Hydrocarbons.

The simplest organic compounds containing carbon and hydrogen only are called hydrocarbons.
On the basis of structure, hydrocarbons can be divided into two types.

(i) Acyclic or open chain hydrocarbons.
(ii) Cyclic or closed chain hydrocarbons.

(i) Acyclic or open chain hydrocarbons — These compounds contain open chain of carbon atoms in their molecules. They are also called aliphatic hydrocarbons. These are further classified into three categories.

a Alkanes. b Alkenes c Alkynes.

An alkanes have only carbon-carbon single bond.
An alkene has only carbon-carbon double bond.
An alkyne has only carbon-carbon triple bond.

(ii) Cyclic or close chain hydrocarbons — These compounds contain closed chain or ring of carbon atom in their molecule they are further divided into two classes.

a. Alicyclic hydrocarbons.
b. Aromatic hydrocarbons.

a. Alicyclic hydrocarbons — Hydrocarbons which contain a ring of three or more carbon atoms and have properties similar to those of aliphatic hydrocarbons are called alicyclic hydrocarbons. these are further divided into three groups.

1. Cycloalkanes — Saturated alicyclic hydrocarbons in which all the carbon atoms are joined by single covalent bonds are called cycloalkanes.
2. Cycloalkenes — unsaturated alicyclic hydrocarbons which contain one-carbon-carbon double bond are called cycloalkenes.

3. cycloalkynes — unsaturated alicyclic hydrocarbons which contain one carbon-carbon triple bond are called cyclic-alkynes.

b. Aromatic hydrocarbons — Arenes — Hydrocarbons and their alkyl, Alkenyl and Alkynyl derivatives which contain one or more benzene rings either fused or isolated in their molecules are called aromatic hydrocarbons. They are also called Arenes.

— Alkanes — General formula — C_nH_{2n+2}.

Methods of Preperation.

1 From unsaturated hydrocarbons — The process of addition of hydrogen to an unsaturated compound in presence of a catalyst is called hydrogenation or reduction.

$$CH_2=CH_2 + H_2 \xrightarrow[\text{or Pt, Pd.}]{\text{Raney Ni}} CH_3-CH_3.$$

2. From alkyl halides —

a Through Grignard reagents — Alkyl halide reacts with magnesium metal in presence of dry ethoxyethane (diethyl ether) to form alkyl magnesium halides. these are commonly called Grignard reagents.

$$R-x + Mg \xrightarrow{\text{Dry ether}} R-Mg-x.$$

Since Carbon is more electronegative than magnesium, therefore C-Mg bond is quite Polar. Hence Grignard reagent react with compound containing active hydrogens to form alkanes.

$$CH_3-CH_2-Br + Mg \xrightarrow{\text{ether}} CH_3-CH_2-MgBr.$$

$$CH_3-CH_2-MgBr + H_2O \longrightarrow CH_3-CH_3 + Mg(OH)Br.$$

b. Wurtz reaction — when an alkyl halide is treated with metalic sodium in presence of dry diethyl ether, a symmetrical alkane, containing double the number of carbon atoms present

the alkyl group is formed. This reaction is called wurtz reaction.

$$R-x + 2Na + x-R \xrightarrow[\text{ether.}]{\text{Dry.}} R-R + 2Nax.$$

Wurtz reaction is used for the synthesis of only symmetrical alkanes, not for the preperation of unsymmetrical alkanes.

C. Corey-House reaction — Wurtz reaction does not give good yields of unsymmetrical alkanes. However Corey-House reaction can be used to prepare both symmetrical and unsymmetrical alkanes in good yields. In this reaction the alkyl halide is first treated with lithium metal in dry ether to form alkyl lithium which is then allowed to react with cuprous iodide to form lithium dialkylcopper. Lithium dialkyl copper on subsequent treatment with a suitable alkyl halide gives the desired alkanes.

$$R-x + 2Li \xrightarrow{\text{Dry ether.}} R-Li + Lix.$$

$$2R-Li + CuI \longrightarrow R_2CuLi + 2LiI$$

$$R_2CuLi + R'-x \longrightarrow R-R' + Lix + RCu$$

where R and R' may be same or different alkyl groups.

D. Reduction of Alkyl halides — Alkanes can also be prepared by the reduction of alkyl halides.

(I) Reduction by dissolving metals such as Zn and CH_3COOH or HCl, Zn and NaOH or Zn-Cu couple and alcohol.

$$R-x \xrightarrow{Zn/HCl} R-H + Hx.$$

$$CH_3Cl + Zn + H^+ \longrightarrow CH_4 + Zn^{+2} + Cl^-$$

(II) Reduction by chemical reagents such as $LiAlH_4$, $NaBH_4$, Ph_3SnH.

$$H^- + R-x \longrightarrow R-H + x^-$$

(III) Catalytic hydrogenolysis implies cleavages of a sigma bond with H_2 in presence of a catalyst. The best catalyst is Pd-C

$$CH_3CH_2-Br + H_2 \xrightarrow{Pd-C} CH_3-CH_3 + HBr.$$

(IV) Reduction with HI and red P

$$CH_3CH_2-I + HI \xrightarrow[red\ P.]{423K} CH_3-CH_3 + I_2.$$

3. From Carboxylic acid — Alkanes can be prepared from Carboxylic acids by the following two methods.

a Decarboxylation :- The process of removal of a molecule of CO_2 from an organic compound is called decarboxylation. When a carboxylic acid is heated with soda-lime at about 630 K, a molecule of CO_2 is lost and an alkane with one carbon atom less than the carboxylic acid is formed.

$$R-COOH + NaOH \longrightarrow R-COONa + H_2O.$$
$$R-COONa + NaOH \longrightarrow R-H + Na_2CO_3.$$

b. Kolbe's electrolytic method — when a concentrated aqueous solution of the sodium or potassium salt of a mono-carboxylic acid is electrolyed an alkane is produced.

$$2R-COONa + 2H_2O \xrightarrow{electrolysis} R-R + 2NaOH + H_2 + 2CO_2.$$

4. By the action of water on beryllium and aluminium carbide — Both these carbides on treatment with water gives methane.

$$Be_2C + 4H_2O \longrightarrow CH_4 + 2Be(OH)_2.$$
$$Al_4C_3 + 12H_2O \longrightarrow 3CH_4 + 4Al(OH)_3.$$

— Physical Properties —

1 Boiling Points — Amongest the straight chain alkanes, the first four members (C_1-C_4) are gases, (C_5-C_{17}) are liquid, and the higher members (C_{18} onwards) are colourless waxy solids.

The boiling Points of straight chain alkanes increases fairly regularly with increase in their molecular mass. The boiling point generally increases by 20-30 K. for the addition of each CH_2 group.

The branched chain isomer has invariably the lower boiling Point than the Corresponding n-alkane.

2. Melting Point — The melting Points of alkanes increases with increase in Carbon Content.

Alkanes with even number of Carbon atoms have higher melting Point and alkanes with odd number of Carbon atoms have lower melting Points.

3. Solubility — Alkanes which are Predominantly non-Polar are insoluble in Polar Solvents but are highly soluble in non-Polar Solvents

4. Density — The densities of alkanes increases with increase in the molecular mass. All the alkanes are lighter than water

— Chemical reactions of Alkanes.

1 Substitution reactions — A reaction in which a hydrogen atom of a hydrocarbon is replaced by an atom or a group of atoms is called a substitution reaction.

a. Halogenation of Alkanes — Halogenation of an alkane is carried out by treating it with a suitable halogen in Presence of Ultraviolet light or by heating the reaction mixture to 520-670 K.

The order of reactivity of different halogens

$$F_2 > Cl_2 > Br_2 > I_2.$$

During halogenation of methane all the four hydrogen atoms are replaced one by one to form a mixture of Products.

b. Nitration — The Process of replacement of a hydrogen atom by a nitro ($-NO_2$) group is Called nitration.

The order of reactivity of different hydrogens.

$$3^0 > 2^0 > 1^0.$$

C. Sulphonation — Substitution of a hydrogen atom of an alkane by Sulphonic acid group ($-SO_3H$) is called Sulphonation.
The order of reactivity of different hydrogen
$3^\circ > 2^\circ > 1^\circ$

— Uses of alkanes.

1. Methane in form of natural gas is used as a fuel.
2. Methane is used to make Carbon black which is used in the manufacture of Printing inks, Paints and automobile tyres.
3. Catalytic oxidation of alkanes gives alcohols, aldehydes etc.
4. Higher alkanes in form of gasoline, kerosene oil, diesel etc. are widely used.
5. Methane is used for the manufacture halogen containing Compounds such as CH_2Cl_2, $CHCl_3$, CCl_4 which are used as Solvents

— Stereoisomerism — Isomers which have the same Structural formula but have different relative arrangement of atoms or group in space are Called Stereoisomers.
It is of the three type.

1. Conformational isomerism.
2. Optical isomerism.
3. Geometrical isomerism.

1. Conformational isomerism — The infinite number of momentary arrangement of the atom in space which result through rotation about a single bond are Called rotational or rotamers or Conformations isomers.

— Torsional Strain — The repulsive interaction between the electron cloud which affects the stability of a Conformation is Called torsional strain. It is depends upon the angle of rotation about C-C bond. this angle is Called dihedral or torsional angle.

Alkenes.

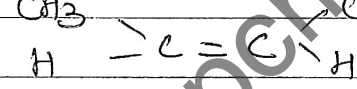
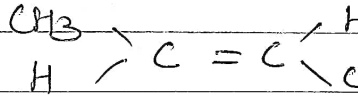
Acyclic unsaturated hydrocarbons containing a carbon-carbon double bond are called alkenes. They are also called olefins. Alkenes are readily attacked by reagents or compounds which are in search of electrons. Such reagents are called electrophiles or electrophilic reagents.

The General formula for alkenes is C_nH_{2n}.

– Isomerism of Alkenes – Alkenes show both Structural isomerism and Stereoisomerism.

a Structural isomerism – Ethene and Propene can have only one structure but alkenes containing four or more carbon atoms can show both Position and Chain isomerism.

b. Geometrical isomerism – Isomers which have the same structural formula but differ in the relative spatial arrangement of atoms or groups around the double bond are called Geometrical isomerism.

ex.  ; 

cis-But-2-ene trans-But-2-ene.

– Properties of Geometrical Isomers.

1 melting points – The melting point of a trans-isomer is higher than that of corresponding cis-isomer.

2. Solubility – The solubility of cis-isomer is higher than that of corresponding trans-isomers.

3. Dipole moments – cis-isomers of alkenes are more polar than of transisomers.

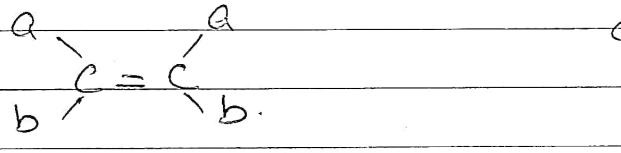
4. Boiling Point – The boiling points of cis-isomers is higher.

than those of the corresponding trans-isomers.

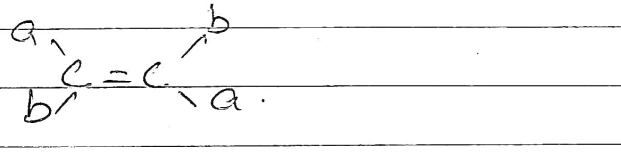
— Necessary and Sufficient Condition for geometrical isomerism -

(i) The molecule must contain a double bond.

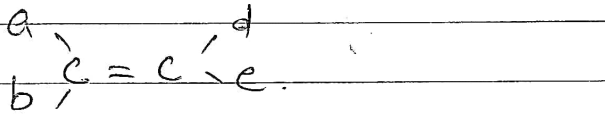
(ii) each of the two carbon atoms of the double bond must have different substituents which may be same or different.



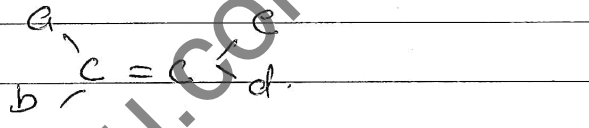
cis-isomer



trans-isomer



Z-isomer.



E-isomer.

Geometrical isomers have the same molecular structure but differ only in the relative position of atoms or group in space, therefore they are stereoisomers.

— Alkenes add on hydrogen in presence of finely divided metals such as Pt, Pd, Ni to form alkanes.

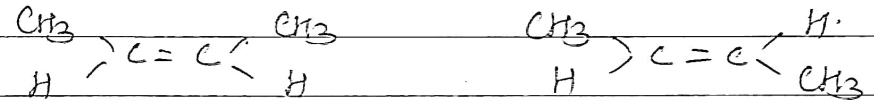
This reaction is called hydrogenation. It is an exothermic reaction and the amount of heat evolved is called heat of hydrogenation.

— General methods of Preparation.

1. By Partial reduction of alkynes — The catalytic hydrogenation of alkynes to alkenes occurs faster than that of alkenes to alkanes.

$CH_3-C\equiv C-CH_3$

H_2-Pd/$CaCO_3$ + S ↓ (Lindlar Catalyst) — Na/liq NH_3 (Birch reduction) ↓



2. From alkyl halides or haloalkanes — Alkyl halides on heating with a strong base such as sodium ethoxide or a concentrated alcoholic solution of potassium hydroxide undergo dehydrohelogenation to give alkenes.

$$CH_3CH_2-I + KOH \longrightarrow CH_2=CH_2 + KI + H_2O$$

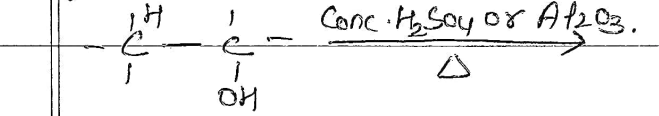
The process of removal of a molecule of a halogen halide (HCl, HBr, HI) from a haloalkanes to form an alkene is called dehydrohalogenation.

3. From vicinal dihalides or 1,2-dihaloalkanes — Dihalogen derivatives of alkanes in which the two halogen atoms are present on adjacent carbon atoms are called vicinal or 1-2 dihaloalkanes. Alkenes can be prepared by heating a suitable dihaloalkanes with zinc dust in methanol or ethanol.

$$\begin{matrix}CH_2-Br\\ |\\ CH_2-Br\end{matrix} + Zn \xrightarrow[\Delta]{CH_3OH} \begin{matrix}CH_2\\ ||\\ CH_2\end{matrix} + ZnBr_2$$

The process of removal of a molecule of halogen (Cl_2, Br_2, I_2) from a dihaloalkane to form an alkene is called dehalogenation.

4. From monohydric alcohols or alkanols by acidic dehydration — monohydric alcohols on heating with a mineral acid such as conc. H_2SO_4 or H_3PO_4 or on passing their vapours over heated alumina at 623-633K, eliminate a molecule of water to form alkenes. This reaction is known an acidic dehydration



5. From Sodium or Potassium salts of saturated dicarboxylic acids – (Kolbe's electrolytic reactions) – Electrolysis of Sodium or Potassium salts of saturated dicarboxylic acids give alkenes.

$$\begin{matrix} CH_2COOK \\ | \\ CH_2COOK \end{matrix} + 2H_2O \xrightarrow{\text{electrolysis}} \begin{matrix} CH_2 \\ || \\ CH_2 \end{matrix} + 2CO_2 + H_2 + 2KOH.$$

– Physical Properties.

1. Physical state, Colour, Smell etc – The first three members of the family, ethene, propene, butene, are colourless gases. Next fourteen members (C_5-C_{18}) are liquid while the higher are solid. Except ethene which has a pleasant smell, all other alkenes are colourless and odourless gases.
2. Solubility – They are insoluble in water but are fairly soluble in non-polar solvents
3. Boiling Points – Their boiling points increases regularly with increase in molecular mass.

– Chemical Reactions of Alkenes –

1. Addition reactions of alkenes.

a. Addition of dihydrogen – Addition of dihydrogen to unsaturated hydrocarbons is called catalytic hydrogenation.

$$CH_2=CH_2 \xrightarrow{Pt/Pd/Ni} CH_3-CH_3.$$

b. Addition of halogens – Halogens such as chlorine and bromine readily add to alkenes to form 1,2 dihaloalkanes.

$$CH_2=CH_2 + Br_2 \xrightarrow{CCl_4} \begin{matrix} CH_2-CH_2 \\ | \quad | \\ Br \quad Br \end{matrix}.$$

During the addition of bromine to alkenes, the orange red colour of bromine is discharged since the dibromide formed is colourless. So this reaction is used as a test for.

for unsaturation in organic compounds.

The order of reactivity of addition of halogens to alkenes.

$F_2 > Cl_2 > Br_2 > I_2$.

C. Addition of hydrogen halides — Alkenes react with halogen (HCl, HBr, HI) to form monohaloalkanes called alkyl halides

$$>C=C< + HX \longrightarrow >\underset{H}{C}-\underset{X}{C}<$$

the order of reactivity.

$$HI > HBr > HCl.$$

D. Addition of the elements of hypohalous acids (HOX where X = Cl, Br, I) - Halohydrin formation - Chlorine and bromine in the presence of water readily add to alkenes to form the corresponding halohydrins.

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

$$>C=C< + \underset{-HX}{X_2/H_2O} \rightarrow >\overset{OH}{C}-\underset{X}{C}<$$

E. Addition of Sulphuric acid - Indirect hydration of alkenes — Cold conc. H_2SO_4 adds to alkenes to form alkyl hydrogen sulphates

$$CH_2=CH_2 + H^+ \bar{O}SO_2OH \rightarrow CH_3-CH_2-OSO_2OH.$$

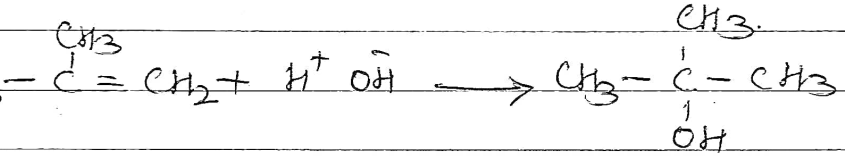
and.

(i) $$CH_3CH=CH_2 + H^+ \bar{O}SO_2OH \rightarrow CH_3-\underset{OSO_2OH}{CH}-CH_3$$

(ii) $$CH_3-\underset{OSO_3H}{CH}-CH_3 + H_2O \xrightarrow{\Delta} CH_3-\underset{OH}{CH}-CH_3 + H_2SO_4.$$

This overall two-step conversion of an alkene first into alkyl hydrogen sulphate followed by hydrolysis with boiling water to form alcohols is called indirect hydration of alcohols.

(F) Addition of water — Direct hydration of alkenes —
By hydration we mean addition of water.
Water does not add directly to most of alkenes, However some reactive alkenes do add water in presence of mineral acid to form alcohols.



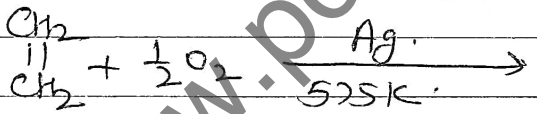
2. Oxidation reactions of alkenes —

a Complete oxidation with oxygen or air — Combustion —
Alkenes burn in oxygen or air to form CO_2 and H_2O. This Process is called Combustion. All combustion reactions are highly exothermic in nature.

$$CH_2=CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$$

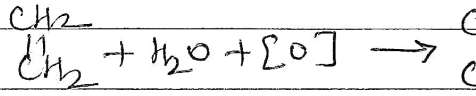
b. Controlled oxidation with oxidising agents —

(i) oxidation with oxygen — Alkenes reacts with O_2 in Presence of Silver as catalyst to form epoxyalkanes.



(ii) oxidation with $KMnO_4$ — Different Products are formed depending upon the reactions Conditions.

(a) with cold dilute neutral or alkaline $KMnO_4$ — Because of the Presence of π-bonds, alkenes are readily oxidised by Cold dilute neutral or alkaline $KMnO_4$ solution to give Vicinal or 1,2-diols ; $2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$



This reaction is called hydroxylation since during this Process two hydroxyl groups are added across the double bond

(ख) oxidation with hot KMnO4 solution — when an alkene is heated with hot KMnO4 solution cleavage of the C=C bond occurs leading to the formation of carboxylic acid, ketones and . Carbon dioxide depending upon the nature of alkene.

→ with terminal alkenes, one of the products is always methanoic acid which on further oxidation gives $CO_2 + H_2O$.

$$CH_2=CH_2 + 4[O] \xrightarrow[373-383K]{KMnO_4/KOH} 2H-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{[O]} 2CO_2 + 2H_2O$$

→ with non-terminal alkenes, carboxylic acids or ketones or both of these are obtained depending upon the nature of the alkene.

$$CH_3CH=CHCH_3 + 4[O] \xrightarrow[373-383K]{KMnO_4/KOH} CH_3COOH + HOOCCH_3$$

(ii) oxidation with ozone — when ozone is passed through a solution of an alkene in some inert solvent such as CH_2Cl_2 etc. at low temperature it oxidises alkenes to ozonides. Ozonides are unstable and explosive compounds, therefore they are not usually isolated but are reduced

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + O_3 \xrightarrow[196-200K]{CH_2Cl_2} O\begin{matrix} \diagup CH_2-O \\ \diagdown CH_2-O \end{matrix} \xrightarrow[-ZnO]{Zn/H_2O} 2H-\overset{O}{\overset{\|}{C}}-H$$

This two-step conversion of an alkene into an ozonied followed by its reductive cleavage to yield carbonyl compound is called ozonolysis.

3 Polymerization Reactions — Polymerization is a process in which a large number of simple molecules combine to form a big molecule. The simple molecules are called monomers. while the big molecule is called a macromolecule or a polymer.

Uses of Alkene.

1. Lower members of the family are used as fuels.
2. Alkenes and substituted alkenes upon polymerization form a number of useful polymers
3. Ethene is employed for the preparation of ethyl alcohol and ethylene glycol (antifreeze)
4. Ethylene is used for artificial ripening of green fruits.
5. Ethylene is also used in oxygen-ethylene flame for cutting and welding of metals.

Alkynes.

Acyclic unsaturated hydrocarbons containing a Carbon-carbon triple bond are called alkynes or acetylenes. Their general formula is: C_nH_{2n-2}

— Isomerism of Alkynes.

1. Position isomerism — The first two members, ethyne and propyne exist in one form only. But butyne and higher alkynes exhibit position isomerism due to different position of the triple bond on the carbon chain.
2. Chain isomerism — Alkynes having five or more carbon atoms show chain isomerism due to different structures of the carbon chain.
3. Functional isomerism — Alkynes are functional isomers of dienes. Compounds containing two double bonds.
4. Ring chain isomerism — Alkynes show ring chain isomerism with cycloalkenes.

— Classification of Alkynes — Alkynes are further classified as terminal or non-terminal alkynes according as the triple bond is present at the end of chain or within the chain.

Methods of Preparation of Alkynes –

1. **By the action of water on Calcium Carbide –**
Ethyne is prepared in the laboratory as well as on a commercial scale by the action of water on calcium carbide.

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

2. **By dehydrohalogenation of dihaloalkanes :–**
Alkynes are prepared by dehydrohalogenation of vicinal-dihaloalkanes by heating them with an alcoholic solution of KOH.

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2KOH(alc.) \xrightarrow{\Delta} \begin{matrix} CH \\ \vert\vert \\ CH \end{matrix} + 2KBr + 2H_2O$$

3. **By dehalogenation of tetrahalides –** Tetrahaloalkanes when heated with zinc dust in methanol undergo dehalogenation to yield alkynes.

$$H-\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-H + 2Zn \xrightarrow[\Delta]{CH_3OH} H-C \equiv C-H + 2ZnBr_2$$

4. **By dehalogenation of haloforms –** chloroform and iodoform on heating with silver powder undergo dehalogenation to form alkynes.

$$CHCl_3 + 6Ag + Cl_3CH \xrightarrow{\Delta} CH \equiv CH + 6AgCl$$

5. **Kolbe's electrolytic reaction –** Acetylene can be prepared by electrolysis of a concentrated solution of sodium or potassium salt of maleic acid or fumaric acid

$$\begin{matrix} H \\ \\ \\ H \end{matrix}\!\!\begin{matrix} COOK \\ \diagdown \\ C \\ \vert\vert \\ C \\ \diagup \\ COOK \end{matrix} \text{ or } \begin{matrix} COOK \\ \diagup \\ C \\ \vert \\ C \\ \diagdown \\ H \end{matrix}\!\!\begin{matrix} H \\ \\ \\ COOK \end{matrix} + 2H_2O \xrightarrow{\text{electrolysis}} \begin{matrix} CH \\ \vert\vert \\ CH \end{matrix} + 2CO_2 + H_2 + 2KOH$$

(cis) (trans)

This reaction is called Kolbe's electrolytic reaction.

6. Synthesis from Carbon and hydrogen – Berthelot Synthesis – Acetylene can be prepared by passing a stream of hydrogen through an electric arc struck Carbon electrode.

$$2C + H_2 \xrightarrow[3270\,K.]{\text{Electric arc}} HC \equiv CH.$$

7. Synthesis of higher alkynes from acetylene – Acetylene is first treated with Sodium metal at 475K or with Sodamide in liquid ammonia at 196K to form Sodium acetylide. This upon treatment with alkyl halides give higher alkynes.

$$H{-}C \equiv CH + NaNH_2 \xrightarrow[196\,K.]{Liq.\ NH_3} HC \equiv C^- Na^+ + NH_3.$$

$$HC \equiv C^- Na^+ + CH_3{-}Br \longrightarrow H{-}C \equiv C{-}CH_3 + NaBr.$$

— Physical Properties of Alkynes

1. Physical state — The first three members of this family (ethyne, propyne, butyne) are colourless gases, the next eight are liquid while higher are solids.

2. Smell – All the alkynes are odourless. However acetylene has garlic smell due to the presence of Phosphine as impurity.

3. Melting and boiling Points — The melting and boiling Points of alkynes are slightly higher than those of the corresponding alkenes and alkanes. this is due to triple bond.

4. Solubility – Alkynes are non-Polar and insoluble in water but readily dissolve in organic solvents.

5. Density — Densities of alkynes increases as the molecules size increases, they are lighter than water.

— Reactivity of alkynes versus alkenes —
Although alkynes contain two π-bonds, yet they are less reactive than alkenes towards electrophilic addition reactions.
reasons:

(1) The π-electrons of alkynes are more tightly held by the carbon atoms than π-electrons of alkenes. and hence are less reactive.

2. The π-electrons of a triple bond are less readily available for reaction than those of double bond.

— Chemical reactions of Alkynes —

1 Acidic character of Alkynes — Unlike alkanes and alkenes, the hydrogen atoms attached to the triple bond of alkynes so acetylenic hydrogens are acidic in nature.
The acidity of alkynes can be explained in term of the sp-hybridization of a triply bonded carbon. An electron in an s-orbital is more tightly held than in a p-orbital. So an sp-hybridized carbon is more electronegative than sp^2 or sp^3.
Due to this greater electronegativity the electrons of C-H bond are displaced more towards the carbon hence H gain + charge. so Alkynes behave as acids.
The acidic character of hydrocarbons decreases in the following order $CH \equiv CH > CH_2 = CH_2 > CH_3 - CH_3$.

2. Electrophilic addition reactions —
The electrophilic addition reactions of alkynes take place in two stages

$$-C \equiv C- + X_2 \longrightarrow \underset{X}{\overset{X}{\diagdown}}C = C\underset{X}{\overset{X}{\diagup}} \xrightarrow{+X_2} \begin{matrix} X & X \\ | & | \\ -C & -C- \\ | & | \\ X & X \end{matrix}$$

Addition of halogens — Chlorine and Bromine readily add to alkynes first forming 1,2 dihaloalkenes and than 1,1,2,2-tetra haloalkanes.

$$H-C\equiv C-H + Cl_2 \longrightarrow \underset{H}{\overset{Cl}{\rangle}}C=C\underset{Cl}{\overset{H}{\langle}} \xrightarrow{Cl_2} H-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-\underset{Cl}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-H$$

$$CH_3-C\equiv CH \xrightarrow{Br_2} \underset{Br}{\overset{CH_3}{\rangle}}C=\langle\underset{H}{\overset{Br}{}} \xrightarrow{Br_2} CH_3-\underset{Br}{\overset{Br}{\underset{|}{\overset{|}{C}}}}-\underset{Br}{\overset{Br}{\underset{|}{\overset{|}{C}}}}-H$$

During this reaction the raddish brown colour of Br_2 is decolourised and hence this reaction is used as a test for unsaturation. The order of reactivity $Cl_2 > Br_2 > I_2$.

b. Addition of halogen halides or halogen acids — Halogen halides add to alkynes in the dark but the addition is catalysed by light or metallic halides.

$$HC\equiv CH \xrightarrow{HCl} CH_2=CHCl \xrightarrow{HCl} CH_3-CHCl_2$$

c. Addition of the elements of hypohalous acids —

$$HC\equiv CH + \overset{\delta+}{Cl}\,\overset{\delta-}{OH} \longrightarrow Cl-CH=CH-OH \xrightarrow{Cl-OH} Cl-\underset{Cl}{\overset{|}{CH}}-\underset{OH}{\overset{|}{CH}}-OH \xrightarrow{-H_2O}$$

$$\underset{Cl}{\overset{Cl}{\rangle}}CH-CH=O.$$

D. Addition of H_2O — Hydration of alkynes —

$$HC\equiv CH + H-OH \xrightarrow[333K.]{H_2SO_4/HgSO_4} \underset{OH}{\overset{|}{CH}}=\underset{H}{\overset{|}{CH}} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-H$$

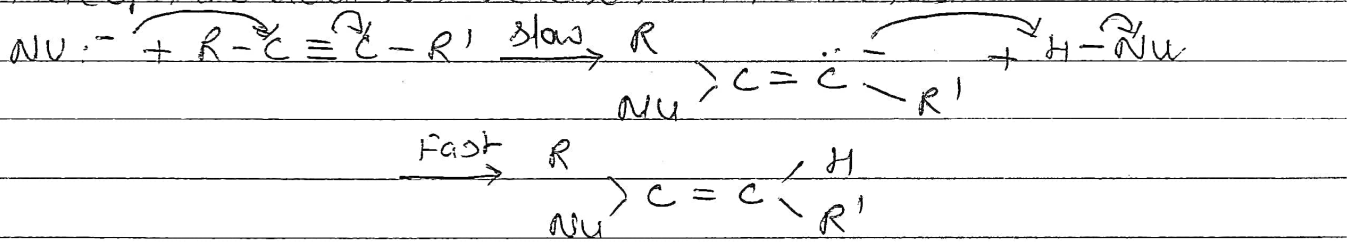
E Addition of Carboxylic acids —

$$R-C\equiv CH + CH_3COO-H \xrightarrow{BF_3} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{R}{\overset{|}{C}}=CH_2$$

F. Addition of hydrogen cyanide —

$$HC\equiv CH + HCN \xrightarrow[CuCl/HCl.]{Ba(CN)_2} CH_2=CH-CN.$$

3. Nucleophilic addition reactions – Because of the greater electronegativity of the sp-hybridized carbon as compared to sp^2-hybridized carbon alkynes are more susceptible to nucleophilic addition reaction than alkenes.



4. Reduction of alkynes – Addition of dihydrogen to alkynes in presence of Nickel at 523–573 gives alkanes.

$$H-C\equiv C-H + H_2 \xrightarrow{Ni} CH_2=CH_2 \xrightarrow{Ni} CH_3-CH_3.$$

5. Oxidation reactions of alkynes.

a. oxidation with air – Combustion – When heated in air alkynes undergo combustion to form CO_2 and H_2O by release of large amount of heat and light energy.

$$2\,CH\equiv CH + 5O_2 \longrightarrow 4CO_2 + 2H_2O.$$

b. Oxidation with cold dilute Potassium Permagnate –

$$\begin{matrix} CH \\ \| \\ CH \end{matrix} + 2[O] \xrightarrow[298\text{-}303K]{KMnO_4,\ H_2O} \begin{matrix} CH=O \\ | \\ CH=O \end{matrix} \xrightarrow[\text{oxidation.}]{+2[O]} \begin{matrix} COOH \\ | \\ COOH. \end{matrix}$$

During this reaction, the pink colour of the $KMnO_4$ solution is discharged and a brown precipitate of manganese dioxide is obtain. So this reaction is used as a test for unsaturation under the name Baeyer's test.

c. oxidation with hot $KMnO_4$ solution — Terminal alkynes when treated with hot $KMnO_4$ solution undergo cleavage of the $C\equiv C$ bond leading to the formation of carboxylic acid and carbon dioxide depending upon the nature of alkynes.

$\equiv CH$ is oxidised to CO_2 and H_2O.

$\equiv CR$ is oxidised to R-COOH.

ex.

$$\underset{\text{CH}}{\overset{\text{CH}}{|||}} + 4[O] \xrightarrow[323-383K.]{KMnO_4/KOH.} \underset{\text{COOH}}{\overset{\text{COOH}}{|}} \xrightarrow{[O]} 2CO_2 + H_2O.$$

$$CH_3-C\equiv CH + 4[O] \xrightarrow[323-383K.]{KMnO_4/KOH.} CH_3COOH + CO_2.$$

D. Oxidation with ozone — Alkynes react with ozone in presence of some inert solvent at low temperature to form ozonides. These ozonides on decomposition with Zn dust and water or H_2/Pd give 1,2-dicarbonyl compounds.

$$HC\equiv CH \xrightarrow[196-200K.]{O_3/CH_2Cl_2} HC(-O-O-)CH \xrightarrow[-ZnO]{Zn/H_2O} H-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-H.$$

6. Polymerization Reaction of Alkynes —

a Linear Polymerization — In this type of Polymerization, two or more molecules of ethyne combine to form products which have linear structure.

b. Cyclic Polymerization — In this type of Polymerization, three or more molecules of an alkyne combine together to form products which have ring structures.

7. Isomerization of alkynes — when alkynes are heated with $NaNH_2$ in an inert solvent, they undergo isomerization.

$$CH_3C\equiv CCH_3 \xrightarrow[\text{inert solv. } \Delta]{NaNH_2 \text{ in.}} CH_3CH_2C\equiv CH.$$

$$CH_3CH_2C\equiv CH \longrightarrow CH_3C\equiv CCH_3.$$