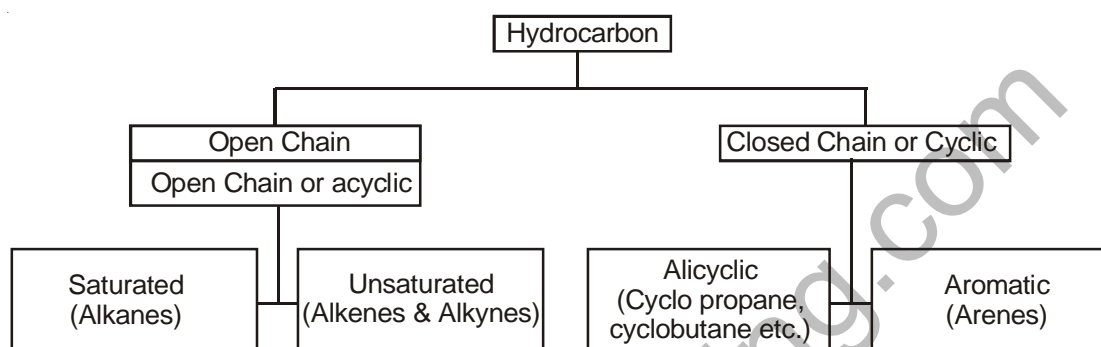


Hydrocarbons

1. HYDROCARBONS

- (i) Organic compound of Carbon and hydrogen only are called **hydrocarbons**.
- (ii) Petroleum and Coal are main source of hydrocarbon.
- (iii) Hydrocarbons are broadly classified as :



Alkanes and Arenes are quite stable compound and gives substitution reaction while alkenes & alkynes are more reactive and give addition reactions.

2. SATURATED HYDROCARBONS OR ALKANES OR PARAFFINS

- v General formula C_nH_{2n+2}
- v Alkanes are also known as **paraffins** due to their less reactive nature.
- v Type of formula : $R-H$, $R-CH_3$, $R(CH_2)_n-R$
- v All the carbon atoms in alkanes are in sp^3 hybridization state.
- v All the bond angles are tetrahedral angles i.e. $H-C-H$ or $H-C-C$ bond angle is $109^\circ 28'$ or 109.5° .
- v Alkanes contain $C-C$ and $C-H$ sigma bonds.

	$C-C (sp^3 - sp^3)$	$C-H (sp^3 - s)$
Bond Length	1.54 Å	1.112 Å
Bond energy	82.67 K Cal/mol	98.67 K Cal/mole

- v Isomerism : Alkanes shown chain and position isomerism.

Examples :

Methane, Ethane & Propane – No isomers.

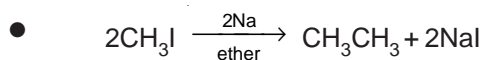
Alkanes with at least 4 carbon atoms show isomerism.

Butane	–	2 isomers
Pentane	–	3 isomers
Hexane	–	5 isomers
Heptane	–	9 isomers

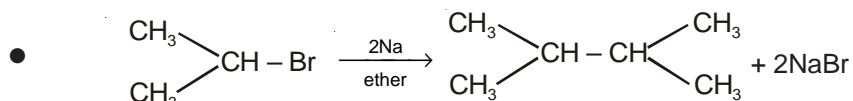
3. METHODS OF PREPARATION OF ALKANES

(a) By Wurtz Reaction

When a solution of an alkyl halide in ether solvent is treated with sodium metal two alkyl groups combine together. Yields of products are best for primary (~60%) halides and poorest for tertiary halides (~3%).



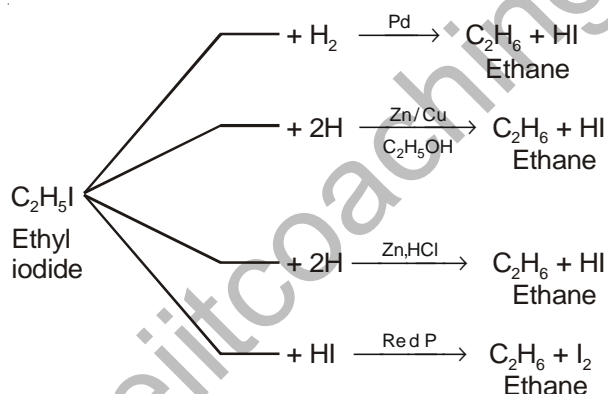
Ethyl iodide Ethane



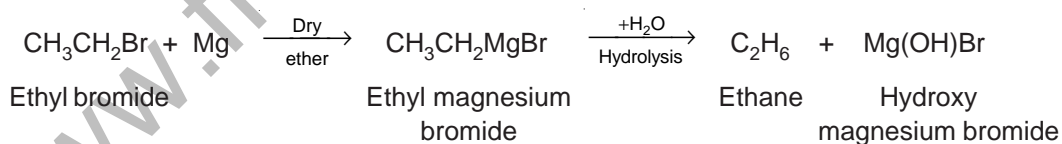
2-bromo propane 2-3- dimethyl butane

This method is suitable for the preparation of symmetrical alkanes. A mixture of products is obtained if two different alkyl halides are reacted. Methane cannot be prepared by this method.

(b) By Reduction of Halides

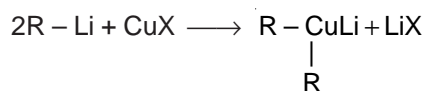
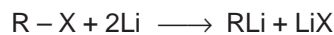


(c) From Alkyl Halides through Grignard Reagents

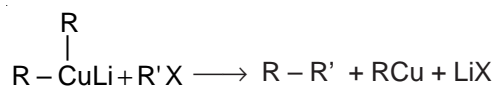


In these reactions, the alkyl group of alkyl magnesium halide gets converted into alkane.

(d) Corey-House Synthesis

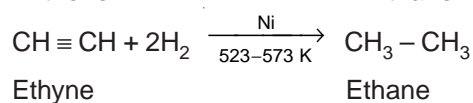
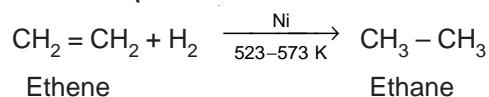
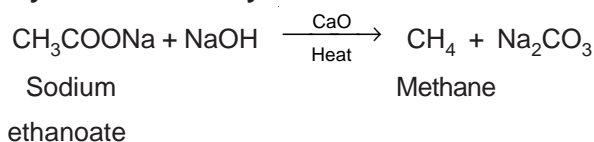


Lithium dialkyl copper



Alkane

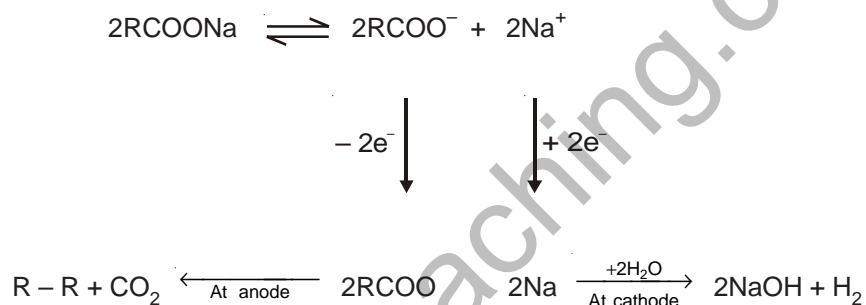
Unlike Wurtz reaction, this reactions can be employed to prepare unsymmetrical alkanes.

(e) From unsaturated hydrocarbons (*Sabatier and Senderen's reaction*)**(f) By Soda-Lime Decarboxylation of Carboxylic Acids**

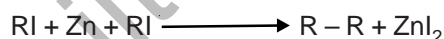
The alkane formed has one carbon less than the starting material.

(g) By Kolbe's Electrolysis

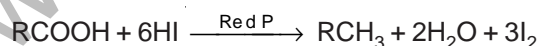
In this method concentrated aqueous solution of sodium or potassium salt of a carboxylic acid is electrolyzed using platinum electrodes.



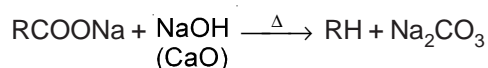
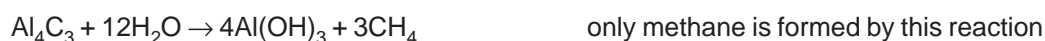
If n is the number of carbon atoms in the acid, the alkane formed has $2(n - 1)$ carbon atoms.

(h) Frankland Reaction**(i) Reduction of Aldehyde and Ketones :**

This is known as **Clemmenson's Reduction**

(j) From Carboxylic Acids :**(a) Reduction :****(b) Decarboxylation :**

It is obtained by heating sodium salts of acids with sodalime (NaOH & CaO).

**(k) From Aluminium Carbide :**

Ex.1 Which of the following reactions can be employed for getting unsymmetrical alkanes in good yield ?

- [1] Wurtz reaction [2] Corey–House reaction
[3] Both [4] None of these

Ans. [2]

Sol. Wurtz reaction is suitable for symmetrical alkanes

Ex.2 Sodium propionate on decarboxylation with sodalime gives

- [1] Propane [2] Ethane [3] Butane [4] Pentane

Ans. [2]

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

Ex.3 Which of the following alkanes cannot be produced by Kolbe electrolysis of sodium or potassium salts of carboxylic acids ?

- [1] Methane [2] Ethane [3] Butane [4] Hexane

Ans. [1]

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

4. PHYSICAL PROPERTIES OF ALKANES

(i) **Melting point and Boiling point**

They have low M.P. and B.P. Their B.P. increase with increase in number of carbons.

(ii) **Physical state**

Alkanes $C_1 - C_4 \rightarrow$ Gaseous state

$C_5 - C_{17} \rightarrow$ Liquid state

C_{18} & above \rightarrow solid like wax

(iii) Alkanes are colourless, odourless and tasteless.

(iv) Alkanes are lighter than water.

(v) These are insoluble in water and soluble in organic solvents.

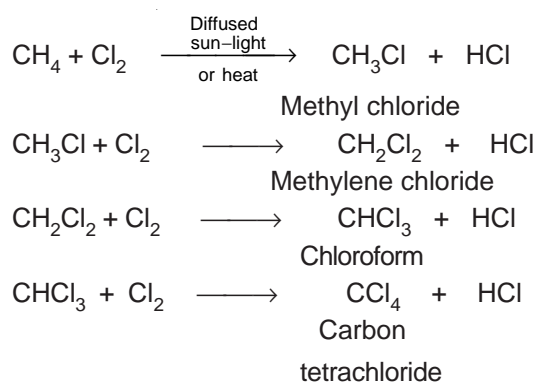
5. CHEMICAL PROPERTIES OF ALKANES

(i) **Alkanes** being saturated hydrocarbons do not have any of the reactive sites. Their molecules have all carbon-carbon or carbon-hydrogen single bonds. Thus, alkanes are the least reactive hydrocarbons and are called **paraffins**.

(ii) **Alkanes** react on strong heating or in presence of light.

(iii) **Alkanes** undergo only substitution type of reactions i.e. they undergo only free radical substitutions.

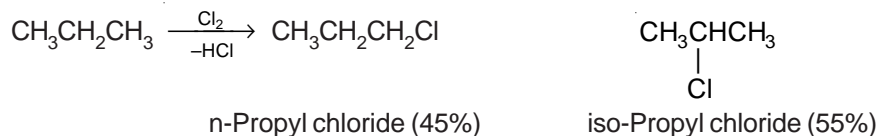
(a) **Halogenation of alkanes**



The reactivity of halogens towards alkanes varies as :

fluorine > chlorine > bromine > iodine.

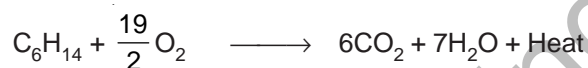
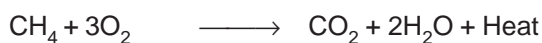
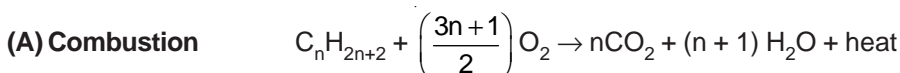
Higher alkanes on halogenation give different isomers of halogen derivatives.



It may be remembered that in general, the order of ease of replacement of hydrogens is

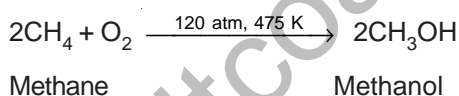
tertiary > secondary > primary.

(b) Oxidation

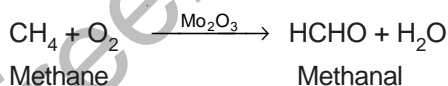


(B) Controlled oxidation

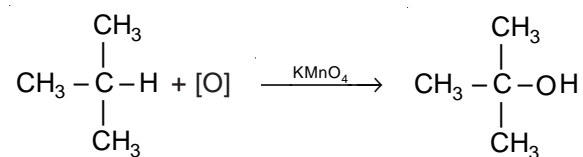
(i) On passing methane and oxygen in the ratio of 9 : 1 under pressure (≈ 120 atm.) through copper tube at 475 K, methane gets oxidized to methanol.



(ii) Methane gets oxidized to methanol on passing its mixture with oxygen over heated molybdenum oxide.



(iii) Alkanes containing tertiary hydrogen atom get converted to alcohol on reaction with KMnO_4 .



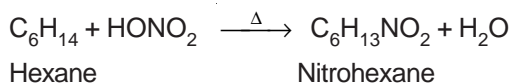
iso-Butane

tert-Butyl alcohol

(c) Nitration

In this reaction, a hydrogen atom of an alkane is replaced by nitro ($-\text{NO}_2$) group.

In liquid phase nitration, the alkane is heated for several hours with conc. HNO_3 under pressure. Consider the nitration of n-hexane,



6. USES OF ALKANES

- [1] Alkanes are used as fuels, e.g. various fractions obtained by fractional distillation of petroleum, such as L.P.G., calor gas, gasoline, diesel oil, kerosene oil, etc. are some important fuels.
- [2] Some alkanes are used for industrial preparation of methane, hydrogen etc.
- [3] Some alkanes are used for the manufacture of organic compounds like methyl chloride, methyl alcohol, methylene dichloride, alkenes, tetramethyllead, etc.
- [4] Carbon black obtained by decomposition of alkanes is very fine powder and is used in the preparation of printer's ink, black paint, black boot polish, carbon paper etc., and for blackening of types.

Ex-4 The homolytic fission of hydrocarbon results in the formation of -

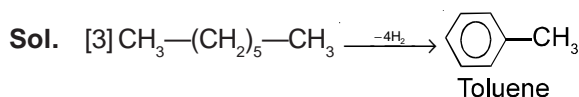
- [1] Free radicals [2] Carbocations [3] Carbanions [4] Carbenes.

Sol. [1] Homolytic fission results in the formation of free radicals.

Ans. [1]

Ex-5 n-Heptane when heated to a temperature of about 800 K under high pressure in the presence of $\text{Cr}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst gives -

- [1] 1-heptene [2] 2-Methylhexane [3] Toluene [4] Xylene.



Ans. [3]

Ex-6 The reaction conditions leading to the best yield of $\text{C}_2\text{H}_5\text{Cl}$ are -

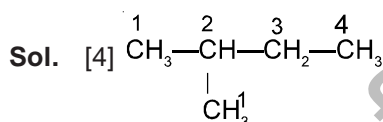
- [1] C_2H_6 (excess) + $\text{Cl}_2 \xrightarrow{\text{UV light}}$ [2] $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow[\text{room temperature}]{\text{Dark}}$
- [3] $\text{C}_2\text{H}_6 + \text{Cl}_2$ (excess) $\xrightarrow{\text{UV light}}$ [4] $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}$

Ans. [1]

Sol. [1] C_2H_6 should be used in excess, otherwise polychlorination will take place

Ex-7 Number of isomer which can be theoretically obtained on monochlorination of 2-methylbutane is -

- [1] 1 [2] 2 [3] 3 [4] 4 **Ans. [4]**



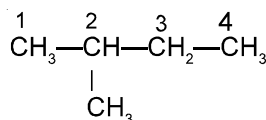
Ex-8 Complete oxidation of ethane yields -

- [1] Ethanol [2] Ethanoic acid [3] Ethanal [4] CO_2 and H_2O

Sol. [4] $2\text{C}_2\text{H}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$

Ans. [4]

Ex-9 In iso-pentane, the H atom that can be most easily substituted is on -



- [1] C—1 [2] C—2 [3] C—3 [4] C—4

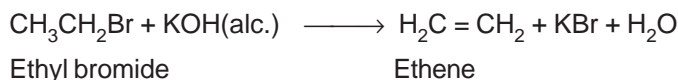
Sol. [2] Ease of substitution of various types of H atoms is $3^\circ > 2^\circ > 1^\circ$.

Ans. [2]

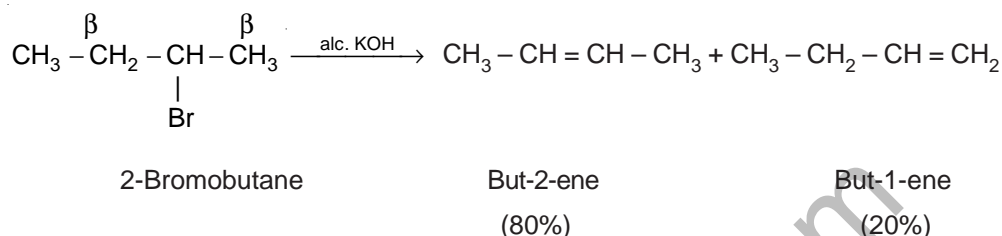
Alkenes are unsaturated hydrocarbons. The characteristic feature of alkenes is the presence of carbon-carbon double bond ($\text{C}=\text{C}$) in their molecules. Alkenes are also known as **olefins** derived from Greek word olefinic (means oil forming). It is because of the fact that lower members of this series form oily products when treated with chlorine.

7. METHODS OF PREPARATION OF ALKENES

(a) By Dehydrohalogenation of Alkyl Halides



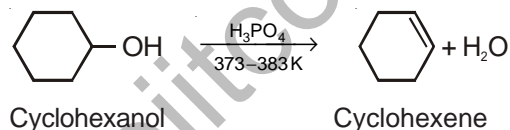
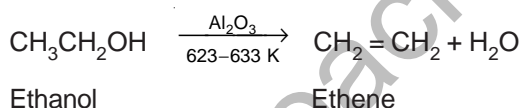
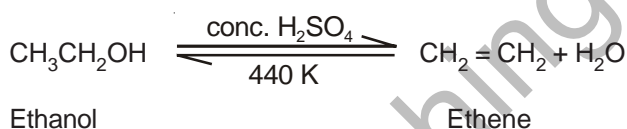
In case an alkyl halide can eliminate hydrogen halide in two different ways, the preferred alkene is the one which is maximum alkylated i.e., which carries more number of alkyl groups attached to the doubly bonded carbon atoms. This generalization is known as **Saytzeff Rule**. For example,



The reactivity of alkyl halides towards elimination reaction follows the order :

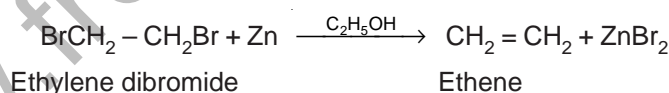
tertiary > secondary > primary

(b) By Dehydration of Alcohols



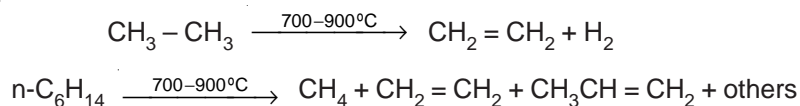
(c) By Dehalogenation :

Vicinal dihalides on treatment with zinc and alcohol give alkenes



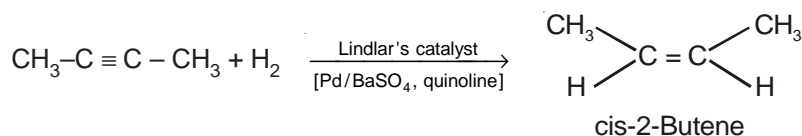
(d) By Cracking of Alkanes

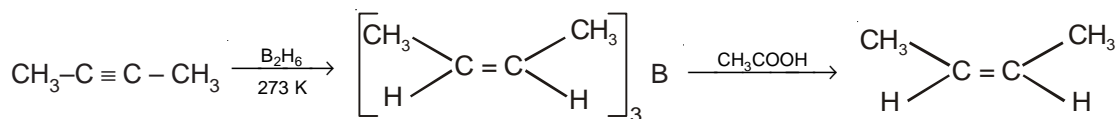
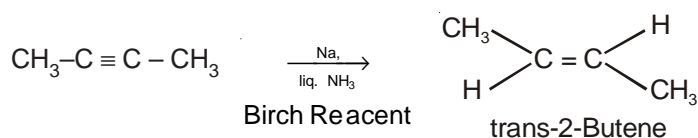
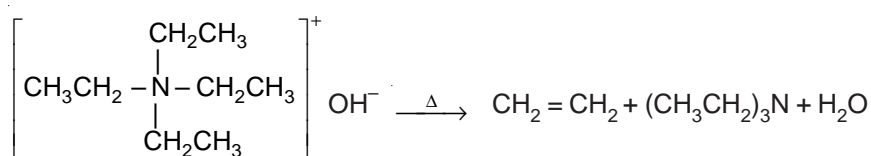
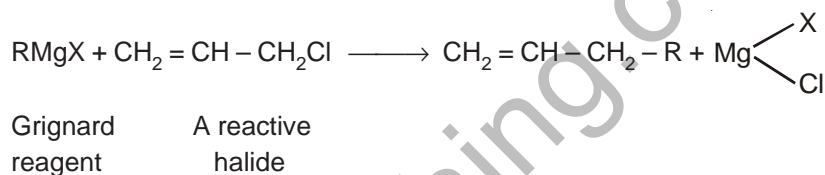
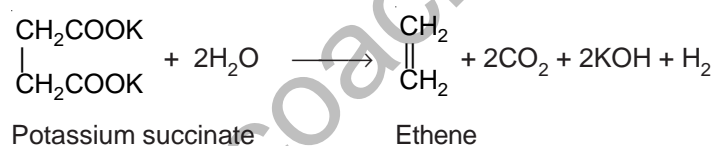
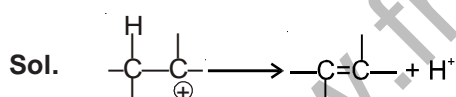
Alkenes are prepared on large scale by cracking of hydrocarbons.



Ethene and propene are used extensively for the production of polymers.

(e) From Alkynes : (By partial hydrogenation of C – C triple bond)



**(f) By Decomposition of Quaternary Ammonium Hydroxides****(g) By use of Organometallic Compounds and Reactive Halides****(viii) By Kolbe Electrolysis of Potassium Succinate****Ex.10** An alkene is formed from a carbocation by[1] Elimination of a H^+ ion[2] Elimination of H^- ion[3] Addition of a H^+ ion[4] Addition of a H^- ion**Ans. [1]**Elimination of H^+ **Ex.11** When ethyl alcohol is heated with conc. H_2SO_4 at 443 K, ethylene is formed by

[1] Intramolecular hydration

[2] Intermolecular hydration

[3] Intermolecular dehydration

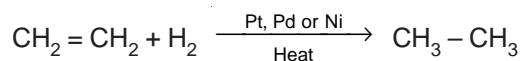
[4] Intramolecular dehydration

Ans. [4]**Sol.** Ethene is formed by removal of water molecule within the molecule of ethanol**8. PHYSICAL PROPERTIES ALKENES****(i) Physical State :** $\text{C}_1 - \text{C}_4 \longrightarrow$ gas $\text{C}_5 - \text{C}_{16} \longrightarrow$ liquid $> \text{C}_{16} \longrightarrow$ Solid wax**(ii) M.P. and B.P. of alkenes are slightly higher than alkanes.**

9. CHEMICAL PROPERTIES OF ALKENES

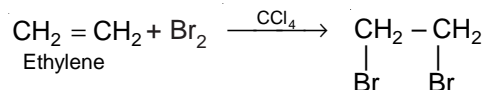
- (i) Alkenes are highly reactive.
 (ii) They undergo addition reactions due to their unsaturated nature.
 (iii) Alkenes undergo electrophilic addition reactions.

a. Addition of Hydrogen



b. Addition of Bromine

Chlorine and bromine add to alkenes at ordinary temperature to form vicinal dihalides.

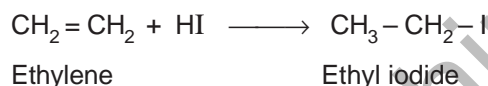


Ethylene dibromide

In the reaction of an alkene with bromine, the red colour of bromine is discharged due to the formation of dibromide which is colourless. Therefore, this reaction is used as a **test** for the presence of carbon-carbon double bond in a molecule.

c. Addition of Hydrogen Halides

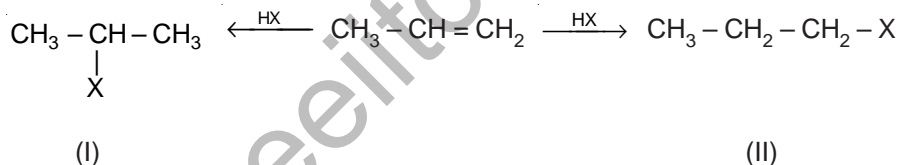
Alkenes readily undergo addition reactions with hydrogen halides (HCl, HBr or HI) to form alkyl halides.



Order of reactivity of different halogen acids in this reaction is :



In case of unsymmetrical alkenes such as propene, a halogen acid can add to give two different products (I) and (II).



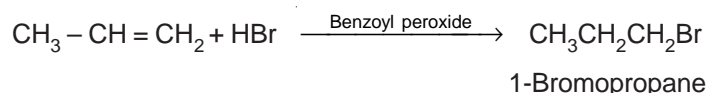
Major product

The product actually obtained is the one which obeys **Markownikoff's Rule** which is stated as :

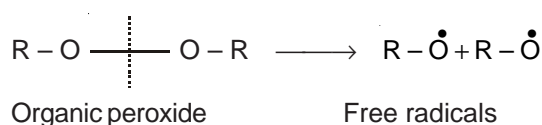
"Electrophilic addition in unsymmetrical alkenes takes place in such a way so that the negative part of the addendum attaches itself to the carbon which carries a smaller number of hydrogen atoms."

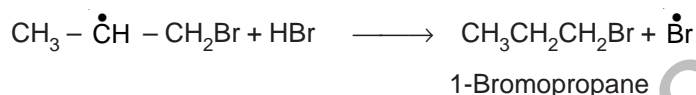
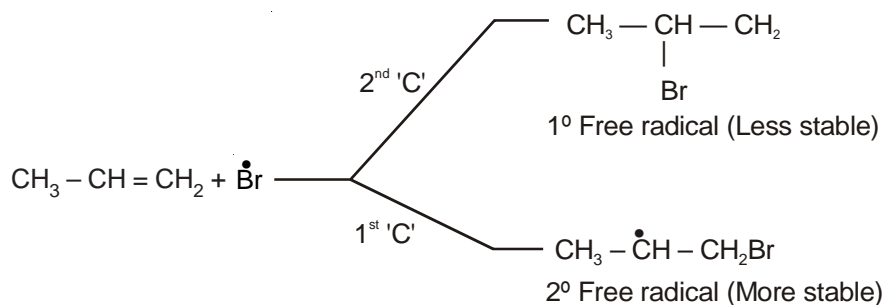
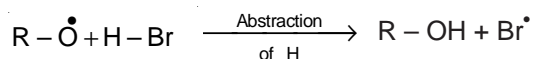
Kharasch Effect or Antimarkownikoff Additions

Kharasch effect deals with antimarkownikoff addition of HBr across an unsymmetrical alkene in the presence of peroxide.



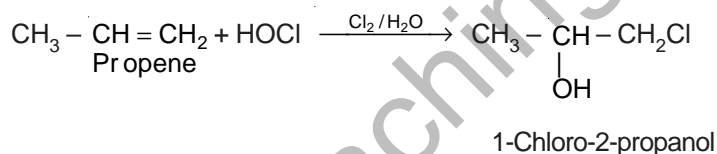
In the presence of peroxide, the addition of HBr follows a free radical mechanism.





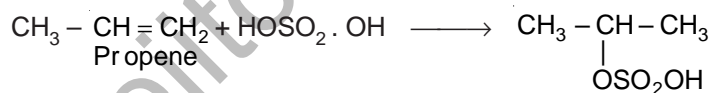
It may be noted that HF and HCl do not follow free radical mechanism even in the presence of peroxide. They add by ionic mechanism-guiding products in accordance with Markownikoff Rule.

d. Addition of Hypohalous Acids (*Formation of Halohydrins*)



e. Addition of Sulphuric Acids

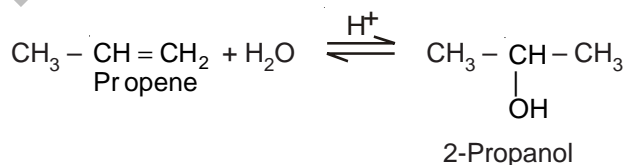
Alkenes add on cold conc. sulphuric acid to form corresponding alkyl hydrogen sulphate.



Isopropyl hydrogen sulphate

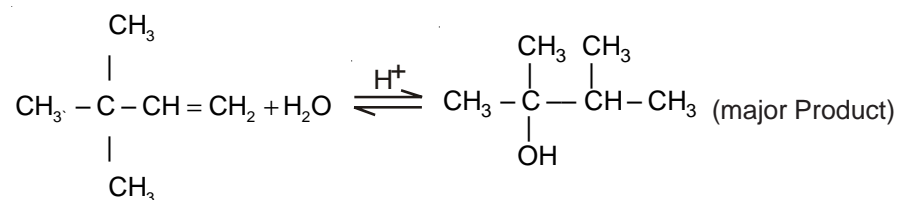
f. Addition of Water (*Hydration*)

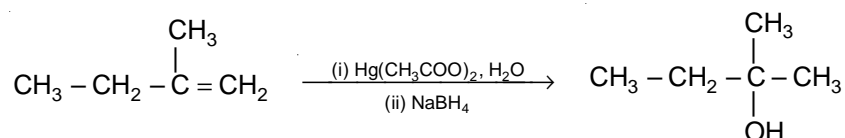
A water molecule gets added to alkenes in the presence of acids to form alcohols.



Addition to unsymmetrical alkenes follows Markownikoff rule.

During hydration of alkenes many times rearranged products are obtained.

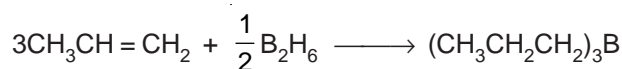


g. **Oxymercuration-demercuration**

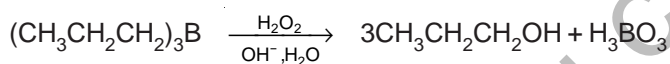
Addition of water here takes place according to Markownikoff's rule but no rearrangement takes place during the reaction.

h. **Hydroboration-Oxidation**

In this reaction alkene is treated with diborane followed by treatment with alkaline solution of H_2O_2 when alcohol is formed.



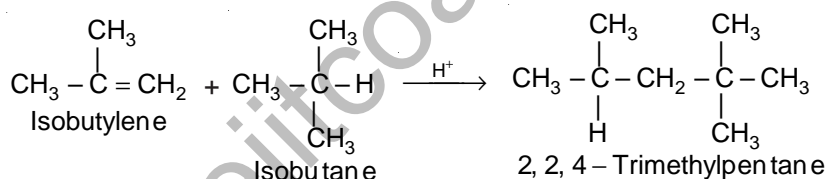
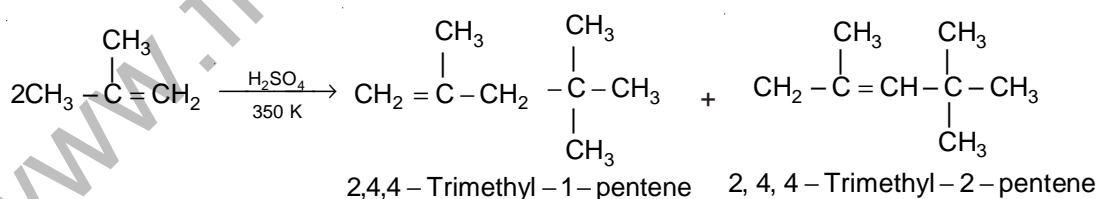
Propene Diborane Tripropyl borane



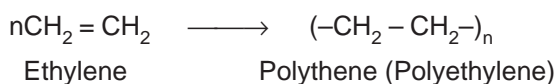
1-Propanol

i. **Additions of Alkanes**

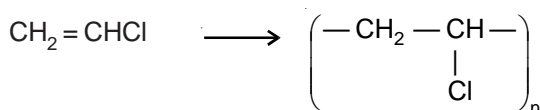
Alkenes can also add on alkanes in the presence of suitable acidic catalysts to form higher alkanes. The reaction known as **alkylation** is employed commercially for the manufacture of alkanes such as 2,2,4-trimethylpentane used as aviation fuel.

j. **Dimerisation**k. **Polymerisation**

When ethene is heated in presence of traces of oxygen at about 500–675 K under high pressure, n molecules of ethene participate in the reaction as shown below :

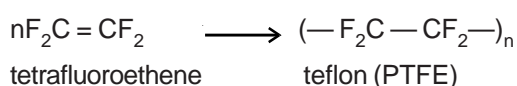
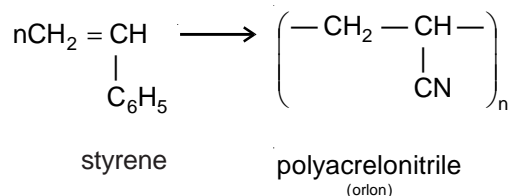
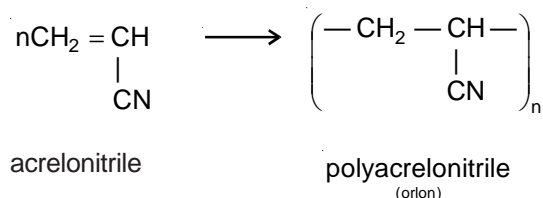


Few polymers :

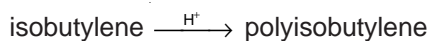


vinyl chloride

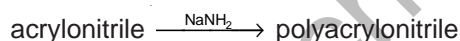
polyvinyl chloride
(PVC)

**Cationic polymerisation :**

Carbocation is formed as an intermediate

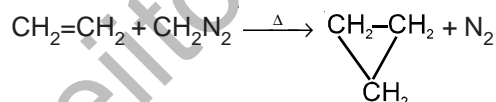
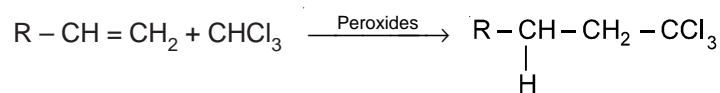
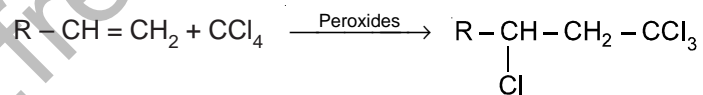
**Anionic polymerisation :**

In the polymerisation of acrylonitrile anion is formed as an intermediate

**I. Addition of Carbenes**

The addition of carbene to alkene is always carried by diazomethane CH_2N_2

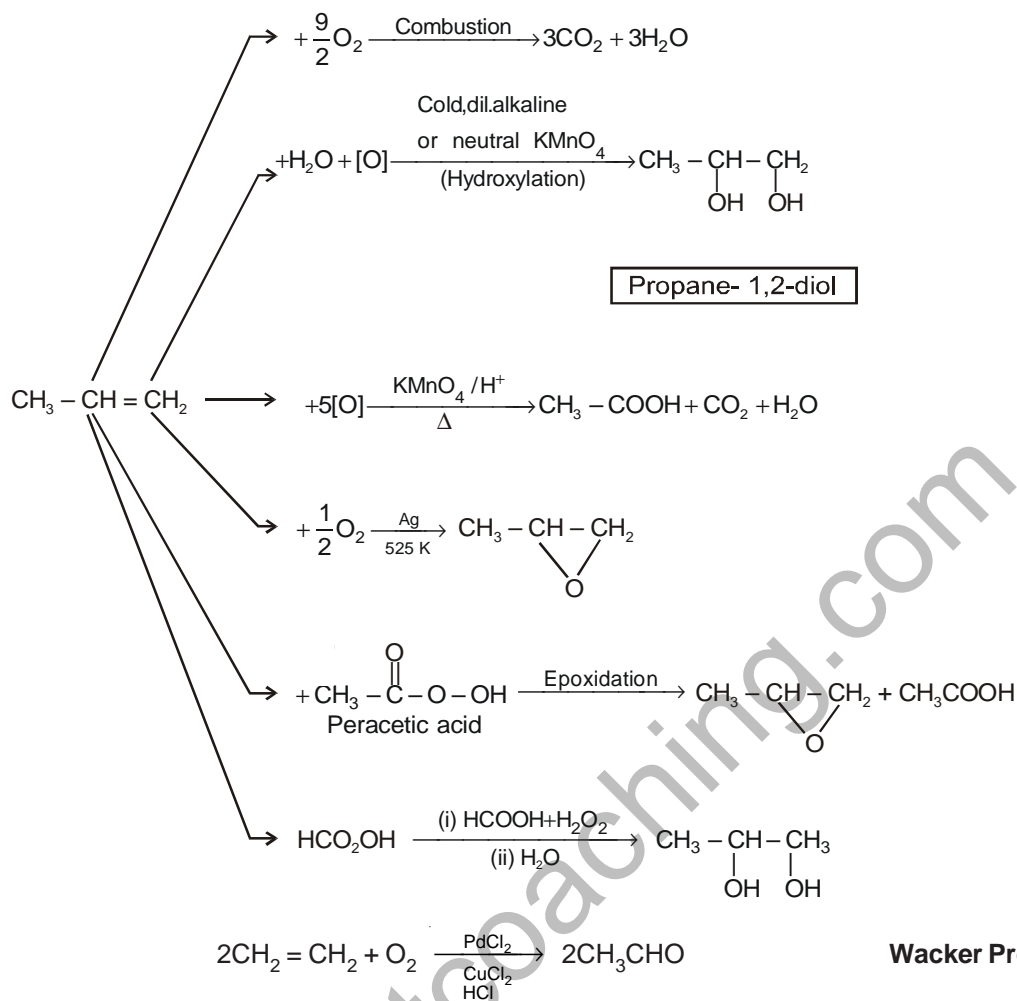
Carbene group obtained from diazomethane is added to alkene & give cyclopropane

**m. Addition of Free Radicals**

This reaction follows free radical addition mechanism similar to that in case of Kharasch effect.

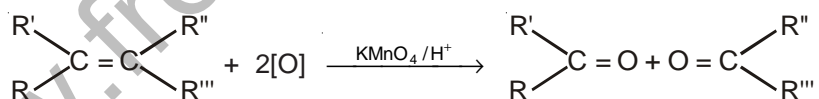
n. Oxidation

Oxidation reactions of alkenes are summarized below

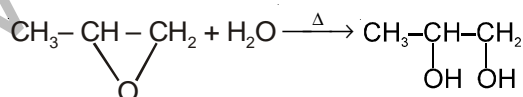


Note : 1. Alkaline solution of KMnO_4 is known as **Baeyer's reagent**. During reaction with alkenes (or alkynes) its colour gets discharged. Therefore, this reagent can be used to detect unsaturation in the molecule.

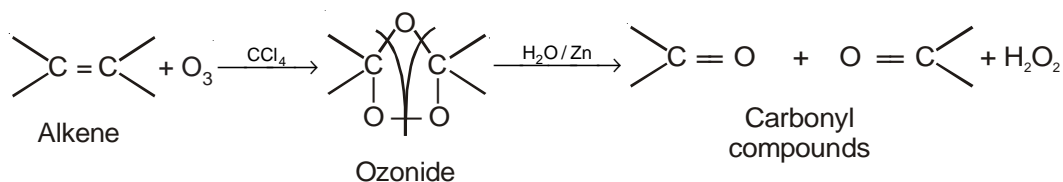
2. Tetra-substituted alkenes on reaction with hot, conc. acidified KMnO_4 solution give ketones as the products



3. Epoxides can be hydrolysed to vicinal diols by boiling water.

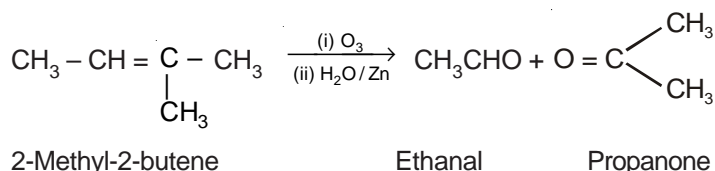
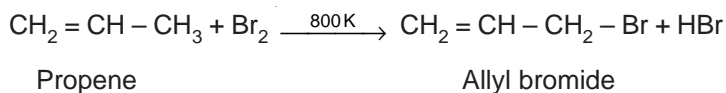


o. Ozonolysis

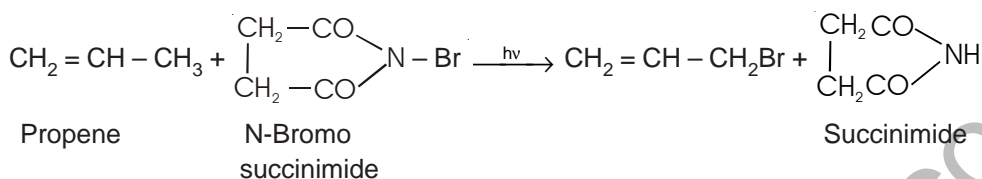


The oxidation of alkenes with ozone followed by the decomposition of the ozonide is called ozonolysis. Ozonolysis is the best method for locating the position of the double bond in alkenes.

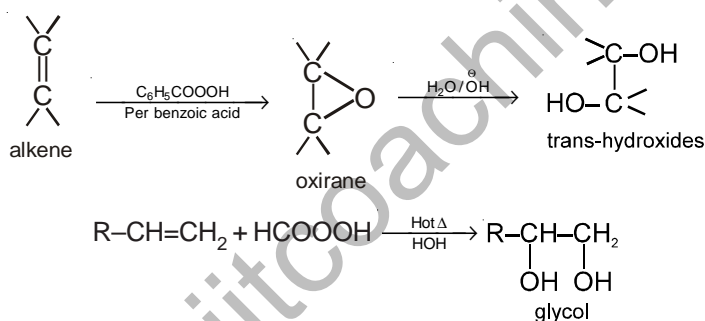
The products of ozonolysis of 2-methyl-2-butene are given below :

**p. Allylic Substitution**

The allylic substitution can also be carried out by treating the alkene with N-Bromo succinimide (NBS)

**q. Prileschaiev Reaction / Reaction with Performic Acid**

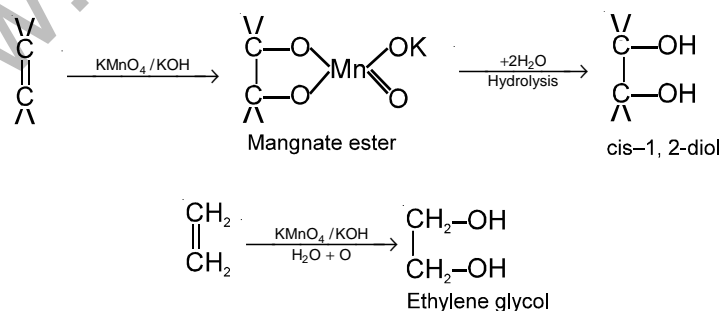
Alkenes react with per acids (per benzoic acid – $\text{C}_6\text{H}_5\text{COOH}$, per formic acid – $99\% \text{H}_2\text{O}_2 + \text{HCHO}$) to form oxiranes (1, 2-epoxide), which on hydrolysis converted into dihydroxy compounds.



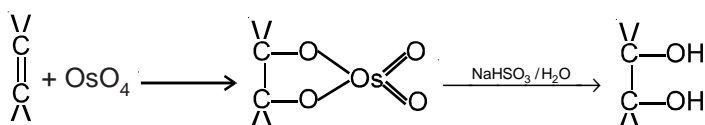
Formation of glycol from alkene is called **hydroxylation**

r. Hydroxylation

[1] In the presence of Bayer's reagent alkene after reacting form mangnate ester which on hydrolysis converted into cis-diols.



[2] Osmium tetra oxide (OsO_4) react with double bond of alkene to form cyclic osmate ester which on hydrolysis with aqueous solution of sodium bisulphite gives cis-diol.



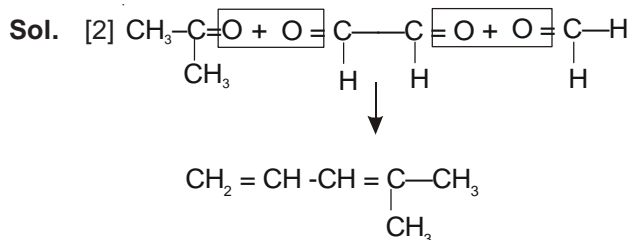
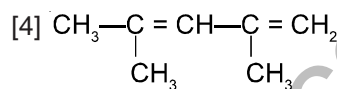
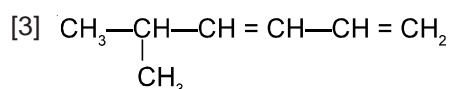
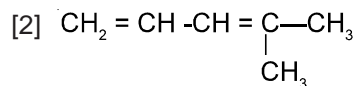
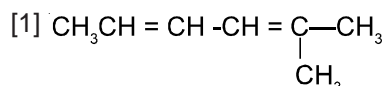
Uses of Propylene

- [1] In the manufacture of polypropylene plastic, commercially known as **Koylene**.
 [2] For the synthesis of **glycerol**.

Uses of Butylenes

- [1] Manufacture of **polyisobutylene adhesive** and **butyl rubber** (a synthetic rubber) from isobutylene.
 [2] Manufacture of diisobutylene and from this **isooctane** (a high quality synthetic fuel) is obtained.

Ex-12 A compound on ozonolysis gives glyoxal, acetone and formaldehyde as the products. The compound could be-



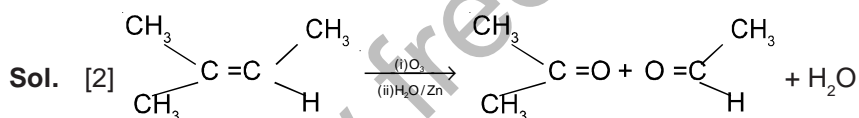
Ex-13 On ozonolysis, an alkene gave acetone and acetaldehyde along with H_2O_2 . The alkene is -

[1] 2, 3-Dimethyl-2-butene

[2] 2-Methyl-2-butene

[3] 3-Methyl-2-butene

[4] 2-Butene.



Ex-14 A hydrocarbon of formula C_6H_{12} on ozonolysis gives only one carbonyl product which does not reduce Fehling's solution. The hydrocarbon is -

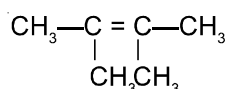
[1] 2-Hexene

[2] 2, 3-Dimethyl-2-butene

[3] 2-Methyl-2-pentene

[4] 2-Hexene

Sol. [2] Both the carbon atom's involved in double bond will have alkyl groups attached in them.



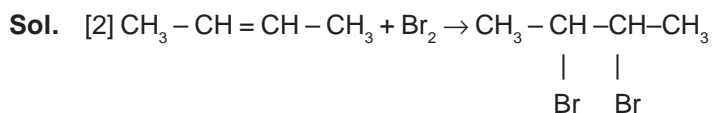
Ex-15 Addition of Br_2 to 2-butene gives -

[1] 1, 2-dibromobutane

[2] 2, 3-Dibromobutane

[3] 1, 3-Dibromobutane

[4] 1, 4-Dibromobutane



Ex-16 The addition of HBr to styrene givesas the major product -

- [1] 1-Bromo-1-phenylethane [2] 2-Bromo-1-Phenylethane
 [3] Benzyl chloride [4] p-Bromophenyl ethylene

Sol. [1] 1-Bromo-1-phenylethane will form. Addition is according to Markownikof's rule.

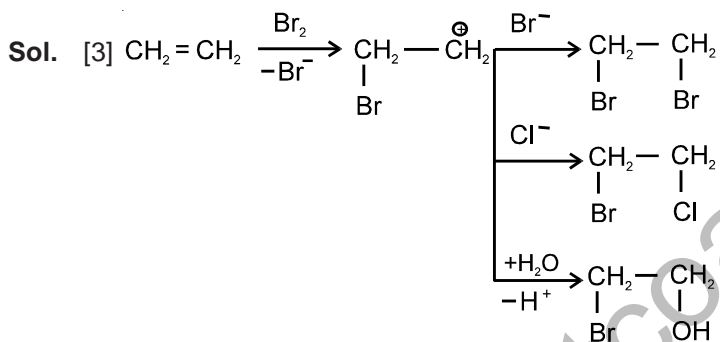
Ex-17 When HBr adds to 1-Butene in the presence of benzoyl peroxide, the products is -

- [1] 1-Bromobutane [2] 2-Bromobutane [3] 1-Bromobutene [4] 2-bromobutene

Sol. [1] 1-Bromobutane. Addition of HBr in the presence of peroxide obeys anti markownikoff's rule.

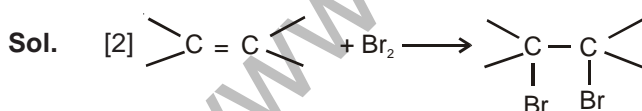
Ex-18 Ethene is shaken with aqueous solution of Br₂ and NaCl. Which of the following is not the possible product -

- [1] $\begin{array}{c} \text{CH}_2\text{---Br} \\ | \\ \text{CH}_2\text{---Br} \end{array}$ [2] $\begin{array}{c} \text{CH}_2\text{---Br} \\ | \\ \text{CH}_2\text{---Cl} \end{array}$ [3] $\begin{array}{c} \text{CH}_2\text{---Cl} \\ | \\ \text{CH}_2\text{---Cl} \end{array}$ [4] $\begin{array}{c} \text{CH}_2\text{---Br} \\ | \\ \text{CH}_2\text{---OH} \end{array}$



Ex-19 2.8 g of pure alkene containing only one double bond per molecule, react completely with 8 g of bromine (in an inert solvent.) What is the molecular formula of the alkene -

- [1] C₂H₄ [2] C₄H₈ [3] C₃H₄ [4] C₆H₁₂



1 mole of alkene reacts with one mole of Br₂

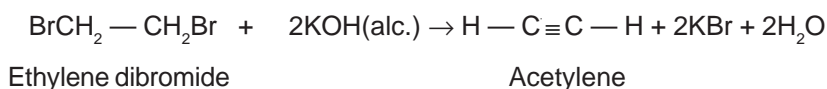
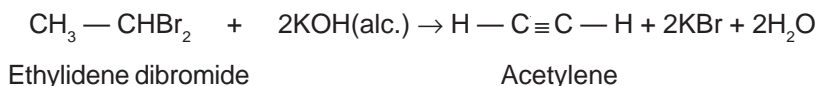
$$\therefore \text{Molecular mass of alkene} = \frac{2.8}{8} \times 160 = 56$$

Hence alkene is C₄H₈.

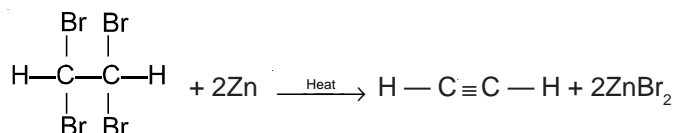
Alkynes are unsaturated hydrocarbons. They have carbon-carbon triple bond ($\text{—C}\equiv\text{C—}$). The carbon atom involved in triple bond are sp-hybridized.

11. METHODS OF PREPARATION OF ALKYNES

a. By Dehydrohalogenation of Dihalides



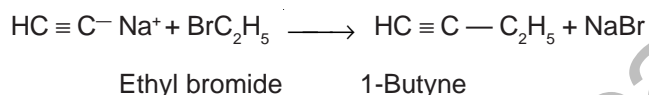
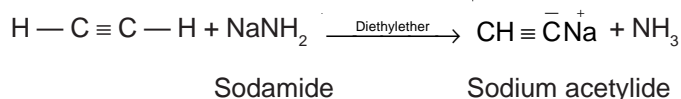
b. By Dehalogenation of Tetrahalides



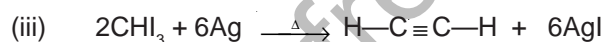
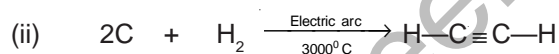
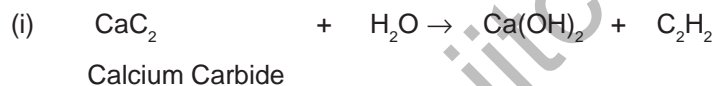
1,1,2,2-Tetrabromoethane

c. Higher alkynes from Acetylene

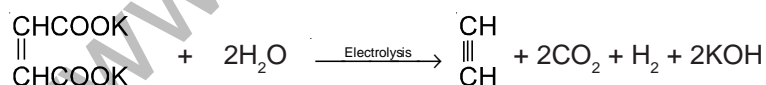
Higher alkynes may be prepared by the action of alkyl halides on sodium acetylide, Sodium acetylide can be obtained from acetylene by the reaction of sodamide.



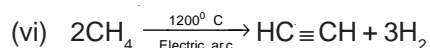
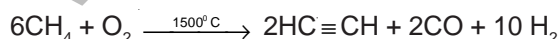
d. Some Special Methods for the Preparation of Acetylene



(iv) By Kolbe electrolysis of potassium fumarate or potassium maleate



(v) By partial oxidation of methane (**Industrial method**)



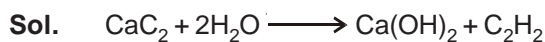
12. PHYSICAL PROPERTIES OF ALKYNES

- (i) Alkynes are colourless, odourless and tasteless.
- (ii) Lower alkynes are partially soluble in H_2O . (It is due to its polarizability)
- (iii) Higher alkynes are insoluble in water due to more % of covalent character.
- (iv) Completely soluble in organic solvents.

- (v) Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.
- (vi) Up to C_4 alkynes are gaseous. $C_5 - C_{11}$ liquid, C_{12} & above are solids.
- (vii) Acetylene & 1-alkyne are acidic in nature. It is due to presence of active H.

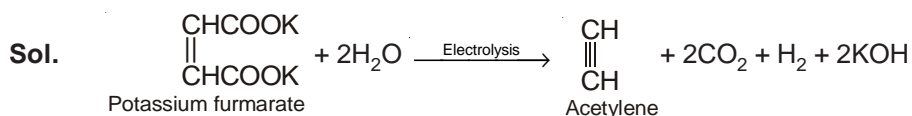
Ex.20 Ethyne can be prepared in a single step from

- [1] Calcium carbide [2] Ethylidene bromide [3] Ethylene bromide [4] All of these **Ans. [4]**



Ex.21 An aqueous solution of potassium salt of fumaric acid is electrolysed. The hydrocarbon produced at anode is

- [1] Ethane [2] Ethene [3] Methane [4] Ethyne **Ans. [4]**



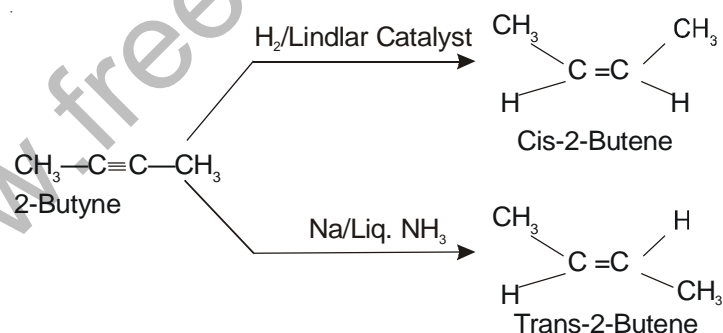
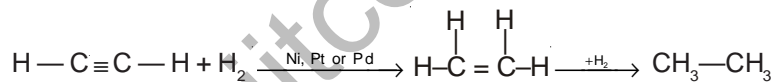
Ex.22 2-Pentyne can be converted into trans-pent-2-ene by reaction with

- [1] H_2/Ni [2] H_2 /Lindlar's catalyst
[3] $Na/Liq : NH_3$ [4] Zn/HCl **Ans. [3]**

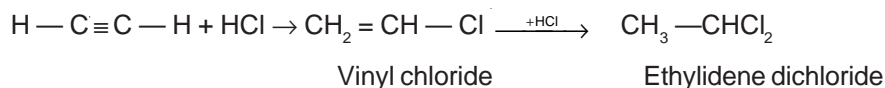
Sol. Sodium in the presence of liquid ammonia converts alkynes to corresponding trans-alkenes.

13. CHEMICAL PROPERTIES OF ALKYNES

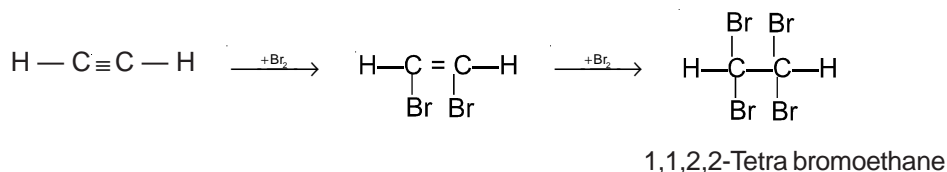
a. Addition of Hydrogen



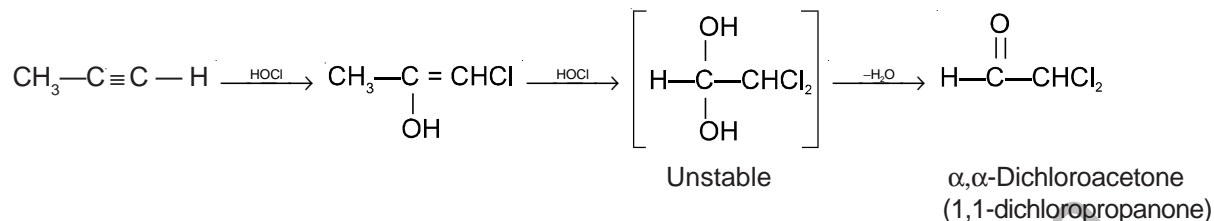
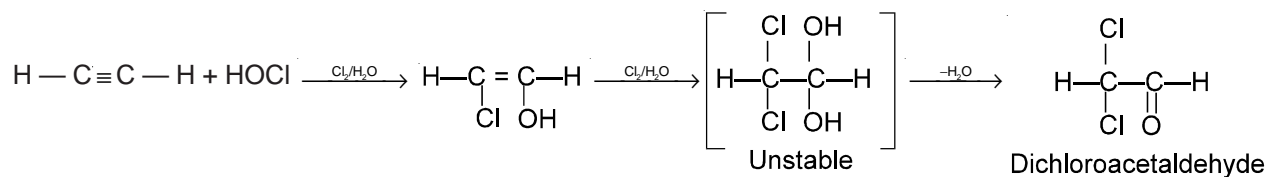
b. Addition of Halogen Acids



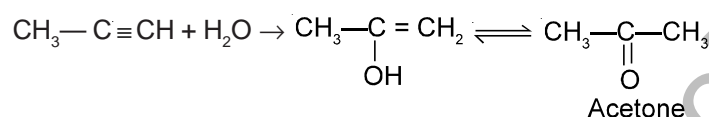
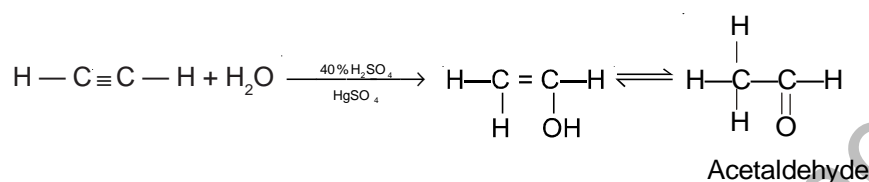
c. Addition of Halogens



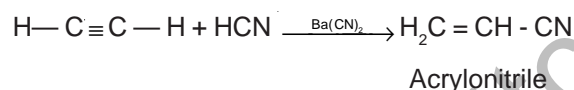
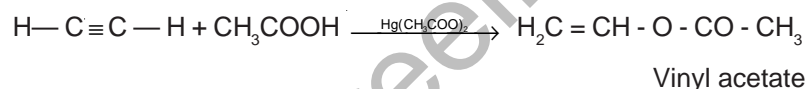
d. Addition of hypohalous Acids



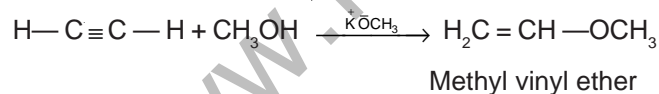
e. Addition of water



f. Addition of HCN

g. Addition of CH_3COOH 

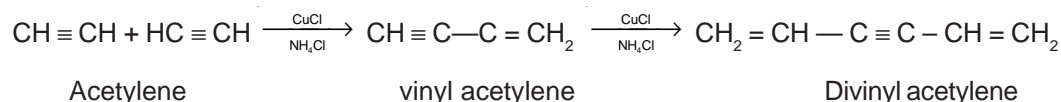
h. Addition of Alcohols



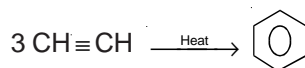
Note : Reactions b,c,d are electrophilic addition reactions whereas reactions e,f,g and h are nucleophilic addition reactions. Nucleophilic addition reactions are catalysed by heavy metal ions.

i. Polymerisation reactions

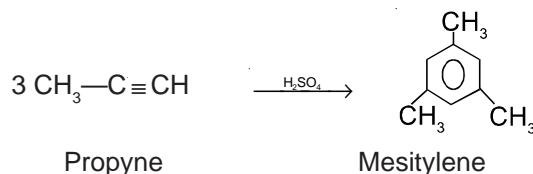
(i) **Dimerisation.** When passed through a solution of cuprous chloride in ammonium chloride, acetylene dimerises to give vinyl acetylene.



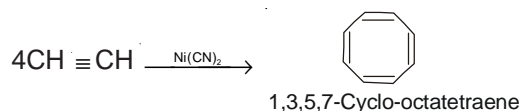
(ii) **Trimerisation.** When passed through a red hot tube, acetylene is partially converted into benzene



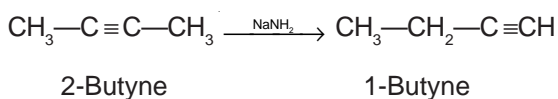
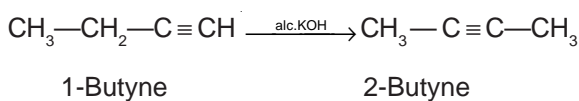
Similarly, propyne trimerises in the presence of sulphuric acid to form sym-trimethyl benzene or mesitylene.



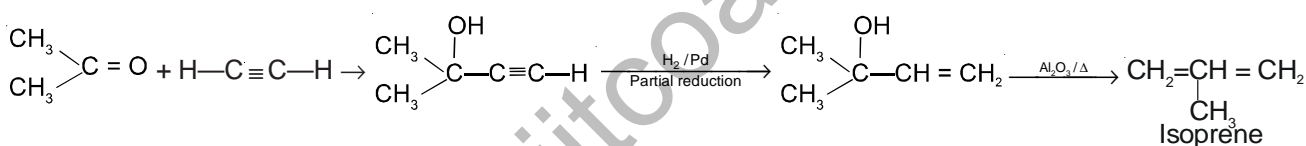
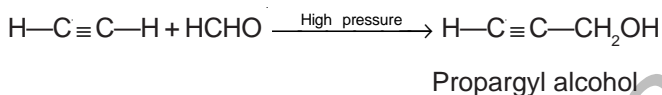
(iii) **Tetramerisation.** Acetylene undergoes tetramerisation under high pressure and in presence of nickel cyanide catalyst to form cyclo-octatetraene.



j. Isomerisation

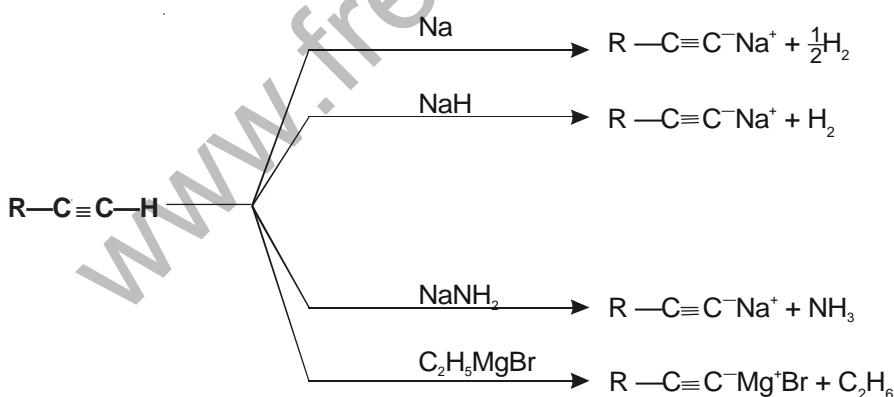


k. Reaction with carbonyl compounds

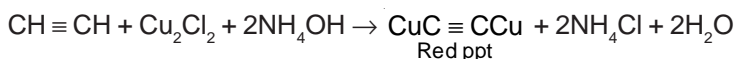
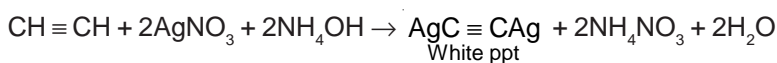


l. Reactions as Acids

The following reactions illustrate the acidic character of terminal alkynes

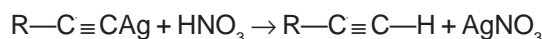


Formation of heavy metal acetylides



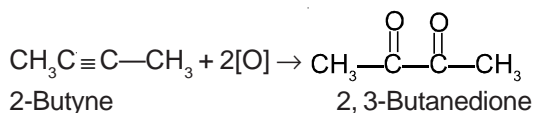
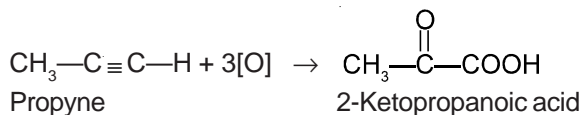
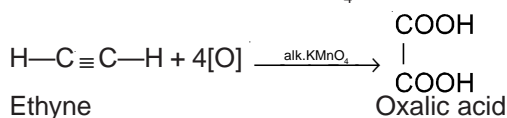
The formation of acetylides can be used for distinguishing terminal alkynes from other hydrocarbons and even from disubstituted alkynes ($\text{R—C}\equiv\text{C—R}$) which do not undergo this reaction.

These acetylides are quite explosive when in the dry state. Therefore, they should be destroyed while still wet by warming with dilute HNO_3 .



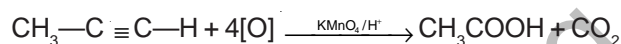
m. Oxidation Reactions

Reaction with alkaline KMnO_4 (Mild conditions)

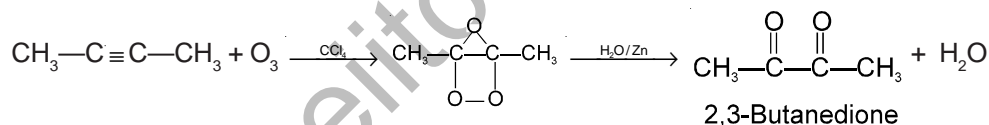
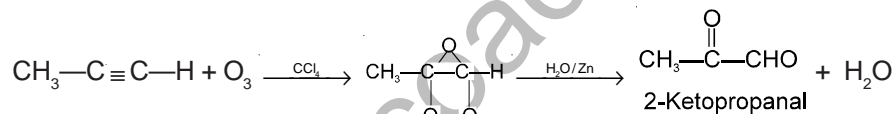
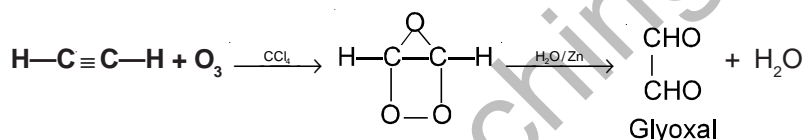


Reaction with acidified KMnO_4 (Drastic conditions)

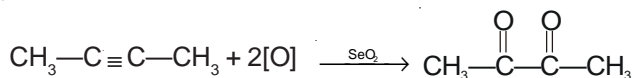
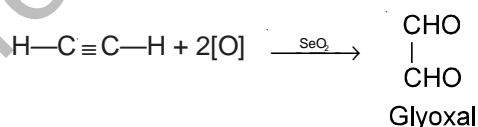
Molecule of alkyne undergoes cleavage at the carbon-carbon triple bond.



Ozonolysis

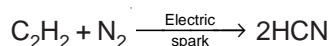


Oxidation with SeO_2

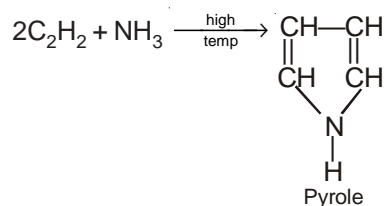


14. IMPORTANT REACTIONS OF ACETYLENE

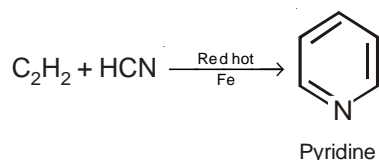
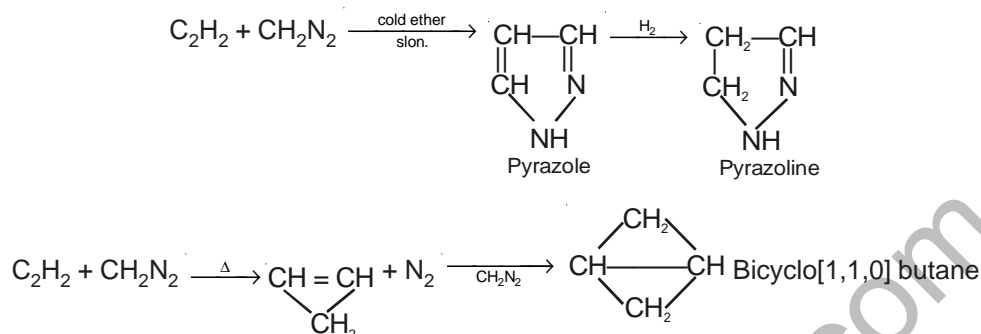
(i) Reaction with N_2



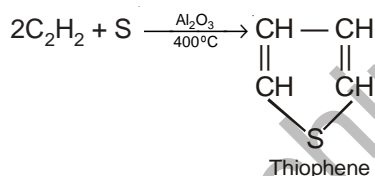
(ii) Reaction with NH_3



(iii) Reaction with HCN

(iv) Reaction with CH_2N_2 

(v) Reaction with sulphur



15. USES OF ACETYLENE

- [1] In ripening of raw fruits.
- [2] For illumination in carbide lamps.
- [3] In oxyacetylene flame from cutting and welding of metals.
- [4] In the manufacture of carbon black.
- [5] Trichloroethylene, obtainable from acetylene, is used in dry-cleaning under the trade name **triclene**.
- [6] Purified acetylene can be used as an anaesthetic under the trade name of **norcilene**.
- [7] In the manufacture of **Lewisite**, which is used as a war gas.
- [8] In the preparation of a synthetic plastic (**P.V.C.**).
- [9] In the preparation of polyacrylonitrile (acrolein or orlon).
- [10] In the manufacture of synthetic polyisoprene rubber.



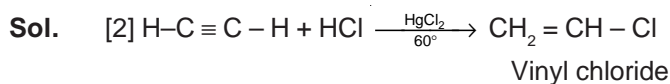
The reagent is -

- [1] Na [2] HCl in H_2O [3] KOH in $\text{C}_2\text{H}_5\text{OH}$ [4] Zn in alcohol.

Sol. [3] Alcoholic KOH brings about dehydrohalogenation

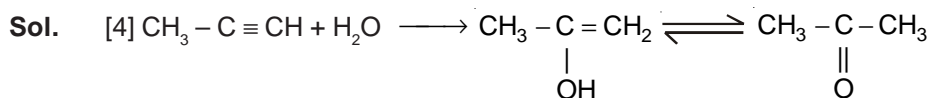
Ex-24 Acetylene when treated with dilute HCl at 60°C (333 K) in presence of HgCl_2 produces -

- [1] Methyl chloride [2] Vinyl chloride [3] Acetaldehyde [4] Formaldehyde



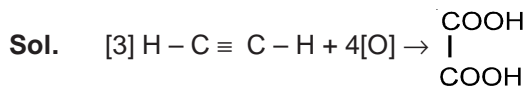
Ex-25 When propyne is treated with aqueous H_2SO_4 in the presence of HgSO_4 , the major product is -

- [1] Acetaldehyde [2] Propanal [3] 2-Propanol [4] Propanone



Ex-26 Alkaline KMnO_4 , oxidizes acetylene to -

- [1] Acetic acid [2] Glyoxal [3] Oxalic acid [4] Ethylene glycol



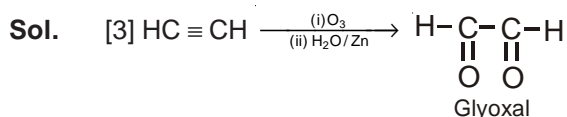
Ex-27 Which of the following is most acidic -

- [1] Ethyne [2] Propyne [3] 1-Butyne [4] 2-Butyne

Sol. [1] Because ethyne gives most stable anion.

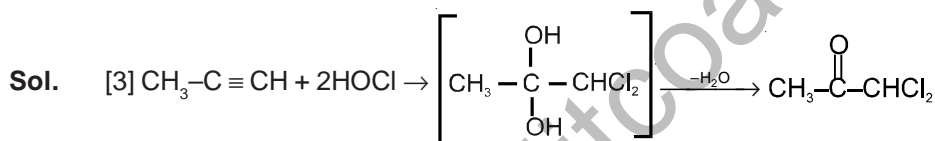
Ex-28 Ozonolysis of acetylene gives -

- [1] Oxalic acid [2] Ethylene glycol [3] Glyoxal [4] CH_3CHO



Ex-29 Propyne on reaction with aqueous chlorine gives -

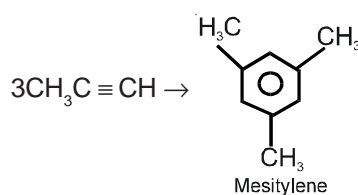
- [1] 1, 1, 2, 2-Tetrachloropropane [2] 1, 2-Dichloropropene
[3] 1, 1-Dichloropropanone [4] 2, 2-Dichloropropanone



Ex-30 Mesitylene can be obtained by polymerization of -

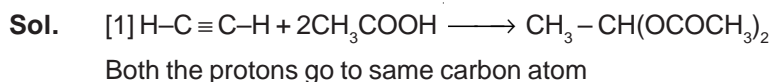
- [1] Ethyne [2] Ethene [3] Propene [4] Propyne

Sol. [4] Propyne on trimerization yields mesitylene



Ex-31 Excess of CH_3COOH is reacted with $\text{CH} \equiv \text{CH}$ in presence of Hg^{2+} , the product is -

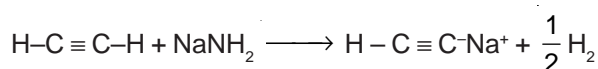
- [1] $\text{CH}_3\text{CH}(\text{OOCCH}_3)_2$ [2] $\text{CH}_2 = \text{CH}(\text{OOCCH}_3)$
[3] $(\text{CH}_3\text{COO})\text{CH}_2 - \text{CH}_2(\text{OOCCH}_3)$ [4] None of these



Ex-32 A compound is treated with NaNH_2 to give sodium salt. Identify the compound -

- [1] C_2H_2 [2] C_6H_6 [3] C_2H_6 [4] C_2H_4

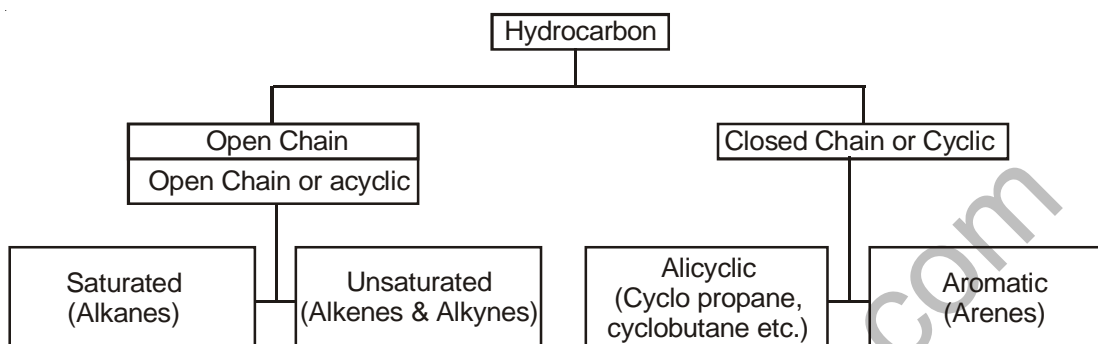
Sol. [1] Ethyne is acidic in character



HYDROCARBONS

HYDROCARBONS :

- (i) Organic compound of Carbon and hydrogen only are called hydrocabons.
- (ii) Petroleum and Coal are main source of hydrocarbon.
- (iii) Hydrocarbons are broadly classified as :



Alkanes and Arenes are quite stable compound and gives substitution reaction while alkenes & alkynes are more reactive and give addition reactions.

SATURATED HYDROCARBONS OR ALKANES OR PARAFFINS :

- ✓ General formula C_nH_{2n+2}
 - ✓ Alkanes are also known as paraffins due to their less reactive nature.
 - ✓ Type formula : $R-H$, $R-CH_3$, $R(CH_2)_n-R$
 - ✓ All the carbon atoms in alkanes are in sp^3 state of hybridization.
 - ✓ The four bonding orbitals are directed towards the four corners of a regular tetrahedron.
 - ✓ All the bond angles are tetrahedral angles i.e. $H-C-H$ or $H-C-C$ bond angle is $109^\circ 28'$ or 109.5° .
 - ✓ Alkanes contain $C-C$ and $C-H$ sigma bonds.
- | | | |
|-------------|---------------------|------------------|
| | $C-C (sp^3 - sp^3)$ | $C-H (sp^3 - s)$ |
| Bond Length | 1.54 Å | 1.112 Å |
| Bond energy | 82.67 K Cal/mol | 98.67 K Cal/mole |
- ✓ The long carbon chains in alkanes are arranged in Zig-Zig manner and not linear as usually shown. It is due to tetrahedral disposition of four bonds made by Carbon.
 - ✓ Isomerism : Alkanes shown chain and position isomerism.

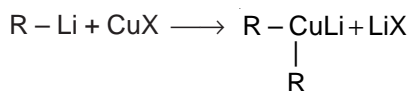
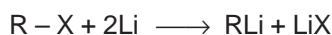
Examples :

Methane, Ethane & Propane – No isomers.

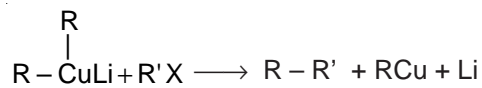
Alkanes with at least 4 carbon atoms show isomerism.

Butane	–	2 isomers
Pentane	–	3 isomers
Hexane	–	5 isomers
Heptane	–	9 isomers
Octane	–	18 isomers
Decane	–	75 isomers

4. COREY-HOUSE SYNTHESIS :

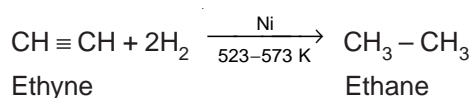
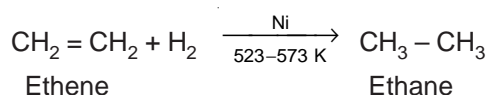


Lithium dialkyl copper

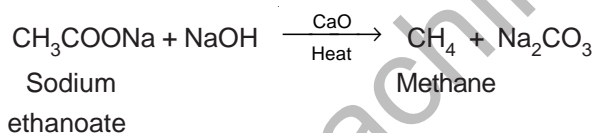


Alkane

Unlike Wurtz reaction, this reactions can be employed to prepare unsymmetrical alkanes.

5. FROM UNSATURATED HYDROCARBONS (*Sabatier and Senderen's reaction*):

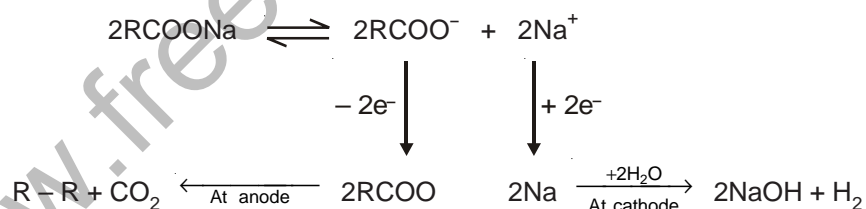
6. BY SODA-LIME DECARBOXYLATION OF CARBOXYLIC ACIDS :



The alkane formed has one carbon less than the starting material.

7. BY KOLBE'S ELECTROLYSIS :

In this method concentrated aqueous solution of sodium or potassium salt of a carboxylic acid is electrolyzed using platinum electrodes.



If n is the number of carbon atoms in the acid, the alkane formed has 2(n - 1) carbon atoms.

PHYSICAL PROPERTIES OF ALKANES :

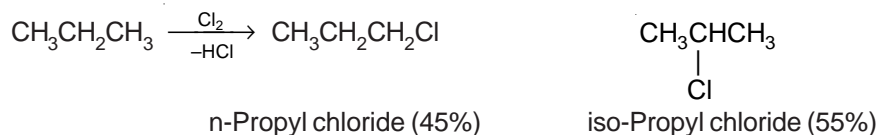
- ✓ **Physical state** : The first four members (C_1 to C_4) are gases ; the next thirteen members, (C_5 to C_{17}) are liquids while the higher members are waxy solids.
- ✓ **Boiling Points** : Alkanes have generally low boiling points. The boiling points of n-alkanes increase regularly with the increase in the number of carbon atoms. There is an increase of 20-30 degrees for each carbon atom added to the chain.
- ✓ Among isomeric alkanes, the branched chain isomers have relatively low boiling points as compared to their corresponding straight chain isomers.
- ✓ **Melting points** : The melting points of alkanes do not show uniform increase with increase in molecular mass as illustrated below.

Fluorination of alkanes takes place violently and hence is seldom done.

The reactivity of halogens towards alkanes varies as :

fluorine > chlorine > bromine > iodine.

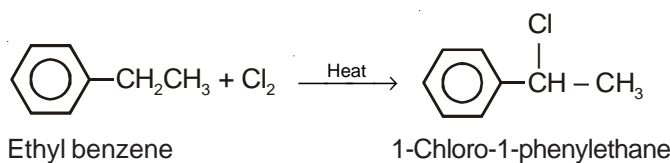
Higher alkanes on halogenation give different isomers of halogen derivatives.



It may be remembered that in general, the order of ease of replacement of hydrogens is

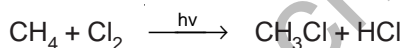
tertiary > secondary > primary.

Benzylic hydrogens are replaced even more easily than tertiary hydrogens



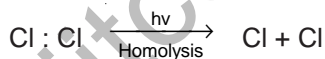
MECHANISM OF HALOGENATION OF ALKANES :

Halogenation of alkanes take place through free-radical mechanism. Let us understand it by taking the example of chlorination of methane to give methyl chloride.

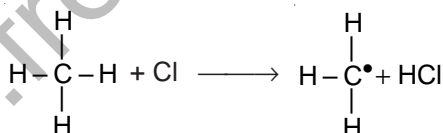


The substitution occurs through the following steps :

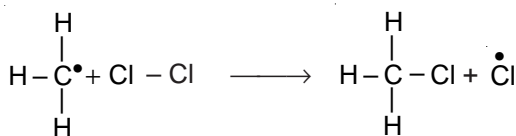
(a) Chain initiation step :



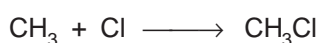
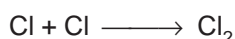
(b) Chain propagation step : Cl[•] radicals attack the methane molecules and abstract H[•] radical to form methyl radicals



Methyl radical in turn abstract Cl radical from Cl₂ molecule

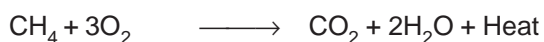


(c) Chain termination step : This involves the combination of two free radicals

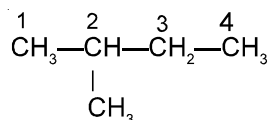


2. OXIDATION :

(a) Combustion



Ex-6 In iso-pentane, the h atom that can be most easily substituted is on -



[1] C—1

[2] C—2

[3] C—3

[4] C—4

Sol. (2) Ease of substitution of various types of H atoms is $3^\circ > 2^\circ > 1^\circ$.

ALKENES

Alkenes are unsaturated hydrocarbons. The characteristic feature of alkenes is the presence of carbon-carbon double bond (C = C) in their molecules. Alkenes are also known as olefins derived from Greek word olefiant (means oil forming). It is because of the fact that lower members of this series form oily products when treated with chlorine.

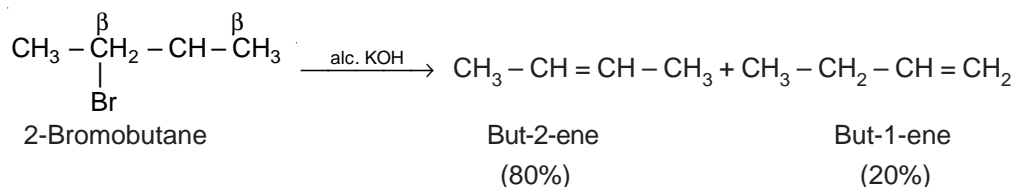
METHODS OF PREPARATION OF ALKENES :

1. By Dehydrohalogenation of alkyl halides
2. By Dehydration of Alcohols
3. By Dehalogenation
4. By Cracking of Alkanes
5. From Alkynes
6. By Decomposition of Quaternary Ammonium Hydroxides
7. By use of Organometallic Compounds and Reactive Halides
8. By Kolbe Electrolysis of Potassium Succinate

1. BY DEHYDROHALOGENATION OF ALKYL HALIDES :

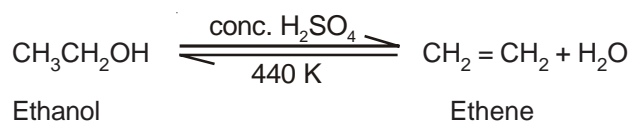


In case an alkyl halide can eliminate hydrogen halide in two different ways, the preferred alkene is the one which is maximum alkylated i.e., which carries more number of alkyl groups attached to the doubly bonded carbon atoms. This generalisation is known as Saytzeff Rule. For example,

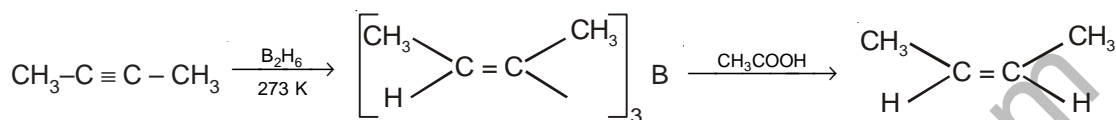
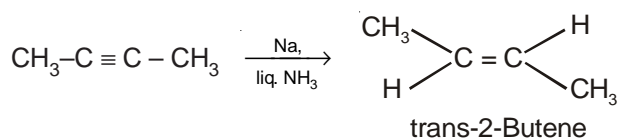
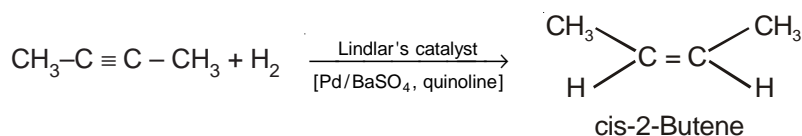


The reactivity of alkyl halides towards elimination reaction follows the order :
tertiary > secondary > primary

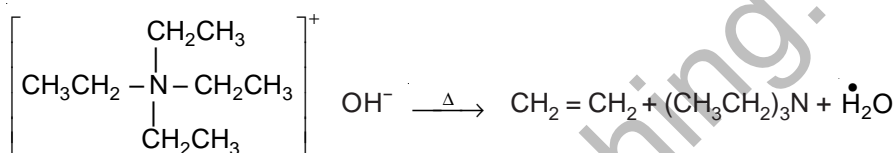
2. BY DEHYDRATION OF ALCOHOLS :



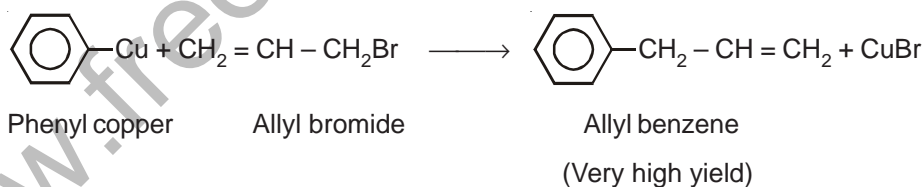
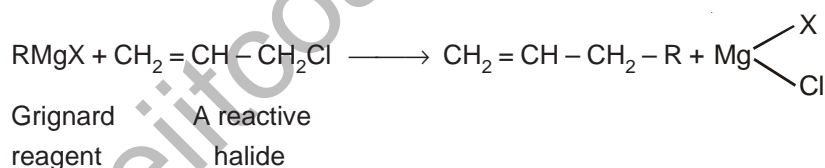
5. From Alkynes : (By partial hydrogenation of C – C triple bond)



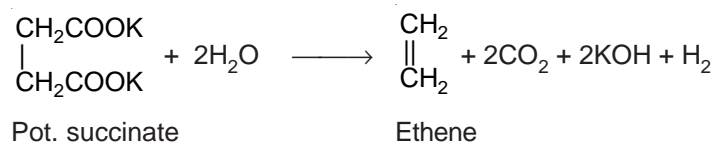
6. By Decomposition of Quaternary Ammonium Hydroxides :



7. By use of Organometallic Compounds and Reactive Halides :



8. By Kolbe Electrolysis of Potassium Succinate :



CHEMICAL PROPERTIES OF ALKENES :

1. Addition of Hydrogen
2. Addition of Bromine
3. Addition of Hydrogen Halides
4. Kharasch Effect of Antimarkownikoff Additions
5. Addition of Hypohalous Acids (*Formation of Halohydrins*)

- v Due to anti addition cis-2-butene on reaction with Br_2 yields a racemic mixture of 2, 3-dibromobutane while trans-2-butene yields meso-2, 3-dibromobutane.

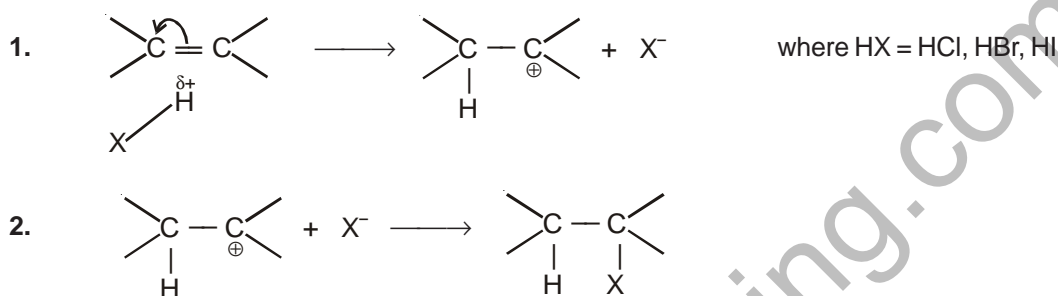
3. ADDITION OF HYDROGEN HALIDES :

Alkenes readily undergo addition reactions with hydrogen halides (HCl, HBr or HI) to form alkyl halides.



MECHANISM OF ADDITION OF HALOGEN ACIDS TO ALKENES :

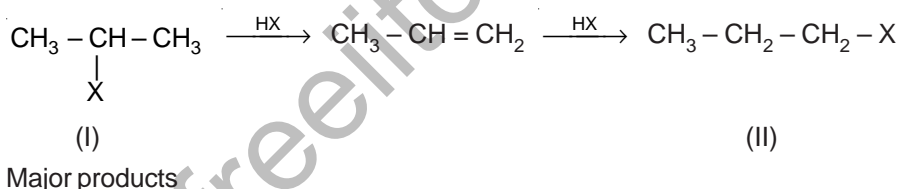
Hydrogen halides easily add to alkenes to form alkyl halides. Addition is believed to proceed through following mechanism.



Order of reactivity of different halogen acids in this reaction is :



In case of unsymmetrical alkenes such as propene halogen acid can add to give two different products (I) and (II).

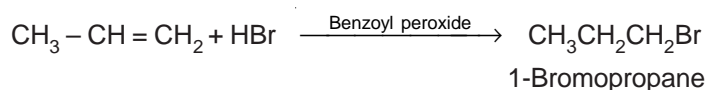


The product actually obtained is the one which obeys Markownikoff's Rule which is stated as :

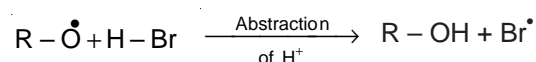
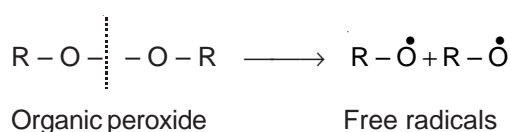
Electrophilic addition in unsymmetrical alkenes takes place in such a way so that the negative part of the addendum attaches itself to the carbon which carries smaller no. of hydrogen atoms.

4. KHARASCH EFFECT OF ANTIMARKOWNIKOFF ADDITIONS :

Kharasch effect deals with antimarkownikoff addition of HBr across unsymmetrical alkene in the presence of peroxide.



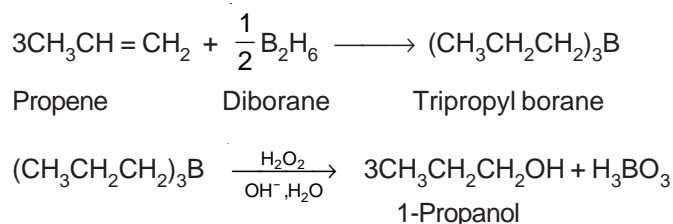
In the presence of peroxide the addition of HBr follows free radical mechanism.



Addition of water here takes place according to Markownikoff's rule but no reorganisation takes place during the reaction.

9. HYDROBORATION-OXIDATION :

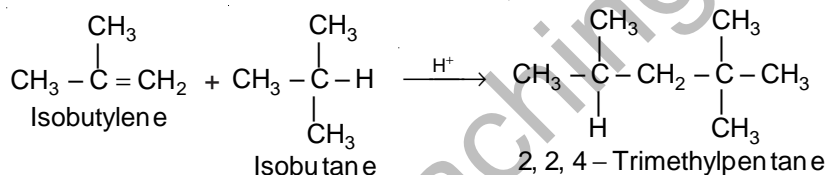
In this reaction alkene is treated with diborane followed by treatment with alkaline solution of H_2O_2 when alcohol is formed.



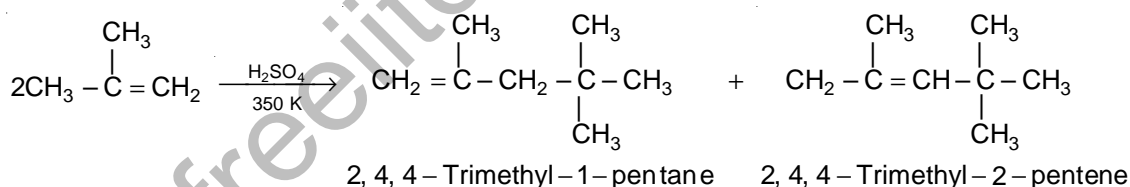
In this method addition of water occurs in an anti-Markownikoff's way.

10. ADDITIONS OF ALKANES :

Alkenes can also add on alkanes in the presence of suitable acidic catalysts to form higher alkanes. The reaction known as alkylation is employed commercially for the manufacture of alkanes such as 2, 2, 4-trimethylpentane used as aviation fuel.

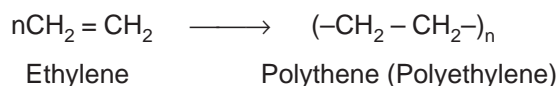


11. DIMERISATION :



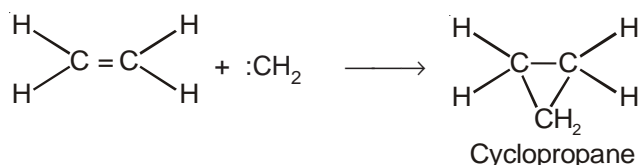
12. POLYMERISATION :

When ethene is heated in presence of traces of oxygen at about 500–675 K under high pressure, n molecules of ethene participate in the reaction as shown below :

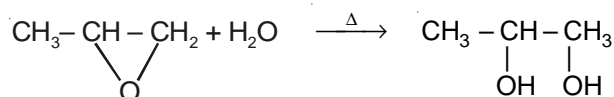


13. ADDITION OF CARBENES :

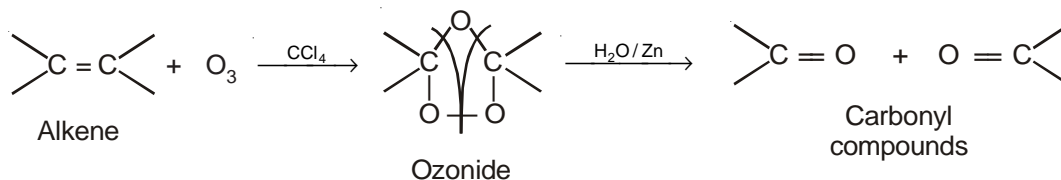
Alkene undergo addition reaction with carbenes (singlet as well as triplet) to form cyclopropanes.



3. Epoxides can be hydrolysed to vicinal diols by boiling water.

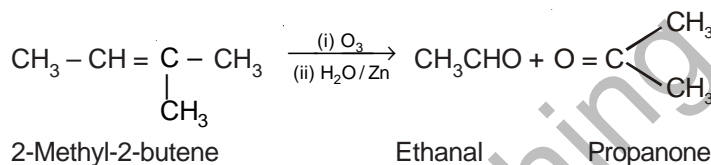


16. OZONOLYSIS :

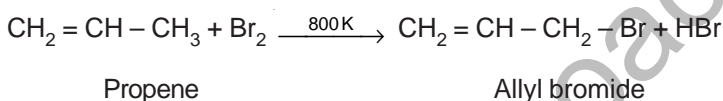


The oxidation of alkenes with ozone followed by the decomposition of the ozonide is called ozonolysis. Ozonolysis is the best method for locating the position of the double bond in alkenes.

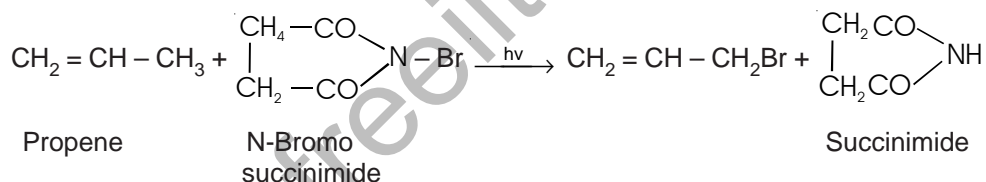
The products of ozonolysis of 2-methyl-2-butene are given below :



17. ALLYLIC SUBSTITUTION :



The allylic substitution can also be carried out by treating the alkene with N-Bromo succinimide (NBS)



USES OF ALKENES

Uses of Ethylene :

- (1) In artificial ripening of Fruits
- (2) In the growth of vegetable and fruit plants
- (3) As an anaesthetic
- (4) In welding by oxy-ethylene flame
- (5) In the manufacture of **mustard gas**, which is very poisonous and is used as a war gas.
- (6) A number of useful polymers are synthesised from ethylene and its derivatives, such as **polythene** from ethylene, **polystyrene** styrene, **polyvinyl chloride** from vinyl chloride, **polyacrylonitrile** from acrylonitrile, **polyvinyl acetate** from vinyl acetate, **polyvinyl alcohol** from hydrolysis of polyvinyl acetate and **polytetrafluoroethylene (Teflon)** from tetrafluoroethylene.

Ex-11 The addition of HBr to styrene givesas the major product -

- [1] 1-Bromo-1-phenylethane [2] 2-Bromo-1-Phenylethane
[3] Benzyl chloride [4] p-Bromophenyl ethylene

Sol. (1) 1-Bromo-1-phenylethane will form. Addition is according to Markownikof's rule.

Ex-12 When HBr adds to 1-Butene in the presence of benzoyl peroxide, the products is -

- [1] 1-Bromobutane [2] 2-Bromobutane [3] 1-Bromobutene [4] 2-bromobutene

Sol. (1) $\text{CH}_2 = \text{CH}_2 + \text{HOCl} \rightarrow \text{ClCH}_2 - \text{CH}_2\text{OH}$

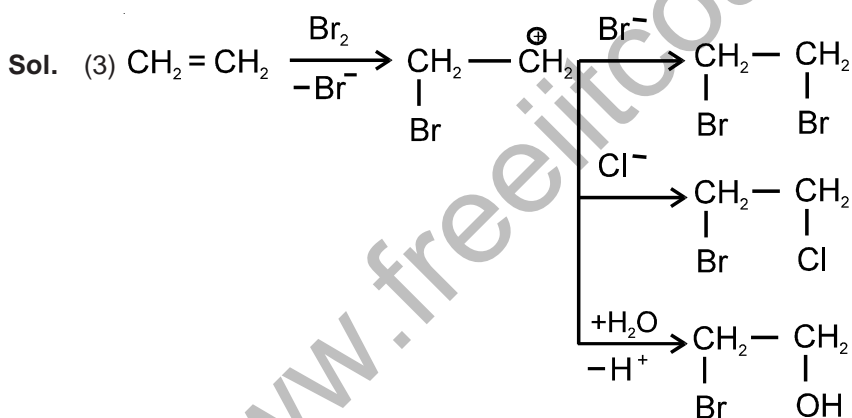
Ex-13 To which of the following compounds Br_2 adds most readily. -

- [1] $\text{CH}_2 = \text{CH}_2$ [2] $\text{CH}_3 - \text{CH} = \text{CH}_2$ [3] $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$ [4] $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH} - \text{CH}_3$

Sol. (4) Intermediate carbocation formed in the case of $\text{CH}_3 - \underset{\text{CH}_3}{\text{C}} = \text{CH} - \text{CH}_3$

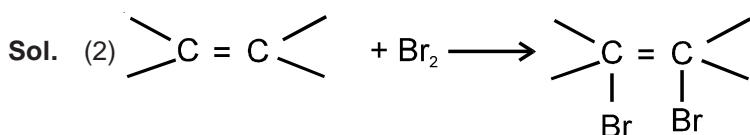
Ex-14 Ethene is shaken with aqueous solution of Br_2 and NaCl. Which of the following is not the possible product -

- [1] $\begin{array}{c} \text{CH}_2 - \text{Br} \\ | \\ \text{CH}_2 - \text{Br} \end{array}$ [2] $\begin{array}{c} \text{CH}_2 - \text{Br} \\ | \\ \text{CH}_2 - \text{Cl} \end{array}$ [3] $\begin{array}{c} \text{CH}_2 - \text{Cl} \\ | \\ \text{CH}_2 - \text{Cl} \end{array}$ [4] $\begin{array}{c} \text{CH}_2 - \text{Br} \\ | \\ \text{CH}_2 - \text{OH} \end{array}$



Ex-15 2.8 g of pure alkene containing only one double bond per molecule, react completely with 8 g of bromine (in an inert solvent.) What is the molecular formula of the alkene -

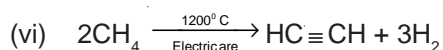
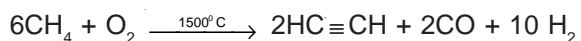
- [1] C_2H_4 [2] C_4H_8 [3] C_3H_4 [4] C_6H_{12}



1 mole of alkene reacts with one mole of Br_2

\therefore Molecular mass of alkene = $\frac{2.8}{8} \times 160 = 56$

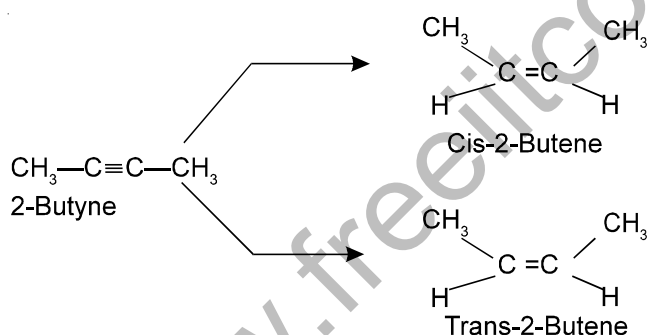
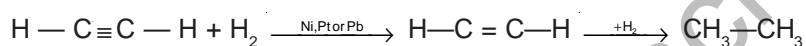
(v) By partial oxidation of methane (**Industrial method**)



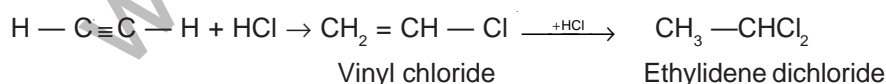
CHEMICAL PROPERTIES OF ALKYNES

1. Addition of Hydrogen
2. Addition of Halogen Acide
3. Addition of Halogens
4. Additon of Hyprohalous acids
5. Adition of water
6. Addition of HCN
7. Addition of CH_3COOH
8. Addition of Alcohols
9. Polymerisation Reactions
10. Isomerisation
11. Reaction with carbonyl compounds
12. Reactions as Acids
13. Oxidation Reactions

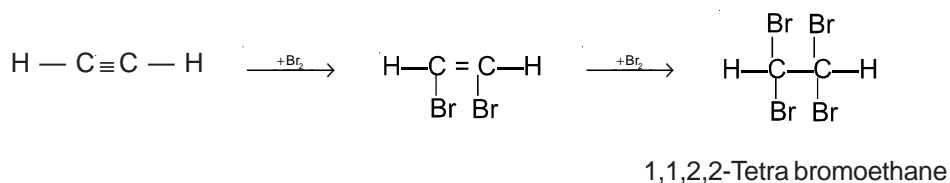
1. ADDITON OF HYDROGEN



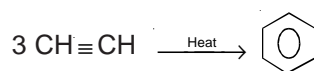
2. ADDITION OF HALOGEN ACIDS



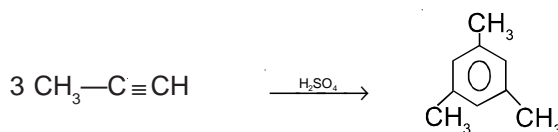
3. ADDITION OF HALOGENS



(ii) **Trimerisation.** When passed through a red hot tube, acetylene is partially converted into benzene



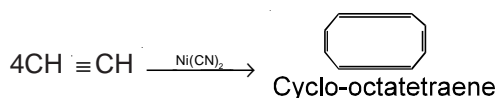
Similarly, propyne trimerises in the presence of sulphuric acid to form sym-trimethyl benzene or mesitylene.



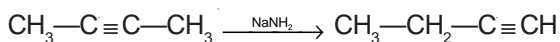
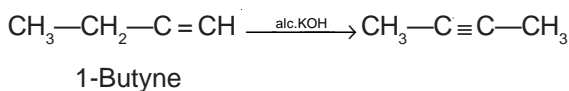
Propyne

Mesitylene

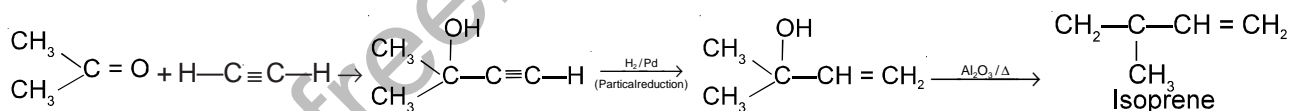
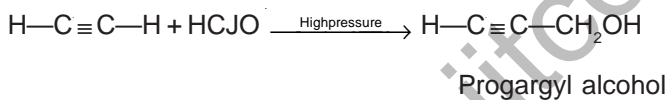
(iii) **Tetramerisation.** Acetylene undergoes tetramerisation under high pressure and presence of nickel cyanide catalyst to form cyclo-octatetraene.



10. ISOMERISATION

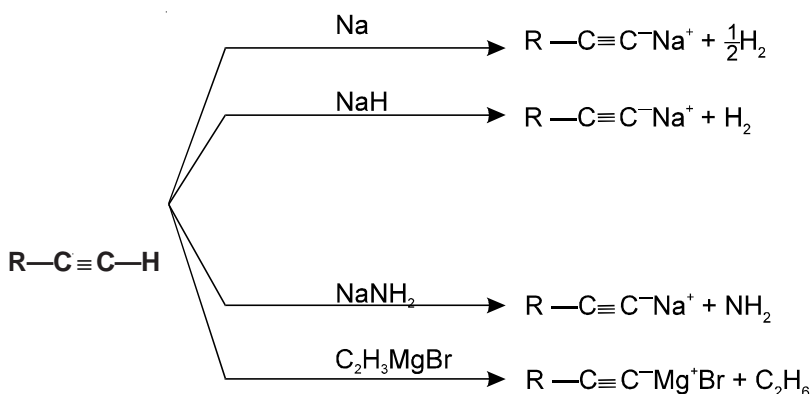


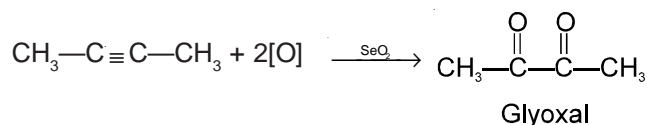
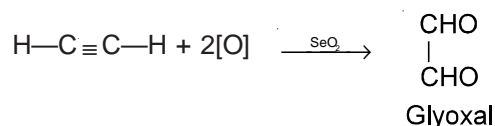
11. REACTION WITH CARBONYL COMPOUNDS



12. REACTIONS AS ACIDS

The following reactions illustrate the acidic character of terminal alkynes



Oxidation with SeO_2 

USES OF ACETYLENE

- (1) In ripening of raw fruits.
- (2) For illumination in carbide lamps
- (3) In oxyacetylene flame from cutting and welding of metals.
- (4) In the manufacture of carbon black.
- (4) Trichloroethylene, obtainable from acetylene, is used in dry-cleaning under the trade name **tricleene**.
- (5) Purified acetylene can be used as an anaesthetic under the trade name of **norcilene**.
- (6) In the manufacture of **Lewisite**, which is used as a war gas.
- (7) In the preparation of a synthetic plastic (**P.V.C.**).
- (8) In the preparation of polyacrylonitrile (acrolein or orlon).
- (9) In the manufacture of synthetic polyisoprene rubber.



The reagent is -

- [1] Na [2] HCl in H_2O [3] KOH in $\text{C}_2\text{H}_5\text{OH}$ [4] Zn in alcohol.

Sol. (3) Alcoholic KOH brings about dehydrohalogenation

Ex-18 Acetylene when treated with dilute HCl at 60°C (333 K) in presence of HgCl_2 produces -

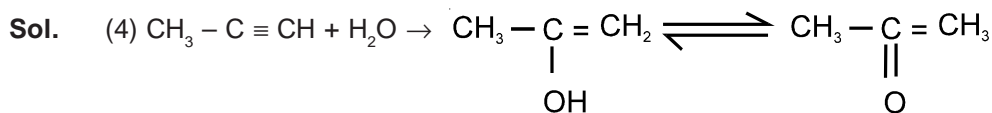
- [1] Methyl chloride [2] Vinyl chloride [3] Acetaldehyde [4] Formaldehyde



Vinyl chloride

Ex-19 When propyne is treated with aqueous H_2SO_4 in the presence of HgSO_4 , the major product is -

- [1] Acetaldehyde [2] Propanal [3] 2-Propanol [4] Propanone



Ex-20 Alkaline KMnO_4 , oxidizes acetylene to -

- [1] Acetic acid [2] Glyoxal [3] Oxalic acid [4] Ethylene glycol

