श्री BalaJi

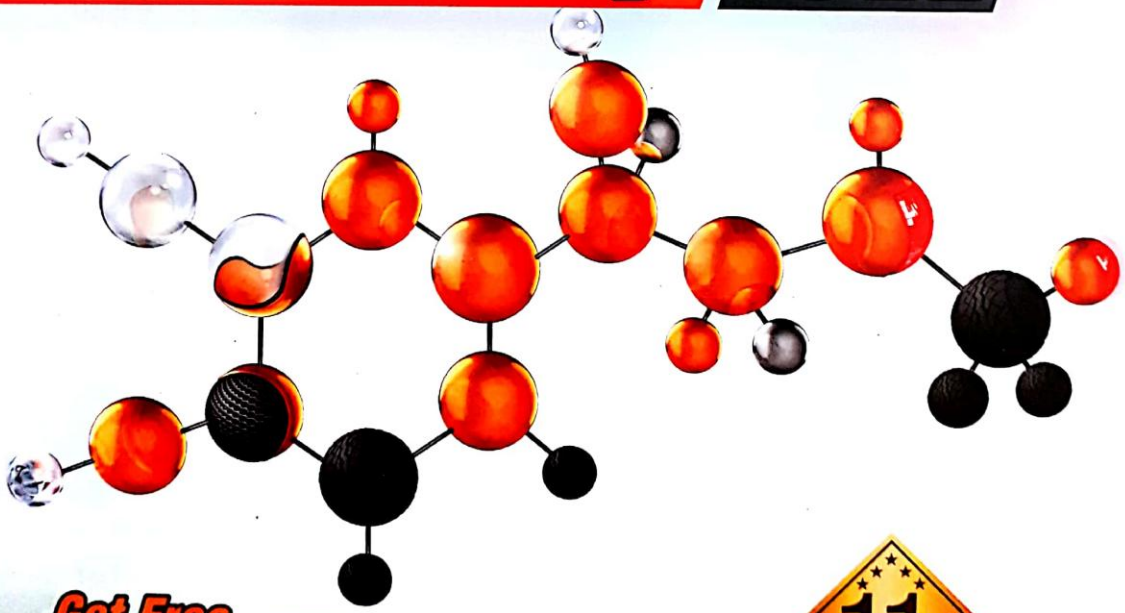
M.S. Chouhan

Solution Manual

Advanced Problems in

Organic Chemistry

for JEE



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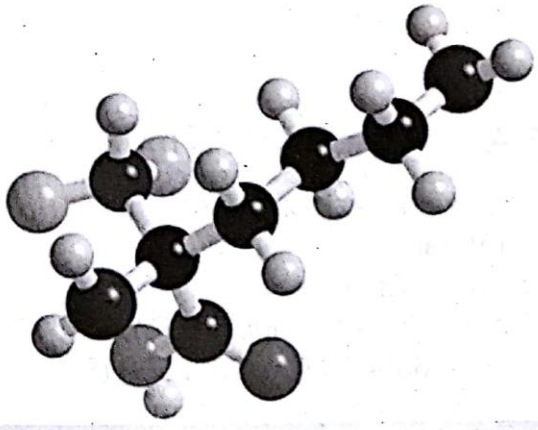

Solution Manual

Advanced Problems *in*

ORGANIC CHEMISTRY

for

JEE

by :

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Important Contribution by :

Akshya Chaudhary
Dr. Sharad Kothari

CONTENTS

About the Author

Mahendra Singh Chouhan (MSC Sir) is a renowned name in the realm of Organic Chemistry. Through a Chemical Engineer from Mumbai University, his great passion for the subject led him to impart guidance to IIT-JEE aspirants on a regular basis. His in depth knowledge and vast experience has helped innumerable students to achieve their dream of excelling at IIT, JEE and other such tough challenges.

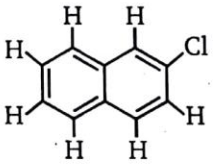
He has launched a website to extend the benefits of his expertise beyond the geographical barriers to all those who dare to dream and seek - www.iitjeeorganic.com.

The website provides expert guidance in all the areas of the subject in a most skillful manner. There are quizzes, challenging questions, notes, e-books and videos etc. This website is a complete guide in itself for organic chemistry and has been designed for IIT-JEE aspirants, keeping in mind the various syllabi and CBSE.

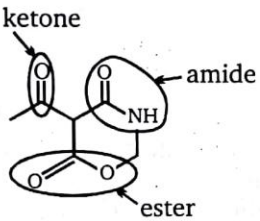
Highly recommended for the high flyers.

1. General Organic Chemistry

Level-1

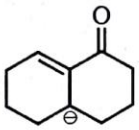
1. (c) 

2° H are seven.

2. (d) 

3. (d) Potential energy of (*A*) and (*B*) is same and transition state has the characteristics of sp^2.

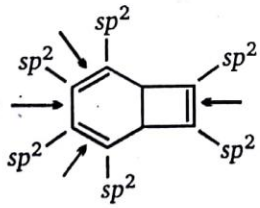
4. (a) More the numbers of carbons more will be the heat of combustion.

5. (d) 
is not the resonating structure of others.

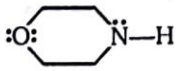
6. (d) Acidic strength ∝ stability of resulting anion. (*i. e.*, conjugate base)

7. (b) $CH_3-\overset{\delta-}{O}-\overset{\delta+}{C}=O-CH_3$

due to resonance this bond has partial double bond characters

8. (c) 

Total 4 σ-bonds
has $sp^2 - sp^2$ overlapping

9. (b) 

Total '3' lone pairs in molecule.

10. (c) Ring strain $\propto \dfrac{1}{\text{size of ring}}$

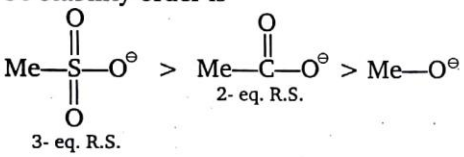
11. (b) Alcohol, ketone, alkene and ether.

12. (b) Acidic strength $\propto -I; -H; -M \propto \dfrac{1}{+I; +H; +R}$

13. (a) $C^{\oplus}$ stability $\propto$ +H on carbocation

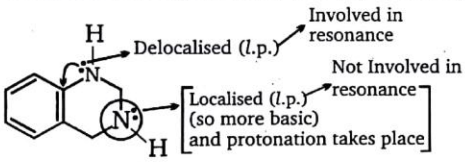
14. (b) Stability of resonance hybrid $\propto$ no. of equivalent R.S.

So stability order is



So Acidic strength order is $x > y > z$ so pK_a is $z > y > x$.

15. (b)

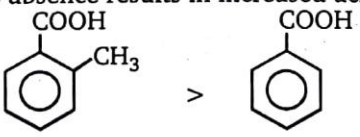


16. (b) **The ortho-effect :** This is a special effect that is shown by *o*-substituents of benzene and its derivatives, but is not necessarily just a steric effect, *e.g.*, the basicities of some *o*-substituted anilines were explained in terms of steric effects and differences in crowding round the nitrogen atom. This ortho-effect also operates with the benzoic acids. Irrespective of the polar type, nearly all o-substituted benzoic acids are stronger than benzoic acid. As we have seen, benzoic acid is a resonance hybrid, and so the carboxyl groups is coplanar with the ring. An o-substituent tends to prevent this coplanarity. Thus resonance is diminished (or prevented), and so the O-atom of the OH groups has a greater positive charge, resulting increased acid strength. It follows from this that the greater the steric inhibition to resonance, the stronger is the acid. Support for this is the following order of strengths of substituted benzoic acids.

2,6-di-Me (pK_a 3.21) > 2-t-Bu (pK_a 3.46) > 2-Me (pK_a 3.91).

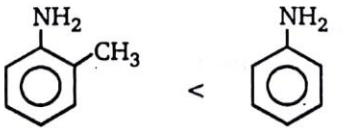
Here again, if we consider the stability of the anion, steric inhibition of resonance prevents the +*R* effect of the ring coming into operation (see above), and since this weakens acid strength, its absence results in increased acid strength.

K_a order:



(due to ortho effect)

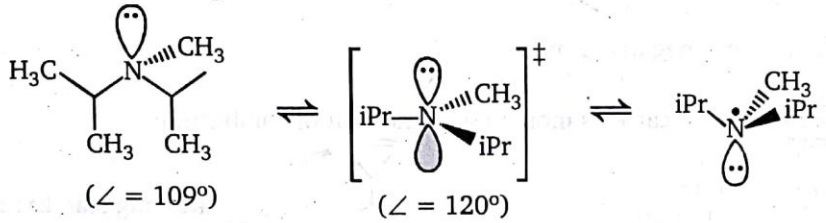
K_b order:



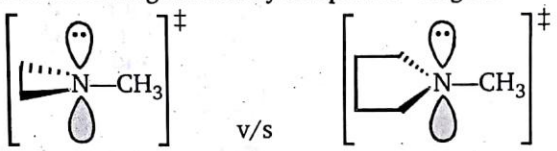
(due to ortho effect)

For options B and D, no ortho effect is valid and order of acidity and basicity is calculated by nearly examining the inductive effect.

17. (a) The barrier to inversion for i-Pr_2 NMe is less than for Me_3N because going from sp^3 (tetrahedral) to sp^2 (trigonal planar) spreads the bulky isopropyl groups further apart and relieves steric crowding. In other words the isopropyl groups destabilize the pyramidal amine more than the planar transition structure.

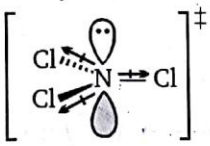


(b) The sp^2 transition state has ideal bond angle of ~ 120°. The three member ring T.S. is highly strained because it cannot achieve 120° due to the small ring locking the angles at ~ 60°. The 5-membered ring can easily adopt 120° angle.



(highly strained) (very little ring strained)

(c) As the nitrogen goes from $sp^3 \rightarrow sp^2$, it becomes effectively more electronegative. (Remember : more s-character means more electronegative) The electronegative chlorine atoms pull electron density away from N more than the methyl groups, creating an electron - deficient N, and destabilising the T.S.



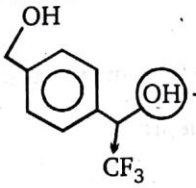
T.S. = transition state

18. (c) $H_2C{=}C{=}CH{-}CH{=}O$

sp^2 sp sp^2 sp^2

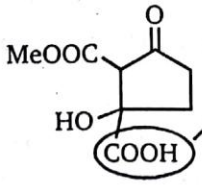
19. (d) All 'N' atoms of circle have localised *l. p.* which do not take part in resonance.

20. (d) (a)

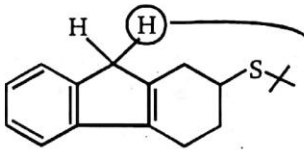


More Acidic due to – *I* of CF_3

(b)



More Acidic because resulting anion has 2-equivalent R.S.

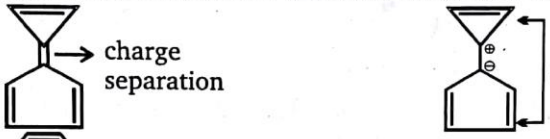
(c) 

After deprotonation ring becomes Aromatic so it is most acidic

21. (c) Due to electronegativity order.

$$O^{\oplus} > N^{+} > O > N$$

22. (c) More the no. of carbons more will be the heat of combustion.

23. (c) 

charge separation

2-Aromatic ring stabilised by resonance

more stable due to extra resonance and has 2-aromatic rings

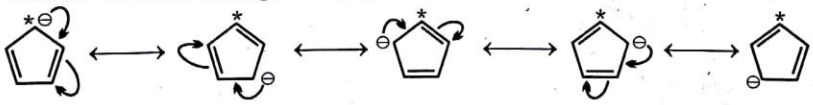
one aromatic & one anti aromatic

so charge separation is less

so bond rotation energy $C > A > B$

so order of rotation is $B > A > C$

24. (a) Weaker acid has stronger conjugate base.

25. (d) 

Final products are

20% 40% 40%

26. (d) Aromatic ring is more stable than non-aromatic ring so 'd' is most stable.

27. (d) 

most acidic because ring is aromatic after deprotonation.

H — C ≡ C — H is next most acidic compound because % s characters are high.

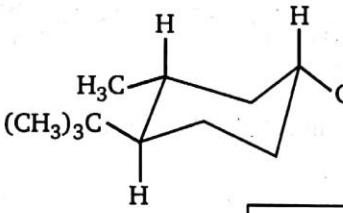
is least acidic because anion is anti aromatic and remaining compounds are arrange on the basis of % s characters.

28. (a) Acid base reactions favours equilibrium towards weak acid & weak base.

29. (d) Acid base reactions favours equilibrium towards weak acid & weak base.

30. (a) Cis molecule has non-zero dipole moment

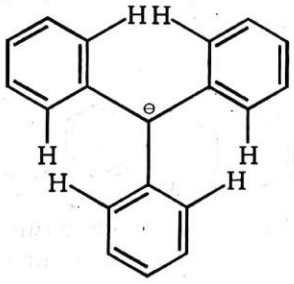
31. (c) Heat of combustion $\propto \boxed{\dfrac{1}{\text{Stability of molecule}}}$



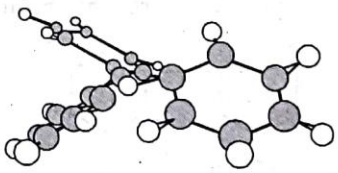
is most stable and so its heat of combustion will be least.

32. (c) Heat of combution $\propto \boxed{\dfrac{1}{\text{stability of molecule}}} \propto \boxed{\text{No. of 'C' atoms in molecule}}$

33. (d) Increasing the number of phenyl groups decreases the pK_a — this is what we expect, since we can delocalize the charge over all the rings. Notice, however, that each successive phenyl ring has less effect on the pK_a : the first ring lowers the pK_a by 8 units, the second by 7, and the third by only 1 unit. In order to have effective delocalization, the system must be planar. Three phenyl rings cannot arrange themselves in a plane around one carbon atom because the ortho-hydrogens clash with each other (they want to occupy the same space) and the compound actually adopts a propeller shape where each phenyl ring is slightly twisted relative to the next.

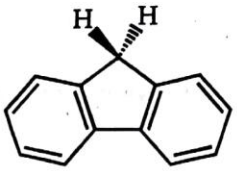


(The hydrogens in the ortho positions try to occupy the same space)

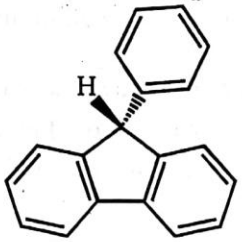


each phenyl ring is staggered relative to the next

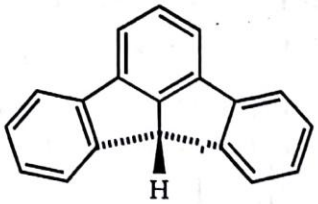
Even though complete delocalization is not possible, each phenyl ring does lower the pK_a because the sp^2 carbon on the ring is electron - withdrawing. If we force the system to planar, as in the compounds below, the pK_a is lowered considerably.



fluorene, pK_a 22.8
in the anion, the whole system is planar



9-phenylfluorene, pK_a 18.5
in the anion, only the two fused fings can be planar



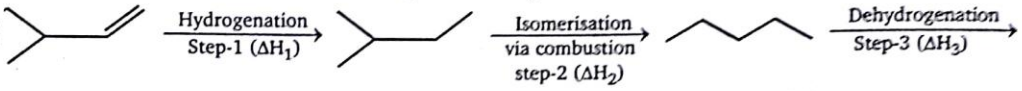
fluoradene pK_a 11
in the anion, the whole system is planar

34. (d) B.P. $\propto$ extent of H bonding $\propto$ surface area of molecule.

35. (d) Acidic strength $\propto$ stability of resulting anion.

36. (d) Degree of unsaturation $= (C+1) - \left(\frac{H+X-N}{2}\right)$

37. (b)

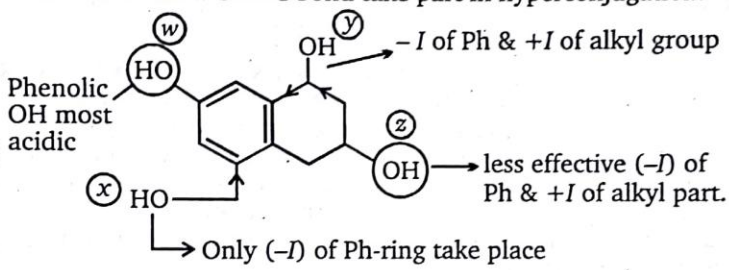


$\Delta H_1 = -30$ kcal/mol, $\Delta H_2 = (-784+782)$ kcal/mol, $\Delta H_3 = 28$ kcal/mol

$\Rightarrow \Delta H_1 + \Delta H_2 + \Delta H_3 = -4$ kcal/mol

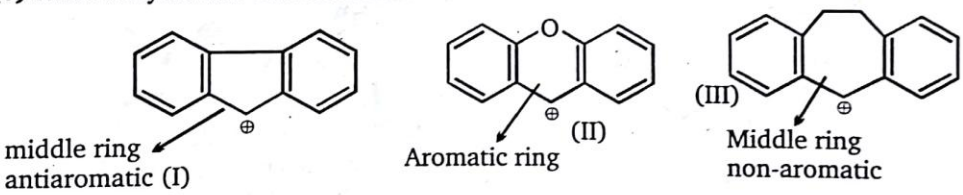
38. (b) $\propto$ 'H' atoms w.r.t. C = C bond take part in hyperconjugation.

39. (a)



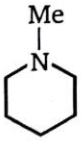
so order is $w > x > y > z$.

40. (c) After dehydration carbocations are formed.



II > III > I

41. (c)



does not participate in H-bonding so has least B.P.

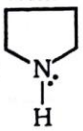
42. (d) In 'd' compound degree of unsaturation is different.

43. (c) Basic strength $\propto \frac{1}{\text{Acidic strength of conjugated acid}}$

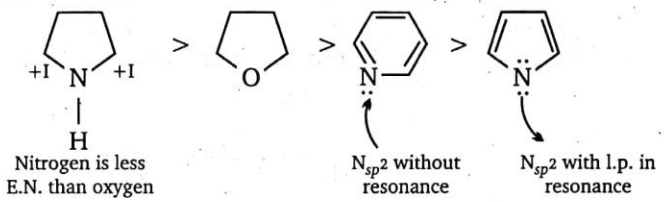
44. (c) Phenol is less acidic than H_2CO_3 so reaction does not favours in forward direction.

45. (c) With the increase in hydrocarbon portion solubility in H_2O decreases.

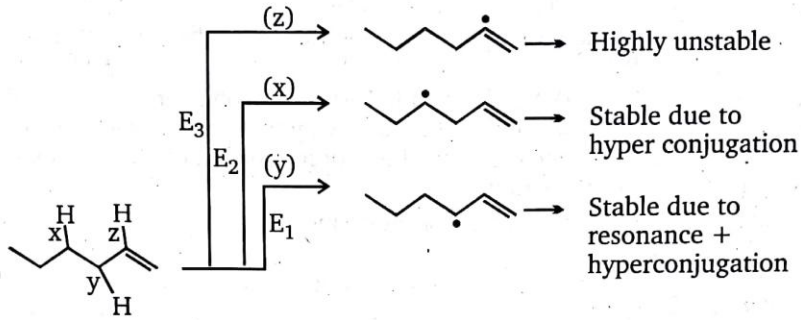
46. (d)



$\longrightarrow$ Most basic compound because it has sp^3 hybridised 'N' atom and has localised lone pair.



47. (b)



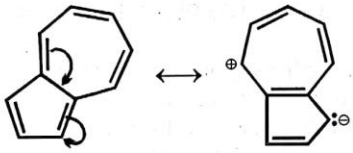
so bond dissociation energy order is

$$E_1 < E_2 < E_3 \quad i.e, \quad (z) > (x) > (y)$$

48. (d) $CH_3—\overset{\curvearrowleft}{O}—H \xrightarrow{Na(1mole\ or\ 23\ gm)} CH_3—O^{\ominus}Na^{\oplus} + \frac{1}{2}\,mole\,H_2 \uparrow$

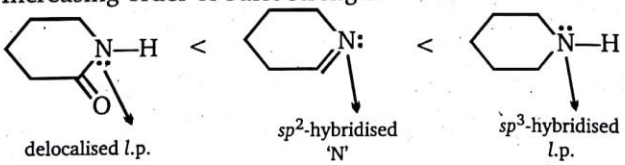
(*i.e.*, 11.2 L of H_2 gas at NTP)

49. (b)

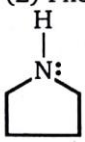


Quasi-aromatic and polar. (Both rings are aromatic)

50. (b) Increasing order of basic strength

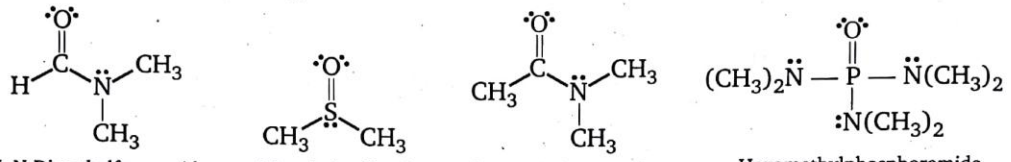


51. (d) (1) Alcohols are more acidic than amines.
(2) Phenols are more acidic than alcohols because of resonance.

52. (d)  is most basic has localised lone pair.

53. (d) **Polar Aprotic Solvents :** Aprotic solvents are those solvents whose molecules do not have a hydrogen atom that is attached to an atom of an electronegative element. A

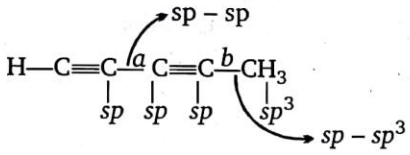
number of polar aprotic solvents have come into wide use by chemists because they are especially useful in S_{N^2} reactions. Several examples are the following:



N, N-Dimethylformamide (DMF) | Dimethyl sulfoxide (DMSO) | Dimethylacetamide (DMA) | Hexamethylphosphoramide (HMPA)

All of these solvents (DMF, DMSO, DMA, and HMPA) dissolve ionic compounds, and they solvate cations very well. They do so in the same way that protic solvents solvate cations : by orienting their negative ends around the cation and by donating unshared electron pairs to vacant orbitals of the cation :

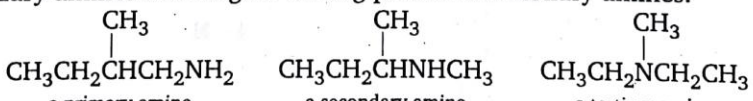
54. (a) With the increase in $-I$ of group, acidic strength increases.

55. (c) 

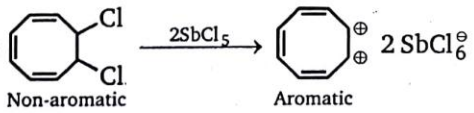
bond 'a' has more s characters.

56. (c) Primary and secondary amines also form hydrogen bonds, so these amines have higher boiling points than alkanes with similar molecular weights. Nitrogen is not as electronegative as oxygen, however, which means that the hydrogen bonds between amine molecules are weaker than the hydrogen bonds between alcohol molecules. Amines, therefore, have lower boiling points than alcohols with similar molecular weights.

Because primary amines have two N — H bonds, hydrogen bonding is more significant for primary amines than for secondary amines. Tertiary amines cannot form hydrogen bonds with each other because they do not have a hydrogen attached to the nitrogen. Consequently, if you compare amines with the same molecular weight and similar structures, primary amines have higher boiling points than secondary amines, and secondary amines have higher boiling points than tertiary amines.



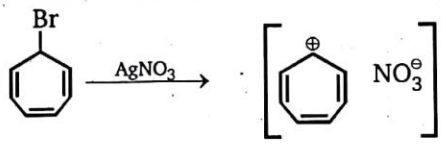
a primary amine b.pt. = 97°C | a secondary amine b.pt. = 84°C | a tertiary amine b.pt. = 65°C

57. (b) 

Non-aromatic | Aromatic

58. (b) 3-ethyl-2-methyl pentane has '8' 'C' atoms while  has only '7' 'C' atoms so it is not isomer of fomer compound.

59. (d) All are isomers of each other.

60. (c) 

Salt has high dipole moment & stable due to aromatisation and has high R.E.

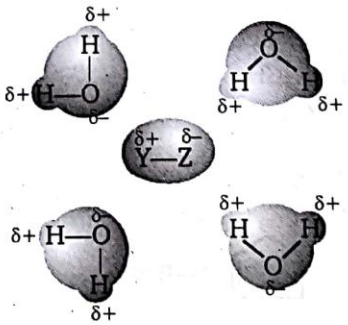
61. (b) $CH_3-CH_2-\overset{\oplus}{C}H-CH_3 > CH_2=CH-CH_2-\overset{\oplus}{C}H_2$

$5\alpha-H$ stabilises by hyper conjugation — $2\alpha-H$ & $-I$ of double bond so less stable

62. (b) B.P. $\propto$ surface area of molecule $\propto$ extent of inter molecular H-bonding $\propto$ dipole moment of molecule.

63. (d) The general rule that explains solubility on the basis of the polarity of molecules is that "like dissolves like." In other words, polar compounds dissolve in polar solvents and nonpolar compounds dissolve in nonpolar solvents. This is generally true because a polar solvent such as water has partial charges that can interact with the partial charges on a polar compound. The negative poles of the solvent molecules surround the positive pole of the polar solute, and the positive poles of the solvent molecules surround the negative pole of the polar solute. Clustering of the solvent molecules around the solute molecules separates solute molecules from each other, which is what makes them soluble. The interaction between a solvent and a molecule or an ion that is dissolved in that solvent is called solvation.

Because nonpolar compounds have no net charge, polar solvents are not attracted to them. In order for a nonpolar molecule to dissolve in a polar solvent such as water, the nonpolar molecule would have to push the water molecules apart, disrupting their hydrogen bonding. Hydrogen bonding is so strong that it excludes the nonpolar compound. In contrast, nonpolar solutes dissolve in non-polar solvents because of the van der Waals interactions between solvent and solute molecules.



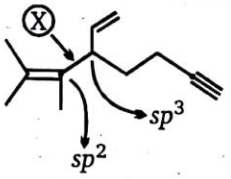
solvation of a polar compound $\overset{\delta+}{Y}-\overset{\delta-}{Z}$ by water

w.r.t. the question asked, 1-pentanol has maximum number of carbons, so it is least soluble in water. {extent of H-bonding decreases}

64. (c) Acidic strength $\propto K_a \propto \frac{1}{pK_a} \propto -I$ of groups attached.

65. (d) Stability of Alkene $\propto$ No. of 'α' H-atoms or more hyper conjugation.

66. (c)



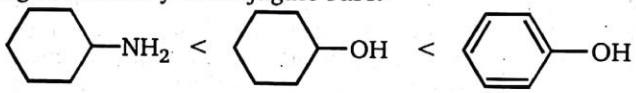
X-bond is formed by $sp^2 - sp^3$ overlapping

67. (a) Acidic strength $\propto$ –I; – H; – M $\propto \dfrac{1}{+I;\ +H;\ +R}$

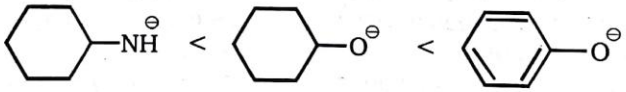
68. (a) $Ph-COOH + NaH\overset{*}{C}O_3 \rightleftharpoons H_2\overset{*}{C}O_3 + Ph-COO^{\ominus}$

$\underset{\text{unstable}}{H_2\overset{*}{C}O_3} \longrightarrow \overset{*}{C}O_2 \uparrow + H_2O$

69. (d) Order of Acidic strength $\propto$ stability of conjugate base.



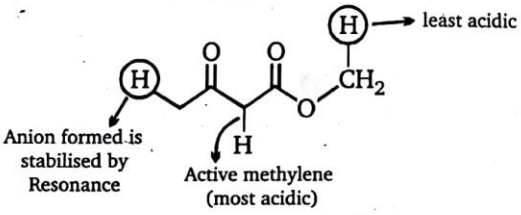
i.e.,



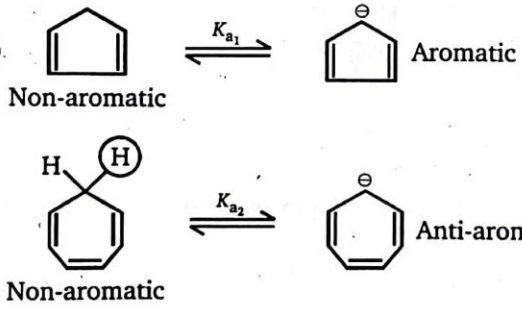
Resonance stabilized {phenoxide ion}

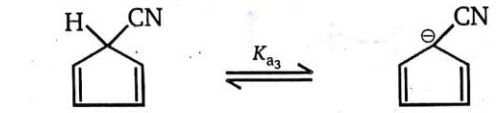
70. (b) Acidic strength $\propto -I \propto \dfrac{1}{+I}$

71. (a)



72. (d)





Aromatic & stabilises by –M of CN group.

so $K_{a_3} > K_{a_1} > K_{a_2}$

Acidic strength $\propto K_a$

73. (d)

+H of CH_3 decreases acidic strength

more acidic

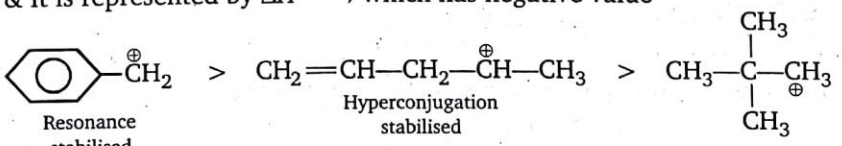
74. (d) $CH_2{=}\underset{\uparrow sp}{C}{=}C\begin{matrix}H\\Cl\end{matrix}$ $\quad H{-}\underset{\uparrow sp}{C}{\equiv}C{-}H \quad CH_3{-}\underset{\uparrow sp}{C}{\equiv}C{-}H$

75. (a)

76. (d) 'OH' group attached to 2° 'C' is known as 2° alcohol

77. (a) Heat of hydrogenation $\propto$ Unstability of Alkene
& It is represented by $\Delta H \longrightarrow$ which has negative value

78. (a)

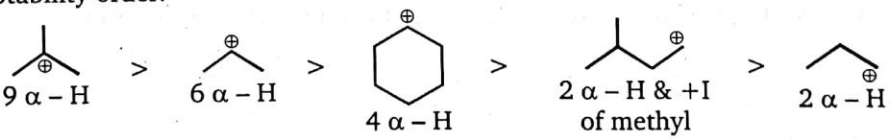


Resonance stabilised

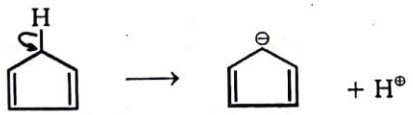
Hyperconjugation stabilised

Inductive effect stabilised

79. (b) Stability order.



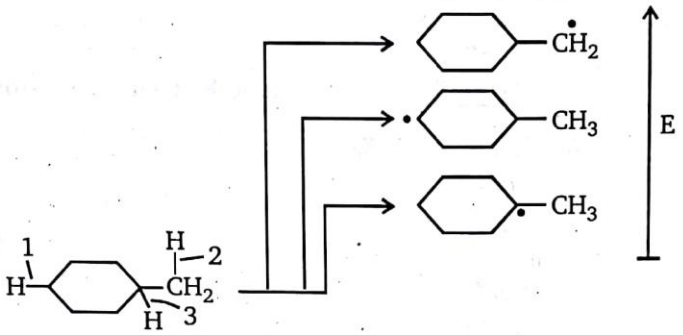
80. (a)



Non-aromatic

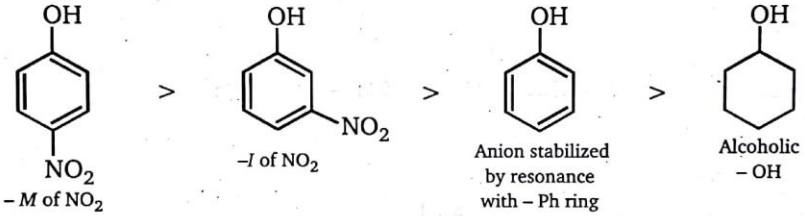
Aromatic

81. (d)



So order of bond energy is 3 < 1 < 2.

82. (d)



83. (d) Acidic strength ∝ electron withdrawing groups at acid.

84. (c) Acidic strength $\propto -M \propto \frac{1}{+M}$

85. (b) $H-\overset{+}{\underset{..}{O}}=C=\overset{\ominus}{N}: \longleftrightarrow H-\underset{..}{\ddot{O}}-C\equiv N:$
are resonating structures.

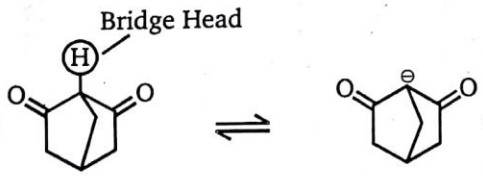
86. (a) Equilibrium favour formation of weak acid and weak base.

87. (a) F – H - - - F is strongest H-bonding.

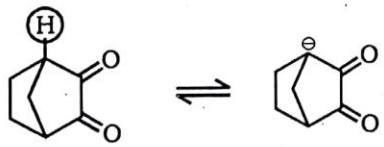
88. (b) Extent of H-bonding ∝ ⊕ δ charge on H.

89. (a) $-\overset{O}{\overset{\|}{C}}-O(H)$ is most acidic 'H' because resulting anion has 2-equivalent R.S.

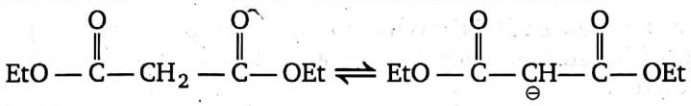
90. (d)



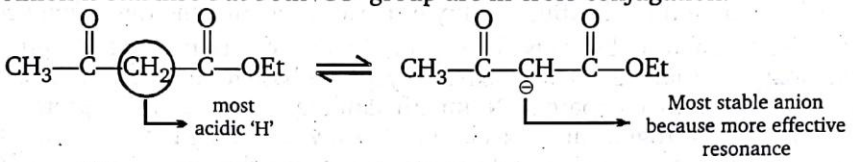
⟶ Unstable. No resonance only –I of 'CO' group. (Bredt's rule)



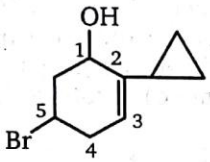
Unstable 'NO' resonance.



Anion is stabilise but both 'CO' group are in cross conjugation.

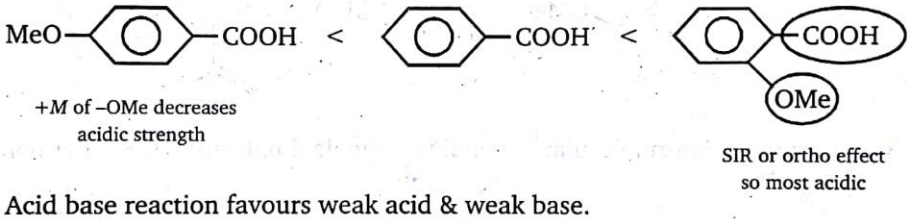


91. (b)



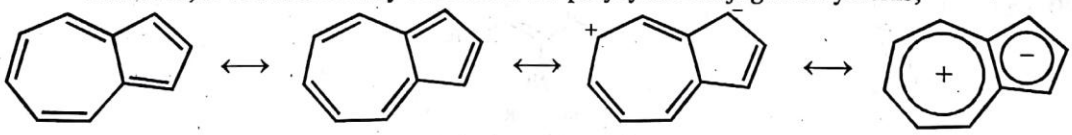
Priority sequence is alcohol > alkene > halide.

92. (c)



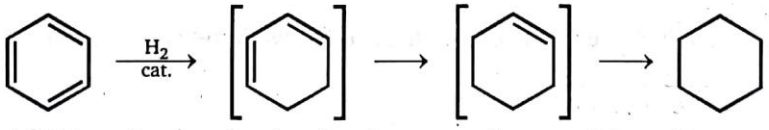
93. (d) Acid base reaction favours weak acid & weak base.

94. (d) Polycyclic systems : Huckel's $(4n + 2)$ rule applies to monocyclic systems. The rule, however, is not necessarily successful for polycyclic conjugated systems;



the $(4n + 2)$ rule should be applied to the peripheral (conjugated) π-electrons. The five-membered ring has five and the seven-membered ring has seven π-electrons (two π-electrons are common to both rings). If one π-electron is transferred from the seven - to the five - ring, each ring will now have a closed shell of six π-electrons (cf. naphthalene). In this condition, the molecule will have a dipolar structure, and this has been shown to be the case from dipole - moment measurements. Azulene also behaves chemically as an aromatic compound.

95. (d)



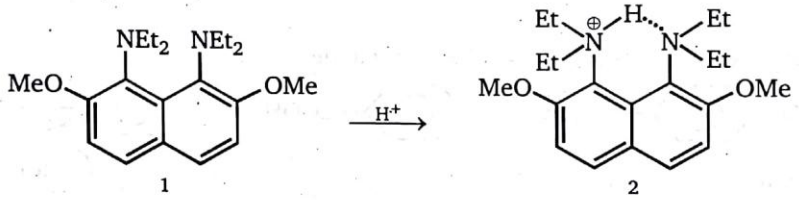
Addition of one molecule of hydrogen produces cyclohexadiene, in which almost all of the resonance energy of benzene has been lost. Hence the activation energy of this step is much greater than that required for each succeeding step, in which the double bonds behave like their acyclic analogues. Thus we have a multi-step reaction in which the first step is ratedetermining. This means that the conditions required for the first step are more vigorous than those required for the successive steps (all steps involve the addition of one

molecule of hydrogen). Because of this, it is not possible to stop the reaction proceeding to complete reduction of benzene to cyclohexane, and consequently it is not possible to isolate the intermediates.

96. (d) Like dissolve like concept.

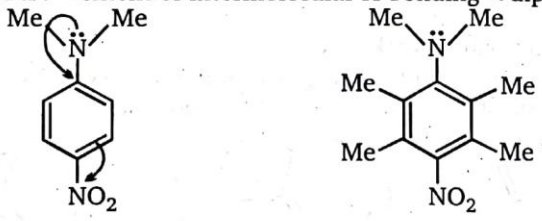
97. (b) Steric effects can indirectly affect acidity or basicity by affecting the resonance.

Steric effects can also be caused by other types of strain. 1,8-bis(diethylamino)-2, 7-dimethoxynaphthalene (1) is an extremely strong base for a tertiary amine (pK_a of the conjugate acid = 16.3; compare N, N-dimethylaniline , pK_a = 5.1), but proton transfers to and from the nitrogen are exceptionaly slow ; enough to be followed by a uv-spectrophotometer. 1 is severely strained because the two nitrogen lone pairs are forced to be near each other. Protonation relieves the strain : one lone pair is now connected to a hydrogen, which forms a hydrogen bond to the other lone pair (shown in 2). The same effects are found in 4, 5-bis (dimethylamino) fluorene (3) and 4, 5-bis(dimethylamino).



98. (d) B.P. ∝ extent of intermolecular H-bonding ∝ dipole-dipole attraction or H-bonding

99. (a)

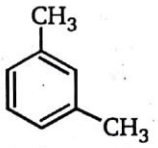


less SIR
so more effective resonance

more SIR
less effective resonance
so has less dipole.

100. (b) Basic strength $\propto \dfrac{1}{\text{acidic strength of conjugated acid.}}$

101. (b)



is thermodynamically more stable due to more effective hyperconjugation.

102. (d) Stability $\propto \dfrac{1}{\text{heat of combution}}$

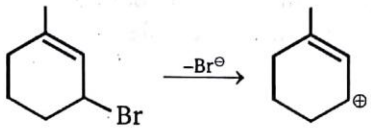
103. (a) Heat of combution ∝ No. of 'C' atoms $\propto \dfrac{1}{\text{Branching}}$ when 'C' atoms are same.

104. (a) 1,3 & 4 compounds are 3-ethyl-4-methyl heptane.

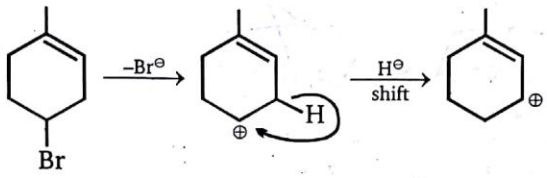
105. (c) Acidic strength ∝ Stability of resulting anion.

106. (c) Basic strength $\propto \dfrac{1}{\text{Stability of anion}} \propto \dfrac{1}{\text{Dispersion of} -\text{ve charge}}$

107. (c)



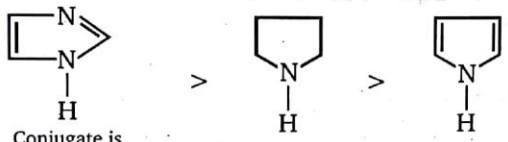
intermediate



same intermediate as above

108. (b) Acidic strength $\propto -I$ of groups attached to acid.

109. (c)

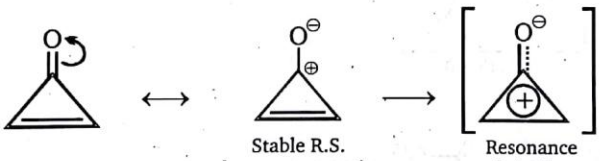


Conjugate is resonance stabilized therefore most basic

(Pyrole are weak base)

(Lone pair is involved in resonance)

110. (c)



Stable R.S. because aromatic

Resonance hybrid

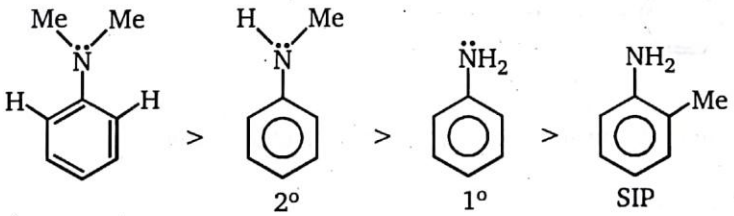
so molecule has high dipole.

111. (d) (a) $\underset{2^\circ}{Me_2NH} > \underset{1^\circ}{MeNH_2} > \underset{3^\circ}{Me_3N} > NH_3$ if ($R = -$Me or Butyl) (in polar protic solvent)

(b) $2^\circ > 3^\circ > 1^\circ > NH_3$ if ($R = -$Et)

(c) $3^\circ > 2^\circ > 1^\circ > NH_3$ (Gas phase)

112. (c)



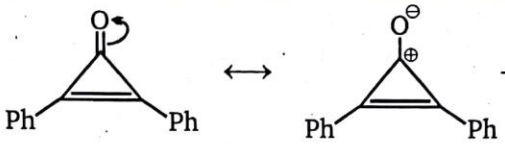
2° 1° SIP

Due to $+I$ of effect of methyl basic strength increases in 3° amine.

113. (c) $(CH_3)_2C{=}C(CH_3)_2$ has highest C — C bond length (B.L.); Because it has maximum hyperconjugation.

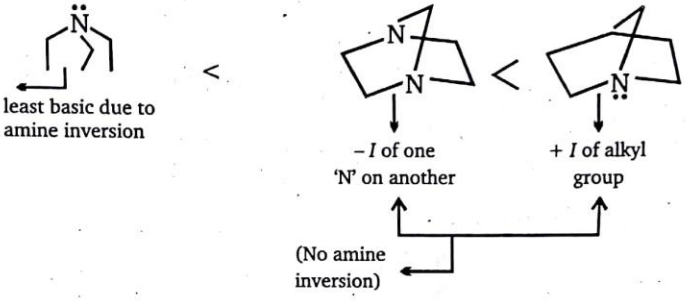
More single bond character by hyperconjugation.

114. (c)

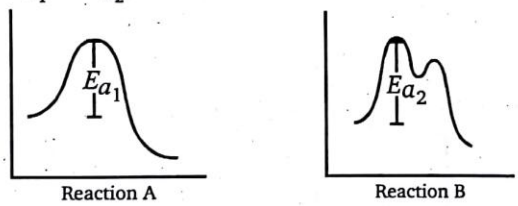


Stable R.S. because aromatic so compound has highest dipole

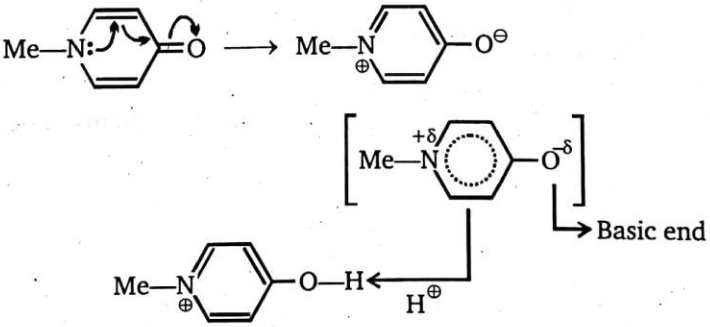
115. (c)



116. (a) $E_{a_1} < E_{a_2}$ and reaction is exothermic.



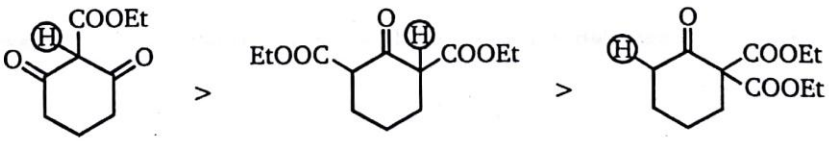
117. (a)



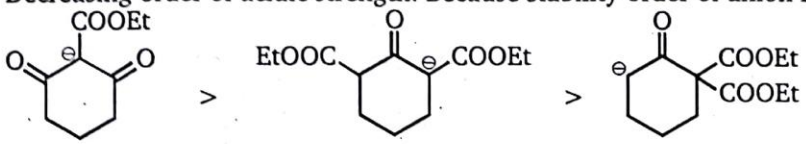
118. (d) $E = h\nu = \frac{hc}{\lambda}$; λ max means less energy, ∴ most stable dienes.

119. (c)  N—*t*-Bu . See 17(a) also.

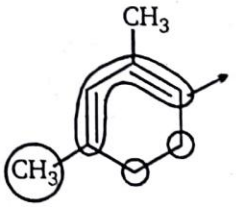
120. (c)



Decreasing order of acidic strength. Because stability order of anion is

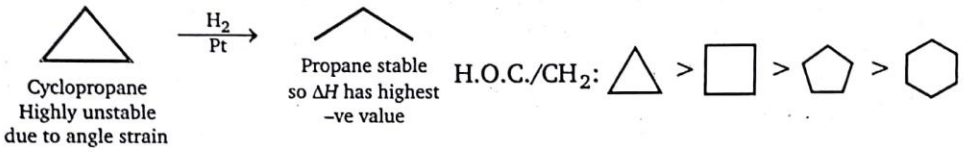


121. (c)

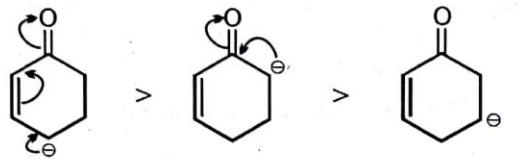


Resonance stabilised C = C & has 10 α – H so stabilise by hyperconjugation.

122. (a)

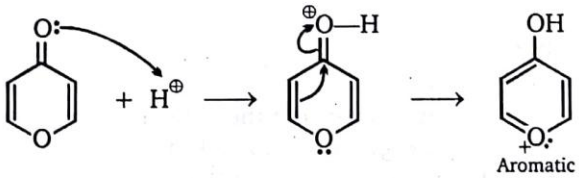


123. (c) Stability of anion is



$$\text{Basic strength} \propto \frac{1}{\text{stability of anion}}$$

124. (c)



125. (d) Stability of $C^{\oplus}$ ∝ extent of conjugation

126. (b) Stability of $C^{\oplus}$ ∝ extent of conjugation

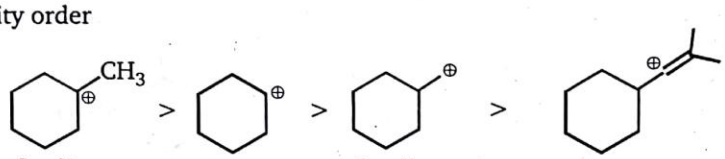
127. (a) $CH_2{=}\underset{\oplus}{C}{-}H$ (sp) It is vinyl cation.

128. (d) $H_2C{=}CH{-}H \longrightarrow H_2C{=}\dot{C}H$

↑ strong bond; unstable vinyl radical

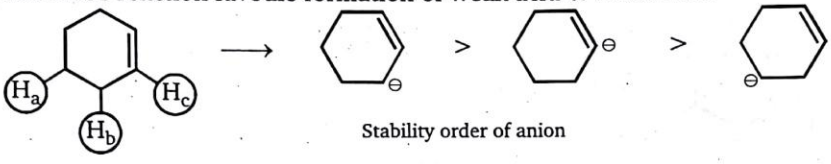
therefore it is endothermic.

129. (b) Stability order



130. (a) Acid base reaction favours formation of weak acid & weak base.

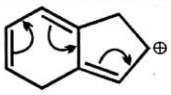
131. (c)



So acidic strength order $H_b > H_c > H_a$

132. (d) Acid base reaction favours weak acid & weak base.

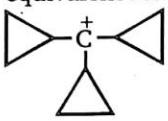
133. (c)



Stabilised by extended conjugation.

134. (d) The more nearly equivalent the resonance contributors are in structure, the greater the resonance energy. The carbonate dianion is particularly stable because it has three equivalent resonance contributors.

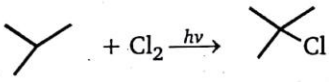
135. (a)



most stable $C^{\oplus}$ due to 'σ' resonance.

136. (d) Heat of hydrogenation or heat of combution $\propto \dfrac{1}{\text{Stability of alkene}}$

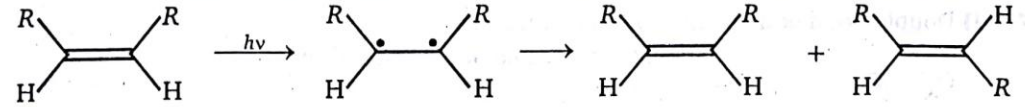
137. (c)



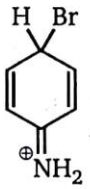
(i) C — Cl Bond energy is highest.

(ii) and 3° free radical is most stable.

138. (d) It is possible to interconvert cis and trans alkenes, but the π-bond must be broken first. This requires a considerable amount of energy - around 260 kJ mol^{-1}. One way to break the π-bond would be to promote an electron from the π-orbital to the π*-orbital. If this were to happen, there would be one electron in the bonding π-orbital and one in the antibonding π*-orbital and hence no overall bonding. Electromagnetic radiation of the correct energy could promote the electron from HOMO to LUMO. The correct energy actually corresponds to light in the ultraviolet (UV) region of the spectrum. Thus, shining UV light on an alkene would promote an electron from its bonding π-molecular orbital to its antibonding π*-molecular orbital, thereby breaking the π-bond (but not the σ-bond) and allowing rotation to occur.



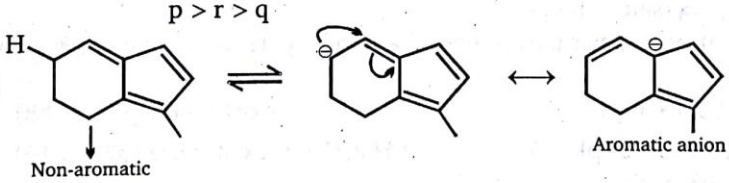
no rotation is possible (*cis* isomer) — UV light breaks π bond rotation is now possible — mixture of both isomers formed (*cis*) (*trans*)

139. (c)  Most stable R.S. because cation has complete octet.

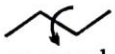
140. (c) Acidic strength of acid $\propto \dfrac{1}{\text{Basic strength of conjugated base}}$

141. (a) (1) Neutral R.S. are most stable.
(2) With the increase in charge separation stability of R.S. decreases.
So stability order is
I > II > III

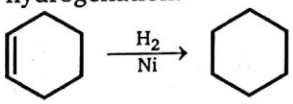
142. (d) (i) –ve charge on electronegative atom increases stability.
(ii) —C ≡ N system is more stable than C = C = N system. So stability order is
p > r > q

143. (b) 

"So" above compound is acidic.

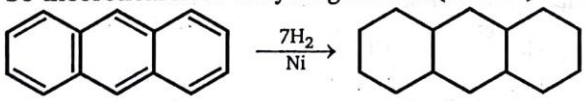
144. (c)  Compound has lowest steric crowding during rotation and doesn't have partial or complete double bonded characters so rotational energy barrier is lowest.

145. (a) Resonance energy = Theoretical heat of hydrogenation – Experimental heat of hydrogenation.



; $\Delta H = -28.6$ kcal/mol

So theoretical heat of hydrogenation (H.O.H.) for anthracene is

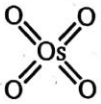


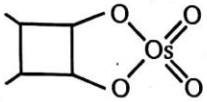
Theoretical $\Delta H = 7 \times (-28.6) = -200.2$ kcal/mol
Experimental $\Delta H = -116.2$ kcal/mol
Resonance energy = 84 kcal/mol

146. (b) Degree of unsaturation = 1 $\quad DU = (C+1) - \left(\dfrac{H + X - N}{2}\right)$

We ignore the oxygen in such calculations.

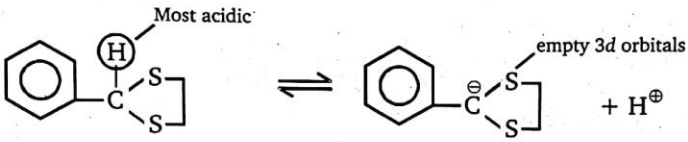
147. (d) Double bond equivalent = Degree of unsaturation
= No. of double bond + no. of rings

148. (b)  → has +8 oxidation state.

 → has +6 oxidation state.

149. (a) Active methylene has most acidic 'H' atom.

150. (b)



Stabilise by simple resonance
& 'd' – orbital resonance.

151. (d) According to Henderson equation.

$$pH = pK_a + \log \frac{[salt]}{[Acid]}$$

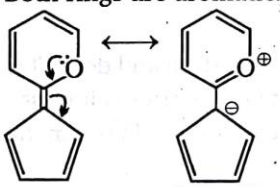
If $pH > pK_a \Rightarrow [salt] > [acid]$

or Concentration of basic part is more than acidic part while if $pH < pK_a$; (Acidic part) > (Basic part).

Thus, for CH_3COOH at pH = 7 ; $CH_3COO^{\ominus}$ exist more ($pK_a = 4.8$)

& for CH_3CH_2OH at pH = 7 ; CH_3CH_2OH exist more ($pK_a = 16$)

152. (b) Both rings are aromatic.

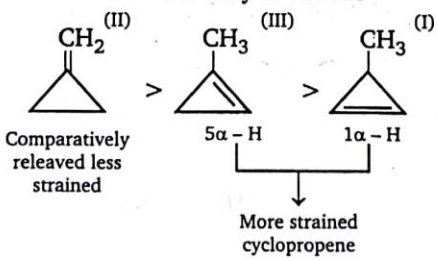


(aromatic)

153. (a) Peak of potential energy (P.E.) is the transition state (T.S.).

154. (a) Heat of hydrogenation $\propto \frac{1}{\text{stability of alkene}}$.

Stability:



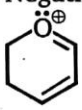
∴ Heat of hydrogenation (H.O.H.) : (I) > (III) > (II)

155. (c) Heat of hydrogenation $\propto \dfrac{1}{\text{stability of alkene}}$.

156. (c) $\overset{\ominus}{C}H_2—\overset{\oplus}{\underset{..}{O}}:$ is highly unstable. (due to incomplete octet of oxygen).

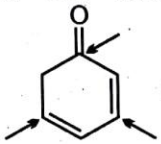
157. (c) Maximum co-valency of N is 4.

158. (b) Negative charge on oxygen is more stable than on carbon.

159. (c)  It has complete octet for all atoms.

160. (c) Resonance energy of extended conjugation is more.

161. (b) Structure III & I has complete octet for all atoms but III is more stable than I because $N^{\oplus} > O^{\oplus}$ is the stability order.

162. (c)  Since conjugate addition can also take place.

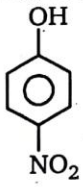
163. (a) More the double bond character, more will be the rotational barrier energy.

164. (a) More the double bond character, more will be the rotational barrier energy.

165. (c) Lone pair will not participate in resonance because of bredt's rule.

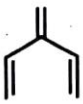
166. (a) Homologes have same functional group and consecutive member has difference of molecular weight by 14 and molecular formula by $—CH_2$.

167. (d) $-M \propto$ acidic strength



($-M$) stabilizes conjugate anion.

168. (c) $+I \propto \dfrac{1}{\text{acidic strength}}$ $—CH_3$ has $+I$ effect which destabilizes conjugate anion.

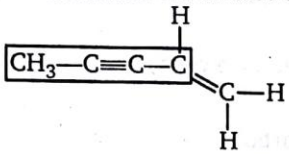
169. (d) 

cross conjugation in which two group not in conjugation with each other but it is in conjugation with 3rd group.

170. (b)

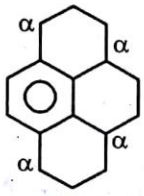
I	>	II	>	III	>	IV
More covalent bond complete octet neutral		More covalent bond complete octet		Less covalent bond incomplete octet ($O^{\ominus} > C^{\ominus}$) stability		Positive charge on highly electronegative O-atom and negative charge on less electronegative C-atom

171. (a) In resonance we cannot change position of atom.

172. (c) 

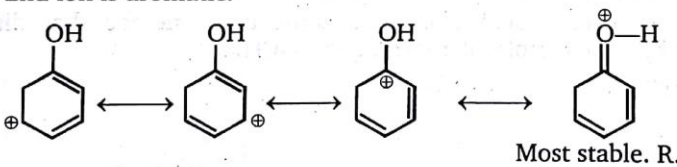
4-carbon are linear

173. (c) II (More resonating structure) > III (resonance) > I (no resonance) > IV (anti-aromatic carbocation)

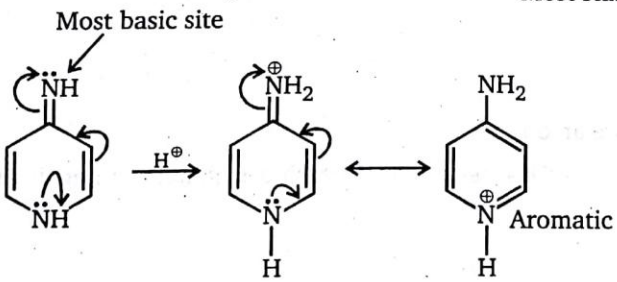
174. (c) 

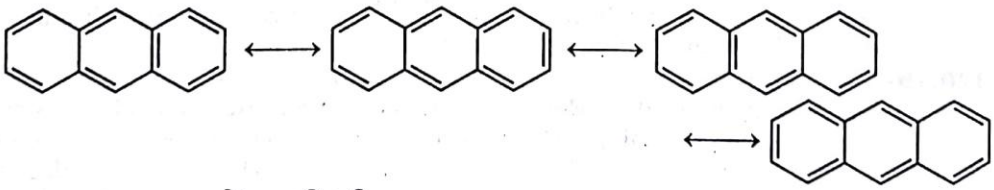
(6α-H)

175. (b) (ii) and (iii)
2nd ion is aromatic.

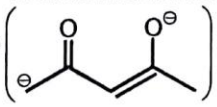
176. (b) 

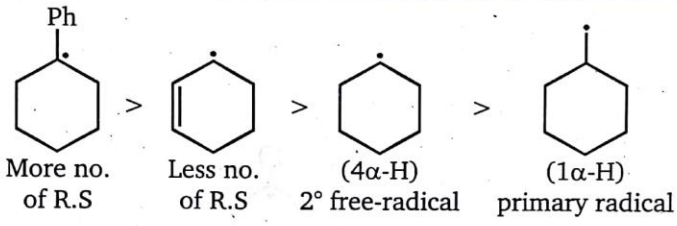
Most stable. R.S

177. (c) 

178. (c) 

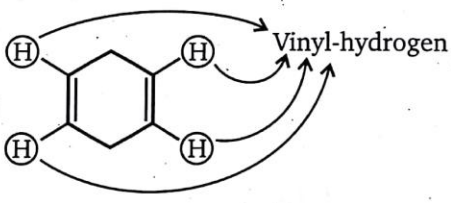
179. (e) Base stronger than $>-O^{\ominus}Na^{\oplus}$ is used in this reaction.

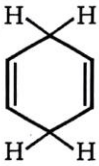
180. (d) Stronger base reaction with $H^{\oplus}$  is strong base.

181. (c) 

182. (b) 

(tert-butyl carbonium ion).

183. (b) 

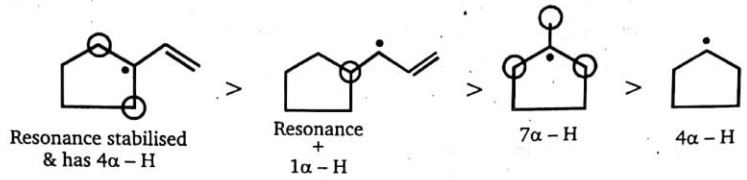


α-hydrogen are allyl.

Level-2

Comprehension-1

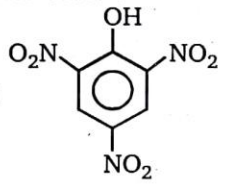
Stability order.

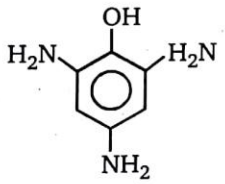


Comprehension-2

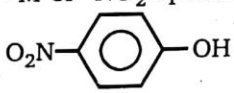
$c > b > a$, acidity $\propto -M \propto \frac{1}{+M}$

Comprehension-3

(A)  is most acidic due to $-M$ of 3 NO_2 groups.

(B)  $+M$ of $-NH_2$ group decreases acidic strength.

(C) $-M$ of $-NO_2$ operates at para position so

 more acidic.

(D) $-\overset{O}{\overset{\|}{C}}-Me$ at para-position has $-M$ so increases acidic strength.

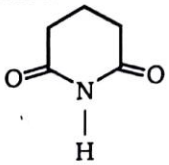
Comprehension-4

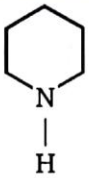
(A) Compounds having L.P. or –ve charge on electronegative atoms are known as H-bond acceptor.

(B) Compounds having L.P. or –ve charge & have active 'H' attached to electronegative elements are known as H-bond acceptor & donor.

(C) Compounds do not have above properties cannot form H-bond.

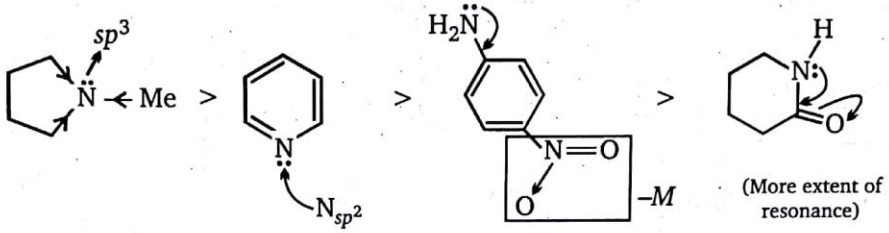
Comprehension-5

(A) **(d)**  (Resonance stabilised anion after deprotonation)

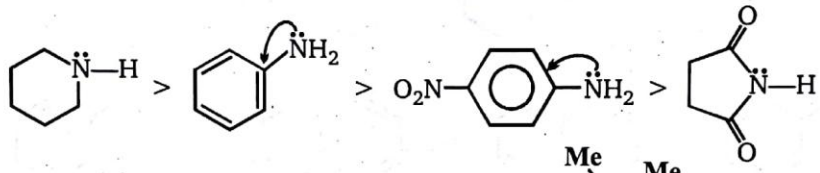
(B) **(a)**  (localised lone pair of electron so readily available for coordination.)

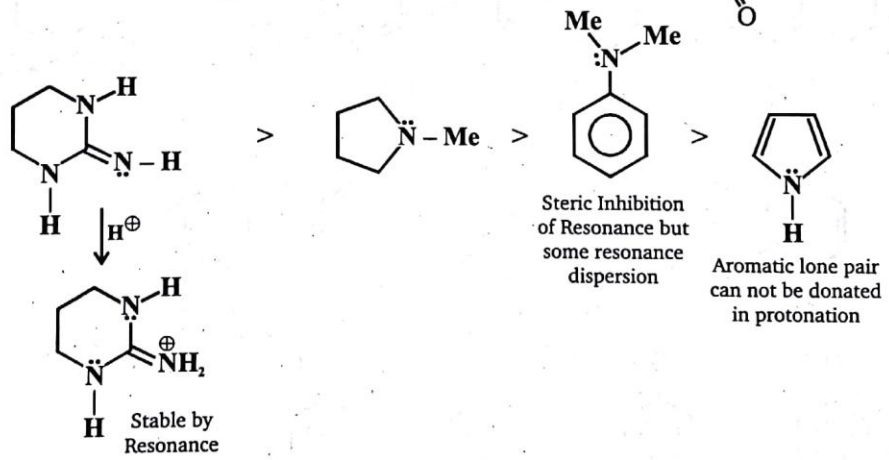
6. C < B < A ; More is the resonance, lesser will be the energy of delocalising electrons.

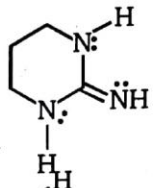
7. a-2, 1, 4, 3; b-1, 2,3,4; c-3,4,1,2; d-3,2,4,1

(a) 

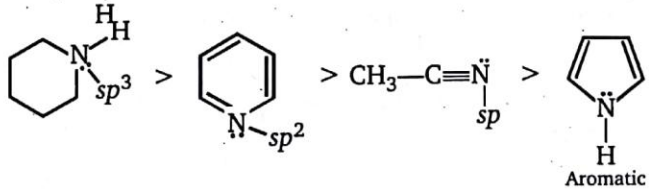
E.N ($N_{sp} > N_{sp^2} > N_{sp^3}$) due to % *s*-character.

(b) 

(c) 

or 

due to +*M* of 2 amino group, electron density on 3rd nitrogen is increasing its basicity.

(d) 

E.N $N_{sp} > N_{sp^2} > N_{sp^3}$

8. a-iv>ii>i>iii, b-iii>iv>i>ii

Comprehension-9

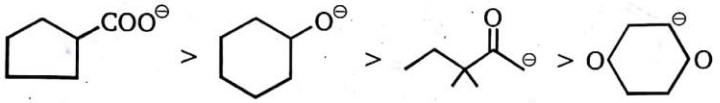
9. (a) 4, 2, 3, 1; (b) 3, 1, 4, 2; (c) 2, 1, 3, 4; (d) 2, 3, 4, 1

(a) Acidic strength $\propto -I$

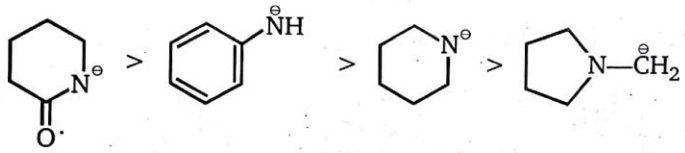
$$\text{Acidic strength} \propto \frac{1}{\text{distance of group from reaction centre}}$$

(b) Acidic strength $\propto$ Stability of conjugated base.

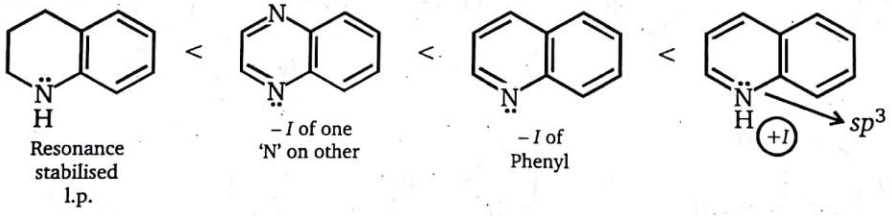
(c)



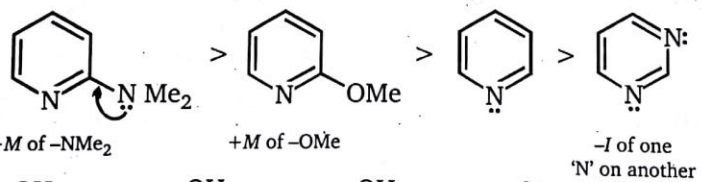
(d) Stability of conjugated base.



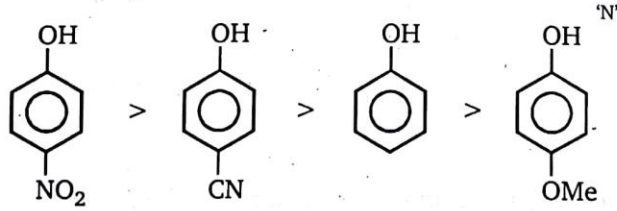
10. (A) (i)



(ii)

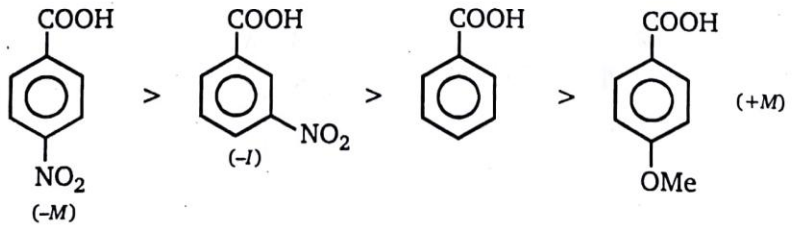


(B) (i)



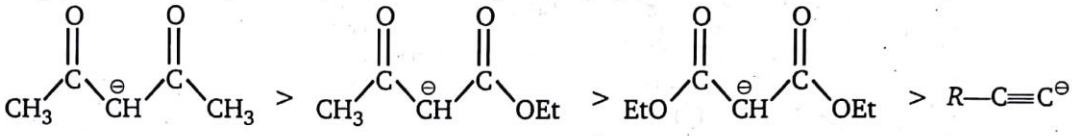
L → R
(1) –M decreases (2) +M Increases.

(ii)



Comprehension-11

(A) Acidic strength $\propto$ –I, $-M \propto$ stability of conjugate base.



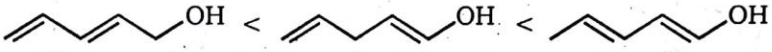
$$\text{Acidic strength} \propto \frac{1}{\text{distance of group from reaction centre}}$$

(B) Acidic strength $\propto$ No. of $-I$ groups $\propto \frac{1}{+I}$

a-3,2,1,4; b-2,1,4,3; c-2,1,3,4; d-2,4,3,1

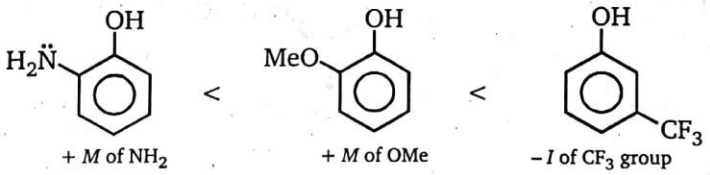
12. Acidic strong $\propto$ stability of conjugate base.
Stability of conjugate base $\propto -M$ and $-I$ on group.

13. (A)

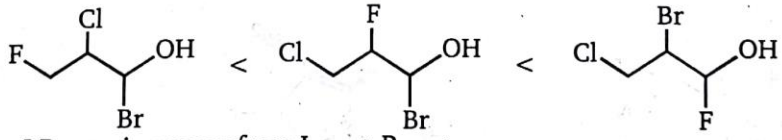


Acidic strength on the basis of stability of conjugate base.

(B)

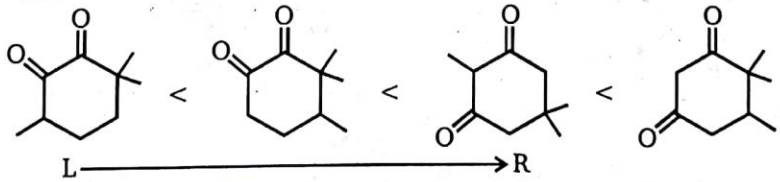


(C)



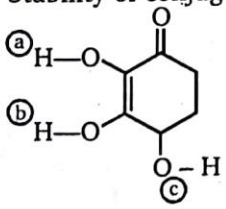
$-I$ Power increases from L $\longrightarrow$ R

(D)



Stability of conjugate base increases.

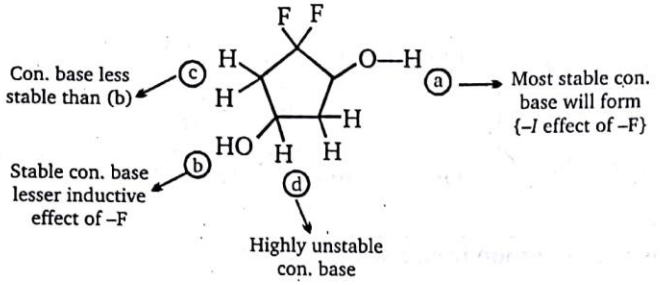
14. (A)



b > a > c

Above order is on the basis of stability of resulting conjugate base.

(B)

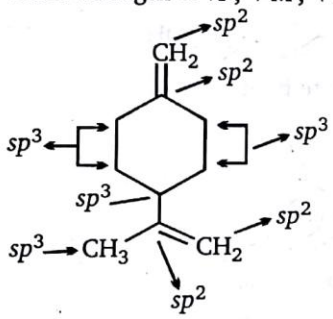


a > b > c > d

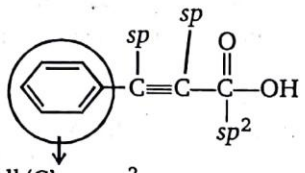
15. A-1,3,4,6,7,8,9 ; B-2,5 ; C-6 ; D-3,4,6,7,9 ; E-6,8,9 ; F-6 ; G-7 ; H-9 ; I-4, 7

16. Acidic strength $\propto -I$; $-M$, $-$H groups on acidic centre.
Basic strength $\propto +I$; $+M$, $+$H groups on basic centre.

17. (a)

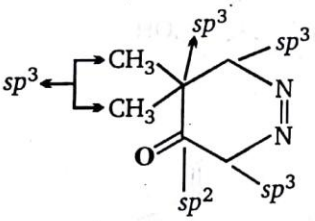


(b)

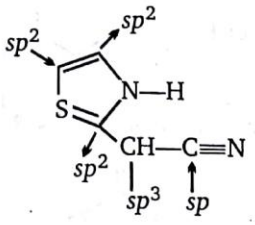


All 'C' are sp^2

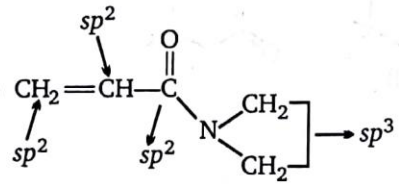
(c)



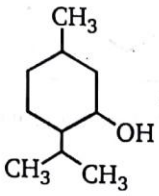
(d)



(e)

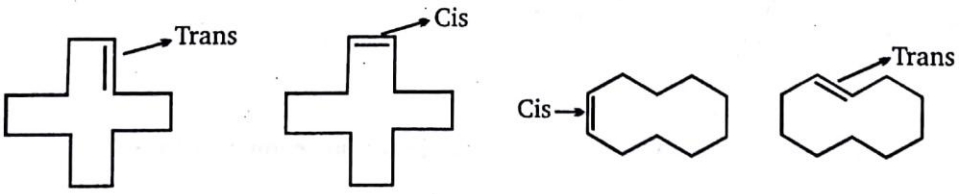


(f)



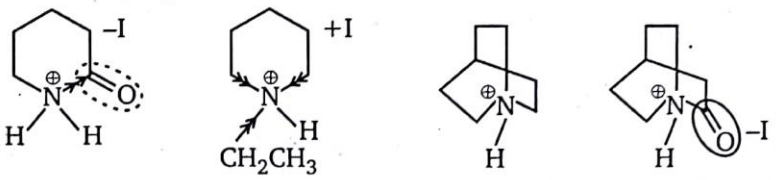
All 'C' atoms are sp^3-hybridised

18.



[Heat of combustion (H.O.C.) $\propto$ no. of carbon atoms $\propto$ 1/stability]

19. Acidity $\propto \dfrac{1}{pK_a}$



(+I) (+I) 2(+I) and 1(–I)

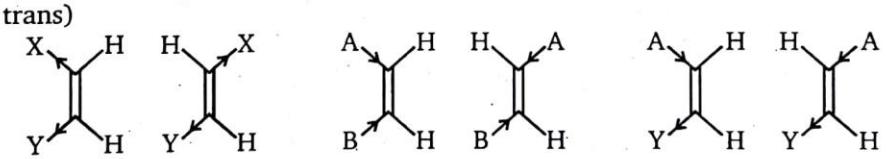
K_a **order :** (1) > (4) > (2) > (3)

20. Consider angle strain and chair structure of six membered ring.

21. Consider hyperconjugation and resonance of C = C in all the parts.

22. a → p, s ; b → q, r ; c → q, s ; d → p, s

23. As shown in fig. the relation of dipole moment to configuration is quite direct. If in a 1, 2 -disubstituted alkene (*X*CH = CH*Y*) *X* and *Y* are both electron donating or both electron withdrawing, the dipole moment of the cis isomer will generally be sizeable, whereas that of the trans isomer will be small or zero (*i.e.*, $\mu_{cis} > \mu_{trans}$). If, on the other hand, *X* is electron donating and *Y* is electron withdrawing, or vice versa, $\mu_{trans} > \mu_{cis}$. In tribustituted alkenes *X*CH = C*YZ* the situation is less clear cut, though if *Z* is alkyl and *X* and *Y* are halogen or other strongly electron withdrawing groups, the disposition (cis or trans)



$\mu_{cis} > \mu_{trans}$ *e.g.*, CHBr = CHBr μ_{cis} = 1.35 D ; μ_{trans} =0

$\mu_{cis} > \mu_{trans}$ *e.g.*, $CH_3CH = CHCH_3$ μ_{cis} = 0.25 D ; μ_{trans} =0

$\mu_{trans} > \mu_{cis}$ *e.g.*, $CH_3CH = CHCN$ μ_{cis} = 4.08 D ; μ_{trans} = 4.53

of *X* and *Y* will be decisive. Except for the case of cyclooctene, configuration can be inferred from dipole moment where known, though in some cases the differences are perhaps uncomfortably small. In the case of 1-chloro-2-iodoethylene the original, seemingly unreasonable order of dipole moments was later reversed. In trans-cyclooctene, the normal C_{2h} symmetry of trans–*X*CH = CH*X* is reduced to at most C_2; therefore the compound can have a dipole moment, whereas compounds of C_{2h} symmetry cannot. That the moment is so large may be related to the highly twisted nature of the double bond (torsion angle between 136° and 157°)

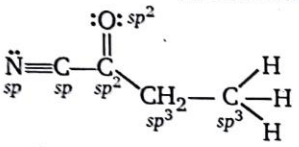
Dipole Moments and the Dipole Rule[a] :

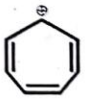
As for as the question is concerned, melting point of (*trans* > *cis*)because *trans* form is more symmetrical than *cis* form.

24. (A) 7 α H in (b) (B) 6 α H in (c) (C) 7 α H in (a) (D) 8 α H in (c)
(E) 6 α H + no van der Waal repulsion in (a) (F) extended conjugation upto 3π-bond in (b)
(G) octet complet is more stable in (d).

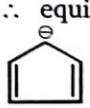
26. Part –(A) ⟶ *d*-orbital resonance in (c)
Part –(B) ⟶ –*M* effect of two keto group in (b)

Part –(C) ⟶ –*M* effect of $-NO_2$ in (b)
Part –(D) ⟶ –*M* effect of two keto group in (b)
Part –(E) ⟶ two equivalent resonating structure in (b)
Part –(F) ⟶ Alcohol are most acidic in (a)
Part –(G) ⟶ –*I* effect of $-\overset{\oplus}{N}H_3$ in (b)
Part –(H) ⟶ –*M* of $-NO_2$ will operate from ortho and para-position in (c)
Part –(I) ⟶ Conjugate base is resonace stabilized in (b)
due sigma bond formation from ortho position rotation is restricted and effective delocalization taking place.

27. 

28. (a)  (Aromatic) (stable tropylinium ion)

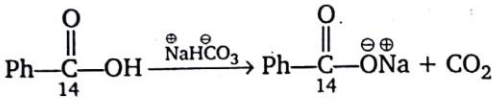
∴ equilibrium in forward direction.

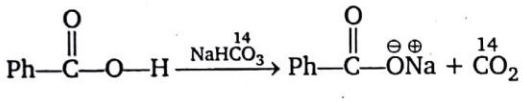
(b)  (Aromatic) (stable)

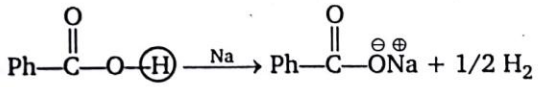
∴ equilibrium in backward direction.

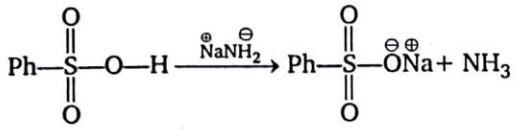
29. (a) $NaHCO_3$ will not react with phenol
(b) Na reacts with compound containing acidic hydrogen
(c) NaOH reacts with compound containing acidic hydrogen
(d) $NaNH_2$ reacts with compound containing acidic hydrogen

30. $pK_a \propto \dfrac{1}{\text{acidic strength}} \propto$ -*I* effect of attached groups.

31. (a) 

(b) 

(c) 

(d) 

32. (b) 90 ; Gas $(A) = \overset{14}{C}O_2$; Gas $(C) = CO_2$; $46 + 44 = 90$

33. $\underset{(pK_a = 4.2)}{PhCOOH} + NaHCO_3 \longrightarrow \underset{(pK_a = 6.4)}{PhCOONa^{\oplus}} + \underset{(A)}{H_2CO_3\ (H_2O + CO_2)}$

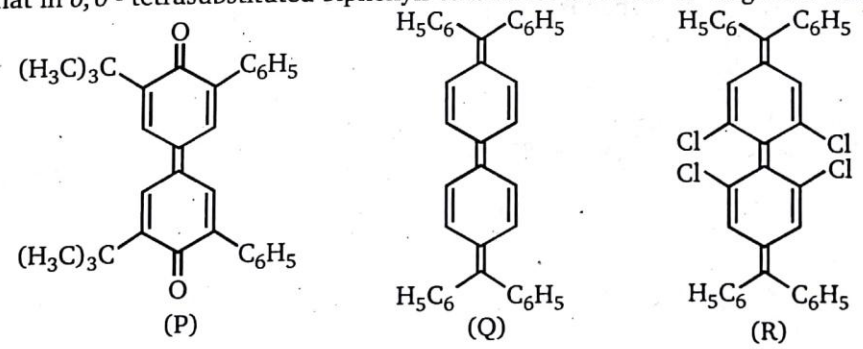
$\underset{(pK_a = 25)}{2Ph-C\equiv CH} + 2Na \longrightarrow 2Ph-C\equiv C^{\ominus}Na^{\oplus} + \underset{(B)}{(H_2\uparrow)}$

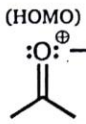
$\underset{pK_a = 10}{PhOH} + NaNH_2 \longrightarrow PhONa + \underset{(C)}{NH_3}$

$\underset{pK_a = 16}{ROH} + NaH \longrightarrow RONa + \underset{(D)}{H_2}$

$\therefore\ A + B + C + D = 44 + 2 + 17 + 2 = 65$

34. In some alkenes, steric crowding in the planar state may be so severe that the latter is no longer an energy minimum but becomes an energy barrier with the ground state becoming twisted. In this context the compounds in figure are of interest. The drop in rotational barrier from stilbene (42.8 kcal mol^{-1}, 179 kJ mol^{-1}) to compound P (21.1 kcal mol^{-1}, 88.3 kJ mol^{-1}) to compound Q ("small barrier", cf.) may be explained by increasing stabilization of the triplet biradical transition state. However, the "negative" barrier in R, that is, the fact that the stable ground state of R is non-planar and that the planar conformation represents the transition state for rotation requires a different explanation ; the difference between Q and R is presumably due to the steric interaction of the four chlorine substituents in the planar conformation of R. This situation resembles that in o, o'- tetrasubstituted biphenyls to alkenes with low or "negative" barriers.

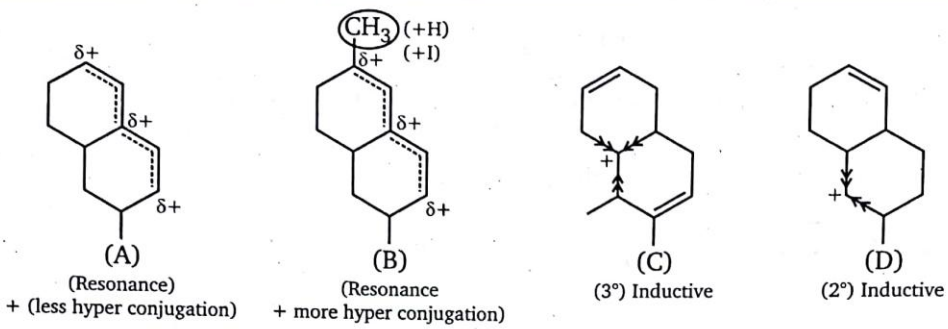


35. 

BF_3, A – d; B – a; C – a

36 to 51 solutions are given in Book

52.



(Stability order : B > A > C > D)

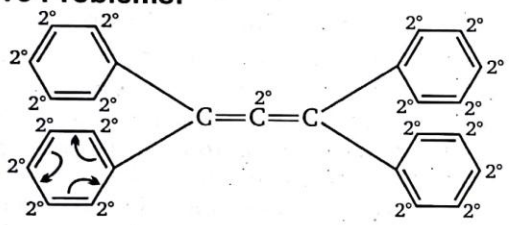
53. Stability order of alkene α no. of α-Hydrogens.

$A \longrightarrow 9\alpha$ - H $\quad B \longrightarrow 1\alpha$ - H $\quad C \longrightarrow 3\alpha$ - H $\quad D \longrightarrow 5\alpha$ - H

54. D.B.E = Number of (π-bonds + Rings).

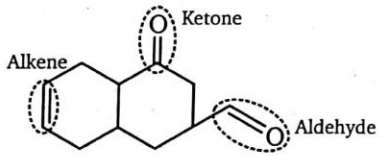
Subjective Problems:

1.

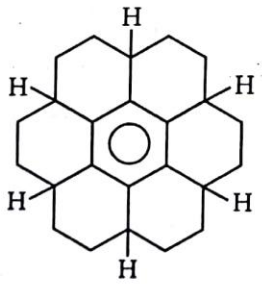


2. D.B.E = Number of π-bonds + rings

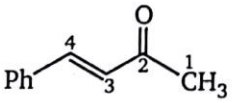
3.



4.



5.



6. No. of π-bonds = 9
No. of rings = 4

7. (a) C—C—C—C—OH (b) C—C—C(OH)—C (c) C—C(C)—C—OH

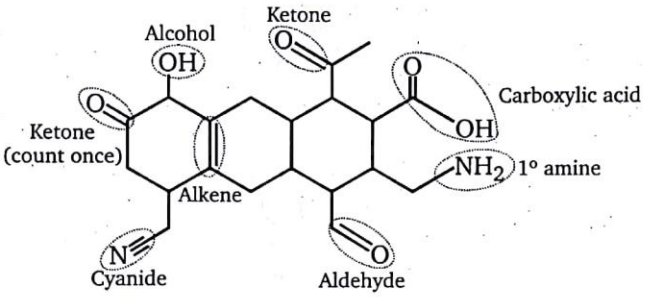
(d) C—C(C)(OH)—C

8. ≃7

9. Benzoic acid and Benzene Sulphonic acid are more acidic compounds than H_2CO_3 so these are capable to react with $NaHCO_3$ to give a salt and CO_2 gas.

10. Compound which gives an stable conjugate base after deprotonation will deprotonate easily.

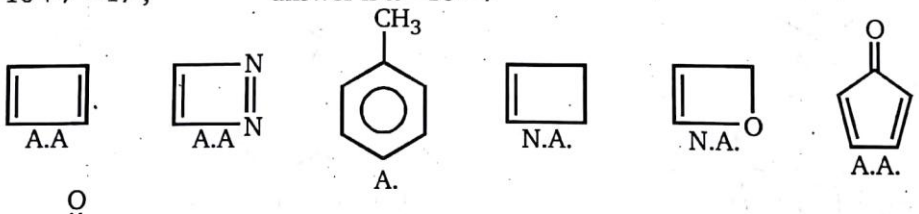
11. (7)

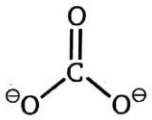


7 F.G. D.B.E. value : 10

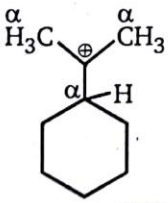
$x = 10 + 7 = 17$; answer is $x - 10 = 7$

12.





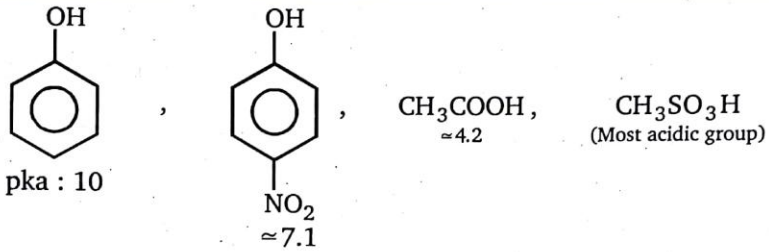
(3 equivalent resonance) ⇒ Q = 3



$7\alpha - H \Rightarrow R = 7$

$CH_3—CH=CH—CH=CH_2$ $n = 1$; (2 geometrical isomers) ⇒ $S = 2$

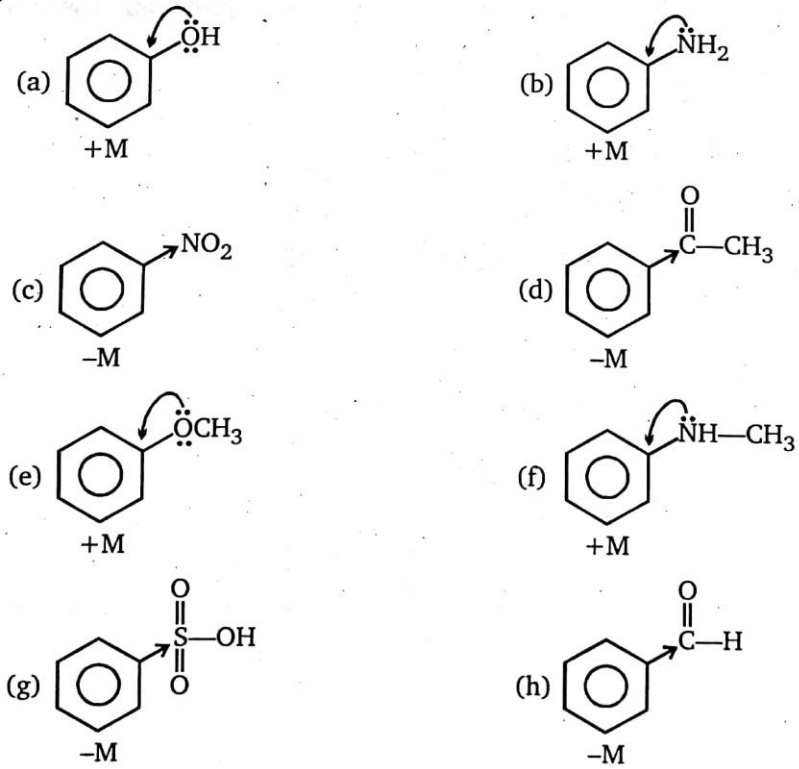
Show G.I. No. G.I.



All are more acidic than ethanol CH_3CH_2OH ($pka \simeq 16$) $\Rightarrow$ $T = 4$

$(P+Q+R+S+T)-15 = 19-15 = 4$

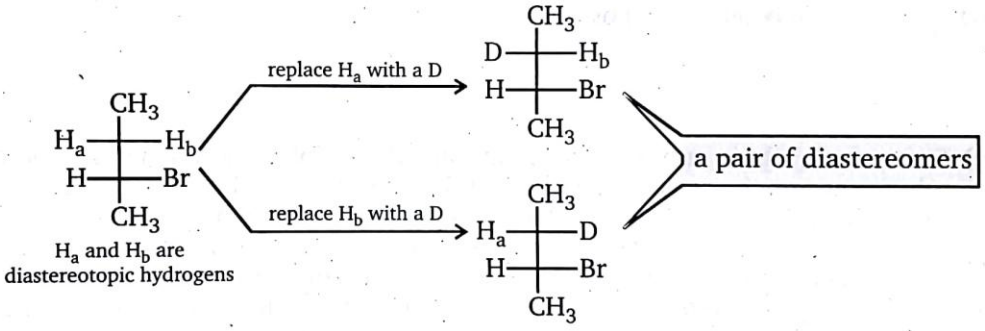
13. (4)



2 Isomerism (Structural and Stereoisomerism)

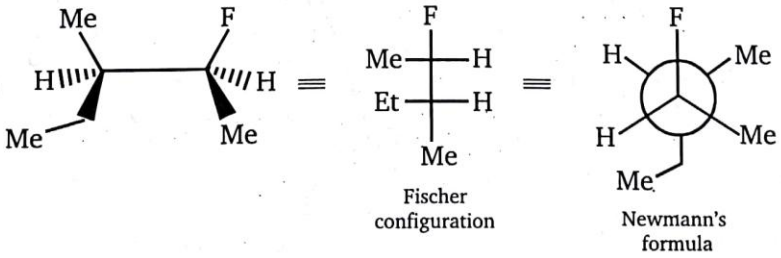
Level-1

1. (b) If a carbon is bonded to two hydrogens and replacing each of them in turn with deuterium (or another group) creates a pair of diastereomers, the hydrogens are called diastereotopic hydrogens.

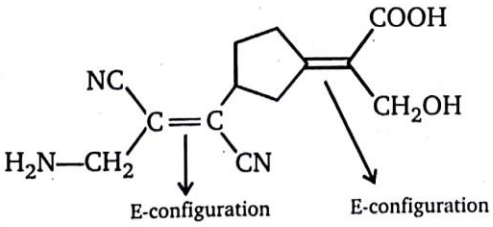


2. (c) P.O.S. (Plane of Symmetry) is present.

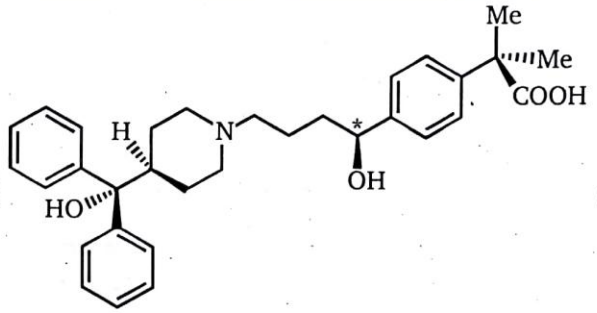
3. (b)



4. (c)

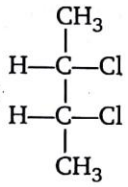


5. (a)



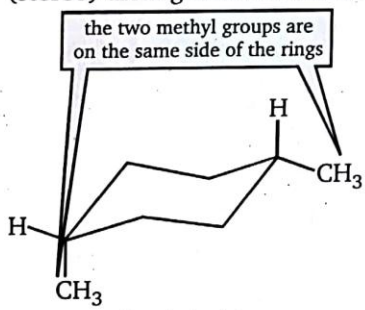
Only one chiral 'C'

6. (b)

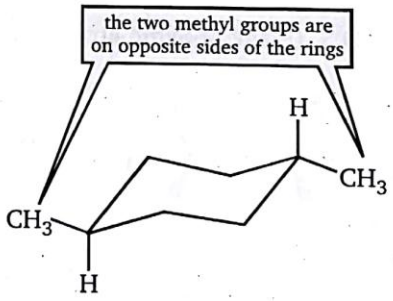


Only one meso possible.

7. (c) First of all, there are two different dimethylcyclohexanes. One has both methyl substituents on the same side of the cyclohexane ring; it is the cis isomer (cis is Latin for "on this side"). The other has the two methyl substituents on opposite sides of the ring ; it is the trans isomer (trans is Latin for "across"). cis-1, 4-dimethylcyclohexane and trans -1, 4-dimethylcyclohexane are called geometric isomers of cis-trans stereoisomers - they have the same atoms, and the atoms are linked in the same order, but they differ in the spatial (stereo) arrangement of the atoms.



cis-1, 4-dimethylcyclohexane

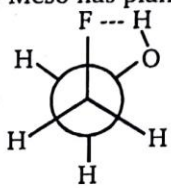


trans-1, 4-dimethylcyclohexane

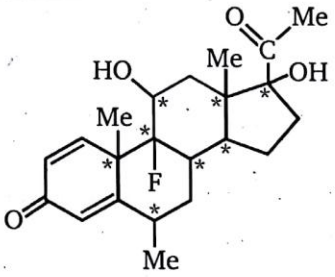
First we will determine which of the two chair conformers of cis- 1, 4-dimethyl-cyclohexane is more stable. One chair conformer has one methyl group in an equatorial position and one methyl group in an axial position. The other chair conformer also has one methyl group in an equatorial position and one methyl group in an axial position. Therefore, both chair conformers are equally stable.

8. (d) Meso has plane of symmetry with chiral centre.

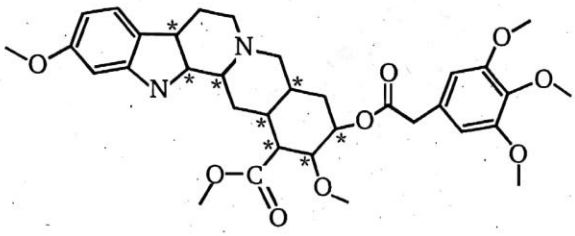
9. (c)



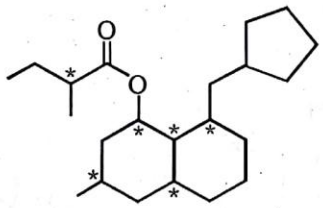
Gauche

10. (d) 

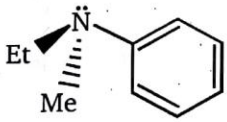
8 — Chiral centre

11. (b) 

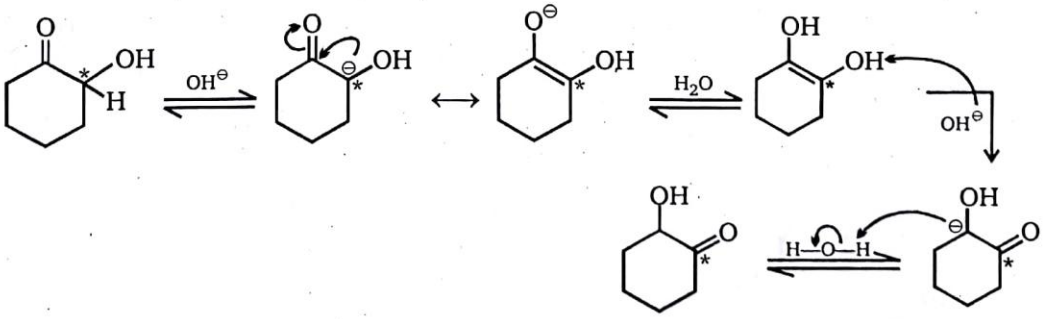
8 Chiral carbons

12. (c) 

6 Chiral centres

13. (a) 

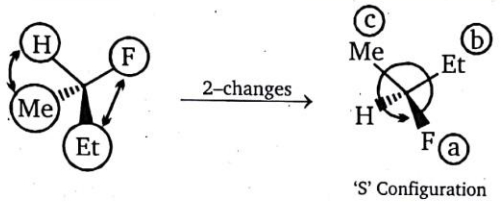
$\longrightarrow$ optically inactive due to resonance.
(N is sp^2-hybridised)

14. (b) 

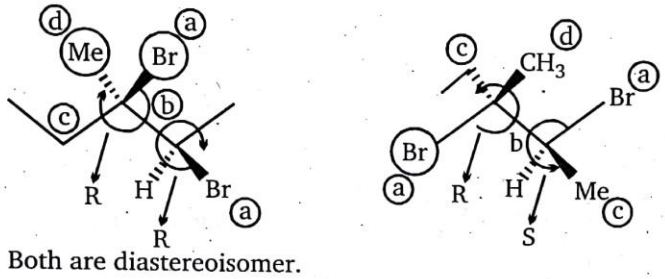
15. (b) Optically active compounds are used for separation or resolution of $dl/(\pm)$ mixture.

16. (d) Compounds do not have plane & centre of symmetry are known as optically active compounds.

17. (c)



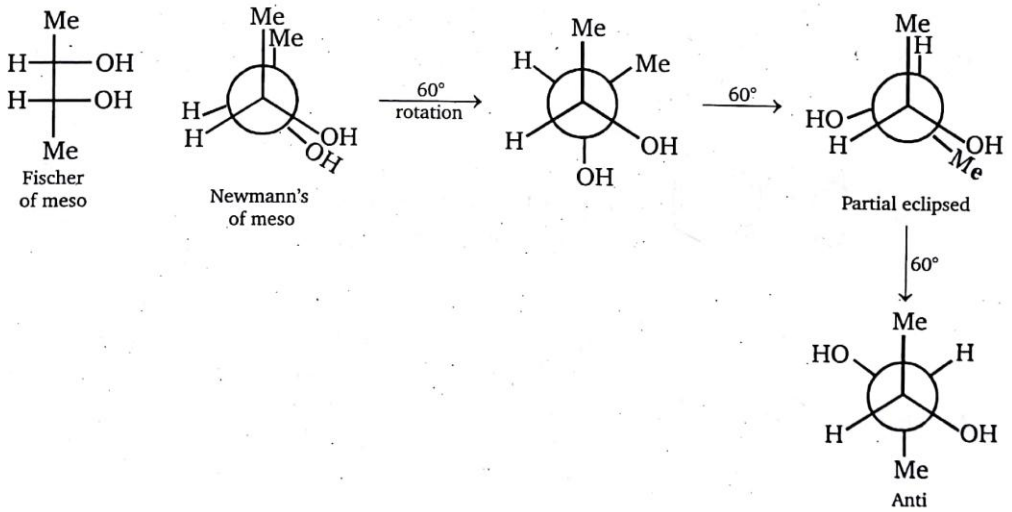
18. (a)



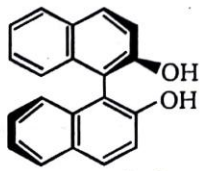
Both are diastereoisomer.

19. (b) $Br-\overset{*}{C}(Cl)(H)-CH_2-CH_2-Br$ 1,3-dibromo-1-chloropropane.

20. (b)

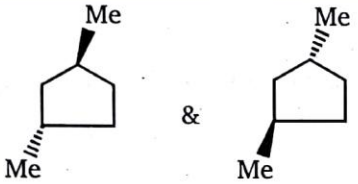


21. (d)



(Bnp)

Compound give Atropi isomerism and is optically active due to absence of plane and centre of symmetry.

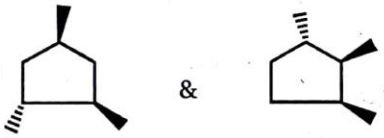
22. (b) 

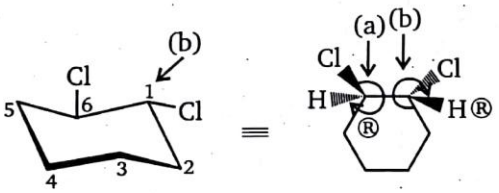
are mirror image and are not superimposable on each other so are enantiomers.

23. (c) When molecule is symmetrical and has even no. of chiral centres then total no. of isomers

$$= \underset{\text{O.A.}}{2^{n-1}} + \underset{\text{meso}}{2^{n/2-1}}$$

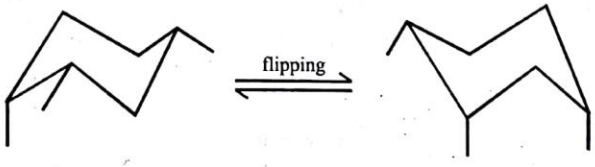
(O.A. -Optically active)

24. (d)  are positional isomers.

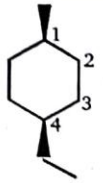
25. (a) 

(a) → *R* (b) → *R*

26. (b) During flipping a ⟷ e e ⟷ a are inter convertible.

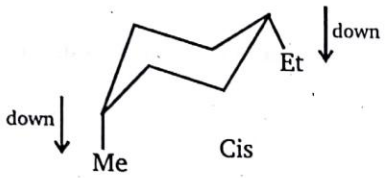


27. (d) Trans-1, 4-disubstituted compound is most stable (ee → most stable) and doesn't have any steric repulsion. (e, e → equatorial, equatorial)

28. (b) 

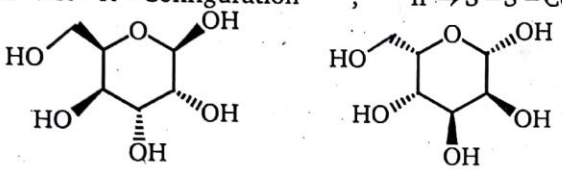
Cis-1, 4-disubstituted compound has a e configuration so 'Et' group is present at 'e'

and 'Me' at 'a'

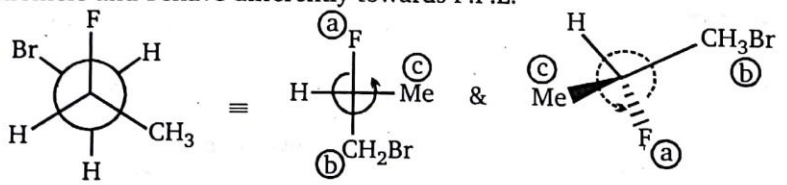


29. (a) Enantiomers have same solubility in optically inactive solvents so (I) & (IV) have same solubility because are enantiomers

I → R – R – Configuration ; II → S – S – Configuration

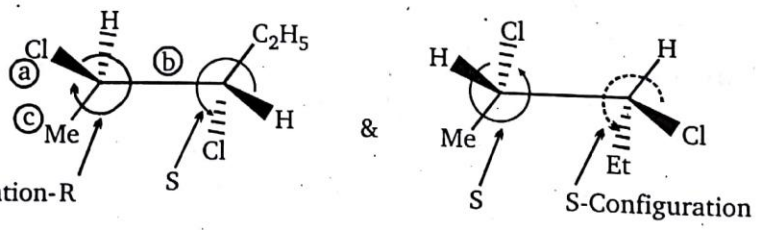
30. (c) 

Above 2 compounds are mirror image of each other and are not superimposable so are enantiomers and behave differently towards P.P.L.

31. (c) (I) 

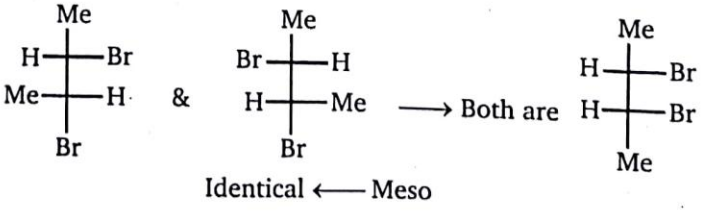
R-Configuration S-Configuration

Enantiomer ←

(II) 

Configuration-R S-Configuration

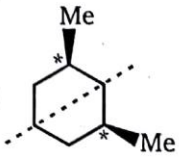
are diastereoisomers.

(III) 

Identical ← Meso

32. (a)

33. (b)

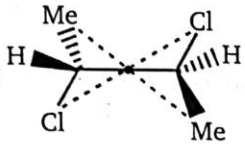


Meso → Compounds having chiral centres and have plane or centre of symmetry are known as meso compound.

34. (c) Resolution.

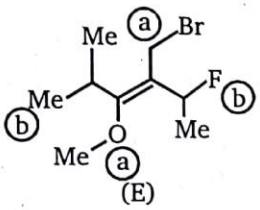
35. (c) Follows CIP rules.

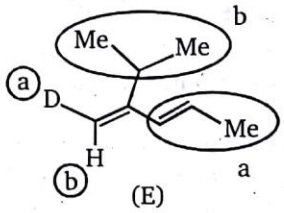
36. (d)



Molecule has centre of symmetry.

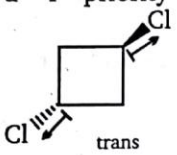
37. (c)





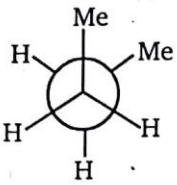
a = Ist priority ; b = IInd priority

38. (d)

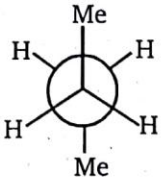


Zero dipole.

39. (b)



Gauche



Anti

If no rotation then these two are not inter convertible and are diastereoisomer.

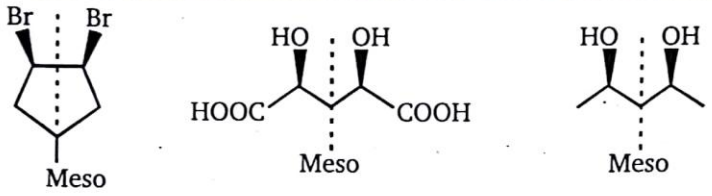
40. (a) (1) Compounds which do not have plane & centre of symmetry are optically active.
(2) 50/50 mixture of diastereoisomers is also optically active.

41. (a)

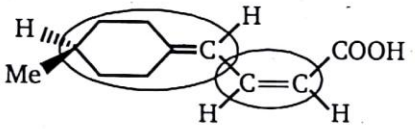
e, e, e form is most stable.

42. (d) Compound which do not have plane and centre of symmetry are optically active.

43. (a)



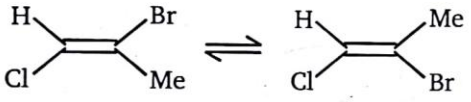
44. (d)



Total isomers $= 2^n = 2^2 = 4$

45. (a) Compounds do not have plane and centre of symmetry are chiral.

46. (b)



Due to C = C ; C — C rotation require very high activation energy for breaking of π-bond and then σ-rotation.

47. (c) Anti conformation of butane is most stable and require lowest energy.

48. (b) I & IV have P.O.S. so are inactive while II, III & V are optically active.
(P.O.S. = plane of symmetry.)

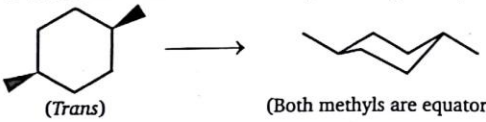
49. (c) Enantiomers are resolved in optically active solvents/compounds and (III)rd compound is optically active.

50. (c) In Fischer most oxidised end remains always on top so rotation of IInd str. by 180°. It is clear that I & II are identical.

51. (d) Given molecule doesn't has C = C bond having different valencies and not has chiral centres so doesn't show stereoisomerism.

52. (d) 'I' molecule has centre of symmetry so optically inactive remain all are active.

53. (e)

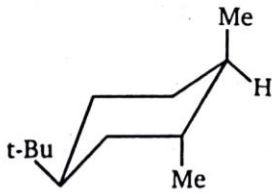


(*Trans*) (Both methyls are equatorial)

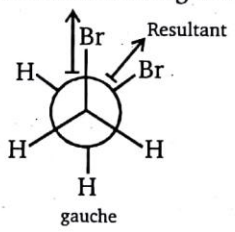
54. (a) Both molecule has same molecular formula $C_6H_{11}Cl$ so have same molecular wt. and composition because both have substituents on same atoms.

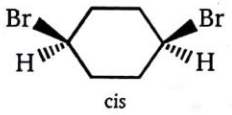
55. (d) aa isomer is most stable (due intramolecular hydrogen bonding).

56. (c) 1, 3-trans cyclohexane has –ae configuration 1, 4-cis cyclohexane has –ae configuration so str. of molecule is



57. (d) Non-zero dipole has following molecules



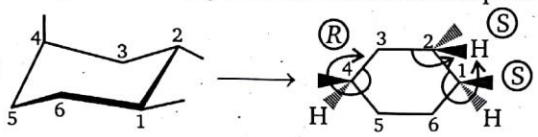


Dibromocyclohexane → stereo chemistry and position are not mentioned so may be cis.

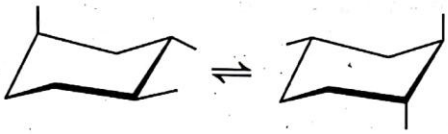
58. (b) $n = 15$

59. (a) Compound '*B*' may be meso but meso has plane of symmetry with chiral centres.

60. (a)



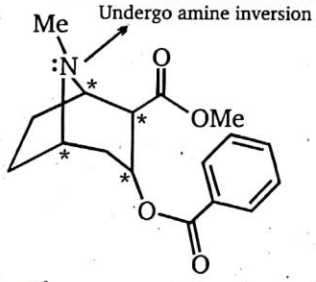
Now,



(2 methyl equatorial and 1 axial) will be more stable.

61. (c) Cis and trans are diastereoisomer of each other.

62. (d)



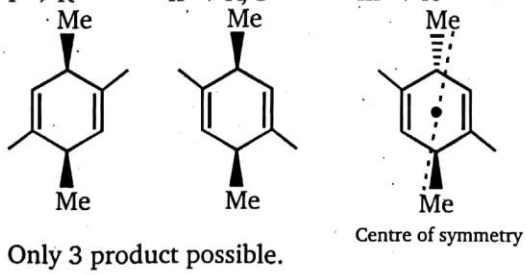
4-chiral 'C' atoms

63. (e) IIIrd compound has plane of symmetry so optically inactive but I and II are optically active and are chiral. I and II are enantiomers whereas III is a meso compound.

64. (d) All molecules have chiral centres and have configurations.

I → R II → R, S III → R IV → R, S (Meso)

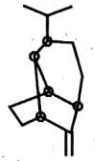
65. (b)



Only 3 product possible.

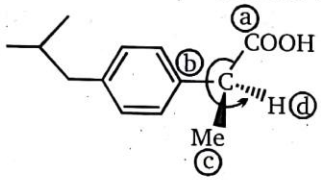
66. (b) I, II → Structural isomer
III → Geometrical (configuration)
IV → Enantiomer (optical)

67. (d) Stereogenic centre = Chiral center



68. (d) Half chair is less stable due to angle strain.

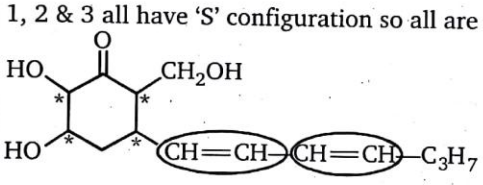
69. (d)



–S – configuration.

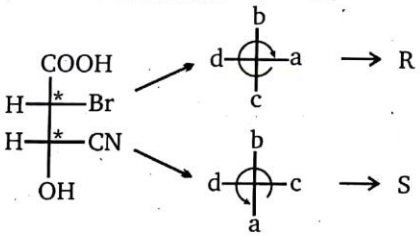
70. (d) 1, 2 & 3 all have 'S' configuration so all are identical.

71. (d)



molecule has (1) chiral centre = 4, (2) C = C along which it can show G. I. = 2.
Total stereoisomers = $2^6 = 64$

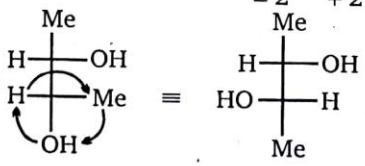
72. (a)



So molecule has 2(R) 3(S)

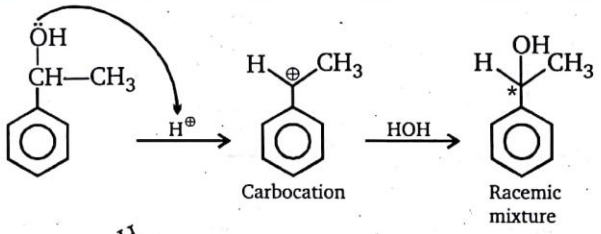
73. (b) For symmetrical molecule total isomers when n = even
$= 2^{n-1} + 2^{n/2-1}$

74. (a)

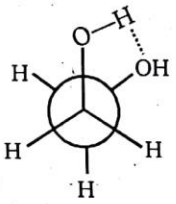


is not meso.

75. (b)



76. (b)

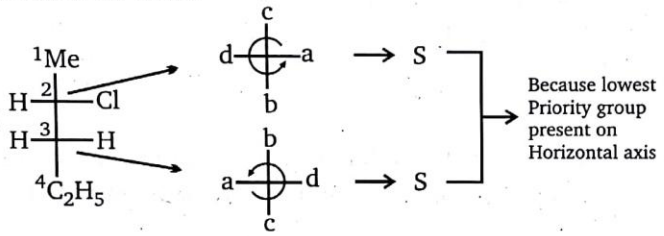


due to intramolecular H-bonding gauche is most stable.

77. (a) Both molecule have same configuration so are identical.

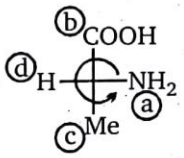
78. (b) Follow CIP rules.

79. (c)



So configuration 2(S) 3(S).

80. (b)

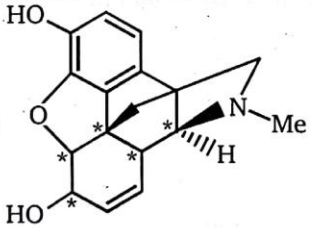


⟶ 'R' Configuration.

81. (d) All compounds have P.O.S. and chiral centre so all are meso.

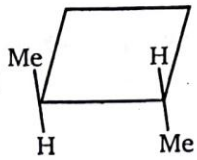
82. (a) When racemic mixture reacts with optically active compound it gives diastereoisomeric mixture.

83. (b)



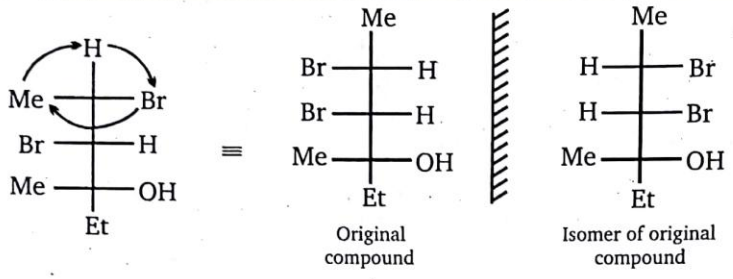
5-chiral 'C' atoms.

84. (a)

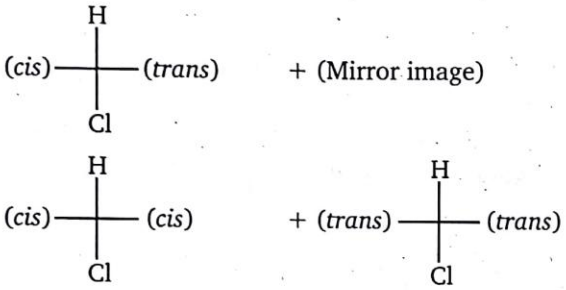


is optically active.

85. (a)



86. (d)



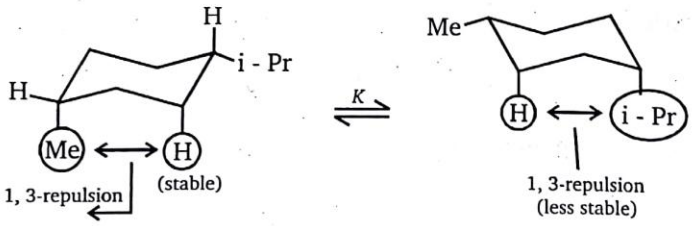
Total 4.

87. (a) No explanation is required.

88. (d) I point of difference is applicable in CIP rule [on the basis of atomic No. or At. mass]

89. (a) Cis has steric crowding between 2-groups in same side so trans is more stable.

90. (b)

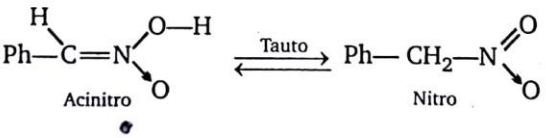


equilibrium favours reactant so $K < 1$.

91. (a) Position isomers.

92. (a) van der Waal's strain is known as strain or repulsion between van der Waal's radius of 2-groups in a molecule.

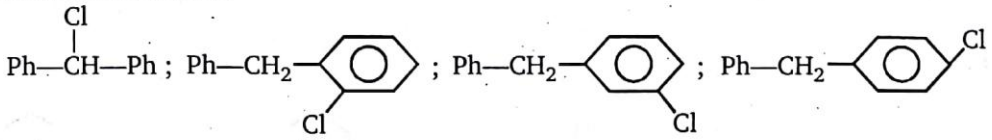
93. (b)



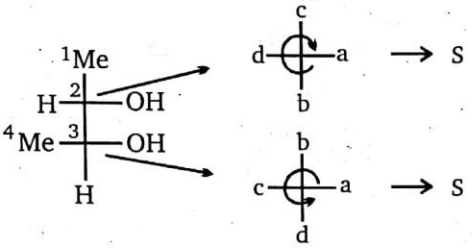
94. (a) Double bonded compounds having same valencies on double bonded 'C' atom do not show G.I.

95. (b) Given 2 compounds are mirror images of each other and are not superimposable on each other so are enantiomers.

96. (b) Isomers obtains are

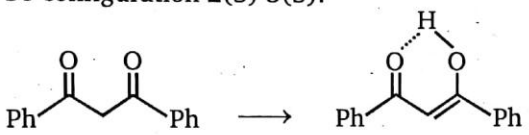


97. (a)



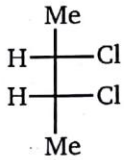
So configuration 2(S) 3(S).

98. (d)



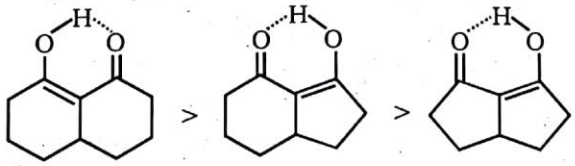
Most stable enol stabilised by resonance and intramolecular H-bonding

99. (b)



(Meso) 2, 3-dichlorobutane

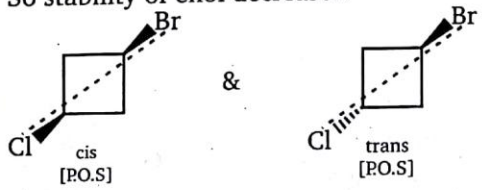
100. (a)



Angle strain L ⟶ R Increases

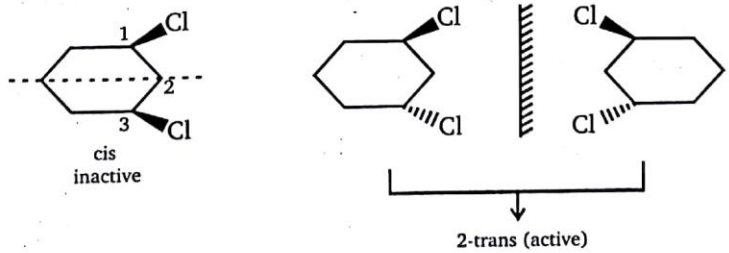
So stability of enol decreases.

101. (c)

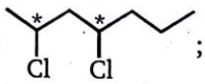


Only 2 Isomers.

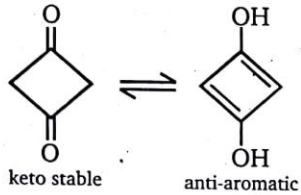
102. (c)



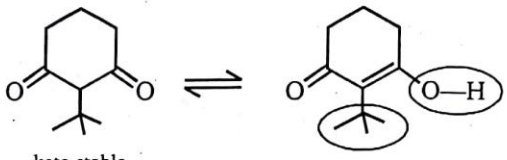
103. (c) Cis and trans only.

104. (d) 

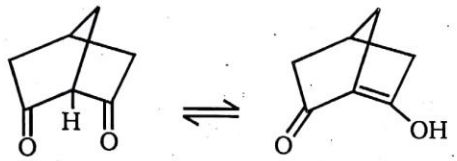
; Total isomers = $2^2 = 4$

105. (d) (a) 

keto stable — anti-aromatic unstable

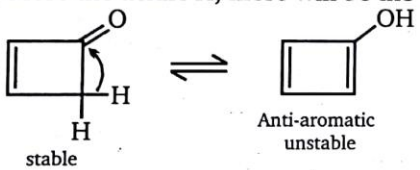
(b) 

keto stable [Non-planner] — Bad steric clash

(c) 

keto (more stable) — violates Bredt's rule

106. (a) More the acidic H, more will be the enol contant.

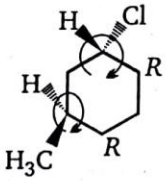
107. (c) 

stable — Anti-aromatic unstable

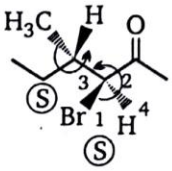
108. (b) Optical purity or enantiomeric excess $= \dfrac{\text{Excess of one enantiomer}}{\text{Total mixutre}} \times 100$

Enantiomeric excess (e. e.) $= \dfrac{6g - 4g}{(6+4)} \times 100 = 20\%$

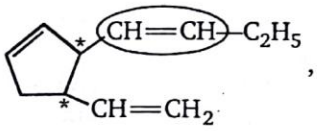
109. (d) Those stereoisomers which are not mirror images of each other are diastereoisomers.

110. (a) 

111. (c) Optical purity $= \dfrac{\text{Optical rotation of mixture}}{\text{Optical rotation of pure compound}} \times 100$; O. P. $= \dfrac{6.76}{13.52} \times 100$

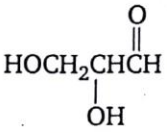
112. (c) 

Molecule has (S) (S) configuration.

113. (a) 

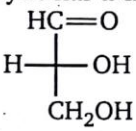
, total isomers = $2^3 = 8$

114. (d) The smallest aldose and the only one whose name does not end in "ose," is glyceraldehyde, an aldotriose.

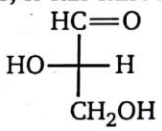


glyceraldehyde

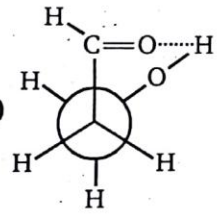
Because glyceraldehyde has a chirality center, it can exist as a pair of enantiomers.



(R)-(+)-glyceraldehyde

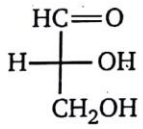


(S)-(–)-glyceraldehyde

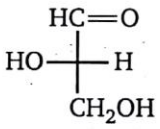
115. (b) 

Gauche is most stable due to intramolecular H-bonding.

116. (b)

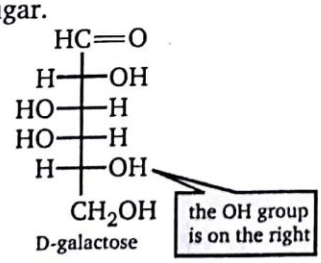


D-glyceraldehyde

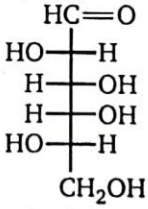


L-glyceraldehyde

D and L notations can be used to describe the configuration of carbohydrates and amino acids, so it is important to learn what D and L signify. In Fischer projections of monosaccharides, the carbonyl group is always placed on top (in the case of aldoses) or as close to the top as possible (in the case of ketoses). From its structure, you can see that galactose has four chirality centers (C-2, C-3, C-4, and C-5). If the OH group attached to the bottom-most chirality center (the second from the left, the compound is an L-sugar. Almost all sugars found in nature are D-sugars. Notice that the mirror image of a D-sugar is an L-sugar.



D-galactose

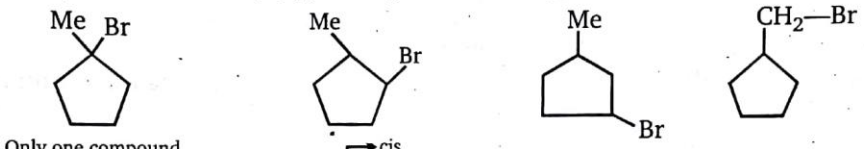


L-galactose
mirror image of D-galactose

D and L, like R and S, indicate the configuration of a chirality center, but they do not indicate whether the compound rotates plane-polarized light to the right (+) or levorotatory. In other words, optical rotation, like melting or boiling points, is a physical property of a compound, whereas "R, S, D and L" are conventions humans use to depict the structure of the molecule.

D-(+)-glyceraldehyde D-(–)-lactic acid

117. (c)



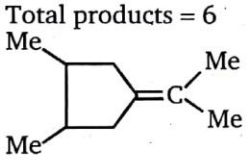
Only one compound 1, 1-disubstituted

Two – cis, trans 1, 2-disubstituted

Two – cis, trans 1, 3-disubstituted

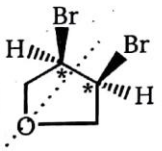
Total products = 6

118. (d)



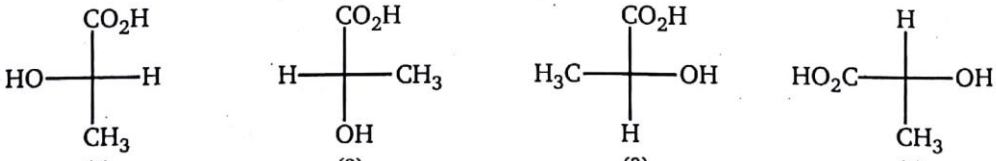
can show G.I. Along the 5-membered ring.

119. (b)

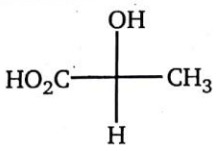


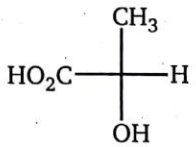
is meso.

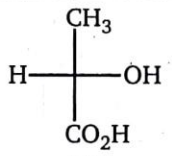
120. (c) There are 24(= 4! this being the number of permutations of 4 ligands among 4 sites) ways of writing the projection formula ; 12 correspond to one enantiomer and 12 to the other. Twelve of these, corresponding to the (+) enantiomer, are depicted in Fig. ; the 12 mirror images of those shown would represent the (–) isomer.

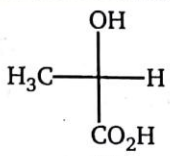


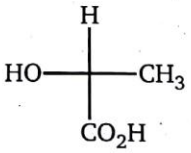
(1) (2) (3) (4)

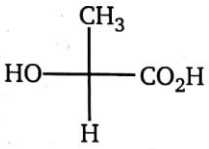

(5)

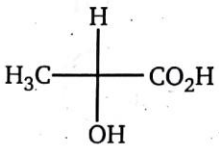

(6)

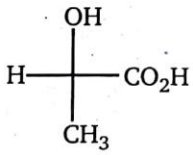

(7)


(8)

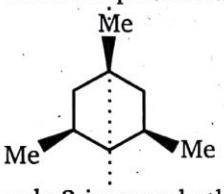
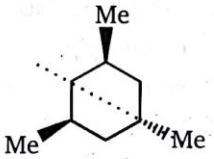

(9)


(10)

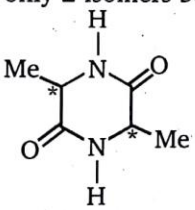

(11)


(12)

Twelve representations of (+)-lactic acid (Fischer projections)

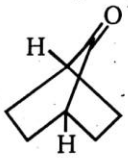
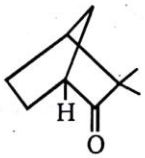
121. (a)  and 

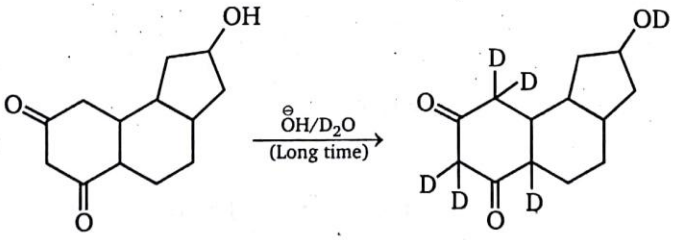
only 2-isomers both are optically inactive.

122. (b) 

Symmetrical and have 2-chiral centres so has

$$2^{n-1} + 2^{n/2-1} = 2^1 + 2^0 = 3 \text{ isomers.}$$

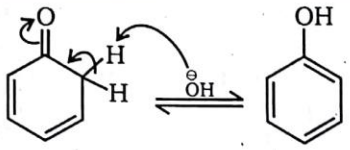
123. (d)   due to Bredt's rule.

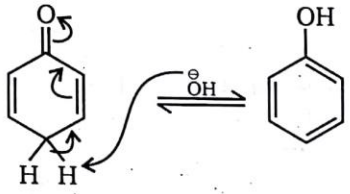
124. (b) 

(All acidic hydrogens are being replaced)

125. (b) This carbon will not get the negative charge.

126. (c)





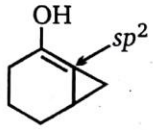
127. (c) γ-H attached with sp^3 and its conjugate base is resonance stabilized.

128. (b) α-hydrogen attached to sp^3 carbon is present in structure II.

129. (d) α-hydrogen attached to sp^3 carbon is present in all structures.

130. (a) Higher the bond energy of $>C=O$.

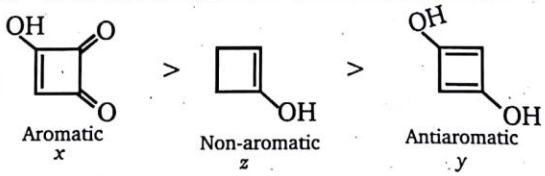
131. (c)



is unstable due to angle strain.

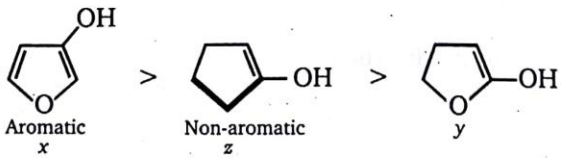
132. (d) I^{st} structure is unstable due to Bredt's rule.

133. (d)



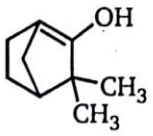
Stability order of enol.

134. (d)



Stability order of enol.

135. (b)

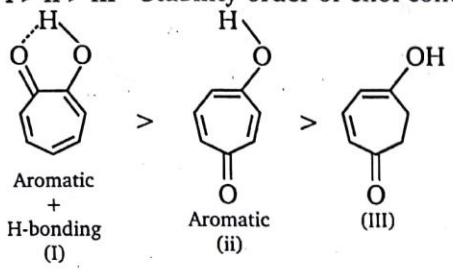


unstable enol due to Bredt's rule.

136. (b) Benzylic carbon gets negative charge. ∴ It exchange its H by D.

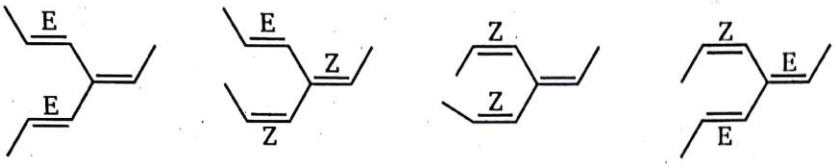
137. (c) II > I > III Stability order of enol form.

138. (a) I > II > III Stability order of enol content.



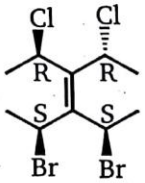
139. (d) II > I > III Stability order of enol form

140. (b)



Total 4 geometrical isomers.

141. (b)



Identical groups are present.

142. (a) Terminal hydrogens are perpendicular to each other $\therefore\ l_1 = l_2$

143. (c) Terminal hydrogens are in same plane $\therefore\ l_2 > l_1$

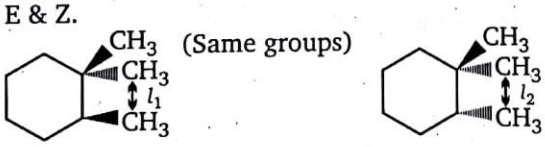
144. (b) cis & trans.

145. (b) E and Z

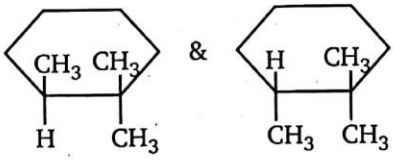
146. (b) cis & trans.

147. (b) E & Z.

148. (a)

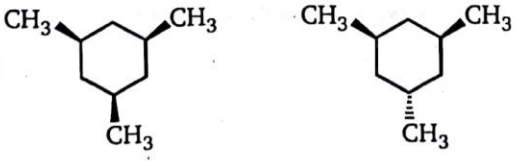


$l_1 = l_2$

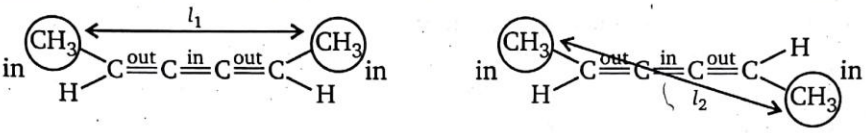


are not Geometrical isomers.

149. (b)



150. (c)



$\Rightarrow \quad (l_2 > l_1)$

151. (a) cis & trans across middle π-bond.

152. (c) Total G. I. $= 2^2 = 4$

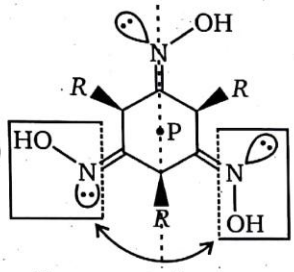
153. (b) Total geometrical isomers

$$= 2^{n-1} + 2^{p-1} \qquad p = \frac{n}{2}$$

$$= 2^1 + 2^\circ$$

$$= 3$$

154. (d)

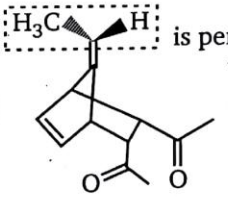


These are not mirror image
POS (not present)

No COS and on rotating 120° along axis passing through centre P perpendicular to plane of molecule, results into identical form. Thus, C_3 axis of symmetry is present.

155. (c) Identical.

156. (a)

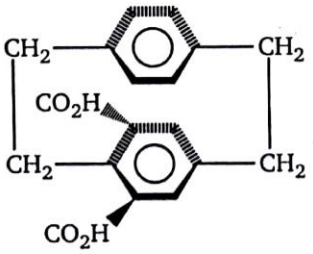


is perpendicular to the ring.

no POS
no COS
Thus, chiral

Plane of symmetry and centre of symmetry is not present in compound (A) $\therefore$ it is chiral.

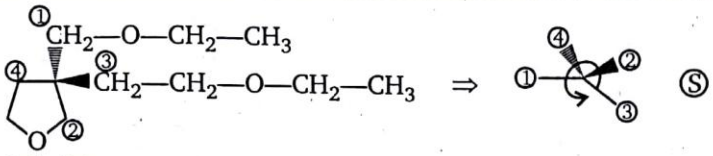
157. (c)



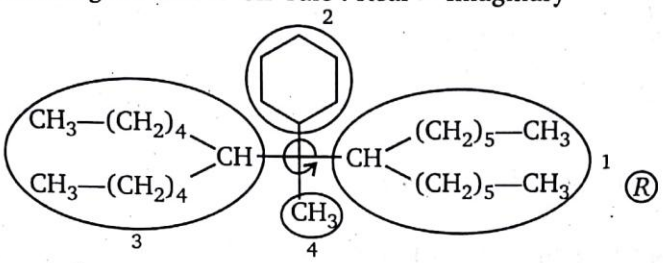
now, plane passing through square will give P.O.S

Plane of symmetry is present.

158. (d)



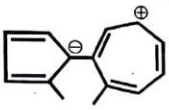
Priorities are assigned acc. to CIP rule : Real > Imaginary



159. (d) All compounds have centre of symmetry.

160. (d) Chiral mixture would rotate plane polarized light.

161. (b)

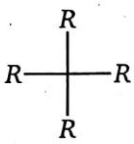


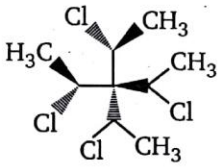
both rings are perpendicular to each other, so plane of symmetry and centre of symmetry is absent.

162. (d) All have plane of symmetry.

163. (d)

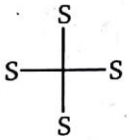
164. (d) Consider



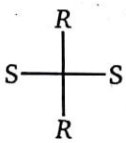


no plane can pass in such a way that molecule has symmetry.

similarly for

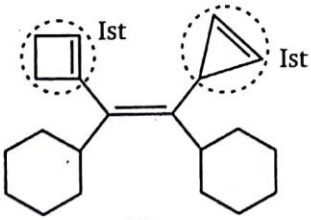


&



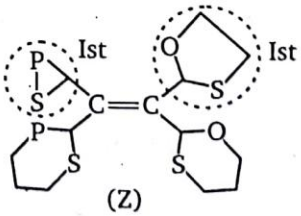
165. (d)

(a)

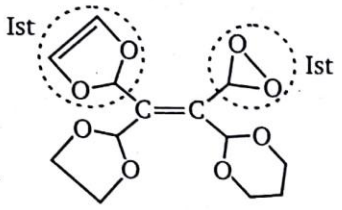


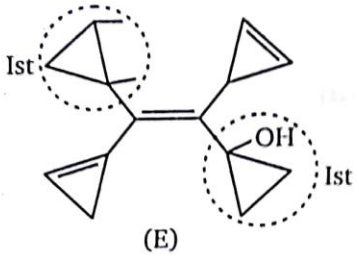
(Z)

(b)



(Z)

(c) 

(d) 

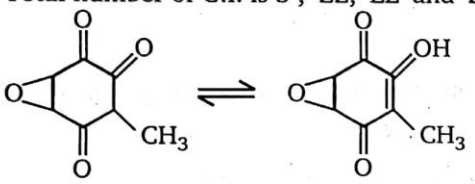
(E)
(real > imaginary)

166. (c) Enol of first compound is aromatic.

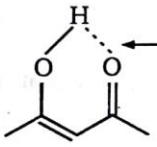
167. (d)

168. (c) Enol from of (*A*) is $Ph-\underset{\underset{OH}{|}}{C}=CH-OH \xrightleftharpoons{\text{Tautomerises}} Ph-\underset{\underset{O}{\|}}{C}-CH_2-OH$

169. (b) Total number of G.I. is 3 ; ZZ, EE and ZE.

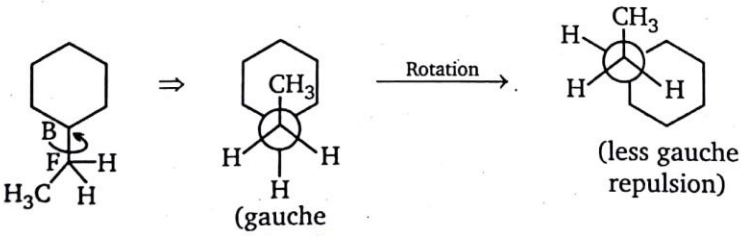
170. (c) 

(resonance stabilised)

171. (c) 

Intramolecular H-bonding

172. (d)

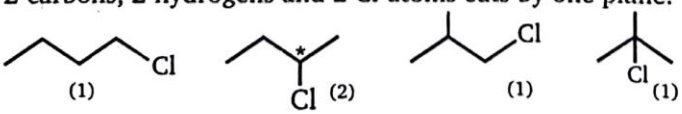
173. (b) 

(gauche repulsion from both sides)

(less gauche repulsion)

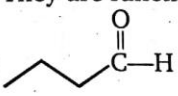
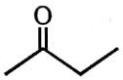
B = Back
F = Front

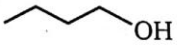
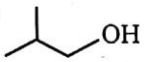
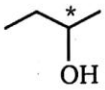
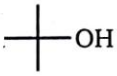
174. (c) 2-carbons, 2-hydrogens and 2 Cl-atoms cuts by one plane.

175. (d) 

; Total = 5

176. (c) They are functional isomers.

177. (b)  aldehyde and  ketone are functional isomers.

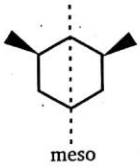
178. (c) (a)  (b)  (c)  (d) 

179. (c) (S) configuration: I, II, IV
(R) configuration: III

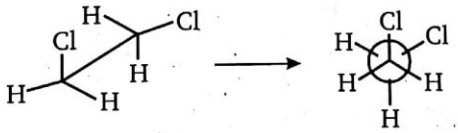
180. (d) Imagine the structure and find out the chirality.

181. (d)

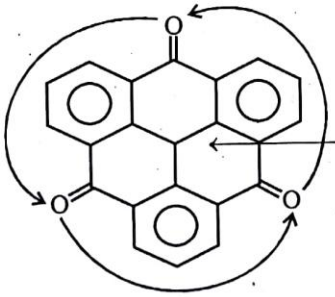
	No. of POS	No. of COS
(a)	–	–
(b)	2	–
(c)	2	–
(d)	1	✓

182. (b) 
meso

Chiral center and symmetry
∴ Internal compensation and meso.

183. (b) 

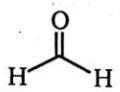
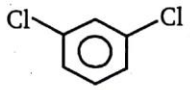
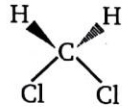
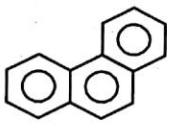
184. (c)



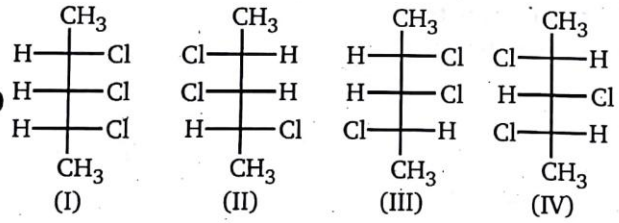
z-axis as C_3axis $\xrightarrow{\pm 120°}$ same configuration reappears.

Molecular plane of symmetry is present in the compound.
Centre of symmetry is absent because same group at the same distance does not meet.

185. (c)

	POS	AOS (C_2)
	✓	✓
	✓	✓
	✓	✓
	✓	✓

186. (b)



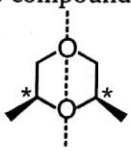
(I) (II) (III) (IV)

3 diastereomers.

187. (b) Check configuration (R or S) with proper orientation.

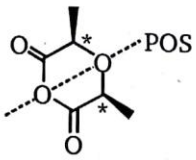
188. (a) Meso compounds are those having 2 or more chiral centres along with symmetry.

(1)



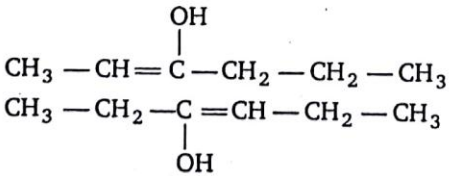
POS
Meso

(3)



Meso

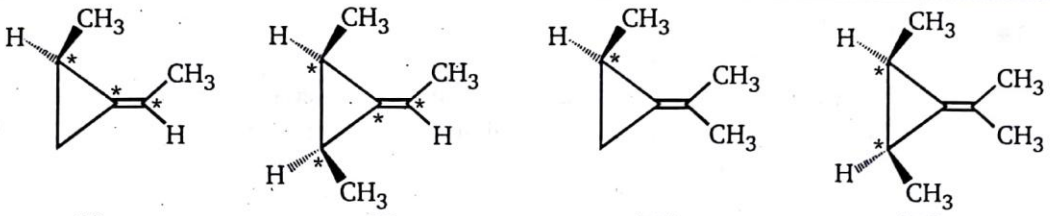
189. (c)



(*E* & *Z*)
(*cis* & *trans*)

Total = 4 enol forms.

190. (c)



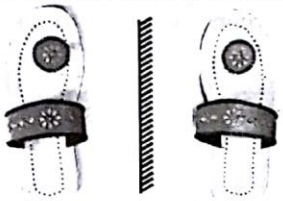
(I) (II) (III) (IV)

Stereocenters are marked with asterisck (*).

191. (c) Stereoisomers are actually configurational isomers. Thus, they might be diastereomers (geometrical/optical) and enantiomers (mirror image non-super imposeable). Stereoisomers are not constitutional isomers, thus, can't be tautomers, positional.

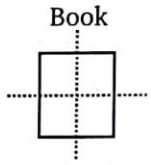
Since, conformational isomers deals with bond rotation without change in configuration, thus, stereoisomers can't be conformational isomers.

192. (b) (I)



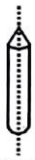
A shoe
(chiral)

(II)



(Achiral)

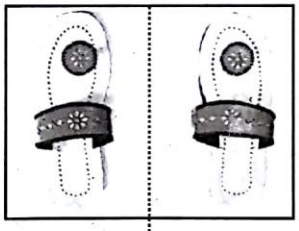
(III)



A pencil
(Achiral)

(IV)

Pair of shoe



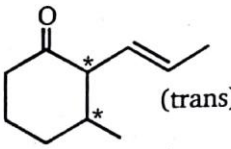
Internal POS
(Achiral)

(V)

(chiral)
(asymmetric)

(a pair of scissors)

193. (c)



(trans) Fixed

Now 2 chiral centres will give 4 stereoisomers having trans alkene.

Level-2

1. (a) Total No. of stereoisomers = 2^n, When molecule is unsymmetrical.

(b) When molecule is symmetrical, total no. of stereoisomers

(I) When n = even

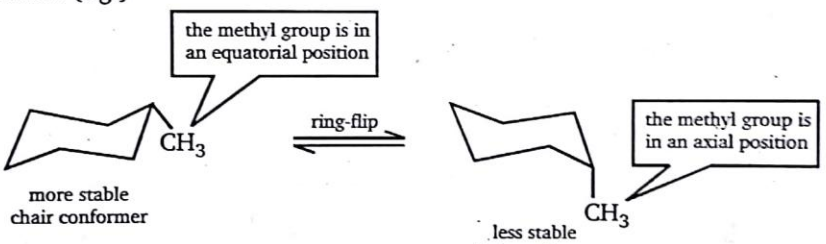
Total isomers = $2^{n-1} + 2^{n/2-1}$

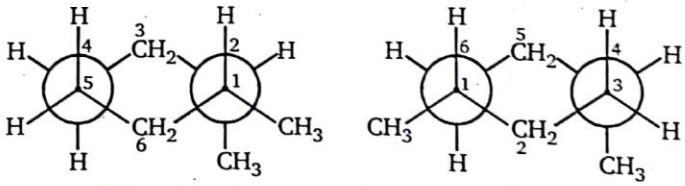
(II) When n = odd.

$$\text{Total isomers} = \underbrace{\left(2^{n-1} - 2^{\frac{n-1}{2}}\right)}_{\text{Optically active}} + \underbrace{2^{\frac{n-1}{2}}}_{\text{meso}}$$

2. The chair conformer with the methyl substituent in an equatorial position is more stable because a substituent has more room and, therefore, fewer steric interactions when it is in an equatorial position. When the methyl group is in an equatorial position, it is anti to the C-3 and C-5 carbons (Figure). Therefore, the substituent extends into space away from the rest of the molecule.

In contrast, when the methyl group is in an axial position, it is gauche to the C-3 and C-5 carbons (fig.)





As a result, there are unfavourable steric interactions between the axial methyl group and both the axial substituent on C-3 and the axial substituent on C-5 (in this case hydrogens). In other words, the three axial bonds on the same side of the ring are parallel to each other, so any axial substituent will be too close to the axial substituents on the other two carbons. Because the interacting substituents are on 1, 3-positions relative to each other, these unfavourable steric interactions are called 1, 3-diaxial interactions

*Alkyl group occupy equational position to achieve maximum stability.

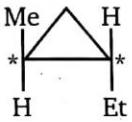
*If the size of alkyl group increase, then stability of conformer will increase and value of equillibrium constant will also increase.

3. **Chiral molecules:** – Those molecules which do not have plane of symmetry, centre of symmetry are optically active and are not superimposable on their mirror images and are known as chiral molecules

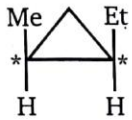
vice-versa are achiral.

Chiral centre: – Tetrahedrally bonded atom having four different groups are known as chiral centres.

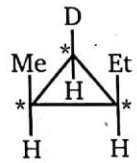
Meso: – Compound having two or more than two chiral center and posses P.O.S./C.O.S. are meso isomer they become optically inactive due to internal compensation P.O.S. absent.

4. (a) 

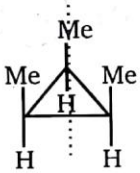
⟶ molecule has chiral centre and can show G.I. and it can show optical isomerism.

(b) 

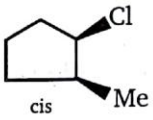
⟶ (1) Chiral centre (2) G.I. (3) Optical Isomerism.

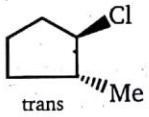
(c) 

⟶ (1) Chiral centre (2) G.I. (3) O.I.

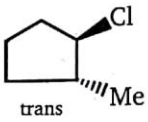
(d) 

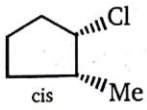
⟶ (1) P.O.S. (2) G.I. (3) Optical Isomerism absent due to presence of P.O.S.

5. (a) 

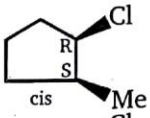
and 

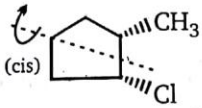
are not mirror image of each other so diastereoisomers.

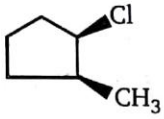
(b) 

and 

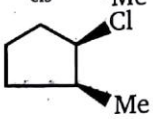
are diastereoisomers.

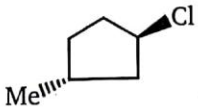
(c) 

and 

≡ 

∴ Both are identical.

(d) 

and 

are positional isomers (position of (Cl) and (CH_3) will be changed that's why they are structural isomer.)

6. (a) Molecule is cis and doesn't has P.O.S. and C.O.S. so optically active. (P.O.S. = Plane of Symmetry)

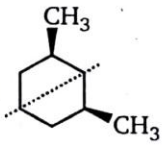
(b) Molecule is trans and has C.O.S. so optically inactive. (C.O.S. = Center of Symmetry)

(c) Molecule is trans and active.
(d) Molecule is cis and inactive.

7. (a) Compound doesn't have chiral centre but has stereocentre and is optically active due to absence of P.O.S.
(b) Compound has P.O.S and has C.O.S. and has 2-stereocentres.
(c) Compound has chiral centre stereocentre and optically active due to absence of P.O.S..
(d) Compound has stereocentre and P.O.S. and optically inactive.

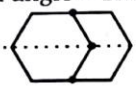
8. (a) Molecule has P.O.S., C.O.S., so non-polar and O.I.
(b) Molecule is O.A. and doesn't has P.O.S., C.O.S. and is polar.
(c) Molecule has P.O.S. and C.O.S. and is non-polar and O.I.
(d) Molecule has P.O.S. so optically inactive and polar. 

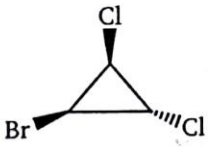
$\mu \neq 0$

9. (a) Molecule has P.O.S. so optically inactive.
(b) Molecule has P.O.S. so optically inactive doesn't has chiral centre so not meso and can show G.I.
(c) Molecule has P.O.S. and chiral centres so it is meso and can show G.I. 

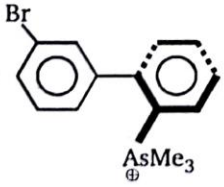
(d) Molecule has P.O.S. and doesn't has chiral centres but can show G.I.

10. (a) Dihedral angle = 0°, 360° ⟶ fully eclipsed
(b) Dihedral angle = 60°, 300°, ⟶ partically eclipsed
(c) Dihedral angle = 180° ⟶ staggered/anti
(d) Dihedral angle = 120°, 240° ⟶ Gauche

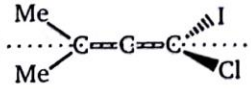
12. (a) P.O.S.  Compound has P.O.S. so cannot rotate plane polorised light.

(b) 

doesn't has P.O.S. and C.O.S. so O.A. and can rotate plane polarise light.

(c) 

doesn't has P.O.S. and C.O.S. so optically active.

(d) 

Compound has P.O.S. so inactive and doesn't has C.O.S.

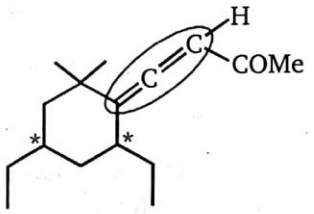
13. (a) $CH_3-\overset{\swarrow}{CH}=\overset{\swarrow}{CH}-\underset{\underset{Br}{|}}{\overset{\swarrow}{CH}}-CH_3 \longrightarrow$ 3-stereocentre

(b) $H-C\equiv C-\overset{\swarrow}{CH}=\overset{\swarrow}{CH}-\overset{*\swarrow}{\underset{\underset{Br}{|}}{CH}}-\overset{*\swarrow}{\underset{\underset{Br}{|}}{CH}}-CH_3 \longrightarrow$ 4-stereocentre

(c) $Ph-\overset{O}{\overset{\|}{S}}-CH=CH-\underset{\underset{Me}{|}}{CH}-Me \longrightarrow$ 3-stereocentres

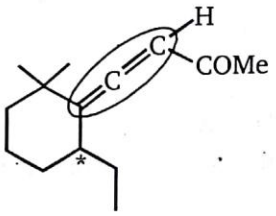
(d) $Ph-\overset{\swarrow}{\underset{\underset{Cl}{|}}{\overset{*}{C}H}}-Et \longrightarrow$ 1-stereocentre

14. (a)



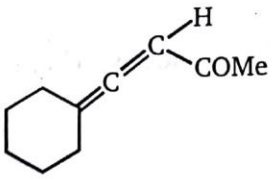
Total isomer $= 2^n = 2^3 = 8$

(b)



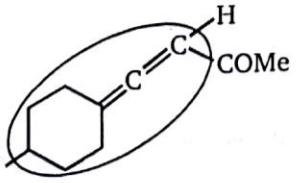
S. I. $= 2^n = 2^2 = 4$ (S. I. = Stereoisomers)

(c)



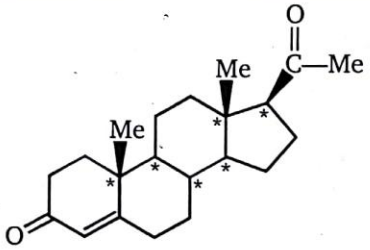
$n = 0$; S. I. $= 2^0 = 1$ (no S.I.)

(d)



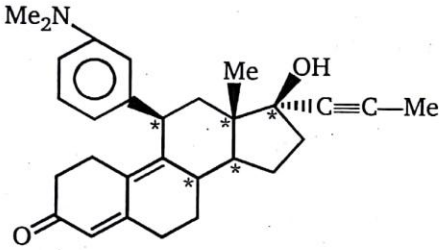
$n = 1$; S. I. $= 2^1 = 2$

15. (a)



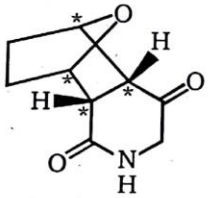
Molecule doesn't has P.O.S. & C.O.S. so it is O.A. (has even no. of chiral centres)

(b)



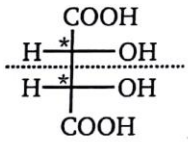
Molecule doesn't has P.O.S. & C.O.S. so O.A. (has odd no. of chiral centres)

(c)



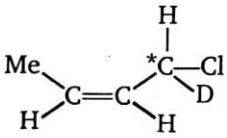
Molecule doesn't has P.O.S. & C.O.S. so O.A. (has even no. of chiral centers)

(d)



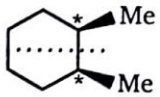
Molecule has P.O.S. so it is O.I. (O. I = optically inactive) 2 chiral centre given form is meso.

16. (a)



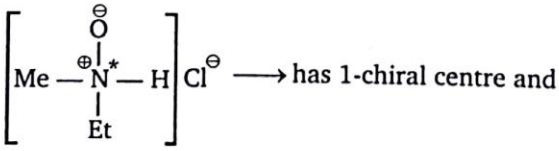
Molecule doesn't has P.O.S. and C.O.S. and has 1-chiral centre so O.A.

(b)

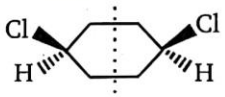


→ Molecule has 2-chiral centre and P.O.S. so it is meso and O.I. and doesn't has C.O.S.

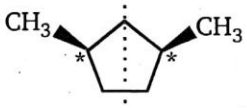
(c)



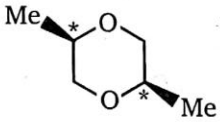
→ has 1-chiral centre and O.A. doesn't has P.O.S. and C.O.S..

(d) 

→Molecule has P.O.S. but doesn't has chiral centre so it cann't be meso but O.I.

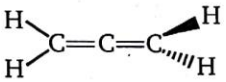
17. (a) 

(1) Molecule has P.O.S. and 2-chiral centre.
(2) Meso so it is achiral.

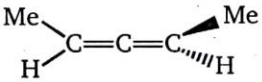
(b) 

(1) Molecule has 2-chiral centre.
(2) Doesn't has P.O.S. and C.O.S. so O.A. that's why it is chiral.

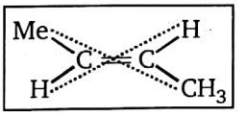
(c) 
(1) Doesn't has chiral centre.
(2) Doesn't has P.O.S. and C.O.S. so chiral and show atropi isomerism.

(d) 

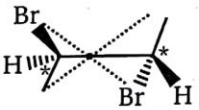
(1) Molecule has P.O.S. but not has C.O.S. so O.I.
(2) Doesn't has chiral centre.

(e) 

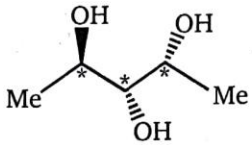
(1) Molecule doesn't has P.O.S. and C.O.S. so chiral.
(2) Doesn't has chiral centre.

(f) 

(1) Molecule has P.O.S. and C.O.S. so O.I. and achiral.
(2) Molecule doesn't has chiral centre.

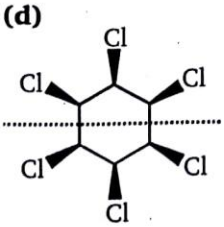
(g) 

(1) Molecule has C.O.S. so O.I. and has 2-chiral centre so it is meso.
(2) Molecule is achiral.

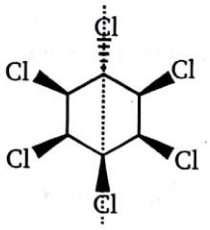
(h) 

(1) Molecule is O.A. and has chiral centres.

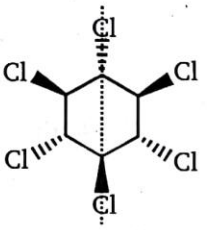
18. (A) (d)

(P) 

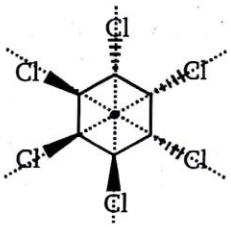
P.O.S. so molecule is optically inactive.

(Q) 

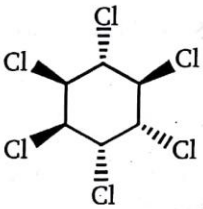
Molecule has P.O.S. so optically inactive.

(R) 

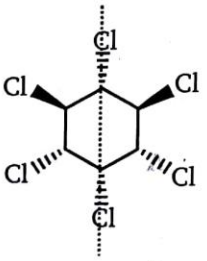
Molecule has P.O.S. & C.O.S. so O.I.

(S) 

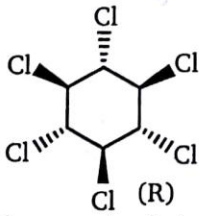
Molecule has P.O.S. & C.O.S. so O.I.

(T) 

Molecule doesn't has P.O.S. & C.O.S. so optically active.

(U) 

Molecule has P.O.S. so O.I.

(B) 

Most stable conformer

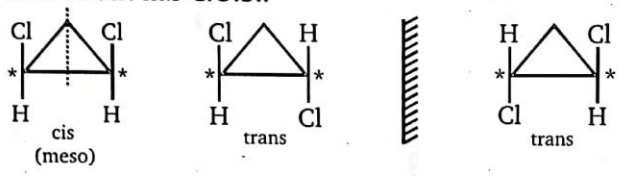
because in chair conformer all chlorine atoms are in equatorial position. It will stabilise the system.

19. (a) Enantiomers $\Rightarrow 1$
(b) identical $\Rightarrow 4$
(c) identical $\Rightarrow 4$
(d) identical $\Rightarrow 4$
$\therefore \quad 1+4+4+4=13$

20. $A \rightarrow b, d, e$; $B \rightarrow a, c, f, h$; $C \rightarrow i, k, p$

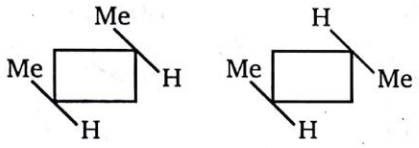
21. (A) e, f, j $\longrightarrow$ Str. do not have P.O.S. & C.O.S. so optically active.
(B) a, b, c, d g, h, i – has P.O.S. so are O.I.
(C) No one str. has C.O.S..

22. (i)



Total = 3

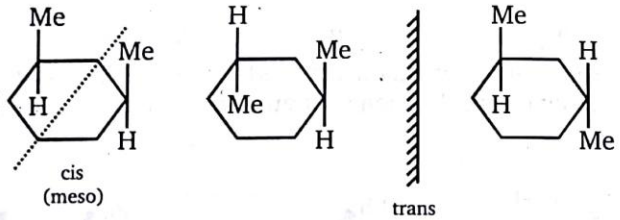
(ii)



Total = 2
doesn't contain chiral centre but is capable to show G.I.

(iii) $\overset{4}{CH_3}-\overset{3}{\underset{*}{CH}}(Cl)-\overset{2}{\underset{*}{CH}}(Br)-\overset{1}{CH_3} = 2^2 = \text{Total} = 4$

(iv)



Total = 3 | $w + x + y + x = 12$

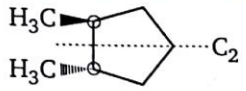
24. A – (a & c) (b & f) ; B – (a & d) or (c & d), (a & e) (c & d) ; C – (d & e)

26. Select optically active compounds do not have P.O.S. and C.O.S..

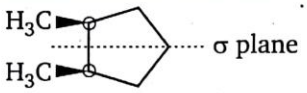
27. A – d, h ; B – d ; C – f, h ; D – h

28.

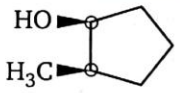
Compound	A	B	C	Compound	A	B	C
I	c	a	a	VI	c	a	a
II	c	b	b	VII	c	a	a
III	c	a	a	VIII	e	b	b
IV	c	b	b	IX	e	a	a
V	c	a	a	X	e	b	b

(I) 

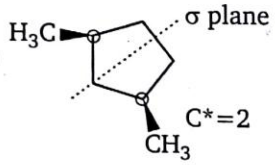
No. of chiral centres = 2

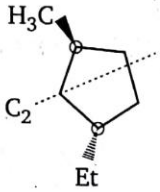
(II) 

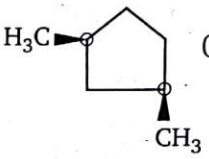
No. of chiral centres = 2

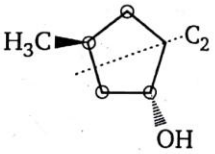
(III) 

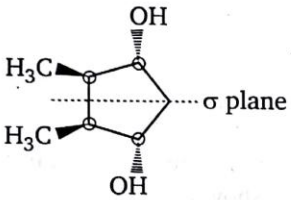
No. of chiral centres = 2

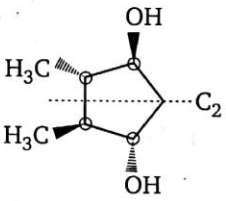
(IV) 

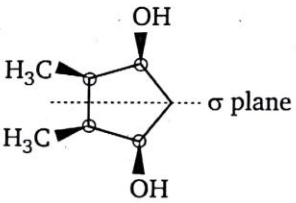
(V) 

(VI) 

(VII) 

(VIII) 

(IX) 

(X) 

29. (a) (R)
Lowest priority atom is present on
Horizontal line so configuration will be (R)

(b) L
NH_2 group is situated on L.H.S.

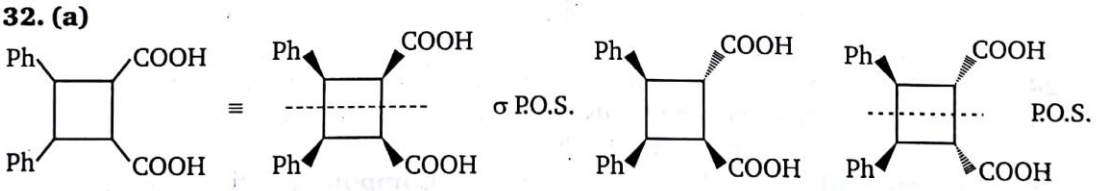
30. (A) 1 – N ; 2 – Z ; 3 – E 4 – Z ; 5 – Z
6 – E ; 7 – N ;

(B) 1 – Z ; 2 – E ; 3 – E ; 4 – Z ; 5 – Z ; 6 – E

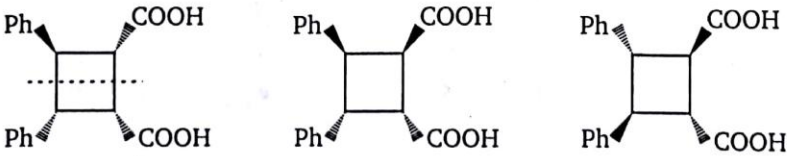
If higher priority atoms/groups are situated on same side then configuration will be (Z) and if these are situated on opposite side, then configuration will be (E).

31. 1 – Z ; 2 – N ; 3 – E

32. (a)



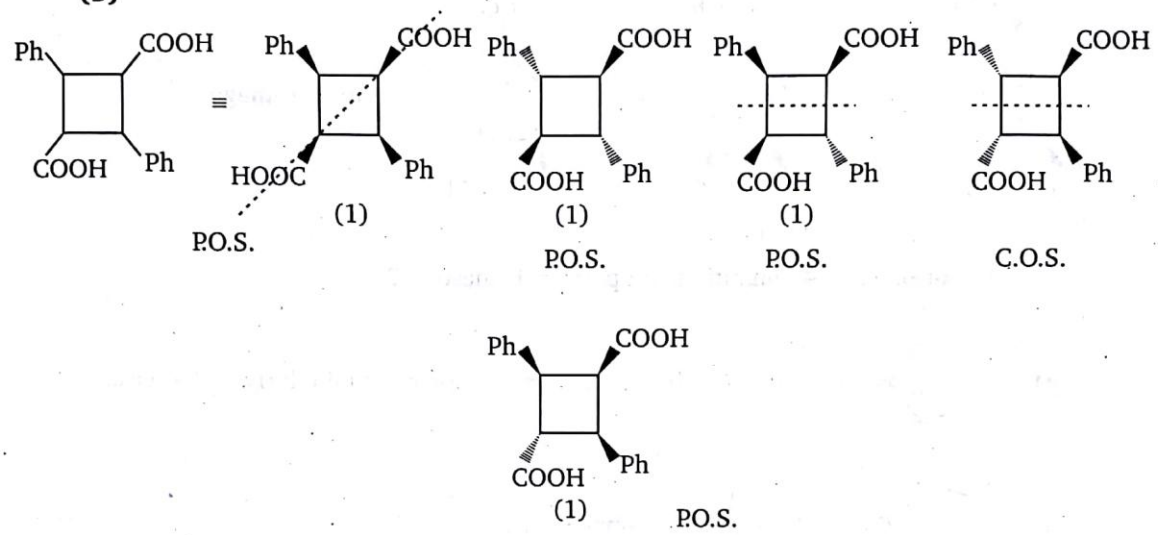
(1) (2) (1)



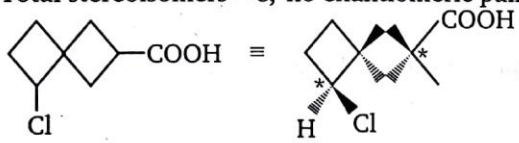
(2) (2) (2)

Total stereoisomer = 10; Enantiomeric pairs = 4; No. of meso = 2

(b)



Total stereoisomers = 5, no enantiomeric pairs, all 5 are meso compounds.

(c) 

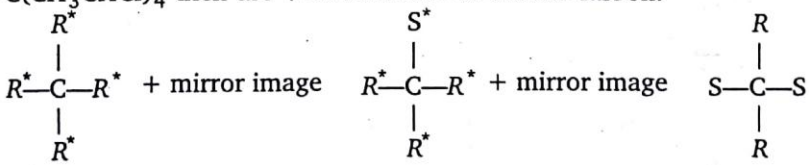
molecule is chiral ($n = 2$)

Total stereoisomers = 4 ; no. of enantiomeric pairs = 2 ;no meso

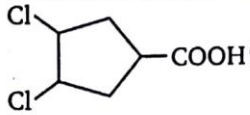
(d) 

(molecules is chiral) ∴ no of stereoisomers = 2
no. of enantiomeric pairs = 1

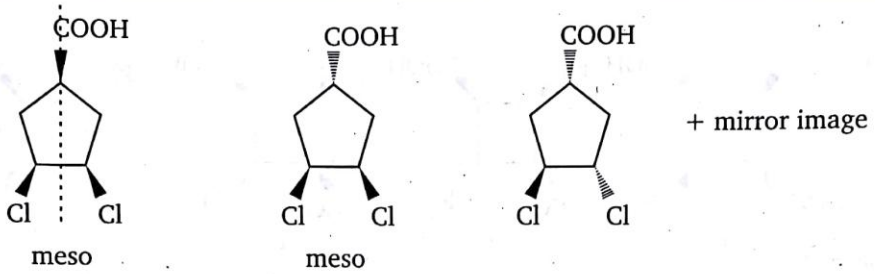
(e) $C(CH_3CHCl)_4$ their are 4 chiral atoms on middle carbon.



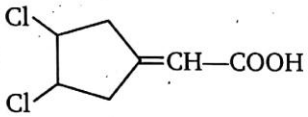
Total stereoisomer = 5 ; No. of enantiomeric pairs = 2 ; No. of meso = 1

(f) 

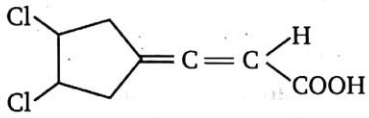
This molecule has 2 chiral centres and a pseudo asymmetric centre.



Total stereoisomer = 4 ; enantiomeric pairs = 1; meso = 2

(g) 

will have 2 enantiomeric pairs (similarly makes cases)

(h) 

(makes cases)

Total stereoisomer = 4 ; enantiomeric pairs = 1; meso = 2

33. Solution in book.

34. Solution in book.

35. Solution in book.

36. (A) (d)

(B) (b)

cis-(meso)

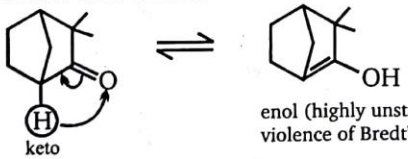
and its mirror image.

trans-(optically active)

P.O.S. ✓ ×

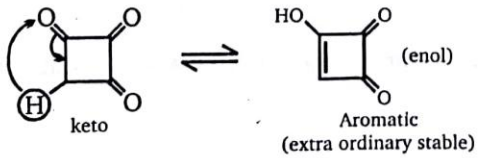
37. Draw and Check.

38. (a)

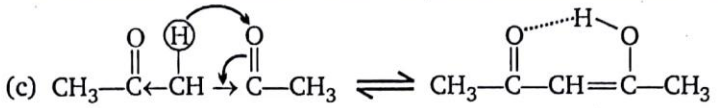


enol (highly unstable)
violence of Bredt's rule

(b)

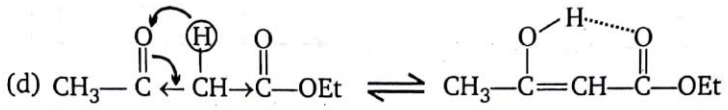


Aromatic
(extra ordinary stable)

(c) 

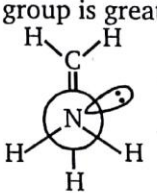
keto

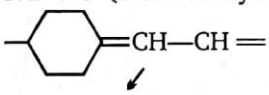
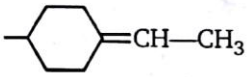
enol form
is stabilised by
(I) Intramolecular Ⓗ- bonding
(II) Resonance stabilised.

(d) 

enol form (stable)

In both compound (c) and (d) active methylene group is present but $-I$ effect of keto group is greater than ester that's why enol content of (c) is greater than (d).

39.  Most stable conformer around (N — C) bond.

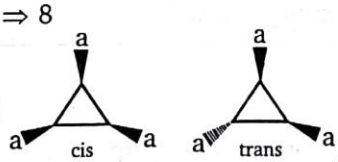
40. (1) $2^4 \Rightarrow 16$; (2) $2^2 \Rightarrow 4$; (3) $2^4 = 16$ ($n = 4$ = stereogenic centre)
(4) $2^2 \Rightarrow 4$ (molecule unsymmetrical) ; (5) $2^2 \Rightarrow 4$
(6) $2^2 \Rightarrow 4$ (molecule unsymmetrical) ; (7) $2^2 = 4$
(8) S. I $\Rightarrow$ 3 (molecule symmetrical)
(9)  ; (10) $2^2 \Rightarrow 4$; (11) 

Show optical isomerism

$n = 2$; $2^2 = 4$

Show O.I. only

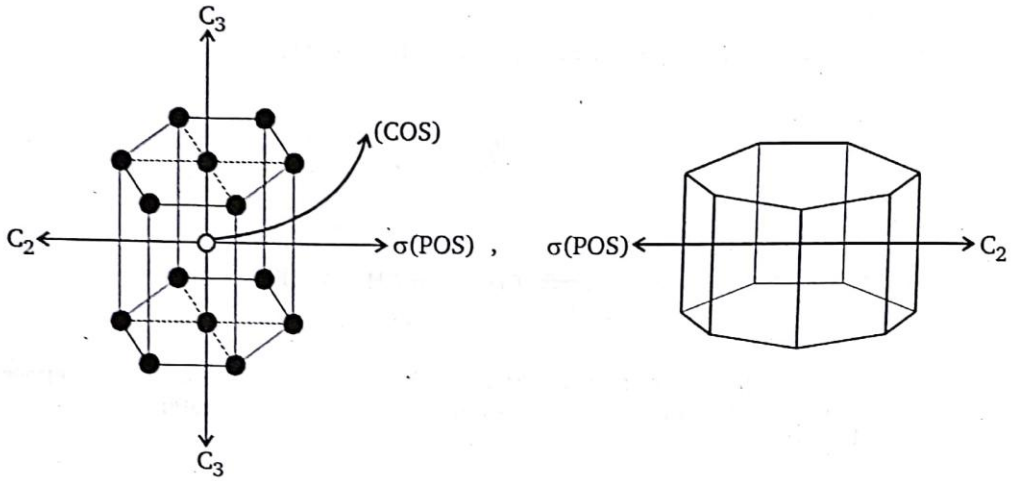
$n = 1$; $2^1 = 2$

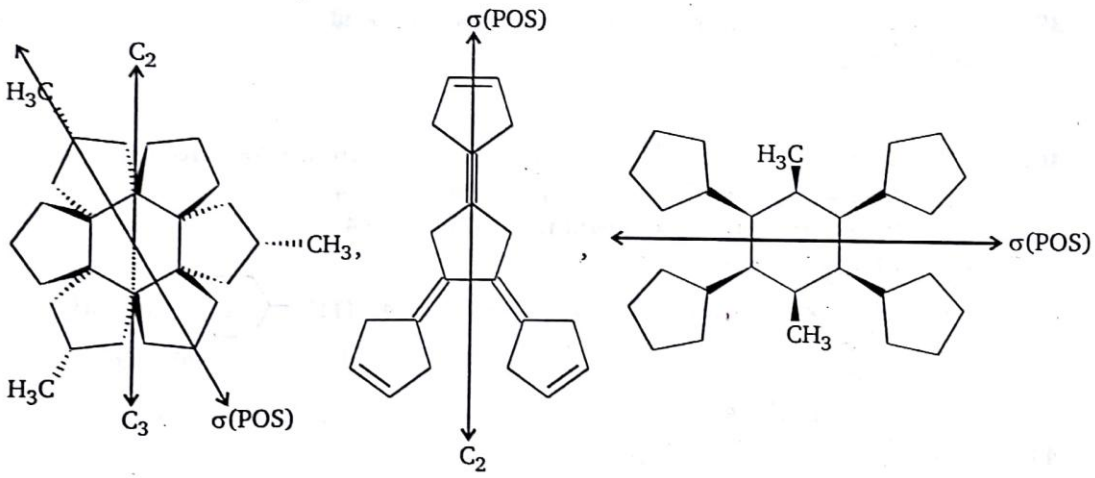
41. (1) $2^1 = 2$
(2) $2^2 = 4$
(3) $2^{n-1} + 2^{(n/2-1)} = 2^{2-1} + 2^{(2/2-1)} = 2^1 + 2^0 = 2^1 + 1 = 3$
(4) 4
(5) $2^3 \Rightarrow 8$
(6) (2) 

cis trans

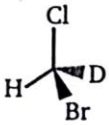
43. (a) $2^5 \Rightarrow 32$ (b) $2^5 \Rightarrow 32$
(c) $a = 2^{n-1} = 2^{8-1} = 2^7 = 128$; $m = 2^{(n/2-1)} = 2^{(8/2-1)} = 2^{(4-1)} = 2^3 = 8$
Total S. I $\Rightarrow 2^7 + 2^3 = 128 + 8 = 136$
(d) $2^9 = 512$
Summing up all stereoisomer : $\underset{(a)}{32} + \underset{(b)}{32} + \underset{(c)}{(128 + 8)} + \underset{(d)}{512} = 712$

46.

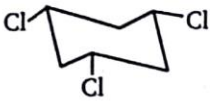




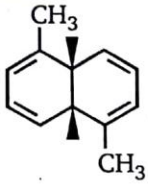
SUBJECTIVE PROBLEMS

1. (c) 

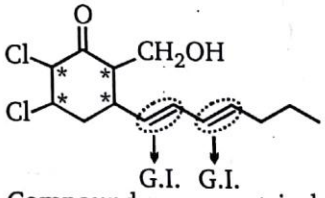
one chiral center is present so compound is chiral (P.O.S. absent).

(f) 

P.O.S. absent so compound is chiral.

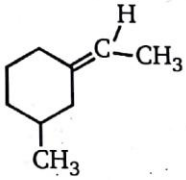
(h) 

No C.O.S.; no P.O.S.

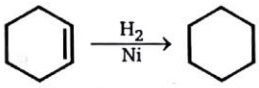
2. 

S. I = $2^6 \Rightarrow 64$

Compound unsymmetrical.

3. (i) 

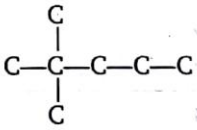
S. I $\Rightarrow 2^2 = 4$

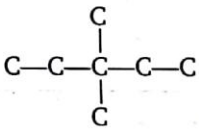
(ii) 

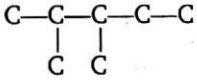
$[C_6H_{12}]$ Degree of unsaturation $\Rightarrow$ 1

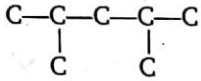
S.I. of (C) + DU of (D) = 5

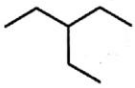
4. $[C_7H_{16}]$

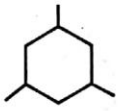
(1) 

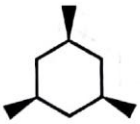
(2) 

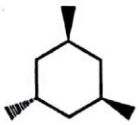
(3) 

(4) 

(5) 

5. 
Possible [G. I.] = 2

(a) 

(b) 

6. $[C_5H_{11}Br]$; Total = 8

(a) C—C—C—C—C—Br

(b) C—C—C—C(Br)—C

(c) C—C—C(Br)—C—C

(d) C—C—C(C)—C—Br

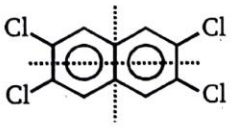
(e) C—C—C(Br)(C)—C

(f) Br—C—C—C(C)—C

(g) C—C(C)(C)—C—Br

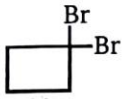
(h) C—C(Br)—C(C)—C

7.

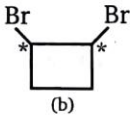


POS (σ) → σ_H, σ_V, $\sigma_{molecular}$ all 3 P.O.S. is present.

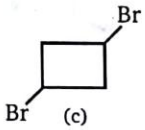
8. $[C_4H_6Br_2]$



(a)



(b)

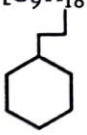


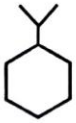
(c)

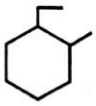
	(a)	(b)	(c)
O.I	×	✓	×
G.I	×	✓	✓
Possible isomers:	1	3	2

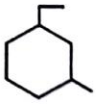
Total S.I. = 1 + 3 + 2 = 6

9. $[C_9H_{18}]$

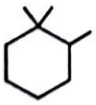
(a) 

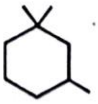
(b) 

(c) 

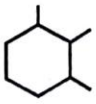
(d) 

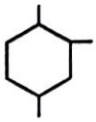
(e) 

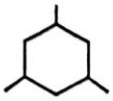
(f) 

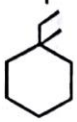
(g) 

(h) 

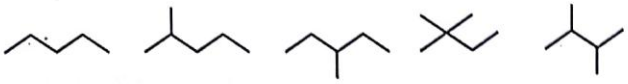
(i) 

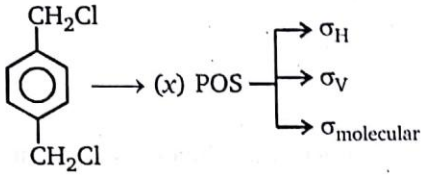
(j) 

(k) 

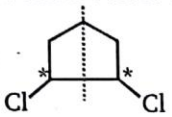
(l) 

10. $[C_4H_{10}O]$ (1) C—C—C—C—OH (2) C—C—C(OH)—C (3) C—C(C)—C—OH (4) C—C(C)(OH)—C

11.  Total = 5

12. (a) 

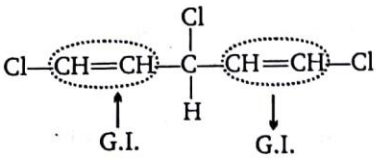
Total 3 P.O.S. are present.

(b) 

$\longrightarrow$ $(y)\ \sigma_V$ is present meso isomer $= 2^{(n/2-1)} = 2^{(2/2-1)} = 2^{1-1} = 2^0 = 1$

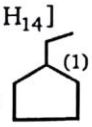
Sum of $x + y = 3 + 1 = 4$

13. $CH_3-\underbrace{CH=CH}_{GI}-\overset{*}{\underset{Br}{CH}}-\overset{*}{\underset{Cl}{CH}}-CH_3$ stereocentres $= 2 + 2 = 4$

14. 

S. I. = 4
(makes cases)

15. $[C_7H_{14}]$

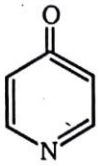
(1) 

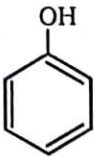
(2) 

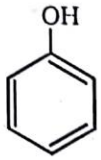
(3) 
(4) 

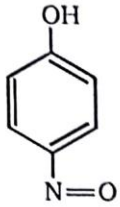
S. I. = 3 (symmetrical) S. I. = 3

Total = 8

16. (a) 

(b) 

(c) 

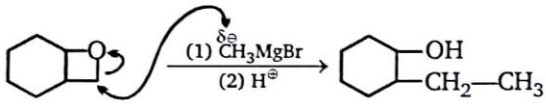
(d) 

17. $x = 6$

3 Grignard Reagent

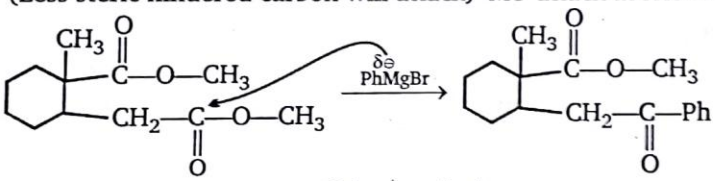
Level-1

1. (b)



(Less steric hindered carbon will attack) 'Me' attack at less hindered 'C' atom

2. (d)



less steric hindered ester will be attacked.

3. (b) Reaction (1) $x = 6$

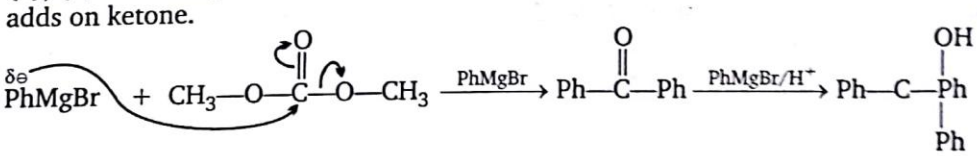
2 mole of CH_3MgBr act as a base 4 mole of CH_3MgBr act as a nucleophile

Reaction (2) $y = 3$

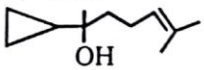
3 mole of CH_3MgBr act as a nucleophile.

4. (d) (a), (b) are example of nucleophilic addition reaction of GR on aldehyde while in (c) GR adds on ketone.

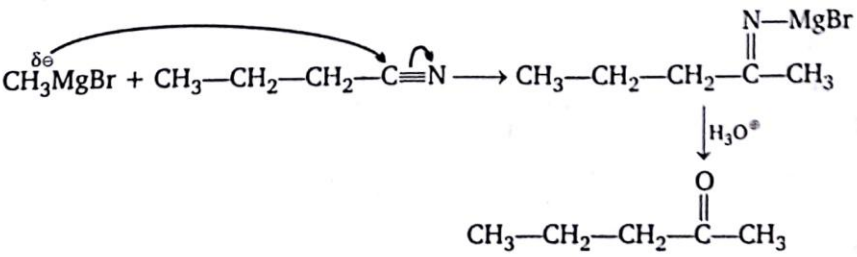
5. (c)



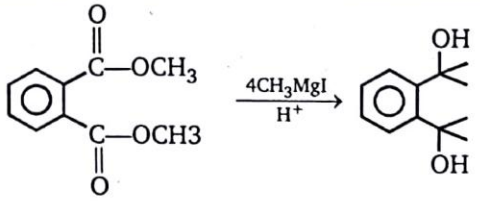
6. (d) In (i), (ii) and (iii), nucleophilic - addition take place to form compound



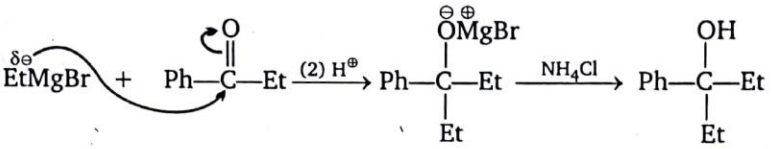
7. (c)



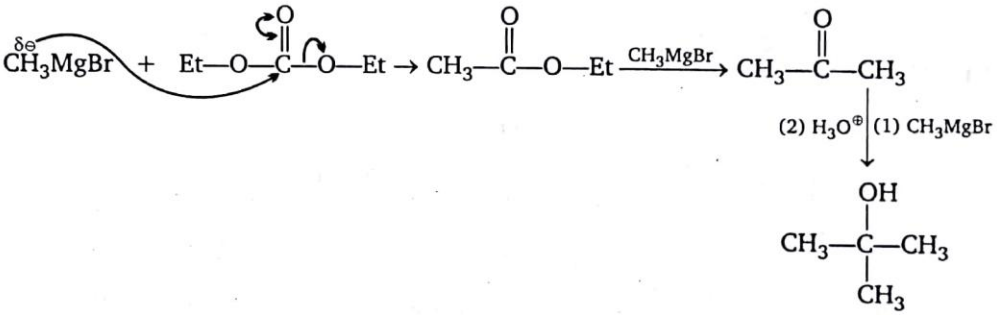
8. (c)



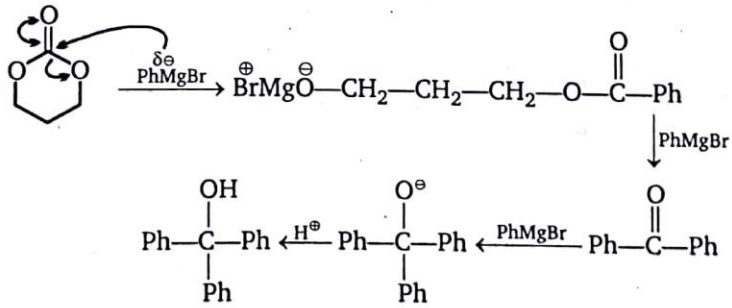
9. (d)



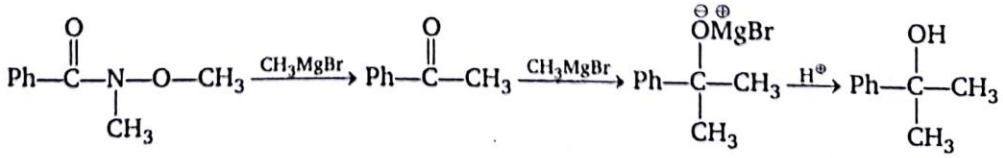
10. (c)



11. (b)

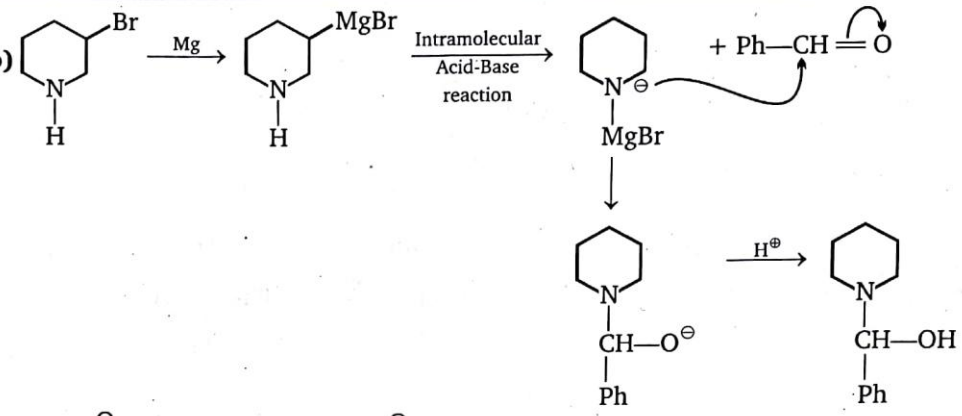


12. (b)

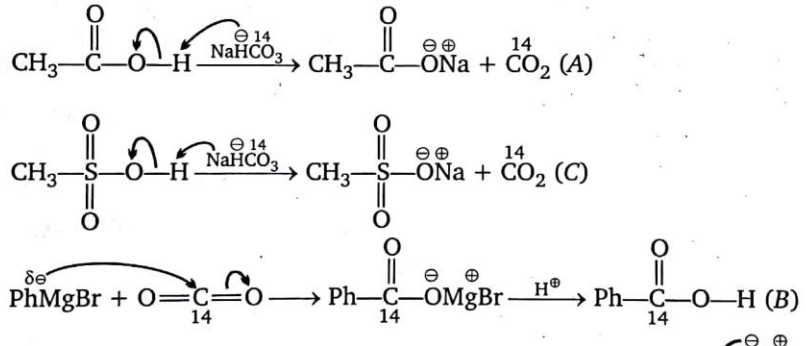


excess of CH_3MgBr is used to maximise the yield.

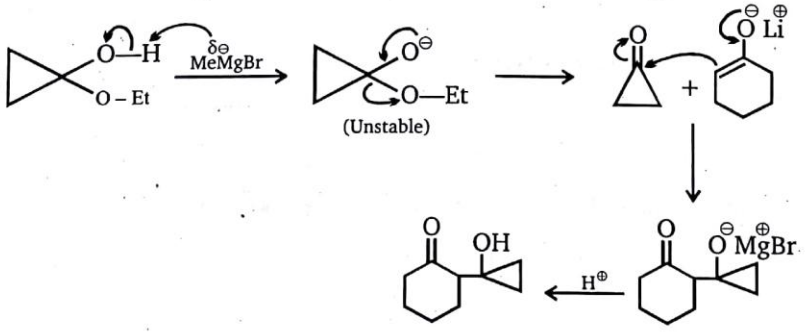
13. (b)



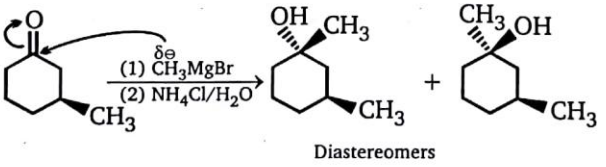
14. (c)



15. (b)

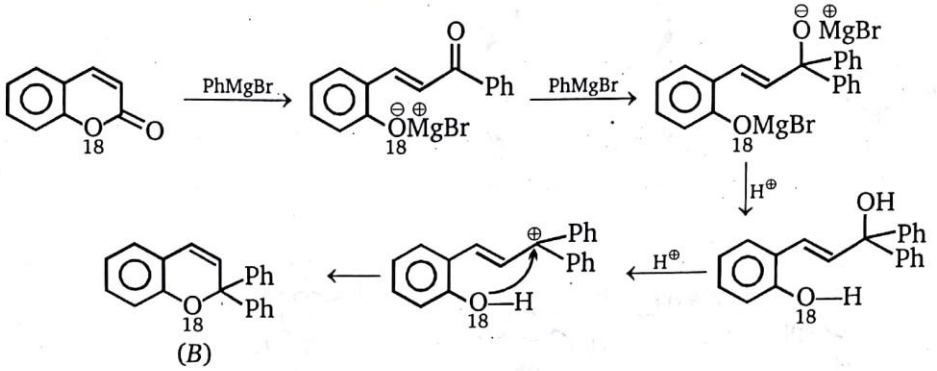


16. (b)



17. (d) All reactions are between Girgnard reagent and the reagents having 'H' or 'D'
∴ all are acid-base reactions.

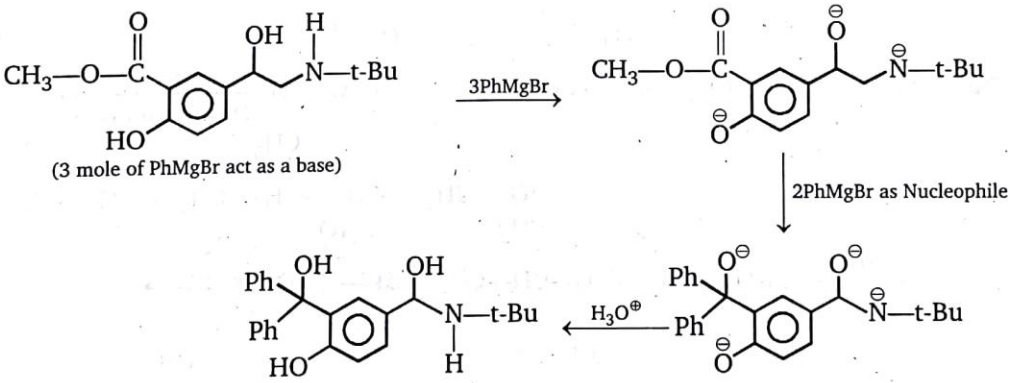
18. (d)



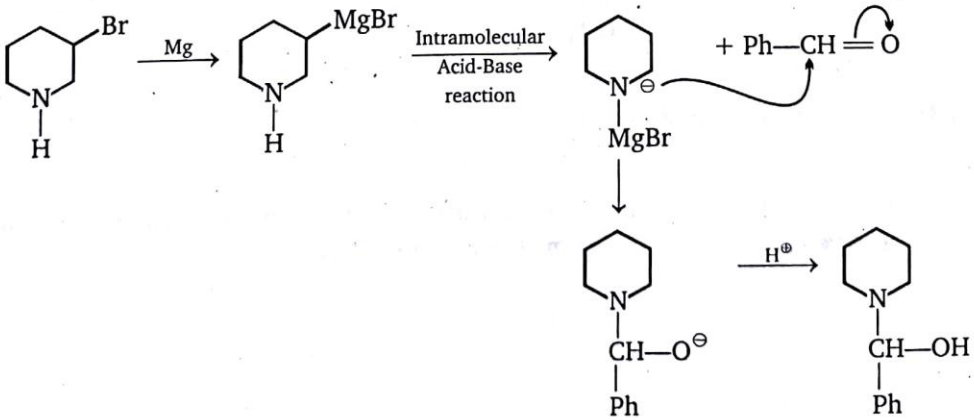
19. (d) $\overset{\ominus}{E}t\overset{\oplus}{M}gBr + H-\overset{\curvearrowright}{O}-\overset{O}{\overset{\|}{C}}-O-Ph \longrightarrow Ph-\overset{\curvearrowleft}{O}-\overset{O}{\overset{\|}{C}}-\overset{\curvearrowright}{\overset{\ominus}{O}}\overset{\oplus}{M}gBr \longrightarrow O=C=O + Ph-OMgBr$

20. (d) Benzene will not react with Grignard reagent.

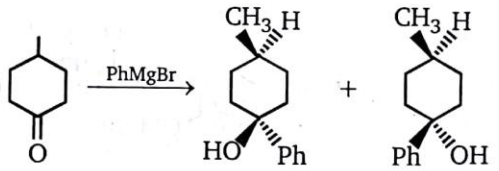
21. (c)



22. (b)

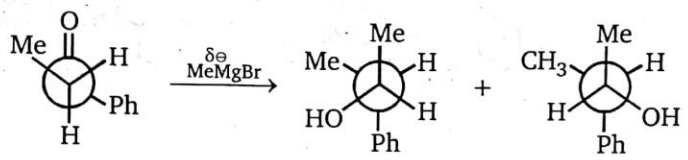


23. (b)

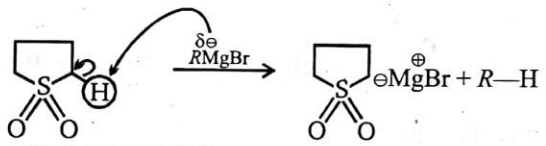


(Geometrical isomers)

24. (c)



25. (c)



(Acid -base reaction)

26. (b) $HO-CH_2-CH_2-\underset{}{\overset{CH_3}{\overset{|}{CH}}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[\text{(Acid-base reaction)}]{CH_3-Li}$

$HO-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus}Li^{\oplus}$

$\xrightarrow[\text{Acid-base}]{CH_3-Li} Li^{\oplus}O^{\ominus}-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O^{\ominus}Li^{\oplus} \xrightarrow{\overset{\delta\ominus}{CH_3}-Li}$

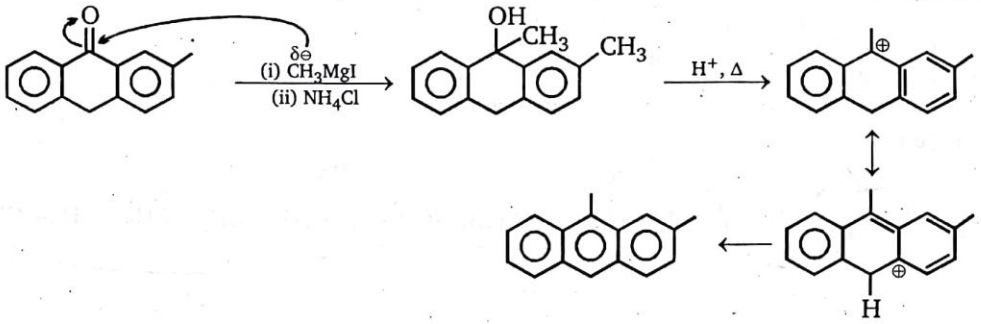
$O^{\ominus}-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\underset{CH_3}{\overset{O^{\ominus}Li^{\oplus}}{\overset{|}{\underset{|}{C}}}}-O^{\ominus}Li^{\oplus} \xrightarrow{NH_4Cl} HO-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

27. (d) $R-\overset{O}{\overset{\|}{C}}-Cl + R_1MgBr \xrightarrow[(2)H^{\oplus}]{} R-\underset{R_1}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-R_1$

at least two like group are attached with 3° alcohol then that alcohol can be prepared.

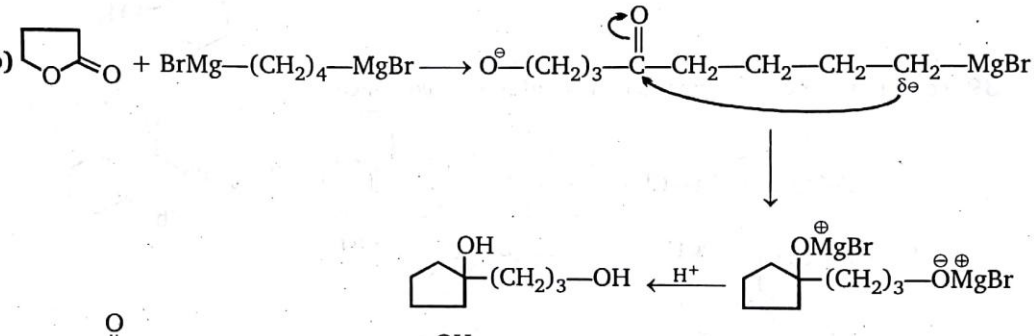
(d) has three unlike group : it cannot be prepared.

28. (d)

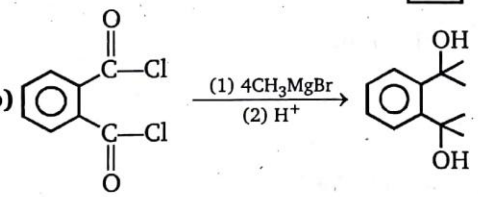


29. (a) $\overset{\delta\ominus}{R}MgBr + S \longrightarrow R-\overset{\ominus\oplus}{S}MgBr \xrightarrow{H^+} R-S-H$

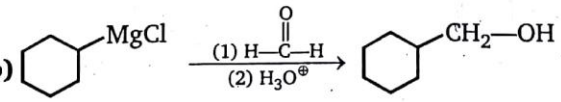
30. (b)



31. (b)



32. (b)



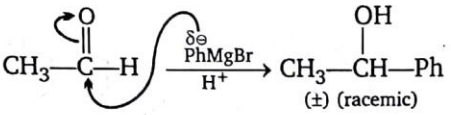
33. (d) In non-polar solvent solution of Grignard reagent is possible.

34. (b)

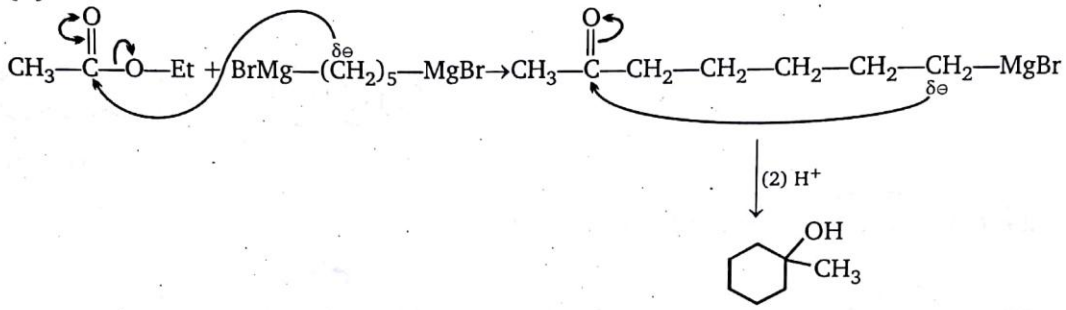
$H_2C{=}CH{-}CH_2{-}Br \xrightarrow{Mg} H_2C{=}CH{-}\overset{\delta\ominus}{CH_2}{-}MgBr + H_2C{=}CH{-}CH_2{-}Br \xrightarrow{S_{N^2}}$ 

35. (c) $\overset{\delta\ominus}{CH_3}MgBr + CH_3{-}C({=}O){-}CH_3 \xrightarrow{H_3O^\oplus} CH_3{-}C(CH_3)_2{-}OH$

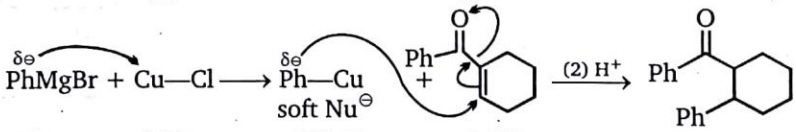
36. (c) $\overset{\delta\ominus}{CH_3}MgBr + CH_3{-}C{\equiv}N \longrightarrow CH_3{-}C({=}N{-}MgBr){-}CH_3 \xrightarrow{H_3O^+} (CH_3)_2C{=}O$

37. (b) 

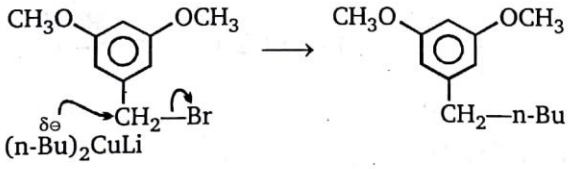
38. (b)



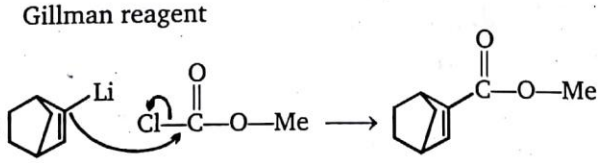
39. (b) In presence of copper salt 1, 4-addition take place.

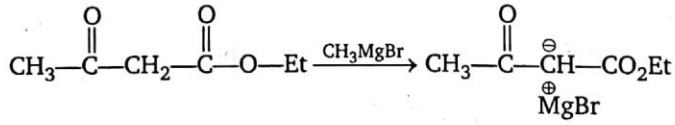


40. (a)

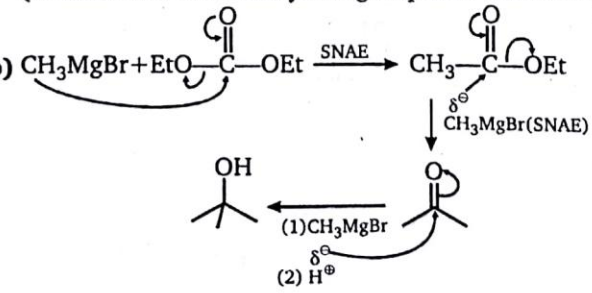


41. (b)

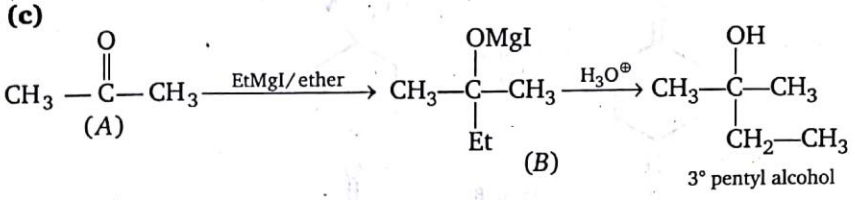


42. (c) 

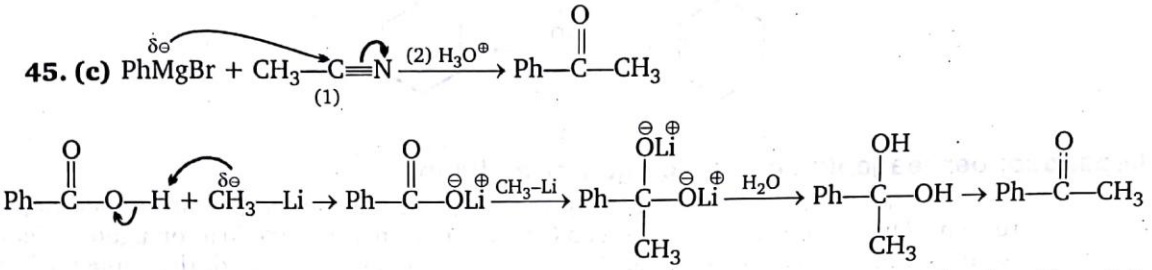
(because of active methylene group acid-base take place).

43. (b) 

44. (c)

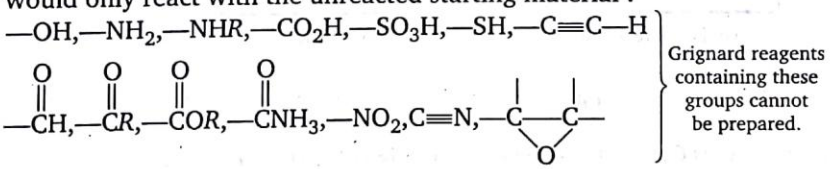


45. (c)



46. (d) The Grignard reagent is a very powerful base ; in effect it contains a carbanion. Thus, it is not possible to prepare a Grignard reagent from an organic group that contains an acidic hydrogen ; by an acidic hydrogen, we mean any hydrogen more acidic than the hydrogen atoms of an alkane or alkene. We cannot, for example, prepare a Grignard reagent from a compound containing an — OH group, an — NH – group, an — SH group, a — CO_2H group, or an — SO_3H group. If we were to attempt to prepare a Grignard reagent from an organic halide containing any of these groups, the formation of the Grignard reagent would simply fail to take place. (Even if a Grignard reagent were to form, it would immediately react with the acidic group.)

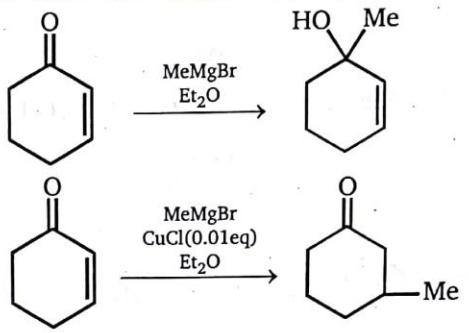
Since Grignard reagents are powerful nucleophiles, we cannot prepare a Grignard reagent from any organic halide that contains a carbonyl, epoxy, nitro, or cyano (– CN) group. If we were to attempt to carry out this kind of reaction, any Grignard reagent that formed would only react with the unreacted starting material :



This means that when we prepare Grignard reagents, we are effectively limited to alkyl halides or to analogous organic halides containing carbon - carbon double bonds, internal triple bonds, ether linkages, and —NR_2 groups.

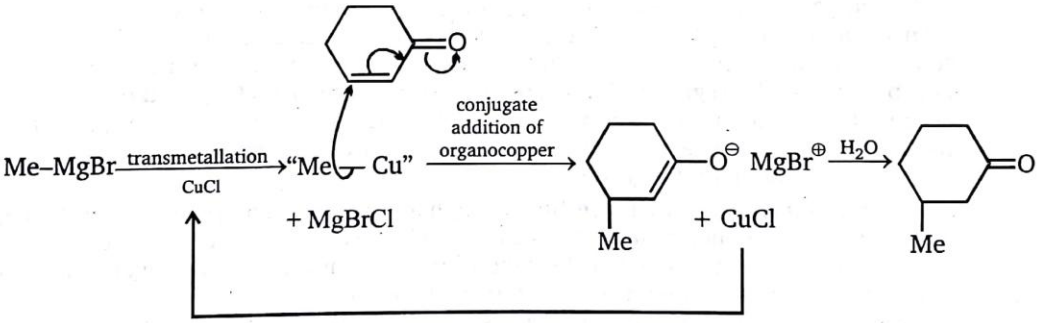
47. (b) Copper (I) salts have a remarkable effect on organometallic reagents.

Grignard reagents add directly to the carbonyl group of α,β-unsaturated aldehydes and ketones to give allylic alcohols : you have seen several examples of this, and you can now explain it by saying that the hard Grignard reagent prefers to attack the harder C = O rather than the softer C = C electrophilic centre. Here is a further example - the addition of MeMgBr to a cyclic ketone to give an allylic alcohol, plus, as it happens, some of a diene that arises from this alcohol by loss of water (dehydration). Below this example is the same reaction to which a very small amount (just 0.01 equivalents, that is 1%) of copper(I) chloride has been added. The effect of the copper is dramatic : it makes the Grignard reagent undergo conjugate addition, with only a trace of the diene.



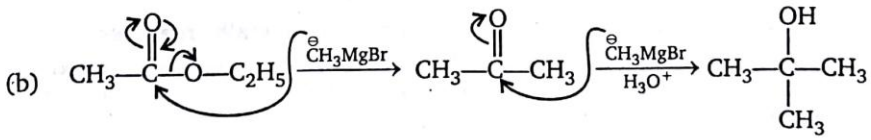
Organocopper reagents undergo conjugate addition:

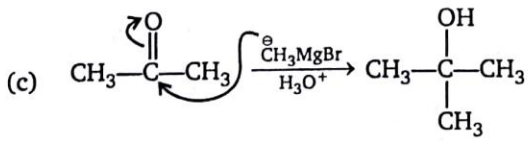
The copper works by transmetallating the Grignard reagent to give an organocopper reagent. Organocoppers are softer than Grignard reagents, and add in a conjugate fashion to the softer C = C double bond. Once the organocopper had added, the copper salt is available to transmetallate some more Grignard, and only a catalytic amount is required.



copper(I) recycled : only a catalytic quantity is required

48. (d) Compound (A) is $CH_3-C(OH)(CH_3)-CH_3$, (b) & (c) give (A)





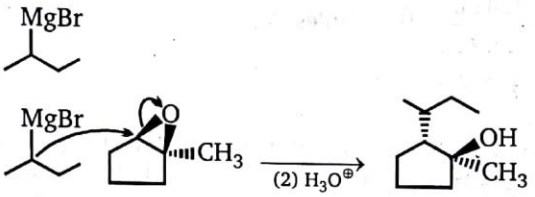
49. (b) $CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow{CH_3MgBr} CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

$\xrightarrow{(1)\ CH_3MgBr,\ (2)\ H_3O^{\oplus}} CH_3-CH_2-CH_2-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-CH_3$

50. (a) $CH_3-CH_2-\overset{\curvearrowleft}{O}-\overset{\curvearrowleft}{H} + \overset{\delta\ominus}{R}-MgBr \longrightarrow R-H + Et-O-MgBr$

(Acid - base reaction)

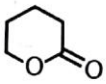
51. (a)



In basic medium less sterichindered carbon will be attacked.

52. (a) $CH_3CH_2MgBr + Ph-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{(2)\ H^+} Ph-\underset{CH_2-CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-CH_3$

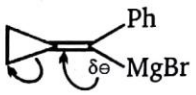
53. (c)



$\xrightarrow{CH_3MgBr} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{-\delta+\delta}{O}MgBr$

$\xrightarrow{(1)\ CH_3MgBr,\ (2)\ H^+} CH_3-\underset{CH_3}{\overset{OH}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_2-CH_2-CH_2-OH$

54. (b)

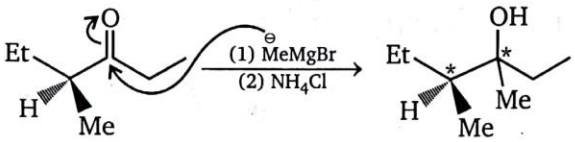


$\rightarrow Ph-C\equiv C-CH_2-\underset{\delta\ominus}{CH_2}-MgBr + H-\overset{O}{\overset{\|}{C}}-H \xrightarrow{H^+} Ph-C\equiv C-CH_2-CH_2-CH_2-OH$

(Strain in the ring)

55. (b) (a) Gives 1-Butanol as the product
(c) Gives 2-methyl-2-hexanol as the product
(d) Gives 2-propyl-1-pentanol as the product
only (b) gives 4-heptanol as the product.

56. (a) attack of Nucleophilic on sp^2 carbon.



Two chiral carbons in the product. Configuration of one carbon is fixed.
Attack on the carbonyl carbon can be from two sides. Hence products obtained will be diastereomers.

57. (c) Because 3 acidic H are present.

58. (c) mol. mass of $A = 12\times 5 + 8 + 16 = 84g$

moles of $A = \dfrac{0.40g}{84g} = 0.005$ moles

moles of gas released at STP $= \dfrac{224\,mL}{22.4\,L} = 0.01$ moles

$\therefore$ 0.005 moles of A release 0.01 moles of gas.

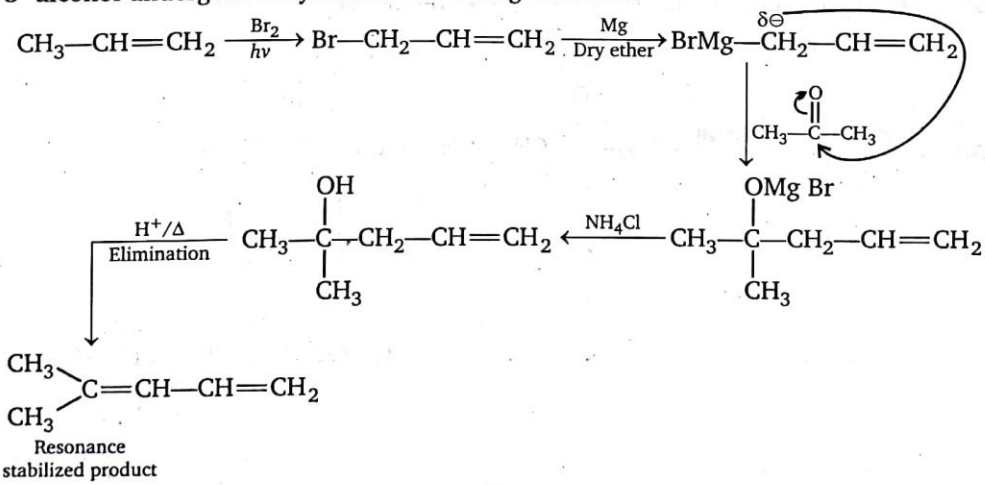
i.e., ratio of 1 : 2.

Hence there must be two acidic H in the compound A. One acidic H is from alcohol the other must be terminal alkyne as only the H attached to terminal alkynes are acidic.

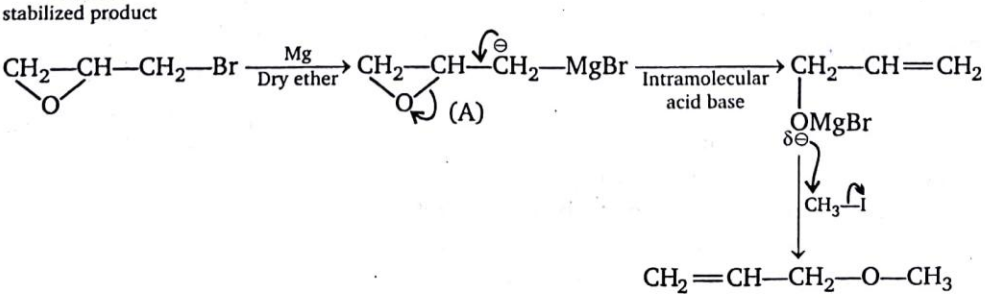
$$A \xrightarrow{\text{Excess } H_2} \text{pentan-1-ol}$$

Hence option (d) is incorrect.

59. (b) 3° alcohol undergoes dehydration on heating with acid.



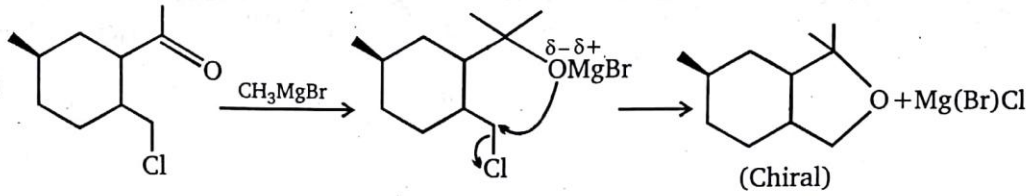
60. (c)



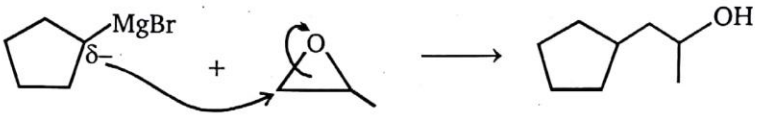
61. (d) $POCl_3$/Pyridine is dehydrating agent. It will cause elimination of H_2O to give alkene.

62. (a) $Y \Rightarrow CH_2{=}CH{-}CH_2{-}C{\equiv}N \xrightarrow[H^{\oplus}/HOH]{\overset{\ominus}{C_6H_5}MgBr} CH_2{=}CH{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}C_6H_5$ (Z)

63. (d)

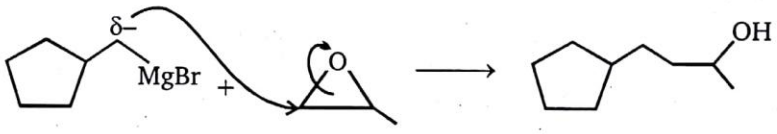


64. (b) (a)

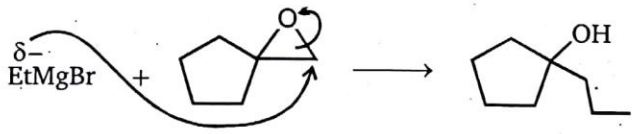


Attack on less steric site

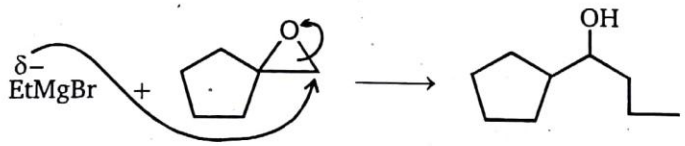
(b)



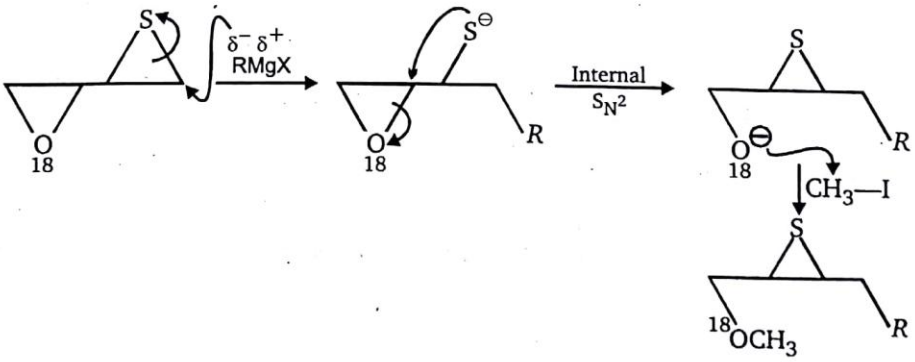
(c)



(d)

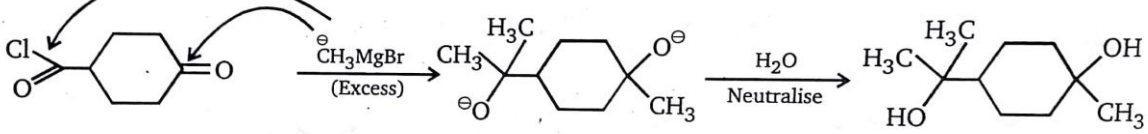


65. (c)



Ring containing sulphur is more strained.

66. (d)



Level-2

1. Grignard reagents are usually prepared by the reaction of an organic halide and magnesium metal (turnings) in an ether solvent.

$$\left.\begin{array}{l} RX + Mg \xrightarrow{Et_2O} RMgX \\ ArX + Mg \xrightarrow{Et_2O} ArMgX \end{array}\right\} \text{Grignard reagents}$$

The order of reactivity of halides with magnesium is also $RI > RBr > RCl$. Very few organomagnesium fluorides have been prepared. Aryl Grignard reagents are more easily prepared from aryl bromides and aryl iodides than from aryl chlorides, which react very sluggishly.

Grignard reagents are seldom isolated but are used for further reactions in ether solution. The ether solutions can be analyzed for the content of the Grignard reagent, however, and the yields of Grignard reagents are almost always very high (85–95%). Two examples are shown here :

$$CH_3I + Mg \xrightarrow[35°C]{Et_2O} \underset{\substack{\text{Methylmagnesium iodide} \\ (95\%)}}{CH_3MgI}$$

$$C_6H_5Br + Mg \xrightarrow[35°C]{Et_2O} \underset{\substack{\text{Phenylmagnesium bromide} \\ (95\%)}}{C_6H_5MgBr}$$

2. Reaction of Grignard reagent with aldehyde or ketone is an example of nucleophilic addition.

a – r; b – q; c – p; d – s

3. Reaction of Grignard reagent with aldehyde or ketone is an example of nucleophilic addition.

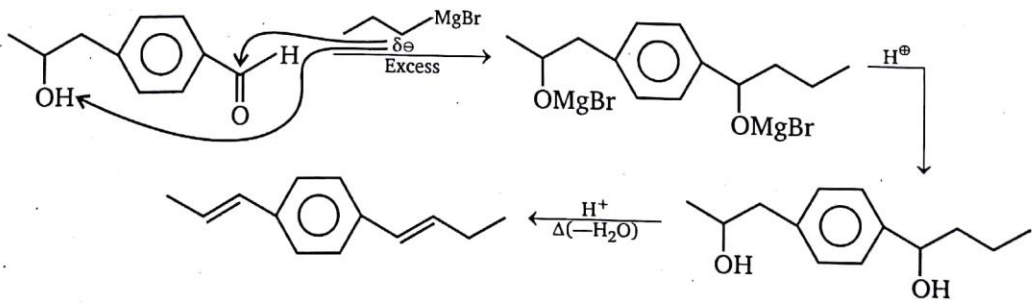
a – s; b – r; c – q; d – p

4. a – r; b – q; c – p; d – s

5. Number of active hydrogen present in organic compound will be four based on mole concept calculation so the answer will be (a) and (b).

SUBJECTIVE PROBLEMS

1.



2. (a) $CH_3 — CH_2 — CH_2CHO \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr} 2°$ alcohol

(b) $CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CHO \xrightarrow[\text{(ii) } H^+]{\text{(i) } CH_3MgBr} 2^\circ$ alcohol

3. Esters and nitrile will consume 2 moles *RMgX* each.
Ketone will consume only one mole.

4. (a) $C-C-C-C-OH$ (with C branch on the second C)

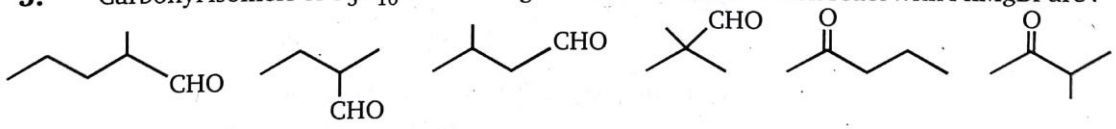
(b) $C-C-\overset{OH}{\overset{|}{C}}-C$ (with C branch on the second C)

(c) $C-\overset{C}{\overset{|}{C}}-C-OH$

(d) $C-\underset{OH}{\underset{|}{\overset{C}{\overset{|}{C}}}}-C$

All these alcohol have active hydrogen so these are capable to react with CH_3MgBr to evolve CH_4 gas.

5. Carbonyl isomers of $C_5H_{10}O$ that will give racemic mixture when react with PhMgBr are :



6. Moles consumed in
- Acid-base reaction = 2
- $Nu^\ominus$ Addition reaction = 6

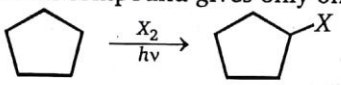
Total = 8

4(A) Hydrocarbons (Alkanes)

Level-1

1. (d) $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \xrightarrow[h\nu]{X_2} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-X$

Both compound gives only one monohalogenated product is possible.



2. (b) $2CH_3-CH_2-Cl \xrightarrow[\text{Dry ether}]{Na} CH_3-CH_2-CH_2-CH_3$

Open chain alkane product having even number of carbons and symmetrical can be achieved by Wurtz reaction.

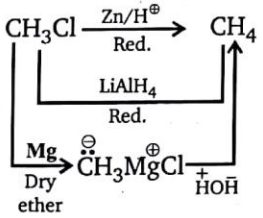
3. (b) Mol. wt. $= 2 \times V.D = 72$

$\therefore$ Mol. formula $= C_5H_{12}$, Structure $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$ neo-pentane

4. (b) $Et-I + CH_3-CH_2-CH_2-I \xrightarrow[DE]{Na} Et-Et + CH_3-CH_2-CH_2-Et$ + hexane

5. (b) $Cl-CH_2-\overset{*}{\underset{CH_3}{CH}}-CH_2-CH_3$, $CH_3-\underset{CH_3}{CH}-\overset{Cl}{\underset{*}{CH}}-CH_3$

6. (d)



7. (b) $CH_3-CH_2-CH_2-CH_2-Cl$ & $CH_3-\overset{*}{\underset{Cl}{CH}}-CH-CH_3$ and mirror image.

8. (a) In order to maximize the amount of monohalogenated product obtained, a radical substitution reaction should be carried out in the presence of excess of alkane. The

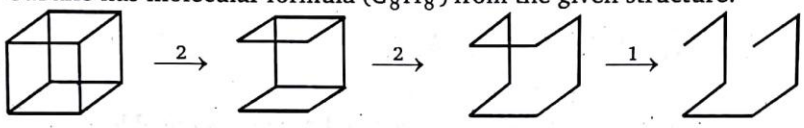
presence of excess alkane in the reaction mixture ensures that there is a greater probability of the halogen radical colliding with a molecule of alkane than with a molecule of alkyl halide. This is true even toward the end of the reaction, by which time a considerable amount of alkyl halide will have been formed. If the halogen radical abstracts a hydrogen from a molecule of alkyl halide rather than from a molecule of alkane, a dihalogenated product will be obtained.

$$Cl^{\bullet} + CH_3Cl \longrightarrow {}^{\bullet}CH_2Cl + HCl$$

$${}^{\bullet}CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^{\bullet}$$

Bromination of alkanes follows the same mechanism as chlorination. The only difference is that chlorination produces alkyl chlorides, whereas bromination forms alkyl bromides.

9. (b) Cubane has molecular formula (C_8H_8) from the given structure.

10. (d) 

Total 5 cleavae.

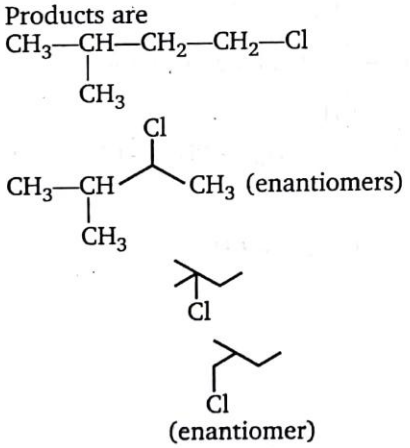
11. (c) Acc. to Arrehenious equation $K = Ae^{-E_a/RT}$

$\therefore$ greater is E_a, the smaller is K *i.e.*, rate of reaction $\propto \dfrac{1}{\text{height of energy barrier}}$.

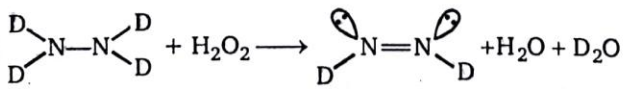
It should be noted that step leading to the height peak will not be rate determining step if the concentration used in some other step is sufficiency high. Since first step is rate determining step.

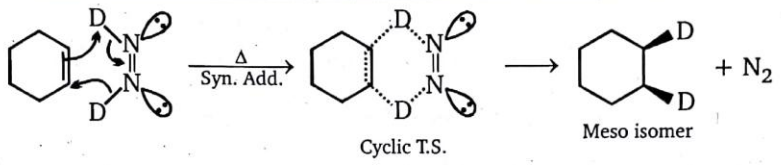
$\therefore$ First peak should be high as is (c).

12. (c) Products are

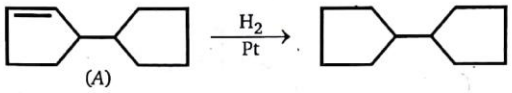


$\therefore$ 6-Products

13. (b) 



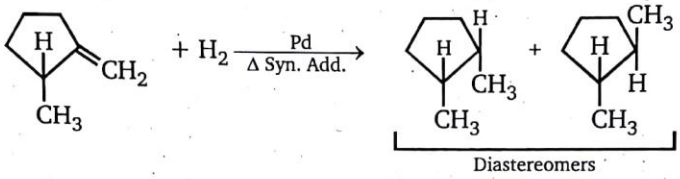
14. (c) Molecular formula



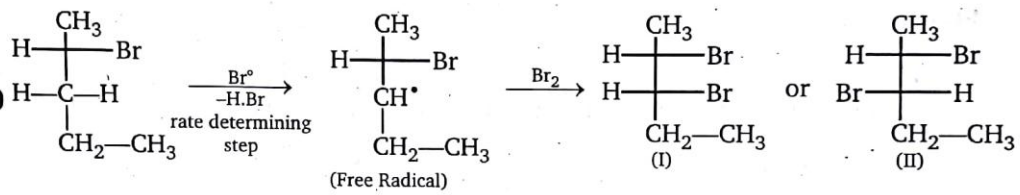
⇒ DBE = 3

15. (c) (iii) is most stable because of less steric repulsion ∴ least heat of combustion.

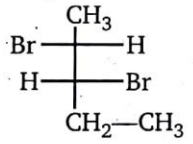
16. (b)



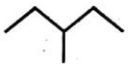
17. (d)



If Free radical (FR) is formed at 3rd carbon,
∴ product I and II are possible, configuration of 2nd carbon will not change. *i. e.*,

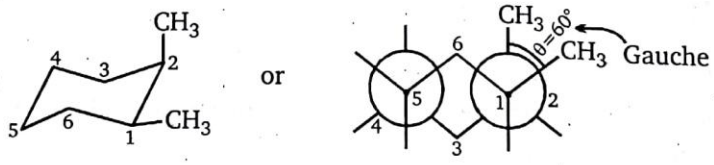


is not possible.

18. (d)  2-ethyl butane is incorrect name.

3-methyl pentane is correct IUPAC name.

19. (c)



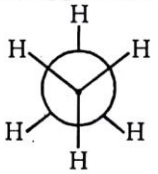
20. (a)

A
cis-1-ethyl-3-methyl cyclohexane

B
trans-1-ethyl-3-methyl cyclohexane

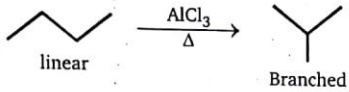
Compound *A* is more stable than compound *B* because in compound *A*, both ethyl and methyl are at equatorial position on the other hand in compound *B*, ethyl is equatorial and methyl is axial.

21. (c) The torsional and steric strain in staggered form is appx. zero.



22. (b) $CH_3-\underset{sp^3}{CH_3} + \frac{7}{2}O_2 \xrightarrow{\Delta} 2\underset{sp}{CO_2} + 3H_2O$

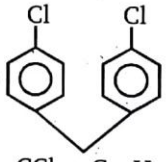
23. (a)



Above reaction is the example of isomerization.

24. (a) CCl_4 pyrene

DDT (Dichloro diphenyl trichloroethane)



CCl_3-C-H
(DDT)

$CCl_3-\overset{O}{\overset{\|}{C}}-H$ chloral $\quad C_6H_6Cl_6$ Gammaxene.

Maximum chlorine content is present in pyrene.

25. (c) $CH_3-CO_2H \xrightarrow[\Delta]{NaOH, CaO} CH_4 + CO_2$

26. (c) $CaC_2 + D_2O \longrightarrow Ca(OD)_2 + D-C\equiv C-D$

27. (c) More the carbon in alkane. More will heat of combustion.

28. (c) Mol. wt. = 86 $\quad\therefore$ Mol. formula $= C_6H_{14}$

site of bromination

site of bromination $\rightarrow CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$

29. (a) EN value $sp > sp^2 > sp^3$ (more the electronegativity more will be the bond strength)

30. (c) I is meso, II and III one mirror image of each other.

31. (b) Cyclopropane is most unstable therefore more reactive toward addition reaction. Cyclopentene is most stable $\therefore$ less reactive.

32. (b) It is an example of intramolecular Wurtz reaction

$$Na \longrightarrow Na^{\oplus} + e^{\ominus}$$

33. (c) $CH_3—Br \xrightarrow{\text{reduction}} CH_4$; $CH_3—Br \xrightarrow{\text{Wurtz}} CH_3—CH_3$

34. (d) $CH_3—\overset{*}{C}H(CH_2—CH_3)—CH_2—CH_2—CH_3$ (or) $CH_3—\overset{*}{C}H(CH_2—CH_3)—CH(CH_3)_2$

35. (b) Bromine is more selective ∴ it will form 3° halide if there is presence of 3° hydrogen.
∴ Q, S, T, form 3° halide as major and P, R, U form 2° halide as major.

36. (b) If reactant (*A*) is added in excess then maximum collission between (*A*) and $Cl^{\bullet}$ in the rate determining step.

37. (a) 2° halide is major, due to formation of sp^2-hybridized free radical racemization take place.

38. (c) Mechanism for the monochlorination of methane

Step-I $:\ddot{Cl}—\ddot{Cl}: \xrightarrow[\text{or } h\nu]{\Delta} 2:\ddot{Cl}\cdot$ [initiation step]

Step-II

$:\ddot{Cl}\cdot + H—CH_3 \longrightarrow HCl: + \cdot CH_3$ (a methyl radical)

$\cdot CH_3 + :\ddot{Cl}—\ddot{Cl}: \longrightarrow CH_3Cl + :\ddot{Cl}\cdot$

} Propagation steps

Step-III

$:\ddot{Cl}\cdot + Cl\cdot \longrightarrow Cl_2$

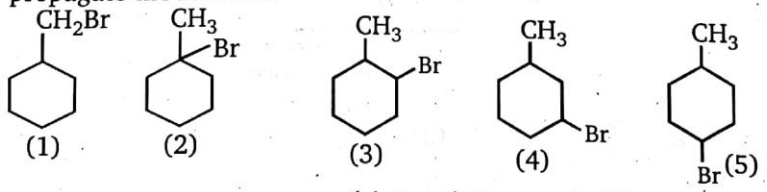
$\cdot CH_3 + \cdot CH_3 \longrightarrow CH_3CH_3$

$:\ddot{Cl}\cdot + \cdot CH_3 \longrightarrow CH_3Cl$

} termination steps

Any two radicals in the reaction mixture can combine to form a molecule in which all the electrons are paired. The combination of two radicals is called a termination step because it brings the reaction to an ends by decreasing the number of radicals available to propagate the reaction.

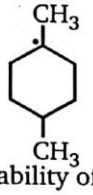
39. (b)



(*cis-trans*) Geometrical isomerism

Excluding stereoisomer = 5

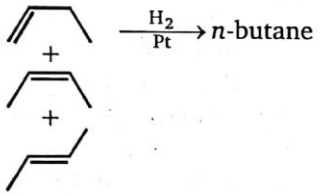
40. (a) Bromine is more selective
∴ abstract that hydrogen which forms stable free-radical

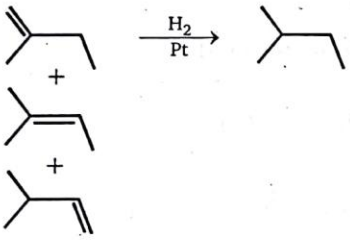
∴ 

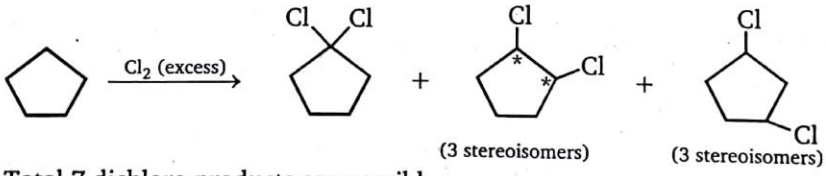
(3° free-radical) is most stable.

41. (d) Stability of cyclic system 6 > 5 > 3 ∴ Heat of combustion i > ii > iii

42. (c) Selectivity of Cl ⟶ 3° > 2° > 1° hydrogen.
as well as –I of F-atom.

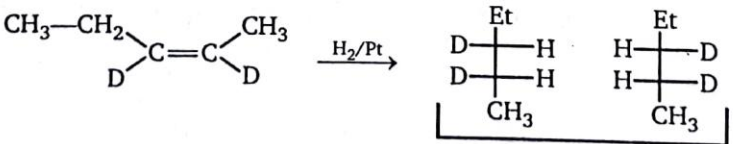
43. (c) 

44. (c) 

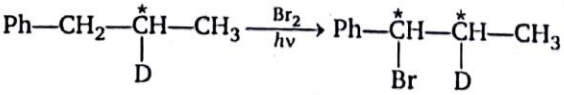
45. (c) 

(3 stereoisomers) (3 stereoisomers)

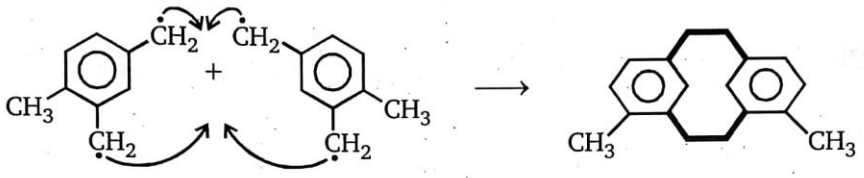
Total 7 dichloro products are possible.

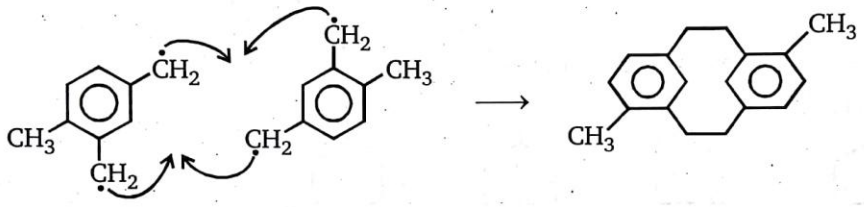
46. (a) 

Enantiomers
(Racemic mixture)

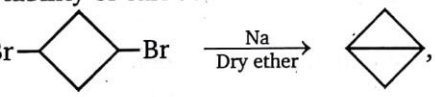
47. (a) 

48. (d) Wurtz reaction :





49. (c) Stability of carbocation 3° > 2° > 1°.

50. (d) 

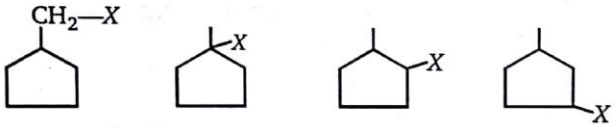
, Major product.

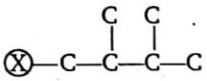
Level-2

Comprehensive-1

1. (A) $X—X \xrightarrow{h\nu} 2X^{\bullet}$ (initiation step)

(B) Br_2 is more selective best yield will obtained.

(C) 

2. 

(A) Cl_2 is less selective ∴ 1° halide will be obtained in better yield.

(B) To obtained 3° halide Br_2 must be used.

(C) $CH_3—\underset{}{\overset{CH_3}{\overset{|}{CH}}}—CH_2—Cl$ Relative formation is = 9 × 1; relative formation of 3° = 5 × 1 (1°)

∴ % yield = 9/14 × 100

(D) (1) $CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—CH_2—CH_2—Cl$

(2) $CH_3—\underset{CH_3}{\underset{|}{CH}}—CH_2—\overset{Cl}{\overset{|}{CH}}—CH_3$

(3) $Cl—CH_2—\underset{CH_3}{\underset{|}{CH}}—CH_2—CH_2—CH_3$

(4) $CH_3—\underset{CH_3}{\underset{|}{CH}}—\overset{Cl}{\overset{|}{CH}}—CH_2—CH_3$

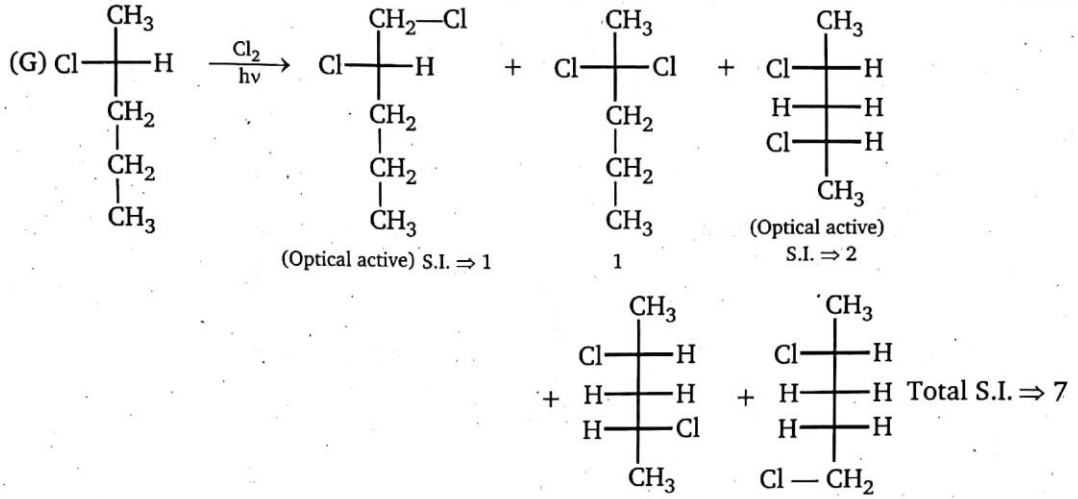
(5) $CH_3—\underset{CH_3}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}—CH_2—CH_2—CH_3$

(E) Relative formation of (X) is = no. of 3° Hydrogen which will form (X) × rate 3° hydrogen

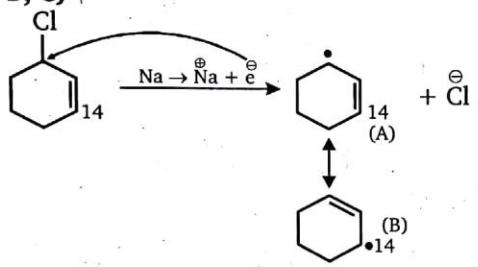
$= 1600 \times 1$ % yield $= \frac{1600}{1779} \times 100 = 90\%$

Total $= 1600 \times 1 + 1 \times 15 + 2 \times 82 = 1779$

(F) $\frac{x}{y} = \frac{6}{2} = \frac{3}{1}$

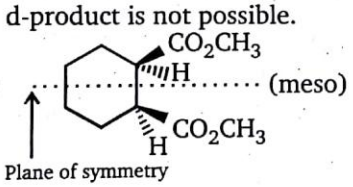


3. (a, b, c)

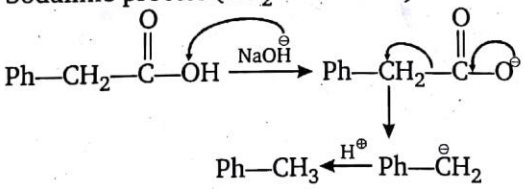


Products a, b and c are obtained by dimerization of radical (A) and (B).
d-product is not possible.

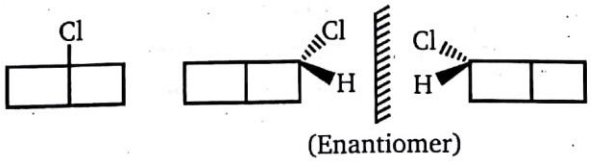
4. (a)



5. (c) Sodalime process (CO_2 will evolve)



6. (a)



3 products

(b) (1) $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-Cl$ (2) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{Cl}{|}}{\underset{*}{C}H}-CH_3$

(3) Mirror image (4) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2-CH_3$

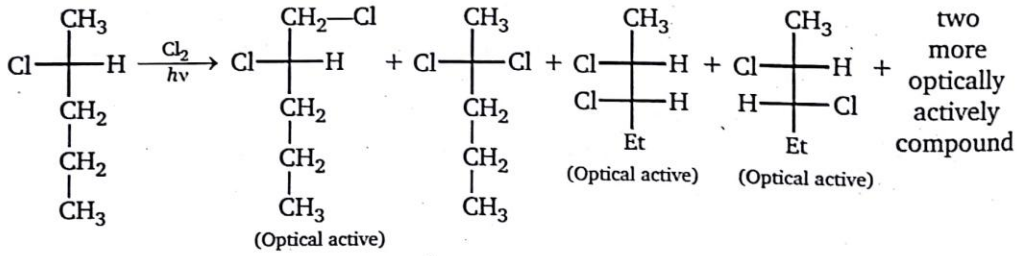
(5) $Cl-CH_2-\underset{\underset{CH_3}{|}}{\overset{*}{C}H}-CH_2-CH_3$ (6) Mirror image

(c) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3-Cl}{|}}{C}}-CH_3$

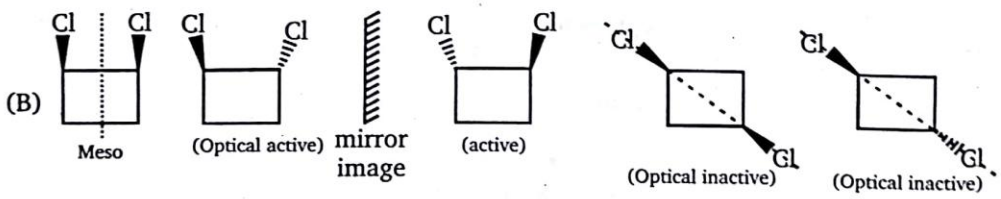
(d) (1) $CH_3-CH_2-CH_2-CH_2-Cl$

(2) $CH_3-CH_2-\underset{\underset{Cl}{|}}{\overset{*}{C}H}-CH_3$ (3) Mirror image

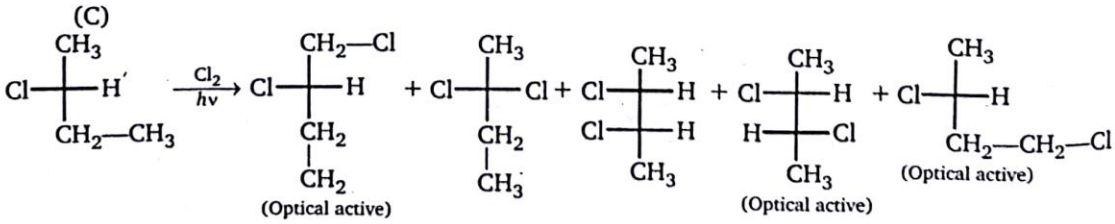
7. (A)



(B)

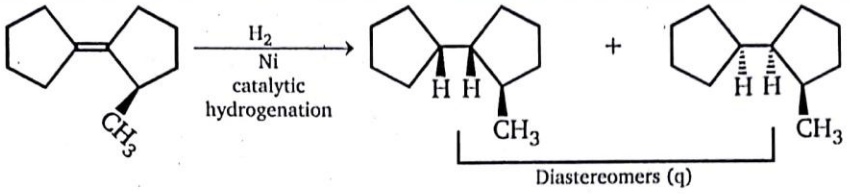


(C)

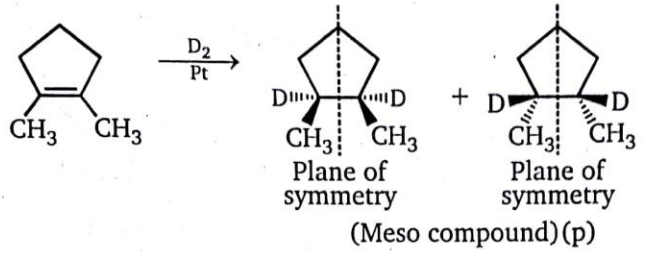


Sum $P+Q+R=5+2+3=10$

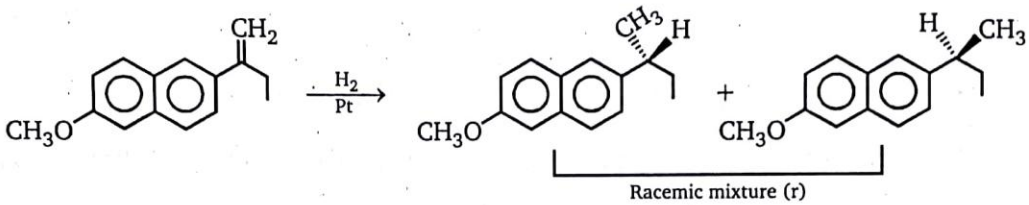
8. (a)



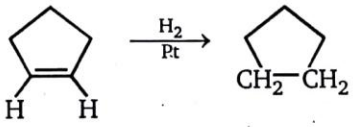
(b)



(c)

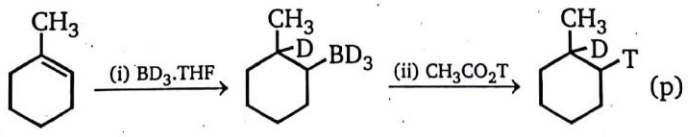


(d)



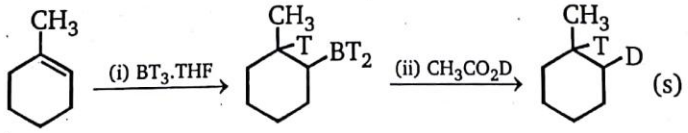
Optically inactive (s)

9. (a)



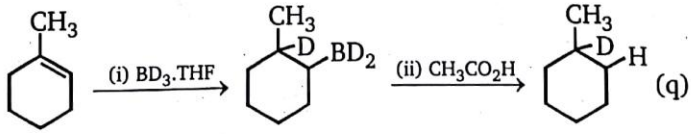
(p)

(b)



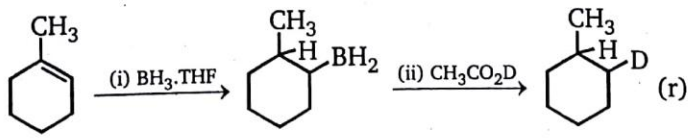
(s)

(c)



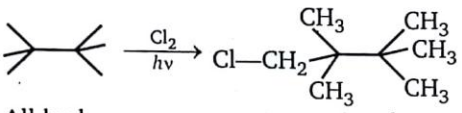
(q)

(d)

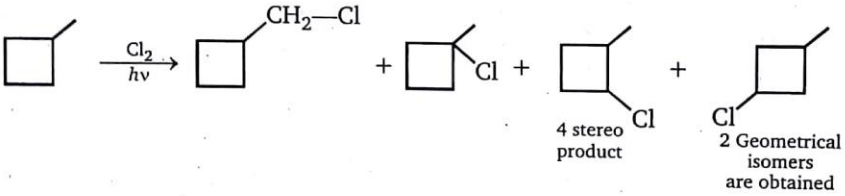


(r)

$\because$ Ist reaction is via transition state so BH_2, BD_2 or BT_2 attached to less sterically hindered carbon (syn. addition) cyclic T.S. is produced during the reaction.

10. (a) 

All hydrogens are same type. $\therefore$only one product is possible.

11. (e) 

12. (a) $CH_3—Cl \xrightarrow[\text{dry ether}]{Na} \dot{C}H_3 \xrightarrow[\text{dimerisation}]{\dot{C}H_3} CH_3—CH_3(s)$

*Number of dimerized products depend on probability of free radical to combine with each other

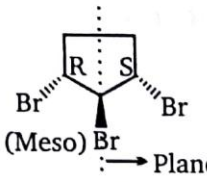
*Similar on different F.R. combine with each other to give product.

13. $x = 9$

4(B) Hydrocarbons (Alkenes)

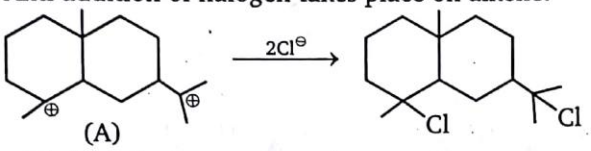
Level-1

1. (c)



Anti addition of halogen takes place on alkene.

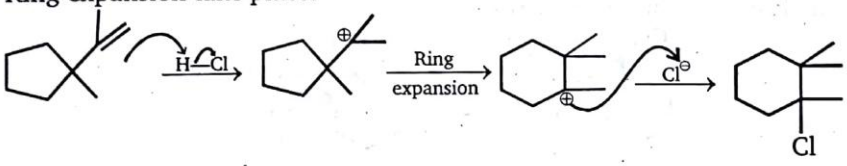
2. (d)



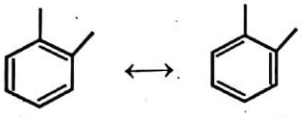
(A)
Carbocation

Source of this carbocation can be (a), (b) and (c).

3. (c) Ring expansion take place.

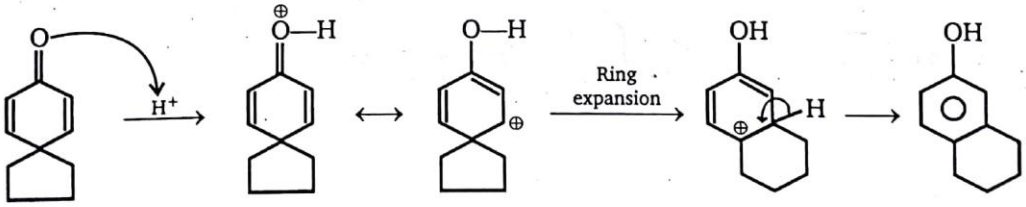


4. (d)

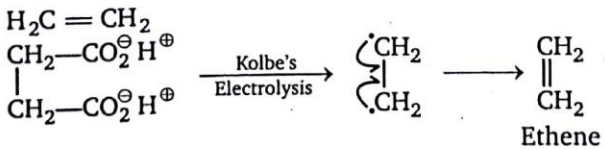


(o-xylene) Which on ozonolysis give a, b and c.

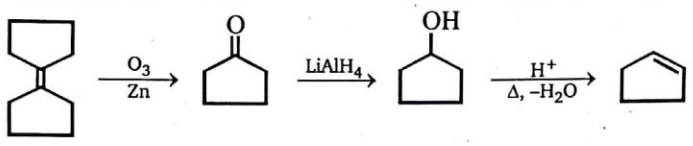
5. (b)



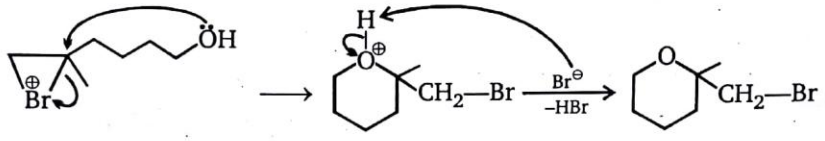
6. (b)



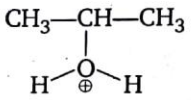
7. (c)



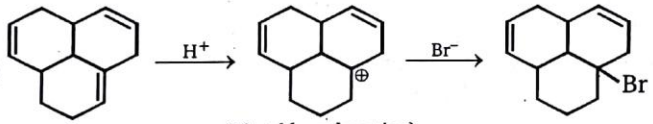
8. (c)



9. (c) $CH_3—CH=CH_2 \xrightarrow{H_3O^\oplus} CH_3—\overset{\oplus}{C}H—CH_3 \xrightarrow{H_2O:}$

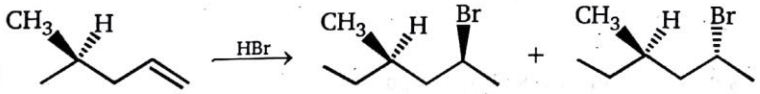


10. (d)



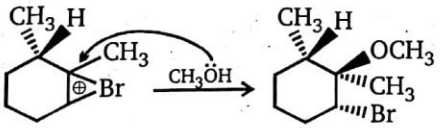
(3° stable carbocation)

11. (b)



(Diastereomers)

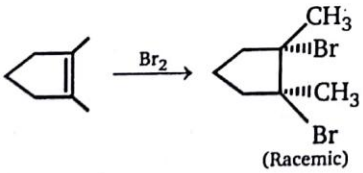
12. (d) Non-classical carbocation will form



13. (c) Because of formation of new chiral center.

14. (b) Transition state = Intermediate +1

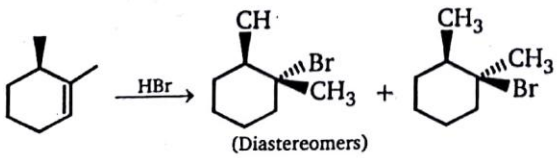
15. (b)



+ Mirror Image

(Racemic)

16. (c)



(Diastereomers)

17. (d) None

This carbocation rearrangement is not favourable.

(σ-resonance stabilized)

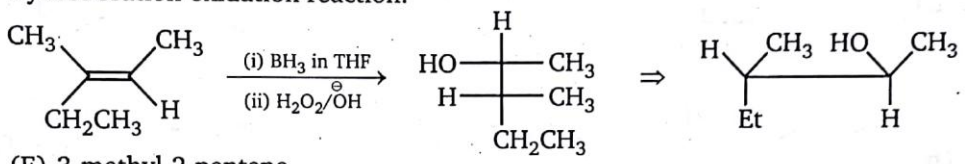
18. (d) Reaction is exothermic because of formation of stable alkene.

19. (b) $H_2C{=}CH{-}O{-}CH_3 \xrightarrow{Br_2} CH_2{-}\overset{\oplus}{C}H{-}O{-}CH_3 \xrightarrow{CH_3\ddot{O}H} CH_2{-}CH(OCH_3){-}OCH_3$ (Br) (+M)

20. (d) 1,2 and 1,4- addition take place.

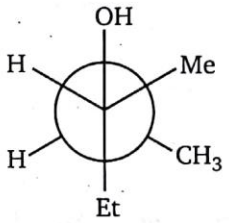
21. (b) NBS + aq. DMSO is used for preparation of halohydrin.

22. (b) Hydroboration oxidation reaction.

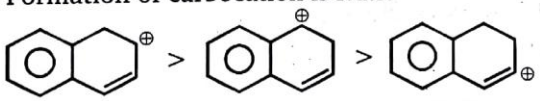


(E)-3-methyl-2-pentene

Hydroboration oxidation is syn addition



23. (b) Formation of carbocation is r.d.s.



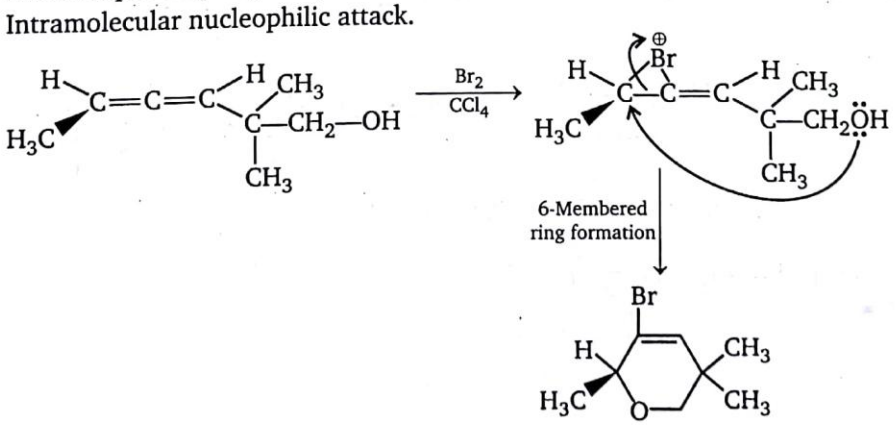
(stability order)

7 R.S 6 R.S Vinylic (least stable)

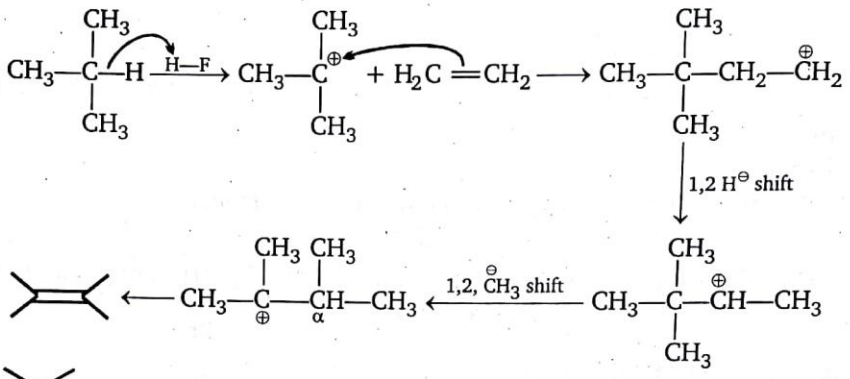
R. S. = Resonating structure.

24. (b) Two products will be obtained by addition reaction above and below the plane of ring. It is the example of syn hydroxylation.

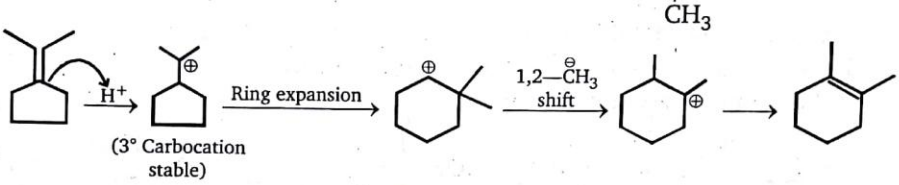
25. (b) Intramolecular nucleophilic attack.



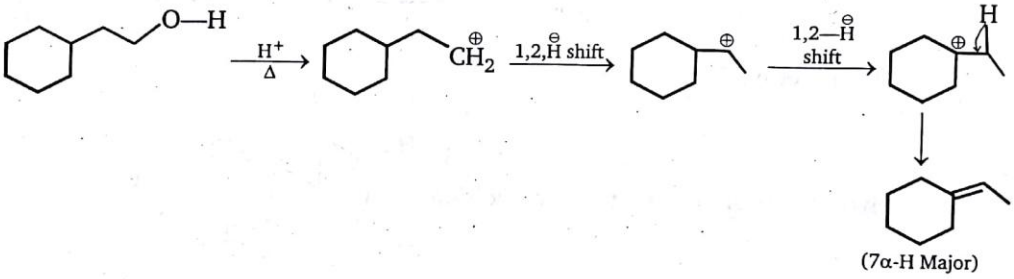
26. (b)



27. (d)



28. (b)



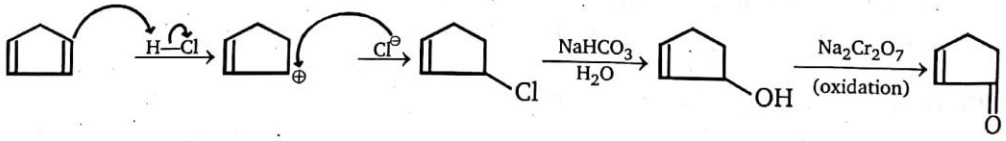
29. (d) Di-imide is used to reduce pi-bond formed between like atom.

For example $\longrightarrow -CH=CH-, -N=N-$

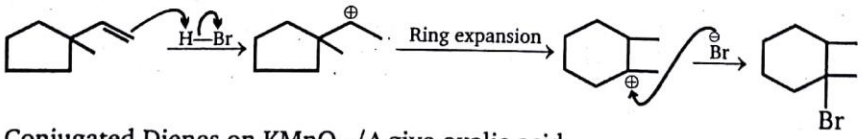
It can not be reduced following gps.

$$\longrightarrow -\overset{O}{\overset{\|}{C}}-, -\overset{N}{\overset{\|}{C}}-, -N=O, -C\equiv N-NC,$$

30. (b)

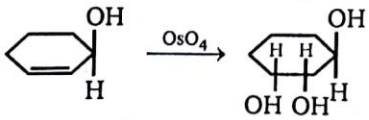


31. (c)



32. (b) Conjugated Dienes on $KMnO_4/\Delta$ give oxalic acid.

33. (a)



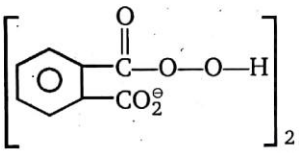
Because of less stric hinderance (a) is major

34. (b) $Ph{-}CH{=}CH{-}Ph \xrightarrow[CCl_4]{Br_2} Ph{-}\underset{\underset{Br}{|}}{CH}{-}\overset{\overset{Br}{|}}{CH}{-}Ph$ (halogenation)

$\downarrow 2NaNH_2 (E_2 \text{ reaction})$

$Ph{-}C{\equiv}C{-}Ph \xrightarrow[Pd/CaCO_3]{H_2} \begin{matrix} Ph \\ H \end{matrix}\!\!>C{=}C<\!\!\begin{matrix} Ph \\ H \end{matrix}$

(syn-addition)
(*cis*-product)

35. (b) MMPP $\longrightarrow$ 

will act as a electrophile so attack on that alkene which has more α-hydrogen or stable epoxide will formed, more substituted epoxide is more stable.

36. (b) More substituted alkene will undergo epoxide formation.

37. (b) Give compound on hydrolysis gives syn-acid.

38. (b) The use of light suggests a free radical mechanism. This means that the methane derivative will undergo homolytic fission. Since the C — Br bond is weaker than the C — Cl bond, it is reasonable to suppose that the former will be broken. Hence :

$$CBrCl_3 \xrightarrow{h\nu} Br\bullet + \bullet CCl_3$$

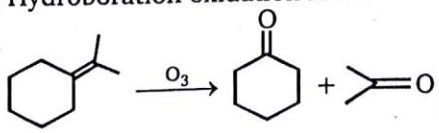
$$PhCH_3 \xrightarrow{\bullet CCl_3} CHCl_3 + PhCH_2\bullet, \xrightarrow{CBrCl_3} PhCH_2Br + \bullet CCl_3, \text{ etc.}$$

Attack by the free radical on toluene occurs at the methyl side - chain and not in the ring because the C — H bond in Me is weaker than that of a ring-hydrogen atom and the benzyl free radical is far more stable than an aryl free radical.

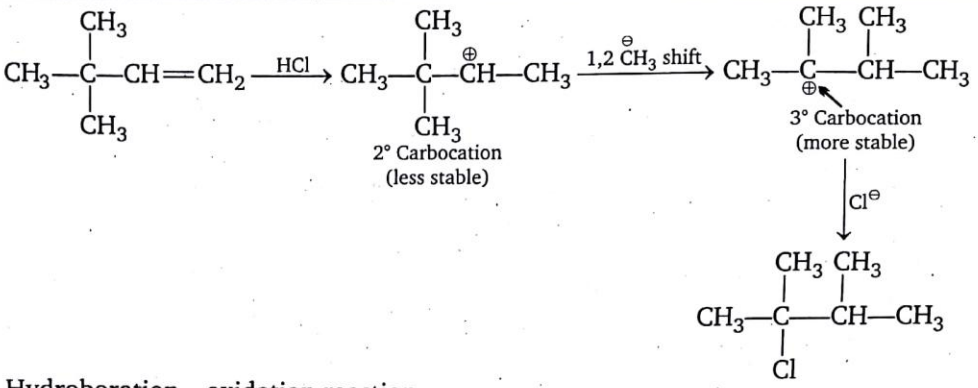
The other point that requires explanation is why toluene is attacked by the CCl_3 free radical and not by the bromine free radical. Activation energies involving free radicals are usually very low and so the controlling factor is the heat of reaction (or, more correctly, the free energy of reaction). The more exothermic the reaction (greater is ΔG), the more favoured is that reaction. If the bromine atom attacks, the result is HBr, the bond of which is much weaker than the C — H bond formed when $^{\bullet}CCl_3$ attacks. Hence, reaction proceeds by the later route.

39. (b) More nucleophilic alkene will react.

40. (b) Hydroboration oxidation reaction.

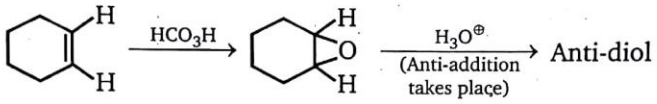
41. (d) 

42. (e)



43. (c) Hydroboration – oxidation reaction.

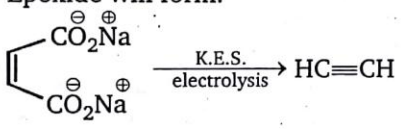
44. (c)



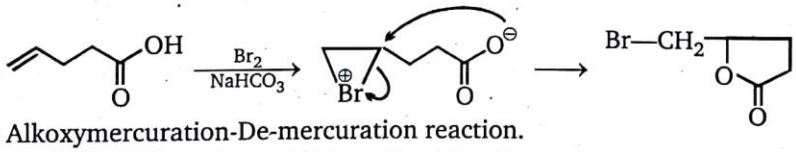
45. (a) Anti-addition take place.

46. (c) Epoxide will form.

47. (c)



48. (b)



49. (b) Alkoxymercuration-De-mercuration reaction.

50. (b) cis-diol will form (syn addition takes place)

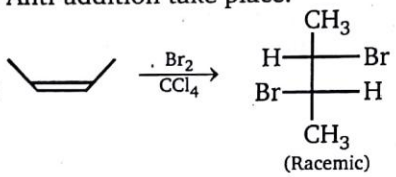
51. (b) $Br_2/h\nu$ (low conc.) (or) N.B.S, Allylic free radical substitution reaction.

52. (a) Alkene will be cleaved by ozonolysis.

53. (b) cis-diol will form

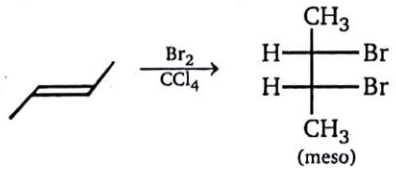
54. (d) Anti-addition take place.

55. (b)



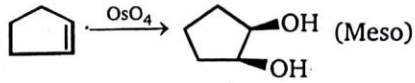
+ mirror image.

56. (c)



(POS) present

57. (c)



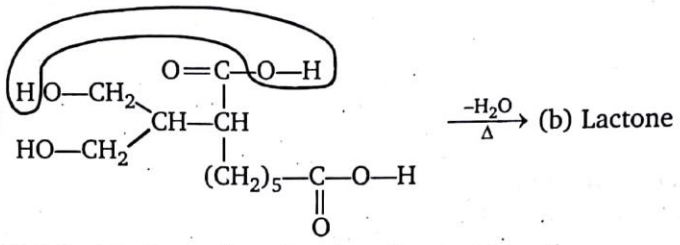
(Meso)

58. (b) Hydroboration - oxidation reaction is a syn-addition.

59. (c) Oxymercuration - Demercuration reaction addition of H_2O molecule is according to Markovnikoff's rule.

60. (a) Anti-Markovnikoff's addition take place (Peroxide effect operates).

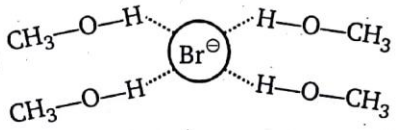
61. (b)



(b) Lactone

62. (d) Halohydrin formation take place (anti-addition).

63. (a)

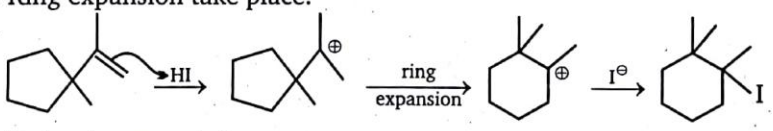


Solvation take place and CH_3 Ö H act as nucleophile.

64. (b) Hot $KMnO_4$ is similar to oxidative ozonolysis.

65. (d) $CH_3—CH=CH_2 \xrightarrow{NBS} Br—CH_2—CH=CH_2 \xrightarrow{Cl_2} Br—CH_2—\underset{Cl}{\underset{|}{CH}}—\overset{Cl}{\overset{|}{CH_2}}$

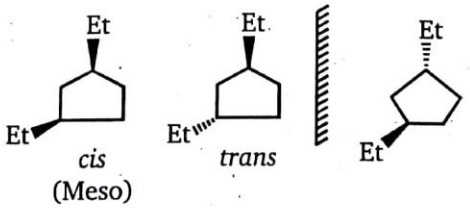
66. (b) Ring expansion take place.



67. (d) Reductive ozonolysis.

68. (a) $H_2C=\overset{CH_3}{\overset{|}{C}}—CH_2—CH_3$

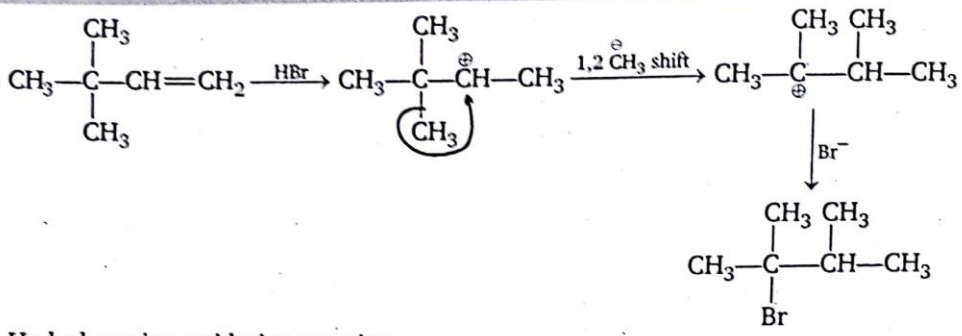
69. (c)



S. I = 3

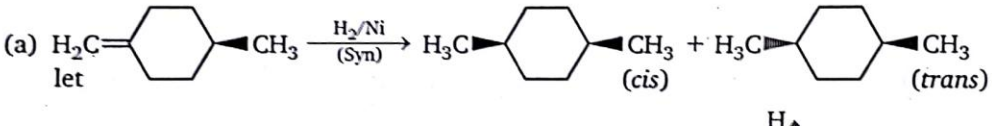
70. (d) Markovnikoff's addition take place.

71. (d)

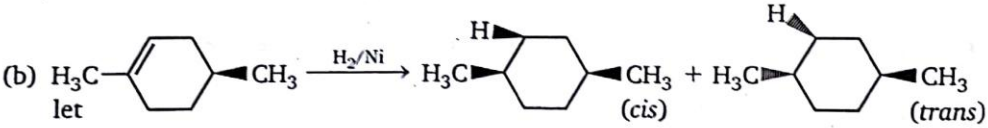


72. (c) Hydroboration-oxidation reaction.
73. (d) Terminal alkyne will reacts with Tollen's reagent.
74. (c) Anti-Markovnikoff's addition take place.
75. (a) Syn-addition take place.
76. (c) Reductive ozonolysis.
77. (d)

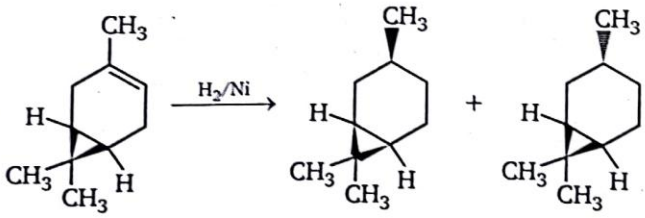
(a)



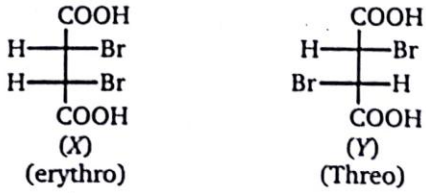
(b)



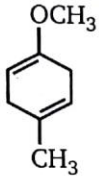
(c)



78. (b) Formation of carbocation is the rate determining step.
79. (d) Corresponding alkene is not possible.
80. (d) Non-classical carbocation will form.
81. (c) Attack of free radical on alkene is an propagation step.
82. (b) Attack of alkene take place of H — Cl.
83. (a) Carbocation formed will attacked by alkene.
84. (a) Hydroboration-oxidation take place (syn addition).
85. (a) Anti-addition take place.

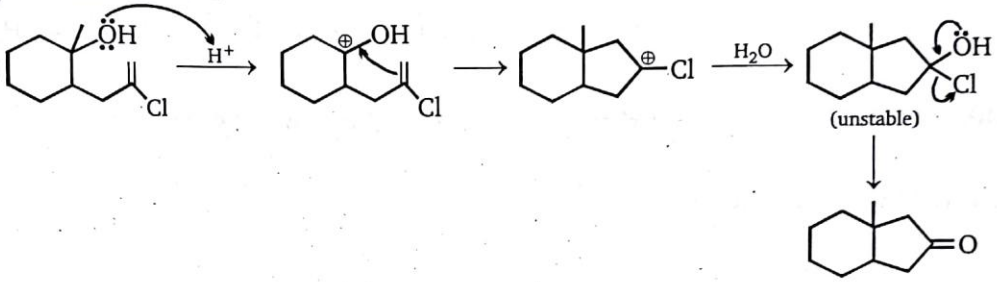


(X) (erythro) (Y) (Threo)

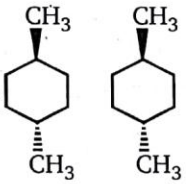
86. (d) (*P*) = 

More nucleophilic alkene will attack.

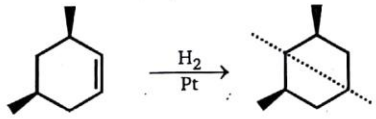
87. (b) Iodo lactonization.

88. (b) 

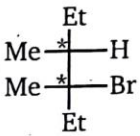
89. (c) (*A*) $Ph-\underset{Br}{\underset{|}{CH}}-CH_2-Br$ (*B*) $Ph-C\equiv C-H$ (*C*) $Ph-C\equiv C-CH_3$

90. (d) (a), (b) and (c) gives 

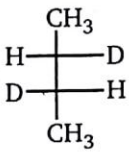
(cis & trans)

91. (b) 

optically active meso (POS) Present

92. (b) 

4-Product

93. (a) 

+ mirror image.

94. (a) $CH_3-CH_2-\overset{*}{\underset{Br}{\underset{|}{C}}}H-CH_3$ (racemic mixture)

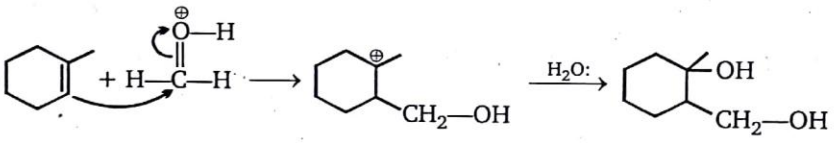
95. (a) Less steric hinderance site will be attacked. Approach of H_2 is more hindered in (b).
96. (d) Reductive ozonolysis.
97. (b) Oxidation take place *i. e.*, epoxidation.
98. (a) Hydroboration-oxidation take place.
99. (c) Hydroboration-reduction take place.

$$CH_3-CH=CH_2 \xrightarrow{THF.\ BD_3} \left(CH_3-\overset{D}{\overset{|}{C}}H-CH_2-\right)_3 B \xrightarrow{CH_3-CO_2T} CH_3-\overset{D}{\overset{|}{C}}H-CH_2T$$

100. (d) $CH_3-CH_2-\underset{Cl}{\underset{|}{C}H}-CH=CH_2 \xrightarrow[Pt]{H_2} Et-\underset{Cl}{\underset{|}{C}H}-Et$ optically inactive.

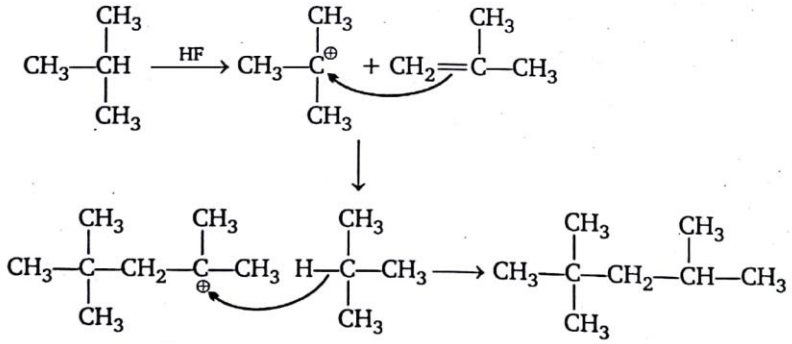
101. (b) Cumulative dienes.

102. (b)

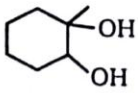
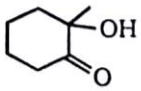


103. (d) (*A*) $CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-OH$ (*B*) $CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2$ (*C*) $CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-Br$
(Anti-markovnikoff's addition take place)

104. (b)



105. (b) $Br-CH_2-\overset{O}{\overset{||}{C}}-Cl\ (P) \xrightarrow{CH_3OH} Br-CH_2-\overset{O}{\overset{||}{C}}-O-CH_3$

106. (c) (*A*)  (*B*)  (*C*) 

107. (b) Markovnikoff's addition.
108. (b) Halohydrin will form (anti-addition).

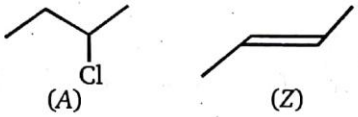
109. (d) Hydroboration-oxidation take place.

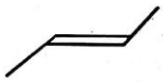
110. (d) Oxymercuration-Demercuration take place.
(Addition of —OH takes place according to Markovnikoff's Rule)

111. (c) Anti-addition take place. (*i. e.*, anti-hydroxylation)

112. (b)

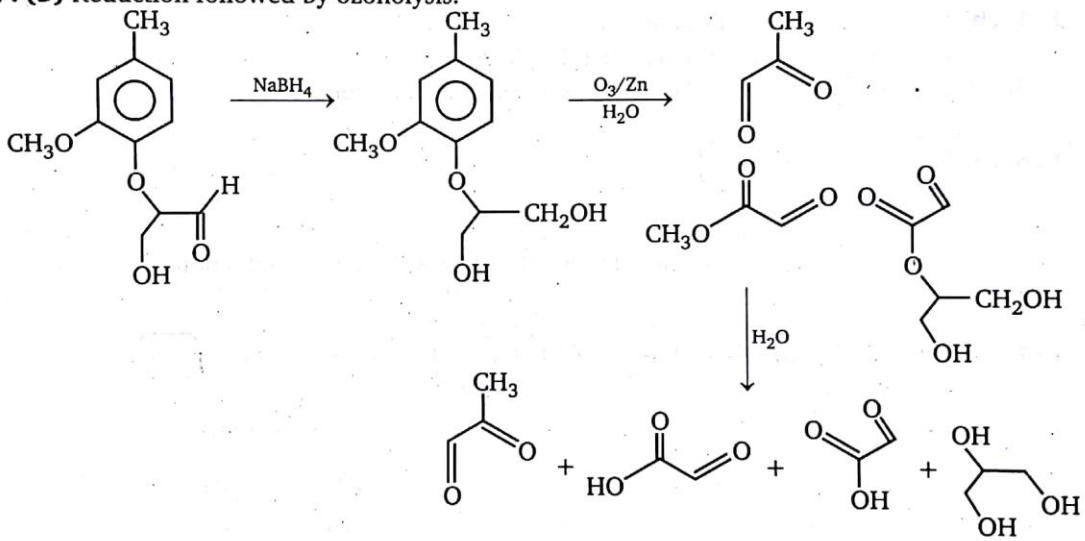
113. (a)

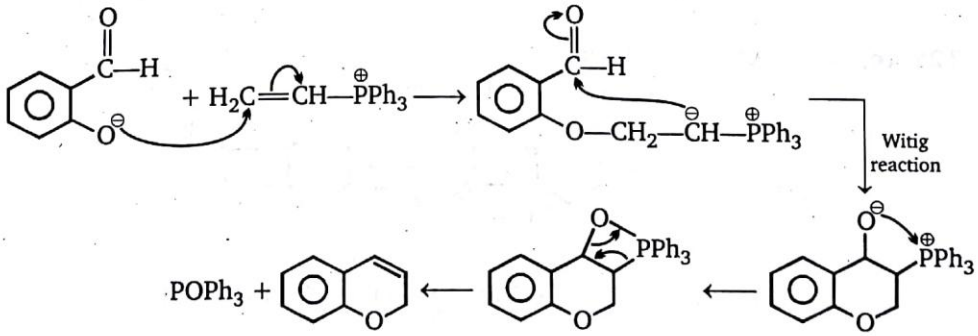
114. (b) 

115. (c)  (trans will be major)

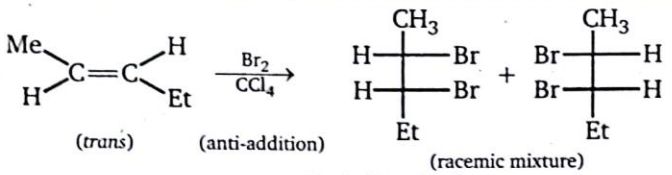
116. (a) *A* and *B* are diastereomers.

117. (b) Reduction followed by ozonolysis.



118. (b) (*X*) 

119. (b) (*P*)



(*trans*) (anti-addition) (racemic mixture)

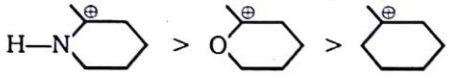
(Optical inactive due to external compensation)

120. (d) Unstable alkene will readily undergo reduction.

121. (b) (*B*) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_3$. It is also obtained by reductive ozonolysis of $C(C_{11}H_{18}O_2)$.

122. (c) Oxidation of alkene followed by ozonolysis take place.

123. (a) Formation of carbocation is the rate determining step so stability of carbocation is.

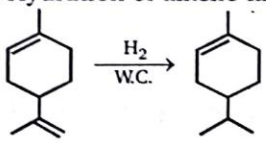


124. (b) II ⟶ Markovnikoff's addition

III ⟶ Halogenation of alkane take place.

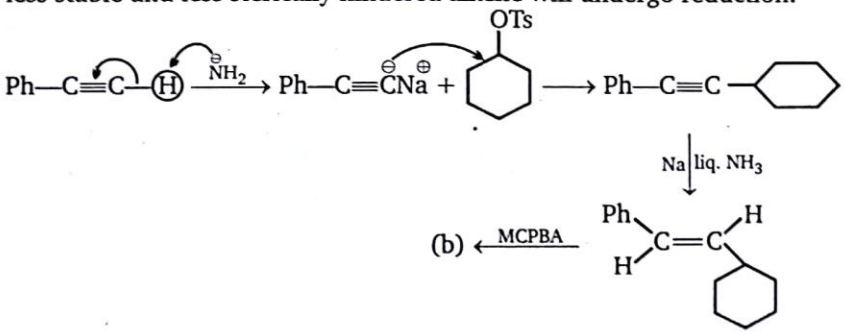
125. (d) Hydration of alkene take place. (Markonikov's addition)

126. (a)



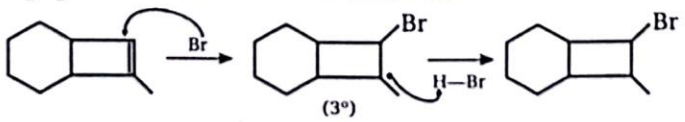
less stable and less sterically hindered alkene will undergo reduction.

127. (b)

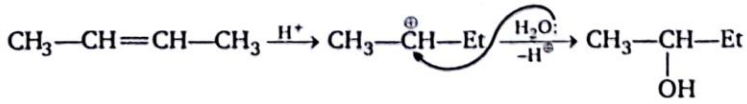


128. (c) Anti-Markovnikoff's rule

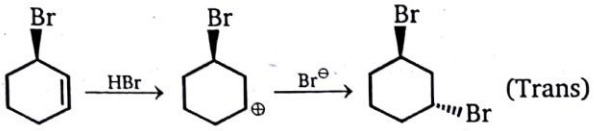
$R_2O_2 \xrightarrow{h\nu} 2RO + HBr \longrightarrow ROH + Br$



129. (d)

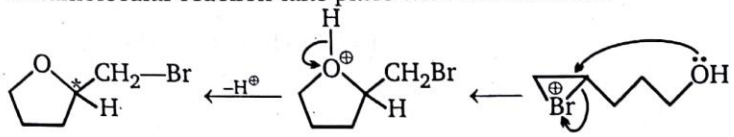


130. (a)



(Trans)

131. (c) Intramolecular reaction take place with intermediate.



R and S configuration.

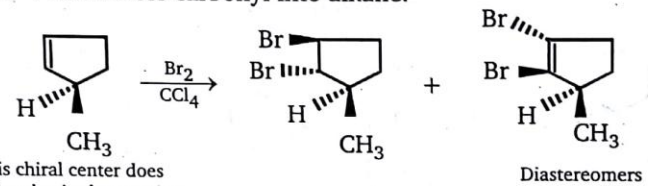
132. (d) More the stable carbocation more is rate.

133. (c) Aryl-halide is used.

∴ It is known as Wurtz fittig reaction.

134. (a) Red P + HI reduces carbonyl into alkane.

135. (d)

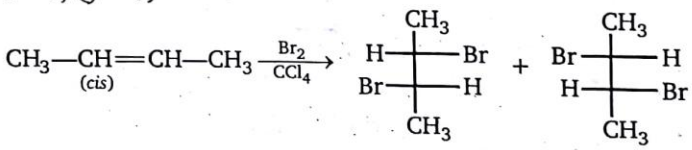


this chiral center does not involve in the reaction

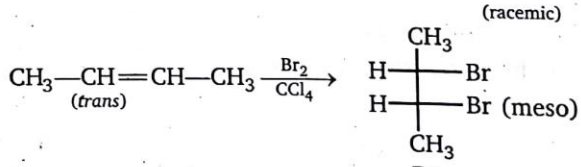
Diastereomers

136. (c) H — C ≡ C — H will precipitate and remaining gas will come out.

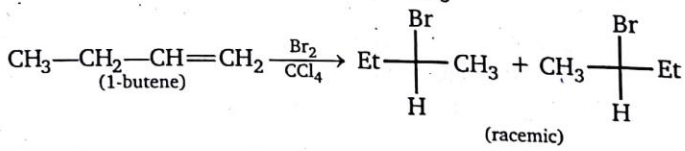
137. (b) $x = 3$, $(y = 5)$



(racemic)



(meso)



(racemic)

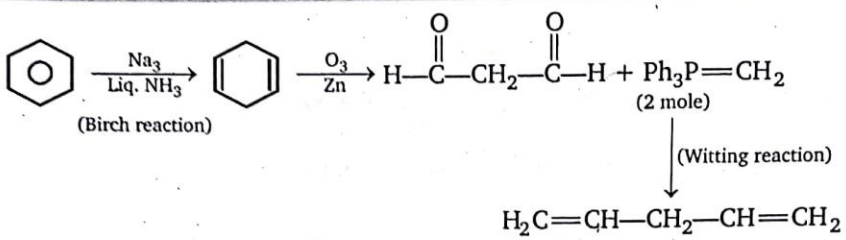
138. (d) $H_2C = CH - \dot{C}H_2 > H_2C = \dot{C}H$
(resonance stabilized)

139. (d) Terminal alkene evolve CO_2 gas when treated with O_3/H_2O_2.

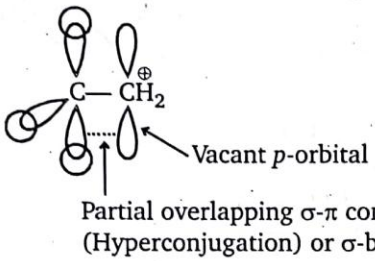
140. (b) a = Cold $KMnO_4$ (syn-addition)

b = $RCO_3H/H_3O^{\oplus}$ (anti-addition)

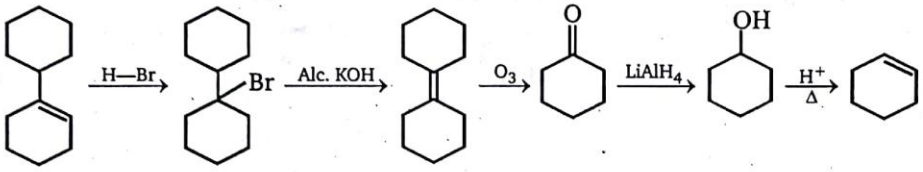
141. (b)



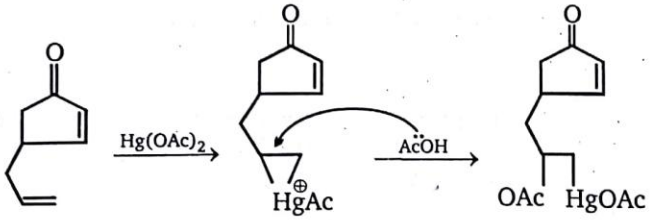
142. (b)



143. (b)



144. (b)



145. (b) Most stable alkene less heat of hydrogenation.

a ⟶ 4α H
b ⟶ 10α H
c ⟶ 6α H
d ⟶ 3α H

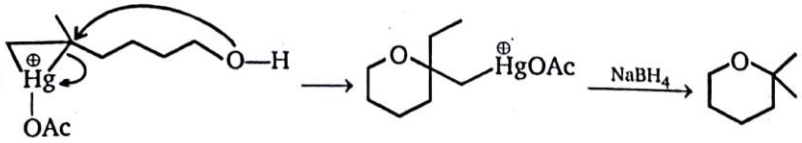
Heat of hydrogenation → d > a > c > b

146. (c) More the stable alkene less heat of hydrogenation.

a ⟶ 4α H
b ⟶ 2α H
c ⟶ 5α H
d ⟶ 8α H

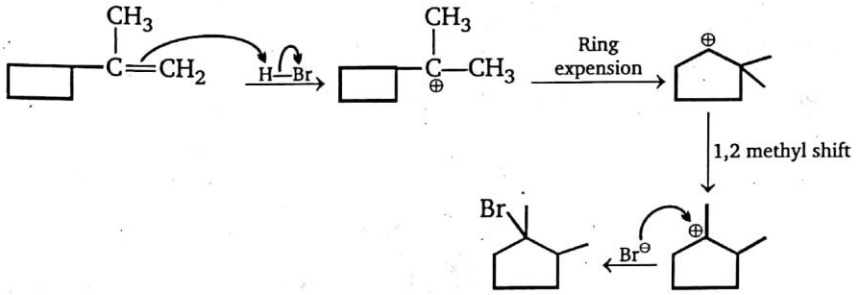
Heat of hydrogenation
$\boxed{b > a > c > d}$

147. (b)

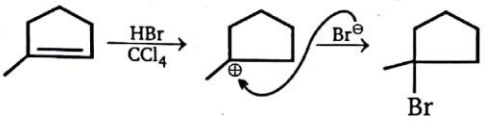


Above reaction is a intramolecular OMDM reaction.

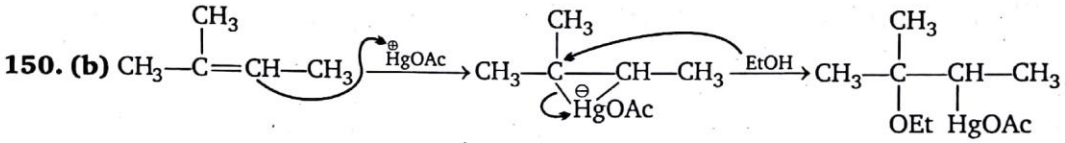
148. (a)



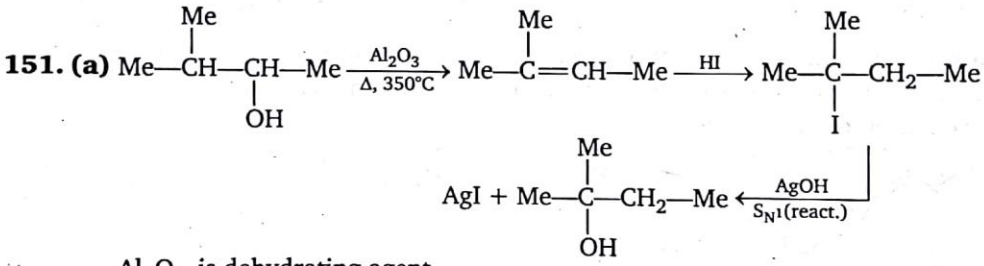
149. (d)



150. (b)

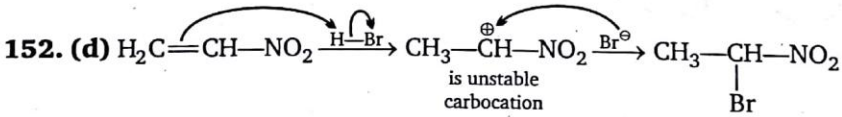


151. (a)

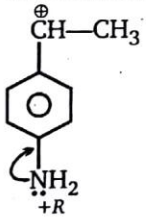


Al_2O_3 is dehydrating agent.

152. (d)



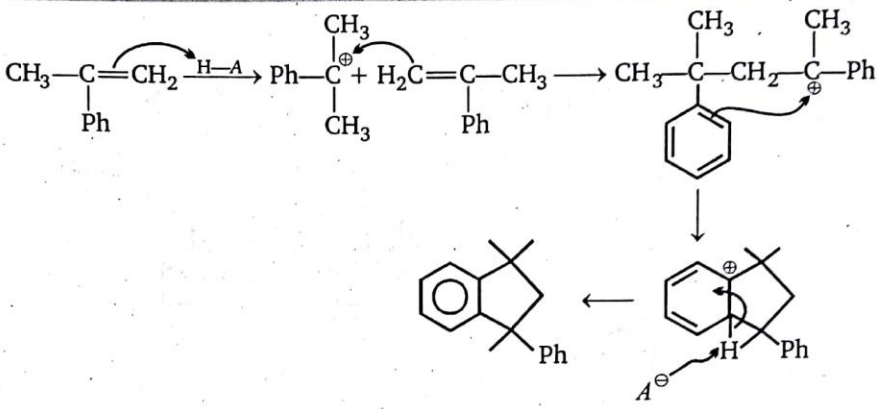
153. (c) Rate determining step is formation of carbocation.



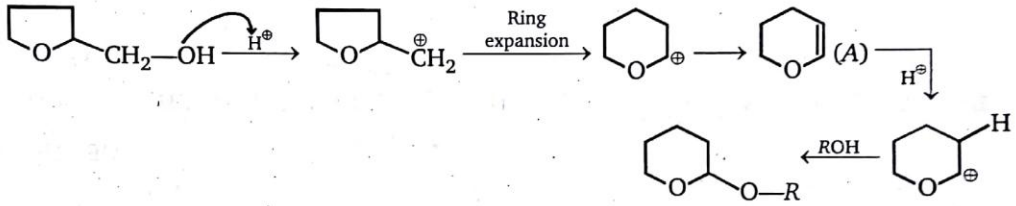
(most stable) because of (+*R*) of NH_2

(a) is least stable due to (–*R*) of —NO_2
(b) +*R* (—OH)
(c) —CH_3 (hyperconjunction)

154. (c)



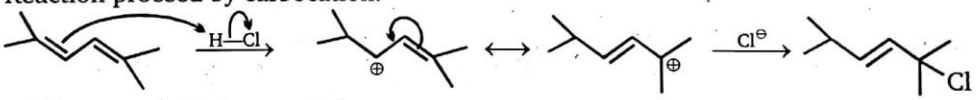
155. (b)



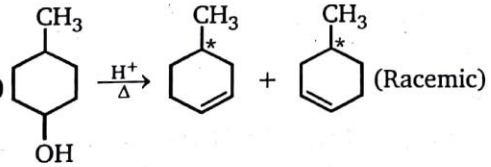
156. (c) Carbocation obtained by reaction (1) and (2) are resonating structure of each other.

157. (a) Low temperature kinetic control high temperature thermodynamic control.

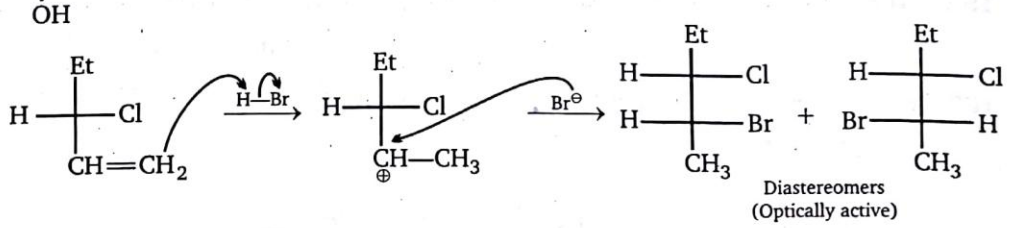
158. (a) Reaction proceed by carbocation.



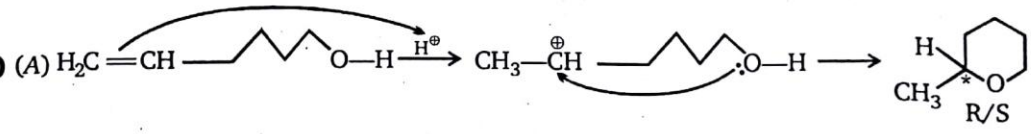
159. (b)



160. (c)



161. (b) (*A*)



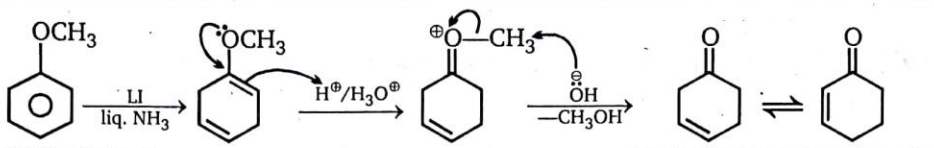
(attack on sp^2-hybridzed carbon) and formation of chiral centre.

∴ Racemic mixture

162. (c) 3 mole of alkene reacts with 1 mole of BH_3

∴ 2 mole of alkene ⟶ 2/3 mole of BH_3

163. (b)



in forward direction.

164. (d) low conc. of Br_2 and high temperature favour substitution reaction, proceed through free radical.

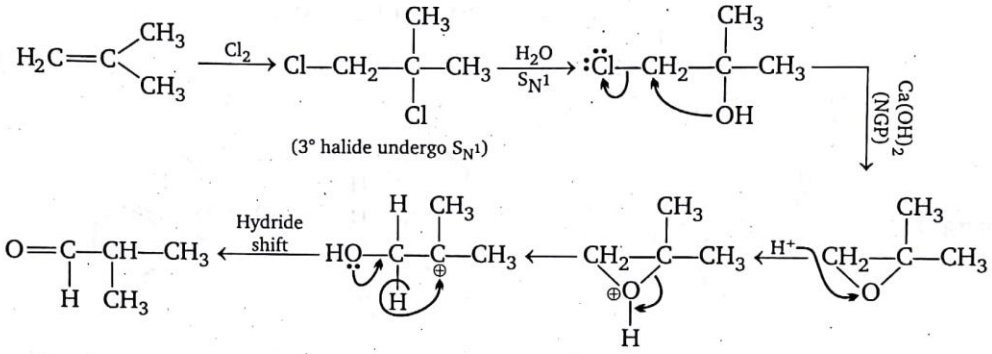
∴ Substitution will be major product.

165. (d) In (a) E_2 reaction take place.

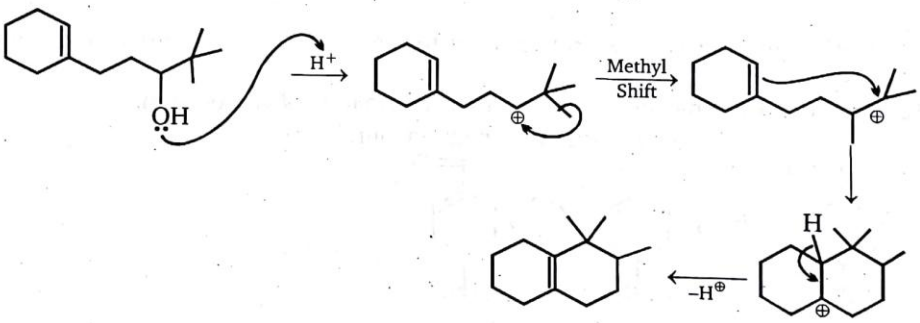
In (b) dehydration take place.

In (c) alkyne is more reactive than alkene toward catalytic reductions.

166. (b)



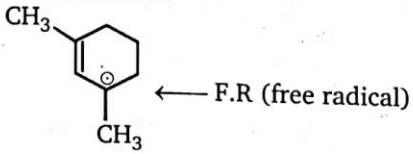
167. (b)



168. (a) Reaction-proceed through stable free radical.

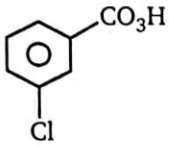
∴ formation of stable 3° free radical at (a)

∴ Bromination of (a) is most favourable.



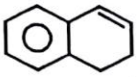
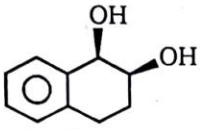
169. (c) Iso-butene is most stable isomer of butene.

∴ It have least heat of combustion.

170. (b) 

(meta-chloro per benzoic acid)

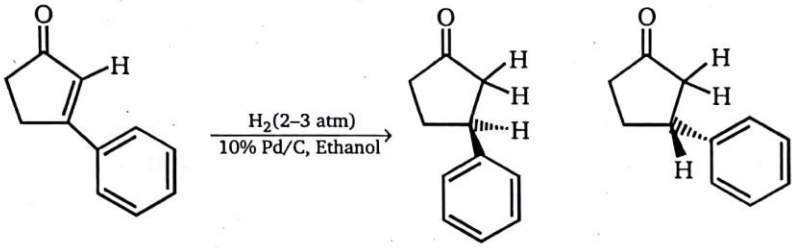
will act as on electrophile and attack on that alkene which has more electron density.
∴ More α-hydrogen

171. (b) 


(Enantiomer) + mirror image

172. (d) Reactant on ozonolysis give

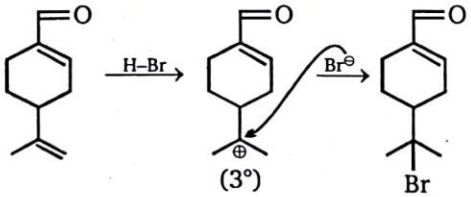
$CH_3—\underset{\underset{CO_2H}{|}}{CH}—(CH_2)_3—CHO$ (*A*) $CH_3—CH_2—CH_2—CHO$ (*B*)

173. (b) 

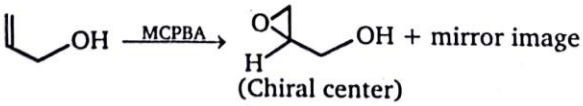
Racemic mixture

Notice that the benzene ring is inert to these conditions; hydrogenation of benzene is discussed.

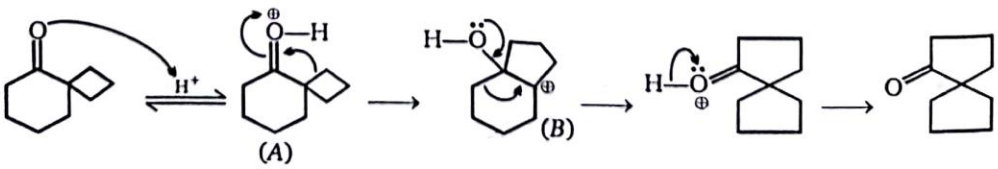
174. (c) Rate determining step of the reaction is formation of carbocation.
∴ formation of 3° carbocation is more favourable.



175. (b) less stable alkene (less α-hydrogen) will undergo reduction first.

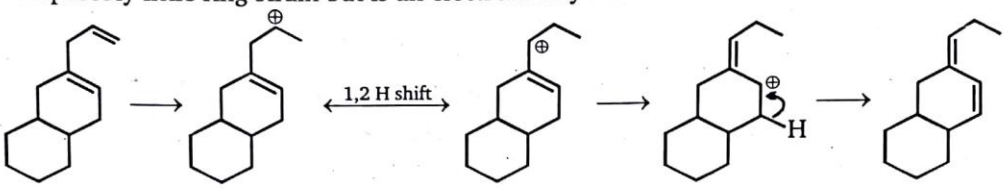
176. (b) 

+ mirror image
(Chiral center)

177. (b) 

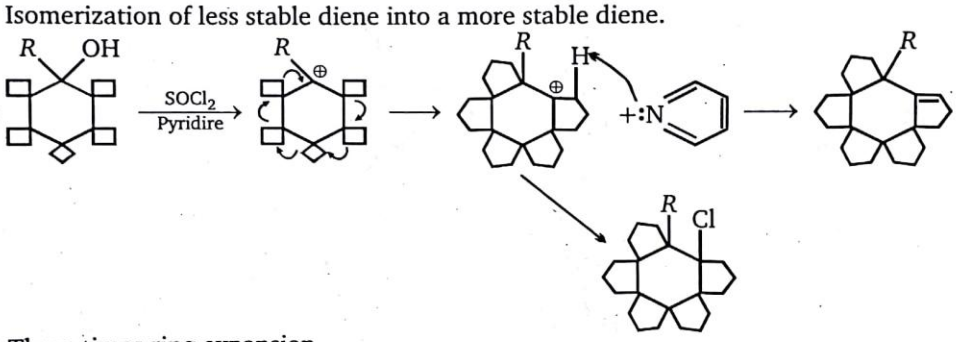
The decrease of ring strain can provide a driving force strong enough to overcompensete for the conversion of a more stable into less stable cationic centre, the carbooxonium ion (*A*) rearranges into the carbonium ion (*B*) because of the release of cyclo butene strain (26 kcal/mol) in the formation of the cyclopentane (ring strain of about 5 cal/mol) cation *B* stablizer itself by way of another 1,2 rearrangement. The resulting action (c) has comparebly little ring strain but is an electronically favourable carboxonium ion.

178. (c)



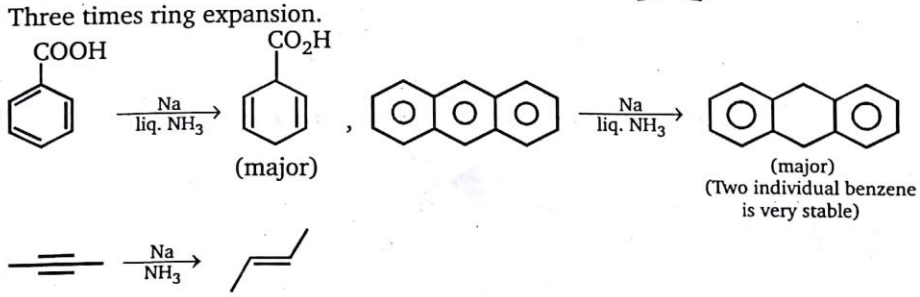
Isomerization of less stable diene into a more stable diene.

179. (b)

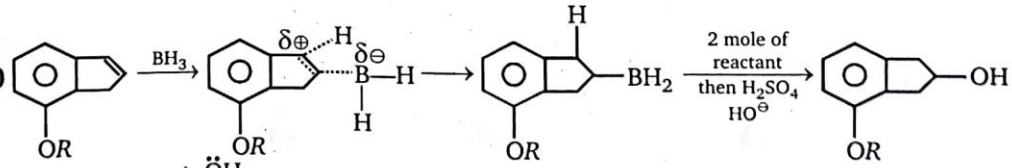


180. (c) Three times ring expansion.

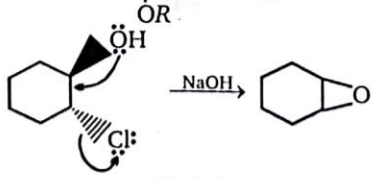
181. (b)



182. (b)

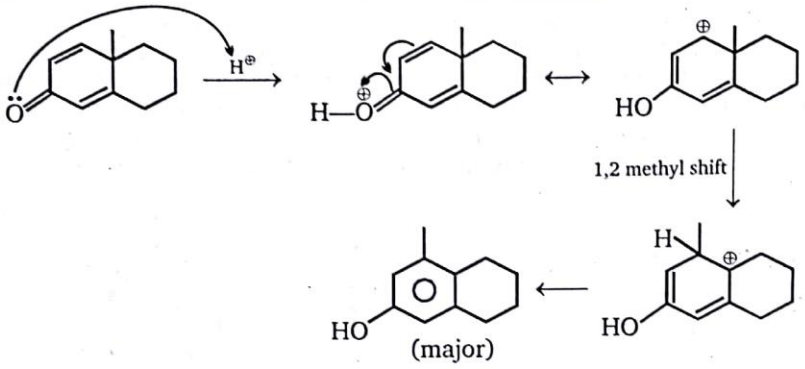


183.(c) (*A*) =

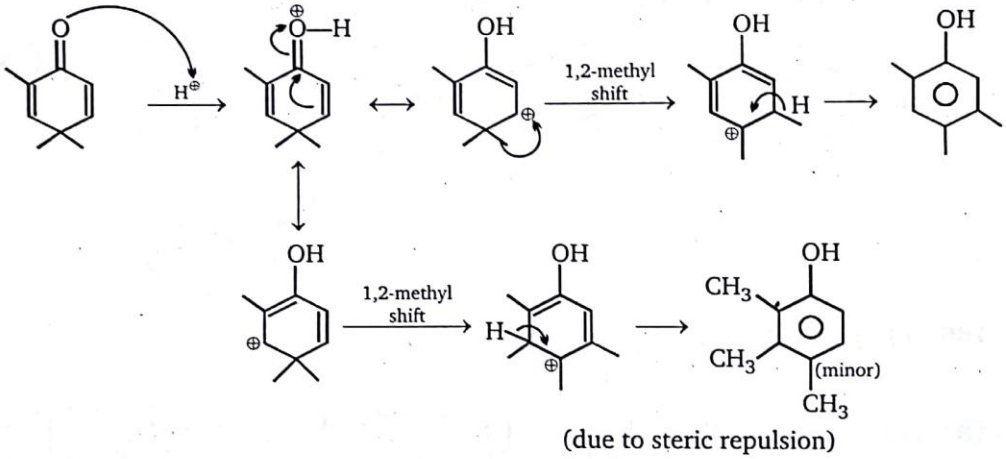


(N.G.P.)
(Neighbouring Group Participation)

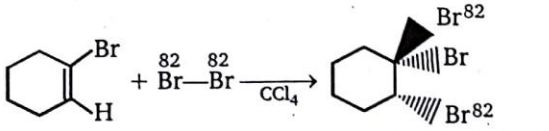
184. (c)



185. (c)

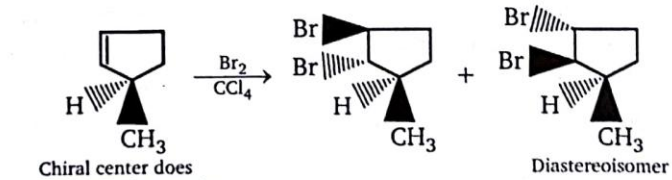


186. (b)



(Anti-addition take place)

187. (a)

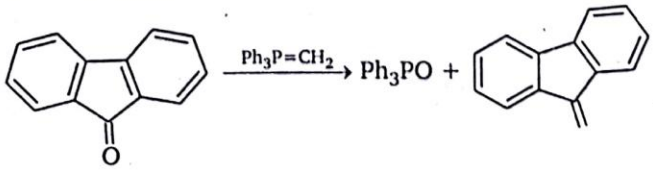


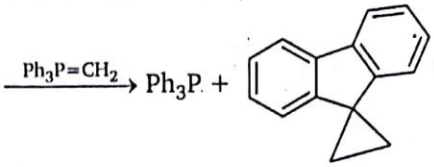
Chiral center does not involve in the reaction

Diastereoisomer

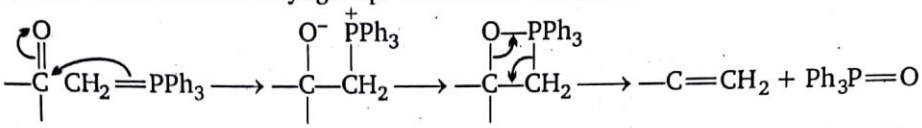
188. (b) Un-symmetrical alkene undergo halogenation to give racemic mixture.

189. (b)

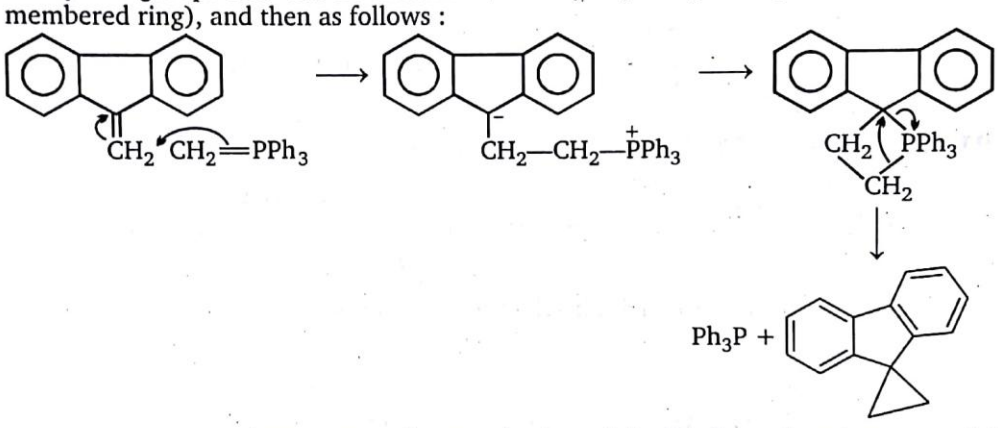




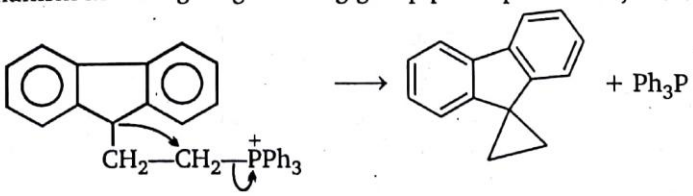
Since there is no carbonyl group in the first product, the double bond of the exocyclic methylene group has reacted with methylenephosphorane. We may therefore propose a mechanism based on the assumption that the exocyclic double bond behaves like the double bond in a carbonyl group. The latter reaction is



However, in the case under consideration, there is no oxygen atom, phosphine and not phosphine oxide is eliminated, and a single and not a double bond is formed with the methylene group. This can be accommodated by replacing O^- by $>C^-$ (of the five - membered ring), and then as follows :

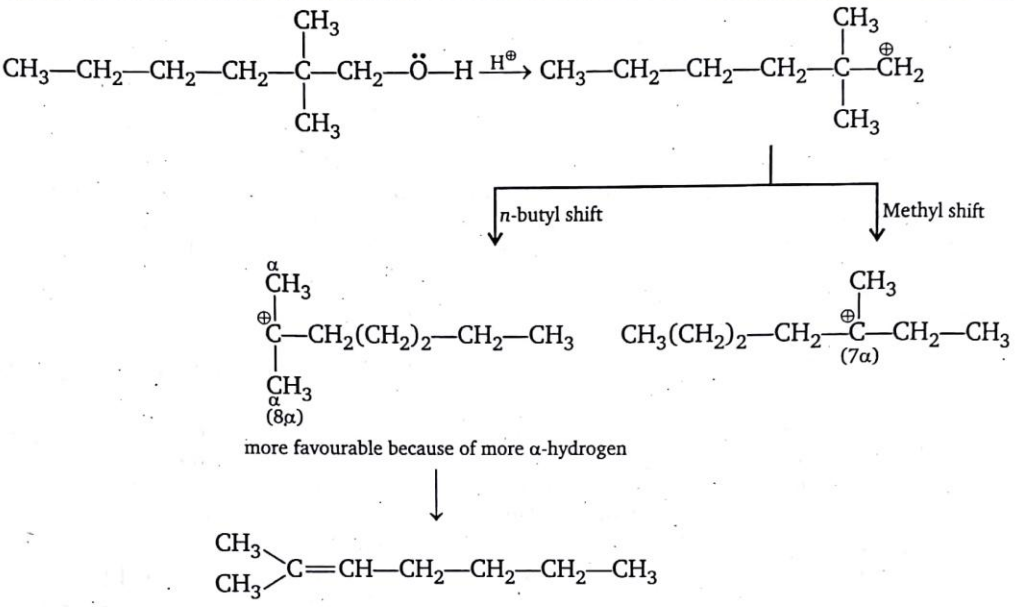


In this sequence, we have proposed a complete parallel with the carbonyl group and this results in the formation of a spiro-compound containing phosphorus in one ring. The final product is also a spiro-compound, but since this contains a three-membered ring, it could be argued that this is less stable than its precursor – which contains a four - membered ring. This can be overcome by assuming that the three - membered ring is formed directly, the mechanism involving neighbouring group participation *i. e.*,

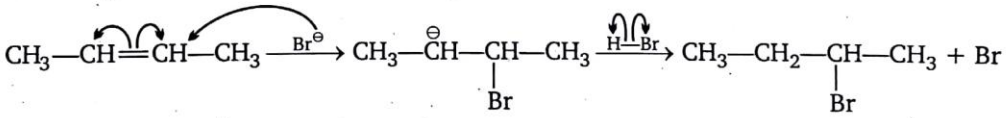


This route would be energetically more favourable than the other one and so is the more likely one.

190. (b)



191. (a) $R_2O_2 \xrightarrow[\Delta]{} 2RO^{\odot} + H-Br \longrightarrow ROH + Br^{\odot}$



Due to attack on sp^2-hybridized reactant and formation of chiral centre, racemization take place.

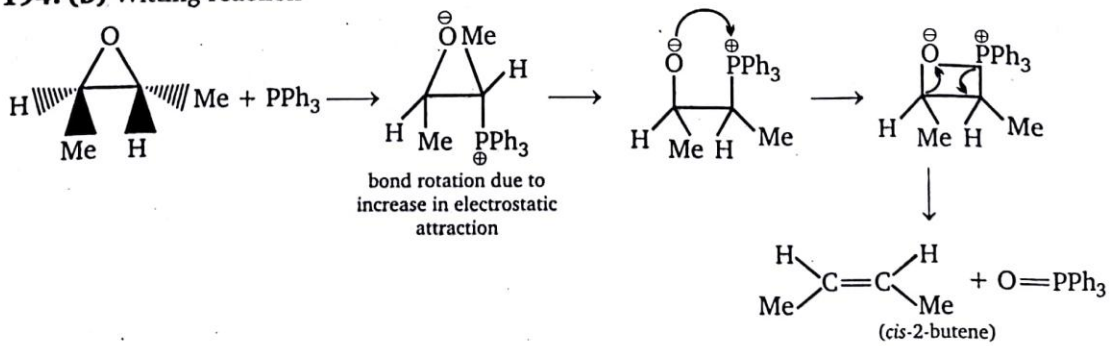
192. (b) $CH_3-\overset{O}{\overset{\|}{C}}-O-O-H$ will act as electrophile.

∴ alkene having more α-hydrogen is better nucleophile it will undergo reaction.

193. (c) Alkene (*A*) must be symmetrical alkene. Which give racemic mixture an anti-addition and meso-compound is syn-addition.

∴ *cis*-4-octene is the answer.

194. (b) Witting reaction



195. (c) Witting reaction :

$$Ph-\overset{\overset{\large O}{\|}}{C}-H + Ph_3P=CH-Ph \longrightarrow Ph-CH=CH-Ph + POPh_3$$

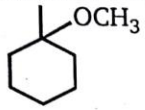
(*cis* and *trans*)

196. (c) $a = Ag_2O, H_2O_2$ (Oxidative ozonolysis)

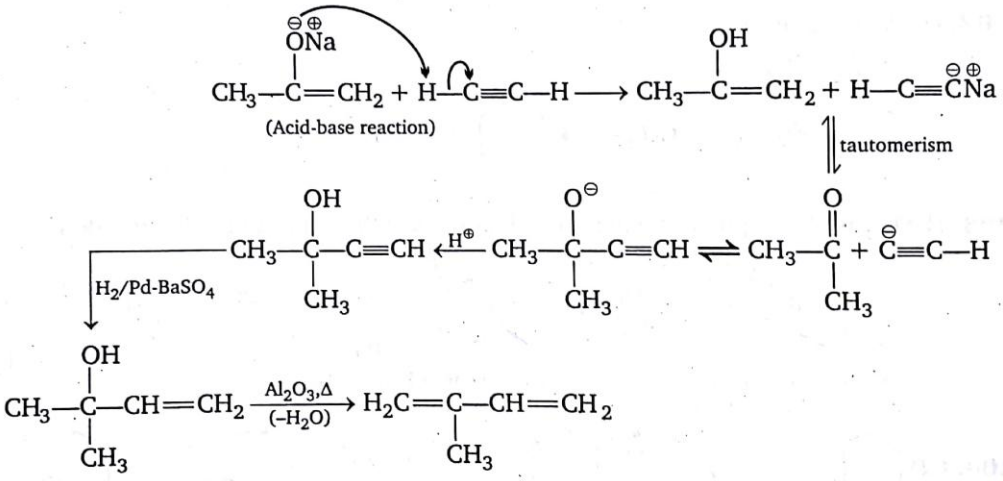
$b = Zn/CH_3CO_2H$ and CH_3-S-CH_3 (reductive ozonolysis)

$c = LiAlH_4$ and $NaBH_4$ (Corresponding alcohol will formed)

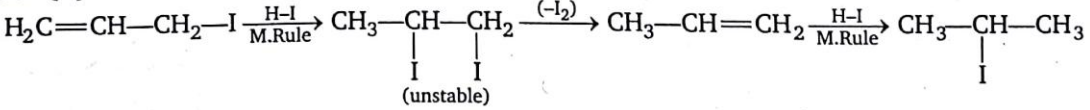
197. (b) Addition of CH_3OH, acc. to Markovnikoff's rule take place

∴ 

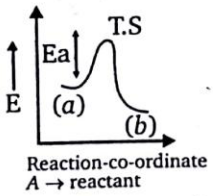
198. (a)



199. (b)

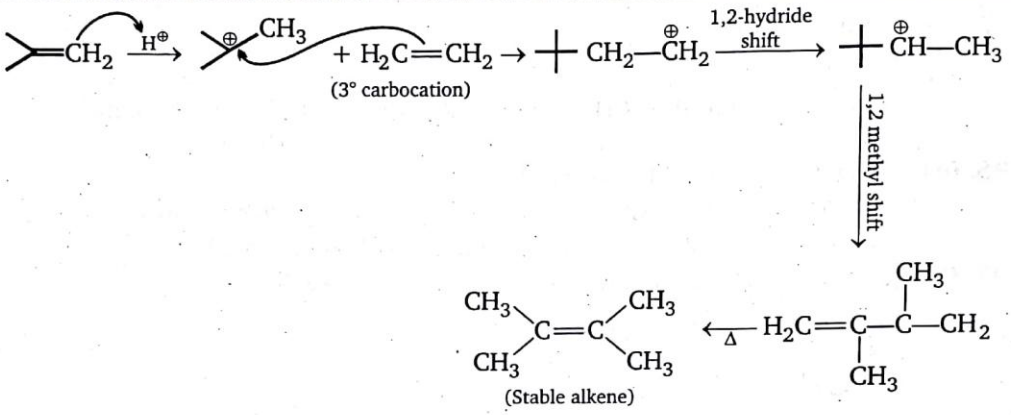


200. (c)

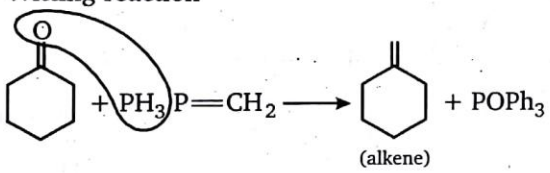


more the stable reactant and more will activation energy less will be rate constant more the stable transition stable less will activation energy more is rate of reaction.

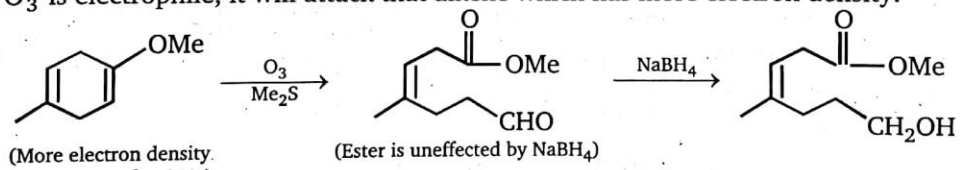
201. (c)



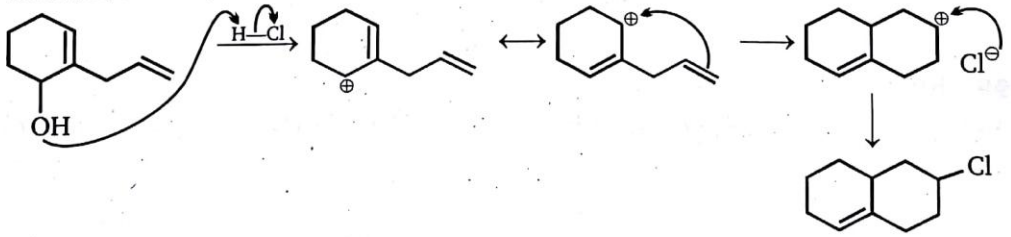
202. (c) Witting reaction



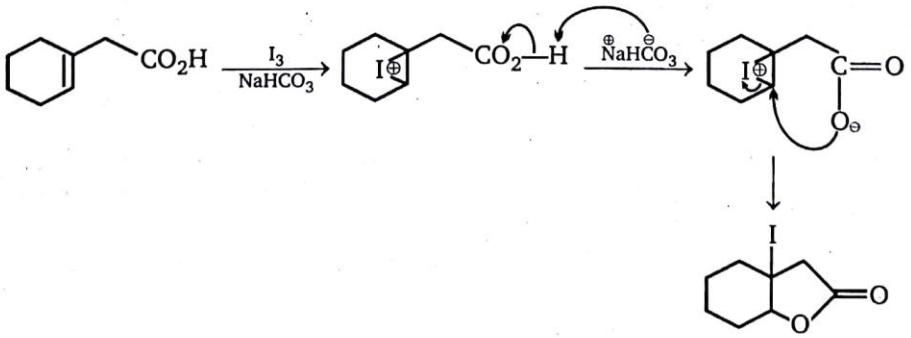
203. (b) O_3 is electrophile, it will attack that alkene which has more electron density.



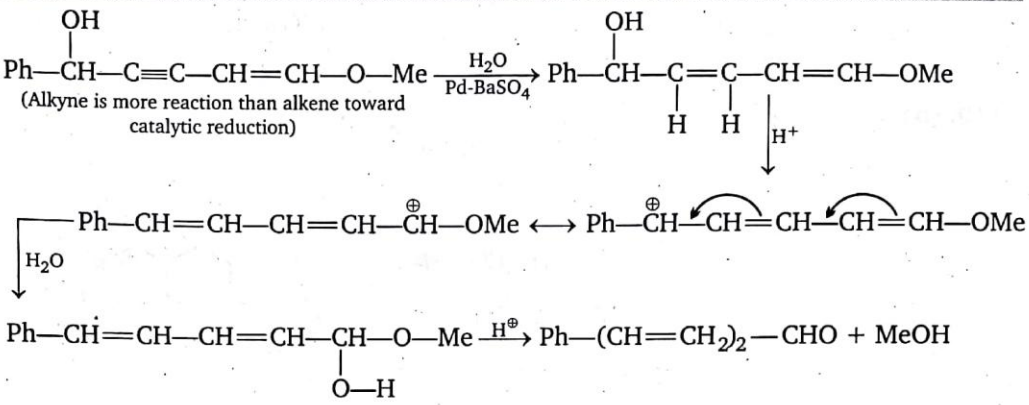
204. (d)



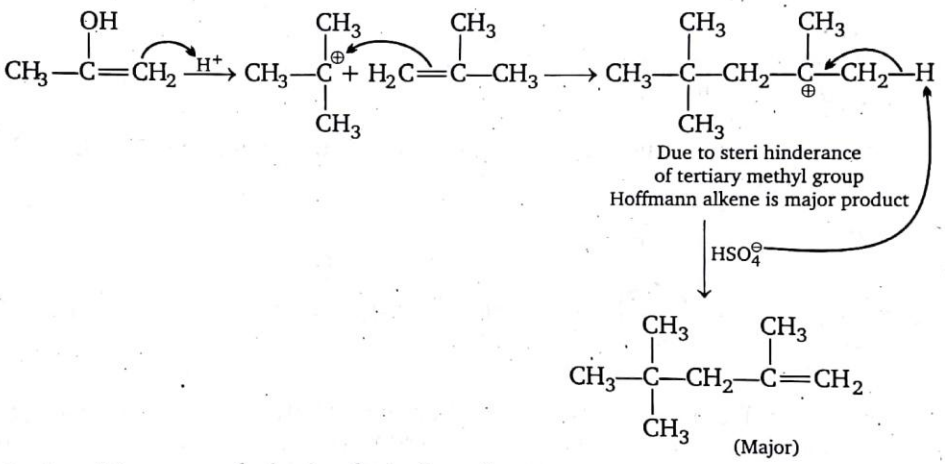
205. (b)



206. (c)

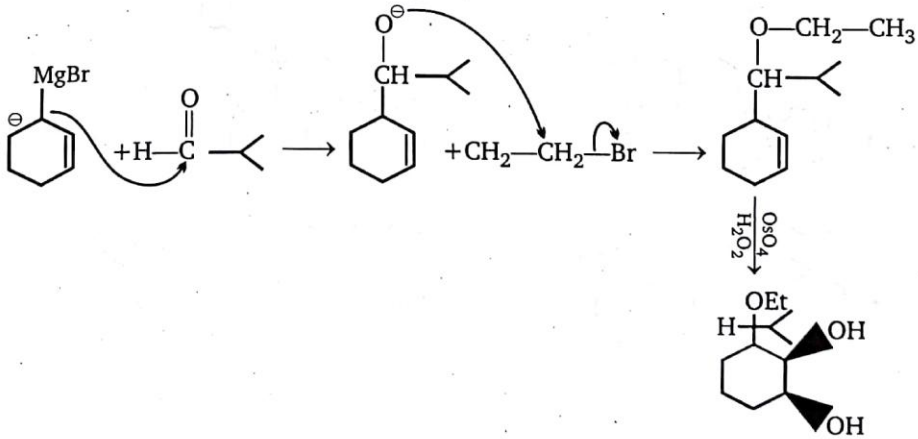


207. (b)

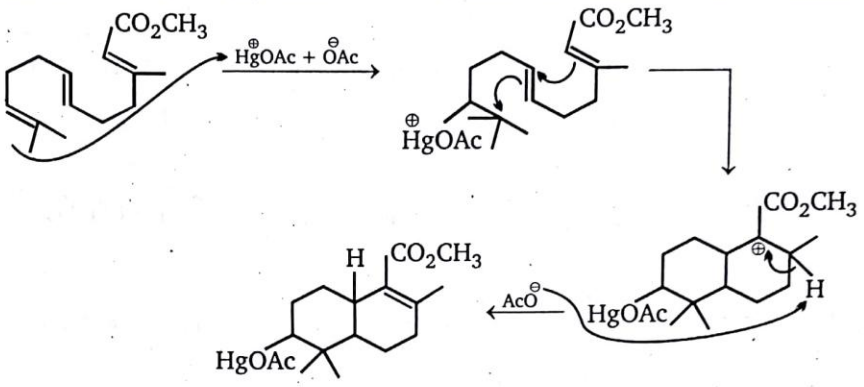


208. (b) Option (b) on ozonolysis give desired product.

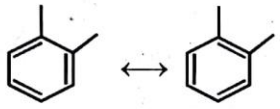
209. (c) (*A*)



210. (b)

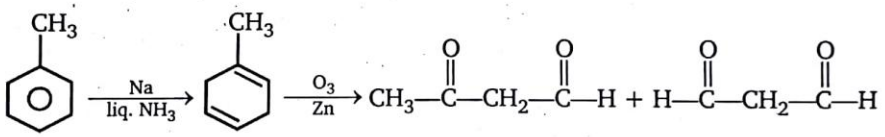


211. (c)



are the canonical structure of *o*-xylene, which on ozonolysis gave 3 mole of glyoxal and 2 mole of pyrualdehyde.

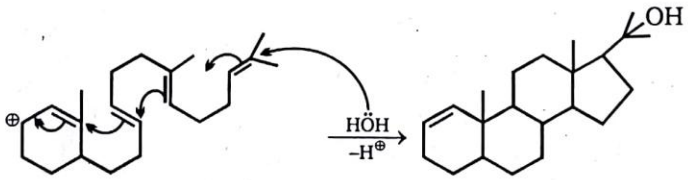
212. (c)



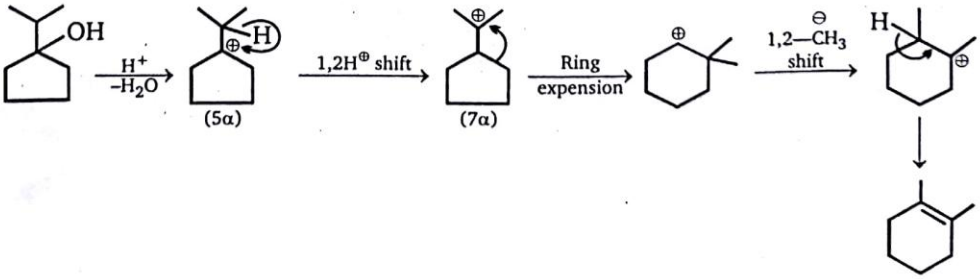
(Birch-reduction)

213. (b) Once a small amount of OsO_4 is used up the Os (VI) by product is oxidized with is the reaction mixture by the amine oxide to re-form OsO_4, thus, a catalytic amount of OsO_4 can be used and the amine oxide acts as the ultimate oxidant.

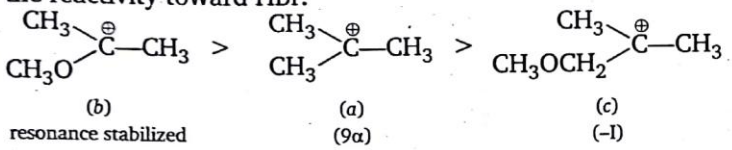
214. (a)

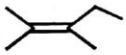


215. (b)

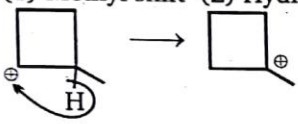


216. (b) Formation of carbocation is the rate determining step more the stable carbocation more is the reactivity toward HBr.

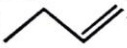


217. (d)  gives more stable is carbocation and this alkene is less stable than 

218. (c) (1) Methyl shift (2) Hydride shift (3) Hydride shift (4) Hydride shift.

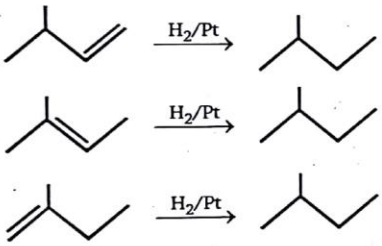
219. (a) 

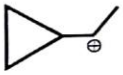
(b) methyl shift (c) No rearrangement (d) Ring expension.

220. (b) Product *a* is 

Product *b* is 

Product *c* is 

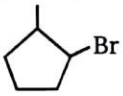
221. (b) 

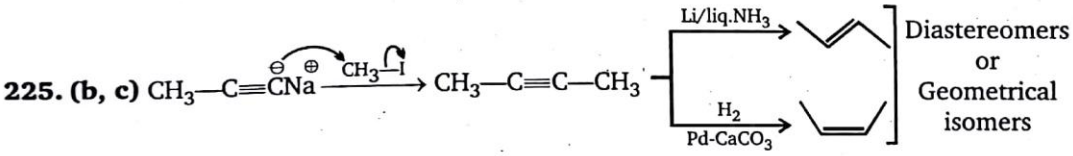
222. (c) 

is stable carbocation due to presence of σ-resonance so it will not rearrange.

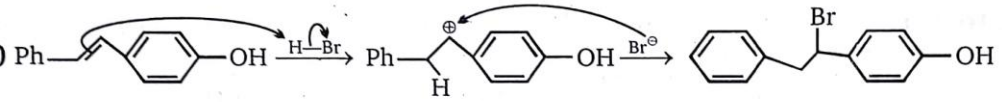
223. (d) SbF_5 is an electrophile which accept the pair of electron in vacant *d*-orbital.

224. (c) $X =$ 

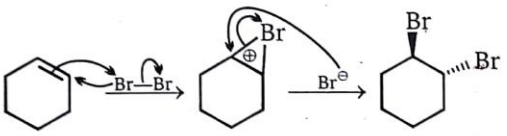
$Y =$ 
$Z =$ 

225. (b, c) 

226. (b)



227. (c)



electophilic addition.

228. (c) (olefins = alkene)

$$-C=C- \xrightarrow[H]{\text{Raney Ni}} -\underset{H}{\underset{|}{CH}}-\underset{H}{\underset{|}{CH}}- \text{ (hydrogenation)}$$

Level-2

Comprehensive-1

1. (i) Markovnikoff 's addition and it is minor product.
(ii) Halogenation of alkene
(iii) Halohydrin formation by (HOBr)
(iv) $C_1H \longrightarrow$ oxymercuration-Demercuration reaction.
(v) Dihydroxylation

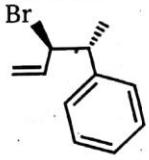
2. (a) Halogenation
(b) Oxymercuration-De-mercuration reaction (OMDM reaction)
(c) Hydroboration-oxidation reaction (HBO reaction)

(e) $CH_3CH=CH_2 \xrightarrow{\text{OMDM}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{oxidising agent}]{\text{HOBr}} CH_3-CH_2-CHO$

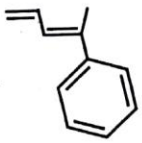
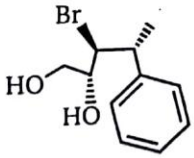
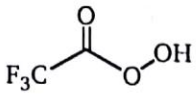
(f) Halohydrin formation
(g) Markovnikoff addition
(h) Oxidation reaction
(i) $CH_3-CH=CH_2 \xrightarrow{\text{HBO}} CH_3-CH_2-CH_2-OH \xrightarrow[\text{Darzene process}]{SOCl_2} CH_3-CH_2-CH_2-Cl + SO_2 + HCl$
(j) Halogenation and elimination.

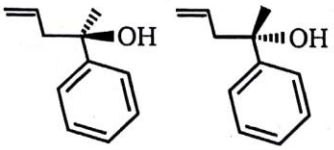
3. Reaction 1: B, D; Reaction 2: E, F, C Reaction 3: I, A
Reaction 4: L, G; Reaction 5: B, L, C

4. Match the reagents a-j with products A-J. There is one best product for each reaction. This molecule



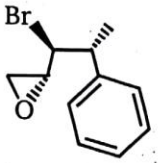
is the starting material for all reactions in problem. Do the ones you know first and then tackle the rest by deductive reasoning

Products	Reagents	Option
(A) 	(a) H_2O heat, pH 7.	C, S_{N1} reaction
(B) 	(b) 	D, Oxidation of alkene

(C) 

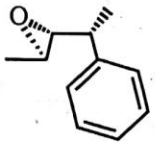
(c) tBuOK, polar aprotic solvent

A E_2 reaction elimination bimolecular

(D) 

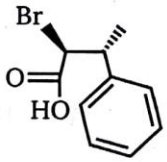
(d) (1) O_3, ether
(2) H_2O, NaOH, H_2O_2

F Oxidative ozonolysis

(E) 

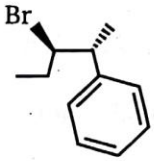
(e) Br_2, CCl_4

I Halogenation of alkene

(F) 

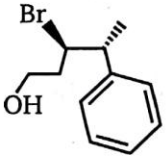
(f) NBS, $h\nu$, CCl_4

J Benzylic substitution

(G) 

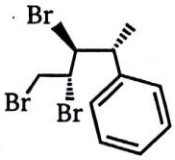
(g) (1) $H_3O(+)$
(2) NaOH, H_2O

E hydration followed by N.G.P.

(H) 

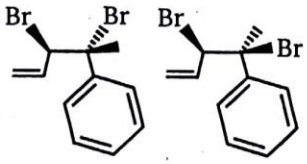
(h) (1) BH_3, ether
(2) H_2O_2

H Hydroboration oxidation

(I) 

(i) (1) OsO_4
(2) NaOH, H_2O

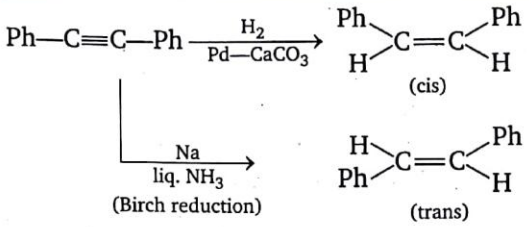
B Oxidation reaction

(J) 

(j) (1) PdC, EtOH, H_2

G Reduction reaction

5. (a)



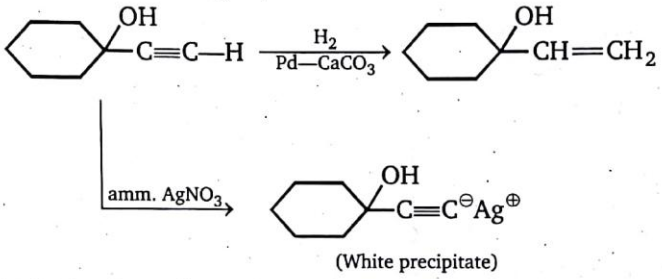
Formula of D.B.E. (Double bond equivalent)

$$\text{DBE} = (C+1) - \left(\frac{H + X - N}{2}\right)$$

X = halogen

$$\text{D. B. E.} = (14+1) - \left(\frac{10}{2}\right) = 10$$

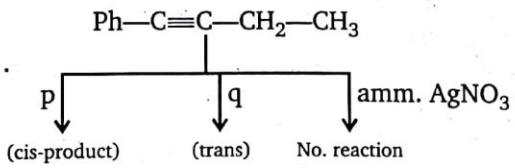
(b)



D. B. E. = 3

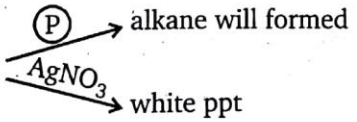
Birch reduction cannot be used for terminal alkyne

(c)



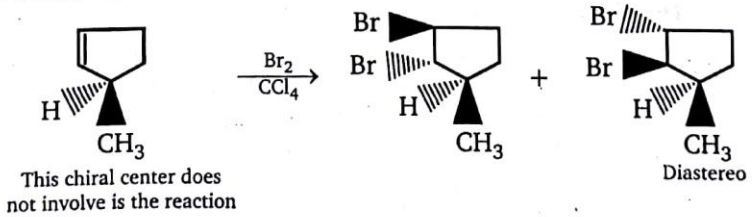
DBE = 6

(d)

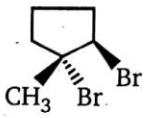


D. B. E. = 6

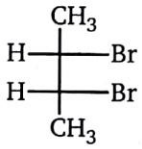
6. (a)



(b) Un-symmetrical alkene undergo halogenation to give racemic mixture.

(c) 

+ Mirror-Image (racemic)

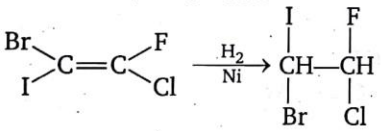
(d) 

(Meso)

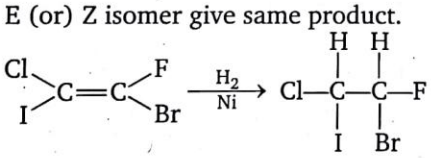
7. (a) OsO_4 will form diol
(b) (HBO)
(c) halohydrin
(d) halogenation

8. $A = B = C = D =$ 

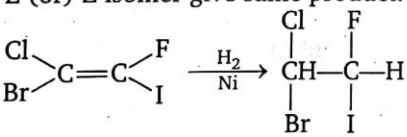
Mol. wt. $= 78 \times 4 = 312$

9. (1) 

E (or) Z isomer give same product.



E (or) Z isomer give same product.

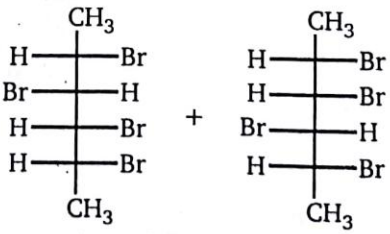


E (or) Z isomer give same product. $(A = 3)$

(2)  (or)  (or)  $\xrightarrow[\text{Ni}]{H_2}$ *n*-Butane

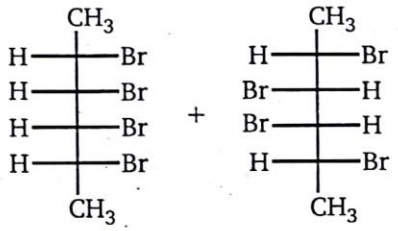
 $\xrightarrow[\text{Ni}]{H_2}$ Iso-butane

$(B = 2) \quad \therefore \quad A + B = 5$

10. Reaction (1) product are $\longrightarrow$ 

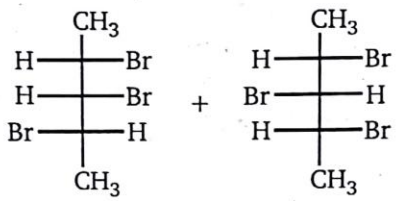
(Diastereomers)

Reaction (2) product are ⟶



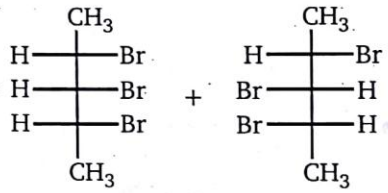
(Diastereomers)

Reaction (3) product are ⟶



(Diastereomers)

Reaction (4) product are ⟶

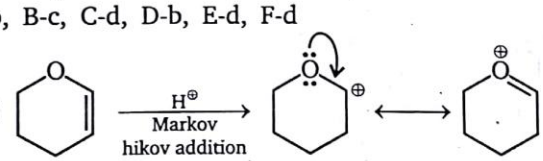


(Diastereomers)

Sum of products (P + Q + R + S) = 8

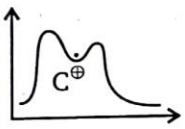
11. A-b, B-c, C-d, D-b, E-d, F-d

(A)



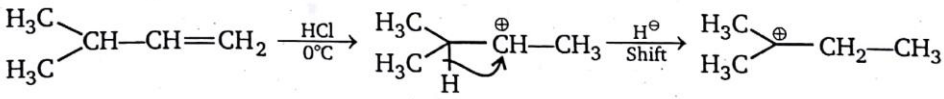
(octet complete carbocation)

(B)

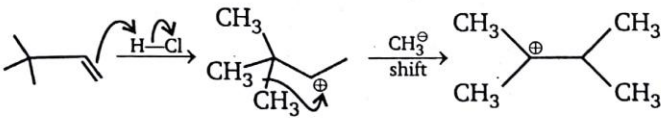


exothermic (1 π-bond breaks and 2σ-bonds are formed)

(C) (a)

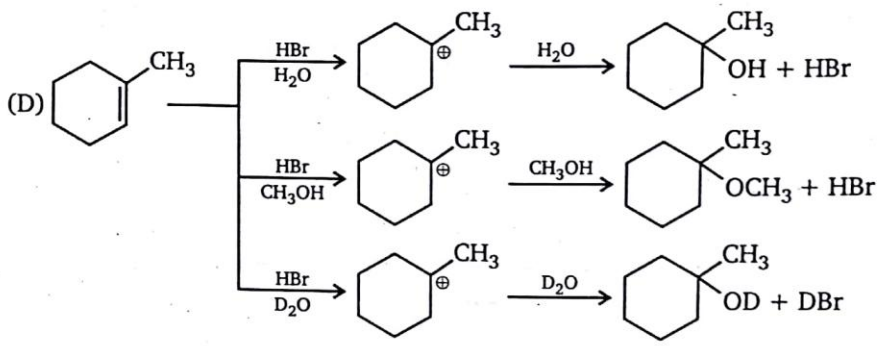


(b)

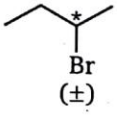


(c) $Ph—CH_2—CH=CH_2 \xrightarrow[CCl_4]{HBr} Ph—CH(H)—\overset{\oplus}{C}H—CH_3 \xrightarrow[Shift]{H^{\ominus}} Ph—\overset{\oplus}{C}H—CH_2CH_3$

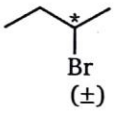
(D)



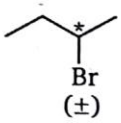
(E) (a)



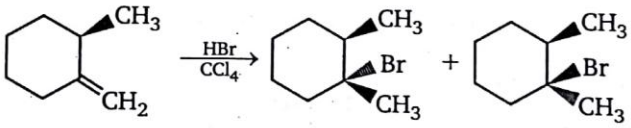
(b)



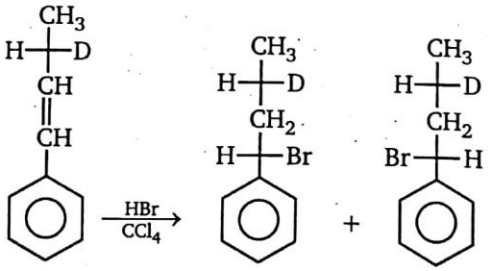
(c)



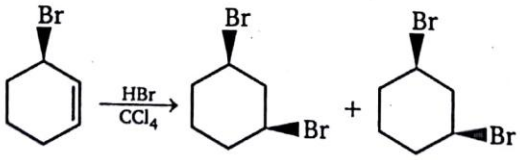
(F) (a)



(b)



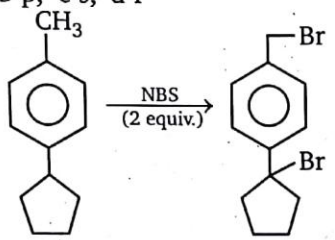
(c)



12. A-b, B-b, C-c, D-b, E-b

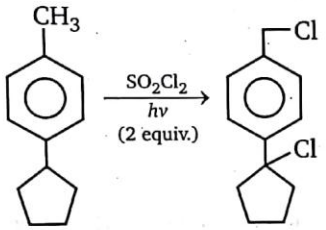
13. a-q, b-p, c-s, d-r

(a)



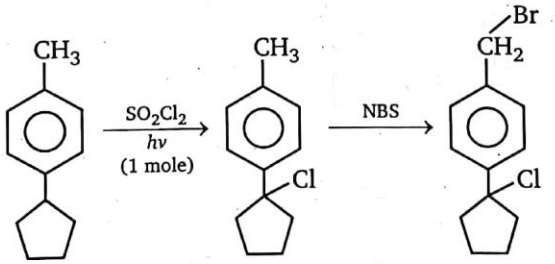
(Benzylic bromination) via free radical formation

(b)

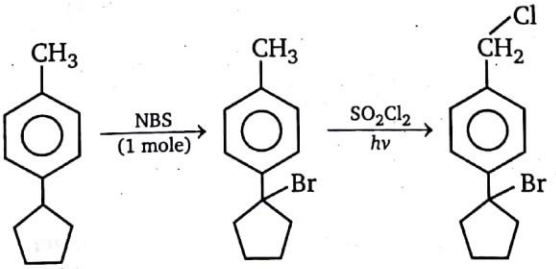


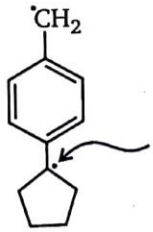
Benzylic chlorination via free radical formation.

(c)



(d)





Most stable radical