FUNDAMENTAL UNIVERSITY ORGANIC AND INORGANIC CHEMISTRY
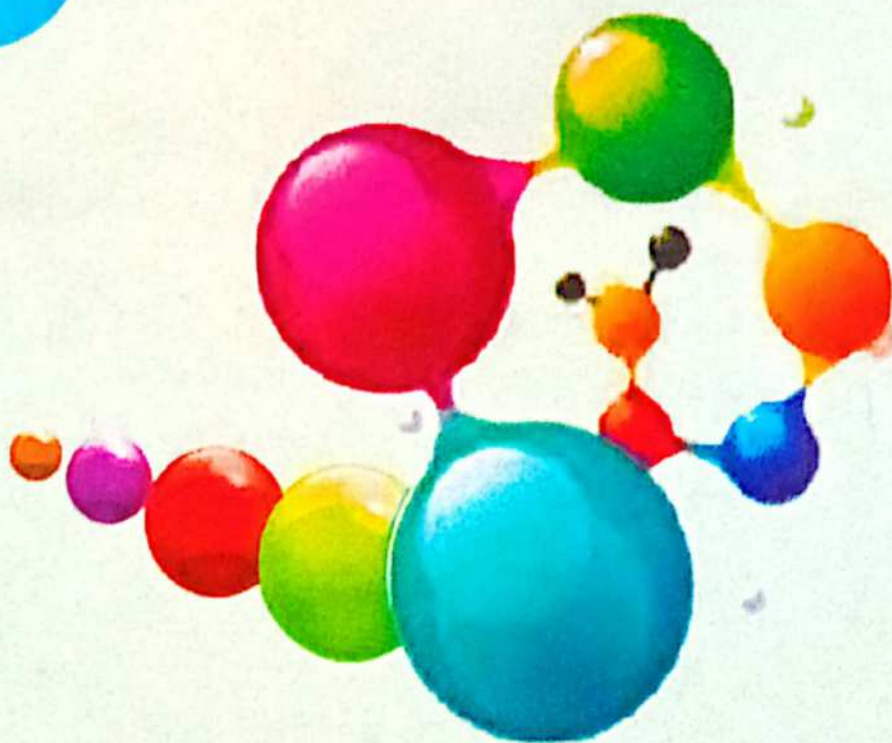
SERIES B

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SECTION TWO

INORGANIC CHEMISTRY

SECTION ONE
(ORGANIC CHEMISTRY)

PART ONE
PHYSICAL AND FUNDAMENTAL
PRINCIPLES OF ORGANIC CHEMISTRY

1

INTRODUCTION

The efforts of organic chemists are aimed at the following objectives:

(a) Isolation and purification of the unknown organic compound.

(b) Thin-layer chromatographic (TLC) analysis of the isolated organic compound to ascertain its purity.

(c) Deducing the molecular structure of the unknown compound by detailed spectroscopic examinations that give clues as to the type of bonds structure and nature of the functional groups present. The spectroscopic techniques commonly employed include:

(i) Infrared spectroscopy
(ii) Ultraviolet/visible spectroscopy
(iii) ^1H and ^{13}C nuclear magnetic resonance spectroscopy
(iv) Mass spectroscopy

If the above-mentioned techniques lead to the determination of structure, the following steps are necessary for further confirmation of the structure of the unknown organic compound.

(d) Preparation of crystalline derivatives, otherwise,

(e) Carrying out degradation reactions to break the molecule into successively smaller fragments until pieces having recognizable structures are obtained.

(f) Synthesis of unknown compound from simpler compounds of known materials and structures. This is then followed by step (d) and in either case, step (e).

(g) X-ray crystallographic analysis.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

This involves methods of identifying elements and functional groups present in unknown organic compounds. Organic compounds are assumed to contain carbon and hydrogen with other elements such as oxygen, nitrogen, sulphur, halogens (normally chlorine, bromine and iodine) and phosphorus, which are often covalently bonded to the carbon atoms. These elements except carbon and hydrogen, which are assumed to be present in organic compounds, can be detected by sodium fusion test (Lassaigne's test). Lassaigne's test does not involve the detection of oxygen; it is always obtained by difference.

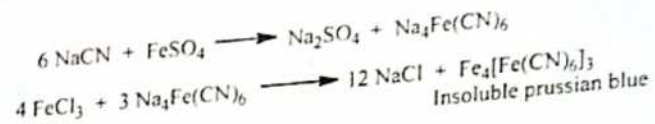## Sodium Fusion Test (Lassaigne's test)

Experimental procedure

Add a little of the substance (about 50 mg if solid, or 2 drops if liquid) to a small pellet of sodium in an ignition tube and heat, gently at first and then more strongly to red heat. Plunge the tube, while still hot into about 15 cm³ of cold distilled water in an evaporating dish and cover immediately with the lid to prevent splashing. Boil the mixture for a short time, while stirring with the unbroken portion of the tube and then filter through a fluted filter paper. The filtrate (known as sodium fusion filtrate or extract) should be clear and colorless if the combustion reaction goes to completion. The test converts any nitrogen, sulphur, phosphorus and halogen present in an organic compound into sodium cyanide, sodium sulphide, sodium phosphide and sodium halide respectively according to the following equation:

$$(C, H, N, S, P, X) + Na_{(s)} \xrightarrow{heat} NaCN + Na_2S + Na_3P + NaX$$
Organic compound   excess
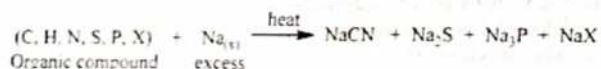
It is essential to use excess sodium metal, otherwise, if sulphur and nitrogen are present, sodium thiocyanate (NaCNS) may be produced instead of sodium cyanide (NaCN) and sodium sulphide (Na₂S) as above. The following qualitative inorganic tests are performed on the sodium fusion filtrate.

(i)   Test for nitrogen

To 4 cm³ of the sodium filtrate, add 0.5 cm³ of cold saturated solution of iron (II) tetraoxosulphate (VI) (FeSO₄). Boil the mixture for thirty minutes, add iron (III) chloride, and acidify by adding concentrated hydrochloric acid (or 3M tetraoxosulphate (VI) acid, (H₂SO₄) dropwise. The formation of a Prussian blue (bluish-green) precipitate indicates the presence of nitrogen. The equations for the reaction are:

$$6 NaCN + FeSO_4 \longrightarrow Na_2SO_4 + Na_4Fe(CN)_6$$
$$4 FeCl_3 + 3 Na_4Fe(CN)_6 \longrightarrow 12 NaCl + Fe_4[Fe(CN)_6]_3$$
Insoluble prussian blue

(ii)   Test for sulphur

To 2.5 cm³ of the sodium fusion filtrate, add few drops of lead ethanoate solution and acidify with dilute ethanoic acid. The formation of a black precipitate of lead (II) sulphide indicates the presence of sulphur.

$$Na_2S + Pb(COOCH_3)_2 \xrightarrow{CH_3COOH} PbS\downarrow + 2 CH_3COONa$$
Black ppt

Alternative test for sulphur

Add a few drops of cold, freshly prepared, dilute solution of sodium pentacyano nitrosyl ferrate (II) (nitroprusside) to a portion of the sodium fusion filtrate. The presence of sulphur is indicated by the production of a rich purple coloration.

(iii)   Test for halogen

If the tests for nitrogen and sulphur are positive, boil the sodium fusion filtrate for some minutes to expel hydrogen cyanide and hydrogen sulphide, which might interfere with the test for halogen. The presence of halogen can be tested for by acidifying a portion of the sodium fusion filtrate with dilute trioxonitrate (V) acid (HNO₃) and adding silver trioxonitrate (V) solution (AgNO₃). The formation of a precipitate indicates the presence of halogen.

$$NaX + AgNO_3 \xrightarrow{HNO_3} AgX\downarrow + NaNO_3$$
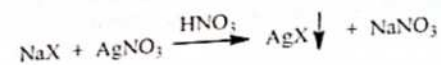
The solubility of the precipitate is then tested in aqueous ammonia to identify the specific halogen present.
If the halogen present is chlorine, the precipitate will be white and readily soluble in aqueous ammonia.

If it is bromine, it will be pale yellow and slightly less soluble in aqueous ammonia.
If it is iodine, it will be yellow and insoluble in aqueous ammonia.

(iv)   Test for phosphorus

To 1 cm³ of the sodium fusion filtrate, add about 2 cm³ concentrated trioxonitrate (V) acid and boil in order to convert any phosphorus present into phosphate (V) ions. Cool the solution, and add ammonium molybdate (VI). The formation of a yellow precipitate on gently warming to a temperature of 50°C indicates the presence of phosphate (V) ions.

SEPARATION AND PURIFICATION OF ORGANIC COMPOUNDS

A compound cannot be properly studied unless it is pure, that is, free from the molecules of any other substance. Purity is ascertained by physical properties such as melting point, boiling point, solubility, density, refractive index, chromatographic behaviour and various spectra studies. A compound is assumed to be 100% pure when processes of purification produce no further change in physical properties. The following are the separation methods used to separate the constituents of a mixture.

A. Filtration

Filtration of a mixture will often be necessary either to isolate a precipitate (e.g. in gravimetric analysis) which has separated out after the completion of a reaction, or to remove insoluble impurities or reactants, in which case the desired product remains in solution. Particles to be filtered must be sufficiently large enough to prevent them from passing through the pores of the filter paper, sintered glass or Gooch fibre.

B. Recrystallization

This is a repeated crystallization of a material from fresh solvent or mixture of solvents to obtain an increasingly pure product, i.e. crystal.

Sublimation

This is the process by which solids are transformed directly to the vapor state without passing through the liquid phase. The success of the method depends upon the compound having high enough vapor pressure at a temperature below the melting point, so that the rate of vaporization from solid will be rapid and the vapor may be condensed back to the solid upon a cooled surface. Impurities should have different vapor pressures from the compound undergoing purification. Sublimation is of considerable importance in the purification of certain substances such as iodine, naphthalene and sulphur.

D. Fractional crystallization

In fractional crystallization, it is desired to separate several solutes present in the same solution. This is generally done by picking crystallization temperatures and solvents such that only one solute is supersaturated and crystallizes out. By changing conditions, other solution may be crystallized subsequently. Repeated crystallization is necessary to achieve desired purities when many inclusions are present or when the solubility of other solutes is significant.

E. Simple distillation

This is the process of producing a gas or vapor from a liquid by heating the liquid in a vessel and collecting and condensing the vapors into liquids at a particular temperature. The liquids can then be collected.

F. Fractional distillation

This is a method of separating a mixture of several volatile components of different boiling points. The mixture is distilled at the lowest boiling point and the average collected as one fraction until the temperature of the vapor rises, showing that a higher boiling component of the mixture is beginning to distill; this component is collected as a separate fraction.

G. Steam distillation

This is a distillation technique in which vaporization of the volatile constituents of a liquid mixture takes place at a lower temperature by the introduction of steam directly into the liquid mixture; steam used in this manner is known as open steam or steam stripping.

H. Steam refining

This is a petroleum refinery distillation process in which crude oil is heated with from steam in open and closed coils near the bottom of the fractionating column to produce gasoline and naphtha where odor and color are of prime importance. It acts as steam distillation where open steam is used.

I. Fractional condensation

This is a method of separation of components of vaporized liquid mixtures by condensing the vapors in stages (partial condensation). The highest-boiling-point components condense in the first condenser stage, allowing the remainder of the vapor to pass on to subsequent condenser stages.

J. Fractional precipitation

This is an analytical method used for separating elements or compounds with similar solubility by a series of analytical precipitations, each one improving the purity of the desired element or compound.

K. Fractionation

This is a method of separation of a mixture in successive stages, each stage removing from the mixture some proportion of one of the substances, as by differential solubility in water-solvent or solvent-solvent mixtures.

L. Solvent refining

This is the process of treating a mixed material with a solvent that preferentially dissolves and removes certain minor constituents (usually the undesired ones). This method is commonly used in the petroleum refining industry.

M. Centrifugation

This process is used to separate two miscible substances. The centrifuge works using the sedimentation principle, where the centripetal acceleration causes denser substances and particles to settle to the bottom of the tube, while low-density substances rise to the top.

N. Chromatography

This is based on the principle of partition of a solute between two immiscible solvents. The solute partitions itself between a mobile phase and a stationery phase. The stationery phase is a solvent adsorbed on a solid, e.g., paper or alumina. The mobile phase is a second solvent or a gas column chromatography, paper chromatography, thin layer chromatography and gas-liquid chromatography all employ principle of partition. The relative distances travelled by the component and solvent front during the separation are used to calculate the retention factor (R_F) as follows:

$$R_f = \frac{Distance\ travelled\ by\ the\ component}{Distance\ travelled\ by\ the\ solvent\ front} \qquad (1.1)$$

The R_f value can be used in identifying components of a mixture by comparing with literature values.

O. Solvent extraction

This is a method of separation of materials of different chemical types and solubility by selective solvent action, that is when some materials are more soluble in one solvent than in another, hence there would be a preferential extractive action. The method is useful for materials that distribute themselves between two immiscible solvents. It is used to refine petroleum products, and purify organic compounds, vegetable oils and vitamins.

Distribution Law- (Nernst's Law)

This law states that the ratio of the concentrations of a solute distributed between immiscible solvents is a constant, provided the temperature remains constant and molecular state of the solute is the same in both solvents.

$$K = \frac{Concentration\ of\ solute\ in\ solvent\ A}{Concentration\ of\ solute\ in\ solvent\ B} \qquad (1.2)$$

where K is the partition coefficient of the solute between solvents A and B. The concentration of the solute can be expressed in g cm^{-3}, g dm^{-3}, mol dm^{-3} or any other concentration units.

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Worked Example

Question 1

100 cm^3 of water containing 10 grams of an organic compound X was extracted with 50 cm^3 of diethylether (a) in one batch (b) in two batches of 25 cm^3 of diethylether each. Knowing fully well that diethyl ether and water are immiscible and that the partition coefficient of X between ether and water is 8.0 at the temperature of 37°C. Calculate the masses of X extracted into diethylether in the two cases at this temperature.

Solution

In one batch

Let y grams of X be extracted into ether and (10 − y) grams of X will remain in water.

$$C_{aq}^x = \frac{10-y}{100}\ g\ cm^{-3} \quad and \quad C_{ether}^x = \frac{y}{50}\ g\ cm^{-3}$$

$$K = \frac{C_{ether}^x}{C_{aq}^x} = 8 = \frac{\frac{y}{50}}{\frac{10-y}{100}}$$

∴

$$\left(\frac{y}{50}\right)\left(\frac{100}{10-y}\right) = 8$$

i.e.

$$\frac{100y}{10-y} = 8$$

$$100y = 4000 - 400y$$

$$500y = 4000$$

$$y = 8\ grams$$

$$y = 8\ g$$

∴ It means 8 grams of X would be extracted into ether.

In two batches of equal volume (i.e. 25 cm^3 of ether each).

Let y grams of X be extracted into ether and (10 − y) grams of X into water in the first extraction;

$$C_{ether}^x = \frac{y}{25}\ g\ cm^{-3} \quad and \quad C_{aq}^x = \frac{10-y}{100}\ g\ cm^{-3}$$

$$K = \frac{C_{ether}^x}{C_{aq}^x} = 8 = \frac{\frac{y}{25}}{\frac{10-y}{100}}$$

∴

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$$\left(\frac{y}{25}\right)\left(\frac{100}{10-y}\right) = 8$$

$$\frac{100y}{250-25y} = 8$$

$$100y = 2000 - 200y$$

$$300y = 2000$$

$$y = 6.67 \text{ grams}$$

It means 6.67 grams of X would be extracted into ether in the first extraction, leaving $(10 - 6.67 = 3.33)$ gram in water layer (i.e. aqueous layer).

In the second extraction:

Let z grams of X be extracted into ether and $(3.33-z)$ grams of X into water.

$$C'_{aq} = \frac{3.33-z}{100} \text{ g cm}^{-3} \quad \text{and} \quad C'_{ether} = \frac{z}{25} \text{ g cm}^{-3}$$

$$\therefore K = \frac{C'_{ether}}{C'_{aq}} = 8 = \frac{\frac{z}{25}}{\frac{3.33-z}{100}}$$

i.e.

$$\left(\frac{z}{25}\right)\left(\frac{100}{3.33-z}\right) = 8$$

$$\frac{100z}{83.25 - 25z} = 8$$

$$100z = 666 - 200z$$

$$300z = 666$$

$$z = 2.22 \text{ grams}$$

It means 2.22 grams of X would be extracted into ether in the second extraction,
$\therefore$ Total amount of X extracted into ether in the two extraction batches is;

$$y + z = 6.67 + 2.22$$
$$= 8.89 \text{ g.}$$

$\therefore 1.11$ grams of X will remain in water (i.e. aqueous layer).

Alternatively, one can use the following formulae:

For one batch extraction (i.e single extraction):

$$W = W_o \left(\frac{V_a}{KV_o + V_a}\right) \tag{1.3}$$

where,

V_o is the volume of the organic solvent in a single batch extraction,
V_a is the volume of aqueous solvent in a single batch extraction
W_o is the amount of solute originally in the aqueous solvent,
W is the amount remaining in water after the extraction,
K is the partition coefficient between the organic solvent and water.

For two batches - extraction with different volumes of organic solvent.

$$W = W_o \left(\frac{V_a}{(KV_1 + V_a)}\right)\left(\frac{V_a}{(KV_2 + V_a)}\right) \tag{1.4}$$

where,

V_a is the volume of aqueous solvent,
V_1 and V_2 are the volumes of organic solvent used for extraction in the first and second batches respectively.

For "n" batches - extraction with equal volumes of organic solvent:

$$W = W_o \left(\frac{V_a}{K\left(\frac{V_o}{n}\right) + V_a}\right)^n \tag{1.5}$$

where, "n" is the number of batches.

NB:

(i) The above formulae hold for partition coefficient between the organic layer and water.

(ii) If the partition coefficient given is between aqueous layer and organic layer, the reciprocal of the value has to be taken before substituting into the formulae above.

Let us now apply the formulae to solve the **Question 1** above:

(a) One batch - extraction using 50 cm³ of diethyl ether;

$V_a = 100 \text{ cm}^3$, $V_o = 50 \text{ cm}^3$, $W_o = 10 \text{ g.}$

Using equation (1.3) to calculate the amount of solute remaining in water after the single batch extraction,

$$W = W_o \left(\frac{V_a}{(KV_o + V_a)}\right)$$

$$= 10 \left(\frac{100}{((8 \times 50) + 100)}\right)$$

$$= 2g$$

$\therefore$ Amount extracted $= W_o - W = (10 - 2)g = 8g.$

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(b) Two batches of equal volume of 25 cm³ of diethylether; i.e, $n = 2$

Use equation (1.5) to calculate the amount of solute remaining in water after the two batch extractions, i.e, $n = 2$.

$$W = W_o \left(\frac{V_o}{K\left(\frac{V_o}{n}\right) + V_o} \right)^2$$

$$= 10 \left(\frac{100}{8\left(\frac{50}{2}\right) + 100} \right)^2$$

$$= 1.11g$$

$$\therefore \text{Amount extracted} = W_o - W = (10 - 1.11)g = 8.89 \, g$$

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

This deals with estimation of the proportion of the elements present in an organic compound by combustion microanalysis as described below;

Combustion analysis

A weighed sample is burnt in excess oxygen, where carbon, hydrogen and nitrogen are oxidized to carbon (IV) oxide, water and nitrogen (IV) oxide respectively. The carbon (IV) oxide is absorbed in soda lime (i.e. KOH) and weighed; the water is absorbed in calcium (II) chloride and weighed and nitrogen (IV) oxide is reduced to nitrogen and measured volumetrically (Dumas method). The nitrogen can also be determined by Khedjahl method. This involves digesting the organic compound with concentrated tetraoxosulphate (VI) acid, which converts the total nitrogen present into ammonium tetraoxosulphate (VI). The solution is then made alkaline. The ammonia thus liberated is distilled and its amount is determined by titration with standard boric acid.
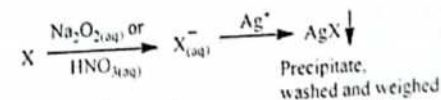
Other elements are converted to inorganic solid compounds and weighed; for example, sulphur in an organic compound is converted into tetraoxosulphate (VI) ion by treatment with sodium peroxide or trioxonitrate (V) acid (Carius method). This is then converted into barium tetraoxosulphate (VI), which is weighed.

$$2 NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
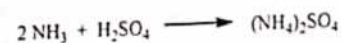
In a similar manner, phosphorus can be estimated by converting to tetraoxophosphate (V) acid.

$$4 P \xrightarrow[H_2O]{10HNO_3} 4 H_3PO_{4(aq)} + 5 NO_{(g)} + 5 NO_{2(g)}$$
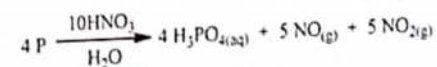
The covalently bonded halogens are converted into halide ions by heating the organic compound either in a bomb with sodium peroxide or in a sealed tube with trioxonitrate (V) acid (Carius method). The halide ion thus formed is treated with silver trioxonitrate (V) to form silver halide, which can then be weighed.

$$X \xrightarrow[HNO_{3(aq)}]{Na_2O_{2(aq)} \text{ or}} X^-_{(aq)} \xrightarrow{Ag^+} AgX\downarrow$$
$$\text{Precipitate,}$$
$$\text{washed and weighed}$$

The oxygen content is obtained by difference. The following worked examples illustrate some of the quantitative methods of analysis of organic compounds.

Worked Examples

Question 1

Determine the molecular formula of compound Y from the following quantitative result. Combustion of 3.54 mg of Y gave 8.03 mg of CO_2 and 3.34 mg of H_2O. The molecular mass of compound Y as determined by mass spectrometry is 116.2.

Solution

44 g of CO_2 contain 12 g of carbon

$$8.03 \text{ mg of } CO_2 \text{ will contain} = \frac{12}{44} \times 8.03 \text{ mg}$$
$$= 2.19 \text{ mg}$$

$$\% \text{ of carbon in the sample} = \frac{2.19}{3.54} \times \frac{100}{1} \%$$
$$= 61.86\%$$

18 g of H_2O contain 2 g of hydrogen

$$3.34 \text{ mg of } H_2O \text{ will contain} = \frac{2}{18} \times 3.34 \text{ mg}$$
$$= 0.37 \text{ mg}$$

$$\% \text{ of hydrogen in the sample} = \frac{0.37}{3.54} \times \frac{100}{1}\%$$
$$= 10.48\%$$

Oxygen is obtained by difference;

$$\% \text{ of oxygen in the sample} = 100 - (61.86 + 10.48)$$
$$= 27.66\%$$

	C	H	O
% Composition:	61.86	10.48	27.66
Ratio of the atom (Divide by atomic mass)	$\frac{61.86}{12}$	$\frac{10.48}{1.0}$	$\frac{27.66}{16.0}$
	= 5.16	= 10.48	= 1.73
Divide by the smallest to get whole number ratio:	$\frac{5.16}{1.73}$	$\frac{10.48}{1.73}$	$\frac{1.73}{1.73}$
	= 2.98	= 6.06	= 1
	= 3	6	1

Empirical formula is $C_3 H_6 O$

To get the molecular formula:
(Empirical formula)$_n$ = molecular mass

$$(C_3H_6O)_n = 116.2$$
$$[(3 \times 12) + (6 \times 1) + (1 \times 16)]_n = 116.2$$

$$58n = 116.2$$
$$n = \frac{116.2}{58} = 2$$

$$\therefore \text{Molecular formula is } (C_3H_6O)_2$$
$$= C_6 H_{12} O_2$$

Question 2

An 8.32 mg sample of aniline yields 1.11 cm^3 of nitrogen at 21°C and 743 mmHg. What is the percentage composition of nitrogen in aniline?

Solution

The first step is to determine the volume of the nitrogen

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$P_1 = 743 \text{ mmHg}, V_1 = 1.11 \quad T_1 = 21 + 273 = 294 \text{ K}$$
$$P_2 = 760 \text{ mmHg}, V_2 = \quad T_2 = 273 \text{ K}$$

$$\therefore V_2 = 1.01 \text{ cm}^3$$

Knowing fully well that volume of any gas at STP is 22.4 $dm^3 \, mol^{-1}$ or 22400 $cm^3 \, mol^{-1}$

22400 cm^3 of N_2 at STP contains 1 mole

$$\therefore 1.01 \text{ cm}^3 \text{ of } N_2 \text{ will contain} = \frac{1 \text{ mol} \times 1.01 \text{ cm}^3}{22400 \text{ cm}^3}$$
$$= 4.5 \times 10^{-5} \text{ mol}$$

$$\therefore \text{mass of } N_2 = \text{mole} \times \text{molar mass of } N_2$$
$$= 4.5 \times 10^{-5} \times 28 = 0.00126 \text{ g}$$
$$= 1.26 \text{ mg}$$

$$\therefore \% \text{ of } N_2 \text{ in the sample} = \frac{1.26 \text{ mg}}{8.32 \text{ mg}} \times \frac{100}{1}\%$$
$$= 15.2\%$$

Question 3

0.530 gram of acetanilide was subjected to Khedjahl determination and the ammonia produced was collected in 50 cm^3 of 0.5M H_2SO_4. On dilution to 250 cm^3, the acid was titrated against 25 cm^3 portion of 0.05M sodium carbonate solution. 13.60 cm^3 of the acid was required for each titration. What is the percentage of nitrogen in acetanilide?

Solution

The equations of reactions are:

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

$$Na_2CO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + CO_2$$
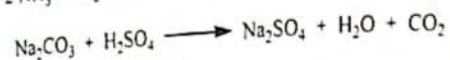
$$n_{H_2SO_4} \text{ (initial)} = 50 \times 10^{-3} \times 0.5 = 0.25 \text{ mol.}$$

$$n_{Na_2CO_3} \text{ (initial)} = 25 \times 10^{-3} \times 0.5 = 1.25 \times 10^{-3} \text{ mol.}$$

From the stoichiometric mole ratio of the above reactions;

$$i.e. \quad n_{H_2SO_4} : n_{Na_2CO_3} = 1 : 1;$$

Na_2CO_3 is the limiting reagent

$$n_{H_2SO_4} = n_{Na_2CO_3} = 1.25 \times 10^{-3} \text{ mol (i.e. 1 : 1)}$$

$$n_{H_2SO_4} \text{ in 250 cm}^3 = \frac{1.25 \times 10^{-3}}{13.60} \times 250$$

$$= 0.025 \text{ mol.}$$

The dilution of the resulting solution to 250 cm³ and titrating with Na_2CO_3 solution is to know the excess number of moles of sulphuric acid left unused and at the same time help to know the amount of H_2SO_4 that have reacted with ammonia.

∴ The number of moles of excess H_2SO_4 = 0.023 mol.

Number of moles of H_2SO_4 that reacted with NH_3 is obtained thus:

$$n_{H_2SO_4} \text{ (initial)} - n_{H_2SO_4} \text{ (excess)}$$

$$= 0.025 - 0.023 = 0.002 \text{ mol.}$$

The stoichiometric mole ratio of NH_3 to H_2SO_4 from the above reaction is;

$$i.e. \quad n_{NH_3} : n_{H_2SO_4} = 2 : 1$$

$$n_{NH_3} = 2n_{H_2SO_4} = 2 \times 0.002 = 0.004 \text{ mol.}$$

∴ Mass of NH_3 = mole × molar mass of NH_3

= 0.004 mol. × (14 + 3) g mol⁻¹

= 0.068 g

Mass of nitrogen in NH_3 = $\frac{14}{17} \times \frac{0.068}{1}$

= 0.056 g

∴% of N in acetanilide

= $\frac{0.056 \text{ g}}{0.530 \text{ g}} \times \frac{100}{1}$

= 10.57 %

Question 4

30 cm³ of a gaseous hydrocarbon, C_xH_y, were mixed with 140 cm³ of excess oxygen and exploded. After cooling to room temperature, the residual gases occupied 95 cm³. By adsorption with potassium hydroxide solution a diminution of 60 cm³ was produced, and the remaining gas was shown to be oxygen. Determine the formula of the hydrocarbon at constant pressure of 1 atmosphere.

Solution

$$C_xH_y + \frac{4x + y}{4}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$
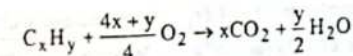
The KOH solution absorbs the CO_2 produced

∴ Volume of CO_2 = 60 cm³

Volume of excess oxygen = 95 – 60 = 35 cm³

Volume of oxygen consumed by the hydrocarbon C_xH_y is: 140 – 35 = 105 cm³

By equating the stoichiometric molar concentrations of the gases CO_2 produced and O_2 consumed, i.e.

$$\frac{\text{Stoichiometric mole of CO}_2}{\text{Volume of CO}_2 \text{ (in cm}^3)} = \frac{\text{Stoichiometric mole of O}_2}{\text{Volume of O}_2 \text{ (in cm}^3)}$$

$$\therefore \quad \frac{x}{60} = \frac{4x + y}{4} \times \frac{1}{105} \quad \text{(By Avogadro's hypothesis)}$$

$$\frac{x}{60} = \frac{4x + y}{4} \times \frac{1}{105}$$

$$420x = 240x + 60y$$

$$180x = 60y$$

$$\therefore \quad x : y = 60 : 180$$

Since the starting volume of the hydrocarbon is 30 cm³

$$\therefore \quad x : y = \frac{60}{30} : \frac{180}{30}$$

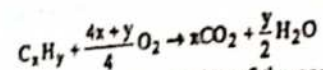$$x \quad : y = 2 : 6$$

$$\therefore \quad x = 2 \text{ and } y = 6$$

∴ Formula of the Hydrocarbon is C_2H_6

Question 5

A hydrocarbon on complete combustion consumed 80 cm³ of oxygen and produced 60 cm³ of carbon (IV) oxide. Deduce the molecular formula of the hydrocarbon.

Solution

Let the hydrocarbon be represented as C_xH_y

$$C_xH_y + \frac{4x+y}{4}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

By equating the stoichiometric molar concentration of the gases CO_2 produced and O_2 consumed; i.e.

$$\frac{\text{Stoichiometric mole of } CO_2}{\text{Volume of } CO_2 \text{ (in cm}^3)} = \frac{\text{Stoichiometric mole of } O_2}{\text{Volume of } O_2 \text{ (in cm}^3)}$$

$$\therefore \quad \frac{x}{60} = \frac{4x+y}{4 \times 80} \quad \text{(By Avogadro's hypoythesis)}$$

$$\frac{x}{60} = \frac{4x+y}{320}$$

$$320x = 240x + 60y$$

$$80x = 60y$$

$$\text{or} \quad \frac{x}{y} = \frac{60}{80} = \frac{3}{4}$$

$$\therefore \quad x : y = 3 : 4$$

$$x = 3, y = 4$$

Molecular formula of the hydrocarbon is C_3H_4

From the molecular formula, first calculate Index of Hydrogen Deficiency (IHD) or Double Bond Equivalent (DBE) using the formula:

$$\text{IHD (or DBE)} = X - \tfrac{1}{2}Y - \tfrac{1}{2}Z + \tfrac{1}{2}J + 1,$$

where X, Y, Z and J are the number of carbon, hydrogen, halogen and nitrogen atoms respectively.

C_3H_4

Here, $X = 3, Y = 4, Z = J = 0$

Therefore, $DBE = 3 - \tfrac{1}{2}(4) + 1 = 2$

This implies that the molecule contains a pair of double bond or a triple bond or a ring and a double bond. Possible structural formulas are:
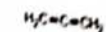
$H_2C=C=CH_2$ $CH_3C\equiv CH$ △
Propa-1,2-diene   Propyne   cyclopropene

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HYBRIDIZATION

This is mixing or blending of two or more different types of orbitals of the same energy level to produce the same number of identical hybrid orbitals with different energies, shapes, etc., than the component atomic orbitals.
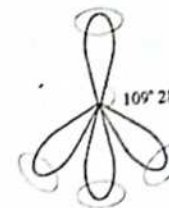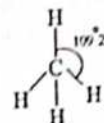
Concept of Hybridization of Carbon Atom

sp^3 Hybridization

This is as a result of mixing $2s$ and three $2p$ orbitals to produce four equivalent sp^3 hybrid orbitals, as in the case of methane (CH_4). Excited state configuration of carbon using Hund's rule is;

C: $1s^2 \quad 2s^1 \quad 2p_x^1 \ 2p_y^1 \ 2p_z^1$

CH_4:

sp^3

H (1s) represented as ↑
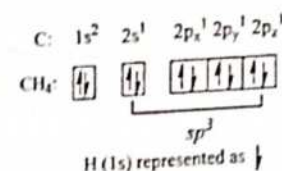
The excited configuration of carbon atom now has four partially filled sp^3 hybrid orbitals as shown in the above diagram, each of which will overlap with the $1s$ orbital of an hydrogen atom to give methane molecule of tetrahedral structure; and bond angle of $109° 28'$. In sp^3 hybridization, four orbitals hybridize in each carbon atom, (i.e. $s + p^3 = sp^3$ hybridization), to give four (4) C–H bonds. The bonds are directed towards the corners of a regular tetrahedron to ensure maximum repulsions between the electron clouds of the 4 C-H bonds.


This process is called hybridization and the orbitals are called sp^3 hybrid orbitals. Each has ¼ (or 25%) 's' character and ¾ (or 75%) 'p' character. The overlap of each sp^3 hybrid atomic orbital with a $1s$ orbital of hydrogen leads to formation of a sigma (σ) bond which is symmetrical about its axis. All single covalent bonds have sigma (σ) bonds.

sp^2 Hybridization

This is as a result of mixing $2s$ and two $2p$ orbitals to form 3 identical sp^2 hybrid orbitals, as in the case of ethene (C_2H_4).

Excited States of carbon atoms are:

The electrons in the $2p_z$ orbitals are unaffected by hybridization

H (1s) represented as ⎮
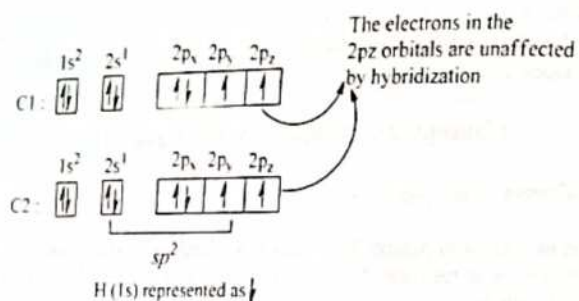
In sp^2 hybridization, only three orbitals are hybridized in each carbon atom, (i.e. $s + p^2 = sp^2$ hybridization). This gives a trigonal carbon atom in order to allow for maximum repulsion. The three equivalent sp^2 orbitals lie at an angle of $120°$ in one plane with unchanged $2p_z$ orbital perpendicular to the sp^2 hybrid orbitals with its lobes sticking above and below the plane.
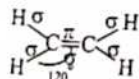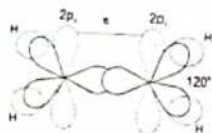
The orbitals are called sp^2 hybrids. Each has $\frac{1}{3}$ (or 33.3%) 's' character and $\frac{2}{3}$ (or 66.7%) 'p' character i.e. more 's' and less 'p' character than sp^3 hybrid orbitals. The overlap of each sp^2 hybrid atomic orbital with a $1s$ orbital of hydrogen leads to a sigma (σ) bond and the carbon-carbon bond is formed by the overlap of two sp^2 hybrid orbitals from each of the adjacent carbon atoms, resulting in a sigma (σ) bond while the overlap of adjacent p (i.e. $2p_z$) orbitals that are unaffected by hybridization forms pi (π) bond

sp Hybridization

This is as a result of mixing the $2s$ and one $2p$ orbitals as in the case of ethyne (C_2H_2). Excited states of carbon atoms are:

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The electrons in the $2p_y$ and $2p_z$ orbitals are unaffected by hybridization

H (1s) represented as ⎮
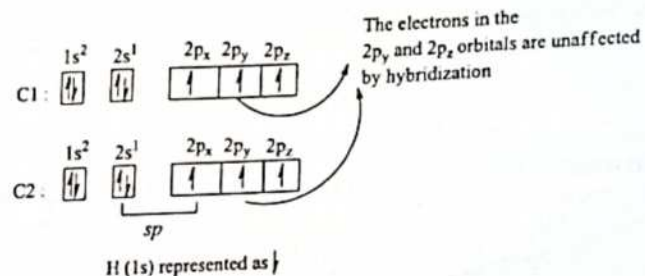
In sp hybridization, only one s and one p orbitals are hybridized to give two equivalent sp hybrid orbitals, (i.e. $s + p = sp$ hybridization). This gives a diagonal carbon atom with two sp orbitals $180°$ apart, and two mutually perpendicular unhybridized p (i.e. $2p_y$ and $2p_z$) orbitals.
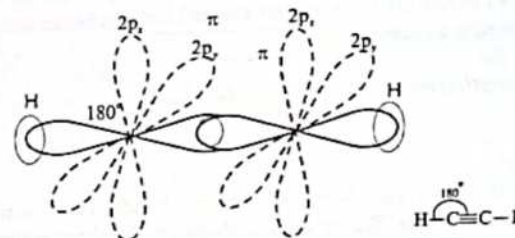
The orbitals are called sp hybrids. Each has ½ (or 50%) 's' character and ½ (or 50%) 'p' character. The sp hybrid orbitals form sigma (σ) bond in the same way as sp^3 with hydrogen atom and the carbon-carbon bond is formed by the overlap of two sp hybrid orbitals from each of the adjacent carbon atoms, resulting in sigma bond. The overlapping of adjacent p (i.e. $2p_y$ and $2p_z$) orbitals that are unaffected by hybridization forms two pi (π) bonds as shown in the above diagram. Thus the triple bond consists of a sigma bond and two pi (π) bonds.

Sigma (σ) and Pi (π) Bonds

Sigma (σ) Bond
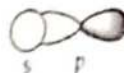
This results from any of the following three possibilities:

(i) The overlapping of two s orbitals

(ii) The overlapping of two p orbitals linearly opposed to each other

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s   p

Pi (π) Bond

This results from the lateral overlap of two parallel p orbitals of adjacent atoms.


P_x P_x

The degree of overlapping in pi (π) bond is less than that in the formation of sigma (σ) bonds. Consequently, pi (π) bonds are weaker than sigma (σ) bonds, and being more exposed, pi (π) bonds are more vulnerable to cleavage by an attacking electron deficient reagent, during a chemical reaction.

The length and strength (energy) of carbon-carbon bonds

Bond length

Double and triple bonds are shorter than single bonds, because of increased 's' character in the multiple bonds. The more the s-character, the closer is the electron cloud of the bond pair to the nucleus, and hence, the shorter the bond. The order of increasing bond length is:

$C≡C$	<	$C=C$	<	$C-C$
50%		33.3%		25%
"s" character		"s" character		"s" character

increasing order of bond length →
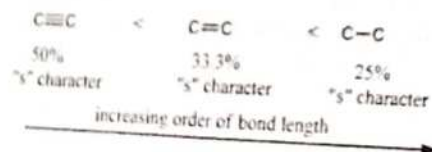
Bond strength (or bond energy)

This is the quantity or amount of energy needed to break the bond concerned in every molecule in one mole of the substance. The shorter the bond, the stronger it is; and thus the order of increasing bond energy is:

$$C-C \quad < \quad C=C \quad < \quad C≡C$$

increasing order of bond energy →
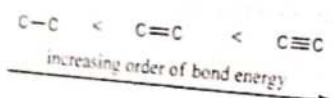
The reason for the above order of bond strength can be explained as follows:

(i) Sigma (σ) bonds are stronger than pi (π) bonds because of the more effective overlap of orbitals in the former.

(ii) The double bond consists of a σ bond and a π bond, each with its own bond strength. The sum of the strengths of both bonds will be expected to be greater than that of a single (σ) bond.

(iii) By the same argument, the triple bond with a σ bond and two π bonds will be expected to have the highest energy.

Table 1.1

Bond properties of organic compounds

Bond	Bond length (nm)	Bond energy (kJ mol^{-1})
C – H	0.108	413
C – C (in ethane)	0.154	349
C = C (ethane)	0.134	681
C≡C (in ethyne)	0.120	815
C – N	0.147	305
C≡N	0.114	890
C – O	0.143	358
C = O (in aldehyde)	0.122	737
C = O (in ketone)	0.122	749
C = O (in methanal)	0.121	695
C – F (in CF₄)	0.136	486
C – Si [in Si(CH₃)₄]	0.193	301
C – S (in C₂H₅SH)	0.181	272
C = S (in CS₂)	0.155	536
C – Cl	0.176	339
C – Br	0.194	285
C – I (in CH₃I)	0.214	213

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BREAKING AND FORMING OF BONDS

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The essence of a chemical change is the breaking and forming of bonds. A covalent bond between two atoms consists of an electron pair, and can be broken in only three ways as follows:
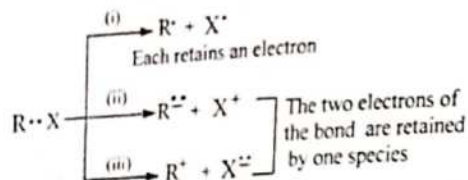

Fig. 1.1 Scheme for the rupturing of bond between R and X

I. Homolytic and Heterolytic Fissions

Homolytic fission

This is a process where rupturing of the bond between two atoms results in the formation of very reactive free radicals as in step (i) above. This occurs when both atoms have similar electronegativity values. The various ways by which radicals can be generated are:

(i) Photolysis

This involves generation of free radical from a molecule or gas in the presence of light. Examples of this method are:

(a) $Cl_2 \xrightarrow{h\nu} Cl^\bullet + Cl^\bullet$

(b) $(CH_3)_2C=O \xrightarrow{h\nu} CH_3^\bullet + CH_3CO^\bullet$
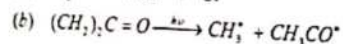
(ii) Thermolysis

This involves generation of free radical by thermal (heat) decomposition of the molecule. Examples of this method are:

(a) Vapor phase decomposition of tetralkyllead

$$PbR_4 \xrightarrow{\Delta} Pb + 4R^\bullet$$
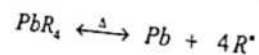
(b) Thermal decomposition of *tert*-butyl peroxide and azomethane

$$(CH_3)_3C-O-O-C(CH_3)_3 \xrightarrow{h\nu} 2(CH_3)_3C-O^\bullet$$
tert-butylperoxide

$$CH_3-N=N-CH_3 \xrightarrow{h\nu} 2CH_3^\bullet + N_2$$
azomethane
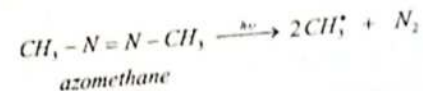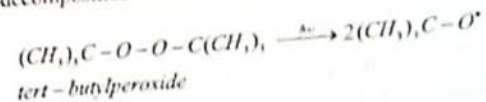
(iii) Redox reaction by inorganic ions involving one-electron transfer from carbanions (or carbonium ions).

(a) The reduction of triphenylmethyl cation to triphenylmethyl radical by vanadous chloride.
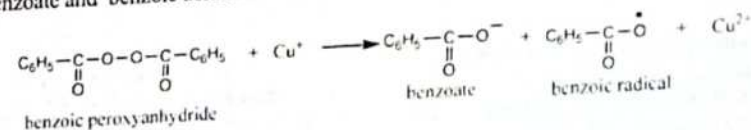
$$(C_6H_5)_3C^\bullet + V^{2+} \rightarrow (C_6H_5)_3C^\bullet + V^{1+}$$
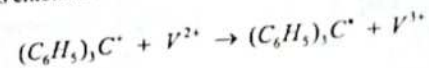
(b) Decomposition of cumyl hydroperoxide

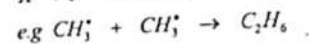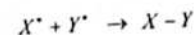Decomposition of αα - Dimethylbenzylhydroperoxide by ferrous salts into alkoxyl) (radicals) and hydroxyl anions.
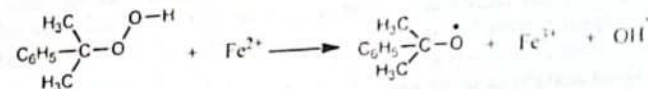
α α - Dimethylbenzylhydroperoxide

Another example is the decomposition of benzoic peroxy anhydride by copper salt into benzoate and benzoic acid radicals.
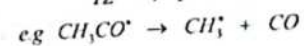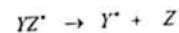

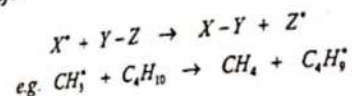Below are reactions that radicals undergo after their formation.
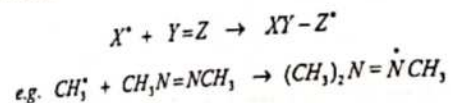
(i) Radical combination(Bond making)

$$X^\bullet + Y^\bullet \rightarrow X-Y$$
$$e.g \; CH_3^\bullet + CH_3^\bullet \rightarrow C_2H_6$$

(ii) Radical fragmentation

$$YZ^\bullet \rightarrow Y^\bullet + Z$$
$$e.g \; CH_3CO^\bullet \rightarrow CH_3^\bullet + CO$$

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(iii) **Radical transfer**

$$X^\bullet + Y{-}Z \rightarrow X{-}Y + Z^\bullet$$

e.g. $CH_3^\bullet + C_4H_{10} \rightarrow CH_4 + C_4H_9^\bullet$

(iv) **Radical addition**

$$X^\bullet + Y{=}Z \rightarrow XY{-}Z^\bullet$$

e.g. $CH_3^\bullet + CH_3N{=}NCH_3 \rightarrow (CH_3)_2N{=}\overset{\bullet}{N}CH_3$

(v) **Radical disproportionation**
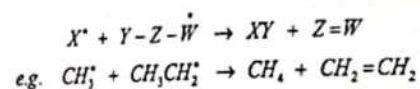
$$X^\bullet + Y{-}Z{-}\overset{\bullet}{W} \rightarrow XY + Z{=}W$$

e.g. $CH_3^\bullet + CH_3CH_2^\bullet \rightarrow CH_4 + CH_2{=}CH_2$

Heterolytic fission

This is a process where rupturing of the bond between two atoms results in the formation of ion-pairs as in steps (ii) and (iii) of Fig. 1.1. This occurs when one atom is distinctly more electronegative than the other, and there is a tendency for both bonding electrons to remain with the more electronegative atom after rupturing of the bond. Consequently, the more electronegative atom becomes negatively charged, and the less electronegative atom becomes positively charged. This is frequently encountered in organic chemistry.

Bond making as in the case of radical combination occurs by the reversal of either of these processes (i.e. bond breaking processes) and any overall chemical reaction consists of a number of bond makings and breakings occurring either in sequence (i.e. stepwise) or simultaneously (concerted reaction).


7

FACTORS INFLUENCING ORGANIC REACTIONS

In heterolytic fission, the reactivity of a molecule depends mainly on:

(i) Its polarity, that is, the extent to which its atoms are electrically charged due to uneven sharing of bonding electrons. Polarity in organic molecules usually stems from atoms such as oxygen, sulphur, nitrogen, phosphorus and halogen, which are more electronegative than carbon, and cause electron-deficiency on any carbon atom to which they are bonded.

(ii) Its polarizability, that is, the extent to which its bonds become polarized in the presence of polar reagents.

(iii) Its size and shape (Steric Effects).

The two ways in which polarization can be transmitted through molecule are: Inductive and mesomeric effects, known as electronic factors.

A Inductive effects

This results from uneven sharing of electrons in a covalent bond due to large difference in the electronegativity values of an atom and the carbon atom to which it is bonded. For example, consider a chlorine atom attached to a carbon chain.

$$\underset{3}{C} \rightarrow \underset{2}{C} \rightarrow \overset{\delta+}{\underset{1}{C}} \rightarrow \overset{\delta-}{Cl}$$
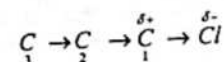
The strong polarization of C–Cl bond renders C–1 electron-deficient and positively charged. The effect continues with diminishing strength along the chain, and is usually too small to be detectable beyond C–2 or C–3. Thus C–1 suffers the greatest inductive effect while C–3 suffers the least. The atoms or groups, which tend to be electron withdrawing with respect to the carbon atom to which they are attached and exert an inductive effect in the same direction as chlorine are said to exert $-I$ effect. The $-I$ effect increases as the electronegativity of the atoms or groups increases.

However, certain groups, notably alkyl groups exert an inductive effect in the opposite direction to chlorine, that is, they are electron-donating (or electron-releasing) and are said to exert $+I$ effect. The bulkier the alkyl group, the greater the $+I$ effect; thus tertiary alkyl groups exert a greater $+I$ effect than secondary which in turn exert a greater $+I$ effect than primary alkyl groups.

Decreasing order of $+I$ effect
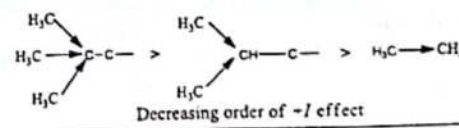
CLASSIFICATION OF REAGENTS USED IN CHEMICAL REACTIONS

The reagents used in chemical reactions can be classified as (a) Electrophilic and (b) Nucleophilic reagents.

(a)   Electrophilic (electron-loving) reagents

These are reagents, which attack electron-rich centres during chemical reaction. They are similar to Lewis acid (i.e. electron-deficient centre). They contain positively charged ions. An electrophile may contain an atom with an incomplete outer shell such as Al or B (in $AlCl_3$ or BF_3). Examples of electrophilic reagents are: H^+, Cl^+, Br^+, I^+, NO_2^+, RN_2^+, R_3C^+, BF_3, $AlCl_3$, Br_2, Cl_2, PhN_2^+, H_3O^+, R_4N^+.

(b)   Nucleophilic (nucleus-loving) reagents

These are reagents, which attack electron-deficient centre during chemical reaction. They are similar to Lewis base (electron-pair donor). They contain negatively charged ions. A nucleophile may contain an atom with lone-pair (non-bonding) electrons, like $\overset{..}{N}H_3$. Examples of nucleophilic reagents are H_2O, NH_3, ROH, OH^-, RO^-, Cl^-, Br^-, I^-, RNH_2, R_2NH, R_3N, CN^-, PbO^-, CH_3MgBr, $CH_3C\equiv C^-$ and CH_3OCH_3 (ROR). In each case, the charge may arise either from an ion or from polarization of the molecule.

TYPES OF ORGANIC REACTIONS

Organic reactions are categorized into four types. They are:

(a) Substitution or Displacement reaction,
(b) Addition reaction
(c) Elimination reaction
(d) Rearrangement reaction.

All the four types may be initiated by electrophilic, nucleophilic or free radical attack on the substrate.

(a) Substitution (or displacement) reaction

When an atom, group or radical attached to carbon is replaced by another one in a chemical compound, without any change in the type of bonding or degree of unsaturation. It occurs either through electrophilic, nucleophilic or free radical mechanisms.

(i) Electrophilic substitution reaction

Example is:
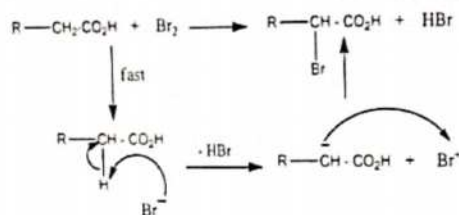
(ii) Nucleophilic substitution reaction

This is more common than electrophilic substitution. Here a nucleophile is leaving for another nucleophile to enter.

$$R-X + OH^- \longrightarrow R-OH + X^- \quad (X = Cl, Br, I)$$

A typical example is:

$$CH_3CH_2Cl + NaOH \longrightarrow CH_3CH_2OH + NaCl$$
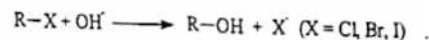
Nucleophilic substitution reaction is one of the methods used for preparation of alcohol. There are basically two types of nucleophilic substitution reactions, i.e. SN^1 and SN^2

Substitution nucleophilic unimolecular reactions (SN^1)

Here, the rate of reaction depends on only one species. It takes place mostly with tertiary alkyl compounds in the presence of weak nucleophiles (e.g. H_2O, NH_3, Br e.t.c).

$$\text{e.g} \quad (CH_3)_3C - Br \; + \; OH^- \longrightarrow (CH_3)_3C - OH \; + \; Br^-$$
$$\text{tert butyl bromide} \qquad \text{tert butyl alcohol}$$
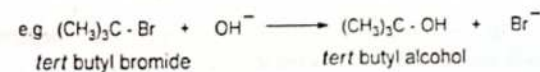
Proposed mechanism
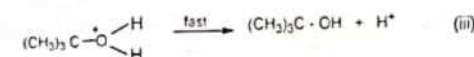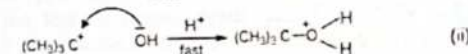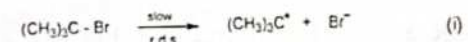
$$Rate = k[(CH_3)_3C - Br]$$

SN^1 reaction is limited mostly to tertiary compounds (or benzylic or allylic compounds) because the rate-determining step (i.e. step (i) above) involves the formation of a carbocation. Any reaction in which stable carbocations (e.g. tertiary carbocation, benzylic or allylic carbocation) can be generated will favor the SN^1 mechanism
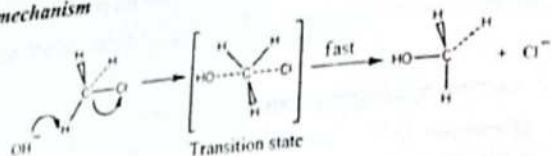
Examples of SN^1 reactions:
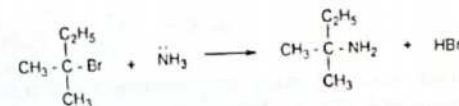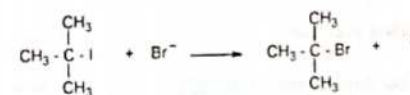
Substitution nucleophilic bimolecular reactions (SN^2)

Here, the rate of reaction depends on two different species, e.g.

$$CH_3Cl + OH^- \longrightarrow CH_3OH + Cl^-$$

Proposed mechanism

Transition state

$$Rate = k[CH_3Cl][OH]$$

The SN^2 reaction is sometimes referred to as a concerted reaction because both the nucleophilic attack and bond breaking are occurring simultaneously.

Conditions for SN^2 reaction

1. The alkyl groups must be primary, i.e. methyl or ethyl and sometimes secondary (i.e. RCHXR). Tertiary alkyl compounds will not undergo SN^2 reaction because the bulkiness will prevent the back-side attack by nucleophile.

2. The nucleophile is usually strong , e.g. OH^-, CH_3O^-, $CH_3CH_2O^-$, NH_2^-, CN^- e.t.c

Examples of SN^2 reaction

$$CH_3CH_2I \xrightarrow[\text{acetone}]{Br^-} CH_3CH_2Br + I^-$$
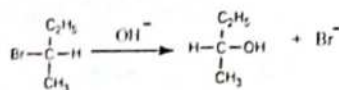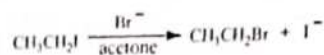
(iii) Free radical substitution reaction

This is a free radical displacement, for example,

$$R-X + n^\bullet \longrightarrow R-n + X^\bullet$$

It is a free radical attack, which also leads to the generation of another radical. A typical example is the halogenation of alkanes, which occurs in the presence of light.

$$Cl_2 \xrightarrow{h\nu} Cl^\bullet + Cl^\bullet$$
$$CH_4 + Cl^\bullet \rightarrow CH_3^\bullet + HCl$$
$$CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet$$
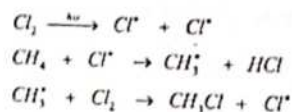
(b) Addition reaction

In addition reaction, extra atoms or groups become attached to an sp or sp^2 hybridized carbon (i.e. unsaturated system) and the molecule becomes more or completely saturated. The addition may occur by electrophilic, nucleophilic or free
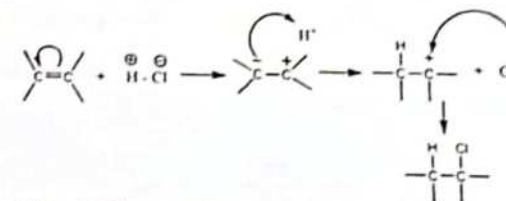
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radical.

(i) Electrophilic addition reaction

Electrophilic addition reaction takes place when the electrophile attacks first. Consider for example:
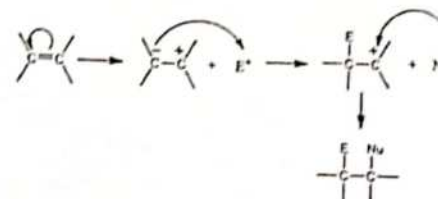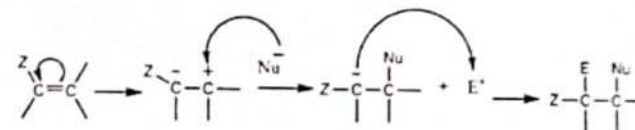

(E^+ = electrophile; Nu^- = nucleophile)
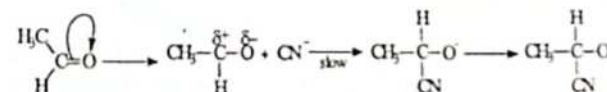
A typical example is:

(ii) Nucleophilic addition reaction

This takes place usually when an electron-withdrawing group is attached to the alkene, where it initiates the nucleophilic addition reaction.
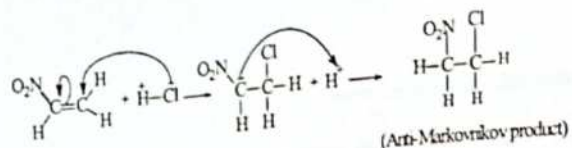

Z is an electron-withdrawing group (Z can be CN, CO_2, SO_2, Cl^-, NO_2 CO_2R, CO, $COCH_3$ and Halogen)

Another example is;

Therefore, if an electron-withdrawing group is attached to the alkene or alkyne, it would go via nucleophilic addition reaction before electrophilic addition reaction. A typical example is:

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(Anti-Markovnikov product)

(iii) **Free radical addition reaction**

Free radical addition reactions also occur in unsaturated system, for example,

$$X_2 \xrightarrow{h\nu} 2X^\bullet \quad \text{Chain initiation}$$
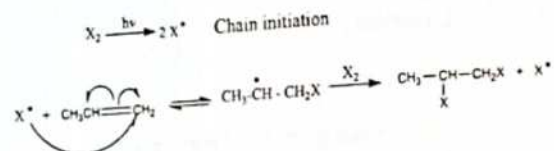
(c) **Elimination reaction**

Elimination reaction is reverse of addition reaction, that is, groups are removed from sp^3-hybridized carbon and the molecule becomes unsaturated. It is one of the methods used for the synthesis of alkenes. It is also called 1, 2-elimination because elimination occurs on the adjacent carbon atoms, for example,
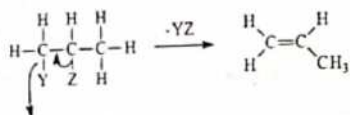
It takes place when we have a good leaving group like bromine. A specific example is:
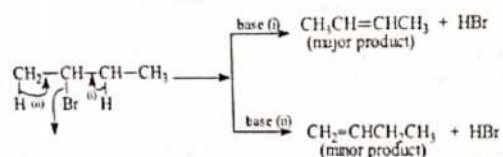

If either of the groups lost is a carbon chain, the reaction is called a fragmentation or cleavage as in the case of cracking or pyrolysis of alkane (to be treated later).

(d) **Rearrangement reaction**

Rearrangement reaction involves the migration of an atom or group from one site to another within the same molecule. The rearrangement may be the migration of a functional group from one position to another within the molecule. It is called 1, 2-shift if the shifting is between two adjacent carbon atoms. For example:
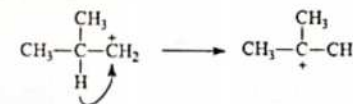

A typical example is:
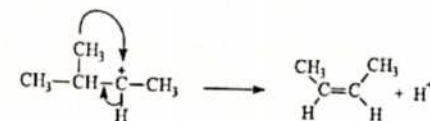
(This is an example of migration of methyl group).

Also, rearrangement may take the form:

(This is an example of rearrangement of positive charge).

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ISOMERISM

Isomerism is the occurrence of two or more compounds with the same molecular formula but different molecular structures. Compounds having the same number and kind of atoms are called isomers. These different isomers will have different physical and chemical properties. There are two main types of isomerism, they are represented on the chart below:
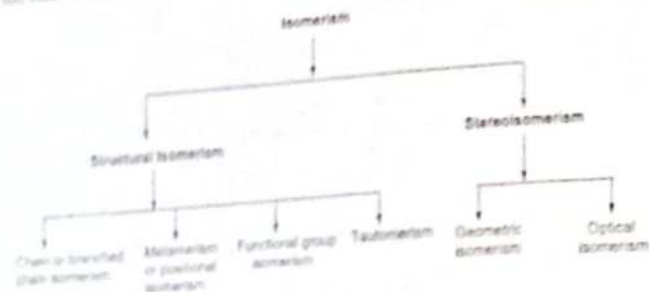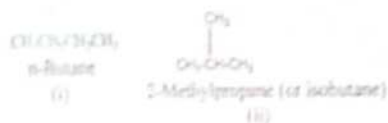

II. Structural Isomerism

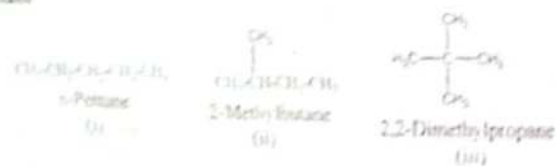This differs in the way atoms or groups are bonded to one another.

(i) *Chain isomerism or branched chain isomerism*

These are isomers having the same number and kind of atoms but having different structures due to the presence of branched chains. For example, butane has two isomers, pentane has three, hexane has five and heptane has eight.
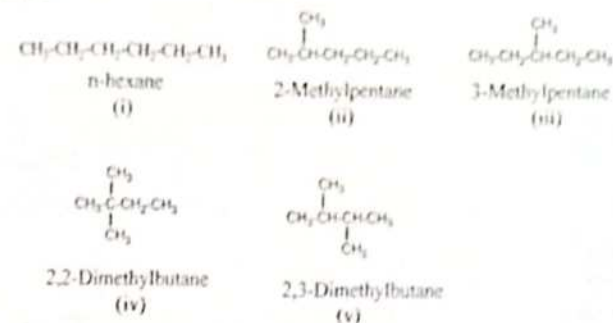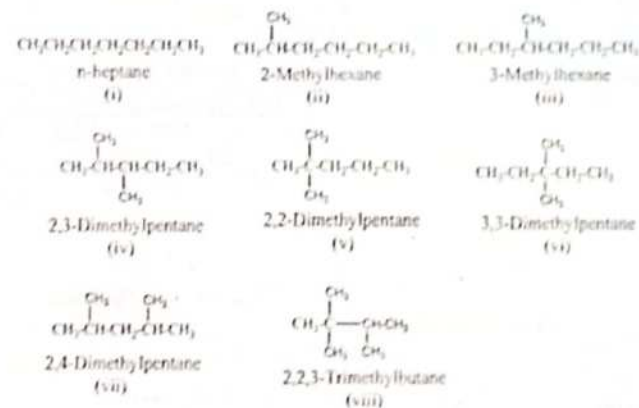
For butane:

CH₃CH₂CH₂CH₃
n-butane
(i)

2-Methylpropane (or isobutane)
(ii)

For pentane

CH₃CH₂CH₂CH₂CH₃
n-Pentane
(i)

2-Methylbutane
(ii)

2,2-Dimethylpropane
(iii)

For hexane

CH₃-CH₂-CH₂-CH₂-CH₂-CH₃
n-hexane
(i)

2-Methylpentane
(ii)

3-Methylpentane
(iii)

2,2-Dimethylbutane
(iv)

2,3-Dimethylbutane
(v)

For heptane

CH₃CH₂CH₂CH₂CH₂CH₂CH₃
n-heptane
(i)

2-Methylhexane
(ii)

3-Methylhexane
(iii)

2,3-Dimethylpentane
(iv)

2,2-Dimethylpentane
(v)

3,3-Dimethylpentane
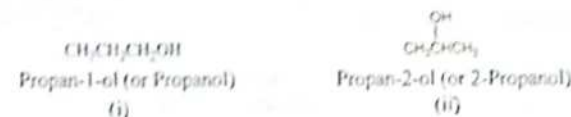(vi)

2,4-Dimethylpentane
(vii)

2,2,3-Trimethylbutane
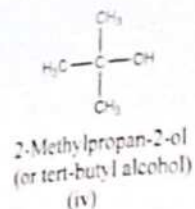(viii)

(ii) Metamerism (position isomerism)

They are isomers, which have substituents in different positions on the same carbon skeleton. It occurs when large alkyl groups are attached to the same functional groups as in alkanol, alkylhalides or ether. For example, there are two and four structural isomeric alcohols corresponding to the formula C_3H_7OH and C_4H_9OH respectively.

C_3H_7OH

CH₃CH₂CH₂OH
Propan-1-ol (or Propanol)
(i)

CH₃CHOHCH₃
Propan-2-ol (or 2-Propanol)
(ii)

C_4H_9OH

CH₃CH₂CH₂CH₂OH
Butan-1-ol
(i)

CH₃CH₂CHOHCH₃
Butan-2-ol
(ii)

2-Methylpropan-1-ol
(or Isobutyl alcohol)
(iii)
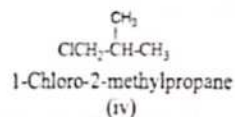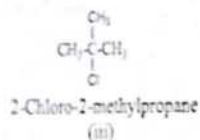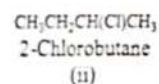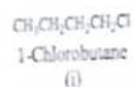
CH₃
|
H₃C—C—OH
|
CH₃

2-Methylpropan-2-ol
(or tert-butyl alcohol)
(iv)

Also, there are three isomers of ether corresponding to the molecular formula, C₄H₁₀O and these include:

CH₃CH₂OCH₂CH₃
Ethoxyethane
(Diethylether)
(i)

CH₃OCH₂CH₂CH₃
1-Methoxypropane
(Methylpropylether)
(ii)

CH₃
|
CH₃OCHCH₃
2-Methoxypropane
(Methylisopropylether)
(iii)
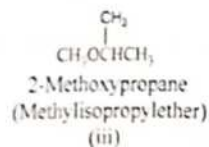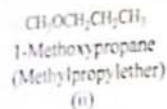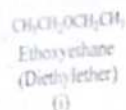
Other examples are cases of Butylchloride and nitrotoluene:

Butylchloride (C₄H₉Cl):

CH₃CH₂CH₂CH₂Cl
1-Chlorobutane
(i)

CH₃CH₂CH(Cl)CH₃
2-Chlorobutane
(ii)

CH₃
|
CH₃-C-CH₃
|
Cl
2-Chloro-2-methylpropane
(iii)

CH₃
|
ClCH₂-CH-CH₃
1-Chloro-2-methylpropane
(iv)

Nitrotoluene: C₇H₇NO₂:

2-Nitrotoluene
(o-Nitrotoluene)

3-Nitrotoluene
(m-Nitrotoluene)

4-Nitrotoluene
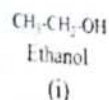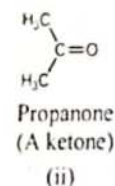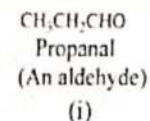(p-Nitrotoluene)
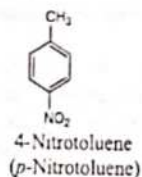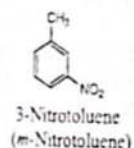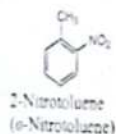
(iii) Functional group isomerism

This is an isomerism between compounds in different homologous series. For example, there are two isomers corresponding to the formula C₂H₆O
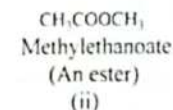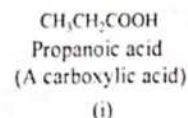
CH₃-CH₂-OH
Ethanol
(i)

CH₃-O-CH₃
Methoxymethane
(or Dimethylether)
(ii)
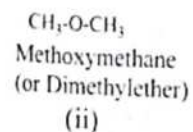
Also there are two isomers each corresponding to the formulae C₃H₆O and C₃H₆O₂

C₃H₆O:

CH₃CH₂CHO
Propanal
(An aldehyde)
(i)

H₃C
  \
   C=O
  /
H₃C
Propanone
(A ketone)
(ii)

C₃H₆O₂:

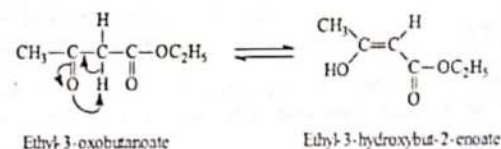CH₃CH₂COOH
Propanoic acid
(A carboxylic acid)
(i)

CH₃COOCH₃
Methylethanoate
(An ester)
(ii)

(iv) Tautomerism

It is a special type of isomerism in which isomers exist together in dynamic equilibrium.

CH₃-C-C-C-OC₂H₅ ⇌ CH₃   H
     ‖ | ‖   \   /
     O H O   C=C
                        /   \
                      HO   C-OC₂H₅
                              ‖
                              O

Ethyl 3-oxobutanoate   Ethyl 3-hydroxybut-2-enoate

III. Stereoisomerism

Isomers in which the same atoms or groups are bonded to carbon but differ in their spatial relationship are called **stereoisomers**. Stereoisomers are subdivided into two types: those that are not mirror images called diastereomers or diastereoisomers and those that are mirror images of each other, called enantiomers or enantiomorphs. The two types of stereoisomerisms are Geometric and Optical Isomerism.

(i) . Geometric isomerism

This is observed in molecules in which there is restriction to free rotation about a carbon-carbon bond, and in which there are different groups attached to both carbon atoms at the point of restriction. This restriction in rotation may be due to double bonds, a ring structure or steric hindrance. The structures of geometric isomers differ only in configuration, that is, spatial arrangement giving rise to a *cis*-isomer, which has identical or similar atoms or groups on the same side of the point of restriction, and a *trans*-isomer, which has them on opposite sides. The *cis*- and *trans*-isomers are not mirror images of each other and are called diastereomers. Organic and inorganic compounds exhibit geometric isomerism. The following are some examples of this type of stereoisomerism:

cis-Dichlorotetraamine cobalt (II)

trans-Dichlorotetraamine cobalt (II)

cis-But-2-ene

trans-But-2-ene

cis-1,2-Dichloroethene

trans-1,2-Dichloroethene

cis-But-2-ene-dioic acid

trans-But-2-ene-dioic acid
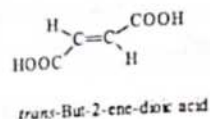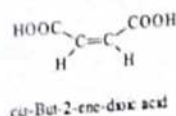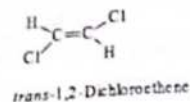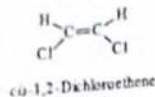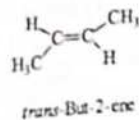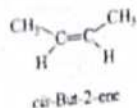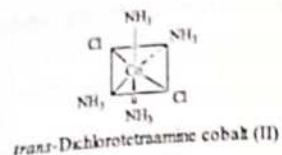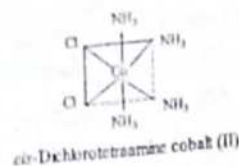
Other types of geometric isomerism

The geometry of molecules containing a nitrogen-nitrogen double bond or carbon-nitrogen double bond makes them also to be capable of *cis-trans* isomerism, for examples, in azobenzene

cis-Azobenzene

trans-Azobenzene
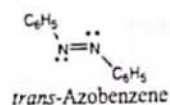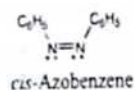
Another example is oximes of benzaldehyde for which a special form of nomenclature is used *syn* (H and OH are *cis* to each other) and *anti* (H and OH are *trans* to each other).

syn-Benzaldoxime

anti-Benzaldoxime
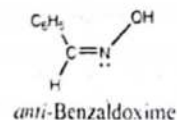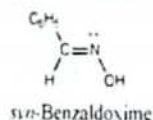
This *cis-trans* isomerism also occurs in ring system, examples are:

cis-1,3-Dichlorocyclobutane

trans-1,3-Dichlorocyclobutane

cis-1,2-Dimethylcyclopropane

trans-1,2-Dimethylcyclopropane

cis-4-Methylcyclohexanol

trans-4-Methylcyclohexanol
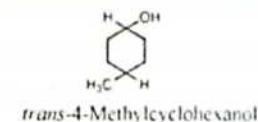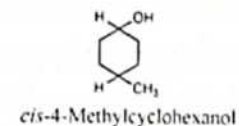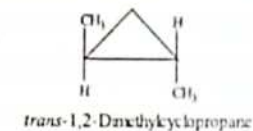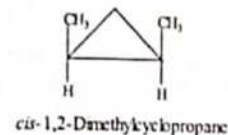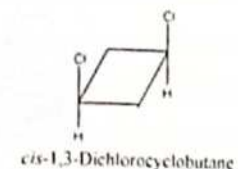
(ii) Optical isomerism

Optical isomerism is observed in compounds in which four different groups are attached to the same carbon atom. There are two isomers that result from this type of isomerism. These isomers are not superimposable on their mirror images, and are referred to as enantiomers, also known as enantiomorphs, optical antipodes, chiral molecules or optical isomers. The central atom, to which the four different atoms or groups are attached, is called a chiral centre. If the central atom is carbon, it is called Asymmetric carbon atom or chiral carbon.
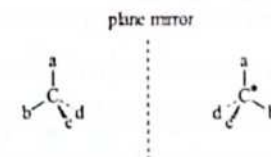
$C^* = $ Asymmetric carbon atom (or chiral carbon)

Examples include:

(a) Optical isomers of bromochlorofluoromethane:
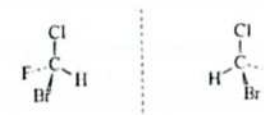
(b) Optical isomers of butan-2-ol:

(c) Optical isomers of hydroxypropanoic acid (lactic acid):
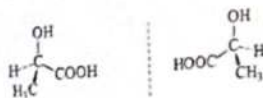
(d) Optical isomers of aminopropanoic acid (alanine):
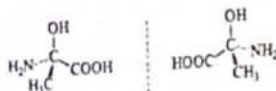
Properties of Enantiomers

Enantiomers are related to one another as a left hand is to a right hand. Such structures are said to be chiral or dissymmetric (i.e. lack of symmetry). Unlike diastereomers, which differ in most physical properties, enantiomers have identical properties other than the sign (+ or –) of their optical activity. Enantiomers like diastereomers have similar chemical properties but may differ in the rate of chemical reaction.

Enantiomers may be distinguished from each other by their ability to rotate the plane of polarized light in opposite directions. It is because they exhibit this property that such isomers are said to be optically active and hence they are optical isomers. Enantiomers are characterized by the sign of their optical activity at a given wavelength, temperature and specific solvent. If the rotation of the plane is in a clockwise direction (i.e. to the right), the substance is said to be DEXTROROTATORY (indicated by a positive sign, +) and if the rotation is in an anticlockwise direction (i.e. to the left), the substance is LAEVOROTATORY (indicated by a negative sign, –). The degree of rotation may be determined by means of a POLARIMETER. Two of the most studied compounds are 2-hydroxypropanoic acid (Lactic acid) and 2-aminopropanoic acid (Alanine) already shown above.

When enantiomers are mixed together in equal proportions, the rotating capacity of one isomer will exactly be cancelled by that of the other. Such a mixture is called a RACEMATE or RACEMIC MIXTURE, and as might be expected, is optically inactive, e.g.,

50 % (R)-2-butanol + 50 % (S) -2-butanol   =   (±) -2-butanol
(optically active)   (optically active)   (optically inactive)
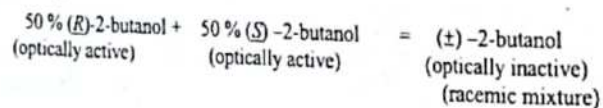   (racemic mixture)

R enantiomer has negative sign (–) while S enantiomer has positive sign (+).

Optical purity

A sample of an optically active material is said to be optically pure (100% optical purity) when only one enantiomer is present in the sample.

$$\text{Optical purity (\%)} = \frac{\text{experimental } [\alpha]_{\lambda}}{[\alpha]_{\lambda} \text{ of pure enantiomer}} \times \frac{100}{1} \qquad (1.10)$$

Optical purity can also be expressed as the *"enantiomeric excess"* or *"ee"* as follows:

$$ee\ (\%) = \frac{([R] - [S])}{([R] + [S])} \times \frac{100}{1} \qquad (1.11)$$

where [ ] indicates the concentration of the species.

In a racemic mixture, [R] = [S], and if we use % as concentration, then [R] = [S] = 50%.

$$\therefore ee(\%) = \frac{0}{([R]+[S])} \times \frac{100}{1} = 0\%$$

For a pure enantiomer, say 100% R;

$$\text{Optical Purity (\%)} = \frac{\alpha_p}{\alpha_p} \times \frac{100}{1} = 100\%$$

where α_p is the specific rotation of pure enantiomer = 100%

$$ee\ (\%) = \frac{100\% - 0\%}{100\% + 0\%} \times \frac{100}{1} = 100\%$$

Worked Example

Question 1

A sample of 2-butanol gave a specific rotation of $-5.68°\ g^{-1}\ cm^3\ dm^{-1}$. Given that pure enantiomer of 2-butanol has a specific rotation of $-15.52°\ g^{-1}\ cm^3\ dm^{-1}$. Calculate the percent of each enantiomer in the sample.

Solution

The experimental specific rotation is –ve (i.e., $-5.68°\ g^{-1}\ cm^3\ dm^{-1}$) and the pure enantiomer has specific rotation of $-15.52°\ g^{-1}\ cm^3\ dm^{-1}$

Well the fact that the sign is negative tells us that in this case the R enantiomer is the dominant one

$$\text{optical purity} = \frac{-5.68}{-15.52} \times \frac{100}{1}\% = 36.6\ \%$$

i.e, there is a 36.6% excess of R over S

If there is a 36.6 % excess of R, then (100% – 36.6 % = 63.4%), i.e, 63.4% left over must be equal amounts of both R and S, i.e 31.7% of each. So the total amount of R is 31.7% + 36.6% = 68.3%

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∴ (S)-2-butanol $= 31.7\%$

(R)-2-butanol $= 68.3\%$

Question 2

The specific rotation for a pure enantiomer is $-39° \, g^{-1} \, cm^3 \, dm^{-1}$. A sample containing both enantiomers is found to have an observed rotation of $-0.62° \, g^{-1} \, cm^3 \, dm^{-1}$ in one dm tube at a concentration of 9.5g/100 cm^3. What is the optical purity of the sample?

Solution

$$\text{Specific rotation} = \frac{observed \ rotation (degrees)}{(concentration \ in \ g/cm^3) \times path \ length \ of \ sample \ cell \ in \ dm}$$

$$\therefore \text{Specific rotation of the sample} = \frac{-0.62°}{(0.095 g/cm^3)(1 dm)}$$

$$= -6.52° \, g^{-1} \, cm^3 \, dm^{-1}$$

$$\text{Optical purity (\%)} = \frac{[\alpha]_{experimental}}{[\alpha]_{pure \ enantiomer}} \times \frac{100}{1}$$

$$= \frac{-6.52° \, g^{-1} \, cm^3 \, dm^{-1}}{-39° \, g^{-1} \, cm^3 \, dm^{-1}} \times \frac{100}{1}$$

$$= 16.73\%$$

The polarimeter

Optical activity in a compound is both detected and measured by means of a POLARIMETER. Plane-polarized light is produced by passing a beam of monochromatic (i.e. of single wavelength) light source (e.g. sodium lamp), through crystals (e.g. Calcite or Polaroid) and sample cell containing a solution of the substance under examination.
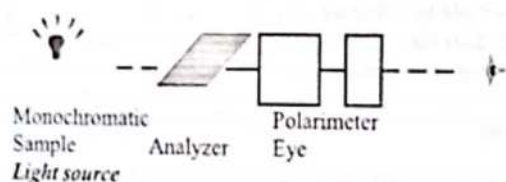

Fig. 1.2: A Simple Polarimeter

Measurement of optical rotation

Optical rotation is measured by a polarimeter (Fig. 1.2). Light from a monochromatic source is polarized by a prism, and passes through the sample cell containing the solution of the substance under examination, and then to rotatable analyzing prism coupled to a 360° scale. The emergent beam is viewed through an eyepiece or measured by a photoelectric cell. The specific rotation is defined as the

rotation produced by a solution of length 10 centimeter and unit concentration (i.e. 1g cm^{-3}) for a given wavelength of light at a given temperature. The angle through which the plane polarized light is turned corresponds to the angle of rotation, α, produced by the sample. The specific rotation, $[\alpha]_\lambda^T$ is given by:

$$[\alpha]_\lambda^T = \frac{\alpha}{c.l} \qquad (1.12)$$

where; T = temperature in °C; λ = wavelength of light used for the observation; α = observed rotation in degree; c = concentration of optically active solute in g cm^{-3}; l = path length in dm. The specific rotation has the unit : (° $g^{-1} \, cm^3 \, dm^{-1}$) or simply in degrees (°).

For a given substance, the value of α varies directly with the number of molecules through which the light passes, that is, with the path length of the cell and the concentration of the solution. It also depends on the wavelength of light used, the temperature and the solvent. The commonest wavelength used is 589 nm, the sodium D-line. Concentration and solvent data is included if relevant. Example: (c = 10, CH_3OH) after rotation means the specific rotation was determined at a concentration of 10 g cm^{-3} in methanol.

Negative rotation (counterclockwise), designated as (–) is sometimes called Levorotatory.

Positive rotation (clockwise), designated as (+), is sometimes called Dextrorotatory.

(N.B: There is no relationship between absolute configuration and the direction of rotation.)

Worked Examples

Question 1

Calculate the specific rotation of a 1.5 M solution of (R)-2-chlorobutane in ether contained in a 10 cm cell that gave a rotation of + 1.84°.

$$[\alpha]_\lambda^T = \frac{\alpha}{c.l}; \qquad l = 10 \ cm = 1 \ dm \ (1 \ dm = 10 \ cm)$$

$$\text{Concentration (mol dm}^{-3}) = \frac{Conc. \ (g/dm^3)}{molar \ mass \ (g \ mol^{-1})}$$

∴ Concentration (g/dm³) = Concentration (mol dm⁻³) × molar mass

molar mass of $CH_3CH(Cl)CH_2CH_3 = 92.5 \ g \ mol^{-1}$

$$\therefore \quad \text{Concentration (g/dm}^3) \quad = 1.5 \ (mol \ dm^{-3}) \times 92.5 \ g \ mol^{-1}$$
$$= 138.75 \ g/dm^3$$

$$\text{Concentration (g/cm}^3) \quad = \frac{Concentration \ (g/dm^3)}{1000} = \frac{138.75}{1000} \ g/cm^3$$
$$= 0.139 \ g/cm^3$$

$$[\alpha]_D = \frac{\alpha}{c \cdot 1} = \frac{+1.84}{0.139 \times 1}$$
$$= +13.23°$$

Question 2

Calculate $[\alpha]_D$ of a solution containing 5 g of 2-butanol in 10 cm³ of dichloromethane that gave a rotation of +7.89° in a 10 cm cell.

Solution

$$[\alpha]_D = \frac{\alpha}{c \cdot 1}; \quad \alpha = +7.89°, \quad c = \frac{5}{10} = \frac{1}{2} = 0.5 \, g/cm^3$$

$$[\alpha]_D = \frac{7.89}{0.5 \times 1 \, dm}; \qquad (10 \, cm = 1 \, dm)$$

$$[\alpha]_D = 15.78°$$

Question 3

How many grams of (S)-2-butanol is contained in a 20 cm³ solution in a 10 cm sample cell that gave an observed rotation of +4.382°; the specific rotation of the solution is +11.64°.

Solution

$$[\alpha]_D = \frac{\alpha}{c \cdot 1}; \quad \alpha = +4.382°, \quad [\alpha]_D = +11.64°; \quad 1 = 10 \, cm = 1 \, dm$$

$$\therefore c = \frac{\alpha}{[\alpha]_D \times 1}$$

$$c = \frac{+4.382}{11.64 \times 1} = 0.376 \, g/cm^3$$

∴ mass of (S)-2-butanol in 20 cm³ solution $= 0.376 \, g/cm^3 \times 20 \, cm^3$
$= 7.52 \, g$

Question 4

What is the expected observed rotation of a 1.0×10^{-4} M methanol solution of the potent anticancer drug Paclitaxel (also called taxol) ? $[\alpha]_D^{20} = -49° \, g^{-1} \, cm^3 \, dm^{-1}$ ($1 = 1$ dm, CH_3OH) Paclitaxel has a molecular mass of 853.93 g mol⁻¹.

Solution

$$[\alpha]_D^{20} = \frac{\alpha}{c \times 1}$$

But,
$$\therefore \alpha = [\alpha]_D^{20} \times c \times 1$$

$$Concentration \, (mol \, dm^{-3}) = \frac{Conc. \, (g/dm^3)}{molar \, mass \, (g \, mol^{-1})}$$

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∴ Concentration (g/dm³) = Concentration (mol dm⁻³) × molar mass
$$= 1 \times 10^{-4} \, mol \, dm^{-3} \times 853.93 \, g \, mol^{-1}$$
$$= 0.085393 \, g/dm^3$$

$$Concentration \, in \, g/cm^3 = \frac{concentration \, in \, g/dm^3}{1000} = \frac{0.085393}{1000}$$

$$= 8.54 \times 10^{-5} \, g/cm^3$$

$$\alpha = (-49° \, g^{-1} \, cm^3 \, dm^{-1})(8.54 \times 10^{-5} \, g \, cm^{-3})(1 \, dm)$$
$$= -0.004°$$

IV. Asymmetric carbon atoms

Asymmetric carbon atom is a carbon atom with four different groups or atoms bonded to it. A molecule containing one asymmetric carbon atom can have two stereoisomer, which are enantiomers. When a compound contains chiral centres, the maximum number of stereoisomeric forms it can have is 2^n, where 'n' is equal to the number of chiral centres. There will be 2^{n-1} enantiomer pairs, which, in relation to each other, are diastereomeric. Consider for example, the various stereoisomers of 3-chlorobutan-2-ol, which has two asymmetric carbon atoms (i.e. n=2). Here, one would expect $2^2 = 4$ stereoisomeric forms.
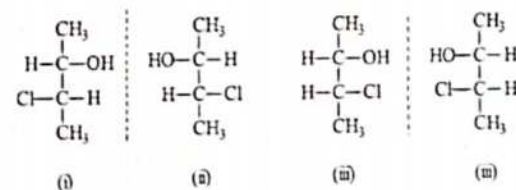
The four stereoisomeric forms consist of two pairs of enantiomers. Each pair is related to the other parts as diastereomers, for example, structure (I) is a diastereomer of (III) and (IV). Structure (III) is a diastereomer of (I) and (II) and so on.

Enantiomers	Diastereomers
I and II	I and III
III and IV	II and III
	I and IV
	II and IV

Consider another example, with three chiral centres (i.e. n=3), that is, the stereoisomers of 4-chloropentan-2, 3-diol, which has three asymmetric carbon atoms (n = 3). Here one would expect $2^3 = 8$ stereoisomeric forms.

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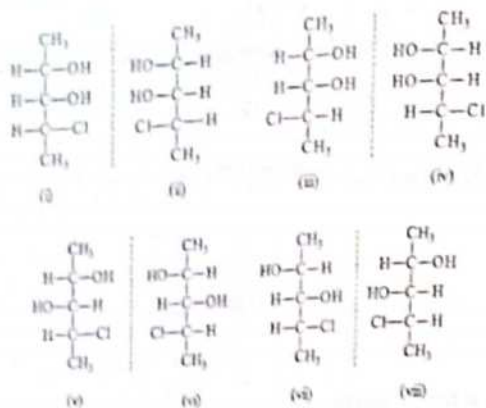
The eight stereoisomeric forms consist of four pairs of enantiomers. Each pair is related to the other parts as diastereomers, for example, structure (I) is a diastereomer of (III) and (IV), (V) and (VI), and (VII) and (VIII). Structure (III) is a diastereomer of (I) and (II), (V) and (VI), and (VII) and (VIII). Structure (V) is a diastereomer of (I) and (II), (III) and (IV), and (VII) and (VIII). Structure (VIII) is a diastereomer of (I) and (II), (III) and (IV), and (V) and (VI), and so on, making a total of four diastereomers (= 2^{n-1}), and each with a pair of enantiomers (= 2^n), where $n = 3$.

| Enantiomers	Diastereomers
I and II	I and III
III and IV	I and IV
V and VI	II and III
VII and VIII	II and IV
	V and VII
	V and VIII
	VI and VII
	VI and VIII

However, when two or more of the chiral centres are equivalent, that is when a compound containing two or more chiral centres has plane of symmetry, the compound will not be optically active. Such compounds are called *meso* isomers. In such cases, the total number of stereoisomers will be less than the maximum predicted by the formula (i.e. 2^n). For example, in butan-2,3-diol, there are only three stereoisomers instead of four (i.e. $n = 2$) that the formula predicted.
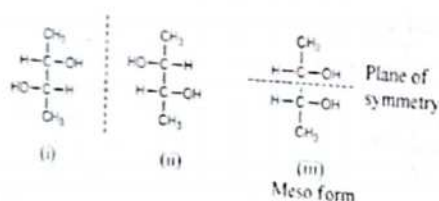
Similarly, for pentan-2, 3, 4-triol, where chiral centres at C-2 and C-4 are alike, there are only four stereoisomers as against eight predicted by the formula for $n = 3$ (i.e. $2^3 = 8$). They are:
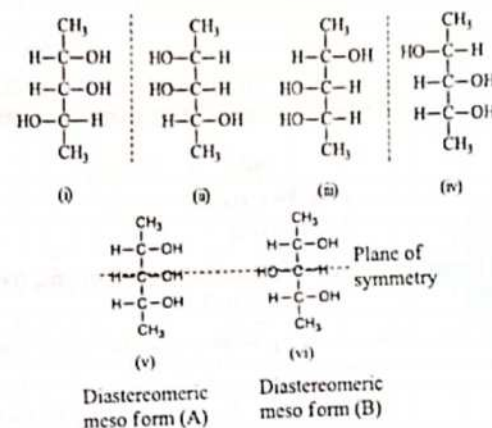
The diastereomeric meso forms (A) and (B) have a plane of symmetry at C-3 (called a pseudoasymmetric carbon atom).

V. Absolute configuration

There are systems of nomenclature for describing the absolute configuration of an asymmetric centre and that of *cis-*and *trans* geometric isomers that are related as diastereomers.

(a) The R/S (Cahn-Ingold-Prelog) system

In the *R/S* system, a chiral carbon is assigned an absolute configuration. Absolute configuration is the exact spatial arrangement of the four groups bonded to the chiral carbon and it is specified as $\underline{R}$ or $\underline{S}$. Thus, if one member of a pair of enantiomers is $\underline{S}$, the other member of the pair (the mirror image) must be $\underline{R}$.

Using a molecule of 1-bromo-1-chloro-1-fluoromethane as an example, the following steps should be followed in order to assign names to enantiomers.

1-Bromo-1-chloro-1-fluoromethane
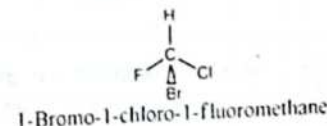
Step 1: Write a Fischer projection involving the chiral carbon

$$
\begin{array}{c}
H \\
| \\
F{-}C{-}Cl \\
| \\
Br
\end{array}
$$

Step 2: Assign priorities (a, b, c, d) to the groups attached to the chiral carbon based on atomic numbers and substitution pattern of the constituent atoms in sequence:

$$
\begin{array}{c}
H(d) \\
| \\
(c)\,F{-}C{-}Cl(b) \\
| \\
Br(a)
\end{array}
$$

If the group with lowest priority (i.e. d) is directed away from you, (i.e. at the top or bottom of the Fischer projection), proceed to step 3

Step 3: Make a circular motion with your pen, from (a) to (b) to (c), ignoring group (d)

Anticlockwise, S

The configuration is *R* if the direction of motion is clockwise "↻" and *S* if the direction of motion is anticlockwise (counterclockwise) "↺"

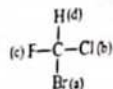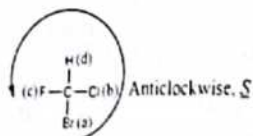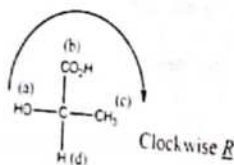**Step 4:** Name the given compound

$$
\begin{array}{c}
H \\
| \\
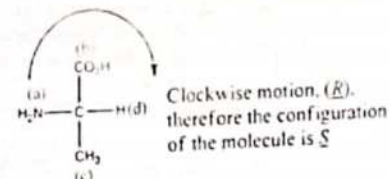F{-}C{-}Cl \\
| \\
Br
\end{array}
$$

S-1-Bromo-1-chloro-1-fluoromethane

Another Example is:

Clockwise *R*

For the case in which the group of lowest priority (i.e., d) is directed towards you (i.e. to the left or right of a Fischer projection), a slight modification of the above method is needed and is as given below:

Make your motion from (a) to (b) to (c), ignoring group (d). The configuration of the chiral carbon is the opposite of the one determined from your motion.

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Examples:

Anticlockwise motion, (*S*), therefore the configuration of the molecule is (*R*)

Clockwise motion, (*R*), therefore the configuration of the molecule is *S*
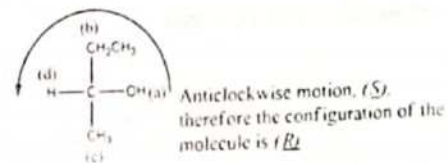
The following rules are used in assigning priorities to the four groups attached to chiral carbon atoms:

(i) Priorities are assigned based on atomic number of the attached groups:

$$I > Br > Cl > S > O > N > C > F > H$$

Decreasing order of priority
(or decreasing order of atomic number) →
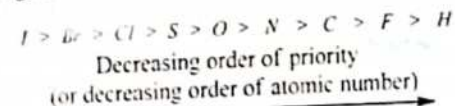
(ii) If two or more first-rank atoms are the same (usually carbon atom), priority between them depends on the atoms directly attached to them (i.e. second-rank atoms), again according to atomic number, for example:

$$-CH_2Cl > -CH_2OH > -CH_2NH_2 > -CH_2CH_3 > -CH_2 H(CH_3)$$

Decreasing order of priority →
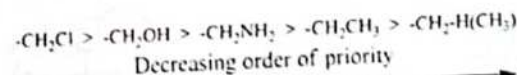
(iii) If two or more groups have the same second-rank atoms, the number of these atoms decides priority, for example,

$$-CHCl_2 > -CH_2Cl > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3$$

Decreasing order of priority →
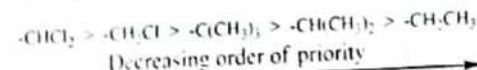
(iv) Multiple bonds are counted as several single bonds
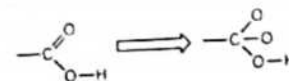
Several asymmetric centres

When several asymmetric centres are present in the molecule, each is treated and specified separately. The following example demonstrates how configuration is

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assigned to molecules with several asymmetric centres.

Step 1: Priority for C-3

$$^{(4)}CO_2H$$
$$HO-^{(3)}C-H$$
$$H-^{(2)}C-OH$$
$$^{(1)}CO_2H$$

Clockwise motion (R), therefore the configuration of the molecule at C-3 is S, i.e, 3S

Step 2: Similarly for C-2,

Clockwise motion (R), therefore the configuration of the molecule at C-2 is S, i.e 2S

The configuration of the molecule is (2S, 3S)

Worked Examples

Question 1

Assign the absolute configuration to all the chiral carbons in the following molecules.

(i)
$$CN$$
$$H-C-OH$$
$$CH_3$$

(ii)
$$CO_2H$$
$$H-CH_3$$
$$HO-H$$
$$CH_3$$

(iii)
$$CH_2CH_3$$
$$H-CH=CH_2$$
$$H-Br$$
$$CH_3$$

Solution

(i)

Anticlockwise motion, S, therefore the configuration of the molecule is R

(ii)

$$^1CO_2H$$
$$H-^2C-CH_3$$
$$HO-^3C-H$$
$$^4CH_3$$

3-Hydroxy-2-methylbutanoic acid

At C-2:

Anticlockwise motion, S, therefore the configuration of the molecule at C-2 is R, (i e 2R

At C-3:

Clockwise motion (R), therefore the configuration of the molecule at C-3 is S (i.e 3S)

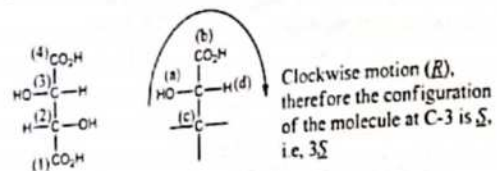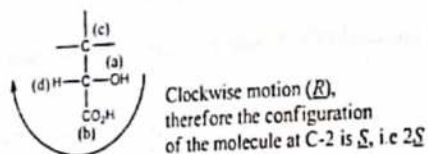∴ (2R, 3S) –3-Hydroxy-2-methylbutanoic acid

(iii)

$$^4CH_2CH_3 \ ^5$$
$$H-^3C-CH=CH_2$$
$$H-^2C-Br$$
$$^1CH_3$$

2-Bromo-3-ethylene pentane

At C-3

Clockwise motion (R), therefore the configuratio of the molecule at C-3 is S, (i.e 3S)

At C-2

Anticlockwise motion, S, therefore the configuration of the molecule at C-2 is R, (i e 2R)

∴ (2R, 3S) –3-Bromo-3-ethylenepentane

(b) The E/Z system

The same priorities may be used in the designation of configurations of diastereomers such as *cis*-and *trans*-1, 2-dichloroethene. When the atoms or groups of highest priority lie on opposite sides of the double bond as in *trans*-1,2-dichloroethene,

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the stereoisomer is designated E (German entgegen = opposite). When the atoms or groups of highest priority are on the same side of the double bond as in cis-1,2-dichloroethene, the stereoisomer is designated Z (means together). This system is less ambiguous than the cis-trans system, which is still applicable in simple cases.

trans- (or E)-1,2-Dichloroethane   cis- (or Z)-1,2-Dichloroethane

(Z)-1-Amino-1,3-dichloro-2-methylprop-1-ene
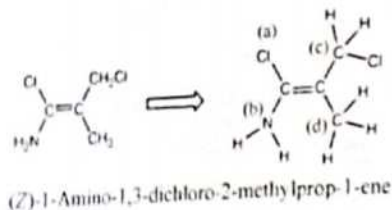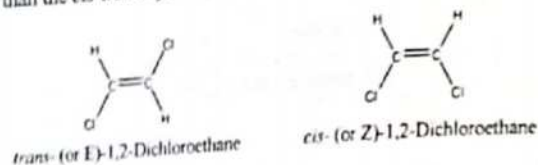
It is also applicable to ring systems, for example

(E)-1-Chloro-1-methyl-2-hydroxyl-2-nitrocyclopropane
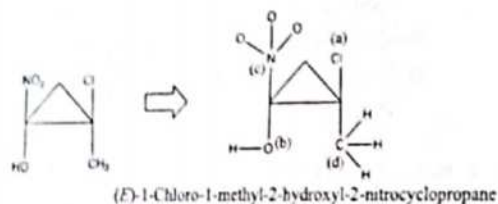
(c)   D/L system (relative configuration)

Emil Fischer determined all configurations relative to the simple molecule, glyceraldehyde, $HOCH_2 \cdot CHOH\text{-}CHO$

D-Series   L-Series

He arbitrarily assigned the configuration as D or L series. If the –OH group on the asymmetric carbon fell on the right in the Fischer projection, he called it D–series, and if on the left it is L–series. To assign a configuration, we draw the molecule in Fischer projection, with C-1 (usually the more highly oxidizable end of the chain) uppermost. If the –OH or NH_2 (or similar) group on the asymmetric carbon lies on the right, the configuration is D, and if on the left, it is L. It must be emphasized that representation of the D and L forms of sugar is merely a convention and has no relation to their direction of rotation. If it is desired to indicate direction of rotation of the compound, the symbols (+), meaning dextrorotatory and (–), meaning laevorotatory, are used. Thus a dextrorotatory sugar with D configuration is indicated by the symbol D (+), while a

laevorotatory sugar of the same configuration is represented as D (–). Examples are:

(i)   D(+)   L(-)
Glyceraldehyde

(ii)   Butan-2-ol, Alanine, L (= S)
(C-1 = easily oxidizable group)

(iii)   (+) Alanine, L (= S)

(iv)   D (-) Lactic acid
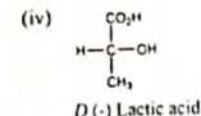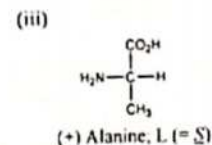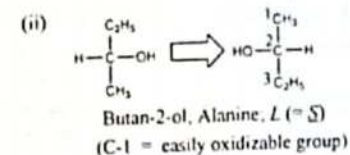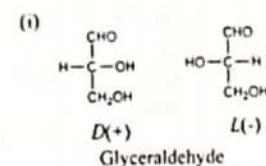
Ambiguities arise in applying the D/L system to more complex molecules, and for molecules with more than one asymmetric centre we must use the R/S system.

1.1 Caderine, an aptly named amine, with a molecular mass of 102 was analyzed for carbon, hydrogen and nitrogen. Analysis of a 0.040 gram sample yielded 0.086 gram of carbon (IV) oxide, 0.051 gram of water and 8.6 cm^3 of nitrogen gas were collected at standard temperature and pressure. Deduce the molecular formula of caderine from these data [molar volume of any gas at STP is 22.4 dm^3].

[$C_5H_{15}N_2$]
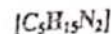
1.2 (a) The molar ratio of carbon to hydrogen of a volatile liquid compound is 1:2. 0.12 gram of the liquid on evaporation at STP gave 32 cm^3 of vapor. Find the molecular formula of the compound.

(b) 45 cm^3 of a gaseous hydrocarbon on combustion consumed 270 cm^3 of oxygen to produce 180 cm^3 of carbon (IV) oxide, all measurements being taken at 25°C and 1 atmosphere pressure.

(i) Determine the molecular formula of the hydrocarbon.

(ii) Give the structural formular and names of all isomers of the hydrocarbon in (b)(i) above.

[(a) C_6H_{12};   b(i) C_4H_8]

1.3 100 cm^3 of water containing 20 grams of an organic compound C was extracted with 200 cm^3 of dichloromethane (a) in one batch (b) in two batches of 100 cm^3 of dichloromethane each. If dichloromethane and water are immiscible, and the partition coefficient of C between water and dichloromethane is 0.4 at 28°C, calculate the masses of C extracted into dichloromethane in each case.

[(a) 16.67 g ; (b) 18.37 g]
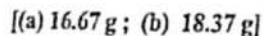
1.4 200 cm^3 of water containing 15 grams of naphthalene was extracted with 150 cm^3 of trichloromethane (chloroform) (a) in one batch (b) in two batches of 100 cm^3 and 50 cm^3 of chloroform each. If chloroform and water are immiscible, and the partition coefficient of naphthalene between chloroform and water is 7.5 at 30°C, calculate the masses of naphthalene extracted into chloroform in each case. Comment on the efficiency of the two extraction methods.

[(a) 12.74 g ; (b) 13.90 g]

1.5 (a) With the aid of appropriate structures, explain the concept of resonance.

(b) Advance three evidences in support of the concept of resonance.

(c) What is (or are) the basic difference(s) between the concepts of resonance and tautomerism? Illustrate with appropriate structures
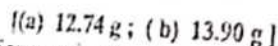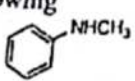
(d) Draw a set of resonance structures for each of the following

(i) CO_3^{2-} (ii) $CH_3CO_2^-$ (iii) $CH_3CH=CH\text{-}COCH_3$ (iv) ⬡-NHCH$_3$

1.6 Explain briefly but clearly, the meaning of the terms sp, sp^2 and sp^3 hybridization, using ethane, ethene and ethyne as illustrated examples.

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Use well labeled diagrams to illustrate your explanation.

1.7 (a) Show how the compound formed between atoms X and Y (i.e X–Y) can be subjected to (i) homolytic fission (ii) heterolytic fission; state the conditions that lead to each type of fission and name the products obtained.

(b) With the aid of examples, mention different ways by which radical can be generated.

(c) Enumerate the various transformations that happen to a radical after its formation.

1.8 (a) Explain briefly, the following statements in terms of hybridization in carbon atom.

(i) pi (π) bonds are generally weaker than sigma (σ) bonds.

(ii) C – C bonds in ethyne (0.12nm) is shorter than C – C bonds in ethane (0.154nm).

(b) A compound named 2-methylpent-1-ene-3-yne was synthesized from petrochemical source.

(i) Draw the graphic formula, showing the bond angles between each carbon atom of the above named compound.

(ii) Which carbon is (are) sp, sp^2 and sp^3 hybridized?

(c) Give three ways by which sigma bonds are formed.

1.9 (a) Name three types of structural isomerism. Write a pair of structural formulae for each named type of structural isomerism for compounds with molecular formula $C_5H_{10}O$

(b) Name the functional groups present in each of the following molecules

(i)   [structure with OH and CHO groups]

(ii) $C_6H_5\text{-}CH\text{-}COCH_3$
              |
             NH$_2$

(iii) $CH_3\text{-}NH(CH_3)CH_2CO_2C_2H_5$ (iv) $CH_3C\equiv CCH(OH)CHO$
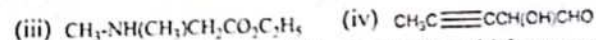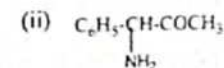
1.10 (a) Copy and complete the following tables which concern the sigma (σ) and pi (π) bonds present in propane, propene and propyne.

Sigma Bonds

Compound X	Number of such bonds (Y)	Overlapping orbitals, and their orientation towards each other (Z)
Propane		
Propene		
Propyne		

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Pi Bonds

Compound X	Number of such bonds (Y)	Overlapping orbitals, and their orientation towards each other (Z)
Propane		
Propene		
Propyne		

(b) Write balanced equations for the complete combustion, in excess oxygen of the compounds
  (i) alkane
  (ii) alkyne, each of which contains n-carbon atoms in the molecule.

(c) (i) Equal volume of the two hydrocarbons in (b) were separately completely combusted in oxygen. The volumes of steam produced in (i) and (ii) were in the ratio 3:2
  Determine the value of n and hence the formula for the alkane and the alkyne. (All measurements were carried out at 120°C).
  (ii) Comment about the properties of the CO_2 produced from the alkane and the alkyne in (b).

[(c) (i) n = 5; Alkane formula is C_5H_{12}; Alkyne formula is C_5H_8]
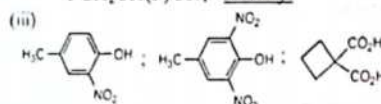
1.11 Arrange the following compounds in the order of increasing indicated property after each group. Give reasons for your order.
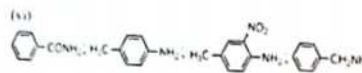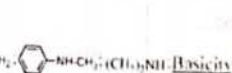 (i) $ClCH_2COOH$; $Cl_2CHCOOH$; CH_3COOH; CH_2FCOOH; $C_6H_5CO_2H$; Acidity
  (ii) FCH_2CH_2OH; CH_3CH_2OH; F_2CHCH_2OH; CH_3CF_2OH; $FCH_2CH(F)OH$; Acidity.
  (iii) ; Acidity
  (iv) $(CH_3)_2CHCO_2H$; $(CH_3)_3CCO_2H$; $CH_3CH(Cl)CO_2H$; $ClCH_2CH_2CO_2H$; $CH_3CH_2CO_2H$; $CH_3CCl_2CO_2H$; Acidity
  (v) NH_3; $(CH_3)_2NH$; $(CH_3)_4N^\oplus$; CH_3NH_2; $(CH_3CH_2)_2NH$; $(CH_3)_3CCH_2NH_2$; $(CH_3)_2CHCH_2NH_2$; $CH_3CH_2CH_2NH_2$; Basicity
  (vi) Basicity
  (vii) Basicity
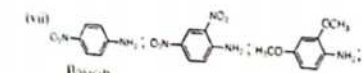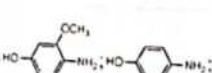
1.12 (a) Explain with appropriate examples in each case, the following terms
  (i) Inductive effect (ii) Mesomeric effect and (iii) Steric effect.
  (b) What are the differences between "inductive and mesomeric effects"

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(c) (i) Is Lewis acid an electrophile or a nucleophile?
  (ii) Classify the following species either as a Lewis acid or a Lewis base

  $C_6H_5N_2^+$; $C_6H_5O^-$; CH_3MgBr; $CH_3C\equiv C^-$; $(C_2H_5)_3N^\oplus$; $CH_3OC_2H_5$ CH_3OH, H_2SO_4, $AlCl_4^-$; BF_3, H_3O^+, Cl^-, I^-, C_2H_4, $CH_3-CO-C_2H_5$ $AlBr_3$; NF_3; $(CH_3)_2NH$, PH_3, NO_2^+; and CN^-

1.13 (a) Which of the following compounds can be resolved into optical isomers
  (i) $(CH_3)_2CHCH_2OH$ (ii) $H_2NCH(CH_3)COOH$, (iii) $H_2N CH_2COOH$
  (iv) $OHCH_2CH(OH)CH(OH)CH_2OH$
  (v) (vi)
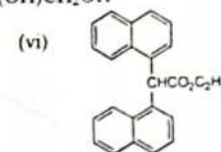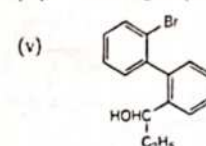
1.14 Draw all the possible geometric isomers (where possible) for each of the following compounds.
  (i) Hexa-2,4-diene (ii) 2, 3- Dimethylbut-2-ene
  (iii) 2-Chloro-3 methylpent-2-ene (iv) 1,4-Dimethylcyclohexanol
  (v) 1,2-Dichlorocyclobutane (vi) 1,2 Dinitrocyclopropane
  (vii)
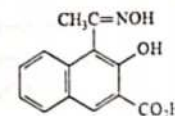
1.15 (a) 20 grams of a table sugar (i e. sucrose) with molecular mass 342 g mol^{-1} was dissolved in 1 dm^3 of distilled water. The solution was put in a curvet of length 10 mm, and the optical activity was measured with a polarimeter. If the specific rotation at 45°C and at 589 nm of sodium D Line was +24.64°, determine the observed angle of rotation, $[\alpha]_\lambda^{45°C}$

  (b) Calculate the specific rotation of a 1.2 M solution of (R)-2-methyl-1-butanol that gave a rotation of +1.307° at 30°C in a 10 cm cell.

  (c) A sample 2-bromobutane gave a specific rotation of +4.23°. Given that (R)-2-bromobutane has a specific rotation of –13.84°. Calculate the percent of each enantiomer in the sample.

[(a) + 0.05° ; (b) + 12.34° ; (c) %(R), 30.6%; %(S), 69.4%]

1.16 (a) A sample of pure (S)-2-butanol was placed in a 10.0 cm polarimeter tube. Using D line of sodium lamp, the observed rotation at 20°C was +104°. The density of this compound is 0.805 g/cm³. What is the specific rotation of (S)-2-butanol? [+129° g⁻¹ cm³ dm⁻¹]

  (b) Calculate the observed rotation of a solution of 0.5245 g of (S)- 1- amino-1-phenylethane diluted to a volume of 10.0 cm3 with methanol at 20°C, using the D- line of a sodium lamp and a 1.0 dm tube. Specific rotation of this material $[\alpha]_D^{20} = -30° g^{-1} cm^3 dm^{-1}$. [$\alpha = -1.57°$]

  (c) A 0.856 g sample of pure (2R, 3R)-tartaric acid was diluted to 10 cm³ with water and placed in a 1. 0 dm polarimeter tube. The observed rotation using

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the 589 nm line of a sodium lamp at 20°C was +1.06°. Calculate the specific rotation of (2R, 3R)-tartaric acid. [+12.38° g^{-1} cm^3 dm^{-1}]

1.17 Assign the absolute configuration to all the chiral carbons in the following molecules.

(i) 3-Bromo-2-hydroxypentane   (ii) 2, 3-Dihydroxybutanedioic acid
(iii) 2-Chloro hexan-3,4,5-triol   (iv) 2,4-Dibromopentan-3-ol
(v) Pentan-1,2,3,4-tetraol   (vi) Pentan-1,2,3,4,5-pentaol

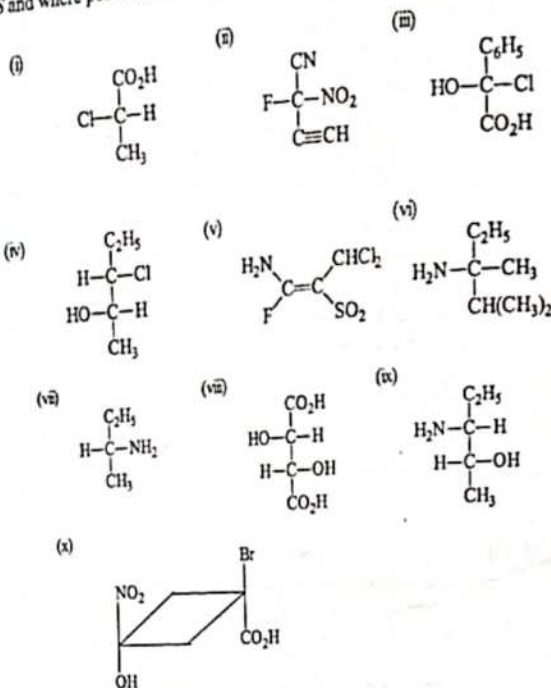**1.18** Deduce the absolute configuration for each of the following structures in *E/Z*; *R/S* and where possible, the *D/L* systems:

(i)
$$CH_3$$
$$Cl-\overset{CO_2H}{\underset{H}{C}}-H$$

(ii)
$$F-\overset{CN}{\underset{C \equiv CH}{C}}-NO_2$$

(iii)
$$HO-\overset{C_6H_5}{\underset{CO_2H}{C}}-Cl$$

(iv)
$$H-\overset{C_2H_5}{\underset{}{C}}-Cl$$
$$HO-\overset{}{\underset{CH_3}{C}}-H$$

(v)
$$\overset{H_2N}{\underset{F}{}}C=C\overset{CHCl_2}{\underset{SO_2}{}}$$

(vi)
$$H_2N-\overset{C_2H_5}{\underset{CH(CH_3)_2}{C}}-CH_3$$

(vii)
$$H-\overset{C_2H_5}{\underset{CH_3}{C}}-NH_2$$

(viii)
$$HO-\overset{CO_2H}{\underset{}{C}}-H$$
$$H-\overset{}{\underset{CO_2H}{C}}-OH$$

(ix)
$$H_2N-\overset{C_2H_5}{\underset{}{C}}-H$$
$$H-\overset{}{\underset{CH_3}{C}}-OH$$

(x)
$$NO_2 \quad Br$$
$$OH \quad CO_2H$$

1.18 Draw Fischer projection formula for each of the following:
(i) (*R*)-2, 3-Dichloropropanol
(ii) (*S*)-1-Bromoethanol
(iii) (*E*)- 1-Amino-1, 3-dibromo-2-methylprop- 1-ene
(iv) (*Z*)-1-Nitroso-1-methyl -2-chloro-2 methylcyclopropane
(v) (*E*)-1-Nitro-4-bromo-4-methylcyclohexanol.

PART TWO

HYDROCARBON CHEMISTRY

Hydrocarbons are compounds containing carbon and hydrogen only. They can be subdivided into aliphatic (or acyclic), alicyclic (or cyclic) and aromatic hydrocarbons.

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ALIPHATIC HYDROCARBONS

These are open-chain compounds which may be saturated or unsaturated. The saturated hydrocarbons are the alkanes (or paraffins) whereas the unsaturated hydrocarbons are the alkenes (or olefins) and alkynes.

VI. Alkanes

Alkanes have the general molecular formula C_nH_{2n+2}. They are saturated hydrocarbons because each carbon atom shows maximum bonding capacity of four and all the bonds present in the molecule are single covalent bonds.

Nomenclature

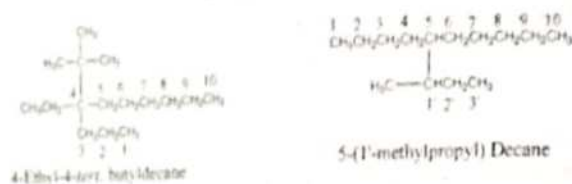Below are the rules used for alkane nomenclature in accordance with I.U.P.A.C. systems of naming.

1. Establish the parent hydrocarbon by counting the longest continuous carbon chain, name the parent compound by taking the Greek prefix appropriate to the number of carbon atoms and adding the ending "-ane". The following are the Greek prefixes (or stems) corresponding to the number of carbon atoms:

C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}
Meth-	Eth-	Prop-	But-	Pent-	Hex-	Hept-	Oct-	Non-	Dec-	Undec-	Dodec-

C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}
Tridec-	Tetradec-	Pentadec-	Hexadec-	Heptadec-	Octadec-	Nonadec-	Eicos-

2. Name the attached group(s) (or substituent(s)). If there are several substituents, separate the numbers by putting comma, and the number from the word by hyphen (–).

3. If the substituents are identical, use the prefix di, tri, tetra, penta, etc.

4. When there are two or more substituents present in a compound, the substituents are cited in alphabetical order, for example, ethyl substituent should be cited

before methyl substituent.

Numbering of the parent hydrocarbon should begin from the end of the carbon
5. chain that is closest to where there is highest branching such that the least
possible numbers are assigned to substituents. Consider the following
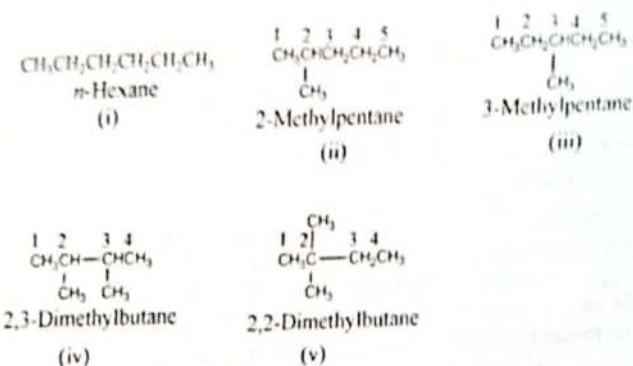examples.

CH₃CH₂CH₂CH₂CH₂CH₃
n-Heptane

3,3,4-Trimethylhexane

CH₃CHCH₂CH₂CH₃
|
CH₃
2-Methylpentane

CH₃CH₂CHCH₂CH₂CH₃
|
CH₂CH₃
3-Ethylhexane

3-Bromo-2,2,4-trimethylpentane

4-Ethyl-4-tert. butyldecane

5-(1'-methylpropyl) Decane
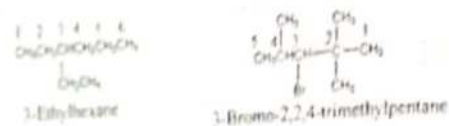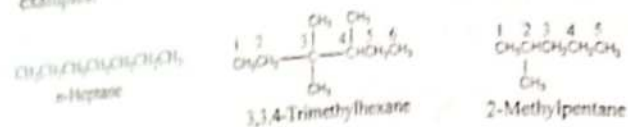
Structural isomerism in alkanes

This is already discussed in part one. They undergo chain or branched chain
isomerism. The following procedures are useful when drawing the structural isomers of
a given compound. We shall use hexane as an example.

1. Start with the isomer having the longest chain with no branching.

2. Take the next longer chain having five carbon atoms by removing a methyl
group, which can be placed in between the carbon chain, but not at the terminal
carbons.

3. Take the shortest possible chain having four carbon atoms, by removing another
methyl group, and the two methyl groups so removed can be placed in between
the carbon chain, but not at the terminal carbons.

CH₃CH₂CH₂CH₂CH₂CH₃
n-Hexane
(i)

1 2 3 4 5
CH₃CHCH₂CH₂CH₃
|
CH₃
2-Methylpentane
(ii)

1 2 3 4 5
CH₃CH₂CHCH₂CH₃
|
CH₃
3-Methylpentane
(iii)

1 2 3 4
CH₃CH—CHCH₃
| |
CH₃ CH₃
2,3-Dimethylbutane
(iv)

1 2 3 4
CH₃C—CH₂CH₃
|
CH₃
2,2-Dimethylbutane
(v)

Classification of carbon atoms

Carbon atoms are classified according to the number of other carbon atoms to which
they are bonded.

Primary (1°) carbon

A carbon is a primary carbon atom when bonded to only one other carbon atom (or
hydrogen atoms).

Secondary (2°) carbon

A carbon is a secondary carbon atom when bonded to two other carbon atoms.

Tertiary (3°) carbon

A carbon is a tertiary carbon atom when bonded to three other carbon atoms.
The following example illustrates the three types of carbon atoms described above.
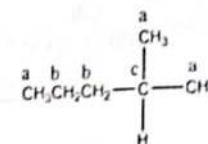
a = Primary carbon atoms,   b = Secondary carbon atoms, c = Tertiary carbon atoms

Physical properties

The straight-chain alkanes, C_1 to C_4 are gases at room temperature and atmospheric
pressure. The C_5 to C_{16} are mostly liquids, with the exceptions of dimethylpropane
which is a gas and tetramethylbutane which is a crystalline solid. Straight-chain alkanes
having greater than sixteen carbon atoms ($> C_{16}$) are waxy solids, with paraffin wax
consisting largely of n-alkanes containing twenty to thirty carbon atoms (i e C_{20}–C_{30}).

Boiling points and melting points

These depend on:

1. Relative molecular mass of the compound
2. Degree of branching.

Generally, the boiling points and melting points of n-paraffins increase with increasing molecular mass.

The boiling point decreases with increasing degree of branching within a family of isomeric alkanes. The lower the boiling point, the higher the volatility, and the boiling point (B pt) is inversely related to volatility as follows:

$$B.pt \ \alpha \ \frac{1}{Volatility} \qquad (2.1)$$

For example,

Name	Formula	Structure	B pt (°C)
Butane	C_4H_{10}	$CH_3CH_2CH_2CH_3$	−0.5°C
2-Methylpropane	C_4H_{10}	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_3$	−10 °C
Pentane	C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	+36 °C
2-Methylbutane	C_5H_{12}	$CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2CH_3$	+28 °C
2,2-dimethylpropane	C_5H_{12}	$CH_3\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}CH_3$	+10 °C

Solubility

Alkanes are soluble in many organic solvents such as alcohols and ether but insoluble in water (like dissolves like). The slight solubility tendency of methane in water is attributable mainly to the very small size of its molecules, which is comparable with water molecules.
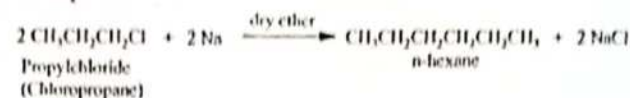
Laboratory synthesis of alkanes

1. Wurtz synthesis

This involves reaction of an alkyl halide with sodium or potassium to afford coupled product; for example;
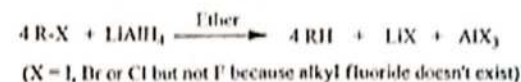
$$2RX + 2Na \xrightarrow{dry \ ether} R-R + 2NaX$$

A specific example is:

$$2 CH_3CH_2CH_2Cl + 2 Na \xrightarrow{dry \ ether} CH_3CH_2CH_2CH_2CH_2CH_3 + 2 NaCl$$
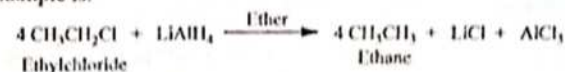Propylchloride   n-hexane
(Chloropropane)

2. Reduction of alkyl halides with common reducing agents

Reduction of alkyl halides with common reducing agents like lithium tetrahydrido aluminate(III) [LiAlH$_4$] or sodium tetrahydridoborate (III) [NaBH$_4$], produces alkane, for example,

$$4 R-X + LiAlH_4 \xrightarrow{Ether} 4 RH + LiX + AlX_3$$

(X = I, Br or Cl but not F because alkyl fluoride doesn't exist)

A specific example is:

$$4 CH_3CH_2Cl + LiAlH_4 \xrightarrow{Ether} 4 CH_3CH_3 + LiCl + AlCl_3$$
Ethylchloride   Ethane

Other useful reducing agents are alkaline metals in liquid ammonia and zinc with mineral acid (Zn/HCl).
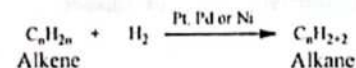
3. Catalytic hydrogenation of alkyl halides

Alkane can be produced by catalytic hydrogenation of alkyl halides with nickel or lead (II) chloride as catalyst.
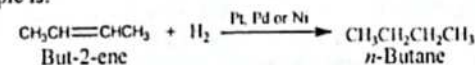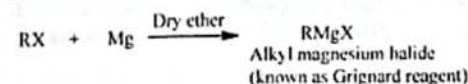
$$CH_3CH_2CH_2Cl + H_2 \xrightarrow[or \ PbCl_2]{Ni \ cat.} CH_3CH_2CH_3 + HCl$$
n-Propane
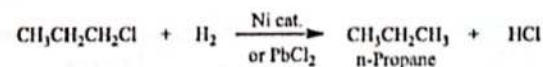
4. Catalytic hydrogenation of alkene

Alkane is produced by catalytic hydrogenation of alkene with platinum, palladium or nickel as catalyst.

$$C_nH_{2n} + H_2 \xrightarrow{Pt, \ Pd \ or \ Ni} C_nH_{2n+2}$$
Alkene   Alkane

A specific example is:

$$CH_3CH=CHCH_3 + H_2 \xrightarrow{Pt, \ Pd \ or \ Ni} CH_3CH_2CH_2CH_3$$
But-2-ene   n-Butane

5. From Grignard reagent

$$RX + Mg \xrightarrow{Dry \ ether} RMgX$$
Alkyl magnesium halide
(known as Grignard reagent)

The Grignard reagent so formed is then hydrolyzed with water in the presence of an acid.

$$RMgX + H_2O \xrightarrow[H_2SO_4]{aq.\ HCl\ or} R\text{-}H + Mg(OH)X$$

A specific example is:

$$CH_3CH_2Br + Mg \xrightarrow[H_2SO_4]{dry\ ether} \underset{\text{Ethylmagnesiumbromide}}{CH_3CH_2MgBr}$$

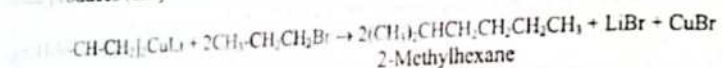$$CH_3CH_2MgBr + H_2O \xrightarrow{HCl_{(aq)}} \underset{\text{Ethane}}{CH_3CH_3} + Mg(OH)Br$$
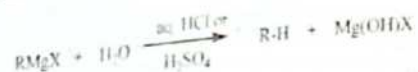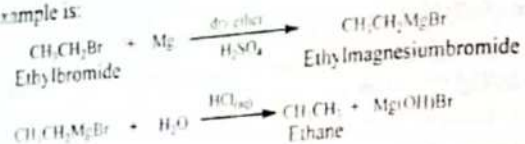
Using lithium dialkyl copper reagents (R₂CuLi)

Treatment of lithium dialkyl copper reagents also known as cuprates with an alkyl halide produces (unsymmetrical) alkanes (R – R').

$$[(CH_3)_2CH\text{-}CH_2]_2CuLi + 2CH_3\text{-}CH_2CH_2Br \rightarrow \underset{\text{2-Methylhexane}}{2(CH_3)_2CHCH_2CH_2CH_2CH_3} + LiBr + CuBr$$
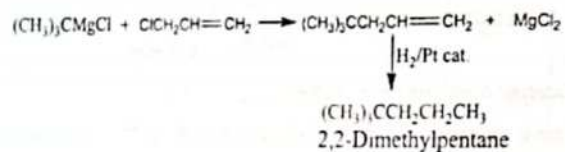
Kolbe synthesis

This is an anodic oxidation of carboxylic acids. The method is useful for the synthesis of symmetrical alkanes (with an even number of carbon atoms).
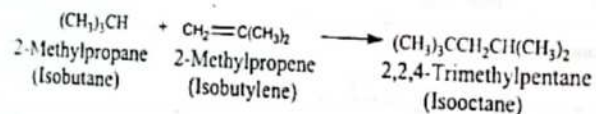
$$2\ RCOOH \longrightarrow R\text{-}R + 2CO_2 + 2H^+ + 2e^-$$

Hydrogenation of corresponding alkene using Grignard's reagents

$$(CH_3)_3CMgCl + ClCH_2CH=CH_2 \longrightarrow (CH_3)_3CCH_2CH=CH_2 + MgCl_2$$
$$\downarrow H_2/Pt\ cat.$$
$$\underset{\text{2,2-Dimethylpentane}}{(CH_3)_3CCH_2CH_2CH_3}$$

Industrial synthesis of Alkanes

Alkylation

Catalytic alkylation of isobutane with gaseous alkene using either tetraoxosulphate (VI) acid or hydrogen fluoride as catalyst provides an economical means for the production of high-octane motor fuel from refinery gases.

$$\underset{\substack{\text{2-Methylpropane}\\(Isobutane)}}{(CH_3)_3CH} + \underset{\substack{\text{2-Methylpropene}\\(Isobutylene)}}{CH_2=C(CH_3)_2} \longrightarrow \underset{\substack{\text{2,2,4-Trimethylpentane}\\(Isooctane)}}{(CH_3)_3CCH_2CH(CH_3)_2}$$
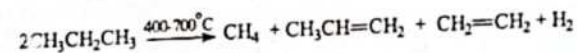
Chemical Reactions

They are very unreactive compared to alkenes and alkynes. However, they may be made reactive under drastic reaction conditions like high temperature and under ultraviolet light or use of peroxide as catalyst. They undergo the following reactions:

(a) Pyrolysis or cracking

This involves heating in the absence of oxygen, leading to cleavage or breaking into smaller hydrocarbons and hydrogen gas.
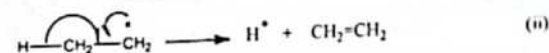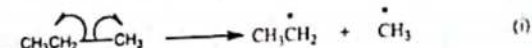
$$Alkane \xrightarrow{400\text{-}700^{\circ}C} \text{mixture of smaller Hydrocarbons} + H_2$$
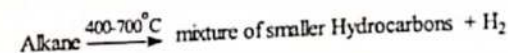
In petroleum industry, it is called *Cracking*. e.g;

$$2CH_3CH_2CH_3 \xrightarrow{400\text{-}700^{\circ}C} CH_4 + CH_3CH=CH_2 + CH_2=CH_2 + H_2$$
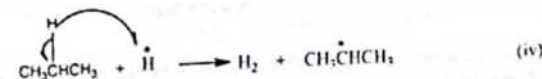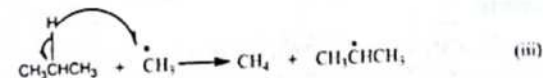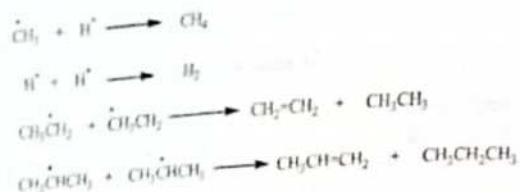
Mechanism of cracking process

Cracking (pyrolysis) takes place via free radical mechanism and it involves homolytic fission of carbon-carbon single bond rather than carbon-hydrogen bond because of lower bond energy of carbon-carbon single bond. Consider for example, the mechanism by which cracking of propane takes place.

$$CH_3CH_2\overset{\frown}{\underset{\frown}{\cdots}}CH_3 \longrightarrow CH_3\dot{C}H_2 + \dot{C}H_3 \qquad (i)$$

$$H\text{-}CH_2\overset{\frown}{\underset{\frown}{\cdots}}CH_2 \longrightarrow H^{\bullet} + CH_2=CH_2 \qquad (ii)$$

The hydrogen and methyl radicals formed above now react with another molecule of propane.

$$CH_3\overset{H}{\underset{|}{C}}HCH_3 + \dot{C}H_3 \longrightarrow CH_4 + CH_3\dot{C}HCH_3 \qquad (iii)$$

$$CH_3\overset{H}{\underset{|}{C}}HCH_3 + \dot{H} \longrightarrow H_2 + CH_3\dot{C}HCH_3 \qquad (iv)$$

Equation (i) is called **chain initiation step** while equation (ii) - (iv) are referred to as **chain propagation steps**. The termination steps, which involve combination of radicals, are as follows:
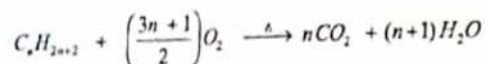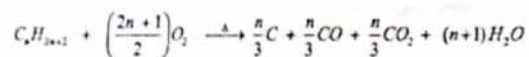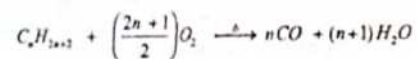
$$\overset{\bullet}{C}H_3 + H^\bullet \longrightarrow CH_4$$

$$H^\bullet + H^\bullet \longrightarrow H_2$$

$$\overset{\bullet}{C}H_2CH_3 + \overset{\bullet}{C}H_2CH_3 \longrightarrow CH_2=CH_2 + CH_3CH_3$$

$$\overset{\bullet}{C}H_2CHCH_3 + CH_3\overset{\bullet}{C}HCH_3 \longrightarrow CH_3CH=CH_2 + CH_3CH_2CH_3$$

(b) Combustion

Alkanes burn at high temperature in excess oxygen to produce carbon (IV) oxide and steam. The reaction is exothermic, for example,

$$C_2H_6 + \frac{7}{2}O_2 \xrightarrow{\;>600^\circ C\;} 2CO_{2(g)} + 3H_2O_{(g)}, \quad \Delta H = -x\,kJ\,mol^{-1}$$
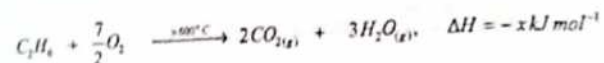
The generalized equation for combustion reaction of alkane is

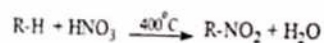$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \xrightarrow{\;\Delta\;} nCO_2 + (n+1)H_2O$$

If the supply of oxygen is deficient, the oxidation of alkane will produce carbon (II) oxide or even carbon in form of carbon black.

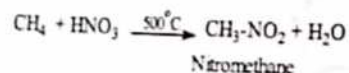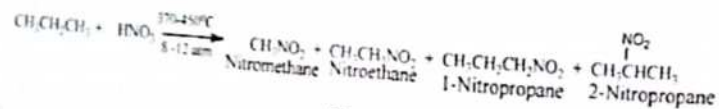$$C_nH_{2n+2} + \left(\frac{2n+1}{2}\right)O_2 \xrightarrow{\;\Delta\;} nCO + (n+1)H_2O$$

$$C_nH_{2n+2} + \left(\frac{2n+1}{2}\right)O_2 \xrightarrow{\;\Delta\;} \frac{n}{3}C + \frac{n}{3}CO + \frac{n}{3}CO_2 + (n+1)H_2O$$

(c) Nitration

Alkanes can be nitrated using nitric acid in the vapor phase at about 400°C or in the liquid phase.

$$R\text{-}H + HNO_3 \xrightarrow{\;400^\circ C\;} R\text{-}NO_2 + H_2O$$

A specific example is:

$$CH_4 + HNO_3 \xrightarrow{\;500^\circ C\;} CH_3\text{-}NO_2 + H_2O$$
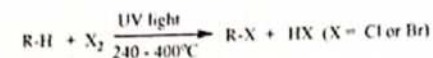$$\text{Nitromethane}$$

Nitration of alkanes occurs via a free-radical mechanism, forming nitroalkane. Reactions involving higher alkanes yield a mixture of smaller nitro products, which results from the cracking, or pyrolysis of the larger molecules. For example, nitration of propane with nitric acid in the vapor phase at a temperature range of 370–450°C and 8 - 12 atmosphere pressure yields a mixture of nitromethane, nitroethane, 1-nitropropane and 2-nitropropane, and these are readily separated by distillation.

$$CH_3CH_2CH_3 + HNO_3 \xrightarrow[\;8\text{-}12\,atm\;]{\;370\text{-}450^\circ C\;} CH_3\text{-}NO_2 + CH_3CH_2NO_2 + CH_3CH_2CH_2NO_2 + CH_3\overset{NO_2}{\underset{|}{C}}HCH_3$$
$$\text{Nitromethane} \quad \text{Nitroethane} \quad \text{1-Nitropropane} \quad \text{2-Nitropropane}$$
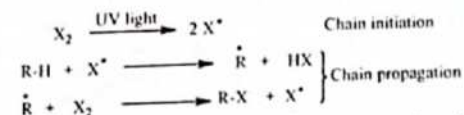
(d) Halogenation

The reaction of alkane with halogen is carried out mainly with chlorine or bromine in the presence of ultraviolet light or visible light.

$$R\text{-}H + X_2 \xrightarrow[\;240\text{ - }400^\circ C\;]{\;UV\ light\;} R\text{-}X + HX \quad (X = Cl\ or\ Br)$$

$$e.g.\quad CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

Mechanism of halogenation

It follows a free radical mechanism as we have in the pyrolysis reaction.

$$X_2 \xrightarrow{\;UV\ light\;} 2X^\bullet \qquad \text{Chain initiation}$$

$$\left.\begin{array}{l} R\text{-}H + X^\bullet \longrightarrow \overset{\bullet}{R} + HX \\ \overset{\bullet}{R} + X_2 \longrightarrow R\text{-}X + X^\bullet \end{array}\right\} \text{Chain propagation}$$
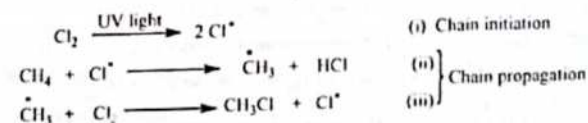
Chain propagation step may continue to give higher chlorinated products.

Consider the following examples.

Example 1

Chlorination of methane

$$Cl_2 \xrightarrow{\;UV\ light\;} 2Cl^\bullet \qquad\qquad\qquad \text{(i) Chain initiation}$$

$$\left.\begin{array}{l} CH_4 + Cl^\bullet \longrightarrow \overset{\bullet}{C}H_3 + HCl \\ \overset{\bullet}{C}H_3 + Cl_2 \longrightarro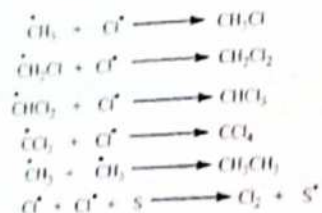w CH_3Cl + Cl^\bullet \end{array}\right\} \begin{array}{l} \text{(ii)} \\ \text{(iii)} \end{array} \text{Chain propagation}$$

Steps (ii) and (iii) are repeated further to give higher chlorinated products as follows:

$$CH_3Cl + Cl^\bullet \longrightarrow \overset{\bullet}{C}H_2Cl + HCl$$

$$\overset{\bullet}{C}H_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^\bullet$$

$$CH_2Cl_2 + Cl^\bullet \longrightarrow \overset{\bullet}{C}HCl_2 + HCl$$

$$\overset{\bullet}{C}HCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl^\bullet$$

$$CHCl_3 + Cl^\bullet \longrightarrow \overset{\bullet}{C}Cl_3 + HCl$$

$$\overset{\bullet}{C}Cl_3 + Cl_2 \longrightarrow CCl_4 + Cl^\bullet$$
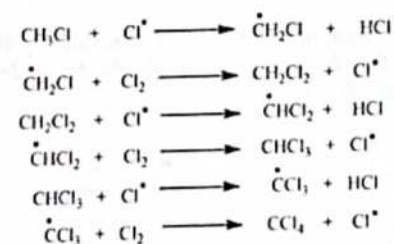
The chain termination steps involve reactions of free radicals generated.

$$\overset{\bullet}{C}H_3 + Cl^\bullet \longrightarrow CH_3Cl$$
$$\overset{\bullet}{C}H_2Cl + Cl^\bullet \longrightarrow CH_2Cl_2$$
$$\overset{\bullet}{C}HCl_2 + Cl^\bullet \longrightarrow CHCl_3$$
$$\overset{\bullet}{C}Cl_3 + Cl^\bullet \longrightarrow CCl_4$$
$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3CH_3$$
$$Cl^\bullet + Cl^\bullet + S \longrightarrow Cl_2 + S^\bullet$$

Example 2

Chlorination of propane

$$Cl_2 \longrightarrow 2Cl^\bullet \qquad \text{(i) Chain initiation}$$

$$CH_3CH_2CH_3 + Cl^\bullet \begin{cases} \longrightarrow CH_3CH_2\overset{\bullet}{C}H_2 + HCl \\ \longrightarrow CH_3\overset{\bullet}{C}HCH_3 + HCl \end{cases} \quad \text{(ii)}$$

$$CH_3CH_2\overset{\bullet}{C}H_2 + Cl_2 \longrightarrow CH_3CH_2CH_2Cl + Cl^\bullet \quad \text{(iii)}$$
$$CH_3\overset{\bullet}{C}HCH_3 + Cl_2 \longrightarrow CH_3CH(Cl)CH_3 + Cl^\bullet \quad \text{(iv)}$$
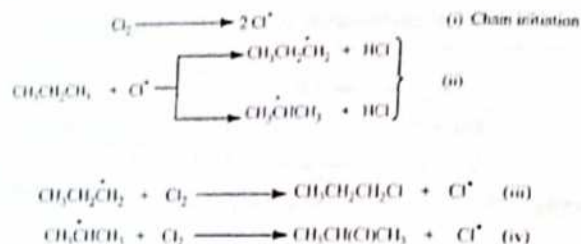
Steps (ii) - (iv) are the chain propagation steps.

The chain termination steps involve the reactions of free radicals generated.

$$CH_3CH_2\overset{\bullet}{C}H_2 + Cl^\bullet \longrightarrow CH_3CH_2CH_2Cl$$
$$CH_3\overset{\bullet}{C}HCH_3 + Cl^\bullet \longrightarrow CH_3CH(Cl)CH_3$$
$$CH_3CH_2\overset{\bullet}{C}H_2 + CH_3CH_2\overset{\bullet}{C}H_2 \longrightarrow CH_3(CH_2)_4CH_3$$
$$CH_3\overset{\bullet}{C}HCH_3 + CH_3\overset{\bullet}{C}HCH_3 \longrightarrow \begin{array}{c} H_2C-CH-CH_3 \\ | \\ H_3C-CH-CH_3 \end{array}$$
$$Cl^\bullet + Cl^\bullet + S \longrightarrow Cl_2 + S^\bullet$$
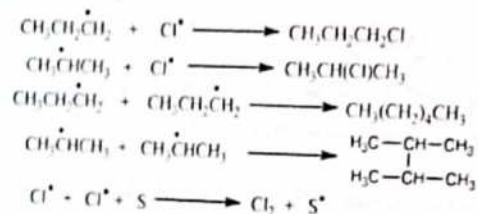
Other chlorinating agent is sulphuryl chloride i.e SO_2Cl_2. Haloalkane is produced when alkane is refluxed with sulphur dichloridedioxide at 40-80°C using di(benzenecarbonyl) peroxide as a catalyst.

$$R\text{-}H + SO_2Cl_2 \xrightarrow[\substack{40\text{-}80°C}]{Peroxide\ cat} RCl + HCl + SO_2$$
$$\text{Haloalkane}$$

A specific example is:

$$CH_3(CH_2)_2CH_3 + SO_2Cl_2 \xrightarrow[\substack{60°C}]{Peroxide\ cat} CH_3(CH_2)_2CH_2Cl + HCl + SO_2$$
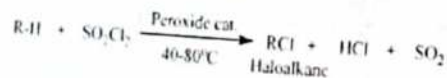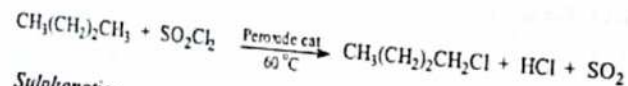
(e) **Sulphonation**

Concentrated tetraoxosulphate (VI) acid (H_2SO_4) does not react appreciably with alkanes at ordinary temperature, but fuming tetraoxosulphate (VI) acid (oleum) reacts

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with higher molecular mass alkanes particularly those containing tertiary carbon atoms, yielding sulphonic acid.

$$RH + H_2SO_4.SO_3 \longrightarrow RSO_3H + H_2SO_4$$

A specific example:

$$(CH_3)_3CH + H_2SO_4.SO_3 \longrightarrow (CH_3)_3C\text{-}SO_3H + H_2SO_4$$

A preferred method for obtaining alkane sulphonic acids from alkanes consists of treating the hydrocarbon with a mixture of chlorine and sulphur (IV) oxide

$$RH + Cl_2 + SO_2 \longrightarrow RSO_2Cl + HCl$$

The alkyl sulphonyl chloride produced is soluble in water

$$RSO_2Cl + H_2O \longrightarrow RSO_3H + HCl$$

A specific example is,

$$CH_3CH_2CH_3 + Cl_2 + SO_2 \longrightarrow CH_3CH_2CH_2SO_2Cl + HCl$$
$$CH_3CH_2CH_2SO_2Cl + H_2O \longrightarrow CH_3CH_2CH_2SO_3H + HCl$$
$$\text{Propylsulphonic acid}$$
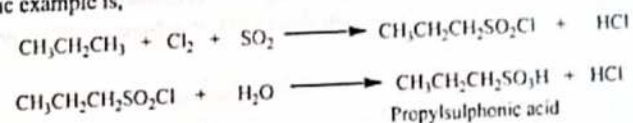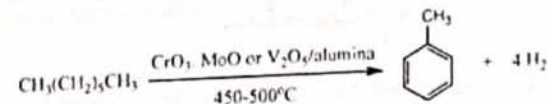
(f) **Dehydrogenation**

Higher alkane members undergo dehydrogenation reaction when treated with chromic (VI) oxide, molybdenum (II) oxide, or vanadium (V) oxide on alumina at 450 - 500° C to give aromatic hydrocarbon.

$$CH_3(CH_2)_5CH_3 \xrightarrow[\substack{450\text{-}500°C}]{CrO_3,\ MoO\ or\ V_2O_5/alumina} \underset{\text{toluene}}{\bigcirc}CH_3 + 4H_2$$

VII. Alkenes

These form homologous series of unsaturated hydrocarbons containing one carbon-carbon double bond (>C=C<) which is the functional group. The general molecular formula is C_nH_{2n}. The unsaturated carbon atoms are sp^2 hybridized and are bonded to each other by a sigma bond and a pi (π) bond (already discussed in part one).
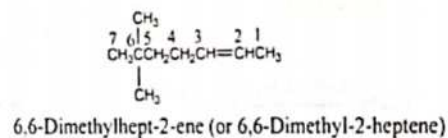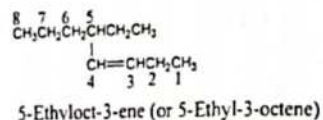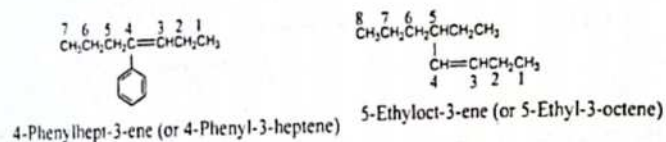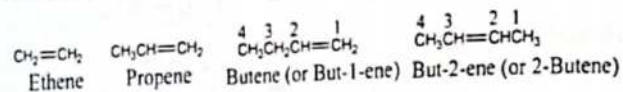
Alkadienes

These are unsaturated hydrocarbons that contain two carbon-carbon double bond units and possess molecular formula, C_nH_{2n-2}, examples include;

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CH₃CH₂CH =C=CH₂, Penta-1,2-diene (called **Cumulative diene**)
CH₃CH = CHCH = CH₂, Penta-1,3-diene (called **Conjugated diene**)
CH₂=CHCH₂CH=CH₂, Penta-1,4-diene (called **Isolated diene**)
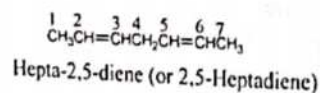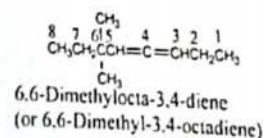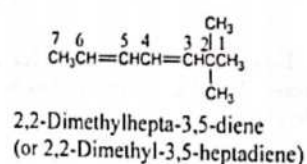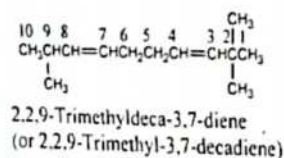
Nomenclature

1. The I.U.P.A.C system of naming these classes of homologous series is similar to alkanes but with ending "-ene", and the position of the double bond is indicated by a number.

2. The longest carbon chain containing the double bond is determined.

3. Numbering of the parent hydrocarbon should begin from the end of the carbon chain that is closest to the functional group.

4. The position of the double bond is indicated by the number of the lower numbered carbon atom containing the double bond.

Consider the following examples:

$CH_2=CH_2$ $CH_3CH=CH_2$ $\overset{4\ 3\ 2\ 1}{CH_2CH_2CH=CH_2}$ $\overset{4\ 3\ 2\ 1}{CH_3CH=CHCH_3}$
Ethene   Propene   Butene (or But-1-ene) But-2-ene (or 2-Butene)

$\overset{7\ 6\ 5\ 4\ 3\ 2\ 1}{CH_3CH_2CH_2C=CHCH_2CH_3}$

4-Phenylhept-3-ene (or 4-Phenyl-3-heptene)

$\overset{8\ 7\ 6\ 5}{CH_3CH_2CH_2CHCH_2CH_3}$
$\overset{|}{CH=CHCH_2CH_3}$
${4\ 3\ 2\ 1}$

5-Ethyloct-3-ene (or 5-Ethyl-3-octene)

$\overset{\ \ \ \ CH_3}{\underset{|}{\overset{7\ 6|5\ 4\ 3\ \ 2\ 1}{CH_3CCH_2CH_2CH=CHCH_3}}}$
CH_3

6.6-Dimethylhept-2-ene (or 6,6-Dimethyl-2-heptene)

The following examples illustrate the system of naming the alkadienes.

$\overset{10\ 9\ 8\ \ 7\ 6\ 5\ \ 4\ \ 3\ 2|1}{CH_3CHCH=CHCH_2CH_2CH=CHCCH_3}$
${|}$
CH_3

2.2.9-Trimethyldeca-3,7-diene
(or 2.2.9-Trimethyl-3,7-decadiene)

$\overset{7\ 6\ \ 5\ 4\ \ 3\ 2|1}{CH_3CH=CHCH=CHCCH_3}$
${|}$
CH_3

2,2-Dimethylhepta-3,5-diene
(or 2,2-Dimethyl-3,5-heptadiene)

$\overset{\ \ \ CH_3}{\underset{|}{\overset{8\ 7\ 6|5\ \ 4\ 3\ 2\ 1}{CH_3CH_2CCH=C=CHCH_2CH_3}}}$
CH_3

6.6-Dimethylocta-3,4-diene
(or 6,6-Dimethyl-3,4-octadiene)

$\overset{1\ 2\ \ 3\ 4\ 5\ \ 6\ 7}{CH_3CH=CHCH_2CH=CHCH_3}$

Hepta-2,5-diene (or 2,5-Heptadiene)

Structural Isomerism in Alkenes

They undergo positional isomerism and sometimes geometrical isomerism due to prevention of free rotation about the carbon-carbon double bond (refer to part one). Ethene and propene have no structural isomers. Higher alkenes have a progressively greater number of isomers corresponding to these two categories of isomerisms as shown by the following example.

Isomers of butene, C_4H_8

$CH_3CH_2CH=CH_2$ $CH_3CH=CHCH_3$ $CH_3C(CH_3)=CH_2$
But-1-ene   But-2-ene   2-Methylpropene
(i)   (ii)   (iii)
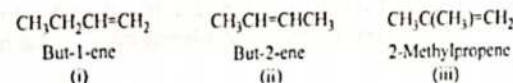
Other two stereoisomers of this compound are:

cis-but-2-ene   trans-but-2-ene

Physical properties

The lower alkenes and alkadienes, which have up to five carbon atoms, are gases at room temperature and pressure. Higher alkenes are colorless liquids or solids. Like other hydrocarbons, alkenes are insoluble in water but soluble in non-polar organic solvents such as trichloromethane (chloroform), ethoxyethane (ether), benzene etc.

Laboratory preparation of Alkenes

The laboratory preparations of alkenes involve elimination reactions, which include the following:

1. *Dehydrohalogenation*

This involves elimination of hydrogen halide from an alkylhalide.

$$CH_3-CH-CH_2 \xrightarrow{KOH/CH_3OH} CH_3CH=CH_2 + HCl$$
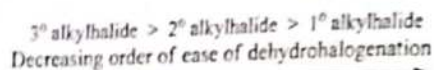$$Propene$$
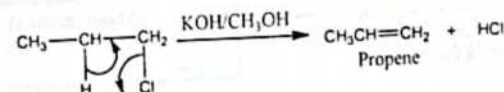
For secondary and tertiary alkylhalides, mixtures of alkenes are usually produced, and their relative proportion (or yield) depends on the respective stability of the individual alkenes produced. The stable product is the one with higher number of hydrogen atoms on the α-carbon atoms (α carbon atom is the carbon atom that is directly bonded to the carbon atoms containing the double bond) or with greater number of alkyl groups bonded to the carbon atoms containing the double bond (Zaytsev's rule). Zaytsev's rule states that "in elimination reactions, the major reaction product is the alkene with the more highly substituted (more stable) double bond.
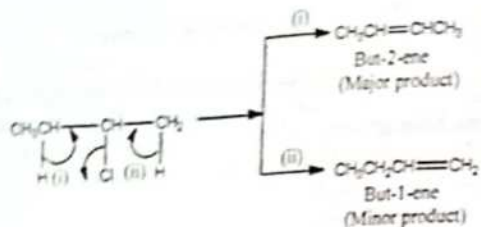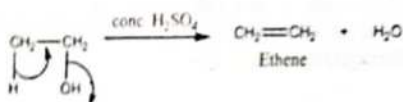
But-2-ene is the major product because it has more hydrogen atoms on the α-carbon atoms (6 hydrogen atoms) and hence more stable, whereas but-1-ene has two hydrogen atoms on the α-carbon atom.

The ease of dehydrohalogenation of alkylhalide is:

$$3° \text{ alkylhalide} > 2° \text{ alkylhalide} > 1° \text{ alkylhalide}$$
Decreasing order of ease of dehydrohalogenation

2. Dehydration

This involves removal of water from alcohol using concentrated tetraoxosulphate (VI) acid (H_2SO_4) as dehydrating agent.

For secondary and tertiary alcohols, mixtures of alkenes are usually produced, and their relative proportion (yield) depends on the respective stability of individual alkenes produced. For example,
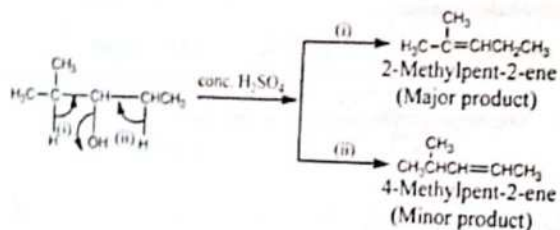
2-Methylpent-2-ene is the major product because it has more hydrogen atoms on the α-carbon atoms (i.e. 8 hydrogen atoms) and hence more stable, whereas 4-Methylpent-2-ene has four hydrogen atoms on the α-carbon atoms. The ease of dehydration of alcohols follows the order:

$$3° \text{ alkylhalide} > 2° \text{ alkylhalide} > 1° \text{ alkylhalide}$$
Decreasing order of ease of dehydration
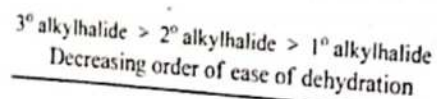
3. Reduction of alkenyl halides
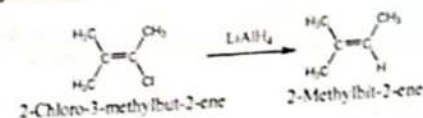
4. Partial hydrogenation of alkynes

Controlled hydrogenation of alkyne using platinum as catalyst or sodium or lithium in liquid ammonia gives alkene.
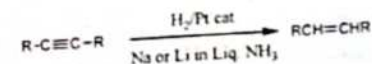
Industrial Preparations

Large quantities of alkenes are obtained by large scale industrial cracking and dehydration processes.
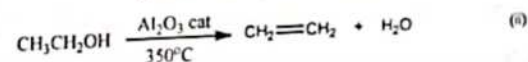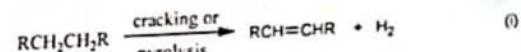
Reaction (i) is a cracking process while reaction (ii) is a dehydration process.

Chemical Reactions

Alkenes are very reactive in comparison with alkanes. The pi (π) electrons of carbon-carbon double bond act as an electron source, and make alkene weak nucleophile. Alkenes undergo mainly addition reactions. The addition may occur by electrophilic, nucleophilic or free radical (already discussed in Part One), however their typical reaction is electrophilic addition.

Electrophilic addition reaction
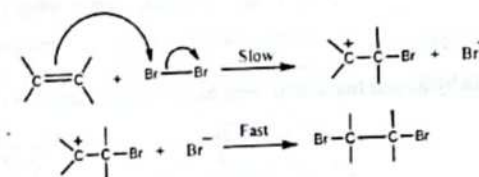
The electrophilic addition leads to formation of electron-deficient carbocation intermediate.

Nucleophilic addition reaction

The nucleophilic addition reaction takes place when an electron-withdrawing group (e.g -COCH₃) is attached to the alkene. This will initiate the attack of nucleophile.
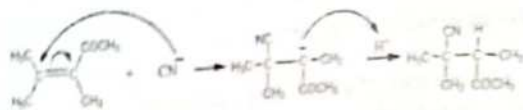
Free radical addition reaction
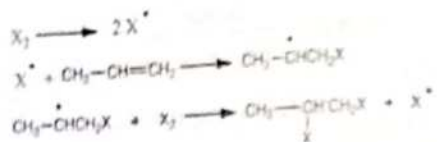
Alkenes generally undergo the following addition reactions:
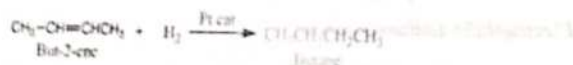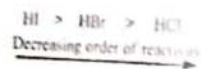
(a) Halogenation

A specific example:
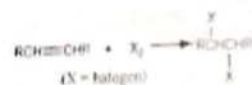
2-Methylpent-2-ene
(or 2-Methyl-2-pentene)   2,3-Dichloro-2-methylpentane
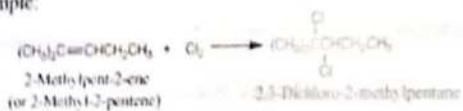
(b) Hydrogenation

Alkenes are converted to the corresponding alkanes by catalytic hydrogenation. The usual catalyst can be finely divided platinum, palladium or nickel.

Example:

But-2-ene   Butane

(c) Addition of hydrogen halides

Alkenes react with hydrogen halides to form haloalkanes. The order of reactivity is;

$$HI > HBr > HCl$$
Decreasing order of reactivity

Examples:

But-2-ene → 2-Chlorobutane

$$CH_3CH_2CH_2CH=CH_2 + HCl \longrightarrow CH_3CH_2CH_2CH_2CH_2Cl + CH_3CH_2CH_2CH(Cl)CH_3$$

But-1-ene   Chloropentane   2-Chloropentane
                                       Major product
                                       (or Markovnikov's product)
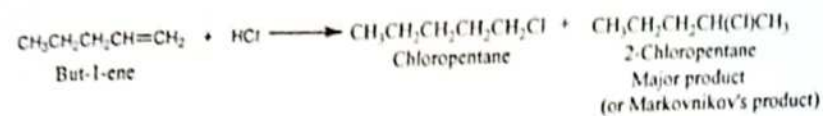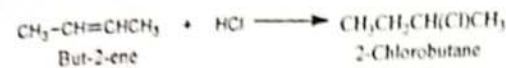
(d) Addition of hypohalous acids

Hypohalous acid (also known as bromine, chlorine or iodine water), is formed when bromine, chlorine or iodine dissolves in water.

$$H_2O + Br_2 \longrightarrow HOBr + HBr$$
Bromic(1) acid
(Hypobromous acid)

$$H_2O + Cl_2 \longrightarrow HOCl + HCl$$
Chloric(1) acid
(Hypochlorous acid)

$$H_2O + I_2 \longrightarrow HOI + HI$$
Iodic(1) acid
(Hypoiodous acid)
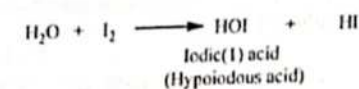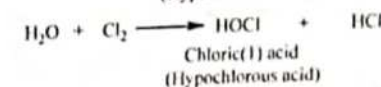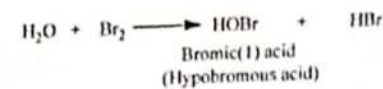
The hypohalous acids add readily to alkenes, forming haloalcohols ("halohydrins").

The HOX polarizes as:

$$\overset{\delta-}{HO}-\overset{\delta+}{X} \quad (X = Cl, Br \text{ or } I).$$

Examples:

$$CH_2=CH_2 + HOBr \longrightarrow CH_2(Br)-CH_2OH$$
Ethene   2-Bromoethanol

$$CH_3CH=CH_2 + HOCl \longrightarrow CH_3CH(Cl)CH_2OH + CH_3CH(OH)CH_2Cl$$
Propene   2-Chloropropan-1-ol   1-Chloropropan-2-ol
                                          Major product
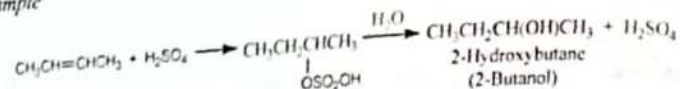   (or Markovnikov's product)
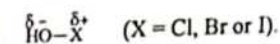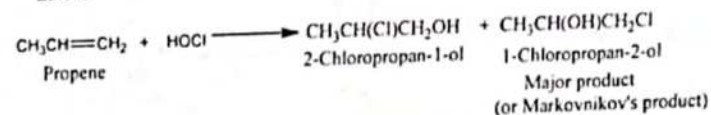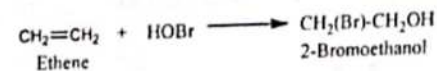
(e) Addition of tetraoxosulphate (VI) acid (H₂SO₄)

Alkenes dissolve in concentrated tetraoxosulphate (VI) acid to form alkylhydrogensulphates, which are hydrolysed by water to alcohols.
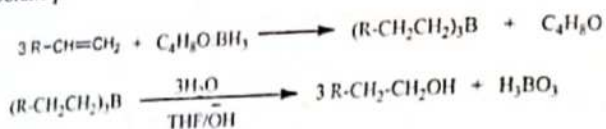
Example

$$CH_3CH=CHCH_3 + H_2SO_4 \longrightarrow CH_3CH_2CHCH_3 \xrightarrow{H_2O} CH_3CH_2CH(OH)CH_3 + H_2SO_4$$
$$\underset{OSO_2OH}{|} \quad \text{2-Hydroxybutane}$$
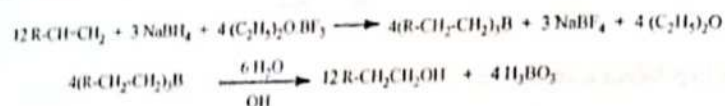$$\text{(2-Butanol)}$$
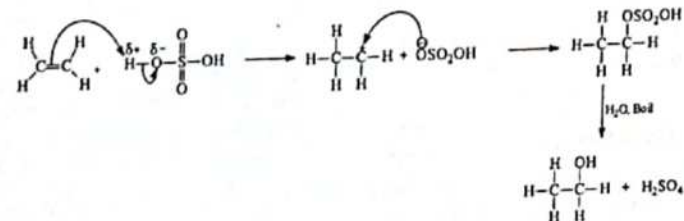
(f) Hydroboration

Diborane is highly soluble in tetrahydrofuran (THF), where it exists as the addition compound, tetrahydrofuran-borane. Such solutions are used for hydroboration, and merely involve bringing the two reactants together as indicated below; and the trialkylborane produced can be oxidized with peroxide, H_2O_2, to give a primary alcohol.

$$3\,R-CH=CH_2 + C_4H_8O\,BH_3 \longrightarrow (R-CH_2CH_2)_3B + C_4H_8O$$

$$(R-CH_2CH_2)_3B \xrightarrow[THF/OH]{3H_2O} 3\,R-CH_2-CH_2OH + H_3BO_3$$

Alternatively, sodium borohydride may be utilized to achieve hydroboration by addition of ethereal solution of boron trifluoride.

$$12\,R-CH-CH_2 + 3\,NaBH_4 + 4\,(C_2H_5)_2O\,BF_3 \longrightarrow 4(R-CH_2-CH_2)_3B + 3\,NaBF_4 + 4\,(C_2H_5)_2O$$

$$4(R-CH_2-CH_2)_3B \xrightarrow[OH]{6\,H_2O} 12\,R-CH_2CH_2OH + 4\,H_3BO_3$$

(g) Hydroxylation

Hydroxylation of alkene may be performed by using osmium (VIII) oxide (osmium tetraoxide), OsO_4 in ether solution to form a cyclic osmate ester, which is hydrolyzed to a 1,2-diol with aqueous sodium trioxosulphate (IV) (or sodium sulphite).

Example
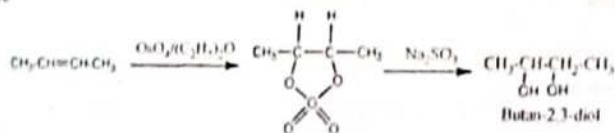
Potassium manganate (VII) ($KMnO_4$), hydrogen peroxide in ethanoic (acetic) acid; (H_2O_2/CH_3COOH) and benzeneperoxocarboxylic (peroxobenzoic) acid (C_6H_5COOOH) give the same end product, a diol.

Example
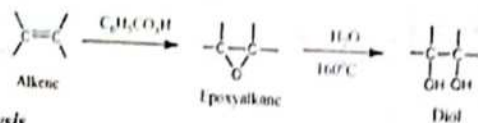
(h) Ozonolysis

Ozone, O_3, reacts rapidly with alkenes to form ozonides, in which both pi (π) and sigma (σ) bonds have been ruptured. The ozonides are unstable, and are usually

decomposed by reduction with zinc and acetic acid giving two carbonyl compounds.

Example
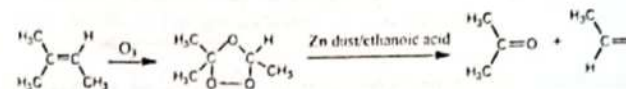
Identification of ozonolysis products helps in locating the position of a double bond in alkene molecules.

(i) Addition of alkanes

Alkanes add across alkenes to form a higher alkane in the presence of an acid catalyst.
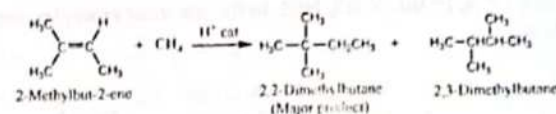
(j) Polymerization of alkenes

At high temperature and pressure and in the presence of catalysts, alkene molecules link up by repeated additions to form long chains called polymers. Polyethene (polythene) is manufactured by using peroxide catalyst.
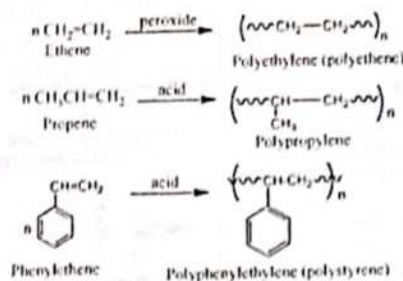
Alkene polymers are widely used as plastic materials, roofing sheet, foam products etc.
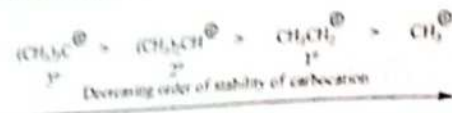
Markovnikov's Rule

The rule states that:

"In the addition of an unsymmetrical reagent to an unsymmetrical alkene, the more electronegative atom or group becomes bonded to the more highly substituted carbon atom, that is, the carbon atom containing fewer hydrogen atoms."
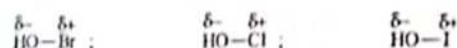
When the double bond is unsymmetrically substituted, two products are possible, and the ratio of the two products formed depends on the relative stability of the electron-deficient carbocation. The stability of a carbocation is enhanced by its attachment to electron-donating groups, which exert inductive effect (i.e. +I effect). Generally, the greater the number of alkyl groups present, the more stable is the

$$(CH_3)_3C^{\oplus} > (CH_3)_2CH^{\oplus} > CH_3CH_2^{\oplus} > CH_3^{\oplus}$$
$$\quad\quad 3° \quad\quad\quad 2° \quad\quad\quad 1°$$

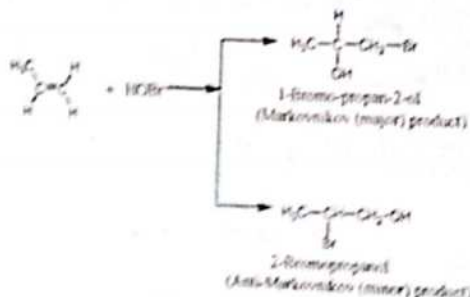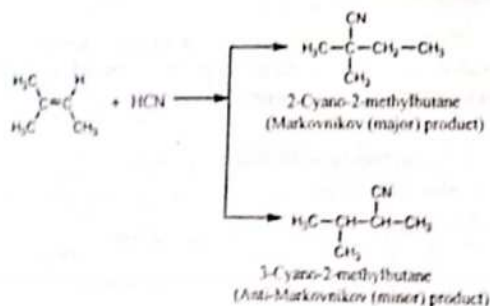Decreasing order of stability of carbocation →

The more stable carbocation forms the more stable product, and hence the major product, which is called the *Markovnikov's product*, while the less stable carbocation forms the less stable product, and hence the minor product, which is called *anti-Markovnikov's product*. Hence a more modern statement of Markovnikov's rule is "In the ionic addition of an unsymmetrical reagent to an unsymmetrical alkene, the positive part of the adding reagent gets bonded to a carbon of the double bond so as to yield more stable carbocation".

The unsymmetrical reagents, which obey Markovnikov's rule, are HBr, HCl, HI, HF, H_2SO_4, H_2O, HCN, HOBr, HOCl, HOI. In the last three examples, the polarization of the reagents is:

$$\overset{\delta-}{HO}-\overset{\delta+}{Br} \; ; \qquad \overset{\delta-}{HO}-\overset{\delta+}{Cl} \; ; \qquad \overset{\delta-}{HO}-\overset{\delta+}{I}$$

Examples:

H₃C—C(CN)(CH₃)—CH₂—CH₃
2-Cyano-2-methylbutane
(Markovnikov (major) product)

H₃C—CH(CN)—CH(CH₃)—CH₃
3-Cyano-2-methylbutane
(Anti-Markovnikov (minor) product)

1-Bromo-propan-2-ol
(Markovnikov (major) product)

2-Bromopropanol
(Anti-Markovnikov (minor) product)

Stability of alkenes

The greater the electron density around a double bond, the more susceptible it will be to electrophilic attack.

(i) *Electron-donating substituents:*

Electron-donating groups like alkyl, increase the rate of electrophilic addition by

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increasing the electron density on the double bond. The carbocation intermediate formed in the transition state is stabilized by the alkyl groups, and hence lowering the activation energy of the reaction. Therefore the more highly alkylated alkenes undergo addition reaction at a greater rate than their less highly substituted counterparts. The relative rates at which alkylated alkenes undergo addition reaction decreases in the order:

$$R_2C=CR_2 > R_2C=CHR > RCH=CHR \approx R_2C=CH_2 > RCH=CH_2 > CH_2=CH_2$$

Decreasing order of rate of addition reaction of alkylated alkenes →
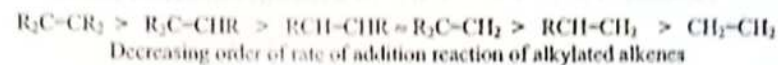
Other electron donating groups that have similar effects like alkyl groups are aryl, -C≡C-, RO-, R_2N-.

(ii) Electron-withdrawing substituents

Electron-withdrawing substituents like Halogen, >C = O, $-CO_2H$, -CN, $-NO_2$ and SO_3H decrease the rate of electrophilic addition reaction by lowering electron density on the double bond, and cause instability of the carbocation intermediate formed at the transition state, thereby raising the activation energy.

Anti-Markovnikov product may be obtained as a result of one or more of the following factors:
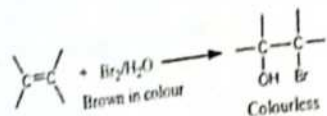
1. The presence of strong electron-withdrawing substituents, such as $-NO_2$ attached to a highly substituted carbon atom; e.g.

2-Nitropropene

1-Chloro-2-nitropropane
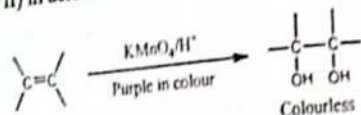(Anti-Markovnikov product)
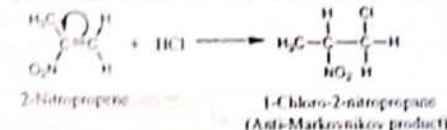
2. Steric hindrance preventing the completion of the reaction by the attachment of a larger, more electronegative species at a highly substituted carbon atom.

3. Addition may take place via a free-radical mechanism, particularly when the reaction is carried out at high temperatures or when organic peroxides, e.g. di(benzenecarbonyl) peroxide and (di(benzoyl) peroxide are present.

Simple Tests for Unsaturation

(1) Unsaturated compounds burn with a luminous, smoky flame, it is also a characteristic property of aromatic compounds.

(2) Unsaturated compounds decolorize brownish color of bromine in water or in tetrachloromethane by the formation of the addition product.

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$$\underset{\text{Brown in colour}}{\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + Br_2/H_2O} \longrightarrow \underset{\text{Colourless}}{-\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{Br}{C}}-}$$

(3) Unsaturated compounds also decolorize the purple color of potassium manganate (VII) in acidic solution by the formation of the addition product.

$$\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} \xrightarrow[\text{Purple in colour}]{KMnO_4/H^+} \underset{\text{Colourless}}{-\overset{|}{\underset{OH}{C}}-\overset{|}{\underset{OH}{C}}-}$$

The depolarization of potassium manganate (VII) also occurs with other reducing agents, such as sulphur (IV) oxide.

The role of simple alkenes in the petrochemical industry

Petrochemicals are chemicals produced from petroleum or natural gas. The main focus of the petroleum industry is the production of liquid fuels and lubricants. However, alongside the production of liquid fuels, there has emerged an industry that has its focus on the large scale production of pure organic compounds. These materials are converted by one or more chemical reactions into more marketable products for chemicals rather than fuel or lubricants.

The abundant supply of simple alkenes from cracking of petroleum and natural gas makes them one of the most important starting reagents for large-scale industrial processes. Ethene, propene and butene are important source of a large number of materials.

Ethene
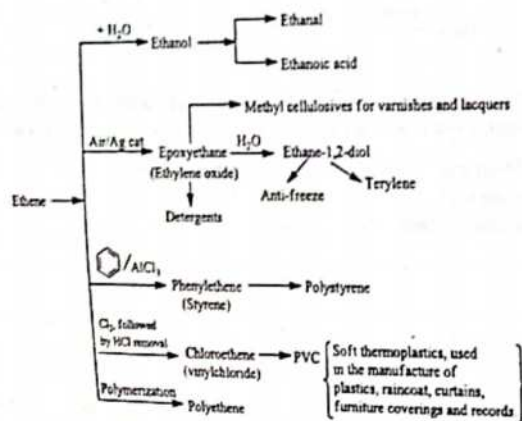
The chemical equations representing the reactions shown in the above chart are:

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(i)

$$CH_2=CH_2 + H_2O \xrightarrow[30^\circ C, 68\text{-}70\text{ atm}]{H_3PO_4\text{ on celite cat}} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[\text{heat}]{[O]} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{[O]} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

(ii)

$$CH_2=CH_2 \xrightarrow{[O]} \underset{O}{\overset{H_2C-CH_2}{\triangle}} \xrightarrow[\text{dil H}^+]{\text{steam}} \underset{\underset{\text{Ethan-1,2-diol}}{OH \quad OH}}{CH_2-CH_2}$$

$$\downarrow \begin{array}{c} + CH_3OH, \\ H_2SO_4 \text{ cat} \end{array}$$

$$\underset{\underset{\text{Methylcellulosive}}{OH \quad OCH_3}}{CH_2-CH_2}$$
(useful solvents for varnishes and lacquers)

(iii)

$$CH_2=CH_2 + Cl_2 \longrightarrow \underset{\text{1,2-Dichloroethane}}{ClCH_2CH_2Cl} \xrightarrow[500^\circ C]{\text{Heat}} \underset{\text{Chloroethene}}{CH_2=CHCl} + HCl$$

$$n\,CH_2=CHCl \xrightarrow[\text{initiator}]{\text{peroxide}} \underset{\underset{\text{(or Polyvinylchloride, PVC)}}{\text{Polychloroethene}}}{\sim(CH_2-CH(Cl)CH_2CH(Cl))_n\sim}$$

(iv)

$$CH_2=CH_2 + \bigcirc \xrightarrow{AlCl_3 \text{ cat}} \underset{\text{Ethylbenzene}}{\bigcirc^{CH_2CH_3}} \xrightarrow[650^\circ C]{Fe_2O_3/Cr_2O_3} \underset{\underset{\text{(Styrene)}}{\text{Phenylethene}}}{\bigcirc^{CH=CH_2}}$$

(v)

$$n\,CH_2=CH_2 \xrightarrow[1,500\text{ atm}, 200^\circ C]{O_2 \text{ initiator}} \underset{\text{Polyethene}}{\{CH_2CH_2CH_2CH_2\}_n}$$

$$n\,\overset{CH=CH_2}{\bigcirc} \xrightarrow{\text{Polymerize}} \underset{\text{Polystyrene}}{\{CH-CH_2\}_n^{\bigcirc}}$$
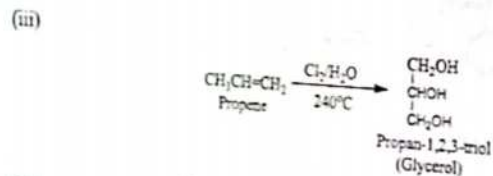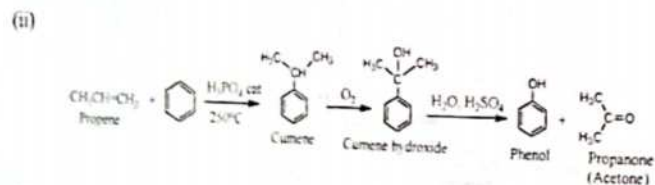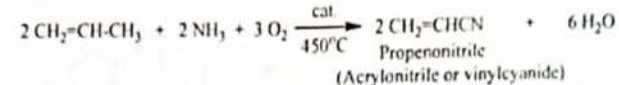
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Propene

The chemical equations for the reactions shown on the above chart are:

(i)
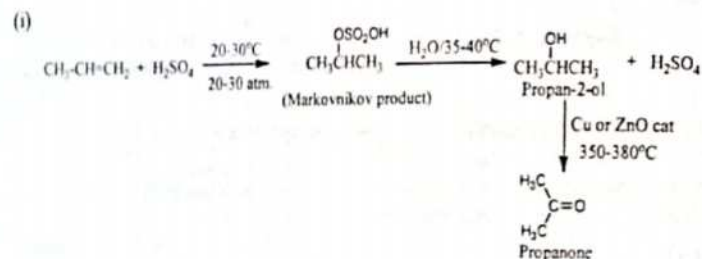
Propanone is an important solvent and it is used in the manufacturing of haloforms and 'Perspex'

(ii)

(iii)

(iv)

(v)

$$2\,CH_2=CH\text{-}CH_3 + 2\,NH_3 + 3\,O_2 \xrightarrow[450^\circ C]{cat.} 2\,CH_2=CHCN + 6\,H_2O$$
Propenenitrile
(Acrylonitrile or vinylcyanide)
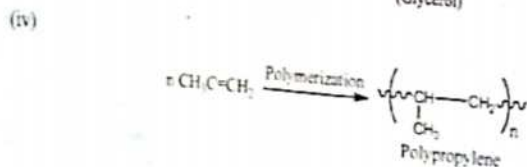
Chemical reactions of conjugated dienes

Conjugated dienes are unique in that both ethylenic linkages in general react as a single unit, in contradistinction to the cumulative and isolated dienes, which can react in an independent manner. They undergo 1, 2 and 1,4 additions, giving *trans* products, but the 1,4 addition of the type below (termed conjugated addition) are the most common for conjugated diene.
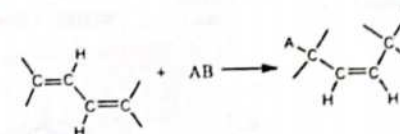
They undergo the following reactions

(a)   *Hydrobromination (addition of hydrogen bromide)*
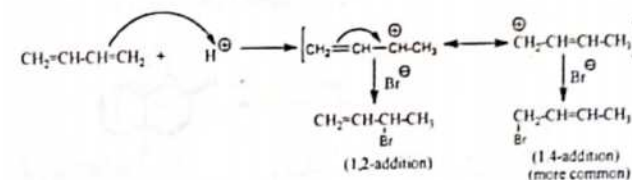
The relative yields of the two products depend on the reaction conditions. High temperatures and polar solvents tend to favor 1,4 -addition while at low temperatures, and in non-polar solvents, 1,2-addition predominates.

(b)   *Diels-Alder reactions*

This is the 1,4-addition of an alkene (the dienophile) to a conjugated diene. The rate of addition is increased by electron-donating groups like alkyls, aryls etc. in the diene and electron-withdrawing groups like -C=O and -C≡ N in the dienophile (diene lover). The following are the examples of Diel-Alder reactions:

(i)

(ii)

Diene
(2,3-dimethyl
buta-1,3-diene)

Dienophile
(Naphthalene-1,4-dione)

(4aR,9aS)-2,3-dimethyl-1,4,4a,9a-tetrahydro
anthracene-9,10-dione

(iii)

Diene
(Cyclopenta-1,3-diene)

Dienophile
(Ethene)

Bicyclo[2.2.1]hept-2-ene

(iv)

Dienophile
(Cyclohexa-3,5-diene
-1,2-dione)

Diene
(Cyclohexa-3,5-diene
-1,2-dione)

1,4,4a,8a-tetrahydro-1,4-ethano
naphthalene-5,6,9,10-tetraone

(v)

Dienophile
(Cyclohexa-3,5-
diene-1,2-dione)

Diene
(Cyclopenta-1,3-diene)

(4aS,8aR)-1,4,4a,8a-tetrahydro-1,4-
methanonaphthalene-5,6-dione

(vi)

Diene
(2,3-dimethyl
buta-1,3-diene)

Dienophile
(4-oxopent-2-ynenitrile)

2-acetyl-4,5-dimethyl
cyclohexa-1,4-dienecarbonitrile

Most common dienophiles consist of compounds containing structure >C = C< or –C ≡ C–. However dienophiles are not restricted to unsaturated carbon compounds and adducts formed with >C = N–, –C ≡ N, –N = N–, and –N = O could also be the dienophile components. The following are some examples:

(vii)

Diene
(Buta-1,3-diene-2,3-
diyldibenzene)

Dienophile
(Propionyl cyanide)

1,4,5-diphenyl-3,6-dihydropyridin-2-yl)
propan-1-one

(viii)

Diene
(3-Methylenepent-1-ene)

Dienophile
((Z)-2-phenylethenol)

4-Ethyl-6-phenyl-5,6-
dihydropyridin-1(2H)-ol

(ix)

Diene
(2-methyl-3-methylene
pent-1-ene)

Dienophile
((Z)-1,2-diphenyldiazene)

4-Ethyl-5-methyl-1,2-diphenyl-
1,2,3,6-tetrahydropyridazine
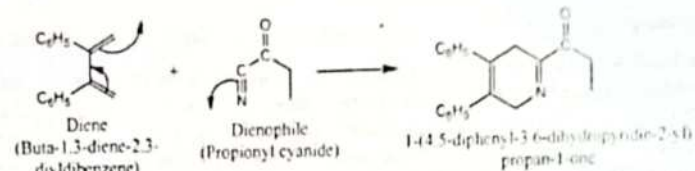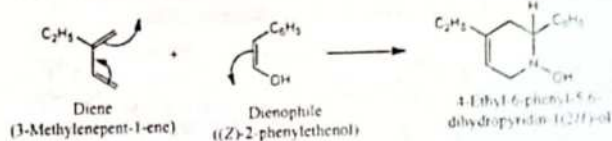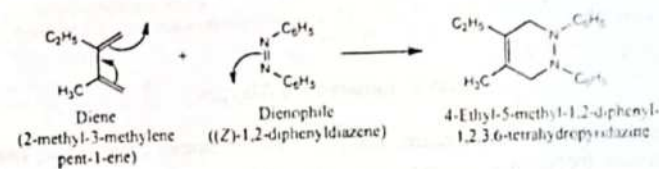
The Diels-Alder reaction is reversible, thus, the product (called an adduct) can be heated to regenerate the original diene and dienophile.
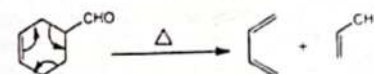
Such reverse reactions are called **retro-Diels-Alder** reactions. The Diels-Alder reaction is also a syn-addition reaction.

Buta-1,3-diene   Malealdehyde   (1R,2S)-cyclohex-4-ene-
1,2-dicarbaldehyde
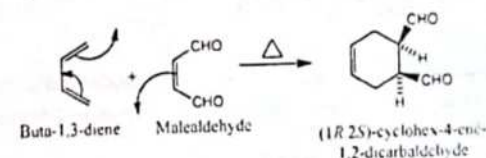
VIII. Alkynes

The alkynes form a homologous series of unsaturated hydrocarbons containing a carbon-carbon triple bond (–C≡C–), which is the functional group. They correspond to a general molecular formula, C_nH_{2n-2}. This is the same molecular formula that alkadienes possess, however, the chemical and physical properties of alkadienes and alkynes are quite different, and thus it is quite easy to distinguish between these classes of compounds. The unsaturated carbon atoms are *sp* hybridized and attached to each other by a sigma (σ) bond and two pi (π) bonds (refer to part one). The simplest alkyne is ethyne, C_2H_2, which is more commonly called acetylene.

Nomenclature

The I.U.P.A.C. system of naming this class of homologous series is similar to corresponding alkanes but replacing the ending "-ane" of the alkane with the suffix "-yne". The position of the triple bond is indicated by inserting the appropriate number between the stem and the ending. Also the position of the triple bond is indicated by the number of the lower numbered carbon atom containing the triple bond. Numbering of the parent hydrocarbon should begin from the end of the carbon chain that is closest to the functional group ($-C\equiv C-$). Consider the following examples:

$$CH_3-C\equiv CH$$
Propyne

5-Methyl-5-phenylhept-3-yne
(or 5-Methyl-5-phenyl-3-heptyne)

4,4-Dimethylhept-2-yne
(or 4,4-Dimethyl-2-heptyne)
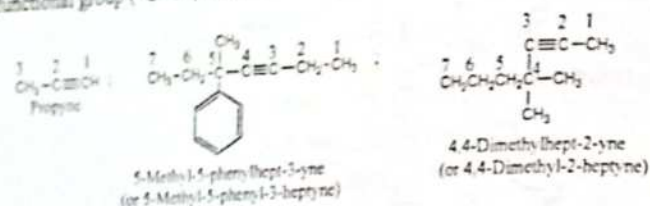
Structural Isomerism in Alkynes

They undergo positional isomerism. There is only one isomer for propyne; two for butyne and three for pentyne.

For propyne

$$CH_3-C\equiv CH$$
Propyne

For butyne

$$CH_3-CH_2-C\equiv CH$$
But-1-yne (or 1-Butyne)
(i)

$$CH_3-C\equiv C-CH_3$$
But-2-yne (or 2-Butyne)
(ii)

For pentyne

$$CH_3CH_2CH_2C\equiv CH;$$
Pent-1-yne
(i)

$$CH_3CH(CH_3)C\equiv CH;$$
3-Methylbut-1-yne
(ii)

$$CH_3CH_2C\equiv C-CH_3$$
Pent-2-yne (or 2-Pentyne)
(iii)
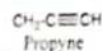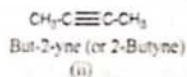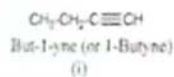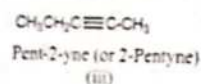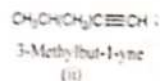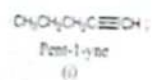
Physical properties

Boiling points increase with increasing molecular mass. The alkynes are virtually insoluble in water but soluble in the non-polar organic solvents.

Synthetic preparations of alkynes

The synthetic preparations of alkynes are as follows:

1. *Dehydrohalogenation of α, β-dihaloparaffins*
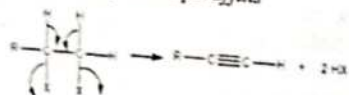
The dihalide can be vicinal (vic.) or geminal (gem.)

2. *From aldehydes or ketones*

Conversion of aldehydes or ketones to dihaloparaffins with subsequent dehydrohalogenation.

$$RCH_2CHO \xrightarrow[\text{(ii) NaX}]{\text{(i) HX}} RCH_2CHX_2 \longrightarrow R-C\equiv CH + 2HX$$
Aldehyde — gem-dihalide

$$RCOCH_3 \xrightarrow[\text{(ii) NaX}]{\text{(i) HX}} RC(X)_2CH_3 \longrightarrow R-C\equiv CH + 2HX$$
Ketone
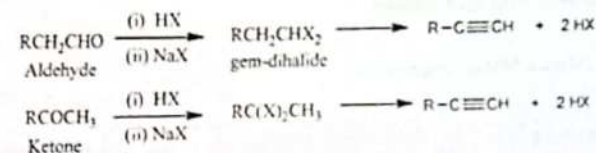
3. *Alkylation of metallic acetylides with alkylhalides in liquids ammonia*

$$RC\equiv \overset{\delta-}{C}-\overset{\delta+}{M} + \overset{\delta+}{R}-\overset{\delta-}{X} \xrightarrow{liq\ NH_3} RC\equiv C-R' + \underset{(M=metal)}{MX}$$
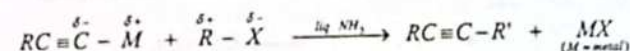
Chemical Reactions

Alkynes undergo similar reactions to those of alkenes. Addition reactions proceed in two stages. For the addition of unsymmetrical reagents across unsymmetrical alkynes, Markovnikov's rule applies in a similar way as it does for alkenes, although light or peroxide catalysed reactions again tend to result in the formation of the Anti-Markovnikov product. Alkynes undergo double addition reaction involving two molecules of the attacking reagent as follows:
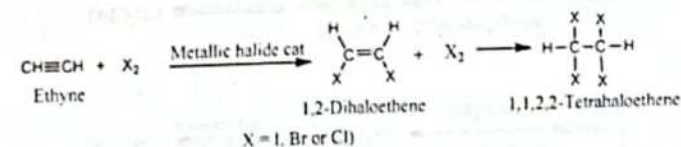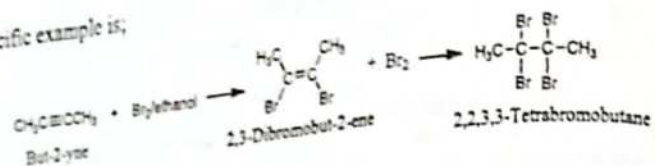

(a) *Hydrogenation*

$$CH_3C\equiv CH + H_2 \xrightarrow{Pt,\ Pd\ or\ Ni\ cat} CH_3CH=CH_2 + H_2 \longrightarrow CH_3CH_2CH_3$$
Propyne — Propene — Propane
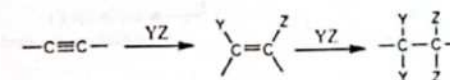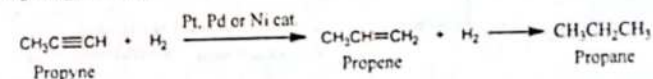
The reaction can be stopped at the alkene stage by using Lindlar's catalyst.

(b) *Halogenation*

$$CH\equiv CH + X_2 \xrightarrow{Metallic\ halide\ cat}$$
Ethyne

1,2-Dihaloethene

1,1,2,2-Tetrahaloethene

(X = I, Br or Cl)

Specific example is;

$$CH_3C\equiv CCH_3 + Br_2 \xrightarrow{\text{Bromoethane}} \underset{\text{2,3-Dibromobut-2-ene}}{\overset{H_3C}{\underset{Br}{C}}=\overset{CH_3}{\underset{Br}{C}}} + Br_2 \longrightarrow \underset{\text{2,2,3,3-Tetrabromobutane}}{H_3C-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{Br}{C}}-CH_3}$$

But-2-yne

(c) *Addition of hydrogen halides*

This follows Markovnikov's rule.

$$CH\equiv CH + HX \xrightarrow[\text{or metallic halide cat}]{\text{UV light}} CH_2=CHX + HX \longrightarrow \begin{cases} \underset{\text{Markovnikov (major) product}}{CH_3CHX_2} \\ \underset{\text{Anti-Markovnikon product}}{XCH_2CH_2X} \end{cases}$$

$$CH_3C\equiv CH + HX \longrightarrow \begin{cases} \underset{\text{Markovnikov route}}{CH_3CX=CH_2} + HX \longrightarrow CH_3CX_2CH_3 \\ \underset{\text{Anti-Markovnikon route}}{CH_3CH=CHX} + HX \longrightarrow CH_3CH_2CHX_2 \end{cases}$$

Specific example is;

$$CH\equiv CH + HCl \longrightarrow CH_2=CHCl + HCl \longrightarrow \begin{cases} \underset{\text{Markovnikov (major) product}}{CH_3CHCl_2} \\ \underset{\text{Anti-Markovnikov product}}{ClCH_2CH_2Cl} \end{cases}$$

$$CH_3C\equiv CH + HCl \longrightarrow \begin{cases} \underset{\text{Markovnikov route}}{CH_3CCl=CH_2} + HCl \longrightarrow \underset{\text{2,2-Dichloropropane}}{CH_3CCl_2CH_3} \\ \underset{\text{Anti-Markovnikov route}}{CH_3CH=CHCl} + HCl \longrightarrow \underset{\text{1,1-Dichloropropane}}{CH_3CH_2CHCl_2} \end{cases}$$

(d) **Hydration**

(i)
$$CH\equiv CH \xrightarrow[HgSO_4 \text{ cat}, 60°C]{\text{dil } H_2SO_4} \underset{\text{Ethenol}}{CH_2=CHOH} \underset{\text{tautomerism}}{\rightleftharpoons} CH_3CHO$$

(ii)
$$CH_3C\equiv CH \xrightarrow[HgSO_4 \text{ cat}, 60°C]{\text{dil } H_2SO_4} \underset{\substack{\text{2-Propenol} \\ \text{(Propen-2-ol)}}}{CH_3C(OH)=CH_2} \underset{\text{tautomerism}}{\rightleftharpoons} \underset{\text{Propanone}}{(CH_3)_2CO}$$

(e) *Addition of hydrogen cyanide*

(i)
$$CH_3-C\equiv CH + HCN \xrightarrow[\text{cat.}]{Ba(CN)_2} CH_3-\overset{}{\underset{CN}{C}}=CH \longrightarrow \underset{\substack{\text{1-Cyanopropene} \\ \text{(Anti-Markovnikov) Product}}}{\underset{CN}{CH_3CH=CH}}$$
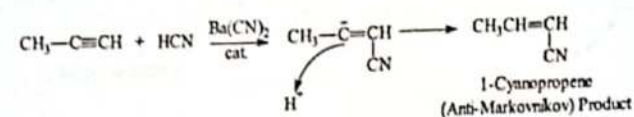
The catalyst used affords the Anti-Markovnikov product as the major product.

(f) *Addition of methanal or carbonyl compounds*

Ethyne and other terminal alkynes react with methanal (formaldehyde) or carbonyl compounds as follows:

$$CH\equiv CH + 2HCHO \xrightarrow[\text{High pressure}]{Cu_2C_2 \text{ cat}} HOCH_2C\equiv CCH_2OH \xrightarrow[\text{Pt cat}]{2H_2} \underset{\text{Butan-1,4-diol}}{HOCH_2CH_2CH_2CH_2OH}$$

$$\xrightarrow[270°C]{-2H_2O} \underset{\text{Buta-1,3-diene (or 1,3-Butadiene)}}{CH_2=CHCH=CH_2}$$

Mechanism

(i)

$$HOCH_2C\equiv CCH_2OH \xrightarrow{2H_2} \underset{\substack{OH \quad H \quad H \quad OH}}{CH_2-CH-CH-CH_2} \xrightarrow{-H_2O} CH_2=CHCH=CH_2$$

Other examples:

(ii)

$$CH_3-C\equiv CCH_2OH \xrightarrow[\text{Pt cat}]{2H_2} \underset{OH}{CH_3CH_2CH-CH_2} \xrightarrow{-H_2O} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2}$$

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(iii)

$$CH_3CH_2C\equiv H \longrightarrow CH_3CH_2C\overset{OH}{\underset{CH_3}{\underset{|}{\overset{|}{C}}}}CH_3 \xrightarrow{\text{H}^+} CH_3CH_2CH_2\overset{OH}{\underset{H}{\underset{|}{\overset{|}{C}}}}\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}CH_2-H$$

2-Methylhexan-2-ol

$$CH_3CH_2CH_2CH = C(CH_3)_2 \quad + \quad CH_3(CH_2)_3C(CH_3) = CH_2$$
2-Methylhex-2-ene   2-Methylhexene
(major product)

(g) Oxidative coupling of two alkynes

Oxidative coupling of two alkynes produces a product having two triple bonds.

$$2RC\equiv CH + \tfrac{1}{2}O_2 \xrightarrow{\text{Cuprous salt}} R-C\equiv C-C\equiv C-R + H_2O$$
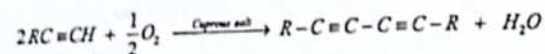
(h) Oxidation of alkynes

Ozone and acidified potassium manganate (VII) oxidize alkynes to give a pair of carboxylic acids:

Example

$$CH_3CH_2C\equiv CCH_2CH_2CH_3 \xrightarrow{KMnO_4/H^+} CH_3CH_2CO_2H + CH_3CH_2CH_2CO_2H$$
Propanoic acid   Butanoic acid
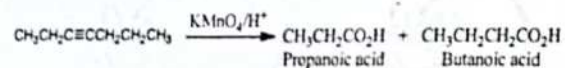
(i) Isomerization

In a strong base, alkynes may be isomerized to a compound with two double bonds on the same carbon atom, allene or to another alkyne.

$$CH_3CH_2C\equiv CH \underset{NaOH}{\overset{NaOH}{\rightleftharpoons}} CH_3CH=C=CH_2 \underset{NaOH}{\overset{NaOH}{\rightleftharpoons}} CH_3C\equiv CCH_3$$
But-1-yne   But-1,2-diene   But-2-yne
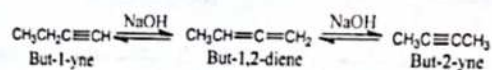
(j) Polymerization of ethyne

(i) Dimerization:

Ethyne dimerizes in a solution of copper (I) chloride and ammonium chloride in hydrochloric acid.

$$2\,CH\equiv CH \xrightarrow{CuCl,\ NH_4Cl/HCl} CH_2=CH-C\equiv CH$$
Ethyne   But-3-ene-1-yne

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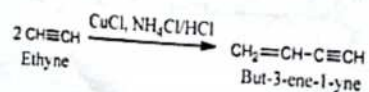
(ii) Trimerization

Ethyne trimerizes to form **benzene** when passed through a heated tube containing a complex organo-nickel catalyst.

$$3\,CH\equiv CH \xrightarrow[\text{organo-nickel cat}]{\substack{\text{heated tube}\\ 60\text{-}70^\circ C}} \text{Benzene}$$
Ethyne
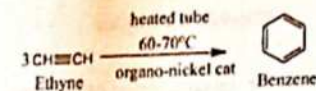
(iii) Tetramerization

Ethyne also tetramerizes to form **cyclooctatetraene** using dicyano nickel (II) complex as catalyst in tetrahydrofuran at 60-70°C and 15-20 atmosphere pressure.

$$CH\equiv CH \xrightarrow[60\text{-}70^\circ C,\ 15\text{-}20\ atm]{Ni(CN)_2/THF\ cat} \text{Cyclooctatetraene}$$
Ethyne
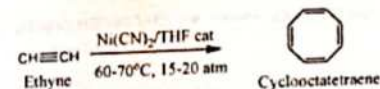
Metal Derivatives of Alkynes

In ethyne or terminal alkynes, that is, those containing the $-C\equiv CH$ group, the hydrogen attached to the triply bonded carbon is acidic. Such alkynes are deprotonated by strong bases such as butyl lithium (LiC_4H_9); sodamide, ($NaNH_2$); ammoniacal solution of copper (I) chloride, and silver ion to form metallic derivatives, which are excellent nucleophiles.

Examples include

(i)
$$CH\equiv CH \xrightarrow{2\ Cu(NH_3)_2Cl} CuC\equiv CCu\downarrow \quad + \quad 2\ HCl$$
Copper(I)dicarbide
or Copper(I)acetylide
(Red precipitate)

(ii)
$$CH\equiv CH \xrightarrow{2\ Ag(NH_3)_2NO_3} AgC\equiv CAg\downarrow \quad + \quad 2\ HNO_3$$
Silver(I)dicarbide
or Silver(I)acetylide
(White precipitate)

(iii)
$$CH_3CH\equiv CH + NaNH_2 \xrightarrow{Liq\ NH_3} CH_3CH\equiv CNa \quad + \quad NH_3$$
Propynyl sodium
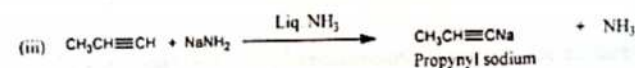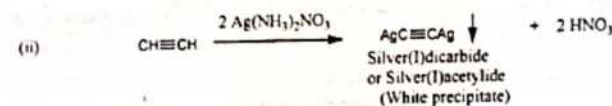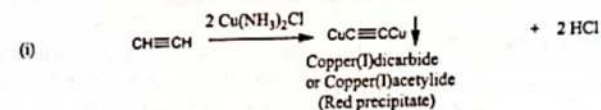
Alkynes of the type $R-C\equiv C-R$ where R is an alkyl or aryl group, do not undergo the above reactions, and therefore these reactions can be used to test for the terminal triple bond.

Alkylation of terminal alkynes

The metal salt of terminal alkynes can behave as a nucleophile and reacts with alkyl halide to form higher homologous of alkynes. This type of reaction is called alkylation of terminal alkyne, and can be used to extend the carbon chain of an alkyne.

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$$RC\equiv CH \xrightarrow{NaNH_2} RC\equiv CNa$$

$$RC\equiv CNa + CH_3CH_2Cl \longrightarrow RC\equiv CCH_2CH_3 + NaCl$$
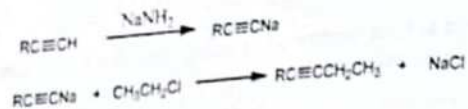
Worked Examples

Question 1

Propose reaction schemes for the conversion of propyne to hex-2-yne

Solution

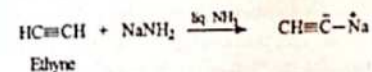$$CH_3C\equiv CH \xrightarrow{NaNH_2} CH_3C\equiv CNa$$

Propyne

$$CH_3C\equiv CNa + CH_3CH_2CH_2Cl \longrightarrow CH_3C\equiv CCH_2CH_2CH_3 + NaCl$$

Hex-2-yne
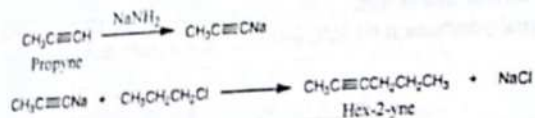
Question 2

Propose reaction schemes for the conversion of ethyne to hex-3-yne.

Solution

$$HC\equiv CH \xrightarrow{2\ NaNH_2} NaC\equiv CNa$$

Ethyne

$$NaC\equiv CNa + 2\ CH_3CH_2Cl \longrightarrow CH_3CH_2C\equiv CCH_2CH_3 + 2\ NaCl$$

Hex-3-yne
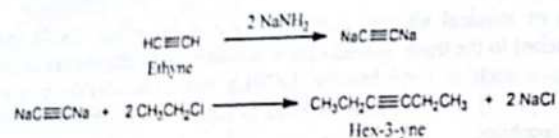
The metal salts of terminal alkynes can also react with carbonyl compounds, to form alcohols.

$$CH_3C\equiv CH + NaNH_2 \xrightarrow{liq\ NH_3} CH_3C\equiv \overset{..}{C}-\overset{+}{N}a$$

$$CH_3C\equiv \overset{..}{C}-\overset{+}{N}a + \underset{R}{\overset{R}{C}}=O \longrightarrow CH_3C\equiv C-\underset{R}{\overset{\overset{-}{O}Na}{C}}-R \xrightarrow{H_2O/H^+} CH_3C\equiv C-\underset{R}{\overset{OH}{C}}-R$$
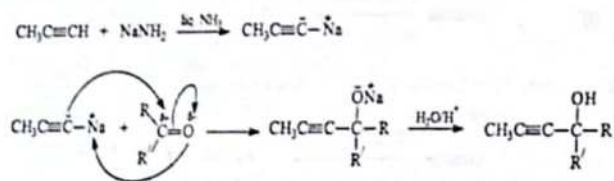
Worked Examples

Question 1

Proposed reaction schemes for the conversion of propyne to but-2-yn-1-ol

Solution

$$CH_3C\equiv CH + NaNH_2 \xrightarrow{liq\ NH_3} CH_3C\equiv \overset{..}{C}-\overset{+}{N}a$$

Propyne

$$CH_3C\equiv \overset{..}{C}-\overset{+}{N}a + \underset{H}{\overset{H}{C}}=O \longrightarrow CH_3C\equiv C-\underset{H}{\overset{\overset{-}{O}Na}{C}}-H \xrightarrow{H_2O/H^+} CH_3C\equiv C-CH_2OH$$

But-2-yn-1-ol
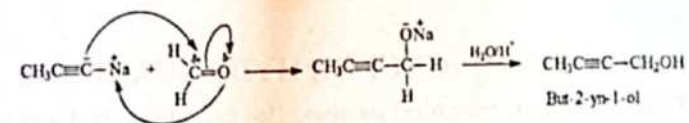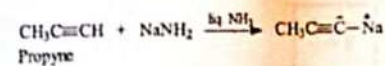
Question 2

Propose reaction schemes for the conversion of ethyne to 3-Methylbut-1-yn-3-ol (or 2-methyl but-3-yn-2-ol)

Solution

$$HC\equiv CH + NaNH_2 \xrightarrow{liq\ NH_3} CH\equiv \overset{..}{C}-\overset{+}{N}a$$

Ethyne

$$HC\equiv \overset{..}{C}-\overset{+}{N}a + \underset{CH_3}{\overset{CH_3}{C}}=O \longrightarrow CH\equiv C-\underset{CH_3}{\overset{\overset{-}{O}Na}{C}}-CH_3 \xrightarrow{H_2O/H^+} CH\equiv C-\underset{CH_3}{\overset{OH}{C}}-CH_3$$

3-Methylbut-1-yn-3-ol
(or 2-Methylbut-3-yn-2-ol)
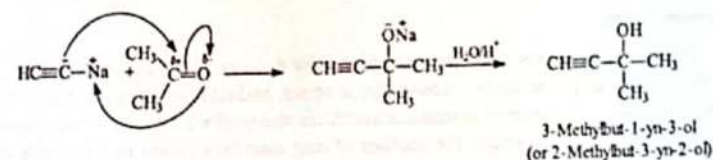
Simple tests for unsaturation in Alkynes

1. Unsaturation in alkynes can be detected by employing the same simple tests used for alkenes, that is, decolourization of bromine water and potassium manganate (VII) solution.

2. Terminal alkynes (i.e. RC≡CH) react with copper (1) ions in aqueous ammonical solution of copper (1) chloride and the silver (1) ions in a solution of silver trioxonitrate (V) to form the insoluble heavy metal dicarbides (acetylides) as given above under the metallic derivatives of alkynes.

ALICYCLIC (CYCLIC) HYDROCARBONS

These non-aromatic cyclic (ring) compounds fall into a larger number of classes than do the aliphatic hydrocarbons because the ring may be of various sizes. They may be saturated or unsaturated and individual members may contain one or more rings.
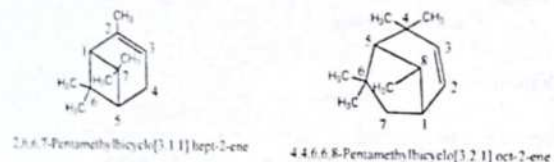
IX. Cycloalkanes

These are saturated monocyclic hydrocarbons, they are also known as cycloparaffins. They have the general molecular formula, C_nH_{2n}. The saturated alicyclic hydrocarbons are sometimes called naphthenes, particularly by petroleum chemists. The word naphthene is related to the fact that cyclopentane and cyclohexane homologues have been isolated from the naphtha fraction of crude petroleum.

Nomenclature

The cycloalkanes are systematically named by denoting the number of carbon atoms in the nucleus as in the straight-chain alkane series, and adding the prefix "cyclo". The fused and bridged two-ring cycloalkanes utilize the prefix "bicyclo" and inserted in brackets, in decreasing order, the number of ring members joined to either side of the common carbon atom. Consider the following examples:

Cyclopropane   1,2-Dimethylcyclopropane   1-Ethylcyclobutane   1,2-Dimethylcyclopentane

1,2,4-Trimethylcyclohexane   Methylenecyclobutane   1-Ethylcyclooctane   Cyclononane

1,2-Dimethylcycloheptane   Bicyclo[4.4.0] decane (Decahydronaphthalene)   Bicyclohexyl   Bicyclopentylmethane
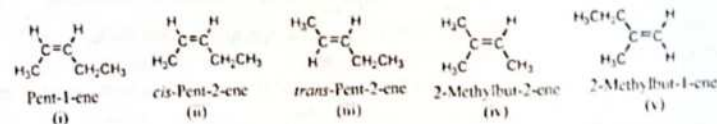
1,7,7-Trimethylbicyclo[2.2.1]heptane
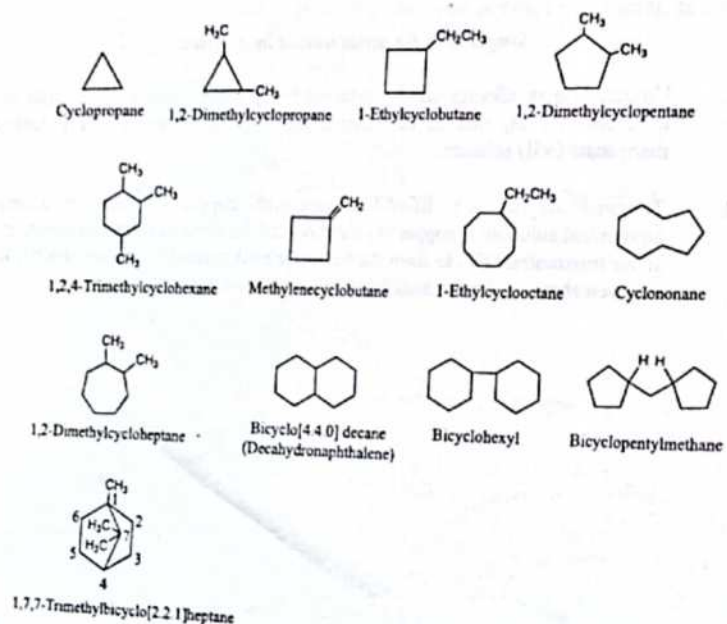
For spiranes, the word 'Spiro' followed, in decreasing order, by the number of atoms connected to the central atom. Consider the following examples
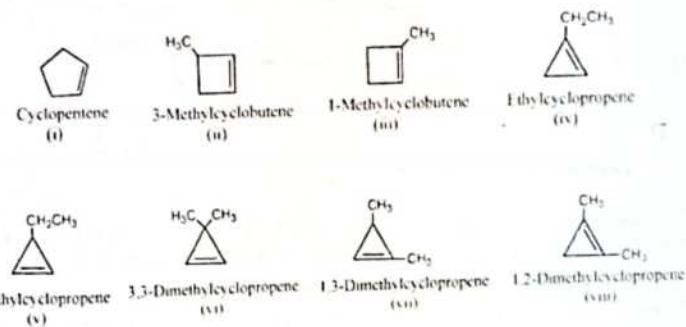

Spiro[5.4]decane   Spiro[3.3]heptane

Isomerism in Cycloalkanes

Cycloalkanes have more isomers than acyclic analogues, since variation in ring size is possible. For example C_5-alkane has three isomers whereas C_5-cycloalkane analogue has five isomers.

C_5-Alkane

$CH_3CH_2CH_2CH_2CH_3$; $(CH_3)_2CHCH_2CH_3$; $CH_3C(CH_3)_2CH_3$
n-Pentane   2-Methylbutane   2,2-Dimethylpropane
(i)   (ii)   (iii)

C_5- Cycloalkanes

Cyclopentane   1-Methylcyclobutane   1-Ethylcyclopropane   1,1-Dimethylcyclopropane
(i)   (ii)   (iii)   (iv)

1,2-Dimethylcyclopropane
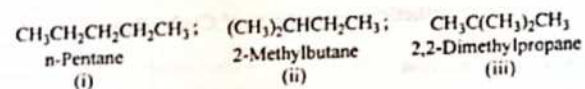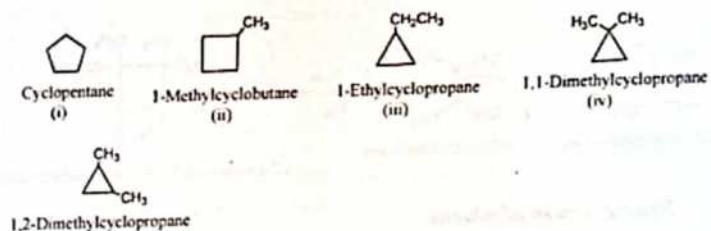
Consider isomers of cyclohexane as another example

Cyclohexane   1-Methylcyclopentane   1-Ethylcyclobutane   1,2-Dimethylcyclobutane
(i)   (ii)   (iii)   (iv)

1,1-Dimethylcyclobutane   1,3-Dimethylcyclobutane   1-Ethyl-1-methylcyclopropane
(v)   (vi)   (vii)

1-Ethyl-2-methylcyclopropane   1,2,3-Trimethylcyclopropane   1-Propylcyclopropane
(viii)   (ix)   (x)

1-Isopropylcyclopropane
(xi)
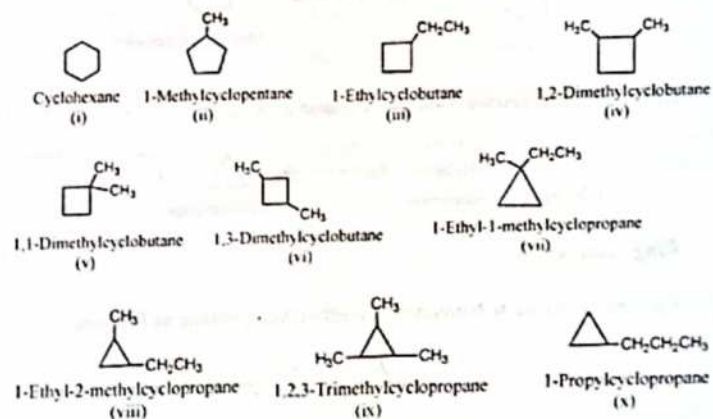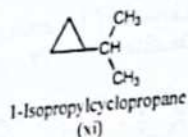
Cyclohexane has eleven isomers whereas C_6 – alkane has only five isomers.

Physical properties

The cycloalkanes boil at a temperature range of 10-20°C higher than the corresponding acyclic alkanes. Cycloalkanes are soluble in many organic solvents such as alcohols and ethers, but insoluble in water.

Synthetic preparations of Cycloalkanes

1. Cycloaddition reaction

Combination of two unsaturated molecules, end to end forms a cyclic molecule with four fewer pi (π) electrons.

2,3-Dimethylbut-2-ene   3,4-Dimethylhex-3-ene   1,2-Diethyl-1,2,3,3,4,4-hexamethylcyclobutane
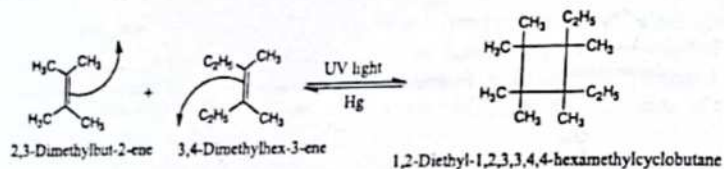
2. Hydrogenation of toluene

Toluene   Methylcyclohexane
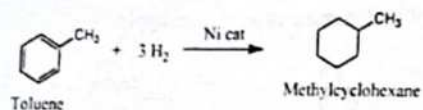
3. Reduction of 1-bromo-3-chloropropane with zinc

$ClCH_2CH_2CH_2Br$ + Zn ⟶ △ + ZnBrCl
1-Bromo-3-chloropropane   Cyclopropane
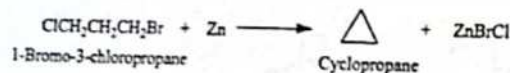
4. Ring contraction

Cyclohexane can be converted to methylcyclopentane as follows:

Cyclohexane   Methylcyclopentane
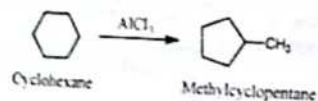
Chemical Reactions

Cycloalkanes in general exhibit a stability towards heat and chemical attack comparable to that of the corresponding alkanes. There is marked ring instability in cyclopropane, and to a lesser extent in cyclobutane. Cyclopropane undergoes the following reactions (Bayer's theory):

A. Hydrogenation

Cyclopropane undergoes catalytic hydrogenation readily to normal propane.

Cyclopropane   n-Propane
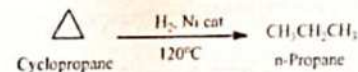
B. Bromination

Cyclopropane undergoes bromination leading to ring opening. The product can then be dehydrobrominated to form 3-bromopropene.

Cyclopropane   3-Bromopropene
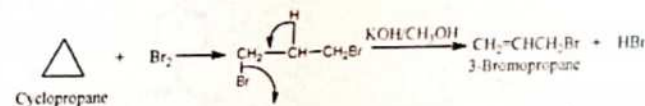
C. Hydrobromination

Cyclopropane undergoes hydrobromination leading to ring opening. The product can then be dehydrobrominated to form propene.

Cyclopropane   Propene
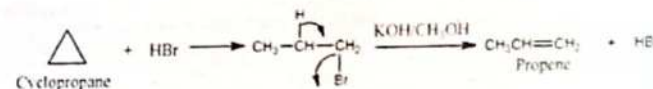
D. Hydration

Cyclopropane can be hydrated with concentrated tetraoxosulphate (VI) acid (H_2SO_4) and this leads to ring opening, and then dehydrated with concentrated tetraoxosulphate (VI) acid to form propene.

Cyclopropane   Propene
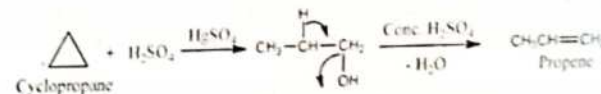
X. Cycloalkenes

These are unsaturated monocyclic hydrocarbons. They are also known as cycloolefins. They also include cyclodiolefins, (or cycloalkadienes); cyclotriolefins, (or cycloalkatrienes); and cyclotetraolefin) (or cycloalkatetraenes). The general molecular

formula for the cycloolefins is C_nH_{2n-2} for cyclodiolefins, C_nH_{2n-4} for cyclotriolefins, C_nH_{2n-6}, and for cyclotetraolefins, C_nH_{2n-8}.

Nomenclature

The cycloalkenes are systematically named by denoting the number of carbon atoms in the nucleus as in the straight-chain alkene series, and adding the prefix "**cyclo**". The position of the double bond within the ring is indicated by numbers. The fused and bridged two-ring cycloalkenes utilize the prefix "**bicyclo**" and inserted in brackets, in decreasing order, the number of ring members joined to either side of the common carbon atom. Consider the following examples:


Cyclopropene

3,4-Dimethylcyclobut-1-ene

3,3-Dimethylcyclohex-1-ene

1,5-Dimethylcyclopentan-1,3-diene
(or 1,5-Dimethyl-1,3-cyclopentadiene)

1-Methyl-4-isopropenylcyclohex-1-ene

1,3-Dimethylcyclooctal,3,5,7-tetraene
(or 1,3-Dimethyl-1,3,5,7-cyclooctatetraene)

3,6-Dimethylcyclohexa-1,4-diene
(or 3,6-Dimethyl-1,4-cyclohexadiene)

2,3,6,7-Pentamethylbicyclo[3.1.1]hept-2-ene

4,4,6,6,8-Pentamethylbicyclo[3.2.1]oct-2-ene

Bicyclo[4.3.0]non-3-ene
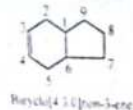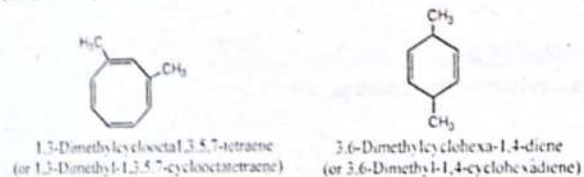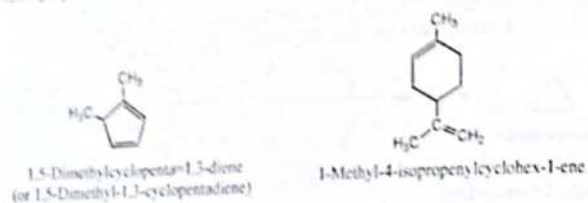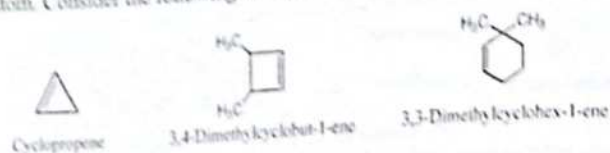
If one of the termini of a double bond in a bicyclic system is a bridgehead carbon, the other terminus is indicated by a number in parentheses to distinguish between the several possibilities. Consider the following examples:

2,4,7-Trimethylbicyclo[4.2.0]oct-1(7)-ene

2,5,3-Trimethylbicyclo[4.3.0]non-1(6)-ene

4,7,8-Trimethylbicyclo[4.3.0]non-1(9)-ene

Bicyclo[3.2.1]hept-1-ene
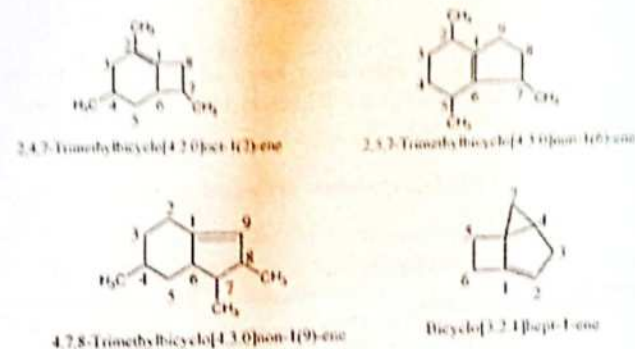
For spirenes, the word 'Spiro' is followed, in decreasing order, by the number of atoms connected to the central atom.

3-Methylspiro[5.2]oct-1-ene

2,3-Dimethylspiro[4.3]oct-1,3-diene
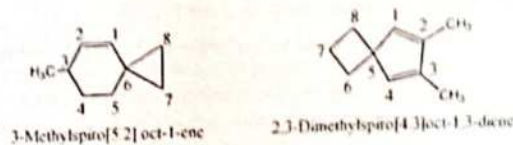
Isomerism in Cycloalkenes

Cycloalkenes have more isomers than the acyclic analogue, since variation in ring size is possible. For example, C_5-alkene has six isomers, whereas the C_5-cycloalkene analogue has eight.

C_5-alkene:

Pent-1-ene
(i)

cis-Pent-2-ene
(ii)

trans-Pent-2-ene
(iii)

2-Methylbut-2-ene
(iv)

2-Methylbut-1-ene
(v)

C_5- Cycloalkene

Cyclopentene
(i)

3-Methylcyclobutene
(ii)

1-Methylcyclobutene
(iii)

Ethylcyclopropene
(iv)

3-Ethylcyclopropene
(v)

3,3-Dimethylcyclopropene
(vi)

1,3-Dimethylcyclopropene
(vii)

1,2-Dimethylcyclopropene
(viii)

Physical properties

The cycloalkenes boil at a temperature range of 10-15°C higher than the corresponding alkenes. Cycloalkenes are soluble in many organic solvents such as alcohols and ether but insoluble in water.

Synthetic preparations of Cycloalkenes

1. Ring expansion

Cycloalkenes are synthesized by ring expansion followed by removal of any existing functional group.

2. Dehalogenation of 1,2-dihalides

1,2-dihalocycloalkanes are converted to cycloalkenes by iodide ion or heating with zinc dust.
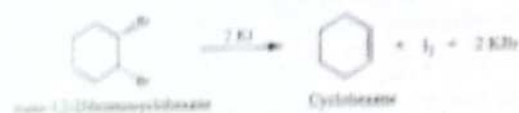
3. Dehydration of cycloalkanol

Cycloalkanol can be converted to cycloalkene by removal of water molecules.
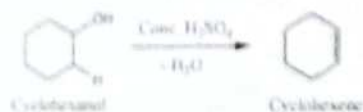
4. Diels-Alder reaction

Ethene undergoes 1,4-addition reaction with conjugated dienes (buta-1,3-diene) to produce cyclohexene.

5. 1,4-Dimerization of buta-1,3-diene

Cyclooctadiene can be synthesized by the 1,4-dimerization of buta-1,3-diene over a complex nickel catalyst.

6. Tetramerization of ethyne

Cyclooctatetraene can be made by tetramerization of ethyne (acetylene) over nickel cyanide catalyst in tetrahydrofuran at 60-70°C and 15-20 atmosphere pressure.
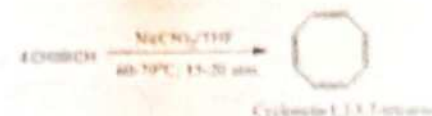
Chemical Reactions

The multiple bond in cycloolefins is generally more reactive than its straight chain counterparts and when cleaved, provides a convenient source of bifunctional organic derivatives. Below are some of the reactions of cycloalkenes.

(a) Halogenation

Halogens add readily to cyclohexene to afford the trans-dihalo compound
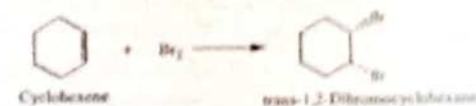
(b) Addition of hypohalous acid

HOCl, HOBr and HOI in aqous solution add readily to cycloalkene forming halo-alcohols. In unsymmetrical cycloalkene, the hydroxyl group becomes attached to the highly substituted carbon atom (Markovnikov's rule)

(i)

(ii)
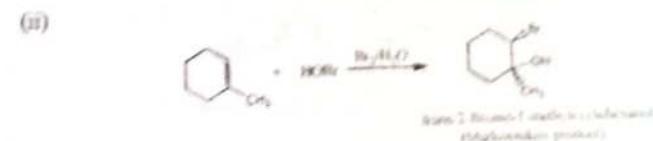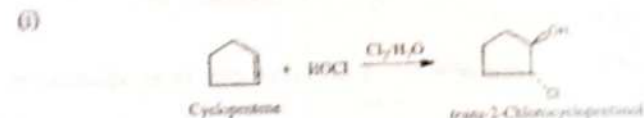
(c) Addition of tetraoxosulphate (VI) acid

Cycloalkene can be converted to cycloalkanol by dissolving the cycloalkenes in concentrated tetraoxosulphate (VI) acid. The cycloalkylhydrogensulphate formed is then hydrolyzed by boiling with water to form the alcohol

Cyclohexene → Cyclohexylhydrogensulphate → Cyclohexanol + H_2SO_4
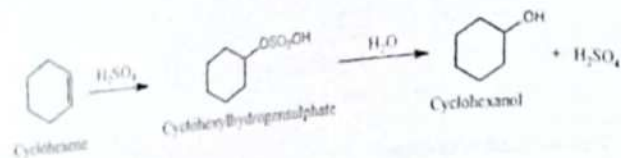
(d) Ozonolysis

Ozone or chromic acid reacts rapidly with cycloalkenes to form bifunctional derivatives. Ozone will give a bicarbonyl compound while chromic acid, which is stronger, will give a dicarboxylic acid.

(i)

Cyclohexene → Hexane-1,6-dial

(ii)

1,2-Dimethylcyclopent-1-ene → Pent-1,5-dione

(iii)

Cyclohexene → Hexane-1,6-dioic acid
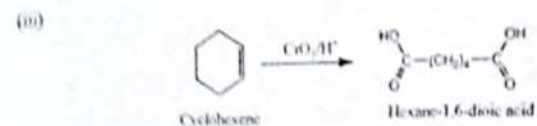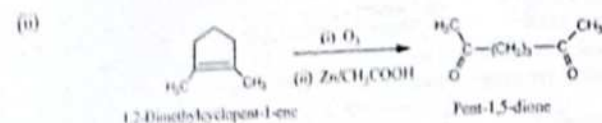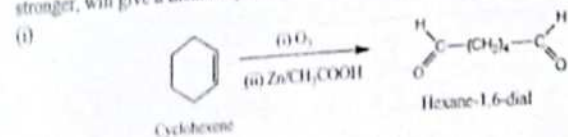
(e) Cis - hydroxylation

cis-Cyclohexane-1,2-diol
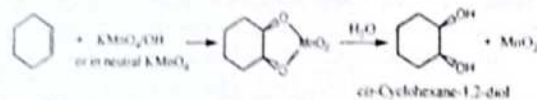
(f) Thermal ring opening

The thermal ring opening of a substituted cyclobutene to an alkadiene is represented below:

cis-3,4-Dimethylcyclobutene → cis-Hexa-2,4-diene

trans-3,4-Dimethylcyclobutene → trans-Hexa-2,4-diene
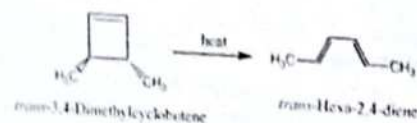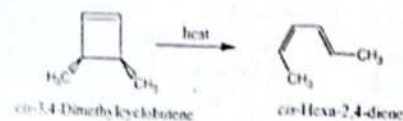
XI. Cycloalkynes

There are very few examples of cycloalkynes. They have the general molecular formula, C_nH_{2n-4}

Nomenclature

The cycloalkynes are systematically named by denoting the number of carbon atoms in the nucleus as in the straight - chain alkyne series, and adding the prefix "cyclo". The position of the triple bond within the ring is indicated by numbers. The fused and bridged two-ring cycloalkynes utilize the prefix "bicyclo" and inserted in brackets, in decreasing order, the number of ring members joined to either side of the common carbon atom. Consider the following examples:

3,4-Dimethylcyclohexyne   3,4-Dimethylcyclopentyne   1,5,5,7-Tetramethylbicyclo[2.2.1]hept-2-yne
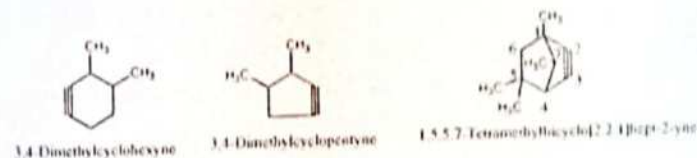
Industrial uses of alicyclic hydrocarbons

1. Cyclopentadiene is used in the preparation of the persistent insecticide chlordane.

2. Cyclohexane is the key intermediate in the preparation of nylon-6 from cyclohexanone and caprolactam.

3. Adipic acid, one of the constituents of nylon 6,6 can be obtained by the oxidation of cyclohexane.

4. Cyclopropane is used as an anaesthetic.

5. The naturally occurring terpenes, limonene and α-pinene are used in flavours and perfumes and as starting materials in the preparation of synthetic camphor, which is a cyclic ketone, and racemic menthol, which is cyclic alcohol.

AROMATIC HYDROCARBONS

These compounds contain at least six-membered ring, incorporating what appears to be three conjugated double bonds. None of the bonds in aromatic hydrocarbons have the olefinic character associated with alkenes and cycloalkenes. They are considered to be a separate class of compounds called the Arenes. The aromatic hydrocarbons (arenes) fall into different types.

Type A

These comprise of benzene, alkylbenzene, alkenylbenzene (styrene) and alkynylbenzene (phenylacetylene).

C_2H_5
$CH=CH_2$
$C\equiv CH$

Ethylbenzene

Vinylbenzene
or Ethenylbenzene (Styrene)

Phenylacetylene
(Ethynylbenzene)
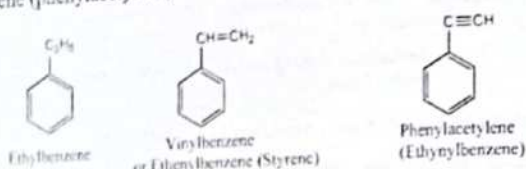
Type B

These comprise of cyccloalkylbenzene (cyclopentylbenzene) and cycloalkenylbenzenes (phenylcyclohexenes).

Cyclopentylbenzene

1-Phenylcyclohexene

Type C

These comprise of fused ring polynuclear hydrocarbons. Examples include, indene, indan, naphthalene, tetrahydronaphthalene, fluorene, anthracene, phenanthrene, pyrene, chrysene, perylene, fluoranthrene, benzo[a] pyrene and benzo[e]pyrene.

Indene (i)

Indan (ii)

Naphthalene (iii)

1,2,3,4-Tetrahydronaphthalene (iv)

Fluorene (v)

Fluoranthrene (vi)

Anthracene (vii)

Phenanthrene (viii)

Pyrene (ix)

Perylene (x)

Chrysene (xi)

Benzo[a]pyrene (xii)

Benzo[e]pyrene (xiii)
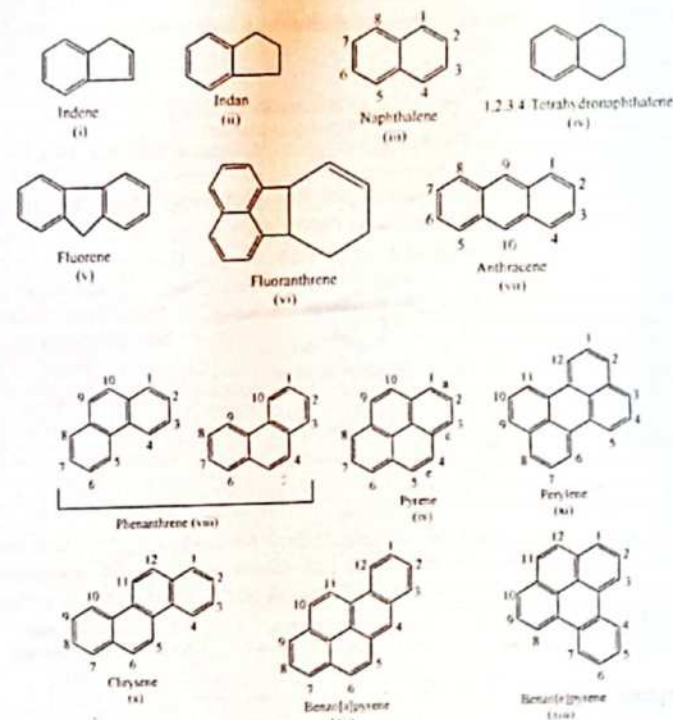
Type D

These comprise of polynuclear aromatic hydrocarbons having directly united rings, e.g. biphenyl, binaphthyl or rings united through aliphatic carbon, e.g. diphenylmethane, 1,2 - diphenylethylene; 1,2 - diphenylacetylene.

Biphenyl (i)

Binaphthyl (ii)

1,2-Diphenylethylene (1,2 - Diphenylethene) (iii)

$C\equiv C$

1,2-Diphenylethyne (1,2-Diphenylacetylene) (iv)

CH_2

Diphenylmethane (v)
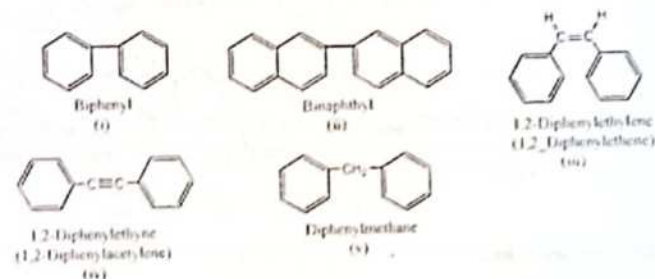
Nomenclature and Isomerism in Arenes

The commonest aromatic hydrocarbon is benzene. Owing to the symmetry of the benzene ring, all the six carbon atoms are equivalent. When one hydrogen atom is replaced by an atom or group, it is referred to as a monosubstituted derivative, and when two and three hydrogens are replaced by atoms or groups, they are referred to as disubstituted and trisubstituted derivatives respectively. A monosubstituted arene like

alkylbenzene has no isomer, a disubstituted derivative has three isomers, namely.

(i) 1,2 or ortho (o) derivative
(ii) 1,3 or meta (m) derivative
(iii) 1,4 or para (p) derivative

The positions of substitution in benzene and its higher homologous are indicated by numbering the carbon atoms in the ring, for example.
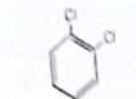
1,2-Dichlorobenzene   1,3-Dichlorobenzene   1,4-Dichlorobenzene

For trisubstituted derivatives
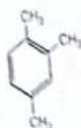
1,2,4-Trimethylbenzene
(or 2,4-Dimethyltoluene)
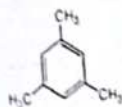
1,3,5-Trimethylbenzene
(or 3,5-Dimethyltoluene)
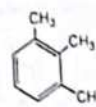
1,2,3-Trimethylbenzene
(or 2,3-Dimethyltoluene)

Other examples include:
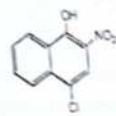
4-Chloro-2-nitronaphthol
(or 4-Chloro-2-nitro-1-naphthol)
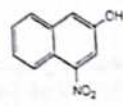
4-Nitronaphthalene-2-ol
(or 4-Nitro-2-naphthol)
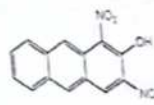
1,3-Dinitroanthracene-2-ol
(or 2-Hydroxy-1,3-dinitroanthracene)
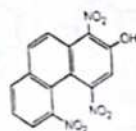
1,4,5-Trinitrophenanthrene-2-ol
or 1,4,5-Trinitro-2-phenanthrol

Physical properties of arenes

Benzene and most alkylbenzenes are liquids at room temperature whereas polycyclic arenes are solids. Boiling points increase as the molecular mass increases, but melting points do not correlate with molecular mass. Arenes are immiscible with water, but are soluble in organic solvents. They are highly flammable with characteristic "aromatic" smell. Arenes burn with a smoky and luminous flame. Arenes are very toxic, and continued inhalation of the vapors is dangerous and can induce anemia and even leukemia. Benzo [a]-pyrene (Bap) is regarded as the most dangerous

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of the polycyclic arenes as it is widely distributed and strongly carcinogenic.

Evidence for stability of arenes

Benzologs of benzene are stable compared to alkenes and alkynes. The extra stability of benzene derivatives is due to delocalization of electrons (refer to part one), with its associated resonance energy, also referred to as delocalization energy.

A quantitative estimate of the stabilization or resonance energy of benzene (which cannot be directly measured) may be obtained by determining the heat evolved when hydrogen is added to cyclohexene and to benzene to yield cyclohexane. The experimentally determined value of the enthalpy change for the hydrogenation of cyclohexene is -121 kJ mol^{-1},

$$\text{Cyclohexene} \xrightarrow{H_2/\text{Ni cat}} \text{Cyclohexane} \quad ; \quad \Delta H = -121 \text{ kJ mol}^{-1}$$
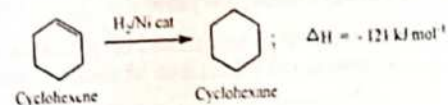
If the three double bonds in benzene were identical to the one in cyclohexene, the heat of hydrogenation of benzene would be three times the heat evolved during hydrogenation of cyclohexene. Thus, for the hypothetical Kekule' structure, one would expect:

$$\text{Benzene} + 3 H_2 \xrightarrow{\text{Ni cat}} \text{Cyclohexane} \quad \Delta H = -(3 \times 121) \text{ kJ mol}^{-1} = -363 \text{ kJ mol}^{-1}$$
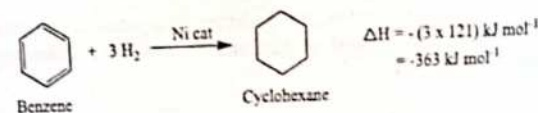
However, experiments showed that:

$$\text{Benzene} \xrightarrow{H_2/\text{Ni cat}} \text{Cyclohexane} \quad ; \quad \Delta H = -209 \text{ kJ mol}^{-1}$$
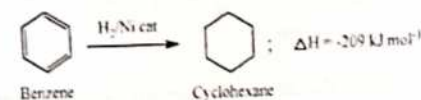
The values given above show that there is a large discrepancy between the "expected" (-363 kJ mol^{-1}) and the measured (-209 kJ mol^{-1}) H values, i.e the difference in H hydrogenation between the Kekule's structure and the real benzene molecule is

$$-363 - (-209) = -154 \text{ kJ mol}^{-1}$$

The resonance energy (or delocalization energy) is -154 kJ mol^{-1}. Hence, benzene is about 154 kJ mol^{-1} more stable than would be expected if there were no resonance interaction between the π electrons. This indicates the extent to which the delocalization of the pi (π) electrons contributes to the overall stability of the molecule.
The evidences in support of the stability of benzene and its derivatives are:

i. Benzene and its derivatives are resistant to oxidation; they are not attacked at 100°C by the usual oxidizing agents, whereas alkenes and alkynes react even at

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ii. $0^\circ C$ with alkaline solution of potassium manganate (VII).
Benzene ring possesses good thermal stability and show little tendency to rearrange during chemical reaction.

Preparation of Benzene

Industrial preparation

Benzene can be prepared industrially by the conversion of any non-aromatic hydrocarbon structures, especially those found in petroleum to aromatic hydrocarbons. The transformation can be accomplished by the following methods.

1. **Dehydrogenation of naphthenes from petroleum**

This is the direct dehydrogenation of naphthenes from petroleum to aromatics using catalysts comprising small amounts of platinum on an acidified alumina support, also known as reforming catalysts.

Cyclohexane → Benzene + 3 H$_2$
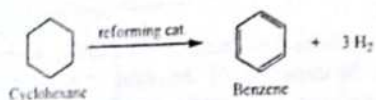
2. **Dehydroisomerization of naphthenes from petroleum**

This is the dehydroisomerization of naphthenes from petroleum to aromatics using catalysts comprising small amounts of platinum on acidified alumina supports, also known as reforming catalysts.

Methylcyclopentane → Benzene + 3 H$_2$
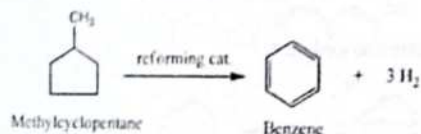
3. **Dehydrocyclization of aliphatic hydrocarbons from petroleum**

This is the dehydrocyclization of aliphatic hydrocarbons from petroleum to aromatics using the same reforming catalysts as in (1) and (2) above.

$CH_3(CH_2)_5CH_3$ (n-heptane) → Methylbenzene (Toluene) + 4 H$_2$
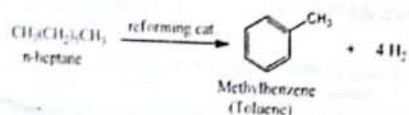
4. **High temperature thermal cracking of petroleum fractions**

Small hydrocarbons from the cracking of heavier components, as well as any component originally present, may be condensed to aromatics, usually with considerable splitting to methane as well as hydrogen.

$$3\ C_2H_2 \xrightarrow{600\ -\ 800^\circ C} \text{Benzene} + 3\ CH_{4(g)} + 4\ H_{2(g)}$$
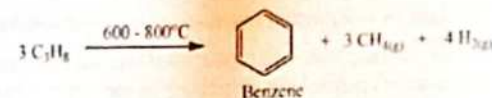
Laboratory preparations

The following laboratory preparations are of chemical interest because the highest abundance of benzene is obtainable from the industrial sources stated above.

1. **Decarboxylation of sodium salt**

Benzene is obtained by fusing sodium benzene carboxylate with sodalime (calcium (II) oxide slaked with sodium hydroxide).

COONa + NaOH $\xrightarrow{fuse}$ Benzene + Na$_2$CO$_3$
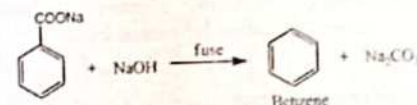
2. **From phenol**

Benzene is produced from phenol by passing phenol vapor over heated zinc dust

Phenol + Zn $\xrightarrow{heat}$ Benzene + ZnO
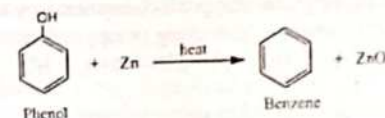
3. **Polymerization of ethyne**

Trimerization of ethyne at 400°C under pressure yields a product containing a small amount of benzene but when a complex organo-nickel catalyst is used at a temperature range of 60 - 70°C, a larger amount of benzene is produced.

$3\ CH\equiv CH$ (Ethyne) $\xrightarrow[60\ -\ 70^\circ C]{\text{Complex organo nickel cat}}$ Benzene
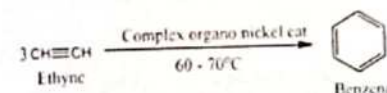
Reactions of Aromatic Hydrocarbons

Aromatic hydrocarbons show a marked tendency to undergo substitution reactions rather than addition reactions, that is, they do not behave chemically like unsaturated compounds that undergo addition reactions. With increasing numbers of fused rings, there is an increasing tendency for addition rather than substitution reactions to occur. This is particularly true if the fused rings are arranged in a linear fashion as in anthracene. However, under drastic reaction conditions, benzene can be made to yield addition products.

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As can be seen from the above resonance structures, the ring becomes electron-deficient, especially at the *ortho* and *para* - positions. Electrophilic (E$^+$) substitution is very slow at these positions and requires rigorous reagents and conditions. The *meta*-positions are the least electron-deficient carbon atom in the ring and electrophilic substitution occurs more at the *meta*-positions.

Consider for example, the structures of the three carbocation intermediate in the nitration of N, N, N-trimethylanilinium cation. They are stabilized only by delocalization with the ring, in which $^+$NR$_3$ group doesn't participate.
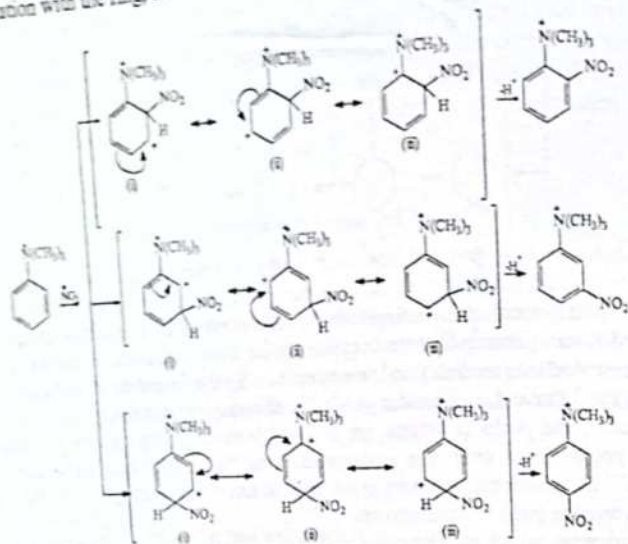
Canonical forms (ii) and (iii) of *para* and *ortho*-intermediates respectively have positive charges on two adjacent atoms, i.e carbon and nitrogen, thus increasing the energy and decreasing the stability of the hybrid. None of the *meta* intermediates has such interaction and is relatively more stable. Thus, *meta* - substitution is the predominant product on the grounds of both electron distribution in the substrate and of the relative stabilities of the three reactive intermediates. The above mechanisms indicate that there are two directing classification for substituted benzenes and they are:

(a) ortho/para- directors   (b) meta- directors

(a) *ortho/para*- directors (electron-donating groups)

The order of decreasing activation of *ortho/para* directors is:

–NH$_2$, ~ –NHR ~ –NR$_2$ > –OH > –NHCOCH$_3$ ~ –NHCOR > –OCH$_3$ ~ –OR > –CH$_3$, ~ –CH$_2$CH$_3$, ~ –R, –Ph > –F, –Cl, –Br, –I.
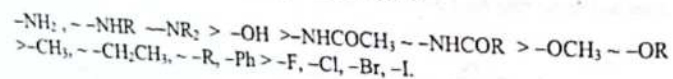
(b) *meta*- directors (electron-withdrawing groups)

The order of decreasing deactivation of *meta* directors is:

–C≡N, –SO$_3$H >–COOH, –COOR > –CHO, –COR, > – CCl$_3$, – CF$_3$ > –NO$_2$, – $^+$NR$_3$
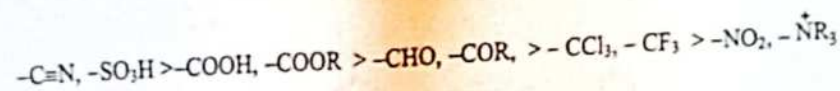
The following are some of the reactions of benzene and its derivatives.

(a) Nitration

A nitrating mixture, containing equal amounts of concentrated nitric acid and sulphuric acid converts benzene to nitrobenzene at 50°C. The sulphuric acid serves to generate a significant concentration of nitryl (nitronium) cation, NO$_2^+$ from a weaker nitric acid, which functions as a base. The NO$_2^+$ generated is a true electrophile and undergoes substitution in the ring.

$$HNO_3 + H_2SO_4 \xrightleftharpoons{slow} NO_2^+ + HSO_4^- + H_2O$$
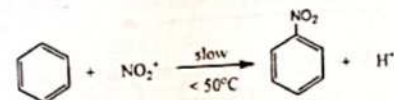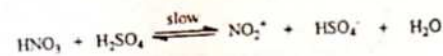
Further nitration of nitrobenzene at 50°C gives 1,3 - dinitrobenzene, because the nitro group is *meta*-directing
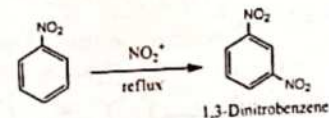
Other examples include
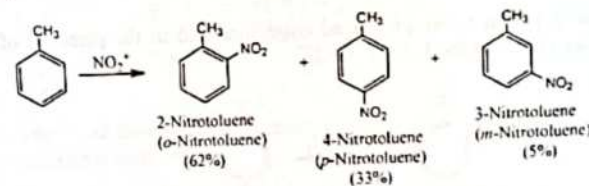
The methyl group is electron releasing by inductive effect *(+I effect)*, and it is therefore *ortho* and *para*-directing and *ortho*-isomer is more stable than *para*-isomer, and hence there is higher percentage yield of *ortho*-isomer than *para*-isomer.

Further nitration of either 2– or 4– nitrotoluene at higher temperatures gives the following products.

1,3,5-Trimethoxybenzene → 1,3,5-Trimethoxy-4-nitrobenzene
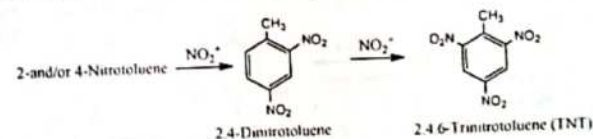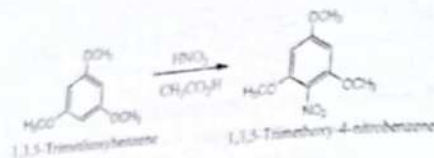
(b) Halogenation

Substitution of halogen atoms in benzene takes place readily at room temperature in the presence of a metal halide catalyst (e.g. $FeBr_3$, $AlCl_3$ or $ZnCl_2$), which polarizes the halogen molecule. The order of reactivity is,

$$F_2 > Cl_2 > Br_2 > I_2$$
Decreasing order of reactivity
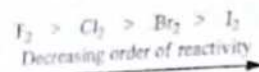
Chlorination may be carried out using aluminium (III) chloride catalyst, which polarizes the chlorine molecule, forming the complex $[Cl^{\delta+}—Cl^{\delta-} \cdots AlCl_3]$, which then ionizes to $Cl^+[AlCl_4]^-$.

The reaction may be represented as follows.

$$Cl_2 + AlCl_3 \rightleftharpoons Cl^+[AlCl_4]^-$$
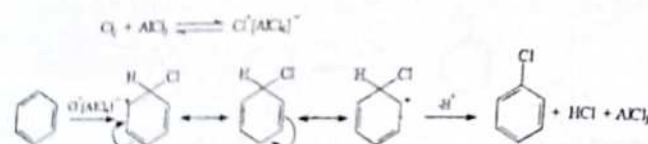
Further halogenation under prolonged conditions and in the presence of higher proportion of halogen gives the 1, 4 – dihalide.

Chlorobenzene → 1,4-Dichlorobenzene
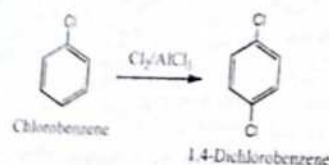
In the presence of light or ultraviolet radiation, benzene behaves as an unsaturated compounds and it reacts with chlorine or bromine at room temperature to form white crystal of 1,2,3,4,5,6- hexachlorocyclohexane or hexabromocyclohexane respectively as addition products.

1,2,3,4,5,6-Hexachlorocyclohexane
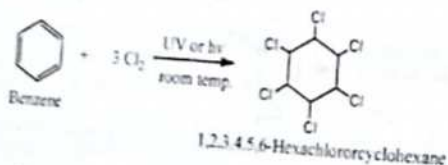
Alkyl benzenes undergo halogen substitution on the alkyl side chain. Attack always occurs at the carbon atom directly attached to the ring.

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Methylbenzene (Toluene) → Chlorophenylmethane (Benzylchloride) → Dichlorophenylmethane → Trichlorophenylmethane

Ethylbenzene → Bromophenylethane + HBr
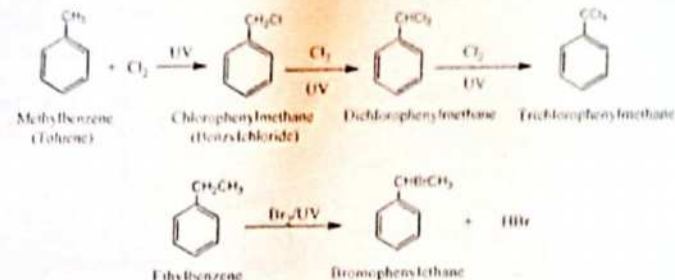
Aniline reacts very fast with an aqueous solution of bromine to precipitate 2,4,6 - tribromoaniline

Aniline → 2,4,6-Tribromoaniline
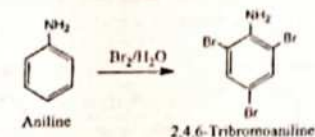
–NH_2 group is *ortho* and *para* - directing

The amino and hydroxyl groups are so activating that it is often not necessary to use a Lewis acid in some reactions (i e. Halogenation).

Phenol → 2,4,6-Tribromophenol
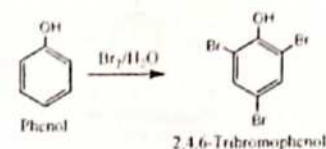
(NB: Mono – and di–bromination is very difficult with these highly activated benzene derivatives.)

Monobromination of aniline can be achieved by producing acetamide derivative first (i.e. it must first be made less activating by a protecting group), and then brominating the amide.

Aniline → 4-Bromoaniline (p-Bromoaniline) + 2-Bromoaniline (o-Bromoaniline)
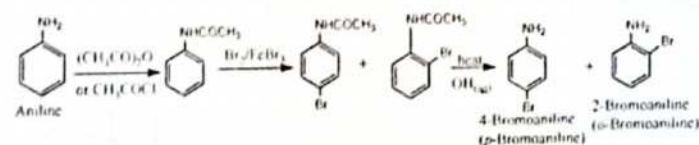
The mixture, i.e *ortho* and *para* - bromo acetanilide can be separated by recrystalization because *ortho*-bromoacetanilide is very much more soluble than the *para*-bromo acetanilide, and they are hydrolyzed separately to give 2- and 4- bromoaniline respectively.

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(c)   **Sulphonation**

Benzene like other hydrocarbons may be sulphonated by oleum, i.e. fuming tetraoxosulphate (VI) acid (a solution of sulphur trioxide in concentrated tetraoxosulphate (VI) acid) at 0°C
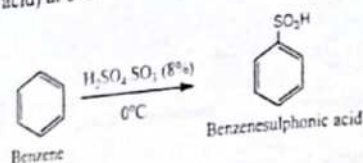
At higher temperatures, benzene sulphonic acid can be converted to Benzene-1,3-disulphonic acid by treatment with 20% oleum.
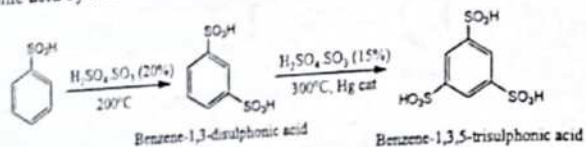
Phenol and toluene can be sulphonated with fuming sulphuric acid as follows:
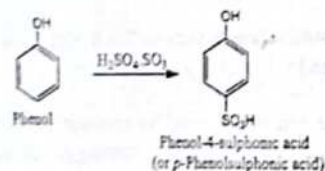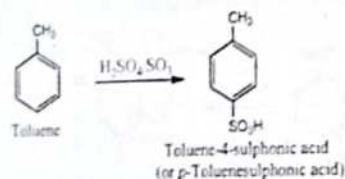
Aniline can be sulphonated with sulphuric acid as follows:
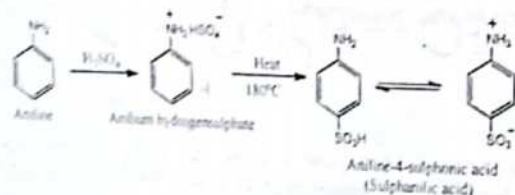
(d)   **Mercuration**

Benzene may be mercurated by treatment with mercuric acetate in glacial acetic acid at 100°C.
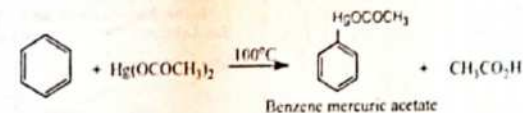
Phenol and aniline likewise can be mercurated by treatment with mercuric acetate in glacial acetic acid.
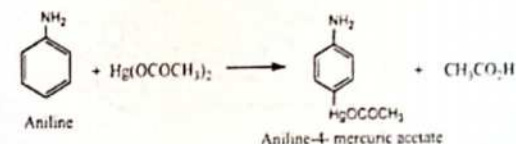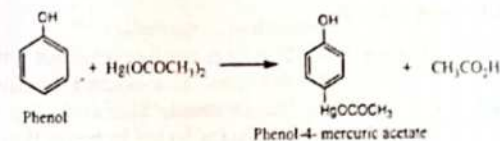
(e)   **Nitrosation**

More reactive aromatic compounds like phenol and N, N-dimethylaniline react with aqueous nitrous acid. With phenols, the nitroso-compound formed only reacts slowly, to give the diazonium salt, because the nitrosophenol is in equilibrium with the quinone monoxime.
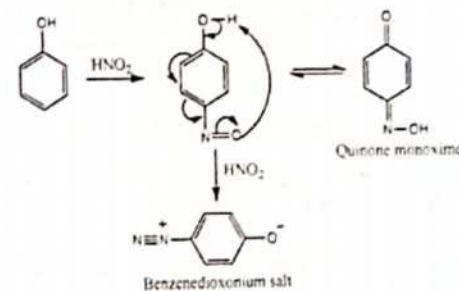
With N, N - dimethylaniline, nitrosation in acidic medium does not proceed to the diazonium salt because the protonated form of nitroso-compound does not react further with nitrous acid.

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N-(4-(hydroxyimino)cyclohexa-2,5-dien-1-ylidene)-N-methylmethanaminium

N-(4-(hydroxyimino)cyclohexa-2,5-dien-1-ylidene)-N-methylmethanaminium

4-(dimethylamino)benzenediazonium
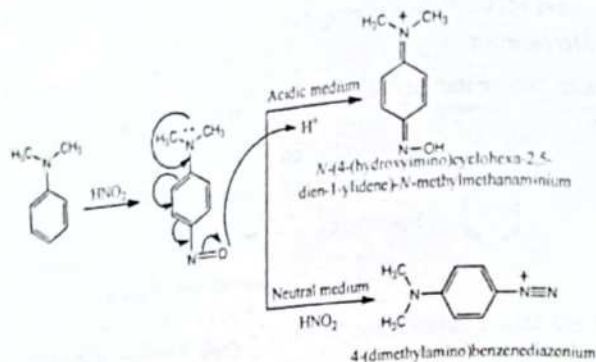
(f) Friedel - Crafts alkylation

Alkylation of benzenes with alkylhalides is usually carried out with aluminium (III) chloride as catalysts to give alkyl benzenes. This reaction is called Friedel-Crafts alkylation. Other suitable catalysts include stannic fluoride (SnF_4); boron trifluoride (BF_3); ferric chloride ($FeCl_3$), zinc chloride ($ZnCl_2$) and hydrogen fluoride (HF).

Specific examples

Ethylbenzene

Isopropylchloride   Isopropylbenzene
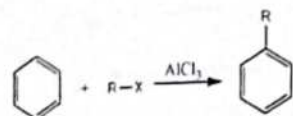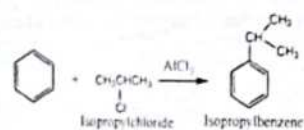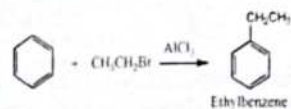
Mechanism
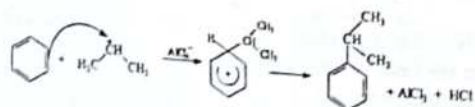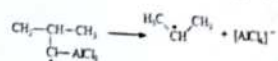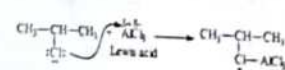
On industrial scale, alkylation is carried out with alkenes in the presence of acid catalyst such as hydrogen fluoride (HF), tetraoxophosphate (V) acid (H_3PO_4), tetraoxosulphate (VI) acid (H_2SO_4) and hydrogen bromide (HBr).

Isopropylbenzene (Cumene)
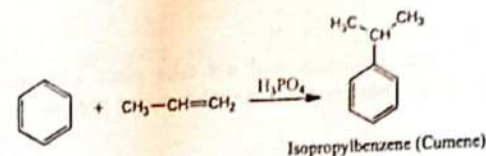
The benzene is obtainable from petroleum, and propene is a product of cracking of heavier fraction of petroleum.

Polysubstitution and Rearrangement

Since monoalkylbenzene is more reactive than benzene itself and more susceptible to attack by an electrophile, polysubstitution occurs readily unless benzene is present in large excess.

Ethylbenzene   1,3,5-Triethylbenzene   1,2,3,4,5,6-Hexaethylbenzene
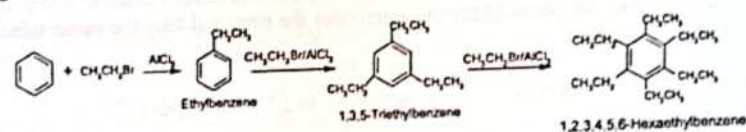
Alkylation of toluene with propylchloride gives 2,4-dipropyltoluene, if the reaction mixture is left to stand in the presence of the aluminium chloride, rearrangement occurs to give the thermodynamically more stable 3,5-dipropyltoluene.

Toluene   2,4-Dipropyltoluene   3,5-Dipropyltoluene
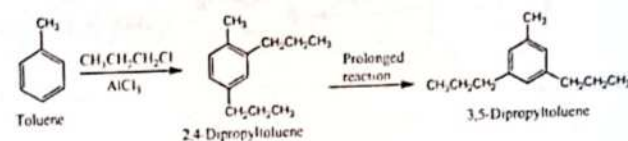
Note the following about Friedel-Craft Alkylation

(i) Any alkyl halide, alkene or alcohol that will form an initial carbocation capable of rearranging to a more stable carbocation should not be used for Friedel-Craft alkylation.

(ii) The following amines will not undergo Friedel-Craft alkylation.
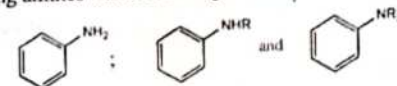
The use of the above amines or their derivatives would result in the formation of a complex with the Lewis acid, which would not undergo further reaction.

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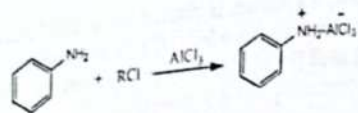
(iii) Friedel-Craft alkylation will not take place with an aromatic ring that is attached to a strongly electron withdrawing groups.
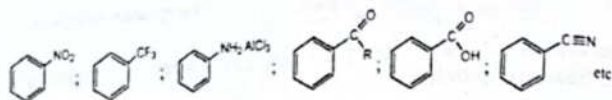
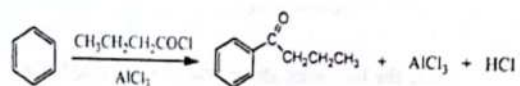### (g) Friedel - Crafts Acylation

Acylhalides or anhydrides react with benzene in the presence of an anhydrous aluminium chloride catalyst to give a good yield of aromatic ketone. The reaction involves the introduction of an acyl group RCO^+, and is called Friedel-Crafts acylation. The acyl group unlike alkyl group, deactivates the ring, and only the mono substituted product is obtained.

$$RCOCl + AlCl_3 \rightleftharpoons RCO^+ + [AlCl_4]^-$$

For anhydride;

$$(RCO)_2O + AlCl_3 \rightleftharpoons RCO^+ + [RCOO\,AlCl_3]^-$$
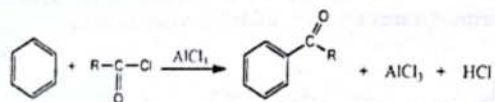
Specific examples

Mechanism
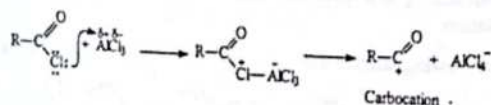
The acylium resonate as;
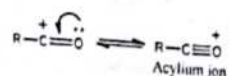
which makes the ion relatively more stable and hence less reactive. The reaction probably takes place through attack of the benzene nucleus by the acylium-aluminium

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halide complex thus:
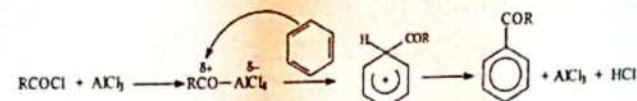
From the resonance form of the acylium ion, it is not surprising that the acylation reaction is slower than alkylation.

Other examples of acylation reactions

Benzophenone
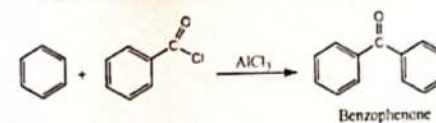
Anhydride can also be used for Friedel Craft acylation.
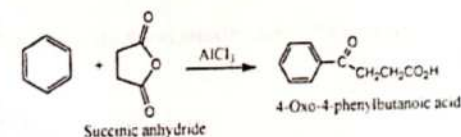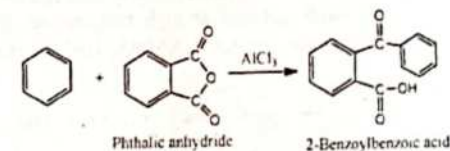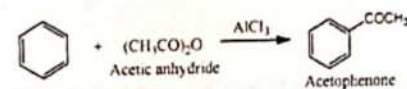
Note the following about the Freidel-Crafts Acylation

The Friedel-Crafts acylation does not work when a strongly electron withdrawing group is attached to the ring. e.g.
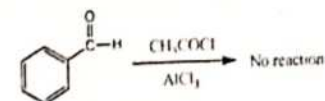
The Freidel-Crafts acylation can be used to synthesize those alkyl benzenes that cannot be efficiently prepared via Friedel-Crafts alkylation.
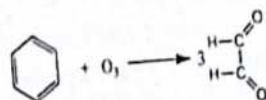
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(h) Reduction

Benzene can be hydrogenated to cyclohexane in the presence of a nickel catalyst at high temperature and pressure.

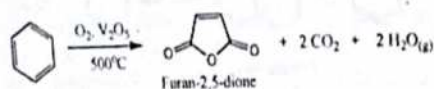
Cyclohexane

Methylcyclohexane
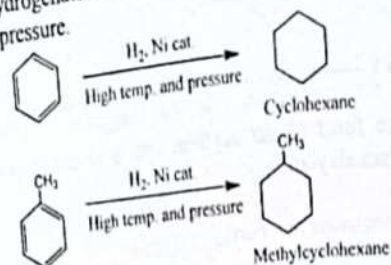
(i) Ozonolysis

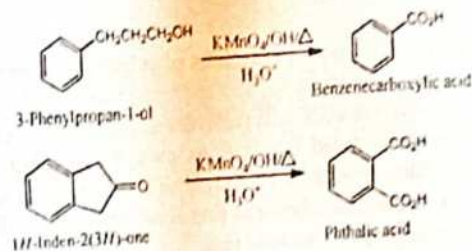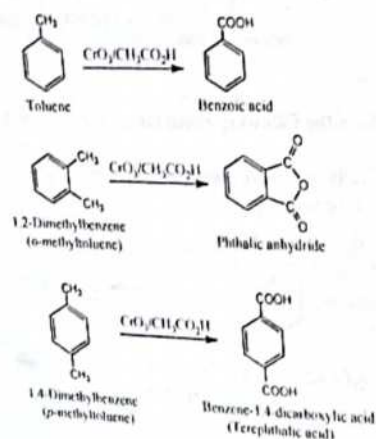Benzene can be ozonolized to ethanedial.

(j) Oxidation

Benzene is oxidized by oxygen to butenedioic anhydride (maleic anhydride) in the presence of vanadium (V) oxide catalyst at high temperature. Benzene cannot be attacked by the usual oxidizing agent (i.e. CrO_3, $KMnO_4$, H_2O_2 and OsO_4).


Furan-2,5-dione

Alkylbenzenes undergo side chain oxidation under the usual oxidizing agent to give either carboxylic acids or anhydrides.

Toluene → Benzoic acid

1,2-Dimethylbenzene (o-methyltoluene) → Phthalic anhydride

1,4-Dimethylbenzene (p-methyltoluene) → Benzene-1,4-dicarboxylic acid (Terephthalic acid)

3-Phenylpropan-1-ol → Benzenecarboxylic acid

1H-Inden-2(3H)-one → Phthalic acid

(k) Hydrogenolysis

This is cleavage of the bond between a benzylic carbon and any heteroatom.
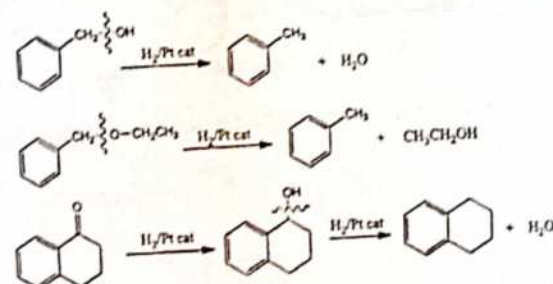

(l) Thallation reactions

Studies of Taylor E.C and Mckillop A showed that Benzene can react with thallium (III) trifluoroacetate in the presence of trifluoroacetic acid at 25°C to give an intermediate compound, phenylthallium bis-trifluoroacetate, which can subsequently be used to synthesize a variety of aromatic compounds.

Phenylthallium bis-trifluoroacetate

Iodobenzene

Phenol

Benzonitrile

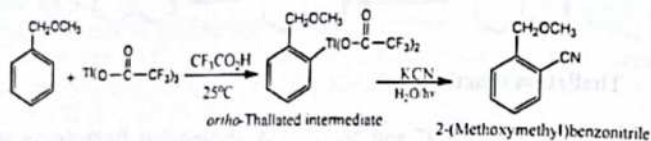Benzonitrile
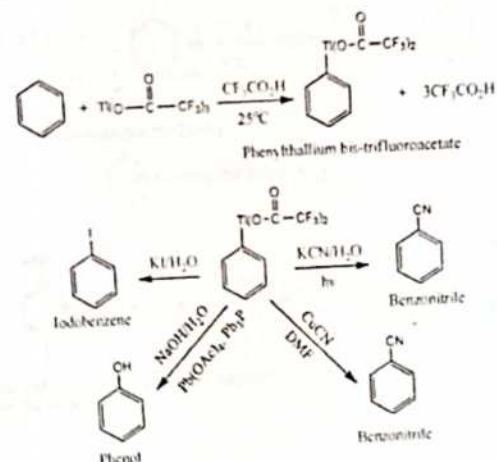
Thallation reactions of substituted benzene

Thallium (III) trifluoroacetate will preferentially attack only one of many possible positions of a mono-substituted benzene, to give *ortho-*, *para-*, or *meta-* thallated compounds, which can similarly be converted to a variety of products as above. This selective attack of a position on a benzene ring is called **regiospecificity**, and it depends on the type of substituent on the benzene ring.
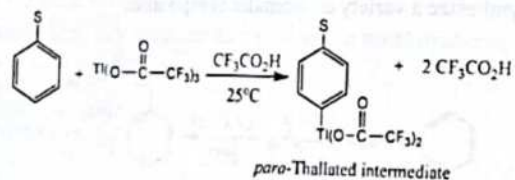
(i) *ortho*-directing

ortho-Thallated intermediate
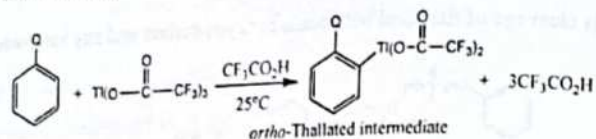
(Q = -CO$_2$H, -CH$_2$CO$_2$H, -CO$_2$CH$_3$; -CH$_2$CO$_2$CH$_3$; -CH$_2$OH; -CH$_2$OCH$_3$; -CH$_2$CH$_2$OH, -CH$_2$CH$_2$OCH$_3$)

Example

ortho-Thallated intermediate   2-(Methoxymethyl)benzonitrile

(ii) *para*-directing

para-Thallated intermediate

(S = alkyl, halogens, -OCH$_3$)

Examples

para-Thallated intermediate   *p*-Iodotoluene
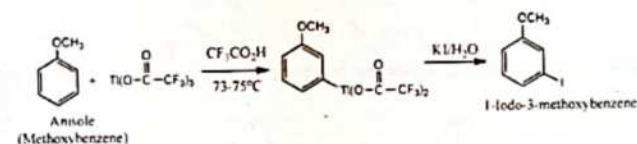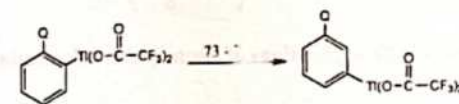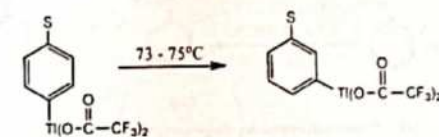   (1-Iodo-4-methylbenzene)

para-Thallated intermediate   4-Methoxyphenol
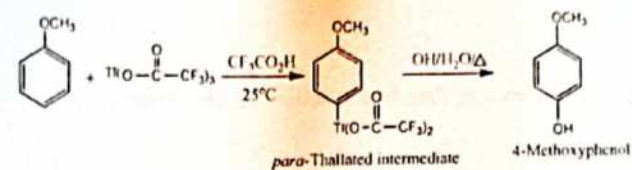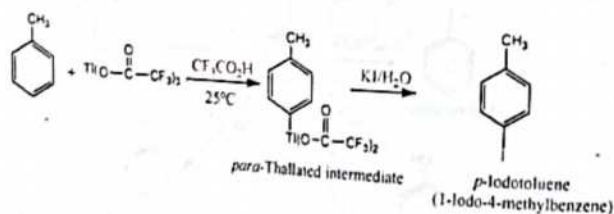
(iii) *meta*-directing

Meta thallated compounds can be obtained by heating the *ortho*- or *para*-thallated intermediate compound to 73 – 75°C.
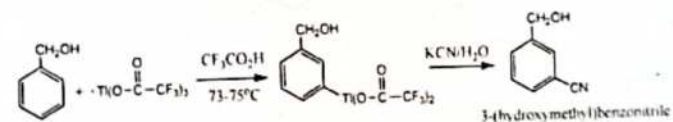

Anisole
(Methoxybenzene)   1-Iodo-3-methoxybenzene

Worked examples on synthetic applications of thallation reactions

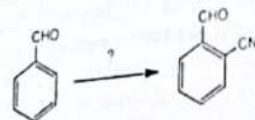### Question 1

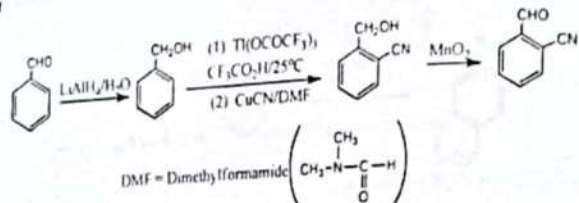How would you effect the following conversion?

Solution

3-(hydroxymethyl)benzonitrile

Question 2

Using thallation reaction, show how to accomplish the following.

Solution

DMF = Dimethylformamide $\left(CH_3-N-\overset{CH_3}{\underset{O}{\overset{|}{\underset{\parallel}{C}}}}-H \right)$

Worked examples on synthetic applications of electrophilic substitution reactions of aromatic compounds
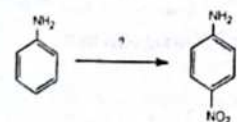
Question 3

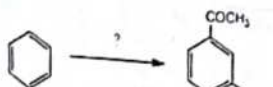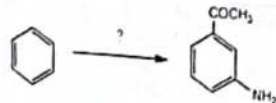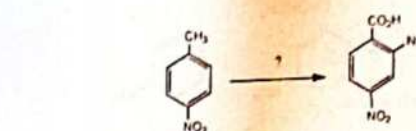How would you effect the following synthetic routes?
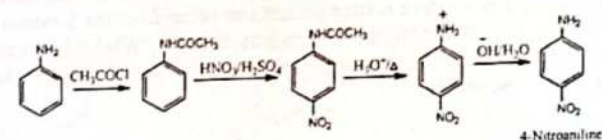
(i)

(ii)

(iii)

(iv)

(v)
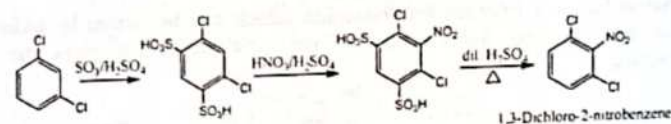

Solution
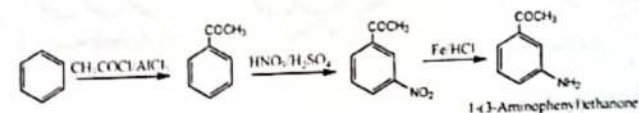
(i)

2-Bromoaniline

(ii)

4-Nitroaniline

(iii)
It is difficult to introduce a group between 1,3-disubstituted benzene when other positions are available because of steric effect (hindrance or crowding). To accomplish the conversion in question (iii) above, one needs to protect other undesirable positions.
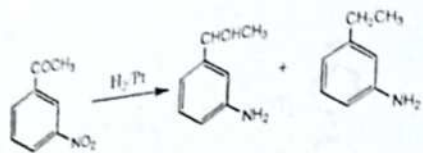

1,3-Dichloro-2-nitrobenzene
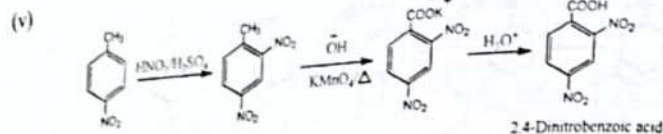
(iv)

1-(3-Aminophenyl)ethanone

N.B:

Therefore, it is better to acylate the benzene ring first before nitration

Also,

Here, it is therefore not advisable to hydrogenate with platinum as a catalyst because it will not give the desired product.

(v)

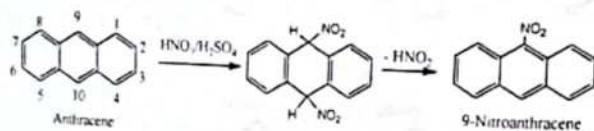2,4-Dinitrobenzoic acid

Reactions of Polycyclic Arenes

Naphthalene, anthracene and phenanthrene react chemically like benzene but they are more reactive than benzene in both substitution and addition reactions.

Substitution normally occurs at the 1 - position but under some reaction conditions, it can take place at the 2-position or rearrangement can occur from the 1-isomer to the 2-isomer. Simple molecular orbital theory predicts that the Wheland intermediate involving attack at the 1-position is the more stable product. The following are some of the reactions of polycyclic arenes.
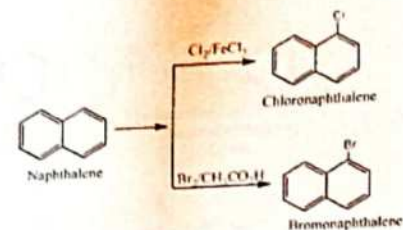
(a) Nitration
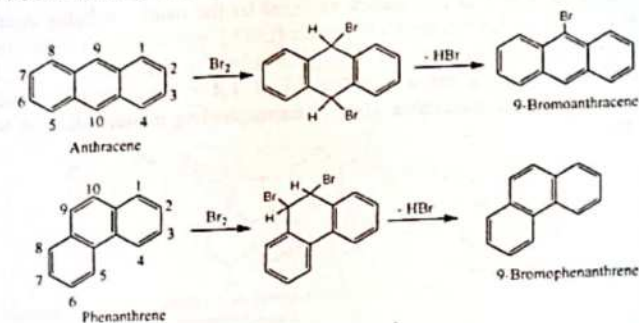
Naphthalene HNO_3/H_2SO_4 Nitronaphthalene
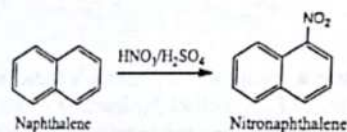
Anthracene becomes substituted at 9-position, which may be formed by addition across the 9,10-positions followed by an oxidation process to yield the 9-nitroanthracene.

(b) Halogenation

Anthracene HNO_3/H_2SO_4 $- HNO_2$ 9-Nitroanthracene

Naphthalene $Cl_2/FeCl_3$ Chloronaphthalene

Br_2/CH_3CO_2H Bromonaphthalene

Anthracene and phenanthrene become substituted predominantly at 9-position which may be formed by addition reaction across the 9,10-positions followed by an oxidation to yield the 9-halo-derivatives. The 9,10-positions undergo electrophilic addition with almost the same ease as that of alkene.

Anthracene Br_2 $- HBr$ 9-Bromoanthracene

Phenanthrene Br_2 $- HBr$ 9-Bromophenanthrene

(c) Sulphonation

H_2SO_4 0-60°C   Naphthalene-1-sulfonic acid $H_2SO_4/180°C$ Naphthalene-2-sulfonic acid

$H_2SO_4/165°C$ Naphthalene-2-sulfonic acid $H_2SO_4 + 15\%\ SO_3$ 165°C   Naphthalene-1,3,6-trisulfonic acid

(d) Friedel-Crafts Acylation

1-(Naphthalen-1-yl)ethanone
(1-Naphthylacetone)
(61%)

1-(Naphthalen-2-yl)ethanone
(2-Naphthylacetone)
(33%)

1-(Naphthalen-2-yl)ethanone
(2-Naphthylacetone)
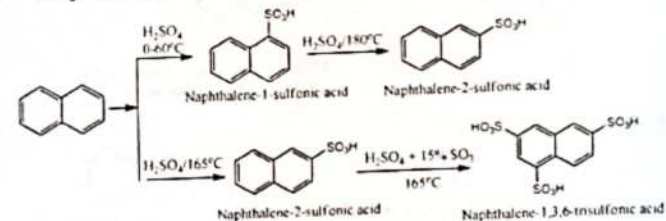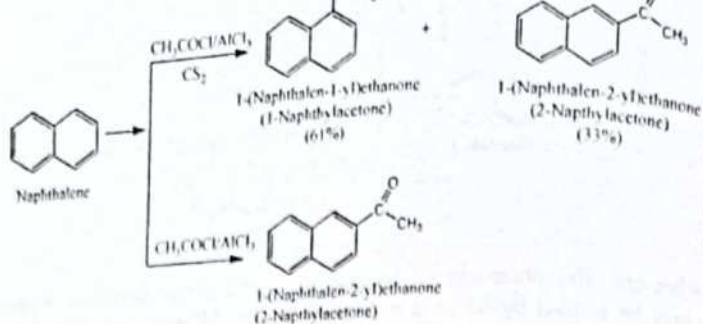
(e) Oxidation

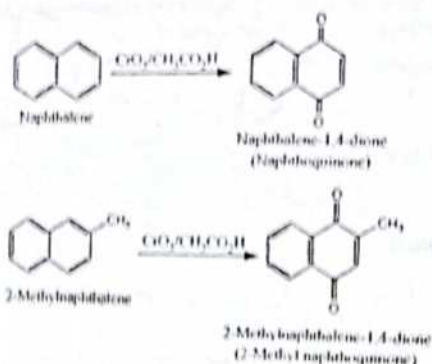Unlike benzene which is not readily oxidized by the usual oxidizing agents like chromic (VI) oxide (CrO_3), Osmium (VIII) oxide (OsO_4), potassium tetraoxomanganate (VII) ($KMnO_4$) and hydrogen peroxide (H_2O_2), treatment of naphthalene with chromic (VI) oxide in acetic acid gives a small yield of 1,4 - naphthoquinone while 2-methylnaphthalene gives a reasonable yield of corresponding naphthoquinone with the same reagents.
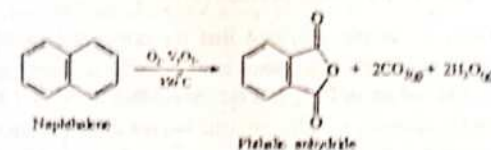

Naphthalene

Naphthalene-1,4-dione
(Naphthoquinone)

2-Methylnaphthalene

2-Methylnaphthalene-1,4-dione
(2-Methyl naphthoquinone)

Compared with:

Toluene

Benzoic acid

Both anthracene and phenanthrene are readily oxidized to 9,10-quinone derivatives.

Anthracene

9,10-Anthraquinone

Phenanthrene

9,10-Phenanthroquinone
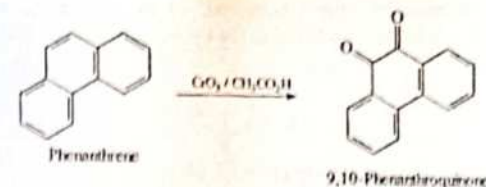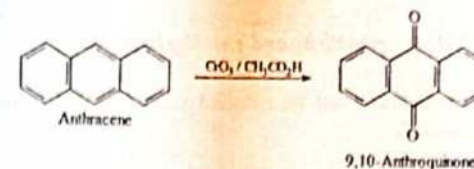
Catalytic oxidation of naphthalene under controlled conditions opens one ring giving phthalic anhydride.

Naphthalene

Phthalic anhydride

(f) Reduction

Naphthalene can be reduced to a dihydro-derivative by sodium and alcohol or sodium amalgam, and to tetrahydro-derivative (tetralin) by sodium in refluxing pentanol.

Naphthalene

1,4-Dihydronaphthalene

1,2,3,4-Tetrahydronaphthalene
(Tetralin)
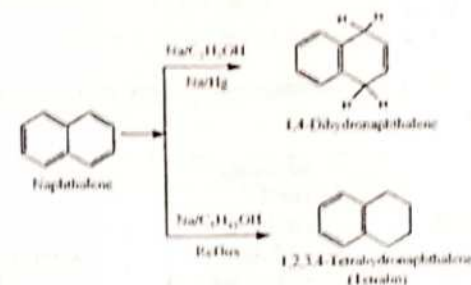
Reduction by catalytic hydrogenation yields decalin.

Naphthalene

Tetralin

Decahydronaphthalene
(Decalin)

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There are four criteria that must be satisfied to ensure that a molecule exhibit aromaticity, and these include

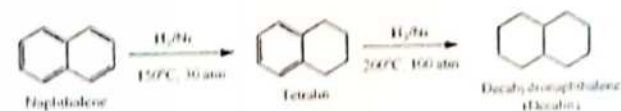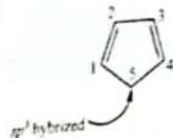a.   The molecule must be cyclical, i.e, must contain at least a ring

b.   The molecule must be fully conjugated, i.e there must be orbital overlap between all the carbon atoms found in the cyclic ring.

Cyclopenta1,3-diene is not fully conjugated because of C5, which is sp^3 hybridized.

c.   The molecule must be planar, continuously lie along the same plane.

d.   Must obey *Huckel's rule*, which is stated below:

Eric Huckel, a German chemist, proposed that for compound to be aromatic, a monocyclic (one ring), planar compounds must have (4n + 2) pi electrons, where 'n' is an integer and it can take values of 0, 1, 2, 3 etc. According to *Huckel's rule*, a ring with 2, 6, 10 or 14 pi (π) electrons may be aromatic but not 4n pi (π) electron (i.e. 4, 8, 12) or any other numbers. Thus, cyclobutadiene, with four pi (π) electrons, and cyclooctatetraene with eight, are not aromatic, whereas benzene, a planar molecule with six pi (π) electrons is aromatic. The rule is generally limited to n = 0 – 5. This rule is derived from the *Huckel* molecular orbital (MO) calculation on planar monocyclic conjugated hydrocarbons $(CH)_m$, where *m* is an integer equal to or greater than 3 according to which (4n + 2)π –electrons are contained in a closed-shell system. The table below differentiates between the characteristic features of aromatic, anti-aromatic and non-aromatic molecules.

Table 2.1. Characteristic features of aromatic, anti-aromatic and non-aromatic molecules

Aromatic	Anti-aromatic	Non-aromatic
Stable	Unstable	Regular
4n + 2 π electrons	4n π electrons	3,5,7,9
2,6,10,14,18 π electrons,	4,8,12, 16	Noncyclic/cyclic
Cyclic, conjugated	Cyclic, conjugated	unconjugated
sp^2 hybridized and planar	sp^2 hybridized and planar	sp^3 hybridized

Benzene has 6π –electrons

$\therefore$ 4n + 2 = 6

$$n = \frac{4}{4} = 1$$

$\therefore$ *Benzene obeys Huckel's rule, hence, it is aromatic*

Other examples include:

(i)   Cyclobutadiene

Cyclobutadiene has 4π –electrons

$\therefore$ 4n + 2 = 4

$$n = \frac{1}{2} \ (\ non-integer)$$

Cyclobutadiene does not obey Hückel's rule, hence it is anti – aromatic.

(ii)   Cycloocta 1,3,5,7-tetraene

Cyclooctatetraene has 8π –electrons

$\therefore$ 4n + 2 = 8

n = 3/2 (non–integer)

Cyclooctatetraene does not obey Hückel's rule, hence it is anti – aromatic

(iii)   Cyclopenta-1,3-diene

Cyclopenta – 1,3 – diene has 4π – electrons but C5 is sp^3 hybridized

$\therefore$ 4n + 2 = 4

n = 1/2 (non–integer)

Cyclopenta – 1,3 – diene does not obey Hückel's rule, and C5 is sp^3 hybridized, hence it is anti – aromatic

(iv)   Cyclopropene

Cyclopropene has 2π - electrons

The top carbon (C3) is sp^3 hybridized

$$\therefore 4n + 2 = 2$$
$$n = 0 (an \ int \, eger)$$

Cyclopropene does obey Hückel's rule, but C3 is sp^3
hybridized, hence it is non - aromatic

(v)   Cyclobutene

Cyclobutene has 2π - electrons and contains sp^3 hybridized carbon atoms

$$\therefore 4n + 2 = 2$$
$$n = 0 (an \ int \, eger)$$

Cyclobutene does obey Hückel's rule, but C3 and C4 are sp^3
hybridized, hence it is non - aromatic

(vi) Cyclododeca-1,3,5,7,9,11-hexaene

Cyclododeca-1,3,5,7,9,11-hexaene

Cyclododeca - 1,3,5,7,9,11 - hexaene has 12π - electrons

$$\therefore 4n + 2 = 12$$
$$n = \frac{5}{2} (non - int \, eger)$$

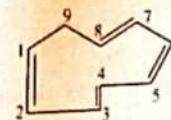*Cyclododeca - 1,3,5,7,9,11 - hexaene does not obey Hückel's rule,*
hence it is anti - aromatic

(vii) Cyclopenta[cd]indene

Cyclopent[cd]indene has 10π - electrons

$$\therefore 4n + 2 = 10$$
$$n = 2 (an \ int \, eger)$$

Cyclopent[cd]indene does obey Hückel's rule, hence it is aromatic
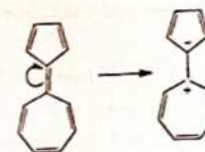
(viii) Cyclonona-1,3,5,7-tetraene

Cyclonona - 1,3,5,7 - tetraene has 8π - electrons and contains sp^3 hybridized carbon atom

$$\therefore 4n + 2 = 8$$
$$n = \frac{3}{2} (non \ int \, eger)$$

Cyclonona - 1,3,5,7 - tetraene does not obey Hückel's rule, and C9 is sp^3 hybridized,
hence it is anti - aromatic / non - aromatic.

(ix) 7-(Cyclopenta-2,4-dien-1-ylidene)cyclohepta-1,3,5-triene

7 (Cyclopenta - 2,4 - dien - 1 - ylidene)cyclohepta - 1,3,5 - triene has 10π - electrons

$$\therefore 4n + 2 = 10$$
$$n = 2 (an \ int \, eger)$$

7 (Cyclopenta - 2,4 - dien - 1 - ylidene)cyclohepta - 1,3,5 - triene does obey
Hückel's rule, hence it is aromatic

(x)   5-(Cycloprop-2-en-1-ylidene)cyclopenta-1,3-diene

5 (Cyclopro - 2 - en - 1 - ylidene)cyclopenta - 1,3 - diene has 6π - electrons

$$\therefore 4n + 2 = 6$$
$$n = 1 (an \ int \, eger)$$

5 (Cyclopro - 2 - en - 1 - ylidene)cyclopenta - 1,3 - diene does obey
Hückel's rule, hence it is aromatic

(xi) *Fulvene*

Fulvene has 4 π – electrons

$$\therefore 4n + 2 = 4$$

$$n = \frac{1}{2} (non\ integer)$$

Fulvene does not obey Hückel's rule, hence it is anti – aromatic

(xii) *Cyclohexa-1,3-diene-5-yne (Benzyne)*

Benzyne unlike normal alkyne contain a weak lateral overlap of two sp^2 orbital at the exterior part of the aromatic ring, which does not provide the required stability expected of a C-C π-bond, and is delocalized as shown above.
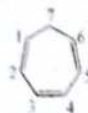
Benzyne has 6 π – electrons

$$\therefore 4n + 2 = 6$$

$$n = 1(an\ integer)$$

Benzyne does obey Hückel's rule, hence it is aromatic

(xiii) *Cyclohepta-1,3,5-triene*

Cyclohepta-1,3,5-triene has 6 π – electrons and contains sp^3 hybridized carbon atom

$$\therefore 4n + 2 = 6$$

$$n = 1(an\ integer)$$

Cyclohepta-1,3,5-triene does obey Hückel's rule, but C7 is sp^3 hybridized, hence it is non – aromatic

(xiv) *Bicyclo[4.4.1]undeca-1,3,5,7,9-pentaene*

Bicyclo[4.4.1]undeca-1,3,5,7,9 – pentaene has 10 π – electrons

$$\therefore 4n + 2 = 10$$

$$n = 2(an\ integer)$$

Bicyclo[4.4.1]undeca-1,3,5,7,9 – pentaene does obey Hückel's rule, hence it is aromatic

Aromatic ions

Hückel's Rule is also applicable to aromatic ions. In as much as the compound has $4n+2$ π electrons, it does not matter if the molecule is neutral or has a charge. For instance, cyclopentadienyl anion is an aromatic ion. As can be seen from the structure below, carbons 2-5 are sp^2 hybridized while carbon 1 with one lone pair is attached to an sp^2 hybridized atom, then C-1 atom is also sp^2 hybridized. Therefore, cyclopentadienyl anion has 6 π electrons and fulfills the $4n+2$ rule.
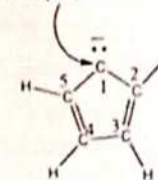
Cyclopentadienyl anion

Other examples include

(i) Cyclopropenyl anion

Cyclopropenyl anion

Cyclopropenyl anion has 4 π – electrons

$$\therefore 4n + 2 = 4$$

$$n = \frac{1}{2}(non\ integer)$$

Cyclopropenyl anion does not obey Hückel's rule, hence it is anti – aromatic

(ii) Cyclopropenyl cation

Cyclopropenyl cation

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Cyclopropenyl cation has 2π - electrons

$$\therefore 4n + 2 = 2$$

$$n = 0 (an\ integer)$$

Cyclopropenyl cation does obey Hückel's rule, hence it is aromatic

(iii) Cyclobut-3-ene-1,2-diide (Cyclobutene dianion)

Cyclobut-3-ene-1,2-diide has 6π - electrons

$$\therefore 4n + 2 = 6$$

$$n = 1 (an\ integer)$$

Cyclobut-3-ene-1,2-diide does obey Hückel's rule, hence it is aromatic

(iv) Cyclobut-3-ene-1,2-diylium (Cyclobutene dication)

Cyclobut-3-ene-1,2-diylium has 2π - electrons

$$\therefore 4n + 2 = 2$$

$$n = 0 (an\ integer)$$

Cyclobut-3-ene-1,2-diylium does obey Hückel's rule, hence it is aromatic

(v) Cyclopenta-2,4-dien-1-ylium (Cyclopentadiene cation)

Cyclopenta-2,4-dien-1-ylium has 4π - electrons

$$\therefore 4n + 2 = 4$$

$$n = \frac{1}{2} (non\ integer)$$

Cyclopenta-2,4-dien-1-ylium does not obey Hückel's rule, hence it is anti-aromatic

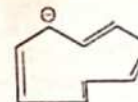(vi) Cyclohepta-2,4,6-trien-1-ylium (Cycloheptatriene cation)

Cyclohepta-2,4,6-trien-1-ylium has 6π - electrons

$$\therefore 4n + 2 = 6$$

$$n = 1 (an\ integer)$$

Cyclohepta-2,4,6-trien-1-ylium does obey Hückel's rule, hence it is aromatic

(vii) Cyclonona-2,4,6,8-tetraen-1-ide (Cyclononatetraene anion)

Cyclonona-2,4,6,8-tetraen-1-ide has 10π - electrons
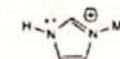
$$\therefore 4n + 2 = 10$$

$$n = 2 (an\ integer)$$

Cyclonona-2,4,6,8-tetraen-1-ide does obey Hückel's rule, hence it is aromatic

Heterocyclic Aromatic Compounds

These are aromatic compounds that contain other atoms in addition to carbon and hydrogen. The following examples illustrate how Hückel's rule is applicable to heterocyclic aromatic compounds.
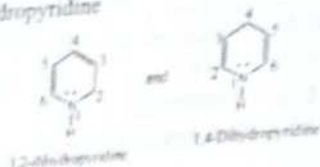
(i) 3-Methyl-1H-imidazol-3-ium

3-Methyl-1-H-imidazol-3-ium has 6π - electrons

$$\therefore 4n + 2 = 6$$

$$n = 1 (an\ integer)$$

3-Methyl-1-H-imidazol-3-ium does obey Hückel's rule, hence it is aromatic
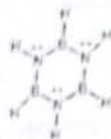
(ii) 1,2 and 1,4-Dihydropyridine

1,2-dihydropyridine   1,4-Dihydropyridine

Both 1,2 and 1,4 - Dihydropyridine has 6π - electrons and contains sp^3 hybridized carbon atoms at C2 and C4 respectively

$$\therefore 4n + 2 = 6$$

$$n = 1 (an\ integer)$$

1,2 and 1,4 - Dihydropyridine do obey Hückel's rule, but C2 and C4 are sp^3 hybridized respectively, hence both is non - aromatic.

(iii) 1,3,5,2,4,6-Triazatriborinane

1,3,5,2,4,6 - Triazatriborinane has 6π - electrons

$$\therefore 4n + 2 = 6$$

$$n = 1 (an\ integer)$$

1,3,5,2,4,6 - Triazatriborinane does obey Hückel's rule, hence it is aromatic.

(iv) 1 H-Borole

1H - Borole has 4π - electrons

$$\therefore 4n + 2 = 4$$

$$n = \frac{1}{2} (non\ integer)$$

1H - Borole does not obey Hückel's rule, hence it is anti - aromatic.

(v) 2,3-Dihydro-1,2,3-thiadiazole

2,3 - Dihydro - 1,2,3 - thiadiazole has 8π - electrons (only 1 of S's lone pairs counts as π - electrons)

$$\therefore 4n + 2 = 8$$

$$n = \frac{3}{2} (non\ integer)$$

2,3 - Dihydro - 1,2,3 - thiadiazole does not obey Hückel's rule, hence it is anti - aromatic.

(vi) Pyrylium

Pyrylium has 6π - electrons (O is using $1p$ orbital for the electrons in the double bond so its lone pairs of electrons are not π electrons, so there are 6π electrons

$$\therefore 4n + 2 = 6$$

$$n = 1 (non\ integer)$$

Pyrylium does obey Hückel's rule, hence it is aromatic.

(vii) Pyrrol-1-ide
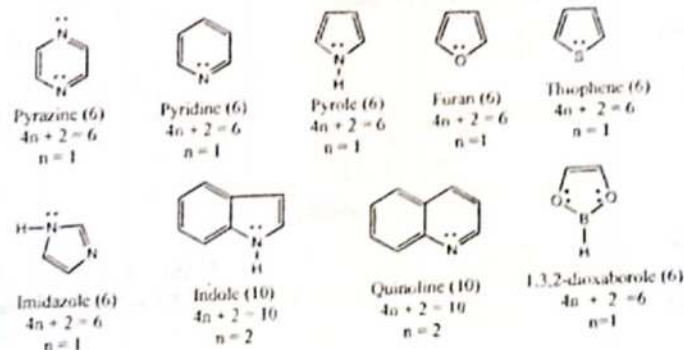

Pyrrol - 1 - ide has 6π - electrons (only one of the N's lone pairs counts as π electrons, so there are 6π electrons)
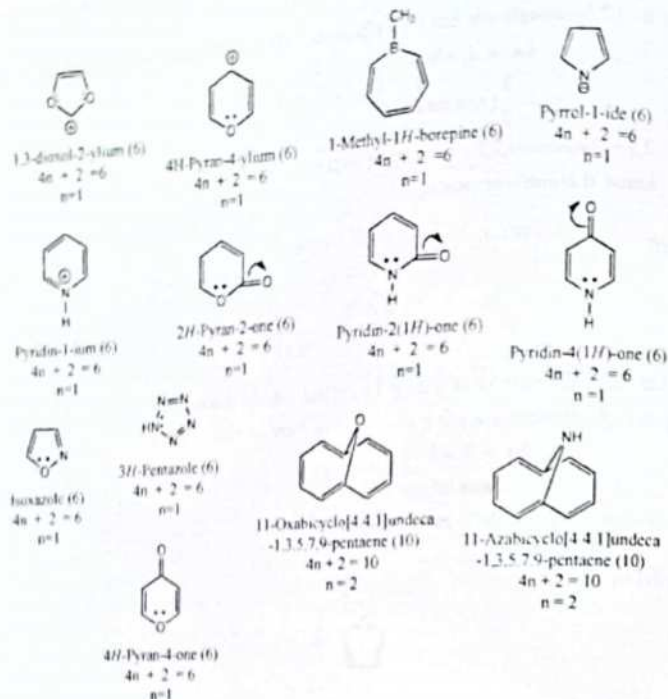
$$\therefore 4n + 2 = 6$$

$$n = 1 (non\ integer)$$

Pyrrol - 1 - ide does obey Hückel's rule, hence it is aromatic.

Other examples of heterocyclic compounds with aromatic character

Pyrazine (6)
$4n + 2 = 6$
$n = 1$

Pyridine (6)
$4n + 2 = 6$
$n = 1$

Pyrole (6)
$4n + 2 = 6$
$n = 1$

Furan (6)
$4n + 2 = 6$
$n = 1$

Thiophene (6)
$4n + 2 = 6$
$n = 1$

Imidazole (6)
$4n + 2 = 6$
$n = 1$

Indole (10)
$4n + 2 = 10$
$n = 2$

Quinoline (10)
$4n + 2 = 10$
$n = 2$

1,3,2-dioxaborole (6)
$4n + 2 = 6$
$n = 1$

CH₃

1,3-dioxol-2-ylium (6)
4n + 2 = 6
n=1

4H-Pyran-4-ylium (6)
4n + 2 = 6
n=1

1-Methyl-1H-borepine (6)
4n + 2 = 6
n=1

Pyrrol-1-ide (6)
4n + 2 = 6
n=1

Pyridin-1-ium (6)
4n + 2 = 6
n=1

2H-Pyran-2-one (6)
4n + 2 = 6
n=1

Pyridin-2(1H)-one (6)
4n + 2 = 6
n=1

Pyridin-4(1H)-one (6)
4n + 2 = 6
n=1

Isoxazole (6)
4n + 2 = 6
n=1

3H-Pentazole (6)
4n + 2 = 6
n=1

11-Oxabicyclo[4.4.1]undeca
-1,3,5,7,9-pentaene (10)
4n + 2 = 10
n = 2

11-Azabicyclo[4.4.1]undeca
-1,3,5,7,9-pentaene (10)
4n + 2 = 10
n = 2

4H-Pyran-4-one (6)
4n + 2 = 6
n=1

Pi (π) molecular orbital theory

This theory explains the reason why a monocyclic compound with six or ten pi (π) electrons is aromatic while a compound with eight pi (π) electrons is non-aromatic. For a molecule to be aromatic, it must have all pi (π) electrons paired, thus providing the maximum and complete overlap required for aromatic stabilization. If some pi (π) orbitals are partially filled (that is there are unpaired pi (π) electrons), overlapping is not maximum and the compound would not be aromatic.

Consider the following examples:

i.   Benzene:

It contains six pi (π) electrons.

Benzene has six pi (π) electrons, three bonding and three antibonding orbitals. The three bonding orbitals are filled to capacity, and all the pi (π) electrons are paired, hence benzene is aromatic.
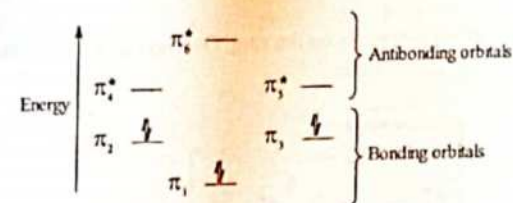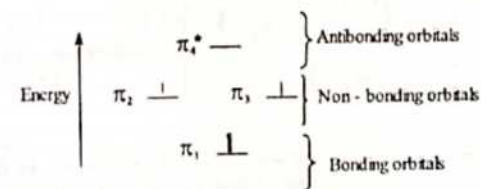
ii.   Cyclodecapentaene:

This has ten pi (π) electrons, five bonding and five antibonding orbitals. The five bonding orbitals are filled to capacity, and all the pi (π) electrons are paired, hence it is aromatic.
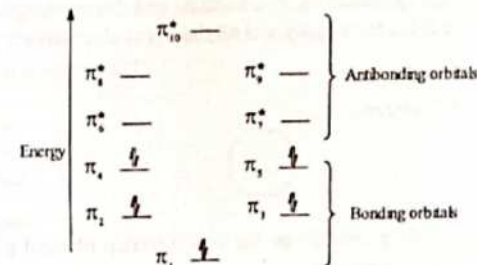
iii. Cyclobutadiene:

This compound has four p orbitals on the ring; overlap of four p orbitals would result in the four pi (π) molecular orbitals.
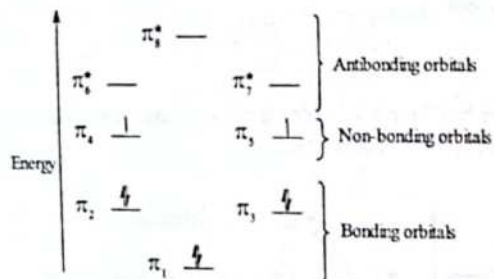
The π₁ is fully filled, the remaining two electrons would be found, one each, in the degenerate π₂ and π₃ orbitals. The pi (π) electrons of butadiene would not all be paired, and the overlapping is not maximum, hence butadiene is not aromatic.

(iv) Naphthalene

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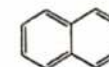
This compound has ten p-orbitals on the ring. Overlays of ten p orbitals would result in ten pi (π) molecular orbitals.
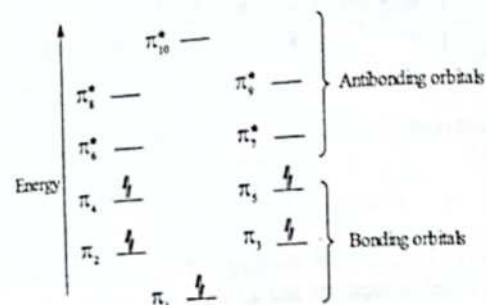
Naphthalene has ten pi (π) electrons, five bonding and five antibonding orbitals. The five bonding orbitals are filled to capacity and all the pi (π) electrons are paired, hence it is aromatic.

v.   *Cycloocta 1,3,5,7-tetraene*

This compound has eight p orbitals on the ring. Overlap of eight p orbitals would result in eight pi (π) molecular orbitals.

If cyclooctatetraene were planar and had a pi (π) system similar to that in benzene, the π_1, π_2 and π_3 orbitals would be completely filled with six of the eight pi (π) electrons. The remaining two would be found, one each, in the degenerate π_4 and π_5 orbitals. The pi (π) electrons of cyclooctatetraene would not all be paired, and the overlapping would not be maximal, and hence the compound cannot be aromatic.
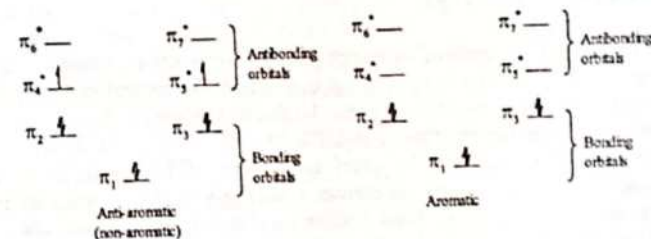
For aromatic ions
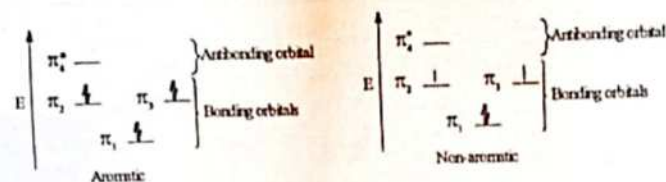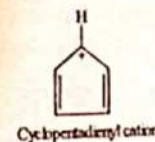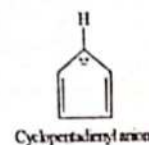
The cyclopentadienyl anion, with six pi (π) electrons conforms with $(4n + 2)$ pi electrons rule. It has three pi (π) orbitals filled and all the pi (π) electrons are paired. The anion is aromatic. The cation, however, has four pi (π) electrons in the three orbitals. The pi (π) electrons would not all be paired, and there would not be maximum overlap. The cation is not aromatic.

Other examples are:

i.   *Cycloheptatrienyl Ions*

The cycloheptatrienyl cation, with six pi (π) electrons conforms with $(4n + 2)$ pi electrons rule. It has three pi (π) orbitals filled and all the pi (π) electrons are paired. The cycloheptatrienyl cation is aromatic. Cycloheptatrienyl anion is anti-aromatic as can be seen above.
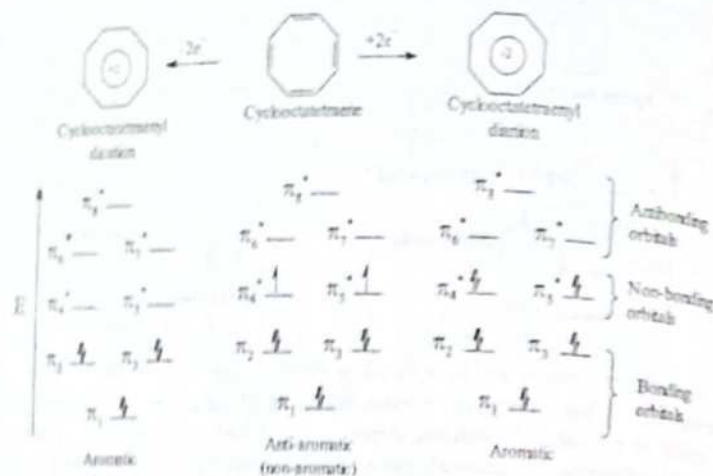
Cyclooctatraene itself is non-aromatic as can be seen from the above pi (π) molecular orbital; the dication, corresponding to a six-electron system, obtained by removing two electrons from the neutral compound (i.e. cyclooctatetraene) and the dianion, corresponding to a ten-electron system, obtained by adding two electrons to the neutral compound are aromatic.

XIII. Natural Sources and uses of Hydrocarbons

(i) Petroleum and natural gas

These are the largest sources of hydrocarbons. The composition of natural gas varies greatly depending on the area from which it is obtained. The natural gas comprises of methane (50-90%), ethane (5-20%), propane (3-18%) and butane (1-7%).

Petroleum is a complex mixture of liquid and solid hydrocarbons; its composition also varies with the sources. The chief component of petroleum is paraffinic hydrocarbons, (saturated five-and six-carbon atoms), alicyclic hydrocarbons (called naphthenes) and aromatic hydrocarbons. Olefins are absent. Petroleum is distilled into a number of useful commercial fractions (Table 2.2).

Table 2.2
Petroleum Distillation Products

Fraction	Temperature range ($^{\circ}$C)	Composition	Uses
Natural gas	< 20	$C_1 - C_4$	Heating
Light naptha	20 - 100	$C_5 - C_6$	Organic Solvent
Heavy naphtha	100 - 150	$C_6 - C_{12}$	Motor fuel
Kerosene	150 - 235	$C_{12} - C_{14}$	Domestic fuel, tractors, & Jet engines, Diesel fuel
Light gas oil	235 - 345	$C_{14} - C_{18}$	Lubrication
Heavy gas oil {Lubricating, {Petroleum jelly {Paraffin wax	345 - 565	> C_{18}	Lubrication Medicine Candles
Residue (Bitumen & asphalt)	-	> C_{40}	Road construction and Roofing

(ii) Destructive distillation of coal

Hydrocarbons are obtained by destructive distillation or carbonization of coal (heating coal in the absence of air) at 1000 - 1300°C to produce coal gas and coal tar. Coal gas contains methane together with smaller amounts of ethane, ethylene, benzene, toluene, cyclopentadiene, naphthalene and nonhydrocarbon products such as hydrogen, ammonia, carbon (II) oxide, hydrogensulphide, hydrogen cyanide, cyanogen and nitric oxide. The normal liquid or solid hydrocarbons in the coal gas, i.e. the cyclopentadiene, benzene, toluene and naphthalene can be recovered. The coal gas is further treated to remove toxic components and then used as a domestic fuel (Table 2.3).
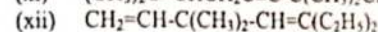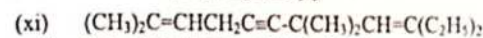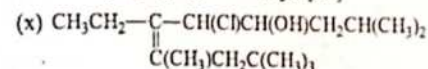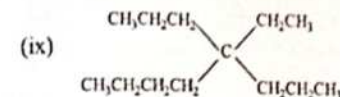
Table 2.3
Coal Distillation Products

Fraction	Composition	Uses
Coal gas	H_2, CH_4, CO, alkene	Fuel
Light oil	Benzene, toluene, xylenes, naphthalene, cyclopentadiene	Solvents, raw materials
Coal tar	Arenes: naphthalene, anthracene, phenanthrene, other polycyclics; heterocyclic; aromatic nitrogen compounds; phenols	Raw materials in organic chemical and pharmaceutical industries and paint industry.
Coke (residue)	Carbon	Fuel, heating, reducing agent in metallurgy and as decolourizer

The volatile oils obtained from certain plants, trees and citrus fruits (lemon or orange) contains members of a large group of hydrocarbons known as terpenes having the formula $C_{10}H_{16}$. These exist both as aliphatic compounds (alkatrienes such as 2, 6-dimethyl-2, 4, 6-octatriene) and more usually as alicyclic compounds (e.g. 1-methyl-4-isopropenylcyclohexene or 2, 6, 6-trimethyl -bicyclo [3.1.1]-2-heptene). Related hydrocarbons include the sesquiterpenes $C_{15}C_{24}$; diterpenes, $C_{20}H_{32}$; triterpenes, $C_{30}H_{48}$ and polyterpenes, $C_{10n}H_{16n}$.

Practice Questions

2.1   (a)   Name the following compounds using I.U.P.A.C. system, and include where necessary the appropriate stereochemical designation.

(i) $CH_3- CH(Cl)-CH = C(CH_3) - C≡C-C(CH_3)_3$

(ii) $(CH_3)_3-C-C≡C-CH(CH_3)C(CH_3)_3$

(iii) $(CH_3)_2-CH- CH(Br) - CH_2- CH_2- C(CH_3)_3$

(iv)   (v)

(vi) $CH≡C-C(CH_3)_2 CH(C_2H_5) C≡CH$

(vii)

(viii)

(ix)

(x) $CH_3CH_2—\underset{\underset{\overset{|}{C(CH_3)CH_2C(CH_3)_3}}{||}}{C}—CH(Cl)CH(OH)CH_2CH(CH_3)_2$

(xi) $(CH_3)_2C=CHCH_2C≡C-C(CH_3)_2CH=C(C_2H_5)_2$

(xii) $CH_2=CH-C(CH_3)_2-CH=C(C_2H_5)_2$

(xiii) $(CH_3)_3C-CH=C(CH_3)-C≡C-C(CH_3)_3$
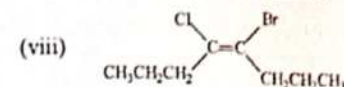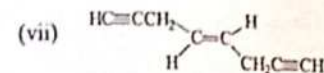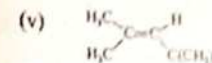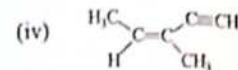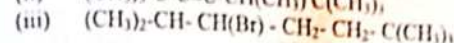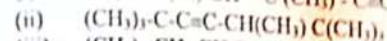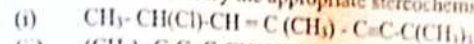
(b)   Give the structures for the following compounds:

(i)   Hexa-1,4-diyne

(ii)   *trans*-t-Butylmethylethylene

(iii)   *p*-Diisopropenylbenzene

(iv)   3-Methylbut-2-ene

(v)   3,3-Diethylhept-2-ene-1-yne

(vi)   *trans*-3-Methylpent-2-ene

(vii)   3-Ethyl-2,5-dimethylhex-3-ene

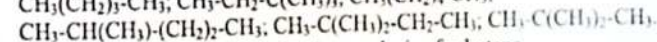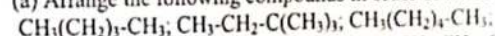(viii)   1,5-Dibromopenta-1,4-diene-3-yne

(ix)   2,5-Dichloro-*cis*-hex-3-ene

(x)   4-Ethyl-6-methyl-(Z)-oct-5-ene-2-yne

(xi)   (E)-1-Isopropyl-1,2-dimethylethylene

(xii)   6-(*trans*-2-Butenyl)-*cis*,*trans*-undeca-2,8-diene

2.2   (a) Arrange the following compounds in order of increasing volatility:
$CH_3(CH_2)_3-CH_3$; $CH_3-CH_2-C(CH_3)_3$; $CH_3(CH_2)_4-CH_3$; $CH_3-CH(CH_3)-(CH_2)_2-CH_3$; $CH_3-C(CH_3)_2-CH_2-CH_3$; $CH_3-C(CH_3)_2-CH_3$.

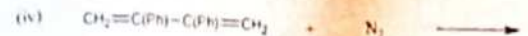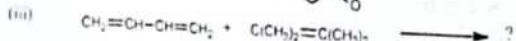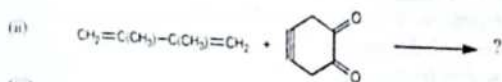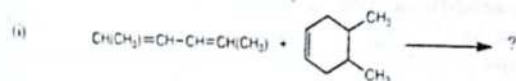(b)   (i) Propose mechanism for the pyrolysis of n-butane
(ii) Name all the products formed when butane is nitrated with nitric acid in the vapor phase at a temperature range of 400-500°C and 10-15 atmosphere pressures.

(c) Name and draw the structures of all isomers of K formed in the following reaction:

$$CH_3(CH_2)_6CH_3 \xrightarrow[450\ C]{CrO_2} K + nH_{2(g)}$$
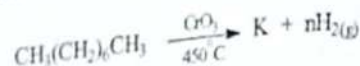
What is the value of n?

2.3 (a) Give a simple chemical test in each case by which you could distinguish between the following pairs of compounds:

(i) 2-Methylpropane and 2-Methylpropene
(ii) 3-Methylbut-1-ene and 3-Methylbut-1-yne
(iii) 4-Methylpent-1-yne and 4-Methylpent-2-yne

(b) In a study of chlorination of propane, four products, A,B, C and D of formula $C_3H_6Cl_2$ were isolated.

(i) What are their possible structures?
(ii) On further chlorination, A gave only one trichloro product, B gave two trichloro products and C can be obtained in an optically active form. Identify A, B, C and D.

2.4 (a) Give the mechanism for the monochlorination of butane.

(b) (i) Give the order for the ease of dehydrochlorination of alkylchloride.
(ii) With the aid of reaction mechanism, outline the dehydrochlorination of 2-chloro-2-ethyl-3-methyl butane.
(iii) Arrange the products formed in b (ii) above in order of increasing stability. Give reasons for your order.

(c) (i) Give the order for the ease of dehydration of alcohols.
(ii) With the aid of reaction mechanisms, outline the dehydration of 2,3 dimethylpent-3-ol.
(iii) Arrange the products formed in c (ii) above in order of increasing stability. Give reasons for your order.

2.5 Give the names and structures of the Markovnikov and anti-Markovnikov products formed when:

(i) CH_3-$C(Br)$=CH-$C(CH_3)_3$ and
(ii) ClC≡C-$CH(CH_3)_2$ are allowed to react with the following reagents:

(a) Hydrogen cyanide
(b) Hypobromous acid
(c) Tetraoxosulphate (VI) acid followed by hydrolysis.
(d) Hydrogen fluoride
(e) Ethane
(f) Propylchloride.

2.6 Using Diel-Alder reaction, draw the structures of the products of the following reactions.

(iv) CH_2=$C(Ph)$-$C(Ph)$=CH_2 + N_2 ⟶ ?

(v) CH_2=CH-CH=CH_2 + (structure) ⟶ ?

(vi) CH_2=CH-CH=$C(CH_3)_2$ + $CH(CN)$=CH_2 ⟶ ?
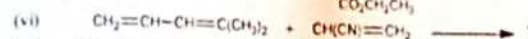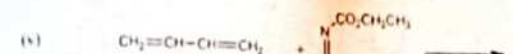
2.7 (a) Propose schemes for the following conversions:

(i) Ethyne to Hex-3-yne
(ii) But-1-yne to Hept-3-ol
(iii) Ethyne to Heptan-2,5-diol-3-yne
(iv) Propyne to propanone
(v) But-1-yne to But-2-yne

(b) Give the structure(s) of the product(s) in each of the following reactions, showing any similarities or differences between them.

(i) Pent-2-yne is reacted with acidified potassium tetraoxomanganate (VII)
(ii) Pent-2-yne is reacted with sodium in liquid ammonia.
(iii) When two moles of ethyne are mixed together in the presence of copper (I) chloride in acidified ammonium chloride.
(iv) When four moles of ethyne are mixed together in the presence of dicyanonickel (II) complex in tetrahydrofuran at 65°C and 20 atmospheres.
(v) When two moles of propyne are oxidatively coupled together in the presence of cuprous salt.

2.8 During the cracking of petroleum, there was abundance production of a compound whose molecular formula is C_5H_{10}. The compound has six isomeric structures A, B, C, D, E and F.

(i) What are their possible structures?
(ii) Isomer A is stable to catalytic hydrogenation, B is less stable while C and D are easily converted to n-pentane and 2-methylbutane respectively when heated with hydrogen in the presence of nickel catalyst.
(iii) E exhibits geometric isomerism while F does not. Identify A, B, C, D, E and F.

2.9 Draw and name all the structural isomers for the following:

(i) C_7-alkanes
(ii) C_7-alkenes
(iii) C_7-alkynes
(iv) C_7-cycloalkanes
(v) C_7-cycloalkenes
(iv) C_7-cycloalkynes

2.10 (a) Name the following compounds using I.U.P.A.C. systems:
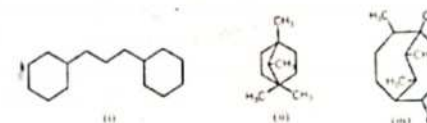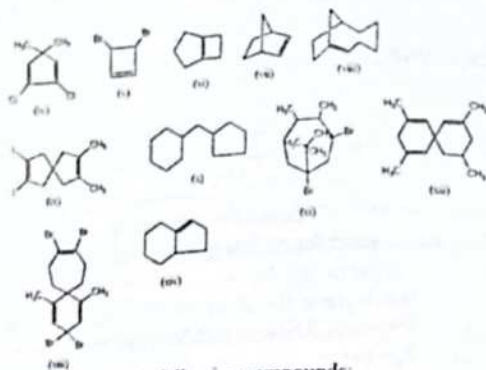
**2.11** Give the structures for the following compounds:
- (i) 2,5,8-Tribromobicyclo [3.2.1] oct-3-ene
- (ii) Bicyclo [3.2.1] oct-2-ene
- (iii) *Spiro* [4.5] dec-2-ene
- (iv) 2,3,4-Trimethylspiro [5.4] dec-2-ene
- (v) 4,7-Dimethylbicyclo [2.2.2] octane
- (vi) 2,3,6,8-Tetramethylspiro [4.3] octa-1,3,5-triene
- (vii) 1,3,5-Trimethylcyclohept-2-ene
- (viii) 4,5,5,7-Tetrabromobicyclo [2.2.1] hept-1-yne
- (ix) *cis*-3,4-Dichlorocyclobutene
- (x) *trans*-2-Chlorocylohexanol
- (xi) 1,3-Diethylcyclopenta-2,4-diene
- (xii) 3,4,7,8-Tetramethylcycloocta-1,5-diene

2.12
- (a) Outline the industrial uses of alicyclic hydrocarbons.
- (b) Propose schemes for the following conversions:
  - (i) 1-Methylcyclopropane to 1-Bromobut-2-ene
  - (ii) 1-Methylcyclopropane to But-2-ol.
  - (iii) 1,1-Dimethylcyclopropane to 2-Methylbutane
  - (iv) Ethylaminecyclobutane to Cyclohexene
  - (v) 1-Methylcyclopropane to But-2-ene
  - (vi) 1,2-Dimethylcyclohexene to Hexan-1,6-dione
  - (vii) Cyclopentene to Penta-1,5-dial
  - (viii) Cyclohexene to Hexan-1,6-dioic acid
  - (ix) Cyclohexene to *cis*-Cyclohexan-1,2-diol
  - (x) 3,4-Dimethylcyclobutene to *trans*-Hexa-2,4-diene
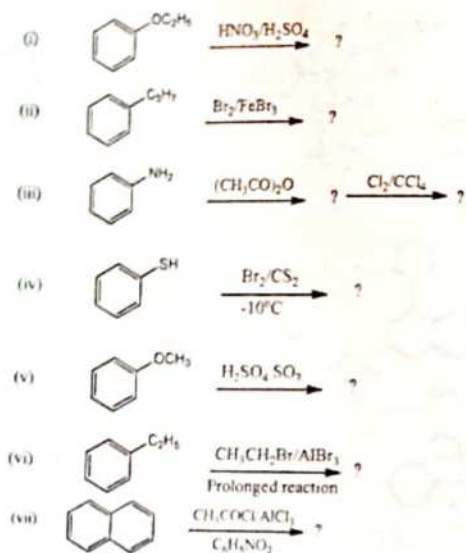
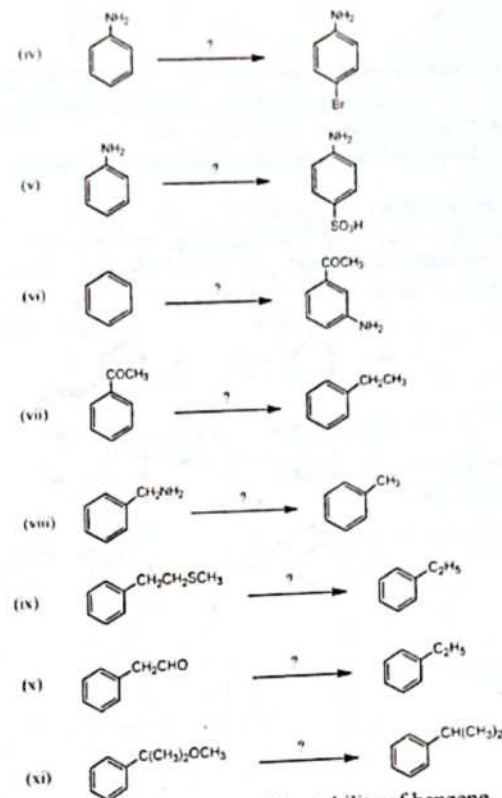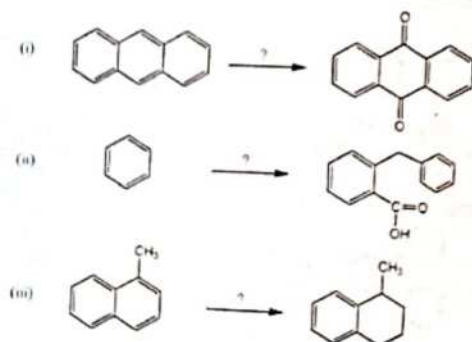**2.13** Name the following aromatic compounds by I.U.P.A.C. systems:
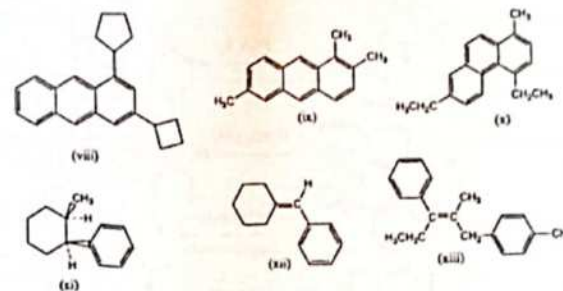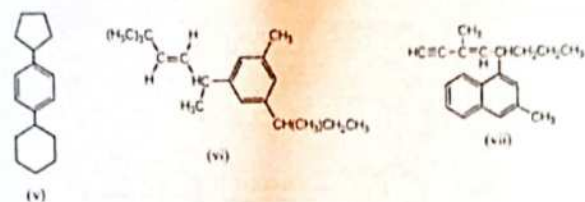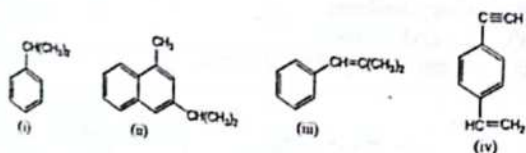
2.14 Predict which of the following structures would be expected to possess aromatic character, and explain using pi (π) molecular orbital theory the basis for your choice.
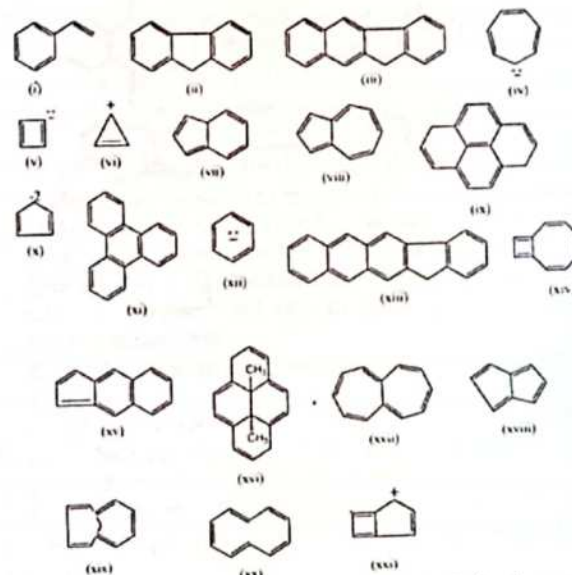
2.15 Give the name and structure of the product(s) of the following reactions:

(i) HNO_3/H_2SO_4 ?

(ii) $Br_2/FeBr_3$?

(iii) $(CH_3CO)_2O$? Cl_2/CCl_4 ?

(iv) Br_2/CS_2 $-10°C$?

(v) H_2SO_4, SO_3 ?

(vi) $CH_3CH_2Br/AlBr_3$ Prolonged reaction ?

(vii) $CH_3COCl, AlCl_3$ $C_6H_5NO_2$?

2.16 How would you effect the following conversions:

(i) ?

(ii) ?

(iii) ?

(iv) ?

(v) ?

(vi) ?

(vii) ?

(viii) ?

(ix) ?

(x) ?

(xi) ?

2.17 (a) Give two evidences in support of the stability of benzene.

(b) Explain, using resonance theory, why electrophilic substitution occurs predominantly at the *ortho*-and *para*-positions of aniline while it occurs more at the *meta*-position of phenylethanone.

(c) Give an account of four reactions in which benzene behaves as a saturated compound and two reactions in which it behaves as unsaturated compound.

(d) How and under what conditions, does naphthalene reacts with the following:

(i) trioxonitrate (V) acid   (ii) tetraoxosulphate (VI) acid
(iii) bromine   (iv) butanoylchloride
(v) chromic (VI) oxide in ethanoic acid
(vi) sodiumethoxide   (vii) hydrogen.

(v) Arrange the following alkenes in order of increasing stability, and give reasons for your order:
$CH_3CH=C(CH_3)CH_2CH_2CH_3$; $CH_3(CH_2)_3CH=CHCH_3$; $CH_2=CH(CH_2)_4CH_3$; $(CH_3)_2C=CHCH_2CH_2CH_3$; $(CH_3)_3C-CH=CHCH_3$; $(CH_3)_2C=C(CH_3)CH_2CH_3$; $(CH_3)_2C=CHCH(CH_3)_2$ and $CH_3CH_2C(CH_3)=C(CH_3)_2$.

2.18 (a) Propose a reaction scheme by which monobromination of aniline could be achieved.

(b) How and under what condition would you expect benzene to react

with:
(i) Ozone   (ii) Oxygen

(c) Compare and contrast the reactions of benzene, toluene and p-methyltoluene with potassium tetraoxomanganate (VII), (KMnO₄) in acidic solution.

(d) Using thallation reaction, show how to accomplish the following.
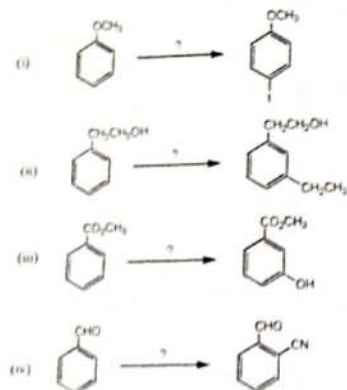
FUNCTIONAL GROUP CHEMISTRY

Functional groups are groups of atoms or bonds common to a series or family of compounds and which govern the principal chemical properties of the series. A series of organic compounds having the same functional group with any member of the series differing from the next by a unit $-CH_2-$ is called homologous series. Below are some common functional groups.

TABLE 3.1

Some Common Functional Groups

Homologous series	General structural formula	Functional Group
Alkanes	$C_nH_{2n+2}(n \geq 1)$	-
Alkenes	$C_nH_{2n}(n \geq 2)$	$>C=C<$
Alkynes	$C_nH_{2n-2}(n \geq 2)$	$-C \equiv C-$
Alcohols	$C_nH_{2n+1}OH (n \geq 1)$	$-OH$
Halides	$C_nH_{2n+1}X (n \geq 1)$	$-X (X = Cl, Br, I, F)$
Ethers	$(C_nH_{2n+1})_2O (n \geq 1)$	$-O-$
Primary amines	$C_nH_{2n+1}NH_2 (n \geq 1)$	$-NH_2$
Secondary amines	$(C_nH_{2n+1})_2NH (n \geq 1)$	$-NH-$
Tertiary amines	$(C_nH_{2n+1})_3N (n \geq 1)$	$-N<$
	$C_nH_{2n+1}NO_2 (n \geq 1)$	$-N\begin{smallmatrix}O^- \\ O\end{smallmatrix}$
Nitrocompound	$C_nH_{2n+1}SH (n \geq 1)$	$-SH$
Thiol	$(C_nH_{2n+1})_2S (n \geq 2)$	$-S-$
Thioether		
Aldehydes	$C_nH_{2n+1}CHO (n \geq 0)$	$\underset{H}{>}C=O$
Ketones	$C_nH_{2n+2}CO (n \geq 2)$	$>C=O$
Carboxylic acids	$C_nH_{2n+1}COOH (n \geq 0)$	$\underset{HO}{>}C=O$
Acid (acyl) chlorides	$C_nH_{2n+1}COCl (n \geq 1)$	$\underset{Cl}{>}C=O$

Table 3.1 contd.

Homologous series	General structural formula	Functional Group
Acid amides	$C_nH_{2n+1}CONH_2(n \geq 1)$	$\underset{}{H_2N}\diagdown C{=}O$
Esters	$C_nH_{2n+1}COOR$ ($n \geq 1$) (R=alkyl or aryl radical)	$RO\diagdown C{=}O$
Anhydrides	$(C_nH_{2n+1}CO)_2O$ ($n \geq 1$)	$-C\diagup^{O}\diagdown_{O}$ $-C\diagup^{O}$
Nitriles	$C_nH_{2n+1}CN$ ($n \geq 1$)	$-C\equiv N$

Alkanes, alkenes and alkynes have been discussed in Part II. We will now deal with polar functional groups, some of these have saturated groups, and others are unsaturated.

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