Unit

13

HYDROCARBONS

I. Multiple Choice Questions (Type-I)

1. Arrange the following in decreasing order of their boiling points.

(A) *n*–butane (B) 2–methylbutane

(C) *n*-pentane (D) 2,2–dimethylpropane

(i) A > B > C > D

(ii) B > C > D > A

(iii) D > C > B > A

(iv) C > B > D > A

2. Arrange the halogens F_2 , Cl_2 , Br_2 , I_2 , in order of their increasing reactivity with alkanes.

(i) $I_2 < Br_2 < Cl_2 < F_2$

(ii) $Br_2 < Cl_2 < F_2 < I_2$

(iii) $F_2 < Cl_2 < Br_2 < I_2$

(iv) $Br_2 < I_2 < Cl_2 < F_2$

3. The increasing order of reduction of alkyl halides with zinc and dilute HCl is

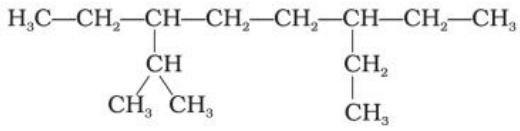
(i) R–Cl < R–I < R–Br

ii) R–Cl < R–Br < R–I

(iii) R–I < R–Br < R–Cl

(iv) R–Br < R–I < R–Cl

4. The correct IUPAC name of the following alkane is



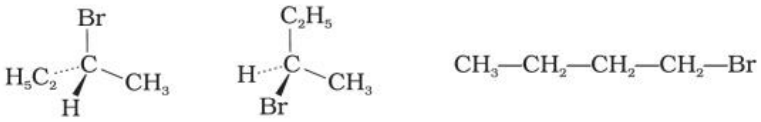
(i) 3,6 – Diethyl – 2 – methyloctane

(ii) 5 – Isopropyl – 3 – ethyloctane

(iii) 3 – Ethyl – 5 – isopropyloctane

(iv) 3 – Isopropyl – 6 – ethyloctane

5. The addition of HBr to 1-butene gives a mixture of products A, B and C



(A) (B) (C)

The mixture consists of

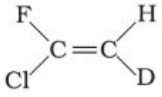
(i) A and B as major and C as minor products

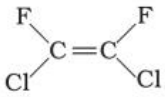
(ii) B as major, A and C as minor products

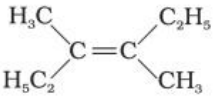
(iii) B as minor, A and C as major products

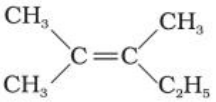
(iv) A and B as minor and C as major products

6. Which of the following will not show geometrical isomerism?

(i) 

(ii) 

(iii) 

(iv) 

7. Arrange the following hydrogen halides in order of their decreasing reactivity with propene.

(i) HCl > HBr > HI

(ii) HBr > HI > HCl

(iii) HI > HBr > HCl

(iv) HCl > HI > HBr

8. Arrange the following carbanions in order of their decreasing stability.

(A) $H_3C - C \equiv C^-$ (B) $H - C \equiv C^-$ (C) $H_3C—\bar{C}H_2$

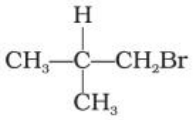
(i) A > B > C

(ii) B > A > C

(iii) C > B > A

(iv) C > A > B

9. Arrange the following alkyl halides in decreasing order of the rate of β– elimination reaction with alcoholic KOH.

(A)  (B) $CH_3—CH_2—Br$ (C) $CH_3—CH_2—CH_2—Br$

(i) A > B > C

(ii) C > B > A

(iii) B > C > A

(iv) A > C > B

10. Which of the following reactions of methane is incomplete combustion:

(i) $2CH_4 + O_2 \xrightarrow{Cu/523\ K/100\ atm} 2CH_3OH$

(ii) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$

(iii) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O\ (l)$

(iv) $CH_4 + 2O_2 \longrightarrow CO_2\ (g) + 2H_2O\ (l)$

II. Multiple Choice Questions (Type-II)

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

11. Some oxidation reactions of methane are given below. Which of them is/are controlled oxidation reactions?

(i) $CH_4\ (g) + 2O_2\ (g) \longrightarrow CO_2\ (g) + 2H_2O\ (l)$

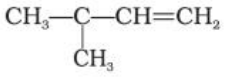
(ii) $CH_4\ (g) + O_2\ (g) \longrightarrow C\ (s) + 2H_2O\ (l)$

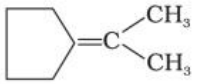
(iii) $CH_4\ (g) + O_2\ (g) \xrightarrow{Mo_2O_3} HCHO + H_2O$

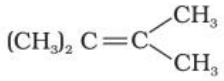
(iv) $2CH_4(g) + O_2(g) \xrightarrow{Cu/523/100\ atm} 2CH_3OH$

12. Which of the following alkenes on ozonolysis give a mixture of ketones only?

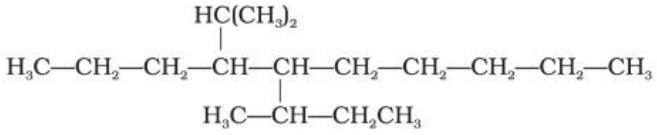
(i) $CH_3—CH=CH—CH_3$

(ii) 

(iii) 

(iv) 

13. Which are the correct IUPAC names of the following compound?



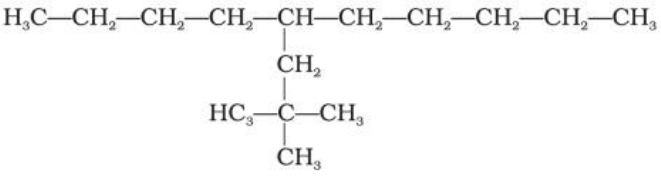
(i) 5– Butyl – 4– isopropyldecane

(ii) 5– Ethyl – 4– propyldecane

(iii) 5– *sec*-Butyl – 4– *iso*-propyldecane

(iv) 4–(1-methylethyl)– 5 – (1-methylpropyl)-decane

14. Which are the correct IUPAC names of the following compound?



(i) 5 – (2′, 2′–Dimethylpropyl)-decane

(ii) 4 – Butyl – 2,2– dimethylnonane

(iii) 2,2– Dimethyl – 4– pentyloctane

(iv) 5 – *neo*-Pentyldecane

15. For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring _____.

(i) deactivates the ring by inductive effect

(ii) deactivates the ring by resonance

(iii) increases the charge density at ortho and para position relative to meta position by resonance

(iv) directs the incoming electrophile to meta position by increasing the charge density relative to ortho and para position.

16. In an electrophilic substitution reaction of nitrobenzene, the presence of nitro group _____.

(i) deactivates the ring by inductive effect.

(ii) activates the ring by inductive effect.

(iii) decreases the charge density at ortho and para position of the ring relative to meta position by resonance.

(iv) increases the charge density at meta position relative to the ortho and para positions of the ring by resonance.

17. Which of the following are correct?

(i) $CH_3—O—\overset{\oplus}{C}H_2$ is more stable than $CH_3—\overset{\oplus}{C}H_2$

(ii) $(CH_3)_2\overset{\oplus}{C}H$ is less stable than $CH_3—CH_2—\overset{\oplus}{C}H_2$

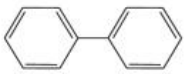
(iii) $CH_2=CH—\overset{\oplus}{C}H_2$ is more stable than $CH_3—CH_2—\overset{\oplus}{C}H_2$

(iv) $CH_2=\overset{\oplus}{C}H$ is more stable than $CH_3—\overset{\oplus}{C}H_2$

18. Four structures are given in options (i) to (iv). Examine them and select the aromatic structures.

(i) 

(ii) 

(iii) 

(iv) 

19. The molecules having dipole moment are _____.

(i) 2,2-Dimethylpropane

(ii) *trans*-Pent-2-ene

(iii) *cis*-Hex-3-ene

(iv) 2, 2, 3, 3 - Tetramethylbutane.

III. Short Answer Type

20. Why do alkenes prefer to undergo electrophilic addition reaction while arenes prefer electrophilic substitution reactions? Explain.

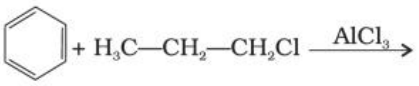
21. Alkynes on reduction with sodium in liquid ammonia form trans alkenes. Will the butene thus formed on reduction of 2-butyne show the geometrical isomerism?

22. Rotation around carbon-carbon single bond of ethane is not completely free. Justify the statement.

23. Draw Newman and Sawhorse projections for the eclipsed and staggered conformations of ethane. Which of these conformations is more stable and why?

24. The intermediate carbocation formed in the reactions of HI, HBr and HCl with propene is the same and the bond energy of HCl, HBr and HI is 430.5 kJ mol^{-1}, 363.7 kJ mol^{-1} and 296.8 kJ mol^{-1} respectively. What will be the order of reactivity of these halogen acids?

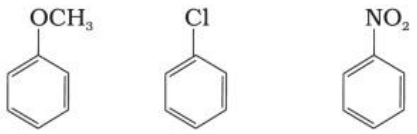
25. What will be the product obtained as a result of the following reaction and why?



26. How will you convert benzene into (i) *p* – nitrobromobenzene

(ii) *m* – nitrobromobenzene

27. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile.Give reason.

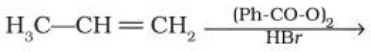


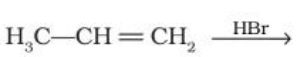
28. Despite their - I effect, halogens are *o*- and *p*-directing in haloarenes. Explain.

29. Why does presence of a nitro group make the benzene ring less reactive in comparison to the unsubstituted benzene ring. Explain.

30. Suggest a route for the preparation of nitrobenzene starting from acetylene?

31. Predict the major product (s) of the following reactions and explain their formation.





32. Nucleophiles and electrophiles are reaction intermediates having electron rich and electron deficient centres respectively. Hence, they tend to attack electron deficient and electron rich centres respectively. Classify the following species as electrophiles and nucleophiles.

(i) H_3CO^- (ii) $H_3C-\overset{\overset{O}{\|}}{C}-O^-$ (iii) $\dot{C}l$ (iv) $Cl_2C:$

(v) $(H_3C)_3C^+$ (vi) Br^- (vii) H_3COH (viii) R–NH–R

33. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. Calculate the percentages of all monochlorinated products obtained from 2-methylbutane.

34. Write the structures and names of products obtained in the reactions of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane.

35. Write hydrocarbon radicals that can be formed as intermediates during monochlorination of 2-methylpropane? Which of them is more stable? Give reasons.

36. An alkane C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. Write the structure of alkane and the tertiary bromide.

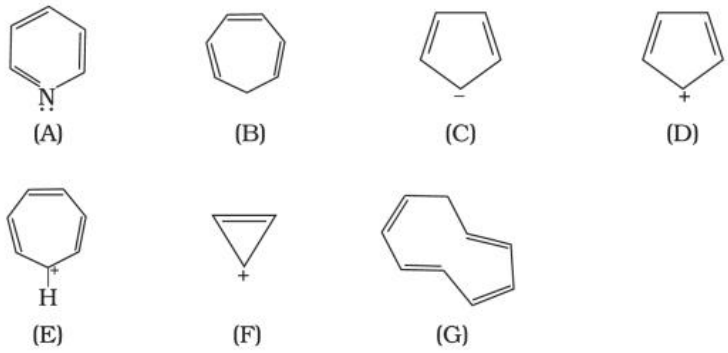
37. The ring systems having following characteristics are aromatic.

(i) Planar ring containing conjugated π bonds.

(ii) Complete delocalisation of the π–electrons in ring system i.e. each atom in the ring has unhybridised *p*-orbital, and

(iii) Presence of (4n+2) π–electrons in the ring where n is an integer (n = 0, 1, 2,.....) [Huckel rule].

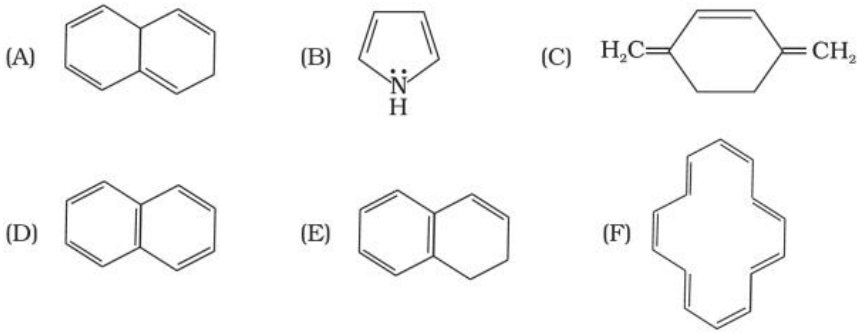
Using this information classify the following compounds as aromatic/nonaromatic.



(A) (B) (C) (D)

(E) (F) (G)

38. Which of the following compounds are aromatic according to Huckel's rule?



39. Suggest a route to prepare ethyl hydrogensulphate (CH_3–CH_2–OSO_2—OH) starting from ethanol (C_2H_5OH).

IV. Matching Type

40. Match the reagent from Column I which on reaction with $CH_3—CH=CH_2$ gives some product given in Column II as per the codes given below :

	Column I		**Column II**
(i)	$O_3/Zn + H_2O$	(a)	Acetic acid and CO_2
(ii)	$KMnO_4/H^+$	(b)	Propan-1-ol
(iii)	$KMnO_4/OH^-$	(c)	Propan-2-ol
(iv)	H_2O/H^+	(d)	Acetaldehyde and formaldehyde
(v)	B_2H_6/NaOH and H_2O_2	(e)	Propane-1,2-diol

41. Match the hydrocarbons in Column I with the boiling points given in Column II.

	Column I		**Column II**
(i)	*n*–Pentane	(a)	282.5 K
(ii)	*iso*-Pentane	(b)	309 K
(iii)	*neo*-Pentane	(c)	301 K

42. Match the following reactants in Column I with the corresponding reaction products in Column II.

	Column I		**Column II**
(i)	Benzene + $Cl_2 \xrightarrow{AlCl_3}$	(a)	Benzoic acid
(ii)	Benzene + $CH_3Cl \xrightarrow{AlCl_3}$	(b)	Methyl phenyl ketone
(iii)	Benzene + $CH_3COCl \xrightarrow{AlCl_3}$	(c)	Toluene
(iv)	Toluene $\xrightarrow{KMnO_4/NaOH}$	(d)	Chlorobenzene
		(e)	Benzene hexachloride

43. Match the reactions given in Column I with the reaction types in Column II.

	Column I		**Column II**
(i)	$CH_2=CH_2 + H_2O \xrightarrow{H^+} CH_3CH_2OH$	(a)	Hydrogenation
(ii)	$CH_2=CH_2 + H_2 \xrightarrow{Pd} CH_3—CH_3$	(b)	Halogenation
(iii)	$CH_2=CH_2 + Cl_2 \longrightarrow Cl—CH_2—CH_2—Cl$	(c)	Polymerisation
(iv)	$3\,CH \equiv CH \xrightarrow[Heat]{Cu\ tube} C_6H_6$	(d)	Hydration
		(e)	Condensation

16-04-2018

V. Assertion and Reason Type

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

44. ***Assertion (A) :*** The compound cyclooctane has the following structural formula :



It is cyclic and has conjugated 8π-electron system but it is not an aromatic compound.

Reason (R) : (4n + 2) π electrons rule does not hold good and ring is not planar.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

45. ***Assertion (A) :*** Toluene on Friedal Crafts methylation gives *o*– and *p*–xylene.

Reason (R) : CH_3-group bonded to benzene ring increases electron density at *o*– and *p*– position.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

46. ***Assertion (A) :*** Nitration of benzene with nitric acid requires the use of concentrated sulphuric acid.

Reason (R) : The mixture of concentrated sulphuric acid and concentrated nitric acid produces the electrophile, NO_2^+.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

47. ***Assertion (A) :*** Among isomeric pentanes, 2, 2-dimethylpentane has highest boiling point.

Reason (R) : Branching does not affect the boiling point.

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

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

(iii) Both A and R are not correct.

(iv) A is not correct but R is correct.

VI. Long Answer Type

48. An alkyl halide $C_5H_{11}Br$ (A) reacts with ethanolic KOH to give an alkene 'B', which reacts with Br_2 to give a compound 'C', which on dehydrobromination gives an alkyne 'D'. On treatment with sodium metal in liquid ammonia one mole of 'D' gives one mole of the sodium salt of 'D' and half a mole of hydrogen gas. Complete hydrogenation of 'D' yields a straight chain alkane. Identify A,B, C and D. Give the reactions invovled.

49. 896 mL vapour of a hydrocarbon 'A' having carbon 87.80% and hydrogen 12.19% weighs 3.28g at STP. Hydrogenation of 'A' gives 2-methylpentane. Also 'A' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone 'B' having molecular formula $C_6H_{12}O$. The ketone 'B' gives a positive iodoform test. Find the structure of 'A' and give the reactions involved.

50. An unsaturated hydrocarbon 'A' adds two molecules of H_2 and on reductive ozonolysis gives butane-1,4-dial, ethanal and propanone. Give the structure of 'A', write its IUPAC name and explain the reactions involved.

51. In the presence of peroxide addition of HBr to propene takes place according to anti Markovnikov's rule but peroxide effect is not seen in the case of HCl and HI. Explain.

16-04-2018

ANSWERS

I. Multiple Choice Questions (Type-I)

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)

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.

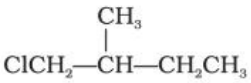
25. Propyl chloride forms less stable $CH_3—CH_2—\overset{\oplus}{C}H_2$ carbocation with anhydrous $AlCl_3$ which rearranges to a more stable $CH_3—\overset{\oplus}{C}H—CH_3$ carbocation and gives isopropylbenzene as the product of the reaction.

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 :

$C_6H_5—OCH_3 > C_6H_5—Cl > C_6H_5–NO_2$

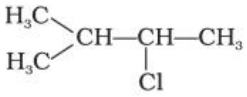
28. Halogens attached to benzene rings exert –I and +R effect. +R effect dominates –I effect and increases the electron density at ortho and para positions of the benzene ring with respect to halogens.

33. 2-Methyl butane is $CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}H—CH_2—CH_3$. Possible compounds are A, B and C given below :



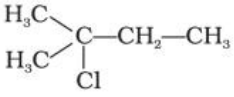
A (1°)

Nine possibilities for compound 'A' because nine methyl hydrogens are present in 2-methylbutane.



B (2°)

Two possibilities for 'B' compound because two CH hydrogens are present in 2-methylbutane.



C (3°)

Only one possibility for 'C' compound because one CH hydrogen is present in 2-methylbutane.

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

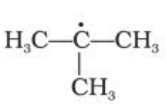
	A (1°)	**B (2°)**	**C (3°)**
Relative amount	9×1= 9	2×3.8 = 7.6	1×5=5

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

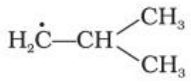
Percentage of A $= \frac{9}{21.6} \times 100 = 41.7\%$

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

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

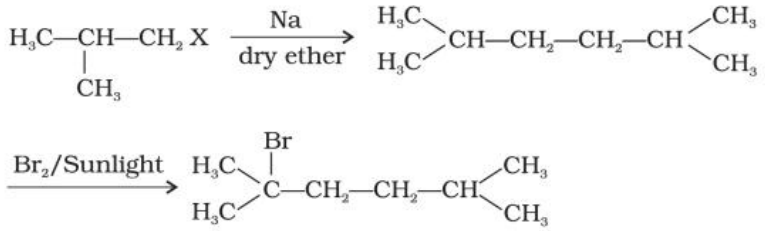
35. 

I



II

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

36. 

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 CH_2- carbon. Hence, not aromatic.

C = Six delocalised π-electrons (4 π 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 2 π electrons i.e. (4n+2) π-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 = 10π electrons in planar rings, aromatic.

E = Out of 8π 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 π 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) → (d) (ii) → (a) (iii) → (e) (iv) → (c) (v) → (b)

41. (i) → (b) (ii) → (c) (iii) → (a)

42. (i) → (d) (ii) → (c) (iii) → (b) (iv) → (a)

43. (i) → (d) (ii) → (a) (iii) → (b) (iv) → (c)

V. Assertion and Reason Type

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

VI. Long Answer Type

48. $C_5H_{11}Br \xrightarrow{\text{alc.KOH}} \underset{\text{(B)}}{\text{Alkene } (C_5H_{10})} \xrightarrow[\text{(C)}]{Br_2 \text{ in } CS_2} C_5H_{10}Br_2$
(A)

$\xrightarrow[-2HBr]{\text{Alc.KOH}} \underset{\text{D (Alkyne)}}{C_5H_8} \xrightarrow{\text{Na–liq.NH}_3} \underset{\text{Sodium alkylide}}{C_5H_7\text{–Na}} + \frac{1}{2}H_2$

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).

$CH_3-CH_2-CH_2-CH_2\equiv CH$ (I)

$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-C\equiv CH$ (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) $CH_3-CH_2-CH_2-CH=CH_2$

(C) $CH_3-CH_2-CH_2-CH(Br)-CH_2Br$

49. *Step I*

896 mL vapour of C_xH_y (A) weighs 3.28 g

22700 mL vapour of C_xH_y (A) weighs $\frac{3.28\times22700}{896}$ g mol^{-1} = 83.1 g mol^{-1}

Step II

Element	*(%)*	*Atomic mass*	*Relative ratio*	*Relative no. of atoms*	*Simplest ratio*
C	87.8	12	7.31	1	3
H	12.19	1	12.19	1.66	4.98≈5

Empirical formula of 'A' C_3H_5

Empirical formula mass = 35 + 5 = 41 u

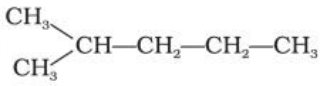
$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{83.1}{41} = 2.02 \approx 2$$

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

$\therefore$ Molecular Formula is C_6H_{10}

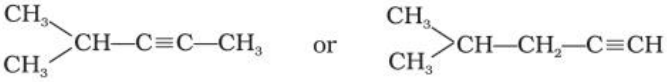
Step III

$$\underset{\text{(A)}}{C_6H_{10}} \xrightarrow{2H_2} \text{2-methylpentane}$$

Structure of 2-methylpentane is 

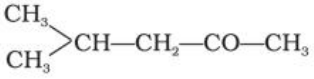
Hence, the molecule has a five carbon chain with a methyl group at the second carbon atom.

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



I or II

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



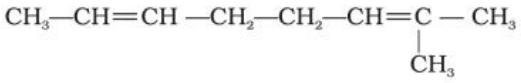
Therefore structure of alkyne is II.

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



(A)

Reactions

