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Organic Chemistry : Some Basic Principles and Techniques

Multiple Choice Questions (MCQs)

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

- (a) 3-ethyl-4, 4-dimethylheptane (b) 4,4-dimethyl-3-ethylheptane
(c) 5-ethyl-4, 4-dimethylheptane (d) 4,4-bis(methyl)-3-ethylheptane

Ans. (a) The structure $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \text{CH}_2 - \text{CH}_3$

While writing IUPAC name, alkyl groups are written in alphabetical priority, thus lower locant 3 is assigned to ethyl.

Note Prefix di, tri, tetra are not included in alphabetical order.

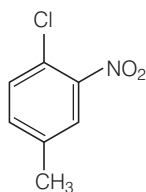
Q. 2 The IUPAC name for $\text{CH}_3 - \overset{\overset{\text{C}}{\parallel}}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \overset{\overset{\text{C}}{\parallel}}{\text{C}} - \text{OH}$ is

- (a) 1-hydroxypentane-1,4-dione
(b) 1,4-dioxopentanol
(c) 1-carboxybutan-3-one
(d) 4-oxopentanoic acid

Ans. (d) When more than one functional group lie in the main chain, nomenclature is done according to that functional group which has higher priority.

Carboxylic acid ($-\text{COOH}$) has more priority than ketone ($>\text{C} = \text{O}$)

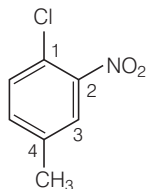
Q. 3 The IUPAC name for



- (a) 1-chloro-2-nitro-4-methylbenzene
 (b) 1-chloro-4-methyl-2-nitrobenzene
 (c) 2-chloro-1-nitro-5-methylbenzene
 (d) *m*-nitro-*p*-chlorotoluene

Ans. (b) For tri or higher substituted benzene derivatives, the compounds are named by identifying substituent, positions on the ring by following the lowest locant rule.

Substituent of the base compound is assigned number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order.



Q. 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?

- (a) $\text{CH}_3 - \text{CH}_2 - \text{*CH}_2 - \text{CH}_3$ (b) $\text{CH}_3 - \text{*CH} = \text{CH} - \text{CH}_3$
 (c) $\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{*CH}$ (d) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{*CH}_2$

Ans. (c) Electronegativity of carbon atom depends on their state of hybridisation. More s-character more the electronegativity.

$$\begin{array}{ccccc} sp^3 & < & sp^2 & < & sp \\ 25\%s & & 33\%s & & 50\%s \end{array}$$

Thus, *sp*-carbon has the highest electronegativity, i.e., option (c) ($\text{CH}_3 - \text{CH}_2 - \text{C} \equiv \text{*CH}$) is correct.

Q. 5 In which of the following, functional group isomerism is not possible?

- (a) Alcohols (b) Aldehydes
 (c) Alkyl halides (d) Cyanides

Ans. (c) Two or more compounds having the same molecular formula but different functional groups are called functional isomers.

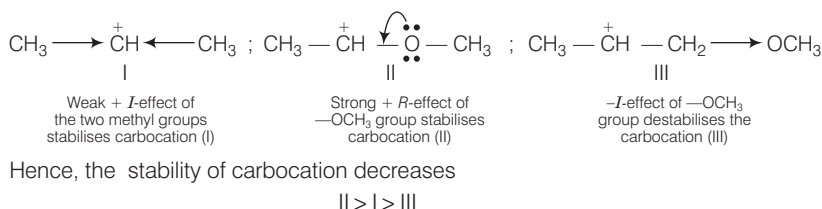
Functional isomer of alcohol is ether.

Functional isomer of aldehyde is ketone.

Functional isomer of cyanide is isocyanide

However, alkyl halides do not show functional isomerism. Hence, option (c) is correct.

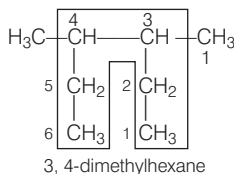
Ans. (a) Stability of the given cations can be understood by the following structures



Q. 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

- (a) 2-ethyl-3-methylpentane (b) 3, 4-dimethylhexane
(c) 2-sec-butylbutane (d) 2, 3-dimethylbutane

Ans. (b)



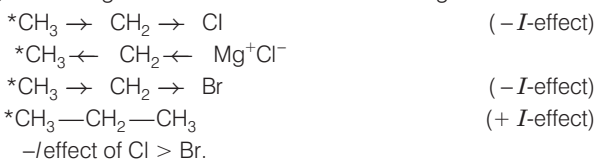
Q. 11 In which of the following compounds the carbon marked with asterisk is expected to have greatest positive charge?

- (a) $^*\text{CH}_3-\text{CH}_2-\text{Cl}$ (b) $^*\text{CH}_3-\text{CH}_2-\text{Mg}^+\text{Cl}^-$
(c) $^*\text{CH}_3-\text{CH}_2-\text{Br}$ (d) $^*\text{CH}_3-\text{CH}_2-\text{CH}_3$

Thinking Process

When a more electronegative atom is attached to carbon, the shared pair of electron moves towards more electronegative atom. Carbon has less electron density and gains partial positive charge.

Ans. (a) Electronegativity of Cl, Br, C and Mg follows the order $\text{Cl} > \text{Br} > \text{C} > \text{Mg}$



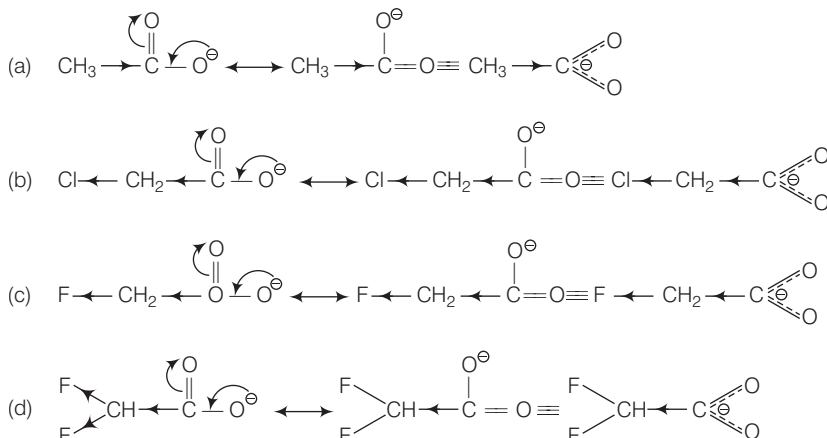
Hence, $\text{CH}_3-\text{CH}_2-\text{Cl}$ has the greatest positive charge.

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



Ans. (d) In all the given carbocations, the negative charge is dispersed which stabilises these carbocations. Here, the negative charge is dispersed by two factors, i.e., +R-effect of the carboxylate ion (conjugation) and I-effect of the halogens.

These effects are shown below in the carbocations



As it is clearly evident from the above structures, that +R-effect is common in all the four structures, therefore, overall dispersal of negative charge depends upon the number of halogen atoms and electronegativity. Since, F has the highest electronegativity and two F-atoms are present in option (d), thus, dispersal of negative charge is maximum in option (d).

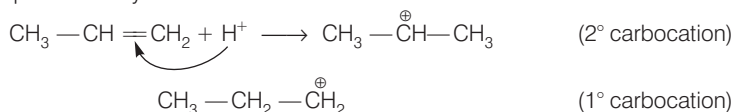
Note In above structure (a), methyl group (CH_3) increases the density on C-atom.

Q. 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.

$\text{H}_3\text{C}-\text{HC}=\text{CH}_2 + \text{H}^+ \longrightarrow ?$

- (a) 2° carbanion (b) 1° carbocation
(c) 2° carbocation (d) 1° carbanion

Ans. (c) When electrophile attacks $\text{CH}_3-\text{CH}=\text{CH}_2$ delocalisation of electrons can take place, in two possible ways



As 2° carbocation is more stable than 1° carbocation thus first addition is more feasible.

Note Stability of carbocations is the basis of Markownikoff's rule.

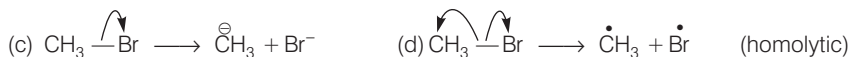
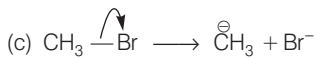
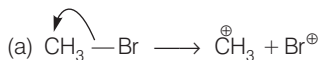
Q. 14 Covalent bond can undergo fission in two different ways. The correct representation involving a heterolytic fission of CH_3-Br is



Thinking Process

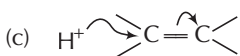
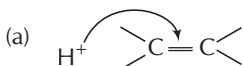
Homolytic fission gives free radical whereas heterolytic fission gives carbocation or carbanion.

Ans. (b) Arrow denotes the direction of movement of electrons



Since, Br is more electronegative than carbon, hence heterolytic fission occurs in such a way that CH_3 gets the positive charge and Br gets the negative charge. Thus, option (b) is correct.

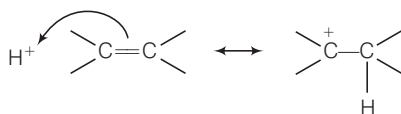
Q. 15 The addition of HCl to an alkene proceeds in two steps. The first step is the attack of H^+ ion to >C=C< portion which can be shown as



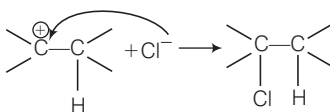
(d) All of these are possible

Ans. (b)

Step I π -bonds creates an electron cloud, Electrophile (H^+) from $\text{H}-\text{Cl}$ attacks the electron cloud, delocalising the electrons. And, a carbocation is formed.

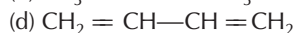
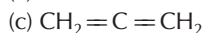
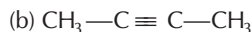


Step II The chloride anion attacks the carbocation.



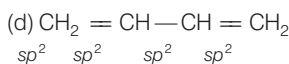
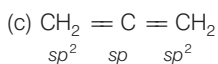
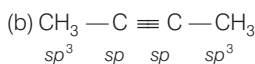
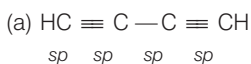
Multiple Choice Questions (More Than One Options)

Q. 16 Which of the following compounds contain all the carbon atoms in the same hybridisation state?



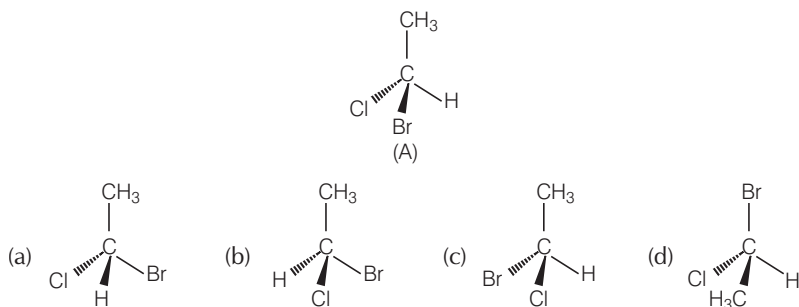
Ans. (a, d)

Hybridisation of carbon atoms in different compounds is shown below



In options (a) and (d), all carbon atoms are in same hybridisation state i.e., in sp and sp^2 hybridisation respectively.

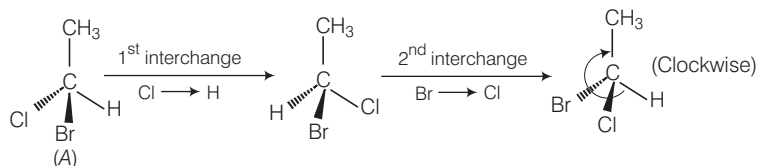
Q. 17 In which of the following representations given below spatial arrangement of group/atom different from that given in structure 'A'?



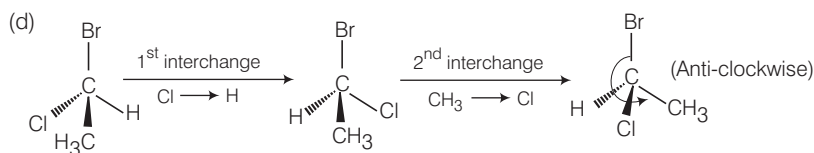
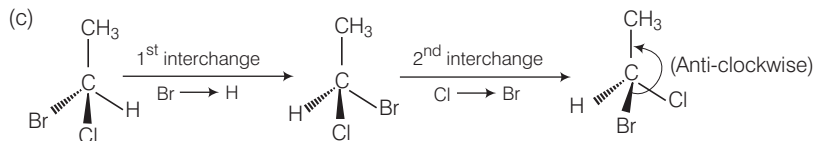
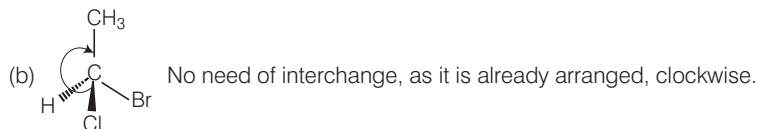
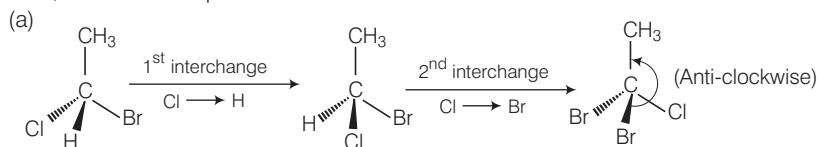
Thinking Process

The spatial arrangement of group/atom can be checked by doing two interchanges of groups/atoms and then by bringing H below the plane of the paper. Then find out the sequence of the remaining groups in a particular order whether clockwise or anti-clockwise starting from atom with highest atomic number towards atoms with lower atomic numbers.

Ans. (a, c, d)



Now, check all the options.



Hence, only option (b) has same spatial arrangement of group/atom as in (A), i.e., clockwise, while in rest of the options (a), (c) and (d) it is different i.e. anti-clockwise.

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

- (a) BF_3 , NH_3 , H_2O (b) AlCl_3 , SO_3 , NO_2^+
 (c) NO_2^+ , CH_3^+ , $\text{CH}_3-\text{C}^+=\text{O}$ (d) C_2H_5^- , $\dot{\text{C}}_2\text{H}_5$, C_2H_5^+

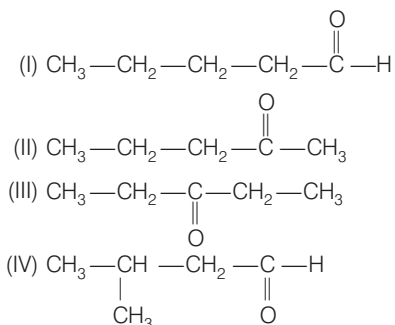
Thinking Process

Electrophiles are electron deficient species. Hence, they are generally Lewis acids or ions with positive charge.

Ans. (b, c)

All AlCl_3 , SO_3 (Lewis acids), NO_2^+ , CH_3^+ , $\text{CH}_3-\text{C}^+=\text{O}$ are electron deficient species. Hence, these are electrophiles.

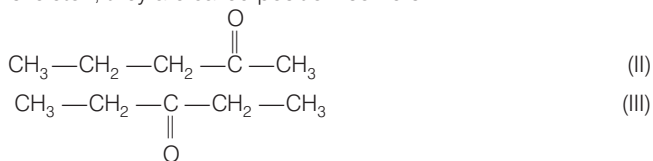
Direction (Q. Nos. 19-20) Consider the following four compounds.



Q. 19 Which of the following pairs are position isomers?

- (a) I and II (b) II and III (c) II and IV (d) III and IV

Ans. (b) When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton, they are called position isomers.



Here, position of $-\overset{\text{O}}{\parallel}\text{C}-$ varies. Thus, II and III are position isomers.

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

- (a) II and III (b) II and IV (c) I and IV (d) I and II

Ans. (a, c)

Two or more compounds having the same molecular formula but different functional groups are called functional isomers.

- I. Aldehyde II. Ketone
 III. Ketone IV. Aldehyde

Here, II and III; I and IV are not functional group isomers. Thus, option (a) and (c) are correct.

Q. 21 Nucleophile is a species that should have

- (a) a pair of electrons to donate (b) positive charge
(c) negative charge (d) electron deficient species

Ans. (a, c)

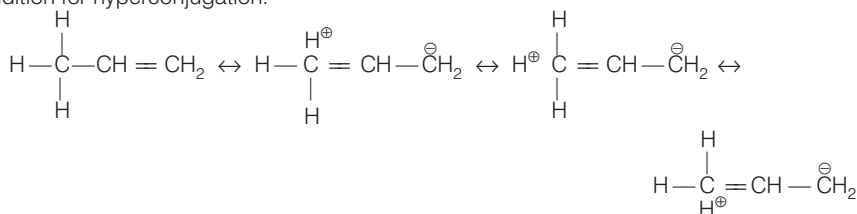
Nucleophile (nucleus-loving) is a chemical species that donates an electron pair to an electrophile (electron-loving). Hence, a nucleophile should have either a negative charge or an electron pair to donate. Thus, option (a) and (c) are correct.

Q. 22 Hyperconjugation involves delocalisation of

- (a) electrons of carbon-hydrogen σ bond of an alkyl group directly attached to an atom of unsaturated system.
(b) electrons of carbon-hydrogen σ bond of alkyl group directly attached to the positively charged carbon atom.
(c) π -electrons of carbon-carbon bond
(d) lone pair of electrons.

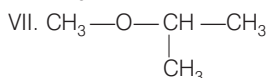
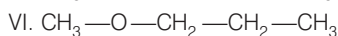
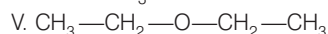
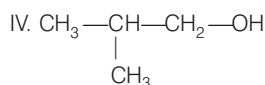
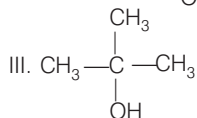
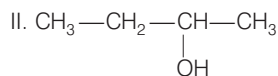
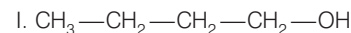
Ans. (a, b)

Hyperconjugation is the delocalisation of sigma electron also known as sigma-pi conjugation. Presence of α -H with respect to double bond, triple bond or carbon containing positive charge (in carbonium ion) or unpaired electron (in free radical) is a condition for hyperconjugation.



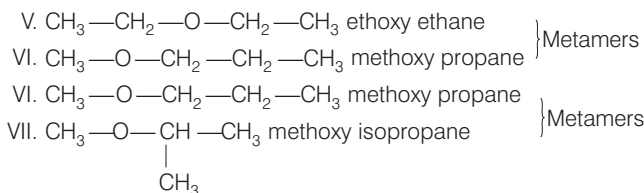
Short Answer Type Questions

Direction (Q. Nos 23 to 26) Consider structures I to VII.



Q. 23 Which of the above compounds form pairs of metamers?

Ans. Metamerism arises due to different alkyl chains on either side of the functional group in the molecule. In the given structures V and VI or VI and VII form a pair of metamers because they differ in carbon atoms on the either side of the functional group, *i.e.*, O-atom.

**Q. 24** Identify the pairs of compounds which are functional group isomers.

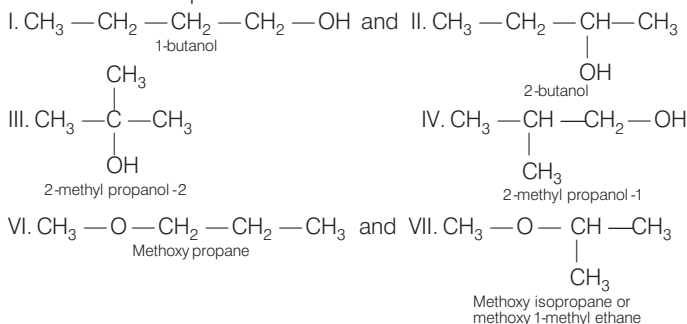
Ans. Two or more compounds having the same molecular formula but different functional groups are called functional isomers.

In the given structure I, II, III, IV represent alcohols as functional group, whereas V, VI, VII are ethers.

Hence, I and V, I and VI, I and VII, II and V, II and VI, II and VII, III and V, III and VI, III and VII, IV and V, IV and VI, IV and VII all are functional group isomers.

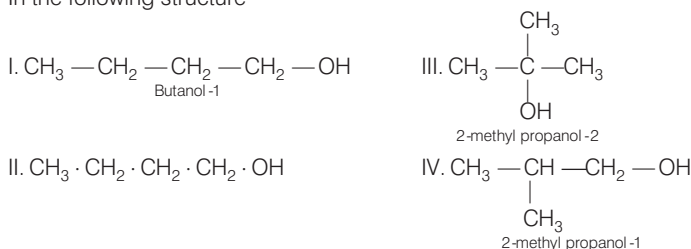
Q. 25 Identify the pairs of compounds that represents position isomerism.

Ans. When two or more compounds differ in position of substituent atom or functional group on the carbon skeleton, they are position isomers. In the given structures, I and II; III and IV, and VI and VII are position isomers.

**Q. 26** Identify the pairs of compounds that represents chain isomerism.

Ans. When two or more compounds have similar molecular formula but different skeletons, these are referred to as chain isomer.

In the following structure



Q. 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 ?

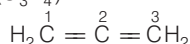
Thinking Process

Nitrogen, sulphur, halogens and phosphorous present in an organic compound are detected by Lassaigne's test. The elements in compound are converted from covalent to ionic form fused with sodium metal.

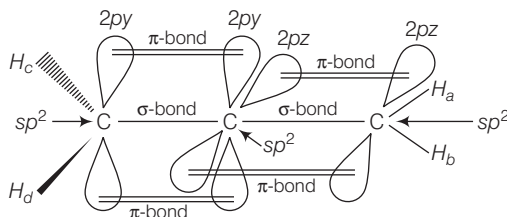
Ans. On adding dilute H_2SO_4 for testing halogens in an organic compound with AgNO_3 , white precipitate of Ag_2SO_4 is formed. This will interfere with the test of chlorine and this Ag_2SO_4 may be mistaken for white precipitate of chlorine as AgCl . Hence, dilute HNO_3 is used instead of dilute H_2SO_4 .

Q. 28 What is the hybridisation of each carbon in $\text{H}_2\text{C}=\text{C}=\text{CH}_2$?

Ans. The given structure is of allene (C_3H_4)



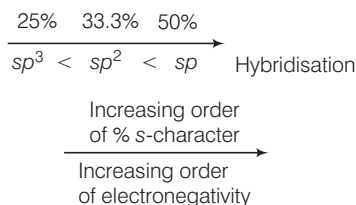
In allene, carbon atoms 1 and 3 are sp^2 -hybridised as each one of them is joined by a double bond. And, carbon atom 2 is sp -hybridised as it has two double bonds at each of its side. Therefore, the two π -bonds are perpendicular to each other, in allene, as shown below.



H_a and H_b lie in the plane of paper while H_c and H_d lie in a plane perpendicular to the plane of the paper. Hence, the allene molecule as a whole is non-planar.

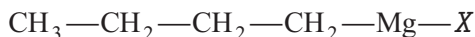
Q. 29 Explain, how is the electronegativity of carbon atoms related to their state of hybridisation in an organic compound?

Ans. Electronegativity of carbon atom, also depends on the hybridisation of the carbon atom. Since, s-electrons are more strongly attracted by the nucleus than p-electrons, thus, electronegativity increases with increase in s-character of the hybridised orbital i.e.,

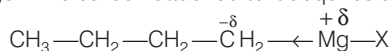


Thus, sp -hybridised carbon is the most electronegative carbon.

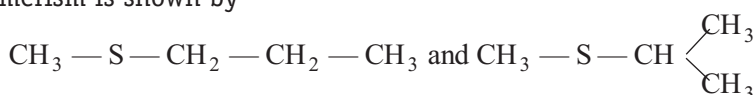
Q. 30 Show the polarisation of carbon-magnesium bond in the following structure.



Ans. Carbon (2.5) is more electronegative than magnesium (1.2) therefore, Mg acquires a partial positive charge while carbon attached to it acquires a partial negative charge.



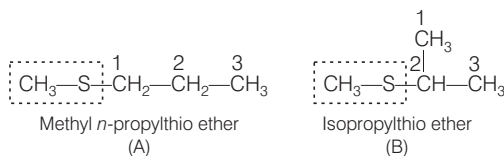
Q. 31 Compounds with same molecular formula but differing in their structures are said to be structural isomers. What type of structural isomerism is shown by



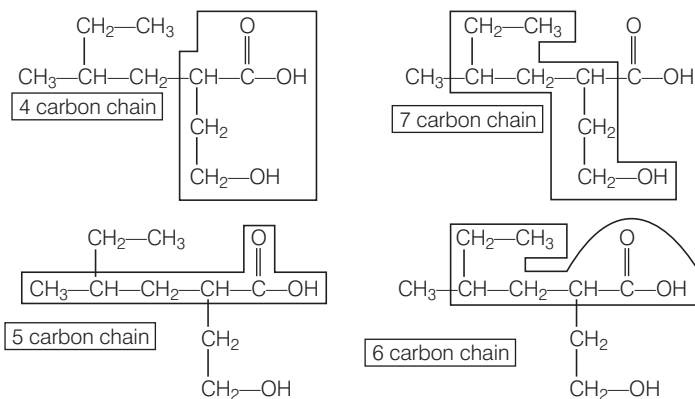
Ans. The two isomers which differ in the position of the functional group on the carbon skeleton are called position isomers and this phenomenon as position isomerism.

Thus, (A) and (B) may be regarded as position isomers and further they cannot be regarded as metamers since metamers are those isomers which have different number of carbon atoms on either side of the functional group.

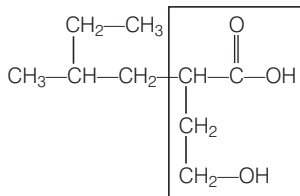
But here, the number of carbon atoms on either side of sulphur atom (functional group) is the same, i.e., 1 and 3.



Q. 32 Which of the following selected chains is correct to name the given compound according to IUPAC system?



Ans. Among the following given compounds, according to IUPAC, the longest carbon chain having maximum number of functional group is being selected.



Thus, carbon-chain containing 4-carbon atoms and which also includes both functional group will be selected. While the other three C-chains are incorrect since none of them contains both the functional groups.

Q. 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.

Ans. DNA and RNA have nitrogen in the heterocyclic rings. Nitrogen present in rings, azo and nitro groups cannot be converted into $(\text{NH}_4)_2\text{SO}_4$. That's why Kjeldahl method cannot be used for the estimation of nitrogen present in DNA and RNA.

Q. 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.

Ans. If a compound decomposes at its boiling point but is steam volatile, water-insoluble and stable at low pressure, steam distillation can be used for its purification. This technique is applied to separate substances which are steam volatile and immiscible with water.

Direction (Q. Nos. 35-38) *On the basis of information given below*

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

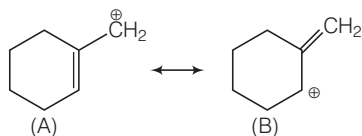
Q. 35 Draw the possible resonance structures for $\text{CH}_3-\ddot{\text{O}}^+-\text{CH}_2$ and predict which of the structures is more stable. Give reason for your answer.

Ans. The given carbocation has two resonance structures.

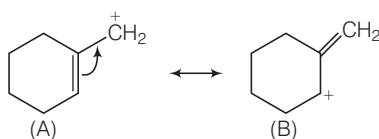


Structure (II) is more stable because both the carbon atoms and the oxygen atom have an octet of electrons.

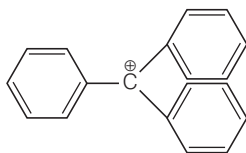
Q. 36 Which of the following ions is more stable? Use resonance to explain your answer.



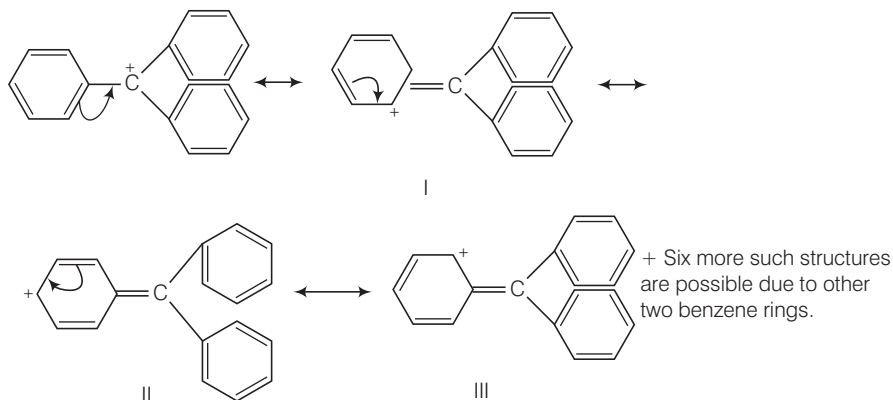
Ans. Carbocation (A) is more stable than carbocation (B). Carbocation (A) is more planar and hence is stabilised by resonance while carbocation (B) is non-planar and hence it does not undergo resonance. Further, double bond is more stable within the ring in comparison to outside the ring.



Q. 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.



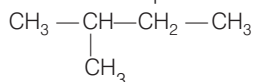
Ans. In triphenylmethyl cation, due to resonance, the positive charge can move at both the *o*- and *p*-position of each benzene ring. This is illustrated below



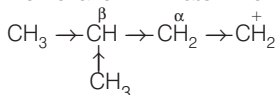
Since, there are three benzene rings, hence, there are, in all, nine resonance structures. Thus, triphenylmethyl cation is highly stable due to these nine resonance structures.

Q. 38 Write structures of various carbocations that can be obtained from 2-methylbutane. Arrange these carbocations in order of increasing stability.

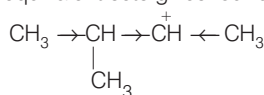
Ans. 2-methyl butane has four different sets of equivalent H-atoms.



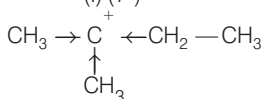
Removal of 1-1 atom from any of these equivalent sets gives four different carbocations.



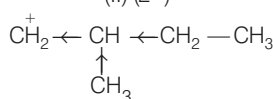
(I) (1°)



(II) (2°)

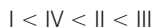


(III) (3°)



(IV) (1°)

Stability of carbocation decreases in the order $3^\circ > 2^\circ > 1^\circ$. So, III (3° carbocation) is most stable followed by II (2° carbocation). Out of I and IV (both are 1° carbocation) I has a CH_3 group at β -carbon while II has a CH_3 group at α -carbon. As +I-effect decreases with distance, hence IV is more stable than I. Therefore, the overall stability of these four carbocations increases in the order.



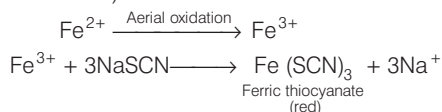
Q. 39 Three students, Manish, Ramesh and Rajni were determining the extra elements present in an organic compound given by their teacher. They prepared the Lassaigne's extract (L.E.) independently by the fusion of the compound with sodium metal. Then they added solid FeSO_4 and dilute sulphuric acid 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.

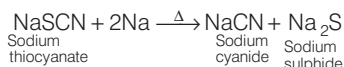
Ans. If the organic compound contains both N and S, then while fusion it may form either a mixture of sodium cyanide (NaCN) and sodium sulphide (Na_2S) or sodium thiocyanate (NaSCN) depending on the amount of Na metal used.

If Less sodium metal is used, only NaSCN is obtained.

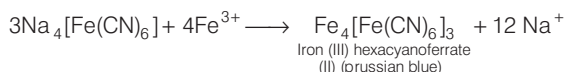
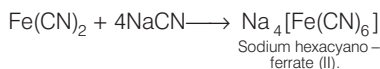
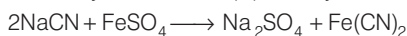
This then gives red colour on reacting with Fe^{3+} ions (produced by oxidation of Fe^{2+} ions while preparing Lassaigne's extract) due to the formation of ferric thiocyanate.



In case, excess of sodium metal is used, the initially formed sodium thiocyanate decomposes as follows:

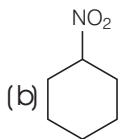
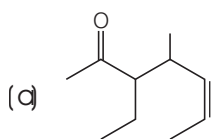


This NaCN then reacts with FeSO_4 , Fe^{3+} ions and NaCN, it gives prussian blue colour due to the formation of ferric ferrocyanide or iron (III) hexacyanoferrate (II).

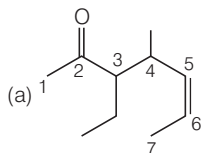


On the basis of above results, it is clear that Ramesh used less sodium and hence NaSCN formed in the Lassaigne's extract which gave red colouration due to $\text{Fe}(\text{SCN})_3$ formation while Manish and Rajni used excess sodium and hence NaCN formed in the Lassaigne's extract which gave prussian blue colour of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

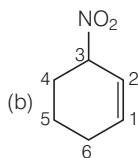
Q. 40 Name the compounds whose line formulae are given below.



Ans.



3-ethyl-4-methylhept-5-en-2-one (C-atoms of the longest possible chain are numbered in such a way that the functional group, $>\text{C}=\text{O}$, gets the lowest possible locant)

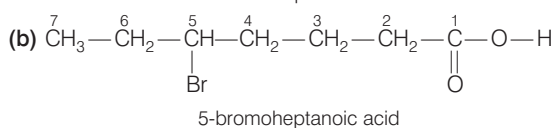
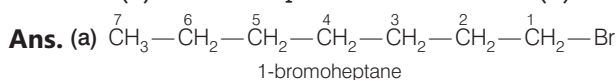


3-nitrocyclohex-1-en (C-atoms of the ring are numbered in such a manner that double bond gets the lowest possible locant followed by the $-\text{NO}_2$ group)

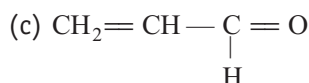
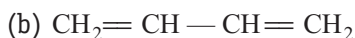
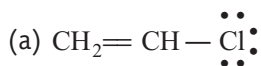
Q. 41 Write structural formulae for compounds named as

(a) 1-bromoheptane

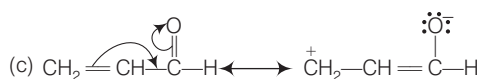
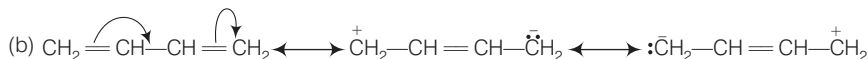
(b) 5-bromoheptanoic acid



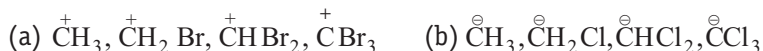
Q. 42 Draw the resonance structures of the following compounds.



Ans.



Q. 43 Identify the most stable species in the following set of ions giving reasons



Ans. (a) CH_3^+ is the most stable species because the replacement of H by Br increases positive charge ($-I$ -effect) on carbon atom and destabilises the species and, more the number of Br-atoms, less stable is the species.

(b) CCl_3^- is the most stable species because on replacing H by Cl, negative charge on carbon is dispersed due to $-I$ -effect of Cl and thus get reduced and species is stabilised. Further, more the number of Cl atoms, more is the dispersal of the negative charge and hence more stable is the species.

Q. 44 Give three points of differences between inductive effect and resonance effect.

Ans. Difference between inductive effect and resonance effect is as follows

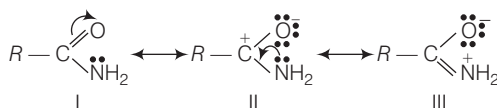
Inductive effect	Resonance effect
Inductive effect involves σ – electrons displacement and occurs only in saturated compounds.	It involves π – electrons or lone pair of electrons and occurs only in unsaturated and conjugated system.
Inductive effect can move upto 3 – carbon atoms.	It is applicable all along the length of conjugated system.
In inductive effect, there is a slight displacement of electrons and thus only partial positive and negative charges appear.	In resonance effect, there is complete transfer of electrons and thus full positive and negative charges appear.

Q. 45 Which of the following compounds will not exist as resonance hybrid. Give reason for your answer.

- (a) CH_3OH
(b) $R-\text{CONH}_2$
(c) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{NH}_2$

Ans. (a) CH_3OH As it lacks π -electrons hence it will not exist as resonance hybrid.

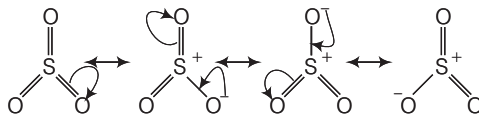
(b) $R-\text{CONH}_2$ Due to the presence of n -electrons on N and π -electrons on $\text{C}=\text{O}$ bond, hence amide can be represented as a resonance hybrid of the following three resonating structures.



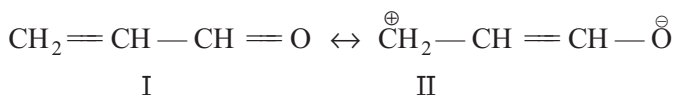
(c) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{NH}_2$ As the lone pair of electrons on the N-atom is not conjugated with the π -electrons of the double bond, thus, resonance is not possible and hence no resonance hybrid will exist.

Q. 46 Why does SO_3 act as an electrophile?

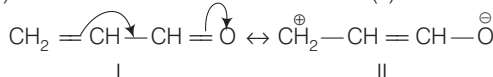
Ans. Three highly electronegative oxygen atoms are attached to sulphur atom in SO_3 which makes sulphur atom electron-deficient. Further, due to resonance, sulphur acquires positive charge. Both these factors, make SO_3 an electrophile.



Q. 47 Resonance structures of propenal are given below. Which of these resonating structures is more stable? Give reason for your answer.



Ans. The structure having more covalent bonds in a resonating structure, has more stability. Further, there is charge separation in structure (II) and the terminal carbon has only a sextet of electrons in (II). These two factors makes structure (II) less stable.



Hence, I > II in terms of stability.

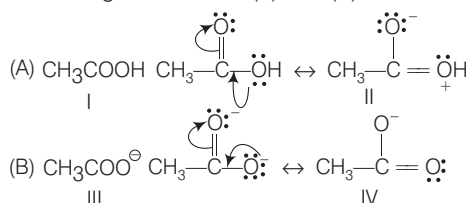
Q. 48 By mistake, an alcohol (boiling point 97°C) was mixed with a hydrocarbon (boiling point 68°C). Suggest a suitable method to separate the two compounds. Explain the reason for your choice.

Ans. The difference in boiling point of two liquids is more than 20°C . Hence, simple distillation can be used and since at the boiling point of low boiling liquid, the vapours would consist entirely of only low boiling liquid without any contamination of vapours of high boiling liquid and *vice-versa*. Thus, both the liquids can be distilled without any decomposition.

Q. 49 Which of the two structures (A) and (B) given below is more stabilised by resonance.

Explain CH_3COOH (A) and $\text{CH}_3\text{COO}^\ominus$ (B)

Ans. Resonating structures of (A) and (B) are as follows



Structure (II) is less stable than structure (I) because it carries separation of positive and negative charges. Therefore, contribution of structure (II) is less than that of (I) towards the resonance hybrid of compound (A), i.e., CH_3COOH . On the contrary, structure (III) and (IV) are of equal energy and hence contribute equally towards the resonance hybrid of compound (B). Therefore, structure (B) is more stable than structure (A) i.e., $\text{CH}_3\text{COO}^\ominus$.

Matching The Columns

Q. 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
A. Two solids which have different solubilities in a solvent and which do not undergo reaction when dissolved in it	1. Steam distillation
B. Liquid that decomposes at its boiling point	2. Fractional distillation
C. Steam volatile liquid	3. Simple distillation
D. Two liquids which have boiling points close to each other	4. Distillation under reduced pressure
E. Two liquids with large difference in boiling points.	5. Crystallisation

Ans. A. $\rightarrow$ (5) B. $\rightarrow$ (4) C. $\rightarrow$ (1) D. $\rightarrow$ (2) E. $\rightarrow$ (3)

Column I	Column II
A. Two solids which have different solubilities in a solvent and which do not undergo reaction when dissolved in it	Crystallisation
B. Liquid that decomposes at its boiling point	Distillation under reduced pressure
C. Steam volatile liquid	Steam distillation
D. Two liquids which have boiling points close to each other.	Fractional distillation
E. Two liquids with large difference in boiling points.	Simple distillation

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

Column I	Column II
A. Carbocation	1. Cyclohexane and 1-hexene
B. Nucleophile	2. Conjugation of electrons of C—H σ bond with empty p -orbital present at adjacent positively charged carbon
C. Hyperconjugation	3. sp^2 hybridised carbon with empty p -orbital
D. Isomers	4. Ethyne
E. sp -hybridisation	5. Species that can receive a pair of electrons
F. Electrophile	6. Species that can supply a pair of electrons.

Ans. A. $\rightarrow$ (3) B. $\rightarrow$ (6) C. $\rightarrow$ (2) D. $\rightarrow$ (1) E. $\rightarrow$ (4) F. $\rightarrow$ (5)

Column I	Column II	Explanation
A. Carbocation	sp^2 -hybridised carbon with empty p -orbital	H_3C^+ is carbocation. Loss of e^- makes its p -orbitals empty (sp^2 -hybridised carbon)
B. Nucleophile	Species that can supply a pair of electron	Nucleus loving <i>i.e.</i> , having negative charge or excess of electrons
C. Hyperconjugation	Conjugation of electrons of C—H σ bond with empty p -orbital present at adjacent positively charged carbon	
D. Isomers	Cyclohexane and 1-hexene	Same molecular formula but different structures
E. sp -hybridisation	Ethyne	$HC \equiv CH$ (sp -hybridisation)
F. Electrophile	Species that receive a pair of electron	Electron loving <i>i.e.</i> , positive charge or lack of electrons

Q. 52 Match Column I with column II.

Column I	Column II
A. Dumas method	1. $AgNO_3$
B. Kjeldahl's method	2. Silica gel
C. Carius method	3. Nitrogen gel
D. Chromatography	4. Free radicals
E. Homolysis	5. Ammonium sulphate

Ans. A. → (3) B. → (5) C. → (1) D. → (2) E. → (4)

	Column I	Column II	Explanation
A.	Dumas method	Nitrogen gel	Used for N containing compounds
B.	Kjeldahl's method	Ammonium sulphate	Nitrogen converts to ammonium sulphate
C.	Carius method	AgNO ₃	Compound is heated in presence of AgNO ₃
D.	Chromatography	Silica gel	Adsorbent used is silica gel
E.	Homolysis	Free radical	Free radicals are formed by homolytic fission

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

	Column I	Column II
A.	Free radical	1. Trigonal planar
B.	Carbocation	2. Pyramidal
C.	Carbanion	3. Linear

Ans. A. → (1) B. → (1) C. → (2)

	Column I	Column II	Explanation
A.	Free radical	Trigonal planar	Free radicals are formed by homolytic fission e.g., $\dot{\text{C}}\text{H}_3$ hybridisation sp^2
B.	Carbocation	Trigonal planar	Formed by heterolytic fission when carbon is attached to a more electronegative atom e.g., $\overset{+}{\text{C}}\text{H}_3$ hybridisation sp^2
C.	Carbanion	Pyramidal	Formed by heterolytic fission when carbon is attached to more electropositive atom e.g., CH_3^- hybridisation sp^3

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

	Column I	Column II
A.	$\text{CH}_3 - \overset{\cdot\cdot}{\underset{\cdot\cdot}{\text{O}}} - \overset{\oplus}{\text{C}}\text{H} - \text{CH}_3$	1. Stable due to resonance
B.	$\text{F}_3 - \text{C}^{\oplus}$	2. Destabilised due to inductive effect
C.	$\text{CH}_3 - \overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}^{\ominus}}}$	3. Stabilised by hyperconjugation
D.	$\text{CH}_3 - \overset{\oplus}{\text{C}}\text{H} - \text{CH}_3$	4. A secondary carbocation

Ans. A. $\rightarrow$ (1, 2) B. $\rightarrow$ (2) C. $\rightarrow$ (2) D. $\rightarrow$ (3, 4)

Column I	Column II	Explanation
A. $\text{CH}_3 - \ddot{\text{O}} - \overset{+}{\text{CH}} - \text{CH}_3$	Stable due to resonance Destabilised due to inductive effect	
B. $\text{F}_3 - \text{C}^+$	Destabilised due to inductive effect	- / effect of F creates electron deficiency at carbon C^+
C. $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C}^\ominus \\ \\ \text{CH}_3 \end{array}$	Destabilised due to inductive effect	+ / effect of CH_3 increases electron density at carbon C^-
D. $\text{CH}_3 - \overset{\oplus}{\text{CH}} - \text{CH}_3$	A secondary carbocation stabilised due to hyperconjugation	$\overset{+}{\text{CH}}$ is attached to two carbon. It can also be stabilised by hyperconjugation.

Assertion and Reason

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 in each question.

Q. 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.

- (a) Both A and R are correct and R is the correct explanation of A
- (b) Both A and R are correct but R is not the correct explanation of A
- (c) Both A and R are not correct
- (d) A is not correct but R is correct

Ans. (a) Both A and R are correct and R is the correct explanation of A.

Simple distillation can be used to separate a mixture of two liquids which do not react and have boiling point difference of more than 20°C . Hence, a mixture of propan-1-ol and propanone can be separated.

Q. 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.

- (a) Both A and R are correct and R is the correct explanation of A
- (b) Both A and R are correct but R is not the correct explanation of A
- (c) Both A and R are not correct
- (d) A is not correct but R is correct

💡 Thinking Process

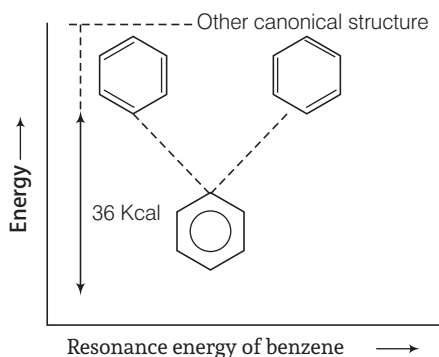
The polarity produced in the molecule by the interaction of two π - bonds or between π - bond and lone pair of electrons present on an adjacent atom is resonance.

Ans. (d) A is not correct but R is correct.

Resonance hybrids are always more stable than any of the canonical structures would be, if they existed. The delocalisation of the electrons lowers the orbital energies, imparting stability. The gain in stability of the resonance hybrid over the most stable of the canonical structure is called resonance energy.

A canonical structure that is lower in energy makes a relating greater contribution to resonance hybrid.

Thus, the correct assertion will be energy of resonance hybrid is equal to the sum of energies of all canonical forms in proportion of their contribution towards the resonance hybrid.

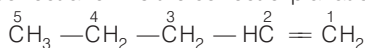


Q. 57 Assertion (A) Pent-1-ene and pent-2-ene are position isomers.

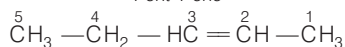
Reason (R) Position isomers differ in the position of functional group or a substituent.

- (a) Both A and R are correct and R is the correct explanation of A
- (b) Both A and R are correct but R is not the correct explanation of A
- (c) Both A and R are not correct
- (d) A is not correct but R is correct

Ans. (a) Both A and R are correct and R is the correct explanation of A.



Pent-1-ene



Pent-2-ene

When two or more compounds differ in the position of substituent atom or functional group on the carbon skeleton then it is position isomerism. Double bond is a functional group whose position varies.

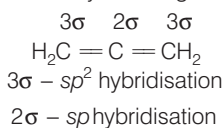
Q. 58 Assertion (A) All the carbon atoms in $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ are sp^2 -hybridised.

Reason (R) In this molecule all the carbon atoms are attached to each other by double bonds.

- (a) Both A and R are correct and R is the correct explanation of A
- (b) Both A and R are correct but R is not the correct explanation of A
- (c) Both A and R are not correct
- (d) A is not correct but R is correct

Ans. (d) A is not correct but R is correct.

Hybridisation can be determined by counting σ -bond



Correct assertion In $\text{H}_2\text{C}=\text{C}=\text{CH}_2$, the central carbon is sp -hybridised whereas the terminal carbons are sp^2 -hybridised.

Q. 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.

- (a) Both A and R are correct and R is the correct explanation of A
- (b) Both A and R are correct but R is not the correct explanation of A
- (c) Both A and R are not correct
- (d) A is not correct but R is correct

Ans. (c) Both A and R are correct but R is not the correct explanation of A.

S present in an organic compound can be estimated quantitatively by Carius method. In this method, a known weight of organic compound is heated with fuming HNO_3 , S present in it gets converted into H_2SO_4 . On adding BaCl_2 , H_2SO_4 gets precipitated as BaSO_4 which may be of light yellow or white in colour.

If light yellow colour is obtained, it means some impurities are present. It is then filtered, washed, purified and then dried and finally pure BaSO_4 of white colour is obtained.

Q. 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.

- (a) Both A and R are correct and R is the correct explanation of A
- (b) Both A and R are correct but R is not the correct explanation of A
- (c) Both A and R are not correct
- (d) A is not correct but R is correct

Ans. (a) Both A and R are correct and R is the correct explanation of A.

In paper chromatography, a chromatography paper is used. It contains water in it, which acts as the stationary phase. A strip of chromatography paper spotted at the base with ink is suspended in a suitable solvent. Solvent acts as the mobile phase.

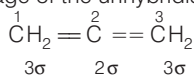
The solvent rises up the paper by capillary action and flows over the spot. The paper selectively retains different components according to their differing partition in two phases.

Hence, components of ink will migrate at different rates and are separated.

Long Answer Type Questions

Q. 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?

Ans. Hybridisation is mixing of atomic orbitals to form new hybrid orbitals. The new orbitals have the same total electron capacity as the old ones. The properties and energies of the new hybridised orbitals are an average of the unhybridised orbitals.

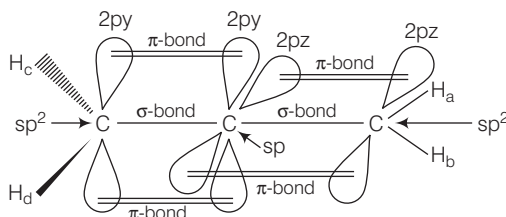


Hybridisation can be found by counting number of σ – bonds around the carbon atom.

$3\sigma = sp^2$ -hybridisation

$2\sigma = sp$ -hybridisation

In allene, carbon atoms 1 and 3 are sp^2 -hybridised as each one of them is joined by a double bond. And, carbon atom 2 is sp -hybridised as it has two double bonds at each of its side. Therefore, the two π -bonds are perpendicular to each other, in allene, as shown below.



H_a and H_b lie in the plane of paper while H_c and H_d lie in a plane perpendicular to the plane of the paper. Hence, the allene molecule as a whole is non-planar.

Q. 62 Benzoic acid is an 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?

Ans. Benzoic acid can be purified by hot water because of following characteristics

- Benzoic acid is more soluble in hot water and less soluble in cold water.
- Impurities present in benzoic acid are either insoluble in water or more soluble in water to such an extent that they remain in solution as the mother liquor upon crystallisation.

Q. 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.

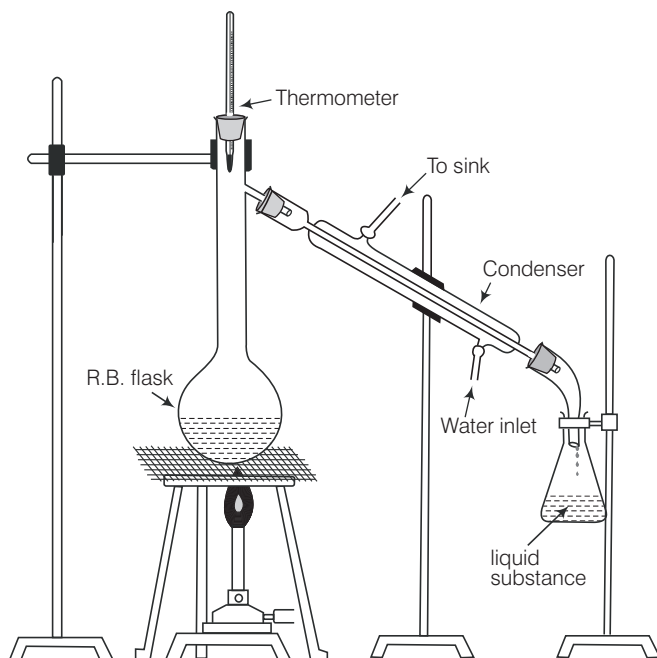
Ans. If the difference in boiling points of two liquids is not much, fractional distillation is used to separate them. In this technique, fractionating column is fitted over the mouth of the round bottom flask.

When vapours of a liquid mixture are passed through a fractionating column, the vapours of the low boiling liquid (A) will move up while those of the high boiling liquid will condense and fall back into the flask. Therefore, liquid (A) with low boiling point will distill first.

Q. 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 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.

Ans. The boiling points are in the order of $A > C > B$.

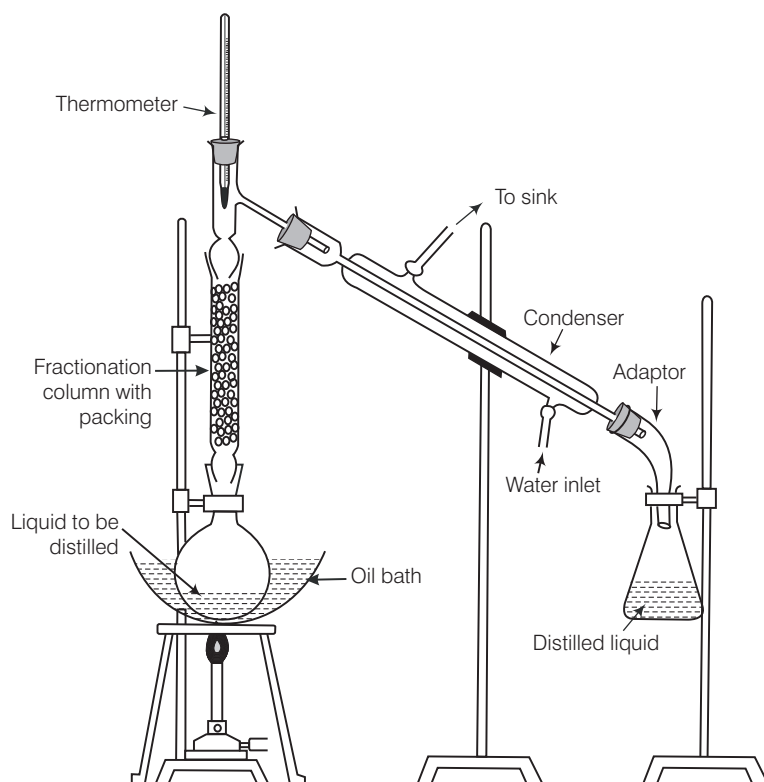
Liquid A can be separated from rest of the mixture of liquid B and C by simple distillation B and C can be separated by fractional distillation.



Simple distillation

The vapours of a substance formed are condensed and the liquid is collected in conical flask.

Due to the fact that boiling point of A is much higher than those of liquids B and C. This can be done by using apparatus as shown in figure (I). As the boiling points of liquid (B) and (C) are quite close but much lower than that of A, hence, mixture of liquids (B) and (C) will distill together leaving behind liquid (A).



Fractional distillation

The vapours of lower boiling fraction reach the top of the column first followed by vapours of higher boiling fractions.

On further heating liquid (A) will distill over. Now, place the mixtures of liquid (B) and (C) in a flask fitted with fractionating column as illustrated in figure (II). On fractional distillation, liquid (B) will distill over first and then liquid (C) as former possess lower boiling point than that of later.

Q. 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?

Ans. If the difference in boiling points of two liquids is not much, fractional distillation is used. The technique is, vapors of liquid mixture are passed through a fractionating column before condensation, fitted over the mouth of the round bottom flask.

Vapours of the liquid with higher boiling point condense before the vapours of the liquid with lower boiling point. The vapours rising up in the fractionating column become rich in more volatile component. Fractionating column provides many surfaces for heat exchange between ascending vapours and descending condensed liquid. The vapours become richer in low boiling component.



One of technological application of fractional distillation is to separate different fraction of crude oil in petroleum industry into various fractions like gasoline, kerosene oil, diesel oil, lubricating oil, etc.

Another application is the separation of acetone and methanol from pyroligneous acid obtained by destructive distillation of wood.

Q. 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 ?

Ans. In steam distillation, the distilling mixture consists of steam and the vapour of organic substance. In steam distillation, the liquid boils when the sum of the vapour pressure of the organic substance (p_1) and that of steam (p_2) becomes equal to the atmospheric pressure (p) at the temperature of distillation.

$$p = p_1 + p_2 \text{ or } p_1 = p - p_2$$

Since, the vapour pressure of the organic substance is lower than p , it vaporises below its normal boiling point without decomposition e.g., aniline which normally boils at 457 K can be distilled at 371.5 K by this process.