SRI MEENAKSHI VIDIYAL
ARTS AND SCIENCE COLLEGE (Co-Education)

(Affiliated to the Bharathidasan University, Trichy)
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INSTRUCTION MATERIAL

2019-2020

DEPARTMENT OF CHEMISTRY

SYLLABUS

GENERAL CHEMISTRY –II

Unit 1: CHEMICAL BONDING

lonic bond–Lattice Energy –Born –Haber Cycle –Pauling and Muliken‘s Scales of electro negativity – Polarizingpower and Polarisability –partial ionic character from electro negativity – Transitions from ionic to covalent character and vice versa –Fajan‘s rule.VESPR Theory–Shapes of simple inorganic molecules ($BeCl_2$, $SiCl_4$, PCl_5, SF_6,IF_7, NH_3, XeF_6, BF_3,H_2O) -VB Theory –Principles of hybridization –$BeCl_2$–MO Theory –Bonding and antibonding orbitals – Application of MO Theory to H_2,He_2,N_2,O_2,HF and CO –Comparison of VB and MO Theories.

Unit 2: CHEMISTRY OF s-BLOCK ELEMENTS

Position of Hydrogen in the Periodic Table, atomic hydrogen, nascent hydrogen, occluded hydrogen, uses of hydrogen. General characteristics of s-block elements –General characteristics of Group IA –diagonal relationship between Li and Mg –Extraction of Lithium –Physical and Chemical properties of Lithium –Uses –Extraction of Sodium –Physical and Chemical properties –Uses –Preparation of NaOH (Laboratory and Industrial methods) –Properties –Uses – Preparation of Na_2CO_3(Laboratory and Industrial methods)–Properties –Uses –Extraction of Potassium –Properties –Uses –Chemistry of KOH,KBr and K1.General characteristics of Elements of Group11A–diagonal relationship between Be and AI –Extraction of Beryllium – Physical and Chemical properties of Be –Uses Extractionof Mg –Physical and Chemical properties –Uses –Chemistry of some compounds of Mg: $MgCO_3$, $MgSO_4$,$MgCl_2$, $Mg(NH_4)PO_4 6H_2O$ –Extraction of Ca –Physical and Chemical properties –Uses –Cement manufacture –Types –Chemistry of setting of cement.

Unit 3:CHEMISTRY OF ALKENES, ALKYNES AND DIENES

Nomenclature –Geometrical Isomerism –Petroleum source of alkenes and aromatics –General methods of preparation of alkenes –Chemical properties –Uses –Elimination mechanisms (E 1,E2,E1cB) –Electrophilic, Free radical additions –Ziegler –Natta Catalytic polymerization of ethylene –polymers of alkene derivatives.Nomenclature General methods of preparation of alkynes –Physical properties –Chemical –Uses –Types of alkadienes –General methods of preparation of Dienes –Physical properties –Chemical properties –Uses –Mechanisms of electrophilic and Free radical addition reactions –Polymers –Rubber as a natural polymer –Types of polymerization reactions –Mechanisms of lonic and Free radical polymerization reactions –Chemistry of Vulcanization of rubber –Chemistry of manufacture of Film sheets, Rayon and Polycyclic fibres –Uses of Polymers.

Unit 4: CHEMISTRY OF BENZENE AND OTHER BENZENOID COMPOUNDS

General methods of preparation of benzene –Chemical properties –Uses –Electrophillic substitution mechanism –Orientation and reactivity in substituted benzenes. Types of Polynuclear Aromatic compounds –Nomenclature –Naphthalene from coal tar and petroleum – Laboratory preparation Structure of Naphthalene –Aromatic character –Physical properties – Chemical properties –Uses –Mechanism of Aromatic electrophilic substitution –Theory of orientation and reactivity –Anthracene, Phenanthrene from tar and petroleum –Laboratory preparation-Molecular Orbital structures –Aromatic Characters –Physical Properties -Chemical properties –Uses –Preparation of biphenyls –Physical and Chemical properties –Uses.

Unit 5: GASEOUS STATE

Maxwell‘s distribution of Molecular velocities (Derivation not required). Types of Molecular velocities –Mean, Most probable and root mean square velocities. Graphical representation and its significance –Collision diameter, Mean free path and collision number –Transport properties–Thermal conductivity, Viscosity and Diffusion –Law of equipartition of energies –Degree of freedom. Molecular basis of Heat capacity –Real gases –vander. Waals equation of states –derivation –significance of critical constants –Virial equations of state –Law of corresponding states –Compressibility factor.

SUBJECT : GENERAL CHEMISTRY – II

CODE : 16SCCCH2

2 MARKS

1) **Define ionic bond**

A type of chemical bond where two atoms or molecules are connected to each other by electrostatic attraction.

2) **What is lattice energy?**

Lattice energy is the energy released when ions in the gas phase are condensed into a solid.

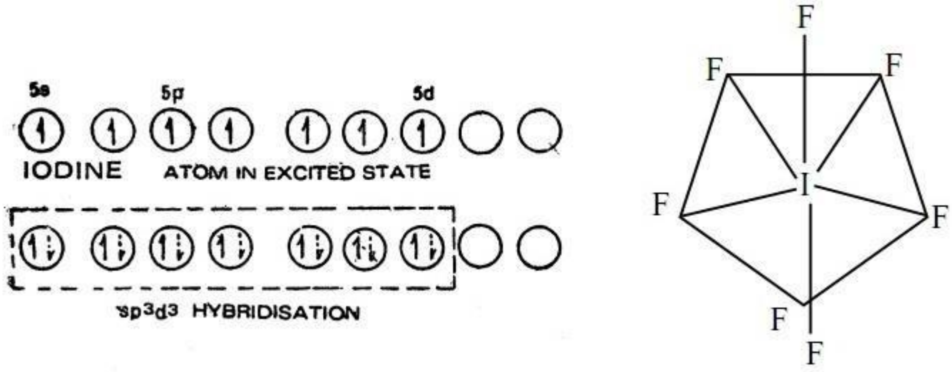
3) **What is** polarizability **?**

The tendency of the anion to become polarized by the cation is known as its **polarizability.**

4) **What is polarizing power**?

The ability of a cation to distort an anion is known as its **polarization power.** 5)

Give the structure of IF_7



Pentagonal bipyramidal structure

6) **Define hybridization**

Mixing a set of atomic orbitals to form a new set of atomic orbitals with the same total electron capacity and with properties and energies intermediate between those of the original unhybridized orbitals.

7) **Define molecular orbital theory**

A theory of chemical bonding based upon the postulated existence of molecular orbitals.

8) **Define VSEPR theory**

Theory assumes that electron pairs are arranged around the central element of a molecular or polyatomic ion so that there is maximum separation among regions of high electron density.

9) **S-block element**

Groups (1 & 2) belong to the s-block of the Periodic Table.

- Group 1 consists of : lithium, sodium, potassium, rubidium, cesium and Francium and collectively known as the alkali metals.
- Group 2 include : beryllium, magnesium,calcium, strontium, barium and Radium except Beryllium, they are known as alkaline metals.

10) **Oxidation state for S – Block elements**

The alkali metals exhibit oxidation state of +1 in their compounds and are strongly electropositive in character. The electropositive character increases from Li to Cs.

11) **Name the chief factors responsible for anomalous behavior of lithium.**

The anomalous behavior of lithium is because of its:

(i)Small size of atom and ion,
(ii)High ionization enthalpy, and
(iii)Absence of d-orbitals in its Valence shell

12) **Why are alkali metals not found in nature?**

Alkali metals are highly reactive in nature due to low ionization enthalpy and strong electropositive character. They do not occur in free state and are always combined with other elements.

13) Why is alkali metals soft and have low melting points?

Alkali metals have only one valence electron per metal atom. As a result, the binding energy of alkali metal ions in the close-packed metal lattices is weak. Therefore, these are soft and have low melting point.

14) Rules for Aromaticity

i. The molecule is cyclic (a ring of atoms) ii. The molecule is planar (all atoms in the molecule lie in the same plane) iii. The molecule is fully conjugated (p orbitals at every atom in the ring)

iv. The molecule has 4n+2 π electrons (n=0 or any positive integer) And, it must have a certain number of π-electrons. This is known as Huckel's rule. The number of π electrons must equal one of the numbers in this series: 2, 6, 10, 14, 18….and so on. **15) What is Benzene?**

i. The chemical formula of benzene is C_6H_6, so it has six carbon (C) atoms and six hydrogen (H) atoms. Its chemical structure can be described as a hexagon ring with alternating double bonds,

ii. Because of its chemical formula, C_6H_6, benzene is classified as a hydrocarbon, which is a compound that consists of only carbon and hydrogen atoms. Its structure and formula reveal benzene to be an aromatic hydrocarbon, which is defined as a compound that is composed of hydrogen and carbon that has alternating double bonds forming a ring.

16) Uses of benzene

- Hydrogenation of benzene results in cyclohexane which is used in caprolactam (a source for Nylon) manufacturing.
- Being alkylated with propylene benzene gives cumin which is used on phenol and acetone industrial preparation.

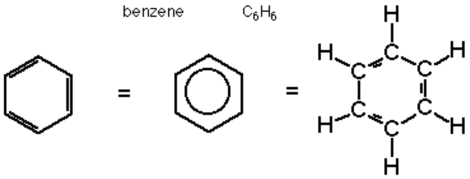
17) Uses of Napthalene

- As an ingredient in the manufacture of the explosive known as gunpowder;
- In the production of lubricants
- In the manufacture of various types of dyes and coloring agents;

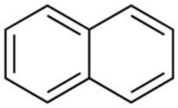
- As a preservative.

18) Structure of benzene and naphthalene

Benzene:



Naphthalene:



19) State haloalkanes

The replacement of hydrogen atom(s) in hydrocarbon, aliphatic by halogen atom(s) results in the formation of alkyl halide (haloalkane)

20) Haloarenes

The replacement of hydrogen atom(s) in hydrocarbon,aromatic, by halogen atom(s) results in the formation of aryl halide (haloarenes)

21) Give the nomenclature of haloalkanes for the following

i. CH_3Br_3 - Tribromomethane ii. $ClCH_2CH_2Cl$
- 1,2-dichloroethane iii. $BrCH_2CH_2Br$ - 1,2-
dibromoethane

22) Give any two uses of iodobenzene

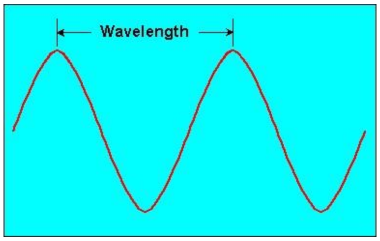
1. It is used in synthetic organic chemistry
2. It is used for substrate for heck reaction

23) Electromagnetic radiation

Energy having both the form of electromagnetic waves and the form of a stream of photons and travelling at the speed of light in a vacuum. The entire range of frequencies and wavelengths of electromagnetic radiation makes up the electromagnetic spectrum

24) wavelength

A wavelength is a measure of distance between two identical peaks (high points) or troughs (low points) in a wave (a repeating pattern of traveling energy like light or sound)

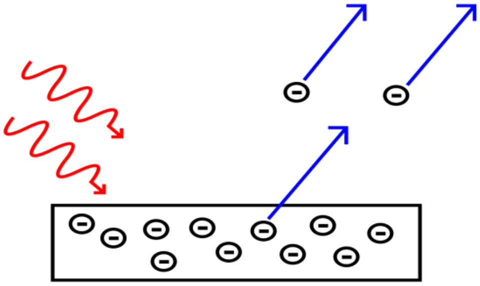


25) velocity

A velocity of an object is the rate of change of the object‘s position with respect to a frame of reference and time, it might sound complicated but velocity is basically speed in a specific direction. It is a vector quantity, which means we need both magnitude (speed) and direction to define velocity. The SI unit of it is meter per second (ms^{-1}) if there is a change in magnitude or the direction in velocity of a body the body is said to be accelerating.

26) photoelectric effect

The photoelectric effect refers to the emission, or ejection, of electrons from the surface of, generally, a metal in response to incident light



27) Compton effect

Compton scattering, discovered by Arthur Holly Compton, is the inelastic scattering of a photon by a charged particle, usually an electron. It results in a decrease in energy (increase in wavelength) of the photon (which may be an X-ray or gamma ray photon), called the Compton effect.

28) black-body radiation

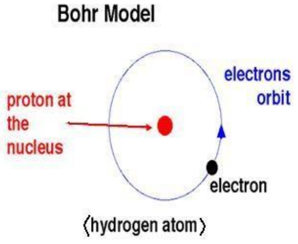
An object that absorbs all radiation falling on it, at all wavelengths, is called a black body. When a black body is at a uniform temperature, its emission has a characteristic frequency distribution that depends on the temperature. Its emission is called black-body radiation

29) Heisenberg uncertainty principle

The statement in quantum mechanics, formulated by Werner Heisenberg, that it is impossible to measure two properties of a quantum object, such as its position and momentum (or energy and time), simultaneously with infinite precision.

30) Bohr theory

A theory of atomic structure in which the hydrogen atom (Bohr atom,) is assumed to consist of a proton as nucleus, with a single electron moving in distinct circular orbits around it, each orbit corresponding to a specific quantized energy state: the theory was extended to other atoms.



5 MARKS

31) Write Postulates of Valence Bond Theory

- The overlapping of two half filled valence orbitals of two different atoms result in the formation of the covalent bond. Due to overlapping, the electron density between two bonded atoms increases and this gives stability to the molecule.
- In case the atomic orbitals possess more than one unpaired electron, more than one bond can be formed and electrons paired in the valence shell cannot take part in such a bond formation.
- A covalent bond is directional and it is parallel to the region of overlapping atomic orbitals.
- Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond and a pi bond. The covalent bond formed by sidewise overlapping of atomic orbitals is known as pi bond whereas the bond formed by overlapping of atomic orbital along the inter nucleus axis is known as a sigma bond.
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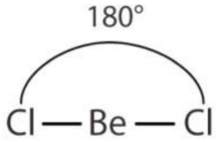
32) Distinguish between bonding and antibonding molecular orbital

Bonding molecular orbital	**Antibonding molecular orbital**
Its energy is less than that of parent atomic orbital.	Its energy is greater than that of parent atomic orbital.
It is more stable than the parent atomic orbital.	It is less stable than the parent atomic orbital.
In B.M.O, the probability of finding electrons	In A.B.M.O, the probability of finding
is maximum.	electrons is minimum.
Contribution of B.M.O is maximum towards the shape of molecule.	It does not contribute towards the shape of molecule.

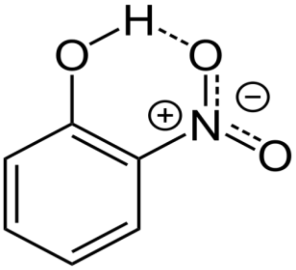
33) Explain about $BeCl_2$ structure

There are only two places in the valence shell of the central atom in $BeCl_2$ where electrons can be found. Repulsion between these pairs of electrons can be minimized by arranging them so that they point in opposite directions. Thus, the VSEPR theory predicts that $BeCl_2$ should be a **linear** molecule, with a 180^o angle between the two Be-Cl bonds.



34) What is Intramolecular Hydrogen Bonding

If a hydrogen bond occurs within two functional group of the same molecule, it is called an intramolecular hydrogen bond. This occurs when the hydrogen donor and the acceptor are both within the same molecule.



Structure of o-Nitrophenol (ortho-Nitrophenol) with intramolecular hydrogen bond

In the O-nitro phenol molecule, the O atom in the –OH group is more electronegative than the H and hence δ-. H atom, on the other hand, is δ+. Therefore, the O atom in the –OH group acts as the H donor whereas O atom on the nitro group acts as the H-acceptor.

35) Difference Between Intermolecular and Intramolecular Hydrogen bonding

Bond Formation

Intermolecular Hydrogen Bonding: Intermolecular hydrogen bonding occurs between two neighbouring molecules.

Intramolecular Hydrogen Bonding: Intramolecular hydrogen bonding occurs within the molecule itself.

Physical Properties

Intermolecular Hydrogen Bonding: Intermolecular hydrogen bonding has high melting and boiling points, and low vapour pressure.

Intramolecular Hydrogen Bonding: Intramolecular hydrogen bonding has low melting and boiling points and high vapour pressure.

Stability

Intermolecular Hydrogen Bonding: The stability is comparatively high.

Intramolecular Hydrogen Bonding: The stability is comparatively low.

Examples

Intermolecular Hydrogen Bonding: Water, methyl alcohol, ethyl alcohol, and sugar are examples of intermolecular hydrogen bonding.
Intramolecular Hydrogen Bonding: O-nitrophenol and salicylic acid are examples of intramolecular hydrogen bonding.

36) Diagonal relationship between lithium and magnesium

i. Li and Mg both are hard matals due to the presence of strong metallic bonds in them.
ii. Li and Mg both are hard, therefore, their melting and boiling points are high. iii. LiOH and Mg(OH)2 both are weak bases.
iv. LiCl and MgCl2 are insoluble in water due to their covalent nature, but soluble in organic solvents.
v. LiCl and MgCl2 get hydrolyzed due to their covalent nature.

vi. Carbonates and nitrates of Li and Mg are unstable and readily decompose to form oxides.

vii. Hydration energies of Li^{+1} and Mg^{+2} ions are higher due to small size.

viii. Li and Mg form complex compounds due to their small size.

37) Analogous behavior of beryllium different from other alkaline earth metals

Beryllium exhibits different behavior due to small size as compared to other elements of its group.

1. Ionization potential and electro negativity of Be are higher than those of other metals.
2. $BeCl_2$ is insoluble in water, due to its covalent nature, but soluble in organic solvents. Other chlorides ($CaCl_2$, $SrCl_2$ and $BaCl_2$) get dissolved in water
3. $BeCl_2$ gets hydrolyzed due to its covalent nature. Chlorides of Ca, Sr and Ba get dissociated.
4. BeO and $Be(OH)_2$ are amphoteric in nature. Therefore they react with acids as well as bases. Otheroxides react onlywith acids due to their alkaline nature

$$BeO + 2NaOH \rightarrow \underset{\text{Sodium berylate}}{Na2BeO2} + H2O$$

$$BeO + 2HCl \rightarrow BeCl2 + H2O$$

5. Beryllium forms single type of oxide (MO), Ca Sr and Ba form peroxides also.
6. Beryllium does not give flame test, Ca, Sr and Ba impart characteriestic colours to the flame.

38) Preparation, Properties and uses of Anthracene

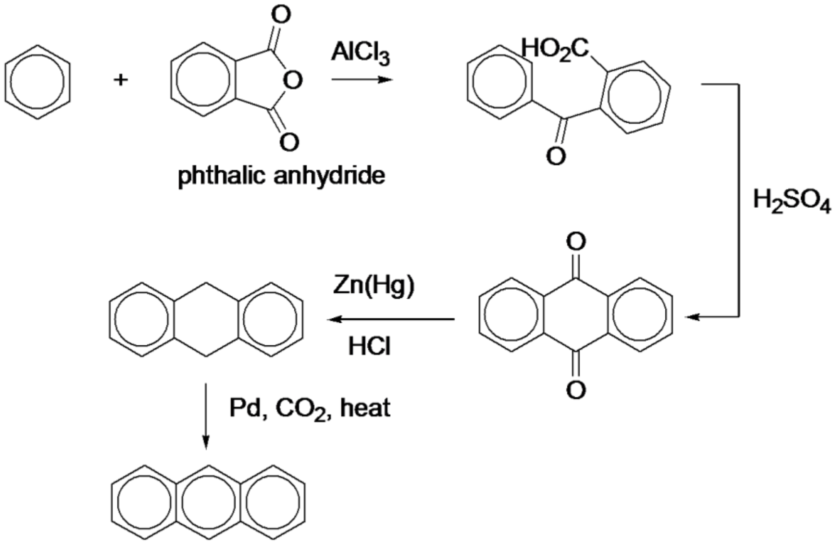
Preparation:

1) From Coal tar:

i. The middle oil fraction (300-350^{o}C) of coal tar is chilled when Anthracene forms crystals.

ii. At this term We get mixture of anthracene, phenanthrene & carbazole iii. Phenanthrene crystals washed with naptha solvent to get final Product.

2) From Haworth Synthesis of Antharacene



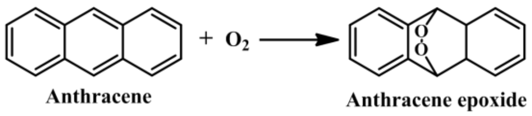
Properties:

i. It is in solid form. It is colorless.
ii. Melting point of anthracene is 270C. *iii.* Boiling point of anthracene is

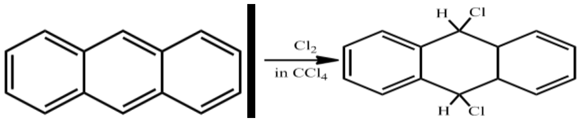
340C. *iv.* It is soluble in alcohol & ether. It is insoluble in water.

Chemical properties:

i. Oxidation



ii. Cholorination



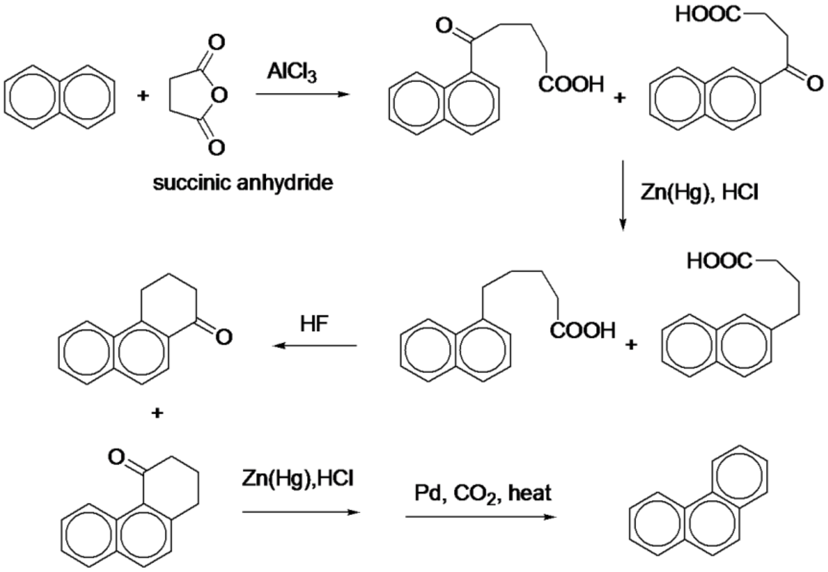
Uses:

i. Anthracene is used for manufacture of anthraquinone.

ii. Anthracene is used for making dyes(Alizarin).

iii. It is also used in smoke screens

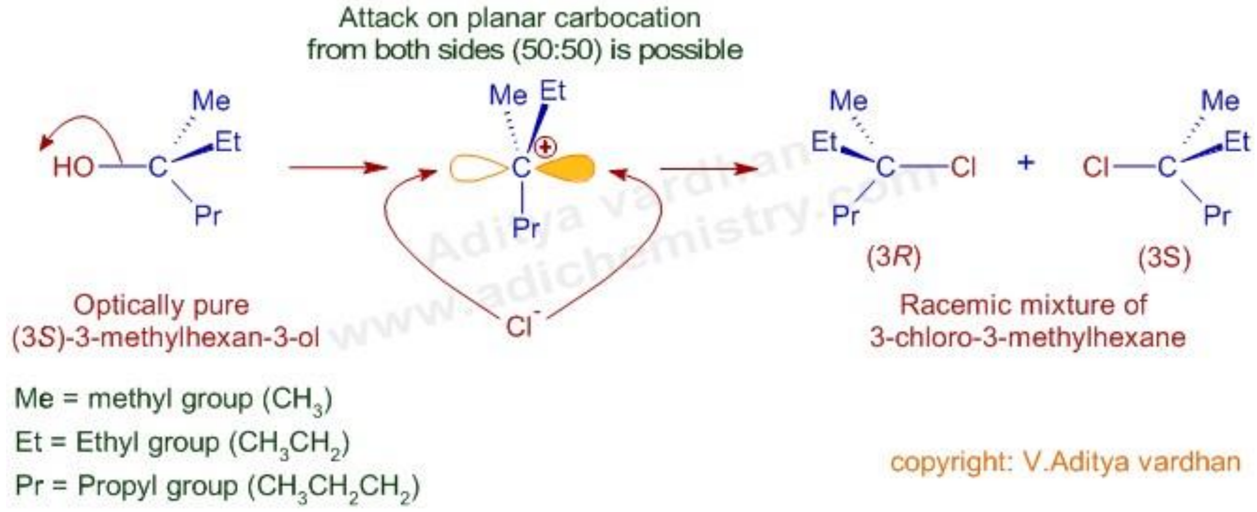
39) Haworth Synthesis of phenanthrene



40) Stereochemistry of SN^1 mechanism

The carbocation is planar with sp2 hybridized central carbon. Hence the attack of the nucleophile from either side is equally probable. Hence, if the starting alcohol is optically active due to chirality of -OH group bearing carbon, a racemic mixture (or sometimes a mixture of diastereomers) of alkyl halide is resulted.

E.g. When optically pure (3S)-3-methyl-3-hexanol is treated with a hydrogen chloride, a racemic mixture (50%:50% R, S) of 3-chloro-3-methylhexane is formed due to formation of carbocation via SN^1 mechanism.

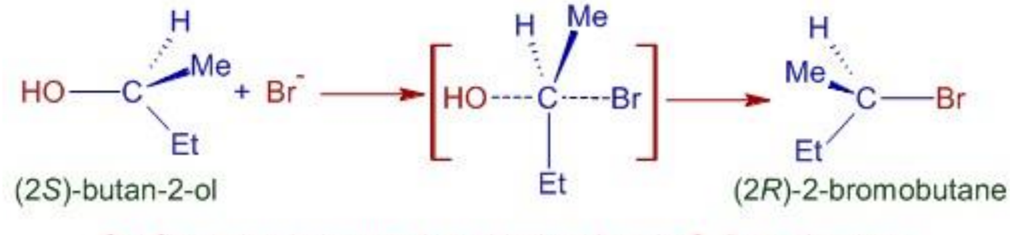


In this reaction, (3R)-3-chloro-3-methylhexane enantiomer is formed due to attack of Cl- ion from the left hand side leading to retention of configuration at chiral center. However, inversion of configuration occurs when the chloride ion attacks from the right hand side to yield (3S)-3chloro-3-methylhexane

41) Stereochemistry of SN^2 mechanism

The SN^2 mechanism involves inversion of configuration at chiral carbon, since the halide ion attacks the carbon (that is bonded to -OH group) from the opposite side of the C-O bond. Hence optically pure alkyl halide is obtained from optically pure alcohol due to complete inversion of configuration if the alcohol reacts by SN^2 mechanism only.

For example, optically pure (2S)-butan-2-ol reacts by SN^2 mechanism with HBr and gives (2R)2-bromobutane as major product. The configuration at chiral carbon (that is bonded to alcoholic group) is inverted from (2S) to (2R) completely because only back side attack is possible in SN^2 mechanism.enantiomer. Hence, a racemic mixture with 50:50 R and S alkyl halide is resulted.



Configuration is inverted at chiral carbon in S_N2 mechanism

42) Preparation,Properties and uses of cholorobenzene

Preparation:

Benzene reacts with chlorine in the presence of a catalyst, replacing one of the hydrogen atoms on the ring by a chlorine atom.

The reaction happens at room temperature. The catalyst is either aluminium chloride or iron.

Strictly speaking iron isn't a catalyst, because it gets permanently changed during the reaction. It reacts with some of the chlorine to form iron(III) chloride, FeCl3.

$$2Fe+3Cl_2 \longrightarrow 2FeCl_3$$

This compound acts as the catalyst and behaves exactly like aluminium chloride, AlCl3, in this reaction.

The reaction between benzene and chlorine in the presence of either aluminium chloride or iron gives chlorobenzene.

$$C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$$

Properties:

i) It is colourless, pleasant smelling liquid ii) B.pt- 13^0C iii) It is insoluble in water iv) It is stem volatile

Uses:

i. Cholorobenzene can be used for preparation of phenol ii. Nitrobenzene required for the manufacture of azo and sulphur dyes iii. It is used for preservation

43) Preparation of cholorobenzene

Preparation:

The reaction between benzene and bromine in the presence of either aluminium bromide (rather than aluminium chloride) or iron gives bromobenzene. Iron is usually used because it is cheaper and more readily available. If we use iron, it is first converted into iron(III) bromide by the reaction between the iron and bromine.

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr$$

Properties:

i) It is colourless ii) Oily liquid iii) Boiling point – 156.43^0c

iv) Melting point – 30.8^0c

v) It is soluble in benzene, alcohols, ether vi) Insoluble in water

Uses:

i. It is used to prepare the corresponding Grignard reagent. ii. It is used as a precursor in the manufacture of phencyclidine

44) Nucleophilic Substitution of haloalkanes

Nucleophilic substitution reaction was first observed by the German chemist, Paul Walden, in 1896. He was able to observe that (+) and (-) malic acid can be interconverted using PCl_5 and Ag_2O. In general, nucleophilic substitution reaction involves the substitution of one nucleophile by another. The general formula for this reaction is as follows:

$R\text{-}X + Nu^– \rightarrow R\text{-}Nu + X^-$

Depending on the molecularity of the reaction, nucleophilic substitution reactions may be classified as SN^1 or SN^2. Depending on the reaction parameters and conditions, either SN^1 or SN2 reactions may occur.

45) Planck's quantum theory :

According to Planck's quantum theory,

1. Different atoms and molecules can emit or absorb energy in discreet quantities only. The smallest amount of energy that can be emitted or absorbed in the form of electromagnetic radiation is known as quantum.
2. The energy of the radiation absorbed or emitted is directly proportional to the frequency of the radiation. The energy of radiation is expressed in terms of frequency as,

$$E = h\,\nu$$

Where,

E = energy of the radiation

h **= Planck's constant ($6.626\times10^{–34}$ J.s)**

ν= Frequency of radiation

10 MARKS

46) Explain about Born-Haber Cycle

There are several important concept in the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

Ionization Energy is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some excepts, usually due to the stability of half-filled and completely filled orbitals.

Electron Affinity is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables.

Dissociation energy is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electro negativity of the atoms involved.

Sublimation energy is the energy required to cause a change of phase from solid to gas, by passing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.

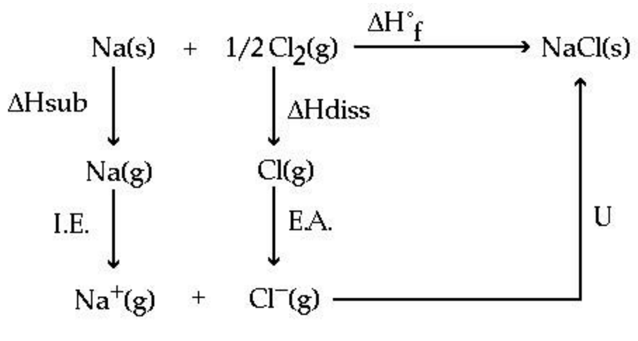
Heat of formation

The heat of formation is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.

Lattice energy

The lattice energy on the formation of sodium chloride from the gaseous ions

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$$

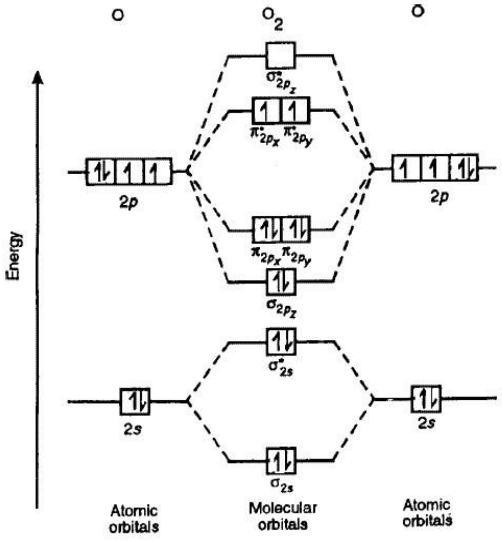


$$\Delta H^\circ_f = \Delta H\text{sub} + \text{I.E.} + \Delta H\text{diss} + \text{E.A.} + U$$

47) Explain MOT for O_2 molecule

The electron configuration of an oxygen atom will be

O: $1s^2 2s^2 2p^4$



The **1s-orbitals** and their corresponding molecular orbitals look exactly like the **2sorbitals**.

The **total number of electrons** available for this diagram will be equal to 12, 6 from each oxygen atom.

Start filling the molecular orbitals by using the **Aufbau Principle**, **Hund's Rule**, and **Pauli's** .

Exclusion Principle

Start from the molecular orbital that's **lowest in energy.**

The **bond order**, which tells you how many bonds you can expect to find between two atoms, is calculated using the formula

B.O =1⁄2 (no. of bonding e− - no. of anti-bonding e−)

The **bond order** for the oxygen molecule will thus be

B.O.=1/2× (10−6)

B.O.=1/2×4=2

This tells that the two oxygen atoms are bonded together via a **double bond**, which of course consists of a **<u>sigma</u> and a <u>pi bond</u>.**

magnetic behavior

The is determined by the presence of **unpaired electrons**.

In the oxygen molecule has **two unpaired electrons** in two anti-bonding MO"s, π*2py and π*2pz.

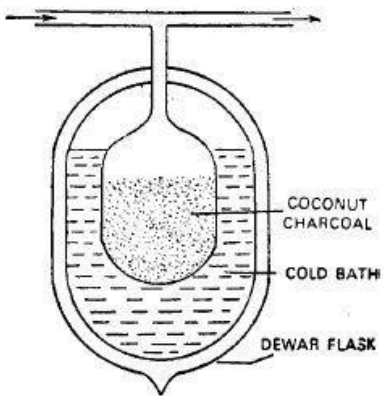
This means that the oxygen molecule will be **paramagnetic**.

48) Describe in detail how noble gases are isolated by Dewar's process. Or How are noble gases separated by Dewar's method?

1. Principle:

The mixture of noble gases obtained by the Ramsay - Rayleigh's method is **separated into individual constituents by the use of coconut charcoal which adsorbs different gases at different temperatures**.

2.



The mixture of noble gases is passed into a double-walled bulb containing coconut charcoal and placed in a low temperature bath at 173K. It is allowed to remain in contact with the charcoal for about half an hour.

3. **At 173K**, only **argon, krypton and xenon are adsorbed** by the charcoal while **helium and neon remain unadsorbed**. These are pumped out and collected.

4. The mixture of helium and neon is kept in contact with coconut charcoal **at 93K** which completely **adsorbs neon leaving free helium**.

5. The charcoal **at 173K** containing argon, krypton and xenon is placed in contact with another charcoal **at the temperature of the liquid air (**temp.77K) when **argon diffuse** into the other charcoal.

6. The temperature of the first charcoal (temp.173K) still containing krypton and xenon is **raised to 183K** when **krypton is set free** while **xenon remain adsorbed** in the charcoal. When it is **heated, xenon is recovered**.

49) **Describe in detail how noble gases are isolated from air by Ramsay - Rayleigh's method.**

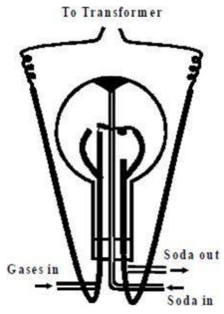
A **mixture of air and oxygen** is constantly admitted into a glass globe of about 50 litres capacity. **Two platinum electrodes** are introduced and a discharge from a transformer of about **6000 - 8000 volts** is passed by the action of which **nitrogen and oxygen rapidly combine to form oxides of nitrogen**. The **oxides are dissolved out in a solution of sodium hydroxide** continuously circulated through the flask.

$N_2 + O_2 \rightarrow 2\,NO$

$2\,NO + O_2 \rightarrow 2NO_2$

$2NO_2 + 2NaOH \rightarrow NaNO_3 + NaNO_2 + H_2O$

Oxygen if any is removed by introducing alkaline pyrogallol in the globe. The supply of air and electric discharge is shut after some time and the remaining mixture of noble gases is pumped out.

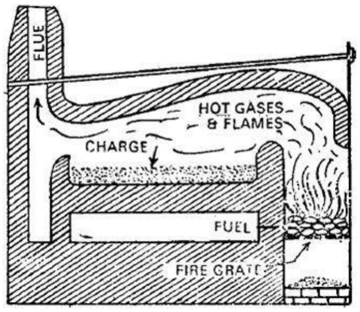


Chemical method for isolation of noble gases

50) Explain the extraction of lead from its ore. Or How is lead extracted from its ore?

Extraction: Lead is mainly **extracted from the sulphide ore galena**. Galena contains lead sulphide and small quantities of silver.

1. **Concentration: Froth floatation process**.
2. **Smelting in a Reverberatory furnace:** The concentrated ore is roasted in a reverberatory furnace at a moderate temperature. The temperature of furnace is controlled by regulating the air supply. During roasting, **galena is partly oxidized to lead monoxide and partly to lead sulphate**.



A reverberatory furnace

$2PbS + 3O2 \rightarrow 2\,PbO + 2SO2$

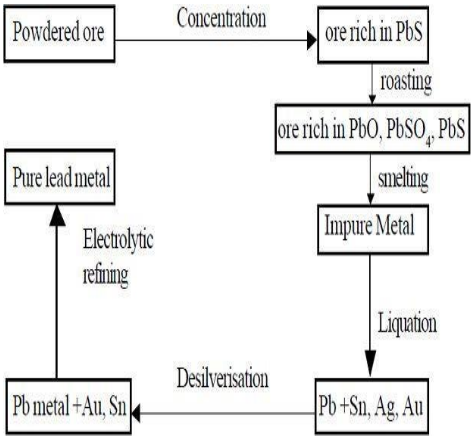
$PbS + 2O2 \rightarrow PbSO4$

More of galena is then added. The temperature is raised and simultaneously the air supply is reduced. Lead sulphide reacts with the two oxidised products giving lead.

$PbS + 2PbO \rightarrow 3Pb + SO2$

$PbS + PbSO4 \rightarrow 2Pb + 2SO2$

Thus in this process roasting and smelting are carried out in the same furnace, at two different temperatures. About 90% of lead is obtained as metal, the rest passes into slag. Led is recovered from the slag by heating with lime and powdered coke.



Purification of Lead

Lead extracted by the above method contains impurities such as silver, copper, tin, bismuth, gold and iron. It is **refined by the following processes**. **a. Liquation**

The impure metal is heated on a sloping hearth. Lead melts and flows down the slope. The infusible impurities remain on the hearth. **b. Desilverisation**

Silver is removed by either Pattinson‘s process or Park‘s process.

c. Electrolytic refining Anode – Impure lead

Cathode – Very pure lead

Electrolyte – Lead fluosilicate ($PbSiF6$) + Hydrofluosilicic Acid ($H2SiF6$)

The metallic impurities which are more electropositive than lead, such as iron and tin, go into the solution while the rest of the impurities are thrown down as anode mud.

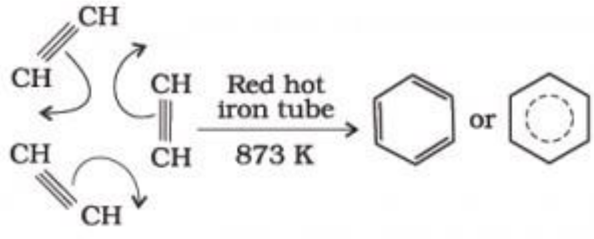
\

51) PREPARATION , PROPERTIES AND USES OF BENZENE

Preparation of benzene

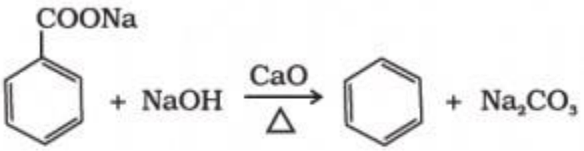
1. **From alkynes**

   Benzene is prepared from ethyne by the process of cyclic polymerization. In this process, Ethyne is passed through a red hot iron tube at 873 K. The ethyne molecule then undergoes cyclic polymerization to form benzene



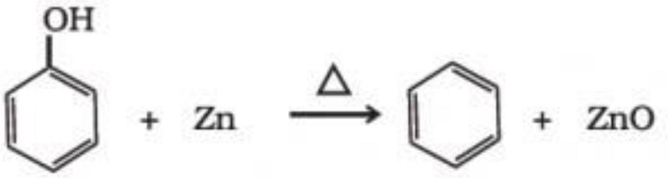
2. From aromatic acids:

   Benzene can be prepared from aromatic acids through their decarboxylation. In this process sodium salt of the benzoic acid (sodium benzoate) is heated with soda lime to produce benzene along with sodium carbonate.



3. From phenol:

   Benzene can be prepared from phenols too through their reduction. In this process vapors of phenol are passed over heated zinc dust. Zinc dust reduces them to form benzene.



4. **From sulphonic acids:**

Benzene can be prepared from sulphonic acids through their hydrolysis. In this process Benzene sulphonic acid is exposed to superheated steam leading to the formation of benzene

$C_6H_5\text{-}SO_3H + H_2O \rightarrow C_6H_6 + H_2SO_4$

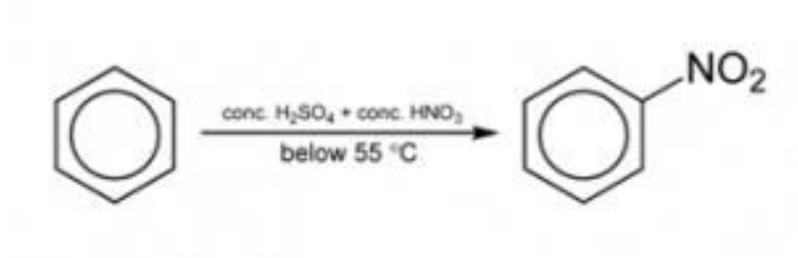
Physical properties of benzene:

1. Benzene belongs to the family of aromatic hydrocarbons which are non-polar molecules and are usually colorless liquids or solids with a characteristic aroma.
2. Benzene being non-polar is immiscible with water but is readily miscible with organic solvents.
3. Combustion of benzene, sooty flame is produced.

Chemical properties of benzene:

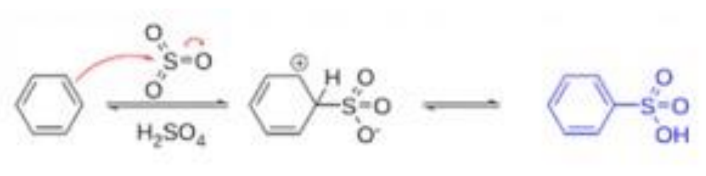
Nitration of Benzene:

Benzene reacts with nitric acid at 323-333 K in the presence of sulphuric acid to form nitrobenzene. This reaction is known as nitration of Benzene.



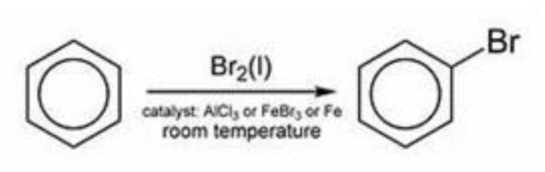
Sulfonation of Benzene:

Sulfonation of benzene is a process of heating benzene with fuming sulphuric acid (H_2SO_4 $+SO_3$) to produce Benzene sulfonic acid. The reaction is reversible in nature.



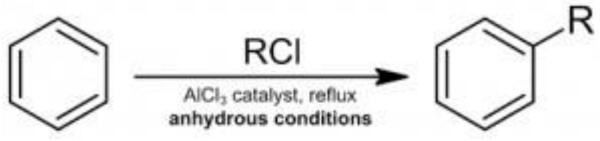
Halogenation of Benzene:

Benzene reacts with halogens in the presence of Lewis acids like $FeCl_3$, $FeBr_3$ to form aryl halides. This reaction is termed as halogenation of benzene



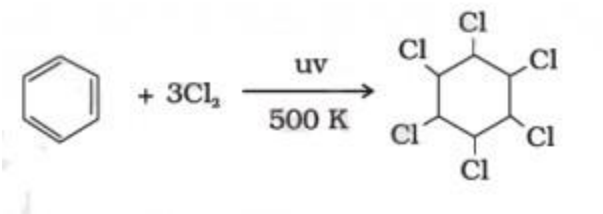
Friedel Craft's alkylation reaction:

When benzene is treated with an alkyl halide in the presence of a Lewis acid such as anhydrous aluminum chloride, alkyl benzene is formed. This reaction is popularly known as Friedel Craft's alkylation reaction.



Addition reactions:

Addition of chlorine in the presence of ultraviolet light produces benzene hexachloride (gammaxene).



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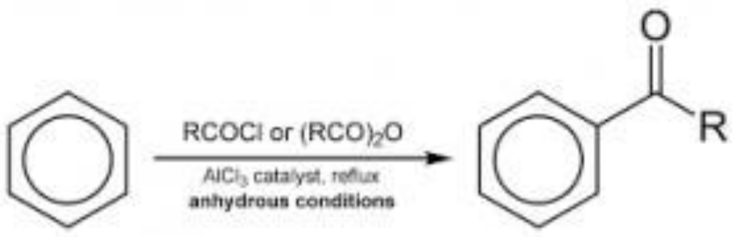


Uses.

- Large amounts of benzene are alkylated with ethylene to obtain ethylbenzene and diethylbenzenes. Ethylbenzene is an intermediate in styrene production.
- Hydrogenation of benzene results in cyclohexane which is used in caprolactam (a source for Nylon) manufacturing.
- Being alkylated with propylene benzene gives cumene which is used on phenol and acetone industrial preparation.
- As a parent compound in industrial synthesis of maleic anhydride.
- As a solvent and extracting agent in a laboratory and industrial chemical processes.
- As a solvent in a laboratory for compound molecular mass determination by cryoscopy method.

52) **Preparation Properties and uses of naphthalene**

1) From Coal tar

i. The middle oil fraction of coal tar is chilled when naphthalene forms *ii.*

Crystals.

iii. The crude crystals are melted & treated with sulfuric acid to remove *iv.*

Basic impurities.

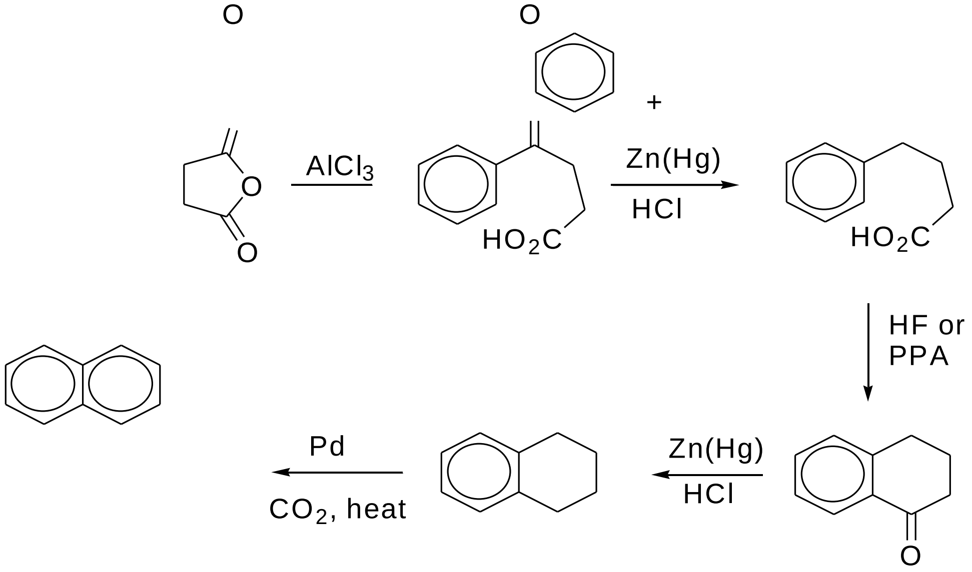
v. The crystals are then washed with aq. Sodium hydroxide to remove Phenol *vi.*

Finally, the naphthalene is distilled to get the pure product.

2) From Petroleum

i. The middle distillates of petroleum on catalytic cracking and catalytic reforming yield naphthalene & methylnaphthalenes. *ii.* The methylnaphthalenes on heating to about 600C in the presence of Hydrogen, are dealkylated to give naphthalene.

From Haworth Synthesis of naphthalene



Physical Properties:

i. Naphthalene is slowly sublimates.

ii. It is volatile matter. *iii.* It is in solid form. *iv.* Melting Point is

80.2C.

v. Boiling Point is 217.9C. *vi.*

Soluble in Benzene & Ether.

vii. Insoluble in Water.

Chemical Properties:

1) **Halogenation**

2) **Sulphonation**

3) **Reduction**

4) **Oxidation Uses of naphthalene**

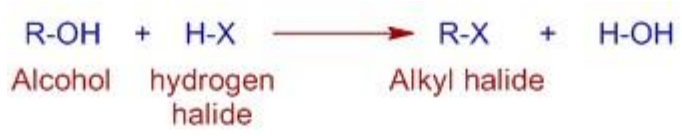
i. It is used in manufacturing of Plastic & resins ii. It is used in Fumigant insecticide iii.

It is used as Pesticides iv. It is used in production of Phthalic Anhydride

53) METHODS OF PREPARATION OF ALKYL HALIDES (HALOALKANES)

Preparation

Alkyl halides can be synthesized from alcohols by treating with hydrogen halides, HX (where X=Cl / Br / I). It is a nucleophilic substitution reaction.



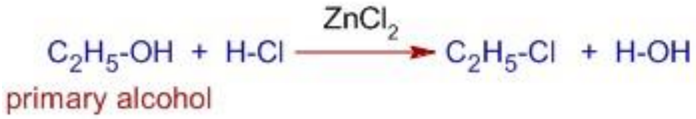
HCl and HBr can be liberated in-situ by using a combination of moderately concentrated sulfuric acid and a halide salt like NaCl, NaBr etc. E.g

However, 95% phosphoric acid is used instead of sulfuric acid to liberate HI from its salt.

* Among hydrohalic acids, HI is more reactive and HF is least reactive. Greater the H-X bond strength lesser is the reactivity. The order of reactivity of hydrogen halides with alcohols is: HF < HCl < HBr < HI

HCl requires a Lewis acid catalyst particularly with primary and secondary alcohols. HBr and HI can react without using any catalyst.

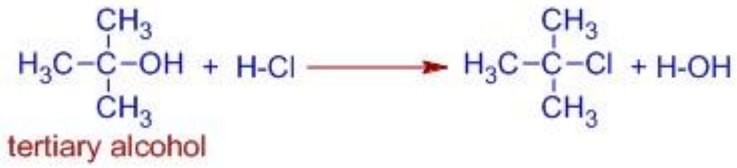
E.g. Conversion of ethyl alcohol, a primary alcohol to ethyl chloride requires ZnCl2, a Lewis acid.



* A combination of dry HCl gas and anhydrous ZnCl2 also known as "Lucas reagent" is employed to get alkyl chlorides. It is used to differentiate between primary, secondary and tertiary alcohols.

* The reactivity of various alcohols follows the order: methyl < primary < secondary < tertiary.Indeed, tertiary alcohols react with HCl even in absence of a catalyst.

E.g. tert-butyl chloride can be synthesized by passing HCl gas into an aqueous solution of tertbutyl alcohol at low temperatures.



$$(CH_3)_3C{-}OH + H{-}Cl \longrightarrow (CH_3)_3C{-}Cl + H{-}OH$$

Physical properties of haloalkanes

i) Melting Point and Boiling Point of haloalkanes

There is large electronegativity difference between halogens and carbon resulting in highly polarized molecules. The higher molecular mass and greater polarity as compared to the parent hydrocarbon results in stronger intermolecular forces of attraction (dipole-dipole and van der Waals) in the halogen derivatives. Boiling Point depends upon the intermolecular forces of attraction and hence the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass. As we go down in homologues series of haloalkanes, the forces of attraction becomes stronger due to increase in molecular size and it‘s mass, hence the boiling point increases down the homologues series. But the boiling point decreases with branching.
Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are gases at room temperature. Higher members are liquids or solids

Melting point of a compound depends upon the strength of lattice structure of a compound.
Melting point also follows the same trend as boiling point. An exception to this is para-isomers. The para-isomers have higher melting as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho– and metaisomers.

ii) Density of haloalkanes

Density is directly proportional to the mass of compound, hence down the homologous series, density increases, also fluoro derivatives are lesser dense than chloro derivatives; chloro derivatives are less dense than bromo derivatives and so on.

iii) Solubility of haloalkanes

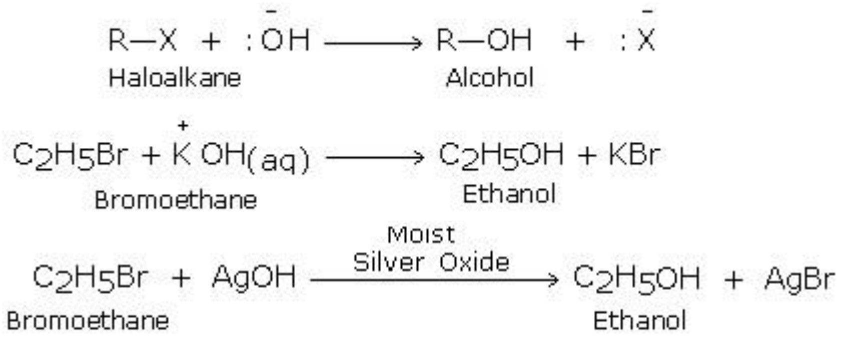
Haloalkanes are slightly soluble in water. This is because of the relatively larger amount of energy required to break bond between halogen and carbon and the smaller amount of energy released, when bond is formed after dissolution ion and water.

Chemical propetirs of haloalkanes

Bond strength: C—F > C—Cl > C—Br > C—I

Bond reactivity: C—F < C—Cl < C—Br < C—I

1. (Formation of alcohols) On treatment with aqueous solution of KOH or moist silver oxide (Ag2O/H2O) haloalkanes give alcohols.

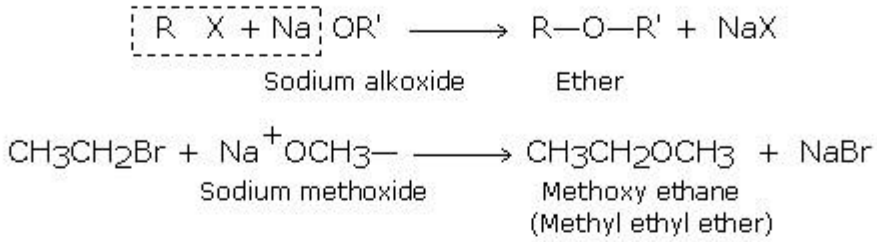


$$\underset{\text{Haloalkane}}{R{-}X} + :\overset{-}{O}H \longrightarrow \underset{\text{Alcohol}}{R{-}OH} + :\overset{-}{X}$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + \overset{+}{K}\,OH_{(aq)} \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KBr$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + AgOH \xrightarrow{\text{Moist Silver Oxide}} \underset{\text{Ethanol}}{C_2H_5OH} + AgBr$$

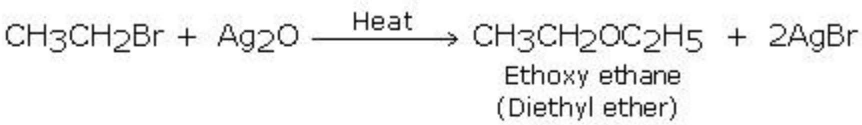
2. (Formation of ethers) - Williamson Synthesis



$$\boxed{R\quad X + Na}\,\underset{\text{Sodium alkoxide}}{OR'} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R'} + NaX$$

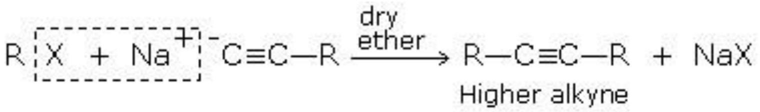
$$CH_3CH_2Br + \underset{\text{Sodium methoxide}}{Na^{+}OCH_3{-}} \longrightarrow \underset{\substack{\text{Methoxy ethane}\\ \text{(Methyl ethyl ether)}}}{CH_3CH_2OCH_3} + NaBr$$

This reaction is called 'Williamson's synthesis' and is quite useful for preparing ethers.
Haloalkanes can also be converted into ethers by heating with dry silver oxide.



$$CH_3CH_2Br + Ag_2O \xrightarrow{Heat} CH_3CH_2OC_2H_5 + 2AgBr$$

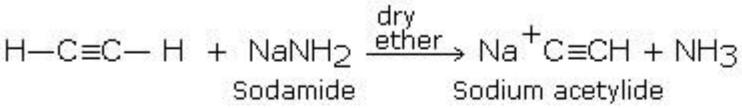
3. (formation of alkynes)The formation of higher alkynes occurs when haloalkane is treated with sodium salt of alkynes (sodium alkynides): the halogen atom is replaced by alkyl group (-C=C-)



$$R\boxed{X + Na^{+}}{}^{-}C\equiv C-R \xrightarrow{\text{dry ether}} R-C\equiv C-R + NaX$$

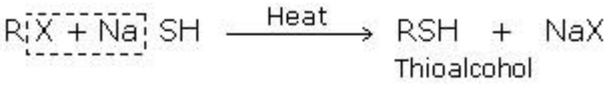
$$CH_3CH_2Br + NaC\equiv CH \longrightarrow CH_3CH_2C\equiv CH + NaBr$$

The sodium alkynides needed for the above reaction are formed by the reaction of sodamide (or sodium in liquid NH3) with alkynes containing terminal triple bond.reaction of sodamide with alkynes

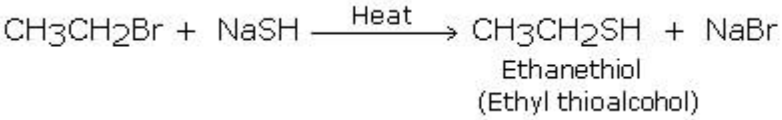


$$H-C\equiv C-H + NaNH_2 \xrightarrow{\text{dry ether}} Na^{+}C\equiv CH + NH_3$$

4. The formation of thioalcohols or thiols takes place when haloalkane is treated withsodium or potassium hydrogen sulphide: the halogen atom gets replaced by hydrosulphide (-SH) group.

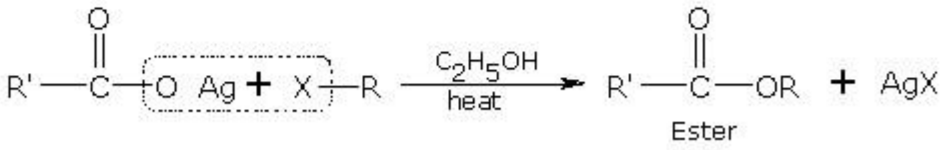


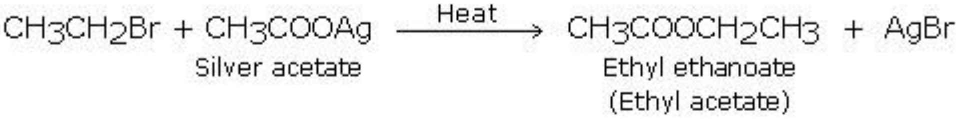
$$R\boxed{X + Na}SH \xrightarrow{Heat} RSH + NaX$$



$$CH_3CH_2Br + NaSH \xrightarrow{Heat} CH_3CH_2SH + NaBr$$

5. (formation of esters)- When Haloalkanes are heated with an ethanolic solution of silver salt of a fatty acid these form esters.





Applications of Haloalkanes

- It is normally used in organic synthesis as asynthon equivalent to alkyl cation.They also take participation in many organic reactions.
- Halo alkanes like tetrachloromethane,dichloromethane,trichloromethane are generally used as a hydrophobic solvent in chemistry. They are commonly used industries.
- CFC‘s were widely used as apropellant and refrigerant because of its high heat of vaporization and low toxicity.CFC‘s lead to ozonedepletion, so HFC‘s is replaced in place of CFC‘s.

54) Orientation of Benzene

Activated rings: Substituent on the ring is groups that donate electrons.

Deactivated rings: Substituent on the ring is groups that withdraw electrons.

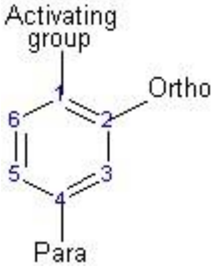
Examples of activating -NH2, -NR2 > -OH, -OR> -NHCOR> -CH3 and other alkyl group with R as alkyl groups (CnH2n+1)

The order of reactivity among Halogens from the more reactive (least deactivating substituent) to the least reactive (most deactivating substituent) halogen is:

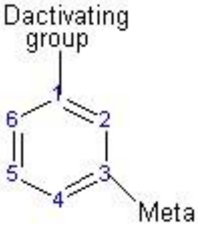
F> Cl > Br > I

The order of reactivity of the benzene rings toward the electrophilic substitution when it is substituted with a halogen groups .The ring that is substituted with the most electronegative halogen is the most reactive ring (less deactivating substituent) and the ring that is substituted with the least electronegatvie halogen is the least reactive ring (more deactivating substituent

The direction of the reaction



The activating group directs the reaction to the ortho or para position, which means the electrophile substitute the hydrogen that is on carbon 2 or carbon 4.

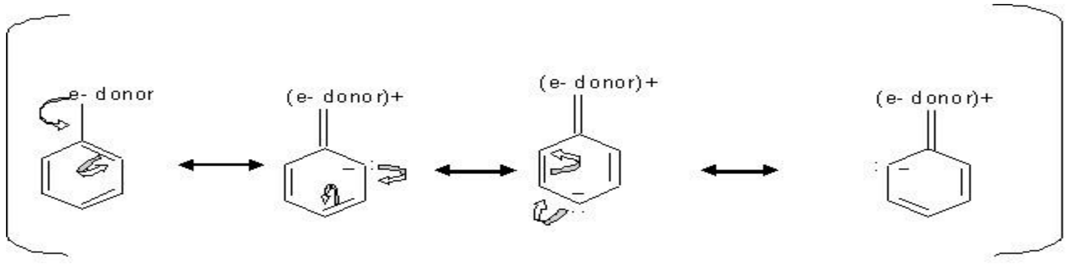


The deactivating group directs the reaction to the meta position, which means the electrophile substitute the hydrogen that is on carbon 3 with the exception of the halogens that is a deactivating group but directs the ortho or para substitution.

- Substituents determine the reaction direction by resonance or inductive effect
- Resonance effect is the conjugation between the ring and the substituent, which means the delocalizing of the π electrons between the ring and the substituent. Inductive effect is the withdraw of the

sigma (the single bond) electrons away from the ring toward the substituent, due to the higher electronegativity of the substituent compared to the carbon of the ring.

Activating groups (ortho or para directors)

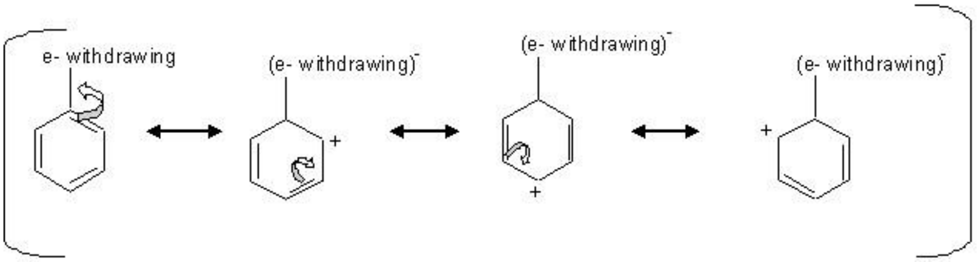


when the substituent like -OH have an unshared pair of electrons, the resonance effect is stronger than the inductive effect which make these substituent stronger activators, since this resonance effect direct the electron toward the ring.

In case, where the substituent is esters or amides, they are less activating because they form resonance structure that pull the electron density away from the ring(Deactivating groupmeta directors

Deactivating groups

Deactivate the ring by the inductive effect in the presence of an electronegative atom that withdraws the electrons away from the ring.



When there is an electron withdrawn from the ring, that leaves the carbons at the ortho, para positions with a positive charge which is unfavorable for the electrophile, so the electrophile attacks the carbon at the meta positions.

Halogens are an exception of the deactivating group that directs the ortho or para substitution. The halogens deactivate the ring by inductive effect not by the resonance even though they have an unpaired pair of electrons. The unpaired pair of electrons gets donated to the ring, but the inductive effect pulls away the s electrons from the ring by the electronegativity of the halogens.

55) Photoelectric effect

The photoelectric effect is the phenomenon due to which electrons are emitted from a metal surface when light of sufficient frequency is incident upon it. Hertz and Lenard‘s observations of the photoelectric effect could not be explained by Maxwell‘s electromagnetic wave theory of light. Hertz (who had proved the wave theory) himself did not pursue the matter as he felt sure it could be explained by the wave theory. It however failed on these accounts:

1. According to wave theory, energy is uniformly distributed across the wave front and is dependent only on the intensity of the beam. This means the kinetic energy of electrons must increase with light intensity. However, the kinetic energy was independent of light intensity.
2. Wave theory implies that light of any frequency should be capable of ejecting electrons. But electron emission occurred only for frequencies larger than a threshold frequency (ν_0).
3. Since energy is dependent on intensity according to wave theory, low intensity light should electrons after sometime so that the electrons can acquire sufficient energy to get emitted. However, electron emission was spontaneous no matter how small the intensity of light.

Einstein resolved this problem using Planck‘s revolutionary idea that light was a particle. The energy carried by each particle of light (called quanta or photon) is dependent on the light‘s frequency (ν) as shown:

$E = h\nu$

Where h = Planck‘s constant = 6.6261×10^{-34} Js.

Since light is bundled up into photons, Einstein theorized that when a photon falls on the surface of a metal, the entire photon‘s energy is transferred to the electron.

A part of this energy is used to remove the electron from the metal atom‘s grasp and the rest is given to the ejected electron as kinetic energy. Electrons emitted from underneath the metal surface lose some of the kinetic energy in collisions. But the surface electrons carry all the kinetic energy imparted by the photon and have the maximum kinetic energy.

We can write this mathematically as:

Energy of photon = energy required to eject electron (work function) + Max. Kinetic energy of electron

$E = W + KE\ hv$

$= W + KE\ KE$

$= hv - w$

At the threshold frequency v_0 electrons are just ejected and do not have any kinetic energy. Below this frequency there is no electron emission. Thus, the energy of a photon with this frequency must be the work function of the metal.

$$\mathbf{w = hv_0}$$

Thus, Maximum kinetic energy equation becomes:

$$\mathbf{KE = 12mv2max=hv-hv_0}$$

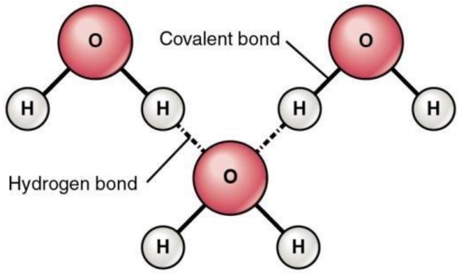
$$\mathbf{12mv2max=h(v-v_0)}$$

V_{max} is the maximum kinetic energy of the electron. It is calculated experimentally using the stopping potential. Please read our article on Lenard‘s observations to understand this part.

$$\mathbf{Stopping\ potential = ev_0 = 12mv2max}$$

56) What is Intermolecular Hydrogen Bonding

Intermolecular hydrogen bonding can occur between like or unlike molecules. The position of the acceptor atom should be properly oriented such that it can interact with the donor.



Hydrogen Bonding in Water Molecule

The pair of electrons shared between H and O atoms are more attracted towards the Oxygen atom. Hence, the O atoms get a slight negative charge compared to H atom. O atom is depicted as δ- and H atom is depicted as δ+. When a second water molecule comes near the former, an electrostatic bond is formed between the δ- O atom of one water molecule with δ+ H atom of the other. The oxygen atoms in the molecules behave as the donor (B) and acceptor (A) where one O atom donates hydrogen to the other.

Water has very special qualities due to hydrogen bonding. It is a good solvent and has a high boiling point and high surface tension. Further, ice at 4-C is of lower density than water. Hence, ice floats on liquid water protecting the aquatic life beneath during the winter. Because of these features in water, it is called the universal solvent and plays a major role in maintaining life on earth.

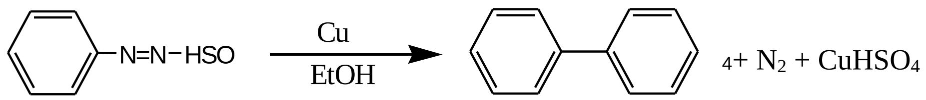
57) Prepation, properties and uses of biphenyl:

Preparation

i. Fittig reaction

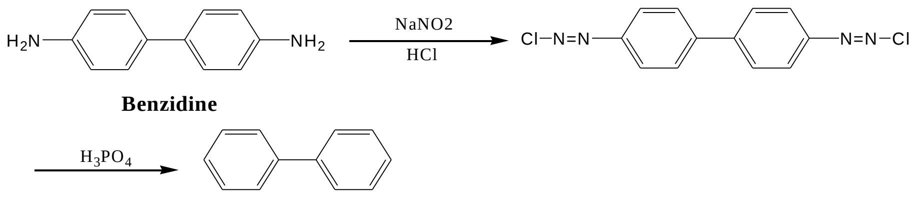
$$2Ph\text{-}Br + 2Na \xrightarrow[\text{soln}]{\text{ether}} Ph\text{-}Ph + 2NaBr$$

ii. From benzene diazonium sulphate

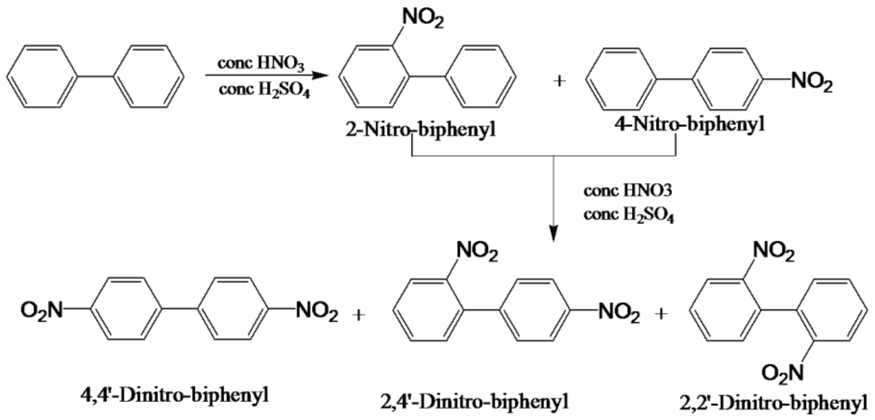


Biphenyl

iii. From benzidine



Properties of biphenyl:

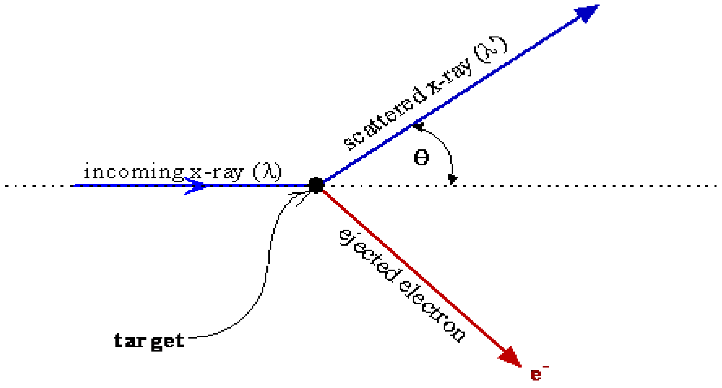


Uses:

Biphenyl is used in organic syntheses, heat transfer fluids, dye carriers, food preservatives, as an intermediate for polychlorinated biphenyls, and as a fungi in the packaging of citrus fruits. BIPHENYL is a clear colorless liquid with a pleasant odor

58) Compton effect

The Compton effect concerns the inelastic scattering of x-rays by electrons. Scattering means dispersing in different directions, and inelastic means that energy is lost by the scattered object in the process. The intensity of the scattered x-ray is measured as a function of the wavelength shift $\Delta\lambda$ where $\lambda' = \lambda + \Delta\lambda$ and the scattering angle θ



The Compton Effect. X-rays scattered from a target at an angle have a different wavelength from the incident x-ray, and produce an ejected electron.

To explain the experimental observations, it is necessary to describe the situation just as one would when discussing two particles, e.g. marbles, colliding and scattering from each other. The x-ray scatters (changes direction) and causes an electron with mass me to be ejected from the object with a direction that conserves the momentum of the system. Momentum and energy conservation equations then explain the scattering angles and the observed wavelength shift of the x-ray when the momentum of the x-rays is taken to be equal to h/λ and the energy is $h\nu$ which describes the experimental data for the variation of $\Delta\lambda$ with θ. The success of using energy and momentum conservation for two colliding particles to explain the experimental data for the Compton effect is powerful evidence that electromagnetic radiation has momentum just like a particle and that the momentum and energy are given by h/λ and $h\nu$ respectively.

$$\Delta\lambda=hmec(1-\cos\theta)$$