ANSWERS

1. (iv)	2. (i)	3. (ii)	4. (i)	5. (i)	6. (iv)
7. (iii)	8. (ii)	9. (iv)	10. (iii)		

II. Multiple Choice Questions (Type-II)

I. Multiple Choice Questions (Type-I)

11. (iii), (iv)	12. (iii), (iv)	13. (iii), (iv)
14. (i), (iv)	15. (i), (iii)	16. (i), (iii)
17. (i), (iii)	18. (i), (iii)	19. (ii), (iii)

III. Short Answer Type

- 20. Both alkenes and arenes are electron-rich. Therefore undergo electrophilic reactions. Olefins undergo addition reactions because addition of a reagent to an olefin gives a more stable product as sp^2 hybridisation changes to sp^3 hybridisation. Addition to the double bond of an arene would give a product with less or no resonance stability hence addition is difficult arenes. On the other hand in substitution reaction resonance stabilisation is retained therefore, arenes undergo substitution reaction.
- 21. 2-Butene is capable of showing geometrical isomerism.
- 22. The rotation about C—C bond is restricted because of repulsion between electron cloud of C—H bonds on either carbon atoms.
- 24. Bond dissociation energy is least for HI and maximum for HCl therefore, order of reactivity will be HI > HBr > HCl.
- 25. Propyl chloride forms less stable $CH_3 CH_2 CH_2^{\oplus}$ carbocation with anhydrous $AlCl_3$ which rearranges to a more stable $CH_3 CH_3 CH_3$ carbocation and gives isopropylbenzene as the product of the reaction.
- 27. The +R effect of $-OCH_3 > -Cl$ and $-NO_2$ has a R effect. Relative reactivity of the substituted benzene rings is as follows :

 $C_{6}H_{5}$ -OCH₃ > $C_{6}H_{5}$ -Cl > $C_{6}H_{5}$ -NO₂

28. Halogens attached to benzene rings exert – I and +R effect. +R effect dominates –I effect and increases the electron density at ortho and para positions of the benzene ring with respect to halogens.

 $^{\circ}H_{3}$

33. 2-Methyl butane is CH_3 —CH— CH_2 — CH_3 . Possible compounds are A, B and C given below :

171 Hydrocarbons

$$\begin{array}{c} \begin{array}{c} CH_{3} \\ CICH_{2}-CH-CH_{2}CH_{3} \\ A (1^{\circ}) \end{array} \end{array} \qquad \begin{array}{c} Nine possibilities for compound 'A' because nine methyl hydrogens are present in 2-methylbutane. \\ A (1^{\circ}) \end{array} \qquad \begin{array}{c} H_{3}C \\ H_{3}C \\ CI \\ H_{3}C \\ CI \\ B (2^{\circ}) \end{array} \qquad \begin{array}{c} Two possibilities for 'B' compound because two CH hydrogens are present in 2-methylbutane. \\ B (2^{\circ}) \end{array} \qquad \begin{array}{c} Only one possibility for 'C' compound because one CH hydrogen is present in 2-methylbutane. \\ \end{array}$$

C (3°)

and C compounds

Relative amounts of A, B = number of hydrogen × relative reactivity

A (1°) **B** (2°) **C (3°)** Relative amount $9 \times 1 = 9$ $2 \times 3.8 = 7.6$ $1 \times 5 = 5$

Total Amount of monohaloginated compounds = 9 + 7.6 + 5 = 21.6

Percentage of A = $\frac{9}{21.6} \times 100 = 41.7\%$

Percentage of B = $\frac{7.6}{21.6} \times 100 = 35.2\%$

Percentage of C =
$$\frac{5}{21.6} \times 100 = 23.1\%$$

35. H_3C — \dot{C} — CH_3 $H_2\dot{C}$ —CH CH_3 I II II

> Radical I is tertiary where as radical II is primary. Radical I is more stable due to hyperconjugation.

Exemplar Problems, Chemistry 172

36.
$$H_{3}C$$
— CH — $CH_{2}X$ \xrightarrow{Na} $H_{3}C$
 $H_{3}C$ — CH_{2} — CH_{3}
 CH_{3}

$$\xrightarrow{\text{Br}_2/\text{Sunlight}} \xrightarrow{\text{H}_3\text{C}} \xrightarrow{\text{Br}} \xrightarrow{\text{CH}_3} \xrightarrow{\text{CH}$$

- 37. A = Planar ring, all atoms of the ring sp^2 hybridised, has six delocalised π electrons, follows Huckel rule. It is aromatic.
 - B = Has six π electrons, but the delocalisation stops at sp^3 hybridised CH₂- carbon. Hence, not aromatic.
 - $C = Six delocalised \pi electrons (4 \pi electrons + 2 unshared electrons on negatively charged carbon) in a planar ring, follows Huckel's rule. It is aromatic.$
 - D = Has only four delocalised π -electrons. It is non aromatic.
 - E = Six delocalised π -electrons follows Huckel's rule. π electrons are in sp^2 hybridised orbitals, conjugation all over the ring because of positively charged carbon. The ring is planar hence is aromatic.
 - F = Follows Huckel's rule, has 2π electrons i.e. $(4n+2)\pi$ -electrons where (n=0), delocalised π -electrons. It is aromatic.
 - G = 8π electrons, does not follow Huckel's rule i.e., (4n+2) π -electrons rule. It is not aromatic.
- 38. A = Has 8π electrons, does not follow Huckel rule. Orbitals of one carbon atom are not in conjugation. It is not aromatic.
 - B = Has 6π delocalised electrons. Hence, is aromatic.
 - C = Has 6π electrons in conjugation but not in the ring. Non aromatic.
 - $D = 10\pi$ electrons in planar rings, aromatic.
 - $E = Out of 8\pi$ electrons it has delocalised 6π electrons in one six membered planar ring, which follows Huckel's rule due to which it will be aromatic.
 - $F = 14 \pi$ electrons are in conjugation and are present in a ring. Huckel's rule is being followed. Compound will be aromatic if ring is planar.

IV. Matching Type

40.	(i) \rightarrow (d)	(ii) \rightarrow (a)	(iii) \rightarrow (e)	$(iv) \rightarrow (c)$
	$(v) \to (b)$			
41.	(i) \rightarrow (b)	(ii) \rightarrow (c)	(iii) \rightarrow (a)	
42.	(i) \rightarrow (d)	(ii) \rightarrow (c)	(iii) \rightarrow (b)	(iv) \rightarrow (a)
43.	(i) \rightarrow (d)	(ii) \rightarrow (a)	(iii) \rightarrow (b)	$(iv) \rightarrow (c)$
				173 Hydrocarbons

V. Assertion and Reason Type

44. (i) 45. (i) 46. (i) 47. (iii)

VI. Long Answer Type

48.
$$C_5H_{11}Br \xrightarrow{alc.KOH} Alkene (C_5H_{10}) \xrightarrow{Br_2 \text{ in } CS_2} C_5H_{10}Br_2$$

(A) (B) (C)
 $\xrightarrow{Alc.KOH} C_5H_8 \xrightarrow{Na-liq.NH_3} C_5H_7-Na + \frac{1}{2}H_2$
D (Alkyne) Sodium alkylide

The reactions suggest that (D) is a terminal alkyne. This means triple bond is at the end of the chain. It could be either (I) or (II).

Since alkyne 'D' on hydrogenation yields straight chain alkane, therefore structure I is the structure of alkyne (D).

Hence, the structures of A, B and C are as follows :

- (A) CH_3 - CH_2 - CH_2 - CH_2 - CH_2Br
- (B) $CH_3 CH_2 CH_2 CH_2 = CH_2$
- (C) CH_3 — CH_2 — CH_2 —CH (Br)— CH_2Br
- 49. Step I

896 mL vapour of $C_{x}H_{y}$ (A) weighs 3.28 g

22700 mL vapour of $C_x H_y$ (A) weighs $\frac{3.28 \times 22700}{896}$ g mol⁻¹ = 83.1 g mol⁻¹

Step II					
Element	(%)	Atomic mass	Relative ratio	Relative no. of atoms	Simplest ratio
С	87.8	12	7.31	1	3
Н	12.19	1	12.19	1.66	4.98≈5

Empirical formula of 'A' C_3H_5 Empirical formula mass = 35 + 5 = 41 u

n =
$$\frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{83.1}{41} = 2.02 \approx 2$$

Exemplar Problems, Chemistry 174

 \Rightarrow Molecular mass is double of the empirical formula mass.

 \therefore Molecular Formula is C₆H₁₀

Step III

$$C_{6}H_{10} \xrightarrow{2H_{2}} 2$$
-methylpentane (A)

Structure of 2-methylpentane is CH_3 CH_-CH_2 $-CH_2$ $-CH_3$

Hence, the molecule has a five carbon chain with a methyl group at the second carbon atom.

'A' adds a molecule of $\rm H_2O$ in the presence of Hg $^{2+}$ and H+, it should be an alkyne. Two possible structures for 'A' are :

$$\begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} CH-C \equiv C-CH_{3} \quad \text{or} \quad \begin{array}{c} CH_{3} \\ CH_{3} \\ CH_{3} \end{array} CH-CH_{2}-C \equiv CH \\ II \end{array}$$

Since the ketone (B) gives a positive iodoform test, it should contain a $-COCH_3$ group. Hence the structure of ketone is as follows :

$$CH_{3}$$

CH-CH₂-CO-CH₃

Therefore structure of alkyne is II.

50. Two molecules of hydrogen add on 'A' this shows that 'A' is either an alkadiene or an alkyne.

On reductive ozonolysis 'A' gives three fragments, one of which is dialdehyde. Hence, the molecule has broken down at two sites. Therefore, 'A' has two double bonds. It gives the following three fragments :

 $OHC-CH_2-CH_2-CHO, CH_3CHO and CH_3-CO-CH_3$

Hence, its structure as deduced from the three fragments must be

$$CH_{3}-CH=CH-CH_{2}-CH_{2}-CH=C-CH_{3}$$

$$\downarrow \\ CH_{3}$$
(A)

Reactions

(A)
$$\xrightarrow{\text{Ozone}} \text{CH}_{3} \xrightarrow{\text{CH}} \text{CH}_{-}\text{CH}_{2} \xrightarrow{\text{CH}_{2}} \text{CH}_{2} \xrightarrow{\text{CH}_{2}} \xrightarrow{\text{CH}_{3}} \text{CH}_{3}$$

 $\xrightarrow{\text{Zn/H}_{2}\text{O}} \text{CH}_{3} \xrightarrow{\text{CHO} + \text{OHC} - \text{CH}_{2} \xrightarrow{\text{CH}_{2}} \xrightarrow{\text{CHO} + \text{O} = \text{C} \overset{\text{CH}_{3}}{\text{CH}_{3}}$
 175 Hydrocarbons