Question 12.1:

What are the hybridisation states of each carbon atom in the following compounds?

i. CH₂=C=O, ii. CH₃CH=CH₂, iii. (CH₃)₂CO, iv. CH₂=CHCN, v. C₆H₆

Answer 12.1:

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$$^{1}_{CH_{2}} = ^{2}_{C} = 0$$

(i)

C-1 is *sp*² hybridised.

C-2 is *sp* hybridised.

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(ii)

C-1 is *sp*³ hybridised.

C–2 is *sp*² hybridised.

C–3 is *sp*² hybridised.

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(iii)

C-1 and C-3 are *sp*³ hybridised.

C-2 is sp² hybridised.

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$$\overset{1}{C}H_{2} = \overset{2}{C}H - \overset{3}{C} \equiv N$$

(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 12.2:

Indicate the σ and π bonds in the following molecules:

i. C_6H_6 , ii. C_6H_{12} , iii. CH_2CI_2 , iv. $CH_2 = C = CH_2$, v. CH_3NO_2 , vi. $HCONHCH_3$

Answer 12.2:

(i) C₆H₆

There are six C–C sigma bonds, six C–H sigma bonds, and three C=C pi resonating bonds in the given compound.

(ii) C₆H₁₂

There are six C–C sigma bonds and twelve C–H sigma bonds in the given compound.

(iii) CH₂Cl₂



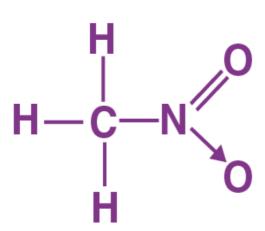
There are two C-Cl sigma bonds and two C-H sigma bonds in the given compound.

(iv)
$$CH_2 = C = CH_2$$



There are two C–C sigma bonds, four C–H sigma bonds, and two C=C pi bonds in the given compound.

(v) CH₃NO₂





There are three C–H sigma bonds, one C–N sigma bond, one N–O sigma bond, and one N=O pi bond in the given compound.

(vi) HCONHCH₃



There are four C–H sigma bonds, two C–N sigma bonds, one N–H sigma bond, and one C=O pi bond in the given compound.

Question 12.3:

Write bond-line formulas for: Isopropyl alcohol, 2, 3-dimethyl butanal, Heptan-4-one.

Answer 12.3:

Isopropyl alcohol

$$\begin{array}{c} H & OH & H \\ \hline + C & C & C \\ \hline + H & H & H \\ \hline \\ OH & \\ \hline \end{array}$$

2, 3-dimethyl butanal



Heptan-4-one

$$H_{3}C-CH_{2}-CH_{2}-C-CH_{2}-CH_{2}-CH_{3}$$

$$\Rightarrow 0$$

Question 12.4:

Give the IUPAC names of the following compounds:

(a)



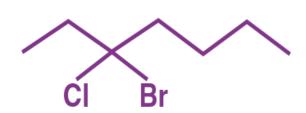
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(b)

(c)

(d)





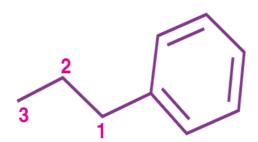
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(e)

(f) CI₂CHCH₂OH

Answer 12.4:

(a)



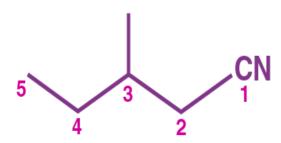
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Propylbenzene

(b)

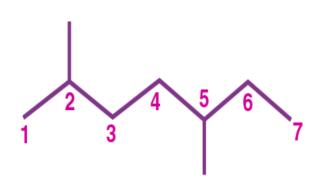






3-methylpentanenitrite

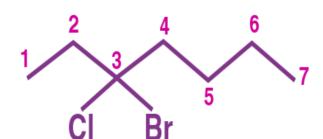
(c)



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2,5-dimethyl heptane

(d)

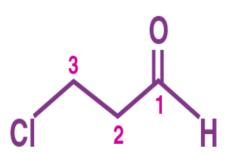


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3-bromo-3-chloroheptane

(e)





- 3-chloropropanal
- (f) Cl₂CHCH₂OH
- 2,2-dichloroethanol

Question 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 12.5:

- (a) The prefix *di* shows that there are two methyl groups in the chain. Thus, the correct IUPAC name would be 2,2-Dimethylpentane.
- (b) The locant number should start from the minimum. Here, 2,4,7 is lower than 2,5,7. Thus, the correct IUPAC name would be 2,4,7-Trimethyloctane.



- (c) If the substituents in the chain are in equivalent positions, then the lower number is given to the substituent group in alphabetical order. Thus, the correct IUPAC name would be 2-Chloro-4-methylpentane.
- (d) Out of the two <u>functional groups</u> present in the given compound, the alcoholic group is the principal functional group. Thus, the parent chain will have an –ol suffix. Since the alkyne group is in C–3, the IUPAC name would be But–3–yn–1–ol.

Question 12.6:

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

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

Answer 12.6:

The first five members of each homologous series beginning with the given compounds, are

(a)

H-COOH: Methanoic acid

CH3-COOH: Ethanoic acid

CH₃-CH₂-COOH: Propanoic acid

CH₃-CH₂-COOH: Butanoic acid

CH₃-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 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 12.7:

(a) 2, 2, 4-Trimethylpentane

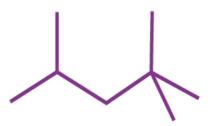
Condensed formula

(CH₃)₂CHCH₂C (CH₃)₃

Bond line formula:





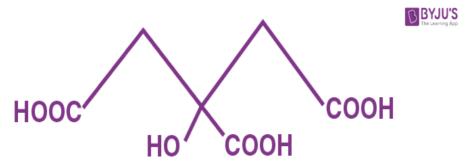


(b) 2-Hydroxy-1, 2, 3-propanetricarboxylic acid

Condensed formula

(COOH)CH₂C(OH) (COOH)CH₂(COOH)

Bond line formula:



Functional groups:

Carboxylic acid (-COOH) and Hydroxyl (-OH) groups

(c) Hexanedial

Condensed formula

(CHO)(CH₂)₄(CHO)

Bond line formula:



Functional groups:

Aldehyde (-CHO)

Question 12.8:

Identify the functional groups in the following compounds.

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(a)

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(b)

(c)





Answer 12.8:

(a) Hydroxyl (-OH), Aldehyde (-CHO), Methoxy (-OMe),

C=C double bond

- (b) Ester -(O = C O)-, 1°Amino (–NH₂) (aromatic), Diethylamine $CH_2N(C_2H_5)_2$ 30 Amine group
- (c) Nitro (-NO₂),

C=C Ethylenic double bond

Question 12.9:



Which one of the two, O₂NCH₂CH₂O⁻ or CH₃CH₂O⁻ is expected to be more stable and why?

Answer 12.9:

Since NO₂ belongs to the electron-withdrawing group, it shows the –I effect. NO₂ tries to decrease the negative charge on the compound by withdrawing the electrons towards it. This stabilises the compound, whereas the ethyl group belongs to the electron-releasing group and shows the +I effect. This results in an increase in the negative charge on the compound, thus destabilising the compound. Hence, O₂NCH₂CH₂O- is expected to be more stable than CH₃CH₂O-.

Question 12.10:

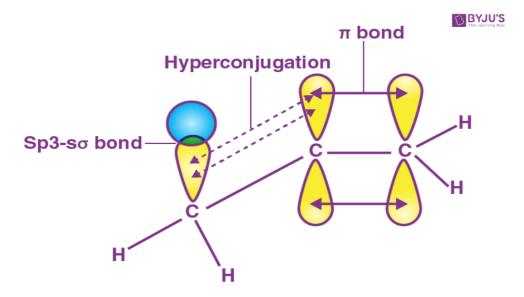
Explain why alkyl groups act as electron donors when attached to a π system.

Answer 12.10:

Due to hyperconjugation, an alkyl group behaves as an electron-donor group when attached to a π system. For example, propane (see the figure above).

The sigma electrons of the C-H bond get delocalised due to hyperconjugation. The alkyl is attached directly to an unsaturated system. The delocalisation happens due to the partial overlap of an sp³-s sigma bond orbital with an empty p orbital of the n bond of an adjacent carbon atom.

This process can be shown as follows:



The overlap, as shown above, results in delocalisation, making the compounds more stable.

Question 12.11:

Draw the resonance structures for the following compounds. Show the electron shift using curved-arrow notation.

- (a) C₆H₅OH
- (b) C₆H₅NO₂
- (c) CH₃CH = CH CHO
- (d) C₆H₅CHO
- (e) C₆H₅-CH₂
- (f)CH₃CH=CHCH₂

Answer 12.11:

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(a) The structure of C₆H₅OH is:

Resonating Structures:

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(b) The structure of $C_6H_5NO_2$ is:

Resonating Structures:

(c) The structure of CH₃CH = CH – CHO is:



$$CH_3$$
— CH — CHO

Resonating Structures:

$$CH_{3}-CH=CH-C-H \longleftrightarrow CH_{3}-CH-CH=C-H$$

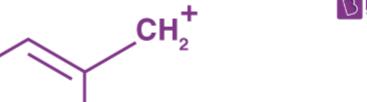
(d) The structure of C₆H₅CHO is:

Resonating Structures:





(e) C₆H₅-CH₂+



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Resonating structures:

$$\begin{array}{c} + \operatorname{CH}_2 & \operatorname{CH}_2 & \operatorname{CH}_2 \\ \hline \end{array} \\ \longleftrightarrow \\ \begin{array}{c} + \operatorname{CH}_2 \\ \hline \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} + \operatorname{CH}_2 \\ \hline \end{array} \\ \end{array}$$



(e) The structure of CH₃CH=CHCH₂⁺ is:



$$CH_3$$
— CH = CH — CH_2^{\oplus}

Resonating Structures:



$$CH_{3}-CH-CH_{2} \longleftrightarrow CH_{3}-CH-CH=CH_{2}$$

$$I \qquad \qquad II$$

Question 12.12:

What are electrophiles and nucleophiles? Explain with examples.

Answer 12.12:

A nucleophile is a reagent that has an electron pair and is willing to donate it. It is also known as a nucleus-loving reagent. For example, NC-, OH-, R₃C- (carbanions), etc.

An electrophile is a reagent which is in need of an electron pair and is also known as an electron-loving pair. For example, carbonyl groups, CH₃CH₂+(Carbocations), and neutral molecules (due to the presence of electron deficiency atom).

Question 12.13:

Identify the reagents in the following equations as nucleophiles or electrophiles:

(a) CH₃COOH + HO-

 \longrightarrow

CH₃COO- + H₂O

(b) CH₃COCH₃+ C-N

 \rightarrow (CH₃)₂C(CN) + (OH)⁻

(c) $C_6H_5 + CH_3C^+O$

C₆H₅COCH₃

Answer 12.13:

A nucleophile is a reagent that has an electron pair and is willing to donate it. It is also known as a nucleus-loving reagent.

An electrophile is a reagent which is in need of an electron pair and is also known as an electron-loving pair.

(a) CH₃COOH + HO-

CH₃COO- + H₂O

It is a nucleophile since HO- is electron rich in nature.

(b) CH₃COCH₃+ C-N

 \rightarrow (CH₃)₂C(CN) + (OH)⁻

It is a nucleophile since C-N is electron rich in nature.

(c) $C_6H_5 + CH_3C^+O$

It is an electrophile since CH₃C+O is electron-deficient in nature.

Question 12.14:

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

(a) CH₃CH₂Br + HS⁻

CH₃CH₂SH + Br

(b) $(CH_3)_2 C = CH_2 + HCI$

 \rightarrow

(CH₃)₂CIC-CH₃

(c) CH₃CH₂Br + HO-

 \rightarrow

CH₂=CH₂ + H₂O + Br⁻

(d) (CH₃)₃C-CH₂OH + HBr

 \longrightarrow

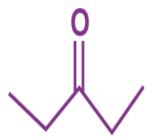
(CH₃)₂ CBrCH₂CH₃ + H₂O

Answer 12.14:

- (a) Substitution (nucleophilic) reaction, since the bromine group gets substituted by the –SH group.
- (b) Addition (electrophilic) reaction, since two reactant molecules combine to form a single product.
- (c) Elimination (bimolecular) reaction, since reaction hydrogen and bromine are removed to form ethene.
- (d) Substitution (nucleophilic) reaction, since rearrangement of atoms takes place.

Question 12.15:

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

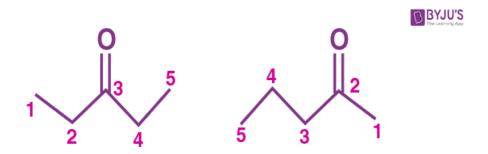




(a)

Answer 12.15:

(a) The given compounds are a pair of structural isomers since they have the same molecular formula but have different structures. These compounds differ in the position of the ketone group. For the first structure, it is in C-3, whereas for the 2nd one, it is in C-2.



(b) The given compounds are a pair of geometrical isomers since they have the same molecular formula, sequence of covalent bonds and same constitution but differ in the relative positioning of the atoms in space. These compounds differ in the positioning of the Deuterium and Hydrogen.

(c) The given compounds are a pair of contributing structures or canonical structures. They do not represent any real molecule and are purely hypothetical. They are also called resonance isomers.

Question 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)

(b)

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(c)



(d)

Answer 12.16:

(a) The bond cleavage can be shown as:





It comes under homolytic cleavage since one of the shared pairs in a covalent bond goes with the bonded atom. A free radical is formed as the reaction intermediate.

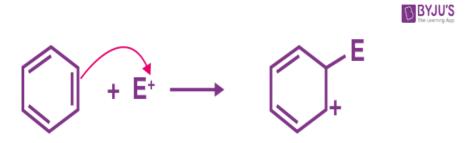
(b) The bond cleavage can be shown as:

It comes under heterolytic cleavage since the shared remains with the carbon atom of propanone. A carbanion is formed as the reaction intermediate.

(c) The bond cleavage can be shown as:

It comes under heterolytic cleavage since the shared remains with the bromine ion. A carbocation is formed as the reaction intermediate.

(d) The bond cleavage can be shown as:



It comes under heterolytic cleavage since the shared remains with one of the fragments. A carbocation is formed as the reaction intermediate.

Question 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) Cl₃CCOOH > Cl₂CHCOOH > CICH₂COOH
- (b) $CH_3CH_2COOH > (CH_3)_2CHCOOH > (CH_3)_3C.COOH$

Answer 12.17:

Electrometric effect

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 is called the electrometric effect. It can either be the – E effect or the +E effect.

- E effect: Occurs when electrons are moved away from the attacking agent
- + E effect: Occurs when electrons are moved towards the attacking agent

Inductive effect

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

It can either be +I effect or –I effect. When an atom or group attracts electrons towards itself more strongly than hydrogen, it is said to possess the –I effect.

When the force with which an atom attracts electrons towards itself is greater than that of hydrogen, it is said to exhibit the +I effect.

(a) Cl₃CCOOH > Cl₂CHCOOH > ClCH₂COOH

The acidity increases with the increase in the –I effect, which is directly proportional to the number of chlorine atoms.

$$CI \leftarrow CI \qquad OH \qquad CI \leftarrow CI \leftarrow OH \qquad CI \leftarrow CI \leftarrow OH \qquad CI \leftarrow CI \leftarrow OH \qquad H \qquad OH \qquad H$$

(b) $CH_3CH_2COOH > (CH_3)_2 CHCOOH > (CH_3)_3C.COOH$



The acidity increases with the increase in the +I effect, which is directly proportional to the number of alkyl groups.

$$CH_{3} \rightarrow CH_{2} \rightarrow C \rightarrow OH$$

$$CH_{3} \rightarrow CH_{3} \rightarrow C \rightarrow OH$$

$$CH_{3} \rightarrow C \rightarrow OH$$

Question 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 12.18:

(a) Crystallisation

Crystallisation is used to purify solid organic compounds.

Principle: The principle on which it works is the difference in the solubility of the compound and impurities in a given solvent. The impure compound is made to dissolve in the solvent at a higher temperature since it is sparingly soluble at lower temperatures. This is continued till we get an almost saturated solution. On cooling and filtering it, we get its' crystals. For example, by crystallising 2-4 g of crude aspirin in 20 ml of ethyl alcohol, we get pure aspirin. It is heated if needed and left undisturbed until it crystallises. The crystals are then separated and dried.

(b) Distillation



This method is used to separate non-volatile liquids from volatile impurities. It is also used when the components have a considerable difference in their boiling points.

Principle: The principle on which it works is that liquids having different boiling points vaporise at different temperatures. They are then cooled, and the formed liquids are separated.

For example, a mixture of aniline (b.p = 457 K) and chloroform (b.p = 334 K) is taken in a round bottom flask having a condenser. When they are heated, chloroform vaporises first due to its high volatility and is made to pass through a condenser, where it cools down. The aniline is left behind in the round bottom flask.

(c) Chromatography

It is widely used for the separation and purification of organic compounds.

Principle: The principle on which it works is that individual components of a mixture move at different paces through the stationary phase under the influence of the mobile phase.

For example, Chromatography can be used to separate a mixture of blue and red ink. This mixture is placed on a chromatogram where the component which is less absorbed by the chromatogram moves faster up the paper than the other component, which is almost stationary.