Chapter – 12 (Organic Chemistry Some Basic Principles)

Exercise Questions:

Question: 1 What are the hybridisation states of each carbon atom in the following compounds?
$CH_2=C=O$, $CH_3CH=CH_2$, $(CH_3)_2CO$, $CH_2=CHCN$, C_6H_6

Answer:
(i) C-1 is sp^2 hybridised.
C-2 is sp hybridised.

(ii) C-1 is sp^3 hybridised.
C-2 is sp^2 hybridised.
C-3 is sp^2 hybridised.

(iii) C -1 and C-3 are sp^3 hybridised.
C-2 is sp^2 hybridised.

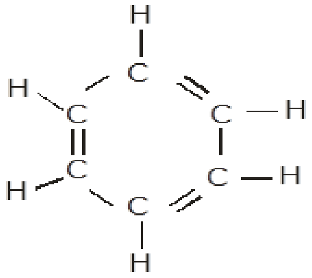
(iv) C-1 is sp^2 hybridised.
C-2 is sp^2 hybridised.
C-3 is sp hybridised.

(v) C_6H_6 All the 6 carbon atoms in benzene are sp^2 hybridised.

Question: 2 Indicate the sigma and π bond in the following molecules:
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2=C=CH_2$, CH_3NO_2, $HCONHCH_3$.

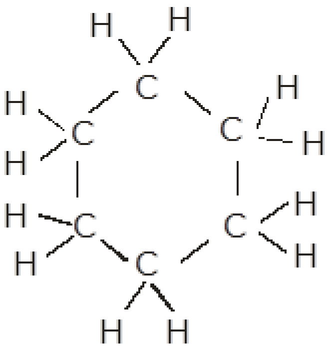
Answer:

(i) C_6H_6



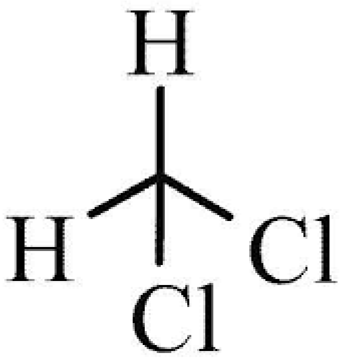
There are six C-C sigma (σC-C) bonds, six C-H sigma (σC-H) bonds and three C=C pi (πC-C) resonating bonds in the given compound.

(ii) C_6H_{12}



There are six C-C sigma (σC-C) bonds and twelve C-H sigma (σC-H) bonds in the given compound.

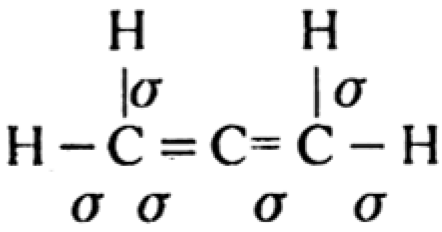
(iii) CH_2Cl_2



There two C-H sigma (σC-H) bonds and two C-Cl sigma (σC-Cl) bonds in the given compound.

(iv) $CH_2=C=CH_2$

$CH_2 = C = CH_2$



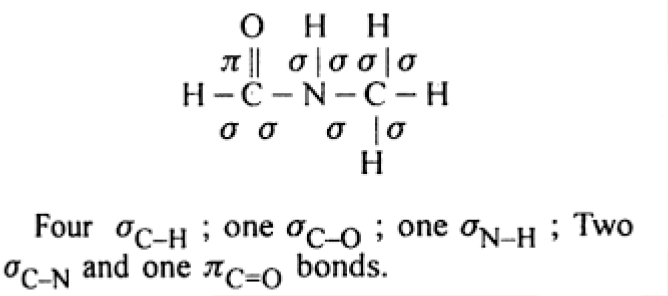
$$\mathrm{H}\underset{\sigma}{-}\overset{\overset{\mathrm{H}}{|\sigma}}{\mathrm{C}}\underset{\sigma}{=}\mathrm{C}\underset{\sigma}{=}\overset{\overset{\mathrm{H}}{|\sigma}}{\mathrm{C}}\underset{\sigma}{-}\mathrm{H}$$

There are two C-C sigma (σC-C) bonds, four C-H sigma (σC-H) bonds, and two C=C pi (πC-C) bonds in the given compound.

(v) CH3NO2

There are three C-H sigma (σC-H) bonds, one C-N sigma (σC-N) bond, one N-O sigma (σN-O) bond and one N=O pi (πN-O) bond in the given compound.

(vi) HCONHCH3



Four σ_{C-H} ; one σ_{C-O} ; one σ_{N-H} ; Two σ_{C-N} and one $\pi_{C=O}$ bonds.

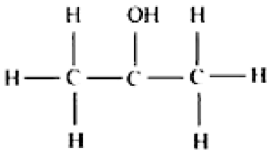
There are two C-N sigma (σC-N) bonds, four C-H sigma (σC-H) bonds, one N-H sigma bond, and one C=O pi (πC-O) bond in the given compound.

Question: 3 Write bond line formula for: Isopropyl alcohol, 2,3 – Dimethyl butanal, Heptanr-4-one.

Answer:

The bond line formula of the given compound are:

a.) Isopropyl alcohol



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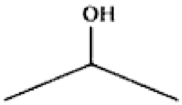
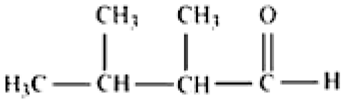
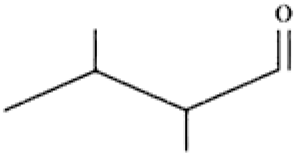


b.) 2,3 – dimethyl butanal

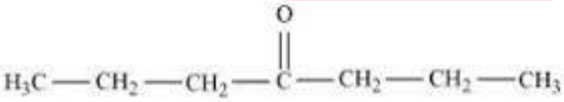


$$H_3C-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{O}{||}}{C}-H$$

⇒

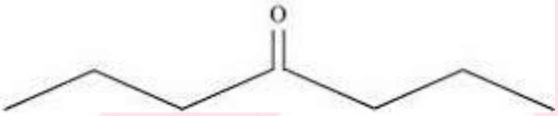


c.) Heptane – 4- one



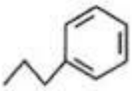
$$H_3C-CH_2-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_2-CH_3$$

⇒



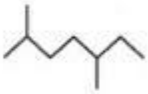
Question: 4 Give the IUPAC names of the following compounds:

(a)

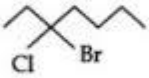


(b)

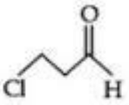
(c)



(d)



(e)



(f) Cl_2CHCH_2OH

Answer:

a.) 3 – phenyl propane.
b.) 2 – methyl – 1 – cyanobutane
c.) 2,5 – dimethyl heptane
d.) 3 – bromo – 3 – chloroheptane
e.) 3 – chloropropanal
f.) 1,1 – dichloro – 2 – ethanol

Question: 5 Which of the following represents the correct IUPAC name for the compounds concerned?

a.) 2,2 – Dimethylpentane or 2 – Dimethylpentane
b.) 2,4,7 – Trimethyloctane or 2,5,7 – Trimethyloctane

c.) 2 – Chloro – 4- methylpentane or 4 – Chloro – 2- methylpentane
d.) But – 3 – yn – 1 – ol or But – 4 – ol – 1 – yne

Answer:

(a) 2,2-Dimethylpentane or 2-Dimethylpentane

Answer : 2,2-Dimethylpentane

Reason : due to two alkyl group on the same carbon its locant is repeated two times .

Hence, 2,2-dimethylpentane is the right answer .

(b) 2,4,7-Trimethyloctane or 2,5,7-Trimethyloctane

Answer : 2,4,7-Trimethyloctane

Reason : due to 2,4,7 locant is set of lower than 2,5,7 . 2,4,7 -Trimethylocatne is the right answer .

(c) 2-Chloro-4-methylpentane or 4-Chloro-2-methylpentane

Answer : 2-Chloro-4-methylpentane

Reason : due to alphabetical order of substituents, 2-chloro - 4-methylpentane is right answer.

(d) But-3-yn-1-ol or But-4-ol-1-yne

Answer : But-3-yn-1-ol

Reason : due to the rule of "lower locant for the principal functional group" { here alcohol is principal functional group}

Question: 6 Draw the formulas for the first five members of each homologus series beginning with the following compounds.

a.) H-COOH
b.) CH3COCH3
c.) H-CH=CH2

Answer:

The first five members of each homologous series beginning with the given compounds are shown as follows:

(a)

H-COOH : Methanoic acid
CH3-COOH : Ethanoic acid
CH3-CH2-COOH : Propanoic acid
CH3-CH2-CH2-COOH : Butanoic acid
CH3-CH2-CH2-CH2-COOH : Pentanoic acid

(b)

CH3COCH3 : Propanone

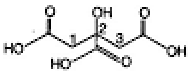
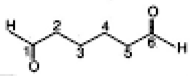
CH3COCH2CH3 : Butanone
CH3COCH2CH2CH3 : Pentan-2-one
CH3COCH2CH2CH2CH3 : Hexan-2-one
CH3COCH2CH2CH2CH2CH3 : Heptan-2-one

(c)
H-CH=CH2 : Ethene
CH3-CH=CH2 : Propene
CH3-CH2-CH=CH2 : 1-Butene
CH3-CH2-CH2-CH=CH2 : 1-Pentene
CH3-CH2-CH2-CH2-CH=CH2 : 1-Hexene

Question: 7 Give condensed and bond line structural formulas and identify the functional group(s) present, if any, for:

- **a.) 2,2,4 – Trimethylpentane**
- **b.) 2 – Hydroxy – 1,2,3 – propanetricarboxylic acid**
- **c.) Hexanedial**

Answer:

S. No.	Condensed formula	Bond line formula	Functional groups
(i)	$(CH_3)_3CCH_2CH(CH_3)_2$		—
(ii)	$HOOCCH_2C(OH)(COOH)CH_2COOH$		$-\overset{O}{\overset{\|}{C}}-OH$ (carboxyl) and —OH (hydroxyl)
(iii)	$OHC(CH_2)_4CHO$		$-\overset{O}{\overset{\|}{C}}-H$ (aldehyde)

The functional group present in the given compound is aldehyde (-CHO).

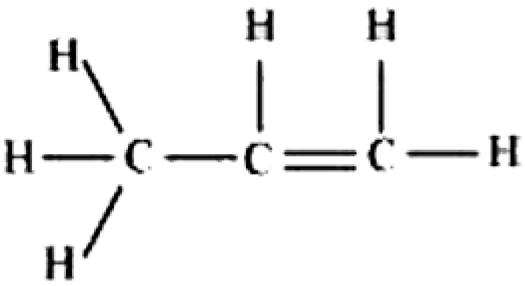
Question: 8 Which of the two:
$O2NCH2CH2O^-$ or $CH3CH2O^-$ is expected to be more stable and why?

Answer:
NO2 group is an electron-withdrawing group. Hence, it shows –I effect. By withdrawing the electrons toward it, the NO2 group decreases the negative charge on the compound, thereby stabilising it. On the other hand, ethyl group is an electron-releasing group. Hence, the ethyl group shows +I effect. This increases the negative charge on the compound, thereby destabilising it. Hence, O2NCH2CH2O– is expected to be more stable than CH3CH2O–.

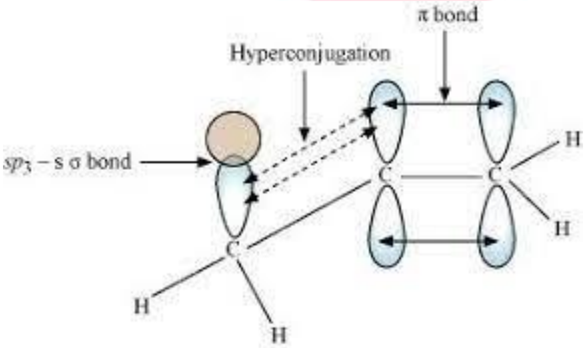
Question: 9 Explain why alkali groups act as electron donors when attached to a π system.

Answer:

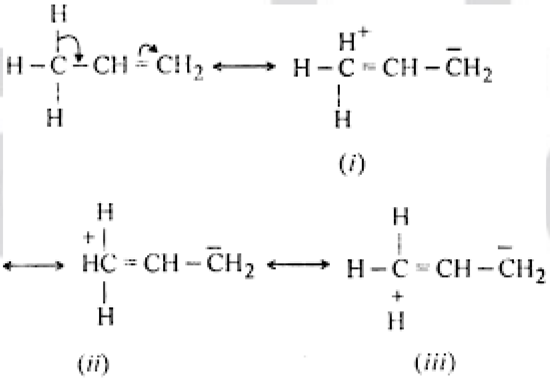
When an alkyl group is attached to a π system, it acts as an electron-donor group by the process of hyperconjugation. To understand this concept better, let us take the example of propene.



In hyperconjugation, the sigma electrons of the C-H bond of an alkyl group are delocalised. This group is directly attached to an atom of an unsaturated system. The delocalisation occurs because of a partial overlap of a sp3-ssigma bond orbital with an empty p orbital of the π bond of an adjacent carbon atom.



The process of hyperconjugation in propene is shown as follows:



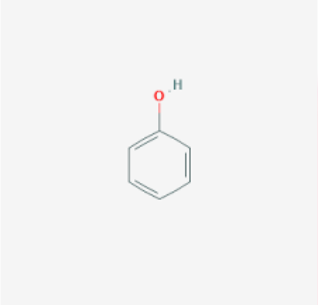
This type of overlap leads to a delocalisation (also known as no-bond resonance) of the π electrons, making the molecule more stable.

Question: 10 Draw the resonance structures for the following compounds. Show the electron shift using curved – arrow notation.

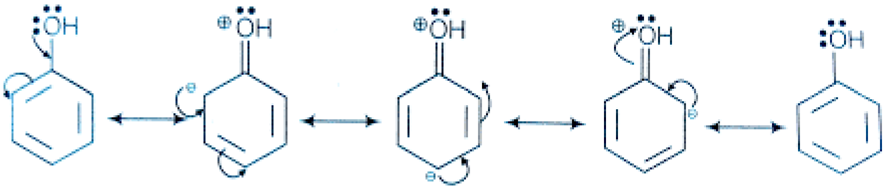
- **a.) C_6H_5OH**
- **b.) $C_6H_5NO_2$**
- **c.) $CH_3CH=CHCHO$**
- **d.) C_6H_5-CHO**
- **e.) $C_6H_5-CH_2$**
- **f.) $CH_3CH=CHCH_2$**

Answer:

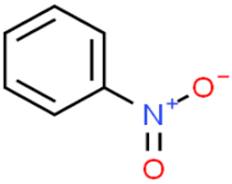
a.) The structure of C_6H_5OH is:



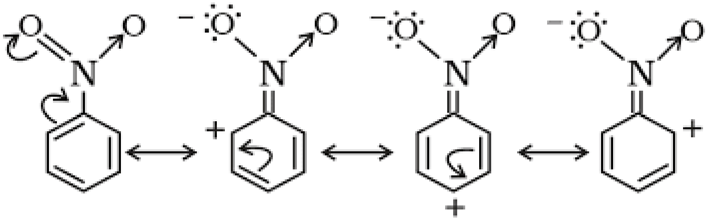
The resonating structures of phenol are represented as:



b.) The structure of $C_6H_5NO_2$ is:

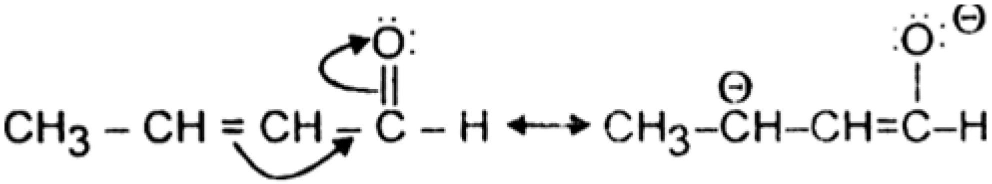


The resonating structures of nitro benzene are represented as:



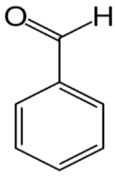
c.) $CH_3CH=CH-CHO$

The resonating structures of the given compound are represented as:

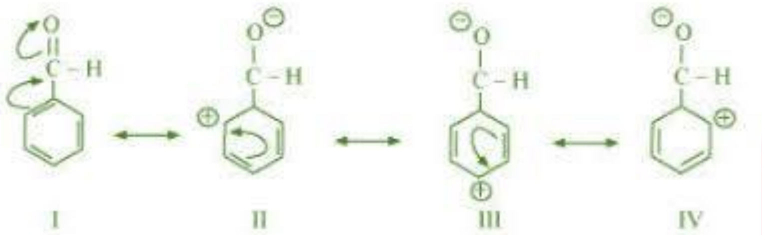


$$CH_3-CH=CH-\overset{\overset{\ddot{O}:}{\|}}{C}-H \longleftrightarrow CH_3-\overset{\ominus}{C}H-CH=\overset{\overset{\ddot{O}:^{\ominus}}{|}}{C}-H$$

d.) The structure of C6H5CHO is:

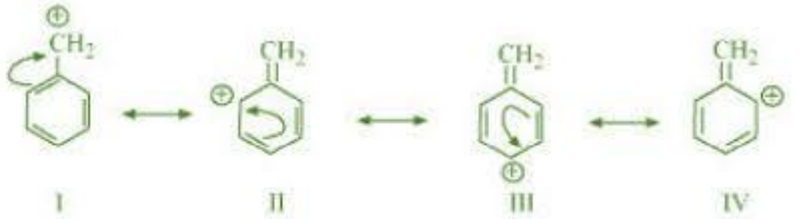


The resonating structures of benzaldehyde are represented as:



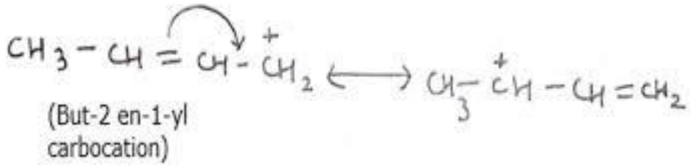
e.) C6H5CH2

The resonating structures of the given compound are:



f.) CH3CH=CHCH2+

The resonating structures of the given compound are:



Question: 11 What are electrophiles and nucleophiles? Explain with examples.

Answer:

An electrophile is a reagent that takes away an electron pair. In other words, an electron-seeking reagent is called an electrophile (E+). Electrophiles are electron-deficient and can receive an electron pair.

Carbocations and (CH3CH+2) neutral molecules having functional groups such as carbonyl group (C=O) are examples of electrophiles.

A nucleophile is a reagent that brings an electron pair. In other words, a nucleus-seeking reagent is called a nucleophile (Nu:).

For example: OH-, NC-, carbanions (R3C-), etc.

Neutral molecules such as H2ö and ammonia also act as nucleophiles because of the presence of a lone pair.

Question: 12 Identify the reagents shown in bold in the following equations as nucleophiles:

- **a.) CH3COOH + HO^{-} → CH3COO^{-} + H2O**
- **b.) CH3COCH3 + CN → (CH3)2C(CN)(OH)**
- **c.) C6H5 + CH3CO → C6H5COCH3**

Answer:

Electrophiles are electron-deficient species and can receive an electron pair. On the other hand, nucleophiles are electron-rich species and can donate their electrons.

(a) CH3COOH + HO- → CH3COO- + H2O

Here, HO- acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleus-seeking species.

(b) CH3COCH3 + C^{-} N → (CH3)2 C (CN) (OH)

Here, C-N acts as a nucleophile as it is an electron-rich species, i.e., it is a nucleus-seeking species.

(c) C6H5 + CH3C^{+} O → C6H5COCH3

Here, CH3C+O acts as an electrophile as it is an electron-deficient species.

Question: 13 Classify the following reactions in one of the reaction type studied in this unit.

- **a.) CH3CH2Br + HS^{-} → CH3CH2SH + Br^{-}**
- **b.) (CH3)2C=CH2 + HCl → (CH3)2ClC-CH3**
- **c.) CH3CH2Br + HO- → CH2=CH2 + H2O + Br-**
- **d.) (CH3)2C-CH2OH + HBr → (CH3)2CBrCH2CH3 + H2O**

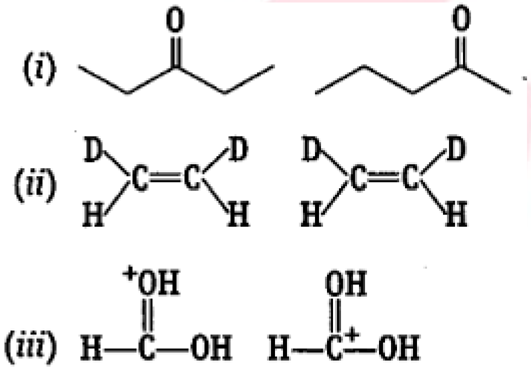
Answer:
(a) Br- and HS- are electron rich species. Hence, it is Nucleophile.
A Nucleophile (Br-) is replaced by other Nucleophile (HS-) . Hence, it is nucleophilic substitution reaction.

(b) HCl is added to the double bond.
HCl is electron- loving species and it addition on double bond (C=C) hence, it is electrophilic addition reaction.

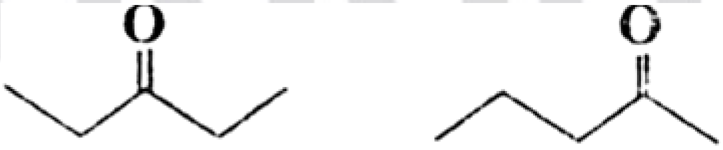
(c) H and Br are eliminated from successive Carbon atoms hence, it is Beta - elimination reaction.

(d) OH- and Br- are electron rich species .hence, it is Nucleophile and we see that Nucleophile (OH-) is replaced by Nucleophile (Br-). Hence, it is nucleophilic substitution reaction with rearrangement {because after reaction products are rearranged }

Question: 14 What is the relationship between the members of the following pairs of structures? Are they structural or geometrical isomers or resonance contribution?

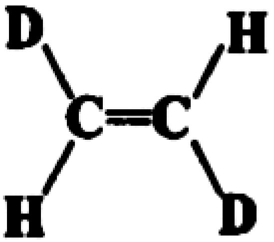


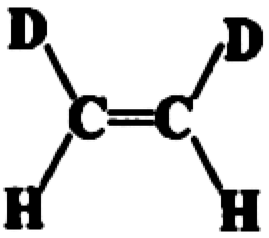
Answer:
(a) Compounds having the same molecular formula but with different structures are called structural isomers. The given compounds have the same molecular formula but they differ in the position of the functional group (ketone group).



In structure I, ketone group is at the C-3 of the parent chain (hexane chain) and in structure II, ketone group is at the C-2 of the parent chain (hexane chain). Hence, the given pair represents structural isomers.

(b) Compounds having the same molecular formula, the same constitution, and the sequence of covalent bonds, but with different relative position of their atoms in space are called geometrical isomers.





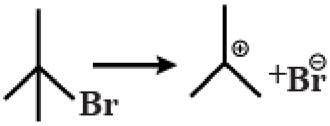
In structures I and II, the relative position of Deuterium (D) and hydrogen (H) in space are different. Hence, the given pairs represent geometrical isomers.

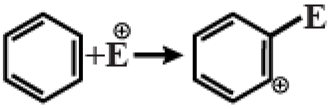
(c) The given structures are canonical structures or contributing structures. They are hypothetical and individually do not represent any real molecule. Hence, the given pair represents resonance structures, called resonance isomers.

Question: 15 For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or hetrolysis. Identify reactive intermediate produced as free radical carbocationb and carbanion.

a. $CH_3O - OCH_3 \rightarrow CH_3O + OCH_3$

b.


c.


d.


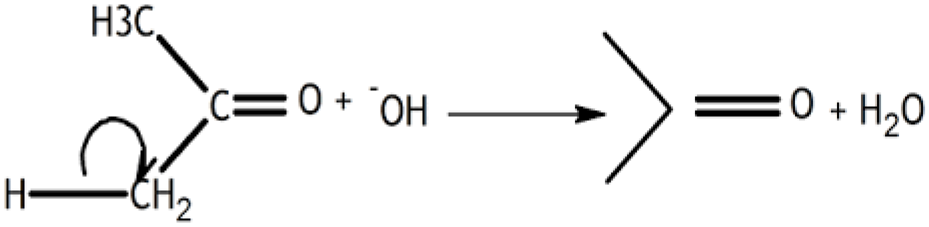
Answer:

(a) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as

$CH3O\text{-}OCH3 \rightarrow CH3O^{+} + {}^{+}OCH3$

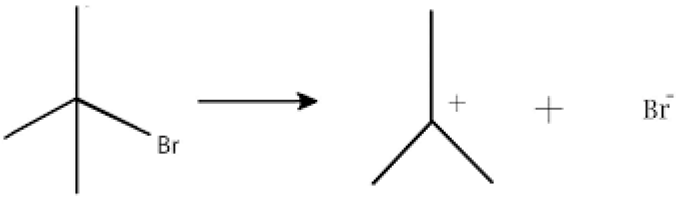
It is an example of homolytic cleavage as one of the shared pair in a covalent bond goes with the bonded atom. The reaction intermediate formed is a free radical.

(b) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



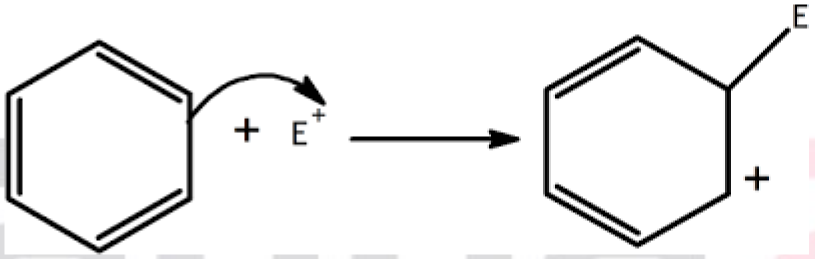
It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the carbon of propanone. The reaction intermediate formed is carbanion.

(c) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is an example of heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with the bromine ion. The reaction intermediate formed is a carbocation.

(d) The bond cleavage using curved-arrows to show the electron flow of the given reaction can be represented as



It is a heterolytic cleavage as the bond breaks in such a manner that the shared pair of electrons remains with one of the fragments. The intermediate formed is a carbocation.

Question: 16 Explain the terms inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

- **a.) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$**
- **b.) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$**

Answer:

Inductive effect

The permanent displacement of sigma (-) electrons along a saturated chain, whenever an electron withdrawing or electron donating group is present, is called inductive effect.

Inductive effect could be + I effect or - I effect. When an atom or group attracts electrons towards itself more strongly than hydrogen, it is said to possess - I effect. For example,

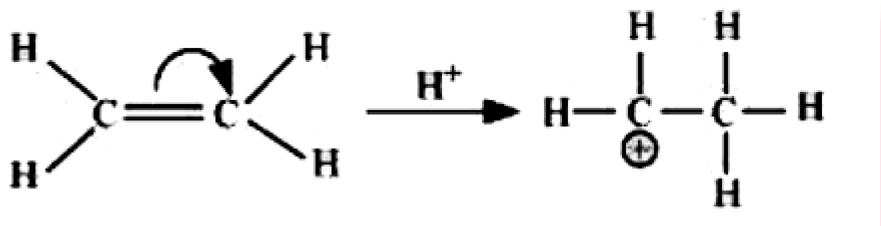
F —← CH_2 —← CH_2 —← CH_2 —←CH_3

When an atom or group attracts electrons towards itself less strongly than hydrogen, it is said to possess + I effect. For example,

CH_3 —→ CH_2 →→— Cl

Electrometric effect

It involves the complete transfer of the shared pair of π-electrons to either of the two atoms linked by multiple bonds in the presence of an attacking agent. For example,



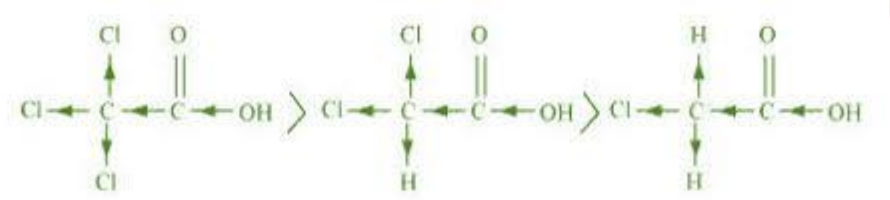
Electrometric effect could be + E effect or - E effect.

+ E effect: When the electrons are transferred towards the attacking reagent

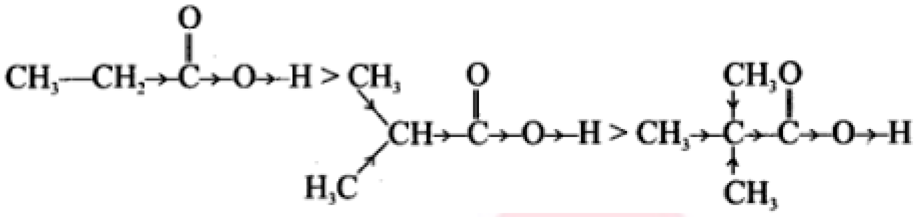
- E effect: When the electrons are transferred away from the attacking reagent

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

The order of acidity can be explained on the basis of Inductive effect (- I effect). As the number of chlorine atoms increases, the - I effect increases. With the increase in - I effect, the acid strength also increases accordingly.



(b) CH3CH2COOH > (CH3)2 CHCOOH > (CH3)3 C.COOH
The order of acidity can be explained on the basis of inductive effect (+ I effect). As the number of alkyl groups increases, the + I effect also increases. With the increase in + I effect, the acid strength also increases accordingly.



Question: 17 Give a brief description of the principles of the following techniques taking an example in each case.

- **a.) Crystallisation**
- **b.) Distillation**
- **c.) Chromatography**

Answer:

Crystallisation:

Crystallisation is the common way of purifying organic solids. It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent. The impure compound is dissolved in a solvent in which it is sparingly soluble at room temperature but appreciably soluble st higher temperature. The solution is concentrated to get a nearly saturated solution. On cooling the solution, pure compound crystallises out and is removed by filtration.

It the compound is highly soluble in one solvent and very little in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents. Coloured impurities are removed by adsorbing them over activated charcoal. The crystals are separated by filtering unnder reduced pressure using Buchner funnel. The crystals are finally dried over sulphuric acid or calcium chloride in vaccum desiccator.
Repeated crystallisation becomes necessary for the purification of compounds containing impurities of comparable solubilities.

Distillation:

Distillation is one of the effective method for separation of liquid type mixture and it work on the principle of difference in boiling point. When two liquids of high boiling point difference are mixed they can be separated out by using this method.
Ex:- Ether presents as impurity in alcohols because of weak inter molecular forces ether are volatile in nature where as alcohols have inter molecular hydrogen bonding and this mixture can be separated by simple heating above 30 C where ether is evaporated first and the vapour's are condensed where alcohols is left over in the flask.

Fractional distillation:-

It is the one of the effective method to separate liquid in liquid solutions of similar boiling point which are having less boiling point difference.

Ex:- Fractional distillation of petroleum. Petroleum is a crude oil is a mixture of different hydrocarbons and this can be separated out different columns of fractional distillations. In the fractional distillation plant the hydro- carbon having less boiling point is separated at the top of the container and the hydro-carbon with high boiling point is separated as the bottom of the container.

Chromatography:

Chromatography is one of the effective separation for liquids and pigments and it work under principle of Adsorption.

Adsorption it is a surface phenomenon where one of the substance get accumulated on the surface of another surface.

Adsorption in separation of a mixture it is taken on a stationary face kept in a mobile phase (solvent) different substance present in a mixture will have different rate of absorption one of the effective method.

Column chromatography:- Column chromatography involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube. The column is fitted with a stopcock as it lower end. The mixture adsorbed is placed on the top of the adsorbent column packed in a glass tube. A suitable eluant, either a single solvent or a mixture of solvents is allowed to flow down the column slowly. Depending upon the degree to which the compounds are adsorbed, complete separation takes place. The most readily adsorbed substances are retained near the top and others come down accordingly to various distances in the column.

Thin layer chromatography is another type of adsorption chromatography, which involves separation of the substances of a mixture over a thin layer of an adsorbent coated on glass plate. A thin layer (about 0.2mm thick) of an adsorbent is spread over a glass plate of suitable size. The plate is known as thin layer chromatography plate or chromaplate. The solution of the mixture to be separated is applied as a small spot about 2 cm above the end of the thin layer chromatography plate.

Partition Chromatography:

Partition chromatography is based on continuous differential partitioning of components of a mixture between stationary and mobile phases. Paper chromatography is an example. In paper chromatography a special quality paper known as chromatography paper is used. This paper contains water trapped in it, which acts as the stationary phase.

A strip of chromatography paper spotted at the base with the solution of the mixture in suspended in a suitable solvent or a mixture of solvents. This solvent acts as the mobile phase. The solvent rises up the paper by capillary action and flows over the spot.

The paper selectively retains different components according to their differing partition in the two phases. The paper strip so developed is known as chromatogram. The spots of the separated coloured compounds are visible at the different heights from the position of initial spot on the chromatogram.

Question: 18 Describe the method, which can be used to separate two compounds with different solubilities in a solvent S.

Answer:

Two compounds which have different solubilities in a solvent S can be separated from each other by Fractional Crystallisation. The process involves a series of repeated-crystallisations. The mixture of the two compounds in the solvent S is heated so as to make it saturated. When the hot solution is allowed to cool, the less soluble substance crsytallises out first while the more soluble substance remains in the solution. The crystals of first compound are separated from the mother liquor and the mother liquor is again concentrated and allowed to cool when the crystals of the 2nd compound are obtained.

Question: 19 What is the difference between distillation, distillation under reduced pressure and steam distillation?

Answer:

The differences among distillation, distillation under reduced pressure and steam distillation rae given in the following table:

Distillation	**Distillation under reduced pressure**	**Steam distillation**
It is used for the purification of compounds that are associated with non – volatile impurities or those liquids, which do not decompose on boiling. In other words, distillation is used to separate volatile liquids form non – volatile impurities or a mixture of those liquids that have sufficient difference in boiling points.	This method is used to purify a liquid that tends to decompose on boiling. Under the conditions of reduced pressure, the liquid will boil at a low temperature than its boiling point and will therefore, not decompose.	It is used to purify an organic compound, which is steam volatile and immiscible in water. On passing steam, the compound gets heated up and the steam gets condensed to water. After some time, the mixture of water and liquid starts to boil and passes through the condenser. This condensed mixture of water and liquid is then separated by using a separating funnel.
Mixture of petrol and kerosene is separated by this method.	Glycerol is purified by this method. It boils with decomposition at a temperature of 593 K. At a reduced	A mixture of water and aniline is separated by steam distillation.

	pressure, it boils at 453 K without decomposition.	

Question: 20 Discuss the chemistry of Lassaigne's test.

Answer:

Lassaigne's test This test is employed to detect the presence of nitrogen, sulphur, halogens, and phosphorous in an organic compound. These elements are present in the covalent form in an organic compound. These are converted into the ionic form by fusing the compound with sodium metal.

$Na + C + N \rightarrow NaCN$

$2Na + S \rightarrow Na2S$

$Na + X \rightarrow NaX$

(X = Cl, Br, I)

The cyanide, sulphide, and halide of sodium formed are extracted from the fused mass by boiling it in distilled water. The extract so obtained is called Lassaigne's extract. This Lassaigne's extract is then tested for the presence of nitrogen, sulphur, halogens, and phosphorous.

(a) Test for nitrogen

Lassaignes's extract + Ferrous Sulphate

↓ Conc. sulphuric acid

Prussian blue colour

(Ferriferro cyanide)

Chemistry of the test

In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

$6CN- + Fe2+ \longrightarrow [Fe(CN)6]4-$

$3[Fe(CN)6]4- + 4Fe3+ \longrightarrow Fe4[Fe(CN)6]3 . xH2O$

Prussian blue colour

(b) Test for sulphur

(i) Lassaignes's extract + Lead acetate ⟶ Black precipitate

Chemistry of the test

In the Lassaigne's test for sulphur in an organic compound, the sodium fusion extract is acidified with acetic acid and then lead acetate is added to it. The precipitation of lead sulphide, which is black in colour, indicates the presence of sulphur in the compound.

$S2- + Pb2+ \longrightarrow PbS$

(Black)

(ii) Lassaignes's extract + Sodium nitroprusside ⟶ Violet colour

Chemistry of the test

The sodium fusion extract is treated with sodium nitroprusside. Appearance of violet colour also indicates the presence of sulphur in the compound.

$S2- + [Fe(CN)5\ NO]2- \longrightarrow [Fe(CN)5NOS]-4$

(Violet)

If in an organic compound, both nitrogen and sulphur are present, then instead of NaCN, formation of NaSCN takes place.

$Na + C + N + S \longrightarrow NaSCN$

This NaSCN (sodium thiocyanate) gives a blood red colour. Prussian colour is not formed due to the absence of free cyanide ions.

$Fe3+ + SCN \longrightarrow [Fe(SCN)]2+$

(Blood Red)

(c) Test for halogens

Chemistry of the test In the Lassaigne's test for halogens in an organic compound, the sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

$X- + Ag+ \longrightarrow AgX$

$(X = Cl,Br,I)$

If nitrogen and sulphur both are present in the organic compound, then the Lassaigne's extract is boiled to expel nitrogen and sulphur, which would otherwise interfere in the test for halogens.

Question: 22 Difference between the principle of estimation of nitrogen in an organic compound by :

- **i.) Dumas method and**
- **ii.) Kjeldahl’s method.**

Answer:

Dumas method:

A known quantity of compound containing nitrogen is heated with excess copper oxide in carbon dioxide atmosphere to form free nitrogen in addition to carbon dioxide and water.

CxHyNz + (2x+y/2)CuO → xCO2 + y/2H2O + z/2 N2 + (2x+y/2)Cu

Nitrogen is collected over an aqueous solution of KOH. Volume of nitrogen produced is measured at room temperature and atmospheric pressure.

Kjeldahl's method: A known amount of compound containing nitrogen is heated with concentric sulphuric. The nitrogen present in the compound is quantitatively converted into ammonium sulphate and distilled with excess NaOH. Ammonia evolved is passed into known volume of sulphuric acid. Unreacted acid is estimated by volumetric analysis and the amount of ammonia produced is determined. The percentage of nitrogen in the compound is estimated. This method is not applicable to compounds containing nitro and azo groups and compounds in which nitrogen is part of ring structure.

$$\text{Organic compound} \xrightarrow{\text{Conc. } H_2SO_4} (NH_4)_2\,SO_4$$

$$(NH_4)_2\,SO_4 + 2NaOH \longrightarrow Na_2\,SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2\,SO_4$$

Question: 22 Discuss the principles of estimation of halogens, sulphur and phosphorus present in an organic compound.

Answer:

Principle of estimation of halogens :

A known mass of the organic compound is heated with fuming nitric acid and a few Crystal of silver nitrate is a sealed hard glass tube .

under the conditions , carbon and Hydrogen are oxidised to carbon dioxide and water respectively while halogens is converted into silver halide. The participate of silver halide is filtered , washed , dried and weighed . Knowing the mass of the substance taken and the mass of precipitate formed , the percentage of halogens is calculated as follow,

% of X = (atomic mass of X/molecule mass of AgX) × {mass of AgX formed /mass of substance taken } × 100

Principle of estimation of sulphur :-

A known mass of the substance is heated with sodium peroxide or fuming nitric acid in a sealed tube . Carbon and Hydrogen are oxidised to CO_2 and H_2O respectively. While sulphur present in the compound is oxidised to H_2SO_4 which is them precipitated as Barium sulphate by adding of barium chloride solution.

The PPT of $BaSO_4$ is filtered , washed , dried and weighed . Knowing the mass of the substance taken and the mass of $BaSO_4$ ppt formed ,

% of S = {32/233} × { mass of $BaSO_4$ formed/mass of substance taken } × 100

Principle of estimation of phosphorus :-

A known mass of organic substance is heated with fuming nitric acid in a sealed tube . Under these conditions , C and H are oxidised to CO_2 and H_2O respectively. While Phosphorus present in organic compound is oxidised to H_3PO_4 which is precipitated as ammonium phosphomolybadate by heating it with conc.HNO_3 and then adding ammonium molybdate.

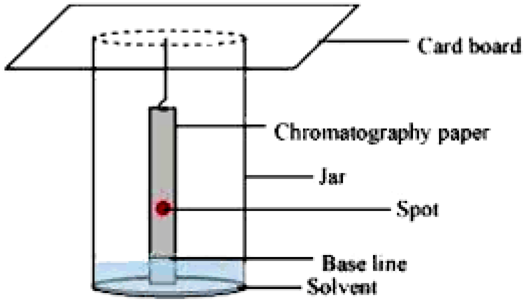
The precipitated of a mm phosphomolybadate are filtered , washed , dried and weighed .

% of P = {31/1877} × {mass of a mm. phosphomolybadate formed /mass of substance taken} × 100

Question: 23 Explain the principle of paper chromatography.

Answer:

In paper chromatography, chromatography paper is used which contains water trapped in it which is the stationary phase. On the base of the paper, a solution (containing the mixture to be separated) is spotted. The paper strip is suspended in suitable solvent which is mobile phase. The solvent rises to the top of the paper by capillary action. During this, it flows over the spot. The components are selectively retained on the paper. The spots of different components travel with the mobile phase to different heights. The developed paper is called chromatogram.



Question: 24 Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

Answer:

Sodium extract is boiled with nitric acid to decompose NaCN and Na_2S if present.

$NaCN + HNO_3 \rightarrow NaNO_3 + HCN \uparrow$

$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S \uparrow$

If cyanide and sulphide are not removed, they will react with $AgNO_3$ and hence, will interfere with the silver nitrate test for halogens.

$NaCN + AgNO_3 \rightarrow AgCN + NaNO_3$

(white ppt.)

$Na_2S + 2AgNO_3 \rightarrow Ag_2S + 2NaNO_3$

(black ppt.)

Question: 25 Explain the reason for the fusion of an organic compound with metallic sodium for testing nitrogen, sulphur and halogens.

Answer:

Nitrogen, sulphur, and halogens are covalently bonded in organic compounds. For their detection, they have to be first converted to ionic form. This is done by fusing the organic compound with sodium metal. This is called “Lassaigne’s test”.

$Na + C + N \rightarrow NaCN$

$Na + S + C + N \rightarrow NaSCN$

$2Na + S \rightarrow Na2S$

$Na + X \rightarrow NaX$

$(X = Cl, Br, I)$

The chemical equations involved in the test are Carbon, nitrogen, sulphur, and halogen come from organic compounds.

Question: 26 Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Answer:

The process of sublimation is used to separate a mixture of camphor and calcium sulphate. In this process, the sublimable compound changes from solid to vapour state without passing through the liquid state. Camphor is a sublimable compound and calcium sulphate is a non-sublimable solid. Hence, on heating, camphor will sublime while calcium sulphate will be left behind.

Question: 27 Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?

Answer:

In steam distillation, the organic liquid starts to boil when the sum of vapour pressure due to the organic liquid (p1) abd the vapour pressure due to water (p2) becomes equal to atmospheric pressure (p), that is, $p = p1 + p2$

Since $p1 < p2$, organic liquid will vapourise at a lower temperature than its boiling point.

Question: 28 Will CCl4 give white precipitate of AgCl on heating it with silver nitrate? Give reason for your answer.

Answer:

CCl4 will not give the white precipitate of AgCl on heating it with silver nitrate. This is because the chlorine atoms are covalently bonded to carbon in CCl4. To obtain the precipitate, it should be present in ionic form and for this, it is necessary to prepare the Lassaigne's extract of CCl4.

Question: 29 Why is a solution of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

Answer:

CO2 is slightly acidic in nature , therefore it reacts with strong base KOH to form K2CO3 and form the weight of CO2 obtained , the percentage of Carbon in the organic compound is calculated .

2KOH + CO2 ----> K2CO3 + H2O

Increases in the weight of U-tube containing KOH gives the weight of CO2 produced and form the weight of the CO2 obtained ,

So, % of Carbon in the organic compound is calculated as

% of Carbon = (12/44) × {mass of CO2 formed/mass of substance taken} × 100

Question: 30 Why is it necessary to use acetic acid and not sulphuric acid for acidification of sodium extract for testing sulphur by lead acetate test?

Answer:

When sulphuric acid is added, lead sulphate is precipitated.

When acetic acid is used, complete precipitation of sulphur in the form of lead sulphate occurs due to common ion effect. Hence, it is necessary to use acetic acid for acidification of sodium extract for testing sulphur by lead acetate test.

Question: 31 An organic compound contains 69 % carbon and 4.8 % hydrogen, the remainder being oxygen. Calculate the mass of the carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Answer:

Percentage of carbon in organic compound = 69 %

That is, 100 g of organic compound contains 69 g of carbon

: 0.2 g of organic compound will contain 69x.02 / 100 = 0.138g of C

Molecular mass of carbon dioxide, CO2 = 44 g

That is, 12 g of carbon is contained in 44 g of CO2.

Therefore, 0.138 g of carbon will be contained in 44x0.138/12 = 0.506 g of CO2

Thus, 0.506 g of CO2 will be produced on complete combustion of 0.2 g of organic compound.

Percentage of hydrogen in organic compound is 4.8.

i.e., 100 g of organic compound contains 4.8 g of hydrogen.

Therefore, 0.2 g of organic compound will contain 4.8x0.2/100 = 0.0096 g of H

It is known that molecular mass of water (H2O) is 18 g.

Thus, 2 g of hydrogen is contained in 18 g of water.

: 0.0096 g of hydrogen will be contained in 18x0.0096/2 = 0.0864g of water

Thus, 0.0864 g of water will be produced on complete combustion of 0.2 g of the organic compound.

Question: 32 A sample of 0.50 g of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.5M H2SO4. The residual acid required 60 mL of 0.5 M solution of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Answer:

Volume of acid taken = 50ml of 0.5M H2SO4 = 25ml of 1M H2SO4

{We know, M1V1 = M2V2 , if M1=1M,M2=0.5M,V2=50ml then,V1=25ml }

Volume of alkali used for the neutralisation of excess acid = 60ml of 0.5M NaOH or, 30ml of 1M NaOH {M1V1=M2V2 use and then you get volume = 30ml for 1M NaOH}

H2SO4 + 2NaOH ---> Na2SO4 + 2H2O

1mole of H2SO4 = 2mole of NaOH

Hence, 30ml of 1M NaOH = 15ml of 1M H2SO4

So, volume of acid used by ammonia = 25ml - 15ml = 10ml

Now, % of nitrogen = 1.4 × Normality of acid × volume of acid/mass of organic compound

= 1.4 × 2 × 10/0.5 {normality = n-factor × molarity , normality of H2SO4 = 2 × 1 = 2 N}

= 56%

Hence, percentage of Nitrogen = 56%

Question: 33 0.3780 g of an organic chloro compound gave 0.5740 g of silver chloride in Carius estimation. Calculate the percentage of chlorine present in the compound.

Answer:

The mass of organic compound taken is 0.3780g

Mass of AgCl formed = 0.5740g

We know,

Atomic mass of Chlorine = 35.5 g/mol

Molecular mass of AgCl = 108 + 35.5 = 143.5 g/mol

Now,

Applying the relation,

The percentage of chlorine = (35.5/143.5) ×{mass of AgCl formed/mass of organic substance taken} ×100

= (35.5/143.5) ×{0.5740/0.3780} × 100

= (35.5 × 574 × 100}/{143.5 × 378}

= 37.566 %

Hence, the percentage of Cl in the compound is 37.566% .

Question: 34 In the estimation of sulphur by Carius method, 0.468 g of an organic sulphur compound afforded 0.668 g of barium sulphate. Find out the percentage of sulphur in the given compound.

Answer:

The mass of organic compound taken = 0.468g

Mass of BaSO4 formed = 0.668g

We know,

Atomic mass of sulphur = 32g/mol

Molecular mass of BaSO4 = 233 g/mol

Applying the relation,

Percentage of sulphur = (32/233) × {mass of BaSO4 formed/mass of organic substance taken } × 100

= (32/233) × {0.668/0.468}×100

= 3200× 668/(233 ×468)

= 19.60 %

Hence, percentage of sulphur in the given compound is 19.6%

Question: 35 In the organic compound CH2=CH-CH2-CH2-C=CH, the pair of hybridised orbitals involved in the formation of: C2-C3 bond as:

a.) Sp-sp2

- **b.) Sp-sp3**
- **c.) Sp2-sp3**
- **d.) Sp3-sp3**

Answer:

We know, when both double and triple bond are present at equivalent positions then we have to give preference of double bond.

Hence, numbering of Carbon chain start near of double bond .

See attachment , here it is clear that which is C2-C3 bond .

Hence, C2-C3 bond is formed by overlap of sp^2 and sp^3 orbitals. hence, option (C) is correct.

Question: 36 In the Lassaigne's test for nitrogen in an organic compound, the Prussian blue colour is obtained due to the formation of:

- **a.) Na4[Fe(CN)6]**
- **b.) Fe4[Fe(CN)6]3**
- **c.) Fe2[Fe(CN)6]**
- **d.) Fe3[Fe(CN)6]4**

Answer:

In the Lassaigne's test for nitrogen in an organic compound, the sodium fusion extract is boiled with iron (II) sulphate and then acidified with sulphuric acid. In the process, sodium cyanide first reacts with iron (II) sulphate and forms sodium hexacyanoferrate (II). Then, on heating with sulphuric acid, some iron (II) gets oxidised to form iron (III) hexacyanoferrate (II), which is Prussian blue in colour. The chemical equations involved in the reaction can be represented as

$$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$$

$$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4[Fe(CN)_6]_3 \cdot xH_2O}$$

Hence, the Prussian blue colour is due to the formation of Fe4[Fe(CN)6]3.

Question: 37 Which of the following carbocation is most stable?

- **a.) (CH3)3C.CH2**
- **b.) (CH3)3C**
- **c.) CH3CH2CH2**
- **d.) CH3CHCH2CH3**

Answer:

The stability of carbocation is 3°-carbocation > 2°-carbocation > 1°-carbocation

(a) (CH3)3C-CH2+ {1°-carbocation}

(b) (CH)3C+ {3°-carbocation}

(c)CH3-CH2-CH2+{1°-carbocation}

(d)CH3CH$^+$CH2CH3 {2°-carbocation}

Because 3°-carbocation is option (b) hence, option (b) is the most stable carbocation.

Question: 38 The best and latest technique for isolation, purification and separation of organic compounds is:

- **a.) Crystallisation**
- **b.) Distillation**
- **c.) Sublimation**
- **d.) Chromatography.**

Answer:

The best and latest technique for isolation, purification, and separation of organic compounds is chromatography which is a method used by scientists for separating organic and inorganic compounds. Chromatography is based on differential migration. The solutes in a mobile phase go through a stationary phase. Solutes with a greater affinity for the mobile phase will spend more time in this phase than the solutes that prefer the stationary phase. As the solutes move through the stationary phase, they separate.

Option (d) is correct.

Question: 39 The reaction:

CH3CH2I + KOH(aq) → CH3CH2OH + KI

Is classified as:

- **a.) Electrophilic substitution**
- **b.) Nucleophilic substitution**
- **c.) Elimination**
- **d.) Addition**

Answer:

CH3CH2I + KOH(aq) ⟶ CH3CH2OH + KI

It is an example of nucleophilic substitution reaction. The hydroxyl group of KOH (OH-) with a lone pair of itself acts as a nucleophile and substitutes iodide ion in CH3CH2I to form ethanol.