Chapter
7

FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY

INTRODUCTION

Organic chemistry is the chemistry of carbon compounds. Most of the organic compounds also contain hydrogen and many compounds also contain oxygen and other elements. There are few compound which contain carbon but they are not organic compounds. e.g., CO, CO_2 metal carbonates, bicarbonates, cyanide, and carbides.

Early chemists believed that the compounds which are obtained from living things: (animals and plants) are called organic compound and which are obtained from minerals are called inorganic compounds.

SYNTHESIS OF FIRST ORGANIC COMPOUND IN THE LABORATORY

For more than 200 years, chemist divided materials into two categories. Those compounds which were isolated from animal and plants were called organic compounds. At one time, chemists believed that organic compounds require a **vital force** for their synthesis which is only present in animals and plants. This theory was called vital force theory. This theory was rejected by Friedrick Wohler when he obtained urea accidentally. Friedrick Wholer was interested in the chemistry of cyanate compounds which contain OCN^-. In 1828, he tried to synthesize ammonium cyanate from silver cyanate and ammonium chloride. What he expected can be described by the following equation.

$$AgOCN + NH_4Cl \longrightarrow AgCl + NH_4OCN$$

The product had isolated from this reaction was white crystalline solid identical to urea which could be isolated from urine.

Actually ammonium cyanate on heating changed to urea.

$$NH_4OCN \longrightarrow O=C\begin{matrix}NH_2\\NH_2\end{matrix}$$

Ammonium cyanate Urea (organic)

He synthesized organic compound from inorganic compound in the laboratory and vital force theory was rejected.

MODERN DEFINITION OF ORGANIC CHEMISTRY

"The branch of chemistry which deals with the study of hydrocarbons and their derivatives is called organic chemistry."

Since the synthesis of urea from ammonium cyanate, millions of organic compounds have been prepared and analyzed. All these compounds contain carbon as an essential element. Apart from carbon, most of the organic compounds also contain hydrogen. Other elements which may also be present include oxygen, nitrogen, sulphur, etc. A few of the carbon compounds such as CO, CO_2, carbonates, bicarbonates, etc. are studied as inorganic compounds. It also has been recognized that the chemical forces in organic compounds are similar to those, which exist, in inorganic compounds. Thus it was felt that organic chemistry should be redefined. According to the modern definition, organic chemistry is the branch of chemistry which deals with the study of hydrocarbons and their derivatives.

SOME FEATURES OF ORGANIC COMPOUNDS

Following are some features of organic compounds:

(1) Peculiar Nature of Carbon:

Carbon forms a large number of compounds. There are millions of organic compounds known at present. The main reason for such a large number of compounds is its unique properly of linking with other carbon atoms to form long chains or rings. This self-linking property of carbon is called **catenation**. Carbon also forms stable single and multiple bonds with other atoms like oxygen, nitrogen and sulphur etc. It can thus form numerous compounds of various sizes, shapes and structures.

(2) Non-ionic Character of Organic Compounds:

Organic compounds are generally covalent compounds, therefore, do not give ionic reactions.

(3) Similarity in Behaviour:

Organic compounds are classified according to their functional groups. The compounds which contain same type of functional group have same properties. This property is called **homologous series**. This similarity in behaviour has reduced the study of millions of compounds to only a few homologous series.

(4) Complexity of Organic Compounds:

Organic molecules are usually large and structurally more complex. For example, starch has the formula $(C_6H_{10}O_5)_n$ where n may be several thousands. Proteins are very complex molecules having molecular masses ranging from a few thousands to a millions.

(5) Isomerism:

Isomerism is a very common phenomenon in organic compounds. Very often more than one compounds are represented by the same molecular formula. However, they have different structural formulas.

(6) Rates of Organic Reactions:

The reactions involving organic compounds are slow and in general the yields are low. The slowness of the organic reactions is due to the molecular nature of organic compounds.

(7) Solubility:

Most organic compounds are insoluble in water and dissolve readily in non-polar organic solvents, such as, benzene, petroleum, ether etc.

IMPORTANCE OF ORGANIC CHEMISTRY

Organic chemistry has a variety of applications in our lives and too much important. A few areas are highlighted here.

(1) All chemical reactions that take place in animals and plants involve life molecules like proteins, carbohydrates, enzymes, lipids, vitamins, fats and oils, nucleic acids.

(2) We are dependent upon the organic compounds in food, clothing and medicines.

(3) Chemists synthesize plastic, rubber, detergents, medicines, paints, varnishes, fertilizers, artificial fibers, pesticides, cosmetics, soap, cement, dyes etc.

SOURCES OF ORGANIC COMPOUNDS

Initially organic compounds were obtained only from animals and plants. Now a days petroleum, coal and natural gas are the major sources of organic compounds. Petroleum, coal and natural gas are called **fossil fuels** and are formed, by the decay of animals and plants over a long period of time.

(1) Animals and Plants:

There are so many compounds which are obtained from animals and plants. e.g., proteins, carbohydrates, fats, oils, enzymes, honey, urea, vitamins, dyes, drugs etc.

(2) Coal:

Coal is one of the mankind's primary energy source. Now a days it is a source of many organic compounds as well.

Formation of Coal:

It is believed that coal is formed from vegetable matter (plants) and rocks. About 500 million year ago, under high temperature and pressure and due to some bacterial decomposition, the vegetative material changed to **peat**. Peat is decomposed organic matter. Then, as a result of high temperature and high pressure inside the earth's crust, peat gets transfer into different forms of coal.

$$\text{Wood} \xrightarrow[\text{Chemical action}]{\text{Bacterial acid}} \text{Peat}$$

(Dead plants)

$$\text{Peat} \xrightarrow[\text{High pressure}]{\text{High temperature}} \text{Lignite}$$

$$\text{Lignite} \xrightarrow{\text{High pressure}} \text{Bituminous coal}$$

$$\text{Bituminous coal} \xrightarrow{\text{High pressure}} \text{Anthracite}$$

Types of Coal:

Coal is usually classified on the basis of percentage of carbon contents present in it. Carbon contents in different coals are as follows:

(1) Peat (59.9%) (2) Lignite (60 – 70%)

(3) Bituminous coal (79%) (4) Anthracite (91%)

Destructive Distillation of Coal (Carbonization):

Coal is fuel as well as a source of many organic compounds. Organic compounds from coal are obtained by destructive distillation or carbonization.

"The thermal decomposition of coal in the absence of air at high temperature (500–1000°C) is called carbonization."

In the absence of air, at high temperature coal changes to coke, coal gas and coal tar. Coal tar contains larger number of organic compounds (mostly aromatic) which are separated from each other by fractional distillation.

Composition of Coal Tar:

Coal tar is liquid component of coal. It contains 215 aromatic organic compounds. It is subjected to fractional distillation to get the following products:

(i) Light oil (150 – 200°C)

(ii) Middle oil (200 – 250°C)

(iii) Heavy oil (250 – 300°C)

(iv) Anthracite oil (300 – 350°C)

Future of Coal in Pakistan:

The total coal resources of Pakistan are estimated by the geological survey of Pakistan to be 184 billion tones. About 80% of this coal is used to bake bricks, in lime kilns, and some quantity is used for domestic purposes.

Sincere efforts are being made by the government to induct coal into industry by setting up coal based power units. The Sindh coal Authority and the directorates of Mineral Development of the Punjab, Baluchistan and NWFP are all keen to expand coal utilization in power generation for which many incentives have been given.

(3) Natural Gas:

Natural gas is a mixture of low boiling hydrocarbons. Major portion of the natural gas is methane (80–85%), 8–10% is ethane and rest of propane and butene, ethene etc.

Natural gas is also formed by the decomposition of organic matter under high pressure.

Natural gas is an important energy source in Pakistan. In Pakistan, natural gas is a cheaper source of energy and used in cement industries, fertilizer industries, thermal power stations and domestic purposes.

(4) Petroleum:

The word "petroleum" means "oil of rocks". Crude petroleum is black or greenish black in colour. It is a mixture of many hydrocarbons from C_1 to C_{40}. Petroleum is also a **fossil fuel** and called **"rock oil"** or **"crude oil"** or **"mineral oil"**.

Fractional Distillation of Petroleum:

"Fractional distillation is a method used to separate components of a mixture on the basis of difference in their boiling points."

The fractions of the petroleum, their boiling point ranges and uses are given below in the table:

Table – Principal fractions obtained from petroleum

Boiling point range °C	No. of carbons atoms in the fraction	Name of the fraction and principal uses
Below 20	C_1–C_4	**Natural gas:** As fuel for heating and cooking. Raw materials for other chemicals.
20–60	C_5–C_6	**Petroleum ether:** As a non-polar solvent and cleansing fluid.

60–100	C_6–C_7	**Ligroin or light naphtha:** As a non-polar solvent and cleansing fluid.
40–200	C_5–C_{10}	**Gasoline or petrol:** Fuel for vehicles.
175–325	C_{11}–C_{12}	**Kerosene:** Used for domestic purposes, jet fuel.
Nonvolatile liquids	C_{18} and up	**Lubrication oil:** Used for lubrications.
Nonvolatile solids M.P. 50–60°C	C_{23}–C_{29}	**Paraffin:** Wax products like candles, polishes.
Solids	Residue	**Asphalt or petroleum coke:** Roofing, paving, fuel, reducing agent.

Oil Refineries in Pakistan:

At present, four oil refineries are in operation in our country. One oil refinery known as Attack Oil refinery is located at Morgah near Rawalpindi. It has about 1.25 million tones oil refining capacity. Similarly two oil refineries have been established at Karachi National Oil Refinery and Pakistan Oil Refinery which have about 2.13 million tones of oil refining capacity. Another refinery known as Pak Arab refinery is located at Mahmud Kot near Multan.

CRACKING

"Thermal decomposition of hydrocarbons in the absence of air is called cracking."

This is the process in which C-C bonds in long chain alkane molecules are broken, producing smaller molecules of both alkanes and alkenes. The composition of the products depends on the condition under which the cracking takes place.

For example, by cracking of natural gas, hydrogen gas is produced.

(i) $$CH_4 \xrightarrow[1200\text{-}1600^\circ C]{\text{Heat}} C + 2H_2$$

(ii) $$2CH_3 - CH_2 - CH_3 \longrightarrow CH_3 - CH = CH_2 + CH_2 = CH_2 + CH_4 + H_2$$

A higher hydrocarbon $C_{16}H_{34}$ splits up as:

$$C_{16}H_{34} \xrightarrow[700^\circ C]{\text{Heat}} C_7H_{16} + CH_2{=}CH_2 + CH_3\text{-}CH{=}CH_2$$

Hexadecane Heptane Ethene Propene

(Such reactions cannot be balanced because products are not fixed)

Significance of Cracking:

(1) With the help of cracking process, industrially, **hydrogen gas** is produced in our country to manufacture vegetable ghee.

(2) Fractional distillation of petroleum yields only 20% gasoline. Due to its greater demand, deficiency of gasoline is recovered by converting higher hydrocarbon such as kerosene to gasoline by cracking process. In other words, **yield of gasoline** is increased by cracking.

(3) With the help of cracking process large amount of useful **by-products** such as ethane, propene, butene, benzene etc., are obtained. These by products are used for the manufacture of drugs, plastics, detergents, synthetic fiber, fertilizers, pesticides, weed killers and important industrial and laboratory chemicals like ethanol, acetone and phenol.

(4) Through cracking process, octane number of gasoline is increased and it is called re-forming process.

TYPES OF CRACKING

(1) Thermal Cracking:

Breaking down of large molecules by heating at high temperature and pressure is called **thermal cracking**. It is particularly useful in the production of unsaturated hydrocarbons such as ethene and propene.

(2) Catalytic Cracking:

Higher hydrocarbons can be cracked at lower temperature (500°C) and lower pressure (2 atm), in the presence of a suitable catalyst. A typical catalyst used for this purpose is a mixture of silica (SiO_2) and alumina (Al_2O_3). Catalytic cracking produces gasoline of higher octane number and, therefore, this method is used for obtaining better quality gasoline.

(3) Steam Cracking:

In this process, higher hydrocarbons in the vapours phase are mixed with steam, heated for a short duration to about 900°C and cooled rapidly. The process is suitable for obtaining lower unsaturated hydrocarbons.

REFORMING OF PETROLEUM

"The process to increase the octane number by conversion of straight-chain alkanes into branched chain alkenes is called reforming of petroleum."

The octane number of any fuel is the percentage by volume of iso-octane in a mixture of iso-octane and n-heptane.

The octane number of n-heptane is zero, it is a bad fuel while that of iso-octane is 100. The mixture that contains the ratio of iso-octane and n-heptane as 8 : 2 have octane number 80. Gasoline having low octane number have greater knocking and vice versa.

*"**Knocking** is a sharp metallic sound produced in the internal combustion engine."*

In reforming process, gasoline is heated to a temperature of about 100°C for a very short time, in the presence of aluminium chloride, $AlCl_3$ or platinum catalyst. The high pressure is maintained in such a way that molecules do not crack but are reformed by isomerization. The purpose of reforming is to increase the octane numbers. For example, n-octane can be converted into iso-octane as follows:

$$\underset{\text{n-octane}}{CH_3-(CH_2)_6-CH_3} \xrightarrow[\text{Catalyst}]{100^\circ C} \underset{\text{2,2,4-trimethyl pentane (iso-octane)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3}$$

n-octane
Octane number = 0

2,2,4-trimethyl pentane (iso-octane)
Octane number = 100

The octane number of a poor fuel can also be improved by blending it with a small amount of additive like tetraehtyl lead (TEL). **Tetraethyl lead** $(C_2H_5)_4Pb$, is an efficient antiknock agent but has one serious disadvantage; its combustion product, lead oxide, is reduced to metallic lead which is discharged into the air through the exhaust pipe and causes air pollution.

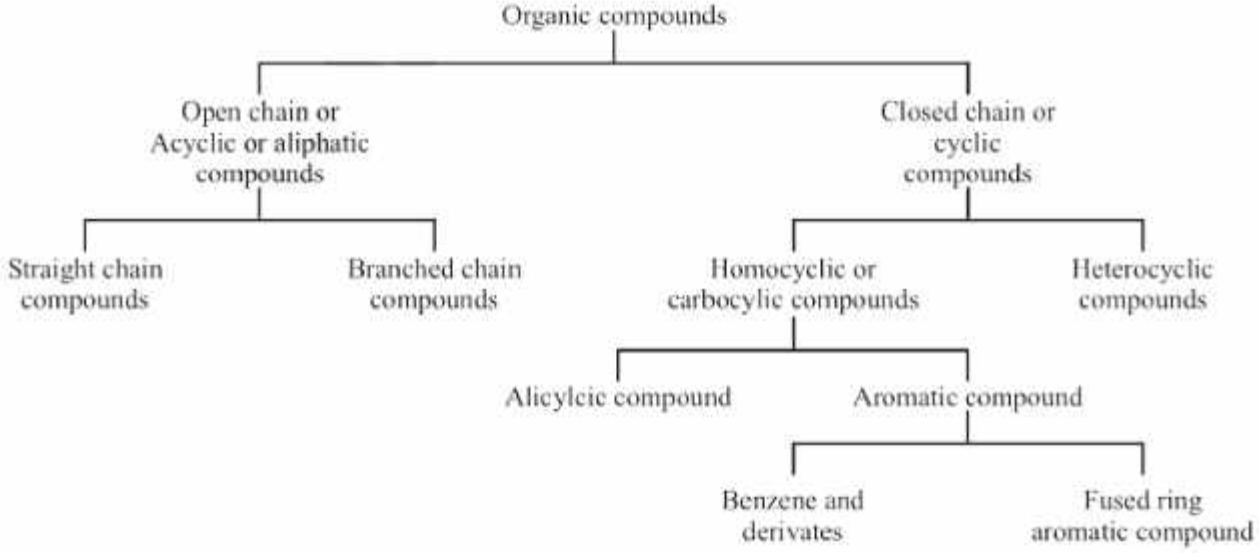
How to Improve Octane Number?

(1) By adding anti-knocking agent (2) Reforming
(3) Hydroforming (4) Isomerization

Regular gasoline has octane number 74. It is used in cars and buses. Octane number of 2, 2, 3 trimethyl butane is 124. It is superior to iso-octane.

CLASSIFICATION OF ORGANIC COMPOUNDS

There are millions of organic confounds. It is not possible to study each individual compound to facilitate their study. Organic compounds are classified into various groups and sub-groups. Organic compounds are classified into following groups.



(1) Open Chain or Acyclic or Aliphatic Compounds:

"Organic compounds with open chain of carbon atoms are called open chain or acyclic or aliphatic compounds."

There are two types of organic compounds:

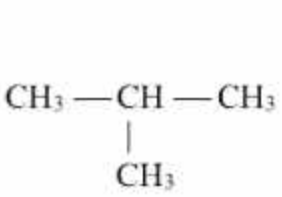
Open chain and closed chain compounds. Open chain compounds are of two types: straight chain and branched chain compounds.

(i) Straight Chain Compounds:

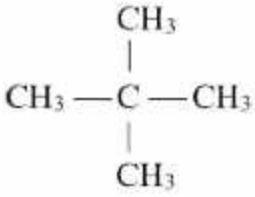
CH_3-CH_2-CH_2-CH_3 H_2C=CH-CH_2-CH_3 CH_3-CH_2-CH_2-CH_2-OH

Butane 1-Butene 1-Butanol

(ii) Branched Chain Compounds:



2-Methylpropane
(iso-Butane)



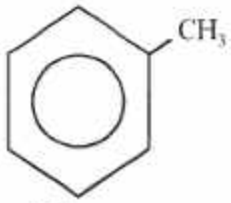
2, 2 Dimethylpropane
(neo-pentane)

(2) Closed Chain or Cyclic Compounds:

The compounds which contain one or more closed ring of carbon atoms or atoms of carbon and one or more other element (N, S or O) are called cyclic compounds.



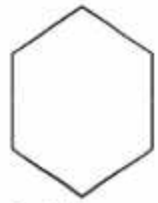
Benzene



Toluene



Pyridine



Cyclohexane

Cyclic compounds are of two types:

(a) Homocyclic or carbocyclic compounds

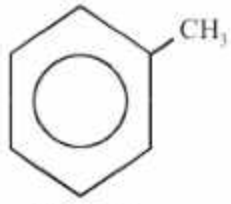
(b) Heterocyclic compounds

(a) Homocyclic or Carbocyclic Compounds:

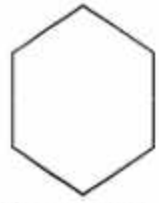
"Organic compounds with closed ring of carbon atoms are called homocyclic or carbocyclic compounds."



Benzene



Toluene

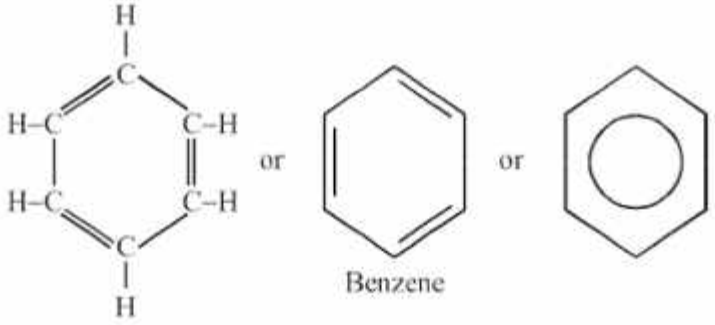


Cyclohexane

Homocyclic compounds are of two types:

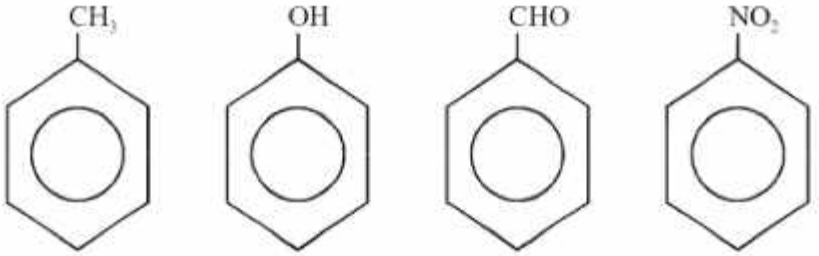
(*i*) ***Aromatic Compounds:***

The carbocyclic compounds which contain at least one benzene ring (six carbon atoms with alternate double and single bonds) are called aromatic compounds. e.g.,



Benzene

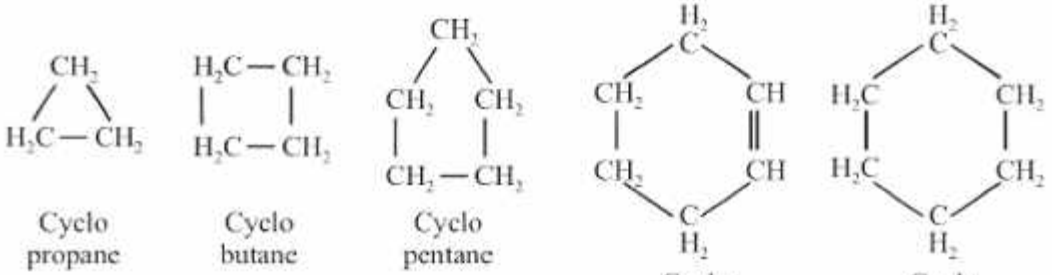
The aromatic compounds may have a side-chain or a functional group attached to the ring. For example:



Toluene Phenol Benzaldehyde Nitrobenzene

(*ii*) ***Alicyclic Compounds:***

"The homocyclic compounds which contain a ring of three or more carbon atoms and resembling aliphatic compounds are called alicyclic compounds." The saturated alicyclic hydrocarbons have the general formula C_nH_{2n}. Typical alicyclic compounds are given below.

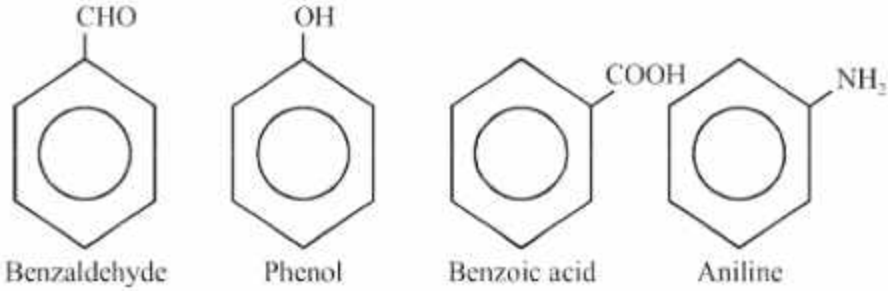


Cyclo propane Cyclo butane Cyclo pentane Cyclo hexene Cyclo hexane

Aromatic compounds are further classified as

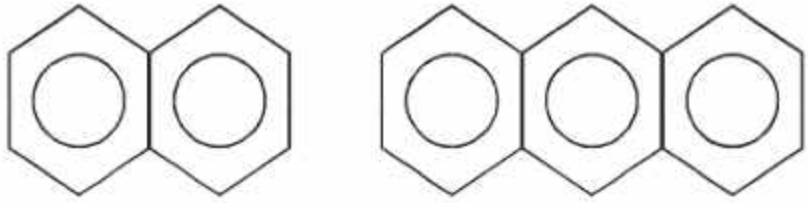
- Single ring compounda or benzene derivatives
- Fused ring aromatic compounds

- **Benzene and its derivatives:** The compounds which contain benzene ring with some functional group are called derivative of benzene. e.g.,



Benzaldehyde Phenol Benzoic acid Aniline

- **Fused ring compounds:** The compounds which contain more than one benzene rings fused together are called fused ring compounds.



Naphthalene Anthracene

(b) Heterocyclic Compounds:

"The compounds in which the ring consists of atoms of more than one kind are called **heterocyclic** compounds or **heterocycles**." In heterocyclic compounds, generally one or more atoms of elements such as nitrogen (N), oxygen (O) or sulphur (S) are present. The atom other than carbon present in the ring is called a **hetro atom**.



Pyridine Furan Pyrrole Thiophene Tetrahydro Furan

HYDROCARBONS

"The compounds which contain carbon and hydrogen are called hydrocarbons." Hydrocarbons may be aliphatic, alicyclic or aromatic.

Alkanes (aliphatic hydrocarbons):

The aliphatic hydrocarbons in which carbon atoms are joined by single covalent bonds only. The compounds in which carbon atoms are joined by single covalent bonds are called saturated hydrocarbons.

All alkanes are saturated hydrocarbons e.g., methane, ethane, propane etc. The general formula of saturated hydrocarbons is C_nH_{2n+2}. Where n is the number of carbon atoms in alkanes.

The term alkane can be split up into two parts.

Alk-This is the general term for meth, eth, prop, but, pent. This indicates the number of carbon atoms in the alkane or alkyl group.

-ane indicates that hydrocarbon is saturated.

Alkane	Formula	Alkane	Formula
Methane	CH_4	Hexane	C_6H_{14}
Ethane	C_2H_6	Heptane	C_7H_{16}
Propane	C_3H_8	Octane	C_8H_{18}
Butane	C_4H_{10}	Nonane	C_9H_{20}
Pentane	C_5H_{12}	Decane	$C_{10}H_{22}$
Ecosane	$C_{20}H_{42}$	Hectane	$C_{100}H_{202}$

Alkyl Radicals:

"A group of atoms formed when a hydrogen atom is removed from an alkane is called alkyl radical."

It is represented by a symbol "R" and the general formula $\mathbf{C_nH_{2n+1}}$. It is a portion of molecule and has no independent existence. The group is named by replacing the **"ane"** of alkane by **"yl"**.

Table – Alkane and Alkyl group

Alkane	Formula	Alkyl group	Formula
Methane	CH_4	Methyl	CH_3^-
Ethane	C_2H_6	Ethyl	$C_2H_5^-$
Propane	C_3H_8	Propyl	$C_3H_7^-$
Butane	C_4H_{10}	Butyl	$C_4H_9^-$

Structure of some alkyl radicals

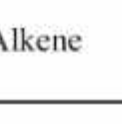
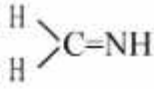
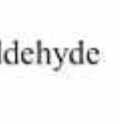
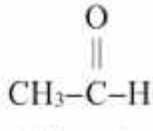
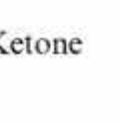
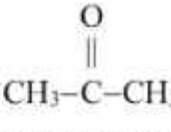
Alkane	Alkyl	
CH_4 methane	H | H—C— | H Methyl or CH_3—	
CH_3–CH_3 Ethane	CH_3–CH_2– Ethyl	
CH_3–CH_2–CH_3 Propane	CH_3—CH_2—CH_2— n-Propyl	CH_3—CH—CH_3 Iso-propyl
CH_3—CH_2—CH_2—CH_3 n-butane	CH_3—CH_2—CH_2—CH_2— n-butyl	CH_2—CH—CH_3—CH_3 Sec-butyl
CH_3 CH_3—CH—CH_3 Iso-butane	CH_3 CH_3—CH—CH_2— Iso-butyl	CH_3 CH_3—C— CH_3 Ter-butyl
CH_3 CH_3—C—CH_3 CH_3 Neopentane	CH_3 CH_3—C—CH_2— CH_3 Neopentyl	

FUNCTIONAL GROUP

"An atom or a group of atoms or a double bond or a triple bond which confers characteristic properties to an organic compounds is called a functional group, because they are chemically functional parts of molecules."

The compounds which have same functional group in them, have same chemical properties. There are about six millions of organic compounds but there are very few functional groups. e.g., –OH alcohol, $-\overset{\overset{O}{\|}}{C}-OH$, carboxylic acid, $-NH_2$ amine, $-\overset{\overset{O}{\|}}{C}-H$ aldehyde, etc.

A list of functional groups and their associated types of compounds are given below. This list is not comprehensive, functional groups are usually written as suffix after the name of root or as prefix (before the name).

Type of compound	Structure of functional group	Suffix or prefix	Examples (common name is in bracket)
Alkane		–ane	$CH_3–CH_3$ Ethane
Alkene		–ene	$CH_2=CH_2$ Ethene
Alkyne	–C≡C–	–yne	HC≡CH Ethyne
Alkyl halide	–X	Halo (chloro, bromo, iodo)	$CH_3–Cl$ Chloromethane
Alcohol	–OH	–ol	$CH_3–OH$ Methanol
Amine	$–NH_2$	amine	$CH_3–CH_2–NH_2$ (Ethyl amine)
Imine	=NH	imine	 (Methyl imine)
Ether	C–O–C	ether	$CH_3–O–CH_3$ (Dimethyl ether)
Aldehyde		–al	 Ethanal
Ketone		–one	 (Dimethyl ketone) 2-Propanone

Carboxylic acid	$-\overset{\overset{O}{\|}}{C}-OH$	–oic acid	CH_3COOH Ethanoic acid (Acetic acid)
Acid halide	$-\overset{\overset{O}{\|}}{C}-X$	–oyl halide	$CH_3-\overset{\overset{O}{\|}}{C}-Cl$ Ethanoyl chloride (Acetyl chloride)
Acidamide	$-\overset{\overset{O}{\|}}{C}-NH_2$	–amide	$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$ Ethanamide (Acetamide)
Ester	$-\overset{\overset{O}{\|}}{C}-OR$	–oate	$CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5$ Ethyl ethanoate (Ethyl acetate)
Acid anhydride	$-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$	–oic anhydride	$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$ Ethanoic anhydride (Acetic anhydride)
Thio alcohol or thiol	–SH	–thiol	CH_3-SH Methanethiol (Methane thio alcohol) (Methyl merceptan)
Alkyl cyanide or alkyl nitrile	$-C\equiv N$	cyano	$CH_3-C\equiv N$ Cyanomethane (Methyl cyanide) (Ethane nitrile) IUPAC name
Nitroalkane	$-\overset{\overset{O}{\|}}{N}\rightarrow O$	nitro	$CH_3-CH_2-NO_2$ Nitroethane

SOME DERIVATIVES OF HYDROCARBONS

"The study of hydrocarbons and their derivatives is called organic chemistry." Definition and examples of some derivatives are given below:

(1) Alkenes (> C = C <):

The hydrocarbon in which double bond is present between two carbon atoms. It is called alkene. Alkenes have general formula C_nH_{2n}. e.g.,

Formula	Common name	IUPAC name	Radical
$CH_2 = CH_2$	Ethylene	Ethene	$CH_2 = CH -$ Vinyl
$CH_2 = CH - CH_3$	Propylene	Propene	$CH_2 = CH - CH_2 -$ Allyl
$CH_2 = CH - CH_2 - CH_3$	Butylene	1-butene	$CH_2 = CH - CH_2 - CH_2 -$ Butenyl
$CH_3 - CH = CH - CH_3$	Butylene	2-butene	$CH_3 - CH = CH - CH_2 -$ Crotyl

(2) Alkynes (– C ≡ C –):

"The hydrocarbon in which triple bond is present between two carbon atoms are called alkynes." The general formula of alkyne is C_nH_{2n-2}. e.g.,

Formula	Common name	IUPAC name
$HC \equiv CH$	Acetylene	Ethyne
$HC \equiv C - CH_3$	Methyl acetylene	Propyne
$CH_3 - C \equiv C - CH_3$	Dimethyl acetylene	2-butyne

(3) Alkyl Halides (R – X):

"If hydrogen atom of hyrocarbon is replaced by halogen atom, it is called alkhyl halides." The general formula of alkyl halides is $C_nH_{2n+1}X$. e.g.,

Formula	Common name	IUPAC name
$CH_3 - Cl$	Methyl chloride	Chloromethane
$C_2H_5 - Cl$	Ethyl chloride	Chloroethane
$CH_3 - \underset{\displaystyle Br}{\underset{\vert}{CH}} - CH_3$	Iso-propyl bromide	2-bromopropane

(4) Alcohol (R – OH):

"If hydrogen atom of hydrocarbon is replaced by hydroxyl group (–OH), it is called an alcohol." The general formula of monohydric alcohol (having one –OH group) is $C_nH_{2n+1}OH$.

Formula	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
C_2H_5OH	Ethyl alcohol	Ethanol
$CH_3 - CH_2 - CH_2 - OH$	n-propyl alcohol	1-propanol

(5) Amines ($R - NH_2$):

If hydrogen atom of hydrocarbon is replaced by amino group, it is called amine. The general formula of primary amine is $C_nH_{2n+1}NH_2$.

Formula	Common name	IUPAC name
$CH_3 - NH_2$	Methyl amine	Aminomethane
$C_2H_5 - NH_2$	Ethyl amine	Aminoethane
$CH_3 - CH_2 - CH_2 - NH_2$	n-propyl amine	1-aminopropane

(6) Ether (R – O – R):

"If oxygen atom is attached with two similar or dissimilar alkyl or aryl group, it is called ether." e.g.,

Formula	Common name	IUPAC name
$CH_3 - O - CH_3$	Dimethyl ether	Methoxy methane
$C_2H_5 - O - C_2H_5$	Diethyl ether	Ethoxyethane
$CH_3 - O - C_2H_5$	Ethyl-methyl ether	Methoxyethane
$C_2H_5-O-CH_2-CH_2-CH_3$	Ethyl n-propyl ether	Ethoxy-propane

(7) Aldehyde ($R - \overset{\overset{O}{\|}}{C} - H$):

If hydrogen atom of hydrocarbon is replaced by aldehydic group (–CHO), it is called aldehyde. Systematic names are obtained by replacing suffix "e" of the alkane by "al". e.g.,

Formula	Common name	IUPAC name
HCHO	Formaldehyde	Methanal
$CH_3 - CHO$	Acetaldehyde	Ethanal
$CH_3 - CH_2 - CHO$	Propinoaldelyde	Propanal

(8) Ketone (R – C – R):

"The carbonyl compound, > C = O, in which two valencies of carbon are satisfied by the two alkyl group are called ketones." Systematic names are obtained by replacing suffix "e" of the alkane by "one". e.g., General formula of ketone is R – CO – R.

Formula	Common name	IUPAC name
$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$	Dimethyl ketone	2-propanone
$CH_3 - \overset{\overset{O}{\|}}{C} - CH_2\,CH_3$	Ethyl-methyl ketone	2-butanone
$CH_3 - CH_2 - \overset{\overset{O}{\|}}{C} - CH_2\,CH_3$	Diethyl ketone	3-pentanone

(9) Carboxylic Acids (R – C – OH):

"The carbonyl compound > C = O in which one valency of carbon is satisfied by –OH and other valency is satisfied by alkyl or hydrogen atom is called carboxylic acid." Systematic names are obtained by replacing "e" of the alkane by suffix "–oic acid". e.g.,

Formula	Common name	IUPAC name
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
CH_3CH_2COOH	Propionic acid	Propanoic acid

(10) Thiols or Thioalcohol or Mercaptans:

"If hydrogen atom of alkane is replaced by SH group, it is called thiols or mercaptans." Systematic names are obtained by adding suffix "thio" with the name of alkane.

Formula	Common name	IUPAC name
$CH_3 - SH$	Methyl mercaptan or Methyl thioalcohol	Methane thiol
$CH_3 - CH_2 - SH$	Ethyl mercaptan or Ethyl thioalcohol	Ethane thiol

HYDRIDIZATION OF ORBITALS AND THE SHAPES OF MOLECULES

Although the most stable electronic configuration of a carbon atom (having two partially filled 2p-orbitals) requires it to be divalent, carbon is tetravalent in the majority of its compounds. In order to explain this apparent anomaly, it is assumed that an electron from the 2s-orbital is promoted to an empty $2p_z$ orbital, giving the electronic configuration.

Ground state electronic configuration of carbon	$1s^2, 2s^2, 2p_x^1, sp_y^1, 2p_z^0$
Excited state electronic configuration of carbon	$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

The excited state configuration can explain the tetravalency of carbon but these four valencies will not be equivalent. Orbital hybridization theory has been developed to explain the equivalent tetravalency of carbon.

According to this theory, four atomic orbitals of carbon belonging to valence shell may be mixed in different ways to explain the bonding and shapes of molecules formed by carbon atoms.

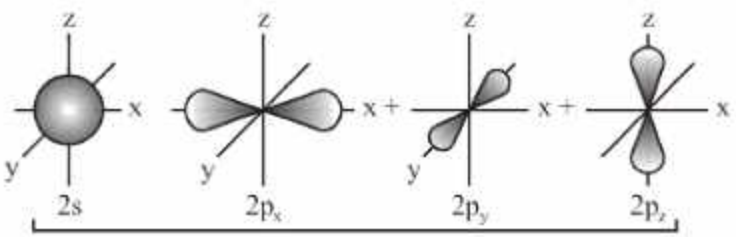
sp^3-hybridization:

"The process of mixing of one s-orbital and three p-orbitals of same shell to form four new equivalent orbital with same energy and shape is called sp^3-hybridization."

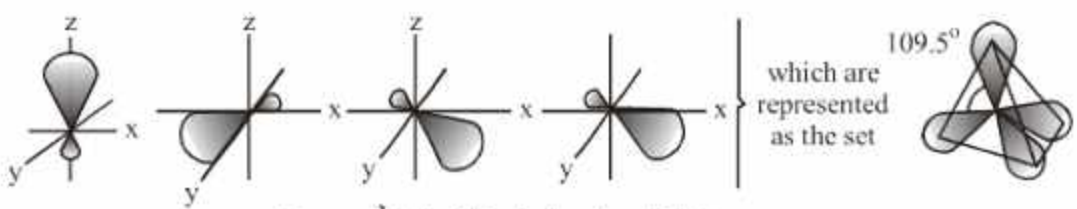
All the carbon atoms which are attached with four atoms are sp^3-hybridized. The electronic configuration of carbon in ground state and excited is given below:

Ground state electronic configuration of carbon	$1s^2, 2s^2, 2p_x^1, sp_y^1, 2p_z^0$
Excited state electronic configuration of carbon	$1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$

One s-orbitals and three p-orbital intermix to four new orbitals.



Unhybridized atomic orbitals of carbon



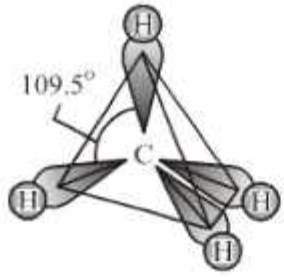
Four sp^3-hybridized atomic orbitals

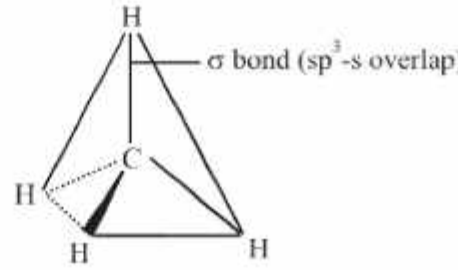
All these sp^3-hybrid orbitals are degenerate (having equal energy) and are directed at an angle of 109.5° in space to give a tetrahedral geometry.

When a carbon atom forms single bonds with other atoms, these hybrid overlap with the orbitals of others atoms to form four sigma bonds. This type of hybridization explains the bonding and shapes of all those compounds in which carbon atom is saturated.

STRUCTURE OF METHANE CH_4

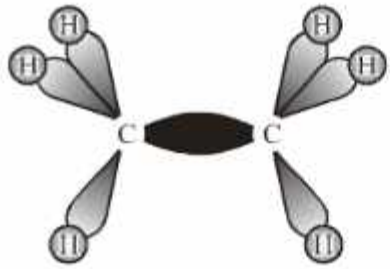
In the formation of methane, the four hybrid atomic orbitals of carbon overlap separately with four 1s atomic orbitals of hydrogen to form four equivalent C-H bonds. The shape of methane thus formed is tetrahedral. All the four hydrogen atoms do not lie in the same plane. Electron density is between two nuclei in case of sigma bonds.

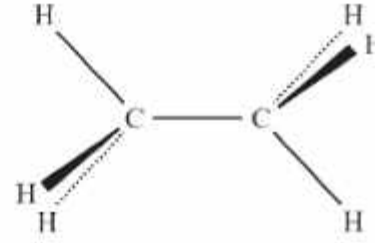




STRUCTURE OF ETHANE (CH_3–CH_3)

In case of ethane, each carbon is sp^3-hybridized. Structure on each carbon is tetrahedral and two tetrahedrons join together. In ethane one sigma bond is formed by the overlapping of sp^3-hybrid orbital one carbon and sp^3-hybrid orbital of other carbon atom. Six sigma bonds are present between carbon and hydrogen atoms. In these bonds sp^3-hybrid orbital of carbon overlap with partially filled s-orbital of hydrogen atoms.





Carbon atoms of all saturated hydrocarbons have sp^3-hybridization. All the bond angles between H–C–H are 109.5°.

Tetravalent carbon atom is more stable than divalent carbon atom, why?

In case of carbon when an electron is promoted from 2s orbital to 2p orbital, same amount of energy is needed. For this purpose 406 kJ/mole^{-1} energy is needed.

C atom (ground state) $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$

C atom (promoted) $1s^2, 2s^1, sp_x^1, 2p_y^1, 2p_z^1$

After mixing of one 2s-orbital and three p-orbitals, four new orbitals of equivalent energy and shape are formed. In CH_4, when four partially filled hybrid orbitals overlap with s-orbital of hydrogen, some amount of energy is released and it becomes stable. When CH_4 molecules is formed, it is an exothermic reaction and -2068 kJ/mol^{-1} energy is released. The amount of energy released is greater than the amount of energy absorbed. So a tetravalent carbon atom is expected to be more stable than divalent carbon.

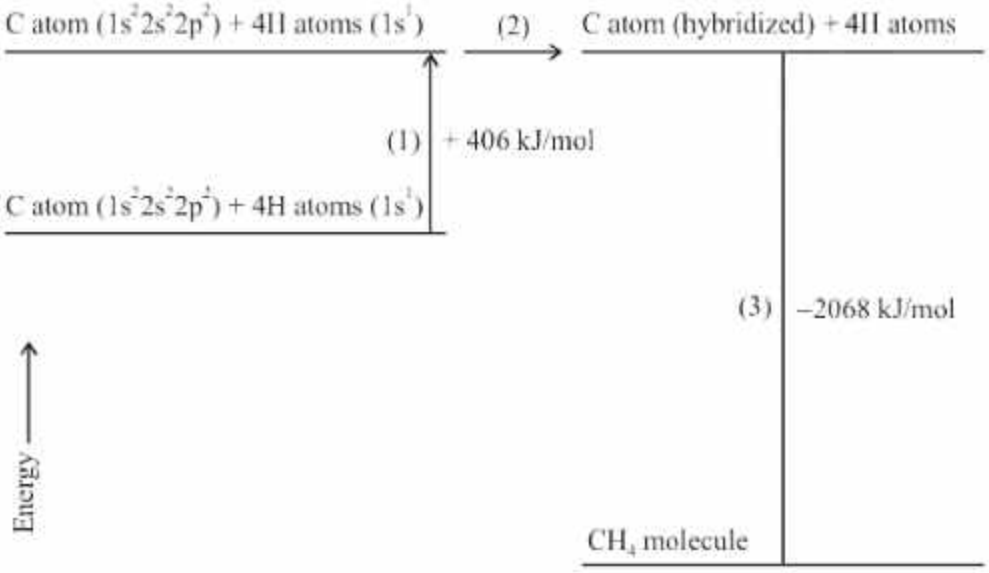


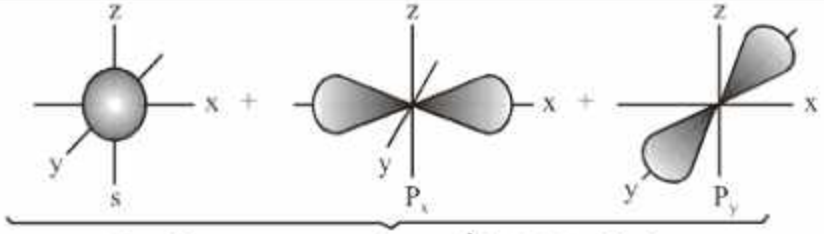
Figure 1 after promotion of electron, orbitals are hybridized 2-formation of CH_4 releases 2068 kJ/mol of energy. These three steps occur simultaneously as bond is formed.

sp^2-HYBRIDIZATION

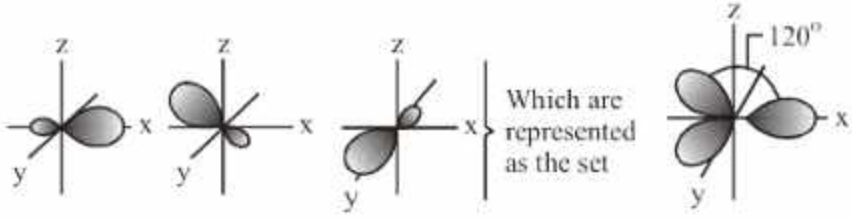
"The process of mixing one s-orbital and two p-orbitals to get three new equivalent sp-hybrid orbitals is called sp^3-hybridization."

The sp^2-hybridization occurs when a carbon atom in a molecule is attached to three other atoms.

The structure of alkenes can be explained by sp^2 mode of hybridization. In this type, one 2s and two 2p-orbitals are mixed together to give three equivalent and coplanar sp^2-hybrdized orbitals.



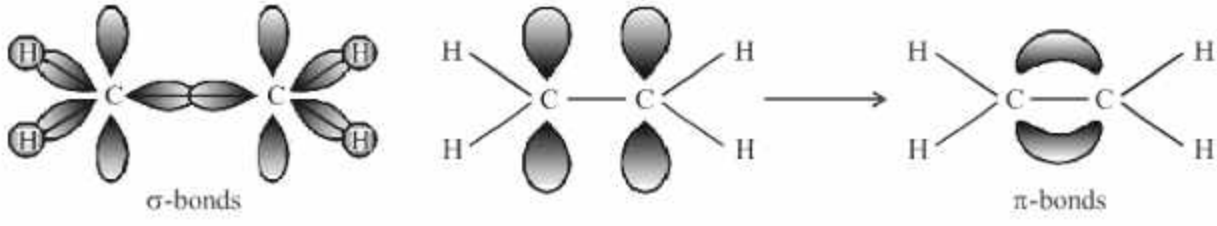
Combine to generate three sp^2-hybrid orbitals



Each sp^2-hybrid orbital is directed from the centre of an equilateral triangle to its three comers. The bond angle between any two sp^2-hybrid orbitals is 120°. The unhbridized $2p_z$ orbital will remain perpendicular to the triangle which is formed.

STRUCTURE OF ETHENE ($CH_2 = CH_2$)

In ethene, each carbon atom is attached to two hydrogen atoms by single bonds and to another carbon atom by a double bond. Since each carbon is attached to three other atoms, it uses sp^2-orbitals and an unhybridized p-orbital to form its bonds. There are four C – H single bonds. Each C – H bond is a σ bond and is formed by the overlap of sp^2-orbital from carbon and 1s orbital from hydrogen. One of the two bonds in the double bond is also a σ bond and forms by the linear overlap of sp^2-orbitals, one from each carbon atom.

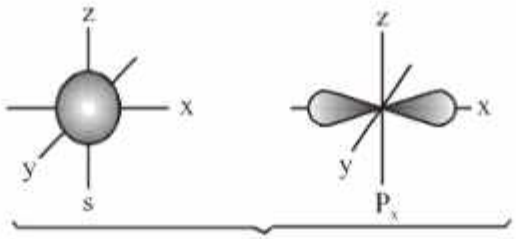


The second bond in the double bond is a π-bond which forms by the parallel overlap of two unhybridized p-orbitals. Ethene is a planar molecule. All bond angles are of 120°. Electron density in case of π-bond is above and below the bond axis. π-bonds is weaker bond than the sigma. Due to this exposed π-bond, alkanes are more reactive than σ-bond. Alkenes are restricted bond and cannot be rotated and gave the idea of geometrical isomers.

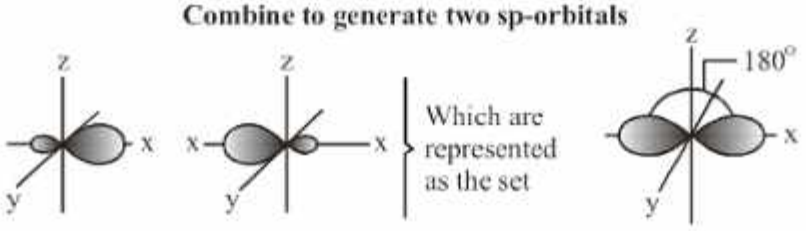
sp-HYBRIDIZATION

"The process of mixing of one s-orbital and one p-orbital to form two new hybrid orbitals of equivalent shape and energy is called sp-hybridization."

Structure of alkynes can be explained with the help of sp-hybridization. The hybridized orbitals have same energy (degenerate). The orbitals have linear shape with a bond angle of 180°. The two unhybrid p-orbitals, $2p_y$ and $2p_x$ are perpendicular to these sp-hybridized orbitals.



Combine to generate two sp-orbitals



STRUCTURE OF ETHYNE (HC ≡ CH)

In ethyne, each carbon atom is attached to one hydrogen atom by a single covalent bond and to another carbon atom by a triple bond. Since each carbon is attached to two other atoms, it uses two sp-hybrid orbitals and two unhybridized 2p-orbitals. There are two C – H single bonds and one carbon-carbon triple bond. Each C – H bond is a σ-bond and is formed by the overlap of sp-orbital from carbon and 1s orbital from hydrogen. One of the three bonds is a σ-bond and is formed by the linear overlap of the two sp-orbitals, one from each carbon. The other two bonds in the triple bond are π-bonds and are formed due to the parallel overlap of the unhybridized p-orbitals on each carbon. Ehtyne is a linear molecule. The bond angle is of 180°.

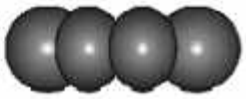
The presence of a σ and two π-bonds between two carbon atoms is responsible for shortening the bond distance.



Formation of σ-bonds



Formation of π-bonds



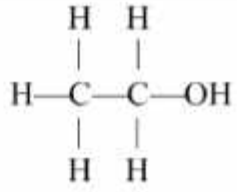
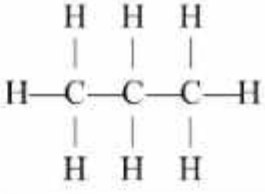
Space-filling model

Molecular Formula:

"The formula which gives the actual number of different atoms of elements in a molecule is called molecular formula." e.g., CH_3OH methanol, C_2H_5OH ethanol, CH_3COOH acetic acid, C_4H_{10} butane etc.

Structural Formula:

The formula which describe the arrangement of atoms of different elements in a molecule is called structural formula. e.g.,

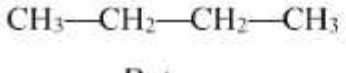
Name of compound	Molecular formula	Structural formula
Ethanol	C_2H_5OH	
Propane	C_3H_8	

ISOMERISM

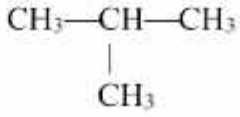
"The compounds which have same molecular formula but different arrangement of atoms are called isomers and phenomenon is called isomerism."

Methane, ethane and propane have only one arrangement of atoms and have no phenomenon of isomerism. Butane has two isomers or two possible arrangements of atoms.

Isomers of Butane (C_4H_{10}):

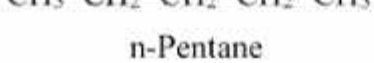


n-Butane

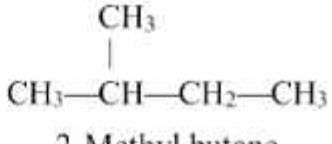


iso-Butane

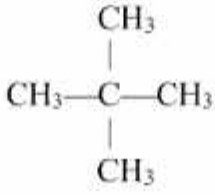
Isomers of Pentane (C_5H_{12}):



n-Pentane

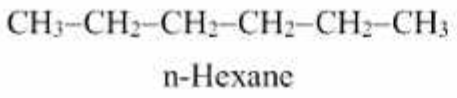


2-Methyl butane

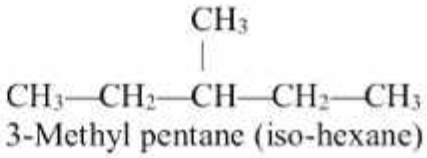


2,2 Dimethyl propane (neo-pentane)

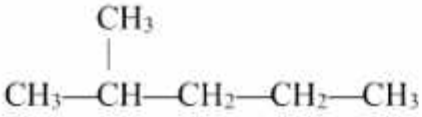
Isomers of Hxane (C_6H_{10}):



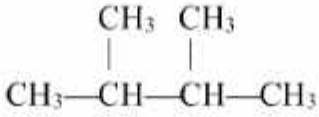
n-Hexane



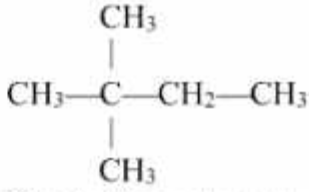
3-Methyl pentane (iso-hexane)



2-Methyl pentane

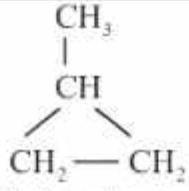
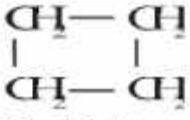


2-3-Dimethyl butane



2-2-Dimethyl butane (neo-hexane)

Isomers of C_4H_8:

$H_2C = CH - CH_2 - CH_3$ 1-butene	 Cis-2-butene	 Trans-2-butene
 Methyl cyclopropane	 Cyclobutane	

As the number of carbon atoms, in a hydrocarbon increases, the number of possible isomers increases very rapidly. Butane has two, pentane has three and hexane has five structural isomers. Decane has 75 isomers and Eicosane has 366319 isomers. When the number of carbon atoms increases to 30, the number of possible isomers (geometrical and structural) should be over four billions.

TYPES OF ISOMERISM

(1) Structural Isomerism:

"The compounds which have same molecular formula but different structural formula are called structural isomers."

The structural isomers are not confined only to hydrocarbons. This isomerism is present in every functional group. The structural isomerism arises due to the difference of arrangement of carbon atoms in a molecule. The structural isomers have following four types:

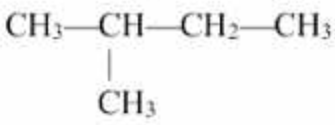
(i) Chain Isomerism (Skeletal Isomerism):

"The compounds which have same molecular formula but different length of chain of carbon atoms, are called chain isomers." And this phenomenon is called chain isomerism. For example, pentane (C_5H_{12}) has three chain isomers.

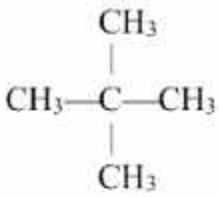
It is also called "Skeletal Isomerism".

$CH_3–CH_2–CH_2–CH_2–CH_3$

(n-Pentane)



2-Methyl butane (iso-pentane)



2,2-Dimethyl propane (neo-pentane)

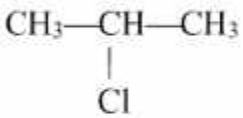
(ii) Positional Isomerism:

"This type of isomerism arises due to the difference in the position of the same functional group on the carbon chain." The arrangement of carbon atoms remains the same. For example:

(a) Chloropropane can have two positional isomers given below:

$CH_3–CH_2–CH_2–Cl$

1-Chloropropane



2-Chloropropane

(b) Butene (C_4H_8) can have two positional isomers.

$CH_3–CH_2–CH=CH_2$

1-Butene

$CH_3–CH=CH–CH_3$

2-Butene

(iii) Functional Group Isomerism:

"The compounds having the same molecular formula but different functional groups are called functional group isomerism." For example, there are two compounds having the same molecular formula C_2H_6O, but different arrangement of atoms.

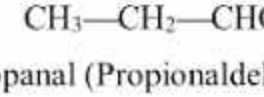
$CH_3–O–CH_3$

Dimethyl ether

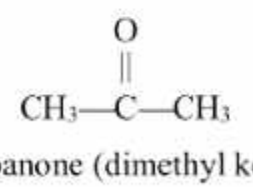
$CH_3–CH_2–OH$

Ethyl alcohol

Isomers of C_3H_6O:



Propanal (Propionaldehyde)



Propanone (dimethyl ketone)

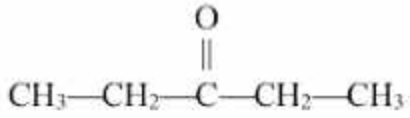
(iv) Metamerism:

"This type of isomerism arises due to the unequal distribution of carbon atoms on either side of the functional group." Such compounds belong to the same homologous series. For example, diethyl ether and methylpropyl ether are metamers.

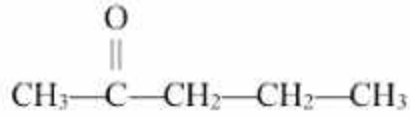
$CH_3–CH_2–O–CH_2–CH_3$ $\qquad$ $CH_3–O–CH_2–CH_2–CH_3$

Diethyl ether $\qquad$ Methyl n-propyl ether

For a ketonic compound having the molecular formula $C_5H_{10}O$, the following two metamers are possible.



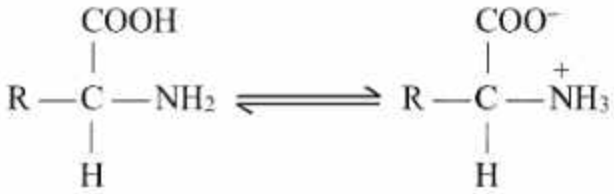
(Diethyl ketone)
3-pentanone



(Methyl n-propyl ketone)
2-pentanone

(v) Tautomerism:

This type of isomerism is due to shifting of proton from one atom to the other in the same molecule.



(Zwitter ion)

(2) Stereo Isomerism:

"The compounds which have same molecular formula but different spatial arrangement of atoms or groups are called stereo isomerism."

There are two kinds of stereo isomerism:

(i) Geometrical isomerism

(ii) Optical isomerism

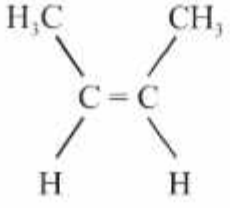
(i) Geometrical Isomerism:

The two carbon atoms joined by a single bond are capable of free rotation. However, when two carbon atoms are joined by a **double bond**, they **cannot rotate** freely. Rotation about carbon-carbon double bond cannot occur without breaking of pi-bonds. This lack of rotation about the double bond give rise to the isomers in certain alkenes. The relative position of various groups attached to double bonded atoms get fixed and give rise to cis-trans isomerism.

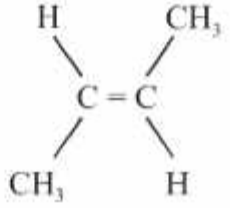
"Such compounds which possess the same structural formula but differ with respect to the positions of the identical groups in space are called cis-trans isomers and the phenomenon is known as the cis-trans or geometric isomerism."

The necessary and sufficient condition for a compound to exhibit geometric isomerism is that two groups attached to the same carbon must be different.

2-butene can exist in the form of cis and trans isomers

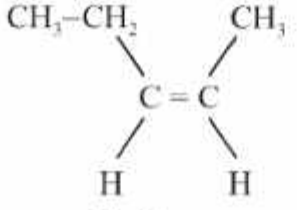


Cis-2-butene

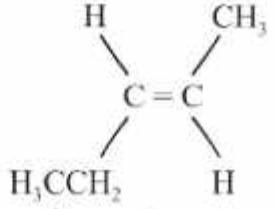


Trans-2-butene

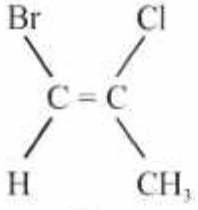
Similarly 2-pentene and 1-bromo-2-chloropropene also show cis-trans isomerism.



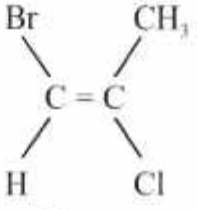
Cis-2-pentene



Trans-2-pentene



Cis



Trans

1-bromo-2-chloropropene

In the **cis-form**, the similar groups lie on the same side of the double bond whereas in the **trans-form**, the similar groups lie on the opposite sides of the double bond.

The rotation of two carbon atoms joined by a double bond could happen only if the pi-bond breaks. This ordinarily costs too much energy, making geometric isomers possible.

EXERCISE

Q.1 Fill in the blanks:

(i) Organic compounds having same molecular formula but different ———— are called isomers.

(ii) The state of hydridization of carbon atom in ———— is sp^2.

(iii) Alkenes show ———— due to restricted rotation around a carbon-carbon double bond.

(iv) Heating an organic compound in the absence of oxygen and in the presence of ———— as a catalyst is called catalytic cracking.

(v) A group of atoms which confers characteristic properties to an organic compound is called ————.

(vi) 2-butene is ———— of 1-butene.

(vii) Carbonyl functional group is present in both ———— and ketones.

(viii) A heterocyclic compound contains an atom other than ———— in its ring.

(ix) The quality of gasoline can be checked by finding out its ————.

(x) A carboxylic acid contains ———— as a functional group.

ANSWERS

(i)	structures	**(ii)**	ethene	**(iii)**	geometrical isomerism
(iv)	$SiO_2 + Al_2O_3$	**(v)**	functional group	**(vi)**	positional isomer
(vii)	aldehyde	**(viii)**	carbon	**(ix)**	octane number
(x)	–COOH				

Q.2 Indicate True or False:

(i) There are three possible isomers for pentane.

(ii) Alkynes do not show the phenomenon of cis-trans isomerism.

(iii) Organic compounds cannot be synthesized from inorganic compounds.

(iv) All close chain compounds are aromatic in nature.

(v) The functional group present in amides is called an amino group.

(vi) Government of Pakistan is trying to use coal for power generation.

(vii) Crude petroleum is subjected to fractional sublimation in order to separate it into different fractions.

(viii) A bond between carbon and hydrogen serves as a functional group for alkanes.

(ix) o-nitrotoluene and p-nitrotoluene are the examples of functional group isomerism.

(x) Almost all the chemical reactions taking place in our body are inorganic in nature.

ANSWERS

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

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

(i) The state of hybridization of carbon atom in methane is:

(a) sp^3 **(b)** sp^2

(c) sp **(d)** dsp^2

(ii) In t-butyl alcohol, the tertiary carbon is bonded to:

(a) Two hydrogen atoms **(b)** Three carbon atoms

(c) One hydrogen atom **(d)** No hydrogen atom

(iii) Which set of hybrid orbitals has planar triangular shape:

(a) sp^3 **(b)** sp

(c) sp^2 **(d)** dsp^2

(iv) The chemist who synthesized urea from ammonium cyanate was:

(a) Berzelius **(b)** Kolbe

(c) Wholer **(d)** Lavoisier

(v) Linear shape is associated with which set of hybrid orbitals:

(a) sp **(b)** sp^2

(c) sp^3 **(d)** dsp^2

(vi) A double bond consists of:

(a) Two sigma bonds **(b)** One sigma and one pi bond

(c) One sigma and two pi bonds **(d)** Two pi bonds

(vii) Ethers show the phenonenom of:

(a) Position isomerism **(b)** Functional group isomerism

(c) Metamerism **(d)** Cis-trans isomerism

(viii) Select from the following the one which is alcohol:

(a) $CH_3–CH_2–OH$ **(b)** $CH_3–O–CH_3$

(c) CH_3COOH **(d)** $CH_3–CH_2–Br$

ANSWERS

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

Q.4 How organic compounds are classified? Give suitable example of each type.

Ans. Descriptive question. See text book for details.

Q.5 What are homocyclic and heterocyclic compounds? Give one example of each.

Ans. For details. See text book.

Q.6 Write the structural formulas of the two possible isomers of C_4H_{10}.

Ans. Two possible isomers of C_4H_{10} are:

(i) $H_3C—CH_2—CH_2—CH_3$ (n-butane)

(ii) $H_3C—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$ (iso-butane)

Q.7 Why is ethene an important industrial chemical?

Ans. (i) It is used for the preparation of chemicals of industrial use like glycols (anti-freezer), ethanol, ethyl halides.

(ii) It is used as general anaesthetic in hospitals.

Q.8 What is meant by a functional group? Name typical functional groups containing oxygen.

Ans. **Functional Group:** A single bond, double bond, triple bond, and atom or group of atoms that imparts specific characteristics to an organic compound is called as function group.

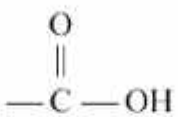
Oxygen containing typical functional groups are:

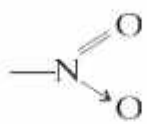
(i) Hydroxyl group —OH

(ii) Ether linkage 

(iii) Carbonyl group 

(iv) Ketonic group 

(v) Carboxyl group 

(vi) Nitro group 

Q.9 What is an organic compound? Explain the importance of Wohler's work in the development of organic chemistry.

Ans. Detailed question. See text book.

Q.10 Write a short note on cracking of hydrocarbons.

Ans. See text book for answer.

Q.11 Explain reforming of petroleum with the help of suitable example.

Ans. See text book for detailed answer.

Q.12 Describe important sources of organic compounds.

Ans. See text book for detailed answer.

Q.13 What is orbital hybridization? Explain sp^3, sp^2 and sp modes of hybridization of carbon.

Ans. Descriptive question. See text book.

Q.14 Explain the type of bonds and shapes of the following molecules using hybridization approach.

$CH_3 - CH_3$, $CH_2 = CH_2$, $CH \equiv CH$, HCHO, CH_3Cl

Ans.

(i) $CH_3 - CH_3$:

Ethane is 2nd member of alkanes having 7-sigma bonds, each carbon is sp^3 hybridized. It has tetrahedral geometry or shape.

(ii) $CH_2 = CH_2$:

Ethene is 2nd member of alkenes having 5-sigma bonds and 1-pi bond. Each carbon is sp^2 hybridized. Its molecule has triangular planar shape.

(iii) $CH \equiv CH$:

Ethyne is first member of alkynes having 3-sigma and 2-pi bonds molecule has linear shape.

(iv) HCHO:

Formaldehyde is first member of aldehyde having 3-sigma and 1-pi bond. Carbon atom is sp^2 hydbridized and molecule have triangular planar shape.

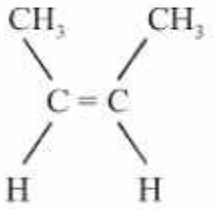
(v) $CH_3 - Cl$:

Methylehloride have all sigma bonds. The carbon is sp^3 hybridized. Its molecule have tetrahedral shape.

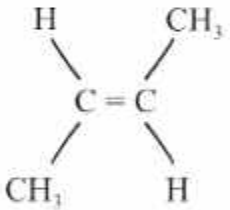
Q.15 Why there is no free rotation around a double and a free rotation around a single bond? Discuss cis-trans isomerism.

Ans. In case of double bond the unhybrid orbitals form π-bond by overlapping in parallel fashion due to which free rotation is restricted around double bond, while in case of single bond which is formed by linear overlapping of hybrid orbitals free rotation is possible due to ease of rotation around single sigma bond.

Due to restriction of rotation, alkenes have different arrangement of groups in space. If identical groups are present on the same side, they are called cis-compounds. If identical groups are present on the opposite side, they are called trans-compounds. For example 2-butene have two arrangements.



Cis-2-butene



Trans-2-butene

DO YOU KNOW?

(1) The first organic compound prepared in the laboratory was urea (Fredrick Wholer in 1828).

(2) Anthracite contains 91% carbon and peat contains 59.9% carbon.

(3) Octane number of iso-octane is 100.

(4) The quality of petrol is checked by its octane number.

(5) Dimethyl ether and ethanol are functional group isomers of each other.

(6) Fractional distillation of petroleum gives 20% of gasoline.

(7) Hetrocyclic compounds contains N, S, O alongwith carbon atoms in the ring.

(8) Molecular formula of cyclo alkanes and alkenes is the same (C_nH_{2n}).

(9) Pyridine, furan, thiophene and pyrrole are hetrocyclic compounds.

(10) sp^3 hybrid orbitals are non-coplanar.

(11) Acetaldehyde and acetone are functional group isomers of each other.

(12) 1-butene and 2-butene are position isomers.

(13) An atom or group of atoms which confers characteristic properties to an organic compound is called functional group.

(14) Decane has 75 isomers.

(15) Eicosane has 366319 isomers.

(16) Octane number of 2, 2, 3 trimethyl butane is 124.

(17) Anti-knocking agent is ethyl fluid. It contains $(C_2H_5)_4Pb$ = 67%, $C_2H_4Br_2$ = 26%, $C_2H_4Cl_2$ = 9%, Red-dye = 2%. 1 – 3 c.c. (cm^3) of this reagent is added to one gallon of petrol.

CHAPTER 7

FUNDAMENTAL PRINCIPLES OF ORGANIC CHEMISTRY

MULTIPLE CHOICE QUESTIONS

1. The state of hybridization of carbon atom in methane is:

(a) sp^3 **(b)** sp^2

(c) sp **(d)** dsp^2

2. The chemist who synthesized urea from ammonium cyanate was:

(a) Berzelius **(b)** Kolbe

(c) Wholer **(d)** Lavoisier

3. Which set of hybrid orbitals has planar triangular shape:

(a) sp^3 **(b)** sp

(c) sp^2 **(d)** dsp^2

4. The reaction $C_8H_{18} \xrightarrow{\Delta} C_3H_6$ + Fragments is:

(a) Catalytic oxidation **(b)** Isomerization

(c) Synthesis **(d)** Cracking

5. The octane number is 100% in petroleum:

(a) Neo-octane **(b)** n-Hexane

(c) Neo-pentane **(d)** Iso-octane

6. Concept of octane number was introduced by:

(a) Kekule **(b)** Edgar

(c) Wholer **(d)** Dalton

7. Which of the following form of coal has maximum %age of carbon:

(a) Peat **(b)** Bituminous

(c) Sub-bituminous **(d)** Anthracite

8. Which of the following is the use of light naptha:

(a) Non-polar solvent **(b)** Lubricant

(c) Roofing **(d)** Polar solute

9. Carbon atom of HCHO (methanal, formaldehyde) is:

(a) sp hybridized **(b)** sp^2 hybridized

(c) sp^3 hybridized **(d)** Not hybridized

10. A double bond consist of:

(a) Two sigma bonds **(b)** One sigma and one pi bond

(c) One sigma and two pi bond **(d)** Two pi bonds

11. Alkanoic acid is another name of:

(a) Aldehyde **(b)** Ketones

(c) Carboxylic acid **(d)** Alcohols

12. An isomer of ethanol is:

(a) Dimethyl ether **(b)** Diethyl ether

(c) Ethylene glycol **(d)** Methanol

13. Ethers shows the phenomenon of:

(a) Position isomerism **(b)** Functional group isomerism

(c) Metamerism **(d)** Cis-trans isomerism

14. Isomerism exhibited by ethanol and dimethyl ether is:

(a) Position isomerism **(b)** Metamerism

(c) Functional group isomerism **(d)** Chain isomerism

15. Which one of the following does not show geometric isomerism:

(a) ClHC = CHCl **(b)** $H_3C - HC = CHCH_3$

(c) $H_2C = CHCl$ **(d)** BrClC = CClBr

16. In t-butyl alcohol, the tertiary carbon is bonded to:

(a) Two H-atoms **(b)** Three H-atoms

(c) One H-atom **(d)** No H-atom

17. Which one is the functional group of esters:

(a) $-\overset{\overset{O}{\|}}{C}-X$ **(b)** $-\overset{\overset{O}{\|}}{C}-OH$

(c) $-\overset{\overset{O}{\|}}{C}-OR$ **(d)** $-\overset{\overset{O}{\|}}{C}-H$

18. Which of the following has zero dipole moment:

(a) 2-methyl-1-propene **(b)** 1-butene

(c) Trans-2-butene **(d)** Cis-2-butene

19. Fractional distillation of petroleum yields only about ———— of gasoline.

(a) 40% **(b)** 20%

(c) 70% **(d)** 10%

20. Which of the following compounds will exhibit cis-trans (isomerism):

(a) Butanal **(b)** 2-butyne

(c) 2-butanol **(d)** 2-butene

answers

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

SOLVED EXERCISE

Q.1 Fill in the blanks:

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(ii) The state of hydridization of carbon atom in ———— is sp^2.

(iii) Alkenes show ———— due to restricted rotation around a carbon-carbon double bond.

(iv) Heating an organic compound in the absence of oxygen and in the presence of ———— as a catalyst is called catalytic cracking.

(v) A group of atoms which confers characteristic properties to an organic compound is called ————.

(vi) 2-butene is ———— of 1-butene.

(vii) Carbonyl functional group is present in both ———— and ketones.

(viii) A heterocyclic compound contains an atom other than ———— in its ring.

(ix) The quality of gasoline can be checked by finding out its ————.

(x) A carboxylic acid contains ———— as a functional group.

answers

(i)	structures	**(ii)**	ethene	**(iii)**	geometrical isomerism
(iv)	$SiO_2 + Al_2O_3$	**(v)**	functional group	**(vi)**	positional isomer
(vii)	aldehyde	**(viii)**	carbon	**(ix)**	octane number
(x)	–COOH				

Q.2 Indicate True or False:

(i) There are three possible isomers for pentane.

(ii) Alkynes do not show the phenomenon of cis-trans isomerism.

(iii) Organic compounds cannot be synthesized from inorganic compounds.

(iv) All close chain compounds are aromatic in nature.

(v) The functional group present in amides is called an amino group.

(vi) Government of Pakistan is trying to use coal for power generation.

(vii) Crude petroleum is subjected to fractional sublimation in order to separate it into different fractions.

(viii) A bond between carbon and hydrogen serves as a functional group for alkanes.

(ix) o-nitrotoluene and p-nitrotoluene are the examples of functional group isomerism.

(x) Almost all the chemical reactions taking place in our body are inorganic in nature.

answers

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

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

(i) The state of hybridization of carbon atom in methane is:

(a) sp^3 **(b)** sp^2

(c) sp **(d)** dsp^2

(ii) In t-butyl alcohol, the tertiary carbon is bonded to:

(a) Two hydrogen atoms **(b)** Three carbon atoms

(c) One hydrogen atom **(d)** None of these

(iii) Which set of hybrid orbitals has planar triangular shape:

(a) sp^3 **(b)** sp

(c) sp^2 **(d)** dsp^2

(iv) The chemist who synthesized urea from ammonium cyanate was:

(a) Berzelius **(b)** Kolbe

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(v) Linear shape is associated with which set of hybrid orbitals:

(a) sp **(b)** sp^2

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(vi) A double bond consists of:

(a) Two sigma bonds **(b)** One sigma and one pi bond

(c) One sigma and two pi bonds **(d)** Two pi bonds

(vii) Ethers show the phenonenom of:

(a) Position isomerism **(b)** Functional group isomerism

(c) Metamerism **(d)** Both (b) and (c)

(viii) Select from the following the one which is alcohol:

(a) $CH_3–CH_2–OH$ **(b)** $CH_3–O–CH_3$

(c) CH_3COOH **(d)** $CH_3–CH_2–Br$

answers

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

Q.4 How organic compounds are classified? Give suitable example of each type.

Ans. Descriptive question. See text book for details.

Q.5 What are homocyclic and heterocyclic compounds? Give one example of each.

Ans. For details. See text book.

Q.6 Write the structural formulas of the two possible isomers of C_4H_{10}.

Ans. Two possible isomers of C_4H_{10} are:

(i) $H_3C—CH_2—CH_2—CH_3$ (n-butane)

(ii) $H_3C—\underset{\displaystyle CH_3}{\underset{|}{CH}}—CH_3$ (iso-butane)

Q.7 Why is ethene an important industrial chemical?

Ans. (i) It is used for the preparation of chemicals of industrial use like glycols (anti-freezer), ethanol, ethyl halides.

(ii) It is used as general anaesthetic in hospitals.

Q.8 What is meant by a functional group? Name typical functional groups containing oxygen.

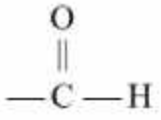
Ans. **Functional Group:** A single bond, double bond, triple bond, and atom or group of atoms that imparts specific characteristics to an organic compound is called as functional group.

Oxygen containing typical functional groups are:

(i) Hydroxal group —OH

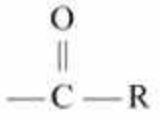
(ii) Ether linkage 

(iii) Aldehydic group



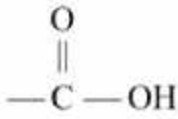
(Formyl)

(iv) Ketonic group

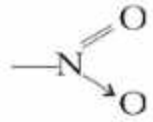


(Carbonyl)

(v) Carboxyl group



(vi) Nitro group



Q.9 What is an organic compound? Explain the importance of Wohler's work in the development of organic chemistry.

Ans. Detailed question. See text book.

Q.10 Write a short note on cracking of hydrocarbons.

Ans. See text book for answer.

Q.11 Explain reforming of petroleum with the help of suitable example.

Ans. See text book for detailed answer.

Q.12 Describe important sources of organic compounds.

Ans. See text book for detailed answer.

Q.13 What is orbital hybridization? Explain sp^3, sp^2 and sp modes of hybridization of carbon.

Ans. Descriptive question. See text book.

Q.14 Explain the type of bonds and shapes of the following molecules using hybridization approach.

$CH_3 - CH_3$, $CH_2 = CH_2$, $CH \equiv CH$, HCHO, CH_3Cl

Ans.

(i) $CH_3 - CH_3$:

Ethane is 2nd member of alkanes having all sigma bonds, each carbon is sp^3 hybridized. It has tetrahedral geometry or shape.

(ii) $CH_2 = CH_2$:

Ethene is 2nd member of alkenes having 7 sigma bonds and 1-pi bond. Each carbon is sp^2 hybridized. Its molecule has triangular shape.

(iii) $CH \equiv CH$:

Ethyne is first member of alkenes having 3 sigma and 2-pi bonds molecule has linear shape.

(iv) HCHO:

Formaldehyde is first member of aldehyde having 3-sigma and 1-pi bond. Carbon atom is sp^2 hydbridized and molecule has triangular shape.

(v) $CH_3 - Cl$:

Methyl chloride have all sigma bonds. The carbon is sp^3 hybridized. Its molecule have tetrahedral shape.

Q.15 Why there is no free rotation around a double and a free rotation around a single bond? Discuss cis-trans isomerism.

Ans. In case of double bond, the unhybrid orbitals form π-bond by overlapping in parallel fashion due to which free rotation is restricted around double bond, while in case of single bond which is formed by linear overlapping of hybrid orbitals free rotation is possible due to ease of rotation around single sigma bond.

Cis-trans isomerism see in text book.

DO YOU KNOW?

1. The first organic compound prepared in the laboratory was urea (Fredrick Wholer in 1828).
2. Anthracite contains 91% carbon and peat contains 59.9% carbon.
3. Octane number of iso-octane is 100.
4. The quality of petrol is checked by its octane number.
5. Dimethyl ether and ethanol are functional group isomers of each other.
6. Fractional distillation of petroleum gives 20% of gasoline.
7. Hetrocyclic compounds contains N, S, O alongwith carbon atoms in the ring.
8. Molecular formula of cyclo alkanes and alkenes is the same.
9. Pyridine, furan, thiophene and pyrrole are hetrocyclic compounds.
10. sp^3 hybrid orbitals are non-coplanar.
11. Acetaldehyde and acetone are functional group isomers of each other.
12. 1-butene and 2-butene are position isomers.
13. An atom or group of atoms which confers characteristic properties to an organic compound is called functional group.

SHORT QUESTIONS

Q.1 Why there is no free rotation around a double and a free rotation around a single bond?

Ans. In case of alkane only sigma bonds are present. In case of alkene two type of bonds are present; sigma and Pi bond. Due to parallel overlapping of p-orbitals in Pi-bond, no free rotation is present. So these double bonds are called restricted bonds. Due to restriction of rotation in alkenes, they have geometrical isomerism (Cis and trans isomerism).

Q.2 How tetraethyl lead acts as knock inhibitor in gasoline?

Ans. Tetraethyl lead acts as negative catalyst and it reduces the speed of combustion of the fuel, hence less knocking is produced.

Q.3 Why members of chain isomers of pentane are greater than butane?

Ans. As the number of carbon atom increase, number of possible arrangement also increases. Butane has two chain isomers while pentane has three isomers.

Q.4 Concept of metamerism is not present in butanone, why?

Ans. In metamerism, alkyl group varies on both side of functional group. In 2-butanone two alkyl groups are present on both side of carboxyl carbon.

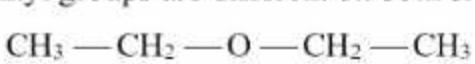


Methyl ethyl ketone or 2-butanone

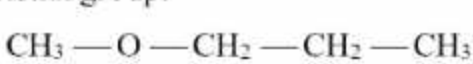
By rearranging the alkyl groups, name of ketone remains same.

Q.5 Ethers show metamerism and functional group isomerism. Explain it.

Ans. Ethers show functional group isomerism with alcohol. C_2H_5OH and CH_3OCH_3 both are functional group isomers. Diethyl ether and higher ethers show metamerism in which alkyl groups are different on both side of functional group.



Diethyl ether



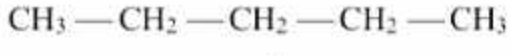
Methyl n-propyl ether

Q.6 Cracking process is used to increases the yield of gasoline, explain it.

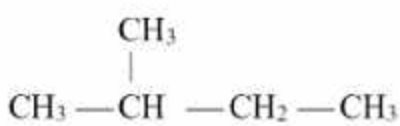
Ans. Fractional distillation of petroleum yields only 20% gasoline. Due to its greater demand, deficiency of gasoline is recovered by converting higher hydrocarbon to gasoline by cracking process. In this way, yield of gasoline is increased by cracking.

Q.7 Give possible isomers of C_5H_{12}.

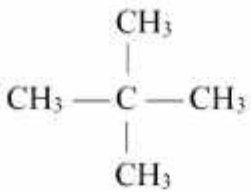
Ans. C_5H_{12} has three isomers.



n-pentane



2 methyl butane or iso-pentane



2, 2 dimethyl propane (Neopentane)

Q.8 On what basis different fractions of petroleum are separated from each other?

Ans. Different fractions of petroleum are separated from each other on the basis of their different boiling points.

Q.9 What is vital force theory?

Ans. Historically the term organic chemistry was applied to the study of those compounds, such as alcohols, sugar and urea that were found in living organism but were not found in non-living matter.

Therefore, for a longer time it was believed that organic compounds could be produced only in living organisms and there is some vital force present only in living organism necessary to generate organic compounds.