

Unit 12

ORGANIC CHEMISTRY SOME BASIC PRINCIPLES AND TECHNIQUES

I. Multiple Choice Questions (Type-I)

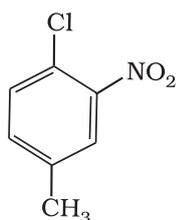
1. Which of the following is the correct IUPAC name?

- (i) 3-Ethyl-4, 4-dimethylheptane
- (ii) 4,4-Dimethyl-3-ethylheptane
- (iii) 5-Ethyl-4, 4-dimethylheptane
- (iv) 4,4-Bis(methyl)-3-ethylheptane

2. The IUPAC name for $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ is _____.

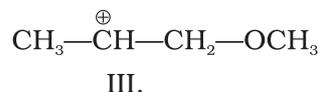
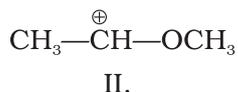
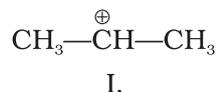
- (i) 1-hydroxypentane-1,4-dione
- (ii) 1,4-dioxopentanol
- (iii) 1-carboxybutan-3-one
- (iv) 4-oxopentanoic acid

3. The IUPAC name for



- (i) 1-Chloro-2-nitro-4-methylbenzene
(ii) 1-Chloro-4-methyl-2-nitrobenzene
(iii) 2-Chloro-1-nitro-5-methylbenzene
(iv) *m*-Nitro-*p*-chlorotoluene
4. Electronegativity of carbon atoms depends upon their state of hybridisation. In which of the following compounds, the carbon marked with asterisk is most electronegative?
- (i) $\text{CH}_3 - \text{CH}_2 - \text{*CH}_2 - \text{CH}_3$
(ii) $\text{CH}_3 - \text{*CH} = \text{CH} - \text{CH}_3$
(iii) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{*CH}$
(iv) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{*CH}_2$
5. In which of the following, functional group isomerism is **not** possible?
- (i) Alcohols
(ii) Aldehydes
(iii) Alkyl halides
(iv) Cyanides
6. The fragrance of flowers is due to the presence of some steam volatile organic compounds called essential oils. These are generally insoluble in water at room temperature but are miscible with water vapour in vapour phase. A suitable method for the extraction of these oils from the flowers is:
- (i) Distillation
(ii) Crystallisation
(iii) Distillation under reduced pressure
(iv) Steam distillation
7. During hearing of a court case, the judge suspected that some changes in the documents had been carried out. He asked the forensic department to check the ink used at two different places. According to you which technique can give the best results?
- (i) Column chromatography
(ii) Solvent extraction
(iii) Distillation
(iv) Thin layer chromatography
8. The principle involved in paper chromatography is
- (i) Adsorption
(ii) Partition
(iii) Solubility
(iv) Volatility

9. What is the correct order of decreasing stability of the following cations.



- (i) II > I > III
- (ii) II > III > I
- (iii) III > I > II
- (iv) I > II > III

10. Correct IUPAC name for $\text{H}_3\text{C}-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{CH}_3$ is _____.

- (i) 2-ethyl-3-methylpentane
- (ii) 3,4-dimethylhexane
- (iii) 2-sec-butylbutane
- (iv) 2,3-dimethylbutane

11. In which of the following compounds the carbon marked with asterisk is expected to have greatest positive charge?

- (i) $^*\text{CH}_3-\text{CH}_2-\text{Cl}$
- (ii) $^*\text{CH}_3-\text{CH}_2-\text{Mg}^+\text{Cl}^-$
- (iii) $^*\text{CH}_3-\text{CH}_2-\text{Br}$
- (iv) $^*\text{CH}_3-\text{CH}_2-\text{CH}_3$

12. Ionic species are stabilised by the dispersal of charge. Which of the following carboxylate ion is the most stable?

- (i) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$
- (ii) $\text{Cl}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$
- (iii) $\text{F}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$
- (iv) $\begin{array}{l} \text{F} \\ \diagdown \\ \text{CH} \\ \diagup \\ \text{F} \end{array} - \overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-$

13. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.



- (i) 2° Carbanion
- (ii) 1° Carbocation
- (iii) 2° Carbocation
- (iv) 1° Carbanion

14. Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of $\text{CH}_3\text{—Br}$ is

- (i) $\overset{\cdot\cdot}{\text{C}}\text{H}_3\text{—Br} \longrightarrow \overset{\oplus}{\text{C}}\text{H}_3 + \text{Br}^{\ominus}$
- (ii) $\text{CH}_3\text{—}\overset{\cdot\cdot}{\text{B}}\text{r} \longrightarrow \overset{\oplus}{\text{C}}\text{H}_3 + \text{Br}^{\ominus}$
- (iii) $\text{CH}_3\text{—}\overset{\cdot\cdot}{\text{B}}\text{r} \longrightarrow \overset{\ominus}{\text{C}}\text{H}_3 + \text{Br}^{\oplus}$
- (iv) $\overset{\cdot\cdot}{\text{C}}\text{H}_3\text{—}\overset{\cdot\cdot}{\text{B}}\text{r} \longrightarrow \overset{\cdot}{\text{C}}\text{H}_3 + \overset{\cdot}{\text{B}}\text{r}$

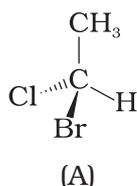
15. The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to $\text{>C}=\text{C}<$ portion which can be shown as

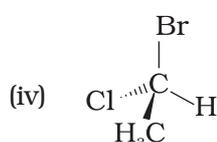
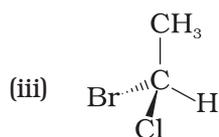
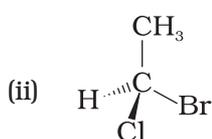
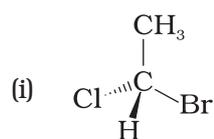
- (i) $\text{H}^+ \curvearrowright \text{>C}=\text{C}<$
- (ii) $\text{H}^+ \curvearrowleft \text{>C}=\text{C}<$
- (iii) $\text{H}^+ \curvearrowright \text{>C}=\text{C}<$
- (iv) All of these are possible

II. Multiple Choice Questions (Type-II)

In the following questions two or more options may be correct.

16. Which of the following compounds contain all the carbon atoms in the same hybridisation state?
- (i) $\text{H—C}\equiv\text{C—C}\equiv\text{C—H}$
 - (ii) $\text{CH}_3\text{—C}\equiv\text{C—CH}_3$
 - (iii) $\text{CH}_2=\text{C}=\text{CH}_2$
 - (iv) $\text{CH}_2=\text{CH—CH}=\text{CH}_2$
17. In which of the following representations given below spatial arrangement of group/ atom **different** from that given in structure 'A'?

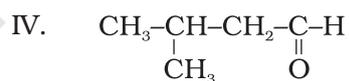
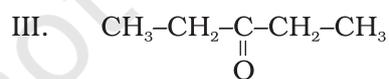
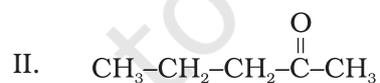




18. Electrophiles are electron seeking species. Which of the following groups contain only electrophiles?

- (i) BF_3 , NH_3 , H_2O
 (ii) AlCl_3 , SO_3 , NO_2^+
 (iii) NO_2^+ , CH_3^+ , $\text{CH}_3 - \overset{+}{\text{C}} = \text{O}$
 (iv) C_2H_5^- , $\overset{\cdot}{\text{C}}_2\text{H}_5$, C_2H_5^+

Note : Consider the following four compounds for answering questions 19 and 20.



19. Which of the following pairs are position isomers?

- (i) I and II

- (ii) II and III
- (iii) II and IV
- (iv) III and IV

20. Which of the following pairs are **not** functional group isomers?

- (i) II and III
- (ii) II and IV
- (iii) I and IV
- (iv) I and II

21. Nucleophile is a species that should have

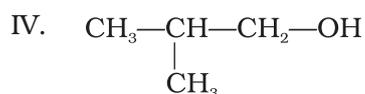
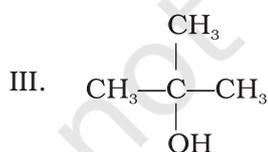
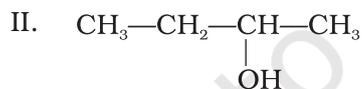
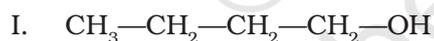
- (i) a pair of electrons to donate
- (ii) positive charge
- (iii) negative charge
- (iv) electron deficient species

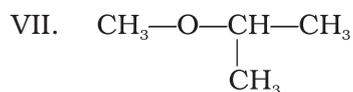
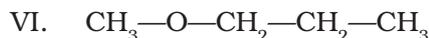
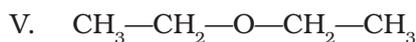
22. Hyperconjugation involves delocalisation of _____.

- (i) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to an atom of unsaturated system.
- (ii) electrons of carbon-hydrogen σ bond of alkyl group directly attached to the positively charged carbon atom.
- (iii) π -electrons of carbon-carbon bond
- (iv) lone pair of electrons

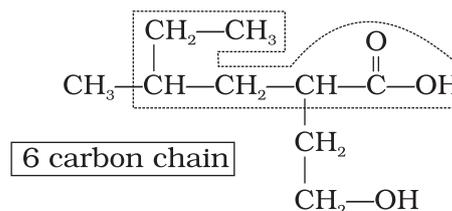
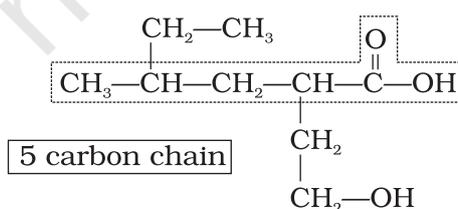
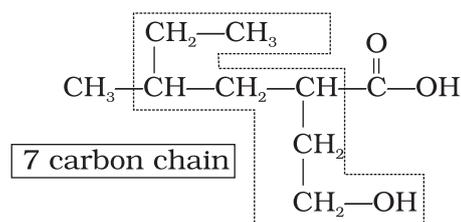
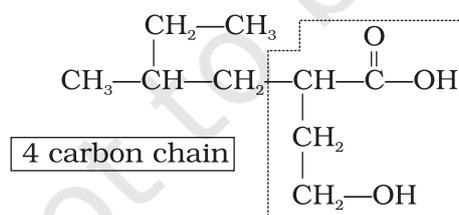
III. Short Answer Type

Note : Consider structures I to VII and answer the questions 23–26.





- 23.** Which of the above compounds form pairs of metamers?
- 24.** Identify the pairs of compounds which are functional group isomers.
- 25.** Identify the pairs of compounds that represents position isomerism.
- 26.** Identify the pairs of compounds that represents chain isomerism.
- 27.** For testing halogens in an organic compound with AgNO_3 solution, sodium extract (Lassaigne's test) is acidified with dilute HNO_3 . What will happen if a student acidifies the extract with dilute H_2SO_4 in place of dilute HNO_3 ?
- 28.** What is the hybridisation of each carbon in $\text{H}_2\text{C} = \text{C} = \text{CH}_2$.
- 29.** Explain, how is the electronegativity of carbon atoms related to their state of hybridisation in an organic compound?
- 30.** Show the polarisation of carbon-magnesium bond in the following structure.
 $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_2\text{—Mg—X}$
- 31.** Compounds with same molecular formula but differing in their structures are said to be structural isomers. What type of structural isomerism is shown by
 $\text{CH}_3\text{—S—CH}_2\text{—CH}_2\text{—CH}_3$ and $\text{CH}_3\text{—S—CH} \begin{array}{l} \text{CH}_3 \\ \text{CH}_3 \end{array}$
- 32.** Which of the following selected chains is correct to name the given compound according to IUPAC system.

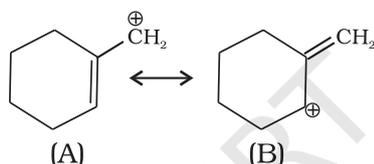


- 33.** In DNA and RNA, nitrogen atom is present in the ring system. Can Kjeldahl method be used for the estimation of nitrogen present in these? Give reasons.
- 34.** If a liquid compound decomposes at its boiling point, which method (s) can you choose for its purification. It is known that the compound is stable at low pressure, steam volatile and insoluble in water.

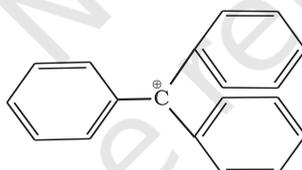
Note : Answer the questions 35 to 38 on the basis of information given below:

“Stability of carbocations depends upon the electron releasing inductive effect of groups adjacent to positively charged carbon atom involvement of neighbouring groups in hyperconjugation and resonance.”

- 35.** Draw the possible resonance structures for $\text{CH}_3-\overset{\oplus}{\underset{\cdot\cdot}{\text{O}}}-\text{CH}_2$ and predict which of the structures is more stable. Give reason for your answer.
- 36.** Which of the following ions is more stable? Use resonance to explain your answer.



- 37.** The structure of triphenylmethyl cation is given below. This is very stable and some of its salts can be stored for months. Explain the cause of high stability of this cation.



- 38.** Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.
- 39.** Three students, Manish, Ramesh and Rajni were determining the extra elements present in an organic compound given by their teacher. They prepared the Lassaigne's extract (L.E.) independently by the fusion of the compound with sodium metal. Then they added solid FeSO_4 and dilute sulphuric acid to a part of Lassaigne's extract. Manish and Rajni obtained prussian blue colour but Ramesh got red colour. Ramesh repeated the test with the same Lassaigne's extract, but again got red colour only. They were surprised and went to their teacher and told him about their observation. Teacher asked them to think over the reason for this. Can you help them by giving the reason for this observation. Also, write the chemical equations to explain the formation of compounds of different colours.

IV. Matching Type

In the following questions more than one correlation is possible between options of Column I and Column II. Make as many correlations as you can.

50. Match the type of mixture of compounds in Column I with the technique of separation/purification given in Column II.

Column I	Column II
(i) Two solids which have different solubilities in a solvent and which do not undergo reaction when dissolved in it.	(a) Steam distillation
(ii) Liquid that decomposes at its boiling point	(b) Fractional distillation
(iii) Steam volatile liquid	(c) Simple distillation
(iv) Two liquids which have boiling points close to each other	(d) Distillation under reduced pressure
(v) Two liquids with large difference in boiling points.	(e) Crystallisation

51. Match the terms mentioned in Column I with the terms in Column II.

Column I	Column II
(i) Carbocation	(a) Cyclohexane and 1-hexene
(ii) Nucleophile	(b) Conjugation of electrons of C-H σ bond with empty p -orbital present at adjacent positively charged carbon.
(iii) Hyperconjugation	(c) sp^2 hybridised carbon with empty p -orbital
(iv) Isomers	(d) Ethyne
(v) sp hybridisation	(e) Species that can receive a pair of electrons
(vi) Electrophile	(f) Species that can supply a pair of electrons

52. Match Column I with Column II.

Column I	Column II
(i) Dumas method	(a) $AgNO_3$

- | | |
|------------------------|-----------------------|
| (ii) Kjeldahl's method | (b) Silica gel |
| (iii) Carius method | (c) Nitrogen gas |
| (iv) Chromatography | (d) Free radicals |
| (v) Homolysis | (e) Ammonium sulphate |

53. Match the intermediates given in Column I with their probable structure in Column II.

Column I

- (i) Free radical
 (ii) Carbocation
 (iii) Carbanion

Column II

- (a) Trigonal planar
 (b) Pyramidal
 (c) Linear

54. Match the ions given in Column I with their nature given in Column II.

Column I

- (i) $\text{CH}_3-\ddot{\text{O}}^{\oplus}-\text{CH}-\text{CH}_3$
 (ii) $\text{F}_3-\text{C}^{\oplus}$
 (iii) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}^{\ominus} \\ | \\ \text{CH}_3 \end{array}$
 (iv) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$

Column II

- (a) Stable due to resonance
 (b) Destabilised due to inductive effect
 (c) Stabilised by hyperconjugation
 (d) A secondary carbocation

V. Assertion and Reason Type

In the following questions a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question.

55. **Assertion (A)** : Simple distillation can help in separating a mixture of propan-1-ol (boiling point 97°C) and propanone (boiling point 56°C).

Reason (R) : Liquids with a difference of more than 20°C in their boiling points can be separated by simple distillation.

- (i) Both A and R are correct and R is the correct explanation of A.
(ii) Both A and R are correct but R is not the correct explanation of A.
(iii) Both A and R are not correct.
(iv) A is not correct but R is correct.
- 56. Assertion (A) :** Energy of resonance hybrid is equal to the average of energies of all canonical forms.
Reason (R) : Resonance hybrid cannot be presented by a single structure.
(i) Both A and R are correct and R is the correct explanation of A.
(ii) Both A and R are correct but R is not the correct explanation of A.
(iii) Both A and R are not correct.
(iv) A is not correct but R is correct.
- 57. Assertion (A) :** Pent- 1- ene and pent- 2- ene are position isomers.
Reason (R) : Position isomers differ in the position of functional group or a substituent.
(i) Both A and R are correct and R is the correct explanation of A.
(ii) Both A and R are correct but R is not the correct explanation of A.
(iii) Both A and R are not correct.
(iv) A is not correct but R is correct.
- 58. Assertion (A) :** All the carbon atoms in $\text{H}_2\text{C} = \text{C} = \text{CH}_2$ are sp^2 hybridised
Reason (R) : In this molecule all the carbon atoms are attached to each other by double bonds.
(i) Both A and R are correct and R is the correct explanation of A.
(ii) Both A and R are correct but R is not the correct explanation of A.
(iii) Both A and R are not correct.
(iv) A is not correct but R is correct.
- 59. Assertion (A) :** Sulphur present in an organic compound can be estimated quantitatively by Carius method.
Reason (R) : Sulphur is separated easily from other atoms in the molecule and gets precipitated as light yellow solid.
(i) Both A and R are correct and R is the correct explanation of A.
(ii) Both A and R are correct but R is not the correct explanation of A.
(iii) Both A and R are not correct.
(iv) A is not correct but R is correct.
- 60. Assertion (A):** Components of a mixture of red and blue inks can be separated by distributing the components between stationary and mobile phases in paper chromatography.

Reason (R) : The coloured components of inks migrate at different rates because paper selectively retains different components according to the difference in their partition between the two phases.

- (i) Both A and R are correct and R is the correct explanation of A.
- (ii) Both A and R are correct but R is not the correct explanation of A.
- (iii) Both A and R are not correct.
- (iv) A is not correct but R is correct.

VI. Long Answer Type

- 61. What is meant by hybridisation? Compound $\text{CH}_2 = \text{C} = \text{CH}_2$ contains sp or sp^2 hybridised carbon atoms. Will it be a planar molecule?
- 62. Benzoic acid is a organic compound. Its crude sample can be purified by crystallisation from hot water. What characteristic differences in the properties of benzoic acid and the impurity make this process of purification suitable?
- 63. Two liquids (A) and (B) can be separated by the method of fractional distillation. The boiling point of liquid (A) is less than boiling point of liquid (B). Which of the liquids do you expect to come out first in the distillate? Explain.
- 64. You have a mixture of three liquids A, B and C. There is a large difference in the boiling points of A and rest of the two liquids i.e., B and C. Boiling point of liquids B and C are quite close. Liquid A boils at a higher temperature than B and C and boiling point of B is lower than C. How will you separate the components of the mixture. Draw a diagram showing set up of the apparatus for the process.
- 65. Draw a diagram of bubble plate type fractionating column. When do we require such type of a column for separating two liquids. Explain the principle involved in the separation of components of a mixture of liquids by using fractionating column. What industrial applications does this process have?
- 66. A liquid with high boiling point decomposes on simple distillation but it can be steam distilled for its purification. Explain how is it possible?

ANSWERS

I. Multiple Choice Questions (Type-I)

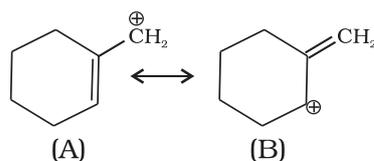
1. (ii) 2. (iv) 3. (ii) 4. (iii) 5. (iii) 6. (iv)
7. (iv) 8. (ii) 9. (i) 10. (ii) 11. (i) 12. (iv)
13. (iii) 14. (ii) 15. (ii)

II. Multiple Choice Questions (Type-II)

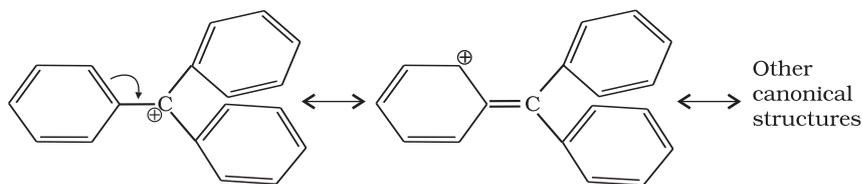
16. (i), (iv) 17. (i), (iii), (iv) 18. (ii), (iii)
19. (ii) 20. (i), (iii) 21. (i), (iii)
22. (i), (ii)

III. Short Answer Type

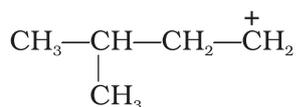
27. White ppt. of Ag_2SO_4 will be formed.
29. Electronegativity increases with increasing 's' character.
 $sp^3 < sp^2 < sp$
30. $\text{CH}_3-\text{CH}_2-\overset{\delta-}{\text{CH}_2}-\overset{\delta+}{\text{CH}_2}-\text{Mg}-\text{X}$. Since electronegativity of carbon is more than magnesium it will behave as $\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{-}{\text{C}}\overset{+}{\text{H}}_2\overset{+}{\text{Mg}}\text{Br}$.
31. Metamerism.
32. The four carbon chain. Selected chain should have maximum number of functional groups.
33. DNA and RNA have nitrogen in the heterocyclic rings. Nitrogen present in rings, azo groups and nitro groups cannot be removed as ammonia.
35. $\text{CH}_3-\text{O}-\overset{\oplus}{\text{C}}\text{H}_2$ $\text{CH}_3-\overset{\oplus}{\text{O}}=\text{CH}_2$
I. II.
Structure II is more stable because every atom has complete octet.
36. Structure I is more stable due to resonance. (See resonance structure 'A' and 'B'). No resonance is possible in structure II.



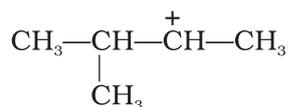
37. Stabilised due to nine possible canonical structures.



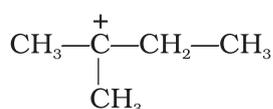
38. Four possible carbocations are



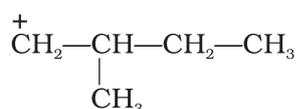
(I)



(II)



(III)



(IV)

Order of increasing stability I < IV < II < III

39. In Lassaigne's test SCN^- ions are formed due to the presence of sulphur and nitrogen both. These give red colour with Fe^{3+} ions. This happens when fusion is not carried out in the excess of sodium. With excess of sodium the thiocyanate ion, if formed, is decomposed as follows:



40. (i) 3-Ethyl-4-methylheptan-5-en-2-one

(ii) 3-Nitrocyclohex-1-ene.

41. (a) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2\text{Br}$

(b) $\text{CH}_3-\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$

42. (i) $\text{CH}_2=\text{CH}-\ddot{\text{C}}\text{l} \longleftrightarrow \overset{\ominus}{\text{C}}\text{H}_2-\text{CH}=\overset{\oplus}{\text{C}}\text{l}$

(ii) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 \longleftrightarrow \overset{\oplus}{\text{C}}\text{H}_2-\text{CH}=\text{CH}-\overset{\ominus}{\text{C}}\text{H}_2$

(iii) $\text{CH}_2=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H} \longleftrightarrow \overset{\oplus}{\text{C}}\text{H}_2-\text{CH}=\overset{\ominus}{\text{O}}-\text{C}-\text{H}$

43. (i) $\overset{\oplus}{\text{C}}\text{H}_3$, The replacement of hydrogen by bromine increases positive charge on carbon atom and destabilises the species.
- (ii) $\overset{\ominus}{\text{C}}\text{—Cl}_3$ is most stable because electronegativity of chlorine is more than hydrogen. On replacing hydrogen by chlorine, negative charge on carbon is reduced and species is stabilised.

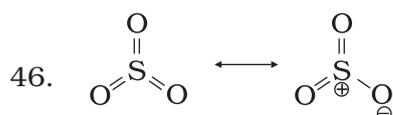
44. **Inductive effect**

- (i) Use σ -electrons
- (ii) Move up to 3-carbon atoms
- (iii) Slightly displaced electrons

Resonance effect

- (a) Use π - electrons or lone pair of electrons
- (b) All along the length of conjugated system
- (c) Complete transfer of electrons

45. CH_3OH ; Any possible contributing structure will have charge separation and incomplete octet of electrons on atoms. So the structure will be unstable due to high energy. e.g., $\overset{\oplus}{\text{C}}\text{H}_3\overset{\ominus}{\text{O}}\text{H}$.

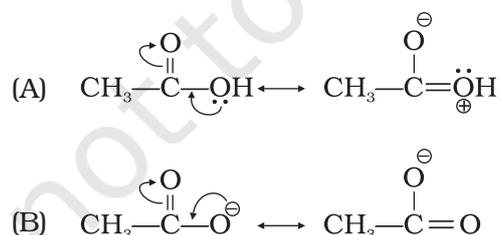


Three highly electronegative oxygen atoms are attached to sulphur atom. It makes sulphur atom electron deficient. Due to resonance also, sulphur acquires positive charge. Both these factors make SO_3 an electrophile.

47. I > II

48. Simple distillation can be used because the two compounds have a difference of more than 20° in their boiling points and both the liquids can be distilled without any decomposition.

49. Resonating structures are as follows:



Structure 'B' is more stabilised as it does not involve charge separation.

IV. Matching Type

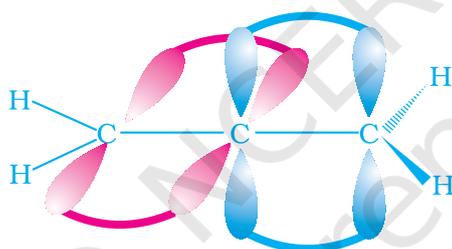
50. (i) → (e) (ii) → (d) (iii) → (a) (iv) → (b) (v) → (c)
51. (i) → (c) (ii) → (f) (iii) → (b) (iv) → (a) (v) → (d)
(vi) → (e)
52. (i) → (c) (ii) → (e) (iii) → (a) (iv) → (b) (v) → (d)
53. (i) → (a), (ii) → (a) (iii) → (b)
54. (i) → (a), (b), (d) (ii) → (b) (iii) → (b) (iv) → (c), (d)

V. Assertion and Reason Type

55. (i) 56. (iv) 57. (i) 58. (iv) 59. (iii) 60. (i)

VI. Long Answer Type

61. No. It is not a planar molecule.



Central carbon atom is sp^2 hybridised and its two unhybridised p -orbitals are perpendicular to each other. The p -orbitals in one plane overlap with one of the p -orbital of left terminal carbon atom and the p -orbital in other plane overlaps with p -orbital of right side terminal carbon atom. This fixes the position of two terminal carbon atoms and the hydrogen atoms attached to them in planes perpendicular to each other. Due to this the pair of hydrogen atoms attached to terminal carbon atoms are present in different planes.