Organic Chemistry–Some Basic Principles and Techniques

CHAPTER 12

EXAM DRILL

ANSWERS

1. By distillation under reduced pressure.

2. Sublimation.

3. $H_2C{=}\underset{\displaystyle Cl}{\underset{|}{C}}{-}CH_2{-}CH_2{-}CH_3$

2-Chloropentene

$\sigma_{C—C} = 4$, $\sigma_{C—H} = 9$, $\sigma_{C—Cl} = 1$, $\pi_{C—C} = 1$

Total no. of σ-bonds = 14

Total no. of π-bonds = 1

4. 1, 1, 2, 2, 3, 3, -Hexamethylcyclopropane.

5. $\overset{6}{C}H_3—\overset{5}{C}H_2—\overset{4}{C}H_2—\overset{3}{\underset{}{C}}(=O)—\overset{2}{C}H_2—\overset{1}{C}HO$

6. (b) : Bond dissociation energy is defined as the standard enthalpy change when *A*–*B* is cleaved by homolysis to give fragments *A* and *B*, which are usually radicals.

$$A—B \longrightarrow \dot{A} + \dot{B}$$

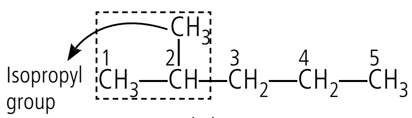
radicals

7. **(a) :** Alkenes like hex-1-ene when flipped from top to bottom they have identical structures and also they have $–C{=}CH_2$ unit which does not exhibit *cis*- *trans* isomerism.

8. **(d) :** In bond breaking, bond making and bond movement, the electrons are moved between atoms or compounds. This is because all of them have the property of electron transfer or we can say the movement of a pair of electrons from an electron rich site (a lone pair of electrons or a bond) to an electron poor site. But revolution of bond will not lead to movement of electron between compounds.

9. **(d) :** Homolysis of a chlorine molecule, to form two chlorine atoms, initiated by ultraviolet radiation or sunlight is done in free radical halogenation. A chlorine atom has an unpaired electron and acts as a free radical.

10. **(d) :**



2-Methylpentane

11. **(b) :** $\underset{sp}{H – C}{\equiv}\underset{sp}{C – H} > \underset{sp^2}{CH_2}{=}\underset{sp^2}{CH_2} > \underset{sp^3}{CH_3}\underset{sp^3}{CH_3}$

(Acidic character)

Conjugate base of the given acid :

$$\bar{C}{\equiv}C – H < \bar{C}H{=}CH_2 < \bar{C}H_2CH_3$$

(Basic character)

Conjugate base of stronger acid is weaker and *vice-versa.*

12. **(a) :** $\underset{sp^2}{H_2C} = \underset{sp^2}{CH} – \underset{sp}{C} \equiv \underset{sp}{CH}$

13. **(b) :** Pentane and 2-methylpentane are homologues as they belong to same homologous series i.e.; alkanes.

14. **(a)**

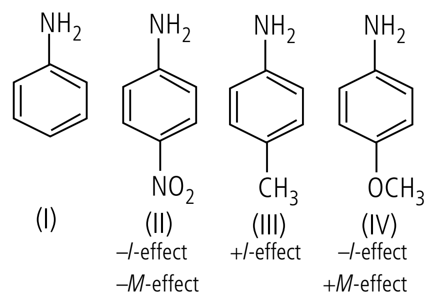
15. **(c) :** All carbon atoms in alkanes are sp^3-hybridised.

16. **(a)**

17. The electromeric effect is noticed in the organic compounds containing multiple bonds *i.e.*, double bond or triple bond ($>C = C<$ or $>C = O$), ($–C \equiv N$) under the influence of the attacking reagent. The moment the attacking reagent is removed, pi (π) electron pair comes back to its original position forming multiple bond again. Therefore, electromeric effect is a temporary effect.

18. An alkyl group is donating only if no other electron withdrawing group is present on it. Therefore, groups like $—CH_2Cl$ and $—CH_2F$ become electron withdrawing group. —F has more stronger –*I*-effect than –Cl group. More the electronegativity of attached group, higher will be the acidic character. So, order of acidic strength is III > II > I.

19.



+*R* or +*M*-effect is stronger than +*I*–effect.

Electron donating groups increase the basic strength while electron withdrawing groups decrease it.

Therefore,the order of basic strength is IV > III > I > II.

20. Diazonium salt($C_6H_5N_2^+ X^-$) readily lose N_2 on heating before reacting with fused sodium metal. Therefore, these do not give positive Lassaigne's test for nitrogen.

OR

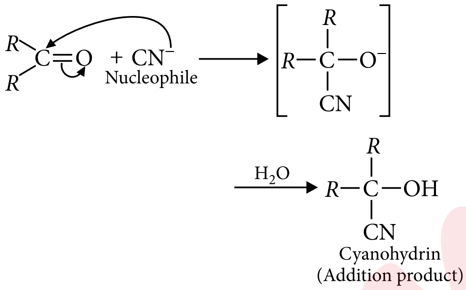
A functional group is defined as an atom or group of atoms bonded together in a specific manner, which gives the characteristic chemical properties of the organic compounds and they are the centres of the chemical reactivity. —COOH will be the principal functional group if present along with $—NH_2$.

21. Since the R_f value of A is 0.65, therefore, it is less strongly adsorbed as compared to component B with R_f value of 0.42. Therefore, on extraction of the column, A will elute first.

22. If the Lassaigne's extract gives a blood red colouration with $FeCl_3$ it indicates that the compound contains both N and S. During fusion sodium thiocyanate is formed which gives blood red colouration of ferric thiocyanate, $[Fe(CNS)_3]$ with $FeCl_3$.

23. Nucleophiles are nucleus loving chemical species. Since the nucleus of any atom is positively charged, therefore, nucleophiles must be electron rich chemical species containing at least one lone pair of electrons.

$$HO^- + H—CN \longrightarrow H_2O + \underset{\text{Nucleophile}}{CN^-}$$



24. (i) Displacement of σ-electrons along a saturated carbon chain whenever an electron withdrawing (or electron donating) group is present at the end of the chain is called the inductive effect or the *I*-effect. There are two types of inductive effects, *i.e.*, –*I*-effect and + *I*-effect.

(a) If the substituent attached to the end of the carbon chain is electron-withdrawing, the effect is called –*I*-effect. For example,

$$\overset{\delta\delta\delta^+}{C} \rightarrow \overset{\delta\delta^+}{C} \rightarrow \overset{\delta^+}{C} \rightarrow \overset{\delta^-}{X}$$

(–*I*-effect)

(Electron-withdrawing substituent)

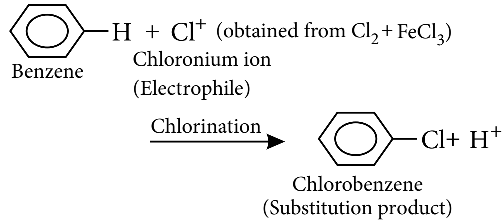
(b) If the substituent attached to the end of the carbon chain is electron-donating, the effect is called +*I*-effect. For example

$$\overset{\delta\delta\delta^-}{C} \leftarrow \overset{\delta\delta^-}{C} \leftarrow \overset{\delta^-}{C} \leftarrow CH_3$$

(+*I*-effect)

(Electron-donating substituent)

(ii) Electrophiles are electron loving chemical species. Their attraction for electrons is due to the presence of an electron deficient atom in them.



25. (a) OH^- is a nucleophile.

(b) CH_3^+ is an electrophile.

(c) CN^- is a nucleophile.

26. Volume of $\frac{M}{10}$ H_2SO_4 taken = 100 mL

Excess volume of $\frac{M}{10}$ H_2SO_4 is

154 mL of $\frac{M}{10}$ NaOH $= \frac{154}{2}$ mL of $\frac{M}{10}$ H_2SO_4

∴ Volume of $\frac{M}{10}$ H_2SO_4 left unused = 77 mL

Volume of $\frac{M}{10}$ H_2SO_4 used for neutralisation of NH_3

= 100 – 77 = 23 mL

Now, 23 mL of $\frac{M}{10}$ $H_2SO_4 = 2 \times 23$ mL of $\frac{M}{10}$ NH_3

= 46 mL of $\frac{M}{10}$ NH_3

Now, 1000 mL of 1 M NH_3 contains 14 g N

∴ 46 mL of $\frac{M}{10}$ NH_3 contains $\frac{14}{1000} \times \frac{46 \times 1}{10}$

∴ % of $N = \frac{14 \times 46 \times 100}{1000 \times 10 \times 0.35} = 18.4\%$

OR

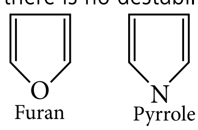
(a) (i) Functional isomerism is shown because they have same molecular formula but different carbon skeletons.

(ii) Chain isomerism is exhibited due to the difference in the position of the carbonyl group in the same carbon chain.

(iii) These two are metamers as these differ in position of functional group.

27. (a) IV > II > III > I

(I) It is destabilised by –*M*-and high –*I*- effect. (II) It is destabilised by –*I*-effect only at meta position. (III) It is destabilised by –*M*-effect and less –*I*-effect. (IV), there is no destabilisation by any group.

(b) 

28. Wt. of organic compound = 0.2475 g

Wt. of CO_2 = 0.4950 g

Wt. of H_2O = 0.2025 g

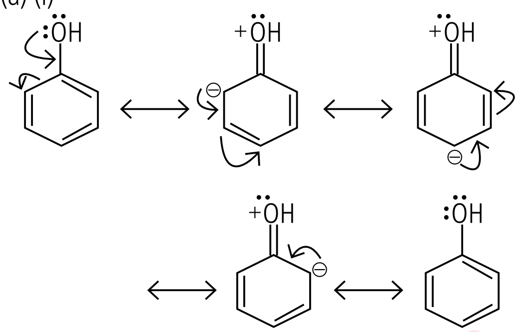
$$\% \text{ of C} = \frac{12}{44} \times \frac{\text{Mass of } CO_2 \text{ formed}}{\text{Mass of compound taken}} \times 100$$

$$= \frac{\frac{12}{44} \times 0.4950}{0.2475} \times 100 = 54.54\%$$

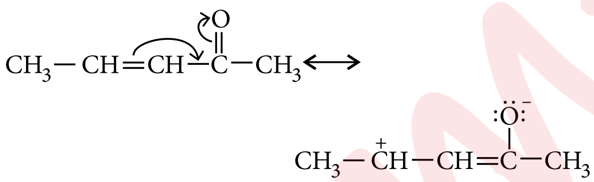
$$\% \text{ of H} = \frac{2}{18} \times \frac{\text{Mass of } H_2O \text{ formed}}{\text{Mass of compound taken}} \times 100$$

$$= \frac{\frac{2}{18} \times 0.2025}{0.2475} \times 100 = 9.09\%$$

29. (a) (i)



(ii)



(b) Since nearly all the organic compounds contain carbon as well as hydrogen it is usually not necessary to carry out tests to detect them and their presence can be assumed without testing for them.

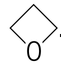
30. (a) A known mass of an organic compound containing sulphur is heated with an excess of fuming nitric acid or sodium peroxide in a sealed Carius tube. The whole of sulphur present in the compound is converted to sulphuric acid which is treated with a slight excess of barium chloride solution. Thus, barium sulphate gets precipitated.

(b) Carbon and hydrogen are detected by heating the organic compound with cupric oxide (CuO) strongly, where carbon is oxidised to carbon dioxide and hydrogen to water. Carbon dioxide is tested by lime water test (turns milky), whereas water is tested by anhydrous copper sulphate test (turns blue).

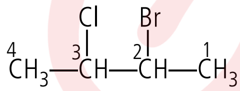
31. Positional isomerism is observed when two molecules have the same functional group, positioned at different places on the carbon chain.

2-Pentanone ($CH_3–\overset{O}{\overset{\|}{C}}–CH_2–CH_2–CH_3$), also known as methyl propyl ketone is a positional isomer of 3-pentanone ($CH_3–CH_2–\overset{O}{\overset{\|}{C}}–CH_2–CH_3$) also known as diethyl ketone. Another example would be *n*-propanol ($CH_3–CH_2–CH_2–OH$) and isopropanol ($CH_3–CH(OH)–CH_3$).

Functional isomerism is observed when two compounds with the same molecular formula have different functional groups.

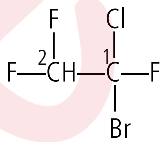
One example would be propionaldehyde ($CH_3–CH_2–\overset{O}{\overset{\|}{C}}–H$) and acetone ($CH_3–\overset{O}{\overset{\|}{C}}–CH_3$), where both compounds have the same molecular formula, C_3H_6O. Yet another functional isomer with C_3H_6O molecular formula would be oxetane, . The same molecular formula C_3H_6O is associated with three different functional groups - an aldehyde, a ketone and a cyclic ether.

32. (i)



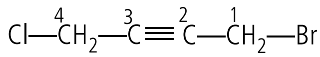
2-Bromo-3-chlorobutane

(ii)



1-Bromo-1-chloro-1, 2, 2-trifluoroethane

(iii)



1-Bromo-4-chloro-2-yne

33. Calculation of volume of nitrogen at S.T.P.

Experimental conditions,

Pressure of dry gas P_1 = 755.8 – 23.8 = 732 mm

V_1 = 31.7 mL, T_1 = 25 + 273 = 298 K

At S.T.P. condition, P_2 = 760 mm, V_2 = ?, T_2 = 273 K

Applying gas equation, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\therefore \quad \frac{732 \times 31.7}{298} = \frac{760 \times V_2}{273} \Rightarrow V_2 = 27.97 \text{ mL}$$

$$\% \text{ of Nitrogen} = \frac{28 \times \text{Volume of } N_2 \text{ at S.T.P.} \times 100}{22400 \times \text{Mass of compound}}$$

$$= \frac{28 \times 27.97 \times 100}{22400 \times 0.2325} = 15.04$$

OR

(a) Compounds having the same molecular formula but different number of carbon atoms on either side of the functional group are called metamers and the phenomenon is called metamerism.

(b) (i) $(CH_3)_3\bar{C}: < CH_3-\ddot{\bar{C}}H-CH_3 < CH_3-\ddot{\bar{C}}H_2$

(ii) $CH_3COOH < H—COOH < Cl—CH_2—COOH$

(c) In steam distillation, the organic liquid boils when the sum of vapour pressures due to organic liquid (P_1) and that due to water (P_2) becomes equal to atmospheric pressure (P) *i.e.*; $P = P_1 + P_2$. Since P_1 is lower than P. Substance vaporises and distils at a temperature lower than its boiling point.

34. (a) (i) **Homocyclic compounds :** The compounds in which the ring consists of only carbon atoms are called homocyclic compounds. Some examples of this type are :

Cyclopropane Cyclohexane

(ii) Aldehyde : $—C(=O)H$

(b) Three functional isomers and their IUPAC names are :

$CH_3CH_2—\overset{+}{N}(=O)O^-$; $CH_3CH_2—O—N=O$

Nitroethane ; Ethyl nitrite

$H_2N—CH_2—\overset{O}{\overset{\|}{C}}—OH$

Aminoethanoic acid (Glycine)

OR

(a) Isomeric alcohols of $C_4H_{10}O$ are given as

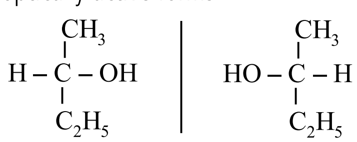
$CH_3–CH_2–CH_2–CH_2OH$; $CH_3–CH_2–CH(OH)–CH_3$;

1-Butanol 2-Butanol

$CH_3–CH(CH_3)–CH_2OH$ $CH_3–C(CH_3)_2–OH$

2-Methyl-1-propanol 2-Methyl-2-propanol

Moreover, butan-2-ol shows optical isomerism and exists in two optically active forms.



(*D*-form) mirror (*L*-form)

(b) The basic concepts on which the stability of carbocations is explained are as follows :

(i) **Inductive effect :** Carbocations are stabilized by neighbouring carbon atoms. The stability of carbocations increases as we go from primary to secondary to tertiary carbons.

(ii) **Pi-donation :** Carbocations are stabilized by neighbouring carbon-carbon multiple bonds. Carbocations adjacent to another carbon-carbon double or triple bond have special stability because overlap between the empty *p*-orbital of the carbocation with the *p*-orbitals of the π bond allows for charge to be shared between multiple atoms.

(iii) **Delocalization effect :** Carbocations are stabilized by adjacent lone pairs. The key stabilizing influence is a neighbouring atom that donates a pair of electrons to the electron-poor carbocation.

35. (a) : (i) $\overset{9}{C}H_3\overset{8}{C}H_2\overset{7}{C}H(CH_3)\overset{6}{C}H_2=\overset{5}{C}H\overset{4}{C}H\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}OOH$

7-Methylnon-4-en-1-oic acid

(ii) 4-Nitrophenol

(iii) 3-Methylhex-1-en-5-yne

(b) Four isomers are possible

1, 1-dichloropropane ($CH_3CH_2CHCl_2$),

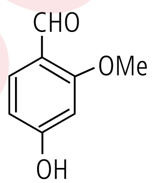
1, 2-dichloropropane ($CH_3CHClCH_2Cl$),

2, 2-dichloropropane ($CH_3CCl_2CH_3$) and

1, 3-dichloropropane ($ClCH_2CH_2CH_2Cl$).

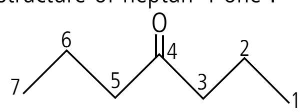
OR

(a)

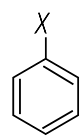


The principal functional group is aldehydic (–CHO) group. The secondary functional groups are alcoholic (–OH) and ether (–O–) group.

(b) Bondiline structure of heptan-4-one :



(c) There is one isomer for mono-substituted benzene



There are three isomers for disubstitued benzene