Chapter

8

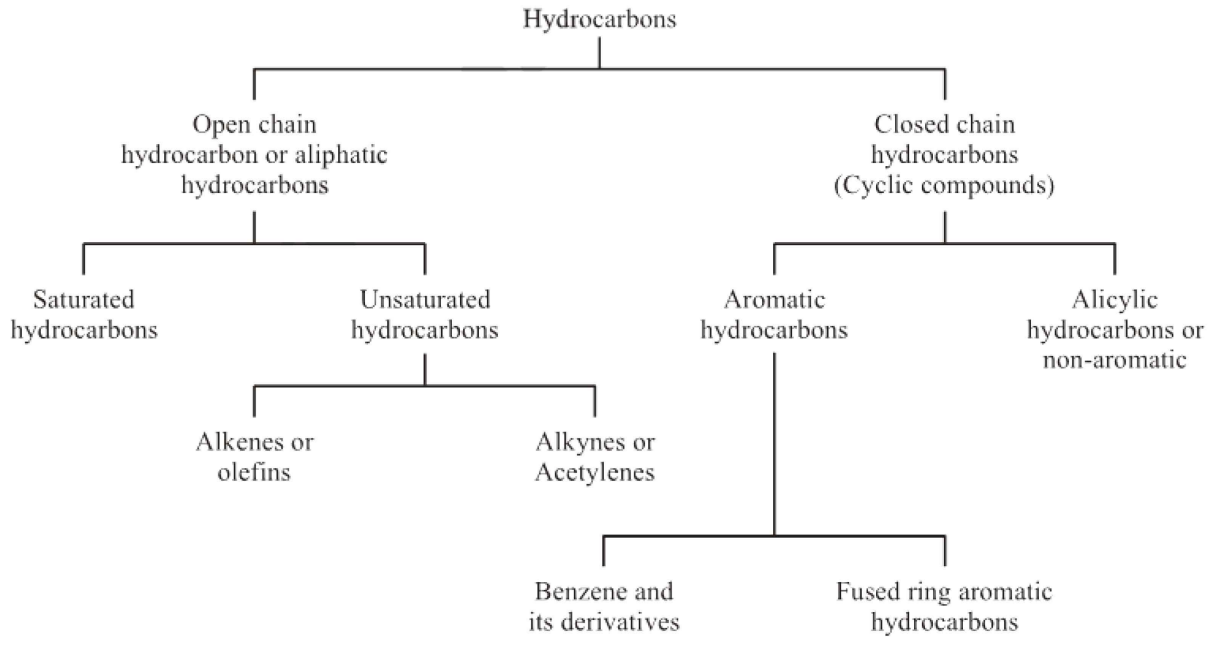
ALIPHATIC HYDROCARBONS

The organic compounds which contain carbon atoms and hydrogen atoms only in them are called hydrocarbons. e.g.,

CH_4, $CH_2 = CH_2$, $CH \equiv CH$, C_6H_6 etc.

Hydrocarbon compounds are in large numbers and divided into various classes. Hydrocarbons are classified on the basis of structure of chain, size of chain and nature of the rings.

CLASSIFICATION OF HYDROCARBONS



Hydrocarbons are classified into two major classes:

(1) Open chain hydrocarbons (aliphatic hydrocarbons)

(2) Closed chain hydrocarbons (cyclic)

(1) Open Chain Compounds:

The hydrocarbons in which both ends of carbon chain are open, are called open chain compounds. e.g.,

$CH_3 — CH_2 — CH_2 — CH_3$ n-butane

$CH_3 — CH_2 — CH = CH_2$ 1-butene

$CH_3 — CH_2 — C \equiv CH$ 1-butyne

These hydrocarbons are of mainly two types:

(a) Saturated hydrocarbons

(b) Unsaturated hydrocarbons

(a) Saturated Hydrocarbons:

"These are the compounds of carbon and hydrogen in which the valency of carbon is fully saturated and there is single bonds between carbon and carbon atoms." Their general formula in C_nH_{2n+2}. e.g.,

CH_4 $H_3C — CH_2 — CH_3$ $CH_3 — CH_2 — CH_2 — CH_2 — CH_3$

Methane Propane n-pentane

Due to their least chemical reactivity, the saturated hydrocarbons are also known as 'Paraffins'. The name 'Paraffins' comes from the combination of Latin word "parum" and "affin".

Parum = Little, Affin = Affinity

(b) Unsaturated Hydrocarbons:

"Compounds of carbon and hydrogen, in which the valency of carbon is not fully saturated, are called unsaturated hydrocarbon."

Unsaturated hydrocarbons are grouped into two categories:

(i) Alkenes or Olefins

(ii) Alkynes or Acetylenes

(i) Alkenes or Olefins:

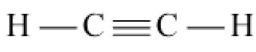
Those hydrocarbons in which there is a double bond between carbon and carbon atoms are called alkenes or olefins. Their general formula is C_nH_{2n}. e.g.,

$CH_2 = CH_2$ $CH_2 = CH — CH_3$

Ethene Propene

(ii) Alkynes or Acetylenes:

"Those hydrocarbons in which there is a triple bond between carbon and carbon atoms are called alkynes or acetylenes." Their general formula is C_nH_{2n-2}. e.g.,



(Ethyne) Acetylene



Propyne

(2) Closed Chain Hydrocarbons:

"Closed chain hydrocarbons are the compounds of carbon and hydrogen which contain rings of carbon atoms."

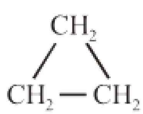
These are of two types of closed chain compounds:

(a) Alicyclic hydrocarbons

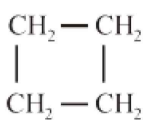
(b) Aromatic hydrocarbons

(a) Alicyclic Hydrocarbons:

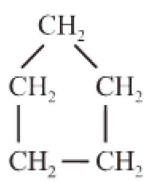
"Cyclic hydrocarbons that do not contain a benzene ring in them are called alicyclic hydrocarbons." e.g.,



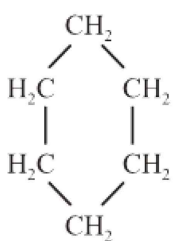
Cyclo propane



Cyclo butane



Cyclo pentane

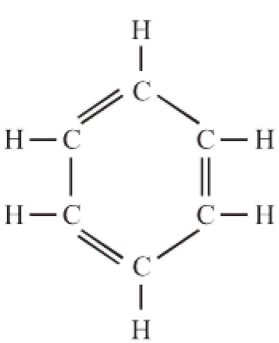


Cyclo hexane

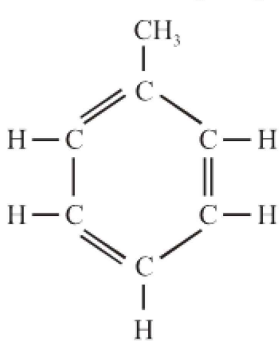
(b) Aromatic Hydrocarbons:

"Cyclic hydrocarbons are those which contain a benzene ring in them, are called aromatic hydrocarbons."

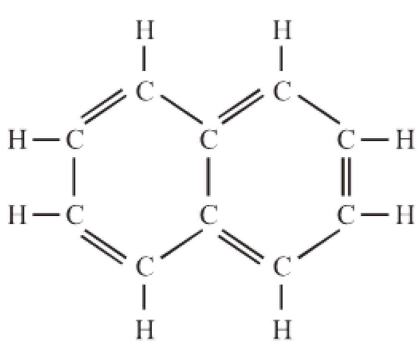
A six-member ring of carbon atoms with alternating single and double carbon-carbon bonds is called a benzene ring. e.g.,



Benzene



Toluene



Naphthalene

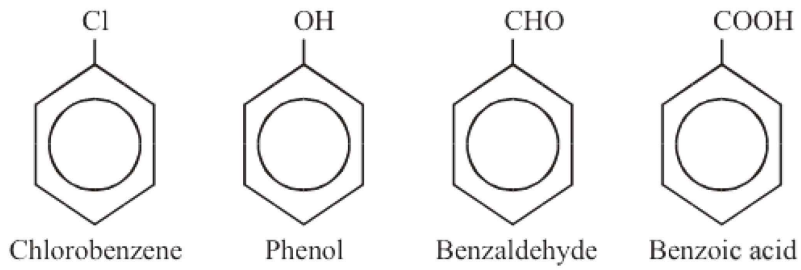
Aromatic compounds are further classified as:

(i) Benzene and its derivative

(ii) Fused ring aromatic compounds

(i) Benzene Ring Derivatives:

"The compounds in which one or more hydrogen atoms of benzene ring are replaced by any functional group or alkyl group are called benzene derivatives." e.g.,



Chlorobenzene Phenol Benzaldehyde Benzoic acid

(ii) Fused Ring Aromatic Compounds:

"The hydrocarbons which have two or more aromatic rings, fused together, called fused ring aromatic compounds." e.g.,



Naphthalene Anthracene

NOMENCLATURE

Common or Trivial Names:

In the early days, the compounds were named on the basis of their history; the method of preparation or name of the person working on it, e.g., the name **marsh gas** as given to methane because it was found in marshy places. Acetic acid derives its name from vinegar (Latin, acetum means vinegar). Organic compounds were named after a person (Barbara) like barbituric acid ($C_4H_4N_2O_3$). Such a system may have a certain charm but is never manageable.

In this system, first four members of the series are known as methane (CH_4), ethane, (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}). Rest of the members are named by prefixing Greek numeral, indication the number of carbon atoms (penta, hexa, hepta, etc.) and the suffix "ane".

TYPES OF CARBON ATOMS IN SATURATED HYDROCARBONS

Usually in saturated hydrocarbons, four types of carbon atoms are present:

(1) **Primary (1°) carbon:** Atom having either one or more of its valencies satisfied with another carbon atom.

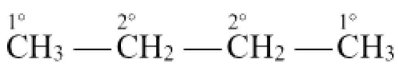
(2) **Secondary (2°) carbon:** Atom having its two valencies satisfied with two other carbon atoms.

(3) **Teritiary (3°) carbon:** Atom having its three valencies satisfied with three other carbon atoms.

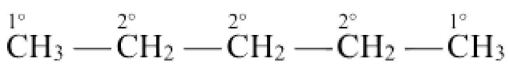
(4) **Quaternary (4°) carbon:** Atom having its all the four valencies satisfied with four carbon atoms.

Some points for common naming are given below:

(i) In open chain hydrocarbons only primary and secondary carbon atoms are present. e.g.,



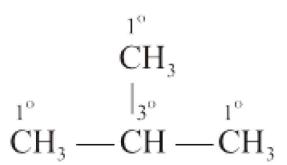
(n-Butane)



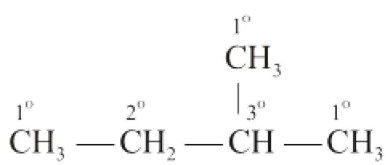
(n-Pentane)

Such carbons are termed as normal and denoted by "n".

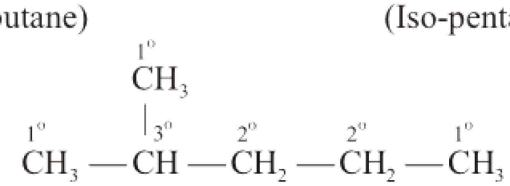
(ii) Branched chain hydrocarbon having tertiary carbon (3°) atom are named as "iso" hydrocarbons. e.g.,



(Iso-butane)

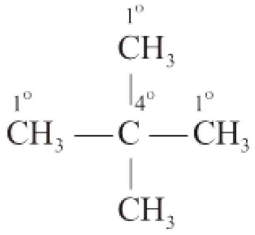


(Iso-pentane)

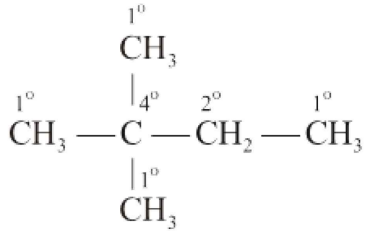


(Iso-hexane)

(iii) The branched chain hydrocarbons having quaternary carbon atom (4°) are named as "neo" hydrocarbons.



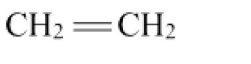
(Neo-pentane)



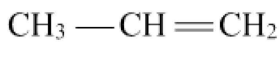
(Neo-hexane)

COMMON NAMES OF ALKENES

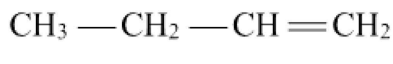
Common name of alkene are formed by replacing **"ane"** of alkane by **"ylene"**. e.g.,



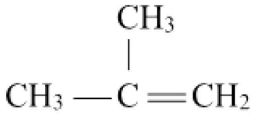
(Ethylene)



(Propylene)



(n-Butylene)



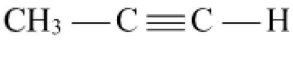
(Iso-butylene)

COMMON NAMES OF ALKYNE

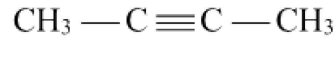
The first member of alkyne series is acetylene, C_2H_2. All the common name of alkynes are derived from acetylene.



(Acetylene)



(Methyl acetylene)



(Dimethyl acetylene)

The prefixes used in the common names have limited used and cannot be applicable for more complex molecules. Moreover, common names give only minimum information about the structure of compound.

IUPAC NAMES

In 1889 the solution for naming the organic compounds systematically was brought by international Chemical Congress. A report was accepted in 1892 in Geneva but it was found incomplete. In 1930, international union of chemistry (IUC) gave a modified report which is also referred as Liege Rules. This report was further modified by International Union of Pure and Applied Chemistry (IUPAC) in the year 1947. Since

that date, the union has issued periodic reports on rules for the systematic nomenclature of organic compounds. The most recent of which was published in the year 1979. IUPAC system of nomenclature is based on the following principle.

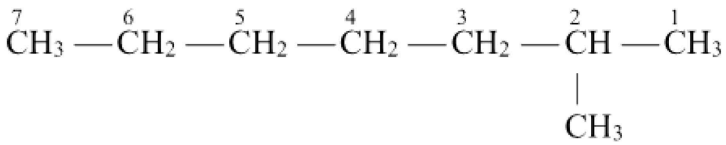
"Each different compound should have a different name."

Thus through a systematic set of rules, the IUPAC system provides different names for more than 7 million known organic compounds.

RULES FOR NAMING ALKANES

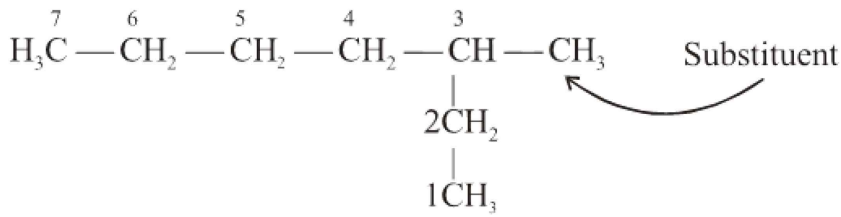
Branched – chain alkanes are named according to the following rules.

(1) Select longest possible chain of carbon atoms. Length of chain determines the parent name e.g., the longest chain in the given formula is heptane.



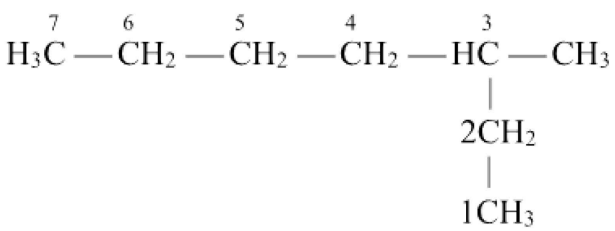
The carbon atoms which are not part of the chain, are called substituent.

(2) Start numbering from that end which is near to the substituent.

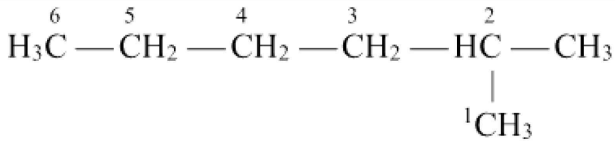




(3) Write the location (number at which substituent is attached) and name of substituent before the parent name or stem name. e.g.,

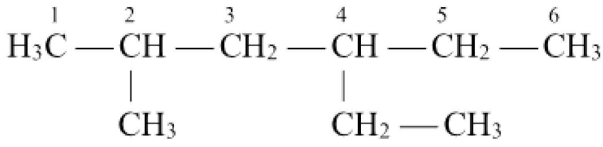


3-Methylheptane



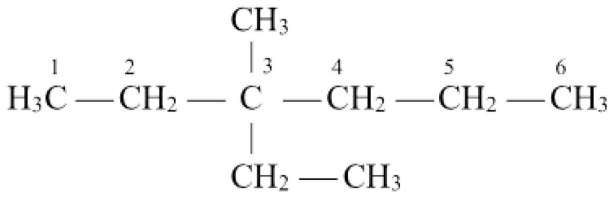
2-Methyl hexane

(4) If more than one substituents of different types are present, they should be named in alphabetic order. (ethyl before methyl). e.g.,



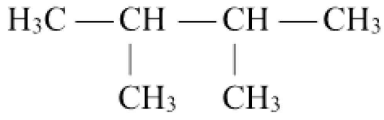
4-Ethyl 2-Methyl hexane

(5) When two substituents are present at the same carbon, write that number twice.

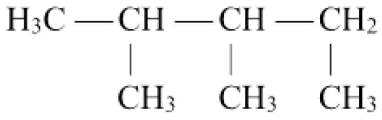


3-Ethyl-3-methylhexane

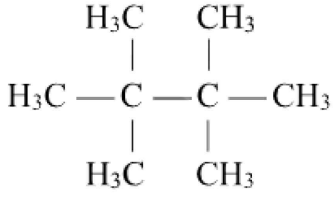
(6) If similar substituents are present more than once, the number of carbon atom to which substituent is attached given each time. Prefixes di, tri, tetra, etc., are used for the same type of substituents.



2,3-Dimethylbutane



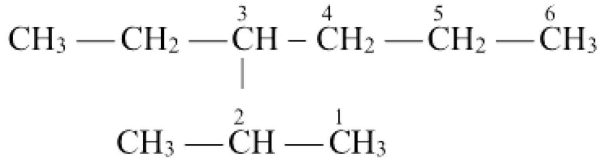
2,3-Dimethylpentane



2,2,3,3, Tetramethylbutane

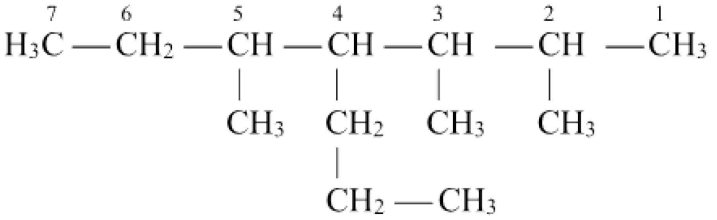
(7) When two chains of equal length compete for selection as the parent chains, choose the chain with greater number of substituents.

(i)



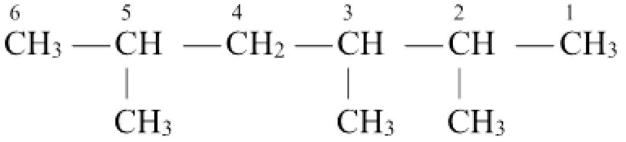
3-Ethyl-2-methyl Hexane (not 3-isopropyl hexane)

(ii)



2,3,5-Trimethyl 4-n-propyl heptane

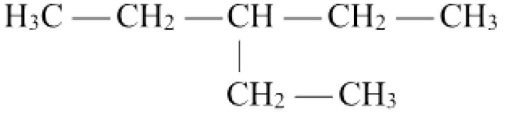
(8) When branching first occurs at an equal distance from either end of the longest chain, choose the name that gives the lower number at the first point of difference.



2,3-5-Trimethylhexane (not 2,4,5-trimethylhexane)

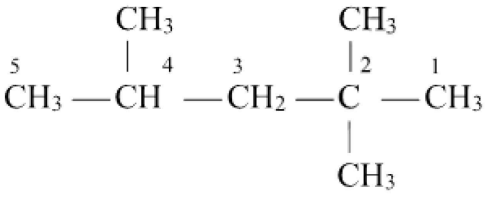
Some Other Examples of Alakens:

(1)



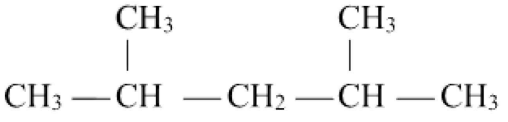
3-Ethyl pentane

(2)



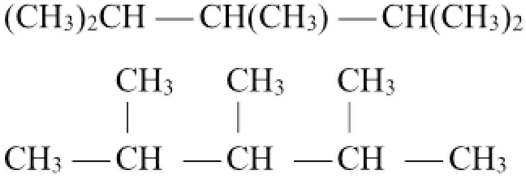
2,2,4-Trimethyl pentane

(3)



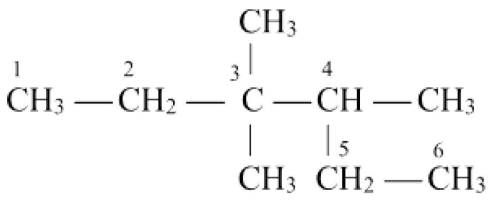
2,4-Dimethyl pentane

(4)



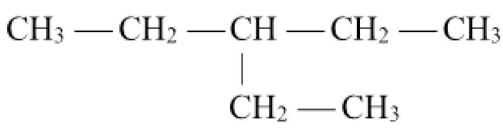
2,3,4-Trimethyl pentane

(5) $CH_3—CH_2—C(CH_3)_2—CH(CH_2—CH_3)—CH_3$



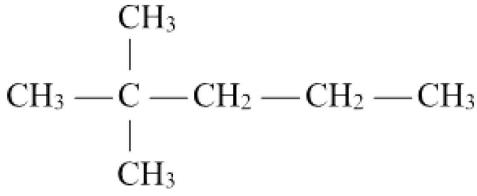
3,3,4 Trimethyl-hexane

(6) $(CH_3CH_2)_3CH$



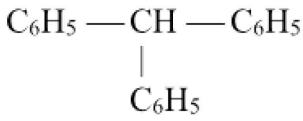
3-Ethyl pentane

(7) $CH_3C(CH_3)_2(CH_2)_2CH_3$



2,2-Dimethyl pentane

(8) $(C_6H_5)_3CH$



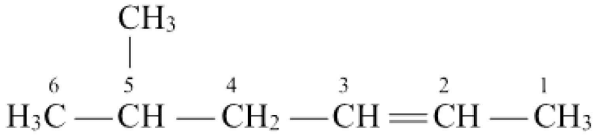
Triphenyl methane

Note: C_6H_5 is an aryl radical and its name is phenyl.

RULES FOR NAMING ALKENE

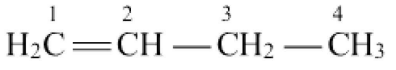
(1) Select longest possible chain of carbon atoms containing C = C double bond.

(2) Start numbering from that end which is nearer to the double bond. Suffix of alkene is **"ene"**. The suffix **"ane"** of alkanes is changed by "ene" for alkenes.

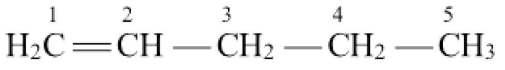


5-Methyl-2-hexene

(3) Mention the location of the double bond by using the number of the first atom of the double bond as a prefix.

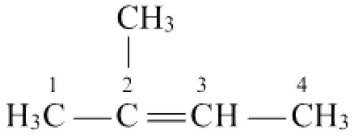


1-Butene

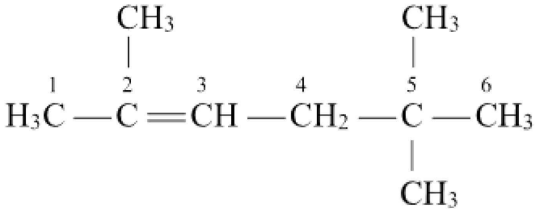


1-Pentene

(4) Indicate the locations of the substituent groups by the numbers of the carbon atoms to which they are attached.

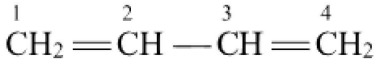


2-Methyl-2-butene

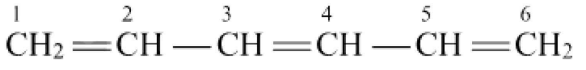


2,5,5-Trimethyl-2-hexene

(5) If more than one double bonds are present, indicate the prefix diene for two, triene for three double bonds. etc.

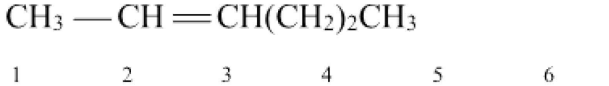


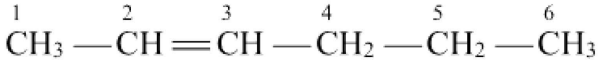
1, 3-Butadiene or Buta-1, 3-diene



1,3,5-Hexatriene or hexa 1,3,5-triene

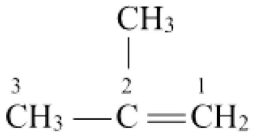
Some Other Examples of Alkenes:

(1) 



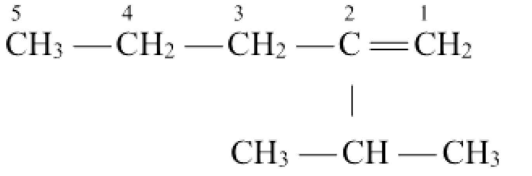
2-Hexene

(2) $(CH_3)_2C=CH_2$



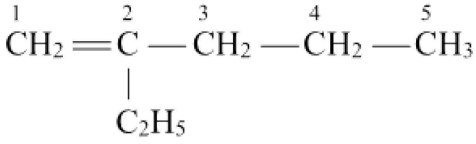
2-Methyl-1-Propene

(3) $CH_3-CH_2-CH_2-C(CH(CH_3)_2)=CH_2$



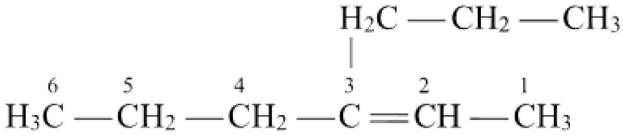
2-Iso propyl-1-pentene

(4) $CH_2=C(C_2H_5)-CH_2-CH_2-CH_3$



2-Ethyl-1-pentene

(5) $H_3C-CH_2-CH_2-C(CH_2-CH_2-CH_3)=CH-CH_3$



3-n-Propyl 2-hexene

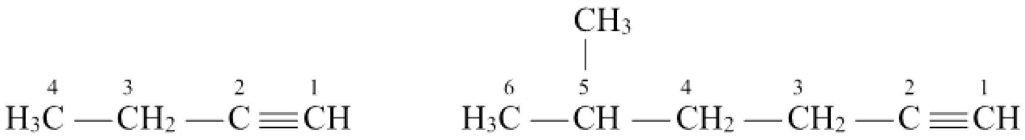
RULES FOR NAMING ALKYNES

(1) Select longest possible chain of carbon atoms containing C ≡ C triple bond. The suffix of alkyne is "yne". The suffix of alkane "ane" is replaced by "yne" for alkynes.



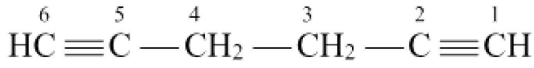
Ethyne Propyne

(2) The position of triple bond is shown by numbering the alkyne, so that minimum number is assigned to the triple bond.



Butyne 5-Methyl-1-hexyne

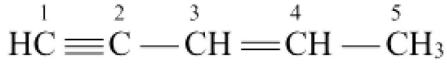
(3) If a hydrocarbon contains more than one triple bonds, it is named as alkadiyne and triyne etc., depending on the number of triple bonds.



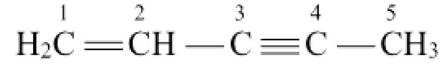
Hex-1, 5-diyne or 1, 5-hexadiyne

(4) If both double and triple bonds are present in the compound then ending "en-yne" is given to the root.

(a) Lowest possible number is assigned to a double or a triple bond irrespective of whether "one" or "yne" gets the lower number.

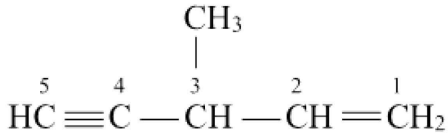


Pent-3-en-1-yne



Pent-1-en-3-yne

(b) If double and triple bonds are present at equal position, double bond will be preferred for numbering and naming.

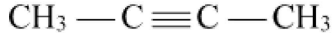


3-Methyl Pent-1-en-4-yne

Suffix of alkene will be "en" instead of "ene" when another functional is also present in a molecule.

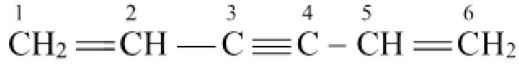
Some Other Examples of Alkynes:

(1)



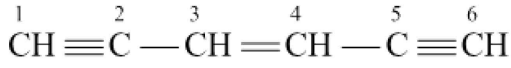
2-Butyne

(2)



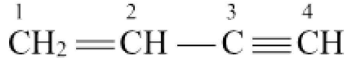
Hex 1,5-dien-3-yne

(3)



Hex-3-en-1,5-diyne

(4)



But-1-en-3-yne

ALKANES OR PARAFFINS

Alkanes are saturated hydrocarbons with general formula C_nH_{2n+2}. Methane (CH_4) is the simplest member of this family. Each carbon atom of saturated hydrocarbon is sp^3-hybridized with tetrahedral geometry.

GENERAL METHOD FOR PREPARATIONS

(1) Hydrogenation of unsaturated hydrocarbons (Sabatier's and Sendern's reaction):

Hydrogenation of alkenes or alkynes in the presence of Nickel catalyst at 200–300°C yields alkanes. e.g.,

$$R - CH = CH_2 + H_2 \xrightarrow[200–300°C]{Ni} R - CH_2 - CH_3$$

Alkene Alkane

$$CH_2 = CH_2 + H_2 \xrightarrow[200–300°C]{Ni} CH_3 - CH_3$$

The hydrogenation can also be carried out with plantinum or palladium at room temperature but they are expensive than Nickel.

This method is of industrial importance. Production of vegetable ghee by the catalytic hydrogenation of vegetable oil (unsaturated fatty acids) is an example of the application of this method on industrial scale.

(2) From Alkyl Halides:

(a) An alkane is produced when an alkyl halide reacts with zinc in the presence of an aqueous acid such as HCl or CH_3COOH.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$

$$R - X + [H] \xrightarrow{HCl + Zn} R - H + HX$$

Alkyl halide Alkane

$$CH_3 - I + 2[H] \xrightarrow{Zn + HCl} CH_4 + HI$$

Methyl iodide Methane

$$CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3 + [H] \xrightarrow{Zn + HCl} CH_3 - CH_2 - CH_2 - CH_3 + HBr$$

2-Bromo-butane Butane

(b) **Hydrogenolysis:** Alkanes can also be prepared from alkyl halides using palladium charcoal as a catalyst. The method is known as Hydrogenolysis (hydrogenation which takes place by cleavage of H-H bond).

$$R - X + H_2 \xrightarrow{Pd/C} R - H + H - X$$

$$CH_3I + H_2 \xrightarrow{Pd/C} CH_4 + HI$$

(3) **Decarboyxlation of Mono-carboxylic Acids:**

(a) When sodium salts of fatty acids are heated with soda-lime (prepared by soaking quick lime (CaO) with caustic soda solution and drying the product). They eliminate a molecule of CO_2 to form alkanes except sodium formate which forms H_2.

$$R-\overset{\overset{O}{\|}}{C}-O^-Na^+ + NaOH \xrightarrow{CaO} R-H + Na_2CO_3$$

(Sodium salt of an acid)

$$CH_3-\overset{\overset{O}{\|}}{C}-ONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

(Sod-acetate)

$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-ONa + NaOH \xrightarrow[\Delta]{CaO} CH_3-CH_3 + Na_2CO_3$$

(Sod-propionate)

Note: Sodium formate forms hydrogen

$$H-\overset{\overset{O}{\|}}{C}-ONa + NaOH \xrightarrow[\Delta]{CaO} H_2 + Na_2CO_3$$

(Sod-formate)

(b) **Kolbe's Electrolytic Method:**

When a concentrated solution of sodium of sodium or potassium salt of a mono carboxylic acid is electrolysed, an alkane is produced. This method is only suitable for the preparation of symmetrical alkanes i.e., those of the type R – R. Methane cannot be prepared by this method.

$$2RCOO^-Na^+ + 2H_2O \xrightarrow{Electrolysis} R - R + 2CO_2 + 2NaOH + H_2$$

Mechanism:

When potassium salt of acetic acid is electrolysed, acetate ions migrate towards the anode gives up one electron to produce free radical (CH_3COO), which decomposes to give a methyl free radical (CH_3) and CO_2. Two such methyl radicals combine to give ethane.

$$2H_3C-\overset{\overset{O}{\|}}{C}-O^-K^+ \rightleftharpoons 2H_3C-\overset{\overset{O}{\|}}{C}-O^- + 2K^+$$

At Anode:

$$2H_3C-\overset{\overset{O}{\|}}{C}-O^- \longrightarrow 2H_3C-\overset{\overset{O}{\|}}{C}-O^{\bullet} + 2e^-$$

$$2H_3C-\overset{\overset{O}{\|}}{C}-O^{\bullet} \longrightarrow 2CH_3^{\bullet} + 2CO_2$$

$$CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow H_3C-CH_3$$

At Cathode:

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

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

(4) From Aldehyde and Ketones (Carbonyl Compounds):

(a) Clemensen Reduction:

In this reaction, ketones react with zinc amalgam and hydrochloric acid to form alkane (an alloy containing mercury as one of the components is called amalgam).

$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + 4[H] \xrightarrow{Zn\text{-}Hg/HCl} CH_3-CH_2-CH_3 + H_2O$$

Acetone Propane

(b) Wolf Kishner's Reduction:

Aldehyde reacts with KOH and hydrazine and changes to alkane.

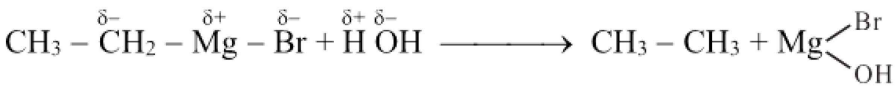
$$CH_3-\overset{\overset{O}{\|}}{C}-H + 4[H] \xrightarrow{N_2H_4/KOH} CH_3-CH_3 + H_2O$$

Acetaldehyde Ethane

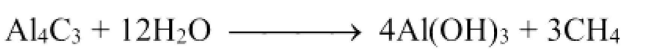
(5) From Grignard Reagent:

Alkyl halides react in anhydrous ether with magnesium to form alkyl magnesium halides, known as Grignard Reagent. They decompose on treatment with water or dilute acid to give alkanes.





(6) Hydrolysis of Al_4C_3 (method for methane only):



PHYSICAL CHARACTERISTICS OF ALKANES

(1) Alkanes containing upto four carbon atoms are colourless, odourless **gasses** while pentane to heptadecane (C_5 to C_{17}) are colourless **liquids**. The higher members from C_{18} onwards are **waxy solids** which are also colourless and odourless.

(2) Alkanes are **non-polar** or very weakly polar and are insoluble in polar solvents like water, but soluble in non-polar solvents like benzene, ether, carbon tetrachloride, etc.

(3) Their physicals constants like boiling points, melting points, density etc., increase with the increase in number of carbon atoms, whereas solubility decreases with increase in molecular mass. The boiling point increases by 20°C to 30°C for addition of each CH_2 group to the molecule.

The boiling points of alkanes having **branched chain** structures are **lower** than their isomeric normal chain alkanes, e.g., n-butane has a higher boiling point (–0.5°C) than isobutane (–11.7°C) B.P of n-pentane = 36°C, Isopentane = 28°C, Neopentane = 9.5°C and Melting point of n-pentane = –130°C.

and M.P. of Iso-pentane –160°C

M.P. of Neo-pentane –17°C

Straight chain alkanes have **greater polarizability** than branched chain alkanes and have greater intermolecular forces in them.

(4) The melting points and boiling points of alkanes also increases with the increase in molecular masses but this increase is not so regular.

REACTIVITY OF ALKANES

The alkanes or paraffins (Latin: parum = little, affins = affinity) under ordinary condition are inert towards acids, alkalis, oxidizing agents and reducing agents. However, under suitable conditions, alkanes do undergo two types of reactions.

(i) Substitution reactions

(ii) Thermal and catalytic reactions

These reactions take place at high temperature or on absorption of light energy through the formation of highly reactive free radicals.

Non-reactivity of alkanes is due to the following reasons:

(1) Non-polar Nature of C – H Bond:

The reactivity of alkanes under normal conditions may be explained on the basis of the non-polarity of the bonds forming them. The electronegativity values of carbon (2.5) and hydrogen (2.1) do not differ appreciably from the ionic reagents such as acids, alkalies, oxidizing agents, etc., and find no reaction site in the alkane molecules to which they could be attached.

(2) Inertness of σ-bond:

The un-reactivity of alkanes can also be explained on the basis of intertness of a σ-bond. In a σ-bond the electrons are very tightly held between the nuclei and electrons present in a σ-bond can neither attack on any electrophile nor a nucleophile can attack on them. Both these facts make alkanes less reactive.

REACTIONS OF ALKANES

(1) Combustion:

Burning of an alkane in presence of oxygen is known as **Combustion**.

Complete combustion of an alkane yields CO_2, H_2O and heat. *"The amount f heat evolved when one mole of a hydrocarbon is burnt to CO_2 and H_2O is called heat of combustion."* e.g.,

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad (\Delta H = -891 \text{ kJ mol}^{-1})$$

Although the reaction is highly exothermic, it required very high temperature to initiate it, e.g., by a flame or a spark.

Combustion is the major reaction occurring in the internal combustion engines of automobiles. A compressed mixture of alkanes and air burns smoothly in the internal combustion engine and increases its efficiency.

(2) Oxidation:

Oxidation of methane under different conditions give different products.

(i) Incomplete oxidation occurs in a limited supply of oxygen or air and results in the formation of CO and carbon black.

$$3CH_{4(g)} + 4O_{2(g)} \xrightarrow{\text{Flame}} 2CO_{(g)} + 6H_2O_{(g)} + C_{(g)}$$

(ii) Catalytic Oxidation: Lower alkanes when burnt in the presence of metallic catalysts, at high temperature and pressure results in the formation of useful products.

$$CH_4 + [O] \xrightarrow[400°C/200\ atm.]{Cu} H_3C - OH \text{ (Methanol)}$$

$$H_3C - OH + [O] \xrightarrow[''']{Cu} HCHO \quad \text{(Methanal)} + H_2O$$

$$HCHO + [O] \xrightarrow[''']{Cu} HCOOH \quad \text{(Methanoic acid)}$$

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

Catalytic oxidation of alkanes is used industrially to prepare higher fatty acids used in soap and vegetable oil industries.

(3) Nitration:

It is a substitution reaction of alkanes in which a hydrogen atom of an alkanes is replaced by nitro group ($-NO_2$). Alkanes undergo vapour-phase nitration under drastic condition (at 400–500°C) to give nitroalkanes. e.g.,

$$CH_4 + HONO_2 \longrightarrow CH_3NO_2 + H_2O$$

Nitromethane

Nitroalkanes generally find use as fuels, solvents, and in organic synthesis.

Nitration of higher alkanes forms number of nitro-alkanes due to cracking. It is called vapour-phase nitration. For example:

$CH_3 - CH_2 - CH_2 - CH_3 + HNO_3 \longrightarrow CH_3 - CH_2 - CH_2 - CH_2$ (with NO_2)

n-butane

1-Nitrobutane

$+ CH_3 - CH_2 - CH(NO_2) - CH_3$

2-Nitrobutane

$+ CH_3 - CH_2 - CH_2 - NO_2$

1-Nitropropane

$+ CH_3 - CH(NO_2) - CH_3$

2-Nitropropane

$+ CH_3 - CH_2 - NO_2$

Nitroethane

$+ CH_3 - NO_2$

Nitromethane

(4) Halogenations (Substitution Reaction):

Alkanes react with chlorine and bromine in the presence of sunlight or UV light or at high temperature resulting in the successive replacement of hydrogen atoms with halogens called **substitution**. Extent of halogenations depends upon the amount of halogen used. If halogen and alkanes are taken with 1 : 1 ratio CH_3Cl is formed. If greater amount of halogen is used, further substitution of halogen will also takes place.

Reaction of alkanes with fluorine is highly violent and results in a mixture of carbon, fluorinated alkanes and hydrofluoric acid. Iodine does not substitute directly because the reaction is too slow and reversible. The order of reactivity of halogens is $F_2 > Cl_2 > Br_2 > I_2$.

Step-I: $Cl - Cl \longrightarrow Cl^{\bullet} + Cl^{\bullet}$ (Initiation)

Step-II: $H_3C - H + Cl^{\bullet} \longrightarrow CH_3^{\bullet} + HCl$

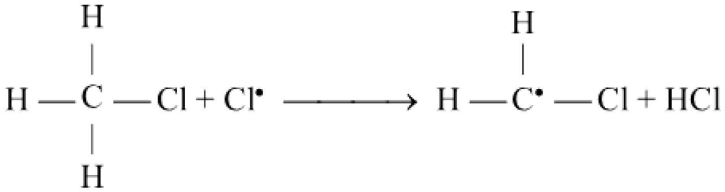
$CH_3^{\bullet} + Cl - Cl \longrightarrow CH_3 - Cl + Cl^{\bullet}$ } (Propagation)

Step-III: $CH_3^{\bullet} + Cl^{\bullet} \longrightarrow CH_3Cl$

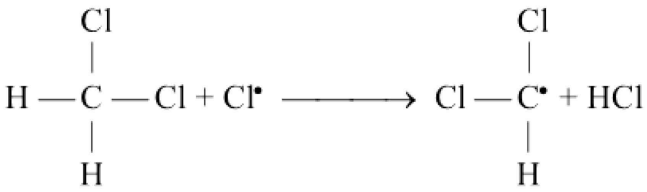
or $Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$ } (Termination)

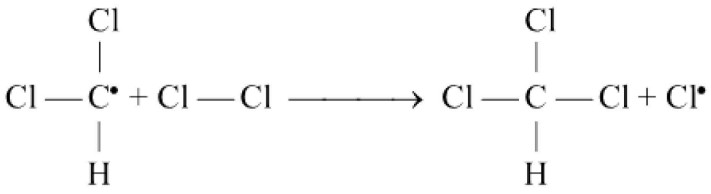
or $CH_3^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3 - CH_3$

By further substitution of halogens, following products are obtained.

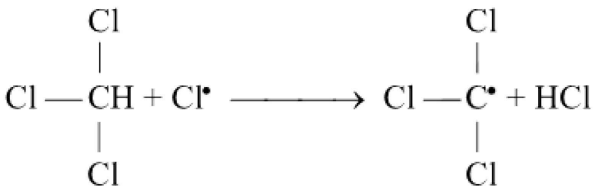


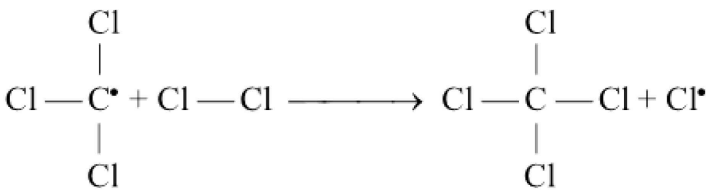
$$CH_2^{\bullet} - Cl + Cl - Cl \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$





Chloroform or trichloromethane





Tetrachloromethane or carbon tetrachloride

Uses of Methane:

(1) Methane is used for the preparation of methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4).

(2) Methane is important constituent of natural gas and used as fuel.

(3) Methane is used for the industrial preparation of methyl alcohol (CH_3OH), formaldehyde (HCHO) and formic acid (HCOOH).

(4) Methane is used for preparation of carbon black used in paint, printing inks and automobile tyres.

(5) By cracking of methane hydrogen gas is produced. This gas is used for the manufacture of vegetable ghee and fertilizers.

(6) In the manufacture of urea.

ALKENES

Alkenes have two hydrogen atoms less than the corresponding saturated hydrocarbons. They are also known as Olefins (derived from Latin word olefins meaning oil forming) because lower members from oily products on treatment with chlorine or bromine. The simplest olefin is C_2H_4, ethene.

Alkene have one double bond are known as mono-enes with general formula C_nH_{2n}. Alkenes containing two double are called dienes.

GENERAL METHODS OF PREPARATION

(1) Dehydrohalogenation of Alkyl Halides (Elimination Reaction):

Alkyl halides on heating with alcoholic potassium hydroxide undergo dehydrohalogenation i.e., elimination of a halogen atom together with a hydrogen atom from adjacent carbon atoms.

(a)
$$CH_3-CH_2-\underset{\displaystyle X}{\underset{|}{CH_2}}+KOH \xrightarrow{\text{Alcoholic}} CH_3-CH=CH_2+KX+H_2O$$

$$\underset{\displaystyle H}{\underset{|}{H_2C}}-\underset{\displaystyle Br}{\underset{|}{CH_2}}+KOH \xrightarrow{\text{Alcoholic}} \underset{\text{Ethene}}{H_2C=CH_2}+KBr+H_2O$$

$$H_3C-CH_2-CH_2-Br+KOH \xrightarrow{\text{Alcoholic}} H_3C-CH=CH_2+KBr+H_2O$$

(b) **Note:** With aqueous KOH, alcohols are formed:

$$CH_3-CH_2-Cl+KOH_{(aq)} \longrightarrow CH_3-CH_2-OH+KCl$$

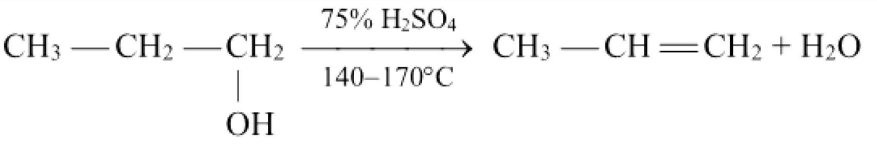
(2) Dehydration Alcohols:

Alcohols when dehydrated in the presence of a catalyst give alkenes. The best procedure is to pass vapours of alcohol over heated alumina.

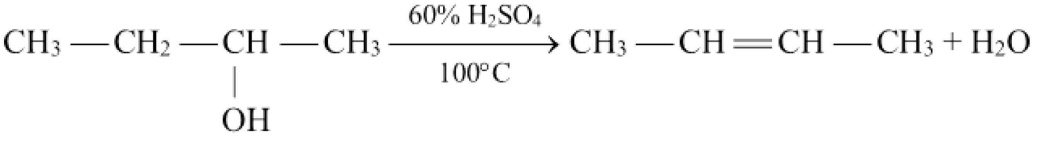
$$CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH_2}} \xrightarrow[340-450^\circ C]{Al_2O_3} \underset{\text{Propene}}{CH_3-CH=CH_2}+H_2O$$

$Al_2O_3.P_4O_{10}$, H_2SO_4 (conc.) H_3PO_4 are dehydrating agent used for preparation of alkane. The ease of dehydration of various alcohols is in the order.

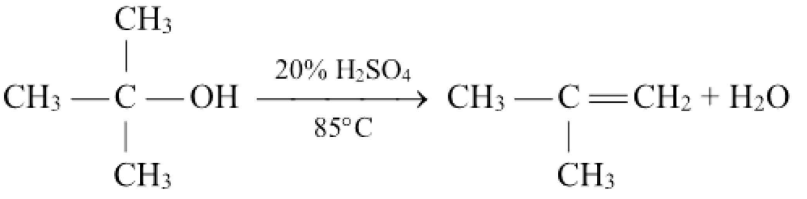
Ter. alcohol > Sec. alcohol > Pri-alcohol



Primary alcohol



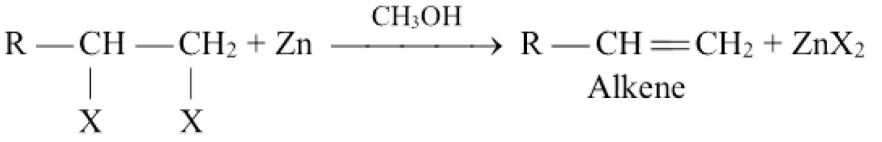
Secondary alcohol



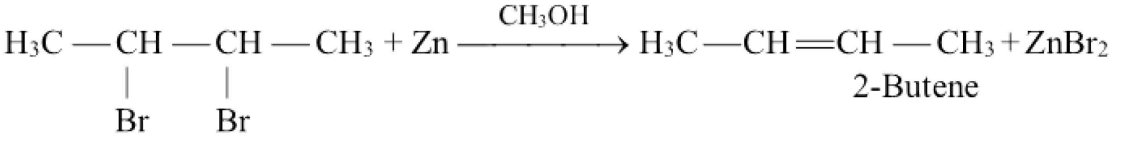
Ter-alcohol Isobutylene

(3) Dehalogenation of Vicinal Dihalides:

Vic-dihalides have halogens on adjacent carbon atoms. Dehalogenation occurs when dihalide is treated with zinc dust in an anhydrous solvent like methanol or acetic acid.



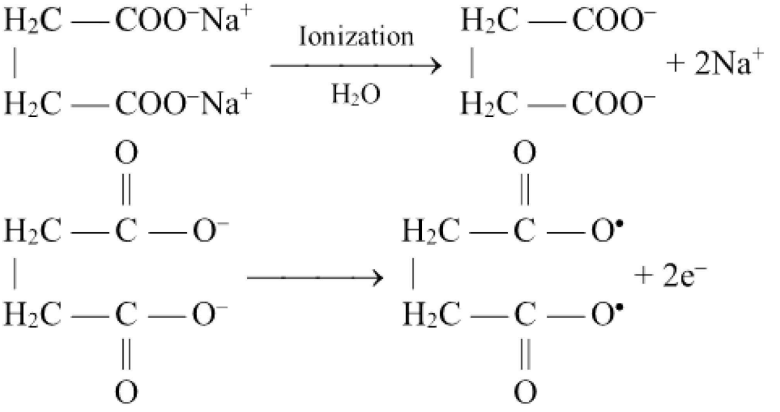
Alkene

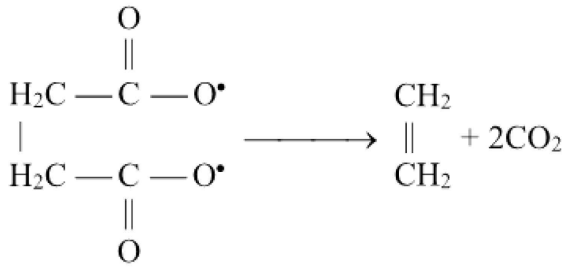


2-Butene

(4) Electrolysis of Salts of Dicarboxylic Acid (Kolbe's Electrolytic Method)

When sodium of potassium salts of the dicarboxylic acid like succinic acid are subjected to electrolysis in an aqueous solution, alkenes are formed.





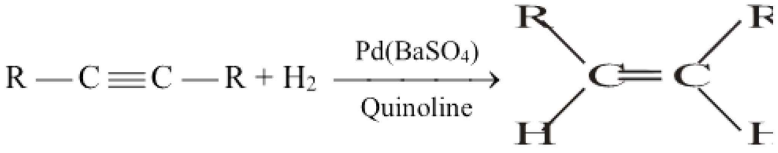
At Cathode:

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

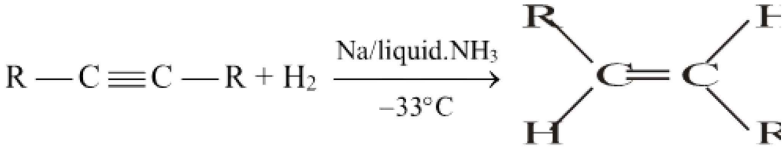
$$2Na^+ + 2OH^- \longrightarrow 2NaOH$$

(5) Partial Hydrogenation of Alkyne:

Controlled hydrogenation of alkynes with hydrogen gas in an equi-molar ratio over heated catalysts, gives alkenes. The catalyst is finely divided palladium supported on $BaSO_4$ and poisoned by treatment with quinoline (Lindler's catalyst).



Cis-Alkene



Trans-alkene

PHYSICAL CHARACTERISTICS

(1) First three members i.e., ethene, propene and butene are gases at room temperature while C_5 to C_{15} are liquids and the higher members are solids.

(2) They are insoluble in water but soluble in alcohol.

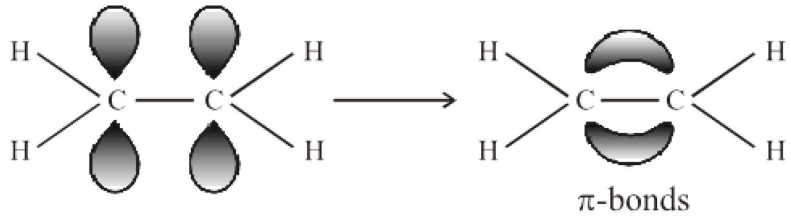
(3) They have characteristic smell and burn with luminous flame.

(4) Unlike alkanes, they show weakly polar properties because of sp^2 hybridization.

REACTIVITY OF ALKENES

In alkenes, double bond is present between two carbon atoms, one is sigma and other is π-bond, σ-bond is formed by linear overlapping of partially filled sp^2 hybrid orbitals and electron density is maximum between two nuclei or at bond axis. π-bond is

formed by the parallel overlapping of p-orbitals of carbon atoms. In π-bond, electron density is maximum above and below the bond axis. Due to less overlapping π electrons are not firmly attached. Due to less overlapping region π-bonds are weaker bond than sigma bonds. π-electrons are more exposed electrons and an electrophile (electron deficient specie) can attack easily on π-electrons. Thus the compounds containing π-bond are more reactive than alkane. Alkenes usually undergo addition reactions.



REACTIONS OF ALKENES

(a) Addition Reactions:

(1) Hydrogenation (addition of hydrogen):

Hydrogenation is a process in which a molecule of hydrogen is added to an alkene in the presence of a catalyst and at moderate pressure (1-5 atm) to give a saturated compound. The process is known as catalytic hydrogenation.

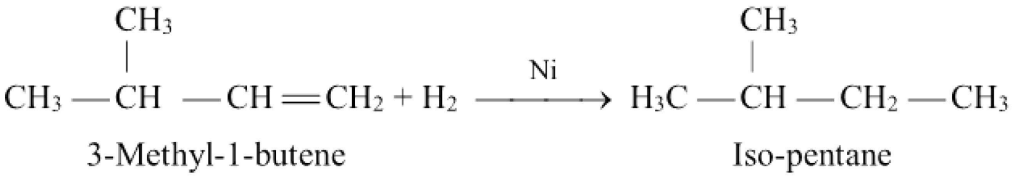
It is a highly exothermic process and the amount of heat evolved when one mole of an alkene is hydrogenated is called heat of hydrogenration. The heat of hydrogenation of most alkenes is about 120 kJ $mole^{-1}$ for each double bond present in a molecule. The catalysts used are Pt, Pd or Raney Nickel.

Raney Nickel:

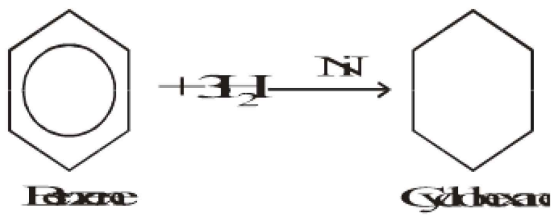
It is prepared by treating a Ni — Al alloy with caustic soda.

$$Ni — Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + \frac{3}{2}H_2$$

Most alkenes are hydrogenated over Raney Nickel at about 100°C and 3-atmospheric pressure.



3-Methyl-1-butene Iso-pentane



Catalytic hydrogenation of alkenes is used in the laboratory as well as in industry. In industry, it is used for the manufacture of **vegetable ghee** from vegetable oils. In the laboratory, it is used to synthesize many chemicals like alkane or cycloalkane. Hydrogenation is also used to determine the degree of unsaturation of compound.

(2) Addition of Hydrogen Halides:

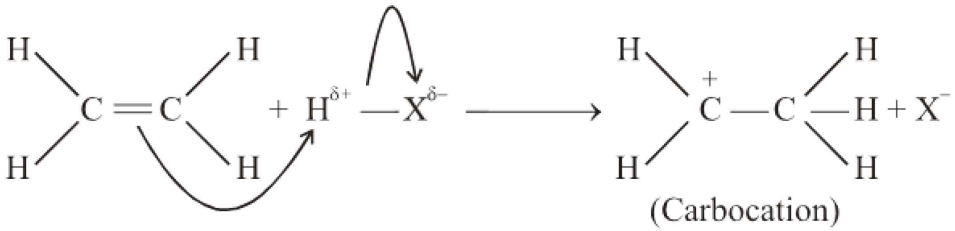
Alkenes react with aqueous solution of halogen acids to form alkyl halides. The order or reactivity of halogen acids is HI > HBr > HCl.

$$R-CH=CH_2 + HX \longrightarrow RCH(X)-CH_3$$

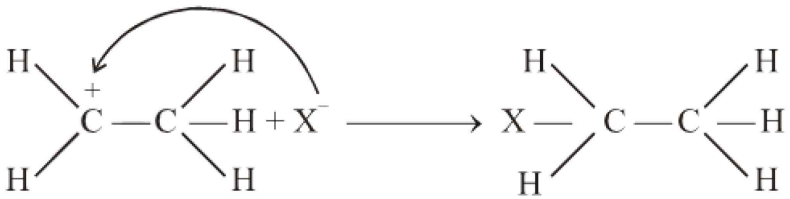
$$H_2C=CH_2 + HCl \longrightarrow H_3C-CH_2Cl$$

Mechanism:

The addition of a hydrogen halides to an alkene takes place in two steps. Alkene accepts the proton of hydrogen halide to form a carbocation.



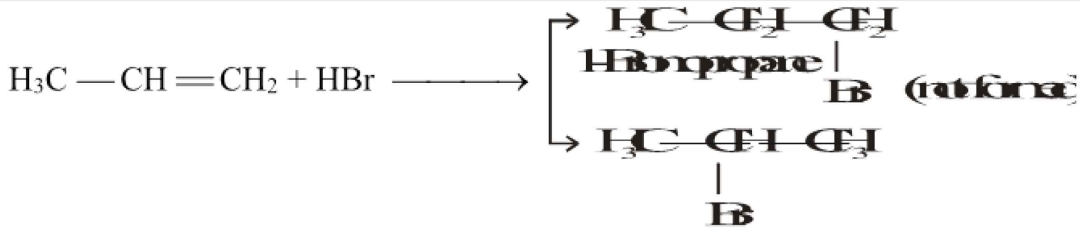
The carbocation the reacts with the halide ion, to form alkyl halide.



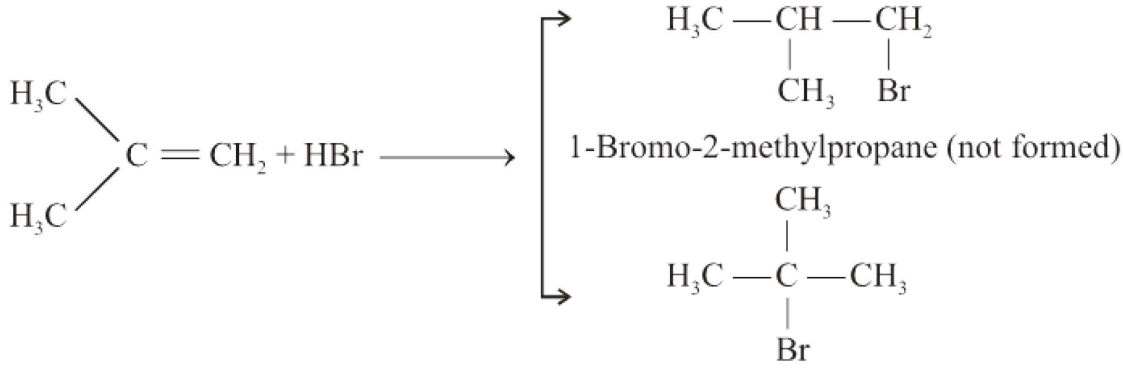
Markownikov's Rules:

"If unsymmetrical reagent is added to unsymmetrical alkene, the negative part of reagent will be added to that carbon which have least number of hydrogen atoms."

Unsymmetrical alkenes are those which have different number of hydrogen on both side of double bond.



2-Bromopropane (Actual product)

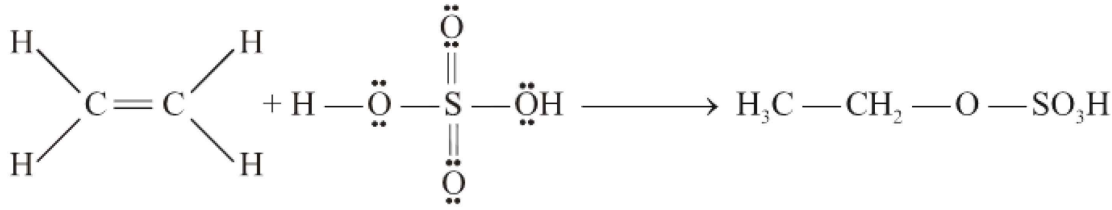


1-Bromo-2-methylpropane (not formed)

2-Bromo-2-methylpropane
(Actual Product)

(3) Addition of Sulphuric Acid:

When alkenes are treated with cold concentrated sulphuric acid, they are dissolved because they react by addition to form alkyl hydrogen sulphate.

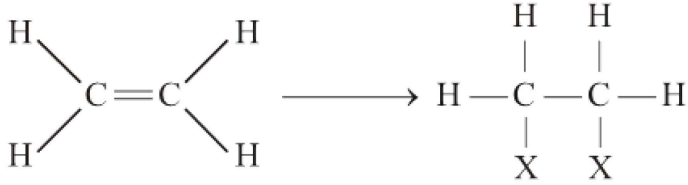


This alkyl hydrogen sulphates on boiling with water decomposes give corresponding alcohols. It is called "hydration".

$$H_3C-CH_2-O-SO_3H + H_2O \xrightarrow{100^\circ C} H_3C-CH_2-OH + H_2SO_4$$

(4) Addition of Halogens:

The alkenes on reacting with halogen in an inert solvent like carbon tetrachloride at room temperature, give vicinal dihalides or 1, 2 dihalogenated products.

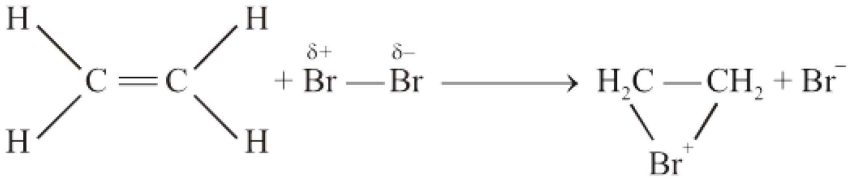


Vicinal dihalide

Br_2 and Cl_2 are effective electrophilic reagents. Fluorine is too reactive to control the reaction. Iodine does not react.

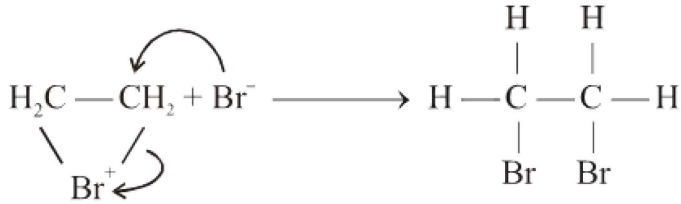
Mechanism:

(a) A bromine molecule becomes polarized as it approaches the alkene. This polarized bromine molecule transfers a positive bromine atom to the alkene resulting in the formation of a bromonium ion.



Bromonium ion

(b) The nucleophilic bromide ion then attacks on the carbon of the bromonium ion to form vicinal dibromide and the colour of bromine is discharged.



Bromonium ion 1,2-dibromoethane

This test is used for the detection of a double bond or detection of unsaturation of a compound.

(5) Addition of Hypohalous Acid (HOX):

If the halogenation of an alkene is carried out in an aqueous solution, halo alcohol is formed called a Halohydrin. In this reaction, molecules of the solvent also become reactants.

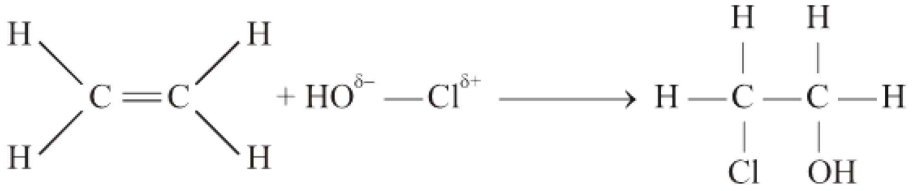
$$X_2 + H_2O \longrightarrow HOX + HX$$



$X_2 = Cl_2$ or Br_2 Halohydrin

For example:

(i) $Cl_2 + H_2O \longrightarrow HCl + HOCl$



Ethylene chlorohydrin

(ii) $CH_3 - CH = CH_2 + \overset{\delta-}{H}O - \overset{\delta+}{C}l \longrightarrow CH_3 - \underset{OH}{CH} - \underset{Cl}{CH_2}$

Propene

(1-chloro-2-propanol)

(Propylene chlorohydrin)

(b) Oxidation Reactions:

(1) Addition of Oxygen:

Alkenes when mixed with oxygen or air and passed over a silver catalyst at high temperature and pressure, add an atom of oxygen to form epoxides. Epoxides serve as the starting substances for the industrial production of glycols.

$$H_2C = H_2C + 1/2O_2 \xrightarrow[300^oC]{Ag_2O} H_2C - CH_2 \quad (O)$$

Ethylene oxide (Epoxide)

$$CH_3 - CH = CH_2 + 1/2O_2 \xrightarrow[300^oC]{Ag_2O} CH_3 - CH - CH_2 \quad (O)$$

Propylene oxide (Epoxide)

(2) Hydroxylation (Baeyers Test):

When alkenes are treated with mild oxidizing reagents like dilute (1%) alkaline $KMnO_4$ solution (Baeyer's Reagent) at low temperature, hydroxylation of double bond occurs resulting in the formation of dihydroxy compounds known as vicinal glycols. The pink colour of $KMnO_4$ solution is discharged during the reaction. It is also a test for the presence of unsaturation in the molecules.

$$3CH_2 = CH_2 + 2KMnO_4 + 4H_2O \longrightarrow \underset{OH}{CH_2} - \underset{OH}{CH_2} + 2MnO_2 + 2KOH$$

Ethylene glycol

$$3CH_3 - CH_2 - CH = CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3CH_3 - CH_2 - \underset{OH}{CH} - \underset{OH}{CH_2} + 2MnO_2 + 2KOH$$

(1,2-Butanediol)

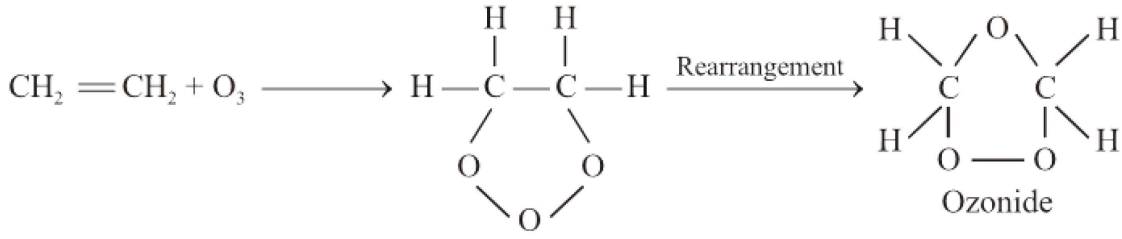
(3) Combustion:

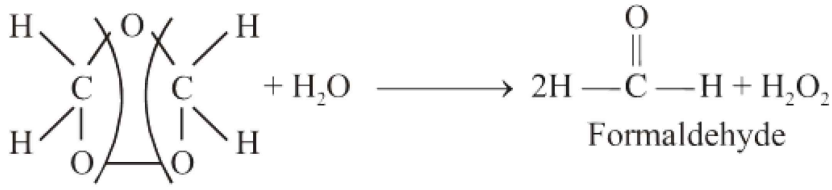
Alkenes burn in air with luminous flame and produce CO_2 and H_2O vapours. Ethene forms a highly explosive mixture with air oxygen.

$$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O + \text{Heat}$$

(4) Ozonolysis:

Ozone (O_3) is a highly reactive allotropic form of oxygen. It reacts vigorously with alkenes to form unstable molozonide. It rearranges spontaneously to form an ozonide.





$$H_2O_2 + Zn \longrightarrow ZnO + H_2O$$

Ozonolysis is used to locate the position of double bond in an alkene.

In the ozonolysis of propene, one molecule of formaldehyde and one molecule of acetaldehyde is formed and ozonolysis of 2-butene forms two molecules of acetaldehyde.

(c) Polymerization:

"In this process small organic molecules (monomers) combine together to form larger molecules known as Polymers."

Ethene at 400°C and 100 atm. pressure, polymerize to polythene or polyethylene.

$$n CH_2 = CH_2 \xrightarrow[\text{100 atm. pressure, traces of } O_2 \text{ (0.1\%)}]{400^\circ C} [-CH_2 - CH_2-]_n$$

A good quality polythene is obtained, when ethene is polymerized in the presence of aluminium triethyl $Al(C_2H_5)_3$ and titanium tetrachloride catalysts ($TiCl_4$).

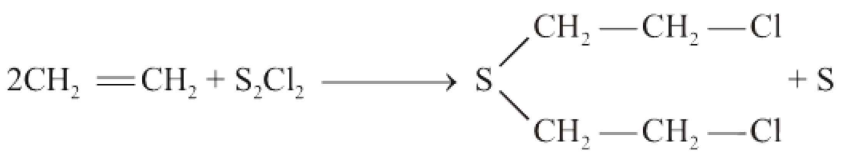
USES OF ETHENE

(1) Ethene is used for the manufacture of polyethene plastic for making, toys, cable insulations, bags, boxes, plastic utensils, etc.

(2) Ethene can also be used for the artificial ripering of fruits.

(3) It is used as general anesthetic in hospitals.

(4) It is used for the preparation of mustard gas. Mustard gas was used in first world war (1914–1918) by german and his allies. The name of the gas is due its maustard order. It is not a gas but a high boiling liquid that is dispersed as mist of tiny droplets. It is a powerful **vesicant or blistering agent**.



β, β-dichloro ethyl sulphide
(Mustard gas)

(5) It is used as a starting material for a large number of chemicals of industrial use such as glycols (antifreeze), ethyl halide, ethyl alcohol, etc.

ALKYNES

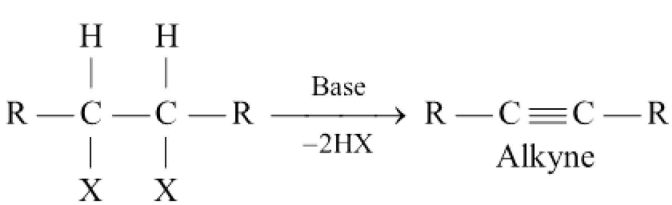
Unsaturated hydrocarbons which contain a triple bond are called Alkynes. They have the general molecular formula C_nH_{2n-2} and contain two hydrogen atoms less than the corresponding alkenes.

The first member of the Alkyne series has the formula C_2H_2 and is known as Ethyne or Acetylene.

General Methods of Preparation:

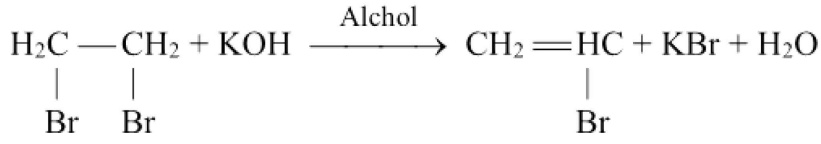
(1) Dehydrohalogenation of Vicinal Dihalides:

Vicinal dihalide on treatment with a strong base, eliminates two molecules of hydrogen halides from two adjacent carbons to give an alkyne.



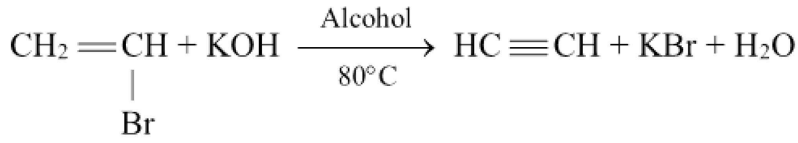
1,2-dihalide

(a) Mechanism:



1,2-dibromoethane Vinyl bromide

(b)

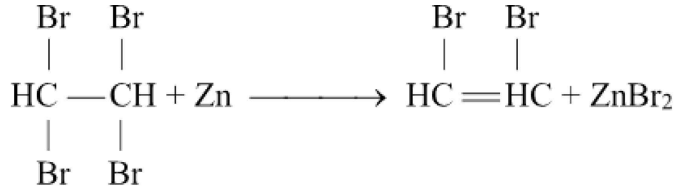


The second molecule of hydrogen halide is removed with great difficulty and requires drastic conditions.

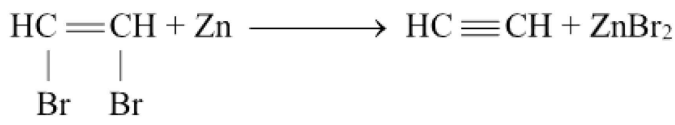
(2) Dehalogenation of Tetra Halides:

Tetra haloalkanes on treatment with active metals like Zn, Mg, etc. form alkynes.

(i)

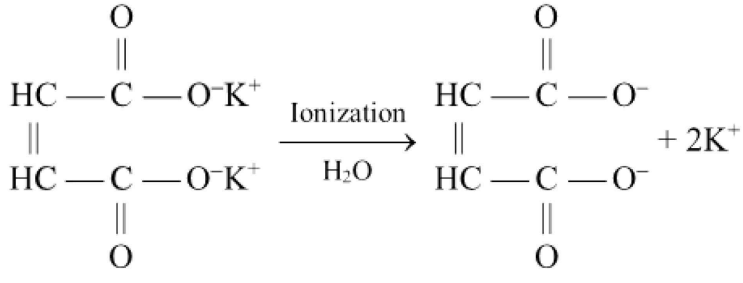


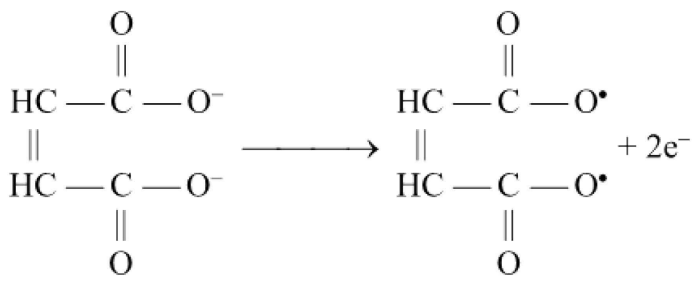
(ii)

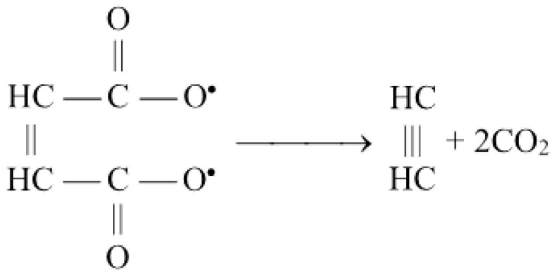


(3) Electrolysis of Salts of Unsaturated Dicarboxylic Acids:

Kolbe's electrolytic method involved electrolysis of aqueous solution of Na of K salts of unsaturated dicarboxylic acids. Electrolysis of aqueous solution of potassium fumerate, give ethyne.







At cathode **Ethyne**

$$2H_2O + 2e^- \longrightarrow 2OH + H_2$$

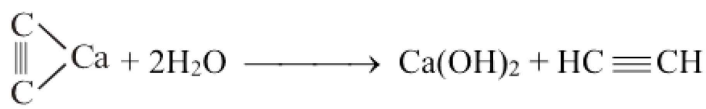
$$K^+ + OH^- \longrightarrow KOH$$

(4) Industrial Preparation (For Acetylene only):

On industrial scale ethyne is prepared by the reaction of calcium carbide (CaC_2) with water.

Calcium carbide is prepared by heating lime (CaO) and coke (C) at a very high temperature in an electric furnace.

$$CaO + 3C \xrightarrow{2000^\circ C} CaC_2 + CO$$



Calcium carbide Ethyne

PHYSICAL CHARACTERS OF ALKYNES

(1) They are colourless, odourless, except acetylene which has a garlic like odour.

(2) The first three members are gases (ethyne, propyne and butyne) at room temperature. The next eight members are liquids and higher members are solids.

(3) The melting points, boiling point and densities increase gradually with the increase in molecule masses.

(4) They are non-polar and dissolve readily in solvents like ether, benzene and carbon tetra chloride.

REACTIVITY OF ALKYNES

In alkynes, triple bond is present between carbon atoms; one sigma bond and two π-bonds. In sigma bond, electron density is maximum between the nuclei and in π-bond electron density is all around the bond axes. Electron density between triple bonded carbon atoms is very high which draws atoms very close to each other. The C – C bond

distance in triple bond is short than single bond. π-electrons of the triple bond are less exposed due to greater attraction. Alkynes give addition reactions with electrophilic reagents but they have less reactivity than alkenes.

Ethene discharge the colour of Br_2 immediately while ethyne reacts slowly with Br_2 and colour of Br_2 discharge after few minutes.

$$CH_2{=}CH_2 + Br_2 \longrightarrow \underset{\displaystyle Br}{\underset{|}{CH_2}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \quad \text{(Immediately)}$$

$$CH{\equiv}CH + Br_2 \xrightarrow{\text{Few minutes}} \underset{\displaystyle Br}{\underset{|}{CH}}=\underset{\displaystyle Br}{\underset{|}{CH}}$$

$$\underset{\displaystyle Br}{\underset{|}{CH}}=\underset{\displaystyle Br}{\underset{|}{CH}} + Br_2 \longrightarrow CHBr_2 - CHBr_2$$

REACTIONS OF ALKYNES

(a) Addition Reaction:

Alkynes undergo addition reaction like alkenes but add two molecules of the reagent instead of one.

(1) Addition of Hydrogen:

Alkynes react with hydrogen gas in the presence of a suitable catalysts like finely divided Ni, Pt or Pd. Initially alkenes are formed which then take up another molecule of hydrogen to form an alkane.

$$HC{\equiv}CH + H_2 \xrightarrow[\text{Heat}]{\text{Ni}} H_2C{=}CH_2$$

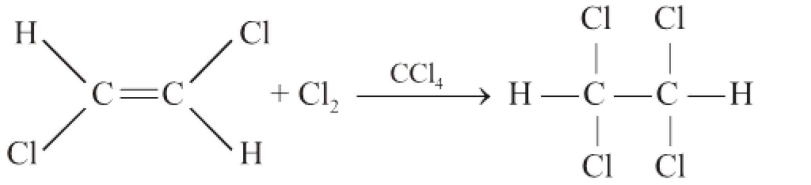
Ethyne Ethene

(2) Addition of Halogens:

One or two molecules of halogens can be added to alkynes giving dihalides and tetra halides respectively. Chlorine and bromine add readily while iodine reacts rather slowly.

$$HC{\equiv}CH + Cl_2 \xrightarrow{CCl_4} \begin{matrix} H & & Cl \\ & C{=}C & \\ Cl & & H \end{matrix}$$

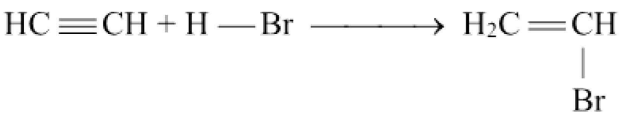
Ethyne 1,2-dichloroethene



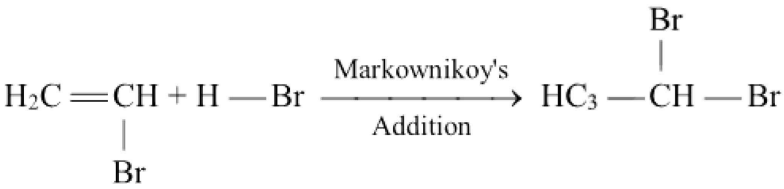
1,1,2,2-tetrachloroethane
(Acetylene tetrachloride)

(3) Addition of Halogen Acids:

Alkynes react with HCl or HBr to form dihaloalkanes. Addition of second molecule in vinyl bromide takes place according to Markonikov's rule.



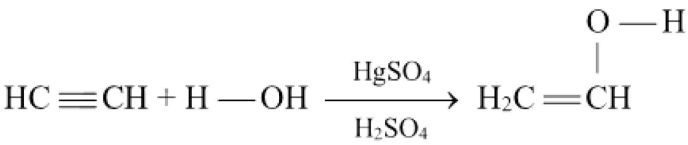
Vinyl bromide



1,1-Dibromoethane (Ethylidene bromide is geminal dihalide)

(4) Addition of Water:

Water adds to acetylene in the presence of mercuric sulphate dissolved in sulphuric acid at 75°C. The reaction is important industrially.

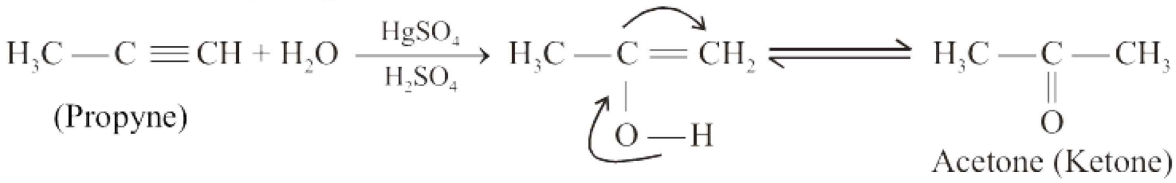


Vinyl alcohol

Vinyl alcohol is an unstable enol. The enol has the hydroxy group attached to a double bonded carbon atom and isomerises to acetaldehyde.



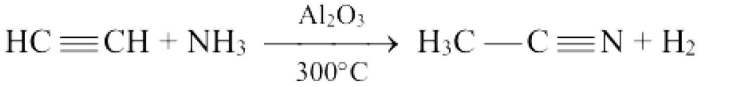
All other alkynes give ketones.



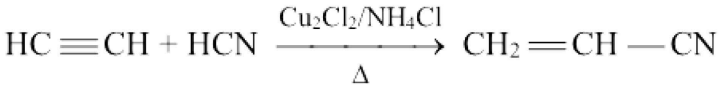
(Propyne) Acetone (Ketone)

(5) Addition of Ammonia and Hydrogen Cyanide:

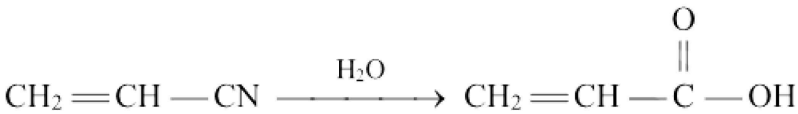
Addition of NH_3 and HCN to ethyne in the presence of suitable catalysts, give nitriles.



Methyl cyanide (Ethane nitrile)



Acrylonitrile

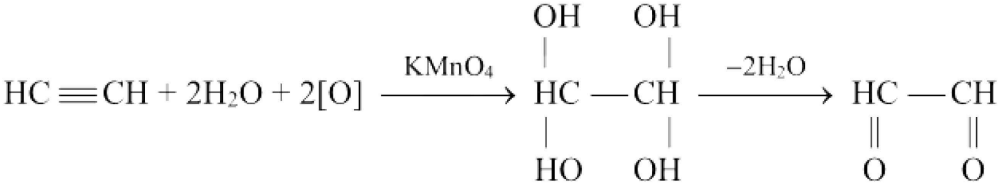


Acrylic acid

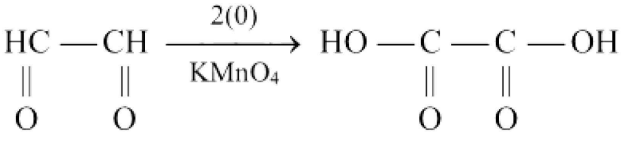
Acrylic acid is used in weather resistant paint.

(b) Oxidation Reactions:

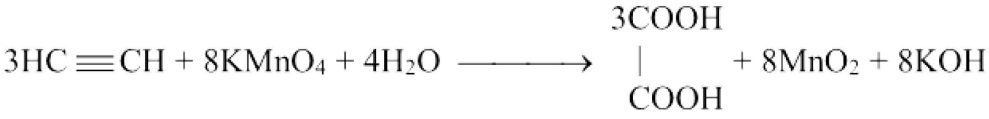
(1) Ethyne on oxidation with strong alkaline $KMnO_4$ gives glyoxal.



Ethnye Glyoxal



Glyoxal Oxalic acid



(2) Combustion:

Ethyne when burnt in air or oxygen, produces heat and evolves CO_2 and H_2O. The reaction is highly exothermic and the resulting oxyacetylene flame is used for welding and cutting of metals.



(c) Polymerization:

Alkynes polymerize to give linear or cyclic compounds depending upon the temperature and catalyst used. However, these polymers are different from the polymers of the alkenes as they are usually low molecular weight polymers.

(1) Acetylene to Divinyl Acetylene:

When aceptene is passed through an acidic solution of cuprous chloride and ammonium chloride and allowed to stand for several hours at room temperature, vinyl acetylene and divinyl acetylene are obtained.

$$HC \equiv CH + HC \equiv CH \xrightarrow{Cu_2Cl_2+NH_4Cl} H_2C = CH - C \equiv CH$$

Vinyl acetylene (But-1-en-3-yne)

$$H_2C{=}CH{-}C{\equiv}CH + HC{\equiv}CH \xrightarrow{Cu_2Cl_2+NH_4Cl} H_2C{=}CH{-}C{\equiv}C{-}CH{=}CH_2$$

Divinyl acetylene
(Hexa-1,5-dien-3-yne)

If HCl is added to vinyl acetylene, chloroprene is obtained which readily polymerize to neoprene, used as synthetic rubber.

$$H_2C = CH - C \equiv CH + \text{Conc. } HCl \xrightarrow{Cu_2Cl_2+NH_4Cl} H_2C = CH - \underset{\displaystyle Cl}{\overset{\displaystyle |}{C}} = CH_2$$

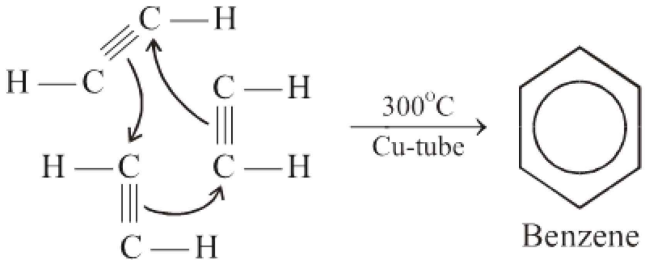
(Chloroprene)

$$\text{Chloroprene} \xrightarrow{\text{Polymeriation}} \text{Neoprene (Synthetic rubber)}$$

$$n\,CH_2 = CH - \underset{\displaystyle Cl}{\overset{\displaystyle |}{C}} = CH_2 \xrightarrow{\text{Polymeriation}} [CH_2 - CH = \underset{\displaystyle Cl}{\overset{\displaystyle |}{C}} - CH_2]_n$$

(2) Acetylene to Benzene:

When acetylene is passed through a copper tube at 300°C, it polymerizes to benzene.



ACIDIC NATURE OF ALKYNES

Alkynes differ from alkenes and alkanes. They have acidic hydrogen in them. The hydrogen atom attached to triple bonded carbon atom or sp hybridized carbon atom is acidic in nature.

In alkynes s-orbital or hydrogen is overlapped with sp-hybrid orbital of carbon which has 50% s characters. sp^2-hybrid orbital has 33% s and sp^3 hybrid orbital has 25% s characters in it. Due to greater s-characters of hybrid orbital of carbon, it attract the electrons to itself and behave as more electronegative than sp^3 or sp^2 carbon atoms. Due to greater attraction of sp carbon, slightly negative charge is present on carbon and slightly positive charge is present on hydrogen.

$$R-C\equiv C^{\delta-}H^{\delta+}$$

This acidic hydrogen can be replaced by a metal ions to form salts called alkynides. Acetylene has two acidic hydrogen while 1-alkynes (1-propyne, 1-butyne, etc) have one acidic hydrogen while 2-butyne has no acidic hydrogen in it.

When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained respectively.

$$R-C\equiv CH + NaNH_2 \xrightarrow{\text{Liq. } NH_3} R-C\equiv C^-Na^+ + NH_3$$

$$HC\equiv CH + 2Na \longrightarrow Na^+C\equiv C^-Na^+ + H_2$$

Disodium acetylide

Sodium actylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

Acetylides of copper and silver are obtained by passing acetylene in the ammonical solution of cuprous chloride and silver nitrate respectively.

$$HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC\equiv CCu + 2NH_4Cl + 2H_2O$$

Dicopperacetylide
(Reddish brown ppt.)

$$HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC\equiv CAg + 2NH_4NO_3 + 2H_2O$$

Disilver acetylide
(White ppt.)

Silver and copper acetylides react with acids to regenerate alkynes.

$$AgC \equiv CAg + H_2SO_4 \xrightarrow{\text{dil.}} HC \equiv CH + Ag_2SO_4$$

$$AgC \equiv CAg + 2HNO_3 \xrightarrow{\text{dil.}} HC \equiv CH + 2AgNO_3$$

These alkynides are used for the preparation, purification, separation and identification of alkynes.

USES OF ETHYNE OR ACETYLENE

(1) Oxyacetylene flame has temperature about 3000°C and is used for metals cutting and welding.

$$2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O + \text{Heat}$$

(2) It is used for the artificial ripening of fruits.

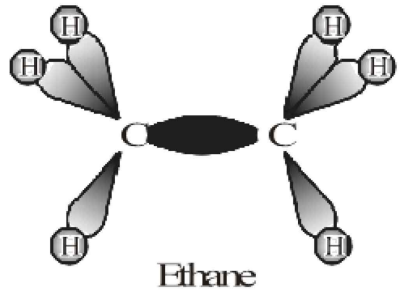
(3) Acetylene is used for the preparation of alcohols, acetaldehyde and acetic acid.

(4) It is also used for manufacture of polyvinyl chloride PVC, polyvinyl acetate, polyviny ethers, neoprene rubber, orlon and benzene.

(5) It is used to prepare acetylene tetrachloride $C_2H_2Cl_4$, which is a solvent for varnishes, resins and rubbers.

COMPARISON OF REACTIVITY OF ALKANES ALKENES AND ALKYNES

(1) Alkanes are the least reactive hydrocarbons. Alkanes have all sigma bonds in them which are strong bonds. In sigma bonds, electrons are very tightly held between the nuclei and makes them stable. A lot of energy is required to break C – C or C – H bond in alkanes.



Ethane

Electrons of the sigma bonds of alkane are not attracted by any nucleophile or electrophile. So alkanes do not react with ionic reagents, acids alkalis, oxidizing agent or reducing agents. However, under suitable conditions, alkanes undergo some substitution, combustion and thermal or catalytic reactions. Alkanes do not go addition reactions.

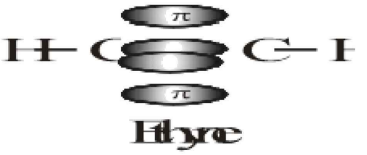
(3) Alkenes are the most reactive hydrocarbons. Alkenes have one sigma and one π-bond between C – C atoms. Each carbon atom of double bond is sp^2 hybridized. π-bond in alkene is weak and can easily be broken by any electrophile.



Ethene

π-electrons of alkene are more exposed and can easily be attached by an electrophilic reagent. Alkenes are more reactive than alkane as well as alkynes.

(4) Alkynes are less reactive than alkenes but more reactive than alkanes. Alkynes have one sigma and two π-bonds between C – C atoms.



The electron density between triple bonded carbon atoms is very high which draws atoms close together. π-electrons of alkynes are less exposed. Therefore alkynes are less reactive toward electrophilic reagents. Alkynes are however more reactive than alkenes toward nucleophilic reagents.

The decreasing reactivity order of alkanes, alknes and alkynes is as follows:

Alkenes > Alkynes > Alkanes

ELECTROPHILES OR ELECTROPHILIC REAGENTS

"The substances which are deficient of electrons and can accept available electrons from another substance are called electrophiles or electrophilic reagents. (electron – lovings)". e.g.,

(1) Positive Electrophiles:

Proton (H^+), Chloronium ion (Cl^+), Bromonium ions (Br^+), Nitronium ion (NO_2^+), Nitrosonium ion (NO^+), Carbonium ion, (CH_2^+, RCH_2^+, R_2CH^+ or R_3C^+).

(2) Neutral Electrophiles:

$AlCl_3$, BF_3, $ZnCl_2$, SO_3, R — $\overset{\overset{O}{\|}}{C}$ — Cl carbonyl carbon of aldehyde and ketone

$\overset{\overset{O}{\|}}{C}$ —, carbon adjacent of halogen in alkyl halides. ($CH_3^{\delta+}$ — $Br^{\delta-}$).

NUCLEOPHILES OR NUCLEOPHILIC REAGENTS

"The substances which donate a pair of electrons to electrophile and form a new covalent bond are called nucleophiles (nucleus – loving)". e.g.,

(1) Negative Nucheophiles:

Halides ions (Cl^-, Br^-, I^-), Alkoxy R — O^- hydroxide $(OH)^-$ cyanide, $(CN)^-$, Amide ion (NH_2^-), Carbanion (CH_3^-, RCH_2^-, R_2CH^-, R_3C^-).

(2) Neutral Nucleophiles:

Ammonia NH_3, Water H — O — H, Alcohol R — OH, Alkyl hydrogen sulphide R — SH. Alkyl amines (R_3N, R_2NH or RNH_2).

EXERCISE

Q.1 Fill in the blanks:

(i) Ozone reacts with ethene to form ————.

(ii) Lindlar's catalyst is used for ———— of alkynes.

(iii) Divinyl acetylene is a ———— of acetylene.

(iv) Vicinal dihalides have two halogens on ———— carbon atoms.

(v) Ethyne is acidic in character because of ———— hybridization.

(vi) Halohydrins are formed due to addition of ———— in ethene.

(vii) Ethylene glycol is produced when ———— reacts with cold alkaline $KMnO_4$ solution.

(viii) Mustard gas is a highly boiling ————.

(ix) Ethyne has ———— like odour.

(x) Ethyne is obtained by the reaction of ———— with calcium carbide.

ANSWERS

(i)	ozonide	**(ii)**	partial hydrogenation	**(iii)**	polymer
(iv)	adjacent	**(v)**	sp	**(vi)**	hypohalous acid HOX
(vii)	ethene	**(viii)**	liquid	**(ix)**	garlic
(x)	water				

Q.2 Indicate True or False:

(i) Addition of HX to unsymmetrical alkanes takes place according to Markownikov's rule.

(ii) Methane reacts with bromine water and its colour is discharged.

(iii) Mustard gas is a blistering agent.

(iv) Methane is also called marsh gas.

(v) Ethyne is a saturated compound.

(vi) Bayer's reagent is used to locate a double bond in an alkene.

(vii) Alkanes usually undergo substitution reactions.

(viii) Benzene is a polymer of ethene.

(ix) Acrylonitrile can be obtained from ethyne.

(x) Ethyne is more reactive towards electrophilic reagents than ethene.

ANSWERS

(i)	False	**(ii)**	False	**(iii)**	True	**(iv)**	True	**(v)**	False
(vi)	True	**(vii)**	True	**(viii)**	False	**(ix)**	True	**(x)**	False

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Preparation of vegetable ghee involves:

(a) Halogenation **(b)** Hydrogenation

(c) Hydroxylation **(d)** Dehydrogenation

(ii) Formula of chloroform is:

(a) CH_3Cl **(b)** CCl_4

(c) CH_2Cl_2 **(d)** $CHCl_3$

(iii) The presence of a double bond in a compound is the sign of:

(a) Saturation **(b)** Unsaturation

(c) Substitution **(d)** None

(iv) Vinyl acetylene combines with HCl to form:

(a) Polyacetylene **(b)** Benzene

(c) Chloroprene **(d)** Divinylacetylene

(v) The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule:

(a) Hund's rule **(b)** Markownikov's rule

(c) Pauli's exclusion principle **(d)** Aufbau principle

(vi) Synthetic rubber is made by polymerization of:

(a) Chloroform **(b)** Acetylene

(c) Divinylacetylene **(d)** Chloroprene

(vii) β-β′-dichloroethyl sulphide is commonly known as:

(a) Mustard gas **(b)** Laughing gas

(c) Phosgene gas **(d)** Bio-gas

(viii) When methane reacts with Cl_2 in the presence of diffused light the products obtained are:

(a) Chloroform only

(b) Carbon tetrachloride only

(c) Chloromethane and dichloromethane

(d) Mixture of (a), (b), (c)

(ix) Which one of the following gases is used for artificial ripening of fruits:

(a) Ethene **(b)** Ethyne

(c) Methane **(d)** Propane

ANSWERS

(i)	(b)	**(ii)**	(d)	**(iii)**	(b)	**(iv)**	(c)	**(v)**	(b)
(vi)	(b)	**(vii)**	(a)	**(viii)**	(d)	**(ix)**	(b)		

Q.4 Write the structural formula for each of the following compounds:

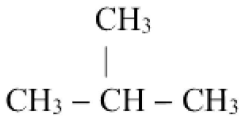
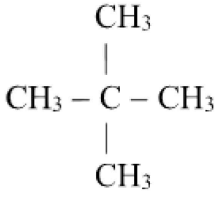
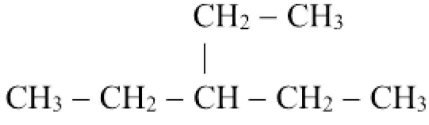
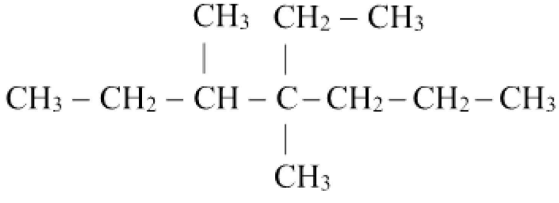
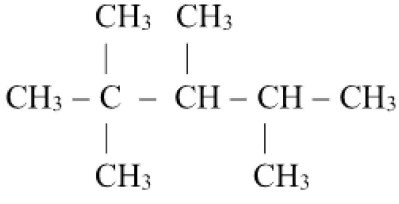
(i) 2-methylpropane **(ii) Neopentane**

(iii) 3-ethylpentane **(iv) 4-ethyl-3, 4-dimethylheptane**

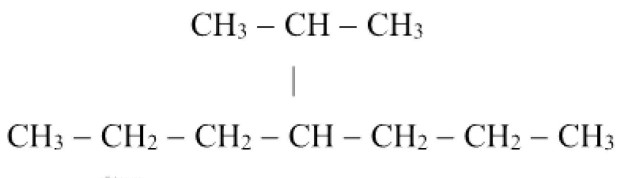
(v) 2, 2, 3, 4-tetramethylpentane **(vi) 2, 2, 3, 4-tetramethylpentane**

(vii) 2, 2-dimethylbutane **(viii) 2, 2-dimethylpropane**

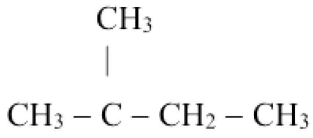
Ans.

	Compound Name	Structural Formula
(i)	**2-methylpropane**	
(ii)	**Neopentane**	
(iii)	**3-ethylpentane**	
(iv)	**4-ethyl-3, 4-dimethylheptane**	
(v)	**2, 2, 3, 4-tetramethylpentane**	

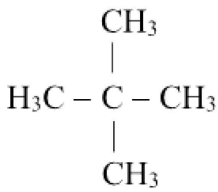
(vi) **4-iso-propylheptane**



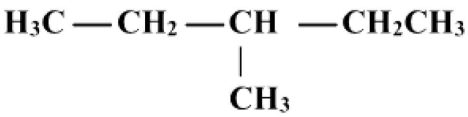
(vii) **2, 2-dimthyl butane**



(viii) **2, 2-dimethylpropane**

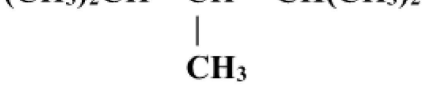


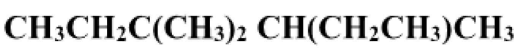
Q.5 Write down names of the following compounds according to IUPAC system:

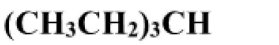
(i) 

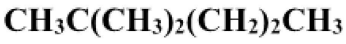
(ii) 

(iii)

(iv) 

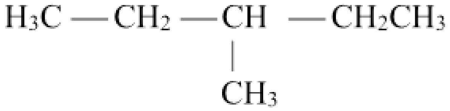
(v) 

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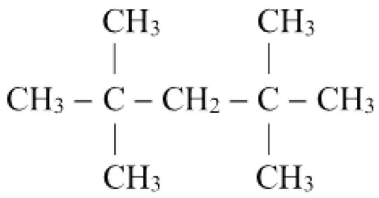
(vii) 

(viii) 

Ans.

	Compound	IUPAC Name
(i)		3-methylpentane

(ii)



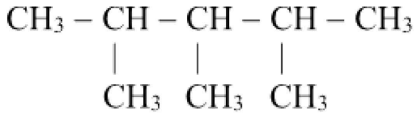
2, 2, 4, 4-Tetramethylpentane

(iii)



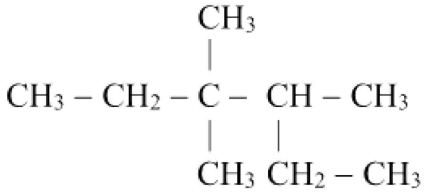
2, 4-Dimethylpentane

(iv)



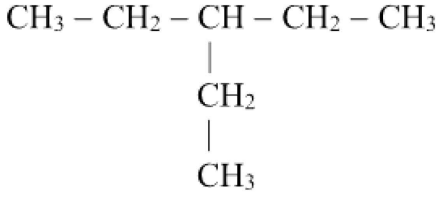
2, 3, 4-Trimethylpentane

(v)



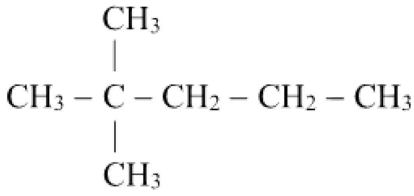
3, 3, 4-Trimethylhexane

(vi)



3-Ethylpentane

(vii)



2, 2-Dimethylpentane

(viii) $(C_6H_5)_3CH$ triphenylmethane

Q.6 What are the rules for naming alkanes? Explain with suitable examples.

Ans. Detailed question. See text book.

Q.7 (a) Write down the structural formulas for all the isomeric hexanes and name them according to IUPAC system.

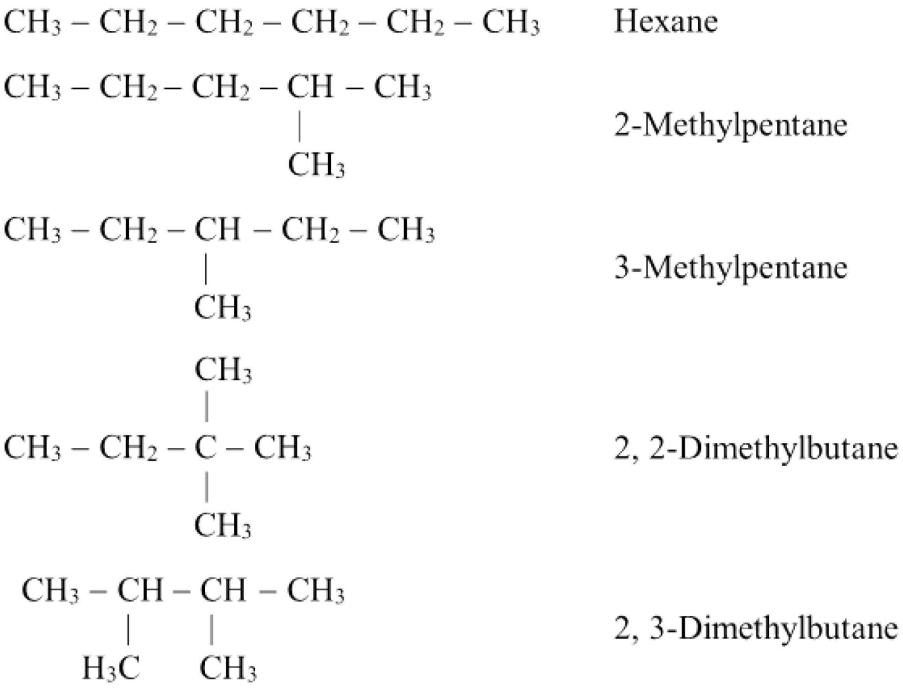
(b) The following names are incorrect. Give the correct IUPAC names:

(i) 4-methylpentane **(ii) 3, 5, 5-trimethylhexane**

(iii) 2-methy-3-ethylbutane

Ans.

(a) The isomeric forms of hexanes and their IUPAC names are as follows:



(b) Correct names:

Given Name	Structure	Correct Name
4-Methylpentane	$CH_3 - \underset{\displaystyle CH_3}{\underset{\vert}{CH}} - CH_2 - CH_2 - CH_3$	2-Methyl pentane
3, 5, 5-Trimethylhexane	$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{\vert}{CH}} - CH_2 - \underset{\displaystyle CH_3}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}} - CH_3$	2, 2, 4-Trimethyl hexane
2-Methyl-3-ethylbutane	$CH_3 - \underset{\displaystyle H_3C}{\underset{\vert}{CH}} - \underset{\displaystyle C_2H_5}{\underset{\vert}{CH}} - CH_3$	2, 3-Dimethyl pentane

Q.8 (a) Explain why alkanes are less reactive than alkenes? What is the effect of branching on the melting point of alkanes?

(b) Three different alkanes yield 2-methylbutane when they are hydrogenated in the presence of a metal catalyst. Give their structures and write equations for the reactions involved.

Ans.

(a) Descriptive question. Consult text book for details.

(b) **(i)** **2-methyl-1-butene:**

$$CH_3 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH_2 + H_2 \xrightarrow{Pt/Pd} CH_3 - CH_2 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_3$$

(ii) **2-methyl-2-butene:**

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} = CH - CH_3 + H_2 \xrightarrow{Pt/Pd} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_2 - CH_3$$

(iii) **3-methyl-1-butene:**

$$CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH = CH_2 + H_2 \xrightarrow{Pt/Pd} CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle |}{CH}} - CH_2 - CH_3$$

Q.9 **(a)** **Out line the methods available for the preparation of alkanes.**

(b) **How will you bring about the following conversions?**

(i) **Methane to ethane** **(ii)** **Ethane to methane**

(iii) **Acetic acid to ethane** **(iv)** **Methane to nitromethane**

Ans.

(a) Descriptive question. Consult text book for details.

(b) **(i)** **Methane into ethane:**

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

$$2CH_3Cl + 2Na \longrightarrow CH_3 - CH_3 + 2NaCl$$

(ii) **Ethane into methane:**

$$CH_3 - CH_3 + Cl_2 \xrightarrow{hv} CH_3 - CH_2Cl + HCl$$

$$CH_3 - CH_2Cl + KOH_{(aq)} \longrightarrow CH_3 - CH_2 - OH + KCl$$

$$CH_3 - CH_2 - OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{\displaystyle O}{\overset{\displaystyle \|}{C}} - H + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3-\overset{\overset{O}{\|}}{C}-OH$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + NaOH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-ONa + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-ONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

(iii) Acetic acid to ethane:

$$CH_3COOH + 6HI \xrightarrow{P} CH_3-CH_3 + 3I_2 + 2H_2O$$

(iv) Methane to nitromethane:

$$CH_4 + HNO_3 \xrightarrow{450°C} CH_3-NO_2 + H_2O$$

Q.10 (a) What is meant by octane number? Why does a high octane fuel has a less tendency to knock in an automobile engine?

(b) Explain free radical mechanism for the reaction of chlorine with methane in the presence of sunlight.

Ans.

(a) (i) Octane Number: It is defined as; the percentage of branched chain hydrocarbon, iso-octane, in gasoline fraction of petroleum is known as octane number.

(ii) Less Tendency to Knock: High octane fuel has less tendency to knock because it contains 100% isooctane.

(b) Descriptive question. Consult text book for details.

Q.11 (a) Write structural formulas for each of the following compounds:

(i) Isobutylene
(ii) 2, 3, 4, 4-tetramethyl-2-pentene
(iii) 2, 5-heptadiene
(iv) 4, 5-dimethyl-2-hexene
(v) Vinylacetylene
(vi) 1, 3-pentadiene
(vii) 1-butyne
(viii) 3-n-propyl-1, 4-pentadiene
(ix) Vinyl bromide
(x) But-1-en-3yne
(xi) 4-methyl-2-pentyne
(xii) Iso-pentane

(b) Name the following compounds by IUPAC system:

(i) $H_3C-CH=CH(CH_2)_2CH_3$

(ii) $(CH_3)_2C=CH_2$

(iii)
$$CH_3-CH_2-CH_2-\underset{\displaystyle CH(CH_3)_2}{\overset{\displaystyle |}{C}}=CH_2$$

(iv) $CH_2=CH-CH=CH_2$

(v)
$$CH_2=\underset{\displaystyle C_2H_5}{\overset{\displaystyle |}{C}}-CH_2CH_2CH_3$$

(vi) $CH\equiv C-CH_3$

(vii) $CH_3-C\equiv C-CH_3$

(viii) $CH_2=CH-C\equiv C-CH=CH_2$

(ix) $CH\equiv C-CH=CH-C\equiv CH$

(x) $CH_2=CH-C\equiv CH$

Ans.

(a)

Name	Structural Formulas
Isobutylene	$\begin{array}{l} \quad CH_3 \\ \quad\ \vert \\ CH_3-C=CH_2 \end{array}$
2, 3, 4, 4-Tetramethyl-2-pentene	$\begin{array}{l} \qquad\qquad\quad CH_3 \\ \qquad\qquad\quad\ \vert \\ CH_3-CH=C-\ C-CH_3 \\ \quad\ \vert \quad\ \vert \quad\ \vert \\ \ H_3C \quad CH_3\ CH_3 \end{array}$
2, 5-Heptadiene	$H_3C-CH=CH-CH_2-CH=CH-CH_3$
4, 5-Dimethyl-2-hexene	$\begin{array}{l} CH_3-CH=CH-C\ -\ CH-CH_3 \\ \qquad\qquad\quad\ \vert \quad\ \vert \\ \qquad\qquad CH_3\ CH_3 \end{array}$
Vinyl acetylene	$CH_2=CH-C\equiv CH$
1, 3-Pentadiene	$CH_2=CH-CH=CH-CH_3$
1-Butyne	$CH\equiv C-CH_2-CH_3$

3-n propyl-1, 4-pentadiene	$CH_2 = CH - CH - CH = CH_2$ | $CH_2 - CH_2 - CH_3$
Vinyl bromide	$CH_2 = CH - Br$
But-1-en-3-yne	$HC \equiv C - CH = CH_2$
4-Methyl-2-pentyne	$CH_3 - C \equiv C - CH - CH_3$ | CH_3
Isopentane	$CH_3 - CH_2 - CH - CH_3$ | CH_3

(b)

Compounds	IUPAC Name
$CH_3 - CH = CH(CH_2)_2CH_3$	2-Hexene
$(CH_3)_2C = CH_2$	2-Methyl-1-propene
$CH_3 - CH_2 - CH_2 - C = CH_2$ | CH / \\ H_3C CH_3	2-Isopropyl-1-pentene
$CH_2 = CH - CH = CH_2$	1, 4-Butadiene
$CH_2 = C - CH_2 - CH_2 - CH_3$ | C_2H_5	2-Ethyl-1-pentene
$HC \equiv C - CH_3$	Propyne
$CH_3 - C \equiv C - CH_3$	2-Butyne
$CH_2 = CH - C \equiv C - CH = CH_2$	1, 5-Hexadiene-3-yne
$HC \equiv C - CH = CH - C \equiv CH$	3-Hexene-1, 5-diyne
$H_2C = CH - C \equiv CH$	1-Butene-3-yne

Q.12 (a) Describe different methods for the preparation of alkenes. How would you establish that ethylene contains a double bond?

(b) Give structure formulas of the alkenes expected to form by the dehydrohalogenation of the following compounds with a strong base:

(i) 1-chloropentane (ii) 2-chloro-3-methylbutane

(iii) 1-chloro-2, 2-dimethyl propane

Ans.

(a) Descriptive question. Consult text book.

"Ethylene contains double bond" it can be established by following reactions:

(i) Baeyer's test (ii) Ozonolysis

(i) **Baeyer's Tests:** Reaction with Bayeyer's reagent i.e., 1% alkaline solution of $KMnO_4$

$$3H_2C = CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\ \underset{OH}{\overset{CH_2}{|}}\!\!-\!\!\underset{OH}{\overset{CH_2}{|}} + 2MnO_2 + 2KOH$$

Result: Discharging of the colour of $KMnO_4$ confirms the presence of double bond.

(ii) **Ozonolysis:**

$$CH_2 = CH_2 + O_3 \longrightarrow \text{(ozonide)} \xrightarrow[\text{ii. Zn}]{\text{i. } H_2O} 2H - \overset{O}{\overset{\|}{C}} - H + ZnO$$

(b)

(i) **1-Chloropentane:**

$$CH_3 - CH_2 - CH_2 - CH_2 - \underset{Cl}{\overset{CH_2}{|}} + KOH \xrightarrow[(alc)]{} \underset{\text{1-Pentene}}{CH_3 - CH_2 - CH_2 - CH = CH_2} + KCl + H_2O$$

(ii) **2-chloro-3-methyl butane:**

$$CH_3 - \underset{Cl}{\overset{CH}{|}} - \underset{CH_3}{\overset{CH}{|}} - CH_3 + KOH \xrightarrow[(alc)]{} \underset{\text{2-Methyl-2-butene}}{CH_3 - CH = \overset{CH_3}{\overset{|}{C}} - CH_3} + KCl + H_2O$$

(iii) **1-chloro-2, 2-dimethyl propane:**

$$CH_3 - \overset{CH_3}{\overset{|}{\underset{CH_3}{\overset{|}{C}}}} - CH_2 - Cl \longrightarrow$$ As β-hydrogen is not available so reaction is not possible.

Q.13 (a) Write down chemical equations for the preparation of propene from the following compounds:

(i) $CH_3 — CH_2 — CH_2 — OH$

(ii) $CH_3 — C \equiv CH$

(iii) Iso-propyl chloride

(b) Write skeleton formula showing only the arrangement of carbon atoms for all the possible alkenes of the molecular formula C_5H_{10}.

Ans.

(a) (i) $CH_3 - CH_2 - CH_2 - OH \xrightarrow[140 - 170°C]{75\% H_2SO_4} CH_3 - CH = CH_2 + H_2O$

(ii) $CH_3 - C \equiv CH + H_2 \xrightarrow[Quinoline]{Pd(BaSO_4)} CH_3 - CH = CH_2$

(iii) $CH_3 - \underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3 + KOH \xrightarrow[100°C]{alcohol} CH_3 - CH = CH_2 + KCl + H_2O$

(b) Possible structures of alkenes having molecular formula C_5H_{10} are as following:

(i) $CH_3 - CH_2 - CH_2 - CH = CH_2$ 1-Pentene

(ii) $CH_3 - CH_2 - CH = CH - CH_3$ 2-Pentene

(iii) $CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$ 2-Methyl-1-butene

(iv) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH = CH_2$ 3-Methyl-1-butene

(v) $CH_3 - CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_3$ 2-Methyl-2-butene

Q.14 (a) How may ethene be converted into ethyl alcohol?

(b) Starting from ethene, outline the reactions for the preparation of following compounds:

(i) 1, 2-ethyldibromide (ii) Ethyne

(iii) Ethane (iv) Ethylene glycol

(c) How will you bring about the following conversions:

(i) 1-butene to 1-butyne (ii) 1-propanol to $CH_3 — \underset{\displaystyle OH}{\underset{|}{CH}} — CH_2Cl$

Ans.

(a) Ethene may be converted into ethyl alcohol by two steps:

(i) Addition of H_2SO_4:

$$CH_2 = CH_2 + H - O - SO_3H \longrightarrow CH_3 - CH_2 - O - SO_3H$$

(ii) Hydration:

$$CH_3 - CH_2 - O - SO_3H + H - OH \xrightarrow{100^\circ C} CH_3 - CH_2 - OH + H_2SO_4$$

(b) (i) Ethylene dibromide:

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} Br - CH_2 - CH_2 - Br$$

(ii) Ethyne:

(a) $$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} Br - CH_2 - CH_2 - Br$$

(b) $$Br - CH_2 - CH_2 - Br + 2KOH \xrightarrow[(alc)]{80^\circ C} CH \equiv CH + 2KBr + 2H_2O$$

(iii) Ethane:

$$CH_2 = CH_2 + H_2 \xrightarrow[250^\circ C]{Ni} CH_3 - CH_3$$

(iv) Ethylene glycol:

$$3H_2C = CH_2 + 2KMnO_4 + 4H_2O \xrightarrow{\bar{O}H} \begin{matrix} 3CH_2 - OH \\ | \\ CH_2 - OH \end{matrix} + 2MnO_2 + 2KOH$$

(c) (i) 1-butene to 1-butyne:

Steps involved:

1. Bromination:

$$CH_3 - CH_2 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - \underset{\displaystyle Br}{\underset{|}{CH_2}}$$

2. Dehydrohlogenation:

$$CH_3 - CH_2 - \underset{\displaystyle Br}{\underset{|}{CH}} - \underset{\displaystyle Br}{\underset{|}{CH_2}} + 2KOH \xrightarrow{100^\circ C} CH_3 - CH_2 - C \equiv CH + 2KBr + 2H_2O$$

(ii) 1-propanol to $CH_3 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2}$

Steps involved:

1. Dehydration:'

$$CH_3 - CH_2 - CH_2 - OH \xrightarrow[140-170°C]{H_2SO_4} CH_3 - CH = CH_2 + H_2O$$

2. Addition of hypochlorus acid:

$$CH_3 - CH = CH_2 + HOCl \longrightarrow CH_3 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2}$$

Q.15 Show by means of chemical equations how the following cycle of changes may be affected:



Ans.

First Step:

$$\text{Ethane} \longrightarrow \text{Ethene}$$

(i) Halogenation in the presence of sunlight:

$$CH_3 - CH_3 + Cl - Cl \xrightarrow{hv} CH_3 - CH_2 - Cl + HCl$$

(ii) Dehydrohalogenation:

$$CH_3 - CH_2 - Cl + \underset{(alc)}{KOH} \xrightarrow{100°C} CH_2 = CH_2 + KCl + H_2O$$

Second Step:

$$\text{Ethene} \longrightarrow \text{Ethyne}$$

(i) Addition of halogen:

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} Br - CH_2 - CH_2 - Br$$

(ii) Dehydrohalogination:

$$Br - CH_2 - CH_2 - Br + \underset{(alc)}{2KOH} \xrightarrow[80°C]{-HBr} CH \equiv CH + 2KBr + 2H_2O$$

Third Step:

Ethyne $\longrightarrow$ Ethane

(i) $CH \equiv CH + H_2 \xrightarrow[250°C]{Ni} CH_2 = CH_2$

(ii) $CH_2 = CH_2 + H_2 \xrightarrow[250°C]{Ni} CH_3 - CH_3$

Q.16 Write down structural formulas for the products that are formed when 1-butene will react with the following reagents:

(i) **H_2, Pt** **(ii)** **Br_3 in CCl_4**

(iii) **Cold dil. $KMnO_4$\OH** **(iv)** **HBr**

(v) **O_2 in the presence of Ag** **(vi)** **HOCl**

(vii) **dil. H_2SO_4**

Ans.

(i) $CH_2 = CH - CH_2 - CH_3 + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3$

n-Butane

(ii) $CH_2 = CH - CH_2 - CH_3 + Br_2 \xrightarrow{CCl_4} \underset{\underset{Br}{|}}{CH_2} - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3$

1-2-Dibromobutane

(iii) $3CH_2 = CH - CH_2 - CH_3 + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{\underset{OH}{|}}{CH_2} - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_3 + 2MnO_2 + 2KOH$

(iv) $CH_2 = CH - CH_2 - CH_3 + HBr \longrightarrow CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3$

2-Bromobutane

(v) $CH_3 - CH_2 - CH = CH_2 + \frac{1}{2} O_2 \xrightarrow[300°C]{Ag_2O} CH_3 - CH_2 - \underset{\diagdown\ \diagup}{CH} - CH_2$

Butylene oxide O

(vi) $CH_3 - CH_2 - CH = CH_2 + HOCl \longrightarrow CH_3 - CH_2 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2}$

1-Chloro-2-butanol

(vii) $CH_3 - CH_2 - CH = CH_2 + H_2SO_4 \longrightarrow CH_3 - CH_2 - \underset{\underset{O - SO_3H}{|}}{CH} - CH_3$

$$CH_3-CH_2-\underset{\displaystyle O-SO_3H}{\underset{|}{CH}}-CH_3 + \overset{+}{H}\overset{-}{O}H \longrightarrow CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 + (H_2SO_4)$$

(2-Butanol)

Q.17 In the following reactions, identify each lettered product:

(i) Ethyl alcohol $\xrightarrow{\text{Conc. } H_2SO_4}$ **A** $\xrightarrow{Br_2}$ **B** $\xrightarrow[KOH]{\text{alcoholic}}$ **C**

(ii) Propene $\xrightarrow{Br_2}$ **D** $\xrightarrow[KOH]{\text{alcoholic}}$ **E** $\xrightarrow{HCN}$ **F**

Ans.

(i) Reactions Involved:

$$CH_3-CH_2-OH \xrightarrow[170^\circ C,\ (-H_2O)]{\text{Conc. } H_2SO_4} CH_2=CH_2 \xrightarrow[CCl_4]{Br_2} \underset{\displaystyle Br}{\underset{|}{CH_2}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} \xrightarrow[-HBr]{\text{KOH (alc)}} HC\equiv CH$$

Products:

A = Ethene

B = 1, 2 Dibromoethane

C = Ethyne

(ii) $CH_3-CH=CH_2 + Br_2 \longrightarrow CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}}$

$$CH_3-\underset{\displaystyle Br}{\underset{|}{CH}}-\underset{\displaystyle Br}{\underset{|}{CH_2}} + 2KOH\ (alc) \longrightarrow CH_3-C\equiv CH + 2KBr + 2H_2O$$

$$CH_3-C\equiv CH + HCN \longrightarrow CH_3-\underset{\displaystyle CN}{\underset{|}{C}}=CH_2$$

D = $CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle Br\ \ Br}{\overset{|\quad|}{C}}}}-CH_2$ 1, 2-Dibromopropane

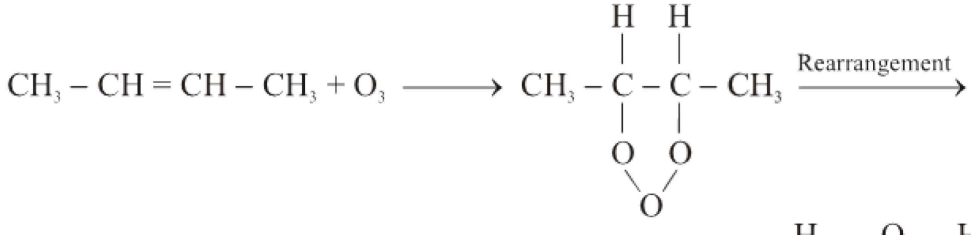
E = $CH_3 - C \equiv CH$ Propyne

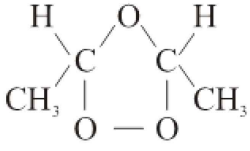
F = $CH_3 - \underset{\displaystyle CN}{\underset{|}{C}} = CH_2$ 2-cyano propene

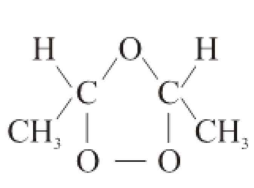
Q.17 After an ozonlysis experiment, the only product obtained was acetaldehyde. The chemist who did the experiment correctly claimed that two possible starting materials could give this product. Can you guess the structural formulas of the compounds?

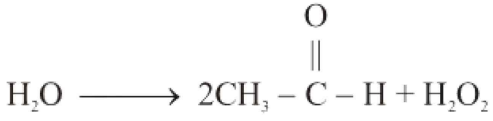
Ans.

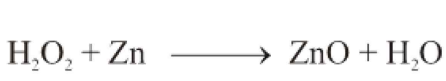
When cis 2-butene or trans 2-butene reacts separately with O_3 the final product will be acetaldehyde.











Q.19 (a) The addition of sulphuric acid to an alkene obeys Markownikov's rule. Predict the structures of the alochols obtained by the addition of the acid to the following compounds:

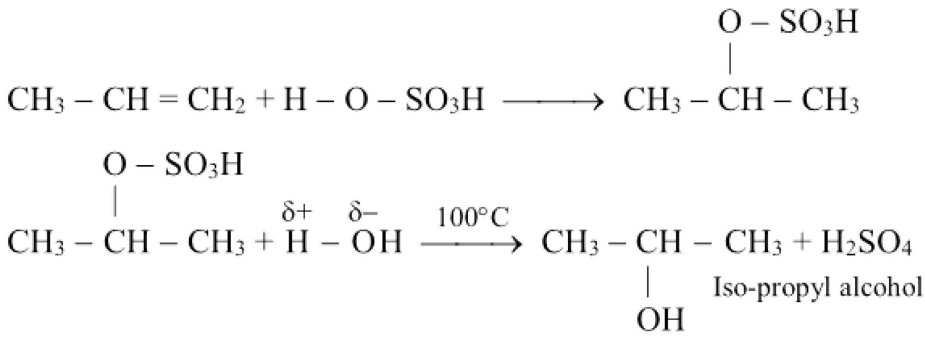
(i) Propene **(ii) 1-butene**

(iii) 2-butene

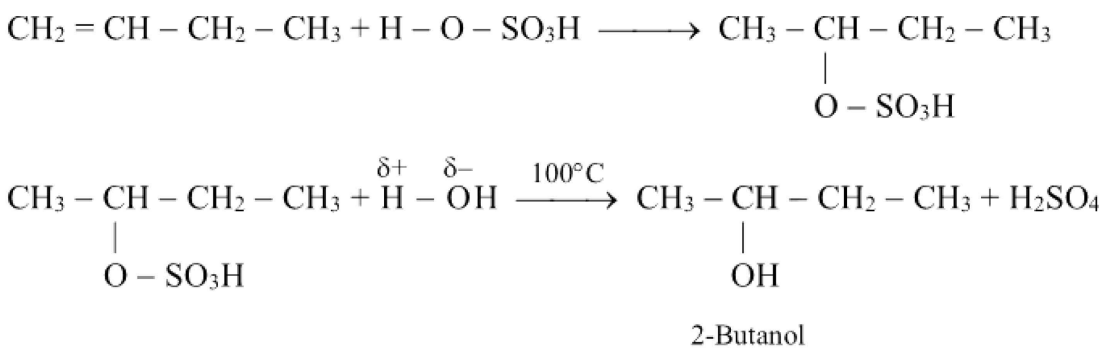
(b) Predict the most likely product of the addition of hydrogen chloride to 2-methyl 2-butene. Explain the formation of this product.

Ans.

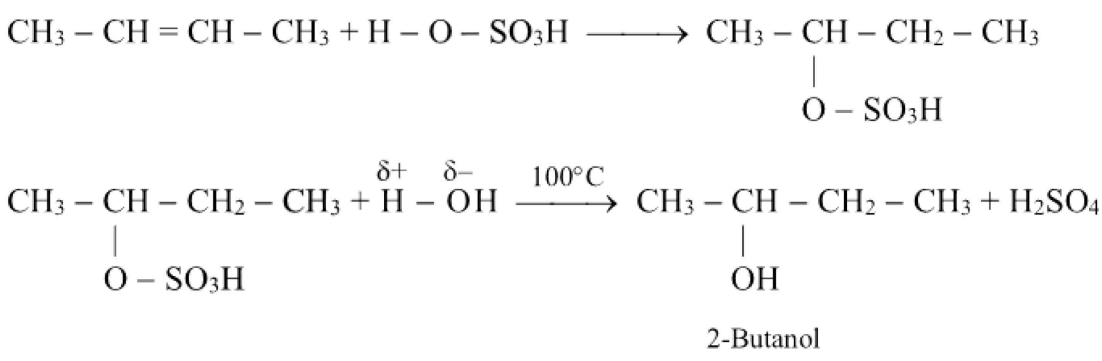
(a) (i) Propene:



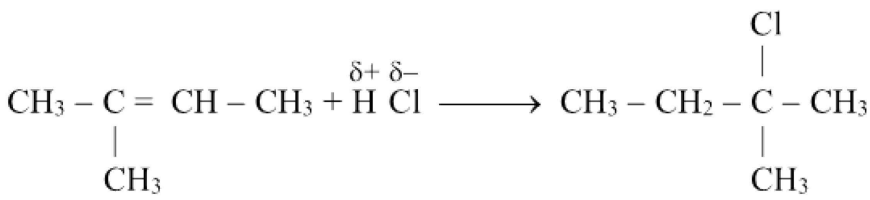
(ii) 1-butene:



(iii) 2-butene:



(b)



As a-methyl-2-butene is an unsymmetrical compound and H-Cl is an unsymmetrical reagent so, the addition will be according to Markownikov's rule and the product will be 2-chloro-2 methyl butane.

Q.20 Why are some hydrocarbons called saturated and others unsaturated? What type of reactions are characteristics of them?

Ans. **Saturated Hydrocarbons:** If all the valencies of the carbon atoms in a molecule are fully satisfied and these cannot further take up any more hydrogen or other atom then this compound is named as saturated hydrocarbon.

Type of Reactions: Saturated hydrocarbons give substitution reactions. e.g.,

$$CH_4 + HNO_3 \xrightarrow{450°C} CH_3 - NO_2 + H_2O$$

substitutional product

Unsaturated Hydrocarbons: If in the compounds of carbon and hydrogen all the four valencies of carbon atom are not fully utilized and they contain either a double or a triple bond then these are called as unsaturated hydrocarbons.

Types of Reactions: Unsaturated hydrocarbons give addition reactions. e.g.,

$$CH_2 = CH_2 + HCl \longrightarrow CH_3 - CH_2 - Cl$$

addition product

Q.21 (a) Describe methods for the preparation of ethyne.

(b) How does ethyne react with:

(i) Hydrogen **(ii) Halogen acid**

(iii) Alkaline $KMnO_4$ **(iv) 10% H_2SO_4 in the presence of $HgSO_4$**

(v) Ammonical cuprous chloride

(c) Mention some important uses of methane, ethene and ethyne.

Ans.

(a) Consult the book.

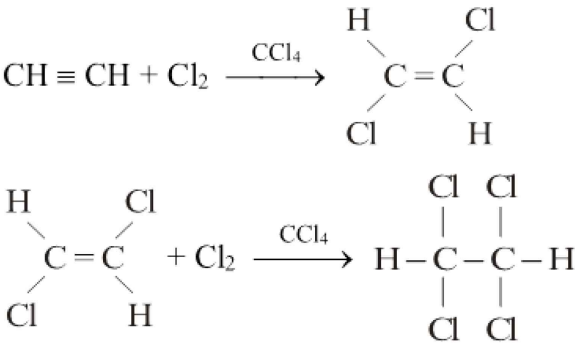
(b)

(i) Hydrogen:

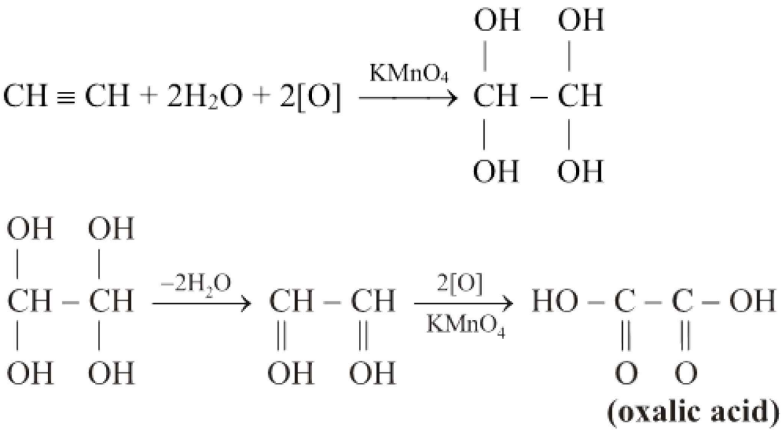
$$CH \equiv CH + H_2 \xrightarrow[250°C]{Ni} CH_2 = CH_2$$

$$CH_2 = CH_2 + H_2 \xrightarrow[250°C]{Ni} CH_3 - CH_3$$

(ii) Halogen:

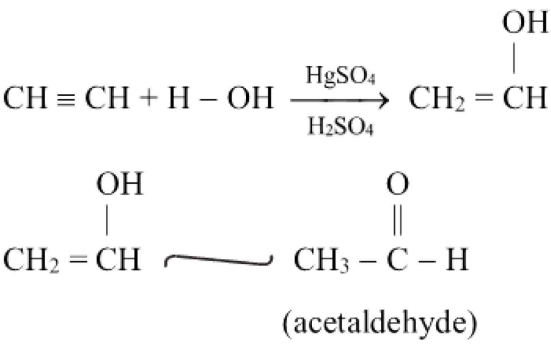


(iii) Alkaline $KMnO_4$:



(oxalic acid)

(iv) 10% H_2SO_4 in the presence of $HgSO_4$:



(acetaldehyde)

(v) Ammonical cuprous chloride:

$$HC \equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow Cu - C \equiv C - Cu + 2NH_4Cl + 2H_2O$$

(vi) Bromine water with:

$$CH \equiv CH + Br_2 \longrightarrow CHBr = CHBr + Br_2 \longrightarrow CHBr_2 - CHBr_2$$

(c) Consult the book.

Q.22 Describe how you could distinguish ethane, ethene and ethyne from one another by means of chemical reactions.

Ans. **Distinction between Ethane, Ethylene and Acetylene:**

Reagent	Ethane	Ethylene	Acetylene
(1) Alkaline $KMnO_4$ soln.	No reaction	Decolourized $3CH_2 = CH_2 + 4H_2O + 2KMnO_4 \rightarrow CH_2(OH) - CH_2(OH) + 2MnO_2 + 2KOH$	Declolourized $3CH \equiv CH + 4H_2O + 8KMnO_4 \rightarrow 3H_2C_2O_4 + 8MnO_2 + 8KOH$
(2) Bromine water	No reaction	Decolourized $CH_2 = CH_2 + Br_2 \rightarrow CH_2Br - CH_2Br$	Decolourized $CH \equiv CH + Br_2 \rightarrow CHBr = CHBr \xrightarrow{Br_2} Br_2CH - Br_2CH$
(3) Ammonical $AgNO_3$	No reaction	No reaction	While ppt. of silver acetylide $CH \equiv CH + 2AgNO_3 + 2NH_4OH \rightarrow AgC \equiv CAg + 2NH_4NO_3 + 2H_2O$
(4) Ammonical Cu_2Cl_2	No reaction	No reaction	Red ppt. of copper acetylide $CH \equiv CH + Cu_2Cl_2 + 2NH_4OH \rightarrow CuC \equiv CCu + 2NH_4Cl + 2H_2O$
(5) 10% H_2SO_4 + $HgSO_4$	No reaction	Ethyl alcohol is formed $CH_2 = CH_2 + H_2O \xrightarrow[H_2SO_4]{10\%\ H_2SO_4} CH_3 - CH_2OH$	Acetaldehyde is formed. $CH \equiv CH + H_2O \xrightarrow[H_2SO_4]{10\%\ H_2SO_4} CH_2 = CH - OH \rightarrow CH_3 - CHO$

Q.23 (a) How will you synthesize the following compounds starting from ethyne:

(i) Acetaldehyde **(ii) Benzene**

(iii) Chloroprene **(iv) Glyoxal**

(v) Oxalic acid **(vi) Acrylonitrile**

(vii) Ethane **(viii) Methyl nitrile**

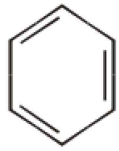
(b) Write a note on the acidity of ethyne.

Ans.

(a) (i) Ethyne $\longrightarrow$ Acetaldehyde

$$HC \equiv CH + \overset{+\ -}{H}OH \xrightarrow[HgSO_4]{10\%\ H_2SO_4} \begin{matrix} CH_2 \\ \| \\ CHOH \end{matrix} \rightleftharpoons CH_3 - \overset{O}{\overset{\|}{C}} - H$$

(ii) Ethyne ⟶ Benzene

$$3HC \equiv CH \xrightarrow[300^\circ C]{\text{Cu-tube}}$$ 

(iii) Ethyne ⟶ Chloroperene

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

Vinyl-acetylene

$$CH_2 = CH - C \equiv CH + HCl \longrightarrow H_2C = CH - \underset{\displaystyle Cl}{\underset{|}{C}} = CH_2$$

(iv) Ethyne ⟶ Glyoxal

$$HC \equiv CH + 2H_2O + 2[O] \xrightarrow{KMnO_4} \begin{matrix} OH & OH \\ | & | \\ HC & - CH \\ | & | \\ OH & OH \end{matrix} \xrightarrow{-2H_2O} \begin{matrix} CH = O \\ | \\ CH = O \end{matrix}$$

(v) Ethyne ⟶ Oxalic acid

$$HC \equiv CH + 2H_2O + 2[O] \xrightarrow{KMnO_4} \begin{matrix} OH & OH \\ | & | \\ HC & - CH \\ | & | \\ OH & OH \end{matrix} \xrightarrow{-2H_2O} \begin{matrix} CH = O \\ | \\ CH = O \end{matrix}$$

$$\begin{matrix} CH = O \\ | \\ CH = O \end{matrix} + 2[O] \xrightarrow{KMnO_4} \begin{matrix} COOH \\ | \\ COOH \end{matrix}$$

(OR)

$$3 \begin{matrix} CH \\ \vdots \\ CH \end{matrix} + 8KMnO_4 + 4H_2O \longrightarrow 3 \begin{matrix} COOH \\ | \\ COOH \end{matrix} + 8MnO_2 + 8KOH$$

(vi) Ethyne ⟶ Acrylonitrile

$$\begin{matrix} CH \\ \vdots \\ CH \end{matrix} + \overset{+\ -}{HCN} \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH - CN \end{matrix}$$

(vii) Ethyne ⟶ Ethane

$$HC \equiv CH + H_2 \xrightarrow[250°C]{Ni} CH_2 = CH_2 + H_2 \xrightarrow[250°C]{Ni} CH_3 - CH_3$$

(viii) Ethyne ⟶ Methyl nitrile

$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + NH_3 \xrightarrow[300°C]{Al_2O_3} \begin{matrix} CH_3 \\ | \\ C \equiv N \end{matrix} + H_2$$

(b) Consult the chapter.

Q.24 (a) Compare the reactivity of ethane, ethene and ethyne.

(b) Compare the physical properties of alkanes, alkenes and alkynes.

Ans.

(a) The general decreasing reactivity order of ethane, ethene and ethyne is as follow:

Ethene > Ethyne > Ethane

Reasons: A π-bond in **ethene** is not only weak but its electrons are more exposed to an attack by an electrophilic reagent. Both these facts make the ethene a very reactive compound. **Ethyne** although contain 2π-bonds but it is less reactive than ethene towards electrophilic reagents. This is because the bond distance between the two triple bonded carbon atoms is very short and hence π-electrons are not easily available to be attacked by electrophilic reagents. Ethyne is, however more reactive than ethene towards nucleophilic reagents. **Ethane** have no π-electrons so, it is much less reactive than ethene or ethyne.

(b) (i) Physical State:

Alkanes: Alkanes containing upto 4 carbon atoms are gases while pentane to heptadecane (C_5 to C_{17}) are liquids. The higher members from C_{18} to onwards are waxy solids.

Alkenes: First 3 members of alkenes are gases while C_5 to C_{15} are liquids and higher members are solids.

Alkynes: The first 3 members of alkynes are gases. C_5 to C_{12} are liquids and higher members are solids.

(ii) Characteristics:

Alkanes: All alkanes are colourless and odourless.

Alkenes: They have characteristic smell.

Alkynes: They are colourless, odourless, except acetylene which has garlic like odour.

(iii) Polarity and Solubility:

Alkanes: They are non-polar or very weakly polar and are insoluble in polar solvents like water but soluble in non-polar solvents like benzene etc.

Alkenes: They show weakly polar properties because of sp^2 hybridization. They are insoluble in H_2O but soluble in alcohol.

Alkynes: They are non-polar and dissolve readily in non-polar solvents like ether, benzene, etc.

(iv) Physical Constants:

Alkane: In alkanes, boiling points, melting points and density increases with the increase in number of carbon atoms, whereas solubility decreases with increase in molecular mass.

Alkenes and Alkynes: In case of physical constants, similar trend for alkenes and alkynes as that for alkanes.

Q.25 How does propyne react with the following reagents:

(a) $AgNO_3/NH_4OH$ **(b) Cu_2Cl_2/NH_4OH**

(c) $H_2O/H_2SO_4HgSO_4$

Ans. Reaction of Propyne:

(a) $CH \equiv C - CH_3 + AgNO_3 + NH_4OH \longrightarrow Ag^+C^- \equiv C - CH_3 + NH_4NO_3 + H_2O$

Silver propylide (Red ppt)

(b) $2HC \equiv C - CH_3 + Cu_2Cl_2 + NH_4OH \longrightarrow 2Cu^+C^- \equiv C - CH_3 + 2NH_4Cl + 2H_2O$

Copper propylide

(c) $CH \equiv C - CH_3 + HOH \xrightarrow[HgSO_4]{H_2SO_4} CH_2 = \underset{\displaystyle OH}{\underset{|}{C}} - CH_3$

$CH_2 = \underset{\displaystyle O-H}{\underset{|}{C}} - CH_3 \xrightarrow{\text{Rearrangement}} CH_3 - \underset{\displaystyle O}{\underset{\|}{C}} - CH_3$

Enol form Acetone

Q.26 A compound has a molecular formula C_4H_6, when it is treated with excess hydrogen in the presence of Ni-catalyst, a new compound C_4H_{10} is formed. When C_4H_6 is treated with ammoniacal silver nitrate a white precipitate is formed. What is the structural formula of the given compound?

Ans.

(1) Reaction of H_2 shows that it has one triple bond in it.

(2) Reaction of compound with ammonical silver nitrate indicates that it has acidic hydrogen in it.

$$CH \equiv C - CH_2 - CH_3 + 2H_2 \xrightarrow{Ni} CH_3 - CH_2 - CH_2 - CH_3$$

1-Butyne

$$CH \equiv C - CH_2 - CH_3 + AgNO_3 + NH_4OH \longrightarrow Ag^+C \equiv C - CH_2 - CH_3 + NH_4NO_3 + H_2O$$

1-Butyne

The possible structure is:

$$HC \equiv C - CH_2 - CH_3$$

(1-Butyne)

and not $CH_3 - C \equiv C - CH_3$

(2-Butyne)

because 2-butyne does not react with ammonical silver nitrate.

Q.27 (a) Identify A and B:

$$\mathbf{CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow{Na/Ether} B}$$

(b) Give the general mechanism of electrophilic addition reactions of alkenes.

Ans.

(a) (i) Dehydration of Alcohol:

$$CH_3 - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 \xrightarrow[Heat]{PCl_5} CH_3CH_2CH_2Cl + POCl_3 + HCl$$

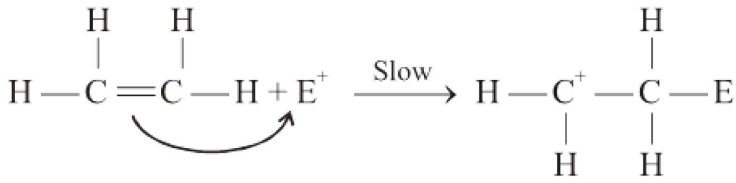
(ii) $$CH_3CH_2CH_2Cl + 2Na \xrightarrow{Ether} CH_3(CH_2)_4CH_3 + 2NaCl$$

n-Hexane

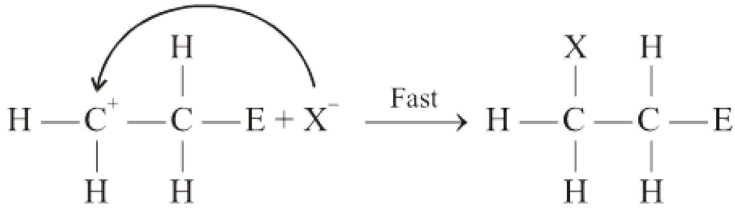
(b) Electrophilic Addition Reaction (Mechanism):

In alkenes, usually electrophilic addition takes place due to the presence of π-bond in it. The electrophilic reagent when approaches to the double bond it break up into negative and positive ions. Each ion (negative and positive) is added to double bond. Although both the ions are added but it is called electrophilic addition because reaction is initiated, when an electrophile approaches the

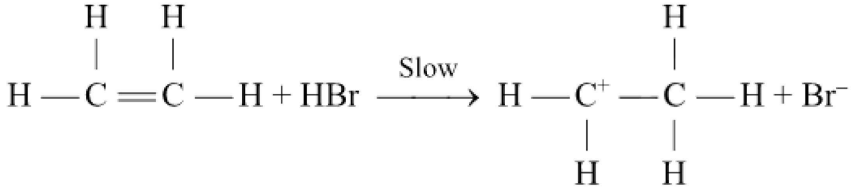
multiple bond. The two electrons of the π-bond form a new sigma bond with incoming electrophile.

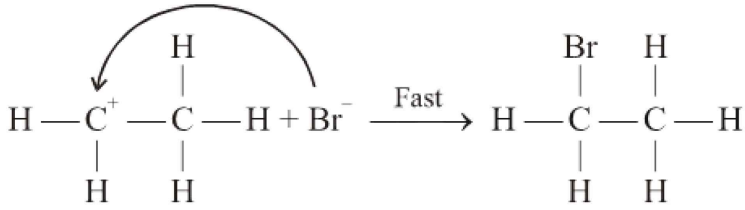


It is a slow step and rate determining step. A carbonium ion (Carbon with positive charge) is formed as the electrophile (E^+) attack on the multiple bond. The carbonium charge becomes satisfied by reacting with the negative ion.



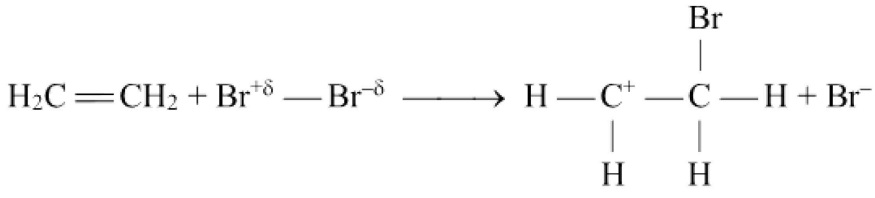
For example, when HBr is added to ethene following mechanism takes place.

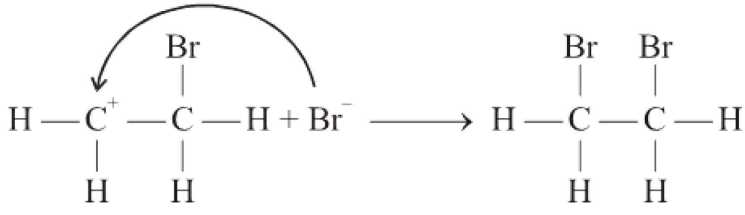




(b) When Br_2 is added to ethene, the following mechanism takes place.

Br_2 is non-polar but when Br_2 approaches to ethene, polarization in molecule takes place due to repulsions of the electron cloud. First an intermediate is formed which changes to dihalide by further attack of Br^-.





(1,2-dibromoethane)

DO YOU KNOW?

(1) Alkanes are also called paraffins.

(2) Alkenes are also called olefines.

(3) $C_{20}H_{42}$ is called eicosane.

(4) $C_{11}H_{24}$ is called undecane.

(5) $C_{12}H_{26}$ is called dodecane.

(6) $C_{16}H_{34}$ is called hexadecane.

(7) $C_{100}H_{202}$ is called hectane.

(8) Wurtz's reaction is used for lengthening the carbon chain.

(9) The boiling point of branched chain alkanes are less than straight chain hydrocarbons.

(10) Kolbe's method is used for the preparation of alkanes, alkenes, alkynes.

(11) Raney Nickel has high surface area and is more reactive.

(12) Bayer's test is used for the identification of double bond.

(13) Mustard gas is highly boiling liquid. It is used as vesicant (blistering agent).

(14) 1-butyne reacts with ammonical $AgNO_3$ but 2-butyne does not react.

(15) Acetylene was prepared accidentally by an American Chemist named Willson.

(16) Ethyne has garlic like odour.

(17) Methane is also called marsh gas.

(18) $-CH_2-$ is methylene radical.

(19) $\equiv CH$ is methylidene radical.

(20) $CH_3 - CH<$ ethylidene.

(21) $CH_2 = CH -$ vinyl radical.

(22) $CH_2 = CH - CH_2 -$ ally radical.

(23) $CH_3 - CH = CH - CH_2$ – cryotyl radical.

(24) Barbituric acid $C_4H_4N_2O_3$.

(25) Two halogen atoms attacked to adjacent C-atoms are vicinal dihalides and if two halogen atoms are attached to the same C-atom, then it is called geminal dihalide. For example:

$CH_2(X) - CH_2(X)$ vicinal dihalide.

$CH_3 - CH(X)_2$ geminal dihalide.

(26) Quinoline



CHAPTER 8

ALIPHATIC HYDROCARBONS

MULTIPLE CHOICE QUESTIONS

1. Preparation of vegetable ghee involves:

(a) Halogenation **(b)** Hydrogenation

(c) Hydroxylation **(d)** Dehydrogenation

2. Which type of reactions are given by alkanes:

(a) Polymerization **(b)** Elimination

(c) Addition **(d)** Substitution

3. The most reactive hydrocarbon is:

(a) Ethene **(b)** Acetylene

(c) Heptane **(d)** Ethane

4. Formula of chloroform is:

(a) CH_3Cl **(b)** CCl_4

(c) CH_2Cl_2 **(d)** $CHCl_3$

5. Cycloalkanes and Alkenes contain which general formula:

(a) C_nH_{2n+2} **(b)** C_nH_{2n}

(c) C_nH_{2n-2} **(d)** C_nH_n

6. Which of the following is not alicyclic:

(a) Cyclohexene **(b)** Cyclobutane

(c) Toluene **(d)** Cyclopentene

7. Unsaturated nature of alkene can be detected by:

(a) Decolorization of red Br_2 water in CCl_4

(b) Decolorization of pink colour of $KMnO_4$ solution

(c) Ozonolysis

(d) All

8. The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule:

(a) Hund's rule **(b)** Mankownikov's rule

(c) Pauli's exclusion principle **(d)** Aufbau principle

9. Vicinal dihalides on treatment with Zn-dust give:

(a) Alkenes **(b)** Alkynes

(c) Alkanes **(d)** All of them

10. Formula of lindlers catalyst is:

(a) $Pb(BaSO_4)$ / Quinoline **(b)** $Ba(PbSO_4)$ / Quinoline

(c) $Pd(BaSO_3)$ / Quinoline **(d)** $Pd(BaSO_4)$ / Quinoline

11. Synthetic rubber is made by the polymerization of:

(a) Chloroform **(b)** Acetylene

(c) Divinyl acetylene **(d)** Chloroprene

12. Ammonical solution of silver nitrate reacts with:

(a) 2-pentyne **(b)** Ethene

(c) 2-butyne **(d)** Ethyne

13. Polymerization of acetylene forms:

(a) Propane **(b)** Butane

(c) Benzene **(d)** Napthalene

14. The number of xylene isomers is:

(a) 2 **(b)** 3

(c) 4 **(d)** 5

15. Number of acidic hydrogens present in 1-butyne is:

(a) 1 **(b)** 2

(c) 3 **(d)** 4

16. Chemically Baeyer's reagent is:

(a) 1% alkaline $KMnO_4$ **(b)** 1% acidic $KMnO_4$

(c) 15% alkaline $KMnO_4$ **(d)** 2% alkaline $KMnO_4$

17. Which of the following gases is used for artificial ripening of fruits:

(a) Ethene **(b)** Ethyne

(c) Methane **(d)** Both (a) and (b)

18. Hydroxylation of alkene can be carried out by:

(a) Alkaline $KMnO_4$ **(b)** O_3

(c) H_2SO_4 **(d)** $K_2Cr_2O_7$

19. Acetylene has a characteristic smell resembling that of:

(a) Rotten egg **(b)** Garlic

(c) Spicy like **(d)** None of the above

20. When ethylene ozonide is treated with Zn-dust we get:

(a) Ethanal **(b)** Methanal

(c) Methanol **(d)** Ethanol

answers

1.	(b)	**2.**	(d)	**3.**	(a)	**4.**	(d)	**5.**	(b)
6.	(c)	**7.**	(d)	**8.**	(b)	**9.**	(a)	**10.**	(d)
11.	(d)	**12.**	(d)	**13.**	(c)	**14.**	(b)	**15.**	(a)
16.	(a)	**17.**	(a, b)	**18.**	(a)	**19.**	(b)	**20.**	(b)

SOLVED EXERCISE

Q.1 Fill in the blanks:

(i) Ozone reacts with ethene to form ————.

(ii) Lindlar's catalyst is used for ———— of alkynes.

(iii) Divinyl acetylene is a ———— of acetylene.

(iv) Vicinal dihalides have two halogens on ———— carbon atoms.

(v) Ethyne is acidic in character because of ———— hybridization.

(vi) Halohydrins are formed due to addition of ———— in ethene.

(vii) Ethylene glycol is produced when ———— reacts with cold alkaline $KMnO_4$ solution.

(viii) Mustard gas is a highly boiling ————.

(ix) Ethyne has ———— like odour.

(x) Ethyne is obtained by the reaction of ———— with calcium carbide.

answers

(i)	ozonide	**(ii)**	partial hydrogenation	**(iii)**	polymer
(iv)	adjacent	**(v)**	sp	**(vi)**	hypohalous acid HOX
(vii)	ethene	**(viii)**	liquid	**(ix)**	garlic
(x)	water				

Q.2 Indicate True or False:

(i) Addition of HX to unsymmetrical alkanes takes place according to Markownikov's rule.

(ii) Methane reacts with bromine water and its colour is discharged.

(iii) Mustard gas is a blistering agent.

(iv) Methane is also called marsh gas.

(v) Ethyne is a saturated compound.

(vi) Bayer's reagent is used to locate a double bond in an alkene.

(vii) Alkanes usually undergo substitution reactions.

(viii) Benzene is a polymer of ethene.

(ix) Acrylonitrile can be obtained from ethyne.

(x) Ethyne is more reactive towards electrophilic reagents than ethene.

answers

(i)	False	**(ii)**	False	**(iii)**	True	**(iv)**	True	**(v)**	False
(vi)	True	**(vii)**	True	**(viii)**	False	**(ix)**	True	**(x)**	False

Q.3 Multiple choice questions. Encircle the correct answer:

(i) Preparation of vegetable ghee involves:

(a) Halogenation **(b)** Hydrogenation

(c) Hydroxylation **(d)** Dehydrogenation

(ii) Formula of chloroform is:

(a) CH_3Cl **(b)** CCl_4

(c) CH_2Cl_2 **(d)** $CHCl_3$

(iii) The presence of a double bond in a compound is the sign of:

(a) Saturation **(b)** Unsaturation

(c) Substitution **(d)** None

(iv) Vinyl acetylene combines with HCl to form:

(a) Polyacetylene **(b)** Benzene

(c) Chloroprene **(d)** Divinylacetylene

(v) The addition of unsymmetrical reagent to an unsymmetrical alkene is in accordance with the rule:

(a) Hund's rule **(b)** Markownikov's rule

(c) Pauli's exclusion principle **(d)** Aufbau principle

(vi) Synthetic rubber is made by polymerization of:

(a) Chloroform **(b)** Acetylene

(c) Divinylacetylene **(d)** Chloroprene

(vii) β-β′-dichloroethyl sulphide is commonly known as:

(a) Mustard gas **(b)** Laughing gas

(c) Phosgene gas **(d)** Bio-gas

(viii) When methane reacts with Cl_2 in the presence of diffused light the products obtained are:

(a) Chloroform only

(b) Carbon tetrachloride only

(c) Chloromethane and dichloromethane

(d) Mixture of (a), (b), (c)

(ix) Which one of the following gases is used for artificial ripening of fruits:

(a) Ethene **(b)** Ethyne

(c) Methane **(d)** Both (a) and (b)

answers

(i)	(b)	**(ii)**	(d)	**(iii)**	(b)	**(iv)**	(c)	**(v)**	(b)
(vi)	(d)	**(vii)**	(a)	**(viii)**	(d)	**(ix)**	(d)		

Q.4 Write the structural formula for each of the following compounds:

(i) 2-methylpropane **(ii) Neopentane**

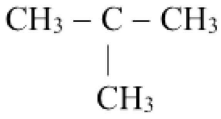
(iii) 3-ethylpentane **(iv) 4-ethyl-3, 4-dimethylheptane**

(v) 2, 2, 3, 4-tetramethylpentane **(vi) 2, 2, 3, 4-tetramethylpentane**

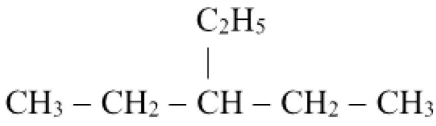
(vii) 2, 2-dimethylbutane **(viii) 2, 2-dimethylpropane**

Ans.

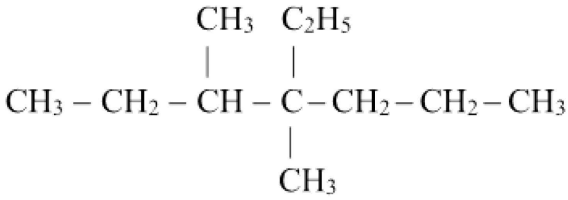
	Compound Name	Structural Formula
(i)	**2-methylpropane**	$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{\underset{\displaystyle \vert}{CH}}}}-CH_3$
(ii)	**Neopentane**	$\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{\displaystyle \vert}{\underset{\displaystyle \vert}{}}}}$



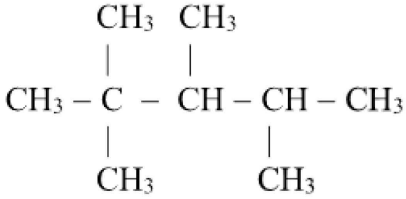
(iii) **3-ethylpentane**



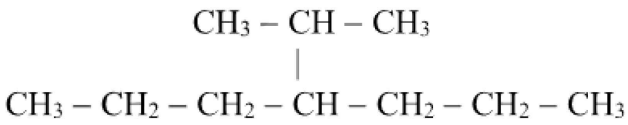
(iv) **4-ethyl-3, 4-dimethylheptane**



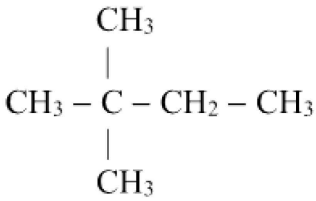
(v) **2, 2, 3, 4-tetramethylpentane**



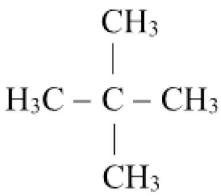
(vi) **4-iso-propylheptane**



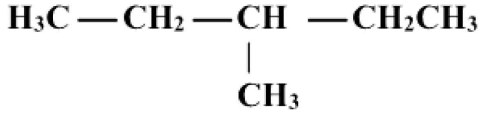
(vii) **2, 2-dimthyl butane**



(viii) **2, 2-dimethylpropane**



Q.5 Write down names of the following compounds according to IUPAC system:

(i) 

(ii) $(CH_3)_3C - CH_2 - C(CH_3)_3$

(iii) 

(iv) $(CH_3)_2CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH(CH_3)_2$

(v) $CH_3CH_2C(CH_3)_2\ CH(CH_2CH_3)CH_3$

(vi) $(CH_3CH_2)_3CH$

(vii) $CH_3C(CH_3)_2(CH_2)_2CH_3$

(viii) $(C_6H_5)_3CH$

Ans.

	Compound	IUPAC Name
(i)	$H_3C - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH_2CH_3$	3-methylpentane
(ii)	$(CH_3)_3C - CH_2 - C(CH_3)_3$	2, 2, 4, 4-tetramethylpentane
(iii)		2, 4-dimethylpentane
(iv)	$(CH_3)_2CH - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH(CH_3)_2$	2, 3, 4-trimethylpentane
(v)	$CH_3CH_2C(CH_3)_2\ CH(CH_2CH_3)CH_3$	3, 3, 4-trimethylhexane
(vi)	$(CH_3CH_2)_3CH$	3-ethylpentane
(vii)	$CH_3C(CH_3)_2(CH_2)_2CH_3$	2, 2-dimethylpentane
(viii)	$(C_6H_5)_3CH$	triphenylmethane

Q.6 What are the rules for naming alkanes? Explain with suitable examples.

Ans. Detailed question. See text book.

Q.7 (a) Write down the structural formulas for all the isomeric hexanes and name them according to IUPAC system.

(b) The following names are incorrect. Give the correct IUPAC names:

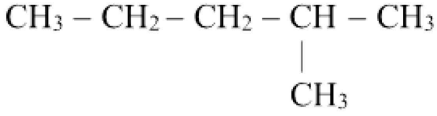
(i) 4-methylpentane (ii) 3, 5, 5-trimethylhexane

(iii) 2-methy-3-ethylbutane

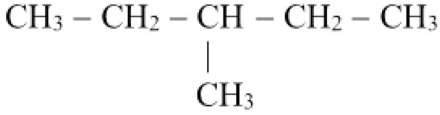
Ans.

(a) The isomeric forms of hexanes and their IUPAC names are as follows:

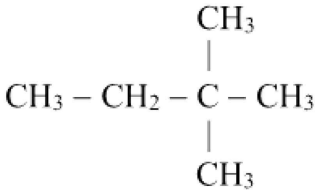
$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$ Hexane



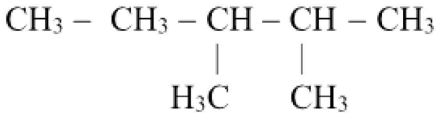
2-methylpentane



3-methylpentane

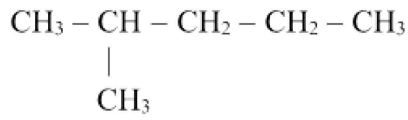
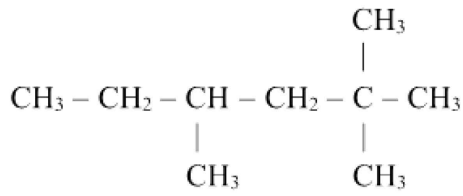


2, 2-dimethylbutane

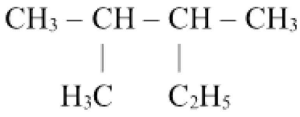


2, 3-dimethylbutane

(b) Correct names:

Given Name	Structure	Correct Name
4-methylpentane		2-methyl pentane
3, 5, 5-trimethylhexane		2, 2, 4-trimethyl hexane

2-methyl-3-ethylbutane



2, 3-dimethyl pentane

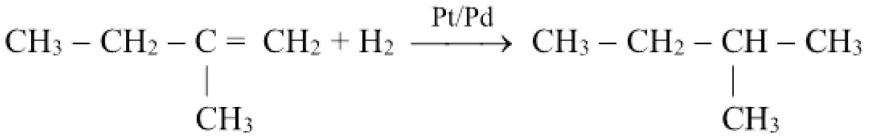
Q.8 (a) Explain why alkanes are less reactive than alkenes? What is the effect of branching on the melting point of alkanes?

(b) Three different alkanes yield 2-methylbutane when they are hydrogenated in the presence of a metal catalyst. Give their structures and write equations for the reactions involved.

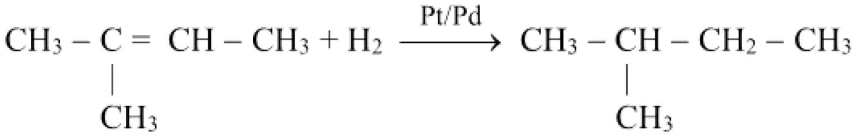
Ans.

(a) Descriptive question. Consult text book for details.

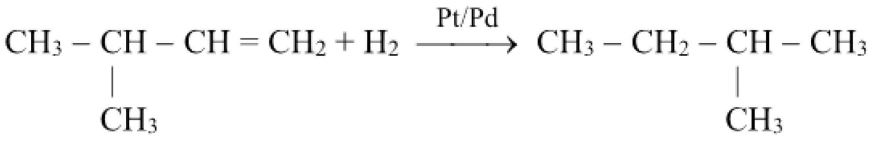
(b) **(i) 2-methyl-1-butene:**



(ii) 2-methyl-2-butene:



(iii) 3-methyl-1-butene:



Q.9 (a) Out line the methods available for the preparation of alkanes.

(b) How will you bring about the following conversions?

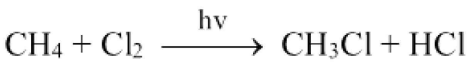
(i) Methane to ethane **(ii) Ethane to methane**

(iii) Acetic acid to ethane **(iv) Methane to nitromethane**

Ans.

(a) Descriptive question. Consult text book for details.

(b) **(i) Methane into ethane:**



$$2CH_3Cl + 2Na \longrightarrow CH_3 - CH_3 + 2NaCl$$

(ii) Ethane into methane:

$$CH_3 - CH_3 + Cl_2 \xrightarrow{hv} CH_3 - CH_2Cl + HCl$$

$$CH_3 - CH_2Cl + KOH_{(aq)} \longrightarrow CH_3 - CH_2 - OH + KCl$$

$$CH_3 - CH_2 - OH + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{\overset{O}{\|}}{C} - H + H_2O$$

$$CH_3 - \overset{\overset{O}{\|}}{C} - H + [O] \xrightarrow[H_2SO_4]{K_2Cr_2O_7} CH_3 - \overset{\overset{O}{\|}}{C} - OH$$

$$CH_3 - \overset{\overset{O}{\|}}{C} - OH + NaOH \longrightarrow CH_3 - \overset{\overset{O}{\|}}{C} - ONa + H_2O$$

$$CH_3 - \overset{\overset{O}{\|}}{C} - ONa + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$

(iii) Acetic acid to ethane:

$$CH_3COOH + 6HI \xrightarrow{P} CH_3 - CH_3 + 3I_2 + 2H_2O$$

(iv) Methane to nitromethane:

$$CH_4 + HNO_3 \xrightarrow{450°C} CH_3 - NO_2 + H_2O$$

Q.10 (a) What is meant by octane number? Why does a high octane fuel has a less tendency to knock in an automobile engine?

(b) Explain free radical mechanism for the reaction of chlorine with methane in the presence of sunlight.

Ans.

(a) (i) Octane Number: It is defined as; the percentage of branched chain hydrocarbon, iso-octane, in gasoline fraction of petroleum is known as octane number.

(ii) Less Tendency to Knock: High octane fuel has less tendency to knock because it contains 100% isooctane.

(b) Descriptive question. Consult text book for details.

Q.11 (a) Write structural formulas for each of the following compounds:

(i) Isobutylene **(ii) 2, 3, 4, 4-tetramethyl-2-pentene**

(iii) 2, 5-heptadiene **(iv) 4, 5-dimethyl-2-hexene**

(v) Vinylacetylene **(vi) 1, 3-pentadiene**

(vii) 1-butyne **(viii) 3-n-propyl-1, 4-pentadiene**

(ix) Vinyl bromide **(x) But-1-en-3yne**

(xi) 4-methyl-2-pentyne **(xii) Iso-pentane**

(b) Name the following compounds by IUPAC system:

(i) $H_3C-CH=CH(CH_2)_2CH_3$

(ii) $(CH_3)_2C=CH_2$

(iii)
$$CH_3-CH_2-CH_2-\underset{\displaystyle CH(CH_3)_2}{\underset{|}{C}}=CH_2$$

(iv) $CH_2=CH-CH=CH_2$

(v)
$$CH_2=\underset{\displaystyle C_2H_5}{\underset{|}{C}}-CH_2CH_2CH_3$$

(vi) $CH\equiv C-CH_3$

(vii) $CH_3-C\equiv C-CH_3$

(viii) $CH_2=CH-C\equiv C-CH=CH_2$

(ix) $CH\equiv C-CH=CH-C\equiv CH$

(x) $CH_2=CH-C\equiv CH$

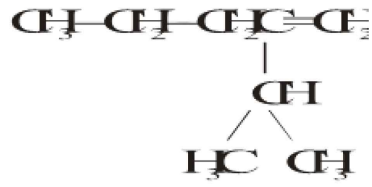
Ans.

(a)

Name	Structural Formulas
Isobutylene	$CH_3-\underset{\displaystyle CH_3}{\underset{\displaystyle \vert}{C}}=CH_2$

2, 3, 4, 4-tetramethyl-2-pentene	$CH_3 - CH = C(CH_3) - C(CH_3)_2 - CH_3$
2, 5-heptadiene	$H_3C - CH = CH - CH_2 - CH = CH - CH_3$
4, 5-dimethyl-2-hexene	$CH_3 - CH = CH - CH(CH_3) - CH(CH_3) - CH_3$
Vinyl acetylene	$CH_2 = CH - C \equiv CH$
1, 3-pentadiene	$CH_2 = CH - CH = CH - CH_3$
1-butyne	$CH \equiv C - CH_2 - CH_3$
3-n propyl-1, 4-pentadiene	$CH_2 = CH - CH(CH_2 - CH_2 - CH_3) - CH = CH_2$
Vinyl bromide	$CH_2 = CH - Br$
But-1-en-3-yne	$HC \equiv C - CH = CH_2$
4-methyl-2-pentyne	$CH_3 - C \equiv C - CH(CH_3) - CH_3$
Isopentane	$CH_3 - CH_2 - CH(CH_3) - CH_3$

(b)

Compounds	IUPAC Name
$CH_3 - CH = CH(CH_2)_2CH_3$	2-hexene
$(CH_3)_2C = CH_2$	2-methyl-1-propene
	2-isopropyl-1-pentene
$CH_2 = CH - CH = CH_2$	1, 4-butadiene

$CH_2 = C(C_2H_5) - CH_2 - CH_3$ — 2-ethyl-1-pentene

$HC \equiv C - CH_3$ — Propyne

$CH_3 - C \equiv C - CH_3$ — 2-butyne

$CH_2 = CH - C \equiv C - CH = CH_2$ — 1, 5-hexadiene-3-yne

$HC \equiv C - CH = CH - C \equiv CH$ — 3-hexene-1, 5-diyne

$H_2C = CH - C \equiv CH$ — 1-butene-3-yne

Q.12 (a) Describe different methods for the preparation of alkenes. How would you establish that ethylene contains a double bond?

(b) Give structure formulas of the alkenes expected to form by the dehydrohalogenation of the following compounds with a strong base:

(i) 1-chloropentane (ii) 2-chloro-3-methylbutane

(iii) 1-chloro-2, 2-dimethyl propane

Ans.

(a) Descriptive question. Consult text book.

"Ethylene contains double bond" it can be established by following reactions:

(i) Baeyer's test (ii) Ozonolysis

(i) Baeyer's Tests: Reaction with Baeyer's reagent i.e., 1% alkaline solution of $KMnO_4$

$$3H_2C = CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\ CH_2(OH)-CH_2(OH) + 2MnO_2 + 2KOH$$

Result: Discharging of the colour of $KMnO_4$ confirms the presence of double bond.

(ii) Ozonolysis:

$$CH_2 = CH_2 + O_3 \longrightarrow \text{ozonide} \xrightarrow[\text{ii. Zn}]{\text{i. } H_2O} 2H-C(=O)-H + ZnO$$

(b)

(i) 1-Chloropentane:

$$CH_3-CH_2-CH_2-CH_2-\underset{\displaystyle Cl}{\underset{|}{CH_2}}+KOH \xrightarrow[(alc)]{} CH_3-CH_2-CH_2-CH=CH_2+KCl+H_2O$$

1-pentene

(ii) 2-chloro-3-methyl butane:

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3+KOH \xrightarrow[(alc)]{} CH_3-CH=\underset{\displaystyle CH_3}{\underset{|}{C}}-CH_3+KCl+H_2O$$

2 methyl-2-butene

(iii) 1-chloro-2, 2-dimethyl propane:

$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-Cl \longrightarrow$$ As β-hydrogen is not available so reaction is not possible.

Q.13 (a) Write down chemical equations for the preparation of propene from the following compounds:

(i) $CH_3—CH_2—CH_2—OH$

(ii) $CH_3—C\equiv CH$

(iii) Iso-propyl chloride

(b) Write skeleton formula showing only the arrangement of carbon atoms for all the possible alkenes of the molecular formula C_5H_{10}.

Ans.

(a) (i) $$CH_3-CH_2-CH_2-OH \xrightarrow[140-170^\circ C]{75\%\ H_2SO_4} CH_3-CH=CH_2+H_2O$$

(ii) $$CH_3-C\equiv CH+H_2 \xrightarrow[Quinoline]{Pd(BaSO_4)} CH_3-CH=CH_2$$

(iii) $$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_3+KOH \xrightarrow[100^\circ C]{alcohol} CH_3-CH=CH_2+KCl+H_2O$$

(b) Possible structures of alkenes having molecular formula C_5H_{10} are as following:

(i) $CH_3-CH_2-CH_2-CH=CH_2$ 1-pentene

(ii) $CH_3-CH_2-CH=CH-CH_3$ 2-pentene

(iii) $CH_3 - CH_2 - \underset{\displaystyle CH_3}{\underset{|}{C}} = CH_2$ 2-methyl-1-butene

(iv) $CH_3 - \underset{\displaystyle CH_3}{\underset{|}{CH}} - CH = CH_2$ 3-methyl-1-butene

(v) $CH_3 - CH = \underset{\displaystyle CH_3}{\underset{|}{C}} - CH_3$ 2-methyl-2-butene

Q.14 (a) How may ethene be converted into ethyl alcohol?

(b) Starting from ethene, outline the reactions for the preparation of following compounds:

(i) 1, 2-ethyldibromide (ii) Ethyne

(iii) Ethane (iv) Ethylene glycol

(c) How will you bring about the following conversions:

(i) 1-butene to 1-butyne (ii) 1-propanol to $CH_3 — CH — CH_2Cl$

Ans.

(a) Ethene may be converted into ethyl alcohol by two steps:

(i) Addition of H_2SO_4:

$$CH_2 = CH_2 + H - O - SO_3H \longrightarrow CH_3 - CH_2 - O - SO_3H$$

(ii) Hydration:

$$CH_3 - CH_2 - O - SO_3H + H - OH \xrightarrow{100°C} CH_3 - CH_2 - OH + H_2SO_4$$

(b) (i) Ethylene dibromide:

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} Br - CH_2 - CH_2 - Br$$

(ii) Ethyne:

(a) $$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} Br - CH_2 - CH_2 - Br$$

(b) $$Br - CH_2 - CH_2 - Br + 2KOH \xrightarrow[(alc)]{80°C} CH \equiv CH + 2KBr + 2H_2O$$

(iii) Ethane:

$$CH_2 = CH_2 + H_2 \xrightarrow[250°C]{Ni} CH_3 - CH_3$$

(iv) Ethylene glycol:

$$3H_2C = CH_2 + 2KMnO_4 + 4H_2O \xrightarrow{\overline{O}H} \underset{\displaystyle CH_2 - OH}{\overset{\displaystyle 3CH_2 - OH}{|}} + 2MnO_2 + 2KOH$$

(c) (i) 1-butene to 1-butyne:

Steps involved:

1. Bromination:

$$CH_3 - CH_2 - CH = CH_2 + Br_2 \xrightarrow{CCl_4} CH_3 - CH_2 - \underset{\displaystyle Br}{\overset{\displaystyle CH}{|}} - \underset{\displaystyle Br}{\overset{\displaystyle CH_2}{|}}$$

2. Dehydrohlogenation:

$$CH_3 - CH_2 - \underset{\displaystyle Br}{\overset{\displaystyle CH}{|}} - \underset{\displaystyle Br}{\overset{\displaystyle CH_2}{|}} + 2KOH \xrightarrow[(alc)]{100^\circ C} CH_3 - CH_2 - C \equiv CH + 2KBr + 2H_2O$$

(ii) 1-propanol to $CH_3 - \underset{\displaystyle OH}{\overset{\displaystyle CH}{|}} - \underset{\displaystyle Cl}{\overset{\displaystyle CH_2}{|}}$

Steps involved:

1. Dehydration:

$$CH_3 - CH_2 - CH_2 - OH \xrightarrow[140-170^\circ C]{H_2SO_4} CH_3 - CH = CH_2 + H_2O$$

2. Addition of hypochlorus acid:

$$CH_3 - CH = CH_2 + HOCl \longrightarrow CH_3 - \underset{\displaystyle OH}{\overset{\displaystyle CH}{|}} - \underset{\displaystyle Cl}{\overset{\displaystyle CH_2}{|}}$$

Q.15 Show by means of chemical equations how the following cycle of changes may be affected:



Ans.

First Step:

Ethane $\longrightarrow$ Ethene

(i) Halogenation in the presence of sunlight:

$$CH_3 - CH_3 + Cl - Cl \xrightarrow{hv} CH_3 - CH_2 - Cl + HCl$$

(ii) Dehydrohalogenation:

$$CH_3 - CH_2 - Cl + KOH \xrightarrow[(alc)]{100^\circ C} CH_2 = CH_2 + KCl + H_2O$$

Second Step:

Ethene $\longrightarrow$ Ethyne

(i) Addition of halogen:

$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} Br - CH_2 - CH_2 - Br$$

(ii) Dehydrohalogenation:

$$Br - CH_2 - CH_2 - Br + 2KOH \xrightarrow[(alc)]{-HBr,\ 80^\circ C} CH \equiv CH + 2KBr + 2H_2O$$

Third Step:

Ethyne $\longrightarrow$ Ethane

(i) $CH \equiv CH + H_2 \xrightarrow[Ni\ (250^\circ C)]{Pd\ /\ BaSO_4} CH_2 = CH_2$

(ii) $CH_2 = CH_2 + H_2 \xrightarrow[250^\circ C]{Ni} CH_3 - CH_3$

Q.16 Write down structural formulas for the products that are formed when 1-butene will react with the following reagents:

(i) H_2, Pt **(ii) Br_3 in CCl_4**

(iii) Cold dil. $KMnO_4$\OH **(iv) HBr**

(v) O_2 in the presence of Ag **(vi) HOCl**

(vii) dil. H_2SO_4

Ans.

(i) $CH_2 = CH - CH_2 - CH_3 + H_2 \xrightarrow{Pt} CH_3 - CH_2 - CH_2 - CH_3$

n-butane

(ii) $CH_2 = CH - CH_2 - CH_3 + Br_2 \xrightarrow{CCl_4} \underset{\underset{Br}{|}}{CH_2} - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3$ (1-2-dibromobute)

(iii) $3CH_2 = CH - CH_2 - CH_3 + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{\underset{OH}{|}}{CH_2} - \underset{\underset{OH}{|}}{CH} - CH_2 - CH_3 + 2MnO_2 + 2KOH$

(iv) $CH_2 = CH - CH_2 - CH_3 + HBr \longrightarrow CH_3 - \underset{\underset{Br}{|}}{CH} - CH_2 - CH_3$ (2-bromobutane)

(v) $CH_3 - CH_2 - CH = CH_2 + \frac{1}{2} O_2 \xrightarrow[300°C]{Ag} CH_3 - CH_2 - \underset{\diagdown\ \diagup}{CH} - CH_2$ (Butylene oxide; O)

(vi) $CH_3 - CH_2 - CH = CH_2 + HOCl \longrightarrow CH_3 - CH_2 - \underset{\underset{OH}{|}}{CH} - \underset{\underset{Cl}{|}}{CH_2}$ (1-chloro-2-butanol)

(vii) $CH_3 - CH_2 - CH = CH_2 + H_2SO_4 \longrightarrow CH_3 - CH_2 - \underset{\underset{O - SO_3H}{|}}{CH} - CH_3$

Q.17 In the following reactions, identify each lettered product:

(i) **Ethyl alcohol** $\xrightarrow{\text{Conc. } H_2SO_4}$ **A** $\xrightarrow{Br_2}$ **B** $\xrightarrow[KOH]{\text{alcoholic}}$ **C**

(ii) **Propene** $\xrightarrow{Br_2}$ **D** $\xrightarrow[KOH]{\text{alcoholic}}$ **E** $\xrightarrow{HCN}$ **F**

Ans.

(i) Reactions Involved:

$$CH_3 - CH_2 - OH \xrightarrow[170°C, -H_2O]{\text{Conc. } H_2SO_4} CH_2 = CH_2 \xrightarrow[CCl_4]{Br_2} \underset{\underset{Br}{|}}{CH_2} - \underset{\underset{Br}{|}}{CH_2} \xrightarrow[-HBr]{2KOH\ (alc)} HC \equiv CH + 2KBr + 2H_2O$$

Products:

A = Ethene

B = 1, 2 dibromoethane

C = Ethyne

(ii) $CH_3 - CH = CH_2 + Br_2 \longrightarrow CH_3 - \underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_2}}$

$CH_3 - \underset{Br}{\underset{|}{CH}} - \underset{Br}{\underset{|}{CH_2}} + 2KOH\ (alc) \longrightarrow CH_3 - C \equiv CH + 2KBr + 2H_2O$

$CH_3 - C \equiv CH + HCN \longrightarrow CH_3 - \underset{CN}{\underset{|}{C}} = CH_2$

D = $CH_3 - \overset{Br}{\overset{|}{CH}} - \overset{Br}{\overset{|}{CH_2}}$ 1, 2-dibromopropane

E = $CH_3 - C \equiv CH$ Propyne

F = $CH_3 - \overset{CN}{\overset{|}{C}} = CH_2$ 2-cyano propene

Q.18 After an ozonolysis experiment, the only product obtained was acetaldehyde, CH_3CHO. Can you guess the structural formula of this compound.

Ans. The only product of acetaldehyde can be obtained by the ozonolysis of 2-butene.

Structural formula: $CH_3 - CH = CH - CH_3$

Q.19 (a) The addition of sulphuric acid to an alkene obeys Markownikov's rule. Predict the structures of the alochols obtained by the addition of the acid to the following compounds:

(i) Propene **(ii) 1-butene**

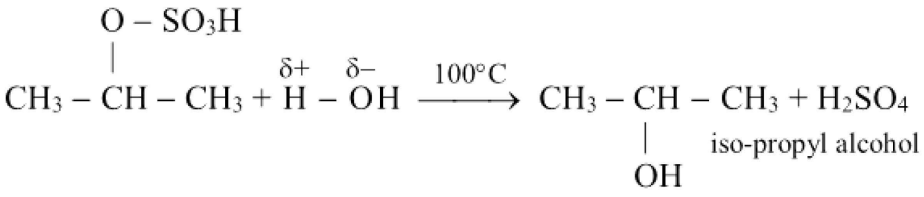
(iii) 2-butene

(b) Predict the most likely product of the addition of hydrogen chloride to 2-methyl 2-butene. Explain the formation of this product.

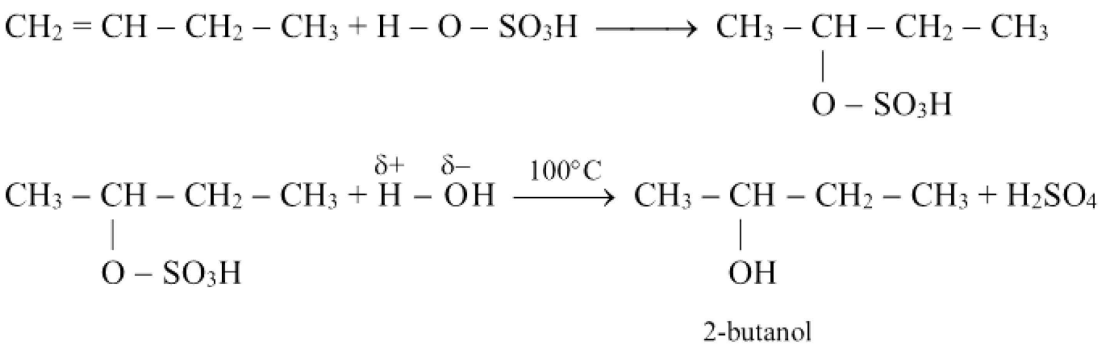
Ans.

(a) (i) Propene:

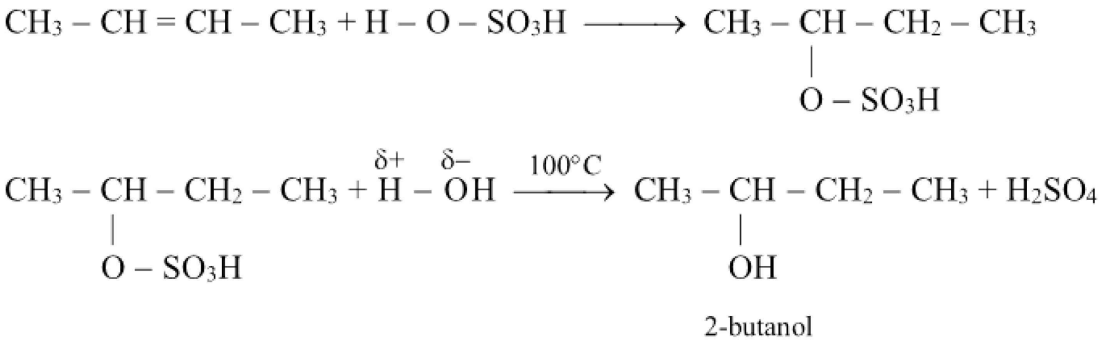
$CH_3 - CH = CH_2 + H - O - SO_3H \longrightarrow CH_3 - \underset{O - SO_3H}{\underset{|}{CH}} - CH_3$



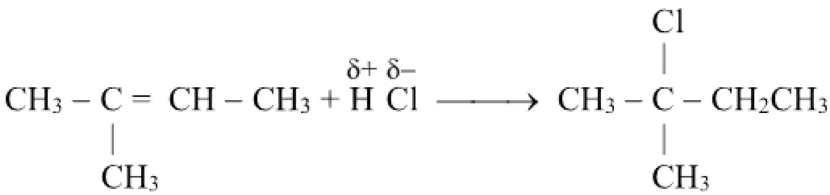
(ii) 1-butene:



(iii) 2-butene:



(b)



As 2-methyl-2-butene is an unsymmetrical compound and H-Cl is an unsymmetrical reagent so, the addition will be according to Markownikov's rule and the product will be 2-chloro-2 methyl butane.

Q.20 Why are some hydrocarbons called saturated and others unsaturated? What type of reactions are characteristics of them?

Ans. **Saturated Hydrocarbons:** If all the valencies of the carbon atoms in a molecule are fully satisfied and these cannot further take up any more hydrogen or other atom then this compound is named as saturated hydrocarbon.

Type of Reactions: Saturated hydrocarbons give substitution reactions. e.g.,

$$CH_4 + HNO_3 \xrightarrow{450°C} CH_3 - NO_2 + H_2O$$

substitutional product

Unsaturated Hydrocarbons: If in the compounds of carbon and hydrogen all the four valencies of carbon atom are not fully utilized and they contain either a double or a triple bond then these are called as unsaturated hydrocarbons.

Types of Reactions: Unsaturated hydrocarbons give addition reactions. e.g.,

$$CH_2 = CH_2 + HCl \longrightarrow CH_3 - CH_2 - Cl$$

addition product

Q.21 (a) Describe methods for the preparation of ethyne.

(b) How does ethyne react with:

(i) Hydrogen **(ii) Halogen acid**

(iii) Alkaline $KMnO_4$ **(iv) 10% H_2SO_4 in the presence of $HgSO_4$**

(v) Ammonical cuprous chloride

(c) Mention some important uses of methane, ethene and ethyne.

Ans.

(a) Preparation of Ethyne:

(i) Hydrolysis of calcium carbide (industrial method):

$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$$

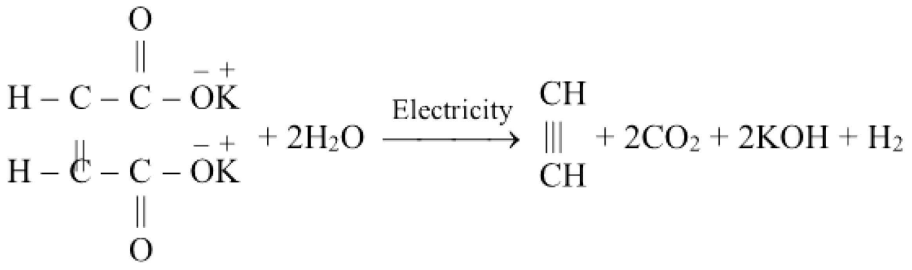
(ii) Dehydrohalogenation of vicinal dihalides:

$$\begin{array}{l} H_2C - CH_2 \\ \quad | \quad\ | \\ \quad Br \quad Br \end{array} + 2KOH \xrightarrow{(alc)} HC \equiv CH + 2KBr + 2H_2O$$

(iii) Dehalogenation of Tetrahalides:

$$\begin{array}{l} \quad Br \quad Br \\ \quad |\quad\ | \\ HC - CH \\ \quad |\quad\ | \\ \quad Br \quad Br \end{array} + 2Zn \longrightarrow HC \equiv CH + 2ZnBr_2$$

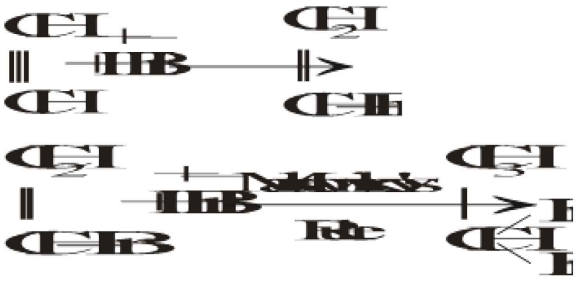
(iv) Kolbe's Method:

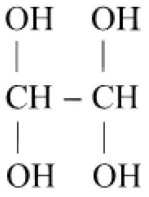


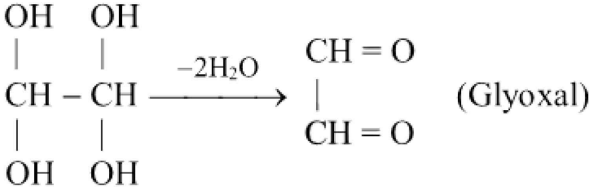
(b) (i) $HC \equiv CH + H_2 \xrightarrow{Ni} CH_2 = CH_2$

$CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$

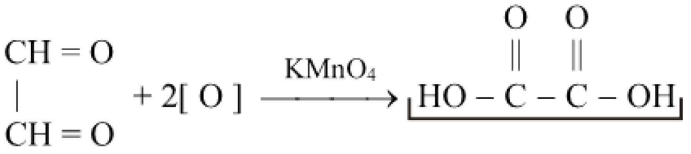
(ii)



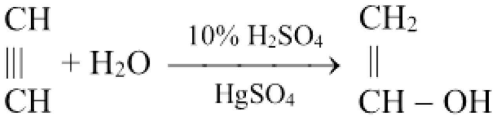
(iii) $HC \equiv CH + 2H_2O + 2[O] \xrightarrow{KMnO_4}$ 



(Glyoxal)



Oxalic acid

(iv) 



(c) Important Uses:

Uses of Methane:

(i) For the preparation of chloroform and carbon tetrachloride.

(ii) Methane is important constituent of natural gas.

(iii) For the industrial preparation of CH_3OH, HCHO, HCOOH.

(iv) Methane is used in the preparation of carbon-black used in paints, automobile tyres and printing inks.

(v) By cracking of methane, H_2 is produced which is used in fertilizers and for the hydrogenation of vegetable oils.

Uses of Ethene:

(i) Artificial ripening of fruits.

(ii) As an anaesthetic.

(iii) In the preparation of mustard gas.

(iv) In the preparation of polyethylene.

Uses of Ethyne:

(i) Oxy-acetylene flame (2800 – 3000°C) is used for welding.

(ii) For artificial ripening of fruits.

(iii) For the preparation of acetaldehyde, ethanol and acetic acid.

(iv) It is used in the preparation of PVC, Neoprene rubber, Orlon.

(v) It is used in the preparation of $C_2H_2Cl_4$ which is used in varnishes, resins, rubber.

Q.22 Describe how you could distinguish ethane, ethene and ethyne from one another by means of chemical reactions.

Ans. We can distinguish between saturated and unsaturated hydrocarbons by means of a chemical test called as Baeyer's test.

BAEYER'S TEST

Ethane / Ethene / Ethyne + $KMnO_4$ + H_2O + $\bar{O}H$

↓

Colour discharge ethene or ethyne is indicated → To differentiate between ethene and ethyne

No colour charge ethane $CH_3 - CH_3$ is confirmed

Ethene / Ethyne + $AgNO_3$ + NH_4OH

No ppt formed ethene $CH_2 = CH_2$ is confirmed

ppt formed ethyne $HC \equiv CH$ is confirmed

Q.23 (a) How will you synthesize the following compounds starting from ethyne:

(i) Acetaldehyde **(ii) Benzene**

(iii) Chloroprene **(iv) Glyoxal**

(v) Oxalic acid **(vi) Acrylonitrile**

(vii) Ethane **(viii) Methyl nitrile**

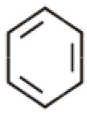
(b) Write a note on the acidity of ethyne.

Ans.

(a) (i) Acetaldehyde:

$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + \overset{+}{H}O\overset{-}{H} \xrightarrow[HgSO_4]{10\%\ H_2SO_4} \begin{matrix} CH_2 \\ \| \\ CHOH \end{matrix} \rightsquigarrow \begin{matrix} O \\ \| \\ CH_3 - C - H \end{matrix}$$

(ii) Benzene:

$$3HC \equiv CH \xrightarrow[300^\circ C]{Cu\text{-}tube}$$ 

(iii) Chlorperene:

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

$$CH_2 = CH - C \equiv CH + HCl \longrightarrow H_2C = CH - \underset{\displaystyle Cl}{\underset{|}{C}} = CH_2$$

(iv) Glyoxal:

$$HC \equiv CH + 2H_2O + 2[O] \longrightarrow \begin{matrix} OH & OH \\ | & | \\ CH & - & CH \\ | & & | \\ OH & & OH \end{matrix}$$

$$\begin{matrix} OH & OH \\ | & | \\ CH & - & CH \\ | & & | \\ OH & & OH \end{matrix} \xrightarrow{-2H_2O} \begin{matrix} CH = O \\ | \\ CH = O \end{matrix}$$

$$\begin{matrix} CH = O \\ | \\ CH = O \end{matrix} + 2[O] \xrightarrow{KMnO_4} \begin{matrix} O & O \\ \| & \| \\ HO - C & - & C - OH \end{matrix}$$

(v) Acrylonitrile:

$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + HCN \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2 = CH - CN$$

(vi) Ethane:

$$HC \equiv CH + H_2 \xrightarrow{Ni} CH_2 = CH_2$$

$$CH_2 = CH_2 + H_2 \xrightarrow{Ni} CH_3 - CH_3$$

(vii) Methyl Nitrile:

$$HC \equiv CH + NH_3 \xrightarrow[300^\circ C]{Al_2O_3} CH_2 - C \equiv N + H_2$$

(b) Consult the text book.

Q.24 (a) Compare the reactivity of ethane, ethene and ethyne.

(b) Compare the physical properties of alkanes, alkenes and alkynes.

Ans.

(a) The general decreasing reactivity order of ethane, ethene and ethyne is as follow:

Ethene > Ethyne > Ethane

Reasons: A π-bond in **ethene** is not only weak but its electrons are more exposed to an attack by an electrophilic reagent. Both these facts make the ethene a very reactive compound. **Ethyne** although contain 2π-bonds but it is less reactive than ethene towards electrophilic reagents. This is because the bond distance between the two triple bonded carbon atoms is very short and hence π-electrons are not easily available to be attacked by electrophilic reagents. Ethyne is, however more reactive than ethene towards nucleophilic reagents. **Ethane** have no π-electrons so, it is much less reactive than ethene or ethyne.

(b) (i) Physical State:

Alkanes: Alkanes containing upto 4 carbon atoms are gases while pentane to heptadecane (C_5 to C_{17}) are liquids. The higher members from C_{18} to onwards are waxy solids.

Alkenes: First 3 members of alkenes are gases while C_5 to C_{15} are liquids and higher members are solids.

Alkynes: The first 3 members of alkynes are gases. Next 8 members C_5 to C_{12} are liquid and higher members are solids.

(ii) Characteristics:

Alkanes: All alkanes are colourless and odourless.

Alkenes: They have characteristic smell.

Alkynes: They are colourless, odourless, except acetylene which has garlic like odour.

(iii) Polarity and Solubility:

Alkanes: They are non-polar or very weakly polar and are insoluble in polar solvents like water but soluble in non-polar solvents like benzene etc.

Alkenes: They show weakly polar properties because of sp^2 hybridization. They are insoluble in H_2O but soluble in alcohol.

Alkynes: They are non-polar and dissolve readily in non-polar solvents like ether, benzene, etc.

(iv) Physical Constants:

Alkane: In alkanes, boiling points, melting points and density increases with the increase in number of carbon atoms, whereas solubility decreases with increase in molecular mass.

Alkenes and Alkynes: In case of physical constants, similar trend for alkenes and alkynes as that for alkanes.

Q.25 How does propyne react with the following reagents:

(a) $AgNO_3/NH_4OH$ **(b) Cu_2Cl_2/NH_4OH**

(c) $H_2O/H_2SO_4HgSO_4$

Ans.

(a) (i) $H-C\equiv C-CH_3 + AgNO_3 + NH_4OH \longrightarrow \underset{\text{(Silver-propylide)}}{Ag-C\equiv C-CH_3} + NH_4NO_3 + H_2O$

(ii) $H-C\equiv C-CH_3 + Cu_2Cl_2 + NH_4OH \longrightarrow 2Cu-C\equiv C-CH_3 + 2NH_4Cl + 2H_2O$

(iii) $H-C\equiv C-CH_3 + \overset{+\ -}{H}OH \xrightarrow[HgSO_4]{10\%\ H_2SO_4} CH_2=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3$

$$CH_2=\underset{\displaystyle OH}{\underset{|}{C}}-CH_3 \rightleftharpoons \underbrace{CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3}_{\text{Acetone}}$$

Q.26 A compound has a molecular formula C_4H_6, when it is treated with excess hydrogen in the presence of Ni-catalyst, a new compound C_4H_{10} is formed. When C_4H_6 is treated with ammoniacal silver nitrate a white precipitate is formed. What is the structural formula of the given compound?

Ans. **Reactions Involved:**

$$\underset{\text{1-butyne}}{CH_3-CH_2-C\equiv CH} + 2H_2 \xrightarrow[250^\circ C]{Ni} \underset{\text{n-butane}}{CH_3-CH_2-CH_2-CH_3}$$

$$CH_3-CH_2-C\equiv CH + AgNO_3 + NH_4OH \longrightarrow CH_3-CH_2-C\equiv CAg + NH_4NO_3 + H_2O$$

Ammonical silver nitrate gives white ppt. with alkynes containing acidic hydrogen. The compound with molecular formula C_4H_6 can be 1-butyne or 2-butyne.

The compound 1-butyne has acidic hydrogen and can be replaced by metal forming alkynides. 2-butyne has no acidic hydrogen and do not form white ppt. So, only 1-butyne can give white ppt. with ammonical silver nitrate.

The possible structure is:

$CH_3 - CH_2 - C \equiv CH$ (1-butyne)

Q.27 (a) Identify A and B:

$$\mathbf{CH_3CH_2CH_2OH \xrightarrow{PCl_5} A \xrightarrow{Na/Ether} B}$$

(b) Give the general mechanism of electrophilic addition reactions of alkenes.

Ans.

(a) $CH_3CH_2CH_2OH + PCl_5 \longrightarrow CH_3 - CH_2 - CH_2 - Cl + POCl_3 + HCl$

$2CH_3 - CH_2 - CH_2Cl + 2Na \longrightarrow CH_3(-CH_2)_4 - CH_3 + 2NaCl$

(n-hexane)

A = $CH_3 - CH_2 - CH_2 - Cl$ (1-chloropropane)

B = $CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$ (n-hexane)

(b) Descriptive question. Consult text book for details.

DO YOU KNOW?

1. Alkanes are also called paraffins.
2. Alkenes are also called olefines.
3. $C_{20}H_{42}$ is called eicosane.
4. $C_{11}H_{24}$ is called undecane.
5. $C_{12}H_{26}$ is called dodecane.
6. $C_{16}H_{34}$ is called hexadecane.
7. $C_{100}H_{202}$ is called hectane.
8. Wurtz's reaction is used for lengthening the carbon chain.
9. The boiling point of branched chain alkanes are less than straight chain hydrocarbons.
10. Kolbe's method is used for the preparation of alkanes, alkenes, alkynes.
11. Raney Nickel has high surface area and is more reactive.
12. Bayer's test is used for the identification of double bond.
13. Mustard gas is highly boiling liquid. It is used as vesicant (blistering agent).
14. 1-butyne reacts with ammonical $AgNO_3$ but 2-butyne does not react.
15. Acetylene was prepared accidentally by an American Chemist named Willson.
16. Ethyne has garlic like odour.
17. Methane is also called marsh gas.

SHORT QUESTIONS

Q.1 Boiling point of straight chain alkane is greater than the boiling point of branched chain hydrocarbons why?

Ans. Boiling point of straight chain hydrocarbon is greater than branched chain hydrocarbon due to greater polarizability and greater intermolecular forces in it. For example, boiling point of n-butane is –0.5°C while isobutane is –11.7°C.

Q.2 Alkanes are less reactive than alkenes. Explain it.

Ans. In alkane, all sigma bonds are present between C – H and C – C atoms. In case of alkenes, Pi bonds are also present. Sigma bond is stronger bond than Pi bond and more energy is required to break this bond. So all alkanes are less reactive than alkenes.

Q.3 Alkenes usually undergo addition reactions while alkanes do not, why?

Ans. Alkenes usually undergo addition reaction due to presence of double bond one sigma and one Pi bond in them. Pi bond is weak and easily break to give electrons to electrophile and acts as nucleophile. Alkanes do not undergo such additions reactions due to lack of Pi bond.

Q.4 What is propagation step in any mechanism?

Ans. Step of mechanism in which same radical is consumed and evolved in the next step is called propagation. For example, in the halogenation of alkane step-II is propagation and step-I is initiation.

Step-I: $Cl - Cl \longrightarrow Cl^{\circ} + Cl^{\circ}$

Step-II: $CH_4 + Cl^{\circ} \longrightarrow HCl + CH_3^{\circ}$

$CH_3^{\circ} + Cl - Cl \longrightarrow CH_3Cl + Cl^{\circ}$

Q.5 Why alkenes are more reactive than alkynes?

Ans. Alkynes are less reactive than alkenes. The electron density between triple bond carbon atoms is high due to the presence of one sigma and two pi-bonds between C-C atoms. Due to high density of electrons in alkynes they are drawn closer to each other and less exposed than alkenes. Therefore, alkynes are less reactive toward electrophilic reagents.

Q.6 Ethyne have acidic hydrogen while ethene does not. Why?

Ans. In alkyne triple bond is present between C-C atoms. Carbon in alkyne is sp-hybridized and have one sigma and two Pi bonds. Due to greater overlapping, distance between C-C is reduced. Due to greater attraction carbon has partial negative charge and hydrogen attached to sp-hybridized carbon is slightly positive.

$$R - C \equiv \overset{-\delta}{C}\,\overset{+\delta}{H} \qquad\qquad \overset{+\delta}{H} - \overset{\delta-}{C} \equiv \overset{-\delta}{C} - \overset{+\delta}{H}$$

Q.7 How will you distinguish between ethene and ethane?

Ans. Ethane does not react with Br_2 or aqueous alkaline $KMnO_4$ solution. Ethene reacts with Br_2 or $KMnO_4$ and their colour is discharged.

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br - CH_2Br$$

$$3CH_2 = CH_2 + 4H_2O + 2KMnO_4 \longrightarrow 3CH_2 - CH_2 + 2MnO_2 + 2KOH$$

$$\begin{array}{cc} | & | \\ OH & OH \end{array}$$

Q.8 How will you distinguish between ethene and ethyne?

Ans. Ethene does not react with ammonical silver nitrate or ammonical cuprous chloride. Ethyne reacts with ammonical silver nitrate to form white precipitate of silver acetylide.

$$HC \equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow AgC \equiv CAg + 2NH_4NO_3 + 2H_2O$$

Ethyne also reacts with ammonical cuprous chloride to form red precipitate of copper acetylide.

$$HC \equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow CuC \equiv CCu + 2NH_4Cl + 2H_2O$$

Q.9 How will you distinguish between 1-butyne or 2-butyne, both have triple bond in them?

Ans. In 2-butyne no acidic hydrogen is present and does not react with ammonical silver acetylide.

$$CH_3 - C \equiv C - CH_3 + AgNO_3 + NH_4OH \longrightarrow \text{No reaction}$$

1-butyne reacts with ammonical silver nitrate to form white precipitate of silver acetylide.

$$HC \equiv C - CH_2 - CH_3 + AgNO_3 + NH_4OH \longrightarrow AgC \equiv C - CH_2CH_3 +$$

$$NH_4NO_3 + H_2O$$

Q.10 If HBr is added to propene, Markonikov's rule is obeyed why?

Ans. When HBr is added to propene, 2 bromo propane is formed and 1-bromo-propane is not formed.

$$CH_3 - CH = CH_2 + HBr \longrightarrow \begin{array}{c} Br \\ | \\ CH_3 - CH - CH_3 \end{array} \quad \text{(actual product)}$$

$$CH_3 - CH = CH_2 + HBr \longrightarrow CH_3 - CH_2 - CH_2 - Br \quad \text{(not formed)}$$

When HBr is added to propene, H^+ is an electrophile and attack at double bond.

$$CH_3 - CH = CH_2 + \overset{+}{H}\overset{-}{Br} \begin{array}{l} \nearrow CH_3 - \overset{+}{C}H - CH_3 + Br^- \\ \searrow CH_3 - CH_2 - \overset{+}{C}H_2 + Br^- \end{array}$$

Secondary carbocation is more stable than primary carbocation and the following reaction takes place.

$$CH_3 - \overset{+}{C}H - CH_3 + Br^- \longrightarrow CH_3 - \underset{|}{\overset{Br}{CH}} - CH_3$$

Q.11 What happens when alkanes are burnt in limited supply of oxygen?

Ans. When methane burns in excess oxygen CO_2 is produced.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{Heat}$$

In limited supply of oxygen, CO is formed. Sometime carbon soot is also formed.

$$3CH_4 + 4O_2 \longrightarrow 2CO + 6H_2O + C$$

Q.12 How Raney nickel is prepared?

Ans. Raney nickel is prepared by the reaction of dilute caustic soda with Ni – Al alloy.

$$Ni - Al + NaOH + H_2O \longrightarrow Ni + NaAlO_2 + \tfrac{1}{2} H_2$$

Q.13 Raney nickel is more effective than ordinary nickel. Why?

Ans. Raney nickel is more effective due to its greater surface area. It is porous and its surface area is greater.

Q.14 How will you bring about the following conversion?

Ans. See Solved Exercise Q.9.

Q.15 How may ethene be converted into following:

Ans

(i) Ethene to ethylene dibromide:

$$CH_2 = CH_2 + Br_2 \longrightarrow \underset{|\quad\quad|}{\overset{Br\quad\quad Br}{CH_2 - CH_2}}$$

(ii) Ethene to ethyne:

$$CH_2 = CH_2 + Br_2 \longrightarrow \underset{|\quad\quad|}{\overset{Br\quad\quad Br}{CH_2 - CH_2}}$$

$$\underset{|\quad\quad|}{\overset{Br\quad\quad Br}{CH_2 - CH_2}} + 2KOH_{(alc)} \longrightarrow CH \equiv CH + 2KBr + 2H_2O$$

(iii) Ethene to ethane:

$$CH_2 = CH_2 + H_2 \xrightarrow[250^\circ C]{\text{Ni/heat}} CH_3 - CH_3$$

(iv) Ethene to ethylene glycol:

$$3CH_2 = CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3CH_2 - CH_2 + 2KOH + 2MnO_2$$

$$\begin{array}{cc} | & | \\ OH & OH \end{array}$$

Q.16 Complete the following reactions.

Ans.

(i) $CH_3 - CH_2 - OH \xrightarrow[180°C]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$

$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2Br - CH_2Br$$

$$\begin{array}{ll} Br & Br \\ | & | \\ CH_2 - & CH_2 \end{array} + 2KOH_{(alc)} \longrightarrow CH \equiv CH + 2H_2O + 2KBr$$

(ii) $CH_3 - CH = CH_2 + Br_2 \longrightarrow \begin{array}{l} Br \\ | \\ CH_3 - CH - \\ \end{array} \begin{array}{l} Br \\ | \\ CH_3 \end{array}$

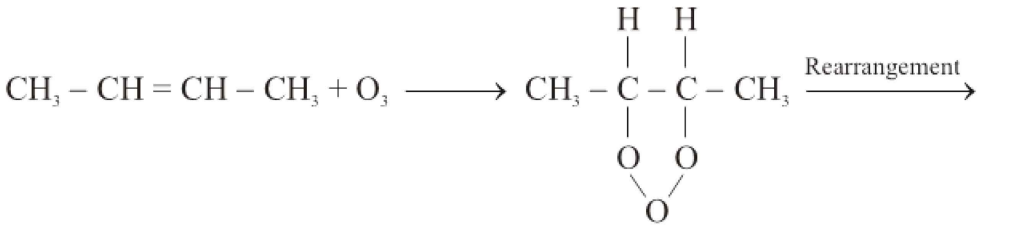
$$\begin{array}{ll} & Br \\ & | \\ CH_3 - & CH \end{array} \begin{array}{l} Br \\ | \\ - CH_3 \end{array} + 2KOH_{(alc)} \longrightarrow CH_3 - C \equiv CH + 2KBr + 2H_2O$$

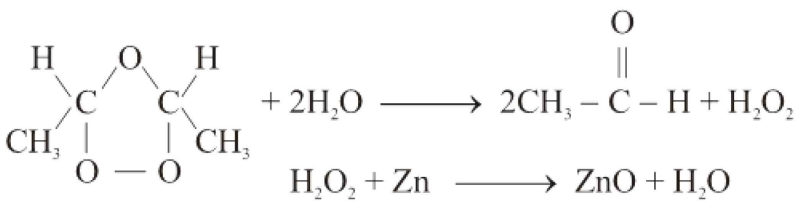
$$CH_3 - C \equiv CH + HCN \longrightarrow \begin{array}{l} CN \\ | \\ CH_3 - C = CH_2 \end{array}$$

Q.17 After an ozonlysis experiment, the only product obtained was acetaldehyde. The chemist who did the experiment correctly claimed that two possible standing materials could give this product. Can you guess the structural formulas of the compounds?

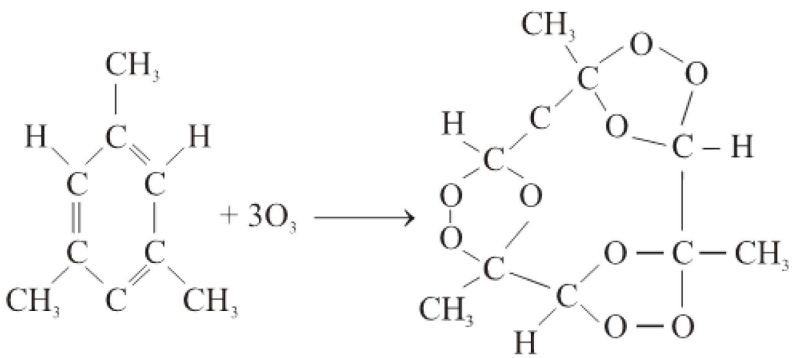
Ans.

(i) When cis 2-butene or trans 2-butene reacts separately with O_3 the final product will be acetaldehyde.

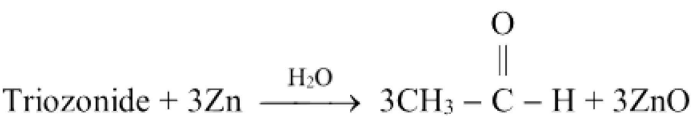




(ii) When 1, 3, 5 trimethyl benzene reacts with O_3, the final product is acetaldehyde.



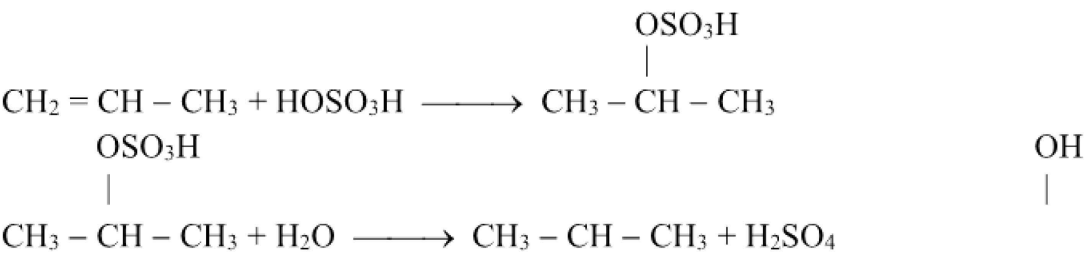
Triozonide



Q.18 The addition of sulphuric acid to an alkene obeys Markownikov's rule. Predict the structures of the alcohols obtained by the addition of the acid to the following compounds.

Ans.

(i) Propene:



(ii) 1-butene:

$$CH_2 = \underset{\displaystyle OSO_3H}{\underset{|}{CH}} - CH_2 - CH_3 + HOSO_3H \longrightarrow CH_3 - \underset{\displaystyle OSO_3H}{\underset{|}{CH}} - CH_2 - CH_3$$

$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3 + H_2O \longrightarrow CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3 + H_2SO_4$$

(iii) 2-butene:

$$CH_3 - CH = CH - CH_3 + H_2SO_4 \longrightarrow CH_3 - \underset{\displaystyle OSO_3H}{\underset{|}{CH}} - CH_2 - CH_3$$

$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3 + H_2O \longrightarrow CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - CH_3 + H_2SO_4$$

Q.19 Predict the most likely product of addition of HCl to 2 methyl 2-butene.

Ans.

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

Q.20 How does ethyne react with?

Ans.

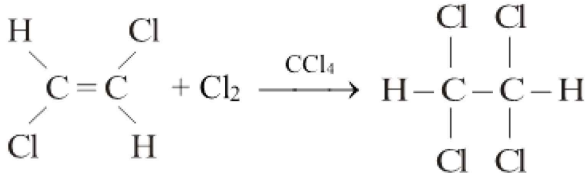
(i) Hydrogen:

$$CH \equiv CH + H_2 \xrightarrow[250°C]{Ni} CH_2 = CH_2$$

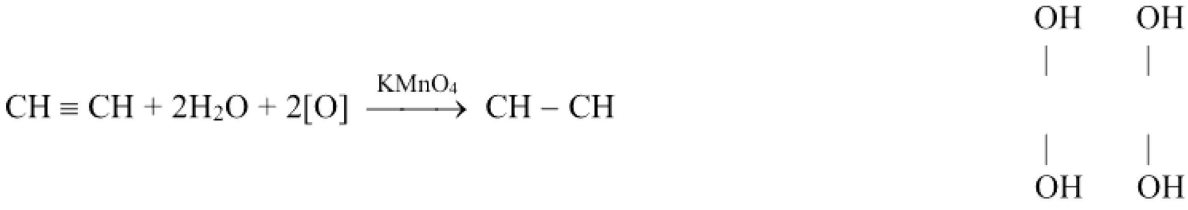
$$CH_2 = CH_2 + H_2 \xrightarrow[250°C]{Ni} CH_3 - CH_3$$

(ii) Halogen:

$$CH \equiv CH + Cl_2 \xrightarrow{CCl_4} \begin{matrix} H & & Cl \\ & \diagdown\ \diagup & \\ & C = C & \\ & \diagup\ \diagdown & \\ Cl & & H \end{matrix}$$

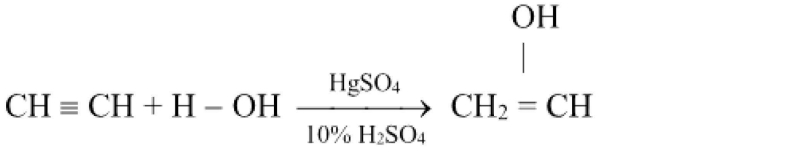


(iii) Alkaline $KMnO_4$:



(oxalic acid)

(iv) 10% H_2SO_4 in the presence of $HgSO_4$:



(acetaldehyde)

(v) Ammonical cuprous chloride:

$$HC \equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow Cu - C \equiv C - Cu + 2NH_4Cl + 2H_2O$$

(vi) Bromine water with:

$$CH \equiv CH + Br_2 \longrightarrow CHBr = CHBr$$

$$BrCH = CHBr + Br_2 \longrightarrow Br_2CH - CHBr_2$$