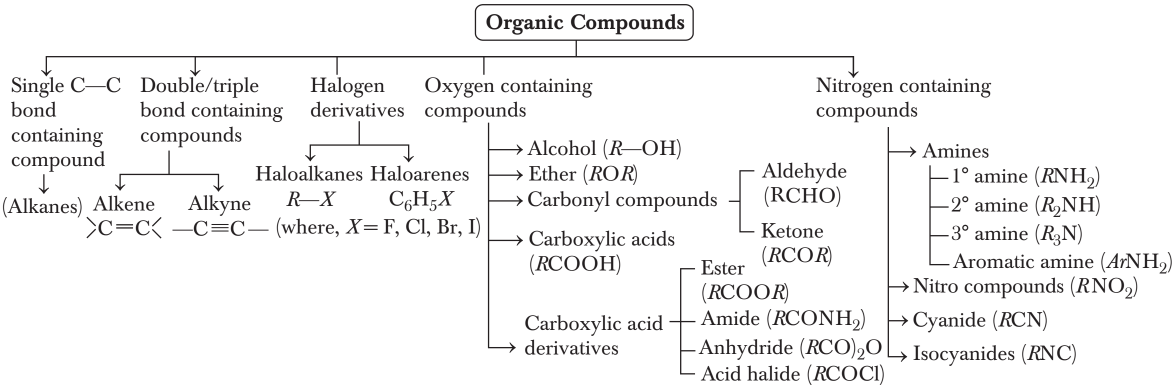
07

Organic Chemistry : Some Basic Principles and Techniques

Quick Revision

1. **Classification** On the basis of functional groups, organic compounds are classified into following families or homologous series:



2. **Nomenclature of Organic Compounds** Steps involved in IUPAC nomenclature are as follows:

***Step* 1** Locate the longest chain with as many possible secondary functional groups along with multiple bonds.

***Step* 2** Select the root word corresponding to the length of longest possible chain.

***Step* 3** Number the longest possible chain according to the rules to give an identification number to each C-atom of longest possible chain.

***Step* 4** Add suitable prefixes and suffixes along with numerals to indicate the number and position of each side chain substituent or functional group present in compound.

Hence, according to these rules the IUPAC name of a compound can be written as :

Prefix	+ Root word	+ Suffix
Tells us about the branches or substituents except in the case of multiple bonds.	Tells us about the length of longest possible chain.	Tells us about the principal functional groups and multiple bonds mostly except in case of halogens.

3. **Fission of a Covalent Bond**

(*i*) **Heterolytic cleavage or heterolysis**

$$X—Y \xrightarrow{\text{Heterolysis}} X^+ + Y^-$$

(when X is less electronegative than Y)

$$X—Y \xrightarrow{\text{Heterolysis}} X^- + Y^+$$

(when Y is less electronegative than X)

Heterolytic cleavage results in formation of two types of species. These are :

(a) **Carbocation or carbonium ion** If the carbon has sextet of electrons and a positive charge, then the species is called carbocation (earlier called carbonium ion), e.g. CH_3^+ (methyl carbonium ion).

It is trigonal planar with C-atom carrying-positive charge is sp^3-hybridised.

The order of stability of carbocations is

$$\overset{+}{C}H_3 < CH_3\overset{+}{C}H_2 < (CH_3)_2\overset{+}{C}H < (CH_3)_3C^+$$

or methyl carbocation < 1° < 2° < 3°.

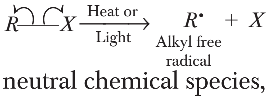
(b) **Carbanion** If the carbon of the obtained species is negatively charged and have octet of electrons in its valence shell, then the species is called carbanion. It is pyramidal in shape with-atom carrying negative charge is sp^3-hybridised.

The order of stability of carbanions is :

$$(C_6H_5)_3\overset{-}{C} > (C_6H_5)_2CH^- > C_6H_5\overset{-}{C}H_2$$

$$> \text{allyl carbanions} > \overset{-}{C}H_3 > (1° > 2° > 3° \text{ carbanions})$$

(ii) **Homolytic cleavage or homolysis** This cleavage involves movement of only one electron, which is represented by half headed (fish hook) curved arrow.

e.g. 

$$R—X \xrightarrow[\text{Light}]{\text{Heat or}} \underset{\text{Alkyl free radical}}{R^\bullet} + X^\bullet$$

The neutral chemical species, thus formed are called the **free radicals**. It is a planar species in which C atom bearing odd electron is sp^2-hydridised. Like carbocations, the order of stability of alkyl free radicals is

$$\underset{\substack{\text{Methyl}\\\text{free radical}\\(1°)}}{\dot{C}H_3} < \underset{\substack{\text{Ethyl}\\\text{free radical}\\(1°)}}{\dot{C}H_2CH_3} < \underset{\substack{\text{Isopropyl}\\\text{free radical}\\(2°)}}{\dot{C}H(CH_3)_2} < \underset{\substack{\textit{tert}\text{-butyl}\\\text{free radical}\\(3°)}}{\dot{C}(CH_3)_3}$$

4. **Nucleophiles and Electrophiles**

(i) **Nucleophiles or nucleophilic reagents** An electron rich species having a lone pair of electrons or is negatively charged species which attacks on electron dificient areas is called a nucleophile ($Nu\mathbf{:}$). e.g.

Negatively charged species like H^-, Cl^-, Br^-, I^-, carbanions, $\overset{-}{O}H$, ^-OR, $\overset{-}{S}R$, CN^-. Nucleophiles can also be seen in the form of neutral molecules with lone pair. e.g.

$$H_2\ddot{\underset{\cdot\cdot}{O}},\ \ddot{N}H_3,\ R\ddot{N}H_2,\ R\ddot{\underset{\cdot\cdot}{O}}H,\ R\ddot{\underset{\cdot\cdot}{S}}H, \text{ etc.}$$

(ii) **Electrophiles or electrophilic reagents** An electrophile is defined as electron deficient species which attacks on electron rich areas. e.g. : Positively charged species like H^+, Cl^+, Br^+, I^+, NO_2^+, SO_3^+ and carbocations.

The electrophiles can also be seen in the form of neutral molecules, e.g. carbenes ($\mathbf{:}CR_2$), nitrenes ($\ddot{N}R$), BF_3, etc.

5. **Inductive Effect** (*I*-effect)

In a polar covalent bond, the electrons are shifted to the more electronegative atom and hence, a polarity is developed in the bond. e.g. In a chain of carbon atoms having C—Cl bond, the C attached directly to the Cl-atom because of its less electronegativity acquires some positive charge (δ^+).

$$\overset{\delta\delta\delta^+}{\underset{3}{C}}H_3 — \overset{\delta\delta^+}{\underset{2}{C}}H_2 \rightarrow— \overset{\delta^+}{\underset{1}{C}}H_2 \rightarrow— \overset{\delta^-}{Cl}$$

This induction of polarity due to presence of polar bold in an organic molecule is called inductive effect.

Types of Inductive Effect

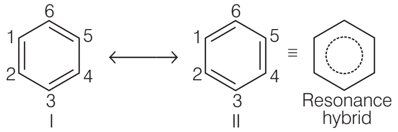
(*i*) **Negative inductive effect** Atoms or groups having greater electron affinity than hydrogen are said to have – ***I*-effect** (electron attracting). Some of the – *I*-effect producing groups in decreasing order of inductive effect are

$$—R_3\overset{+}{N} > —\overset{+}{N}H_3 > —NO_2 > —CN >$$
$$—SO_3H > —CHO > —CO > —COOH >$$
$$—COCl > —COOR > —CONH_2 > —F >$$
$$—Cl > —Br > —I > —OH > —OR >$$
$$—NH_2 > —C_6H_5 > —H$$

($-I$ power in decreasing order with respect to H.)

(ii) **Positive inductive effect** Atoms or groups having lower electron affinity than hydrogen are said to have + *I* effect (electron withdrawing).
The order of +*I*-effect of some groups is as follows : 3° > 2° > 1° or CH_3.

6. **Resonance Structure**
These structures are hypothetical and individually don't represent any real molecule. Benzene is a resonance hybrid of following two canonical forms

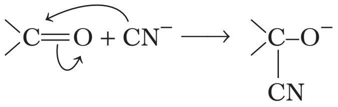


7. **Resonance Effect** (*R*-effect)
The polarity developed with in a molecule due to interaction of two π-bond or of a π-bond with the lone pair of electrons present on a fix atom is called resonance effect.
   (i) **Positive resonance effect** (+ *R*-effect)
   When the electrons move away from the atom or substituent group attached to the conjugated system, the effect is called positive resonance effect.In this effect, electron density increases at certain places. e.g. Groups like halogen, —OH, —O*R*,—OCO*R*,—NH_2, —NH*R*, —NR_2 show + *R*-effect.
   (ii) **Negative resonance effect** (–*R*-effect)
   When the electrons are transferred towards the atom or substituent group attached to the conjugated system, the effect is called negative resonance effect.
   e.g. —C═O, — CN and —NO_2 show –*R*-effect.

8. **Electromeric Effect** (*E*-effect)
The polarity developed due to complete transfer of a shared pair of π-electrons to any of the atoms linked directly to the multiple bond in the presence of an attacking reagent is called the electromeric effect.
   (i) **Positive electromeric effect** (+ *E*-effect)
   If the electrons of the π-bond are transferred to that atom of the double bond to which the reagent gets finally attached, then that effect is known as + *E*-effect. e.g.

$$CH_3 — CH{=}CH_2 + H^+ \longrightarrow CH_3—\overset{+}{C}H—CH_3$$

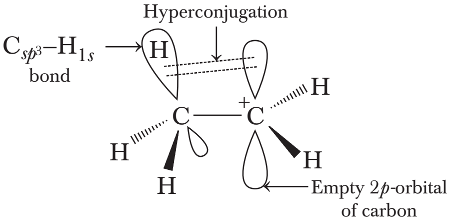
   (ii) **Negative electromeric effect** (– *E*-effect)
   If the electrons of the double (π) bond are transferred to an atom of the double bond other than the one to which the reagent gets finally attached, then that effect is known as – *E*-effect.



$$>C{=}O + CN^- \longrightarrow >\underset{|\atop CN}{C}–O^-$$

9. **Hyperconjugation**
The stabilising interaction that involves delocalisation of σ-electrons of C—H bond of an alkyl group linked directly to an atom of unsaturated system or to an atom having unshared *p*-orbital, is called hyperconjugation.

$CH_3\overset{+}{C}H_2$ has empty *p*-orbital, with which one of the C—H bonds of the methyl group align in its plane and thus, the electrons of the C—H bonds can be delocalised into the empty *p*-orbital as shown below.



Orbital diagram showing hyperconjugation in ethyl cation

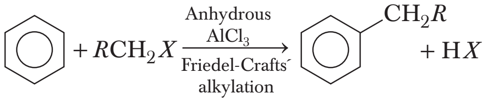
10. **Types of Organic Reactions and Mechanism**
The organic reactions can be categorised into following five categories:
   (i) **Substitution reactions**

$$R—CH_3 + X_2 \xrightarrow[\text{520-670 K}]{h\nu \text{ or}} \underbrace{R–CH_2\overset{\text{Substituent}}{\boxed{X}}}_{\text{Substitution product}} + HX$$

   These are further classified as follows :
   (a) **Free-radical substitution** The reaction brought by free radicals are called free radical substitutions. e.g. Halogenation of alkenes.

$$\underset{\text{Methane}}{CH_4} + Cl_2 \xrightarrow[HCl]{h\nu} \underset{\text{Chloromethane}}{CH_3Cl}$$

(b) **Electrophilic substitution reactions**

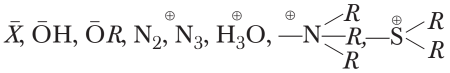


(c) **Nucleophilic substitution reactions** These are usually written as S_N (S-substitution, N-nucleophile) and are of two types, i.e. unimolecular (shown as S_N1) and bimolecular (shown as S_N2).

These reactions are generally seen in alkyl halides and alcohols.

e.g. $RX + KOH(aq) \longrightarrow ROH + KX$

(ii) **Elimination reactions** An elimination reaction is one that involves the loss of two atoms or groups of atoms from the same or adjacent atoms of a substance leading to the formation of a multiple (double or triple) bond.
Elimination reaction is given by those compounds which have a nucleophile as a leaving group, i.e.



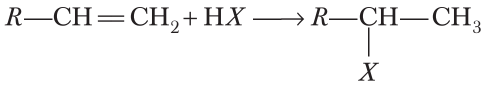
$$\bar{X}, \bar{O}H, \bar{O}R, N_2, \overset{\oplus}{N}_3, H_3\overset{\oplus}{O}, -\overset{\oplus}{N}R_3, -\overset{\oplus}{S}R_2$$

Elimination reactions are of two types :
(a) α-elimination reactions
(b) β-elimination reactions

e.g. $\underset{\text{2-methylpropan-2-ol}}{(CH_3)_3COH} \xrightarrow[\text{(ii) Heat}]{\text{(i) } H_3O^+} \underset{\text{2-methyl propene}}{(CH_3)_2C{=}CH_2} + H_2O$

(iii) **Addition reactions** Reactions which involve combination between two reacting molecules to give a single molecule of the product are called addition reactions.

Such reactions are of typical compounds containing multiple bonds.



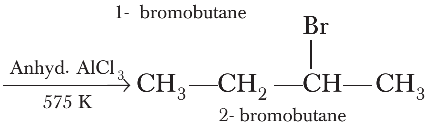
$$R{-}CH{=}CH_2 + HX \longrightarrow R{-}\underset{\displaystyle X}{\underset{|}{C}H}{-}CH_3$$

(iv) **Addition-elimination reactions** These reactions involve addition of two molecules with elimination of smaller molecules like H_2O, e.g. esterification.

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Ethanoic acid}}{CH_3COOH} \overset{H^+}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

(v) **Rearrangement reactions** These reaction involve the migration of an atom or a group from one atom to another within the same molecule.

e.g. $\underset{\text{1- bromobutane}}{CH_3{-}CH_2{-}CH_2{-}CH_2{-}Br}$



$$\xrightarrow[\text{575 K}]{\text{Anhyd. } AlCl_3} \underset{\text{2- bromobutane}}{CH_3{-}CH_2{-}\overset{\displaystyle Br}{\overset{|}{C}H}{-}CH_3}$$

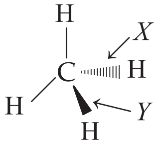
Objective Questions

Multiple Choose Questions

1. Which of the following is a correct representation of condensed formula for $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$?

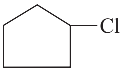
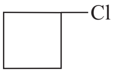
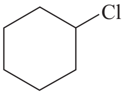
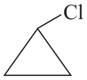
(a) $HO(CH_2)_2CHCH_3CH(CH_3)_2$
(b) $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$
(c) $HOCH_2CHCH_3CH(CH_3)_2$
(d) None of the above

2. Consider the following methane molecule on paper.

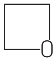
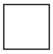
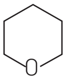
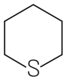


Here, X and Y are respectively
(a) dashed wedge, solid wedge
(b) solid wedge, dashed wedge
(c) both are bonds in the plane of paper
(d) both are dashed wedge

3. In cyclic compounds, the bond-line formula for chlorocyclohexane is represented by which of the following representations?

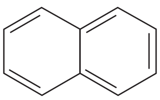
(a) 
(b) 
(c) 
(d) 

4. Which of the following is a homocyclic alicyclic compound ?

(a) 
(b) 
(c) 
(d) 

5. Which of the following compounds is/are heterocyclic aromatic compound?

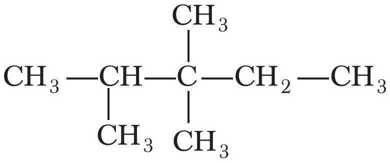
(a) Furan
(b) Thiophene
(c) Pyridine
(d) All of these

6. Which type of compound is shown by the following structure  ?

(Naphthalene)

(a) Alicyclic compound
(b) Benzenoid aromatic compound
(c) Non-benzenoid aromatic compound
(d) Acyclic compound

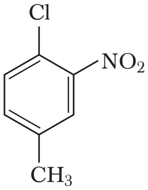
7. In the following compounds, number of 1° (primary) carbons is



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

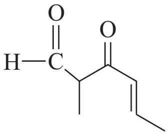
(a) 3
(b) 4
(c) 5
(d) 6

8. 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

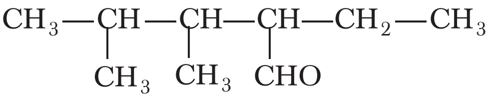
9. The IUPAC name of the compound



is ....

(a) 3-keto-2-methylhex-4-enal
(b) 5-formylhex-2-en-3-one
(c) 5-methyl-4-oxohex-2-en-5-al
(d) 3-keto-2-methylhex-5-enal

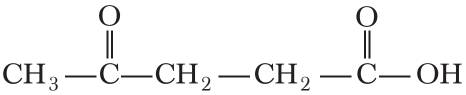
10. The IUPAC name of following compound is



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

(a) 2-ethyl-3,4-dimethylpentanal
(b) 2,3-dimethyl-4-aldohexane
(c) 3-aldol-4,5-dimethyl hexane
(d) 1,3,4,5-tetraethyl butanal

11. The IUPAC name for



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

is

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

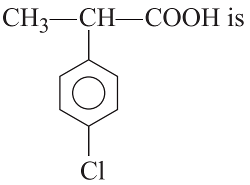
12. The IUPAC name of the following compound.
$HOCH_2(CH_2)_3CH_2COCH_3$ is

(a) 7-hydroxyheptan-2-ol
(b) 7-hydroxyheptan-2-one
(c) 2-oxoheptan-7-ol
(d) Heptan-2-oxo-7-ol

13. Neo-pentyl group is named as based on IUPAC system on

(a) *iso*-pentyl
(b) *neo*-pentyl
(c) 2,2-dimethyl propyl
(d) 1,1-dimethyl

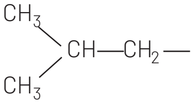
14. The IUPAC name of



(a) 2-(1-chlorophenyl) propanoic acid
(b) 2-methyl-(2-chlorophenyl) ethanoic acid
(c) 1-methyl-(2-chlorophenyl) ethanoic acid
(d) 2-(4-chlorophenyl) propanoic acid

15. The structure of *iso*-butyl group in an organic compound is

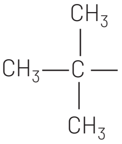
(a)



(b) $CH_3—CH_2—CH_2—CH_3$

(c) $CH_3—CH_2—CH_2—CH_2—$

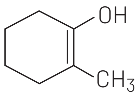
(d)



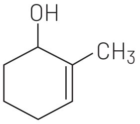
$CH_3—C(CH_3)_2—$

16. Structure of 2-methyl-2-cyclohexen-1-ol is

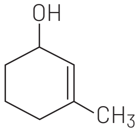
(a)



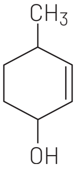
(b)



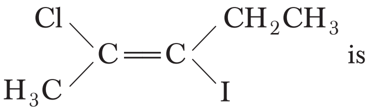
(c)



(d)



17. IUPAC name of the compound

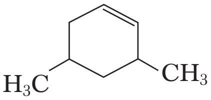


(a) *trans*-3-iodo-4-chloro-3-pentene
(b) *cis*-2-chloro-3-iodo-2-pentene
(c) *trans*-2-chloro-3-iodo-2-pentene
(d) *cis*-3-iodo-4-chloro-3-pentene

18. 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

19. IUPAC name of the following compound is



(a) 3,5-dimethylcyclohexene
(b) 3,5-dimethyl-1-cyclohexene
(c) 1,5-dimethyl-5-cyclohexene
(d) 1,3-dimethyl-5-cyclohexene

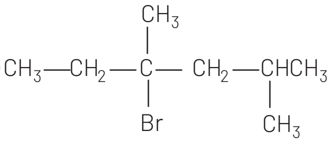
20. IUPAC name of $(CH_3)_2CH—CH_2—CH_2Br$ is

(a) 1-bromopentane
(b) 2-methyl-1-4-bromobutane
(c) 1-bromo-3-methylbutane
(d) 2-methyl-3-bromopropane

21. Which of the following is not in accordance to IUPAC system?

(a) $Br—CH_2—CH=CH_2$
1-bromoprop-2-ene

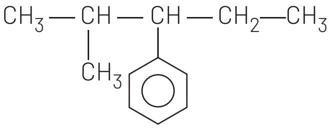
(b)



$CH_3—CH_2—C(CH_3)(Br)—CH_2—CH(CH_3)CH_3$

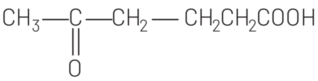
4-bromo-2, 4-dimethylhexane

(c)



2-methyl-3- phenylpentane

(d)



$CH_3—C(=O)—CH_2—CH_2CH_2COOH$

5-oxohexanoic acid

22. Cl—Cl heterolytic fission gives

(a) two free radicals (b) two carbonium ion
(c) two carbanion
(d) one carbocation and one carbanion

23. The most stable carbocation, among the following is

(a) $(CH_3)_3C—\overset{\oplus}{C}H—CH_3$

(b) $CH_3—CH_2—\overset{\oplus}{C}H—CH_2—CH_3$

(c) $CH_3—\overset{\oplus}{C}H—CH_2—CH_2—CH_3$

(d) $CH_3—CH_2—\overset{\oplus}{C}H_2$

24. Which of the following free radicals is the most stable ?

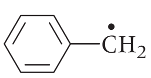
(a) Primary (b) Methyl
(c) Secondary (d) Tertiary

25. When CH_3Cl undergoes homolytic bond-fission

(a) carbon undergoes a geometric change from tetrahedral to planar
(b) hybridisation changes from sp^3 to sp^2
(c) Both (a) and (b)
(d) None of the above

26. Compare stability of free radicals.

I. $CH_3—\overset{\bullet}{C}H—CH_3$

II. 

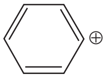
III. $CH_3—\overset{\bullet}{C}(CH_3)_2$

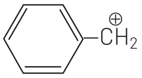
IV. $\overset{\bullet}{C}H_2—CH_3$

(a) II > I > III > IV (b) II > III > I > IV
(c) I > II > III > IV (d) IV > III > I > II

27. Which is the most stable carbocation ?

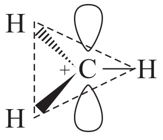
(a) $(CH_3)_3\overset{\oplus}{C}$

(b) 

(c) 

(d) $(CH_3)_2\overset{\oplus}{C}H$

28. Look at the figure below and find the hybridisation of carbon atom.



Shape of methyl cation

(a) sp^3 (b) sp^2
(c) sp (d) None of these

29. The most stable carbocation, among the following is

(a) $(CH_3)_3C—\overset{\oplus}{C}H—CH_3$

(b) $CH_3—CH_2—\overset{\oplus}{C}H—CH_2—CH_3$

(c) $CH_3—\overset{\oplus}{C}H—CH_2—CH_2—CH_3$

(d) $CH_3—CH_2—\overset{\oplus}{C}H_2$

30. Among the following carbocations $Ph_2C^+CH_2Me$ (I), $PhCH_2CH_2CH^+Ph$ (II), $Ph_2CHCH_2^+$ (III), $Ph_2C(Me)^{\bullet}CH_2^{\oplus}$ (IV) the order of stability is

(a) IV > II > I > III (b) I > II > III > IV
(c) II > I > IV > III (d) I > IV > III > II

31. What is the correct order of decreasing stability of the following cations?

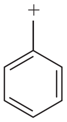
$CH_3—\overset{\oplus}{C}H—CH_3$ (I) $CH_3—\overset{\oplus}{C}H—OCH_3$ (II)

$CH_3—\overset{\oplus}{C}H—CH_2—OCH_3$ (III)

(a) II > I > III (b) II > III > I
(c) III > I > II (d) I > II > III

32. Which one of the following is an intermediate in the reaction of benzene with CH_3Cl in the presence of anhydrous $AlCl_3$?

(a) Cl^+ (b) CH_3

(c) CH_3^+ (d) 

33. 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

Codes

	A	B	C		A	B	C
(a)	1	1	2	(b)	1	2	3
(c)	1	3	2	(d)	2	1	3

34. Select the incorrect comparison as nucleophile.

(a) $(CH_3)_3CO^{\ominus} < OH^{\ominus}$ (b) $H_2O < NH_3$
(c) $RO^{\ominus} < RS^{\ominus}$ (d) $R_3P < R_3N$

35. Which has the highest nucleophilicity ?

(a) F^- (b) OH^-
(c) CH_3^- (d) NH_2^-

36. Which of the following compounds can react with the Lewis base Cl^- in a Lewis acid-base reaction ?

(a) CH_4 (b) $AlCl_3$
(c) OH^- (d) CH_3^-

37. An example of electrophile is

(a NO_2 (b) NH_3 (c) $\overset{+}{N}O_2$ (d) H_2O

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

(a) $BF_3, \overset{+}{C}H_3, NO_2$
(b) $AlCl_3, SO_3, NO_2^+$
(c) $NO_2^+, CH_3^+, CH_3-C^+=O$
(d) $C_2H_5^-, C_2H_5, C_2H_5^+$

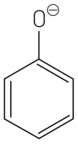
39. Match the terms mentioned in Column I with the terms in Column II.

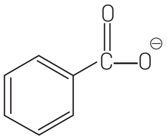
Column I	Column II
A. Carbocation	1. sp^2 hybridised carbon with empty *p*-orbital
B. Nucleophile	2. Ethyne
C. *sp*-hybridisation	3. Species that can receive a pair of electrons
D. Electrophile	4. Species that can supply a pair of electrons.

Codes

	A	B	C	D
(a)	1	4	2	3
(b)	1	3	4	2
(c)	1	3	4	2
(d)	2	3	4	1

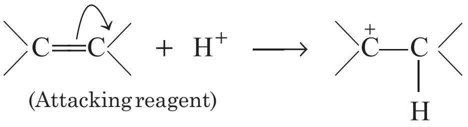
40. Which has maximum stabilisation energy as a result of resonance ?

(a)


(b)


(c) $CH_2=CH\overset{\ominus}{C}H_2$ (d) $CH_3\overset{\ominus}{C}H_2$

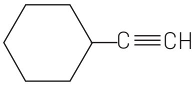
41. Observe the effect carefully and predict the nature of it.

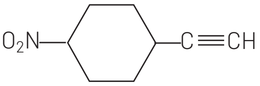


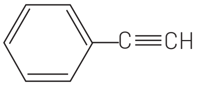
Choose the correct option.

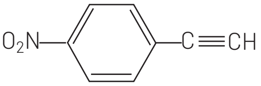
(a) Negative electromeric effect
(b) Resonance effect
(c) Positive electromeric effect
(d) Inductive effect

42. Ethynic hydrogen is released most easily in

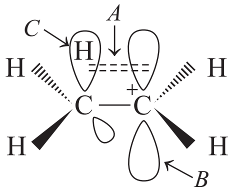
(a)


(b)


(c)


(d)


43. Observe the orbital diagram showing hyperconjugation in ethyl cation. Here *A, B* and *C* refer to



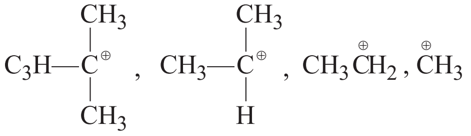
(a) $A\rightarrow$ hyperconjugation, $B\rightarrow$ empty $2p$-orbital of carbon, $C\rightarrow C_{sp^3}-H_{1s}$ bond

(b) $A \rightarrow$ inductive effect, $B \rightarrow i$ 2p-orbital of carbon, $C \rightarrow C_{sp^2} - H_{1s}$ bond

(c) $A \rightarrow$ electromeric effect, $B \rightarrow$ empty 2p-orbital of carbon, $C \rightarrow C_{sp^3} - H_{1s}$ bond

(d) $A \rightarrow$ resonance effect, $B \rightarrow i$ 2p-orbital of carbon, $C \rightarrow C_{sp^3} - H_{1s}$ bond

44. Choose the correct order of stability of carbocation using the concept of hyperconjugation.

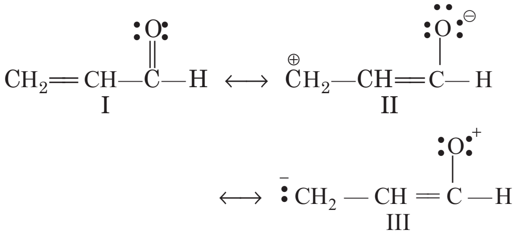


$C_3H-\overset{CH_3}{\underset{CH_3}{C^{\oplus}}}$, $CH_3-\overset{CH_3}{\underset{H}{C^{\oplus}}}$, $CH_3\overset{\oplus}{C}H_2$, $\overset{\oplus}{C}H_3$

I II III IV

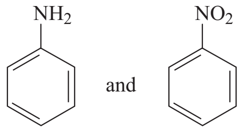
(a) I < II < III < IV
(b) IV < III < II < I
(c) III < IV < II < I
(d) None of these

45. The order of relative stability of the contributing structures are



(a) II > I > III
(b) I > II > III
(c) III > II > I
(d) I = II = III

46. Consider the following compounds,

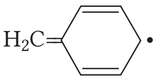


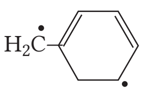
Aniline (I) Nitrobenzene (II)

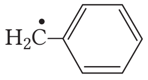
Which of the following option is/are true regarding I and II ?

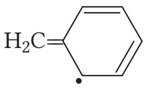
(a) I shows + R -effect, whereas II shows –R-effect
(b) I shows –R -effect, whereas II shows + R-effect
(c) Both I and II show +R -effect
(d) Both I and II show –R -effect

47. Which is the incorrect resonating structure ?

(a) 

(b) 

(c) 

(d) 

48. The stability of $Me_2C{=}CH_2$ is more than that of $MeCH_2CH{=}CH_2$ due to

(a) inductive effect of the Me group
(b) resonance effect of the Me group
(c) hyperconjugative effect of the Me group
(d) resonance as well as inductive effect of the group

49. Hyperconjugation involves overlapping of which of the following orbitals.

(a) σ-σ
(b) σ-p
(c) p-p
(d) π-π

50. Formic acid is a stronger acid than acetic acid. This can be explained using

(a) +M effect
(b) –I effect
(c) +I effect
(d) –M effect

51. The arrangement of $(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3CH_2- when attached to benzene or unsaturated group in increasing order of inductive effect is

(a) $(CH_3)_3C- < (CH_3)_2CH- < CH_3CH_2-$
(b) $CH_3CH_2- < (CH_3)_2CH- < (CH_3)_3C-$
(c) $(CH_3)_2CH- < (CH_3)_3C- < CH_3CH_2-$
(d) $(CH_3)_3C- < CH_3CH_2- < (CH_3)_2CH-$

52. Which of the following does not show electromeric effect ?

(a) Alkene
(b) Ether
(c) Aldehyde
(d) Ketone

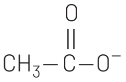
53. Match the ions given in Column I with their nature given in Column II.

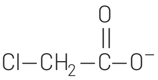
	Column I		Column II
A.	CH_3NO_2	1.	Stable due to resonance
B.	$F_3-C^{\oplus}$	2.	Destabilised due to inductive effect
C.	$CH_3-\overset{\oplus}{C}H-CH_3$	3.	Stabilised by hyperconjugation

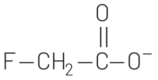
Codes

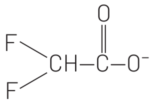
	A	B	C		A	B	C
(a)	1	2	3	(b)	2	3	1
(c)	3	1	2	(d)	3	2	1

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

(a) 
$CH_3-\overset{\overset{O}{\|}}{C}-O^-$

(b) 
$Cl-CH_2-\overset{\overset{O}{\|}}{C}-O^-$

(c) 
$F-CH_2-\overset{\overset{O}{\|}}{C}-O^-$

(d) 

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

(a) $^{*}CH_3-CH_2-Cl$

(b) $^{*}CH_3-CH_2-Mg^{+}Cl^{-}$

(c) $^{*}CH_3-CH_2-Br$

(d) $^{*}CH_3-CH_2-CH_3$

56. Dichlorocarbene is generated by the action of potassium-1- butoxide on chloroform. This is an example of

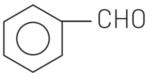
(a) α-elimination

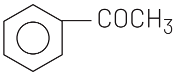
(b) β-elimination

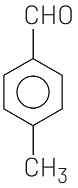
(c) addition reaction

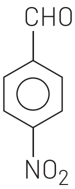
(d) rearrangement reaction

57. Which one is most reactive towards nucleophilic addition reaction ?

(a) 

(b) 

(c) 

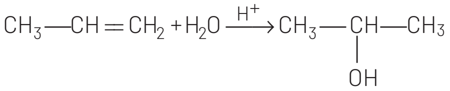
(d) 

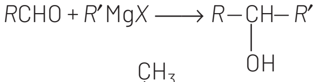
58. Electrophilic addition reactions proceed in two steps. The first step involves the addition of an electrophile. Name the type of intermediate formed in the first step of the following addition reaction.
$H_3C-HC=CH_2+H^+\longrightarrow ?$

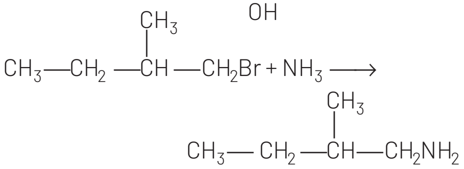
(a) 2° carbanion
(b) 1° carbocation
(c) 2° carbocation
(d) 1° carbanion

59. Which one is a nucleophilic substitution reaction among the following ?

(a) $CH_3CHO+HCN\longrightarrow CH_3CH(OH)CN$

(b) 
$CH_3-CH=CH_2+H_2O\xrightarrow{H^+}CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$

(c) 
$RCHO+R'MgX\longrightarrow R-\underset{\underset{OH}{|}}{CH}-R'$

(d) 
$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2Br+NH_3\longrightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2NH_2$

60. Dehydration of alcohol is an example of which type of reaction?

(a) Substitution
(b) Elimination
(c) Addition
(d) Rearrangement

Assertion-Reasoning MCQs

Directions In the following questions (Q.No. 61-75) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(a) Both Assertion and Reason are correct statements and Reason is the correct explanation of the Assertion.
(b) Both Assertion and Reason are correct statements, but Reason is not the correct explanation of the Assertion.
(c) Assertion is correct, but Reason is incorrect statement.
(d) Assertion is incorrect but Reason is correct statement.

61. Assertion Acyclic compounds consist of straight or branched chain compounds.

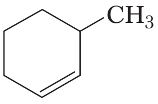
Reason Alicyclic compounds contain carbon atoms joined in the form of a ring.

62. Assertion When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond.

Reason Shift of electron density results in a polar covalent bond.

63. Assertion All the carbon atoms in $H_2C = C = CH_2$ are sp^2- hybridised.

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

64. Assertion  is

3-methylcyclohexene.

Reason In numbering, double bonded carbon atoms get preference to the alkyl group in cycloalkenes.

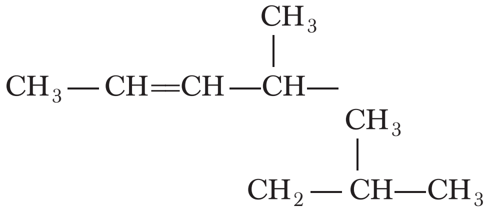
65. Assertion In bond-line structural representations, only atoms specifically written are oxygen, chlorine, nitrogen etc.

Reason In bond-line structural representations, line junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms.

66. Assertion The names of straight chain compounds are based on their chain structure and carry a prefix indicating the number of carbon atoms present in the chain.

Reason From CH_4 to C_4H_{10}, the prefixes are derived from common or trivial names.

67. Assertion 2, 3-dimethylhept-5-ene is



$CH_3—CH{=}CH—CH(CH_3)—CH_2—CH(CH_3)—CH_3$

Reason The alkyl group do not get preference to the double bond.

68. Assertion Heterolytic fission involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are carried away by one of the atoms.

Reason Heterolytic fission occurs readily in polar covalent bonds.

69. Assertion A covalent bond may be cleaved either by heterolytic cleavage or by homolytic cleavage.

Reason Heterolytic cleavage of CH_3Br will give $\overset{+}{C}H_3$ and $\overset{-}{B}r$.

70. Assertion Carbanion has an octet of electorns.

Reason In carbanion, negatively charged carbon atom is sp^3-hybridised.

71. Assertion Free radicals are short lived and highly reactive.

Reason Free radicals are highly unstable.

72. Assertion Inductive effect and resonance effect cause permanent polarisation of bond.

Reason These involve electron displacements due to the influence of an atom or a substituted group present in the molecule.

73. **Assertion** Conjugated system show abnormal behaviour, it contains alternate single and double bonds in an open chain or cyclic system.

Reason In conjugated system, π-electrons are delocalised and the system develops polarity.

74. **Assertion** Energy of resonance hybrid is equal to the average of energies of all canonical forms.

Reason Resonance hybrid cannot be presented by a single structure.

75. **Assertion** Polarisation of one σ bond caused by the polarisation of adjacent σ bond is referred to as the inductive effect.

Reason The substituents can be classified as electron withdrawing or electron donating groups relative to hydrogen.

Case Based MCQs

76. Read the passage given below and answer the following questions :

The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarisation of the bond (called electronic effect), e.g. $CH_3 — \overset{\delta\delta+}{CH_2} — \overset{\delta+}{CH_2} — \overset{\delta-}{F}$.

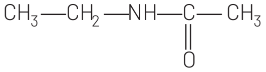
In above example, polar C—F bond induce polarity in the adjacent bonds. Such polarisation of adjacent σ- bond is referred to as the inductive effect. This effect decreases rapidly as the number of intervening bonds increases.

The resonance effect is defined as the polarity produced in the molecule by the interaction of two π-bonds or in conjugated system.

When the group or atom release electron density then electron density of conjugated system increases while the group or atom attract/withdraw electron density then electron density of conjugated system decreases.

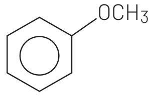
The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer :

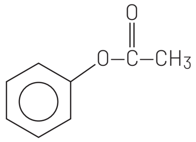
(i) In which molecule dipole moment is the maximum?

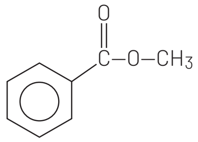
(a) $CH_3CH_2CH_2 — Cl$
(b) $CH_3CH_2CH_2 — NO_2$
(c) $CH_3CH_2CH_2 — OH$
(d) 

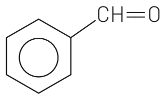
$CH_3—CH_2—NH—\underset{\underset{O}{\|}}{C}— CH_3$

(ii) In which benzene ring electron density is maximum?

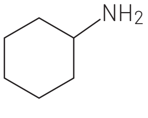
(a) 

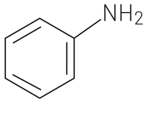
(b) 

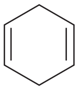
(c) 

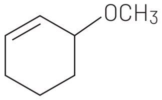
(d) 

(iii) Which of the following system show abnormal behaviour in their properties (like-stability, polarity … etc.) ?

(a) 

(b) 

(c) 

(d) 

(iv) The permanent displacement of electron through a chain involving only σ-bonds is called

(a) inductive effect
(b) hyperconjugation effect
(c) electromeric effect
(d) mesomeric effect

Or

Which of the following is correct with respect to $-I$-effect of the substituents? (R = alkyl)

(a) $—NH_2 > —OR > —F$
(b) $—NR_2 < —OR < —F$
(c) $—NH_2 > —OR < —F$
(d) $—NH_2 > —OR > —F$

77. Read the following passage and answer the question accordingly.

An intermediate is a molecular entity, that is formed from the reactants and reacts further to give the directly observed products of a chemical reaction. Most chemical reactions are stepwise, that is they take more than one elementary step to complete. An intermediate is the reaction product of each of these steps, except for the last one, which forms the final very isolated. Also, owing to the short lifetime, they do not remain in the product mixture.

In certain cases, they are separated and stored. For example matrix isolation and low temperature.

Matrix isolation is a technique that is used experimentally in physics and chemistry that includes a material that has been trapped with in an unreactive material. Host matrix generally comprises guest particles that are generally embedded. Guest particles can be molecules, atoms and ions. The guest is isolated within the host matrix.

The following questions (i-iv) are multiple choice questions. Choose the most appropriate answer:

(i) Relative stabilities of the following carbocations will be in the order

$$\underset{(A)}{\overset{\oplus}{C}H_3},\ \underset{(B)}{CH_3\overset{\oplus}{C}H_2},\ \underset{(C)}{\overset{\oplus}{C}H_2OCH_3}$$

(a) $C > B > A$
(b) $C < B < A$
(c) $B > C > A$
(d) $C > A > B$

(ii) CH_3CH_2Cl undergoes homolytic fission, produces

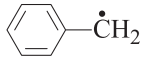
(a) $CH_3\dot{C}H_2$ and $\dot{Cl}$
(b) $CH_3\overset{\oplus}{C}H_2$ and Cl^-
(c) $CH_3\overset{\oplus}{C}H_2$ and $\overset{\oplus}{Cl}$
(d) $CH_3\dot{C}H_2$ and Cl^-

(iii) The shape of carbocation is

(a) square planar
(b) trigonal planar
(c) octahedral
(d) trigonal pyramidal

(iv) Compare stability of free radicals

I. $CH_3—\dot{C}H—CH_3$

II. 

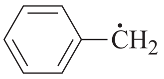
III. $\dot{C}H_2—CH(CH_3)_2$

IV. $\dot{C}H_2—CH_3$

(a) II > I > III > IV
(b) II > I > IV > III
(c) I > II > III > IV
(d) IV > III > I > II

Or

The radical is aromatic because it has



(a) 6p-orbitals and 6 unpaired electrons
(b) 7p-orbitals and 6 unpaired electrons
(c) 7p-orbitals and 7 unpaired electrons
(d) 6p-orbitals and 7 unpaired electrons

78. Read the passage given below and answer the following questions :

When a single Lewis dot structure is unable to explain all the properties of a compound, two or more structures, called the canonical forms or resonating structures, are drawn to explain all the properties of that compound, then the actual structure of the compound is in between these canonical form and is called the resonance hybrid of these canonical forms. This phenomenon is called resonance.

The resonating structure are hypothetical, i.e. have no real existence. The energy of actual structure or resonance hybrid is lower than, that of any of the canonical forms. The difference between hybrid and the energy of most stable (lowest energy) canonical form is called the resonance stabilisation energy or resonance energy.

The more the number of important canonical forms more is the resonance energy. In case of resonating structures of equivalent energy, resonance is of great importance.

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices :

(i) Which rules of resonating structures is true ?

I. The overall charge of system remains same.

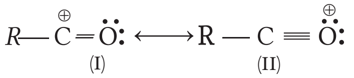
II. The arrangement of atoms must be identical or almost same in resonance structure.

(a) Rule I
(b) Rule II
(c) Both the rules
(d) Neither rule I nor rule II

(ii) There are how many resonance structure of phenoxide ion ?

(a) 4 (b) 5
(c) 6 (d) 3

(iii) Which is more stable among the following pair of resonance contributing structures.



$$\underset{\text{(I)}}{R-\overset{\oplus}{C}=\ddot{O}:} \longleftrightarrow \underset{\text{(II)}}{R-C\equiv\overset{\oplus}{\ddot{O}}:}$$

(a) Structure I
(b) Structure II
(c) Both are equally stable
(d) Can't say

(iv) The relation between resonance and bond order is

(a) $\text{B.O.} = \dfrac{\text{no. of bonds}}{\text{no. of resonating structure}}$

(b) $\text{B.O.} = \dfrac{\text{no. of } \pi \text{ - bond}}{\text{no. of } \sigma \text{ - bond}}$

(c) $\text{B.O.} = \dfrac{\text{no of } \sigma \text{ - bond}}{\text{no. of resonating structure}}$

(d) $\text{B.O.} = \text{no. of } (\sigma + \pi) \text{ bond}$

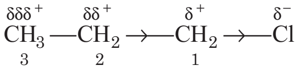
Or

Which of the following show $-R$-effect ?

(a) $—OR_2$ (b) $—NHCOR$
(c) $—NH_2$ (d) $—COOH$

79. Read the passage given below and answer the following questions:

In a polar covalent bond, the electrons are shifted to the more electronegative atom and hence, a polarity is developed in the bond. e.g. In a chain of carbon atoms having C—Cl bond, the C attached directly to the Cl-atom because of its less electronegativity acquires some positive charge (δ^+). The carbon (C_2) that is bonded directly to the C^{δ^+} also loose some of its electron density due to more polar C^{δ^+} and hence, acquires somewhat less positive charge (δ^{++}). Similarly, the next carbon (C_3) also acquires some positive charge but less than (δ^{++}) as shown below :



$$\underset{3}{\overset{\delta\delta\delta^+}{CH_3}}-\underset{2}{\overset{\delta\delta^+}{CH_2}}\rightarrow-\underset{1}{\overset{\delta^+}{CH_2}}\rightarrow-\overset{\delta^-}{Cl}$$

This induction of polarity, due to the presence of polar bond in an organic molecule, is called **inductive effect**.

In these questions (i-iv) a statement of Assertion followed by a statement of Reason is given.

Choose the correct answer out of the following choices :

(a) Assertion and Reason both are correct statements and Reason is correct explanation for Assertion.
(b) Assertion and Reason both are correct statements but Reason is not correct explanation for Assertion.
(c) Assertion is correct statement but Reason is incorrect statement.
(d) Assertion is incorrect statement but Reason is correct statement.

(i) **Assertion** Polarisation of one σ-bond caused by the polarisation of adjacent σ-bond is referred to as the inductive effect.

Reason The substituents can be classified as electron withdrawing or electron donating groups relative to hydrogen.

(ii) **Assertion** Formic acid is a stronger acid than benzoic acid.

Reason +*R*-effect phenyl group is greater than −*I*-effect.

(iii) **Assertion** Allyl and benzyl carbonium ions are stable than propyl carbonium ions.

Reason Electron releasing groups stabilise carbonium ions.

(iv) **Assertion** When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond.

Reason Shift of electron density results in a polar covalent bond.

Or

Assertion Inductive effect and resonance effect cause permanent polarisation of bond.

Reason These involve electron displacements due to the influence of an atom or a substituted group present in the molecule.

80. Read the following passage and answer the questions accordingly.

The name carbon is derived from the latin word 'carbo' which means coal. This is because it is the main constituent of coal. The amount of carbon present in the earth's crust and atmosphere is very small. In fact, all the living things, plants and animals, are made up of carbon compounds.

The compounds having organic origin are known as organic compounds. In morden days organic compounds are not restricted to living systems. Various organic compounds are known which came from non-living systems.

Carbon is known to form more than five million compounds. The existence of such a large number of compounds is due to some unique properties of carbon.

In these questions (i-iv), a statement of Assertion followed by a statement of Reason is given. Choose the correct answer out of the following choices.

(i) **Assertion** Saturated hydrocarbons are chemically less reactive.

Reason All isomeric paraffins have same parent name.

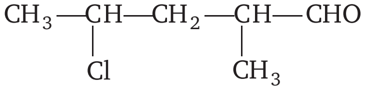
(ii) **Assertion** Olefins are unsaturated hydrocarbons containing two hydrogen atoms less than the corresponding paraffin.

Reason There is one triple bond between two carbon atoms in olefin molecules.

(iii) **Assertion** The IUPAC name for $CH_3CH=CH—C\equiv CH$ is pent-3-en-1-yne and not pent-2-en-4-yne.

Reason While deciding the locants for double and triple bonds, lowest sum rule is always followed.

(iv) **Assertion**



$$CH_3—\underset{\substack{|\\Cl}}{CH}—CH_2—\underset{\substack{|\\CH_3}}{CH}—CHO$$

is 4-chloro-2-methylpentanal.

Reason Numbering is to be given according to the alphabetical order of substituents.

Or

Assertion *neo*-hydrocarbons contain a quaternary carbon atom.

Reason Whenever a carbon atom is bounded to four carbon atoms it is quaternary.

ANSWERS

Multiple Choice Questions

1. (b) 2. (a) 3. (c) 4. (b) 5. (d) 6. (b) 7. (c) 8. (b) 9. (a) 10. (a)

11. (d) 12. (b) 13. (c) 14. (d) 15. (a) 16. (b) 17. (c) 18. (a) 19. (a) 20. (c)

21. (a) 22. (d) 23. (c) 24. (d) 25. (c) 26. (b) 27. (c) 28. (b) 29. (c) 30. (b)

31. (a) 32. (c) 33. (a) 34. (d) 35. (c) 36. (b) 37. (c) 38. (b) 39. (a) 40. (b)

41. (c) 42. (d) 43. (a) 44. (b) 45. (b) 46. (a) 47. (b) 48. (c) 49. (b) 50. (c)

51. (a) 52. (b) 53. (a) 54. (d) 55. (a) 56. (a) 57. (d) 58. (c) 59. (d) 60. (b)

Assertion-Reasoning MCQs

61. (b) 62. (b) 63. (d) 64. (a) 65. (b) 66. (b) 67. (d) 68. (b) 69. (b) 70. (b)

71. (b) 72. (a) 73. (a) 74. (d) 75. (b)

Case Based MCQs

76. (i)-(b), (ii)-(a), (iii)-(b), (iv)-(a) or-(b)

77. (i)-(a), (ii)-(a), (iii)-(b), (iv)-(b) or-(c)

78. (i)-(c), (ii)-(b), (iii)-(a), (iv)-(a) or-(d)

79. (i)-(b), (ii)-(a), (iii)-(b), (iv)-(b) or-(b)

80. (i)-(b), (ii)-(c), (iii)-(a), (iv)-(c) or-(b)

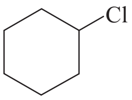
EXPLANATIONS

1. The correct condensed formula for $HOCH_2CH_2CH_2CH(CH_3)CH(CH_3)CH_3$ is $HO(CH_2)_3CH(CH_3)CH(CH_3)_2$.

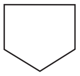
2. X is dashed wedge (bond away from observer) and Y is solid wedge (bond towards observer). In these formulas, the solid wedge is used to indicate a bond projecting out of the plane of paper towards the observer.

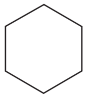
The dashed wedge is used to depict the bond projecting out of the plane of paper and away from the observer.

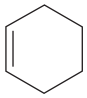
3. In cyclic compounds, the bond-line formula for chloro-cyclohexane is represented by following formula :

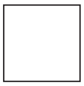


4. Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring but do not have aromatic character. Homocyclic means it contains only C-atoms in ring, e.g.


Cyclopentane


Cyclohexane

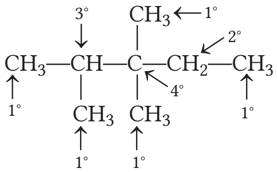

Cyclohexene


Cyclobutane

5. All the given compounds, i.e. furan, thiophene, pyridine are known as heterocyclic aromatic compounds.

6. Since, the given compounds contains benzene nucleus, so naphthalene is a benzenoid aromatic compound.

7. 1° carbons are attached directly to one carbon



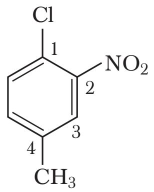
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2-CH_3$$

So, there are 5 primary carbons.

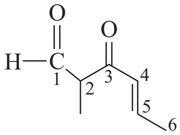
8. For tri or higher substituted benzene derivatives, the compounds are named by identifying substituent, positions on the ring by following the lowest locant rule.

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.



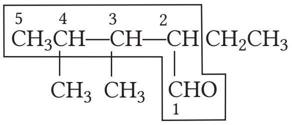
9.



— CHO group gets higher priority (act as principal group) over $>C=O$ and $C=C$ group in numbering of principal carbon chain.

IUPAC name 3-keto-2-methylhex-4-enal.

10.



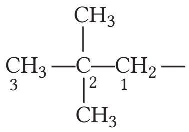
IUPAC name is 2-ethyl-3, 4-dimethylpentanal.

11. 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 (—COOH) has more priority than ketone (> C═O).

12. The correct IUPAC name of the given compound $HOCH_2(CH_2)_3CH_2COCH_3$ is 7-hydroxyheptan-2-one.

A compound containing both an alcohol and a keto group is named as hydroxy alkanone since the keto group is preferred over hydroxy group.

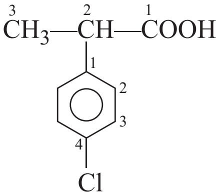
13.



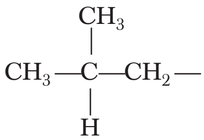
2, 2-dimethyl propyl

Longest chain is of three carbons; two alkyl groups at C_2.

14. The IUPAC name of compound is 2-(4-chlorophenyl) propanoic acid.

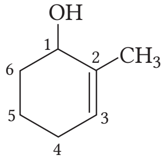


15 '*iso*' means one Me group is present at side chain. Hence, the structure of *iso*-butyl group is

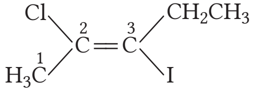


'yl' suffix is used to represent one — H less than the parent hydrocarbon.

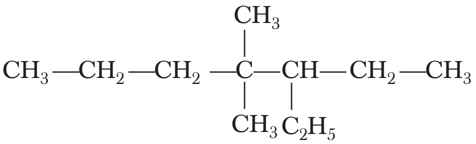
16. Option (b) is the correct structure of 2-methyl 2-cyclohexen-1-ol.



17. *trans*-2-chloro-3-iodo-2-pentene



18. The structure

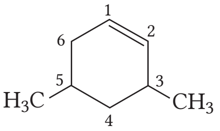


$$CH_3-CH_2-CH_2-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-\underset{C_2H_5}{\underset{|}{CH}}-CH_2-CH_3$$

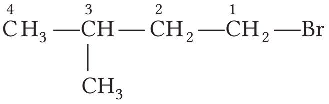
While writing IUPAC name, alkyl groups are written in alphabetical priority, thus lower locant 3 is assigned to ethyl.

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

19. The IUPAC name of given compound is 3, 5-dimethyl cyclohexene.



20.



$$\overset{4}{C}H_3—\overset{3}{C}H(CH_3)—\overset{2}{C}H_2—\overset{1}{C}H_2—Br$$

IUPAC name is 1-bromo-3-methylbutane.

21. Option (a) is not in accordance with IUPAC system. In IUPAC system of nomenclature, preference is given to multiple bond than halogen substituent, so the correct name is

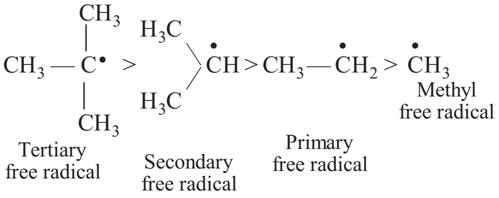
$$Br—\overset{3}{C}H_2—\overset{2}{C}H=\overset{1}{C}H_2$$

3-bromoprop-1-ene

22. Heterolytic fission of Cl_2 gives one carbocation and one carbanion due to transfer of electron from shared pair of bonded electrons.

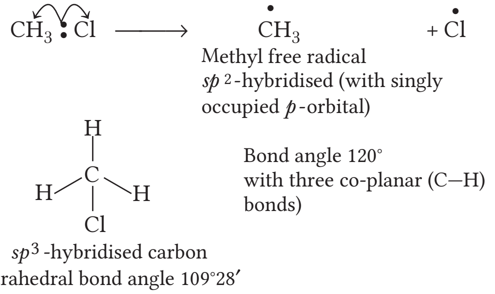
23. $CH_3\overset{+}{C}HCH_2CH_2CH_3$ is the most stable carbocation among the given carbocations. It is because the number of α-H atom attached to carbocation is maximum in $CH_3\overset{+}{C}HCH_2CH_2CH_3$. Thus, it has maximum number of hyperconjugating structure hence, it is most stable.

24. Stability order of free radical is as

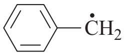


Greater the number of alkyl groups attached to the carbon atom carrying the odd electrons, greater is the delocalisation of odd electron and hence, more stable is the free radical.

25.

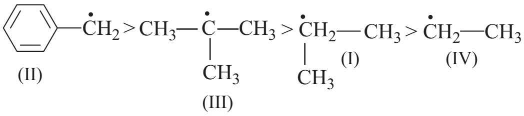


26. Among the given free radicals,

 is most stable due to resonance.

In the remaining free radicals, more the alkyl groups bonded to the electron deficient carbon, the more stable is the radical.

Thus, the correct order of stability of given free radicals is



27. Benzyl carbocation is most stable due to resonance

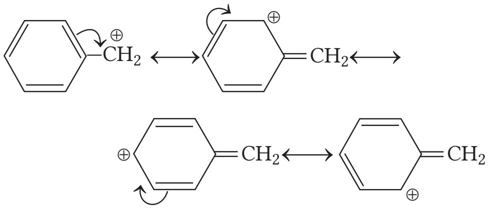
(a) 3° alkyl

(b) 3° vinylic least stable

(c) 1° benzyl most stable

(d) 2° alkyl

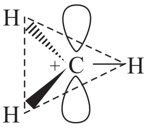
Order is : (b) < (d) < (a) < (c)



28. The shape of CH_3^+ may be considered as being derived from the overlap of three equivalent C-(sp^2)-hybridised orbitals with 1s-orbital of each of the three hydrogen atoms.

Each bond may be represented as $C(sp^2)$ –H (1s) sigma bond.

The remaining carbon orbital is perpendicular to the molecular plane and contains no electrons.



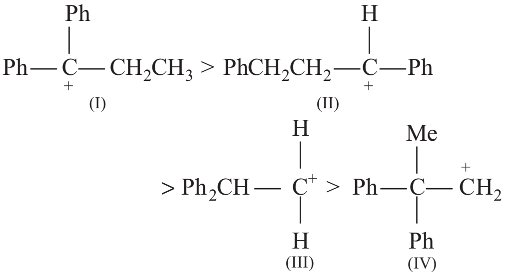
= 3σ-bonds

⇒ sp^2-hybridisation

Shape of methyl cation

29. $CH_3\overset{+}{C}HCH_2CH_2CH_3$ is the most stable carbocation among the given carbocations.
It is because the number of α-H atom attached to carbocation is maximum in
$CH_3\overset{\oplus}{C}HCH_2CH_2CH_3$. Thus, it has maximum number of hyperconjugating structure.
Hence, it is most stable.

30. The order of stability of carbocation is
3° benzylic > 2° benzylic >3° >2° > 1°.
Thus, the correct order of stability will be



$$\underset{\text{(I)}}{Ph-\overset{Ph}{\underset{+}{C}}-CH_2CH_3} > \underset{\text{(II)}}{PhCH_2CH_2-\overset{H}{\underset{+}{C}}-Ph}$$

$$> \underset{\text{(III)}}{Ph_2CH-\overset{H}{\underset{H}{C^+}}} > \underset{\text{(IV)}}{Ph-\overset{Me}{\underset{Ph}{C}}-\overset{+}{C}H_2}$$

31. Stability of the given cations can be understood by the following structures

$$\underset{\text{I}}{CH_3\longrightarrow\overset{+}{C}H\longleftarrow CH_3}\ ;\ \underset{\text{II}}{CH_3-\overset{+}{C}H-\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}-CH_3};$$

Weak + *I*-effect of the two methyl groups stabilises carbocation (I)

Strong + *R*-effect of $-OCH_3$ group stabilises carbocation (II)

$$\underset{\text{III}}{CH_3-\overset{+}{C}H-CH_2\longrightarrow OCH_3}$$

$-I$-effect of $-OCH_3$ group destabilises the carbocation (III)

Hence, the stability of carbocation decreases
II > I > III.

32. $\overset{+}{C}H_3$ group acts as an intermediate in the reaction of benzene with CH_3Cl in the presence of anhydrous $AlCl_3$. This reaction is called as Friedel-Craft alkylation.

33. 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. $\overset{\circ}{C}H_3$ hybridisation sp^2
B. Carbocation	Trigonal planar	Formed by heterolytic fission when carbon is attached to a more electronegative atom e.g. $\overset{+}{C}H_3$ 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

34. Nucleophilic strength increases down the group then

$$R_3P > R_3N$$

but given comparison $R_3P < R_3N$ is incorrect.

35. $\text{Electronegativity} \propto \dfrac{1}{\text{nucleophilicity}}$

∴ CH_3^- has the highest nucleophilicity.

36. (a) $CH_4 + Cl^- \longrightarrow$ No reaction

(b) $\underset{\substack{\text{Electron-deficient}\\ \text{Al (Lewis acid)}}}{AlCl_3} + \underset{\text{Lewis base}}{Cl^-} \longrightarrow AlCl_4^-$

(c) $OH^- + Cl^- \longrightarrow$ No reaction

(d) $CH_3^- + Cl^- \longrightarrow$ No reaction

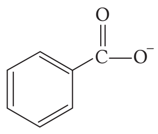
37. Electrophiles are electron deficient species. Hence, among the given species, nitronium ion $(\overset{+}{N}O_2)$ due to lack of electrons act as electrophile while all other given species due to the presence of lone pair of electrons, act as nucleophile.

38. $AlCl_3$, SO_3 (Lewis acids), NO_2^+, CH_3^+,
$CH_3-\overset{+}{C}{=}O$ are electron deficient species.
Hence, these acts as electrophiles.

39. A → (1); B → (4); C → (2); D → (3)

	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.e. having negative charge or excess of electrons.
C.	sp-hybridisa-tion	Ethyne	$HC\equiv CH$ (sp-hybridisation)
D.	Electrophile	Species that receive a pair of electron	Electron loving, i.e. positive charge or lack of electrons

40.



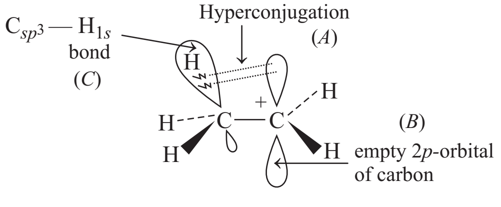
Resonance in benzene nucleus as well as in carboxylate ion. Thus, maximum stable.

Thus, maximum resonance energy.

41. In the given reaction, π-electrons of the multiple bond are transferred to that atom on which the attacking reagent get attached. So, it is an example of positive electromeric effect ($+E$ -effect). e.g.

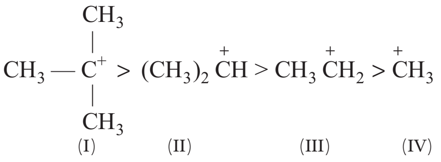
42. Ethynic H is attached to ($-C\equiv C-$) system. $-NO_2$ is electron-withdrawing and (C—H) bond strength is weakened to a greater extent. Since, benzene nucleus is also resonance stabilised, hence (d) is correct option.

43. In $CH_3\overset{+}{C}H_2$ (ethyl cation), the positively charged carbon atom has an empty p -orbital . One of the C—H bonds of the methyl group can align in the plane of this empty p-orbital and the electrons constituting the C—H bond in plane with this p-orbital can then be delocalised into the empty p-orbital as depicted below :



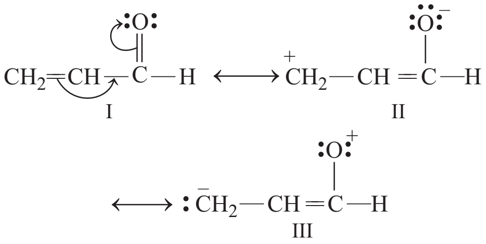
44. Greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation.

Thus, the correct order of stability of carbocation using the concept of hybridisation is



$$\underset{\text{(I)}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^+}}} > \underset{\text{(II)}}{(CH_3)_2\overset{+}{C}H} > \underset{\text{(III)}}{CH_3\overset{+}{C}H_2} > \underset{\text{(IV)}}{\overset{+}{C}H_3}$$

45. The order of relative stability of the contributing structures are I > II > III.



The reason for this order is

I. The resonating structure which is most stable has more number of covalent bonds, each carbon and oxygen atom has complete octet and no separation of opposite charges.

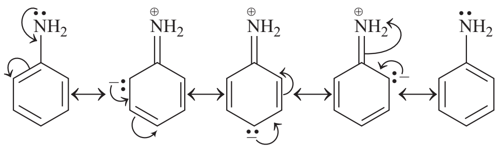
II. Negative charge on more electronegative atom and positive charge on more electropositive atom.

III. Structure does not contribute as oxygen has positive charge and carbon has negative charge, hence least stable.

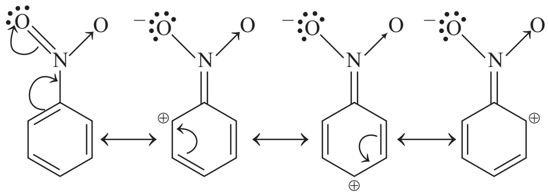
46 Aniline (I) shows $+R$ -effect, whereas nitrobenzene (II) shows $-R$ -effect. In $+R$ -effect, the transfer of electrons is away from an atom or substituent group attached to the conjugated system.

This electron displacement make certain positions in the molecule of high electron densities.

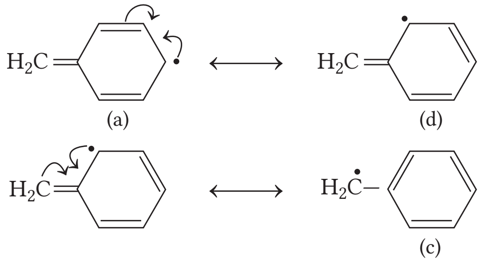
This effect in aniline is shown as :



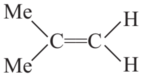
$-R$ -effect is observed when the transfer of electrons is toward the atom or substituent group is attached to the conjugated system, e.g. in nitrobenzene this electron displacement can be depicted as.



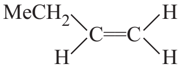
47.



48.



has 6- hyperconjugate forms while



has 2- hyperconjugate forms

Therefore, $Me_2C{=}CH_2$ is more stable than $MeCH_2CH{=}CH_2$.

49. Hyperconjugation involves overlapping of the σ-p-orbitals. It is a general stabilising interaction. It involves delocalisation of σ-electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared system or to an atom with an unshared p -orbital.

The σ-electrons of C—H bond of the alkyl group enter into partial conjugation with the attached unsaturated system or with the unshared p-orbital. It is a permanent effect.

50. Due to + I effect, electron density increases, which results in decrease in acidic character. Acetic acid, CH_3 — COOH has $—CH_3$ group that shows + I effect, whereas no such group is present in formic acid. Therefore, formic acid is a stronger acid than acetic acid.

51. The inductive effect of the alkyl group on a saturated carbon chain follows the order

$(CH_3)_3C— > (CH_3)_2CH— > CH_3CH_2—$

However, when an alkyl group is attached to an unsaturated system such as double bond or a benzene ring, the order of inductive effect is actually reversed.

This effect is called hyperconjugation effect or Baker-Nathan effect. Now, the reactivity order is

$(CH_3)_3C— < (CH_3)_2CH— < CH_3—CH_2—$

52. Electromeric effect implies complete transfer of π-electrons in presence of a reagent. Since, simple ethers do not contain any multiple bond, hence they do not show electromeric effect.

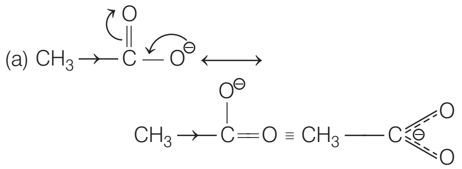
53. A → (1); B → (2); C → (3)

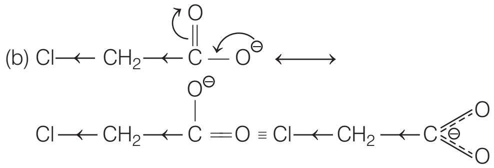
Column I	Column II	Explanation
A. CH_3NO_2	Stable due to resonance	
B. $F_3—C^+$	Destabilised due to inductive effect	$-I$ effect of F creates electron deficiency at carbon C^+.
D. $CH_3—\overset{\oplus}{C}H—CH_3$	Stabilised due to hyperconjugation	$\overset{+}{C}H$ is attached to two carbon. It can also be stabilised by hyperconjugation.

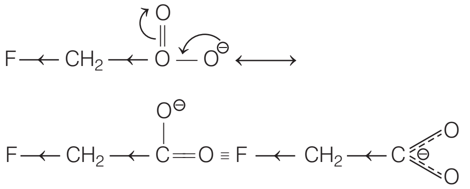
54. In all the given carbocations, the negative charge is dispersed which stabilises these carbocations.

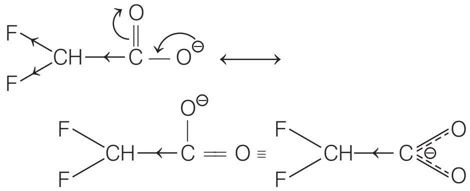
Here, the negative charge is dispersed by two factors, i.e. $+R$-effect of the carboxylate ion (conjugation) and I-effect of the halogens.

These effects are shown below in the carbocations





(c) 

(d) 

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.

55. Electronegativity of Cl, Br, C and Mg follows the order Cl > Br > C > Mg

$^*CH_3 \rightarrow CH_2 \rightarrow Cl$ $\quad$ ($-I$-effect)

$^*CH_3 \leftarrow CH_2 \leftarrow Mg^+Cl^-$

$^*CH_3 \rightarrow CH_2 \rightarrow Br$ $\quad$ ($-I$-effect)

$^*CH_3—CH_2—CH_3$ $\quad$ ($+I$-effect)

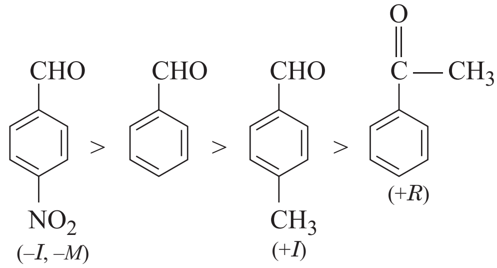
$-I$ effect of Cl > Br.

Hence, $CH_3—CH_2—Cl$ has the greatest positive charge.

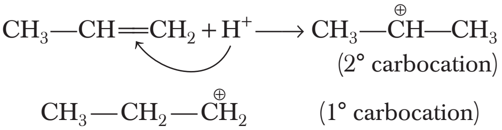
56. $\underset{\text{Chloroform}}{CHCl_3} \xrightarrow{K\ (t\text{-butoxide})} \underset{\text{Dichlorocarbene}}{:CCl_2}$

Since, the dominating group, i.e. hydrogen and chlorine, here are lost from the same carbon atom, it is an example of α-elimination.

57. Reactivity of carbonyl compounds towards nucleophilic addition reactions depends on the presence of substituted group. Electron withdrawing ($-I$, $-M$) groups increases reactivity towards nucleophilic addition reactions.



58. When electrophile attacks $CH_3—CH{=}CH_2$ delocalisation of electrons can take place, in two possible ways

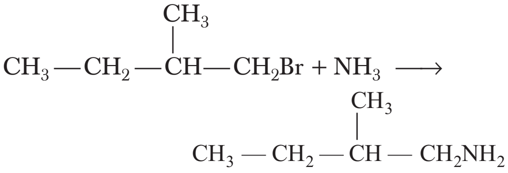


$$CH_3—CH{=}CH_2 + H^+ \longrightarrow \underset{(2° \text{ carbocation})}{CH_3—\overset{\oplus}{C}H—CH_3}$$

$$CH_3—CH_2—\overset{\oplus}{C}H_2 \quad (1° \text{ carbocation})$$

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.

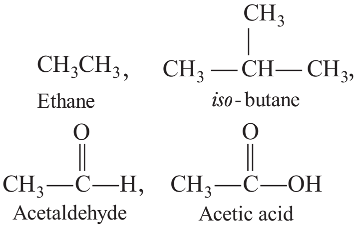
59. 

$$CH_3—CH_2—\overset{\overset{CH_3}{|}}{C}H—CH_2Br + NH_3 \longrightarrow CH_3—CH_2—\overset{\overset{CH_3}{|}}{C}H—CH_2NH_2$$

It is an example of nucleophilic substitution reaction.

60. Dehydration of alcohol involves the loss of two atoms or groups from the adjacent carbon atoms, hence it is an example of β-elimination reaction.

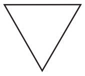
61. Acyclic or open chain compounds are also called aliphatic compounds and consist of straight or branched chain of carbon atoms.

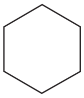


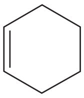
$$\underset{\text{Ethane}}{CH_3CH_3}, \quad \underset{iso\text{-butane}}{CH_3—\overset{\overset{CH_3}{|}}{C}H—CH_3},$$

$$\underset{\text{Acetaldehyde}}{CH_3—\overset{\overset{O}{\|}}{C}—H}, \quad \underset{\text{Acetic acid}}{CH_3—\overset{\overset{O}{\|}}{C}—OH}$$

Alicyclic or closed chain or ring compounds contain carbon atoms joined in the form of a ring (homocyclic). Some examples of this type of compounds are


Cyclopropane


Cyclohexane


Cyclohexene

Thus, both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

62. When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond. Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Thus, both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

63. Assertion is not correct but Reason is correct.

Hybridisation can be determined by counting σ-bond

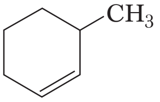
$$\overset{3\sigma}{H_2C}=\overset{2\sigma}{C}=\overset{3\sigma}{CH_2}$$

3σ - sp^2 hybridisation

2σ - sp hybridisation

Correct assertion In $H_2C=C=CH_2$, the central carbon is sp-hybridised whereas the terminal carbons are sp^2-hybridised.

64. In naming cycloalkenes, number the ring to specify the position of the double bonded carbons and choose the direction of numbering so that the substituents get the lowest number. The position of the double bond is not indicated because it is known to be between C - 1 and C - 2.

So,  is 3-methycyclohexene.

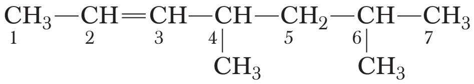
65. In bond-line structural representations only atoms specifically written are oxygen, chlorine, nitrogen etc. Also the terminal position denote methyl ($-CH_3$) group while line-junctions denote carbon atoms bonded to appropriate number of hydrogens required to satisfy the valency of the carbon atoms.

Thus, bond Assertion and Reason correct and Reason is not the correct explanation of Assertion.

66. The names of straight chain compounds are based on their chain structure and end with suffix '-ane', carry a prefix indicating the number of carbon atoms present in the chain (except from CH_4 to C_4H_{10} where the prefixes are derived from trivial names).

Thus, both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

67. In numbering to carbon chain, the parent carbon chain is numbered in a manner so as to give lowest number to that carbon atom linked by double or triple bond even it violates the rules of saturated hydrocarbons so,



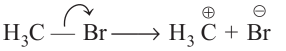
$$\underset{1}{CH_3}-\underset{2}{CH}=\underset{3}{CH}-\underset{\underset{CH_3}{|}}{\overset{}{\underset{4}{CH}}}-\underset{5}{CH_2}-\underset{\underset{CH_3}{|}}{\underset{6}{CH}}-\underset{7}{CH_3}$$

is 4, 6-dimethylhept-2-ene.

68. Heterolytic fission occurs when the two atoms differ considerable in their electronegativities and shared pair of electrons is carried by more electronegative atom.

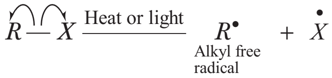
69. A covalent bond may be cleaved either by heterolytic cleavage or by homolytic cleavage.

In heterolytic cleavage, the bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.



$$H_3C-Br \longrightarrow H_3\overset{\oplus}{C}+\overset{\ominus}{Br}$$

In homolytic cleavage, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms.



$$R-X \xrightarrow{\text{Heat or light}} \underset{\text{Alkyl free radical}}{R^\bullet} + \overset{\bullet}{X}$$

Thus, both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

70. Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion.

71. Since free radicals contain odd electrons, so they are short lived and they readily try to pair up the odd electrons to form neutral molecules, that is why they are highly reactive.

72. The electron displacements in an organic molecule due to the influence of an atom or a substituted group present in the molecule cause permanent polarisation of the bond. Inductive effect and resonance effect are examples of this type of electronic displacement.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

73. Presence of alternate single and double bonds in an open chain or cyclic system is termed as conjugated system. These systems often show abnormal behaviour as in them the π- electrons are delocalised and the develops polarity. Examples are 1, 3- butadiene, aniline and nitrobenzene etc.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

74. Assertion is incorrect but Reason 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.

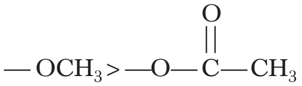
A canonical structure that is lower in energy makes a relating greater contribution to resonance hybrid.

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.

75. When a covalent bond is formed between atoms of different electronegativity, the bonding electrons are shifted towards the more electronegative atom. This is known as inductive effect and this unequal sharing of electrons results in polar covalent bond.

76. (i) Maximum polarity present in $C—NO_2$ bond so dipole moment of nitropropane is the maximum amongst the given molecules.

(ii) Electron donor tendency :



$$—OCH_3 > —O—\overset{\overset{\displaystyle O}{||}}{C}—CH_3$$

(iii) Aniline is a conjugated system and it is more polar than expected because NH_2 group release electron density towards benzene nucleus rather than attract from benzene.

(iv) The permanent displacement of electron through a chain involving only σ-bonds is called inductive effect. It involves the electron displacement along the chain of saturated carbon atoms due to the presence of a polar covalent bond at one end of the chain.

Or

– *I*-effect is related to the ability of substituent for the electron attraction capacity from the attached carbon atom, i.e. it is based on electronegativity of an atom. This effect increases with increase in the electronegativity of an atom.

From above, we can conclude that option (b) is correct.

$$-NR_2 < -OR < -F \ (-I\text{-effect})$$

77. (i) The dispersal of the charge stabilises the carbocation. More the number of alkyl groups, the greater is the dispersal of positive charge and therefore, more is the stability of carbocation.

Thus, the correct order is

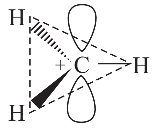
$$\underset{C}{\overset{\oplus}{C}H_2OCH_3} > \underset{B}{CH_3\overset{\oplus}{C}H_2} > \underset{A}{\overset{\oplus}{C}H_3}$$

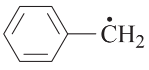
(ii) Homolytic cleavage results in the formation of free radical.

$$CH_3CH_2—Cl \xrightarrow[\text{fission}]{\text{Homolytic}} CH_3\dot{C}H_2 + {}^{\bullet}Cl$$

(iii) The shape of carbocation is trigonal planar with positively charged carbon being sp^2-hybridised.

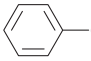
It is shown below :



(iv) Among the given free radicals, 

is most stable due to resonance. In the remaining free radicals, more the alkyl groups bonded to the electron deficient carbon, more stable is the radical.

Thus, the correct order of stability of given free radicals is



$-\dot{C}H_2 > CH_3\dot{C}HCH_3$

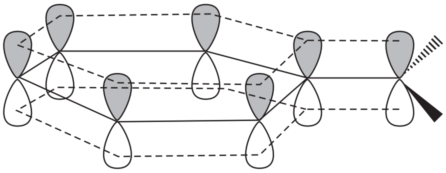
(II) (I)

$> \dot{C}H_2-CH_3 > \dot{C}H_2-CH(CH_3)_2$

(IV) (III)

Or Because of the presence of 7 p-orbitals and 7 unpaired electrons. It is aromatic in nature as these unpaired electrons delocalise in p-orbitals.

The structure of benzyl free radical is

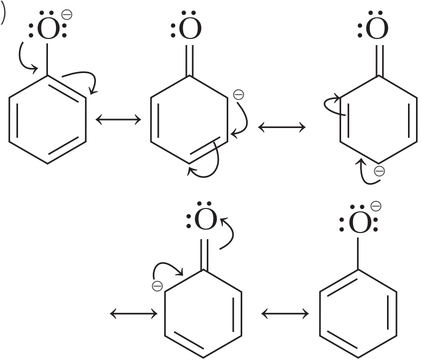


78. (i) Both the rules are correct for resonating structure.

I. The overall charge of system must remain same.

II. The arrangement of atoms must be identical or almost same in every resonance structures.

(ii)



(Phenoxide ion)

(iii) Structure I is more stable than structure II as in structure II, the positive charge is present on the highly electronegative oxygen.

(iv) $+R$-effect is shown by :

Halogen, —OH, OR, —OCOR, NH_2, COR, OR_2

- $-R$-effect is shown : —COOH, —CHO, $>C{=}O$, —CN, —NO_2 etc.

Or

In compounds exhibiting resonance, bond order can be given by the formula.

79. (i) When a covalent bond is formed between atoms of different electronegativity, the bonding electrons are shifted towards the more electronegative atom. This is known as inductive effect and this unequal sharing of electrons results in polar covalent bond.

Thus, both (A) and (R) are correct but (R) is not the correct explanation of (A).

(ii) Formic acid (HCOOH) is a stronger acid than benzoic acid (PhCOOH) although (Ph-) group is e^-- attracting ($-I$-effect). This is due to the $+R$ effect of phenyl group which is greater than $-I$-effect.

Hence, it decreases the acidic nature of benzoic acid.

(iii) The stability of carbonium ions is influenced by both resonance and inductive effects. Allyl and benzyl show resonance effect.

Thus, both (A) and (R) are correct and (R) is the correct explanation of (A).

(iv) When a covalent bond is formed between atoms of different electronegativity, the electron density is more towards the more electronegative atom of the bond.

Such a shift of electron density results in a polar covalent bond. Bond polarity leads to various electronic effects in organic compounds.

Thus, both Assertion and Reason are correct and Reason is not the correct explanation of Assertion.

Or

The electron displacements in an organic molecule due to the influence of an atom or a substituted group present in the molecule cause permanent polarisation of the bond. Inductive effect and resonance effect are examples of this type of electronic displacement.

Thus, both Assertion and Reason are correct and Reason is the correct explanation of Assertion.

80. (i) Both Assertion and Reason are correct but Reason is not the correct explanation of Assertion. Less reactivity of saturated hydrocarbons is due to the presence of single bonds between carbon atoms.

(ii) Assertion is correct but Reason is incorrect. There is one double bond between two carbon atoms in their molecules and they have the general formula C_nH_{2n}.

(iii) Both Assertion and Reason are correct and Reason is the correct explanation of Assertion. When double and triple bonds are present in a single compound lowest sum rule is followed. Thus in

$$\overset{5}{C}H_3\overset{4}{C}H=\overset{3}{C}H-\overset{2}{C}\equiv\overset{1}{C}H$$

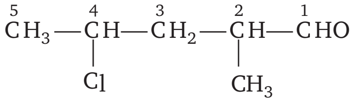
Sum of locants $(1 + 3) = 4$.

In $\underset{1}{C}H_3\underset{2}{C}H=\underset{3}{C}H-\underset{4}{C}\equiv\underset{5}{C}H$

Sum of locants $(2 + 4) = 6$

So it is named as pent-3-en-1-yne.

(iv) Assertion is correct but Reason is incorrect. IUPAC name of



$$\overset{5}{C}H_3-\underset{\underset{Cl}{|}}{\overset{4}{C}}H-\overset{3}{C}H_2-\underset{\underset{CH_3}{|}}{\overset{2}{C}}H-\overset{1}{C}HO$$

is 4-chloro-2-methylpentanal, the compound consists of $-CHO$ as functional group. The numbering is done from the functional group. The numbering is done from the functional group side, Cl and CH_3 are substituents.

When writing the names of the compounds, it is written in alphabetical order.

Thus, the name is given as 4-chloro-2-methyl pentanal.

Or Assertion and Reason both are correct statement but Reason is not the correct explanation of Assertion. *neo*-hydrocarbons contain a quaternay carbon atom, i.e. $(CH_3)_3C-$.