# **Topic 1** Saturated Hydrocarbons

## **Objective Questions I** (Only one correct option)

**1.** In the following skew conformation of ethane,



- (a) 58° (b) 149° (c) 151° (d) 120°
  2. Which of these factors does not govern the stability of a conformation in acyclic compounds? (2019 Main, 10 April II)
  - (a) Electrostatic forces of interaction
  - (b) Torsional strain
  - (c) Angle strain
  - (d) Steric interactions
- **3.** Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure. (2014 Adv.)



The correct order of their boiling point is

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

4. 
$$\begin{array}{c} CH_3 \\ H_3C \\ CH_3 \end{array} \xrightarrow{Cl_2, hv} N \text{ (isomeric products) } C_5H_{11}Cl \\ CH_3 \end{array}$$

Fractional distillation 
$$M$$
 (isometric products)

	·	*	,	
What are N and M?				(2006, 5M)
(a) 6, 6		(b) 6, 4		
(c) 4, 4		(d) 3, 3		

1-bromo-3-chlorocyclobutane when treated with two equivalents of Na, in the presence of ether which of the following will be formed? (2005, 1M)



- 6. How many chiral compounds are possible on mono chlorination of 2-methyl butane? (2004, 1M)
  (a) 2 (b) 4
  (c) 6 (d) 8
- **7.** Consider the following reaction

$$\begin{array}{ccc} H_{3}C & - CH - CH - CH_{3} + Br & \longrightarrow X + HBr \\ & | & | \\ D & CH_{3} \end{array}$$

Identify the structure of the major product X (2002, 3M)

(a) 
$$H_3C$$
— $CH$ — $CH$ — $\dot{C}H_2$  (b)  $H_3C$ — $CH$ — $\dot{C}$ — $CH_3$   
D  $CH_3$  D  $CH_3$  (c)  $H_3C$ — $\dot{C}$ — $CH$ — $CH_3$   
D  $CH_3$  (d)  $H_3C$ — $\dot{C}H$ — $CH$ — $CH_3$   
D  $CH_3$  (d)  $H_3C$ — $\dot{C}H$ — $CH_3$ 

- 9. (CH<sub>3</sub>)<sub>3</sub>CMgCl on reaction with D<sub>2</sub>O produces (1997)
   (a) (CH<sub>3</sub>)<sub>3</sub>CD (b) (CH<sub>3</sub>)<sub>3</sub>OD
   (c) (CD<sub>3</sub>)<sub>3</sub>CD (d) (CD<sub>3</sub>)<sub>3</sub>OD
- 10. When cyclohexane is poured on water, it floats because

  (a) cyclohexane is in 'boat' form
  (b) cyclohexane is in 'chair' form
  (c) cyclohexane is in 'crown' form
  (d) cyclohexane is less dense than water

- **12.** The compound which has one isopropyl group, is (1989, 1M) (a) 2,2,3,3-tetramethyl pentane (b) 2,2-dimethyl pentane (c) 2,2,3-trimethyl pentane (d) 2-methyl pentane
- **13.** The highest boiling point is expected for (1986, 1M) (a) iso-butane (b) n-octane (c) 2, 2, 3, 3-tetramethyl butane (d) n-butane
- 14. Which of the following compounds does not dissolve in conc. H<sub>2</sub>SO<sub>4</sub> even on warming? (1983, 1M) (a) Ethylene (b) Benzene (c) Hexane (d) Aniline

# **Topic 2** Unsaturated Hydrocarbons

**Objective Questions I** (Only one correct option)

**1.** Consider the following reactions,

$$A \xrightarrow[Hg^{2^+/H^+}]{D} ppt$$

$$A \xrightarrow[Hg^{2^+/H^+}]{B} \xrightarrow[C]{2nCl_2} C_{Conc. HCl} Turbidity within 5 minutes$$

A is

- (2019 Main, 12 April II) (a)  $CH \equiv CH$ (b)  $CH_2 - C \equiv C - CH_3$ (c)  $CH_3 - C \equiv CH$ (d)  $CH_2 = CH_2$
- **2.** But-2-ene on reaction with alkaline  $KMnO_4$  at elevated temperature followed by acidification will give

(2019 Main, 12 April I)

(b) one molecule of CH<sub>3</sub>CHO and one molecule of CH<sub>3</sub>COOH (c) 2 molecules of CH<sub>3</sub>COOH

- (d) 2 molecules of CH<sub>3</sub>CHO
- **3.** The major product of the following addition reaction is

$$H_3C$$
— $CH$  =  $CH_2 \xrightarrow{Cl_2/H_2O}$ 

(2019 Main, 12 April I)

(a) 
$$CH_3 - CH - CH_2$$
  
 $CI OH$   
(b)  $CH_3 - CH - CH_2$   
 $OH CI$   
(c)  $H_3C - O$   
(d)  $O$   
 $H_3C - CH_3$ 

(c) CH<sub>3</sub>CD(I)CHD(Cl)

**4.** The major product of the following reaction is  $CH_3C \equiv CH \xrightarrow{(i) DCl (l equiv.)}$ (ii) DI (2019 Main, 9 April I) (b) CH<sub>3</sub>CD<sub>2</sub>CH(Cl)(I) (a)  $CH_3CD(Cl)CHD(I)$ 

(d) CH<sub>3</sub>C(I)(Cl)CHD<sub>2</sub>

15.	The compound with highes	t boiling point is	(1982, 1M)
	<ul><li>(a) 2-methyl butane</li><li>(c) 2, 2-dimethyl propane</li></ul>	<ul><li>(b) <i>n</i>-pentane</li><li>(d) <i>n</i>-hexane</li></ul>	
16.	Marsh gas mainly contains (a) $C_2H_2$ (c) $H_2S$	(b) CH <sub>4</sub> (d) CO	(1980, 1M)

# **Integer Answer Type Question**

- **17.** The maximum number of isomers (including stereoisomers) that are possible on mono-chlorination of the following compound, is CH<sub>3</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub> (2011)
  - 5. Which one of the following alkenes when treated with HCl yields majorly an anti Markownikov product?

(2019 Main, 8 April II)

(a) 
$$Cl-CH = CH_2$$
 (b)  $H_2N-CH = CH_2$   
(c)  $CH_3O-CH = CH_2$  (d)  $F_3C-CH = CH_2$ 

6. The correct order for acid strength of compounds  $CH \equiv CH, CH_3 - C \equiv CH and CH_2 = CH_2 is as follows:$ (2019 Main, 12 Jan I) (a)  $CH_3 - C \equiv CH > CH_2 = CH_2 > HC \equiv CH$ 

(b)  $CH_3 - C \equiv CH > CH \equiv CH > CH_2 = CH_2$ (c)  $\text{HC} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2$ (d)  $CH \equiv C H > CH_2 = CH_2 > CH_3 - C \equiv CH$ 

- 7. The *trans*-alkenes are formed by the reduction of alkynes with (2018 Main) (a) H<sub>2</sub>-Pd/C, BaSO<sub>4</sub> (b) NaBH<sub>4</sub>
  - (c) Na/liq. NH<sub>3</sub> (d) Sn-HCl
- **8.** The reaction of propene with HOCl ( $Cl_2 + H_2O$ ) proceeds through the intermediate (2016 Main) (a)  $CH_{a} = \stackrel{\dagger}{C}H = CH_{a} = CI$  (b)  $CH_{a} = CH(OH) = \stackrel{\dagger}{C}H$

(c) 
$$CH_3 - CHCl - CH_2$$
 (d)  $CH_3 - CH(OH) - CH_2$   
(c)  $CH_3 - CHCl - CH_2$  (d)  $CH_3 - CH_2 - CH_2$  OH

- 9. Which of the following compounds will exhibit geometrical isomerism? (2015 Main) (a) 1-phenyl-2-butene (b) 3-phenyl-1-butene (d) 1, 1-diphenyl-1-propane (c) 2-phenyl-1-butene
- **10.** Which compound would give 5-keto-2-methyl hexanal upon ozonolysis? (2015 Main)



- **11.** The major organic compound formed by the reaction of 1,1,1-trichloroethane with silver powder is (2014 Main) (a) acetylene (b) ethene
  - (c) 2-butyne (d) 2-butene

OII

**12.** The number of optically active products obtained from the complete ozonolysis of the given compound, is (2012)

- **13.** The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are (2010)(a) BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>C  $\equiv$  CH (b)  $BrCH_2CH_2CH_3$  and  $CH_3CH_2CH_2C \equiv CH$ (c)  $BrCH_2CH_2CH_2CH_2CH_3$  and  $CH_3C \equiv CH$ (d)  $BrCH_2CH_2CH_2CH_3$  and  $CH_3CH_2C \equiv CH$
- **14.** The number of stereoisomers obtained by bromination of trans-2-butene is (2007)
  - (a) 1 (b) 2 (c) 3 (d) 4
- **15.** The reagent(s) for the following conversion,

is/are

Br

(a) alcoholic KOH

(b) alcoholic KOH followed by NaNH<sub>2</sub>

(c) aqueous KOH followed by NaNH<sub>2</sub> (d) Zn/CH<sub>3</sub>OH

**16.**  $CH_3 - CH = CH_2 + NOCl \longrightarrow P$ ; Identify the adduct.

(2006, 3M)

(2007, 3M)

(a) 
$$CH_3$$
— $CH$ — $CH_2$   
(b)  $CH_3$ — $CH$ — $CH_2$   
(c)  $NO$   
(c)  $CH_3$ — $CH_2$ — $CH$   
NO  
(d)  $CH_2$ — $CH_2$ — $CH_2$   
NO  
NO  
Cl

- **17.** Cyclohexene is best prepared from cyclohexanol by which of the following? (2005) (a) conc. H<sub>3</sub>PO<sub>4</sub> (b) conc. HCl / ZnCl<sub>2</sub> (d) conc. HBr (c) conc. HCl
- **18.** 2-hexyne gives *trans*-2-hexene on treatment with (2004, 1M) (a) Li/NH<sub>3</sub> (b) Pd/BaSO<sub>4</sub> (c) LiAlH<sub>4</sub> (d)  $Pt/H_2$
- **19.** 2-phenyl propene on acidic hydration, gives (2004, 1M) (a) 2-phenyl-2-propanol (b) 2-phenyl-1-propanol

  - (c) 3-phenyl-1-propanol
  - (d) 1-phenyl-2-propanol



- **21.** Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne. (2002, 3M) (a) bromine,  $CCl_4$ (b) H<sub>2</sub>, Lindlar catalyst (c) dilute H<sub>2</sub>SO<sub>4</sub>, HgSO<sub>4</sub> (d) ammoniacal CuCl<sub>2</sub> solution
- **22.** In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because (2001, 1M) (a) both are highly ionic (b) one is oxidising and the other is reducing (c) one of the steps is endothermic in both the cases
  - (d) all the steps are exothermic in both the cases
- 23. The reaction of propene with HOCl proceeds via the addition (2001) of (a)  $H^+$  in the first step (b)  $Cl^+$  in the first step
  - (c) OH<sup>-</sup> in the first step (d) Cl<sup>+</sup> and OH<sup>-</sup> single step
- 24. Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives



(a) an optically active compound (b) an optically inactive compound (c) a racemic mixture

(d) a diastereomeric mixture

- **25.** Propyne and propene can be distinguished by (2000) (a) conc. H<sub>2</sub>SO<sub>4</sub> (b) Br<sub>2</sub> in CCl<sub>4</sub> (c) dil. KMnO<sub>4</sub> (d) AgNO<sub>3</sub> in ammonia
- **26.** Which one of the following alkenes will react fastest with  $H_2$ under catalytic hydrogenation condition ? (2000, 1M)



**27.** The product(s) obtained *via* oxymercuration  $(HgSO_4 + H_2SO_4)$  of 1-butyne would be (1999, 2M)

- (a)  $CH_3 CH_2 \ddot{C} CH_3$
- (b) CH<sub>3</sub>— CH<sub>2</sub>— CH<sub>2</sub>— CHO
- (c)  $CH_3 CH_2 CHO + HCHO$
- (d)  $CH_3 CH_2 COOH + HCOOH$

- **28.** In the compound, // H, the C2-C3 bond is of the type (1999, 2M) (a)  $sp - sp^2$  (b)  $sp^3 - sp^3$  (c)  $sp - sp^3$  (d)  $sp^2 - sp^3$
- **29.** The reaction of CH<sub>3</sub>CH=CH OH with HBr gives (1998, 2M)



- 30. Which one of the following has the smallest heat of hydrogenation per mole? (1993, 1M)
  (a) 1-butene (b) trans-2-butene
  (c) cis-2-butene (d) 1, 3-butadiene
- 31. The number of structural and configurational isomers of a bromo compound, C<sub>5</sub>H<sub>9</sub>Br, formed by the addition of HBr to 2-pentyne respectively, are (1988, 1M)
  (a) 1 and 2
  (b) 2 and 4
  (c) 4 and 2
  (d) 2 and 1
- 32. Acidic hydrogen is present in (1985, 1M) (a) ethyne (b) ethene (c) benzene (d) ethane
  33. Baeyer's reagent is (1984, 1M) (a) alkaline permanganate solution (b) acidified permanganate solution
  - (c) neutral permanganate solution
  - (d) aqueous bromine solution
- 34. When propyne is treated with aqueous H<sub>2</sub>SO<sub>4</sub> in the presence of HgSO<sub>4</sub>, the major product is (1983, 1M)
  (a) propanal (b) propyl hydrogen sulphate
  (c) acetone (d) propanol
- **35.** The compound 1, 2-butadiene has (1983, 1M) (a) only *sp*-hybridised carbon atoms (b) only *sp*<sup>2</sup>-hybridised carbon atoms (c) both *sp* and *sp*<sup>2</sup>-hybridised carbon atoms (d) *sp*, *sp*<sup>2</sup> and *sp*<sup>3</sup>-hybridised carbon atoms
- 36. Which of the following will decolourise alkaline KMnO<sub>4</sub> solution? (1980, 1M)
  (a) C<sub>3</sub>H<sub>8</sub> (b) CH<sub>4</sub> (c) CCl<sub>4</sub> (d) C<sub>2</sub>H<sub>4</sub>

# **Objective Questions II**

(One or more than one correct option)

37. The correct statement(s) for the following addition reactions is (are) (2017 Adv.)



- (a) (M and O) and (N and P) are two pairs of enantiomers
- (b) Bromination proceeds through *trans*-addition in both the reactions
- (c) *O* and *P* are identical molecules
- (d) (M and O) and (N and P) two pairs of diastereomers

## **Assertion and Reason**

Read the following questions and answer as per the direction given below :

- (a) Statement I is correct Statement II is correct Statement II is a correct explanation of Statement I.
- (b) Statement I is correct Statement II is correct Statement II is not the correct explanation of Statement I.
- (c) Statement I is correct Statement II is incorrect.
- (d) Statement I is incorrect Statement II is correct.
- **38.** Statement I Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromo butane.

Statement II Bromine addition to an alkene is an<br/>electrophilic addition.(2001, 1M)

**39.** Statement I Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compound.

**Statement II** It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. (2001, 1M)

- 40. Statement I 1-butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.
   Statement II It involves the formation of a primary radical. (2000, 1M)
- **41.** Statement I Addition of Br<sub>2</sub> to 1-butene gives two optical isomers.

Statement II The product contains one asymmetric carbon.

(1998,1M)

## **Passage Based Questions**

#### Passage 1



**42.** Compound *X* is



#### **43.** The major compound *Y* is



#### Passage 2

An acyclic hydrocarbon P, having molecular formula  $C_6H_{10}$ , gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.



**44.** The structure of the compound Q is



**45.** The structure of compound *P* is

(a) 
$$CH_3CH_2CH_2CH_2-C \equiv C-H$$
  
(b)  $H_3CH_2C-C \equiv C-CH_2CH_3$   
(c)  $H-C-C \equiv C-CH_3$   
 $H_3C$   
(d)  $H_3C-C-C \equiv C-H$   
 $H_3C$ 

#### Passage 3

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both schemes.



46. The correct statement with respect to product Y is
(a) it gives a positive Tollen's test and is a functional isomer of X
(b) it gives a positive Tollen's test and is a geometrical isomer of X
(c) it gives a positive iodoform test and is a functional isomer of X

(d) it gives a positive iodoform test and is a geometrical isomer of X



# Fill in the Blanks

- **48.** 1,3-butadiene with bromine in molar ratio of 1 : 1 generate predominantly ..... (1997, 1M)
- **49.** Addition of water to acetylene compounds is catalysed by ..... and ..... (1993, 1M)
- **50.** Kolbe's electrolysis of potassium succinate gives  $CO_2$  and .....

(1993, 1M)

- **51.** The terminal carbon atom in 2-butene is ..... hybridised. (1985, 1M)
- **53.** ..... is most acidic. (Ethane, Ethene, Ethyne) (1981, 1M)

## **True/False**

**54.** Moist ethylene can be dried by passing it through concentrated sulphuric acid. (1981)

## **Integer Answer Type Question**

**55.** The total number of cyclic isomers possible for a hydrocarbon with the molecular formula  $C_4H_6$  is (2010)

#### **Subjective Questions**

- **56.** Monomer *A* of a polymer on ozonolysis yields two moles of HCHO and one mole of  $CH_3COCHO$ .
  - (a) Deduce the structure of A.
  - (b) Write the structure of all *cis* form of polymer of compound *A*. (2005, 2M)
- **57.** A biologically active compound, Bombykol ( $C_{16}H_{30}O$ ) is obtained from a natural source. The structure of the compound is determine by the following reactions.
  - (a) On hydrogenation, Bombykol gives a compound A, C<sub>16</sub>H<sub>34</sub>O, which reacts with acetic anhydride to give an ester.
  - (b) Bombykol also reacts with acetic anhydride to give another ester, which on oxidative ozonolysis (O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>) gives a mixture of butanoic acid, oxalic acid and 10-acetoxy decanoic acid.

Determine the number of double bonds in Bombykol. Write the structures of compound *A* and Bombykol. How many geometrical isomers are possible for Bombykol?

**58.** Identify *X*, *Y* and *Z* in the following synthetic scheme and write their structures.

$$CH_{3}CH_{2} - C \equiv C - H \xrightarrow{(i) \text{ NaNH}_{2}} (ii) CH_{3}CH_{2}Br$$
$$X \xrightarrow{H_{2}/Pd BaSO_{4}} Y \xrightarrow{Alkaline KMnO_{4}} Z$$

Is the compound Z optically active? Justify your answer. (2002)

**59.** (a) Identify (A), (B), (C), (D) and (E) in the following schemes and write their structures :

$$A \xrightarrow{\text{NaNH}_2} B \xrightarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} C$$

$$C \xrightarrow{\text{H}_2\text{NHNCONH}_2} D \xrightarrow{\text{NaOD/D}_2\text{O} \text{ (excess)}} E$$

(b) Identify (X), (Y) and (Z) in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H<sub>2</sub>C\*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed. Mark the C\* carbon in the entire scheme. BaC\*O<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → (X) gas [C\* denotes C<sup>14</sup>]

$$H_2C = CH - Br \xrightarrow{(i) Mg/ether}_{(ii) X} (Y) \xrightarrow{\text{LiAlH}_4} (Z)$$

$$\xrightarrow{(iii) X}_{(iii) H_2O^+} (2001)$$

**60.** An alkene (*A*)  $C_{16}H_{16}$  on ozonolysis gives only one product (*B*)  $C_8H_8O$ . Compound (*B*) on reaction with NaOH/I<sub>2</sub> yields sodium benzoate. Compound (*B*) reacts with KOH/NH<sub>2</sub>NH<sub>2</sub> yielding a hydrocarbon (*C*)  $C_8H_{10}$ . Write the structures of compounds (*B*) and (*C*). Based on

this information two isomeric structures can be proposed for alkene (*A*). Write their structures and identify the isomer which on catalytic hydrogenation  $(H_2/Pd - C)$  gives a racemic mixture. (2001)

**61.** What would be the major product in the following reaction?



62. Complete the following reactions with appropriate reagents :



**63.** Complete the following reactions with appropriate structures of products/reagents :

$$C_6H_5CH = CH_2 \xrightarrow{Br_2} [A] \xrightarrow{(i) \text{ NaNH}_2 (3 \text{ equivalent})} [B]$$
(1998, 2M)

64. Write the intermediate steps for each of the following reactions :

(i) 
$$C_6H_5CH(OH)C \equiv CH \xrightarrow{H_3O^+} C_6H_5 - CH = CH - CHO$$
  
(ii)  $H^+ \rightarrow H^+$ 

- 65. The hydrocarbon A, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When A is oxidised
- of a platinum catalyst to form *n*-hexane. When A is oxidised vigorously with KMnO<sub>4</sub>, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of A and explain. (1997, 2M)
- **66.** Complete the following, giving the structures of the principal organic products : (1997, 1M)



**67.** An alkyl halide, *X*, of formula  $C_6H_{13}Cl$  on treatment with potassium tertiary butoxide gives two isomeric alkenes *Y* and *Z* ( $C_6H_{12}$ ). Both alkenes on hydrogenation gives 2, 3-dimethyl butane. Predict the structures of *X*, *Y* and *Z*. (1996, 3M)

- **68.** Give the structure of the major organic products obtained from 3-ethyl-2-pentene under each of the following reaction conditions : (1996)
  - (a) HBr in the presence of peroxide
  - (b)  $\operatorname{Br}_2/\operatorname{H}_2O$
  - (c) Hg(OAc)<sub>2</sub> / H<sub>2</sub>O, NaBH<sub>4</sub>
- **69.** Write down the structure of the stereoisomers formed when *cis*-2-butene is reacted with bromine. (1995)
- **70.** An organic compound  $E(C_5H_8)$  on hydrogenation gives compound  $F(C_5H_{12})$ . Compound E on ozonolysis gives formaldehyde and 2-keto propanal. Deduce the structure of compound E. (1995)
- **71.** When gas *A* is passed through dry KOH at low temperature, a deep red coloured compound *B* and a gas *C* are obtained. The gas *A*, on reaction with but-2-ene, followed by treatment with  $Zn / H_2O$  yields acetaldehyde. Identify *A*, *B* and *C*.

#### (1994, 3M)

- **72.** Give the structures of A, B and C (explanation are not required)
  - A (C<sub>4</sub>H<sub>8</sub>) which adds on HBr in the presence and in the absence of peroxide to give same product.
  - (ii)  $B(C_4H_8)$  which when treated with  $H_2O/H_2SO_4$  gives  $C_4H_{10}O$  which cannot be resolved into optical isomers.
  - (iii) C ( $C_6H_{12}$ ), an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound  $C_6H_{14}$ . (1993,1M × 3 = 3M)
- 73. Write the balanced chemical equation for the following"Ethylene glycol is obtained by the reaction of ethylene with potassium permanganate." (1991, 1M)
- **74.** Give a chemical test and the reagents used to distinguish between cyclohexane and cyclohexene. (1991, 1M)
- **75.** A white precipitate was formed slowly when silver nitrate was added to compound *A* with molecular formula  $C_6H_{13}$ Cl. Compound *A* on treatment with hot alcoholic potassium hydroxide gave a mixture of two isomeric alkenes *B* and *C*, having formula  $C_6H_{12}$ . The mixture of *B* and *C*, on ozonolysis, furnished four compounds

(i) CH<sub>3</sub>CHO (ii) C<sub>2</sub>H<sub>5</sub>CHO

#### (iii) $CH_3COCH_3$ (iv) $CH_3$ —CH— CHO| $CH_3$

What are the structures of A, B and C?

76. How would you convert acetylene to acetone? (1985, 1M)

(1986, 4M)

- 77. Give the chemical test to distinguish between 2-butyne and 1-butyne. (1985, 1M)
- **78.** Following statements are true, only under some specific conditions. Write the condition for each subquestion in not more than two sentences :
  - (i) 2-methyl propene can be converted into isobutyl bromide by hydrogen bromide.
  - (ii) Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution.  $(1984,1M \times 2 = 2M)$
- **79.** Give reasons for the following in one or two sentences :
  - (i) Methane does not react with chlorine in the dark.
  - (ii) Propene reacts with HBr to give isopropyl bromide but does not give *n*-propyl bromide.  $(1983,1M \times 2 = 2M)$
- 80. State with balanced equation, what happens when "propene is bubbled through a hot aqueous solution of potassium permanganate."? (1982, 1M)
- **81.** One mole of a hydrocarbon A reacts with one mole of bromine giving a dibromo compound,  $C_5H_{10}Br_2$ . Compound A on treatment with cold dilute alkaline potassium permanganate solution forms a compound,  $C_5H_{12}O_2$ . On ozonolysis A gives equimolar quantities of propanone and ethanal. Deduce the structural formula of A. (1981, 1M)
- **82.** Write the structural formula of the major product in each of the following cases
  - (i) Ethene mixed with air is passed under pressure over a silver catalyst.
  - (ii) The compound obtained by hydration of ethyne is treated with dilute alkali. (1981,  $2 \times 1/2 M = 1M$ )
- 83. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). (1981, 1M)
- **84.** Give one characteristic test which would distinguish  $CH_4$  from  $C_2H_2$ . (1979, 1M)

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

**55.** (5)

# Answers

Topic 1				<b>17.</b> (a)	<b>18.</b> (a)	<b>19.</b> (a)	20.
<b>1.</b> (b)	<b>2.</b> (c)	<b>3.</b> (b)	<b>4.</b> (b)	<b>21.</b> (d)	<b>22.</b> (c)	<b>23.</b> (b)	24.
<b>5.</b> (d)	<b>6.</b> (c)	<b>7.</b> (b)	<b>8.</b> (c)	<b>25.</b> (d)	<b>26.</b> (a)	<b>27.</b> (a)	28.
<b>9.</b> (a)	<b>10.</b> (d)	<b>11.</b> (c)	<b>12.</b> (d)	<b>29.</b> (c)	<b>30.</b> (b)	<b>31.</b> (b)	32.
<b>13.</b> (b)	14. (c)	<b>15.</b> (d)	<b>16.</b> (b)	<b>33.</b> (a)	<b>34.</b> (c)	<b>35.</b> (d)	36.
17. (8)				<b>37.</b> (a,b,d)	<b>38.</b> (b)	<b>39.</b> (a)	40.
Topic 2				<b>41.</b> (a)	<b>42.</b> (c)	<b>43.</b> (d)	44.
	9 ()	9 (1)	<b>A</b> (1)	<b>45.</b> (d)	<b>46.</b> (c)	<b>47.</b> (a)	
<b>I.</b> (c)	<b>Z.</b> (c)	<b>3.</b> (b)	<b>4.</b> (d)	<b>48.</b> 3,4-dibro	mo-1-butene	<b>49.</b> H <sub>2</sub> SO <sub>4</sub>	, HgSO₄
<b>5.</b> (d)	<b>6.</b> (c)	<b>7.</b> (c)	<b>8.</b> (a)	50 others	<b>51</b> an <sup>3</sup>	<b>59</b> 0 hutra	
<b>9.</b> (a)	<b>10.</b> (b)	<b>11.</b> (c)	<b>12.</b> (a)	<b>30.</b> etnene	<b>31.</b> sp	<b>32.</b> 2-Dutyr	le
<b>13.</b> (d)	<b>14.</b> (a)	<b>15.</b> (b)	<b>16.</b> (a)	<b>53.</b> Terminal	alkyne (ethyne)	<b>54.</b> False	55.

# **Hints & Solutions**

# **Topic 1 Saturated Hydrocarbons**

**1.** A dihedral angle is the angle between two C—H bonds projected on a plane orthogonal to the C—C bond. In the given skew conformation, having Newman's projection the dihedral angle is

The four types of strains *viz* (a) electrostatic force of attraction,
 (b) torsional strain, (c) angle strain, (d) steric stain, are responsible for the stability or energy barriers of conformers. In cyclic compounds, all types of strains may be present.

Compound	Type of strains/forces
	a + c
	a + b + c
OH F	a+b+c+d

In a cyclic or open-chain compounds, angle strain (c) is absent. e.g.



**3. PLAN** This problem is based on boiling point of isomeric alkanes. As we know more the branching in an alkane, lesser will be its surface area and lesser will be the boiling point



#### On moving left to right (III to I)

- branching increases
- surface area decreases
- boiling point decreases
- Hence, correct choice is (b).



Since, fractional distillation cannot separate enantiomers (II + III and V + VI), M = 4 and N = 6.



Out of the four products formed above, II and IV are chiral, produced in pairs, giving total of six mono-chlorination products.

**7.** Bromination is highly selective, occur at the carbon, where the most stable free radical is formed :

$$CH_{3} - CHD - CH - CH_{3} + Br^{\bullet} \longrightarrow$$

$$CH_{3} - CHD - \overset{\bullet}{C} - CH_{3} + HBr$$

$$CH_{3} - CHD - \overset{\bullet}{C} - CH_{3} + HBr$$

$$(a \text{ tertiary free radical})$$

**8.** Toluene on treatment with Cl<sub>2</sub> in the presence of heat or light undergo free-radical chlorination at benzylic position, giving benzyl chloride

$$\begin{array}{c} CH_{3} \\ \hline \\ Toluene \end{array} + Cl_{2} \xrightarrow{h\nu} \\ \hline \\ H_{3} \end{array} \xrightarrow{CH_{2}Cl} + HCl \\ HCl \\$$

9. 
$$(CH_3)_3CMgCl + D_2O \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \longrightarrow D + Mg(OD)Cl$$

- 10. Alkanes are all less dense than water, floats over water.
- **11.** C—H bond with  $sp^3$ -C will be longest in C<sub>2</sub>H<sub>6</sub>.

- **13.** Boiling point of alkane increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-octane has highest boiling point, higher than 2, 2, 3, 3-tetramethyl-butane (an isomer of *n*-octane).
- 14. Ethylene absorb  $H_2SO_4$  forming  $CH_3$ — $CH_2OSO_3H$  and dissolve. Benzene, with warm  $H_2SO_4$ , undergo sulphonation and dissolve.

Aniline, with  $H_2SO_4$ , forms anilinium sulphate salt and dissolve. Hexane, a hydrophobic molecule, does not react with  $H_2SO_4$ , remains insoluble.

- **15.** Among alkanes, boiling point increases with molar mass. Among isomeric alkanes, branching decreases boiling point. Therefore, *n*-hexane has highest boiling point among these.
- **16.** Methane is produced due to the decay of vegetables or animal organisms present in swamps and marsh, by the action of bacteria.

Due to this method of formation, methane is also known as marsh gas.



I has one chiral carbon = two isomers II has two chiral carbons and no symmetry = four isomers. III and IV have no chiral carbon, no stereoisomers.

# **Topic 2** Unsaturated Hydrocarbons

 According to the given conditions, the compound should be alkyne with triple bond present at the terminal. The chemical reactions involved are as follows: Step 1

$$\begin{array}{c} CH_3 \longrightarrow C \Longrightarrow CH \xrightarrow{Ag_2O} CH_3 \longrightarrow C \boxplus C \longrightarrow Ag_3 \\ Prop-1-yne \\ (A) \end{array} (Precipitates) \end{array}$$

Step 2

$$\begin{array}{c} \mathsf{CH}_{3} - \mathsf{C} \equiv \mathsf{CH} \xrightarrow[]{\mathsf{Hg}^{2+}} \\ \hline \mathsf{CH}_{3} - \mathsf{C} \equiv \mathsf{CH}_{2} \xrightarrow[]{\mathsf{merisation}} \mathsf{CH}_{3} - \mathsf{C} \mathsf{CH}_{3} \\ \hline \mathsf{CH}_{3} - \mathsf{C} = \mathsf{CH}_{2} \xrightarrow[]{\mathsf{merisation}} \mathsf{CH}_{3} - \mathsf{C} \mathsf{CH}_{3} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} - \mathsf{CH}_{3} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} - \mathsf{CH}_{3} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} - \mathsf{CH}_{3} \\ \hline \mathsf{OH} \\ \mathsf{(C)} (2^{\circ} \text{ alcohol}) \\ \hline \mathsf{Ch}_{3} - \mathsf{CH} - \mathsf{CH}_{3} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} - \mathsf{CH} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} - \mathsf{CH}_{3} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} - \mathsf{CH} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} - \mathsf{CH} \\ \hline \mathsf{CH}_{3} - \mathsf{CH} \\ \hline \mathsf{CH} \\ \hline \mathsf{C$$

In step-1, prop-1-yne reacts with  $Ag_2O$  to form  $CH_3 - C = C - Ag$ , that forms white precipitates.

In step 2, prop-1-yne in presence of mercuric sulphate and dil  $H_2SO_4$  produces carbonyl compound  $(CH_3)_2C = O$  which produces  $(CH_3)_2CH$ —OH in presence of NaBH<sub>4</sub>. 2°alcohol on reaction with Lucas reagent produces turbidity in about 5 min.

**2.** But-2-ene on reaction with alkaline  $KMnO_4$  at elevated temperature followed by acidification will give acetic acid (CH<sub>3</sub>COOH). Hot alkaline solution of potassium permanganate followed by acidification oxidatively cleaved alkenes. The reaction proceed as follows :

$$CH_{3} - CH = CH - CH_{3} \xrightarrow{Alk. KMnO_{4}, heat} 2CH_{3}COOH$$
  
But-2-ene 
$$H_{3}O^{+} \xrightarrow{Alk. cond} 2CH_{3}COOH$$

- 3. The major product of the given addition reaction is  $H_3C CH CH_2$ .
  - о́н <sub>Cl</sub>

In this reaction,  $H_2O$  is used as a solvent and the major product of the reaction will be a *vicinal* halohydrin. A halohydrin is an organic molecule that contains both OH group and a halogen. In a *vicinal* halohydrin, the OH and halogen are bonded to adjacent carbons.

$$\begin{array}{c} \mathrm{H_3C}-\mathrm{CH}=\mathrm{CH_2} \xrightarrow{\mathrm{Cl_2/H_2O}} \mathrm{H_3C}-\mathrm{CH}-\mathrm{CH_2} + \\ | & | \\ \mathrm{OH} & \mathrm{Cl} \\ \end{array} \\ & \text{A chlorohydrin (major product)} \\ & \mathrm{CH_3}-\mathrm{CH}-\mathrm{CH} \\ & | \\ \mathrm{Cl} & \mathrm{Cl} \end{array}$$

(Minor product)

The reaction proceeds through following mechanism :





**4.** The major product obtained in the given reaction is CH<sub>3</sub>C (I) (Cl) CHD<sub>2</sub>.

$$CH_{3}C \equiv CH \xrightarrow{1. DCI (1 \text{ equiv.})}{2. DI} CH_{3}C (I)(Cl)CHD_{2}$$

Addition in unsymmetrical alkynes takes place according to Markovnikov's rule.

01

Reaction proceed as follows :

$$CH_{3} C \equiv CH \xrightarrow{DCl (1 \text{ equiv.})} CH_{3} C \equiv CHD \xrightarrow{DI} Cl$$

$$CH_{3} C = CHD \xrightarrow{DI} Cl$$

$$CH_{3} \xrightarrow{C} CHD_{2}$$

$$CH_{3} \xrightarrow{C} CHD_{2}$$

**5.** Attachment of electron donating group (+ R or + I) with  $sp^2$ -carbon of an unsymmetrical alkene supports Markownikov's addition rule through electrophilic-addition-pathway.

But, attachment of electron-withdrawing group (-R or -I) for the same will follow anti-Markownikov's pathway (even in absence of organic peroxide which favours free radical addition) through electrophilic addition pathway.

The product formed by given alkenes when treated with HCl.



Similarly,

$$H_{2}\overset{\frown}{N} \xrightarrow{C} CH \xrightarrow{CH_{2}} CH_{2} \xrightarrow{\delta_{+} \delta_{-}} NH_{2} \xrightarrow{CH_{-} CH_{3}} CH_{3} \xrightarrow{CH_{-} CH_{2}} NH_{2} \xrightarrow{CH_{-} CH_{3}} HH_{2} \xrightarrow{CH_{2} CH_{3}} HH_{2} \xrightarrow{CH_{3} CH_{3}}$$

$$\begin{array}{c} \overbrace{CI}^{\bullet} \rightarrow H \overleftarrow{} \\ F_{3}C \leftarrow CH = CH_{2} \xrightarrow{HCI} Slow} F_{3}C - CH_{2} - C\overset{\#}{H_{2}} \\ \xrightarrow{(-1)} - CI^{\circ} \\ \xrightarrow{CI}^{\circ} \\ \overline{Slow}} F_{3}C - CH_{2}CH_{2}CH_{2}CI \end{array}$$

**6.** Ethene  $(H_2C = CH_2)$  is  $sp^2$ -hybridised and ethyne (HC = CH) is sp-hybridised. In ethyne, the sp-hybridised carbon atom possesses maximum s-character and hence, maximum electronegativity. Due to which, it attracts the shared electron pair of C—H bond to a greater extent and makes the removal of proton easier. Hence, alkyne is much more acidic than alkene.

Presence of electron donating group in alkyne ( $H_3C$ —C  $\equiv$  CH) decreases the acidic strength of compound. Hence, the correct order of acidic strength is:

 $HC \equiv CH > H_3C - C \equiv CH > CH_2 = CH_2$ 

**7.** Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.

#### Mechanism







**11.** The reaction is

$$2CH_3 - CCl_3 - \frac{6Ag}{\Delta} CH_3 - C \equiv C - CH_3 + 6 AgCl$$
  
But-2-vne

**12.** Ozonolysis of the given triene occur as follows :

Since, none of the above dial is chiral, no optically active product is obtained.

- **13.**  $CH_3CH_2C \equiv CH + Br CH_2CH_2CH_2CH_3$  $\xrightarrow{-HBr} CH_3CH_2 - C \equiv C - CH_2CH_2CH_2CH_3$  $\xrightarrow{-HBr} CH_3CH_2 - C \equiv C - CH_2CH_2CH_2CH_3$
- 14. Br<sub>2</sub> undergo anti-addition on C = C bonds as:



**16.** NOCl undergo electrophilic addition on alkene as: NOCl  $\longrightarrow {}^{+}N = O + Cl^{-}$ 

$$CH_{3} - CH = CH_{2} + {}^{+}NO \longrightarrow CH_{3} - {}^{+}CH - CH_{2} \xrightarrow[NO]{} NO$$
$$CH_{3} - {}^{CH} - CH_{2} \xrightarrow[CI]{} NO$$
$$CH_{3} - {}^{CH} - CH_{2} \xrightarrow[CI]{} NO$$

**17.** Cyclohexanol on treatment with concentrated H<sub>3</sub>PO<sub>4</sub> undergo acid catalysed dehydration giving cyclohexene.



**18.** Alkynes on treatment with alkali metals in liquid ammonia gives *trans* hydrogenation product:

$$CH_{3} - C \equiv C - CH_{2} - CH_{2} - CH_{3} \xrightarrow{L1/NH_{3}}$$

$$H_{3}C = C \xrightarrow{H}_{CH_{2}CH$$

19. Reaction proceeds through carbocation intermediate:

CH<sub>3</sub>—C—CH<sub>3</sub> | Ph 2-phenyl-2-propanol

20. Reaction proceeds through carbocation intermediate :

С

$$Ph-C \equiv C-CH_{3} + H^{+} \longrightarrow Ph-C^{+} = CH-CH_{3} \xrightarrow{H_{2}O} Resonance stabilised} \xrightarrow{OH} Ph-C = CH-CH_{3} \xrightarrow{(Tautomerisation)} Ph-C-CH_{2}-CH_{3}$$

**21.** Ammoniacal CuCl<sub>2</sub> forms red precipitate with terminal alkynes, can be used to distinguish terminal alkynes from internal alkynes:

$$H_{3} - CH_{2} - C \equiv C - H + CuCl_{2} \xrightarrow{NH_{3}(aq)} CH_{3} - CH_{2} - C \equiv C^{-}Cu^{+} \downarrow$$
  
red ppt.

22. In addition of HBr to an alkene, in the presence of peroxide, both the propagation steps are exothermic :

$$HBr + HO^{\bullet} \longrightarrow H_2O + Br$$

Propagation

IIOCI

$$\begin{cases} CH_3 - CH = CH_2 + Br^{\bullet} \longrightarrow CH_3 - CH - CH_2Br; \ \Delta H < 0 \\ CH_3 - CH - CH_2Br + HBr \longrightarrow CH_3 - CH_2 - CH_2Br \\ + Br^{\bullet}; \ \Delta H < 0 \end{cases}$$

In case of addition of HCl and HI, one of the propagation step is endothermic, reaction fail to occur.

**23.** HOC1 
$$\longrightarrow$$
 HO<sup>-</sup> + Cl<sup>+</sup>  
CH<sub>3</sub>—CH=CH<sub>2</sub> + Cl<sup>+</sup>  $\longrightarrow$  CH<sub>3</sub>—CH $\xrightarrow{\text{Cl}^+}$ CH<sub>2</sub>  
 $\xrightarrow{\text{HO}^-}$ CH<sub>3</sub>—CH $\xrightarrow{\text{CH}^-}$ CH<sub>2</sub>

i.e. reaction is initiated by Cl<sup>+</sup> (chloronium ion electrophile)

24. Hydrogenation with poisoned palladium brings about cis hydrogenation of alkyne and does not affect double bonds :



25. Terminal alkynes forms silver salt with Tollen's reagent while alkene does not react with Tollen's reagent.

$$CH_3 - C \equiv C - H + AgNO_3 \xrightarrow{NH_3(aq)} CH_3 - C \equiv CAg \downarrow$$
  
white ppt.

Therefore, Tollen's reagent can be used to distinguish a terminal alkyne like propyne from alkene as well as from internal alkynes.

- **26.** Ease of catalytic hydrogenation depends upon the size of groups present at the doubly bonded carbon. Larger the size of groups, difficult the hydrogenation. Therefore, in the given situation, disubstituted reacts at faster rate than tri and tetra substituted alkenes. Among disubstituted, the stability order is : *cis* < *geminal* < *trans.*
- 27. Oxymercuration-demercuration brings about Markownikoff's addition of water as :

$$CH_{3} - CH_{2} - C \equiv C - H + H_{2}SO_{4} \xrightarrow{HgSO_{4}}$$

$$\begin{bmatrix} OH \\ | \\ CH_{3} - CH_{2} - C \equiv CH_{2} \end{bmatrix} \longleftrightarrow CH_{3} - CH_{2} - C - CH_{3}$$
butanone
unstable enol

28. According to the IUPAC conventions, compound can be numbered as: .

$$H_2\dot{C} = \dot{C}H - \dot{C}H_2 - \dot{C}H_2 - \dot{C} = \dot{C} - H$$

Here, C-2 is  $sp^2$  and C-3 is  $sp^3$ -hybridised.

29. Electrophilic addition on C=C is governed by stability of carbocation:



- **30.** Among alkenes-heat of hydrogenation depends on :
  - (a) The number of double bonds-greater, greater the amount of heat evolved in hydrogenation.

Hence, 1, 3-butadiene has highest heat of hydrogenation among these.

(b) Relative stability of alkenes-greater the stability, smaller the heat evolved in hydrogenation. trans-2-butene is most stable among three given butenes, has least heat of hydrogenation.

**31.** 
$$CH_3 - C \equiv C - CH_2CH_3 + HBr$$

$$\underbrace{\begin{array}{c} H_{3}C \\ H \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} C_{2}H_{5} \\ H \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} Br \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical isomers} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical} C = C \underbrace{\begin{array}{c} H \\ C_{2}H_{5} \end{array}}_{geometrical} C$$

Therefore, two structural and four configurational isomers.

**32.** Terminal alkynes are slightly acidic, forms salt with very strong base like Na, NaNH<sub>2</sub> etc.

$$H \longrightarrow C \equiv C \longrightarrow H + Na \xrightarrow{\Delta} H \longrightarrow C \equiv C^{-}Na^{+} + \frac{1}{2}H_{2}^{\uparrow}$$

- **33.** Baeyer's reagent is cold, dilute, alkaline permanganate solution, used to detect presence of olefinic bonds.
- 34. Alkynes undergo Markownikoff's addition of water in the presence of  $H_2SO_4 / HgSO_4$ :

$$CH_{3}-C \equiv C-H+H_{2}SO_{4} \xrightarrow{HgSO_{4}} \begin{bmatrix} OH \\ | \\ CH_{3}-C \equiv CH_{2} \end{bmatrix}$$

$$(Tautomerisation) \xrightarrow{O} CH_{3}-C-CH_{3}$$

$$(Tautomerisation) \xrightarrow{O} CH_{3}-C-CH_{3}$$

**35.** Structural formula of 1, 2-butadiene is :

$$\begin{array}{c} H_2C = C = CH - CH_3 \\ \uparrow & \uparrow & \uparrow \\ sp^2 & sp & sp^2 & sp^3 \end{array}$$

**36.** Unsaturated compounds which contain C=C or C=C, decolourises the purple colour of alkaline KMnO<sub>4</sub> solution.

$$CH_2 = CH_2 + KMnO_4 \xrightarrow{HO^-} | CH_2 - OH \\ \downarrow \\ coloured \\ CH_2 - OH \\ CH_2 - OH \\ HnO_2 \downarrow$$

37. Addition of halogen at double bond occur in antiorientation *via* cyclic halonium ion intermediate.(i)



Here, (M + O) and (N + P) are pair of diastereomers.



Statement I is correct. Statement II is also correct. *Meso* form of the product is due to *anti* addition of Br<sup>-</sup> on cyclic bromonium ion intermediate, hence Statement II is not correct explanation of Statement I.



Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

**40.** 
$$CH_3 - CH_2 - CH = CH_2 + Br^{\bullet}$$
 ----

 $CH_3$  —  $CH_2$  — CH —  $CH_2Br$ a secondary radical

Therefore, Statement I is correct but Statement II is incorrect.

41. 
$$CH_3 - CH_2 - CH = CH_2 + Br_2 \longrightarrow$$
  
 $CH_3 - CH_2 - CH_2 - CH_2Br$   
Br  
has one chiral carbon

Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

#### Passage 1

The reaction condition indicates that starting compound is phenyl acetylene.

42.



Hydroboration oxidation brings about anti-Markonikoff's hydration of alkene.





#### Passage 2

The final ozonolysis product indicates that the alkene before ozonolysis is



Also  $P(C_6H_{10})$  has two degree of unsaturation and oxymercuration demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with NaBH<sub>4</sub> gives a 2° alcohol.

$$-C \equiv C - + H_2O \longrightarrow -C - CH_2 - \xrightarrow{(i) \text{ NaBH}_4} - C - CH_2 - H_2O \xrightarrow{(i) \text{ NaBH}_4} - C - CH_2 - H_2O \xrightarrow{(i) \text{ NaBH}_4} + H_2O \xrightarrow{(i) \text{ NaBH}_4} - C - CH_2 - H_2O \xrightarrow{(i) \text{ NaBH}_4} + H_2O \xrightarrow{(i)$$

The secondary alcohol that can give above shown alkene on acid catalysed dehydration is



44. Explained in the beginning.

#### Passage 3

**46. PLAN** This problem can be solved by using the concept of iodoform test and functional isomerism.

**Iodoform test** The compound containing — COCH<sub>3</sub> or —CH(OH) group will undergo iodoform test



- Thus, X and Y are functional isomers of each other and Y gives iodoform test due to the presence of CH<sub>3</sub>CO group as Indicated. Hence, correct choice is (c).
- **47. PLAN** This problem can be solved by using the concept of nucleophilic substitution reaction, oxidation reaction and reduction reaction including strength of nucleophile and regioselectivity.

Reaction of Scheme 1 can be completed as



Among two nacked nucleophilic group I and II, II is more nucleophilica and then will react selectively as follows



Hence, using the concept of regioselectivity we come on the conclusion that final product is correctly represented by structure (a).

**48.** 3, 4-dibromo-1-butene :

$$+ Br_2 \longrightarrow Br Br$$

**49.** 
$$CH \equiv CH + H_2SO_4 \xrightarrow{HgSO_4} CH_3CHO$$
  
 $CH_2 \longrightarrow COOK$ 

**50.** 
$$| \stackrel{2}{\underset{\text{CH}_2 \longrightarrow \text{COOK}}{\longrightarrow}} \xrightarrow{\text{Electrolysis}} \underset{\text{ethene}}{\underset{\text{CH}_2 \implies \text{CH}_2 + 2\text{CO}_2}} CH_2 = CH_2 + 2\text{CO}_2$$

**51.** 
$$CH_3 - CH = CH_3 - CH_3$$
  
2-butene

**52.** 2-butyne :

$$H - C \equiv C - H + \underset{excess}{Na} \longrightarrow \overset{+}{Na} \stackrel{-}{C} \equiv C^{-}Na^{+} \xrightarrow{CH_{3}I} \underset{excess}{excess}$$
$$CH_{3} - C \equiv C - CH_{3}$$

- **53.** Terminal alkyne (ethyne) is most acidic among these.
- 54. Sulphuric acid undergo addition to alkene.





**57.** From oxidation products, structure of starting compound can be deduced as :

$$C_{3}H_{8} - COOH + HOOC - COOH$$
  
butanoic acid oxalic acid O  
+ HOOC - (CH<sub>2</sub>)<sub>8</sub> - CH<sub>2</sub>O - C - CH<sub>3</sub>  
10-acetoxy decanoic acid  
 $\uparrow O_{3} / H_{2}O_{2}$   
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=CH-CH=CH-(CH<sub>2</sub>)<sub>8</sub>  
- CH<sub>2</sub>OCOCH<sub>2</sub>

Therefore, Bombykol is :





 $R = (CHl_3)_2 CHCH_2$ 





**73.** 
$$CH_2 = CH_2 + KMnO_4 + H_2O \longrightarrow CH_2 - CH_2 + MnO_2$$
  
 $| | | OH OH$   
Ethylene glycol

- **74.** Baeyer's reagent (cold, dilute, alkaline permanganate) can be used to distinguish between alkanes and alkenes. Alkenes decolourises purple colour of Baeyer's reagent while alkanes do not.
- **75.** The alkenes are :

$$CH_{3}-CH=O+O=CH-CH(CH_{3})_{2}$$

$$CH_{3} \qquad CH_{3} \qquad CH_{3}$$

$$CH_{3}-CH=CH-CH-CH_{3}; CH_{3}CH_{2}CH=O+O=C-CH_{3}$$

$$I(B) \qquad CH_{3}-CH_{2}-CH=C-CH_{3}$$

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

$$I(C)$$

Since, both alkenes I and II are obtained by  $\beta$ -elimination of same halides, the halides must be :

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

76. H—C=C—H + Na  $\xrightarrow{\text{Heat}(\Delta)} \xrightarrow{\text{CH}_3\text{I}} \text{CH}_3$ —C=CH  $\xrightarrow[\text{H}_2\text{SO}_4]{} \xrightarrow[\text{H}_2\text{SO}_4]{} \xrightarrow[\text{H}_3\text{C}]{} \xrightarrow[\text{C}]{} \xrightarrow[\text{C}]{}$ 

**77.** 1-butyne (terminal) can be distinguished from 2-butyne (internal) by either Tollen's test or through Fehling's test.

$$CH_{3} - CH_{2} - C \equiv C - H \xrightarrow{AgNO_{3}} CH_{3} - CH_{2} - C \equiv CAg \downarrow$$

$$White ppt.$$

$$CuCl_{2} \rightarrow CH_{3} - CH_{2} - C \equiv CCu \downarrow$$

$$Red ppt.$$

**78.** (i) 
$$CH_3 - C = CH_2 + HBr \xrightarrow{Peroxide} CH_3 - CH - CH_2Br$$
  
 $\downarrow \\ CH_3 \\ 2 - methyl propene Isobutyl bromide$ 

In the absence of peroxide, HBr would be added giving tertiary butyl bromide.

(ii) Tertiary alkynes are slightly acidic, forms silver salt with ammoniacal solution of silver nitrate :

$$R - C \equiv C - H + AgNO_3 \xrightarrow{NH_3(aq)} R - C \equiv CAg \downarrow$$
  
White ppt.

79. (i) Free radical chlorination of alkane require energy which is supplied either in the form of heat or radiation.(ii) Addition of HBr proceeds through carbocation intermediates.

$$\begin{array}{ccc} \mathrm{CH}_{3} & - \mathrm{CH} = \mathrm{CH}_{2} + \mathrm{H}^{+} & \longrightarrow & \mathrm{CH}_{3} & - \overset{+}{\mathrm{CH}} - \mathrm{CH}_{3} & \overset{\mathrm{Br}^{-}}{\longrightarrow} \\ & & & 2^{\circ} \text{ carbocation} \\ & & & \mathrm{CH}_{3} - \overset{-}{\mathrm{CH}} - \mathrm{CH}_{3} \\ & & & & Br \\ & & & & \mathrm{Isopropyl bromide} \end{array}$$

**80.** 
$$CH_3CH = CH_2 + KMnO_4(aq) \xrightarrow{\Delta} CH_3 - CH_2 - CH_2 + MnO_2$$

81. Ozonolysis products are the key of identification :

$$CH_{3} \xrightarrow[Propanone]{CH_{3}} CH_{3} \xrightarrow[CH_{3}]{CH_{3}} CH_{3} \xrightarrow[CH_{3}]{CH_{3}} CH_{3} \xrightarrow[CH_{3}]{CH_{3}} CH_{3} \xrightarrow[A]{CH_{3}} CH_{3} CH_{$$

Other products are:

82. (i) 
$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow{Ag}{heat} H_2C \xrightarrow{CH_3}{Cold, OH^-} A \xrightarrow{Br_2}{CH_3 Br}$$

(ii) 
$$CH \equiv CH + H_2SO_4 \xrightarrow{HgSO_4} CH_3 \longrightarrow CH_3 \xrightarrow{OH} OH \xrightarrow{OH} CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \xrightarrow{OH} CH_3 \longrightarrow CH_3 \longrightarrow CH_3 \xrightarrow{OH} CH_2 \longrightarrow CHO$$
(Aldol)

83. 
$$CH_2 = CH_2 + Br_2 \longrightarrow CH_2 - CH_2 \xrightarrow{NaNH_2} H - C \equiv C - H$$
  
Br Br Br

84. Acetylene can be distinguished from methane using Tollen's reagent :

$$C_2H_2 + AgNO_3 \xrightarrow{NH_3(aq)} H - C \equiv CAg \downarrow$$
  
White ppt.

No such reaction occur with methane.