Chapter: Organic Chemistry: Some basic principles and techniques

Exercise

12.1. What are 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) $\overset{1}{C}H_2 = \overset{2}{C} = O$

In the given compound, carbon-1 is bonded to two hydrogen atoms and one carbon atom. So, according to the VSEPR theory, the steric number is 3 which corresponds to sp^2 hybridization. Carbon-2 is bonded to one carbon atom and one oxygen atom. So, the steric number is 2 which corresponds to sp hybridization.

(ii) $\overset{1}{C}H_3\overset{2}{C}H = \overset{3}{C}H_2$

In the given compound, carbon-1 is bonded to three hydrogen atoms and one carbon atom. So, according to the VSEPR theory, the steric number is 4 which corresponds to sp^3 hybridization. Carbon-2 is bonded to two carbon atoms and one hydrogen atom. So, the steric number is 3 which corresponds to sp^2 hybridization.

(iii) $\overset{1}{C}H_3\overset{2}{C}O\overset{3}{C}H_3$

In the given compound, carbon-1 and carbon-3 are bonded to three hydrogen atoms and one carbon atom. So, according to the VSEPR theory, the steric number is 4 which corresponds to sp^3 hybridization. Carbon-2 is bonded to two carbon atoms and one oxygen atom. So, the steric number is 3 which corresponds to sp^2 hybridization.

(iv) $\overset{1}{C}H_2 = \overset{2}{C}H\overset{3}{C}N$

In the given compound, carbon-1 is bonded to two hydrogen atoms and one carbon atom. So, according to the VSEPR theory, the steric number is 3 which corresponds to sp^2 hybridization. Carbon-2 is bonded to two carbon atoms and one hydrogen atom. So, the steric number is 3 which corresponds to sp^2 hybridization. Carbon-3 is bonded to one carbon atom and one nitrogen atom. So, the steric number is 2 which corresponds to sp hybridization.

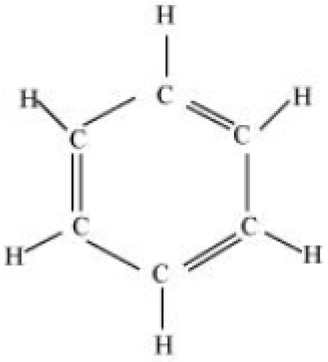
(v) C_6H_6

In the given compound, all carbon atoms are bonded to two carbon atoms and one hydrogen atom. So, according to the VSEPR theory, the steric number is 3 which corresponds to sp^2 hybridization.

12.2. Indicate the σ and π bonds in the following molecules:

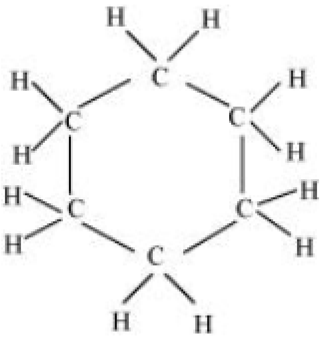
C_6H_6, C_6H_{12}, CH_2Cl_2, $CH_2 = C = CH_2$, CH_3NO_2, $HCONHCH_3$

Answer: The structure of C_6H_6 is shown below.



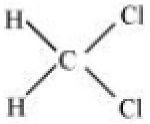
Single bond contains only one sigma bond and double bond contains one sigma and one pi bond. In this structure, nine single bonds and three double bonds are present. So, there are $12\ \sigma$ and $3\ \pi$ bonds present.

The structure of C_6H_{12} is shown below.



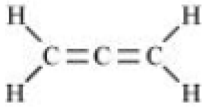
In this structure, eighteen single bonds are present. So, there are only $18\ \sigma$ bonds present.

The structure of CH_2Cl_2 is shown below.



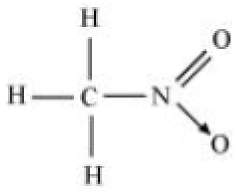
In this structure, four single bonds are present. So, there are only $4\ \sigma$ bonds present.

The structure of $CH_2 = C = CH_2$ is shown below.



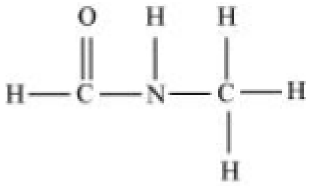
In this structure, four single bonds and two double bonds are present. So, there are $6\ \sigma$ and $2\ \pi$ bonds present.

The structure of CH_3NO_2 is shown below.



In this structure, five single bonds and one double bond are present. So, there are $6\ \sigma$ and $1\ \pi$ bonds present.

The structure of $HCONHCH_3$ is shown below.



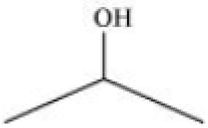
In this structure, seven single bonds and one double bond are present. So, there are $8\ \sigma$ and $1\ \pi$ bonds present.

12.3. Write bond line formulas for:

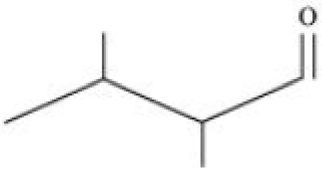
Isopropyl alcohol, $2,3-$ Dimethylbutanal, Heptan $-4-$ one

Answer: The bond line formulas for the given compounds are shown below.

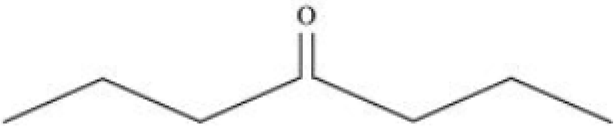
(a) Isopropyl alcohol:



(b) $2,3-$ Dimethylbutanal

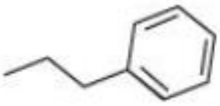


(c) Heptan $-4-$ one

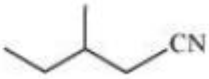


12.4. Give the IUPAC names of the following compounds:

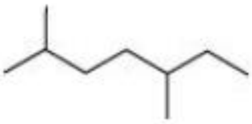
(a)



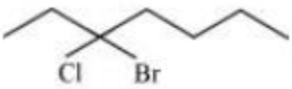
(b)



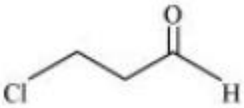
(c)



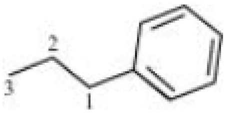
(d)



(e)



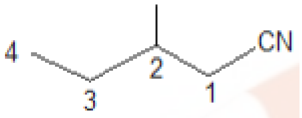
(f) Cl_2CHCH_2OH



Answer: (a)

In this structure, the longest chain of carbon contains 3 carbon atoms and one phenyl group is present. So, the IUPAC name is 1-phenyl propane.

(b)

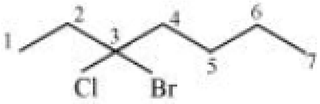


In this structure, the longest chain of carbon contains four carbon atoms. Also, one methyl and one cyanide groups are attached with carbon-2 and carbon-1 respectively. So, the IUPAC name is 2-methyl-1-cyanobutane.

(c)

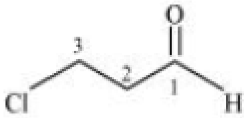
In this structure, the longest chain of carbon contains 7 carbon atoms and 2 methyl are positioned at carbon-2 and carbon-5. So, the IUPAC name of the compound is 2, 5-dimethyl heptane.

(d)



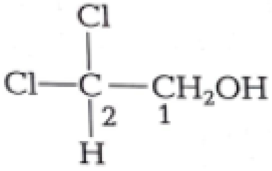
In this structure, the longest chain of carbon contains 7 carbon atoms. Also, 1 chloro and 1 bromo groups are present at carbon-3. So, the IUPAC name of the compound is 3-bromo-3-chloroheptane.

(e)



In this structure, the longest chain of carbon contains 3 carbon atoms. Also, 1 aldehyde and 1 chloro functional groups are present at carbon-1 and carbon-3 respectively. So, the IUPAC name of the compound is 3-chloropropanal.

(f)



$$Cl-\overset{\overset{Cl}{|}}{\underset{\underset{H}{|}}{C}}-CH_2OH$$

In this structure, the longest chain of carbon contains 2 carbon atoms. Also, 1 alcohol and 2 chloro functional groups are present at carbon-1 and carbon-2 respectively. So, the IUPAC name of the compound is 2,2-dichloro-1-ethanol.

12.5. 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) In the IUPAC nomenclature, the prefix Di- denotes that the parent chain has two identical substituent groups. As there are two methyl groups in the C–2 of the parent chain of the given chemical compound, the correct IPUAC name is $2,2-$ Dimethylpentane.

(b) The locant number 2, 4, 7 is less than the locant number 2, 5, 7. As a result, the given compound's IUPAC nomenclature is $2,4,7 - \text{Trimethyloctane}$

(c) If the functional groups are present at the parent chain's equivalent position, the lower number is assigned to the one that appears first in the name in alphabetical order. As a result, the proper IUPAC nomenclature for the given compound is $2 - \text{Chloro} - 4 - \text{methylpentane.}$

(d) The given molecule contains two functional groups: alcoholic and alkyne. The alcoholic group is the principal functional group. As a result, the parent chain will be terminated with ol. The alkyne group can be found in the parent chain's C–3. As a result, $\text{But} - 3 - \text{yn} - 1 - \text{ol}$ is the correct IUPAC nomenclature for the given compound.

12.6. Draw formulas for the first five members of each homologous series beginning with the following compounds.

(a) $H - COOH$

(b) CH_3COCH_3

(c) $H - CH = CH_2$

Answer: The following are the first 5 members of each homologous series, starting with the given compounds:

(a) $H - COOH$: Methanoic acid
$CH_3 - COOH$: Ethanoic acid
$CH_3 - CH_2 - COOH$: Propanoic acid
$CH_3 - CH_2 - CH_2 - COOH$: Butanoic acid
$CH_3 - CH_2 - CH_2 - CH_2 - COOH$: Pentanoic acid

(b) CH_3COCH_3 : Propanone
$CH_3COCH_2CH_3$: Butanone
$CH_3COCH_2CH_2CH_3$: Pentan-2-one
$CH_3COCH_2CH_2CH_2CH_3$: Hexan-2-one
$CH_3COCH_2CH_2CH_2CH_2CH_3$: Heptan-2-one

(c) $H - CH = CH_2$: Ethene
$CH_3 - CH = CH_2$: Propene
$CH_3 - CH_2 - CH = CH_2$: 1-Butene
$CH_3 - CH_2 - CH_2 - CH = CH_2$: 1-Pentene
$CH_3 - CH_2 - CH_2 - CH_2 - CH = CH_2$: 1-Hexene

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

(a) 2,2,4 – Trimethylpentane

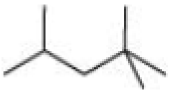
(b) 2 – Hydroxy – 1,2,3 – propanetricarboxylic acid

(c) Hexanedial

Answer: (a) 2,2,4 – Trimethylpentane

Condensed formula: $(CH_3)_2CHCH_2C(CH_3)_3$

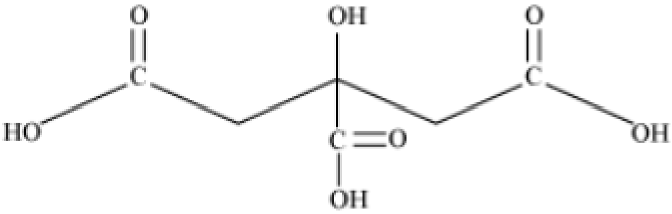
Bond line formula:



(b) 2 – Hydroxy – 1,2,3 – propanetricarboxylic acid

Condensed Formula: $(COOH)CH_2C(OH)(COOH)CH_2(COOH)$

Bond line formula:

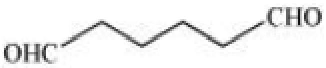


In the given compound, the functional groups present are carboxylic acid $(-COOH)$ and alcoholic group $(-OH)$.

(c) Hexanedial

Condensed Formula: $(CHO)(CH_2)_4(CHO)$

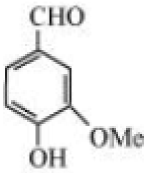
Bond line Formula:

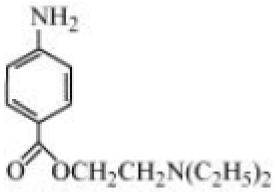


In the given compound, the functional group present is aldehyde $(-CHO)$.

12.8. Identify the functional groups in the following compounds.

(a)





(b)

(c)

Answer: (a) In the given compound, aldehyde $(-\mathrm{CHO})$, hydroxyl $(-\mathrm{OH})$ and methoxy $(-\mathrm{OMe})$ functional groups are present.

(b) In the given compound, amino $(-\mathrm{NH}_2)$, ketone $(\mathrm{C}=\mathrm{O})$, diethylamine $\left(\mathrm{N}(\mathrm{C}_2\mathrm{H}_5)_2\right)$

functional groups are present.

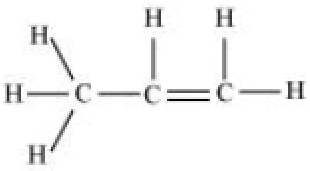
(c) In the given compound, nitro group $(-\mathrm{NO}_2)$ and $\mathrm{C}=\mathrm{C}$ double bond are present.

12.9. Which of the two: $\mathrm{O_2NCH_2CH_2O}-$ or $\mathrm{CH_3CH_2O}-$ is expected to be more stable and why?

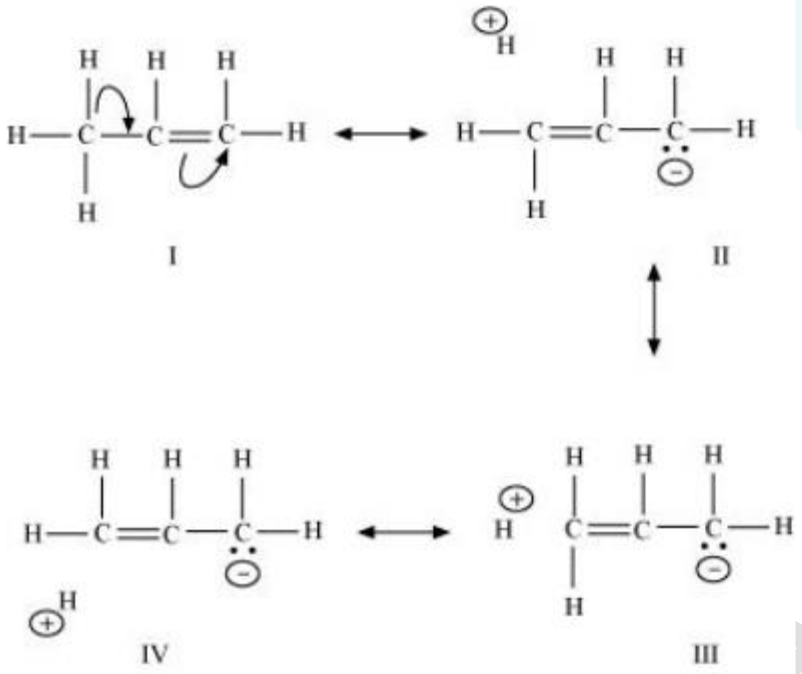
Answer: The nitro group is an electron-withdrawing group. As a result, it exhibits the -I effect. This group reduces the compound's negative charge by attracting electrons towards it and stabilizing it. The ethyl group, on the other hand, is an electron-releasing group. As a result, the ethyl group exhibits the +I effect. This raises the compound's negative charge, making it unstable. As a result, $\mathrm{O_2NCH_2CH_2O}-$ is projected to be more stable than $\mathrm{CH_3CH_2O}-$.

12.10. Explain why alkyl groups act as electron donors when attached to a π system.

Answer: When an alkyl group is linked to a π system, the process of hyperconjugation causes it to act as an electron-donor group. Let us use propene as an example to better comprehend this topic.



The sigma electrons of an alkyl group's C-H bond are delocalised during hyperconjugation. This group is directly connected to an unsaturated system's atom. The delocalisation happens as a result of a partial overlap of a sp^3 sigma bond orbital with an empty p orbital of the pi bond of a nearby carbon atom's bond.



12.11. 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) $CH_3CH = CHCHO$

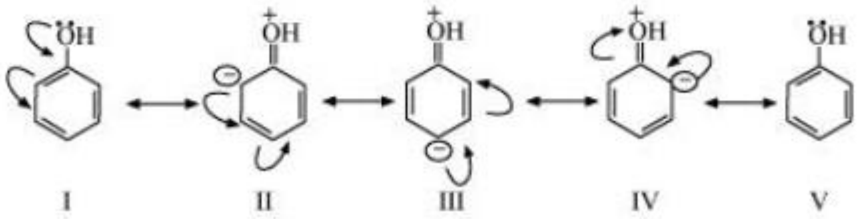
(d) $C_6H_5 - CHO$

(e) $C_6H_5 - \overset{+}{C}H_2$

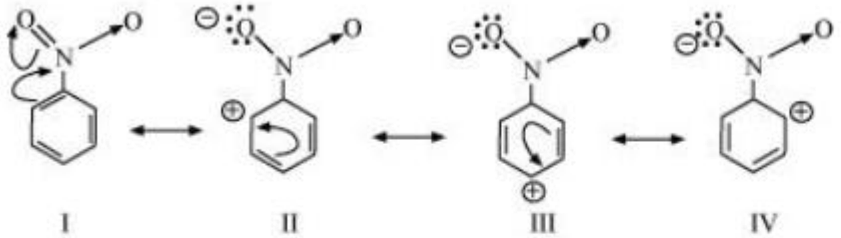
(f) $CH_3CH = CH\overset{+}{C}H_2$

Answer:

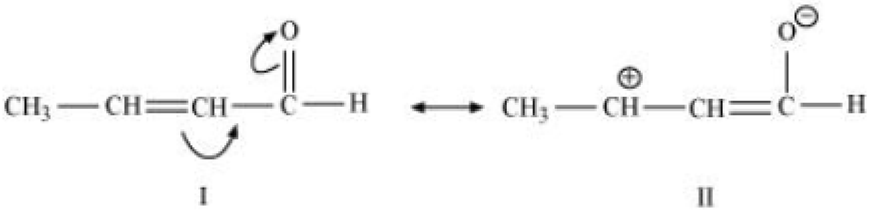
(a) The resonating structures for C_6H_5OH are shown below.



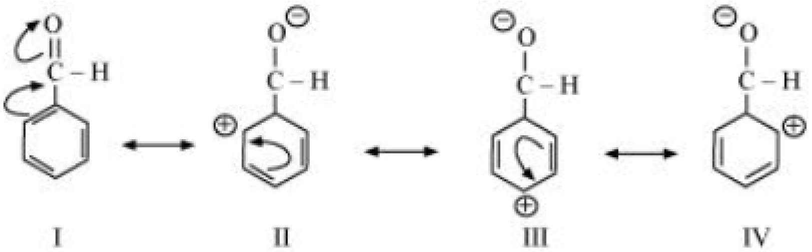
(b) The resonating structures for $C_6H_5NO_2$ are shown below.



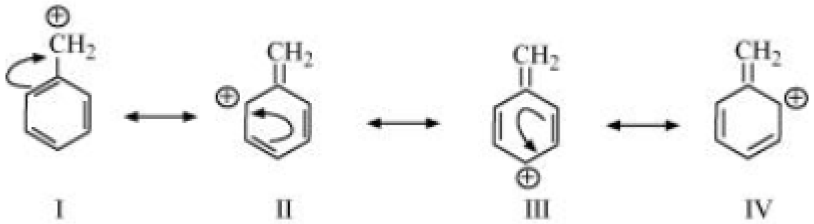
(c) The resonating structures for $CH_3CH = CHCHO$ are shown below.



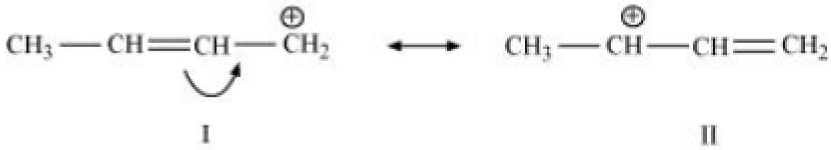
(d) The resonating structures of $C_6H_5 - CHO$ are shown below.



(e) The resonating structures of $C_6H_5 - \overset{+}{C}H_2$ are shown below.



(f) The resonating structures of $CH_3CH = CH\overset{+}{C}H_2$ are shown below.



12.12. What are electrophiles and nucleophiles? Explain with examples.

Answer: An electrophile is a reagent that removes a pair of electrons. In other words, an electrophile $\left(E^+\right)$ is a reagent that seeks electrons. Electrophiles are electron-deficient and receiver of an electron pair.

Electrophiles include carbocations and $\left(CH_3CH_2{}^+\right)$ neutral compounds with functional groups such as the carbonyl group.

A reagent that produces an electron pair is known as a nucleophile. A nucleus-seeking reagent is referred to as a nucleophile (Nu:).

For instance, OH^-, NC^-, carbanions $\left(R_3C^-\right)$, and so on.

Because of the presence of a lone pair, neutral molecules such as water and ammonia also serve as nucleophiles.

12.13. Identify the reagents shown in bold in the following equations as nucleophiles or electrophiles:

$$(a)\ CH_3COOH + \mathbf{OH^-} \rightarrow CH_3COO^- + H_2O$$

$$(b)\ CH_3COCH_3 + \mathbf{CN^-} \rightarrow (CH_3)_2C(CN)(OH)$$

$$(c)\ C_6H_6 + \mathbf{CH_3\overset{+}{C}O} \rightarrow C_6H_5COCH_3$$

Answer: Electrophiles are entities that are electron-deficient and can accept an electron pair. Nucleophiles, on the other hand, are electron-rich entities that can transfer their electrons.

(a) In this equation, OH^- serves as a nucleophile because it is an electron-rich species.

(b) In this equation, CN^- serves as a nucleophile because it is an electron-rich species.

(c) In this equation, $CH_3\overset{+}{C}O$ serves as an electrophile because it is an electron-deficient species.

12.14. Classify the following reactions in one of the reaction types studied in this unit.

$$(a)\ CH_3CH_2Br + HS^- \rightarrow CH_3CH_2HS + Br^-$$

$$(b)\ (CH_3)_2C=CH_2 + HCl \rightarrow (CH_3)_2ClC-CH_3$$

$$(c)\ CH_3CH_2Br + HO^- \rightarrow CH_2=CH_2 + H_2O + Br^-$$

$$(d)\ (CH_3)_3C-CH_2OH + HBr \rightarrow (CH_3)_2CBrCH_2CH_3 + H_2O$$

Answer: (a) The given reaction is a type of a substitution reaction because the bromine group in bromoethane is substituted by thionyl group.

(b) The given reaction is a type of an addition reaction because two reactant molecules react to produce a single product.

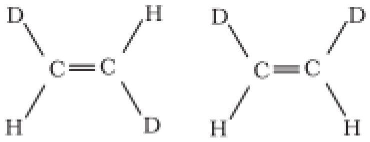
(c) The given reaction is a type of an elimination reaction because hydrogen and bromine are eliminated by bromoethane in order to produce ethene.

(d) Substitution takes place in this reaction, followed by atom and atom group rearrangement.

12.15. What is the relationship between the members of following pairs of structures? Are they structural or geometrical isomers or resonance contributors?

(a)

(b)



(c)


$H-\overset{^{+}OH}{\overset{\|}{C}}-OH$ $H-\overset{OH}{\overset{|}{C^{+}}}-OH$

Answer: (a) Compounds with the same chemical formula but different structures are referred to as structural isomers. The mentioned compounds have the same molecular formula, but the position of the functional group differs (ketone group).

The ketone group is at C-3 of the parent chain (hexane chain) in structure I, and at C-2 of the parent chain in structure II (hexane chain). As a result, the given pair of compounds are structural isomers.

(b) Geometrical isomers are compounds that have the same chemical formula, composition, and series of covalent bonds but have different relative positions of their atoms in space.

The relative positions of Deuterium (D) and hydrogen (H) in space differ in structures I and II. As a result, the given pairs are geometrical isomers.

(c) The structures shown are either canonical or contributing structures. They are fictitious and do not represent any actual molecule. As a result, the given pair represents resonance structures known as resonance isomers.

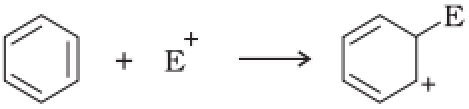
12.16. For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.

(a) $CH_3O - OCH_3 \rightarrow CH_3\dot{O} + \dot{O}CH_3$

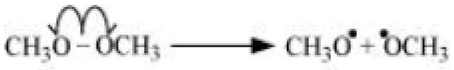
(b)

(c)

(d)

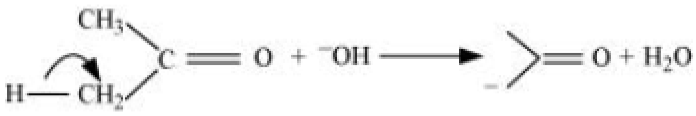


Answer: (a) The bond cleavage can be illustrated using curved arrows to show the electron flow of the given reaction as



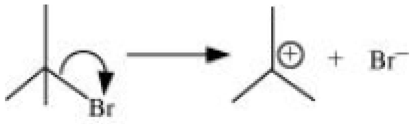
As one of the shared pairs in a covalent bond travels with the connected atom, it is an example of homolytic cleavage. A free radical is produced as a reaction intermediate.

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



It is an example of heterolytic cleavage because the bond breaks in such a way that the shared pair of electrons stay with the carbon of propanone. The reactive intermediate created is carbanion.

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



It is an example of heterolytic cleavage because the bond breaks in such a way that the bromine ion retains the shared pair of electrons. A carbocation is produced as a reaction intermediate.

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

The bond breaks in such a way that the shared pair of electrons stays with one of the fragments, resulting in a heterolytic cleavage. A carbocation is created as an intermediate.

12.17. Explain the terms Inductive and Electromeric effects. Which electron displacement effect explains the following correct orders of acidity of the carboxylic acids?

(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

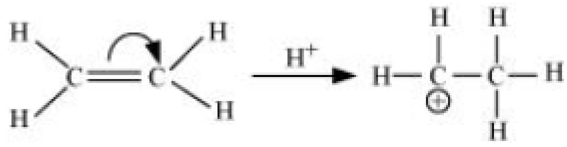
(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

Answer: Inductive effect: It refers to the permanent shift of sigma electrons along a saturated chain whenever an electron withdrawing or electron donating group is present. The inductive effect could be either a $+I$ effect or $-I$ effect. When an atom or group attracts electrons more strongly than hydrogen, it is said to have the $-I$ effect. Example,

$F-\leftarrow CH_2-\leftarrow CH_2-\leftarrow CH_2-\leftarrow CH_3$

When an atom or set of atoms attracts electrons less strongly than hydrogen, this is referred to as the $+I$ effect. For instance, $CH_3-\rightarrow CH_2-\rightarrow Cl$

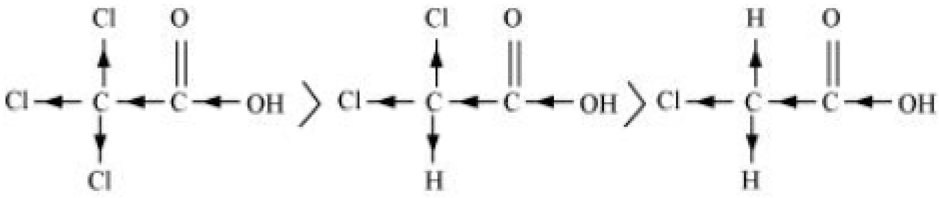
Electromeric effect: In the presence of an attacking agent, it involves the complete transfer of the shared pair of pi electrons to either of the two atoms joined by multiple bonds. For example,



Electrometric effects might be $+E$ or $-E$. The $+E$ effect occurs when electrons are transferred to the assaulting reagent. Whereas when electrons are moved away from the attacking reagent, this is referred to as the $-E$ effect.

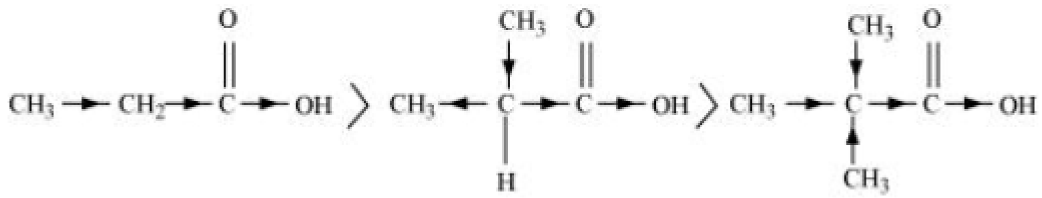
(a) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH$

On the basis of the inductive effect $(-I)$, the order of acidity can be explained. The $-I$ effect increases as the number of chlorine atoms increases. The acid strength increases in proportion to the increase in $-I$ effect.



(b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

The inductive effect ($+I$ effect) can be used to explain the order of acidity. The $+I$ effect increases in proportion to the quantity of alkyl groups. The acid strength increases in proportion to the increase in $+I$ effect.



12.18. Give a brief description of the principles of the following techniques taking an example in each case. (a) Crystallisation (b) Distillation (c) Chromatography

Answer: (a) Crystallisation: It is one of the most widely used methods for purifying solid chemical molecules.

Principle: The differential in the solubilities of the compound and the impurities in a solvent. The impure substance dissolves in the solvent, which is only sparingly soluble at ambient temperature but completely soluble at higher temperatures. The Answer is concentrated until it is virtually saturated. When the Answer is cooled, the pure compound crystallises and is extracted by filtration.

Pure aspirin, for example, is created by recrystallising crude aspirin. 2 - 4 g of crude aspirin is dissolved in approximately 20 mL of ethyl alcohol. To ensure complete decomposition, the Answer is heated.

(b) Distillation: This approach is used to separate volatile liquids from nonvolatile contaminants or a mixture of those liquids with a large enough difference in boiling points.

Principle: It works on the principle that liquids with different boiling points vapourize at different temperatures. The vapours are then cooled, and the liquids that form are separated.

For example: Distillation can be used to separate a combination of chloroform and aniline. The mixture is placed in a condenser-equipped round bottom flask. After that, it is heated. Because chloroform is more volatile, it vaporizes first and enters the condenser. The vapours condense in the condenser, and chloroform trickles down. Aniline is left in the round bottom flask.

(c) Chromatography: It is one of the most effective technologies for organic chemical separation and purification.

Principle: The differential in movement of separate components of a mixture through the stationary phase under the influence of the mobile phase is the basis for the principle.

Example: Chromatography, can separate a combination of red and blue ink. On the chromatogram, a drop of the combination is inserted. The component of the ink that is less adsorbed on the chromatogram travels with the mobile phase, whereas the component that is more adsorbed remains stationary.

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

Answer: The process of fractional crystallisation is used to separate two compounds with varying solubilities in a solvent S. The fractional crystallisation process is divided into four phases.

(a) Answer's preparation: The powdered combination is placed in a flask, and the solvent is slowly and simultaneously added and agitated. The solvent is added until the solute is completely dissolved in it. This saturated Answer is then boiled.

(b) Answer's filtration: In a China dish, the hot saturated Answer is filtered through filter paper.

(c) Fractional crystallisation: Allow the Answer in a China dish to cool. To begin with, the less soluble molecule crystallizes, while the more soluble compound remains in Answer. During the separation of these crystals from the liquor, the latter is concentrated once more. The hot Answer is allowed to cool, resulting in the formation of crystals of the more soluble chemical.

(d) Isolation and drying: Filtration is used to separate the crystals from the mother liquor. The crystals are finally dried.

12.20. What is the difference between distillation, distillation under reduced pressure and steam distillation?

Answer: The differences between distillation, reduced pressure distillation, and steam distillation are shown below.

Distillation: It is used to purify chemicals that are related with non-volatile impurities or liquids that do not disintegrate when heated. In other words, distillation is used to separate volatile liquids from nonvolatile contaminants or a mixture of such liquids with significant boiling point difference. This process separates a mixture of fuel and kerosene.

Reduced pressure distillation: This procedure is used to purify a liquid that decomposes when heated. Under reduced pressure, the liquid will boil at a lower temperature than its boiling point and so will not decompose.

This process is used to purify glycerol. At a temperature of $593\ \mathrm{K}$, it boils with decomposition. It boils at $453\ \mathrm{K}$ without breakdown at a lower pressure.

Steam distillation: It is used to purify an organic molecule that is steam volatile and water immiscible. The compound is heated by passing steam, and the steam is condensed to water. After some time, the water-liquid mixture begins to boil and flows through the condenser. A separating funnel is then used to separate this condensed mixture of water and liquid.

A Answer of water and aniline can be separated by this method.

12.21. Discuss the chemistry of Lassaigne’s test.

Answer: Lassaigne's test: This test detects the presence of nitrogen, sulfur, halogens, and phosphorus in an organic compound. An organic compound has these elements in covalent form. By fusing the chemical with sodium metal, these are transformed into the ionic form.

$$\mathrm{Na + C + N \rightarrow NaCN}$$

$$\mathrm{Na + S + C + N \rightarrow NaSCN}$$

$$\mathrm{2Na + S \rightarrow Na_2S}$$

$$\mathrm{Na + X \rightarrow NaX}$$

The sodium cyanide, sulphide, and halide are removed from the fused material by boiling it in distilled water. Lassaigne's extract is the name given to the extract obtained in this manner. The presence of nitrogen, sulphur, halogens, and phosphorous is then determined in this Lassaigne's extract.

(a) Chemistry of nitrogen test: The sodium fusion extract is heated with iron (II) sulphate and then acidified with sulphuric acid in the Lassaigne's test for nitrogen in an organic molecule. Sodium cyanide first interacts with iron (II) sulphate to generate sodium hexacyanoferrate in this method (II). The iron (II) is then oxidized by sulphuric acid to generate iron (III) hexacyanoferrate (II), which is Prussian blue. The reactions involved are shown below.

$$\mathrm{6CN^- + Fe^{2+} \rightarrow \left[Fe(CN)_6\right]^{4-}}$$

$$\mathrm{3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \rightarrow Fe_4\left[Fe(CN)_6\right]_3}$$

(b) Test for sulphur:

$$\text{(i) Lassaignes's extract} + \text{Lead acetate} \rightarrow \text{Black precipitate}$$

Chemistry of the test: The sodium fusion extract is acidified with acetic acid and then lead acetate is added to it in the Lassaigne's test for sulphur in an organic compound. The presence of sulphur in the combination is shown by the precipitation of lead sulphide, which is black in color.

$$\mathrm{S^{2-} + Pb^{2+} \rightarrow PbS}$$

(ii) Lassaignes's extract + Sodium nitroprusside $\rightarrow$ Violet colour

Chemistry of the test: Sodium nitroprusside is used to treat the sodium fusion extract. The presence of sulphur in the compound is also indicated by the presence of violet color.

$$S^{2-} + [Fe(CN)_5 NO]^{2-} \rightarrow [Fe(CN)_5 NOS]^{-4}$$

If both nitrogen and sulphur are present in an organic molecule, $NaSCN$ is formed instead of $NaCN$.

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

This $NaSCN$ (sodium thiocyanate) color is blood red. The absence of free cyanide ions prevents the formation of prussian color.

(c) Test for halogen: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate in the Lassaigne's test for halogens in an organic molecule. If the organic compound contains both nitrogen and sulphur, the Lassaigne's extract is heated to remove the nitrogen and sulphur, which would otherwise interfere with the halogen test.

12.22. Differentiate between the principle of estimation of nitrogen in an organic compound by (i) Dumas method and (ii) Kjeldahl’s method.

Answer: In the Dumas method, a specified amount of a nitrogen-containing organic molecule is burned strongly with an excess of copper oxide in a carbon dioxide atmosphere to yield free nitrogen as well as carbon dioxide and water.

The process can also yield traces of nitrogen oxides, which can be converted to dinitrogen by passing the gaseous mixture over a heated copper gauge. The dinitrogen generated is collected over a potassium hydroxide aqueous Answer. At room temperature and atmospheric pressure, the volume of nitrogen generated is then measured.

Kjeldahl's method, on the other hand, involves heating a known quantity of a nitrogen-containing organic molecule with concentrated sulphuric acid. The compound's nitrogen is quantitatively transformed into ammonium sulphate. It is then distilled with a high concentration of sodium hydroxide. The ammonia produced by this method is injected into a known volume of H_2SO_4. The chemical equations involved are shown below.

Volumetric analysis (titration against a standard alkali) is used to measure the quantity of acid that is left unused, and the amount of ammonia produced can be calculated. As a result, the percentage of nitrogen in the compound can be calculated. This approach is inapplicable to compounds with nitrogen in a ring structure, and it is also inapplicable to compounds with nitro and azo groups.

12.23. Discuss the principle of estimation of halogens, sulphur and phosphorus present in an organic compound.

Answer: Estimation of halogens: The Carius method is used to calculate halogens. In this approach, a known amount of organic chemical is heated with fuming nitric acid in the presence of silver nitrate in a Carius tube, which is placed in a furnace. The carbon and hydrogen in the compound are oxidized to generate CO_2 and H_2O, respectively, while the halogen in the compound is transformed into the form of AgX. After that, the AgX is filtered, washed, dried, and weighed.

Estimation of sulphur: In this approach, a known amount of organic substance is heated in a hard glass tube called the Carius tube with either fuming nitric acid or sodium peroxide. The compound's sulphur is oxidized to generate sulphuric acid. The precipitation of barium sulphate occurs when an excess of barium chloride is added to it. After that, the precipitate is filtered, washed, dried, and weighed.

Estimation of phosphorus: A known amount of organic substance is heated with fuming nitric acid in this procedure. The compound's phosphorus is oxidized to generate phosphoric acid. Phosphorus can be precipitated as ammonium phosphomolybdate by adding ammonia and ammonium molybdate to the Answer. Phosphorus can also be measured by precipitating it as $MgNH_4PO_4$ and then on igniting it yeild $Mg_2P_2O_7$.

12.24. Explain the principle of paper chromatography.

Answer: Paper chromatography employs the use of chromatography paper. This paper includes trapped water, which behaves as the stationary phase. The Answer of the mixture is spotted on the base of this chromatography paper. The paper strip is then hung in a suitable solvent, which serves as the mobile phase. By capillary action, this solvent moves up the chromatography paper and flows over the spot during the procedure. Different component spots travel to different heights with mobile phase. The resulting paper is known as a chromatogram.

12.25. Why is nitric acid added to sodium extract before adding silver nitrate for testing halogens?

Answer: The Lassaigne's extract is first heated with weak nitric acid before being tested for the presence of halogens. This is done to convert $NaCN$ to HCN and Na_2S to H_2S and then expel these gases. If there is any nitrogen or sulphur present in the form of $NaCN$ or Na_2S, it is eliminated. The chemical equations involved are shown below.

$$NaCN + HNO_3 \rightarrow HCN + NaNO_3$$
$$Na_2S + 2HNO_3 \rightarrow H_2S + 2NaNO_3$$

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

Answer: Organic chemicals are covalently bonded to nitrogen, sulfur, and halogens. They must first be changed to ionic form in order to be detected. This is accomplished by combining the organic chemical with sodium metal. This is known as the "Lassaigne's test." The chemical equations used in the test are as follows:

$$Na + C + N \rightarrow NaCN$$
$$Na + S + C + N \rightarrow NaSCN$$
$$2Na + S \rightarrow Na_2S$$
$$Na + X \rightarrow NaX$$

Here, X is halogen like chlorine, bromine, iodine.

Organic compounds contain carbon, nitrogen, sulfur, and halogen.

12.27. Name a suitable technique of separation of the components from a mixture of calcium sulphate and camphor.

Answer: A combination of camphor and calcium sulphate is separated by sublimation. The sublimable chemical converts from solid to vapour without going through the liquid state throughout this procedure. Camphor is a sublimable molecule, whereas calcium sulphate is a non-sublimable solid. As a result, when heated, camphor will sublime while calcium sulphate will remain.

12.28. Explain, why an organic liquid vaporises at a temperature below its boiling point in its steam distillation?

Answer: In the process of steam distillation, the organic liquid begins to boil when the total of the organic liquid's vapour pressure $\left(p_1\right)$ and the water's vapour pressure $\left(p_2\right)$ equals atmospheric pressure (p), i.e. $p = p_1 + p_2$. Therefore,

$$p_1 < p_2$$

Hence, organic liquid will vapourize at a lower temperature than its boiling point.

12.29. Will CCl_4 give white precipitate of $AgCl$ on heating it with silver nitrate? Give reason for your answer.

Answer: When CCl_4 heated with silver nitrate, it does not produce the white precipitate of $AgCl$. This is because the chlorine atoms in CCl_4 are covalently connected to carbon. It must be present in ionic form in order to obtain the precipitate, which requires preparing the Lassaigne's extract of CCl_4.

12.30. Why is a Answer of potassium hydroxide used to absorb carbon dioxide evolved during the estimation of carbon present in an organic compound?

Answer: Carbon dioxide is an acidic substance, whereas potassium hydroxide is a strong basic. As a result, when carbon dioxide combines with potassium hydroxide, potassium carbonate and water are formed.

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

As a result, the mass of the KOH containing U-tube increases. This rise represents the amount of CO_2 created. The proportion of carbon in the organic compound can be determined based on its mass.

12.31. 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: Due to the common ion effect, the addition of sulphuric acid would precipitate lead sulphate, but the addition of acetic acid would assure complete precipitation of sulphur in the form of lead sulphate. As a result, acetic acid must be used to acidify sodium extract before testing for sulphur using the lead acetate test.

12.32. An organic compound contains $69\ \%$ carbon and $4.8\ \%$ hydrogen, the remainder being oxygen. Calculate the masses of carbon dioxide and water produced when 0.20 g of this substance is subjected to complete combustion.

Answer: The percentage of carbon in organic compound is $69\ \%$.

It means $100\ \text{g}$ of organic compound contains $69\ \text{g}$ of carbon. So, the mass of carbon contained in $0.20\ \text{g}$ of organic compound is calculated as

$$\begin{aligned}\text{Mass of C} &= \frac{69 \times 0.20}{100}\\ &= 0.138\ \text{g of C}\end{aligned}$$

The molecular mass of carbon dioxide is $44\ \text{g/mol}$. Therefore, 12 g of carbon is contained in 44 g of CO_2.

Therefore, the mass of CO_2 contained in $0.138\ \text{g}$ of carbon is calculated as

$$\begin{aligned}\text{Mass of } CO_2 &= \frac{44 \times 0.138}{12}\\ &= 0.506\ \text{g}\end{aligned}$$

Thus, 0.506 g of CO_2 will be produced on complete combustion of 0.2 g of organic compound.

The percentage of hydrogen in organic compound is $4.8\ \%$. It means $100\ \text{g}$ of organic compound contains $4.8\ \text{g}$ of hydrogen.

Therefore, the mass of hydrogen contained in $0.20\ \text{g}$ of organic compound is calculated as

$$\begin{aligned}\text{Mass of H} &= \frac{4.8 \times 0.20}{100}\\ &= 0.0096\ \text{g of H}\end{aligned}$$

It is known that the molecular mass of water is $18\ \text{g/mol}$.

Thus, $2\ \text{g}$ of hydrogen is contained in $18\ \text{g}$ of water. Therefore, the mass of water contained in $0.0096\ \text{g}$ of hydrogen is calculated as

$$\begin{aligned}\text{Mass of } H_2O &= \frac{18 \times 0.0096}{2}\\ &= 0.0864\ \text{g}\end{aligned}$$

12.33. A sample of $0.50\ \text{g}$ of an organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in $50\ \text{ml of } 0.5\ \text{M}\ H_2SO_4$. The residual acid required $60\ \text{mL of } 0.5\ \text{M}$ Answer of NaOH for neutralisation. Find the percentage composition of nitrogen in the compound.

Answer: Given: The total mass of organic compound is $0.50\ \text{g}$.

$60\ \text{mL of } 0.5\ \text{M}$ Answer of NaOH was required for neutralisation by residual acid.

$$60 \text{ mL of } 0.5 \text{ M NaOH solution} = \frac{60}{2} \text{ mL of } 0.5\text{M } H_2SO_4$$

$$\frac{60}{2} \text{ mL of } 0.5\text{M } H_2SO_4 = 30 \text{ mL of } 0.5 \text{ M } H_2SO_4$$

Therefore, acid consumed in absorption of evolved ammonia is calculated as

$$=(50\text{-}30) \text{ mL}$$
$$= 20 \text{ mL}$$

Again, $20 \text{ mL of } 0.5 \text{ M } H_2SO_4 = 40 \text{ mL of } 0.5 \text{ M } NH_3$

Also, since $1000 \text{ mL of } 1 \text{ M } NH_3$ contains 14 g of nitrogen, the mass of nitrogen in $40 \text{ mL of } 0.5 \text{ M } NH_3$ is calculated as

$$\text{Mass of N} = \frac{14 \times 40 \times 0.5}{1000}$$
$$= 0.28 \text{ g}$$

Therefore, the percentage of nitrogen in 0.50 g of organic compound is calculated as

$$\text{Percentage of nitrogen} = \frac{0.28}{0.5} \times 100\%$$
$$= 56 \%$$

12.34. 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: Given: The mass of organic compound is 0.3780 g and the mass of silver chloride formed is 0.5740 g.

The molar mass of AgCl is 143.32 g/mol and the molar mass of chlorine is 35.5 g/mol.

One mole of silver chloride contains one mole of chlorine. So, the mass of chlorine in 0.5740 g of silver chloride is calculated as

$$\text{Mass of AgCl} = \frac{35.5 \times 0.5740}{143.32}$$
$$= 0.1421 \text{ g}$$

Thus, the percentage of chlorine is calculated as

$$\text{Percentage of chlorine} = \frac{0.1421}{0.3780} \times 100\%$$
$$= 37.59 \%$$

Hence, the percentage of chlorine is 37.59%.

12.35. 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: Given: The total mass of organic compound is 0.468 g and the mass of barium sulphate formed is 0.668 g.

The molar mass of $BaSO_4$ is 233 g/mol and the molar mass of sulphur is 32 g/mol.

So,

$$\begin{aligned}1\text{ mol of }BaSO_4 &= 233\text{ g of }BaSO_4\\ &= 32\text{ g of sulphur}\end{aligned}$$

Thus,

$$\begin{aligned}0.668\text{ g of }BaSO_4 &= \frac{32 \times 0.668}{233}\text{ g of sulphur}\\ &= 0.0917\text{ g of sulphur}\end{aligned}$$

Therefore, the percentage of sulphur is calculated as

$$\begin{aligned}\text{Percentage of sulphur} &= \frac{0.0917}{0.468} \times 100\%\\ &= 19.59\ \%\end{aligned}$$

Hence, the percentage of sulphur is $19.59\ \%$.

12.36. In the organic compound $CH_2=CH-CH_2-CH_2-C\equiv CH$, the pair of hydridised orbitals involved in the formation of: $C2-C3$ bond is:

(a) $sp - sp^2$

(b) $sp - sp^3$

(c) $sp^2 - sp^3$

(d) $sp^3 - sp^3$

Answer: The given organic compound is shown below.

$$\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}\equiv\overset{6}{C}H$$

The hybridization of carbon atoms numbered as 1, 2, 3, 4, 5 and 6 are sp, sp, sp^3, sp^3, sp^2, and sp^2 respectively. Therefore, the pair of hybridized orbitals involved in the formation of $C2-C3$ bond is $sp - sp^3$.

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

(a) $Na_4\left[Fe(CN)_6\right]$

(b) $Fe_4\left[Fe(CN)_6\right]_3$

(c) $Fe_2\left[Fe(CN)_6\right]$

(d) $Fe_3\left[Fe(CN)_6\right]_4$

Answer: The sodium fusion extract is heated with iron (II) sulphate and then acidified with sulphuric acid in the Lassaigne's test for nitrogen in an organic molecule. Sodium cyanide initially interacts with iron (II) sulphate to generate sodium hexacyanoferrate (II). The iron (II) is then oxidized by sulphuric acid to generate iron (III) hexacyanoferrate (II), which is Prussian blue. The chemical reactions involved are shown below.

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

$$3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \xrightarrow{x.H_2O} \underset{\text{Prussian Blue}}{Fe_4\left[Fe(CN)_6\right]_3.xH_2O}$$

Therefore, the Prussian blue color is formed due to the formation of complex $Fe_4\left[Fe(CN)_6\right]_3$.

12.38. Which of the following carbocation is most stable?

(a) $(CH_3)_3C.\overset{+}{C}H_2$

(b) $(CH_3)_3\overset{+}{C}$

(c) $CH_3CH_2\overset{+}{C}H_2$

(d) $CH_3\overset{+}{C}HCH_2CH_3$

Answer: $(CH_3)_3\overset{+}{C}$ is a tertiary carbocation. Because of the electron-releasing effect of three methyl groups, a tertiary carbocation is the most stable carbocation. Three methyl groups increase the + I effect, which stabilizes the positive charge on the carbocation. The stability of tertiary carbocations is also due to hyperconjugation and resonance energy.

12.39. The best and latest technique for isolation, purification and separation of organic compounds is:

(a) Crystallisation

(b) Distillation

(c) Sublimation

(d) Chromatography

Answer: Chromatography is the most effective and up-to-date method of separating and purifying organic molecules. Initially, it was employed to separate a combination of colored substances.

12.40. The reaction: $CH_3CH_2I + KOH_{(aq)} \rightarrow CH_3CH_2OH + KI$ is classified as:

(a) electrophilic substitution

(b) nucleophilic substitution

(c) elimination

(d) addition

Answer: The reaction is given as:

$$CH_3CH_2I + KOH_{(aq)} \rightarrow CH_3CH_2OH + KI$$

It shows a nucleophilic substitution reaction. The hydroxyl group of potassium hydroxide with a lone pair serves as a nucleophile, substituting iodide ion in CH_3CH_2I to produce ethanol.

Solved Examples

12.1. How many σ and π bonds are present in each of the following molecules?

(a) $HC{=}CCH{=}CHCH_3$

(b) $CH_2{=}C{=}CHCH_3$

Answer:

(a) σ_{C-C}: 4; σ_{C-H} : 6; $\pi_{C=C}$:1; $\pi_{C\equiv C}$:2

(b) σ_{C-C}: 3; σ_{C-H}: 6; $\pi_{C=C}$: 2

12.2. What is the type of hybridisation of each carbon in the following compounds?

(a) CH_3Cl, (b) $(CH_3)_2CO$, (c) CH_3CN, (d) $HCONH_2$, (e) $CH_3CH{=}CHCN$

Answer:

(a) sp^3,

(b) sp^3, sp^2,

(c) sp^3, sp,

(d) sp^2,

(e) sp^3, sp^2, sp^2, sp

12.3. Write the state of hybridisation of carbon in the following compounds and shapes of each of the molecules.

(a) $H_2C=O$, (b) CH_3F, (c) $HC\equiv N$

Answer:

(a) sp^2 hybridised carbon, trigonal planar

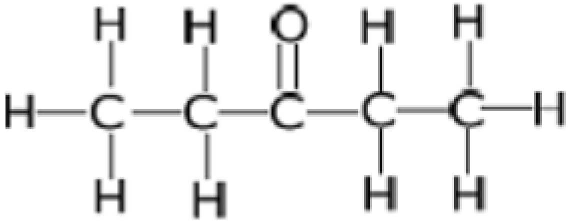
(b) sp^3 hybridised carbon, tetrahedral

(c) sp hybridised carbon, linear

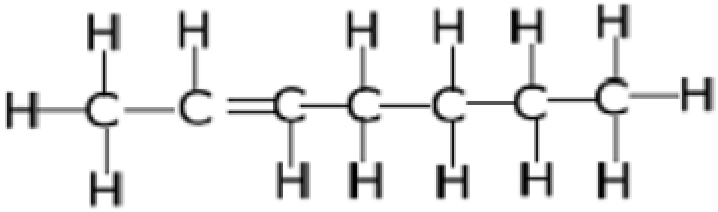
12.4. Expand each of the following condensed formulas into their complete structural formulas.

(a) $CH_3CH_2COCH_2CH_3$ (b) $CH_3CH=CH(CH_2)_3CH_3$

Answer:



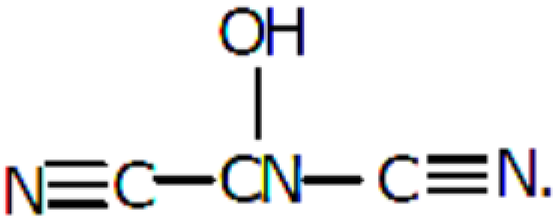
(a)



(b)

12.5. For each of the following compounds, write a condensed formula and also their bond-line formula.

(a) $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$



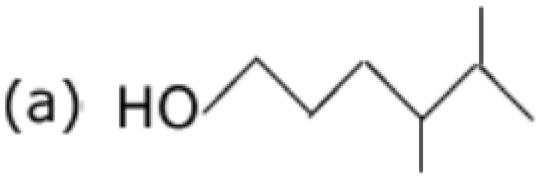
(b)

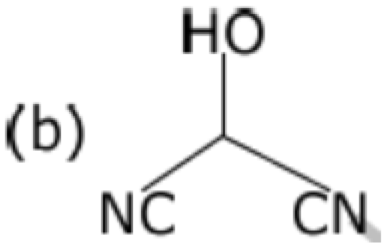
Answer: Condensed formula

(a) $HO(CH_2)_5CHCH_3CH(CH_3)_2$

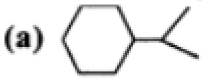
(b) $HOCH(CN)_2$.

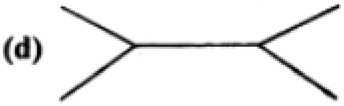
Bond line formula





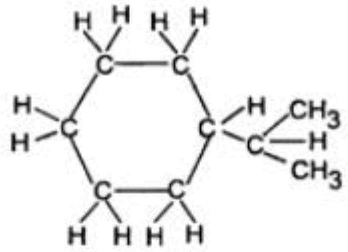
12.6. Expand each of the following bond-line formulas to show all the atoms including carbon and hydrogen



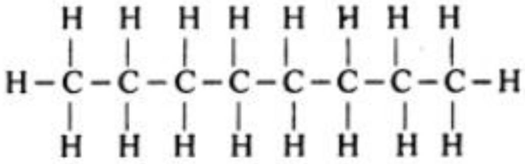


Answer:

(a)

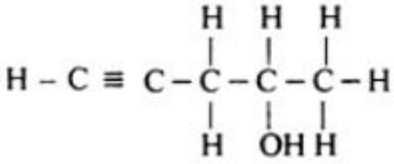


(b)



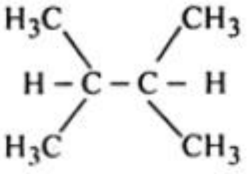
$$H-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$$

(c)



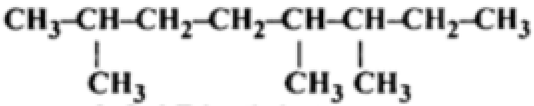
$$H-C\equiv C-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-\overset{H}{\overset{|}{\underset{H}{\underset{|}{C}}}}-H$$

(d)



12.7. Structures and IUPAC names of some hydrocarbons are given below. Explain why the names given in the parentheses are incorrect

(a)

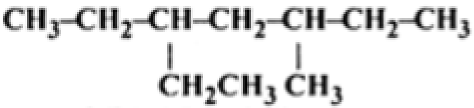


$$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_2-\underset{CH_3}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

2, 5, 6-Trimethyloctane

[and not 3, 4, 7-Trimethylocatane]

(b)



$$CH_3-CH_2-\underset{CH_2CH_3}{\underset{|}{CH}}-CH_2-\underset{CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

3-Ethyl-5-methylheptane

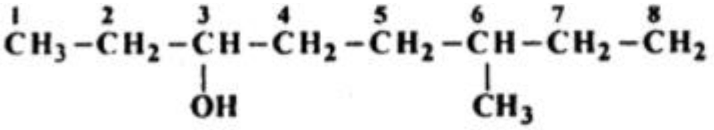
[and not 5-Ethyl-3-methylheptane]

Answer:

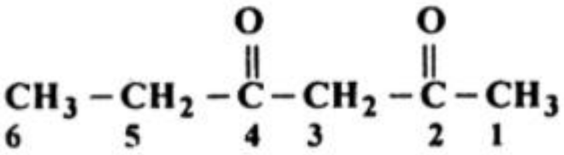
(a) The sum of locant number, 2,5,6 is lower than that of 3,5,7,

(b) The substituents are in equivalent positions; the lower number is assigned to the one that appears first in the name in alphabetical order.

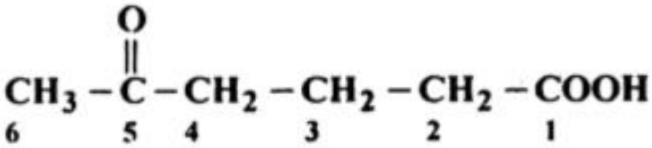
12.8. Write the IUPAC names of the compounds i-iv from their given structures.

(i) 

$$\overset{1}{C}H_3-\overset{2}{C}H_2-\underset{OH}{\overset{3}{C}H}-\overset{4}{C}H_2-\overset{5}{C}H_2-\underset{CH_3}{\overset{6}{C}H}-\overset{7}{C}H_2-\overset{8}{C}H_2$$

(ii) 

$$\underset{6}{CH_3}-\underset{5}{CH_2}-\underset{4}{\overset{\overset{\displaystyle O}{\|}}{C}}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{\displaystyle O}{\|}}{C}}-\underset{1}{CH_3}$$

(iii) 

$$\underset{6}{CH_3}-\underset{5}{\overset{\overset{\displaystyle O}{\|}}{C}}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{CH_2}-\underset{1}{COOH}$$

(iv) $\underset{6}{CH}\equiv\underset{5}{C}-\underset{4}{CH}=\underset{3}{CH}-\underset{2}{CH}=\underset{1}{CH_2}$

Answer:

(i) An alcohol functional group is present (OH). As a result, the suffix is '-ol'.

- The longest -OH chain has eight carbon atoms. As a result, the corresponding saturated hydrocarbon is octane.

- The -OH is on carbon atom number three. A methyl group is also attached to the sixth carbon.

As a result, this compound's systematic name is 6-Methyloctan-3-ol.

(ii) The present functional group is ketone $(>C=O)$, hence the suffix '-one'. Because the presence of two keto groups is indicated by 'di,' the suffix becomes 'dione.' Carbons 2 and 4 contain the two keto groups. Because the longest chain has six carbon atoms, the parent hydrocarbon is hexane.

Hexane2,4-dione is thus the systematic name.

(iii) There are two functional groups present here: ketone and carboxylic acid.

Because the carboxylic acid group is the most important functional group, the parent chain will be suffixed with 'oic' acid.

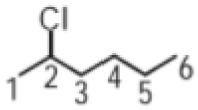
The chain's numbering begins with the carbon of the – COOH functional group. The 'oxo' symbol represents the keto group in the chain at carbon 5. The parent hydrocarbon is hexane because the longest chain, including the principal functional group, has 6 carbon atoms. As a result, the compound is known as 5-Oxohexanoic acid.

(iv) The two C=C functional groups can be found at carbon atoms 1 and 3, while the C functional group can be found at carbon atom 5. These groups are denoted by the suffixes 'diene' and 'yne'. The parent hydrocarbon is hexane because the longest chain containing the functional groups has 6 carbon atoms. As a result, the compound's name is Hexa-1,3-dien-5-yne.

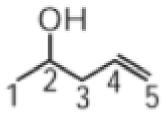
12.9. Derive the structure of (i) 2-Chlorohexane, (ii) Pent-4-en-2-ol, (iii) 3- Nitrocyclohexene, (iv) Cyclohex-2-en-1-ol, (v) 6-Hydroxyheptanal.

Answer:

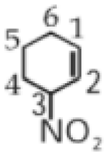
(i) ‘The term 'hexane' denotes the presence of six carbon atoms in the chain. At carbon 2, the functional group chloro is present.



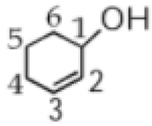
(ii) The suffix 'pent' denotes that the parent hydrocarbon has 5 carbon atoms in its chain. The functional groups C=C and -OH at carbon atoms 4 and 2, respectively, are represented by 'en' and 'ol.'



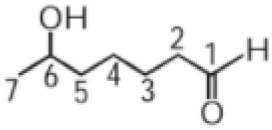
(iii) Cyclohexene, which is numbered as shown in, implies a six-membered ring with a carbon-carbon double bond (I). The prefix 3-nitro denotes the presence of a nitro group on C-3. As a result, the compound's complete structural formula is (II). Because double bond is a suffixed functional group and NO_2 is a prefixed functional group, double bond takes precedence over $-NO_2$ group.



(iv) The term '1-ol' denotes the presence of a -OH group at C-1. The suffixed functional group OH takes precedence over the C=C bond. As a result, the structure is as shown:



(v) The term 'heptanal' refers to an aldehyde with 7 carbon atoms in the parent chain. The '6-hydroxy' denotes the presence of a -OH group at carbon 6. When numbering the carbon chain, the carbon atom of the –CHO group is included.

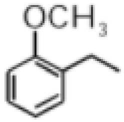


12.10. Write the structural formula of:

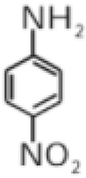
(a) o-Ethylanisole, (b) p-Nitroaniline, (c) 2,3 - Dibromo -1 - phenylpentane, (d) 4-Ethyl-1-fluoro-2-nitrobenzene

Answer:

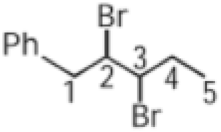
(i)



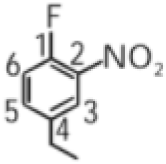
(ii)



(iii)



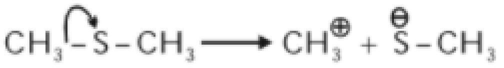
(iv)



12.11. Using curved-arrow notation, show the formation of reactive intermediates when the following covalent bonds undergo heterolytic cleavage.

(A) CH_3–SCH_3, (B) CH_3–CN, (C) CH_3–Cu

Answer:

(A)


(B)


(C)


12.12. Giving justification, categorise the following molecules/ions as nucleophile or electrophile:

$HS^-, BF_3, C_2H_5O^-, (CH_3)_3N, Cl^+, CH_3\overset{+}{C}=O, H_2N:^-, \overset{+}{N}O_2$

Answer: Nucleophiles: $HS^-, H_2N:^-, C_2H_5O^-, (CH_3)_3N$

These species have a pair of unshared electrons that can be donated and shared with an electrophile.

Electrophiles: $Cl^+, CH_3\overset{+}{C}=O, BF_3, \overset{+}{N}O_2$

Reactive sites have only six valence electrons and can accept a nucleophile's electron pair..

12.13. Identify electrophilic centre in the following: $CH_3CH=O, CH_3CN, CH_3I.$

Answer: The starred carbon atoms in $CH_3H\overset{*}{C}=O, CH_3\overset{*}{C}\equiv N, H_3\overset{*}{C}-I.$ are electrophilic centers, as they will have a partial positive charge due to the polarity of the bond.

12.14. Which bond is more polar in the following pairs of molecules:

$(a) H_3C\text{-}H, H_3C\text{-}Br$ $(b) H_3C\text{-}NH_2, H_3C\text{-}OH$ $(c) H_3C\text{-}OH, H_3C\text{-}SH$

Answer: (a) C–Br, since Br is more electronegative than H, (b) C–O, (c) C–O

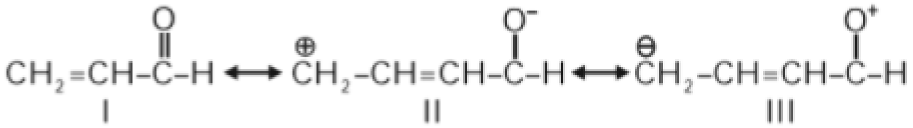
12.15. In which C–C bond of $CH_3CH_2CH_2Br$, the inductive effect is expected to be the least?
Answer: As the number of intervening bonds increases, the magnitude of the inductive effect decreases. As a result, the effect is minimal in the bond between carbon-3 and hydrogen.

12.16. Write resonance structures of CH_3COO- and show the movement of electrons by curved arrows.

Answer: First, sketch out the structure and place unshared pairs of valence electrons on the appropriate atoms. Then, one at a time, draw the arrows, moving the electrons to obtain the other structures.

12.17. Write resonance structures of $CH_2{=}CH{-}CHO$. Indicate relative stability of the contributing structures.

Answer:



Stability: I > II > III

[I: Most stable, has the most covalent bonds, each carbon and oxygen atom has an octet, and there is no charge separation. II: negative charge on more electronegative atoms and positive charge on more electropositive atoms; III: no contribution because oxygen has a positive charge and carbon has a negative charge, making it the least stable].

12.18. Explain why the following two structures, I and II cannot be the major contributors to the real structure of CH_3COOCH_3.

Answer: Because they involve charge separation, the two structures are less important contributors. Structure I also contains a carbon atom with an incomplete octet.

12.19. Explain why $(CH_3)_3\overset{+}{C}$ is more stable than $CH_3\overset{+}{C}H_2$ and $\overset{+}{C}H_3$ is the least stable cation.

Answer: Since $(CH_3)_3\overset{+}{C}$ has nine C-H bonds, the hyperconjugation interaction is greater than in $CH_3\overset{+}{C}H_2$. The vacant p orbital in $\overset{+}{C}H_3$ is perpendicular to the plane in which C-H bonds exist and thus cannot overlap with it. As a result, $\overset{+}{C}H_3$ lacks hyperconjugative stability.

12.20. On complete combustion, 0.246 g of an organic compound gave 0.198 g of carbon dioxide and 0.1014 g of water. Determine the percentage composition of carbon and hydrogen in the compound.

Answer:

$$\text{Percentage of carbon} = \frac{12\times 0.198\times 100}{44\times 0.246}$$

$$= 21.95\%$$

$$\text{Percentage of hydrogen} = \frac{2\times 0.1014\times 100}{18\times 0.246}$$

$$= 4.58\%$$

12.21. In Dumas' method for estimation of nitrogen, 0.3 g of an organic compound gave 50 mL of nitrogen collected at 300 K temperature and 715 mm pressure. Calculate the percentage composition of nitrogen in the compound. (Aqueous tension at $300\text{ K}=15\text{ mm}$)

Answer:

Volume of nitrogen collected at 300K and 715mm pressure is 50 mL.

Actual pressure = 715-15

= 700 mm

$$\text{Volume of nitrogen at STP}=\frac{273\times 700\times 50}{300\times 760}$$

$$= 41.9\text{ mL}$$

22,400 mL of nitrogen at STP weighs = 28 g

$$41.9\text{ mL of nitrogen weighs} = \frac{28\times 41.9}{22400}\text{g}$$

$$\text{Percentage of nitrogen} = \frac{28\times 41.9\times 100}{22400\times 0.3}$$

$$=17.46\%$$

12.22. During estimation of nitrogen present in an organic compound by Kjeldahl's method, the ammonia evolved from 0.5 g of the compound in Kjeldahl's estimation of nitrogen, neutralized 10 mL of 1 M H_2SO_4. Find out the percentage of nitrogen in the compound.

Answer:

1 M of 10 mL H_2SO_4 = 1 M of 20 mL NH_3

1000 mL of 1M ammonia contains 14 g nitrogen.

$$\text{20 mL of 1M ammonia contains } \frac{14\times 20}{1000}\text{ g nitrogen}$$

$$\text{Percentage of nitrogen} = \frac{14\times20\times100}{100\times0.5}$$
$$=56.0\%$$

12.23. In Carius method of estimation of halogen, 0.15 g of an organic compound gave 0.12 g of AgBr. Find out the percentage of bromine in the compound.

Answer:

Molar mass of AgBr = 108 + 80

= 188 g mol^{-1}

188 g AgBr contains 80 g bromine.

0.12 g AgBr contains $\frac{80\times0.12}{188}$ g bromine.

$$\text{Percentage of bromine} = \frac{80\times0.12\times100}{188\times0.15}$$
$$=34.04\%$$

12.24. In sulphur estimation, 0.157 g of an organic compound gave 0.4813 g of barium sulphate. What is the percentage of sulphur in the compound?

Answer:

Molar mass of $BaSO_4$ = 137 + 32 + 64

= 233 g mol^{-1}

233 g $BaSO_4$ contains 32 g sulphur.

0.4813 g $BaSO_4$ contains $\frac{32\times0.4813}{233}$ g sulphur.

$$\text{Percentage of sulphur} = \frac{32\times0.4813\times100}{233\times0.157}$$
$$=42.10\%$$