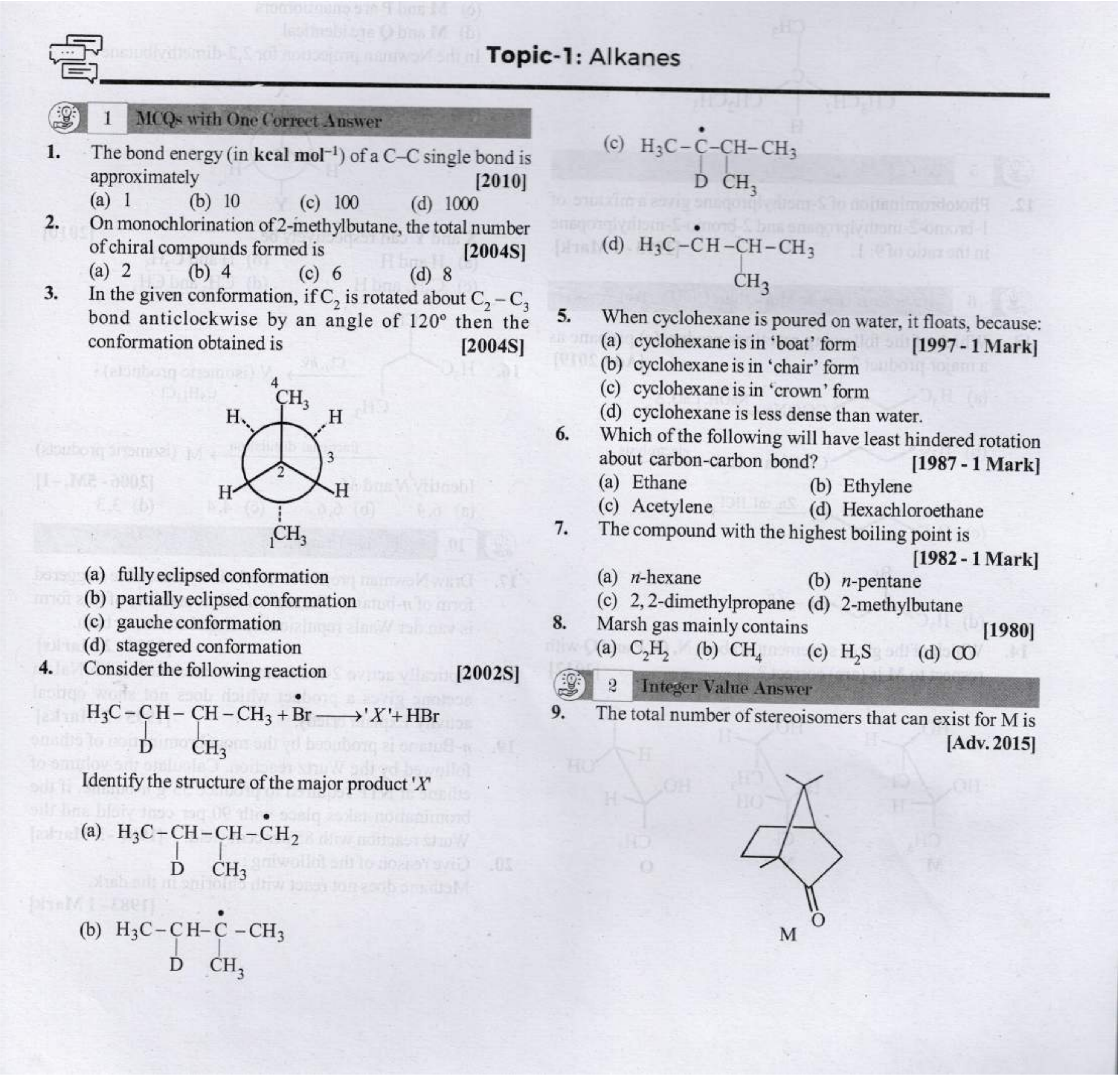
Chapter
Hydrocarbons



Topic-1: Alkanes

1 MCQs with One Correct Answer

1. The bond energy (in **kcal mol^{-1}**) of a C–C single bond is approximately **[2010]**
   (a) 1 (b) 10 (c) 100 (d) 1000
2. On monochlorination of 2-methylbutane, the total number of chiral compounds formed is **[2004S]**
   (a) 2 (b) 4 (c) 6 (d) 8
3. In the given conformation, if C_2 is rotated about C_2-C_3 bond anticlockwise by an angle of 120° then the conformation obtained is **[2004S]**

   (a) fully eclipsed conformation
   (b) partially eclipsed conformation
   (c) gauche conformation
   (d) staggered conformation
4. Consider the following reaction **[2002S]**

$$H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-CH_3+\dot{Br}\longrightarrow 'X'+HBr$$

   Identify the structure of the major product '*X*'

   (a) $H_3C-\underset{D}{CH}-\underset{CH_3}{CH}-\dot{C}H_2$

   (b) $H_3C-\underset{D}{CH}-\underset{CH_3}{\dot{C}}-CH_3$

   (c) $H_3C-\underset{D}{\dot{C}}-\underset{CH_3}{CH}-CH_3$

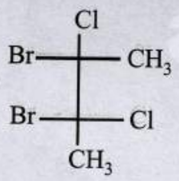
   (d) $H_3C-\dot{C}H-\underset{CH_3}{CH}-CH_3$

5. When cyclohexane is poured on water, it floats, because: **[1997 - 1 Mark]**
   (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.
6. Which of the following will have least hindered rotation about carbon-carbon bond? **[1987 - 1 Mark]**
   (a) Ethane (b) Ethylene
   (c) Acetylene (d) Hexachloroethane
7. The compound with the highest boiling point is **[1982 - 1 Mark]**
   (a) *n*-hexane (b) *n*-pentane
   (c) 2, 2-dimethylpropane (d) 2-methylbutane
8. Marsh gas mainly contains **[1980]**
   (a) C_2H_2 (b) CH_4 (c) H_2S (d) CO

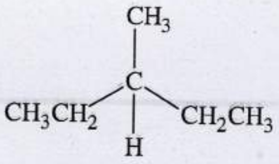
2 Integer Value Answer

9. The total number of stereoisomers that can exist for M is **[Adv. 2015]**

10. The total number(s) of **stable** conformers with **non-zero** dipole moment for the following compound is (are) **[Adv. 2014]**



11. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is **[2011]**

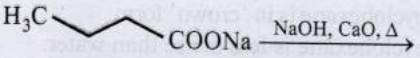


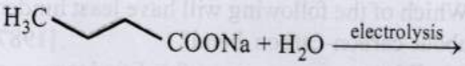
5 True / False

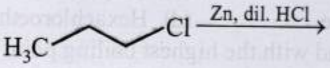
12. Photobromination of 2-methylpropane gives a mixture of 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio of 9: 1. **[1993 - 1 Mark]**

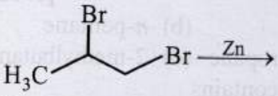
6 MCQs with One or More than One Correct Answer

13. Which of the following reactions produce(s) propane as a major product ? **[Adv. 2019]**

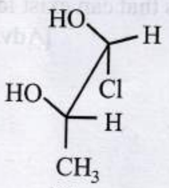
(a) 

(b) 

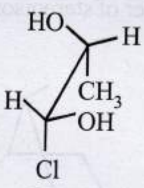
(c) 

(d) 

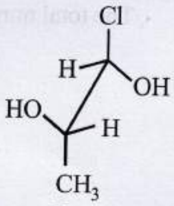
14. Which of the given statement(s) about **N, O, P** and **Q** with respect to **M** is (are) correct ? **[2012]**



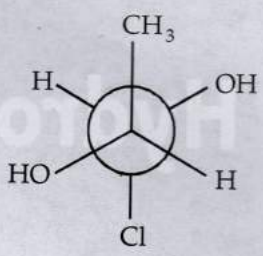
M



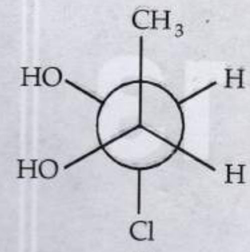
N



O



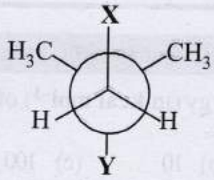
P



Q

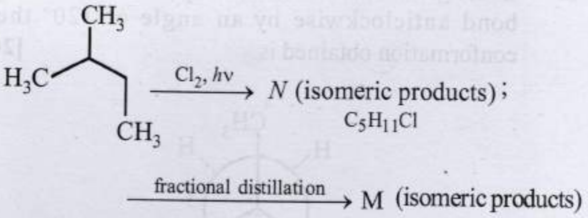
(a) **M** and **N** are non-mirror image stereoisomers
(b) **M** and **O** are identical
(c) **M** and **P** are enantiomers
(d) **M** and **Q** are identical

15. In the Newman projection for 2,2-dimethylbutane



X and **Y** can respectively be **[2010]**

(a) H and H
(b) H and C_2H_5
(c) C_2H_5 and H
(d) CH_3 and CH_3

16. 

Identify *N* and *M* **[2006 - 5M, –1]**

(a) 6, 4 (b) 6, 6 (c) 4, 4 (d) 3, 3

10 Subjective Problems

17. Draw Newman projection of relatively less stable staggered form of *n*-butane. The reason of low stability of this form is van der Waals repulsion, torsional strain, or both. **[2004 - 2 Marks]**

18. Optically active 2-iodobutane on treatment with NaI in acetone gives a product which does not show optical activity. Explain briefly. **[1995 - 2 Marks]**

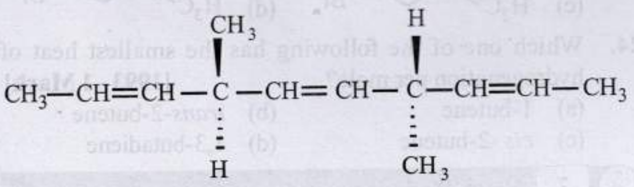
19. *n*-Butane is produced by the monobromination of ethane followed by the Wurtz reaction. Calculate the volume of ethane at NTP required to produce 55 g *n*-butane, if the bromination takes place with 90 per cent yield and the Wurtz reaction with 85 per cent yield. **[1989 - 3 Marks]**

20. Give reason of the following :
Methane does not react with chlorine in the dark. **[1983 - 1 Mark]**

Topic-2: Alkenes

1 MCQs with One Correct Answer

1. The number of optically active products obtained from the **complete** ozonolysis of the given compound is: **[2012]**



$$CH_3-CH=CH-\overset{CH_3}{\underset{H}{C}}-CH=CH-\overset{H}{\underset{CH_3}{C}}-CH=CH-CH_3$$

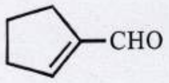
(a) 0 (b) 1 (c) 2 (d) 4

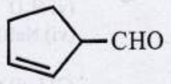
2. In allene (C_3H_4), the type(s) of hybridisation of the carbon atoms is (are) : **[2012]**

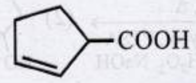
(a) sp and sp^3 (b) sp and sp^2

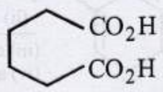
(c) only sp^3 (d) sp^2 and sp^3

3. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound **E**. Compound **E** on further treatment with aqueous KOH yields compound **F**. Compound F is **[2007]**

(a) 

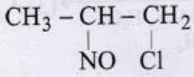
(b) 

(c) 

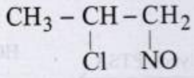
(d) 

4. Identify the product, *P* in the following reaction : **[2006 - 3M, –1]**

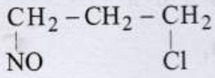
$CH_3-CH=CH_2+NOCl \longrightarrow P$

(a) 

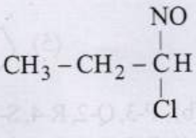
$CH_3-\underset{NO}{CH}-\underset{Cl}{CH_2}$

(b) 

$CH_3-\underset{Cl}{CH}-\underset{NO}{CH_2}$

(c) 

$\underset{NO}{CH_2}-CH_2-\underset{Cl}{CH_2}$

(d) 

$CH_3-CH_2-\overset{NO}{\underset{Cl}{CH}}$

5. The nodal plane in the π-bond of ethene is located in **[2002S]**

(a) the molecular plane

(b) a plane parallel to the molecular plane

(c) a plane perpendicular to the molecular plane which bisects the carbon - carbon σ -bond at right angle

(d) a plane perpendicular to the molecular plane which contains the carbon - carbon σ -bond.

6. The reaction of propene with HOCl proceeds via the addition of **[2001S]**

(a) H^+ in the first step

(b) Cl^+ in the first step

(c) OH^- in the first step

(d) Cl^+ and OH^- in a single step

7. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give *anti*-Markovnikov addition to alkenes because **[2001S]**

(a) both are highly ionic

(b) one is oxidizing and the other is reducing

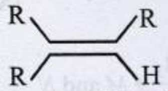
(c) one of the steps is endothermic in both the cases

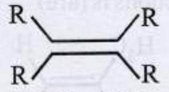
(d) all the steps are exothermic in both the cases

8. Which one of the following will react fastest with H_2 under catalytic hydrogenation condition ? **[2000S]**

(a) 

(b) 

(c) 

(d) 

9. Which of the following compounds will exhibit geometrical isomerism ? **[2000S]**

(a) 1-Phenyl-2-butene (b) 3-Phenyl-1-butene

(c) 2-Phenyl-1-butene (d) 1,1-Diphenyl-1-propene

10. *anti*-Markovnikoff addition of HBr is not observed in :

(a) propene (b) 1-butene **[1985 - 1 Mark]**

(c) but-2-ene (d) pent-2-ene

11. Baeyer's reagent is : **[1984 - 1 Mark]**

(a) alkaline permanganate solution

(b) acidified permanganate solution

(c) neutral permanganate solution

(d) aqueous bromine solution

12. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism? **[1983]**

(a) 2-butene (b) 2-butyne

(c) 2-butanol (d) butanal

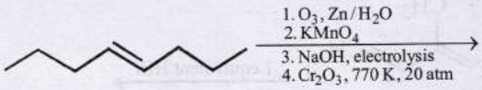
13. Which of the following decolourises alkaline $KMnO_4$ solution **[1980]**

(a) C_3H_8 (b) C_2H_4

(c) CH_4 (d) CCl_4

2 Integer Value Answer

14. The number of -CH_2- (methylene) groups in the product formed from the following reaction sequence is _______.



[Adv. 2022]

15. The total number of chiral molecules formed from one molecule of **P** on complete ozonolysis (O_3, Zn/H_2O) is ______. **[Adv. 2022]**

16. The maximum number of possible isomers (including stereoisomers) which may be formed on *mono*-bromination of 1-methylcyclohex-1-ene using Br_2 and UV light is ______. **[Adv. 2021]**

17. The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} is **[2009]**

4 Fill in the Blanks

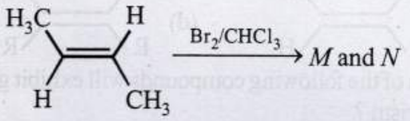
18. 1, 3-Butadiene with bromine in molar ratio of 1 : 1 generates predominantly .... **[1997 - 1 Mark]**

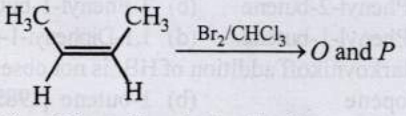
19. Addition of water to acetylenic compounds is catalyzed by.........and.......... **[1993 - 1 Mark]**

20. Kolbe electrolysis of potassium succinate gives CO_2 and .... **[1993 - 1 Mark]**

6 MCQs with One or More than One Correct Answer

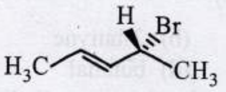
21. The correct statement(s) for the following addition reactions is (are) **[Adv. 2017]**

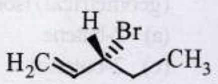
(i) 

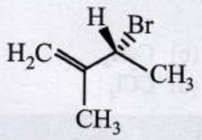
(ii) 

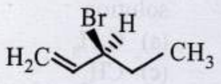
(a) *O* and *P* are identical molecules
(b) (*M* and *O*) and (*N* and *P*) are two pairs of diastereomers
(c) (*M* and *O*) and (*N* and *P*) are two pairs of enantiomers
(d) Bromination proceeds through *trans*-addition in both the reactions

22. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is (are) **[Adv. 2015]**

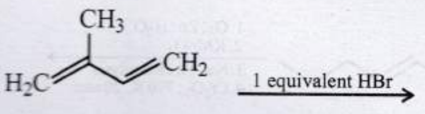
(a) 

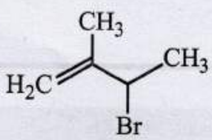
(b) 

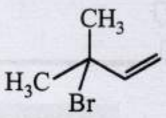
(c) 

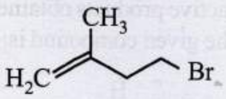
(d) 

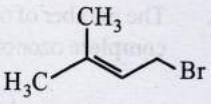
23. In the following reaction, the major product is **[Adv. 2015]**



(a) 

(b) 

(c) 

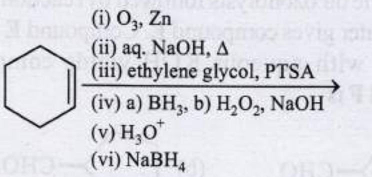
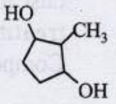
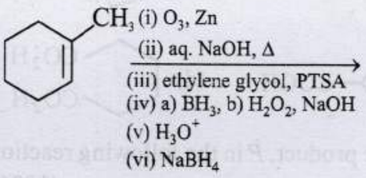
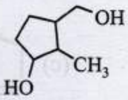
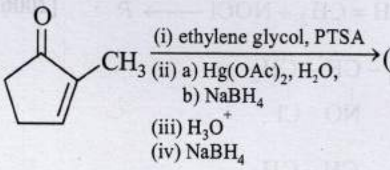
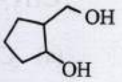
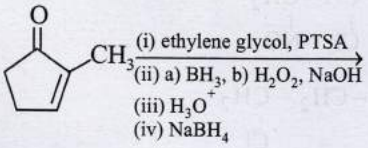
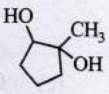
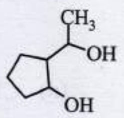
(d) 

24. Which one of the following has the smallest heat of hydrogenation per mole? **[1993 - 1 Mark]**

(a) 1-butene (b) *trans*-2-butene
(c) *cis*-2-butene (d) 1,3-butadiene

7 Match the Following

25. **List-I** contains various reaction sequences and **List-II** contains the possible products.
Match each entry in **List-I** with the appropriate entry in **List-II** and choose the correct option. **[Adv. 2024]**

List-I	List-II
(P)  (i) O_3, Zn (ii) aq. NaOH, Δ (iii) ethylene glycol, PTSA (iv) a) BH_3, b) H_2O_2, NaOH (v) H_3O^+ (vi) $NaBH_4$	(1) 
(Q)  CH_3 (i) O_3, Zn (ii) aq. NaOH, Δ (iii) ethylene glycol, PTSA (iv) a) BH_3, b) H_2O_2, NaOH (v) H_3O^+ (vi) $NaBH_4$	(2) 
(R)  (i) ethylene glycol, PTSA (ii) a) $Hg(OAc)_2$, H_2O, b) $NaBH_4$ (iii) H_3O^+ (iv) $NaBH_4$	(3) 
(S)  (i) ethylene glycol, PTSA (ii) a) BH_3, b) H_2O_2, NaOH (iii) H_3O^+ (iv) $NaBH_4$	(4) 
	(5) 

(a) P-3, Q-5, R-4, S-1 (b) P-3, Q-2, R-4, S-1
(c) P-3, Q-5, R-1, S-4 (d) P-5, Q-2, R-4, S-1

9 Assertion and Reason Statement Type Questions

STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (a), (b), (c) and (d) out of which ONLY ONE is correct. Mark your answer as

(a) If both Statement-1 and Statement-2 are correct, and Statement-2 is the correct explanation of the Statement-2.
(b) If both Statement-1 and Statement-2 are correct, but Statement-2 is not the correct explanation of the Statement-1.
(c) If Statement-1 is correct but Statement-2 is incorrect.
(d) If Statement-1 is incorrect but Statement-2 is correct.

26. **Assertion :** Addition of bromine to *trans*–2–butene yields *meso*–2,3–dibromobutane.
Reason : Bromine addition to an alkene is an electrophilic addition. **[2001S]**

27. **Assertion :** 1-Butene on reaction with HBr in the presence of a peroxide produces 1-bromobutane.
Reason : It involves the formation of a primary radical. **[2000S]**

28. **Assertion :** Addition of Br_2 to 1-butene gives two optical isomers.
Reason : The product contains one asymmetric carbon. **[1998 - 2 Marks]**

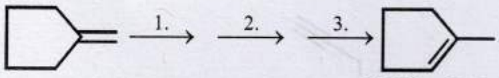
10 Subjective Problems

29. An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compund (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 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 - 5 Marks]**

30. Complete the following reactions with appropriate structures of products/reagents.

(*i*) $C_6H_5CH=CH_2 \xrightarrow{Br_2} [A] \xrightarrow[\text{(ii) } CH_3I]{\text{(i) } NaNH_2 \text{ (3.0 equiv.)}} [B]$

[1998 - 2 + 2 Marks]

(*ii*) 

[1999 - 3 Marks]

31. The hydrocarbon *A*, adds one mole of hydrogen in the presence of a platinum catalyst to form *n*-hexane. When *A* is oxidized vigorously with $KMnO_4$, a single carboxylic acid, containing three carbon atoms, is isolated. Give the structure of *A* and explain. **[1997 - 2 Marks]**

32. Give the structures of the major organic products from 3-ethyl-2-pentene under each of the following reaction conditions. **[1996 - 3 Marks]**
(a) HBr in the presence of peroxide
(b) Br_2/H_2O
(c) $Hg(OAc)_2/H_2O$; $NaBH_4$

33. An organic compound $E(C_5H_8)$ on hydrogenation gives compound $F(C_5H_{12})$. Compound E on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce the structure of compound E. **[1995 - 2 Marks]**

34. 1, 4–Pentadiene reacts with excess of HCl in the presence of benzoyl peroxide to give compound *X* which upon reaction with excess of Mg in dry ether forms *Y*. Compound *Y* on treatment with ethyl acetate followed by dilute acid yields *Z*. Identify the structures of compounds *X*, *Y* and *Z*. **[1995 - 4 Marks]**

35. 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 - 3 Marks]**

36. Identify, $D(C_6H_{12})$, an optically active hydrocarbon which on catalytic hydrogenation gives an optically inactive compound, C_6H_{14}. **[1993 - 1 Mark]**

37. Identify, $B(C_4H_8)$ which adds on HBr in the presence and in the absence of peroxide to give the same product, C_4H_9Br. **[1993 - 1 Mark]**

38. How would you distinguish between cyclohexane and cyclohexene. **[1988 - 1 Mark]**

39. 2-Methylpropene can be converted into isobutyl bromide by hydrogen bromide, is true under what conditions? **[1984 - 1 Mark]**

40. Give reasons for the following :
(i) Propene reacts with HBr to give isopropyl bromide but does not give *n*-propyl bromide. **[1983 - 1 Mark]**
(ii) The central carbon-carbon bond in 1, 3 – butadiene is shorter than that in *n*-butane. **[1998 - 2 Marks]**

41. State with balanced equations, what happens when propene is bubbled through a hot aqueous solution of potassium permanganate. **[1982 - 1 Mark]**

42. Write the structural formula of the major product in the following case : **[1997 - 1 Mark]**


$+ CHBr_3 + t-BuOK \longrightarrow$ - - - -

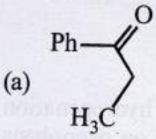
Topic-3: Alkynes

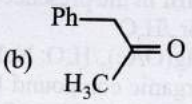
1 MCQs with One Correct Answer

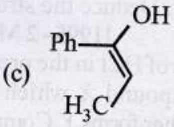
1. The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are **[2010]**
(a) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$
(b) $BrCH_2CH_2CH_3$ and $CH_3CH_2CH_2C\equiv CH$
(c) $BrCH_2CH_2CH_2CH_2CH_3$ and $CH_3C\equiv CH$
(d) $BrCH_2CH_2CH_2CH_3$ and $CH_3CH_2C\equiv CH$

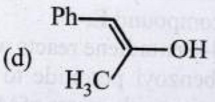
2. Which of the following is used for the conversion of 2-hexyne into *trans*-2-hexene ? **[2004S]**
(a) $H_2/Pd/BaSO_4$
(b) H_2, PtO_2
(c) $NaBH_4$
(d) $Li-NH_3/C_2H_5OH$

3. $Ph-C\equiv C-CH_3 \xrightarrow{Hg^{2+}/H^+} A$. A is: **[2003S]**

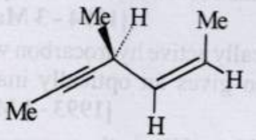
(a)


(b)


(c)


(d)


4. Identify the reagent from the following list which can easily distinguish between 1-butyne and 2-butyne **[2002S]**
   (a) bromine, CCl_4
   (b) H_2, Lindlar catalyst
   (c) dilute H_2SO_4, $HgSO_4$
   (d) ammonical Cu_2Cl_2 solution

5.


Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives **[2001S]**
   (a) an optically active compound
   (b) an optically inactive compound
   (c) a racemic mixture
   (d) a diastereomeric mixture

6. Propyne and propene can be distinguished by **[2000S]**
   (a) conc. H_2SO_4
   (b) Br_2 in CCl_4
   (c) dil. $KMnO_4$
   (d) $AgNO_3$ in ammonia

7. The product(s) obtained via oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be **[1999 - 2 Marks]**
   (a) $CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$
   (b) $CH_3-CH_2-CH_2-CHO$
   (c) $CH_3-CH_2-CHO+HCHO$
   (d) $CH_3CH_2COOH+HCOOH$

8. Acidic hydrogen is present in : **[1985 - 1 Mark]**
   (a) ethyne (b) ethene
   (c) benzene (d) ethane

9. When propyne is treated with aqueous H_2SO_4 in presence of $HgSO_4$ the major product is **[1983 - 1 Mark]**
   (a) propanal
   (b) propyl hydrogensulphate
   (c) acetone
   (d) propanol

4 Fill in the Blanks

10. The starting material for the manufacture of polyvinyl chloride is obtained by reacting HCl with .... **[1983 - 1 Mark]**

11. Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is .... **[1983 - 1 Mark]**

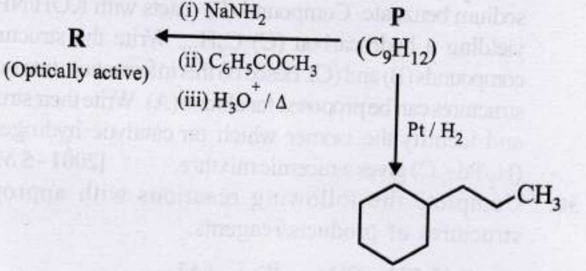
12. .... is most acidic.
(Ethane, Ethene, Ethyne) **[1981 - 1 Mark]**

5 True / False

13. Moist ethylene can be dried by passing it through concentrated sulphuric acid. **[1982 - 1 Mark]**

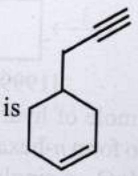
6 MCQs with One or More than One Correct Answer

14. Consider the following transformations of a compound P. **[Adv. 2020]**

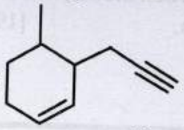


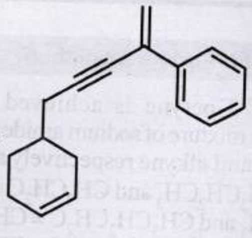
$$P \xrightarrow[\text{(ii) } KMnO_4 / H_2SO_4 / \Delta]{\text{(i) X (reagent)}} \underset{\text{(Optically active acid)}}{\underset{(C_8H_{12}O_6)}{Q}}$$

Choose the correct option(s).

(a) P is


(b) X is Pd-C/quinoline/H_2

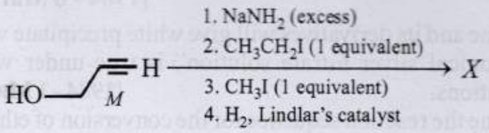
(c) P is


(d) R is


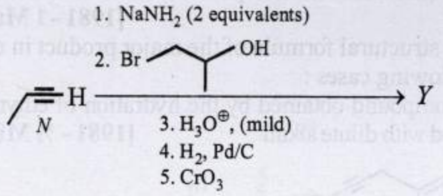
8 Comprehension Passage Based Questions

Passage-I

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



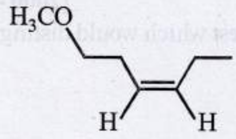
Scheme-1



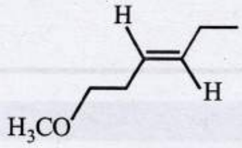
Scheme-2

15. The product *X* is **[Adv. 2014]**

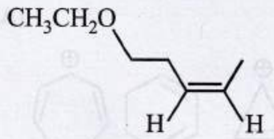
(a)



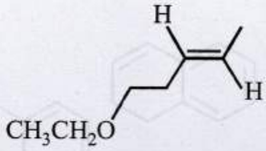
(b)



(c)



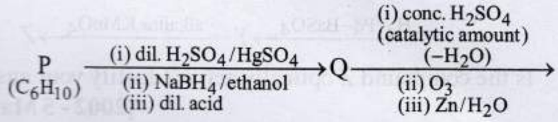
(d)

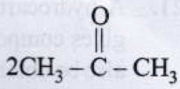


16. The correct statement with respect to product *Y* is **[Adv. 2014]**
   (a) It gives a positive Tollen's test and is a functional isomer of *X*
   (b) It gives a positive Tollen's test and is a geometrical isomer of *X*
   (c) It gives a positive iodoform test and is a functional isomer of *X*
   (d) It gives a positive iodoform test and is a geometrical isomer of *X*

Passage-II

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.

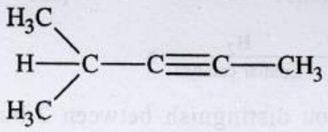




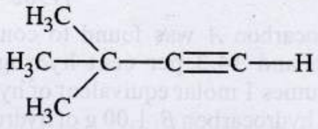
$$2CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

[2011 - I]

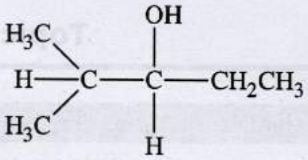
17. The structure of compound **P** is
   (a) $CH_3CH_2CH_2CH_2C\equiv CH$
   (b) $CH_3CH_2C\equiv CCH_2CH_3$
   (c)



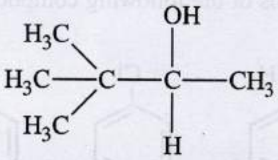
   (d)



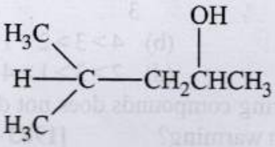
18. The structure of the compound **Q** is
   (a)



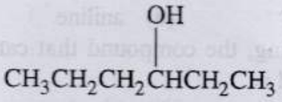
   (b)



   (c)



   (d)



$$CH_3CH_2CH_2\overset{OH}{\overset{|}{C}}HCH_2CH_3$$

10 Subjective Problems

19. Write down the heterogeneous catalyst involved in the polymerisation of ethylene. **[2003 - 2 Marks]**

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

$$CH_3CH_2C\equiv C-H \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2} X$$

$$\xrightarrow{H_2/Pd-BaSO_4} Y \xrightarrow{\text{alkaline } KMnO_4} Z$$

Is the compound Z optically active? Justify your answer. **[2002 - 5 Marks]**

21. A hydrocarbon A, of the formula C_8H_{10}, on ozonolysis gives compound $B(C_4H_6O_2)$ only. The compound B can also be obtained from the alkyl bromide, $C(C_3H_5Br)$ upon treatment with magnesium in dry ether, followed by carbon dioxide and acidification. Identify A, B and C and also give equations for the reactions. **[1996 - 3 Marks]**

22. Draw the stereochemical structures of the products in the following reactions : **[1994 - 4 Marks]**

$$R-C\equiv C-R \xrightarrow[\text{Lindlar catalyst}]{H_2}$$

23. How would you distinguish between 2-butyne and 1-butyne. **[1985 - 1 Mark]**

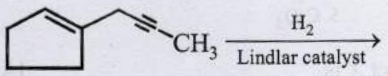
24. A certain hydrocarbon A was found to contain 85.7 percent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.00 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by weight) of Br_2 in CCl_4. Compound A, on oxidation with concentrated $KMnO_4$, gave compound C (molecular formula C_4H_8O) and acetic acid. Compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2- butyne. Determine the molecular formula of A and deduce the structure of A, B and C. **[1984 - 6 Marks]**

25. 'Ethyne and its derivatives will give white precipitate with ammonical silver nitrate solution', is true under what conditions. **[1984 - 1 Mark]**

26. Outline the reaction sequence for the conversion of ethene to ethyne (the number of steps should not be more than two). **[1981 - 1 Mark]**

27. Write the structural formula of the major product in each of the following cases :

(*i*) the compound obtained by the hydration of ethyne is treated with dilute alkali **[1981 - ½ Mark]**

(*ii*) 

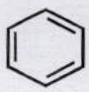
[2000 - 1 Mark]

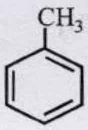
28. Give one characteristic test which would distinguish. CH_4 from C_2H_2 **[1979]**

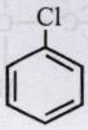
Topic-4: Aromatic Hydrocarbons

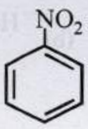
1 MCQs with One Correct Answer

1. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds **[2002S]**


1


2


3


4

(a) 1>2>3>4 (b) 4>3>2>1
(c) 2>1>3>4 (d) 2>3>1>4

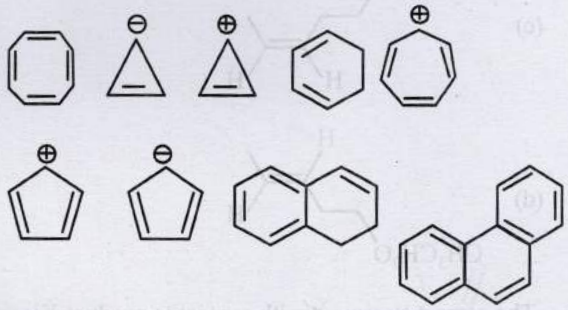
2. Which of the following compounds does not dissolve in conc. H_2SO_4 even on warming? **[1983 - 1 Mark]**
(a) ethylene (b) benzene
(c) hexane (d) aniline

3. Among the following, the compound that can be most readily sulphonated is **[1982]**
(a) benzene (b) nitrobenzene
(c) toluene (d) chlorobenzene

4. The bond order of individual carbon-carbon bonds in benzene is **[1981]**
(a) one (b) two
(c) between one and two (d) one and two, alternately

2 Integer Value Answer

5. Among the following, the number of aromatic compound(s) is **[Adv. 2017]**



4 Fill in the Blanks

6. The bond dissociation energy needed to form the benzyl radical from toluene is........than the formation of the methyl radical from methane. **[1994 - 1 Mark]**

7. Kolbe electrolysis of potassium succinate gives CO_2 and .... **[1993 - 1 Mark]**

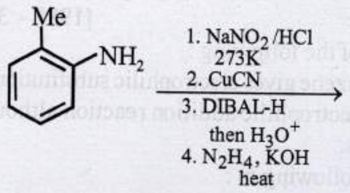
8. .... ring is most strained. **[1981]**
(Cyclopropane, Cyclobutane, Cyclopentane)

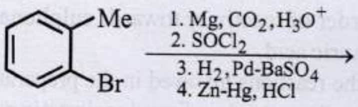
5 True / False

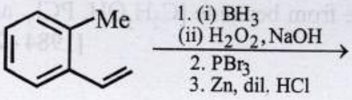
9. An electron donating substituent in benzene orients the incoming electrophilic group to the meta position. [1987]

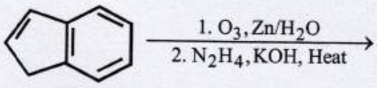
6 MCQs with One or More than One Correct Answer

10. The reaction sequence(s) that would lead to *o*-xylene as the major product is (are) [Adv. 2021]

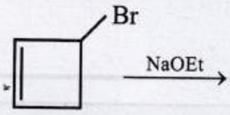
(a) 

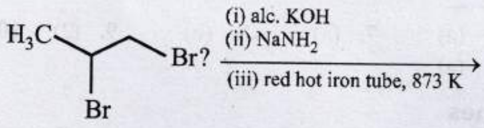
(b) 

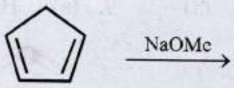
(c) 

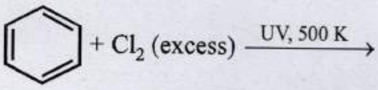
(d) 

11. Choose the correct option(s) that give(s) an aromatic compound as the major product. [Adv. 2019]

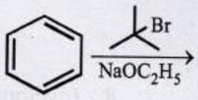
(a) 

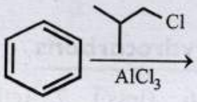
(b) 

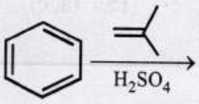
(c) 

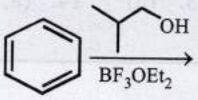
(d) 

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

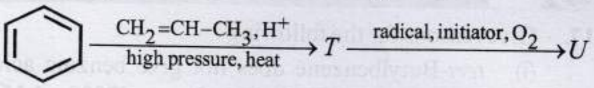
(a) 

(b) 

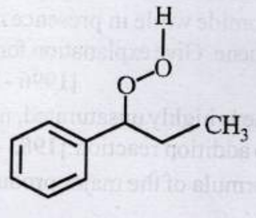
(c) 

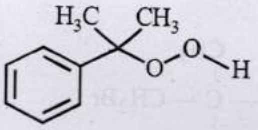
(d) 

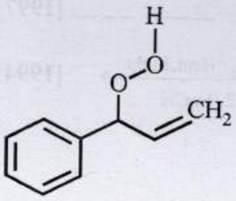
13. The major product *U* in the following reactions is

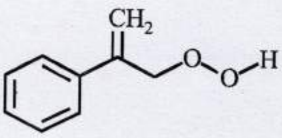


[Adv. 2015]

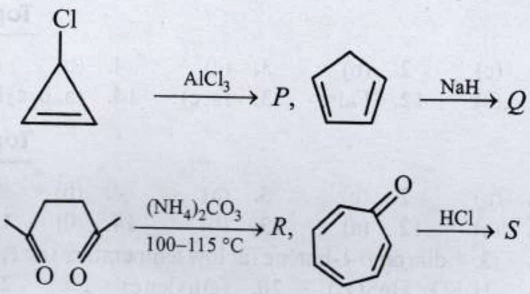
(a) 

(b) 

(c) 

(d) 

14. Among *P*, *Q*, *R* and *S*, the aromatic compound(s) is/are [Adv. 2013-I]



(a) *P* (b) *R* (c) *Q* (d) *S*

15. Toluene, when treated with Br_2/Fe, gives *p*-bromotoluene as the major product because CH_3 group

(a) is para directing [1999 - 3 Marks]

(b) is meta directing

(c) activates the ring by hyperconjugation

(d) deactivates the ring

16. An aromatic molecule will [1999]

(a) have $4n$ π electrons (b) have $(4n+2)$ π electrons

(c) be planar (d) be cyclic

10 Subjective Problems

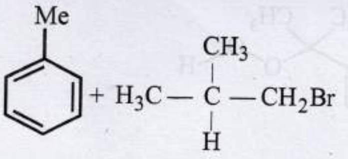
17. Give reasons for the following :

(i) *tert*-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$. **[2000 - 1 Mark]**

(ii) Toluene reacts with bromine in the presence of light to give benzyl bromide while in presence of $FeBr_3$ it gives *p*-bromotoluene. Give explanation for the above observations. **[1996 - 2 Marks]**

(iii) Although benzene is highly unsaturated, normally it does not undergo addition reaction. **[1983 - 1 Mark]**

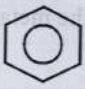
18. Write the structural formula of the major product in each of the following cases :

(i) 

$+ \text{Anhyd. } AlCl_3 \longrightarrow ---$ **[1997 - 1 Mark]**

(ii) $C_6H_5C_2H_5 \xrightarrow[\text{2. NaCN}]{\text{1.}Br_2\text{, Heat, Light}}$ **[1994 - 1 Mark]**

(iii) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$ **[1994 - 1 Mark]**

(iv)  $+ (CH_3)_2CHCH_2Cl \xrightarrow{AlCl_3}$ **[1992 - 1 Mark]**

19. Show the steps to carry out the following transformations.

(i) Ethylbenzene → benzene **[1998 - 2 Marks]**

(ii) Ethylbenzene → 2-phenylpropionic acid. **[1998 - 3 Marks]**

20. Give reason of the following :
Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. **[1994]**

21. Arrange the following in :
benzene, toluene, methoxybenzene, chlorobenzene in increasing order of reactivity towards sulphonation with fuming sulphuric acid. **[1988]**

22. Write down the reactions involved in the preparation of the following, using the reagents indicated against it in parenthesis. Ethylbenzene from benzene [C_2H_5OH, PCl_5, anhydrous $AlCl_3$]. **[1984 - 2 Marks]**

Answer Key

Topic-1 : Alkanes

1. (c) **2.** (b) **3.** (c) **4.** (b) **5.** (d) **6.** (a) **7.** (a) **8.** (b) **9.** (2) **10.** (3)
11. (8) **12.** False **13.** (a, c) **14.** (a, b, c) **15.** (b, d) **16.** (a)

Topic-2 : Alkenes

1. (a) **2.** (b) **3.** (a) **4.** (b) **5.** (a) **6.** (b) **7.** (c) **8.** (a) **9.** (a) **10.** (c)
11. (a) **12.** (a) **13.** (b) **14.** (0) **15.** (2) **16.** (13) **17.** (7)
18. (3, 4-dibromo-1-butene (at low temperature) or 1, 4- dibromo-2-butene (at high temperature))
19. (H_2SO_4, $HgSO_4$) **20.** (ethylene) **21.** (b, d) **22.** (b, d) **23.** (d) **24.** (b) **25.** (a) **26.** (b)
27. (c) **28.** (a)

Topic-3 : Alkynes

1. (d) **2.** (d) **3.** (a) **4.** (d) **5.** (b) **6.** (d) **7.** (a) **8.** (a) **9.** (c) **10.** (C_2H_2)
11. (2-butyne) **12.** (Ethyne) **13.** (False) **14.** (b, c) **15.** (a) **16.** (c) **17.** (d)
18. (b)

Topic-4 : Aromatic Hydrocarbons

1. (c) **2.** (c) **3.** (c) **4.** (c) **5.** (4) **6.** (less) **7.** (ethylene) **8.** (cyclopropane)
9. (False) **10.** (a, b) **11.** (b, c) **12.** (b, c, d) **13.** (b) **14.** (a, b, c, d) **15.** (a, c)
16. (b, c, d)

Hints & Solutions

Topic-1 : Alkanes

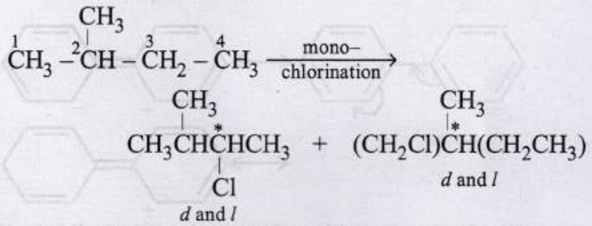
1. (c) $C-C$ bond energy $= 348$ kJ/mol $= \frac{348}{4.2}$ kcal/mol

$= 82.85$ kcal/mol ≈ 100 kcal/mol.

2. (b) (i) Chlorination at C-2 and C-4 produces no chiral compounds

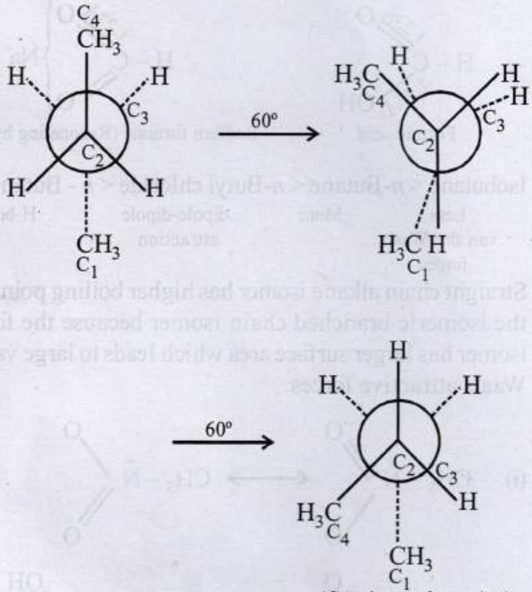
(ii) Chlorination at C-3 produces a chiral carbon marked with star (*d* and *l* form).

(iii) Chlorination at C-1 also produces a chiral carbon marked with star (*d* and *l* form).



$$\overset{1}{C}H_3-\overset{2}{C}H(CH_3)-\overset{3}{C}H_2-\overset{4}{C}H_3 \xrightarrow[\text{chlorination}]{\text{mono–}} \underset{d \text{ and } l}{CH_3CH(CH_3)\overset{*}{C}H(Cl)CH_3} + \underset{d \text{ and } l}{(CH_2Cl)\overset{*}{C}H(CH_3)(CH_2CH_3)}$$

3. (c) Any conformation between two extreme positions i.e. eclipsed and staggered is known as gauche or skew form.



(Gauche conformation)

4. (b) $Br^{\bullet}$ is less reactive and more selective and so the most stable free radical (3°) will be the major product.

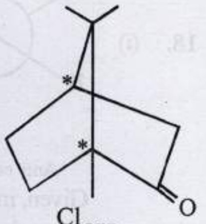
5. (d)

6. (a) Ethylene has restricted rotation [due to $C = C$], acetylene has no rotation [due to $C \equiv C$], hexachloroethane has more rotation than ethylene but less than ethane because of greater size of the substituent (chlorine) than in ethane (substituent is hydrogen).

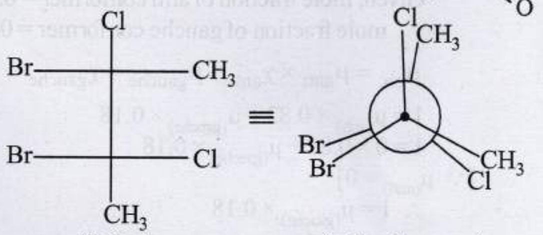
7. (a) In a homologous series, higher the number of C-atoms, higher is the b.p.

8. (b)

9. (2) The molecule cannot show geometrical isomerism, so only its mirror image will be the other stereoisomer.

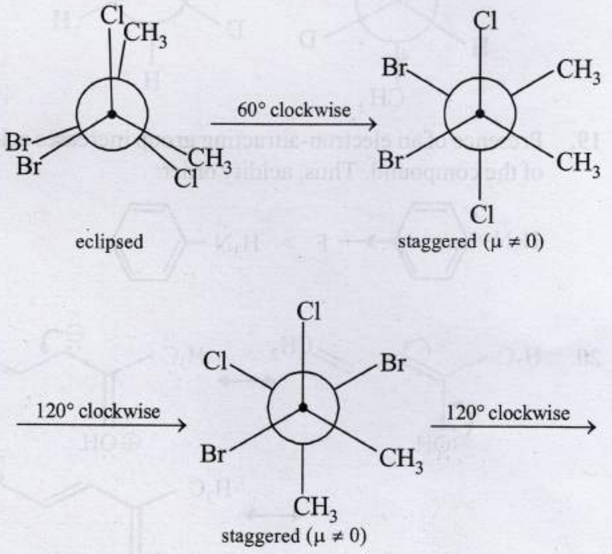


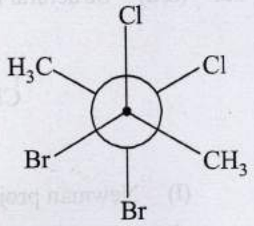
10. (3)



(fischer) (eclipsed newman)

A fischer projection always represents an eclipsed conformation which is least stable. Now, converting this to stable staggered conformation by keeping one carbon atom fixed and other by rotating, we get

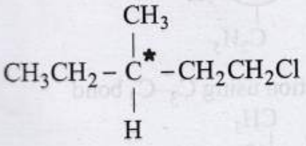




staggered ($\mu \neq 0$)

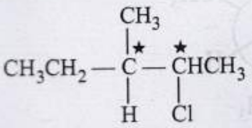
Hence, only 3 different staggered conformers are possible.

11. (8)



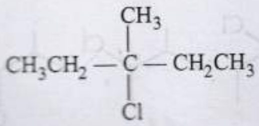
$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C^*}}-CH_2CH_2Cl$$

Enantiomeric pair = 2

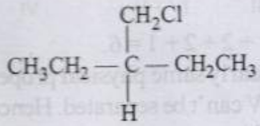


$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C^*}}-\underset{\underset{Cl}{|}}{\overset{*}{C}}HCH_3$$

Two enantiomeric pairs = 4



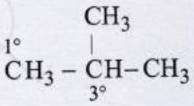
$$CH_3CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_2CH_3 = 1$$



$$CH_3CH_2-\overset{\overset{CH_2Cl}{|}}{\underset{\underset{H}{|}}{C}}-CH_2CH_3 = 1$$

Total = 2 + 4 + 1 + 1 = 8

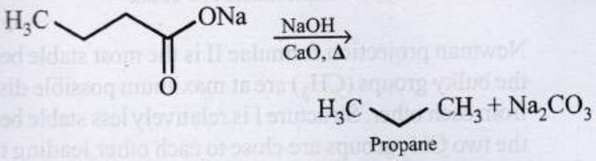
12. **False :** Bromine is less reactive, hence it is more selective and thus 3° hydrogen will be removed more easily than the 1° hydrogen leading to 2-bromo-2-methylpropane as the main product.



$$\overset{1^\circ}{CH_3}-\underset{3^\circ}{\overset{\overset{CH_3}{|}}{CH}}-CH_3$$

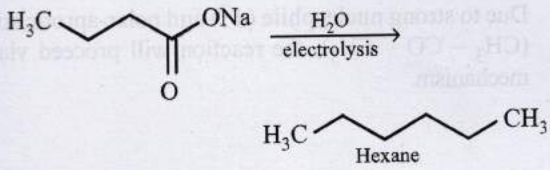
13. (a, c)

(a)



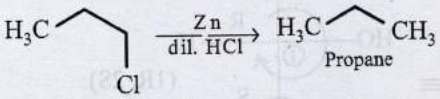
This process of elimination of carbon dioxide from a carboxylic acid is known as decarboxylation.

(b)



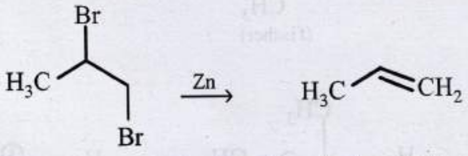
This is Kolbe's electrolytic method.

(c)



Alkyl halides (except fluorides) on reduction with zinc and dilute hydrochloric acid give alkanes.

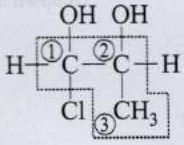
(d)



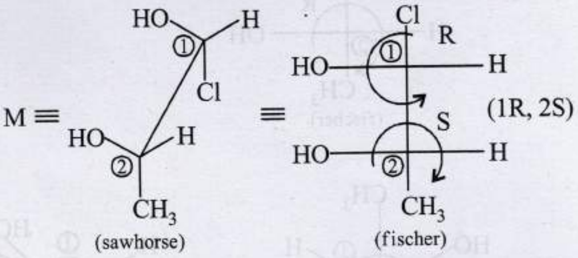
This is a dehalogenation reaction of vicinal dihalide. In this reaction, an alkene is produced on treatment of dihalide with Zn metal by loosing a molecule of ZnX_2.

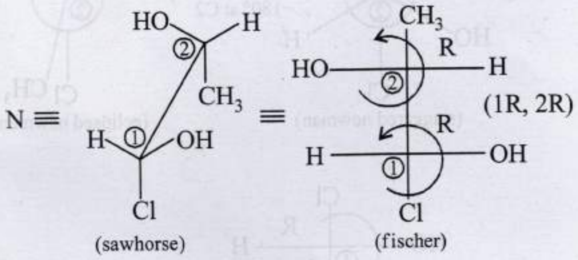
14. (a, b, c)

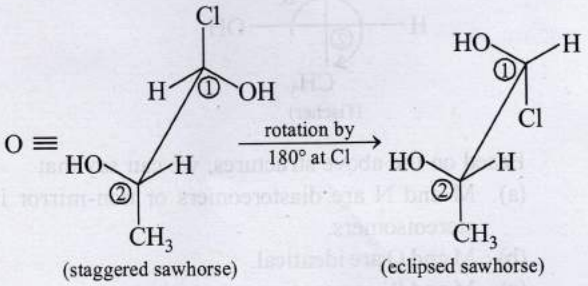
The given conformation are of the following compound



1-Chloro propane-1, 2-diol

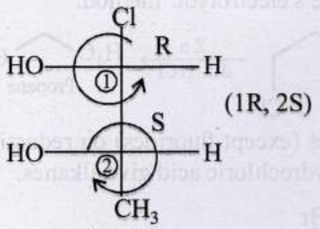






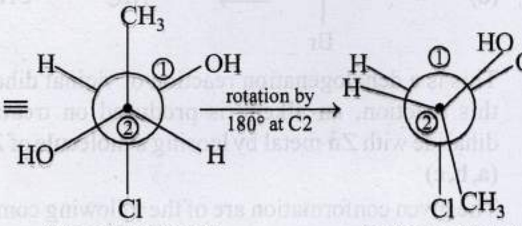
Fisher conformation always show the eclipsed form of molecule. Thus, we have to convert the given staggered conformation of 'O' to an eclipsed conformation.

O ≡



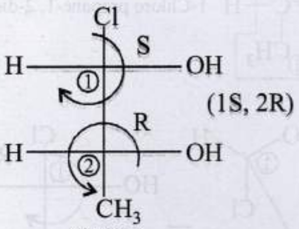
(fischer)

P ≡



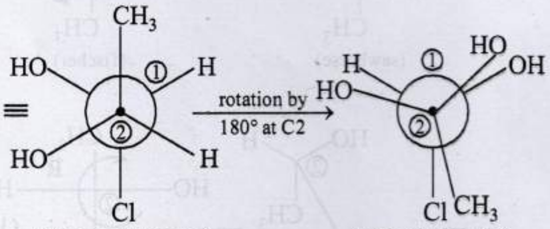
(staggered newman) (eclipsed newman)

P ≡



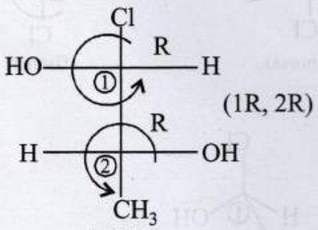
(fischer)

Q ≡



(staggered newman) (eclipsed newman)

Q ≡



(fischer)

Based on the above structures, we can say that

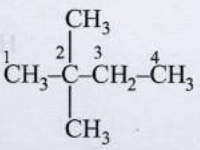
(a) M and N are diastereomers or non-mirror image stereoisomers.

(b) M and O are identical.

(c) M and P are enantiomers.

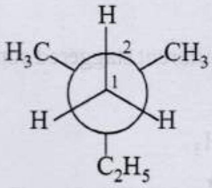
(d) M and Q are diastereomers and therefore not identical.

15. **(b,d)** Structural formula of 2, 2-dimethylbutane is

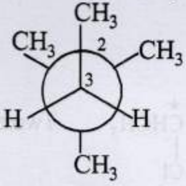


$$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}H_2-\overset{4}{C}H_3$$

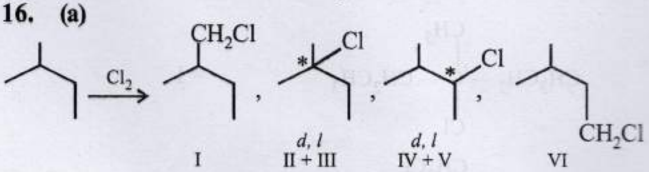
(I) Newman projection using C_1-C_2 bond



(II) Newman projection using C_3-C_2 bond



16. **(a)**

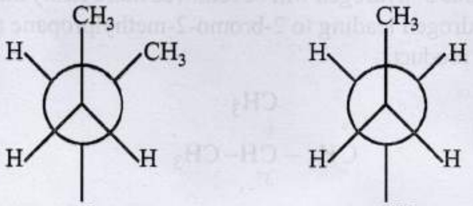


So, the value of N will be $1+2+2+1=6$.

Since, enantiomers have nearly same physical properties, II and III as well as IV and V can't be separated. Hence, the number of isomers (M) will be

$$1+1+1+1=4.$$

17.



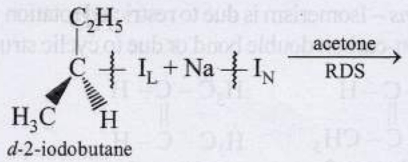
I (Less stable) II (Most stable)

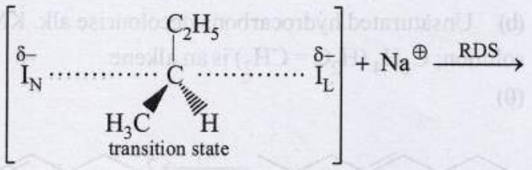
Staggered conformations of n-butane

Newman projection formulae II is the most stable because the bulky groups (CH_3) are at maximum possible distance from each other. Structure I is relatively less stable because the two CH_3 groups are close to each other leading to van der Waal's repulsion between the two methyl groups.

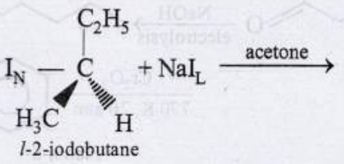
18. In this reaction, the leaving group and attacking nucleophile both are $I^{\ominus}$.

Due to strong nucleophile ($I^{\ominus}$) and polar-aprotic solvent ($CH_3-CO-CH_3$), the reaction will proceed via S_N2 mechanism.





$I_N^\ominus$ is attacking nucleophile and $I_L^\ominus$ is leaving group. Thus, attacking nucleophile can attack only from the near side.



Hence, inversion will take place. If the starting product was *d*-2-iodobutane then the above compound will be *l*-2-iodobutate.

Now, the same process will happen again and again and the final product will be a equimolar mixture of *d*- and *l*-forms *i.e.* a recemic mixture.

Therefore, the final product will not show optical activity.

19. $2C_2H_6 \xrightarrow{\text{monobromination}} 2C_2H_5Br$ (yield 90%) (given)

$2C_2H_5Br \xrightarrow[\text{reaction}]{\text{Wurtz}} C_4H_{10} + 2HBr$ (yield 85%) (given)

Moles of *n*-butane to be produced

$= \frac{55\text{ g}}{58\text{ g mol}^{-1}} = 0.948\text{ mol}$

(∵ molecular mass of $C_4H_{10} = 58$)

Amount of C_2H_5Br (100%) required to obtain 0.948 mol. of $C_4H_{10} = 2 \times 0.948$ mol.

Hence, the amount of C_2H_5Br (85%) required

$= \frac{2 \times 0.948 \times 100}{85}$ mol. ...(1) [∵ yield is 85% only]

Further, 1 mole of C_2H_6 gives one mole of C_2H_5Br, hence number of moles of C_2H_6 reqd. for C_2H_5Br in (1)

$= \frac{2 \times 0.948 \times 100 \times 100}{85 \times 90}$ mol. = 2.48 mol [∵ yield is 90%]

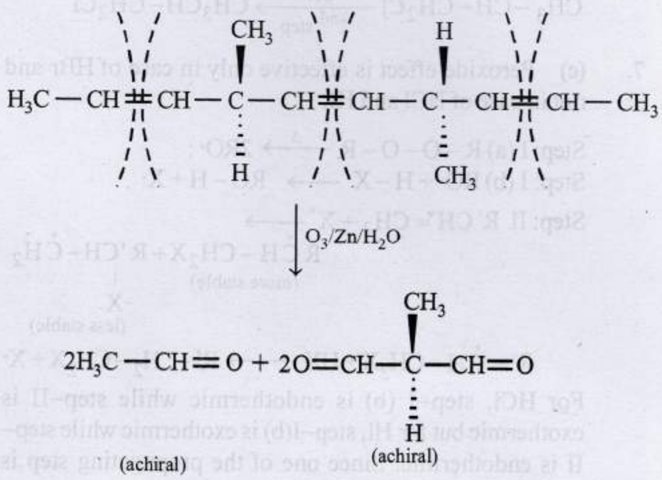
∴ Required volume of ethane at NTP
= 22400 × 2.48 = 55552 mL = **55.55 litres**

20. Chlorination of methane is a free radical substitution reaction.

In dark, chlorine is unable to be converted into free radicals, hence the reaction does not occur.

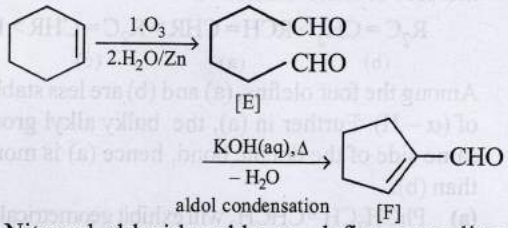
Topic-2 : Alkenes

1. **(a)**

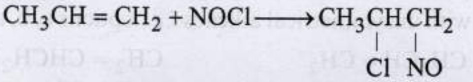


2. **(b)** **Allene (C_3H_4) is** $\overset{sp^2}{H_2C} = \overset{sp}{C} = \overset{sp^2}{CH_2}$

3. **(a)**



4. **(b)** Nitrosyl chloride adds on olefins according to Markovnikov's rule, where NO^+ constitutes the positive part of the addendum.



$CH_3CH = CH_2 + NOCl \longrightarrow CH_3\underset{Cl}{CH}\underset{NO}{CH_2}$

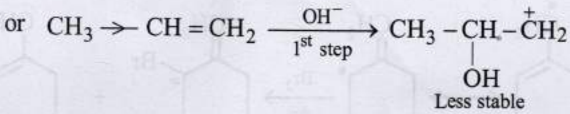
5. **(a)** The π bond is formed by the sideways overlapping of two *p*-orbitals of the two carbon atoms.

The molecular plane does not have any π electron density as the *p*-orbitals are perpendicular to the plane containing the ethene molecule. The nodal plane in the π-bond of ethene is located in the molecular plane.

6. **(b)** Alkenes undergo electrophilic addition reaction. With HOCl.

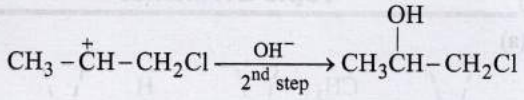
$HOCl \longrightarrow OH^- + Cl^+$

$CH_3 \rightarrow CH = CH_2 \xrightarrow[1^{st}\text{ step}]{Cl^+} CH_3 - \overset{+}{C}H - CH_2Cl$
More stable



or $CH_3 \rightarrow CH = CH_2 \xrightarrow[1^{st}\text{ step}]{OH^-} CH_3 - \underset{OH}{CH} - \overset{+}{C}H_2$
Less stable

So, it is the Cl^+ that attacks in the first step

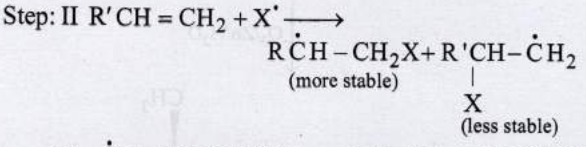


$$CH_3-\overset{+}{C}H-CH_2Cl \xrightarrow[2^{nd}\text{ step}]{OH^-} CH_3\overset{OH}{\overset{|}{C}}H-CH_2Cl$$

7. **(c)** Peroxide effect is effective only in case of HBr and not in case of HCl and HI.

Step: I (a) $R-O-O-R \xrightarrow{\Delta} 2RO\cdot$;

Step: I (b) $RO\cdot + H-X \longrightarrow RO-H + X\cdot$



$$\text{Step: II } R'CH=CH_2+X^{\bullet} \longrightarrow \underset{\text{(more stable)}}{R\dot{C}H-CH_2X} + \underset{\text{(less stable)}}{\underset{X}{\underset{|}{R'CH}}-\dot{C}H_2}$$

$$R'-\dot{C}H-CH_2X+HX \longrightarrow R'-CH_2-CH_2X+X\cdot$$

For HCl, step–I (b) is endothermic while step–II is exothermic but for HI, step–I(b) is exothermic while step–II is endothermic. Since one of the propagating step is endothermic, the reaction does not occur.

8. **(a)** The relative rates of hydrogenation decreases with increase of steric hindrance.

$$\underset{(b)}{R_2C=CH_2} > \underset{(a)}{RCH=CHR} > \underset{(c)}{R_2C=CHR} > \underset{(d)}{R_2C=CR_2}$$

Among the four olefins, (a) and (b) are less stable (less no. of ($\alpha-H$). Further in (a), the bulky alkyl groups are on same side of the double bond, hence (a) is more reactive than (b).

9. **(a)** $PhCH_2CH=CHCH_3$ will exhibit geometrical isomerism because in others one of the doubly bonded carbon atom has two similar groups.

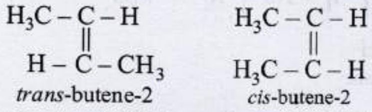
10. **(c)** *anti*-Markovnikoff's addition of HBr is observed only with unsymmetrical alkenes *i.e.*, options a, b, and d.

$\underset{(a)}{CH_3CH=CH_2}$ $\underset{(b)}{CH_2=CHCH_2CH_3}$

$\underset{(c)}{CH_3CH=CHCH_3}$ $\underset{(d)}{CH_3CH=CHCH_2CH_3}$

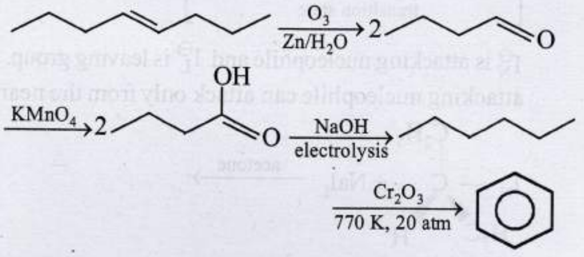
11. **(a)** Cold alkaline $KMnO_4$

12. **(a)** *cis-trans* – Isomerism is due to restricted rotation either due to carbon-carbon double bond or due to cyclic structure.



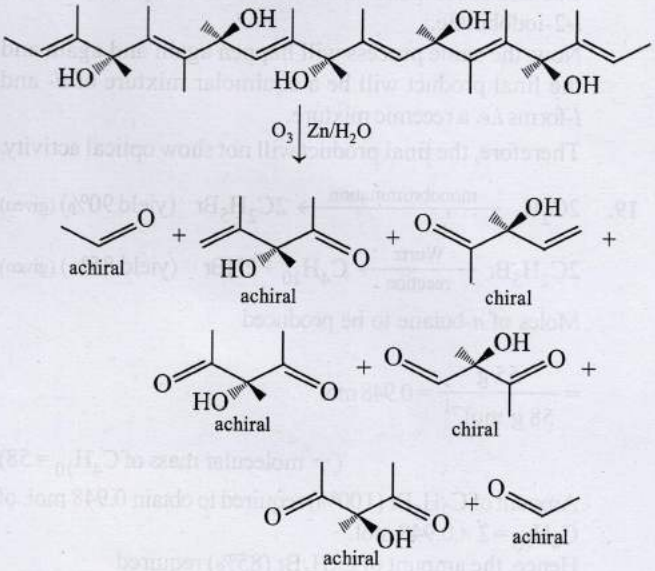
13. **(b)** Unsaturated hydrocarbons decolourise alk. $KMnO_4$ solution; C_2H_4 ($H_2C=CH_2$) is an alkene.

14. **(0)**

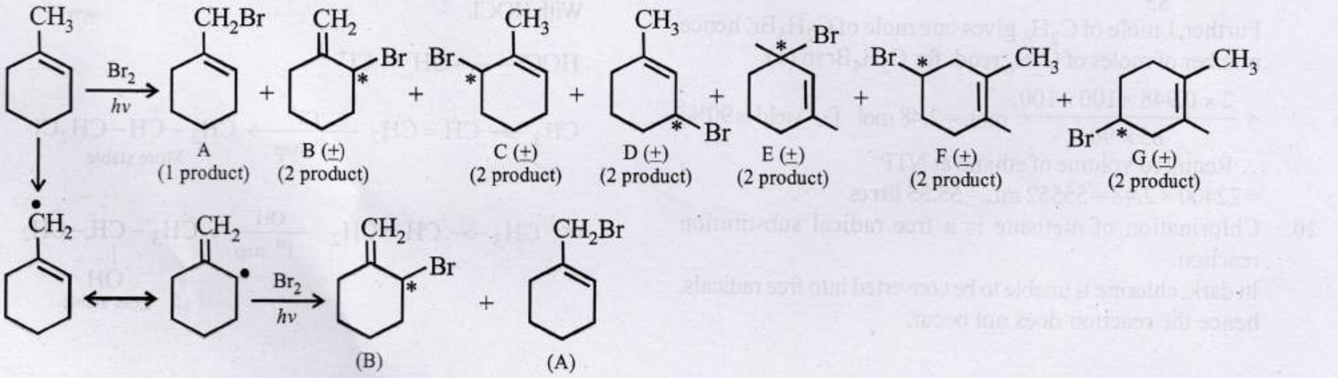


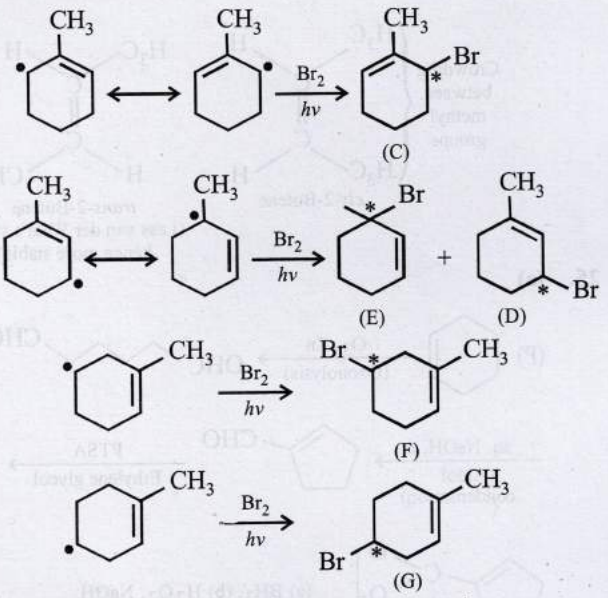
Number of $-CH_2-$ groups in the product = 0.

15. **(2)**



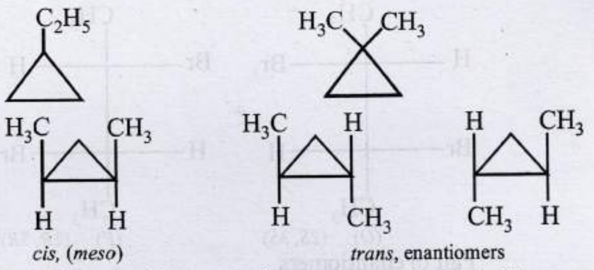
16. **(13)**





So, total 13 possible isomers are formed.

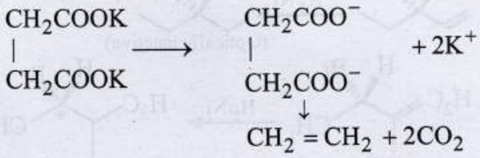
17. (7) The seven possible cyclic structural and stereoisomers are



18. **3, 4-dibromo-1-butene** (at low temperature) or **1, 4-dibromo-2-butene** (at high temperature). These products are formed by 1, 2-addition and 1-4 addition respectively.

19. **H_2SO_4, $HgSO_4$**

20. **ethylene**



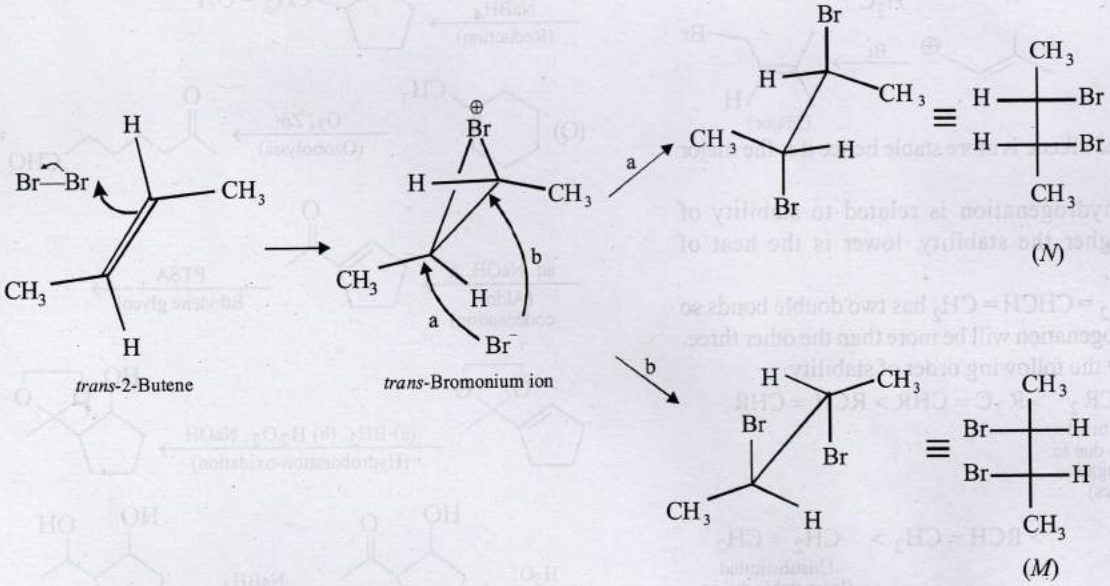
$$\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array} \longrightarrow \begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \\ \downarrow \\ CH_2=CH_2 + 2CO_2 \end{array} + 2K^+$$

21. **(b,d)**

(b) *M* and *N* are identical. Further, *O* and *P* are enantiomers. Hence, *M* and *O* and *N* and *P* are two sets of diastereomers.

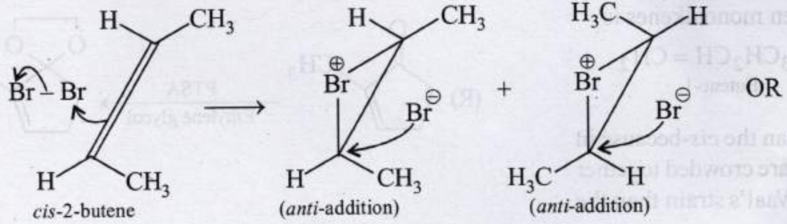
(d) Bromination proceeds through *trans*- or *anti*-addition on alkenes, *i.e.,* in both the reactions. Thus upon addition of bromine, *trans*-alkenes give *meso*-product, while *cis*-alkenes give enantomeric pair.

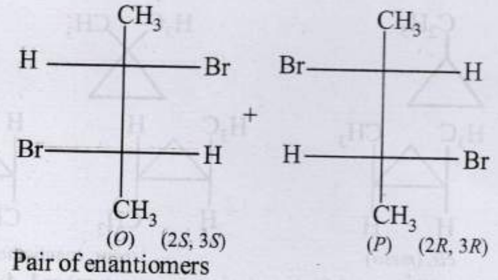
(i)



M and N are same
(*meso*-2, 3-Dibromobutane)

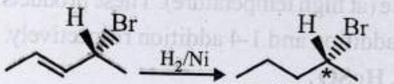
(ii)

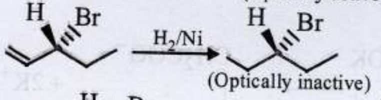


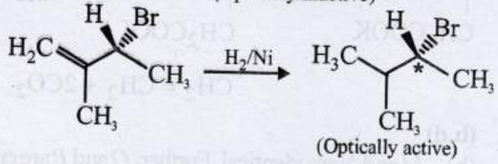


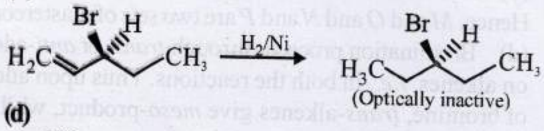
Pair of enantiomers

22. **(b,d)**

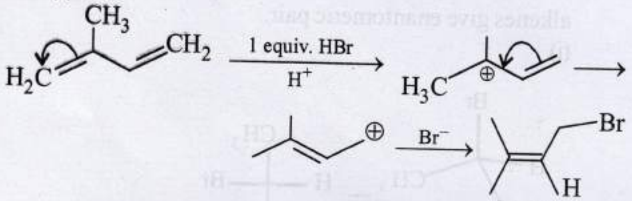
(a)


(b)


(c)


(d)


23. **(d)**



more substituted alkene is more stable hence it is the major product.

24. **(b)** Heat of hydrogenation is related to stability of molecules; higher the stability, lower is the heat of hydrogenation.

Butadiene, $CH_2=CHCH=CH_2$ has two double bonds so its heat of hydrogenation will be more than the other three.

Alkenes follow the following order of stability

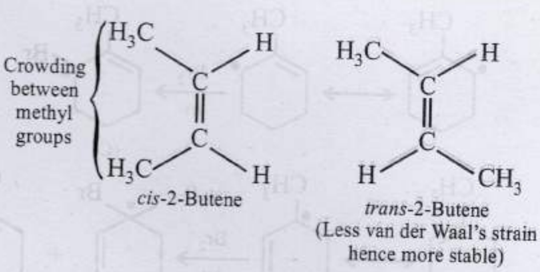
$$\underset{\text{tetrasubstituted (most stable due to hyper conjugative sturctures)}}{R_2C=CR_2} > R_2C=CHR > RCH=CHR$$

$$> RCH=CH_2 > \underset{\text{Unsubstituted (least stable due to no hyperconjugation)}}{CH_2=CH_2}$$

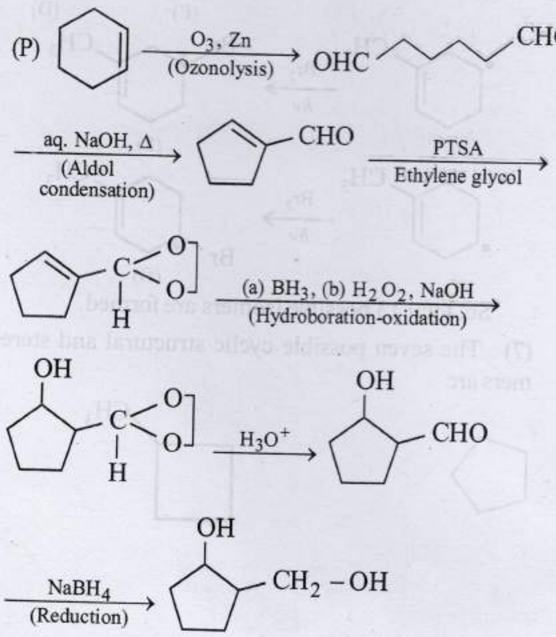
Thus here, stability order of the given monoalkenes is

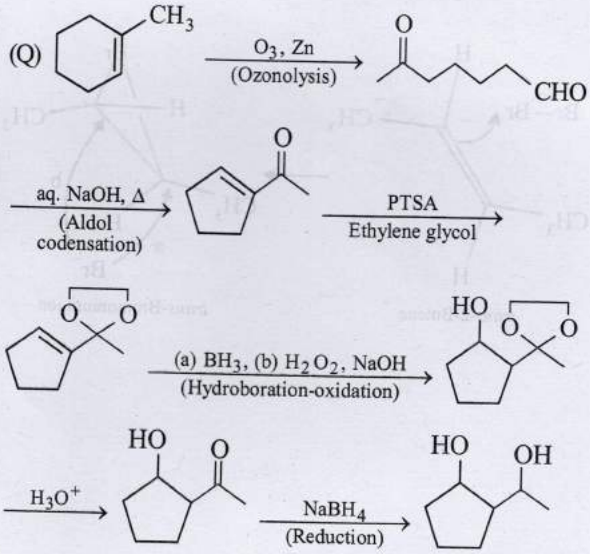
$$\underset{\text{Butene-2 (trans- and cis-)}}{CH_3CH=CHCH_3} > \underset{\text{Butene-1}}{CH_3CH_2CH=CH_2}$$

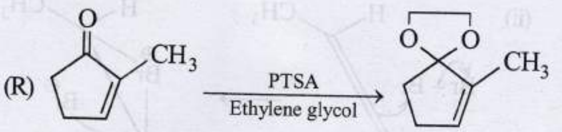
The *trans*-2-butene is more stable than the *cis*-because in the *cis*-isomer the two bulky groups are crowded together with the result, it has more van der Waal's strain than the *trans*-isomer.

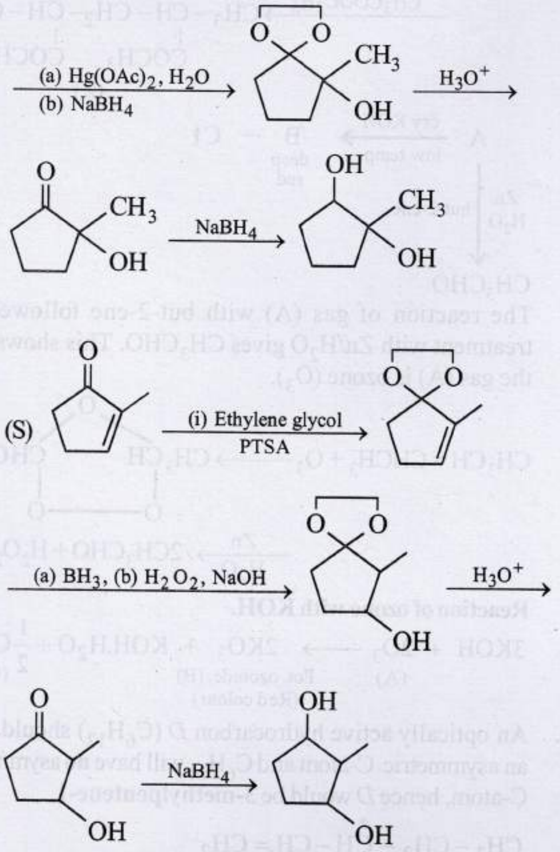


25. **(a)**

(P)


(Q)


(R)


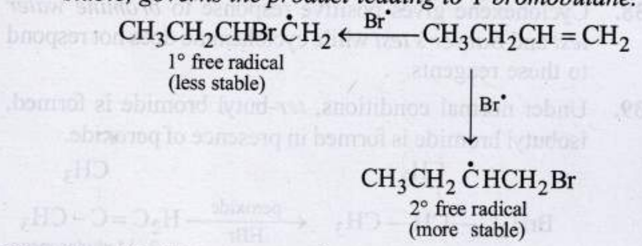


26. **(b)** With *trans*-2-butene, the product of Br_2 addition is optically inactive.

Even though, both assertion and reason are correct the correct reason for the formation of *meso*–2,3–dibromobutane from *trans*–2–butene is *anti* addition of Br_2.

27. **(c)** In presence of peroxide, addition of HBr on alkenes takes place via free radicals.

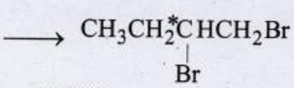
Here, assertion is correct but reasoning is incorrect. Here, two free radical are formed, 2° *free radical, being more stable, governs the product leading to 1-bromobutane.*



$$CH_3CH_2CHBr\dot{C}H_2 \xleftarrow{Br} CH_3CH_2CH=CH_2 \xrightarrow{Br^\bullet} CH_3CH_2\dot{C}HCH_2Br$$

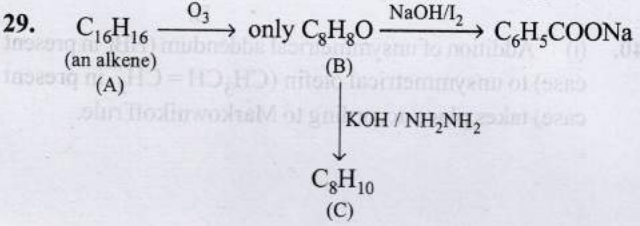
1° free radical (less stable); 2° free radical (more stable)

28. **(a)** $CH_3CH_2-CH=CH_2+Br_2 \longrightarrow CH_3CH_2\overset{*}{C}HCH_2Br$



$$CH_3CH_2\overset{*}{\underset{\substack{|\\Br}}{C}}HCH_2Br$$

29.

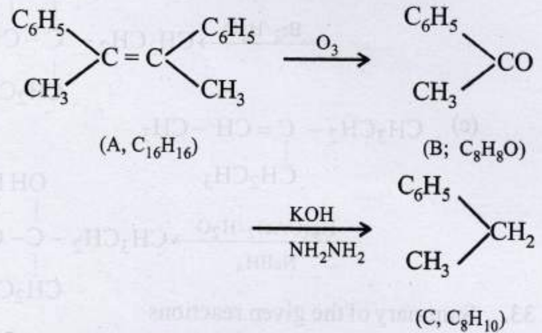


$$\underset{\substack{\text{(an alkene)}\\(A)}}{C_{16}H_{16}} \xrightarrow{O_3} \text{only } \underset{(B)}{C_8H_8O} \xrightarrow{NaOH/I_2} C_6H_5COONa$$

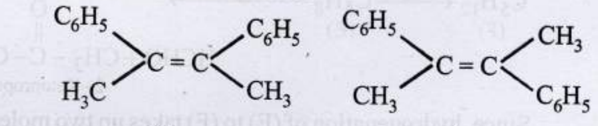
$$C_8H_8O\ (B) \xrightarrow{KOH/NH_2NH_2} \underset{(C)}{C_8H_{10}}$$

(i) Conversion of B (C_8H_8O) to sodium benzoate involves iodoform reaction, hence (B) must contain $-COCH_3$ group leading to $C_6H_5COCH_3$ (C_8H_8O) as its molecular formula.

(ii) Since, the given alkene gives only one product (B) or $C_6H_5-COCH_3$ on ozonolysis, so the given alkene must be a symmetrical alkene containing a double bond in centre. Thus, the alkene (A) must have following structure:

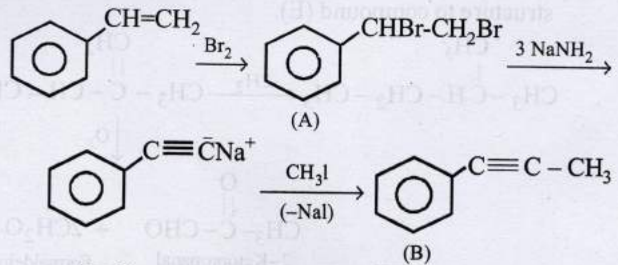


Isomeric structures of A

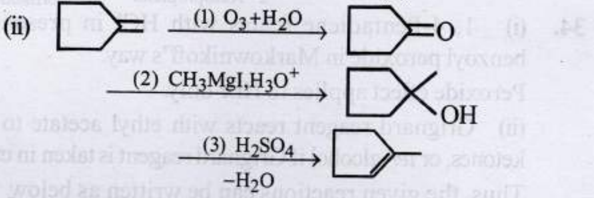


Since catalytic hydrogenation of alkenes takes place in (*syn-*) manner; hence recemic mixture will be formed by the *trans*-isomer.

30. (i)



(ii)

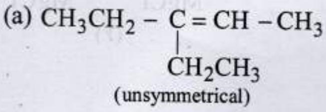


31. (i) It should be an alkene as it adds one mole of H_2 to form *n*-hexane.

(ii) The C_6 alkene should be symmetrical because on oxidation it gives a single carboxylic acid having three carbon atoms.

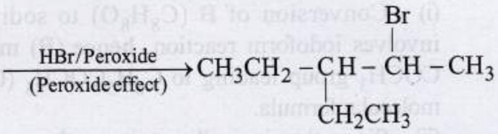
$$\underset{n\text{–Hexane}}{CH_3(CH_2)_4CH_3} \xleftarrow{H_2} \underset{(A)}{CH_3CH_2CH=CHCH_2CH_3} \xrightarrow[KMnO_4]{(O)} 2CH_3CH_2COOH$$

32. (a)

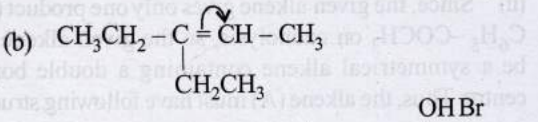


$$CH_3CH_2-\underset{\substack{|\\CH_2CH_3}}{C}=CH-CH_3$$

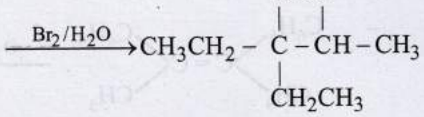
(unsymmetrical)



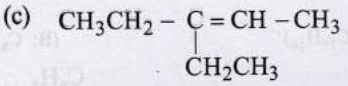
$\xrightarrow[\text{(Peroxide effect)}]{\text{HBr/Peroxide}} CH_3CH_2-\underset{CH_2CH_3}{CH}-\overset{Br}{CH}-CH_3$

(b) 

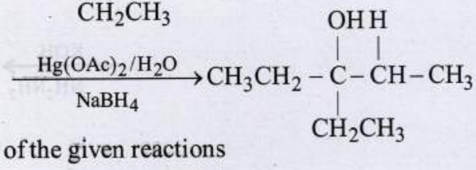
$CH_3CH_2-\underset{CH_2CH_3}{C}=CH-CH_3$



$\xrightarrow{Br_2/H_2O} CH_3CH_2-\underset{CH_2CH_3}{\overset{OH}{C}}-\overset{Br}{CH}-CH_3$

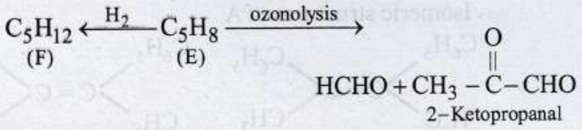
(c) 

$CH_3CH_2-\underset{CH_2CH_3}{C}=CH-CH_3$



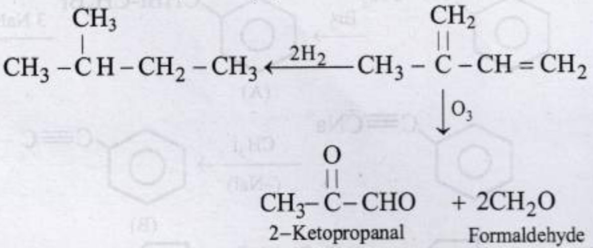
$\xrightarrow[NaBH_4]{Hg(OAc)_2/H_2O} CH_3CH_2-\underset{CH_2CH_3}{\overset{OH}{C}}-\overset{H}{CH}-CH_3$

33. Summary of the given reactions



$\underset{(F)}{C_5H_{12}} \xleftarrow{H_2} \underset{(E)}{C_5H_8} \xrightarrow{\text{ozonolysis}} HCHO + \underset{\text{2-Ketopropanal}}{CH_3-\overset{O}{\overset{\|}{C}}-CHO}$

Since, hydrogenation of (E) to (F) takes up two molecules of hydrogen, it indicates the presence of two double bonds in (E) which is further supported by its ozonolysis to form two products having three carbonyl groups. Further, structure of ozonolysis product leads to following structure to compound (E).



$CH_3-\overset{CH_3}{CH}-CH_2-CH_3 \xleftarrow{2H_2} CH_3-\overset{CH_2}{\overset{\|}{C}}-CH=CH_2 \xrightarrow{O_3} \underset{\text{2-Ketopropanal}}{CH_3-\overset{O}{\overset{\|}{C}}-CHO} + \underset{\text{Formaldehyde}}{2CH_2O}$

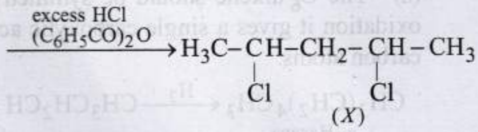
34. (i) 1, 4-Pentadiene reacts with HCl in presence of benzoyl peroxide in Markownikoff's way.

Peroxide effect applies to HBr only.

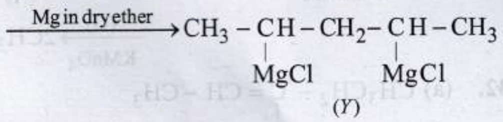
(ii) Grignard reagent reacts with ethyl acetate to form ketones, or *ter*-alcohol if Grignard reagent is taken in excess.

Thus, the given reactions can be written as below.

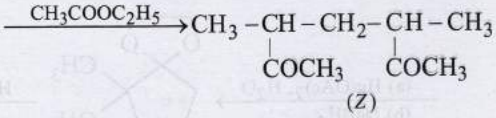
$H_2C=CH-CH_2-CH=CH_2$



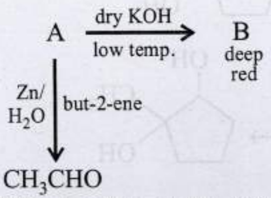
$\xrightarrow[(C_6H_5CO)_2O]{\text{excess HCl}} \underset{(X)}{H_3C-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_3}$



$\xrightarrow{\text{Mg in dry ether}} \underset{(Y)}{CH_3-\underset{MgCl}{CH}-CH_2-\underset{MgCl}{CH}-CH_3}$



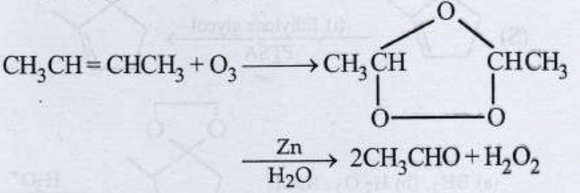
$\xrightarrow{CH_3COOC_2H_5} \underset{(Z)}{CH_3-\underset{COCH_3}{CH}-CH_2-\underset{COCH_3}{CH}-CH_3}$

35. 

$A \xrightarrow[\text{low temp.}]{\text{dry KOH}} \underset{\text{deep red}}{B} + C\uparrow$

$A \xrightarrow[\text{but-2-ene}]{Zn/H_2O} CH_3CHO$

The reaction of gas (A) with but-2-ene followed by treatment with Zn/H_2O gives CH_3CHO. This shows that the gas (A) is ozone (O_3).

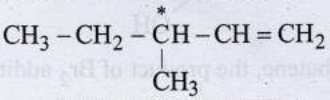


$CH_3CH=CHCH_3 + O_3 \longrightarrow$ ozonide $\xrightarrow[H_2O]{Zn} 2CH_3CHO + H_2O_2$

Reaction of ozone with KOH.

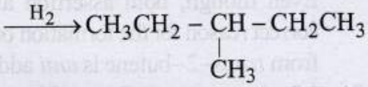
$$3KOH + \underset{(A)}{2O_3} \longrightarrow \underset{\substack{\text{Pot. ozonide, (B)}\\ \text{(Red colour)}}}{2KO_3} + KOH.H_2O + \underset{(C)}{\frac{1}{2}O_2\uparrow}$$

36. An optically active hydrocarbon *D* (C_6H_{12}) should have an asymmetric C-atom and C_6H_{14} will have **no** asymmetric C-atom, hence *D* would be **3-methylpentene-1**.



$CH_3-CH_2-\underset{CH_3}{\overset{*}{C}H}-CH=CH_2$

(*D*) Optically active (C_6H_{12})



$\xrightarrow{H_2} CH_3CH_2-\underset{CH_3}{CH}-CH_2CH_3$

Optically inactive (C_6H_{14})

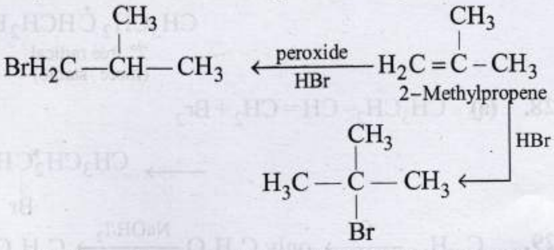
37. B should be a symmetric alkene (**butene-2**)

$CH_3CH=CHCH_3$ gives same product

$CH_3-CH(Br)-CH_2-CH_3$ in presence/absence of peroxide.

38. Cyclohexene gives positive response to *bromine water test* and *Baeyer's test* while cyclohexane does not respond to these reagents.

39. Under normal conditions, *ter*-butyl bromide is formed, isobutyl bromide is formed in presence of peroxide.

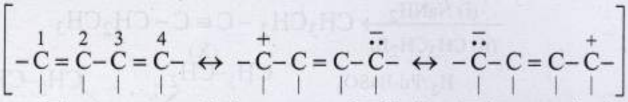


$BrH_2C-\overset{CH_3}{CH}-CH_3 \xleftarrow[HBr]{\text{peroxide}} \underset{\text{2-Methylpropene}}{H_2C=\overset{CH_3}{C}-CH_3} \xrightarrow{HBr} H_3C-\underset{Br}{\overset{CH_3}{C}}-CH_3$

40. (i) Addition of unsymmetrical addendum (HBr in present case) to unsymmetrical olefin ($CH_3CH=CH_2$, in present case) takes place according to Markownikoff rule.

$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \rightarrow \underset{\textit{iso}\text{-Propyl bromide}}{CH_3.CHBr.CH_3}$$

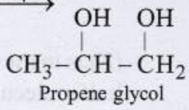
(ii) 1, 3 - Butadiene is a conjugated diene and is a reasonance hybrid:



$$\left[\overset{1}{-C}=\overset{2}{C}-\overset{3}{C}=\overset{4}{C}- \leftrightarrow -\overset{+}{C}-C=C-\overset{\overline{\cdot\cdot}}{C}- \leftrightarrow -\overset{\overline{\cdot\cdot}}{C}-C=C-\overset{+}{C}-\right]$$

Thus resonance induces some double bond character in the central C-C bond leading to the shortening of this bond. **Alternatively**, all the four C atoms of 1, 3–butadiene are sp^2 hybridised and thus their C – C bond length will be lower than that of *n*-butane in which all the four C atoms are sp^3 hybridised.

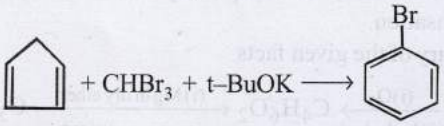
41. $\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O + [O] \xrightarrow{KMnO_4}$



$$\underset{\text{Propene glycol}}{CH_3-\underset{}{\overset{OH}{\overset{|}{C}H}}-\overset{OH}{\overset{|}{C}H_2}}$$

[Colour of $KMnO_4$ is discharged]

42.



Topic-3 : Alkynes

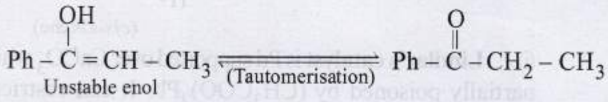
1. **(d)** Only (d) can form 3-octyne

$$CH_3CH_2C\equiv CH \xrightarrow[-NH_3]{NaNH_2} CH_3CH_2C\equiv C^-Na^+$$
$$\xrightarrow[(S_N2)]{CH_3CH_2CH_2CH_2Br} CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3 + NaBr$$

2. **(d)** $H_2/Pd/BaSO_4$ reduces an alkyne to *cis*-alkene, H_2/Pt reduces it to alkane, $NaBH_4$ does not reduce an alkyne. Reduction of an alkyne by active metal in liq. NH_3 gives *trans*-alkene.

3. **(a)** Reaction proceeds through carbocation intermediate:

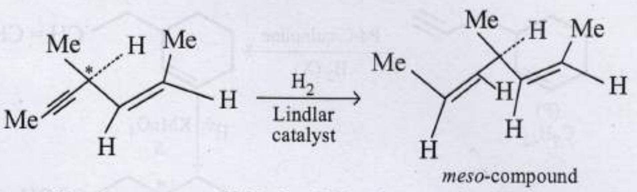
$$Ph-C\equiv C-CH_3 + H^+ \longrightarrow Ph-\overset{+}{C}=CH-CH_3 \xrightarrow[\text{Resonance stabilised}]{H_2O}$$



$$\underset{\text{Unstable enol}}{Ph-\overset{OH}{\overset{|}{C}}=CH-CH_3} \xrightleftharpoons[\text{(Tautomerisation)}]{} Ph-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$$

4. **(d)** 1-Butyne has terminal hydrogen which is acidic whereas in 2-butyne there is no terminal hydrogen. Thus, 2-butyne will not react with ammonical Cu_2Cl_2, while 1-butyne, will give red ppt. with ammonical cuprous chloride

5. **(b)** Addition on triple bond takes place by the *syn*-addition of hydrogen due to Lindlar catalyst. Since the configuration of the double bond already present is *cis*, the compound formed will not remain chiral and hence, optically inactive.

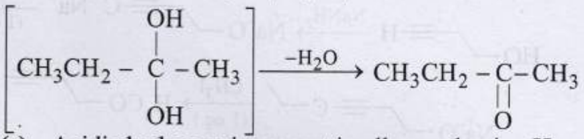


meso-compound

6. **(d)** In propyne ($CH_3C\equiv CH$), the terminal hydrogen is acidic and reacts with ammonical $AgNO_3$.

7. **(a)** Hydration of alkynes via mercuration takes place in accordance with Markovnikov's rule.

$$CH_3CH_2C\equiv CH \xrightarrow[HgSO_4/H_2SO_4]{+2H_2O}$$



$$\left[CH_3CH_2-\overset{OH}{\underset{OH}{\overset{|}{\underset{|}{C}}}}-CH_3\right] \xrightarrow{-H_2O} CH_3CH_2-\underset{O}{\underset{\|}{C}}-CH_3$$

8. **(a)** Acidic hydrogen is present in alkynes, having H on the triply bonded C-atom. They can be easily removed by means of a strong base.

9. **(c)** $CH_3C\equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4}$

$$[CH_3CH(OH)=CH_2] \rightarrow \underset{\text{acetone}}{CH_3COCH_3}$$

10. **C_2H_2**

$$CH\equiv CH + HCl \longrightarrow CH_2=CHCl \longrightarrow PVC$$

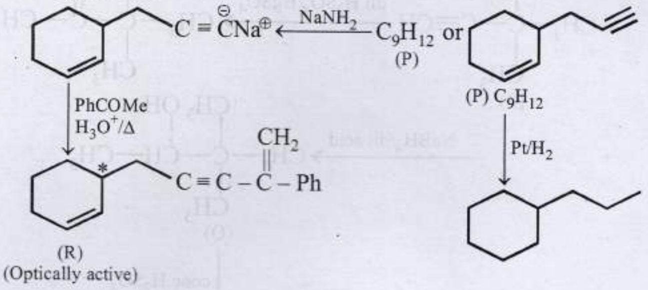
11. **2-butyne**

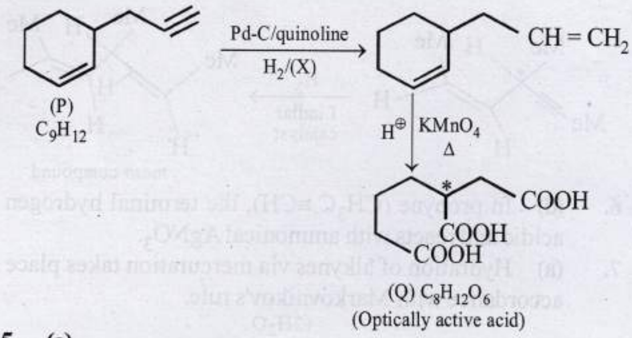
$$CH\equiv CH + Na \xrightarrow[\text{Liq }NH_3]{} CH\equiv CNa \xrightarrow{NaNH_2} NaC\equiv CNa$$
$$NaC\equiv CNa + 2CH_3I \rightarrow \underset{\text{2-Butyne}}{CH_3C\equiv CCH_3}$$

12. **Ethyne,** because of the high *s* character of the carbon of the – C ≡ H bond in ethyne (*sp* hybridisation).

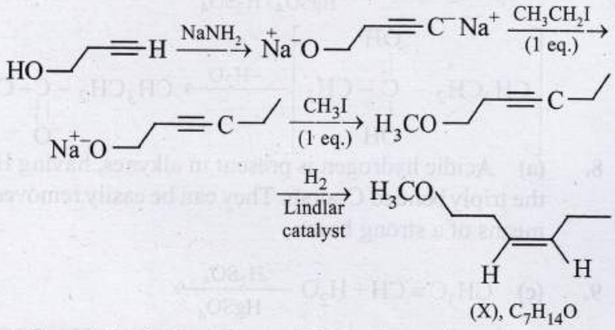
13. **False :** Ethylene reacts with sulphuric acid to form ethyl hydrogen sulphate. It can be dried by passing it through phosphorus pentoxide.

14. **(b,c)**



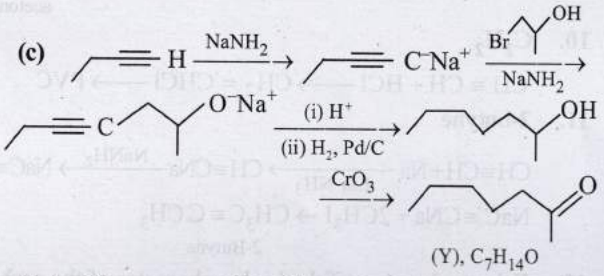


15. (a)



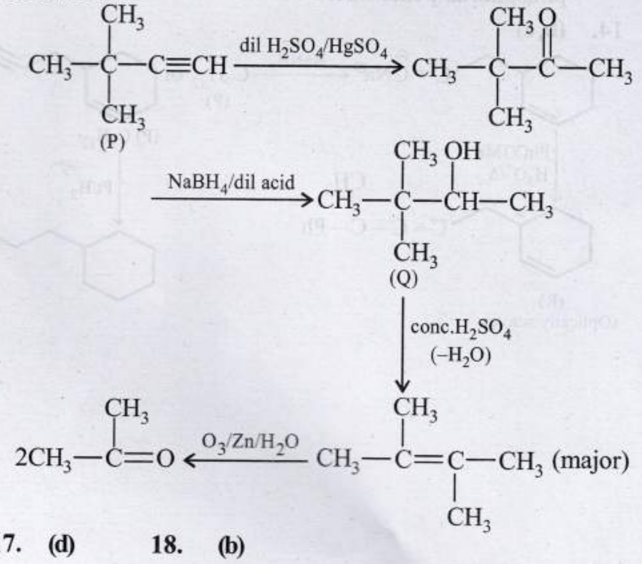
Note : Lindlar's catalyst will form the *cis*-isomer.

16. (c)



Note: The compounds with $-\underset{\underset{O}{\|}}{C}-CH_3$ group, gives positive iodoform test.

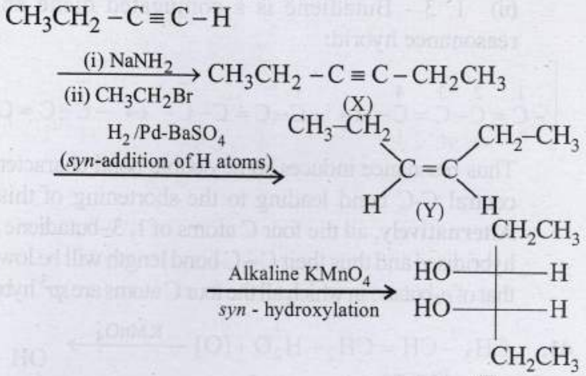
For 17 & 18



17. (d) **18.** (b)

19. Ziggler – Natta catalyst ($R_3Al + TiCl_4$)

20. Meso forms are optically inactive.

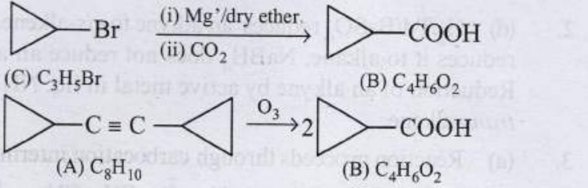


(Z) is in meso form having plane of symmetry. The upper half molecule is mirror image of the lower half molecule. The molecule is, therefore, optically inactive due to internal compensation.

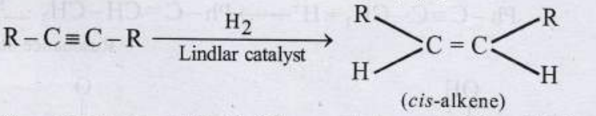
21. Summary of the given facts

$$\underset{(A)}{C_8H_{10}} \xrightarrow[\text{(ii)hydrolysis}]{\text{(i)}O_3} \underset{(B)}{C_4H_6O_2} \xleftarrow[\text{(ii)}CO_2,\ \text{(iii)}H^+]{\text{(i) Mg in dry ether}} \underset{(C)}{C_3H_5Br}$$

Since compound (B) is obtained from compound (C) C_3H_5Br through reaction with Mg and CO_2, it seems that compound (B) is a carboxylic acid formed via the formation of Grignard reagent. Hence, compound (C) should be an alkyl halide having three carbon atoms. The alkyl halide (C) is unsaturated (indicated by number of hydrogen atoms) which is present in the form of ring and thus (C) should be bromocyclopropane.



22.



(i) **Lindlar's catalyst** is Pd supported over $CaCO_3$ which is partially poisoned by $(CH_3COO)_2Pb$. It can restrict the hydrogenation of alkyne to alkene stage. It yields a *cis*-alkene.

23. (i) By amm. $AgNO_3$ or by acidic-H tests : Terminal alkynes give white precipitate with amm. $AgNO_3$ or red ppt. with amm. Cu_2Cl_2 (H atom attached on *sp* hybridized carbon is acidic).

$\underset{\text{1-Butyne}}{2CH_3CH_2C\equiv CH} + Ag_2O \rightarrow 2CH_3CH_2C\equiv CAg + H_2O$

$\underset{\text{2-Butyne}}{CH_3-C\equiv C-CH_3} + Ag_2O \rightarrow$ No reaction

Only terminal alkynes respond to these reactions.

24. **Calculation of molecular formula of *A*.**

Element	Percentage of atoms	Relative No. ratio	Simplest whole
C	85.7	85.7/12 = 7.14	7.14/7.14 = 1
H	14.3	14.3/1 = 14.3	14.3/7.14 = 2

$\therefore$ Empirical formula of $A = CH_2$

Determination of molecular weight of A

1 g of A consumes = 38.05 g of 5% Br_2 (in CCl_4)

$$= \frac{38.05 \times 5}{100} \text{ g of 100\% } Br_2 = 1.90 \text{ g of 100\% } Br_2.$$

Now since, 1.90 g of Br_2 is consumed by 1 g of compound A.

$\therefore$ 160 g (1 mole) of Br_2 will be consumed by

$$= \frac{1}{1.90} \times 160 = 84.2 \text{ g of A} = 84.0 \text{ (app.)g of A}$$

$\therefore$ Molecular weight of A = **84**

$$\text{Hence, } n = \frac{84}{12+2} = 6$$

$\therefore$ Molecular formula of $A = (CH_2)_6 = \mathbf{C_6H_{12}}$

Since, the hydrocarbon A consumes 1 molar equivlaent of hydrogen, it must contain one double bond. Oxidation of compound A with $KMnO_4$ to form compound C (C_4H_8O) and acetic acid indicates $= CH.CH_3$ fragment in A, *i.e.*

$$\underset{A(C_6H_{12})}{C_4H_8 \,|= CHCH_3} \xrightarrow{KMnO_4} \underset{C}{C_4H_8O} + \underset{\text{Acetic acid}}{CH_3COOH}$$

Now the fragment C_4H_8 of A on oxidation forms the compound 'C' (C_4H_8O) which may be easily obtained from butyne-2 and acidic aq. $HgSO_4$, the compound 'C' must be ethylmethyl ketone.

$$\underset{\text{Butyne}-2}{CH_3.C \equiv C.CH_3} \xrightarrow{H^+/HgSO_4} \underset{\text{Ethylmethyl ketone }(C)}{CH_3.\overset{O}{\overset{\|}{C}}.CH_2CH_3}$$

The formation of ketone 'C' (uthyl methyl ketone) and acetic acid from C_4H_8 fragment of 'A' can be explained by the following structure of A.

$$\underset{(A)}{CH_3.CH_2.\overset{CH_3}{\overset{|}{C}} = CH.CH_3} \xrightarrow{KMnO_4} \underset{\substack{\text{Ethylmethyl ketone}\\(C)}}{CH_3.CH_2\overset{CH_3}{\overset{|}{C}} = O} + \underset{\text{Acetic acid}}{COOH.CH_3}$$

Hence, formation of 'B' can be represented as below.

$$\underset{'A'}{CH_3.CH_2.\overset{CH_3}{\overset{|}{C}} = CH.CH_3} + H_2 \longrightarrow \underset{'B'}{CH_3.CH_2\overset{CH_3}{\overset{|}{C}}H.CH_2.CH_3}$$

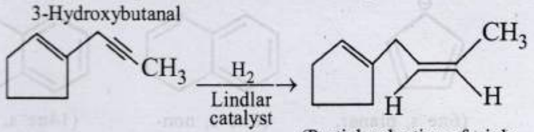
25. Ethyne (HC ≡ CH) and only those derivatives which have at least one acetylenic hydrogen atom ($\equiv C-H$) *i.e.* terminal alkynes, will give white precipitate with ammonical silver nitrate solution.

26. $$\underset{\text{Ethene}}{CH_2 = CH_2} \xrightarrow{Br_2} \underset{Br\quad Br}{CH_2\,CH_2} \xrightarrow[(-2HBr)]{2KOH,\text{ alcoholic}} \underset{\text{Ethyne}}{CH \equiv CH}$$

27. (*i*) $$\underset{\text{Ethyne}}{CH \equiv CH} \xrightarrow{\text{hydration}} CH_3CHO \xrightarrow[\text{Aldol cond.}]{OH^-}$$

$$\underset{\text{3-Hydroxybutanal}}{CH_3\overset{OH}{\overset{|}{C}}HCH_2CHO} \xrightarrow{-H_2O} CH_3CH = CHCHO$$

(*ii*)

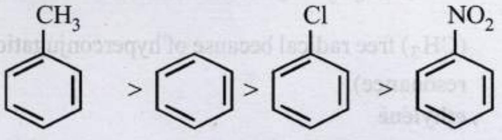


(Partial reduction of triple bond in *syn*-manner)

28. Bromine water test : C_2H_2 decolourises bromine water while CH_4 does not decolourise bromine water.

Topic-4 : Aromatic Hydrocarbons

1. **(c)**



(Activated by + I, and hyperconjugation) Deactivated due to –I Deactivated due to –I, –M, –E

2. **(c)** $CH_2 = CH_2 + H_2SO_4 \rightarrow CH_3CH_2OSO_3H$

$C_6H_6 + H_2SO_4 \rightarrow C_6H_5SO_3H + H_2O$

$C_6H_{14} + H_2SO_4 \rightarrow$ No reaction

$C_6H_5NH_2 + H_2SO_4 \rightarrow C_6H_5\overset{+}{N}H_3H\overset{-}{S}O_4$

Only hexane does not dissolve in conc. H_2SO_4 even on warming.

3. **(c)** $-NO_2$, –Cl and –OH are electron-attracting or withdrawing groups due to –M, –E and/or –I effects whereas $-CH_3$ shows +I effect (electron releasing). Because of the + I effect of the CH_3 group, toluene has the highest electron density in the *o*- and *p*- positions and hence, can be most readily sulphonated.

4. **(c)** The phenomenon of resonance gives identical bonding and hence identical bond lengths.

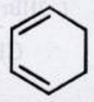
C – C bond order in benzene = 1.5

5. **(4)**

(8πe⁻s, non-planar) Non-aromatic

(4πe⁻s, planar) Anti-aromatic

(2πe⁻s, planar, conjugated) Aromatic

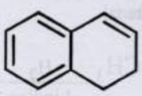


(4πe⁻s non-planar) Non-aromatic

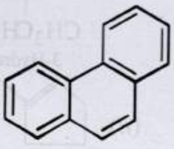
(6πe⁻s, conjugated, planar) Aromatic

(4πe⁻s, conjugated, planar) Anti-aromatic

(6πe⁻s, planar, conjugated) Aromatic



(8πe⁻s, non-planar, non-conjugated) non-Aromatic



(14πe⁻s, planar, conjugated) Aromatic

6. **less;**

$$\text{Stability of free radical} \propto \frac{1}{\text{Bond dissociation energy}}$$

Benzyl ($C_6H_5\dot{C}H_2$) free radical is more stable than methyl ($\dot{C}H_3$) free radical because of hyperconjugation (no bond resonance).

7. **ethylene**

$$\begin{array}{l} CH_2COOK \\ | \\ CH_2COOK \end{array} \longrightarrow \begin{array}{l} CH_2COO^- \\ | \\ CH_2COO^- \\ \quad\downarrow \\ CH_2 = CH_2 + 2CO_2 \end{array} + 2K^+$$

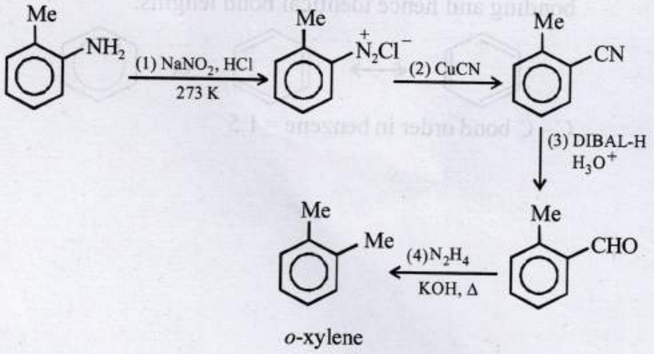
8. **cyclopropane,** because it has maximum deviation, from the normal bond angle of 109°28′ present in alkanes. In cyclopropane bond angle is 60°, therefore deviation *d*,

$$d = \frac{1}{2}(109°28' - 60°).$$

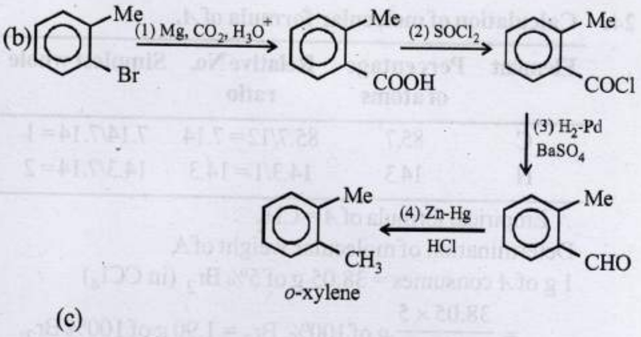
9. **False :** An electron-donating group increases the electron density in *o*- and *p*- positions due to +M, and/or +I effects and hence, orients the new electrophile to *o*- and *p*-positions.

10. **(a,b)**

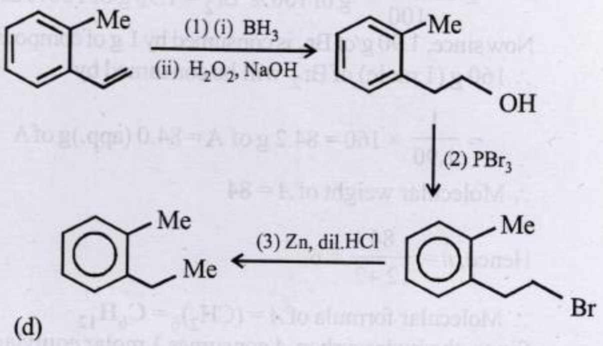
(a)



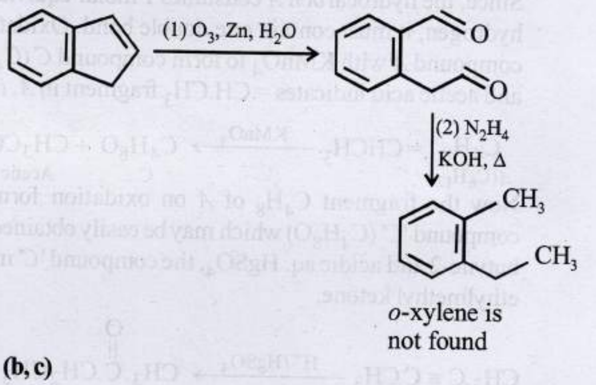
(b)



(c)

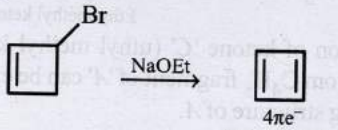


(d)

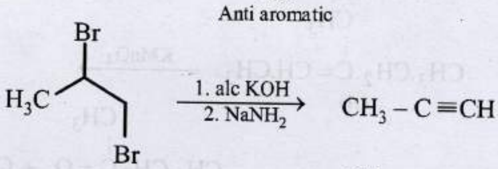


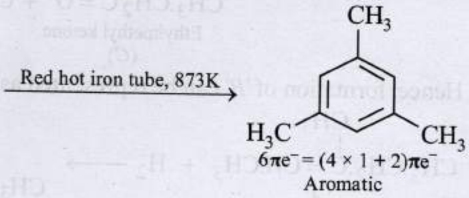
11. **(b, c)**

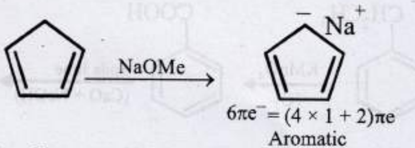
(a)

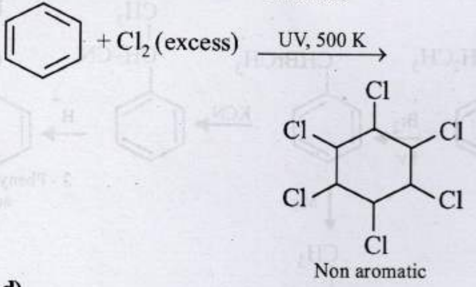


(b)

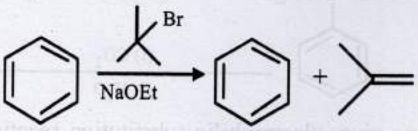


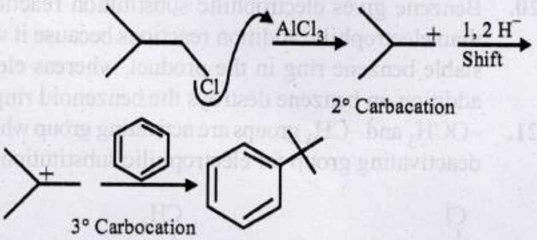


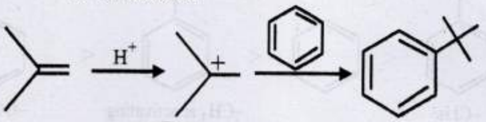
(c) 

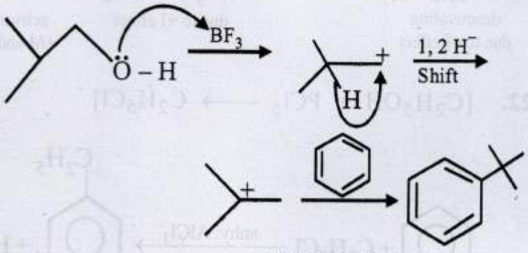
(d) 

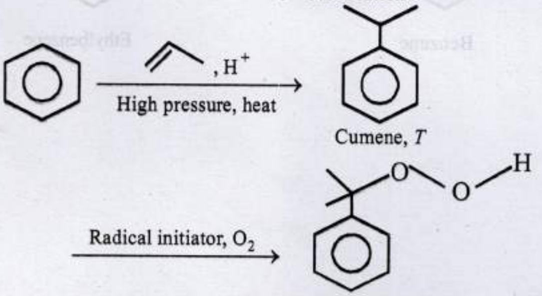
12. **(b, c, d)**

(a) 

(b) 

(c) 

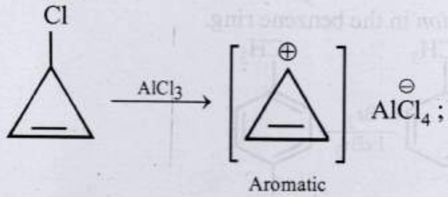
(d) 

13. **(b)** 

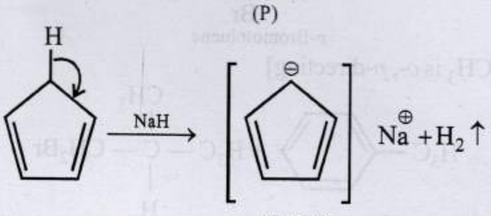
Cumene, *T*

Cumene hydroperoxide, *U*

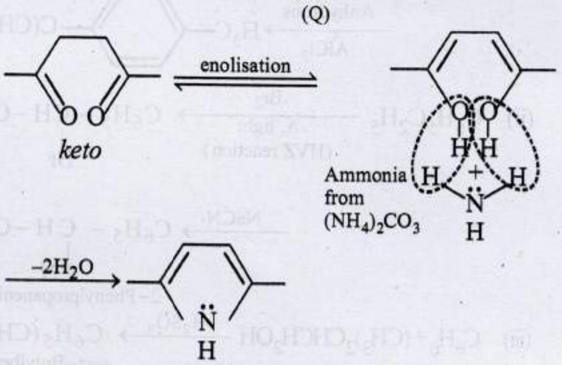
14. **(a, b, c, d)**



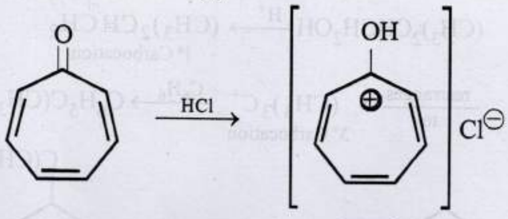
Aromatic (P)



Aromatic (Q)



Aromatic (R)



Aromatic (S)

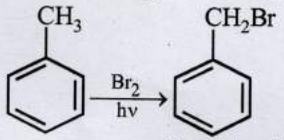
15. **(a, c)** Hyperconjugation in toluene also activates the benzene ring for electrophilic substitution.

Methyl group is activating group and activates *o*- and *p*-positions for electrophilic substitution.

16. **(b, c, d)** An aromatic species will have : $(4n + 2)$ π electrons (by Huckel's Rule), planar structure (to exhibit resonance) and cyclic structure

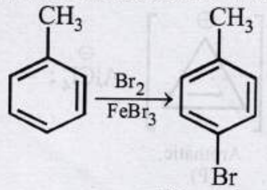
17. (i) *tert*-Butylbenzene does not give benzoic acid on treatment with acidic $KMnO_4$ because it does not contain benzylic hydrogen Ca hydrogen atom on the key carbon atom.

(ii) In presence of light, toluene undergoes *side chain bromination* through a free radical mechanism.



Benzyl bromide

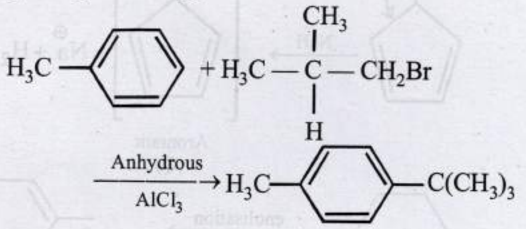
In presence of $FeBr_3$, toluene undergoes *electrophilic substitution* in the benzene ring.



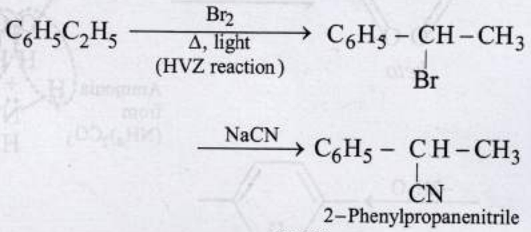
p-Bromotoluene

[$-CH_3$ is *o*-, *p*-directing]

18. (i)



(ii)



$$C_6H_5C_2H_5 \xrightarrow[\text{(HVZ reaction)}]{Br_2,\ \Delta,\ \text{light}} C_6H_5-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{NaCN} C_6H_5-\underset{\underset{CN}{|}}{CH}-CH_3$$

2–Phenylpropanenitrile

(iii) $C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4} C_6H_5(CH_3)_3$ *tert*–Butylbenzene

Explanation :

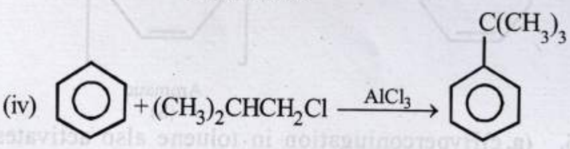
$$(CH_3)_2CHCH_2OH \xrightarrow{H^+} (CH_3)_2CH\overset{+}{C}H_2$$

1° Carbocation

$$\xrightarrow[\text{to}]{\text{rearranges}} (CH_3)_3C^+ \xrightarrow{C_6H_6} C_6H_5C(CH_3)_3$$

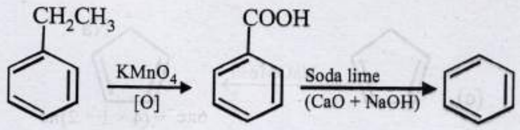
3° Carbocation

(iv)

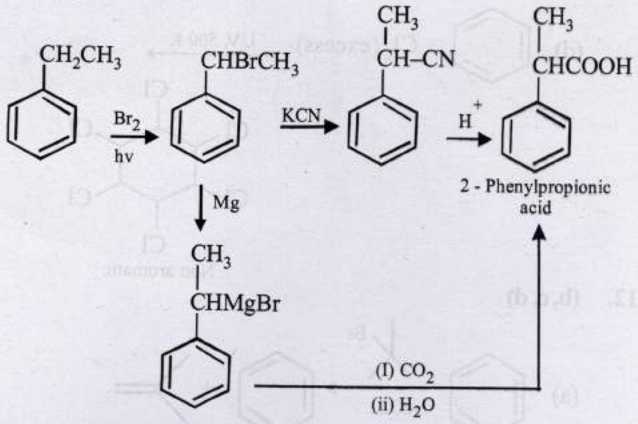


1° carbocation, $(CH_3)_2CH\overset{+}{C}H_2$ formed during reaction rearranges to the more stable, 3° carbocation, $(CH_3)_3\overset{+}{C}$ and hence the above product is formed.]

19. (i)

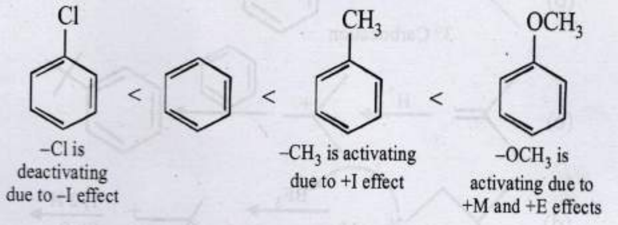


(ii)

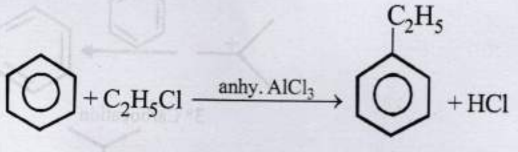


20. Benzene gives electrophilic substitution reactions rather than electrophilic addition reactions because it will have a stable benzene ring in the product, whereas electrophilic addition on benzene destroys the benzenoid ring.

21. $-OCH_3$ and $-CH_3$ groups are activating group while $-Cl$ is a deactivating group for electrophilic substitution.



22. $[C_2H_5OH + PCl_5 \longrightarrow C_2H_5Cl]$



Benzene Ethylbenzene