Solved Examples

JEE Main/Boards

Example 1: Give the total number of isomers, including stereoisomers, obtained on Monochlorination of isopentane.
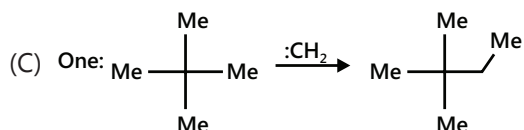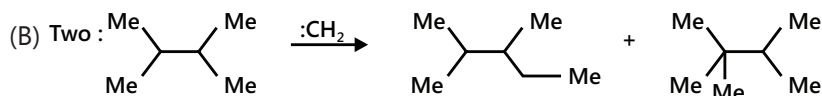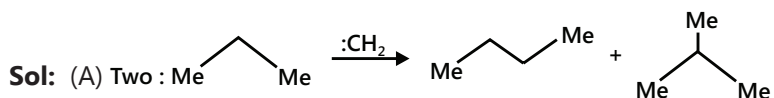
Sol: There are three possible ways of monochlorination. It can take place at C_1, C_2 and C_3. Attack on C_2 produces optically active enantiomer.
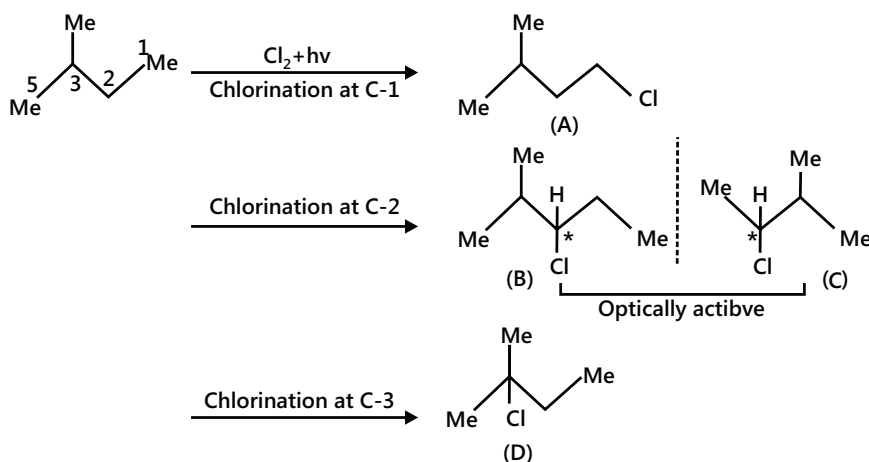
Example 2: Give the number of products obtained inserting methylene in the following alkanes.

Sol: (A) Two :

(B) Two :

(C) One:
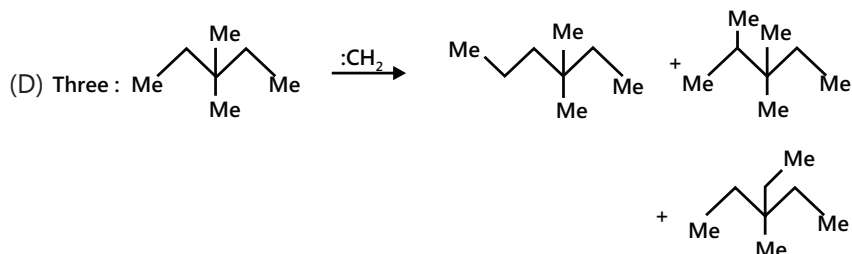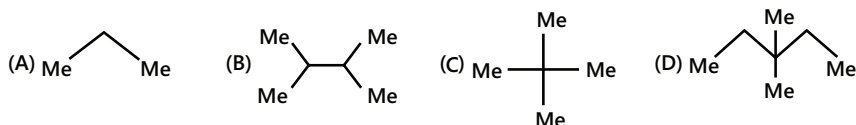
(D) Three :

Example 3: Name the alkane having the lowest molecular mass and is optically active.

Sol: In order to show optical activity, the molecule should contain a chiral carbon i.e. the carbon should have four different groups and to have the lowest molecular mass, one of the groups should be H.
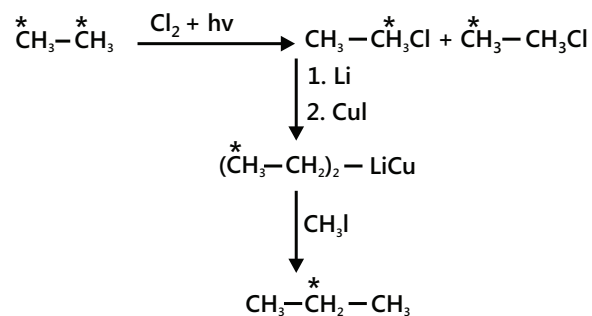

and

In bond line, they are represented as :

3-Methyl hexane

2,3-Dimethyl pentane

Example 4: Synthesize the following compounds starting with CH_3I.

$\overset{*}{C}H_3 - CH_3$ (A)

$\overset{*}{C}H_3 - \overset{*}{C}H_3$ (B)

$\overset{*}{C}H_3 - \overset{*}{C}H_2 - CH_3$ (C)

$\overset{*}{C}H_3 - \overset{*}{C}H_2 - \overset{*}{C}H_3$ (D)

$\overset{*}{C}H_3 - CH_2 - CH_3$ (E)

$\overset{*}{C}H_3 - \overset{*}{C}H_2 - CH_3$ (F)

Sol: The compound can be synthesized By Corey–House synthesis:

Starting with:

$$\overset{*}{C}H_3-\overset{*}{C}H_3 \xrightarrow{\ Cl_2 + h\nu\ } CH_3-\overset{*}{C}H_2Cl + \overset{*}{C}H_3-CH_2Cl$$

with steps:

1. Li
2. CuI

$$(\overset{*}{C}H_3-CH_2)_2-LiCu$$

$$\downarrow CH_3I$$

$$CH_3-\overset{*}{C}H_2-CH_3$$

Example 5: Give the decreasing order of stability at the room temperature of the three isomeric pentanes.

Sol: The possible Isomers of pentanes are:

(A) Me~~~~~~Me
Pentane

(B) Me / Me / Me
Isopentane

(C) Me—|—Me with Me top and Me bottom
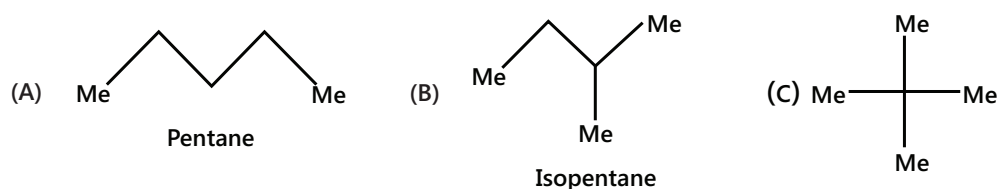
We all know that as the branching increases the stability of isomers increases.

Thus, the order is (c) > (b) > (a).

Example 6: How many geometrical isomers are possible for the following:
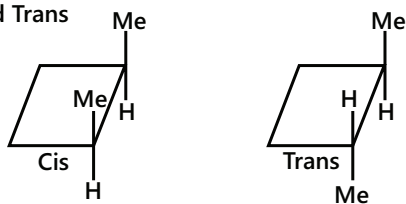
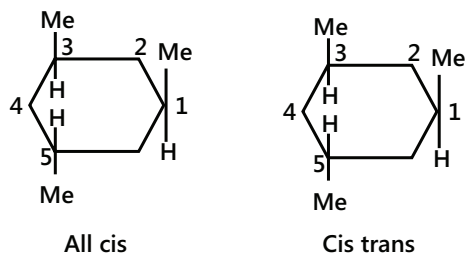(A) 1, 2–Dimethylcyclobutane   (B) 1, 3, 5–Trimethylcyclohexane   (C) 1, 1, 2–Trimethylcycloproane
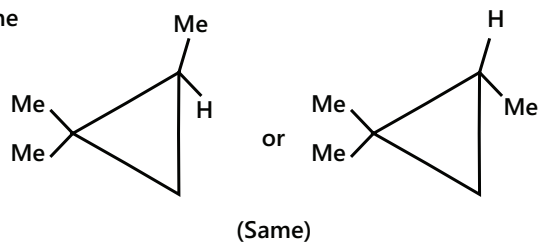
Sol: (A)   Two:
Cis and Trans

Cis   Trans

(B) Two

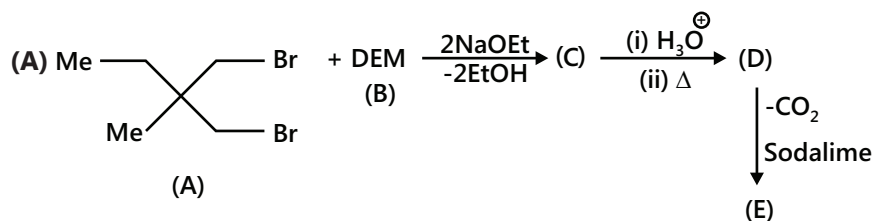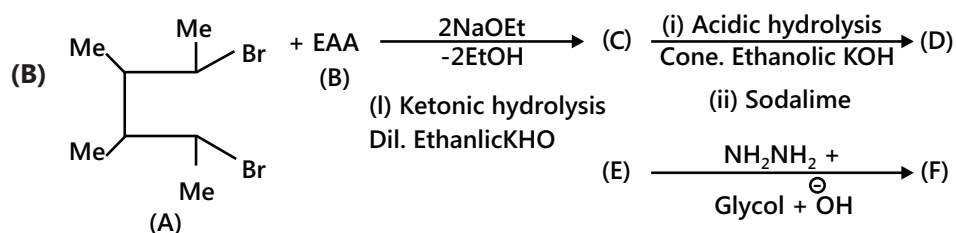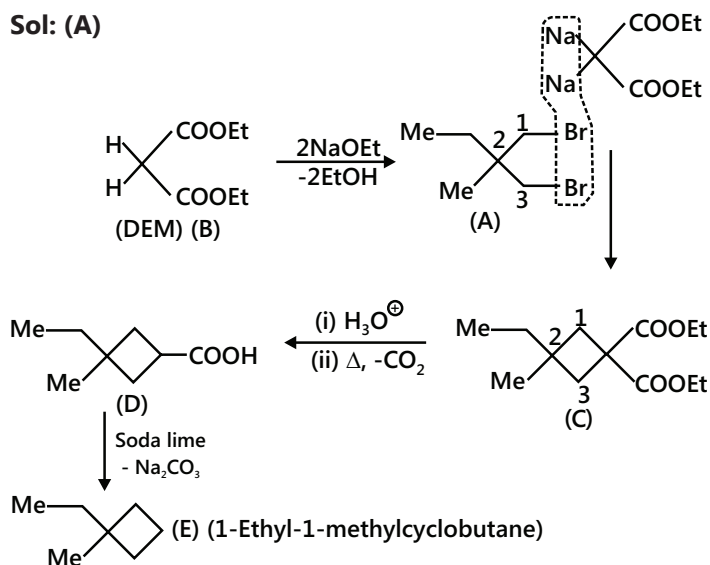All cis   Cis trans
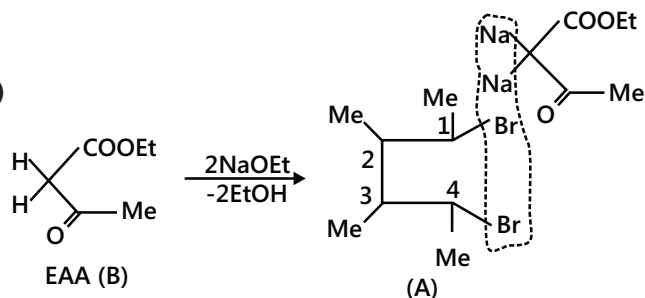
(C)   None

Me ... H   Me ... Me

or

(Same)
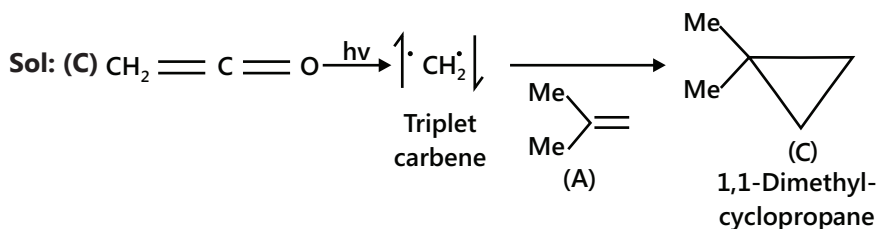
JEE Advanced/Boards

Example 1: Complete the following reactions

(A) Me ⟶ Br + DEM $\xrightarrow[\text{-2EtOH}]{\text{2NaOEt}}$ (C) $\xrightarrow[\text{(ii) }\Delta]{\text{(i) H}_3\overset{\oplus}{\text{O}}}$ (D)

(B)

Me ⟶ Br

(A)

$\downarrow$ -CO$_2$

Sodalime

(E)

Sol: (A)

(E) (1-Ethyl-1-methylcyclobutane)

(B)

Me ⟶ Br + EAA $\xrightarrow[\text{-2EtOH}]{\text{2NaOEt}}$ (C) $\xrightarrow[\text{Cone. Ethanolic KOH}]{\text{(i) Acidic hydrolysis}}$ (D)

(B)

(l) Ketonic hydrolysis
Dil. EthanlicKHO

(ii) Sodalime

(E) $\xrightarrow[\text{Glycol + }\overset{\ominus}{\text{OH}}]{\text{NH}_2\text{NH}_2\text{ +}}$ (F)

(A)

Sol: (B)

EAA (B)

(A)

(B)

(E) ← Ketonic hydrolysis gives ketone ← (C)

(E) → Wolff-Kishner reduction $\left(\overset{\diagdown}{\diagup}C = O \Rightarrow CH_2\right)$ → (F)

(F)
1-Ethyl-2,3,4,5-tetramethyl cyclopentane

(C) → i. Acidic hydrolysis / ii. Soda lime (-CO$_2$) → (D)

(D)
1,2,3,4,-Tetramethyl cyclopentane

(C)

$$\overset{Me}{\underset{Me}{\diagup}}\!\!\diagdown = \quad + \quad CH_2 = C = O \xrightarrow{hv} C$$

(A)   (B)

Sol: (C) $CH_2 = C = O \xrightarrow{hv} |^{\cdot}CH_2^{\cdot}|$

Triplet carbene

$\overset{Me}{\underset{Me}{\diagup}}\!\!\diagdown =$ (A)

⟶

(C)
1,1-Dimethyl-cyclopropane

Example 2: Which of the following compounds are isolable?

(A) (B) (C)

(D) (E) (F) (G)
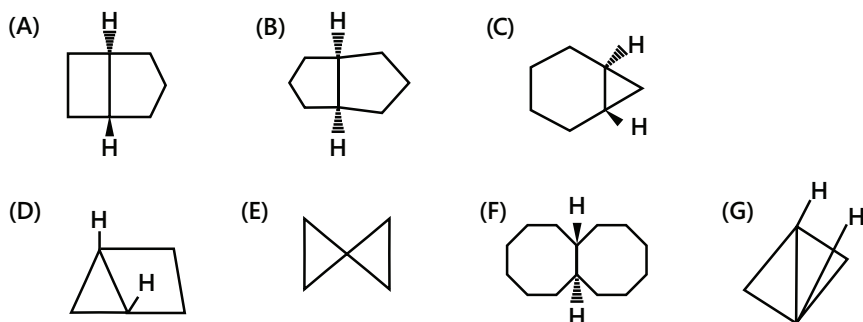
Sol: Any sized rings can be fused in cis but two five–membered or longer rings can be fused in Trans also.

(A) No, (B) Yes, (C) No, (D) Yes, (E) Yes, (F) Yes, (G) Yes

(A) Four and five–membered rings cannot be fused in Trans.

(B) Two five–membered and larger rings can be fused in Trans because the Trans bonds in the bridgehead C atoms are in a position for a 3C–bridge.

(C) Three– and six–membered rings cannot be fused in Trans. The trans bonds on the bridgehead C atoms are too far apart to be bridged by a single C–bridge.

(D) Any sized rings can be fused in cis.

(E) Spiranes for any sized ring are known if they are able to be at right angles.

(F) Two larger rings can be fused in Trans.
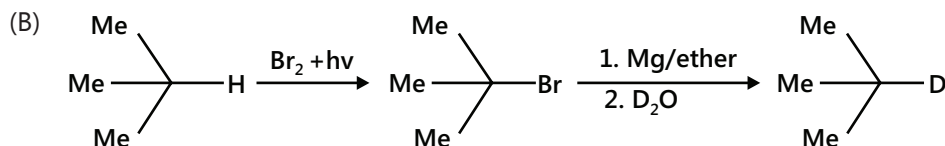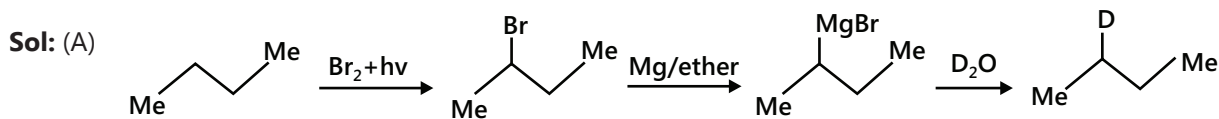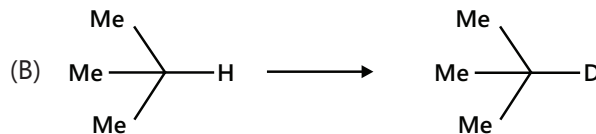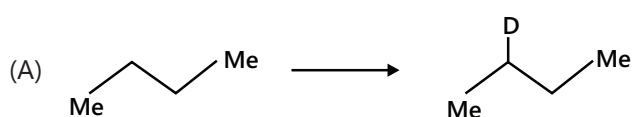
(G) Any sized rings can be fused in cis.

Q.3 Complete the following reaction

(A)

(B)

Sol: (A)

(B)

In (A) and (B), bromination gives the desired products because of the larger difference in the rate of bromination [3° > 2° > 1° (1600: 82: 1)

Example 4: Intramolecular ring closure to form Cyclobutane is unfavorable, how would you synthesize Cyclobutane from open–chain compounds?

Sol: Cyclobutane is synthesized by electrocyclic reaction. (One of the type of pericyclic reaction)

(A)
Ethene

(B)
Buta-1,3-diene
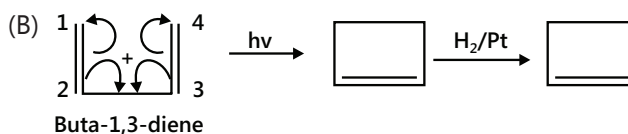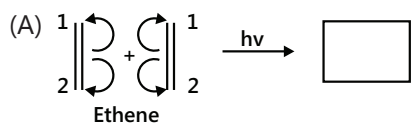
Example 5: Complete the following. Also name the reaction and reaction type

(A)
1,3-Dibromopropane

(B)
1,4-Dibromopropane

(C)
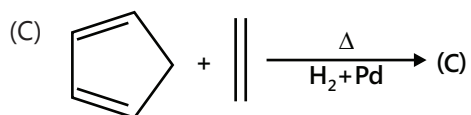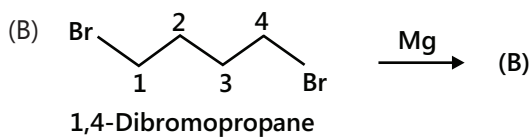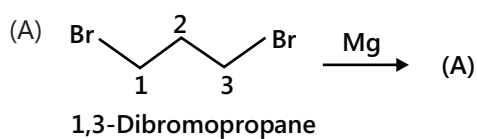
Sol: (A)   A ⇒   (Cyclopropane) (Freud reaction)

Intramolecular ring closure is possible

(B)   B. ⇒ MgBr MgBr
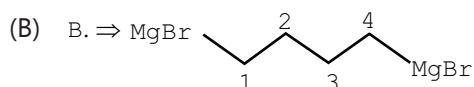
Intramolecular ring closure is not possible, since four–membered ring formation is unfavorable.

(c)
Norborane
(C)

Diels–Alder and cycloaddition reaction.

JEE Main/Boards

Exercise 1

Q.1 (A) Write the IUPAC name of the following compounds.

(B) Identify 1° (primary), 2° (secondary), 3° (tertiary), and 4° (quaternary) C atoms.

(C) Identify all the 1°, 2° and 3 ° H atoms.

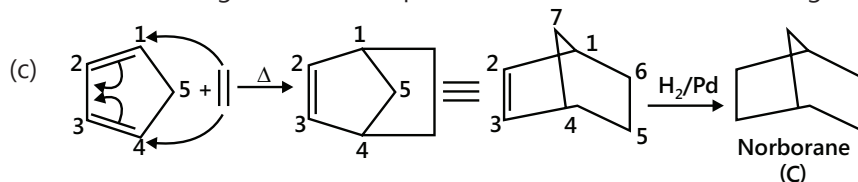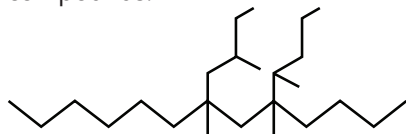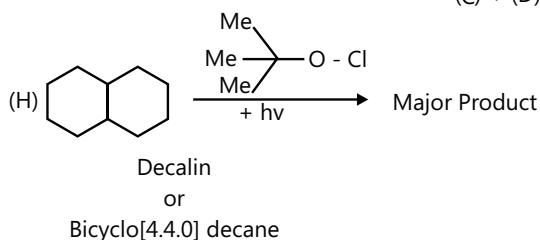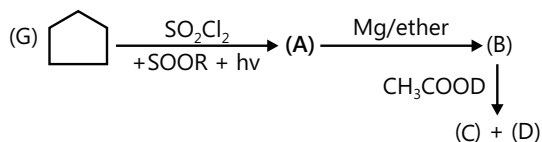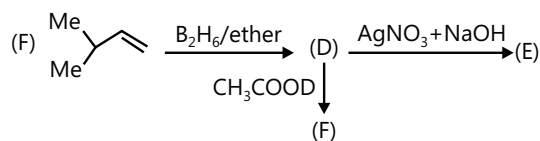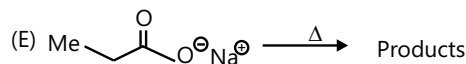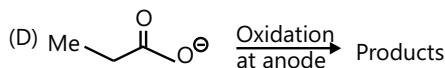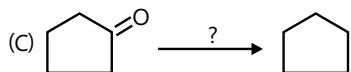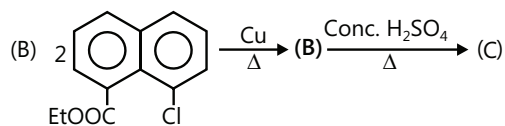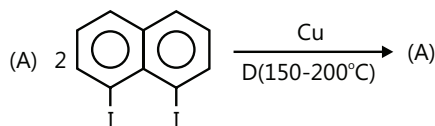**Q.2** Complete the following reactions:

(A)

(B)

(C)

(D)

(E)

(F)

(G)

(H)

Decalin
or
Bicyclo[4.4.0] decane

Q.3 (A) Compound A (molecular formula C_5H_{10}) gives only one monochlorinated product. Write the structure of compound A.

(B) How many monochlorinated products can be obtained from all the isomeric alkanes having the formula C_5H_{10} (excluding stereoisomers)?

Q.4 Why does a fuel with high octane number have less tendency to knock, whereas fuel with higher cetane number has more tendency to knock in an automobile engine?

Q.5 (A) What is the relative abstraction of H and D?
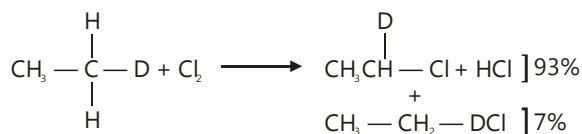
(B) Why free-radical chlorination of CH_4 is nearly 11 times faster than CD_4?

Q.6 There are six isomeric alkenes (A, B, C, D, E and F) that require 1 mol of H_2 per mole of alkene for hydrogenation and give the same product (G) on hydrogenation. G is an alkane having the lowest molecular mass and is optically active. Write the structure of compounds from A to G.

Q.7 There are five isomeric alkenes (A, B, C, D, and E) that require 1 mol of H_2 per mole of alkene for hydrogenation and give the same product (F) on hydrogenation. F is an alkane having the lowest molecular mass and is optically active. Write the structure of the compounds from A to F.

Q.8 Write the structures of all the alkenes that can be hydrogenated to from 2–methyl pentane.

Q.9 Write the reaction of benzyl magnesium bromide with CH_3OD and also identify the conjugate acid–base pairs.

Q.10 Calculate the percentage of compounds obtained by monobromination of isobutene. The relative reactivity of 1°, 2°, 3° H atoms to bromination is 1: 82: 1600.

Q.11 Which factors determine the reactivity of halogens in the substitution reaction?

Q.12 Predict the percentage of isomers formed during monochlorination of 2, 3–dimethyl butane at room temperature. Relative reactivity of 1°, 2°, 3°H atoms to chlorination is (1.0: 3.8: 5.0).

Q.13 In the study of chlorination of propane, four products A, B, C and D of the following $C_3H_6Cl_2$ were isolated. Each of them was further chlorinated to provide trichloro products, $C_3H_5Cl_3$. It was found that A provided one trichloro product, B gave two and C and D each gave three. What are the structural formulae of A, B, C and D?

Q.14 A chloro derivative (A) on treatment with zinc–copper couple gives a hydrocarbon with five C atoms. When 'A' is dissolved in ether and treated with sodium, 2, 2, 5, 5–tetramethyl hexane is obtained. What is the original compound 'A'?

Q.15 An alkyl halide is reduced to the corresponding alkane by tributyl stannane $(C_4H_9)_3SnH$ and by a free radical mechanism in the presence of an initiator, an azo compound.
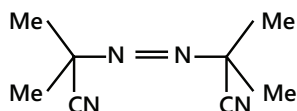

Exercise 2

Single Correct Choice Type

Q.1 The decreasing order of the anti-knocking value of octane number of the following is
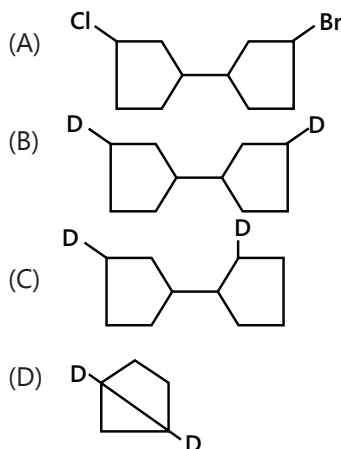
(I) CH_4 (II) C_2H_6 (III) C_3H_8 (IV) C_4H_{10}

(A) (I) > (II) > (III) > (IV)   (B) (IV) > (III) > (II) > (I)

(C) (I) > (III) > (II) > (IV)   (D) (IV) > (II) > (III) > (I)

Q.2 When aqueous solution of sodium ethanoate is electrolysed, the volume of gases obtained at cathode at a pressure of 1.0 bar and 298 K temperature when 2.0 Faraday of electricity is passed is:

(A) 67.2 litres   (B) 68.1 litres

(C) 73.2 litres   (D) 74.1 litres

Q.3

The compound (X) is

(A)

(B)

(C)

(D)
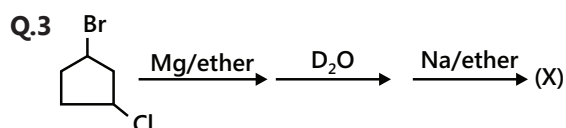
Q.4 Which of the statement is correct?

I. Melting point of alkane increases with increase of C atoms and with increase in branching

II. Boiling point of alkane increases with increase of C atoms but with decrease in branching

III. Cycloalkane have lower boiling point than normal alkane with same number of C atoms

IV. Alkanes have lower boiling point than same number of C atoms in alkanes.

(A) (I), (II)   (B) (I), (II), (III)

(C) (III), (IV)   (D) (IV)

Q.5 Arrange the following in the decreasing order of their boiling points:

I.   II.   III.   IV.

(A) (I) > (II) > (IV) > (III)   (B) (I) > (II) > (III) > (IV)

(C) (III) > (IV) > (II) > (I)   (D) (IV) > (III) > (II) > (I)

Q.6 Arrange the following in the decreasing order of their boiling points:

I. C_9H_{20} II. C_8H_{18}
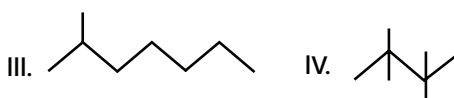
III.   IV.

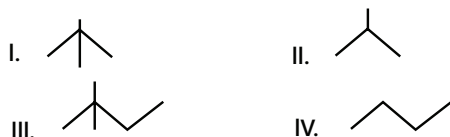(A) (I) > (II) > (III) < (IV)   (B) (IV) > (III) > (II) < (I)

(C) (I) > (II) > (IV) < (III)   (D) (III) > (IV) > (II) < (I)

Q.7 Arrange the following in the decreasing order of their melting points:

I. Decane   II. Nonane   III. Octane   IV. Heptane

(A) (I) > (II) > (III) > (IV)   (B) (IV) > (III) > (II) > (I)

(C) (I) > (III) > (II) > (IV)   (D) (IV) > (II) > (III) > (I)

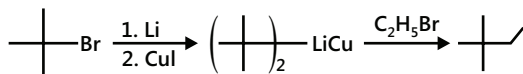**Q.8** Which one of the following products would produce a racemic mixture on monochlorination?

I.   II.

III.   IV.

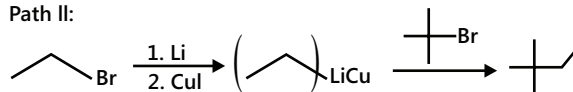(A) I, II   (B) III, III   (C) II, IV   (D) III < IV

Q.9 There are two ways for the preparation of 2, 2–dimethyl butane

$\left(1-\overset{4}{\underset{2\ \ 3}{\vert}}\right)$ by Corey–House synthesis.

Path I:

$\overset{\vert}{\underset{\vert}{\vert}}-Br \xrightarrow[\text{2. CuI}]{\text{1. Li}} \left(\overset{\vert}{\underset{\vert}{\vert}}\right)_2 LiCu \xrightarrow{C_2H_5Br}$

Path II:

$\underset{Br}{\diagdown} \xrightarrow[\text{2. CuI}]{\text{1. Li}} \left(\diagup\right) LiCu \xrightarrow{\overset{Br}{\vert}}$

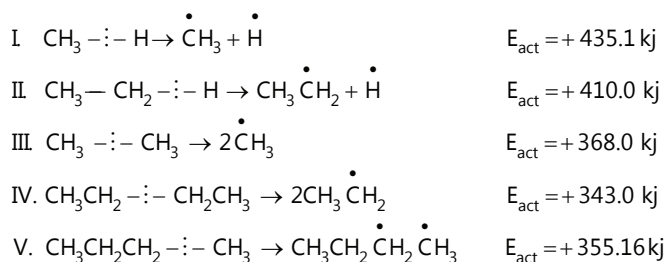Which of the following statements is correct?

(A) Both Path I and Path II are feasible

(B) Path I is feasible

(C) Path II is feasible

(D) Both Path I and Path II are not feasible

Q.10 Which of the statements is/are true about the reactivity of halogenation of alkanes? The reactivity order is $F_2 > Cl_2 > Br_2 > I_2$

I. Lower the activation energy for the chain initiation step, more reactive is the halogen

II. Lower the activation energy for the first chain propagation step, more reactive is the halogen

III. More negative is the overall heat of the reaction (ΔH_r^0) of halogenation of alkane, more reactive is the halogen

IV. Lower the activation energy for the second chain propagation step, more reactive is the halogen.

(A) (I), (II)   (B) (I), (II), (III)

(C) (II), (III)   (D) (II), (III), (IV)

Q.11 With the help of the following equations and data choose the wrong statement

I. $CH_3 -\colon- H \rightarrow \overset{\bullet}{C}H_3 + \overset{\bullet}{H}$ $E_{act} = +435.1\ kj$

II. $CH_3 - CH_2 -\colon- H \rightarrow CH_3 \overset{\bullet}{C}H_2 + \overset{\bullet}{H}$ $E_{act} = +410.0\ kj$

III. $CH_3 -\colon- CH_3 \rightarrow 2\overset{\bullet}{C}H_3$ $E_{act} = +368.0\ kj$

IV. $CH_3CH_2 -\colon- CH_2CH_3 \rightarrow 2CH_3 \overset{\bullet}{C}H_2$ $E_{act} = +343.0\ kj$

V. $CH_3CH_2CH_2 -\colon- CH_3 \rightarrow CH_3CH_2 \overset{\bullet}{C}H_2 \overset{\bullet}{C}H_3$ $E_{act} = +355.16\ kj$
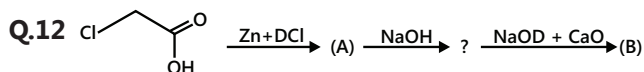
(A) The thermal cracking of (C – H) bond of methane occurs at 1500K and that of (C – H) bond of ethane breaks at 800–900 K

(B) During homolysis of ethane at high temperature, the (C – C) bond breaks more readily than (C – H) bonds.

(C) During the cracking of n–butane, reaction (IV) occurs more readily than reaction (V)

(D) Formation of CH_3CH_2 radical by reaction (II) will take place at lower temperature than the formation of $\overset{\bullet}{C}_2 H_5$ radical by reaction (IV)
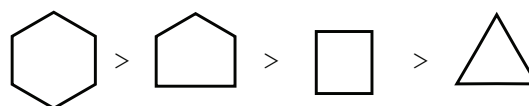
Q.12 $Cl\diagup\diagdown\overset{O}{\underset{OH}{\diagdown}} \xrightarrow{Zn+DCl} (A) \xrightarrow{NaOH} ? \xrightarrow{NaOD + CaO} (B)$

The compounds (A) and (B) in the equation given above are

(A)	(B)
a. CH_3COOH	CH_3CH_3
b. $DCH_2 - COOD$	CH_4
c. $DCH_2 - COOH$	CH_2D_2
d. $CH_3 - COOD$	CH_3D

Q.13 Which of the following statements is wrong?

(A) The decreasing order of the numerical value of heat of combustions is

⬡ > ⬠ > □ > △

(B) Cycloalkanes are planar

(C) Cyclopropane has higher heat of combustion per methylene ($- CH_2 -$) group than that of cyclobutane

(D) With the exception of cyclopropane, cycloalkanes are non–planar.

Previous Years' Questions

Q.1 Marsh gas mainly contains: *(1980)*

(A) CO   (B) H_2S (C) C_2H_2 (D) CH_4

Q.2 The compound with the highest boiling point is: *(1982)*

(A) n–Pentane   (B) n–Hexane

(C) 2–Methyl butane   (D) 2, 2–Dimethyl propane

Q.3 The highest boiling point is expected for: *(1986)*

(A) Isooctane   (B) n–Octane

(C) 2, 2, 3, 3–Tetramethyl butane   (D) n–Butane

Q.4 The compound that has one isopropyl group is: *(1989)*

(A) 2–Methyl pentane

(B) 2, 2, 3, 3–Tetramethyl pentane

(C) 2, 2–Dimethyl pentane

(D) 2, 2, 3–Tetramethyl pentane

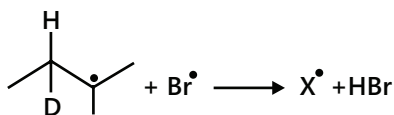**Q.5** The (C – H) bond distance is longest in *(1983)*

(A) $C_2H_2Br_2$ (B) C_2H_4 (C) C_2H_6 (D) C_2H_2

Q.6 When cyclohexane is poured in water, it floats because: *(1997)*
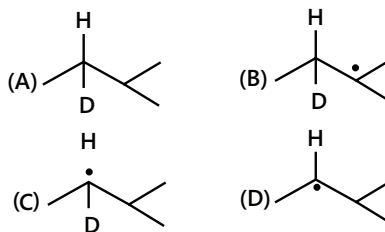
(A) Cyclohexane is in boat form

(B) Cyclohexane is denser than water

(C) Cyclohexane is in chair form

(D) Cyclohexane is in crown form

Q.7 Kolbe's electrolysis of potassium succinate gives CO_2 and ..... *(1993)*

Q.8 Consider the following reaction: *(2002)*

Identify the structure of the major product X.

Q.9 How many chiral compounds are possible on monochlorination of 2–Methyl butane? *(2012)*

(A) 2   (B) 4   (C) 6   (D) 8

(A) Statement-I and statement-II are true, and statement-II is the correct explanation of statement-I

(B) Statement-I and statement-II are true, and statement-II is NOT the correct explanation of statement-I

(C) Statement-I is true, and statement-II is false

(D) Statement-I is false, and statement-II is true

(E) Statement-I is false, and statement-II is false

Q.10 Statement-I: Addition of Br_2 to 1–butane gives two optical isomers.

Statement-II: The product contains one asymmetric carbon. *(1998)*

Q.11 Statement-I: 1–butane on reaction with HBr in the presence of a peroxide produces 1–bromobutane.

Statement-II: It involves the formation of a primary radical. *(2000)*

Q.12 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 the excess of it evaporates. *(2001)*

Q.13 The IUPAC name of neopentane is *(2009)*

(A) 2-methylbutane   (B) 2,2-dimethylpropane

(C) 2-methylpropane   (D) 2, 2-dimethylbutane

Q.14 The treatment of CH_3MgX with $CH_3C \equiv C - H$ produces

(A) $CH_3 - CH = CH_2$ (B) $CH_3C \equiv C - CH_3$

(C) $CH_3 - \overset{H}{\underset{|}{C}} = \overset{H}{\underset{|}{C}} - CH_3$ (D) CH_4 *(2008)*

JEE Advanced/Boards

Exercise 1

Q.1 When a mixture of 2–methyl propane and CCl_4 is reacted at 403–413K in the presence of a radical initiator, t–butyl peroxide, 2–chloro–2–methyl propane and chloroform ($CHCl_3$) are formed. Give the mechanism of the reaction.

Q.2 Alkanes are monochlorinated with t–butyl hypochlorite $\left(\begin{array}{c} Me \\ Me \longrightarrow O \longrightarrow Cl \\ Me \end{array} \right)$ as a radical initiator.

Give the mechanism of the reaction.

Q.3 $\Delta H_C^{\ominus}$ (the standard enthalpy of combustion) of butane and 2–methyl propane is –2877.0 and –2868.0 kJ mol/L, respectively. Explain the relative stabilities of the two isomers.

Q.4 Arrange the following compounds according to the decreasing order of heat of combustion.

(A) i. Pentane   ii. Hexane iii. 2–Methyl butane

iv. 2, 2–Dimethyl propane

(B)

(i)
Me
Me—⟨—Me
Me— ⟩—Me
Me

(ii)
Me
Me—⟨—Me
Me— ⟩
Me

(iii)
Me⌒⌒⌒⌒Me

(iv) Me⌒⌒⌒⌒
Me
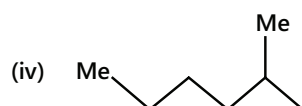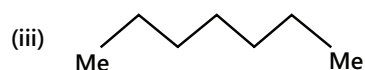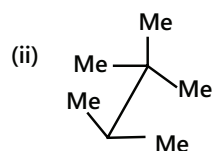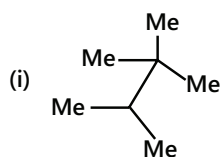
Q.5 (A) Which of the following has highest boiling point?

i. 2–Methyl pentane

ii. 2, 3–Dimethyl butane

iii. 2, 2–Dimethyl butane

(B) What effect does branching of an alkane chain has on its melting point?

Q.6 How many geometrical isomers are possible for the following compounds?
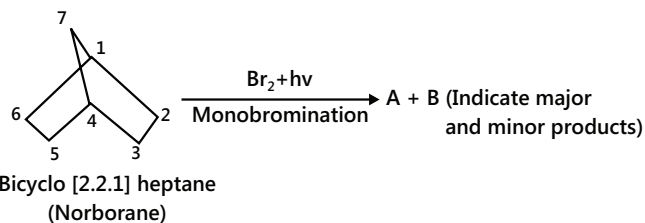
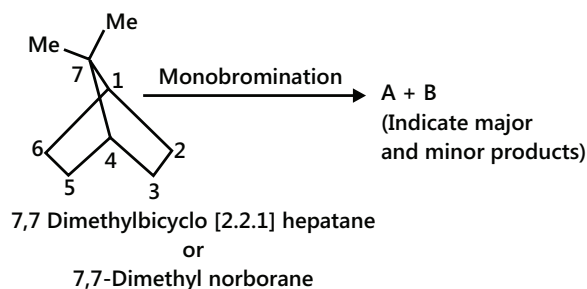(A) 3–Bromo–5–iodo methyl cyclohexane

(B) 5–Bromo–1, 3–dimethyl cyclohexane

(C) 1, 2, 4–Trimethyl cyclohexane

Q.7 Complete the following reaction:

i.

$$\xrightarrow[\text{Monobromination}]{Br_2+h\nu}$$ A + B (Indicate major and minor products)

Bicyclo [2.2.1] heptane
(Norborane)

ii.

$$\xrightarrow{\text{Monobromination}}$$ A + B (Indicate major and minor products)

7,7 Dimethylbicyclo [2.2.1] hepatane
or
7,7-Dimethyl norborane

Q.8 Equal amounts of (e, e) and (a, a) conformers of trans–1, 2–dichloro cyclohexane exist in non–polar solvents but the (e, e) conformers exists in polar solvents. Explain.

Q.9 Which isomer has the lower energy and which is flexible in cis- and trans-decalin?

Exercise 2

Single Correct Choice Type

Q.1 Arrange the following compounds in the increasing order of homolytic (C – C) bond dissociation energy.

I. Propane

II. Ethane

III. 2, 2–Dimethyl propane

IV. 2–Methyl propane

(A) (III) < (IV) < (II) < (I)

(B) (II) < (I) < (IV) < (III)

(C) (III) < (IV) < (I) < (II)

(D) (I) < (III) < (II) < (IV)

Q.2 There is no ring strain in cyclohexane, but cyclobutane has an angle strain of 9° 44'. If ΔH_c^o of cyclohexane per (CH_2) group is 660kJ mol/L and ΔH_c^o of cyclobutane is 2744 kJ mol/L, what is the ring strain in kJ mol/L of cyclobutane?

(A) –104 (B) 104

(C) –2084 (D) 2084

Q.3 Octane number can be changed by

(A) Alkylation (B) Cyclisation

(C) Isomerization (D) All of these

Q.4 Which of the following yields both alkane and alkene?

(A) Williamson's synthesis

(B) Kolbe's reaction

(C) Wurtz reaction

(D) Sandmeyer's reaction

Q.5 Hydrocarbon that is liquid at room temperature is

(A) Ethane (B) Propane

(C) Butane (D) Pentane

Q.6 In the free–radical chlorination of methane, the chain–initiation step involves the formation of

(A) HCl (B) CH_3

(C) CH_2Cl (D) $Cl^{\bullet}$

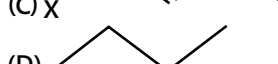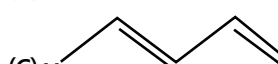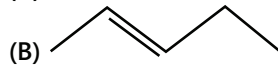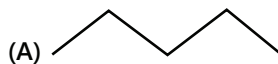**Q.7** 2–methyl butane on reacting with Br_2 in sunlight mainly gives:

(A) 1–Bromo–2–methyl butane

(B) 2–Bromo–2–methyl butane

(C) 2–Bromo–3–methyl butane

(D) 1–Bromo–1–methyl butane

Q.8 Which of the following has the lowest boiling point

(A)

(B)

(C) X

(D)

Q.9 Which hydrocarbon is mainly present in gobar gas?

(A) Methane (B) Ethane

(C) Propane (D) Butane

Q.10 How many diastereomers are possible among all the possible stereoisomers of 2, 3–dibromopentane?

(A) 2 (B) 1 (C) 3 (D) 4

Multiple Correct Choice Type

Q.11 An automobile engine fuel has cetane number of 80. Which of the following statement is/are true?

(A) Fuel contain 80% of α–methyl naphthalene and 20% of $C_{16}H_{34}$

(B) Fuel contains 80% of cetane and 20% of a–methyl naphthalene

(C) Knocking property of the given fuel compared to the knocking property of a fuel with cetane number of 90 is high

(D) Cetane number determines the quality of diesel fuel in terms of ignition properties

Q.12 CH_4 can be prepared by the reaction of H_2O with

(A) Mg_2C_3 (B) CaC_2 (C) Be_2C (D) Al_4C_3

Q.13 When aqueous solution of sodium ethanoate is electrolyzed, the product(s) at anode is/are
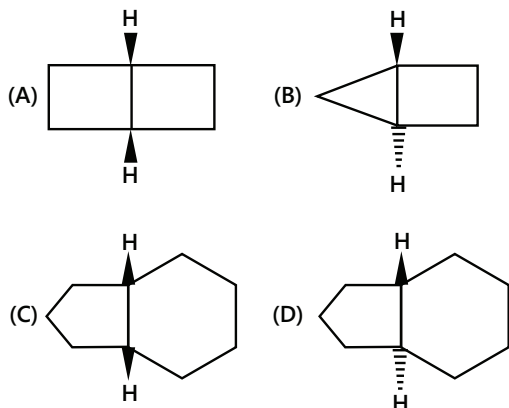
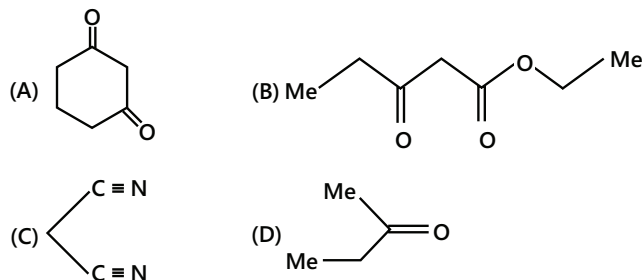(A) Ethane (B) Methyl ethanoate

(C) CO_2 (D) H_2

Q.14 In the destructive distillation of coal, at 443–503 K temperature, a middle oil or carbolic oil fraction is obtained. This fraction contains:

(A) Phenol

(B) Xylene

(C) Naphthalene

(D) Benzene

Q.15 Which of the following compounds is/are isolable?

Q.16 Which of the following compounds contain active methylene group?

Q.17 Which of the following simplest alkanes with fewest number of C atoms contains 1°, 2°, 3° and 4°C atoms?

(A) 2, 2, 3–Trimethyl pentane

(B) 2, 2, 4–Trimethyl pentane

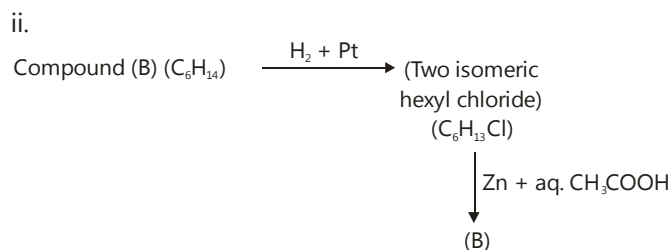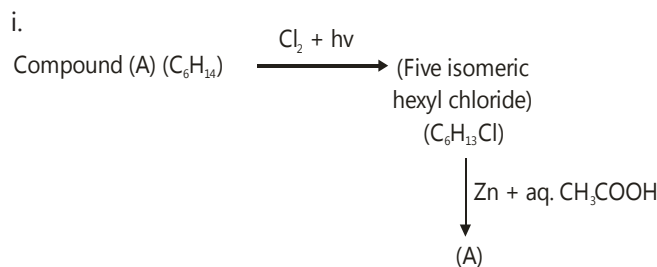(C) 2, 3, 3–Trimethyl pentane

(D) 2, 2, 3–Trimethyl butane

Q.18 Which of the following statement is/are correct?

(A) Decalin exists in two geometrical isomers, cis and trans

(B) Cis- form is flexible and has (a, e) conformer

(C) Trans form is rigid and has (e, e) conformer and is more stable than cis form.

(D) Cis form is rigid and trans form is flexible, also trans form has lower energy
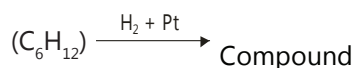
Q.19 Which of the following statements is/are correct in the synthesis of cycloalkanes by intramolecular cyclisation?

(A) Large rings with more six C atoms are stable but difficult to prepare

(B) Decreasing order of thermal stability of cyclic rings is 6 > 7, 5 > 8, 9 >> 4, 4 > 3

(C) Decreasing order of probability of rings closure is 3 > 4 > 5, > 6 > 7 > 8 > 9

(D) Ease of synthesis of cyclo compounds is 5 > 3, 6 > 4, 7, 8, 9

Comprehension Type (20 - 23)

i.

Compound (A) (C_6H_{14}) $\xrightarrow{Cl_2 + hv}$ (Five isomeric hexyl chloride) ($C_6H_{13}Cl$)

$\downarrow$ Zn + aq. CH_3COOH

(A)

ii.

Compound (B) (C_6H_{14}) $\xrightarrow{H_2 + Pt}$ (Two isomeric hexyl chloride) ($C_6H_{13}Cl$)

$\downarrow$ Zn + aq. CH_3COOH

(B)

iii. Alkene (C) and alkene (D)

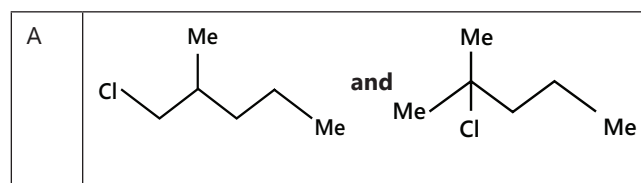(C_6H_{12}) $\xrightarrow{H_2 + Pt}$ Compound

Q.20 Compound (A) is

(A) 2, 3–Dimethylbutane

(B) 2–Methylpentane

(C) 2, 2–Dimethylbutane

(D) 3–Methylpentane

Q.21 Compound (B) is

(A) 2, 3–Dimethylbutane

(B) 2–Methylpentane

(C) 2, 2–Dimethylbutane

(D) 3–Methylpentane

Q.22 Two isomeric hexyl chlorides obtained from (B) are:

B	
C	
D	

Q.23 The alkanes (C) and (D) are:

A	
B	
C	
D	

Comprehension Type (24-25)

(A) Statement-I and statement-II are true, and statement-II is the correct explanation of statement-I

(B) Statement-I and statement-II are true, and statement-II is NOT the correct explanation of statement-I

(C) Statement-I is true, and statement-II is false

(D) Statement-I is false, and statement-II is true

(E) Statement-I is false, and statement-II is false

Q.24 Statement-I: Compound (I) is formed not (II)
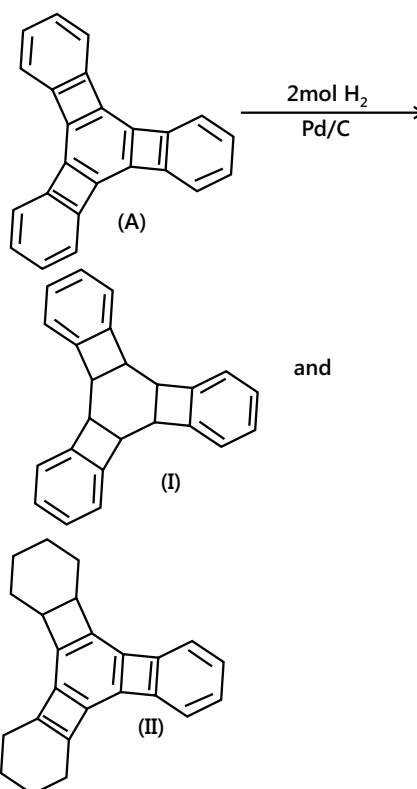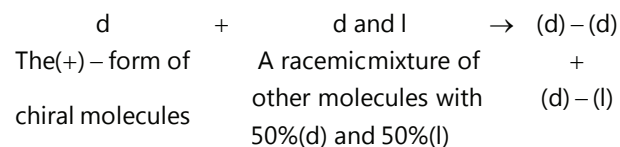

Statement-II: Due to the reduction of central ring, 3 four–membered anti–aromatic rings become stable to form (I). In (II), due to the reduction of terminal ring, only one anti–aromatic ring can be stabilized.

Q.25 Referring to Q. No. 14, which of the statement is wrong?

(A) In compound (A) number of aromatic, antiaromatic, and non–aromatic rings are 4, 3, and 0, respectively.

(B) In product (I) number of aromatic, antiaromatic, and non–aromatic rings are 3, 0, and 4, respectively.

(C) In product (II) number of aromatic, antiaromatic and non–aromatic rings are 3, 2, and 2, respectively.

(D) The stability order is: aromatic > antiaromatic > Non-aromatic

Paragraph Type 26–27

A schematic analysis of the reaction of one enantiomer with racemic mixture is shown below:

$$d \quad + \quad d \text{ and } l \quad \rightarrow \quad (d)-(d)$$

The(+) – form of   A racemicmixture of   +

chiral molecules   other molecules with   (d) – (l)

          50%(d) and 50%(l)

The products (d – d) and (d – *l*) are clearly neither identical nor enantiomers (non–superimposable mirror image) as the mirror image of (d – d) is (*l* – *l*) not

(d – l). They are diastereomers, 'stereoisomers that are not mirror images'

The formation of diastereomers allows the separation of enantiomers (called resolution) which is not easy as enantiomers have identical physical properties. One general procedure for separating enantiomers is to allow them to react with naturally occurring chiral molecule to form a pair of Diastereomers. These can be separated easily as they have different physical properties. If the original chemical reaction be reversed, the enantiomers can be isolated

Q.26 Which of the following is an example of diastereomers?

(A) Two gauche forms of butane

(B) Products of bromination of cis–2–butane in the presence of CCl_4

(C) Gauche and anti–form of butane

(D) Both (A) and (C)

Q.27 Which of the following is not true?

(A) Diastereomers have different melting points and solubilities in a given solvent

(B) Diastereomers have similar chemical properties

(C) Diastereomers are optically active compounds with same or opposite sign of rotation

(D) Diastereomers differ in adsorption

True or False

State whether each of the following is true or false:

Q.28 Photobromination of 2–methylpropane gives a mixture of
1–bromo–2–methylpropane and
2–bromo–2–methylpropane in the ratio 9: 1.

Q.29 The percentage of n–propyl chloride obtained in the chlorination of propane is about 56%.

**Q.30** The percentage of 1–chloro–2–methylpropane obtained in the chlorination of isobutene is about 64%.

Q.31 The percentage of n–propyl bromide in the bromination of propane is 44%. The relative reactivities of 3°, 2° and 1° H atoms are 1600: 82: 1.

Match the Columns

Q.32

| Column I	Column II
Compounds	**Anti–knocking rating value**
(A) n–Heptane	(p) 130
(B) Triptane	(q) Zero (octane number)
(C) 2, 2, 4–Trimethyl pentane	(r) 116
(D) $C_{16}H_{34}$	(s) Zero (cetane number)
(E) α–Methyl naphthalene	(t) 100 (octane number)
(F) Natural gas	(u) 100 (cetane number)
(G) n–Nonane	(v) –45

Q.33

Column I	Column II
Reactant and product	**Reagent**
(A) n-Hexane $\xrightarrow{?}$ ⬡	(p) O_2 at 100 atm, 470 K in the presence of Cu tube
(B) ⬡ $\xrightarrow{?}$ ⬡	(q) O_2 + MoO_2 (Molybdenum oxide)
(C) $CH_4 \xrightarrow{?} CH_3OH$	(r) Al_2O_3 + Cr_2O_3 at 600°C
(D) $RCH_3 \xrightarrow{?} RCOOH$	(s) S or Se or Pt at 600°C
(E) $CH_4 \xrightarrow{?} HCHO$	(t) O_2 in the presence of catalyst $(CH_3COO)_2Mn$ (Manganese acetate at 370–430 K)

Previous Years' Questions

Q.1 What would be the product formed when 1–bromo–3–chlorocyclobutane reacts with two equivalents of metallic sodium in water?

(2005)

(A) ⊡

(B) Cl — [structure] — Br

(C) Cl — [structure] — Cl

(D) Br — [structure] — Cl
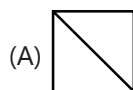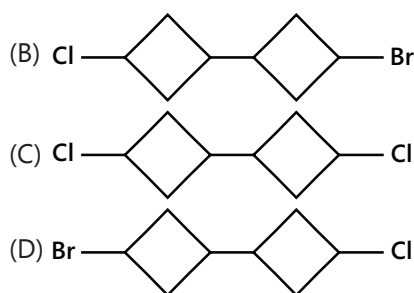
Q.2 μ observed = Sm_iX_i where m_i is the dipole moment of the stable conformer and X_i is the mole fraction of that conformer.
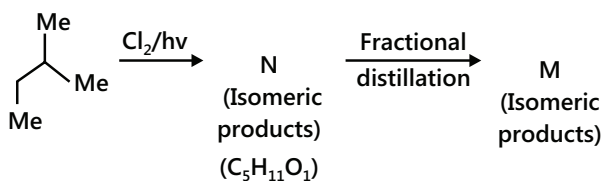
(A) Write the stable conformer for $(Z - CH_2 - CH - Z)$ in Newman's projection.

If $m_{solution}$ = 1.0 D and mole fraction of the antiform

= 0.82, find the μ gauche form.

(B) Write the most stable meso conformer of

$$\begin{array}{c} CHDY \\ | \\ CHDY \end{array}$$

If (i) Y = CH_3 about $C_2 - C_3$ rotation and (ii) Y = OH, about $C_1 - C_2$ rotation. *(2005)*

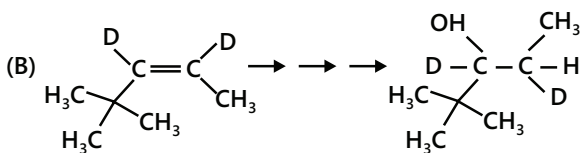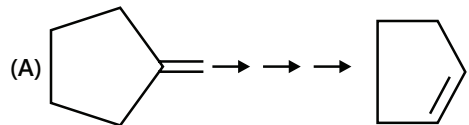**Q.3** The value of N and M are: *(2006)*

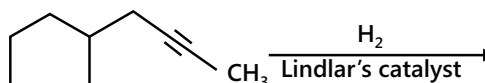(A) 3, 3   (B) 4, 4   (C) 6, 6   (D) 6, 4

Q.4 The total number of cyclic structural as well as stereoisomers possible for a compound with the molecular formula C_5H_{10} is *(2009)*

(A) 7   (B) 9   (C) 12   (D) 13

**Q.5** Complete the following reactions with appropriate reagents: *(1999)*

(A)

(B)

Q.6 What would be the major product in the following reaction? *(1998)*


Q.7 An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compound (B) on reaction with $NaOH/I_2$ yields sodium benzoate. Compound (B) reacts with KOH/NH_2NH_2 yielding a hydrocarbon (C) C_8H_{10}. Write the structure 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)*

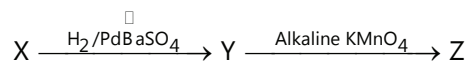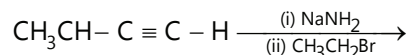**Q.8** (A) Identify A, B, C, D and E in the following schemes and write their structure:
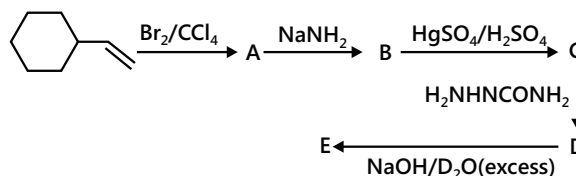
(B) Identify X, Y and Z in the following synthetic scheme and write their structures. Explain the formation of labelled formaldehyde (H_2C^*O) as one of the products when compound (Z) is treated with HBr and subsequently ozonolysed.

Mark the C* carbon in the entire scheme. $BaC^*O_3 + H_2SO_4$ (X) gas [C* denotes C^{14}] *(2001)*

$$H_2C = CH - Br \xrightarrow[\text{(ii) X}]{\text{(i) LiAlH}_4} (Y) \xrightarrow{\text{LiAlH}_4} (Z)$$
$$\text{(iii) } H_3O^+$$
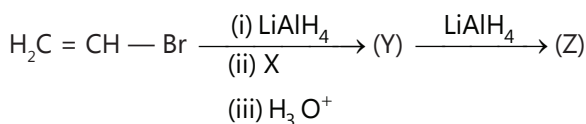
Q.9 Identify X, Y and Z in the following synthetic scheme and write their structures. *(2002)*

$$CH_3CH - C \equiv C - H \xrightarrow[\text{(ii) CH}_3CH_2Br]{\text{(i) NaNH}_2}$$

$$X \xrightarrow{H_2/PdBaSO_4} Y \xrightarrow{\text{Alkaline KMnO}_4} Z$$

Is the compound Z optically active? Justify you answer.

Q.10 Monomer A of a polymer on ozonolysis yields two moles of HCHO and one mole of CH_3COCHO. *(2005)*

(A) Deduce the structure of A.

(B) Write the structure of all 'cis' form of polymer of compound A.
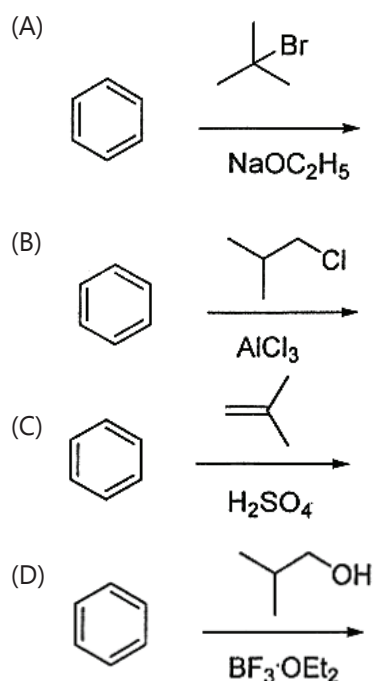
Q.11 Isomers of hexane, based on their branching divided into three distinct classes as shown in the figure
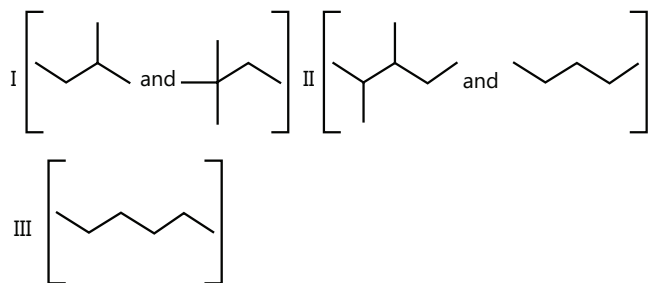
The correct order of their boiling point is: **(2014)**

(A) I > II > III   (B) III > II > I

(C) II > III > I   (D) III > I > II

Q.12 Among the following, reaction(s) which gives(give) *tert*-butyl benzene as the major product is(are) **(2016)**

MASTERJEE Essential Questions

JEE Main/Boards

Exercise 1

Q.2 (f,g)	Q.4	Q.7
Q.12	Q.15	

Exercise 2

Q.3	Q.9	Q.11

Previous Years' Questions

Q.4	Q.6	Q.12

JEE Advanced/Boards

Exercise 1

Q.7	Q.8

Exercise 2

Q.4	Q.13	Q.21
Q26	Q.27	

Previous Years' Questions

Q.5

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Chioce Type

Q.1 A	**Q.2** D	**Q.3** B	**Q.4** A	**Q.5** A	**Q.6** A	**Q.7** C
Q.8 D	**Q.9** B	**Q.10** C	**Q.11** D	**Q.12** C	**Q.13** B	

Previous Years' Questions

Q.1 D	**Q.2** B	**Q.3** B	**Q.4** A	**Q.5** C	**Q.6** B	**Q.7** ETHENE
Q.8 B	**Q.9** B	**Q.10** A	**Q.11** C	**Q.12** A	**Q.13** B	**Q.14** D

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 C	**Q.2** A	**Q.3** D	**Q.4** B	**Q.5** D	**Q.6** D	**Q.7** B
Q.8 D	**Q.9** A	**Q.10** D				

Multiple Correct Choice Type

Q.11 B,D	**Q.12** C,D	**Q.13** A,B,C	**Q.14** A,C	**Q.15** A,C,D	**Q.16** A,B,C	**Q.17** A,B,C
Q.18 A,B,C	**Q.19** A,B,C,D					

Comprehension Type

Q.20 B	**Q.21** A	**Q.22** D	**Q.23** A	**Q.24** D	**Q.25** C

Paragraph Type

Q.26 C	**Q.27** C

True or False

Q.28 False	**Q.29** False	**Q.30** True	**Q.31** False

Match the Column

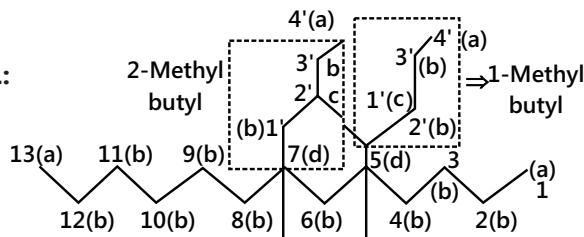|	
Q.32 A → q; B → r; C → t; D → u; E → s; F → p; G → v	**Q.33** A→ r, s; B → r, s; C → p; D → t; E → q

Previous Years' Questions

Q.1 C	**Q.3** D	**Q.4** A	**Q.11** B	**Q.12** B, C, D

Solutions

JEE Main/Boards

Exercise 1

Sol 1:

4'(a)
2-Methyl butyl
4'(a)
3' b
2' c
3'(b)
1'(c) ⇒ 1-Methyl butyl
(b)1'
2'(b)

13(a) 11(b) 9(b) 7(d) 5(d) 3
12(b) 10(b) 8(b) 6(b) 4(b) 2(b) (a) 1 (b)

(A) Out of 1 – and 2 – methyl butyl, the first compound has the lower locant number. So, the numbering of the C chain should start from the side where the locant is at the lowest position of C chain.

Hence, the IUPAC name of the compound is 5-(1-methyl butyl) – 7 (2- methyl butyl) tridecane).

(B) 1° C is bonded to only one other C a = 1°

2° C is bonded to two other C atoms b = 2°

3° C is bonded to three other C atoms c = 3°

4° C is bonded to four other C atoms d = 4°

(C) 1° H atoms are those attached to 1°C atoms

2° H atoms are those attached to 2°C atoms

3° H atoms are those attached to 3°C atoms

4° H atoms do not exist because al four bonds of 4°C are attached to other C atoms.

Sol 2: (A) It is Ullmann reaction
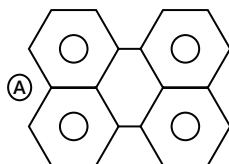
(B) Formation of B is Ullmann reaction.
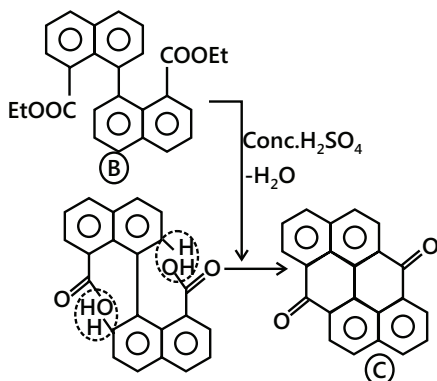
(C) [(> C = O) group is reduced to (-CH$_2$-) group]

(D) It is Kolbe's electrolysis reaction.

(E)

(Clemmensen Redn.) Zn-Hg+HCl
Or
(Wolf-Kishner Redn.) NH$_2$NH$_2$+EtONa
Or
(P+HI)

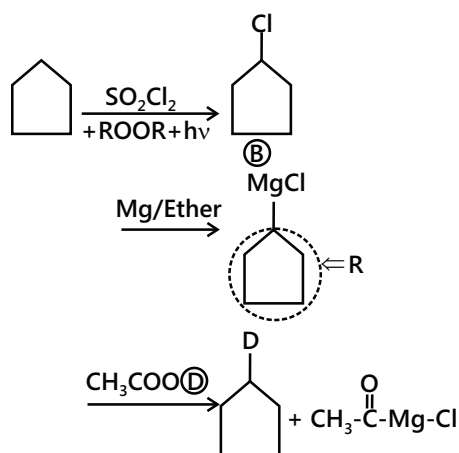$\xrightarrow{\Delta}$ C$_2$H$_6$+C$_2$H$_4$
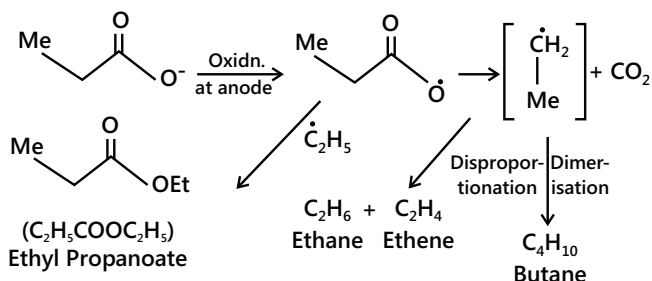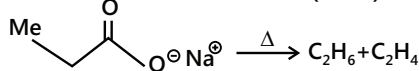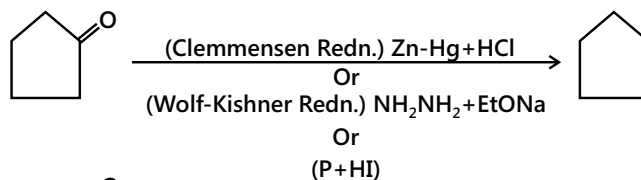
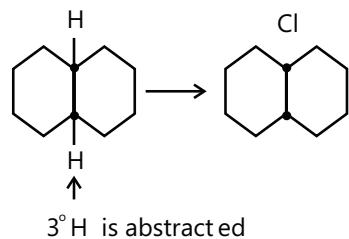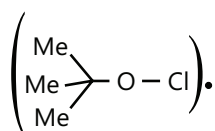(F) It is hydroboration reaction
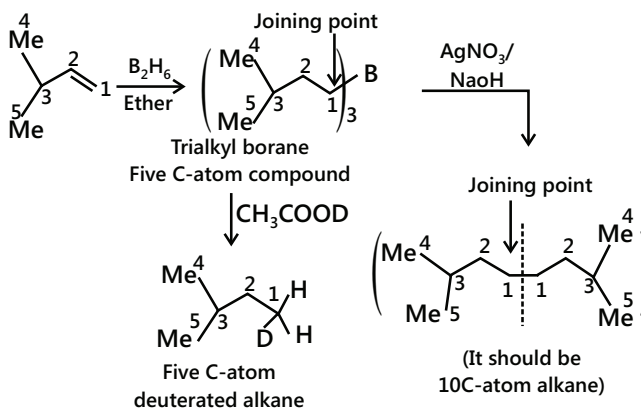
Note: Numbering of C atoms is not in accordance with naming but with counting total C atoms in the compound.

(G) Chlorination of alkane can also be done by SO$_2$Cl$_2$ (sulphuryl chloride) in the presence of peroxide and light.

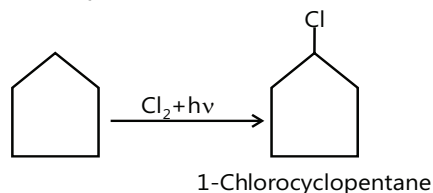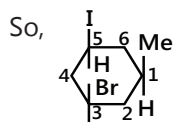(H) Chlorination can also be done by tert-butyl hypochlorine.

3° H is abstracted

Sol 3: (A) C_5H_{10} has 1° of unsaturation. It should have either one double bond or should be a cyclic compound. If it has one double bond, then it should give many monochlorinated products . So, it is a cyclic compound. Thus, it should be cyclopentane.
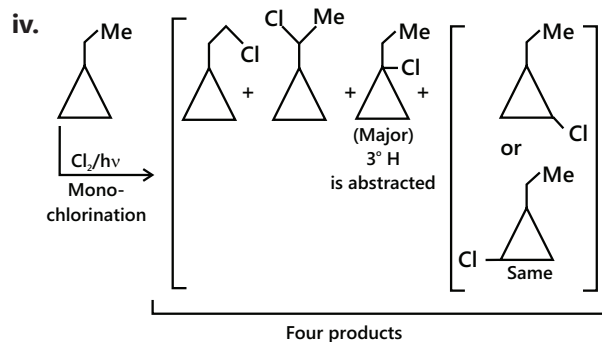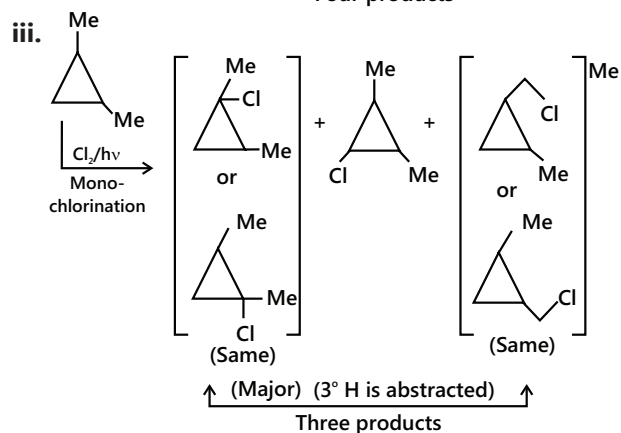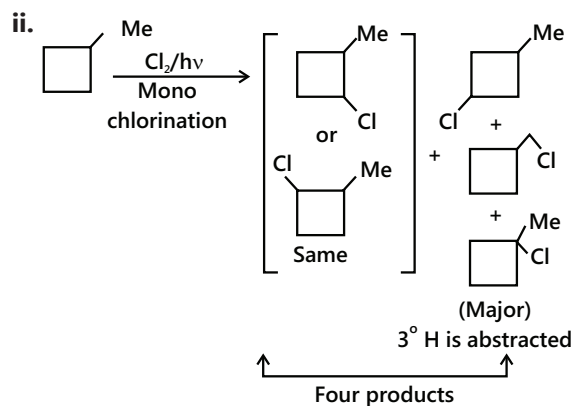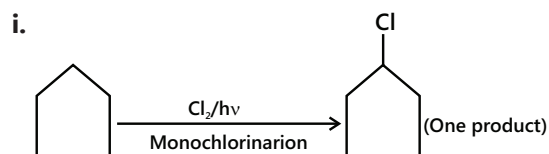
 Will give only one monochloro

product, while other cyclic isomers will give several products

So,

1-Chlorocyclopentane

(B) The different isomers can be

i. Cyclopentane
ii. 1-Methylcyclo butane
iii. 1,2-Dimethyl cyclopropane
iv. 1-Ethylcyclopropane
v. 1,1-Dimethylcyclopropane

i.

ii.

(Major) 3° H is abstracted

Four products

iii.

(Major) (3° H is abstracted)

Three products

iv.

Four products

v.
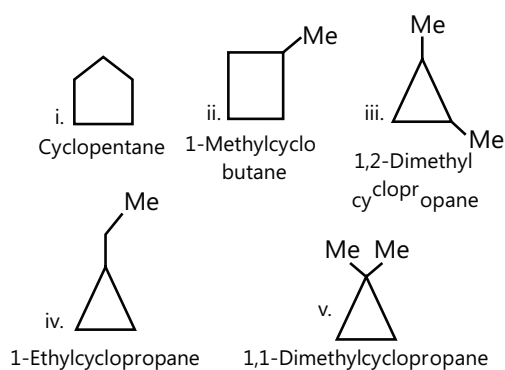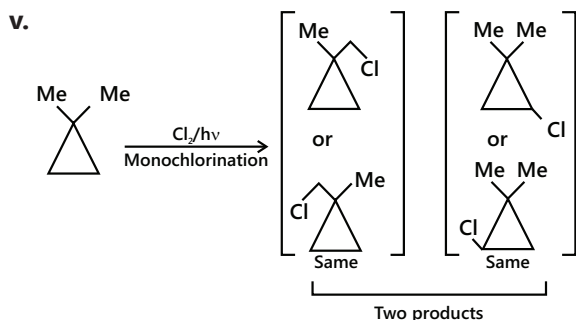
Therefore, total number of isomers = 1 + 4 + 3 + 4 + 2 = 14 (excluding stereoisomers).

Sol 4. Octane number is the percentage of isooctane in the mixture of isooctane and n-heptane. Octane number is for gasoline (petrol) fuel. A gasoline with octane number of 80 means 80% of isooctane and 20% of n-heptane, i.e., branched-chain alkane is more, so knocking is less.

Branched-chain hydrocarbons burn more smoothly to form more stable, less reactive 3° radicals, whereas straight-chain hydrocarbons (e.g. n-heptane) from less stable, more reactive 1° and 2° radicals

In contrast, cetane number is used for diesel fuel and is defined as the percentage of cetane in a mixture of cetane and α-methyl naphthalene. A diesel fuel with cetane number 80 means 80% of cetane (C_6H_{34}) (a straight chain hydrocarbon) and 20% of α-methyl naphthalene (aromatic compound). So, it will not burn smoothly and produce high knocking

But straight –chain hydrocarbons, e.g., cetane, ignite spontaneously in comparison to aromatic compounds.

So, cetane number determines the ignition of fuel. Higher cetane number means fuel will ignite faster but will produce higher knocking. Lower cetane number means fuel will ignite slowly and will produce knocking (rattling sound).

Sol 5: (A) i. Number of H atoms abstracted by D = 5 and percentage of compound formed = 96 %

Therefore, reactivity factor for replacement of H atoms = 93/5 = 18.6

ii. Number of D abstracted by Cl = 1 and percentage of compound formed = 7%.

Therefore, reactivity for D replacement = 7/1 = 7

iii. Relative reactivity of H: D abstraction = 18.6/7 = 2.7: 1 , i.e. , each H is abstracted 2.7 times faster than D.

(B) The C-D bond in CD_4 is slightly stronger than C-H bond in CH_4, thus (delta) H for abstraction of D is slightly greater than for H. The abstraction being the slow step, the removal of H will be faster.

Chemically, H and D are identical but (C-D) bonds; therefore the energy of activation of D is greater than that of H. Since abstraction is a slow step, removal of H will be faster.
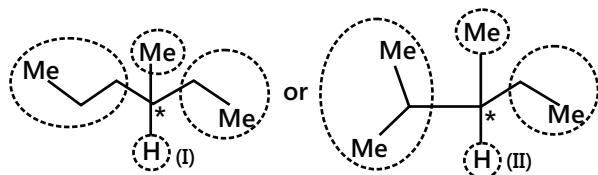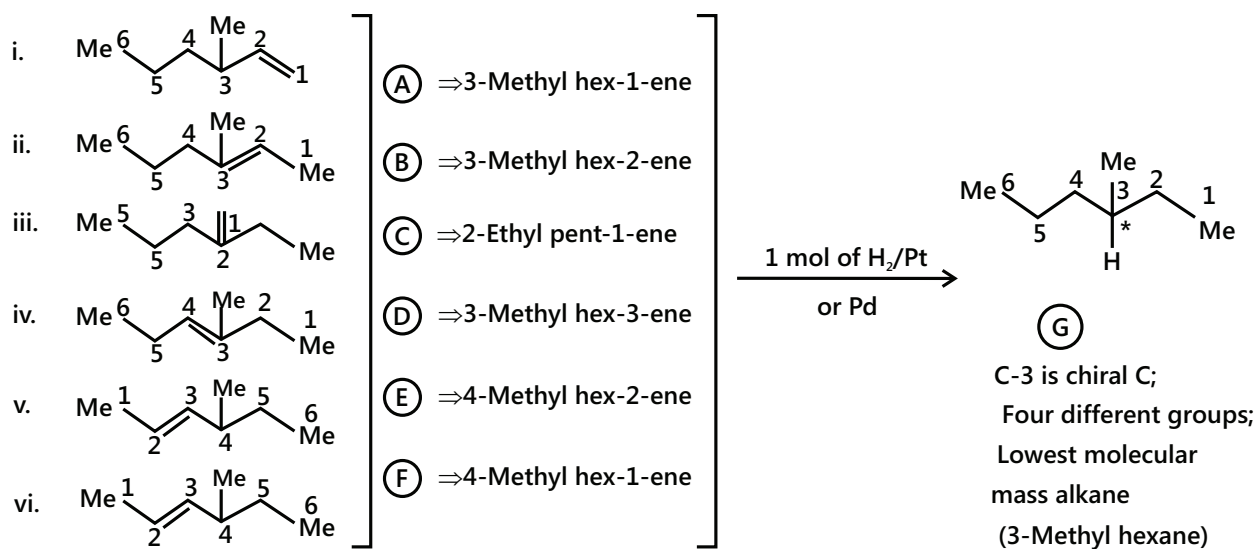
Relative abstraction of H:D = 2.7:1

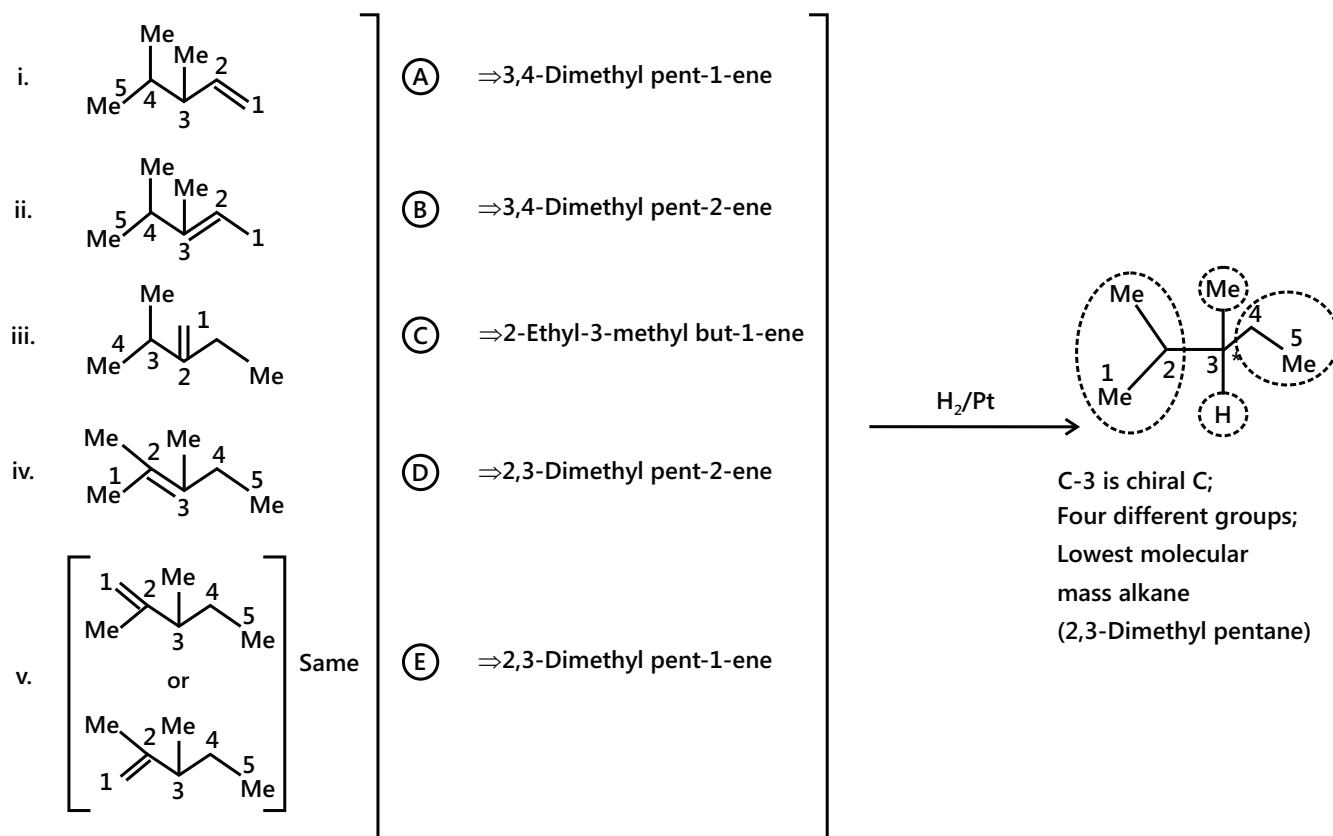Relative abstraction of 4H:D ⊔ 10.8:1

$$⊔ \quad 11:1$$

Sol 6: First, write the structure of G. It can be:

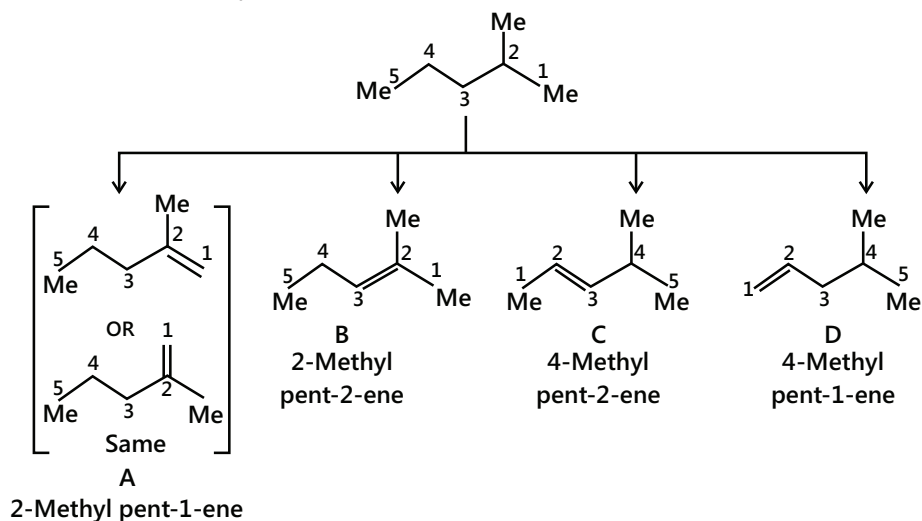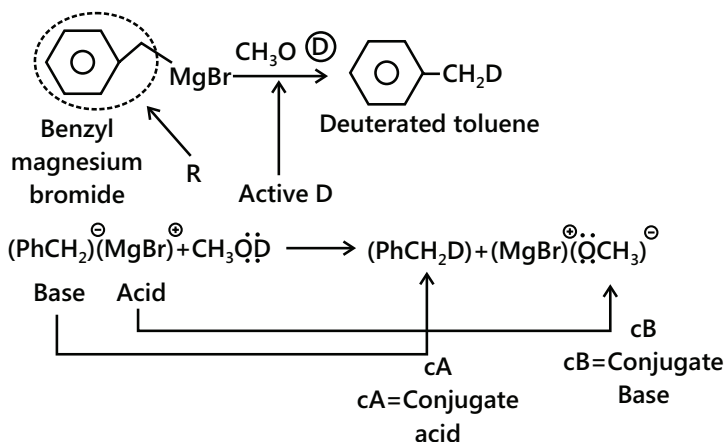(I) Can be obtained by six different alkene but (II) can be obtained by five different alkene. So G is (I).

i.

(A) ⟹3-Methyl hex-1-ene

ii.

(B) ⟹3-Methyl hex-2-ene

iii.

(C) ⟹2-Ethyl pent-1-ene

iv.

(D) ⟹3-Methyl hex-3-ene

v.

(E) ⟹4-Methyl hex-2-ene

(F) ⟹4-Methyl hex-1-ene

vi.

1 mol of H_2/Pt
or Pd
→

(G)

C-3 is chiral C;
Four different groups;
Lowest molecular
mass alkane
(3-Methyl hexane)

Sol 7: Proceed as in Q. No. 6 Compound (F) will be (II). Therefore, five isomeric alkenes are:

i.

(A) ⟹3,4-Dimethyl pent-1-ene

ii.

(B) ⟹3,4-Dimethyl pent-2-ene

iii.

(C) ⟹2-Ethyl-3-methyl but-1-ene

iv.

(D) ⟹2,3-Dimethyl pent-2-ene

v.

Same

(E) ⟹2,3-Dimethyl pent-1-ene

H_2/Pt
→

C-3 is chiral C;
Four different groups;
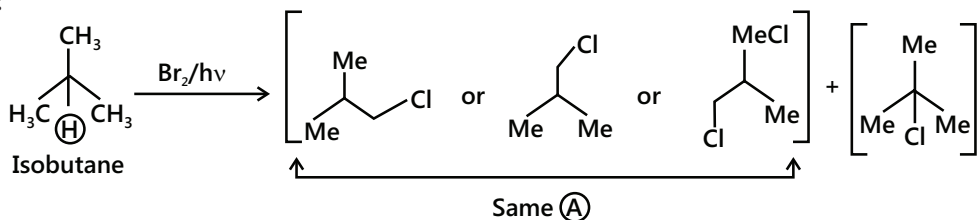Lowest molecular
mass alkane
(2,3-Dimethyl pentane)

Sol 8: First, write the structure of 2-methyl pentane and put double bond between the available (C-C) bond and find isomers. There are four different positions for double bond. Hence, four isomers are:

Sol 9:

$(PhCH_2)^{\ominus}(MgBr)^{\oplus}+CH_3\ddot{O}\dot{D} \longrightarrow (PhCH_2D)+(MgBr)^{\oplus}(\ddot{O}CH_3)^{\ominus}$

Base   Acid

cA

cA=Conjugate acid

cB

cB=Conjugate Base

Sol 10:

Reactivity order of bromination = $3°:2°:1°=1600:82:1$

(A) is obtained from the reaction of none equivalent 1° H atoms.

(B) is obtained from the reaction of one 3° H atoms

Percentage of (A) (isobutyl bromide) $\dfrac{9\times100}{1609} = 0.56\%$

Percentage of (B) (tert-butyl bromide) $= \dfrac{1600\times100}{1609} = 99.4\%$

Ratio = 177.7:1

Formation of t-Butyl bromide is 177.7 times to that of Isobutyl bromide.

Relative amount 9×1

$1600 \times 1 = 1600.0$

Total $= \overline{1609.0}$

Sol 11: Reactivity order of halogens in the reaction of alkene is:
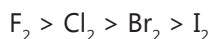
$F_2 > Cl_2 > Br_2 > I_2$

Two factors that are responsible:

a. Low energy of activation for the chain-propagating steps

b. More negative heat of reaction (ΔH_r^o) of the overall reaction.

$E_{activation}$ for the chain-propagation steps ($X+CH_4 \rightarrow HX + CH_3$) for F_2, Cl_2, Br_2 and I_2 is +5.1, +15.9, + 77.8, and + 140.2 kJ mol/L, respectively, and ΔH_r^o of overall reaction for fluorination, chlorination, bromination, and iodination is − 426.8, -102.5, -31.4 and +60.0 kJ mol/L, respectively. Therefore, it is clear that the chain-initiating step is not responsible for the observed order of reactivities, but the two factors discussed above are responsible.

As $E_{activation}$ for the chain-propagating step increases from F to I, the fraction of collision with energies greater than $E_{activation}$ decreases, consequently, the reactivity decreases as shown below in the plot of $E_{activation}$ versus fraction of the collision with the given energy.
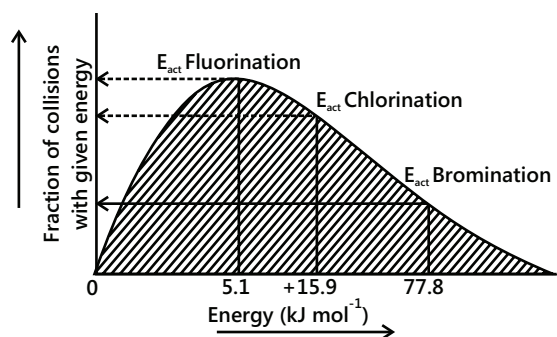
Sol 12:
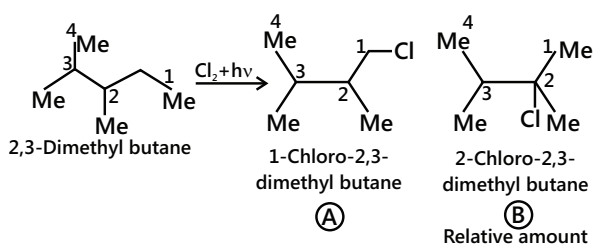
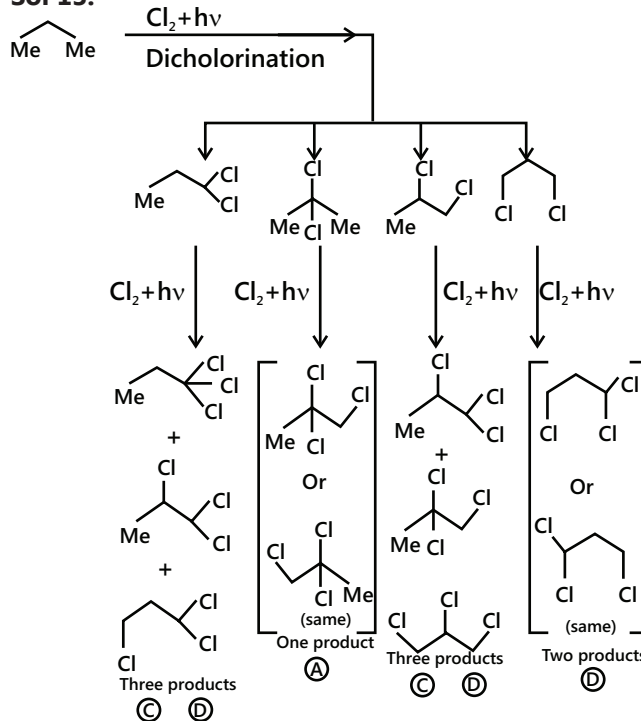(A) is obtained from the reaction of 12 equivalent 1° H atoms $12 \times 1 = 12.0$

(B) Is obtained from the reaction of two equivalent 3° H atoms $2 \times 5 = 10.0$
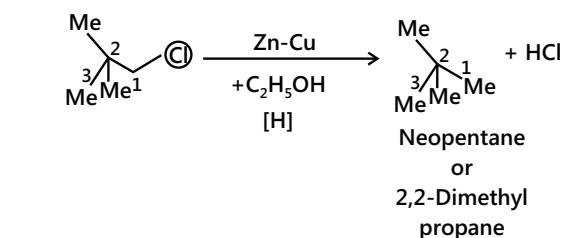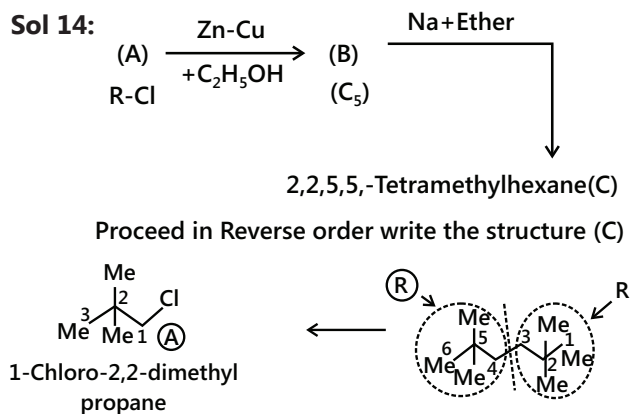
$$\text{Total} = \overline{22.0}$$

Percentage of (A) $= \dfrac{12 \times 100}{22} = 54.5\%$

Percentage of (B) $= \dfrac{10 \times 100}{22} = 45.5\%$

Sol 13:

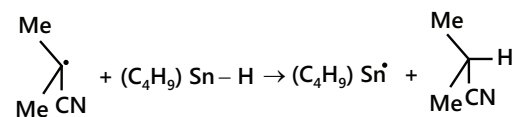

Sol 14:

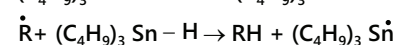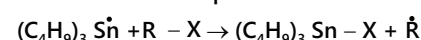2,2,5,5,-Tetramethylhexane(C)

Proceed in Reverse order write the structure (C)

1-Chloro-2,2-dimethyl propane (A)

Neopentane or 2,2-Dimethyl propane

Sol 15: Chain-initiation step:

Chain-initiation step:

$(C_4H_9)_3 \ \overset{.}{S}n + R - X \rightarrow (C_4H_9)_3 \ Sn - X + \overset{.}{R}$

$\overset{.}{R} + (C_4H_9)_3 \ Sn - H \rightarrow RH + (C_4H_9)_3 \ \overset{.}{S}n$
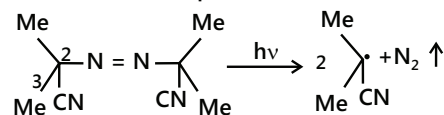
Exercise 2

Single Correct Choice Type

Sol 1: (A) As the number of C atoms increases, knocking power increases or anti-knocking power decreases.

Sol 2: (D) For 2e⁻ or 2F, 3 mol of gases [2 mol of CO_2 +1 mol of CH_3-CH_3(g)] are produced. At 10 bar pressure and 298 K , volume of 1 mol of gas = 247 litres.

∴ Volume of gases at anode $= 24.7 \times 3 = 74.1$ litres

Sol 3: (B) (C-Br) bond is weaker than (C –Cl) bond. Grignard reagent is formed more predominantly with (C –Br).
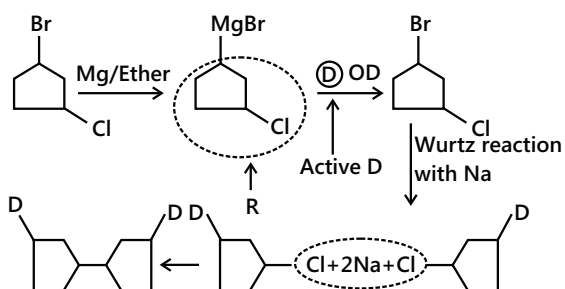
Sol 4: (A) The boiling point order is alkynes > alkenes > straight chain hydrocarbon > branched – chain hydrocarbon > cycloalkane (with the same number of C atom). So, the answer is (a).

The melting point order is : alkynes > trans-alkene > cis-alkene > cycloalkane > branched –chain hydrocarbon > straight-chain hydrocarbon.

Sol 5: (A) Due to polarity in pi bond B.P of alkene is more than alkane. Open chain have higher than branched and cyclic have lowest, due to decreased surface area.

Sol 6: (A) The greater the number of C atoms and straight chain, the higher is the boiling point. So, I is greater than II. More is the branching, less is the surface area, so lower is the boiling point. Therefore, III is greater than IV.

Sol 7: (C) The melting point of even number of C atoms is greater than the next higher C atom (due to the alternation effect).

So, $C_{10} > C_8 > C_9 > C_7$

Sol 8: (D)
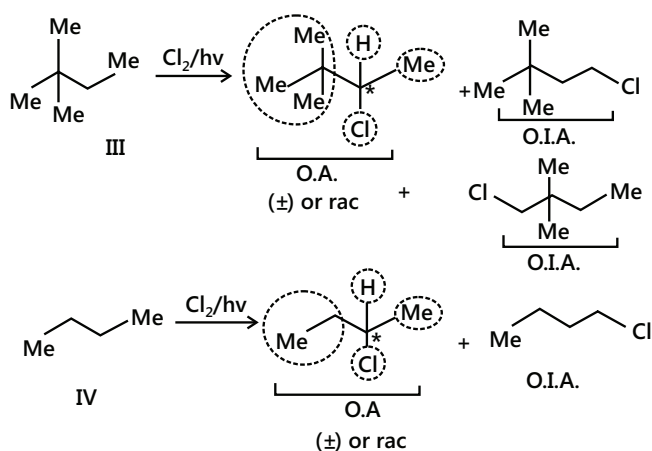
Sol 9: (B) In the second step of Path I, alkyl halide ($C_2 H_5 Br$) is 1°, Corey- House synthesis proceeds via SN²mehanism.

In the second step of path II, alkyl halide

is 3°, So, the reaction will not take place.

Sol 10: (C) There are two factors that determine the reactivity of the halogenation of alkanes.

1. Lesser the position value of E_{act} of the first chain propagating step, more reactive is the halogen.

2. Higher the negative values of overall heat of reaction ($\Delta H_r°$), more reactive is the halogen. This explains high reactivity and explosive violence with which F_2 reacts with CH_4

Sol 11: (D) Lower the E_{act} . of first step of chain propagation reaction, more easily the bond can be broken. Also this bond breaking will take place comparatively at a lower temperature.

Sol 12: (C)
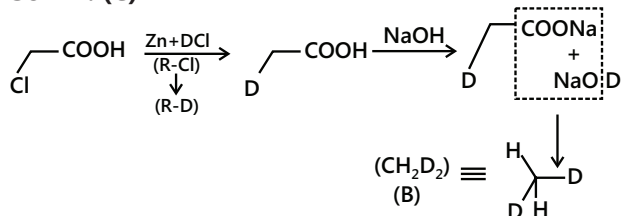
Sol 13: (B)

(A) More the number of C atoms, more is the heat of combustion. So, the order is correct

(B) Other than cyclopropane which is planar, cyclo-alkanes are puckered to relieve some ring strain.

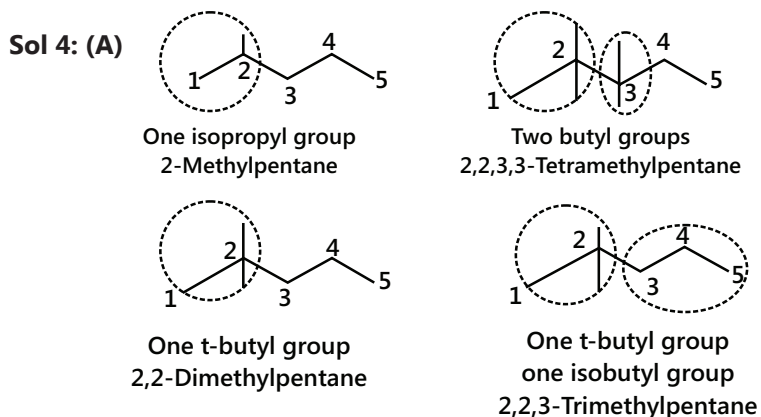(C) Except cyclopropane, cycloalkanes are non-planar.

(D) With the exception of cyclopropane, cycloalkanes are non–planar.
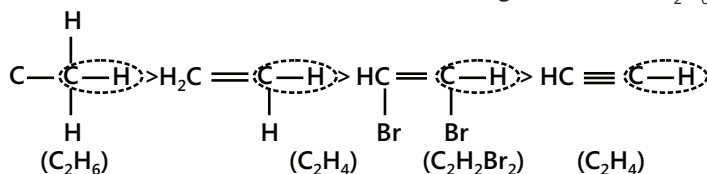
Previous Years' Questions

Sol 1: (D) By the decay of plants or animals present in wet or spongy land (called swamps or marsh) and by the action of bacteria on them, methane gas is produced. Because of this method of formation, methane gas is also called marsh gas.

Sol 2: (B) With the increase in C atoms and decrease in branching (or straight chain), the boiling points of alkanes increase. So, n–hexane has the highest boiling point.

Sol 3: (B) All have the same number of C atoms. n–Octane is a straight–chain compound that has a larger surface area. So, there are more Vander Waals forces of attraction resulting in a high boiling point.

Sol 4: (A)

One isopropyl group
2-Methylpentane

Two butyl groups
2,2,3,3-Tetramethylpentane

One t-butyl group
2,2-Dimethylpentane

One t-butyl group
one isobutyl group
2,2,3-Trimethylpentane

Sol 5: (C) (C – H) bond distance is the longest alkanes (C_2H_6)

$$C{-}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}{-}H > H_2C = \overset{\overset{}{}}{\underset{\underset{H}{|}}{C}}{-}H > HC = \overset{}{\underset{\underset{Br}{|}}{C}}{-}\overset{}{\underset{Br}{H}} > HC \equiv C{-}H$$

(C_2H_6) (C_2H_4) $(C_2H_2Br_2)$ (C_2H_4)

Sol 6: (B) As alkanes and cycloalkanes are non–polar molecules and are insoluble in H_2O, they are also less denser than H_2O and that is why they can float on water
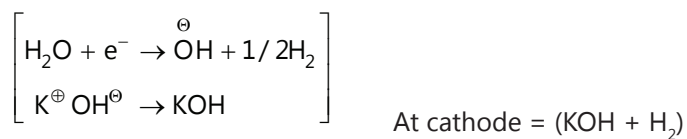
Sol 7: Ethene.
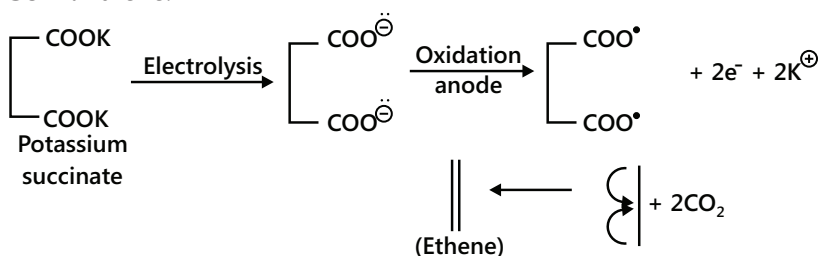
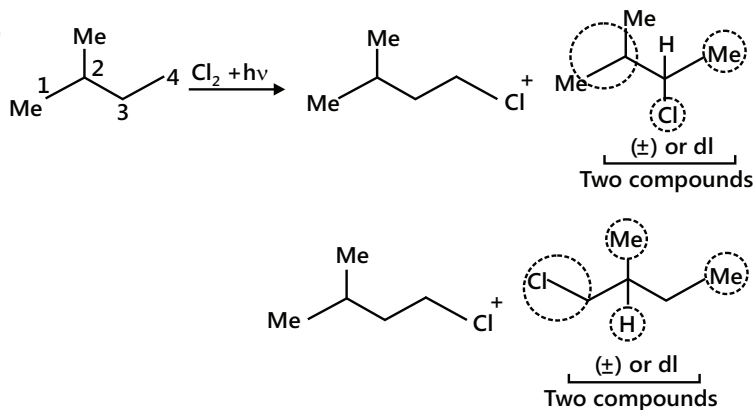Anode = $(2CO_2 + CH_2 = CH_2)$
Cathode = Reduction of H_2O

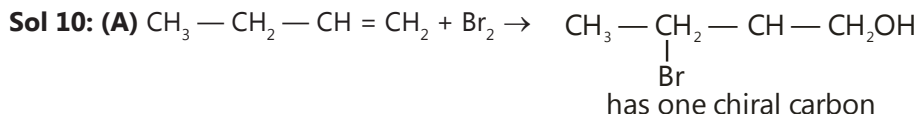Anode = $(2CO_2 + CH_2 = CH_2)$

Cathode = Reduction of H_2O

$$\left[\begin{array}{l} H_2O + e^- \rightarrow \overset{\ominus}{O}H + 1/2H_2 \\ K^{\oplus}OH^{\ominus} \rightarrow KOH \end{array} \right]$$

At cathode = (KOH + H_2)

Sol 8: (B) Abstraction of 3°H by Br gives (B)

Sol 9: (B)

(±) or dl

Two compounds

(±) or dl

Two compounds

Four chiral compounds are possible.

Sol 10: (A) $CH_3 — CH_2 — CH = CH_2 + Br_2 \rightarrow$

$$CH_3 — CH_2 — \underset{\underset{Br}{|}}{CH} — CH_2OH$$

has one chiral carbon

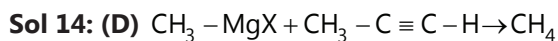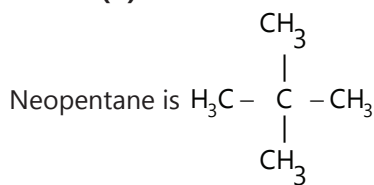Both statement-I and statement-II are correct, and statement-II is the correct explanation of statement-I.

Sol 11: (C) $CH_3 — CH_2 — CH = CH_2 + Br^- \rightarrow CH_3 — CH_2 — \overset{\bullet}{C}H — CH_2Br$

a secondary radical
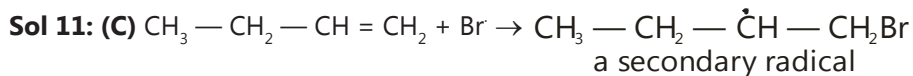
There statement-I is correct but statement-II is incorrect.

Sol 12: (A)
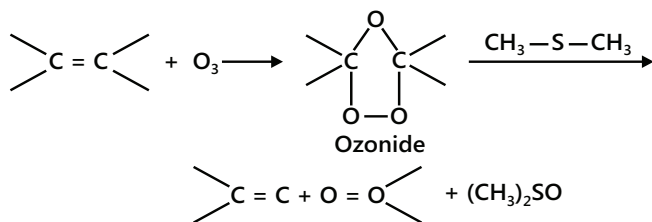
Ozonide

$$\text{C = C} + O = O \quad + (CH_3)_2SO$$

Both statement-I and statement-II are correct, and statement-II is the correct explanation of statement-I

Sol 13: (B)

$$\text{Neopentane is } H_3C - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

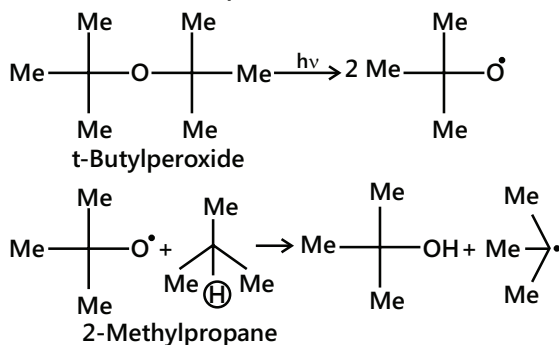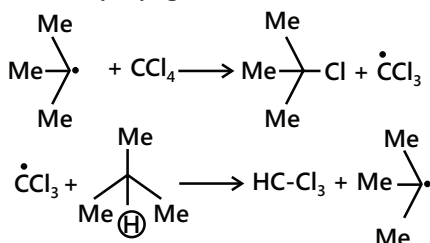**Sol 14: (D)** $CH_3 - MgX + CH_3 - C \equiv C - H \rightarrow CH_4$

JEE Advanced/Boards

Exercise 1

Sol 1: Chain-initiaion step :

t-Butylperoxide

2-Methylpropane
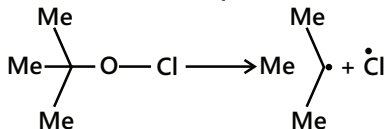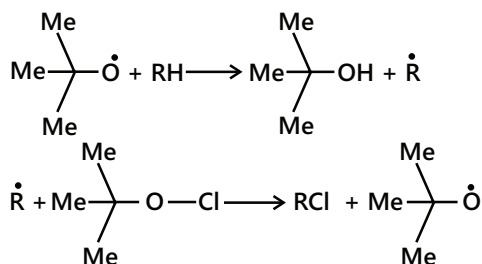
Chain-propagation :

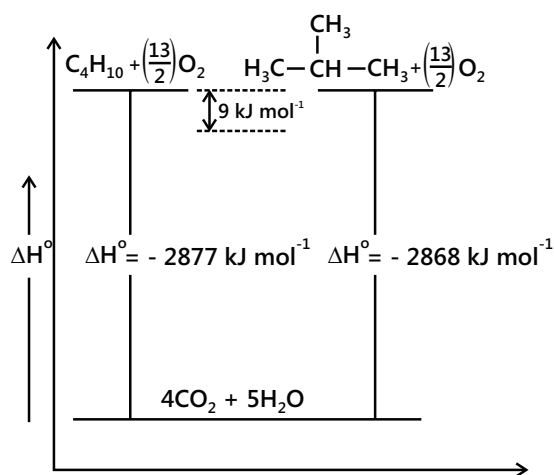**Sol 2:** Chain-initiaion step :

Chain-propagation step :

Sol 3: On combustion, the same number of C atoms gives the same number of moles of CO_2 and H_2O. So a direct comparison is not possible.

Greater the negative value of combustion, thermodynamically less stable is the compound. As butane liberates more heat on combustion than isobutene (2-methyl propane). It must contain relatively more potential energy. Isobutene, therefore, is more stable than butane by 9 kJ mol/L as shown in the graph below.

Sol 4: As discussed in Q. No. 3, greater the number of C atoms, more is the heat of combustion ; but when the number of C atoms is same, the order is straight chain > less branching > more branching:

Hexane > Pentane > 2-Methyl butane (isobutane) > 2, 2-Dimethyl propane (neopentane).

More is the branching, lesser is the heat of combustion, and greater is the stability of compound.

iii>iv>i>ii
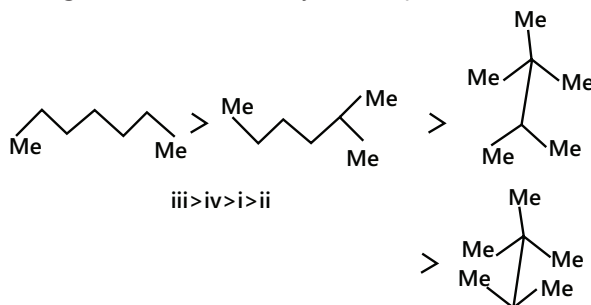
All the isomers react to give the same number of moles of CO_2 and H_2O, so a direct comparision is not possible. Structure (iii) releases more heat on combustion than others, thus, it contains relatively more potential energy and must be thermodynamically less stable. (Higher the energy in a compound, less stable is that compound compared to the products and to its isomers.) or more reactive it is and, hence, more heat of combustion will be released .

In structures (i) and (ii), (i) has higher potential energy than (ii) and, thus is less stable and release more energy. Since structure (i) is an eclipsed structure, whereas (ii) is Gauche structure, hence, (i) is less stable than (ii).
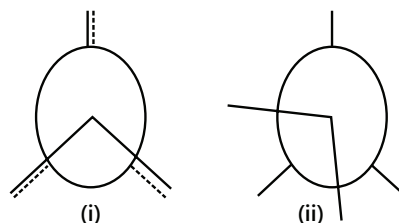
Sol 5: (A) 2-Methyl pentane has the highest point because the boiling point in alkene depends upon the chains of atoms and the molecular mass of the molecules. Straight-chain molecules have higher boiling point than the branched-chain compounds. Also, the lesser branched chain has low boiling point because in higher branched molecules, the molecular mass increases and boiling point also increases.

The boiling point order is as follows:

2-Methyl pentane > 2, 3-Dmethyl butane > 2, 2-Dimethyl butane.
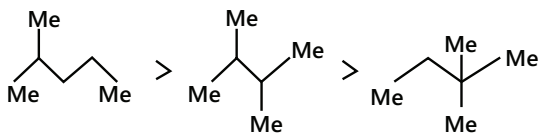
The boiling point decreases because branching increases.

(B) The melting point of alkanes with even number of carbon atoms is higher than that of the odd numbered from the immediate next lower alkanes. For example, the melting point of C_3H_8 is 85.9 k while that of C_6H_{14} is 179 K. Since the packing is symmetrical in even-numbered alkanes, they have melting point.

Therefore, neopentane with a spherical molecules has the highest melting point out of the three isomers due to more compact packing.

The melting point order is:
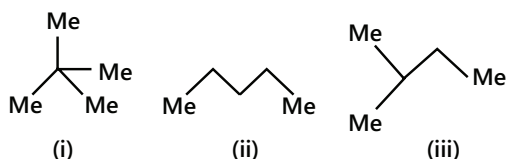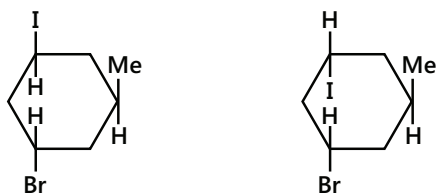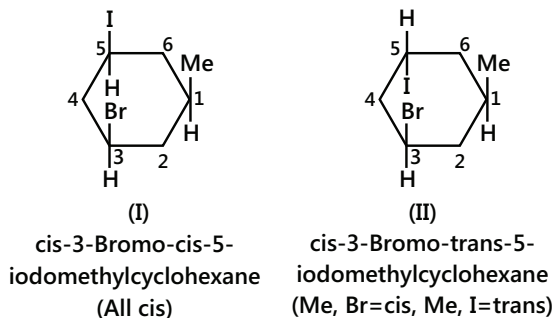

(i) > (ii) > (iii)

(256.4 K > 143.3 K > 113.1 K)

The boiling point order is:
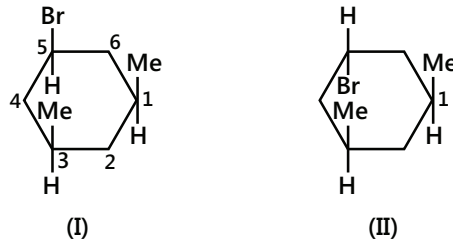
(ii) > (iii) > (i)

(309 K > 300.9 K > 282.5 K)

Sol 6: (A) Four geometrical isomers:

(I)
cis-3-Bromo-cis-5-iodomethylcyclohexane
(All cis)

(II)
cis-3-Bromo-trans-5-iodomethylcyclohexane
(Me, Br=cis, Me, I=trans)

(III)
trans-3-Bromo-cis-5-iodomethylcyclohexane
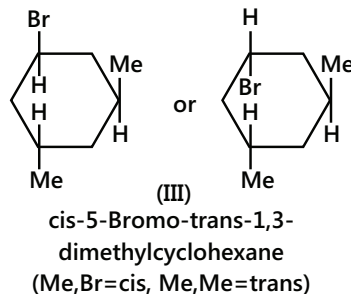(Me, Br=trans, Me,I=cis)

(IV)
trans-3-Bromo-trans-5-iodomethylcyclohexane
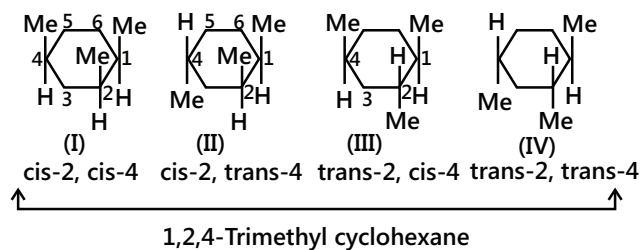(Me,Br=trans, Me,I=cis)

(B) Three geometrical isomers:

(I)
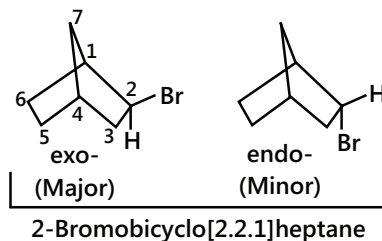cis-5-Bromo-cis-1,3-dimethylcyclohexane
(All cis)

(II)
trans-5-Bromo-cis-1,3-dimethylcyclohexane
(Me, Br=trnas, Me,Me=cis)

(III)
cis-5-Bromo-trans-1,3-dimethylcyclohexane
(Me,Br=cis, Me,Me=trans)

(C) Four geometrical isomers:

(I) cis-2, cis-4
(II) cis-2, trans-4
(III) trans-2, cis-4
(IV) trans-2, trans-4

1,2,4-Trimethyl cyclohexane

Sol 7:
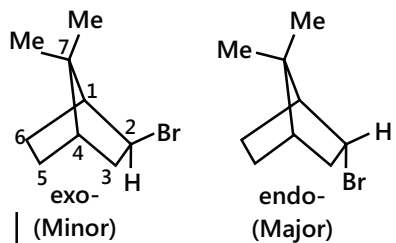

exo-
(Major)

endo-
(Minor)

2-Bromobicyclo[2.2.1]heptane

Major product is exp. Br_2 approaches the intermediate norbornyl radical from the exo side rather than endo

side, which is hindered by the transannular H atoms.

2-Brom-7,7-dimethyl[2.2.1]heptane

Major product is endo; exo approach is more hindered by gem-dimethyl groups than the endo approach hindered by the transannular H atoms.

Sol 8: In (I), there is dipole-dipole repulsion between two equatorial Cl atoms. It partially destabilises the sterically more favoured (e, e) conformer but not the (a, a) conformer (II) where Cl atoms are further apart. Therefore, the conformers (I) and (II) coexist together because their energies are very close. But the polar solvent molecules surround the Cl atoms by dipole – dipole attraction and relieve the dipole-dipole repulsion between Cl atoms themselves. Hence, the lower energy (e, e) conformer (I) predominates in polar solvents.
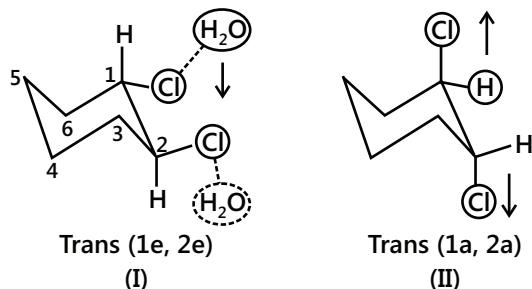
Sol 9:
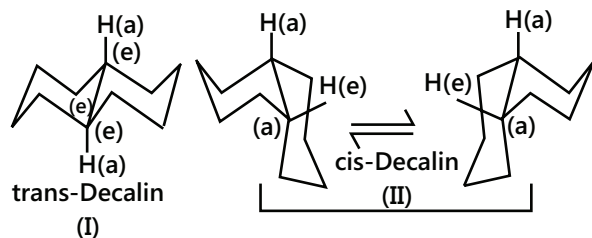
In trans-decalin, only the rigid (e, e) conformer is possible. Flipping to (a, a) orientation is impossible, because the diaxial bonds point $180°$ away from each other and cannot be bridged by only four C atoms to complete the second ring. In cis-conformation, fusion is (e, a) and flipping can give the equilibrating (e, e) conformer. Therefore, cis-form is flexible. The trans conformer (e, e) has lower energy than cis conformer (e, a).

Exercise 2

Single Correct Choice Type

Sol 1: (C). Making and breaking of bonds is the basis of all chemical transformation. Bond dissociation energy is the measure of the strength of a chemical bond. According to the experimental bond enthalpies the order is III < IV < I < II.

Sol 2: (A) Ring strain = ($\Delta H_c°$ of cyclobutane $-4 \times \Delta H_c°$ of per (CH_2) group of cyclohexane). $= 2744 - (4 \times 660) = 104 kJ\ mol^{-1}$.

Sol 3: (D) All the three reactions, i.e., alkylation, cyclisation, and isomerization convert straight –chain hydrocarbons to branched –chain or cyclic compounds, which changes the percentage of straight-chain hydrocarbon. Hence, the octane number is changed.

Sol 4: (B) (i) Williamson's synthesis is used for the preparation of ether.

(ii) Kolbe's reaction is used for the preparation of alkanes, alkenes, and alkynes.

(iii) Wurtz reaction is used for the preparation of higher alkanes (even number and symmetrical alkanes when R group is the same). With two different R group mixed, alkanes and alkenes are obtained.

(iv) Sandmeyer reaction is used for the preparation of various compounds from diazo compounds.

Sol 5: (D) C_1 -C_4 are gases, C_5 –C_{17} are liquids, and C_{18} onwords are colourless waxy solids.

Sol 6: (D) $Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$ (Chain – initiation step).

Sol 7: (B)
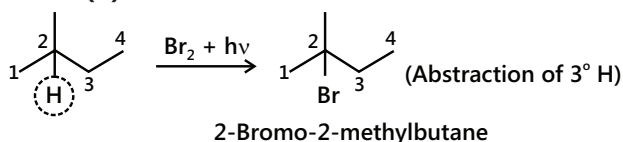
2-Bromo-2-methylbutane

Sol 8: (D) For C atom alkane, van der Waals forces of attraction are weak and boiling point is the lowest. As far as the boiling points are concerned, alkenes have more boiling point than alkanes with the same number of C atoms. due to of the presence of π -bond, alkenes are slightly polar. More is the number of π -bonds, more is the polarity and higher is the boiling point. Thus, the decreasing order of boling points is:

c > b > a> d.

Sol 9: (A) Methane

Sol 10: (D) (So, in total, four isomers exist.)
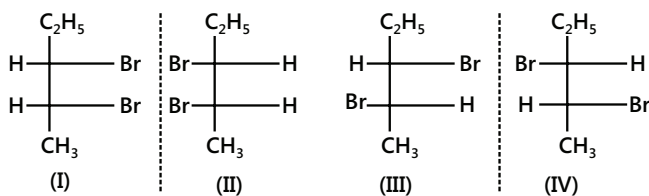
$$\text{I and II} \atop \text{III and IV}\Bigg]\text{Enantiomers}$$

$$\left.\begin{array}{l}\text{I and III}\\ \text{I and IV}\\ \text{II and III}\\ \text{II and IV}\end{array}\right]\text{Diastereomers}$$

Multiple Correct Choice Type

Sol 11: (B, D)

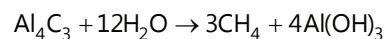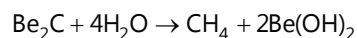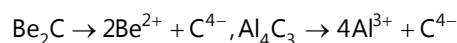A. Wrong (by the definition of cetane number).

B. True (by the definition of cetane number).

C. Wrong (higher cetane number means higher percentage of straight –chain hydrocarbon ($C_{16}H_{32}$), whose knocking property is high). Therefore, cetane number of 90 has high knocking property (makes more rattling sound).

D. True (cetane number determines the quality of diesel fuel in terms of spontaneous ignition).

Higher cetane number means that fuel ignites faster but makes more rattling sound (i.e., more knocking).

Sol 12: (C, D) Carbides of Be and Al contain methinide ion (C^{4-}) and thus give CH_4 gas (due to the diagonal relationship of Be and Al).

$$Be_2C \rightarrow 2Be^{2+} + C^{4-}, Al_4C_3 \rightarrow 4Al^{3+} + C^{4-}$$

$$Be_2C + 4H_2O \rightarrow CH_4 + 2Be(OH)_2$$

$$Al_4C_3 + 12H_2O \rightarrow 3CH_4 + 4Al(OH)_3$$

Whereas the carbides of Mg, i.e., Mg_2C_3, contain propynide ion (C_3^{4-}) and hence give propyne gas.

$$Mg_2C_3 + 4H_2O \rightarrow CH_3 - C \equiv CH + 2Mg(OH)_2$$
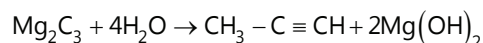
The carbides of rest of the second group, i.e., Ca, Sr, and Ba(CaC_2, SrC_2 and BaC_2) give ethyne (acetylene) gas because they contain acetylide or ethynide ion (C_2^{2-}).

$$CaC_2 \rightarrow Ca^{2+} + C_2^{2-}$$
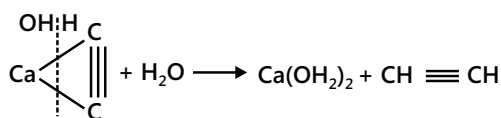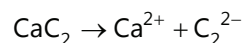
Sol 13: (A, B, C)
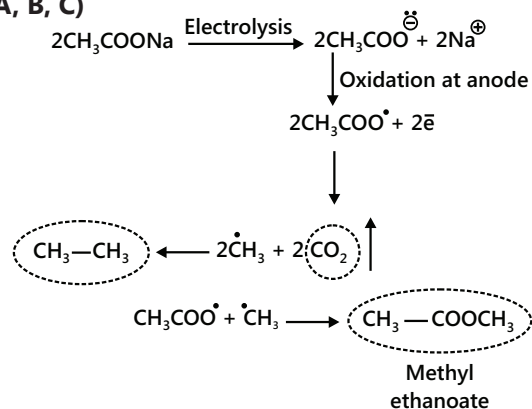
The products at anode are (a), (b), and (c).

At cathode reduction of H_2O gives $H_2(g)$.

Sol 14: (A,C) In destructive distillation of coal, at 443-503 K a middil oil or carbolic oil fraction contains phenol and naphthalene

Sol 15: (A, C, D) Any membered ring can be fused cis, but two five- membered or large rings can also be fused trans.

**Sol 16: (A, B, C)** Active methylene group should have EWG around it.

**Sol 17: (A,B,C)** All the three contains 1°, 2°, 3° and 4°C atoms

Sol 18: (A,B,C) (A) Decalin exists in two geometrical isomers, cis and trans- Correct

(B) cis- form is flexible and has (a, e) conformer- Correct

(C) trans form is rigid and has (e, e) conformer and is more stable than cis form.-Correct

Sol 19: (A,B,C,D) All the four statements iare correct in the synthesis of cycloalkanes by intramolecular cyclisation.

Comprehension Type (20-23)

Sol 20: (B)

Five isomeric hexyl chloride
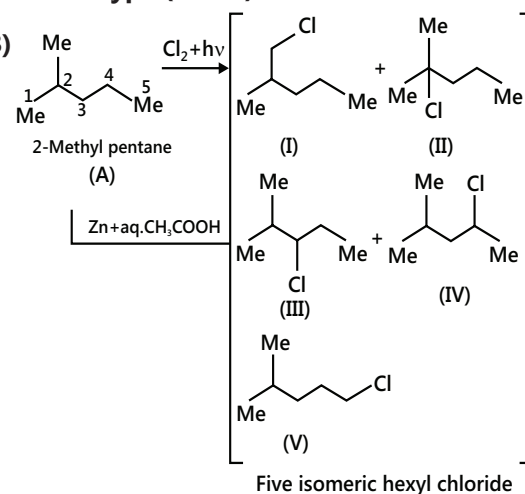
Sol 21: (A)
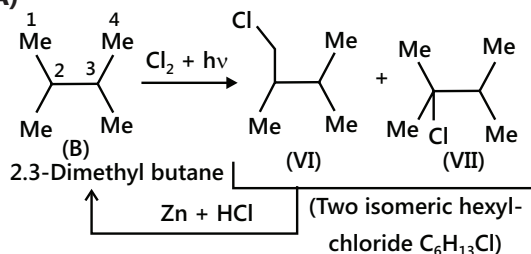
Sol 22: (D) Isomeric hexyl chlorides obtained from (B) are (VI) and (VII).

Sol 23: (A) Alkene (C) and (D) on hydrogenation should give compound (B).

Alkene (C) and (D) are:
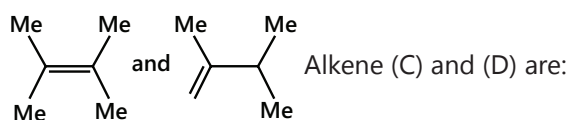
Comprehension Type (24-25)

Sol 24: (D) Due to the reduction of central ring, 3 four–membered anti–aromatic rings become stable to form (I). In (II), due to the reduction of terminal ring, only one anti–aromatic ring can be stabilized.

Sol 25: (C) The stability order is Aromatic > Non-aromatic > Antiaromatic. . Aromatic compounds follow Huckel's rule and ar highly stable, whereas antiaromatic compounds are highly unstable and highly reactive.

Paragraph for Problems (26–27)

**Sol 26: (C)** Two gauche forms of butane are same.
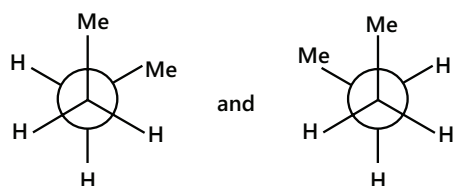
But gauche and anti-forms are different. So, they are diastereomers. So the answer is (C).

Sol 27: (C) (a) is true, (b) is true, and (d) is true, (Adsorption is a physical property. So it is different for diastereomers.) (c) is not true.1 Diastereomers can be optically inactive, e.g., cis- 2- butene and trans are geometrical isomers and are diastereomers.

So the answer is (c)
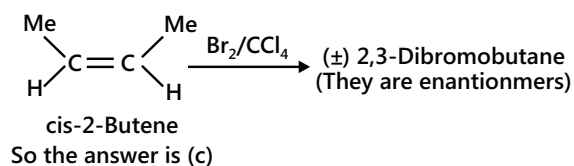
True or False

Sol 28: False Br radical less reactive is less influenced by the probability factor. The bromination primarily depends on the reactivity of H atom which is 3°>2°>1°.

Sol 29: (B) False The chlorination of propane gives two isomeric products -1- chloropropane and 2-chloropropane. Their relative ration would be given as:

$$\frac{1-\text{Chloropropane}}{2-\text{Chloropropane}} = \frac{\text{No. of } 1°H}{\text{No. of } 2°H} \times \frac{\text{Reactivity of } 1°H}{\text{Reactivity of } 2°H}$$

$$= \frac{6}{2} \times \frac{1.0}{3.8} = \frac{6.0}{7.6}$$

Percentage of 1° isomer $= \dfrac{6.0}{6.0 + 7.6} \times 100 = 44\%$

Sol 30: (C) True : - Isobutane is

$$CH_3 \!-\! CH \!-\! CH_3$$
$$\mid$$
$$CH_3$$
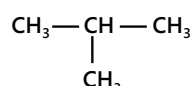
Its chorination would give two isomers:

$$\frac{1-\text{isomer}}{2-\text{isomer}} = \frac{\text{No. of } 1°H}{\text{No. of } 3°H} \times \frac{\text{Reactivity of } 1°H}{\text{Reactivity of } 3°H}$$

$$= \frac{9}{1} \times \frac{1}{5.0} = \frac{9}{5}$$

Percentage of 1° isomer $= \dfrac{9}{9+5} \times 100 = 64.3\%$

Sol 31: False The propane is $CH_3CH_2CH_3$. The relative ratio of the two isomers is

$1°H = 6H = 6 \times 1 = 6, 2°H = 2 \times 82 = 164$

Total reactivity = 6 +164 =170

Percentage of 1° isomer $= \dfrac{6}{170} \times 100 = 6.52\%$

Match the Column

Sol 32: A → q; B → r; C → t; D → u; E → s; F → p; G → v.
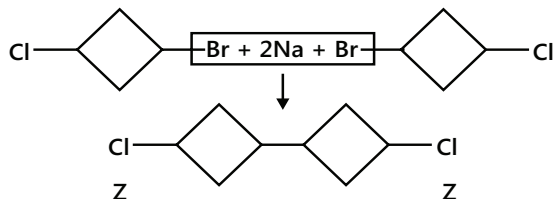
Sol 33: A→ r, s; B → r, s; C → p; D → t; E → q

(a) And (b) reactions are cyclisation and aromatization. Both reactions are carried out as given in (r) and (s).

∴(a) and (b) ⇒(c) and (d).

For (r), (s), and (t) refer to theory.

Previous Years' Questions

Sol 1: (C) (C – Br) bond is weaker than (C – Cl) bond; hence, Wurtz reaction will take place with (C – Br) bond.

Sol 2: Mole fraction of anti–form = 0.82

Mole fraction of gauche form = (1 – 0.82) = 0.18

μ_{obs} =1.0

$\mu_{obs} = \mu_1 X_1 + \mu_2 X_2$

1.0 = μ(anti) × 0.82 + μ(gauche) × 0.18

μ(anti) = 0 (from Newmann's projection, two Z vectors cancel and all H vectors cancel)

1.0 = 0 × 82 + μ(gauche) × 0.18
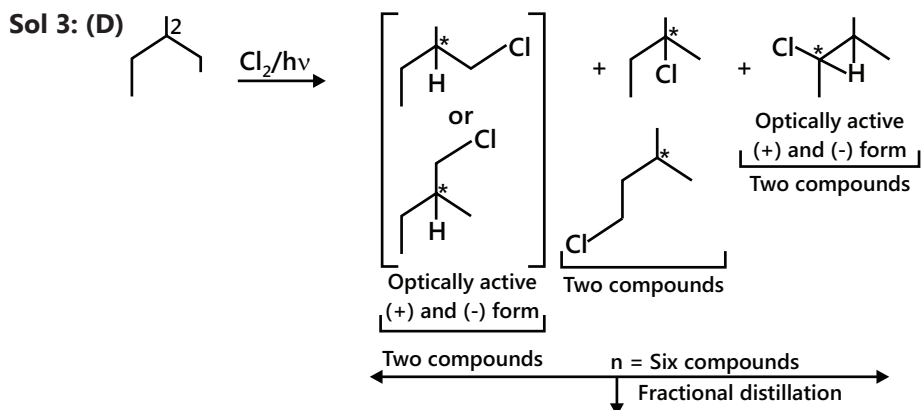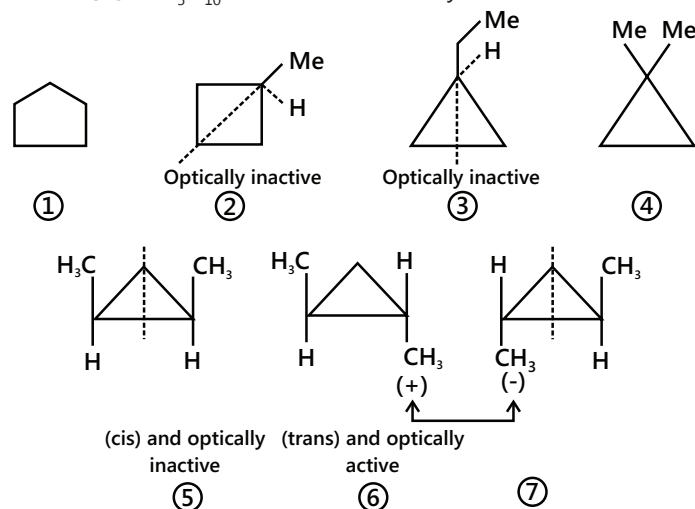
$\mu(gauche) = \dfrac{1.0}{0.18}$ = 5.55D

a.

In (i), anti–form is a stable conformer.

In (ii), gauche form is a stable conformer due to the intramolecular H–bonding.

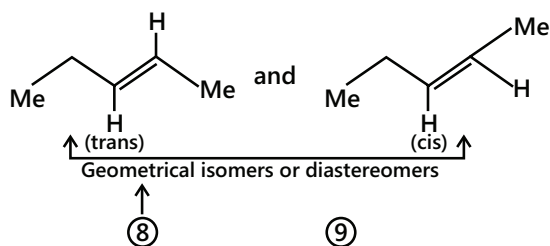**Sol 3: (D)**

Sol 4: (A) a. C_5H_{10} = 1 DU. It can be cyclic and can be alkene.

①   ② Optically inactive   ③ Optically inactive   ④

⑤ (cis) and optically inactive   ⑥ (trans) and optically active   ⑦

Therefore, total cyclic and stereoisomers = 7

If it is alkene:

⑧ (trans)   ⑨ (cis)

Geometrical isomers or diastereomers

Other alkene structures :

⑩   ⑪ or   Same

⑫ and   ⑬ Total numbers of cyclic acyclic, and stereoisomers
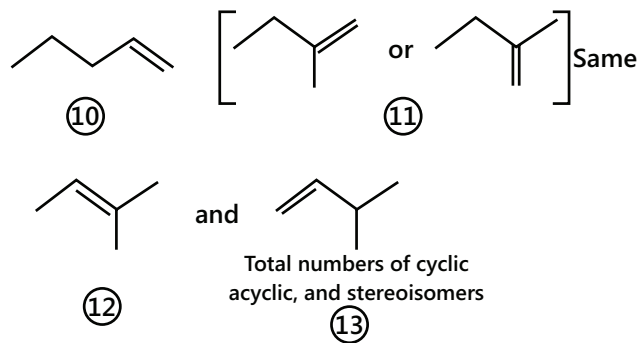
Total Number of cyclic, acyclic, and stereoisomers is 13. However, in the problem only cyclic structural and stereoisomers have been asked. So the total number of isomers would be seven.

Sol 5: (A)

+ O_3 $\xrightarrow{\text{Zn-H}_2\text{O}}$ $\xrightarrow{\text{LiAlH}_4}$

$\xrightarrow[\Delta]{\text{H}_2\text{SO}_4}$

(B)

$+BHR_2$ $\xrightarrow[\text{HO}^-]{\text{H}_2\text{O}_2}$

Sol 6:

R = $(CH_3)_2CHCH_2$ —
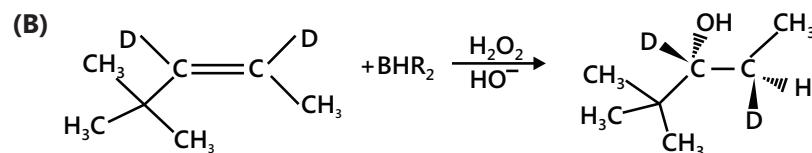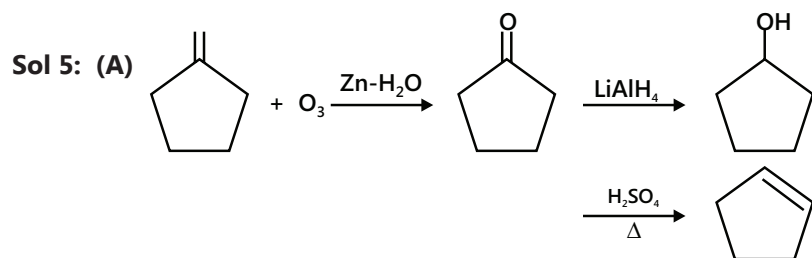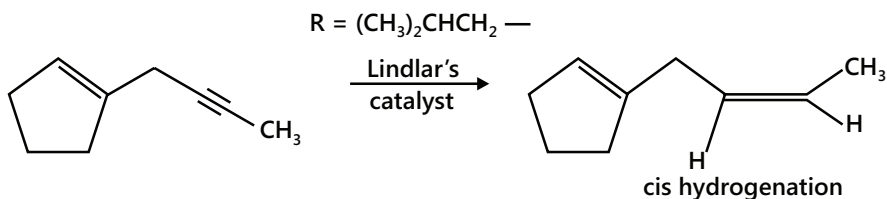
cis hydrogenation

Sol 7: (B) + NaOH + I_2 C_6H_5 — COONa (Iodoform reaction)

B is

$$C_6H_5 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$
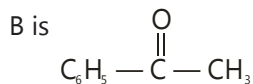
∴ B + N_2H_4 $\xrightarrow{\text{KOH}}$ Hydrocarbon (c) C_8H_{10}

"Wolff–Kishner Reduction"

∴ C is C_6H_5 — CH_2 — CH_3

Hence, A can be one of the following :

or
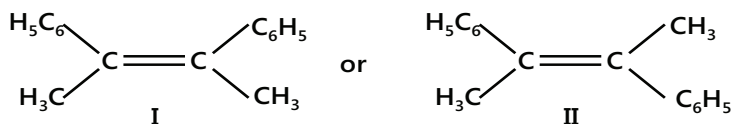
I on catalytic hydrogenation, would give meso compound while II on catalytic hydrogenation, would produce racemic mixture.

Sol 8:

(B) $Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow \overset{*}{C}O_2 + BaSO_4$
$\phantom{Ba\overset{*}{C}O_3 + H_2SO_4 \longrightarrow} X$

$CH_2 = CH \text{—} Br$

(i) Mg/ether
(ii) X
(iii) H_3O^+
$\longrightarrow$

$$CH_2 = CH \text{—} \underset{Y}{C} \overset{\overset{\displaystyle CH_3}{|}}{\underset{}{}} \overset{\overset{\displaystyle O}{||}}{\underset{*}{C}} \text{—} OH$$

$\xrightarrow{\text{LiAlH}_4} CH_2 = CH \text{—} \underset{Z}{\overset{*}{C}H_2} \text{—} OH$
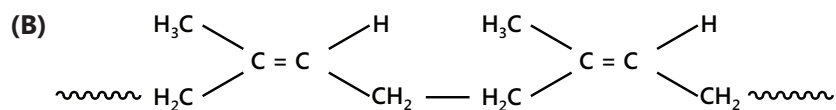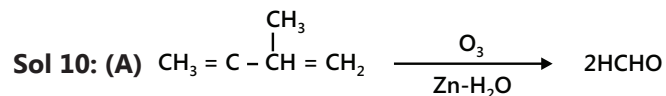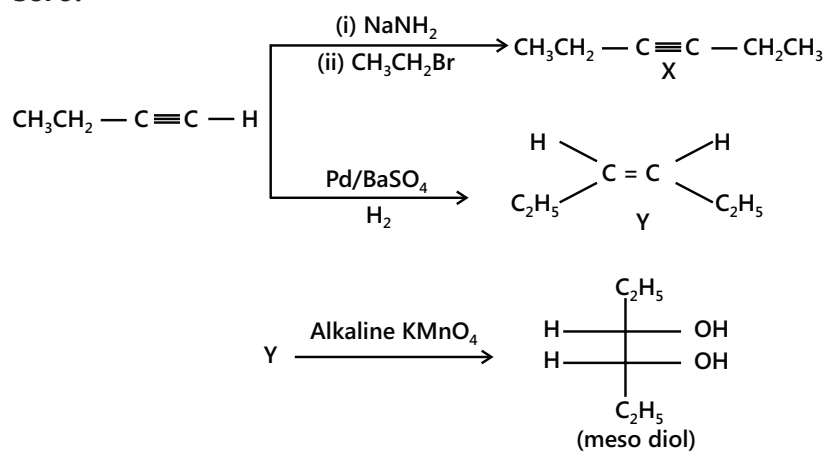
Sol 9:

$CH_3CH_2 \text{—} C \equiv C \text{—} H$

$\xrightarrow[\text{(ii) CH}_3\text{CH}_2\text{Br}]{\text{(i) NaNH}_2} CH_3CH_2 \text{—} C \equiv C \text{—} CH_2CH_3$
$ X$

$\xrightarrow[\text{H}_2]{\text{Pd/BaSO}_4}$

$$\underset{C_2H_5}{\overset{H}{\diagdown}} C = C \underset{\underset{Y}{\diagup}\diagdown C_2H_5}{\overset{H}{\diagup}}$$

$Y \xrightarrow{\text{Alkaline KMnO}_4}$

$$\begin{array}{c} C_2H_5 \\ H\text{———}OH \\ H\text{———}OH \\ C_2H_5 \\ \text{(meso diol)} \end{array}$$

Sol 10: (A) $CH_3 = C \text{–} \overset{\overset{\displaystyle CH_3}{|}}{CH} = CH_2 \xrightarrow[\text{Zn-H}_2\text{O}]{O_3} 2HCHO$

(B)

$$\underset{\wwww H_2C}{\overset{H_3C}{\diagdown}} C = C \underset{\diagup\diagdown CH_2}{\overset{H}{\diagup}} \text{—} H_2C \underset{}{\overset{H_3C}{\diagdown}} C = C \underset{\diagup\diagdown CH_2 \wwww}{\overset{H}{\diagup}}$$
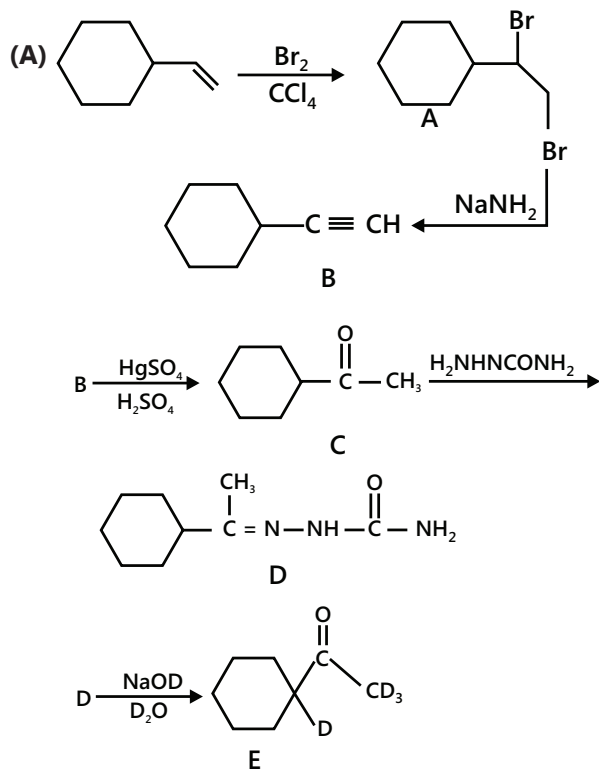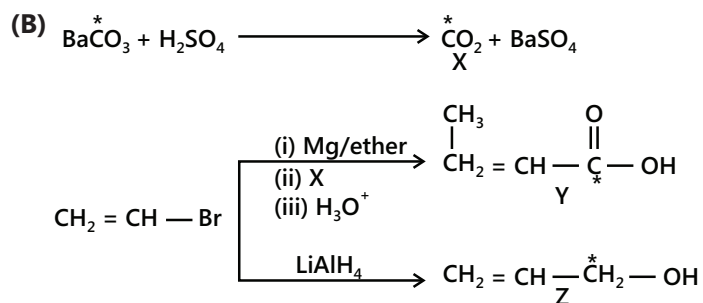
Sol 11: (B) With increase in branching boiling point decreases.

Sol 12: (B,C,D)

(B) ⬡ + ⟩—Cl $\xrightarrow{\text{AlCl}_3}$ ⬡

(C) ⬡ + =⟨ $\xrightarrow{\text{A}_2\text{SO}_4}$ ⬡

(D) ⬡ + ⟩—OH $\xrightarrow{\text{BF}_3.\text{OEt}_2}$ ⬡