2O

Example :

(i)



(ii)



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

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

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

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

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

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

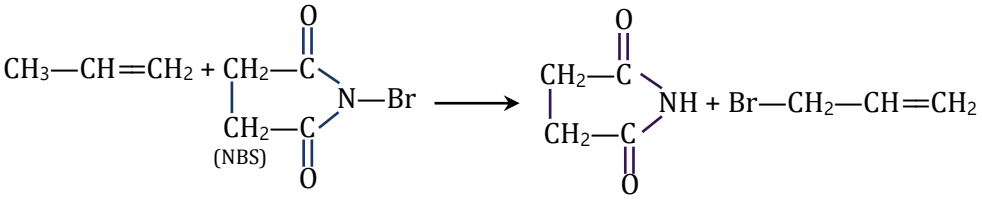
$$CH_2{=}CH_2 + H_2O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

(C) SUBSTITUTION REACTION (Allylic substitution) :

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

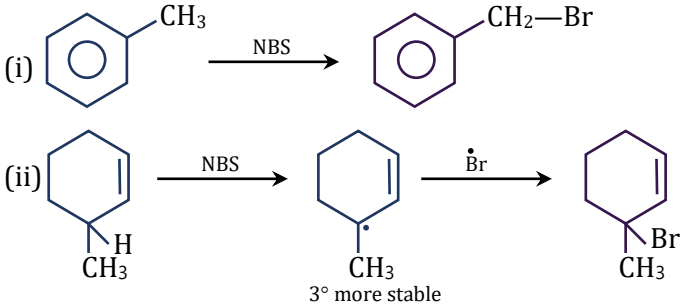
$$CH_3{-}CH{=}CH_2 + Cl_2 \xrightarrow{500°C} \underset{\text{Allyl chloride}\\\text{(3–Chloro–1–propene)}}{ClCH_2{-}CH{=}CH_2} + HCl$$

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



Substitution reaction is not given by ethene.

Example :



(D) POLYMERIZATION :

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

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

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

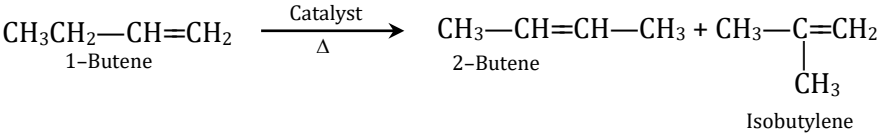
(iv) The presence of oxygen initiates free radical mechanism.

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

Name of Polymer	Structure of monomer	Structure of Polymer	Properties	Uses Properties
1. Polyvinyl Chloride (PVC)	$CH_2=CH_2—Cl$	$+H_2C—HC+_n$ (Cl)	Piliable (easily moulded)	Used in handbag, raincoats, vinyl flooring, good electrical insulator for wires
2. Polytetrafluor-ethylene or Teflon (PTFE)	$F_2C=CF_2$	$+F_2C—CF_2+_n$	Flexible and inert to solvents, boiling acids, even aqua regia stable up to 598K.	For making non-stick utensils coating
3. Natural rubber	$CH_2=CH–C(CH_3)=CH_2$ isoprene	$+CH_2–CH=C(CH_3)–CH_2+_n$	Waxy and non–elastic	Used as raw material for making vulcanised rubber which is strong and elastic. Vulcanised rubber is used in making tyres hose, pipes etc.
4. Orlon	acrylonitrile	$+H_2C—HC+_n$ (CN)	Fibrous	Used in making Fabrics
5. Poly methyl methacrylate (PMMA)	$CH_2=C(CH_3)COOCH_3$ Methyl methacrylate	$+CH_2–C(CH_3)(C=O(OCH_3))+_n$		

(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.



Uses :

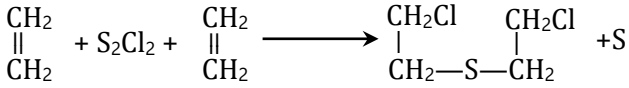
(a) In plastic formation.

(b) In oxy ethylene welding

(c) As food preservatives and ripening fruits.

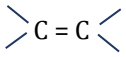
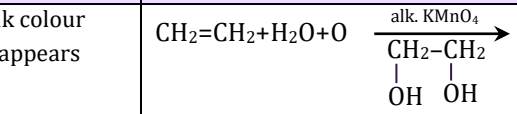
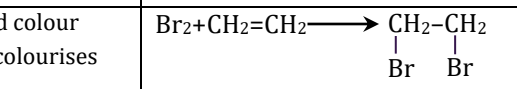
(d) As general anaesthetic (C_2H_4 with 10% O_2)

(e) In preparation of mustard gas



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

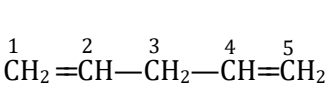
Laboratory test of alkene :

Functional Group	Reagent	Observation	Reaction	Remarks
	(1) Baeyer's Reagent alk. dil. cold $KMnO_4$	Pink colour disappears		Dihydroxylation
	(2) Br_2/H_2O	Red colour decolourises	 White ppt.	Dibromination
	(3) O_3 (ozone)	 Compounds		Ozonolysis

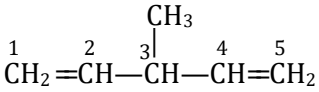
Dienes :

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

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

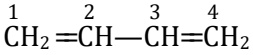


Penta–1,4–diene

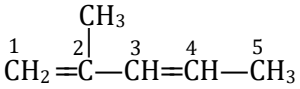


3–Methylpenta–1, 4–diene

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

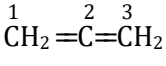


Buta-1,3-diene

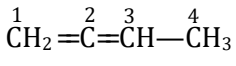


2-Methylpenta-1,3-diene

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



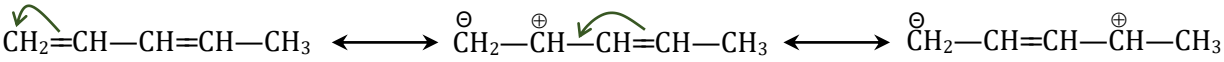
Propa-1,2–diene



Buta–1, 2–diene

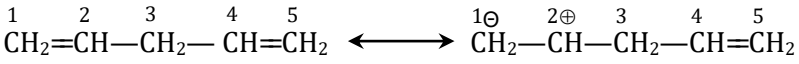
Comparison of relative stabilities of isolated and conjugated dienes :

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



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.



(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.

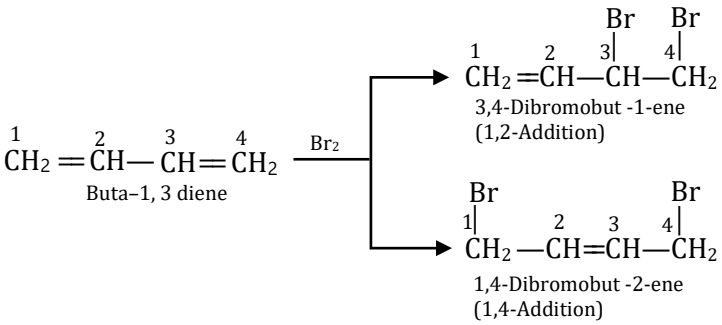
Properties of Conjugated Dienes :

The properties of the isolated dienes are similar to those of simple alkene but those of conjugated dienes are somewhat 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.

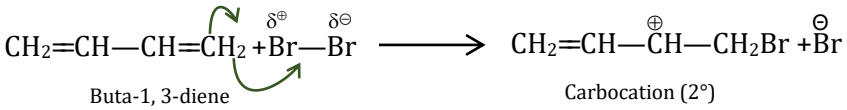
   (A) Electrophilic Addition Reactions : The electrophilic addition is illustrated by the attack of halogen and halogen acid on buta–1,3–diene, a conjugated diene.

   (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,

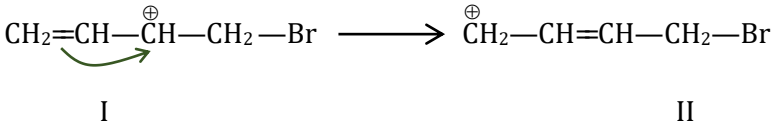


1, 2–addition is a normal addition in which one mole of halogen has been added to one of the double bond. But 1, 4-addition is somewhat unexpected.

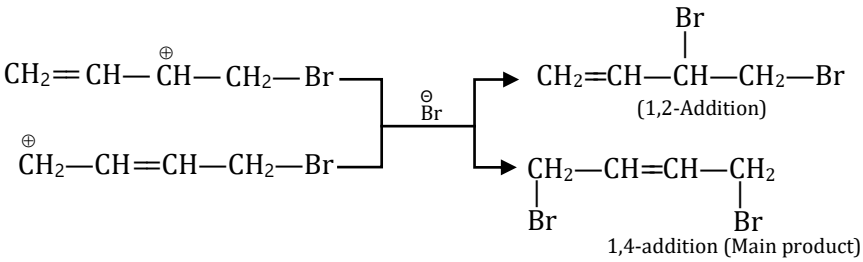
Mechanism : The addition is electrophilic in nature and the halogen molecule (bromine) provides the electrophile for the attack.



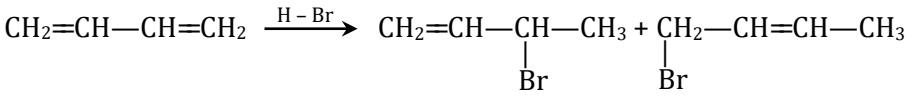
The 2° carbocation get stabilised by resonance as follows –



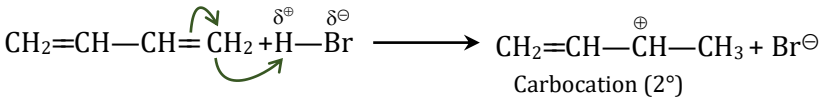
The attack of $\overset{\ominus}{Br}$ ion on carbocation (I and II)



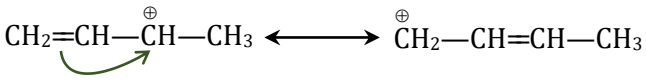
(b) Addition of H – X :



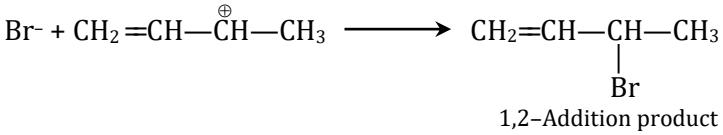
Mechanism : The addition is electrophilic in nature as $H^{\oplus}$ ion is the electrophile.

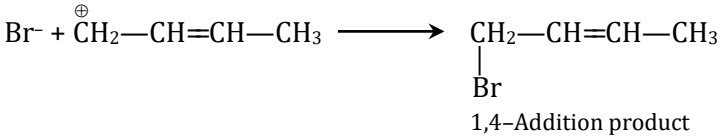


The carbocation gets resonance stabilised as follows :

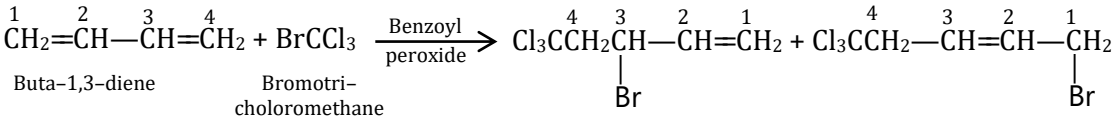


The attack of Br^- ion on the carbocation (I) gives 1,2-addition product whereas the attack on the carbocation (II) yields 1,4-addition product.



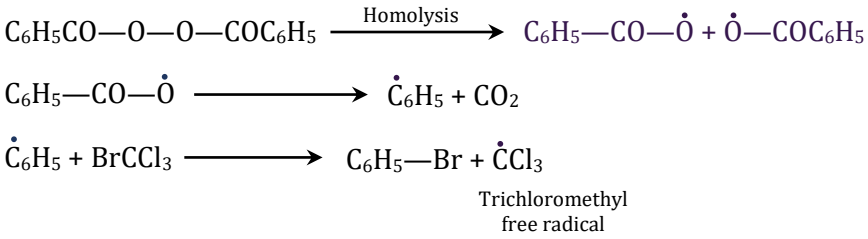


(B) Free Radical Addition Reaction : The addition to conjugated dienes can also proceed by free radical mechanism provided it is carried in the presence of a suitable reagent which can help in forming a free radical. However, the addition also yields 1,2 and 1,4 addition products. The free radical addition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

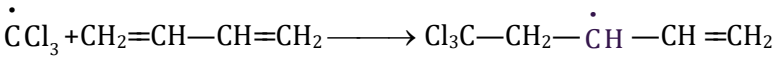


Mechanism : The mechanism of addition is free radical in nature which is initiated by benzoyl free radical. It is explained in the following steps :

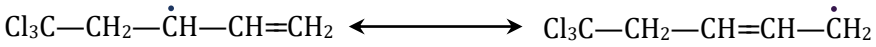
Step I Generation of free radical



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

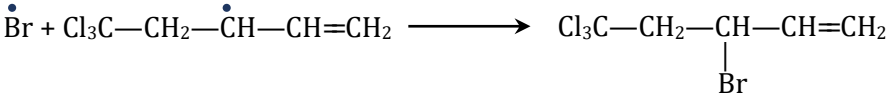


The free radical gets resonance stabilised



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.



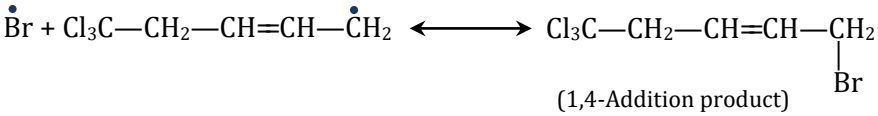


Illustration 32:

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

Solution:

Density of 1 litre hydrocarbon = 2.5 gram/litre

$\therefore$ molecular weight of hydrocarbon = 2.5 x 22.4 = 56

After molecular weight , we calculate the molecular formula.

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

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

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

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

14n = 56 (Alkene) $\because$ Hydrocarbon is C_4H_8 (Butene).

n = 4

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

What is hydrocarbon is to be asked.

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

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

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

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

Illustration 33:

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

Solution:

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

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 (22.4 L) of propene as product.

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

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

$\therefore$ 2.24 L of propene can be get from dehydration of $\frac{60}{22.4} \times 2.24$ g of propanol

Ans. = 6 g

ALKYNE

Introduction:

A triple bond gives an alkyne four fewer hydrogen atoms than the corresponding alkane. Therefore, the triple bond contribute two degree of unsaturation (DU).

Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock, but its largest use is as the fuel for the oxyacetylene welding torch.

Structure and bonding in Alkynes

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

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

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

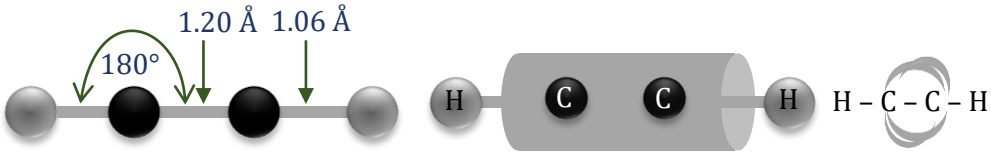
(d) In alkyne C ≡ C bond length is 1.20 Å

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

(f) The hybridization of carbon atoms having triple bond (C ≡ C) in alkynes is sp.

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

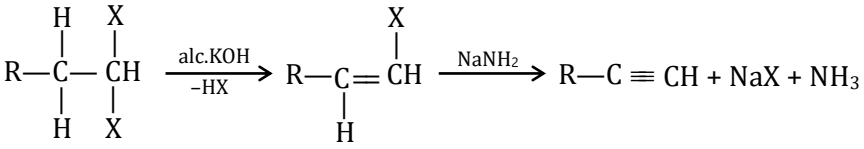
(h) Two π bonds result form overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90°) to each other, forming one π bond with electron density above and below the C-C sigma bond, and the other with electron density in front and in back of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



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

General Methods of Preparation :

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



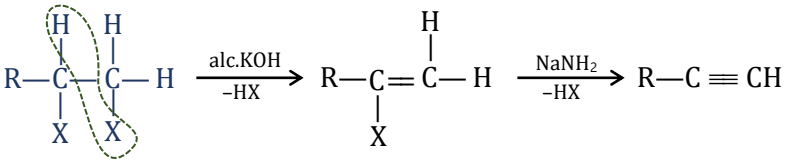
(Stable by resonance)
Vinyl halide

(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.

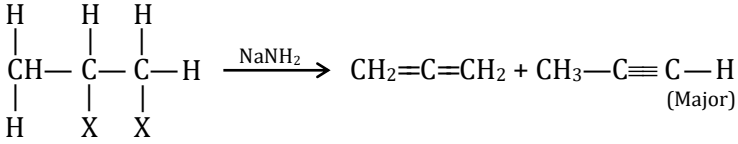
(b) Basic strength : $\overset{\ominus}{N}H_2$ is stronger base than $RO^{\ominus}$

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

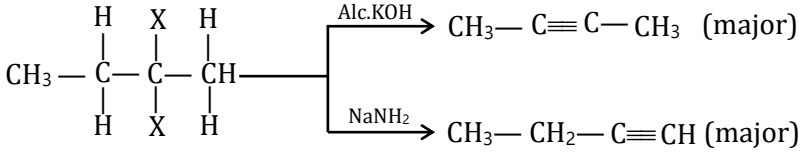
2. From Vicinal dihalides (by dehydrohalogenation) :



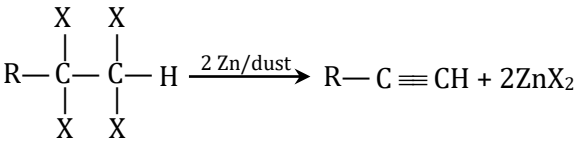
(a) Elimination of Vic. dihalides gives also alkadiene (1, 2 and 1, 3 alkadienes) but the major product is alkyne.

Example : 

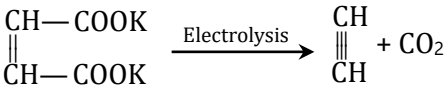
(b) Non terminal gem dihalide gives 2-Alkyne in presence of alc. KOH while gives 1-alkyne in presence of $NaNH_2$.

Example : 

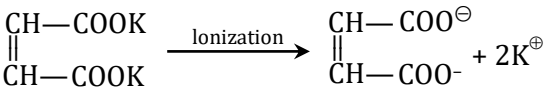
3. Dehalogenation of tetrahalo alkane : By heating 1, 1, 2, 2 - tetra halo alkane with Zn dust.



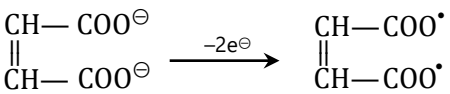
4. From Kolbe's electrolysis : By the electrolysis of aqueous solution of sodium or potassium fumarate or maleate, acetylene is formed at anode.



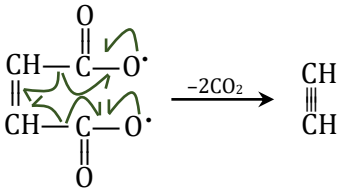
Mechanism :



at anode (Alkyl and CO_2 gas is formed)



(Oxygen free radical)



at cathode (KOH and H_2 gas is formed)

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

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

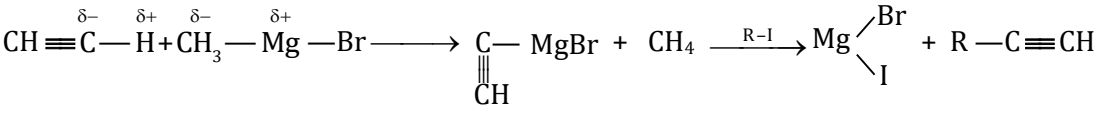
Illustration 34

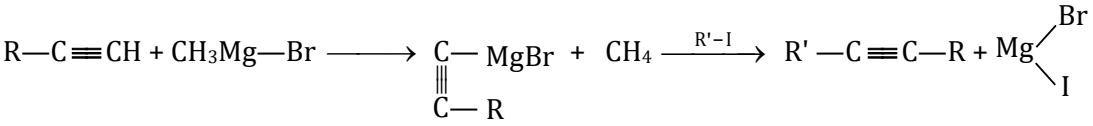
Is PH of solution changed in Kolbe's electrolysis.

Solution:

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 into higher alkyne





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.

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

$Ca^{2\oplus} + {}^{\ominus}C \equiv C^{\ominus} + 2H^{\oplus} + 2OH^{\ominus} \longrightarrow CH \equiv CH + Ca(OH)_2$

(b) Manufacture : Acetylene is manufactured by heating methane or natural gas at 1500°C in an electric arc

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

(c) Berthelot's process : Acetylene is synthesized by striking an electric arc between carbon electrodes in presence of hydrogen. $2C + H_2 \xrightarrow{1200°C} CH \equiv CH$

(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 :

(a) Alkynes are relatively non polar (w.r.t. alkyl halides and alcohols) and nearly insoluble in water (but they are more polar than alkenes and alkanes). They are quite soluble in most organic solvents, (acetone, ether, ethylene chloride, chloroform and alcohols).

(b) Acetylene, propyne, and the butyne are gases at room temperature, just like the corresponding alkanes and alkenes. In fact, the boiling points of alkynes are nearly the same as those of alkanes and alkenes with same number of carbon atoms.

Chemical Properties :

The chemical properties of alkynes are due to two factors

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

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

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

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

$\equiv C-H$	$=C-H$	$-C-H$
50%	33%	25%

Since s electrons are closer to the nucleus than the p electrons, the electrons present in a bond having more s-character will be 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

$\equiv C-H$ (sp) > $=C-H$ (sp^2) > $-C-H$ (sp^3)

Relative acidic order

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

Addition Reaction :

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

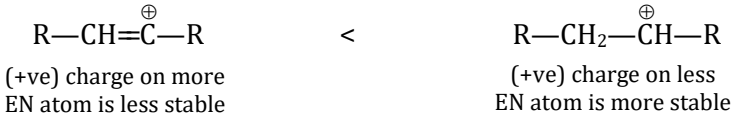
Reactivity order of hydrocarbons for electrophilic addition | Alkenes > Alkynes > Alkanes |

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

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

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

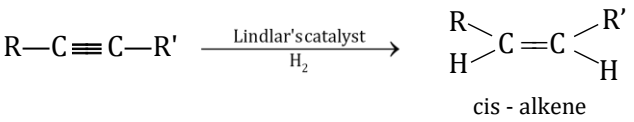
Stability of intermediates :



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

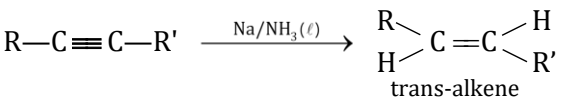
(a) Addition of hydrogen : Alkynes reacts with H_2

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



(Stereo specific reaction)

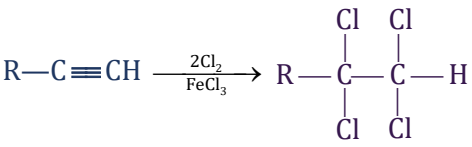
In presence of Na/NH_3 alkynes give trans-alkene. (Birch Reduction)



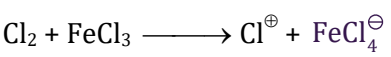
(Stereo specific reaction)

(b) 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 derivatives.

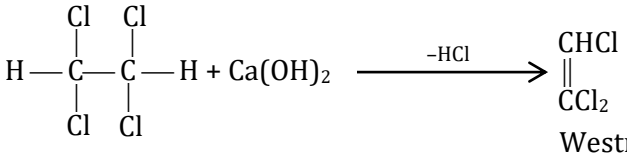


Mechanism :



Acetylene tetrachloride is also called as westron

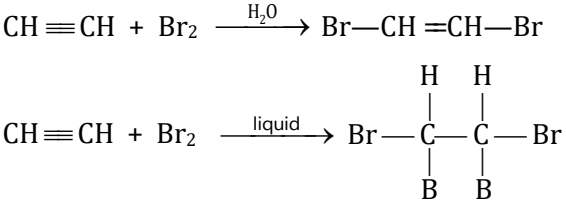
When westron is treated with $Ca(OH)_2$ then we get westrosol



Westrosol or triclene

Both westron and westrosol are used as solvents in cloth industries

Reaction with dilute Br_2 or bromine water:



Reaction with Iodine :

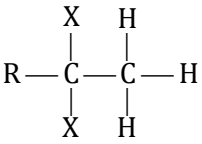
$CH \equiv CH + I_2 \xrightarrow{\text{ethanol}} CHI = CHI$ (addition reaction)

$CH \equiv CH + I_2 \xrightarrow{NH_3} I-C \equiv C-I + NH_4I$ (substitution reaction)

Di iodoacetylene

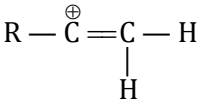
(c) Addition of halogen acids (H – X) : Addition according to Markovnikov Rule.

Reactivity order of H – X : HI > HBr > HCl > HF

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

(Gem dihalides major product)

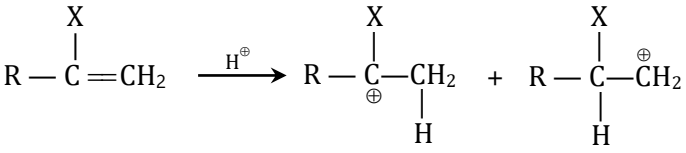
Mechanism :

$R-C \equiv CH \xrightarrow[[H-X]]{H^{\oplus}}$ 

(Intermediate is carbocation)

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

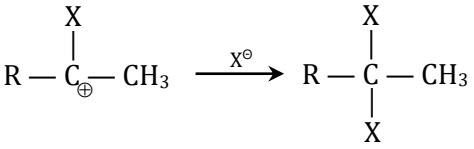
Further



(more stable due to +M of X)

(only –I of X) (Less stable)

So



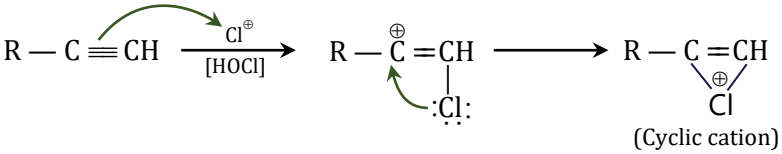
(Major Product)

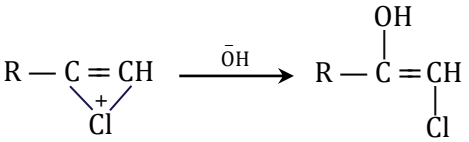
(d) Addition of HOX : Alkynes react with hypohalous acids according to Markovnikov rule and form gem diol, which are unstable, lose a molecule of water and form halo aldehyde or halo ketones.

Reactivity order HOCl > HOBr > HOI

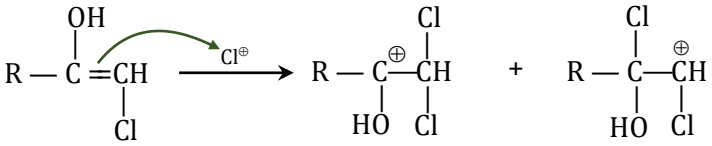
$R-C \equiv CH + HOCl \longrightarrow R-\underset{\underset{O}{\|}}{C}-CHCl_2$

Mechanism :

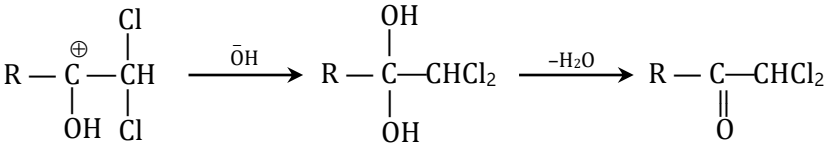




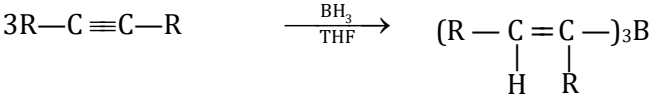
Further



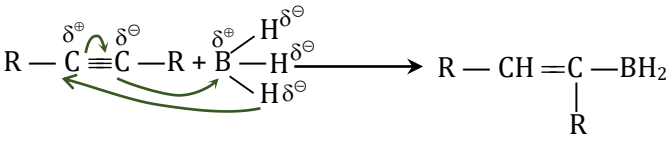
so

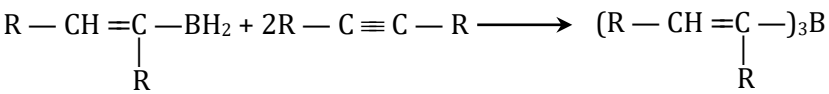


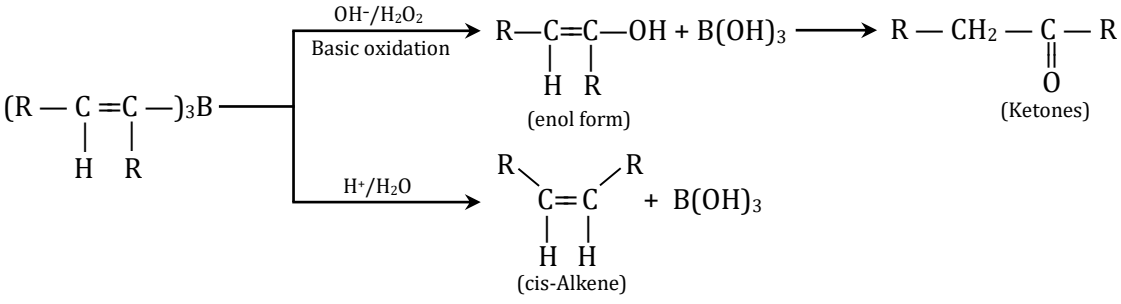
(e) Addition of BH_3 / THF or B_2H_6 (Hydroboration) : THF - Tetrahydrofuran is used as solvent.



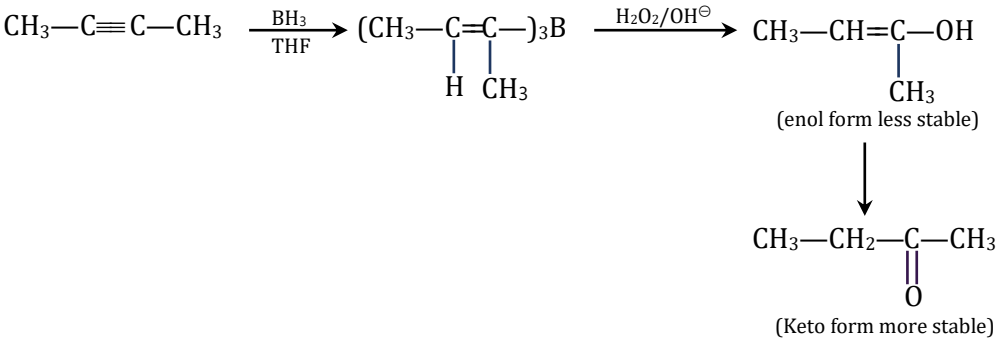
Since BH_3 is not available as monomer so a solvent THF is used for the stability of BH_3.





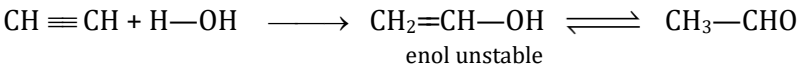


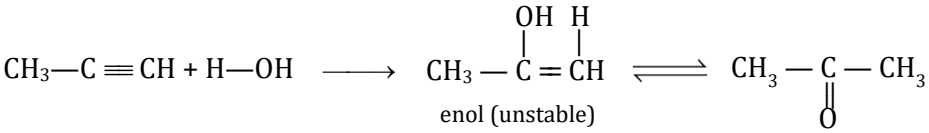
Example :



(2) Nucleophilic addition reaction : In these reactions some heavy metal cation like $Hg^{2\oplus}$, $Pb^{2\oplus}$, $Ba^{2\oplus}$ are used. These cations attracts the $\pi e^{\ominus}$ of alkynes and decrease the $e^{\ominus}$ density and hence a nucleophile can attack on alkynes.

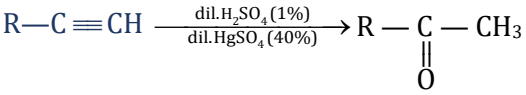
(a) Addition of dil. H_2SO_4 (Hydration) : The addition of water takes place in the presence of $Hg^{2\oplus}$ and H_2SO_4 [1% $HgSO_4$+40% H_2SO_4]. In this reaction carbonyl compounds are obtained .



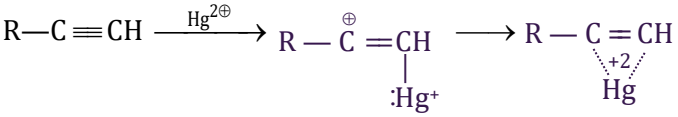


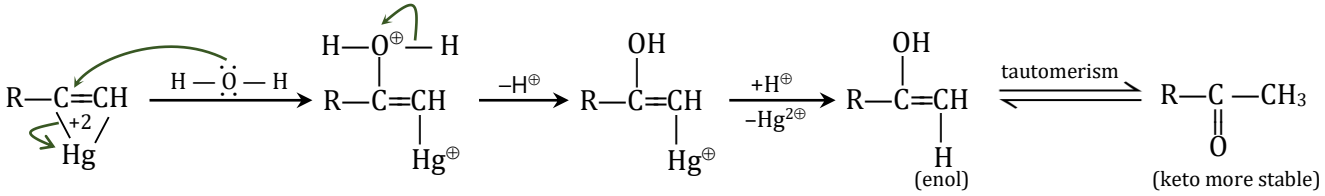
A structure in which –OH group is attached to double bond carbon is called as enol (ene + ol).

This reaction is used for preparation of aldehyde and ketone.

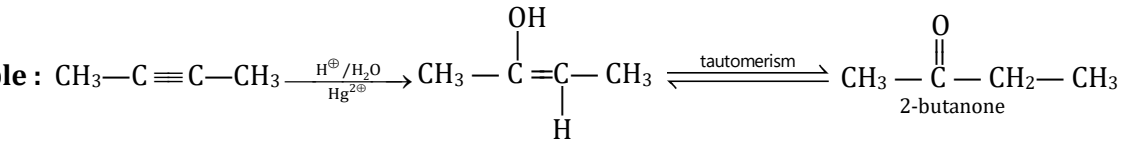


Mechanism :





Example :



(b) 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.

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

Orlon

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

$$CH \equiv CH + CH_3OH \xrightarrow[HgO]{BF_3} CH_2=CHOCH_3 \xrightarrow{CH_3OH} CH_3-CH\begin{matrix}OCH_3\\OCH_3\end{matrix}$$

Methylal (acetal)

$$R-C \equiv CH + CH_3-OH \xrightarrow[HgO]{BF_3} R-\underset{\displaystyle OCH_3}{\underset{|}{C}}=CH_2 \xrightarrow{CH_3OH} R-\underset{\displaystyle OCH_3}{\underset{|}{\overset{\displaystyle OCH_3}{\overset{|}{C}}}}-CH_3$$

Ketal

Acetylene forms acetal while other alkynes form ketal.

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°C) is produced.

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

$$\begin{matrix}CH\\\|\\CH\end{matrix} + 4[O] \xrightarrow{alk.KMnO_4} \begin{matrix}COOH\\|\\COOH\end{matrix}$$

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.

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

$$\begin{matrix}CH\\\|\\CH\end{matrix} + 2[O] \longrightarrow \begin{matrix}CHO\\|\\CHO\end{matrix} \xrightarrow{H_2O+[O]} 2HCOOH$$

glyoxal

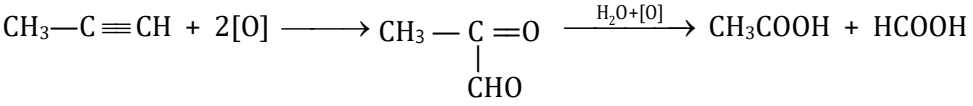
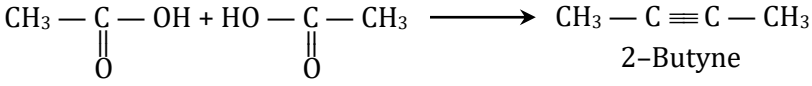


Illustration 35:

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

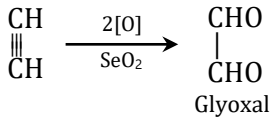
Solution:

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

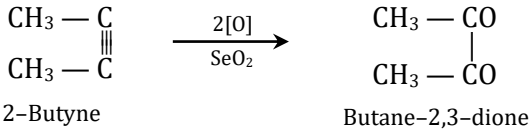


2–Butyne

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

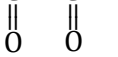


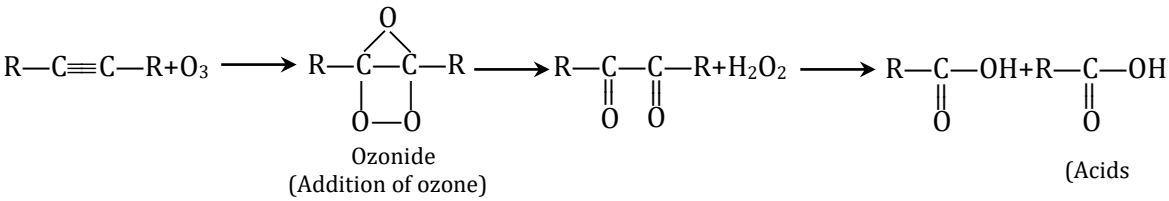
Glyoxal



2–Butyne

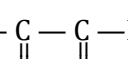
Butane–2,3–dione

(e) Oxidation with ozone (O3) : In the ozonolysis both sp-C-atoms are converted into  group.



Ozonide
(Addition of ozone)

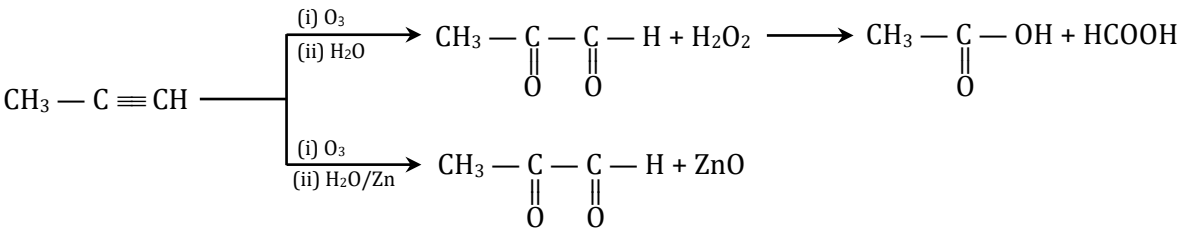
(Acids

In this reaction H_2O_2 is oxidant which oxidise R—  —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

$H_2O_2 + Zn \longrightarrow ZnO + H_2O$

Example :



Substitution Reaction : (Formation of metallic derivatives)

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

Acetylene is dibasic acid where as propyne is monobasic means acetylene can give two $H^{\oplus}$ where as propyne can give one $H^{\oplus}$.

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

$$H-C\equiv C-H \xrightarrow{NaNH_2} \underset{\text{Mono sodium acetylide}}{NaC\equiv C-H} \xrightarrow{NaNH_2} \underset{\text{Disodium acetylide}}{NaC\equiv CNa}$$

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) respectively.

$$R-C\equiv C-H + Cu_2Cl_2 + NH_4OH \longrightarrow \underset{\text{copper acetylide [Red ppt.]}}{R-C\equiv CCu} + NH_4Cl + H_2O$$

(ammonical cuprous-chloride)

$$R-C\equiv C-H + AgNO_3 + NH_4OH \longrightarrow \underset{\text{White ppt.}}{R-C\equiv CAg} + NH_4NO_3 + H_2O$$

Tollen's reagent

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.

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

$$\underset{\text{1–Butyne}}{CH_3-CH_2-C\equiv CH} \xrightarrow[\Delta]{\text{alc.KOH}} \underset{\text{2–Butyne}}{CH_3-C\equiv C-CH_3}$$

When 2–alkyne is heated with $NaNH_2$, 1–alkyne is obtained

$$\underset{\text{2–Butyne}}{CH_3-C\equiv C-CH_3} \xrightarrow[\Delta]{NaNH_2} \underset{\text{1–Butyne}}{CH_3-CH_2-C\equiv CH}$$

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.

$$CH_2=CH-C\equiv C-H \xrightarrow{HCl} CH_2=CH-\underset{\displaystyle Cl}{\overset{\displaystyle |}{C}}=CH_2 \xrightarrow{\text{Polymerisation}}$$

Neoprene (Synthetic rubber)

2–chloro–1,3–butadiene

[chloroprene]

Trimerisation : 3 molecules of acetylene.

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

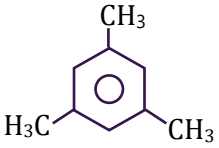
Divinyl acetylene

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

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

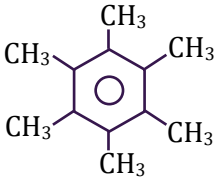
Benzene

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



Mesitylene

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

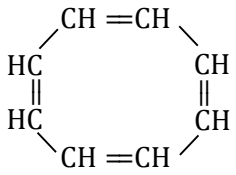


Hexa methyl benzene

$$3\ HC\equiv CH \xrightarrow[(C_6H_5)_3P]{Ni(CO)_4} \text{benzene (90\% yield)}$$

(triphenyl – 1 – phosphene)

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



1,3,5,7–cyclooctatetraene

Uses of Acetylene :

(i) Oxyacetylene flame used in welding and cutting

(ii) Acetylene is used as an illuminant

(iii) Acetylene is used for artificial ripening of fruits

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

(v) It is used as a general anaesthetic.

Laboratory Test for alkynes :

Functional Group	Reagent	Observation	Reaction	Remarks
R – C ≡ C – H	(1) Bayer's reagent alk.dil.Cold $KMnO_4$	Pink colour disappears	$CH_2 = CH_2 + H_2O + O \xrightarrow{alk.KMNO_4} \underset{\vert\quad\vert}{CH_2 - CH_2}$ (OH OH)	Hydroxylation
	(2) Br_2/H_2O	Red colour decolourises	$Br_2 + CH_2 = CH_2 \rightarrow \underset{\vert\quad\vert}{CH_2 - CH_2}$ (Br Br) white ppt.	Bromination
	(3) O_3(ozone)	Acid Formed	$R - C \equiv C - R' \xrightarrow{O_3} RCOOH + R'COOH$	Ozonolysis

Laboratory test of terminal alkynes :

When triple bond comes at the end of a carbon chain. The alkyne is called a terminal alkyne.

acetylenic hydrogen

$\boxed{H} - C \equiv C - CH_2CH_3$

1–Butyne, a terminal alkyne

Functional Group	Reagent	Observation	Reaction
R–C≡C–H	(1) Cuprous chloride + NH_4OH	Red ppt.	$R - C \equiv CH + CuCl \xrightarrow{NH_4OH} R - C \equiv CCu \downarrow$ (red)
	(2) $AgNO_3$+NH_4OH	White ppt.	$R - C \equiv CH + Ag \rightarrow R - C \equiv C\bar{A}g$ (white)
	(3) Na in ether	Colourless gas	$HC \equiv CH + 2Na \rightarrow Na - C \equiv C - Na + H_2 \uparrow$

(i) Decolourization of Br_2 in CCl_4 solution.

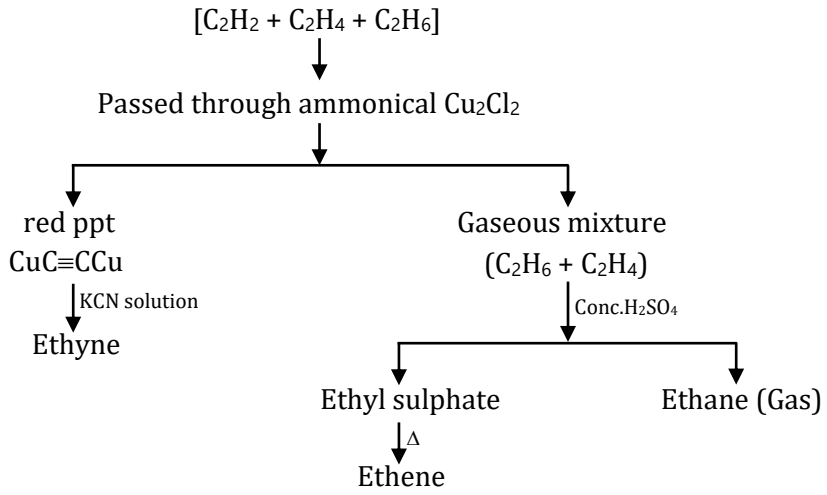
(ii) Decolourisation of 1% alkaline $KMnO_4$ solution.

(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 :



Solved examples

Illustration 36:

$R—CH_2—CCl_2—R \xrightarrow{\text{Reagent}} R—C \equiv C—R$. The reagent is -

(A) Na (B) HCl in H_2O (C) KOH in C_2H_5OH (D) Zn in alcohol.

Ans.(C)

Solution:

Alcoholic KOH brings about dehydrohalogenation

Illustration 37:

Acetylene when treated with dilute HCl at 60°C (333 K) in presence of $HgCl_2$ produces -

(A) Methyl chloride (B) Vinyl chloride (C) Acetaldehyde (D) Formaldehyde

Ans.(B)

Solution:

$$H–C \equiv C – H + HCl \xrightarrow[60°]{HgCl_2} \underset{\text{Vinyl chloride}}{CH_2 = CH – Cl}$$

Illustration 38:

When propyne is treated with aqueous H_2SO_4 in the presence of $HgSO_4$ the major product is -

(A) Acetaldehyde (B) Propanal (C) 2-Propanol (D) Propanone

Ans.(D)

Solution:

$$CH_3 – C \equiv CH + H_2O \longrightarrow CH_3 — \underset{\underset{OH}{|}}{C} = CH_2 \rightleftharpoons CH_3 — \underset{\underset{O}{\|}}{C} — CH_3$$

Illustration 39:

Alkaline $KMnO_4$, oxidizes acetylene to -

(A) Acetic acid (B) Glyoxal (C) Oxalic acid (D) Ethylene glycol

Ans.(C)

Solution:

$$H - C \equiv C - H + 4[O] \longrightarrow \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

Illustration 40:

Which of the following is most acidic -

(A) Ethyne (B) Propyne (C) 1-Butyne (D) 2-Butyne

Ans.(A)

Solution:

Because ethyne gives most stable anion.

Illustration 41:

Ozonolysis of acetylene gives -

(A) Oxalic acid (B) Ethylene glycol (C) Glyoxal (D) CH_3CHO

Ans.(C)

Solution:

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

Glyoxal

Illustration 42:

Propyne on reaction with aqueous chlorine gives -

(A) 1,1,2,2–Tetrachloropropane (B) 1,2–Dichloropropene

(C) 1,1–Dichloropropanone (D) 2,2–Dichloropropanone

Ans.(C)

Solution:

$$CH_3{-}C \equiv CH + 2HOCl \rightarrow \left[CH_3 - \underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{C}} - CHCl_2 \right] \xrightarrow{-H_2O} CH_3 - \overset{\overset{O}{\|}}{C} - CHCl_2$$

Illustration 43:

Mesitylene can be obtained by polymerization of -

(A) Ethyne (B) Ethene (C) Propene (D) Propyne

Ans.(D)

Solution:

Propyne on trimerization yields mesitylene

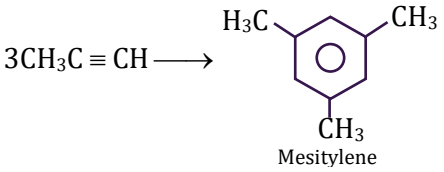


Illustration 44:

Excess of CH_3COOH is reacted with $CH \equiv CH$ in presence of $Hg^{2\oplus}$, the product is -

(A) $CH_3CH(OOCCH_3)_2$ (B) $CH_2 = CH(OOCCH_3)$

(C) $(CH_3COO)CH_2—CH_2(OOCCH_3)$ (D) None of these

Ans.(A)

Solution:

$H–C \equiv C–H + 2CH_3COOH \longrightarrow CH_3 – CH(OCOCH_3)_2$

Both the protons go to same carbon atom

Illustration 45:

A compound is treated with $NaNH_2$ to give sodium salt. Identify the compound -

(A) C_2H_2 (B) C_6H_6 (C) C_2H_6 (D) C_2H_4

Ans.(A)

Solution:

Ethyne is acidic in character

$$H–C \equiv C–H + NaNH_2 \longrightarrow H – C \equiv C^{\ominus}Na^{\oplus} + \frac{1}{2} H_2$$

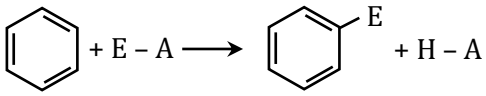
ELECTROPHILIC AROMATIC SUBSTITUTION REACTION

Introduction:

Aromatic hydrocarbons are known generally as arenes. An aryl group is one derived from an arene by removal of a hydrogen atom and its symbol is Ar—. Thus, arenes are designated ArH just as alkanes are designated RH.

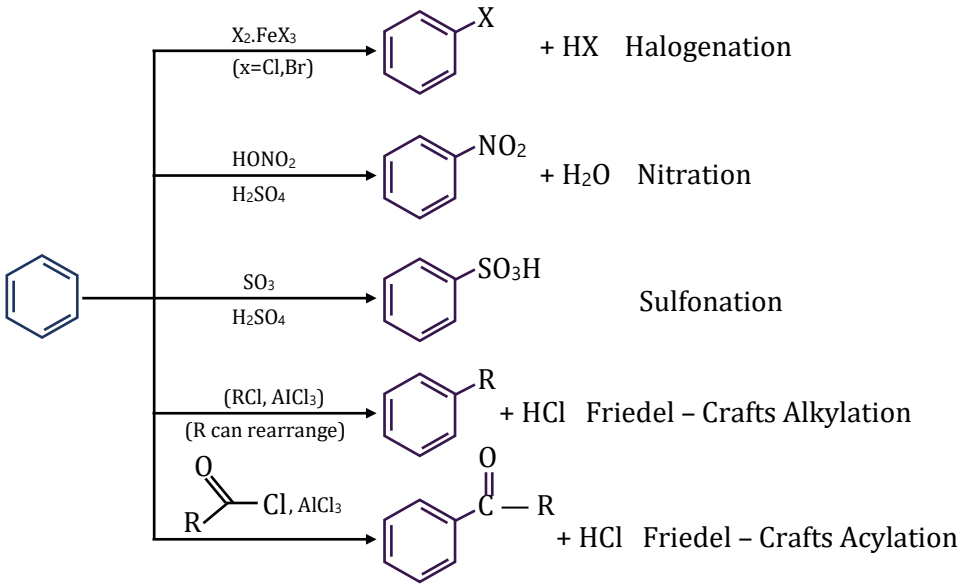
The most characteristic reactions of benzenoid arenes are the substitution reactions that occur when they react with electrophilic reagents. These reactions are of the general type shown below.

$$Ar – H + E – A \longrightarrow Ar – E + H – A$$



The electrophiles are either a positive ion ($E^{\oplus}$) or some other electron- deficient species with a large partial positive charge. For example, benzene can be brominated when it reacts with bromine in the presence of $FeBr_3$. Bromine and $FeBr_3$ react to produce positive bromine ions, $Br^{\oplus}$. These positive bromine ions act as electrophiles and attack the benzene ring, replacing one of the hydrogen atoms in a reaction that is called an electrophilic aromatic substitution (EAS).

Electrophilic aromatic substitutions allow the direct introduction of a wide variety of groups into an aromatic ring, and because of this they provide synthetic routes to many important compounds. The five electrophilic aromatic substitutions that we shall study in this chapter are outlined in figure .



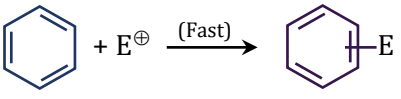
Electrophilic Aromatic Substitution Reactions

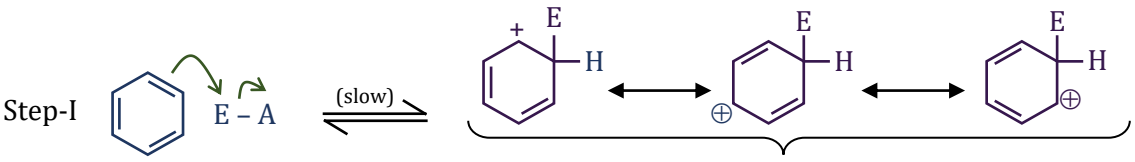
(1) A General Mechanism for electrophilic Aromatic substitution :

Benzene is susceptible to electrophilic attack primarily because of its exposed π-electrons. In this respect benzene resembles an alkene, for in the reaction of an alkene with an electrophilic the site of attack is the exposed π bond.

We saw in however, that benzene differs from an alkene in a very significant way. Benzene's closed shell of six π electrons gives it a special stability. So, although benzene is susceptible to electrophilic attack, it undergoes substitution reactions rather than addition reactions. Substitution reactions allow the aromatic sextet of π electrons to be regenerated after attack by the electrophile was occurred. We can see how this happens of we examine a general mechanism for electrophilic aromatic substitution.

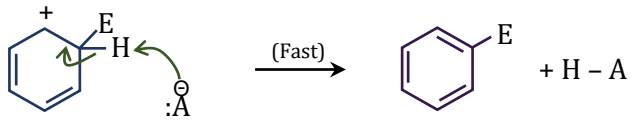
Once the electrophilic, $E^{\oplus}$ is generated in the reaction, it enters into some kind of a weak interaction with the π cloud of benzene ring leading to the formation of a π - complex. This π - complex is a donor-acceptor type of a complex, benzene being the donor and electrophile, the acceptor. These adducts are known as charge transfer complexes. In the complex that benzene forms with bromine, it has been shown that the halogen molecule is located centrally and at right angles to the plane of the benzene ring.





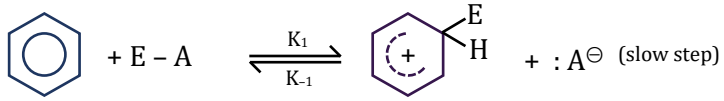
In step 1 the electrophile takes two electrons of the six- electron π system to form a σ bond to one carbon atom of the benzene ring. Formation of this bond interrupts the cyclic system of π - electrons, because in the formation of the arenium ion the carbon that forms a bond to the electrophile becomes sp^3 hybridized and therefore, no longer has an available p-orbital. Now only five carbon atoms of the ring are still sp^2 hybridized and still have p-orbitals. A calculated electrostatic potential map for the arenium ion formed by electrophilic addition of bromine to benzene indicates that positive charge is distributed in the arenium ion ring (figure) just as was shown in the contributing resonance structures.

In step 2 a proton is removed from the carbon atom of the arenium ion that bears the electrophile. The two electrons that bonded this proton to carbon becomes a part of the π system. The carbon atom that bears the electrophile becomes sp^2 hybridized again and a benzene derivative with six fully delocalized π electrons is formed. We can represent step 2 with any one of the resonance structures for the arenium ion.

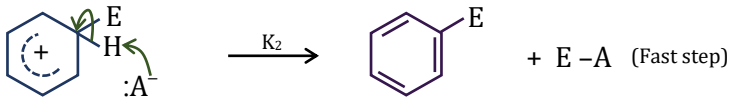
Step -II 

(The proton is removed by any of the bases present, for example, by the anion derived from the electrophile).

Kekule structure are more appropriate for writing mechanisms such as electrophilic aromatic substitution because they permit the use of resonance theory, it can be described however, using the modern formula for benzene in the following way.

Step- I 

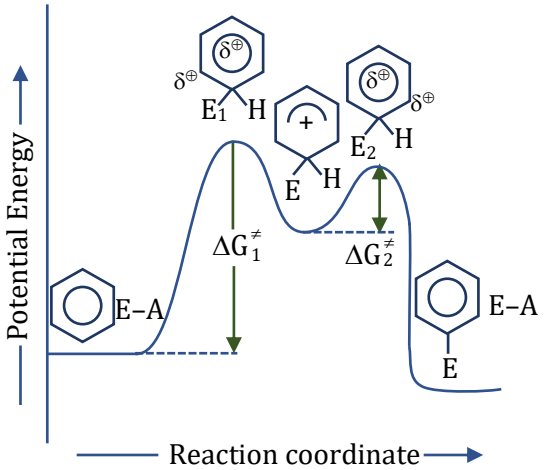
Arenium ion

Step-II 

Where k_1 and k_{-1} is the rate constant of the forward and backward reactions in step-I, k_2 is the rate constant of the step-II.

There is firm experimental evidence that the arenium ion is a true intermediate in electrophilic substitution reactions. It is not a transition state. This means that in a free energy diagram (figure shown below) the arenium ion lies in an energy valley between two transition states.

The free energy of activation, $\Delta G^{\neq}_{(1)}$, for the reaction leading from benzene and the electrophile, $E^{\oplus}$, to the arenium ion has been shown to be much greater than the free energy of activation, $\Delta G^{\neq}_{(2)}$, leading from the arenium ion to the final product. This is consistent with what we would expect. The reaction leading from benzene and an electrophile to the arenium ion is high endothermic, because the benzene ring loses its resonance energy. The reaction leading from the arenium ion to the substituted benzene, by contrast, is highly exothermic because in it the benzene ring regains its resonance energy.



Of the above two steps, step 1 the formation of the arenium ion – is usually the rate determining step in electrophilic aromatic substitution.

Step 2, the removal of a proton, occurs rapidly relative to step 1 and has no effect on the overall rate of reaction.

Isotope Effects :

The next question which comes up is how do we ascertain the presence of two discrete steps in the mechanism and also that the formation of σ - complex is the rate determining step. Answer to this question can be obtained from the study of kinetic isotope effect. If the rate of a reaction depends on a step which involves breaking of a C—H bond, then a kinetic isotope effect (K_H/K_D) of 6 to 7 is expected. Absence of any significant isotope effect in aromatic electrophilic substitution (except sulphonation) suggests that the proton is lost in the fast step, subsequent to rds. We see that the isotope effect study has provided two pieces of important information regarding the mechanism. Firstly, it has shown that the reaction takes place in two steps and secondly, that the first step is slower than the second step.

(2) Nitration :

Nitration reaction is generally carried out with a mixture of concentrated nitric acid and sulphuric acid.

The reagents which cause nitration are called nitrating agents.

The various nitrating agents which are commonly employed are :

(a) N_2O_5 in CCl_4 in the presence of P_2O_5 is used when anhydrous conditions are required.

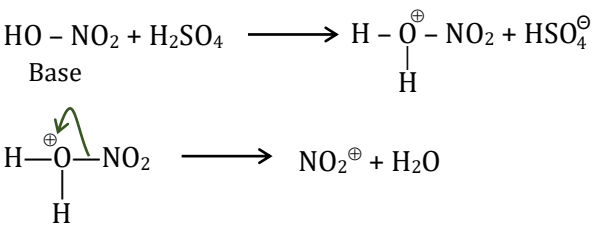
(b) Ethyl nitrate ($C_2H_5ONO_2$) is used to carry out nitration in alkaline medium.

(c) In the case of polycyclic hydrocarbons N_2O_4 and nitronium salts such as $NO_2^{\oplus}BF_4^{\ominus}$, $NO_2^{\oplus}PF_6^{\ominus}$, $NO_2^{\oplus}SO_3^{\ominus}$, can be used. The electrophile involved in nitration reaction is nitronium ion $\left(NO_2^{\oplus}\right)$.

Mechanism :

Generation of electrophile from nitrating agent.

(a) In a mixture of nitric acid and sulphuric acid, an acid base reaction takes place in which nitric acid acts as the base.



$$H_2O + H_2SO_4 \longrightarrow H_3O^{\oplus} + HSO_4^{\ominus}$$

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}$$

(b) N_2O_5 in CCl_4 when used, results in a spontaneous dissociation reaction.

$$N_2O_5 \rightleftharpoons NO_2^{\oplus} + NO_3^{\ominus}$$

(c) With concentrated HNO_3 alone

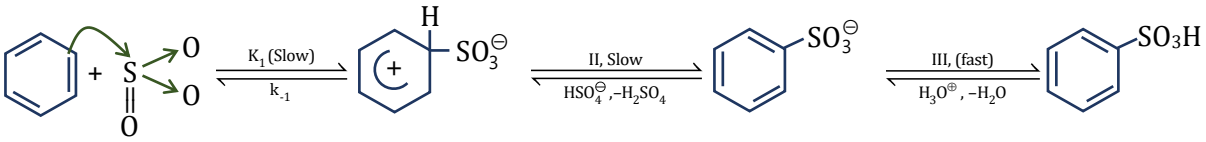
$$2HNO_3 \rightleftharpoons NO_2^{\oplus} + NO_3^{\ominus} + H_2O$$

The electrophile generated in this case is obtained by the behaviour of one nitric acid as the base and other molecule as the acid, but the equilibrium lies in the reactant side.

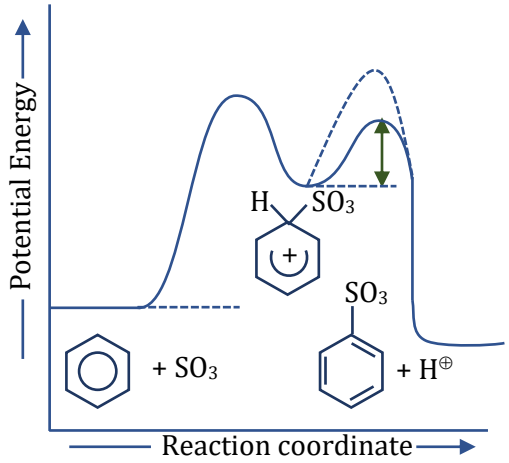
(3) Sulphonation :

Sulphonation is another synthetically important reaction. It is often accomplished with concentrated sulphuric acid or fuming sulphuric acid containing excess of SO_3 or chlorosulphonic acid, HSO_3Cl.

It is believed that the electrophile varies with the reagent, though in all cases SO_3, is involved either free or along with a carrier, like in H_2SO_4 ($SO_3 + H_3O^{\oplus}$) or $H_2S_2O_7$. Sulphur trioxide is generated from sulphuric acid as follows $2H_2SO_4 \rightleftharpoons HSO_4^- + H_3O^{\oplus} + SO_3$. The mechanism of sulphonation of benzene is given below :



Sulphonation is different from other aromatic electrophilic substitution reactions, Firstly, it is reversible and secondly, it shows some amount of isotope effect which is totally absent in other cases. Let us have a look at the potential energy diagram, Fig. of sulphonation reaction to understand these anomalies.



We see that once the σ - complexed benzenium intermediate is formed ; the energy barriers on either side of the intermediate are roughly of the same magnitude. This means that the intermediate can cross over to the product and can also come back to the reactant. This accounts for a reversible nature. Now, if we have the deuterated substrate, then the potential energy diagram gets slightly modified (dotted curve). The barrier to step II becomes higher as it now involves the cleavage of C—D bond. The barrier for step I, on the other hand, remains the same as it pertains to σ - complex formation. The rate of its reverting back to reactants is higher than its crossover to the product. Therefore, there is a net decrease in the overall rate of sulphonation for deuterated substrate-it shows a kinetic isotope effect. The loss of proton (Step II) is the slowest step (rds). The equilibrium in step III lies to the left as aryl sulphonic acids are strong acids.

In the case of other electrophilic substitutions, in contrast, energy barrier for the first step is much higher than that for the second step even for a deuterated substrate.

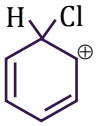
(4) Halogenation :

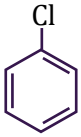
Halogenation of an aromatic ring is a synthetically important reaction. It takes place in the presence of varied reaction condition depending on the reactivity of the aromatic ring. For very reactive aromatic compounds in polar solvents, the molecular halogens themselves may acts as electrophiles. In the case of nonpolar solvents, halogenation is catalysed by a Lewis acid like $AlCl_3$, or $FeCl_3$, Reactivity of halogens has the following order,

$$I_2 < Br_2 < Cl_2$$

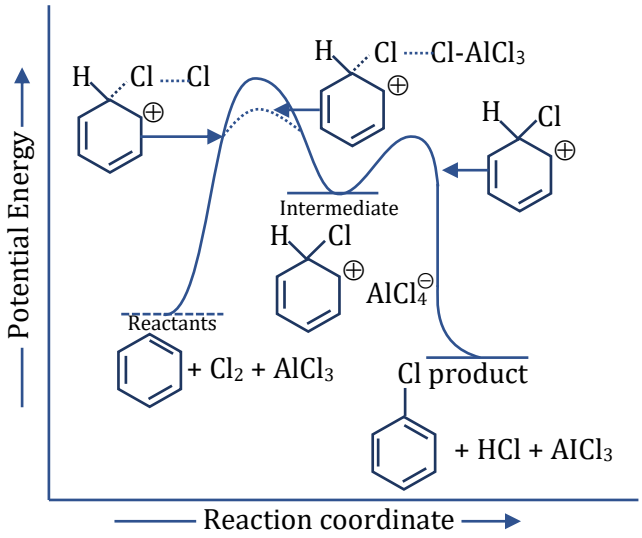
Let us take chlorination as a representative reaction to understand the mechanism of halogenation. Chlorine, in the presence of $AlCl_3$ or $FeCl_3$ forms a complex, Cl_2—$AlCl_3$. This complex can itself be the reactive electrophile or it may dissociate to give $Cl^{\oplus}$.

Step-I : $Cl-\ddot{Cl}: + AlCl_3$ (anhydrous) $\rightleftharpoons AlCl_3 \rightleftharpoons Cl-\overset{\oplus}{Cl}-\overset{\ominus}{AlCl_3}$

Step-II :  $+ Cl-\overset{\oplus}{Cl}-\overset{\ominus}{AlCl_3} \xrightarrow{slow}$  $+ \overset{\ominus}{AlCl_4}$

Step-III :  $+ \overset{\ominus}{AlCl_4} \xrightarrow{Fast}$  $+ AlCl_4 + HCl$

However, there is no significant evidence for the involvement of $Cl^{\oplus}$ as an electrophile and it is likely that the complex itself attacks the substrate. In the Cl_2—$AlCl_3$ complex, role of the Lewis acid is to polarize the halogen molecule and weaken the Cl—Cl bond. This lowers the activation energy for the formation of σ-complex.



Bromination follows a similar mechanism. As said above, Iodine is weakest of the three halogens and even in the presence of a Lewis acid, it can halogenate reactive aromatics only. Therefore, in most other cases iodine-monochloride is used in the presence of Lewis acid, $ZnCl_2$.

Halogenation may be effected by hypohalous acids, $\overset{\delta-}{HO}—\overset{\delta+}{X}$, also. This is markedly slower than with molecular halogens as $HO^{\ominus}$ is a poorer leaving group from $\overset{\delta-}{HO}—\overset{\delta+}{X}$, than, $X^{\ominus}$ is from $\overset{\delta+}{X}—\overset{\delta-}{X}$. The reaction is speeded in the presence of X^-, however, as HO—X is then converted into the more reactive X_2,

e.g. : $^{\ominus}OCl + Cl^{\ominus} + 2H^{\oplus} \longrightarrow Cl_2 + H_2O$

In the presence of strong acid, however, HO—X becomes a very powerful halogenating agent due to the formation of a highly polarized complex :

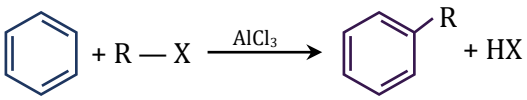
$$H\ddot{O}—X + H^{\oplus} \longrightarrow H_2\overset{\oplus}{O}—X \longrightarrow H_2O + X^{\oplus}$$

The evidence is that this species is the effective electrophile under these conditions and does not support the further conversion of complex into $X^{\oplus}$, i.e. unlike the case with $H_2O^{\oplus}$ —NO_2. F_2 reacts vigorously with benzene, but C—C bond breaking occurs and the reaction is of no preparative significance.

(5) Fridel-Crafts Alkylation :

Alkyl halides react with benzene in presence of aluminium chloride to yield alkyl benzenes. Alkylation of benzene with alkyl halides in the presence of aluminium chloride was discovered by Charles Friedel and James. M. Crafts in 1877.

A general equation for a friedel-Crafts alkylation reaction is the following

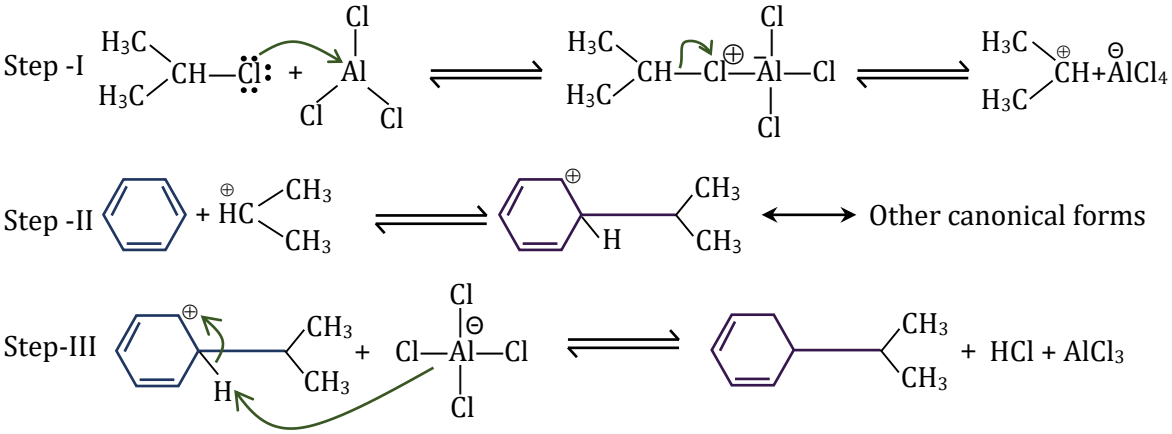


Alkyl halides by themselves are insufficiently electrophilic to react with benzene. $AlCl_3$ serves as a Lewis acid catalyst to enhance the electrophilicity of the alkylating agent. The mechanism for the reaction

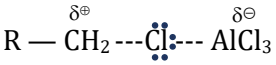
(shown in the following steps, with isopropyl chloride as R—X) starts with the formation of carbocation

(step I). The carbocation then acts as an electrophile (step II) and attacks the benzene ring to form an arenium ion. The arenium ion (Step III) then loses a proton to generate isopropyl benzene. Some times carbocation rearrange to a more stable carbocation.

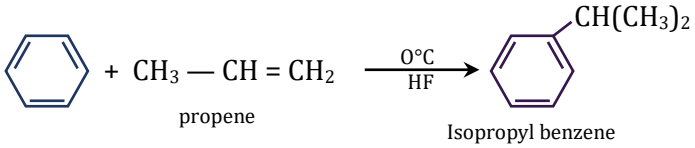
Mechanism for the Reaction:



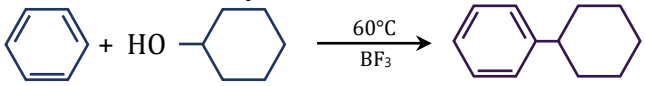
With R–X is a primary halide, a simple carbocation probably does not form. Instead, the $AlCl_3$ forms a complex with the alkyl halide and this complex acts as the electrophile. In the complex the carbon halogen bond is nearly broken and one in which the carbon atom has a considerable +ve charge.



These complexes are so carbocation like that they also undergo typical carbocation rearrangements. Friedel-Crafts alkylations are not restricted to the use of alkyl halides and $AlCl_3$. Many other pairs of reagents that form carbocations (or carbocation like species) may be used as well. These possibilities include the use of a mixture of an alkene and an acid.



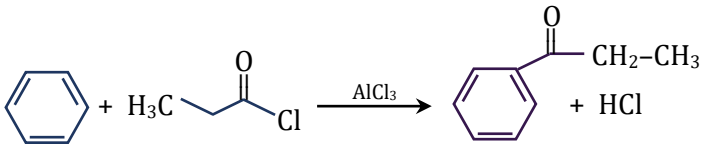
A mixture of an alcohol and an acid may also be used.



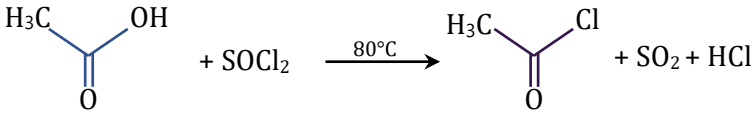
(6) Friedel-crafts Acylation :

The group is called an acyl group and a reaction whereby an acyl group is introduced into a compound is called an acylation reaction.

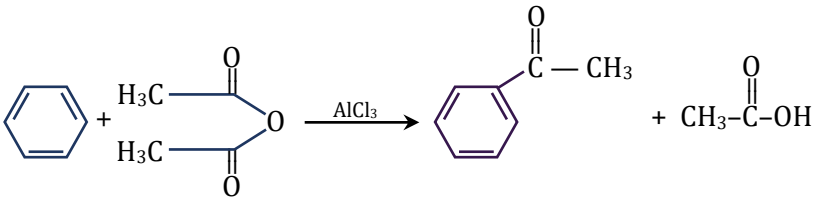
The Friedel-Crafts acylation reaction is an effective means of introducing an acyl group into an aromatic ring. The reaction is often carried out by treating the aromatic compound with an acyl halide.



Acyl chlorides (also called acid chlorides) are early prepared by treating carboxylic acids with thionyl chloride ($SOCl_2$) or phosphorous pentachloride (PCl_5).



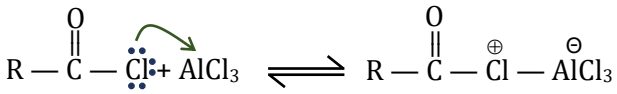
Friedel-Crafts acylations can also be carried out using carboxylic acid anhydrides. eg.



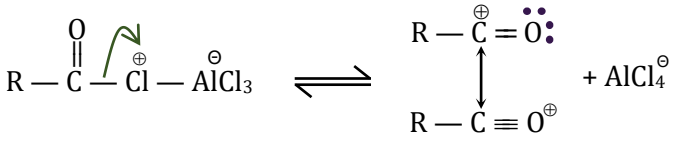
Mechanism of the Reaction :

In most Friedel-Crafts acylation reactions the electrophile appears to be an acylium ion formed from an acyl halide in the following way.

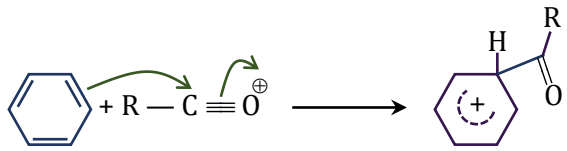
Step-I



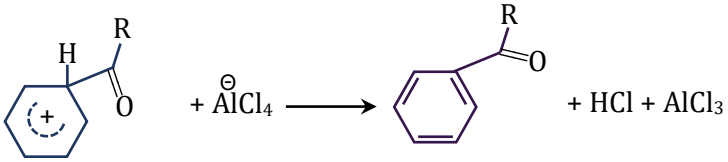
Step-II



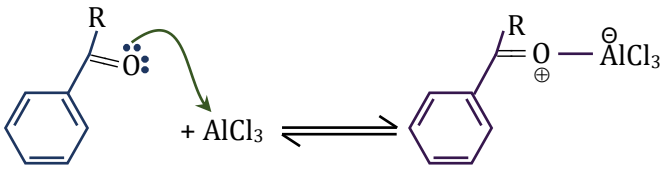
Step-III



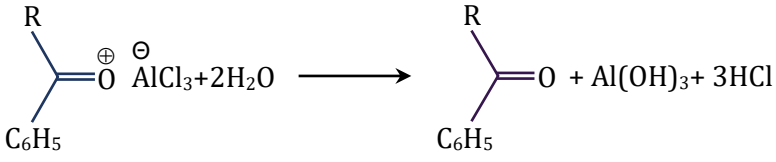
Step-IV



Step-V



In the last step, $AlCl_3$ (a Lewis acid) forms a complex with the ketone (a Lewis base). After the reaction is over, treating the complex with water liberates the ketone.

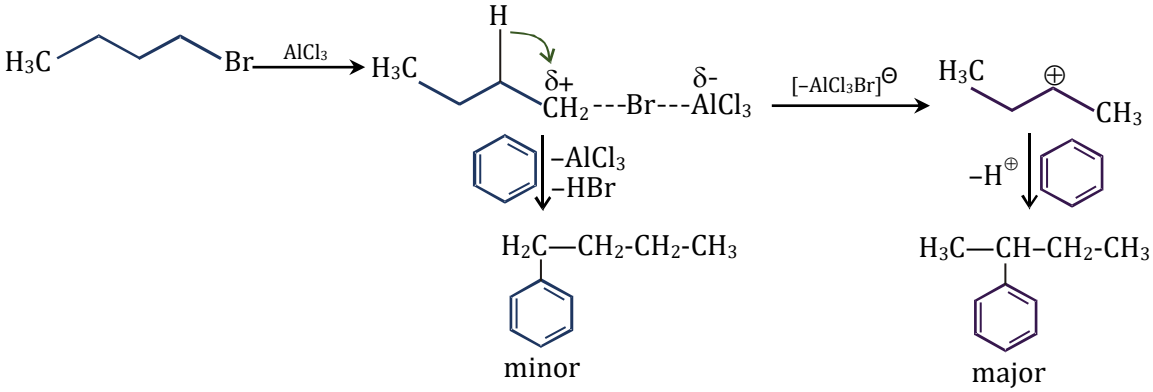


Limitations of Friedel - Crafts Reactions :

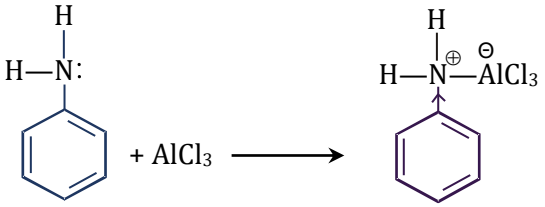
Several restrictions limit the usefulness of Friedel- Crafts reactions.

(a) When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation, it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation.

When benzene is alkylated with butyl bromide, for example, some of the developing butyl cations rearrange by a hydride shift-some developing 1° carbocations (see following reactions) become more stable 2° carbocations. The benzene reacts with both kinds of carbocations to form both butylbenzene and sec-butylbenzene.

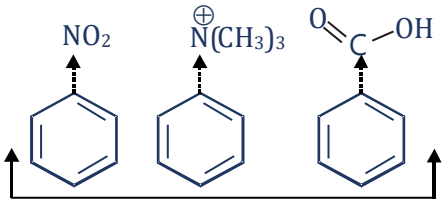


(b) An aromatic ring less reactive than that of halobenzene don't undergo Friedel Craft's reaction. Aromatic ring containing - NH_2, –NHR, $–NR_2$, groups does not undergo Friedel craft's alkylation due to formation of anilinium complex which is meta directing and has more electron withdrawing power than halogen in benzene ring.



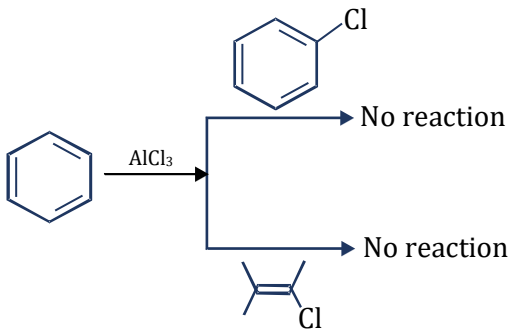
Meta directing group
and does not go
Friedal Craft's reaction

(c) Friedel-Crafts reactions do not occur when powerful electron-withdrawing groups are present on the aromatic ring or when the ring bears an $–NH_2$, –NHR or $–NR_2$ group. This applies to both alkylation and acylation.

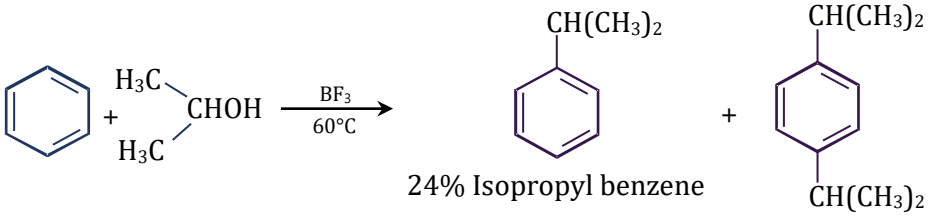


These do not undergo Friedel -Crafts reactions

(d) Aryl and vinylic halides cannot be used as the halide component because they do not form carbocations readily.



(e) Polyalkylations often occur - Alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activates the ring towards further substitution.



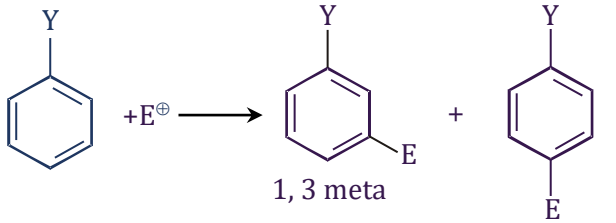
24% Isopropyl benzene

14% Di–isopropylbenzene

Polyacylation are not a problem in Friedel-Crafts acylation however. The acyl group (RCO–) by itself is an electron-withdrawing group, and when it forms a complex with $AlCl_3$ in the last step of the reaction, it is made even more electron withdrawing. This strongly inhibits further substitution and makes monoacylation easy.

(7) Orientation and reactivity in electrophilic aromatic substitution :

In the case of benzene we get just one monosubstituted product in electrophlic aromatic substitution as all the positions are equivalent. However, for substitution in a compound which already has a group attached to the ring, three disubstituted products, (1, 2), (1, 3) (1, 4) commonly called ortho, meta and para meaning next to, between and opposite respectively are possible. These are abbreviated as o, m and P.



1, 3 meta

1, 4 Para

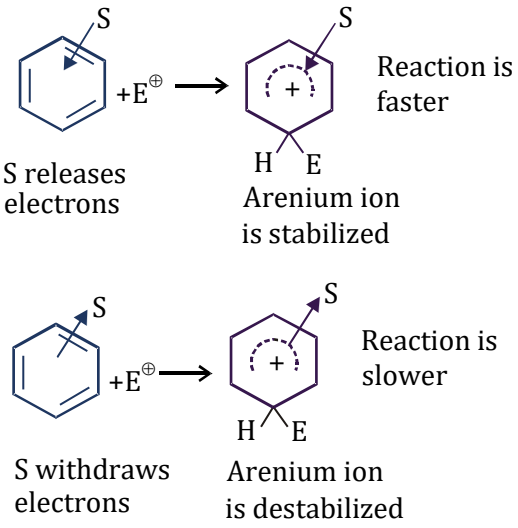
Reactivity :

We have now seen that certain groups activate the benzene ring toward electrophilic substitutions, while other groups deactivate the ring. We mean that an aromatic compound with an activating group reacts faster in electrophilic substitutions than benzene. When we say that a group deactivates the ring, we mean that an aromatic compound with a deactivating group reacts slower than benzene.

We have also seen that we can account for relative reaction rates by examining the transition state for the rate-determining steps. Any factor that increases the energy of the transition state relative to that of the reactants decreases the relative rate of the reaction. It does this because it increases the free energy of activation of the reaction. In the same way, any factor that decreases the energy of the transition state relative to that of activation and increases the relative rate of the reaction.

The rate-determining step in electrophilic substitutions of substituted benzene compounds is the step that results in the formation of arenium ion. We can write the formula for a substituted benzene in a generalized way if we use the letter S to represent any ring substituent including hydrogen, (if S is hydrogen, the compound is benzene). We can also write the structure for the arenium ion in the way shown here. By this formula we mean that S can be in any position -ortho, meta or para - relative to the electrophile, E. Using these conventions, we can write the rate-determining step for electrophilic aromatic substitution in the following way.

When we examine this step for a large number of reactions, we find that the relative rates of the reactions depend on whether S withdraws or release electrons. If S is an electron-releasing group (relative to hydrogen), the reaction occurs faster than the corresponding reaction of benzene. If S is an electron withdrawing group, the reaction occurs slower than that of beznene.



It appears, that the substituent (S) must affect stability of the transition state relative to that of the reactants. Electron-releasing groups apparently make the transition state more stable, while electron withdrawing groups make it less stable. that is entirely reasonable, because the transition state resembles the arenium ion, and the arenium ion is a delocalized carbocation.

The effects of substituents on the reactivity of a benzene ring toward electrophilic substitution:

Strong activating groups : —NH_2, —NHR, —NR_2, —OH, —OR

Moderately activating groups : —NHC(=O)R — OC(=O)R

Weakly activating groups :—R, —Ar, —$CH=CR_2$

Weakly deactivating groups :—F, —Cl, —Br, —I

] Ortho/para directing

Moderately deactivating groups : —CHO, —COR, —COOR, —COOH, —COCl

Strong deactivating groups : —C≡N, —SO_3H, — $\overset{\oplus}{N}H_3$, — $\overset{\oplus}{N}H_2R$, — $\overset{\oplus}{N}HR_2$, — $\overset{\oplus}{N}R_3$, —NO_2

Meta directing

(8) Heterocyclic aromatic compound :

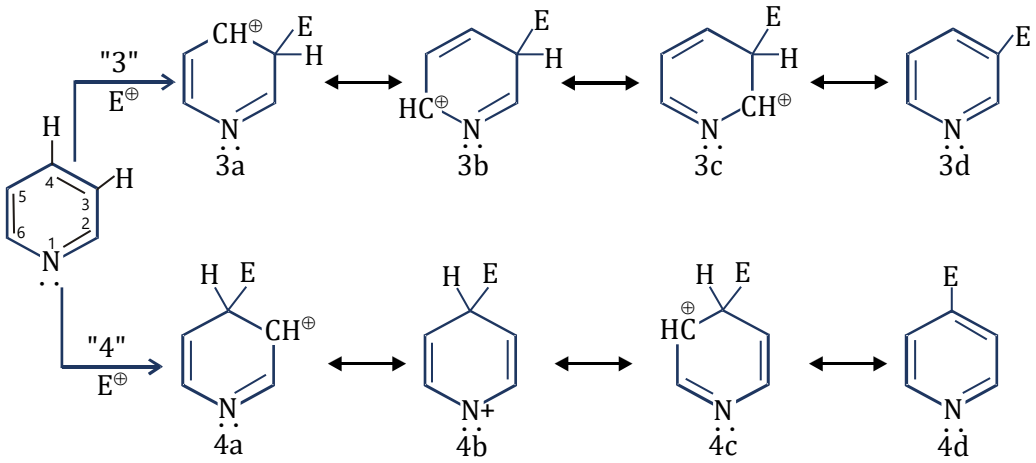
This is a class of compounds with aromatic properties, in which one or more of the ring carbons has been replaced by a heteroatom (an atom other than carbon) such as nitrogen, oxygen or sulphur. Some of these compounds preserve the six-membered ring and are therefore called benzenoid aromatic. In other, the (4n +2) π-electron reside in a five- membered ring, so these are called non-benzenoid. A key difference between these two classes of aromatic compounds is that in non-benzenoid heteroaromatic compounds a formally non-bonding pair of electrons on the heteroatom becomes part of the (4n +2) π-electron of the aromatic π-system, whereas in benzenoid aromatic compounds, the non-bonding pairs on heteroatoms are normally separated from the aromatic system. Here are a few examples :

Benzenoid heteroaromatic compounds: Pyridine, Quinoline, Pyrimidine

Benzenoid heteroaromatic compounds: Pyrrole, Furan, Thiophene

Electrophilic Substitution in Pyridine :

In pyridine the attack may takes place at "3" or "4" position in general.

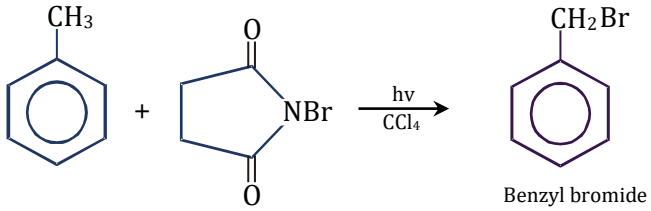


At first glance the two sets of resonance structures look quite similar. But notice how in 4b (one of the resonance structures of the intermediate that results from attack at the 4th position) the valence of nitrogen is left unfilled, an unfavourable situation not encountered in the intermediate formed by attack at the 3rd position. Again, it is the electronegativity of the nitrogen that reduces the reactivity of pyridine (relative to benzene) toward electrophiles.

(9) Reactions of Alkyl Benzenes :

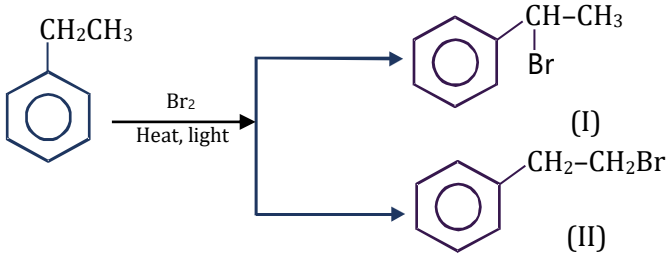
Halogenation of the side chain :

The side chain halogenation of alkyl benzenes takes place in the presence of light or high temperatures. Side chain halogenation is mostly carried out by using the reagent N-bromosuccinamide (NBS) in the presence of light.

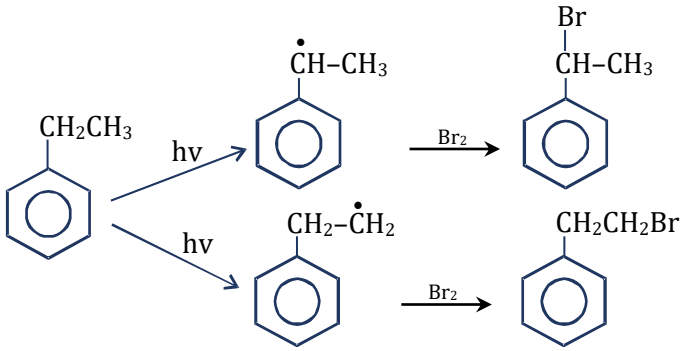


Benzyl bromide

An alkyl benzene with side chain other than methyl may lead to the formation of more than one products



Product (I) is the only product obtained, and formation of such product can be attributed to mechanism governing this reaction. Side chain halogenation has a similar mechanism as that of alkanes. It involves the formation of free radical intermediates. Now if we observe the free radicals formed by attack of bromine free radical on ethyl benzene, we will find that product (I) involves formation of benzyl free radical and (II) involves formation of primary free radical.



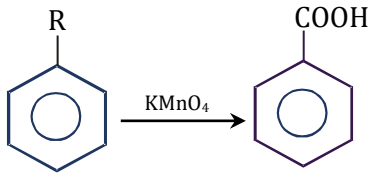
The benzyl free radical is more stable than primary free radical because its bond dissociation energy is 19 kcal/mole less than that of primary free radical.

Order of stability of free-radials.

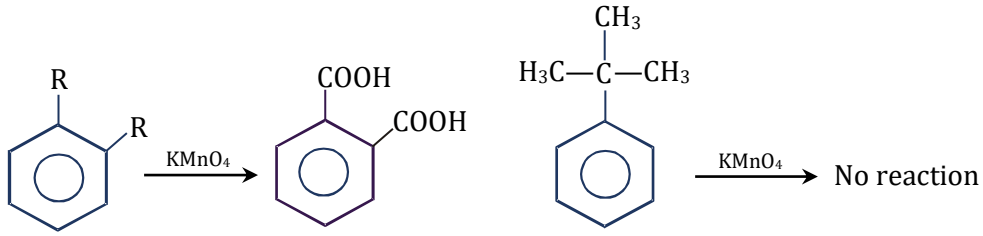
Benzyl > allyl > 3° > 2° > 1° >CH_3 vinyl (from bond dissociation energy data)

Oxidation of side chain :

Although benzene itself is not susceptible to oxidation but side chain attached to the benzene ring undergoes oxidation and converts itself into a —COOH group. Oxidation of side chain takes place after substance is heated for a long time with $KMnO_4$.



The above reaction can be used for identifying substitution pattern in aromatic compound. If any compound gives pthalic acid on heating with $KMnO_4$, then we can infer that it is ortho disubstituted benzene.



There is no reaction because of the absence of a benzylic hydrogen.

Illustration 46:

Which of the following is not correctly matched :

(A) Hydrolysis of phenyl magnesium iodide – benzene

(B) γ–Isomer of BHC – lindane

(C) $(2n + 4)\pi$ Rule – aromaticity

(D) Trimerisation of propyne – mesitylene

Ans.(C)

Solution:

The Huckel rule to account for aromaticity is closed ring of $(4n + 2)\pi$ electrons.

Illustration 47:

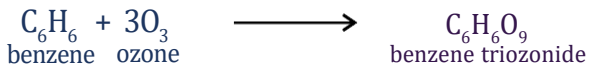
Ozonolysis of benzene in vigorous condition yields :

(A) Glyoxal (B) Glycerine (C) Glycol (D) Glycerol

Ans.(A)

Solution:

Ozonolysis of benzene yields glyoxal. Benzene adds three molecules of ozone and forms benzene triozonide which on decomposition with water gives three molecules of glyoxal.



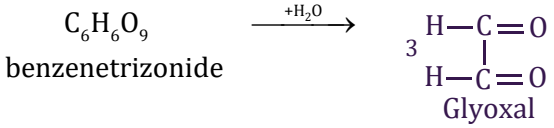


Illustration 48:

Benzene undergoes substitution reaction more easily than addition because :

(A) It has cyclic structure (B) It has three double bonds

(C) It has six hydrogen atoms (D) Of resonance

Ans.(D)

Solution:

If there were no resonance in benzene, π electrons would have not been delocalised and hence easily available to undergo addition reactions as in ethylene. Further the substituted benzene is stable due to resonance.

Illustration 49:

Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give predominantly :

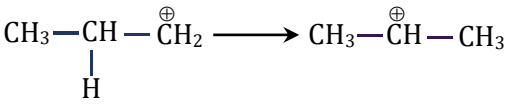
(A) n–Propylbenzene (B) Isopropylbenzene

(C) 3–Propyl–1–chlorobenzene (D) No reaction

Ans.(B)

Solution:

Propyl carbonium ion, $CH_3CH_2\overset{\oplus}{C}H_2$ is primary carbonium ion, it rearranges to the more stable secondary carbonium ion $CH_3\overset{\oplus}{C}HCH_3$, which then reacts to form isopropylbenzene.



Propyl carbonium ion(1°) Iso Propyl carbonium ion(2°)

Illustration 50:

Which of the following reactions of benzene does not account for the three 'C = C' bonds in the molecule–

(a) Benzene + $Br_2 \xrightarrow[\text{conc. } H_2SO_4]{FeBr_3}$ bromobenzene + HBr

(b) Benzene + $HNO_3 \longrightarrow$ nitrobenzene + H_2O

(c) Benzene + $3O_3 \longrightarrow$ Triozonide

(d) Benzne + $3H_2 \xrightarrow{Ni}$ cyclohexane

(A) a, c (B) b, d (C) b, c, d (D) a, b

Ans.(D)

Solution:

a and b are the electrophilic substitution reactions and do not account for the C = C bond reaction.

Illustration 51:

In which of the following reaction t–butylbenzene is formed :

(A) Benzene + t–butyl chloride $\xrightarrow{AlCl_3}$ (B) Benzene + $(CH_3)_2C = CH_2$ $\xrightarrow{BF_3.HF}$

(C) Benzene + t–butyl alcohol $\xrightarrow{H_2SO_4}$ (D) All of these

Ans.(D)

Solution:

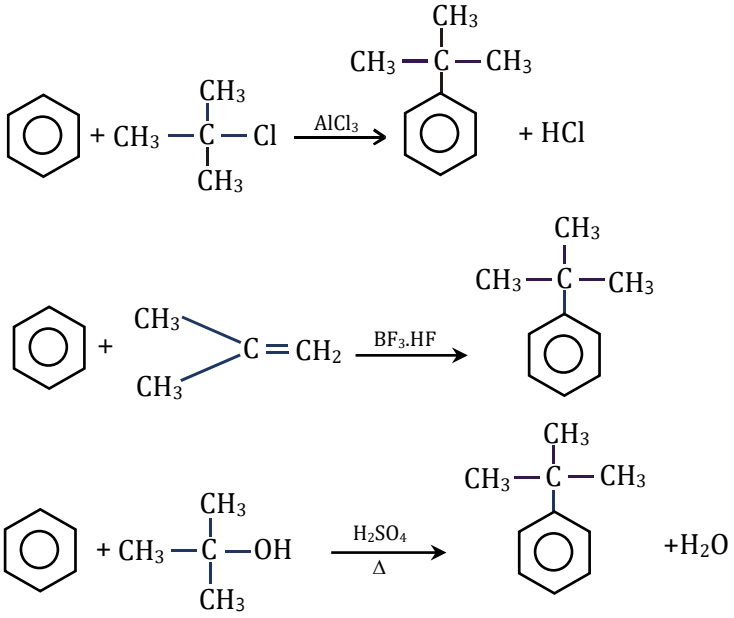


Illustration 52:

The order of reactivity of :

ϕ–CH_3 (I), ϕ–CH_2–CH_3 (II), ϕ–$CH(CH_3)_2$ (III) and ϕ–$C(CH_3)_3$ (IV)

Where $\phi = C_6H_5$

(A) I > II > III > IV (B) IV > III > II > I (C) II > I > III > IV (D) III > II > I > IV

Ans.(A)

Solution:

More are the number of α–hydrogen present in the alkyl group attached to the benzene ring more pronounced will be the hyperconjugation and the benzene ring will be more electron rich and easily be attacked by an electrophile. α–hydrogen in $-CH_3$, $-CH_2-CH_3$, $-CH(CH_3)_2$ and $-C(CH_3)_3$ respectively are three, two, one and zero.

Illustration 53:

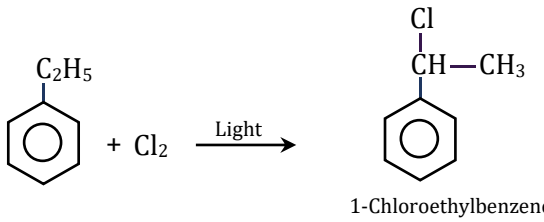
Ethylbenzene + Cl_2 $\xrightarrow{Light}$ (main) compound is :

(A) o– & p– Chloroethylbenzene (B) 1–Chloroethylbenzene

(C) 2–Chloroethylbenzene (D) m–Chloroethylbenzene

Ans.(B)

Solution:



1-Chloroethylbenzene

Illustration 54:

$\phi-CH_3 \xrightarrow[\Delta]{KMnO_4} A \xrightarrow[\Delta]{\text{Soda Lime}} B$

(Where $\phi = C_6H_5$)

Compound B is :

(A) Toluene (B) Benzene (C) Cresol (D) Benzaldehyde

Ans.(B)

Solution:

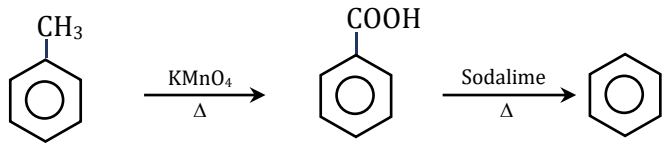


Illustration 55:

Formation of which of the following compound confirms the unsaturation character of benzene :

(A) Cyclohexane (B) Gammexane (C) Triozonide (D) All the above

Ans.(D)

Solution:

Formation of all the three compounds are the result of addition reaction. Hence confirm the unsaturation nature of benzene.

Illustration 56:

Toluene may be prepared by :

(A) Toluic acid (B) Cresol

(C) Toluene sulphonic acid (D) All the above

Ans.(D)

Solution:

Toluene may be prepared by all the above compounds described earlier.

Illustration 57:

Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives :

(A) o–Cresol (B) p–Cresol

(C) 2,4–Dihydroxy toluene (D) Benzoic acid

Ans.(D)

Solution: