

## A Fill in the Blanks

1. Among the given cations, ..... is most stable. (1981)  
(*sec*-butyl carbonium ion; *tert*-butyl carbonium ion; *n*-butyl carbonium ion)
2. The compound having both  $sp$  and  $sp^2$  hybridized carbon atoms is ..... (1981)  
(propene, propane, propadiene)
3. .... ring is most strained. (1981)  
(Cyclopropane, Cyclobutane, Cyclopentane)
4. The terminal carbon atom in butane is ..... hybridised. (1985)
5. A ..... diol has two hydroxyl groups on ..... carbon atoms. (1986)
6. Isomers which are ..... mirror images are known as ..... (1988)  
(superimposable, non-superimposable, enantiomers, diastereomers, epimers)
7. The valence atomic orbitals on carbon in silver acetylide is ..... hybridized. (1990)
8. The kind of delocalization involving sigma bond orbitals is called ..... (1994)
9. The IUPAC name of succinic acid is ..... (1994)

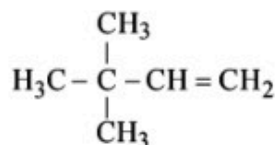
## B True / False

1. Iodide is a better nucleophile than bromide. (1985 - 1/2 Mark)
2. An electron donating substituent in benzene orients the incoming electrophilic group to the meta position. (1987)
3. 2, 3, 4-Trichloropentane has three asymmetric carbon atoms. (1990)
4. During  $S_N1$  reaction, the leaving group leaves the molecule before the incoming group is attached to the molecule. (1990)

## C MCQs with One Correct Answer

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

2. Molecule in which the distance between the two adjacent carbon atoms is largest is (1981)  
(a) Ethane (b) Ethene  
(c) Ethyne (d) Benzene
3. The compound which is not isomeric with diethyl ether is (1981)  
(a) *n*-propyl methyl ether (b) butan-1-ol  
(c) 2-methylpropan-2-ol (d) butanone
4. Among the following, the compound that can be most readily sulphonated is (1982)  
(a) benzene (b) nitrobenzene  
(c) toluene (d) chlorobenzene
5. The compound 1, 2-butadiene has (1983)  
(a) only  $sp$  hybridized carbon atoms  
(b) only  $sp^2$  hybridized carbon atoms  
(c) both  $sp$  and  $sp^2$  hybridized carbon atoms  
(d)  $sp$ ,  $sp^2$  and  $sp^3$  hybridized carbon atoms
6. Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism? (1983)  
(a) 2-butene (b) 2-butyne  
(c) 2-butanol (d) butanal
7. The IUPAC name of the compound having the formula



- is: (1984)
- (a) 3, 3, 3-Trimethyl-1-propene  
(b) 1, 1, 1-Trimethyl-2-propene  
(c) 3, 3-Dimethyl-1-butene  
(d) 2, 2-Dimethyl-3-butene
  8. An isomer of ethanol is: (1986)  
(a) methanol (b) diethyl ether  
(c) acetone (d) dimethyl ether
  9. Out of the following compounds, which will have a zero dipole moment? (1987)  
(a) 1, 1-dichloroethylene  
(b) *cis*-1, 2-dichloroethylene  
(c) *trans*-1, 2-dichloroethylene  
(d) None of these compounds

10. The bond between carbon atom (1) and carbon atom (2) in compound  $N \equiv C - \underset{1}{CH} = \underset{2}{CH_2}$  involves the hybrids as

- (a)  $sp^2$  and  $sp^2$  (b)  $sp^3$  and  $sp$   
(c)  $sp$  and  $sp^2$  (d)  $sp$  and  $sp$

11. The IUPAC name of the compound  $CH_2 = CH - CH(CH_3)_2$  is

- (a) 1,1-dimethyl-2-propene (b) 3-methyl 1-butene  
(c) 2-vinylpropane (d) 1-isopropylethylene

12. The number of isomers of  $C_6H_{14}$  is

- (a) 4 (b) 5  
(c) 6 (d) 7

13. The  $Cl - C - Cl$  angle in 1,1,2,2-tetrachloroethene and tetrachloromethane respectively will be about

- (a)  $120^\circ$  and  $109.5^\circ$  (b)  $90^\circ$  and  $109.5^\circ$   
(c)  $109.5^\circ$  and  $90^\circ$  (d)  $109.5^\circ$  and  $120^\circ$

14. In  $CH_3CH_2OH$ , the bond that undergoes heterolytic cleavage most readily is

- (a)  $C - C$  (b)  $C - O$   
(c)  $C - H$  (d)  $O - H$

15. The compound which has one isopropyl group is :

- (a) 2,2,3,3-tetramethylpentane (b) 2,2-dimethylpentane  
(c) 2,2,3-trimethylpentane (d) 2-methylpentane

16. The  $C - H$  bond distance is the longest in :

- (a)  $C_2H_2$  (b)  $C_2H_4$   
(c)  $C_2H_6$  (d)  $C_2H_5Br$

17. The number of sigma and pi-bonds in 1-butene-3-yne are :

- (a) 5 sigma and 5 pi (b) 7 sigma and 3 pi  
(c) 8 sigma and 2 pi (d) 5 sigma and 4 pi

18. The compound which gives the most stable carbonium ion on dehydration is :

- (a)  $CH_3 - \underset{\text{CH}_3}{\underset{|}{CH}} - CH_2OH$  (b)  $CH_3 - \overset{\text{CH}_3}{\underset{|}{C}} - OH$   
(c)  $CH_3 - CH_2 - CH_2 - CH_2OH$   
(d)  $CH_3 - \underset{\text{OH}}{\underset{|}{CH}} - CH_2 - CH_3$

19. The hybridization of carbon atoms in  $C - C$  single bond of  $HC \equiv C - CH = CH_2$  is

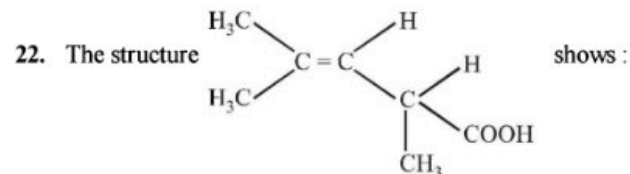
- (a)  $sp^3 - sp^3$  (b)  $sp^2 - sp^3$   
(c)  $sp - sp^2$  (d)  $sp^3 - sp$

20. The products of combustion of an aliphatic thiol (RSH) at 298 K are

- (a)  $CO_2(g)$ ,  $H_2O(g)$  and  $SO_2(g)$   
(b)  $CO_2(g)$ ,  $H_2O(l)$  and  $SO_2(g)$   
(c)  $CO_2(l)$ ,  $H_2O(l)$  and  $SO_2(g)$   
(d)  $CO_2(g)$ ,  $H_2O(l)$  and  $SO_2(l)$

21. Isomers which can be interconverted through rotation around a single bond are

- (a) Conformers (b) Diastereomers  
(c) Enantiomers (d) Positional isomers



- (a) geometrical isomerism (b) optical isomerism  
(c) geometrical & optical isomerism (d) tautomerism.

23. Allyl isocyanide has :

- (a)  $9\sigma$  and  $4\pi$  bonds (b)  $8\sigma$  and  $5\pi$  bonds  
(c)  $9\sigma$ ,  $3\pi$  and 2 non-bonded electrons  
(d)  $8\sigma$ ,  $3\pi$  and 4 non-bonded electrons

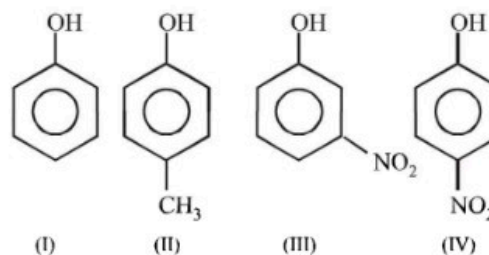
24. Arrange in order of decreasing trend towards  $S_E$  reactions :

- Chlorobenzene (I), benzene (II), anilinium chloride (III), toluene (IV)  
(a)  $II > I > III > IV$  (b)  $III > I > II > IV$   
(c)  $IV > II > I > III$  (d)  $I > II > III > IV$

25. Most stable carbonium ion is :

- (a)  $p\text{-NO}_2\text{-C}_6\text{H}_4\text{-CH}_2^+$   
(b)  $\text{C}_6\text{H}_5\text{CH}_2^+$   
(c)  $p\text{-Cl-C}_6\text{H}_4\text{-CH}_2^+$   
(d)  $p\text{-CH}_3\text{O-C}_6\text{H}_4\text{-CH}_2^+$

26. In the following compounds,



The order of acidity is :

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

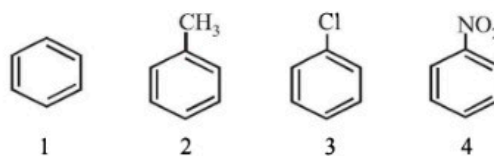
27. Arrange the following compounds in order of increasing dipole moment.

- Toluene (I), *m*-dichlorobenzene (II), *o*-dichlorobenzene (III), *p*-dichlorobenzene (IV)  
(a)  $I < IV < II < III$  (b)  $IV < I < II < III$   
(c)  $IV < I < III < II$  (d)  $IV < II < I < III$

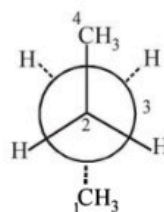
28. How many optically active stereoisomers are possible for butane-2,3-diol?

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

29. In the compound  $\text{CH}_2 = \text{CH}-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{CH}$ , the  $\text{C}_2-\text{C}_3$  bond is of the type, (1999)  
 (a)  $sp-sp^2$  (b)  $sp^3-sp^3$   
 (c)  $sp-sp^3$  (d)  $sp^2-sp^3$
30. The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive (1999)  
 (a) optical rotation and is derived from D-glucose  
 (b) pH in organic solvent  
 (c) optical rotation and is derived from D-(+)-glyceraldehyde  
 (d) optical rotation only when substituted by deuterium
31. Which of the following compounds will exhibit geometrical isomerism? (2000S)  
 (a) 1-Phenyl-2-butene (b) 3-Phenyl-1-butene  
 (c) 2-Phenyl-1-butene (d) 1,1-Diphenyl-1-propene
32. Which of the following has the highest nucleophilicity? (2000S)  
 (a)  $\text{F}^-$  (b)  $\text{OH}^-$   
 (c)  $\text{CH}_3^-$  (d)  $\text{NH}_2^-$
33. The order of reactivities of the following alkyl halides for a  $\text{S}_{\text{N}}2$  reaction is (2000S)  
 (a)  $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$  (b)  $\text{RF} > \text{RBr} > \text{RCl} > \text{RI}$   
 (c)  $\text{RCl} > \text{RBr} > \text{RF} > \text{RI}$  (d)  $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$
34. Which of the following has the most acidic hydrogen? (2000S)  
 (a) 3-Hexanone (b) 2,4-Hexanedione  
 (c) 2,5-Hexanedione (d) 2,3-Hexanedione
35. The number of isomers for the compound with molecular formula  $\text{C}_2\text{BrClFI}$  is (2001S)  
 (a) 3 (b) 4  
 (c) 5 (d) 6
36. An  $\text{S}_{\text{N}}2$  reaction at an asymmetric carbon of a compound always gives (2001S)  
 (a) an enantiomer of the substrate  
 (b) a product with opposite optical rotation  
 (c) a mixture of diastereomers  
 (d) a single stereoisomer
37. Which of the following compounds exhibits stereoisomerism? (2002S)  
 (a) 2-methylbutene-1 (b) 3-methylbutyne-1  
 (c) 3-methylbutanoic acid (d) 2-methylbutanoic acid
38. Which of the following acids has the smallest dissociation constant? (2002S)  
 (a)  $\text{CH}_3\text{CHF}\text{COOH}$  (b)  $\text{FCH}_2\text{CH}_2\text{COOH}$   
 (c)  $\text{BrCH}_2\text{CH}_2\text{COOH}$  (d)  $\text{CH}_3\text{CHBr}\text{COOH}$
39. Identify the correct order of boiling points of the following compounds; (2002S)  
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ ,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$   
 1 2 3  
 (a)  $1 > 2 > 3$  (b)  $3 > 1 > 2$   
 (c)  $1 > 3 > 2$  (d)  $3 > 2 > 1$
40. Identify the correct order of reactivity in electrophilic substitution reactions of the following compounds (2002S)

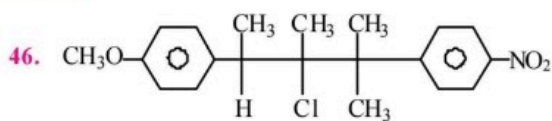


- (a)  $1 > 2 > 3 > 4$  (b)  $4 > 3 > 2 > 1$   
 (c)  $2 > 1 > 3 > 4$  (d)  $2 > 3 > 1 > 4$
41. Which of the following hydrocarbons has the lowest dipole moment? (2002S)  
 (a) (b)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$   
 (c)  $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$  (d)  $\text{CH}_2 = \text{CH} - \text{C}\equiv\text{CH}$
42. Which of the following represents the given mode of hybridisation  $sp^2 - sp^2 - sp - sp$  from left to right? (2003S)  
 (a)  $\text{H}_2\text{C} = \text{CH} - \text{C}\equiv\text{N}$  (b)  $\text{HC}\equiv\text{C} - \text{C}\equiv\text{CH}$   
 (c)  $\text{H}_2\text{C} = \text{C} = \text{C} = \text{CH}_2$  (d)  $\text{H}_2\text{C} = \text{CH} - \text{CH} = \text{CH}_2$
43. Among the following, the molecule with the highest dipole moment is: (2003S)  
 (a)  $\text{CH}_3\text{Cl}$  (b)  $\text{CH}_2\text{Cl}_2$   
 (c)  $\text{CHCl}_3$  (d)  $\text{CCl}_4$
44. In the given conformation, if  $\text{C}_2$  is rotated about  $\text{C}_2 - \text{C}_3$  bond anticlockwise by an angle of  $120^\circ$  then the conformation obtained is (2004S)

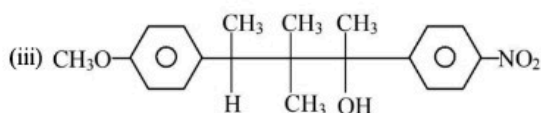
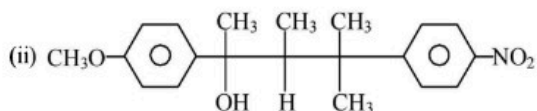
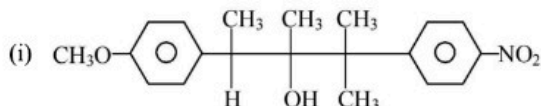


- (a) fully eclipsed conformation  
 (b) partially eclipsed conformation  
 (c) gauche conformation  
 (d) staggered conformation
45. Which of the following resonating structures of 1-methoxy-1,3-butadiene is least stable? (2005S)  
 (a)  $\ominus\text{CH}_2 - \text{CH} = \text{CH} - \text{CH} = \text{O}^{\oplus} - \text{CH}_3$   
 (b)  $\text{CH}_2 = \text{CH} - \text{CH}^{\ominus} - \text{CH} = \text{O}^{\oplus} - \text{CH}_3$   
 (c)  $\ominus\text{CH}_2 - \text{CH}^{\oplus} - \text{CH} = \text{CH} - \text{O} - \text{CH}_3$   
 (d)  $\text{CH}_2 = \text{CH} - \text{CH}^{\ominus} - \text{CH}^{\oplus} - \text{O} - \text{CH}_3$





compound on hydrolysis in aqueous acetone will give (2005S)

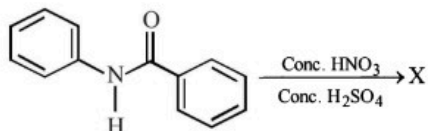


- (a) Mixture of (i) and (ii) (b) Mixture of (i) and (iii)  
(c) Only (iii) (d) Only (i)

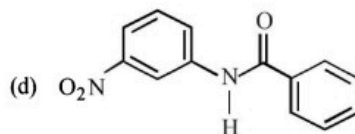
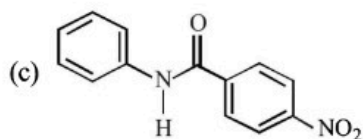
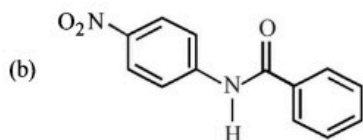
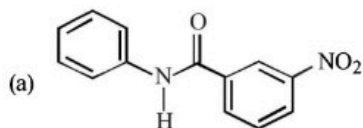
47. The IUPAC name of  $C_6H_5COCl$  is (2006 - 3M, -1)

- (a) Benzene chloro ketone  
(b) Benzoyl chloride  
(c) Chloro phenyl ketone  
(d) Benzene carbonyl chloride

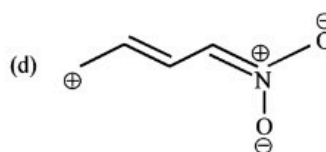
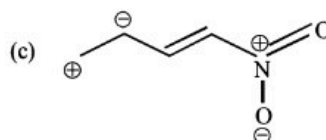
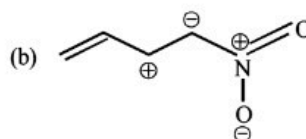
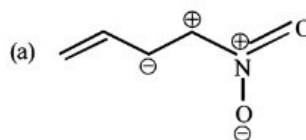
48. In the following reaction,



the structure of the major product 'X' is



49. Among the following, the least stable resonance structure is (2007)



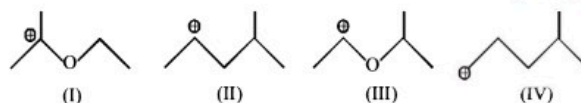
50. The number of stereoisomers obtained by bromination of *trans*-2-butene is (2007)

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

51. Hyperconjugation involves overlap of the following orbitals (2008)

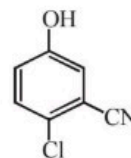
- (a)  $\sigma$ - $\sigma$  (b)  $\sigma$ - $\pi$   
(c) p-p (d)  $\pi$ - $\pi$

52. The correct stability order for the following species is (2008)



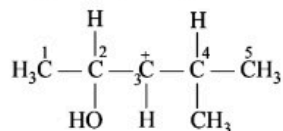
- (a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)  
(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

53. The IUPAC name of the following compound is (2009)

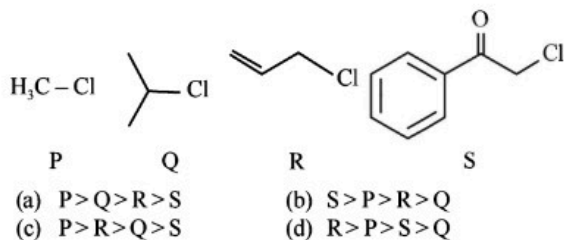


- (a) 4-Bromo-3-cyanophenol  
(b) 2-Bromo-5-hydroxybenzonitrile  
(c) 2-Cyano-4-hydroxybromobenzene  
(d) 6-Bromo-3-hydroxybenzonitrile

54. In the following carbocation, H/CH<sub>3</sub> that is most likely to migrate to the positively charged carbon is (2009)

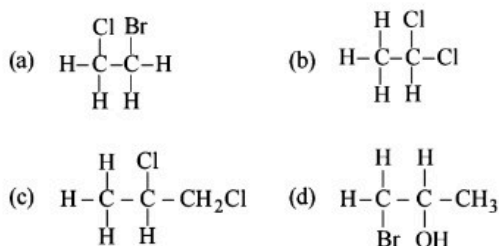


- (a) CH<sub>3</sub> at C-4 (b) Hat C-4  
(c) CH<sub>3</sub> at C-2 (d) Hat C-2
55. Among the following compounds, the most acidic is (2011)
- (a) *p*-nitrophenol (b) *p*-hydroxybenzoic acid  
(c) *o*-hydroxybenzoic acid (d) *p*-toluic acid
56. KI in acetone, undergoes S<sub>N</sub>2 reaction with each of P, Q, R and S. The rates of the reaction vary as (JEE Adv. 2013)



### D MCQs with One or More Than One Correct

1. Resonance structures of a molecule should have : (1984)
- (a) identical arrangement of atoms  
(b) nearly the same energy content  
(c) the same number of paired electrons  
(d) identical bonding
2. Phenol is less acidic than : (1986)
- (a) acetic acid (b) *p*-methoxyphenol  
(c) *p*-nitrophenol (d) ethanol
3. Dipole moment is shown by : (1986)
- (a) 1,4-dichlorobenzene  
(b) *cis*-1,2-dichloroethane  
(c) *trans*-1,2-dichloroethene  
(d) *trans*-1,2-dichloro-2-pentene
4. Only two isomeric monochloro derivatives are possible for: (1986)
- (a) *n*-butane (b) 2,4-dimethylpentane  
(c) benzene (d) 2-methylpropane
5. Which of the following have asymmetric carbon atom? (1989)



6. What is the decreasing order of strength of the bases OH<sup>-</sup>, NH<sub>2</sub><sup>-</sup>, HC≡C<sup>-</sup> and CH<sub>3</sub>CH<sub>2</sub><sup>-</sup> ? (1993)

- (a) CH<sub>3</sub>-CH<sub>2</sub><sup>-</sup> > NH<sub>2</sub><sup>-</sup> > H-C≡C<sup>-</sup> > OH<sup>-</sup>  
(b) H-C≡C<sup>-</sup> > CH<sub>3</sub>-CH<sub>2</sub><sup>-</sup> > NH<sub>2</sub><sup>-</sup> > OH<sup>-</sup>  
(c) OH<sup>-</sup> > NH<sub>2</sub><sup>-</sup> > H-C≡C<sup>-</sup> > CH<sub>3</sub>-CH<sub>2</sub><sup>-</sup>  
(d) NH<sub>2</sub><sup>-</sup> > H-C≡C<sup>-</sup> > OH<sup>-</sup> > CH<sub>3</sub>-CH<sub>2</sub><sup>-</sup>

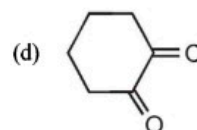
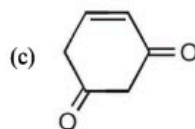
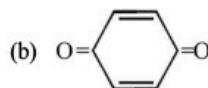
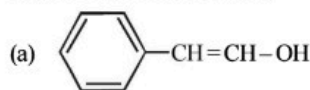
7. Which of the following compounds will show geometrical isomerism? (1998)

- (a) 2-butene (b) propene  
(c) 1-phenylpropene (d) 2-methyl-2-butene

8. Among the following compounds, the strongest acid is (1998)

- (a) HC≡CH (b) C<sub>6</sub>H<sub>6</sub>  
(c) C<sub>2</sub>H<sub>6</sub> (d) CH<sub>3</sub>OH

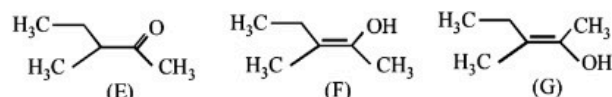
9. Tautomerism is exhibited by (1998)



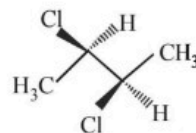
10. An aromatic molecule will (1999)

- (a) have 4n π electrons (b) have (4n + 2) π electrons  
(c) be planar (d) be cyclic

11. The correct statement(s) concerning the structures E, F and G is (are) – (2008)

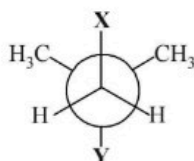


- (a) E, F, and G are resonance structures  
(b) E, F and E, G are tautomers  
(c) F and G are geometrical isomers  
(d) F and G are diastereomers
12. The correct statement(s) about the compound given below is (are) (2008)

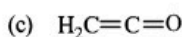
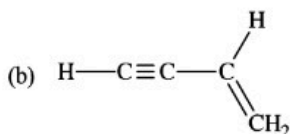
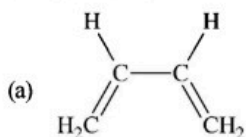


- (a) The compound is optically active  
(b) The compound possesses centre of symmetry  
(c) The compound possesses plane of symmetry  
(d) The compound possesses axis of symmetry

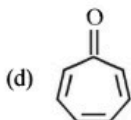
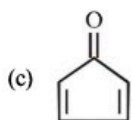
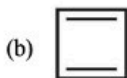
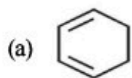
13. The correct statement(s) about the compound (2009)  
 $\text{H}_3\text{C}(\text{HO})\text{HC}-\text{CH}=\text{CH}-\text{CH}(\text{OH})\text{CH}_3$  (X) is(are)  
 (a) The total number of stereoisomers possible for X is 6  
 (b) The total number of diastereomers possible for X is 3  
 (c) If the stereochemistry about the double bond in X is *trans*, the number of enantiomers possible for X is 4  
 (d) If the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2
14. In the Newman projection for 2,2-dimethylbutane



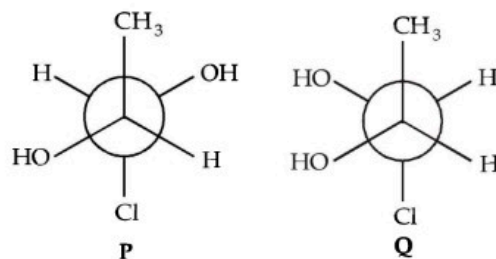
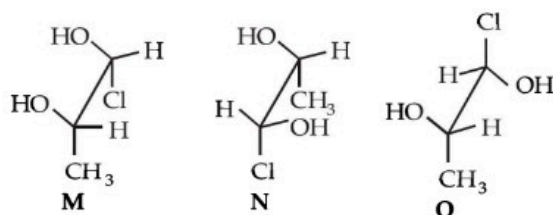
- X and Y can respectively be (2010)  
 (a) H and H (b) H and  $\text{C}_2\text{H}_5$   
 (c)  $\text{C}_2\text{H}_5$  and H (d)  $\text{CH}_3$  and  $\text{CH}_3$
15. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are) (2011)



16. Which of the following molecules, in pure form, is (are) unstable at room temperature? (2012)



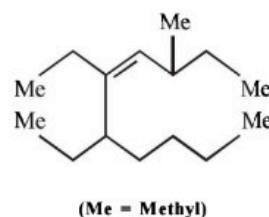
17. Which of the given statement(s) about N, O, P and Q with respect to M is (are) correct? (2012)



- (a) M and N are non-mirror image stereoisomers  
 (b) M and O are identical  
 (c) M and P are enantiomers  
 (d) M and Q are identical
18. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to (JEE Adv. 2013)  
 (a)  $\sigma \rightarrow p$  (empty) and  $\sigma \rightarrow \pi^*$  electron delocalisations  
 (b)  $\sigma \rightarrow \sigma^*$  and  $\sigma \rightarrow \pi$  electron delocalisations  
 (c)  $\sigma \rightarrow p$  (filled) and  $\sigma \rightarrow \pi$  electron delocalisations  
 (d)  $p$  (filled)  $\rightarrow \sigma^*$  and  $\sigma \rightarrow \pi^*$  electron delocalisations

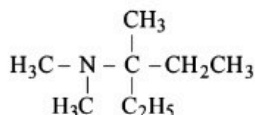
## E Subjective Problems

1. Arrange the following in :
- (i) Increasing reactivity towards HCN (1985)  
 $\text{CH}_3\text{CHO}$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{HCHO}$ ,  $\text{C}_2\text{H}_5\text{COCH}_3$
- (ii) *n*-butane, *n*-butanol, *n*-butyl chloride, isobutane in increasing order of boiling point. (1988)
- (iii) benzene, toluene, methoxybenzene, chlorobenzene in increasing order of reactivity towards sulphonation with fuming sulphuric acid. (1988)
- (iv) Increasing order of acid strength : (1991)  
 $\text{ClCH}_2\text{COOH}$  (I),  $\text{CH}_3\text{CH}_2\text{COOH}$  (II),  
 $\text{ClCH}_2\text{CH}_2\text{COOH}$  (III),  $(\text{CH}_3)_2\text{CHCOOH}$  (IV),  
 $\text{CH}_3\text{COOH}$  (V)
- (v) Increasing reactivity in nucleophilic substitution reactions (1992)  
 $\text{CH}_3\text{F}$ ,  $\text{CH}_3\text{I}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{Cl}$
2. (i) Write the IUPAC name of : (1986)  
 $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCOOH}$
- (ii) Give the IUPAC name of the following compound : (1990)

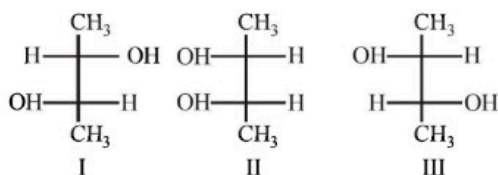


- (iii) Write the IUPAC name for the following :



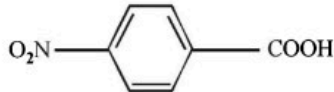
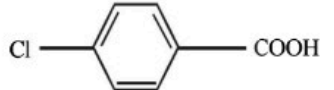

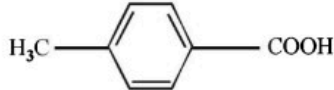


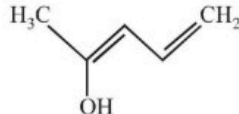
3. For nitromethane molecule, write structure(s).  
 (i) showing significant resonance stabilisation. (1986)  
 (ii) indicating tautomerism. (1986)
4. Give reasons for the following :  
 (i) Carbon oxygen bond lengths in formic acid are 1.23 Å and 1.36 Å and both the carbon oxygen bonds in sodium formate have the same value i.e. 1.27 Å. (1988)  
 (ii) Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl ( $\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$ ) is more reactive than benzene towards electrophilic substitution. (1992)  
 (iii) Aryl halides are less reactive than alkyl halides towards nucleophilic reagents (1994)  
 (iv)  $\text{CH}_2=\text{CH}^-$  is more basic than  $\text{HC}\equiv\text{C}^-$ .  
 (v) Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds.
5. Write the structural formula of 4-chloro-2-pentene. (1988)
6. Write tautomeric forms for phenol. (1992)
7. Write down the structures of the stereoisomers formed when *cis*-2-butene is reacted with bromine. (1995)
8. Discuss the hybridisation of carbon atoms in allene ( $\text{C}_3\text{H}_4$ ) and show the  $\pi$ -orbital overlaps. (1999)
9. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III (2000)



10. Which one is more soluble in diethyl ether - anhydrous  $\text{AlCl}_3$  or hydrous  $\text{AlCl}_3$ ? Explain in terms of bonding. (2003)

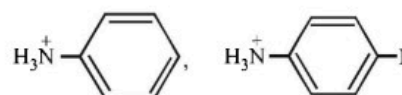
- (1991) 11. Match the  $K_a$  values

|  |  | (2003)                |
|--|--|-----------------------|
|  |  | $K_a$                 |
| (a) Benzoic acid   |  | $6.4 \times 10^{-5}$  |
| (b)  |  | $30.6 \times 10^{-5}$ |
| (c)  |  | $10.2 \times 10^{-5}$ |
| (d)  |  | $3.3 \times 10^{-5}$  |
| (e)  |  | $4.2 \times 10^{-5}$  |

12.  (2003)

Write resonance structure of the given compound.

13. Which of the following is more acidic and why? (2004)



14. (i)  $\mu_{\text{obs}} = \sum_i \mu_i x_i$ , where  $\mu_i$  is the dipole moment of a stable conformer of the molecule,  $\text{Z}-\text{CH}_2-\text{CH}_2-\text{Z}$  and  $x_i$  is the mole fraction of the stable conformer.  
 Given :  $\mu_{\text{obs}} = 1.0 \text{ D}$  and  $x_{(\text{Anti})} = 0.82$   
 Draw all the stable conformers of  $\text{Z}-\text{CH}_2-\text{CH}_2-\text{Z}$  and calculate the value of  $\mu_{(\text{Gauche})}$ .
- (ii) Draw the stable conformer of  $\text{Y}-\text{CHD}-\text{CHD}-\text{Y}$  (meso form), when  $\text{Y} = \text{CH}_3$  (rotation about  $\text{C}_2-\text{C}_3$ ) and  $\text{Y} = \text{OH}$  (rotation about  $\text{C}_1-\text{C}_2$ ) in Newmann projection. (2005)

## F Match the Following

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labelled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column-I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example :

If the correct matches are A-p, s and t; B-q and r; C-p and q; and D-s then the correct darkening of bubbles will look like the given.

|   | p                                   | q                                   | r                                   | s                                   | t                                   |
|---|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| A | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> |
| B | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | <input type="checkbox"/>            |
| C | <input checked="" type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/>            | <input type="checkbox"/>            | <input type="checkbox"/>            |
| D | <input type="checkbox"/>            | <input type="checkbox"/>            | <input type="checkbox"/>            | <input checked="" type="checkbox"/> | <input type="checkbox"/>            |

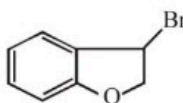
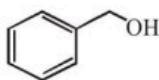
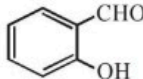
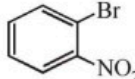
1. Given below are certain matching type questions, where two columns (each having 4 items) are given. Immediately after the columns the matching grid is given, where each item of Column I has to be matched with the items of Column II, by encircling the correct match(es). Note that an item of **Column I** can match with more than one item of **Column II**. All the items of **Column II** must be matched. Match the following : (2006 - 6M)

| Column I   | Column II                |
|--|--------------------------|
| (A) $C_6H_5CH_2CD_2Br$ on reaction with $C_2H_5O^-$ gives $C_6H_5-CH=CD_2$                           | (p) E1 reaction          |
| (B) $PhCHBrCH_3$ and $PhCHBrCD_3$ , both react with the same rate                                    | (q) E2 reaction          |
| (C) $C_6H_5CH_2CH_2Br$ on treatment with $C_2H_5O^-$ and $C_2H_5OD$ gives $C_6H_5CD=CH_2$            | (r) E1cB reaction        |
| (D) $C_6H_5CH_2CH_2Br$ reacts faster than $C_6H_5CD_2CH_2Br$ on reaction with $C_2H_5O^-$ in ethanol | (s) First order reaction |

2. Match the compounds/ions in **Column I** with their properties/reactions in **Column II**. Indicate your answer by darkening the appropriate bubbles of the  $4 \times 4$  matrix given in the ORS. (2007)

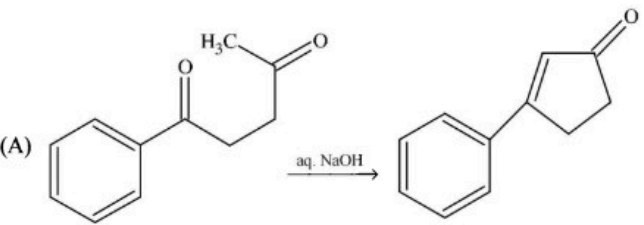
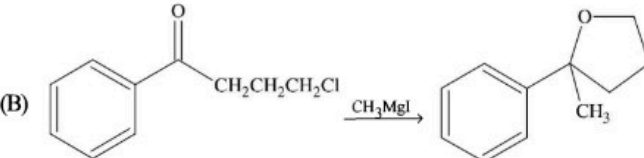
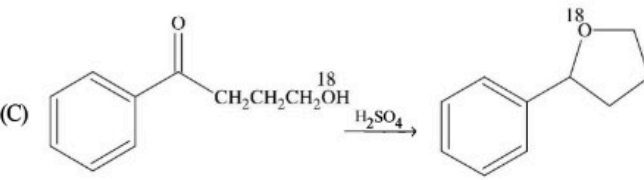
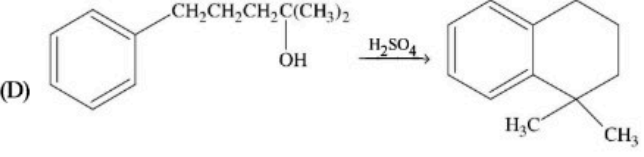
| Column I              | Column II  |
|-----------------------|--|
| (A) $C_6H_5CHO$       | (p) gives precipitate with 2, 4-dinitrophenylhydrazine |
| (B) $CH_3C \equiv CH$ | (q) gives precipitate with $AgNO_3$                    |
| (C) $CN^-$            | (r) is a nucleophile                                   |
| (D) $I^-$             | (s) is involved in cyanohydrin formation               |

3. Match each of the compounds given in **Column-I** with the reaction(s), that they can undergo, given in **Column-II**. (2009)

| Column-I  | Column-II                                |
|---|--|
| (A)  | (p) Nucleophilic substitution            |
| (B)  | (q) Elimination                          |
| (C)  | (r) Nucleophilic addition                |
| (D)  | (s) Esterification with acetic anhydride |
|   | (t) Dehydrogenation                      |



4. Match the reactions in **Column I** with appropriate types of steps/reactive intermediate involved in these reactions as given in **Column II**. (2011)

| Column I   | Column II                                  |
|--|--|
| <p>(A) </p>   | (p) Nucleophilic substitution              |
| <p>(B) </p>   | (q) Electrophilic substitution             |
| <p>(C) </p>  | (r) Dehydration                            |
| <p>(D) </p> | (s) Nucleophilic addition<br>(t) Carbanion |

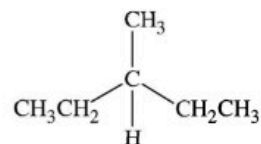
## II Assertion & Reason Type Questions

Read the following Statement-1 (Assertion) and Statement -2 (Reason) and answer as per the options given below :

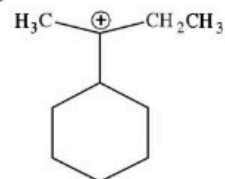
- (a) If both Statement -1 and Statement -2 are correct, and Statement -2 is the correct explanation of the Statement-2.  
 (b) If both Statement -1 and Statement -2 are correct, but Statement -2 is not the correct explanation of the Statement-1.  
 (c) If Statement -1 is correct but Statement -2 is incorrect.  
 (d) If Statement -1 is incorrect but Statement -2 is correct.
- Statement -1:** Aryl halides undergo nucleophilic substitution with ease.  
**Statement -2:** The carbon-halogen bond in aryl halides has partial double bond character. (1991)
  - Statement -1:** Phenol is more reactive than benzene towards electrophilic substitution reactions.  
**Statement -2:** In the case of phenol, the intermediate carbocation is more resonance stabilized. (2000S)
  - Statement -1:** Molecules that are not superimposable on their mirror images are chiral.  
**Statement -2:** All chiral molecules have chiral centres. (2007)

## I Integer Value Correct Type

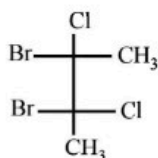
- The total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula  $C_5H_{10}$  is (2009)
- The total number of cyclic isomers possible for a hydrocarbon with the molecular formula  $C_4H_6$  is 5. (2010)
- The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound is (2011)



- The total number of contributing structures showing hyperconjugation (involving C-H bonds) for the following carbocation is (2011)



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



6. The total number of stereoisomers that can exist for M is (JEE Adv. 2015)



## Section-B JEE Main / AIEEE

1. Arrangement of  $(\text{CH}_3)_3\text{C}-$ ,  $(\text{CH}_3)_2\text{CH}-$ ,  $\text{CH}_3-\text{CH}_2-$  when attached to benzyl or an unsaturated group in increasing order of inductive effect is [2002]
- $(\text{CH}_3)_3\text{C}- < (\text{CH}_3)_2\text{CH}- < \text{CH}_3-\text{CH}_2-$
  - $\text{CH}_3-\text{CH}_2- < (\text{CH}_3)_2\text{CH}- < (\text{CH}_3)_3\text{C}-$
  - $(\text{CH}_3)_2\text{CH}- < (\text{CH}_3)_3\text{C}- < \text{CH}_3-\text{CH}_2-$
  - $(\text{CH}_3)_3\text{C}- < \text{CH}_3-\text{CH}_2- < (\text{CH}_3)_2\text{CH}-$
2. A similarity between optical and geometrical isomerism is that [2002]
- each forms equal number of isomers for a given compound
  - if in a compound one is present then so is the other
  - both are included in stereoisomerism
  - they have no similarity.
3. Which of the following does not show geometrical isomerism? [2002]
- 1,2-dichloro-1-pentene
  - 1,3-dichloro-2-pentene
  - 1,1-dichloro-1-pentene
  - 1,4-dichloro-2-pentene
4. The functional group, which is found in amino acid is [2002]
- $-\text{COOH}$  group
  - $-\text{NH}_2$  group
  - $-\text{CH}_3$  group
  - both (a) and (b).
5. Which of the following compounds has wrong IUPAC name? [2002]
- $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{COO}-\text{CH}_2\text{CH}_3 \rightarrow$  ethyl butanoate
  - $\text{CH}_3-\underset{\text{CH}}{\text{CH}}-\text{CH}_2-\text{CHO} \rightarrow$  3-methyl-butanal
  - $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}_3 \rightarrow$  2-methyl-3-butanol
6. The IUPAC name of  $\text{CH}_3\text{COCH}(\text{CH}_3)_2$  is [2003]
- 2-methyl-3-butanone
  - 4-methylisopropyl ketone
  - 3-methyl-2-butanone
  - Isopropylmethyl ketone
7. In which of the following species is the underlined carbon having  $sp^3$  hybridisation? [2002]
- $\text{CH}_3\text{C}\underline{\text{O}}\text{OH}$
  - $\text{CH}_3\text{C}\underline{\text{H}}_2\text{OH}$
  - $\text{CH}_3\text{C}\underline{\text{O}}\text{CH}_3$
  - $\text{CH}_2=\underline{\text{C}}\text{H}-\text{CH}_3$
8. Racemic mixture is formed by mixing two [2002]
- isomeric compounds
  - chiral compounds
  - meso compounds
  - enantiomers with chiral carbon.
9. Following types of compounds (as I, II) [2002]
- $$\begin{array}{cc} \text{CH}_3\text{CH}=\text{CHCH}_3 & \text{CH}_3\text{CHOH} \\ \text{I} & | \\ & \text{CH}_2\text{CH}_3 \\ & \text{II} \end{array}$$
- are studied in terms of isomerism in:
- chain isomerism
  - position isomerism
  - conformers
  - stereoisomerism
10. The reaction: [2002]
- $$(\text{CH}_3)_3\text{C}-\text{Br} \xrightarrow{\text{H}_2\text{O}} (\text{CH}_3)_3\text{C}-\text{OH}$$
- elimination reaction
  - substitution reaction
  - free radical reaction
  - displacement reaction.

## 9

# Organic Chemistry — Some Basic Principles & Techniques

## Section-A : JEE Advanced/ IIT-JEE

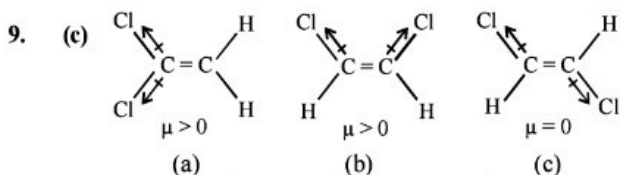
- A** 1. tert-butyl carbonium ion 2. propadiene 3. cyclopropane 4.  $sp^3$   
 5. vicinal, adjacent 6. non-superimposable, enantiomers 7.  $sp$   
 8. hyperconjugation 9. butane-1, 4-dioic acid
- B** 1. F 2. F 3. F 4. T
- C** 1. (c) 2. (a) 3. (d) 4. (c) 5. (d) 6. (a) 7. (c) 8. (d) 9. (c) 10. (c)  
 11. (b) 12. (b) 13. (a) 14. (d) 15. (d) 16. (c) 17. (b) 18. (b) 19. (c) 20. (b)  
 21. (a) 22. (b) 23. (c) 24. (c) 25. (d) 26. (d) 27. (b) 28. (b) 29. (d) 30. (c)  
 31. (a) 32. (c) 33. (d) 34. (b) 35. (d) 36. (d) 37. (d) 38. (c) 39. (b) 40. (c)  
 41. (b) 42. (a) 43. (a) 44. (c) 45. (c) 46. (a) 47. (b) 48. (b) 49. (a) 50. (a)  
 51. (b) 52. (d) 53. (b) 54. (d) 55. (c) 56. (b)
- D** 1. (a,b,c) 2. (a, c) 3. (b, d) 4. (a, d) 5. (c, d) 6. (a) 7. (a, c) 8. (d) 9. (a, c, d) 10. (b, c, d)  
 11. (b, c, d) 12. (a, d) 13. (a, d) 14. (b, d) 15. (b, c) 16. (b, c) 17. (a, b, c) 18. (a)
- E** 1. (i)  $C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$  (ii) isobutane < n-butane < n-butyl chloride < n-butanol  
 (iii) chlorobenzene < benzene < toluene < methoxybenzene (iv) IV < II < III < V < I  
 (v)  $CH_3F < CH_3Cl < CH_3Br < CH_3I$
2. (i) Pent-2-en-1-oic acid or 2-Pentenoic acid (ii) 5, 6-diethyl-3-methyl-4-decene  
 (iii) 3-(N, N dimethylamino)-3-methylpentane
5.  $CH_3-\underset{\text{Cl}}{\text{CH}}-\underset{\text{Cl}}{\text{CH}}=CH-CH_3$  9. enantiomers - I & III; diastereomers - I & II and II & III.
10. Anhydrous  $AlCl_3$  14. (i)  $\mu_{\text{gauche}} = 5.55 \text{ D}$
- F** 1. (A) - (q), (B) - (p, s), (C) - (r, s), (D) - (q) 2. (A) - (p, s); (B) - (q); (C) - (q, r, s); (D) - (q, r)  
 3. (A) - (p, q, t); (B) - (p, s, t); (C) - (r, s); (D) - (p) 4. (A) - (r, s, t); (B) - (p, s); (C) - (r, s); (D) - (q, r)
- H** 1. (d) 2. (a) 3. (c)
- I** 1. 7 2. 5 3. 8 4. 6 5. 3 6. 2

## Section-B : JEE Main/ AIEEE

1. (b) 2. (c) 3. (c) 4. (d) 5. (c) 6. (c) 7. (b) 8. (d) 9. (d) 10. (b)  
 11. (d) 12. (a) 13. (a) 14. (d) 15. (a) 16. (a) 17. (b) 18. (c) 19. (a) 20. (d)  
 21. (d) 22. (c) 23. (d) 24. (a) 25. (d) 26. (a) 27. (b) 28. (c) 29. (b) 30. (a)  
 31. (a) 32. (b) 33. (a) 34. (b) 35. (b) 36. (b) 37. (a) 38. (a) 39. (b) 40. (b)  
 41. (b) 42. (d) 43. (c) 44. (c) 45. (c) 46. (d) 47. (b) 48. (c) 49. (c) 50. (d) 51. (b)

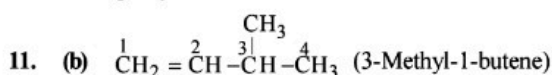






[Note : dipole moment is a vector quantity].

10. (c) Carbon bonded with a triple bond (i.e.  $C_1$ ) is  $sp$  hybridised. Carbon bonded with a double bond ( $C_2$ ) is  $sp^2$  hybridised.

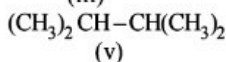
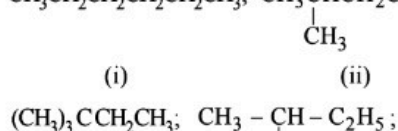
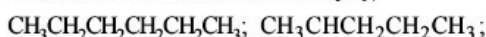


12. (b) **TIPS/Formulae :**

For knowing the possible isomers of the compound follow the following points.

- (i) First write down the possible number of isomeric parent alkane.  
 (ii) Introduce the given functional group at different positions so as to get different isomeric compound.

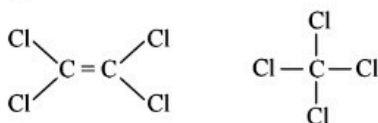
There are 5 isomers possible for  $C_6H_{14}$ .



13. (a) **TIPS/Formulae :**

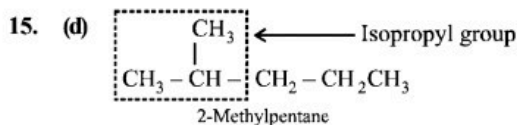
The bond angle in  $sp^3$ ,  $sp^2$  and  $sp$  hybridization is respectively  $109.28^\circ$ ,  $120^\circ$  and  $180^\circ$ .

Tetrachloroethene being an alkene has  $sp^2$  hybridised C-atoms and hence the Cl-C-Cl angle is  $120^\circ$ , whereas in tetrachloromethane, carbon is  $sp^3$  hybridised, so the angle is  $109.28^\circ$ .



14. (d) **NOTE :** Heterolytic fission occurs when the two atoms differ considerably in their electronegativities.

O-H bond undergoes cleavage most readily because O and H differ markedly in their electronegativity and further oxygen being highly electronegative can accommodate the negative charge more effectively developed after the cleavage.



16. (c)  $C_2H_6$  is a saturated hydrocarbon and its carbon is  $sp^3$  hybridised. Hence it is least electronegative among alkanes, alkenes and alkynes with the result C-H bond length will be maximum.

17. (b)  $CH_2 = CH - C \equiv CH$ ;

No of  $\sigma$  bonds =  $2 + 1 + 1 + 1 + 1 + 1 = 7$ ;

No of  $\pi$  bonds =  $1 + 2 = 3$

18. (b) **NOTE :** The order of stability of carbonium ion is  
 tertiary > secondary > primary > methyl

Tertiary carbonium ions (formed in *b*) are more stable because of electron repelling (+I effect) nature of  $CH_3$  group due to which the +ve charge gets dispersed and also due to hyperconjugation.

19. (c)  $HC \equiv C - \overset{sp}{C} - \overset{sp^2}{CH} = CH_2$

20. (b)  $C_2H_5SH + \frac{9}{2} O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l) + SO_2(g)$

At 298 K,  $CO_2$  and  $SO_2$  exist as gases while  $H_2O$  exists as liquid.

21. (a) Stereoisomers which are mirror image of each other are *enantiomers* and the one which are not mirror images are *diastereomers*. **Conformation** of the molecule is the spatial arrangement of the atoms of a given molecular structure that are obtained merely by rotation about a sigma bond in the molecule.

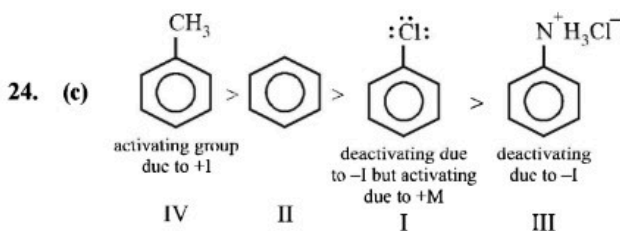
22. (b) **NOTE :**

A compound which consists of at least one asymmetric carbon atom is capable of showing the phenomenon of optical isomerism.

The structure cannot show geometrical isomerism as one of the carbons along the double bond has identical group (methyl). Tautomerism is not possible because of the absence of -CO, group. It shows optical isomerism because it has chiral C atom with four different groups, H,  $CH_3$ , COOH and  $(CH_3)_2C = CH$ .

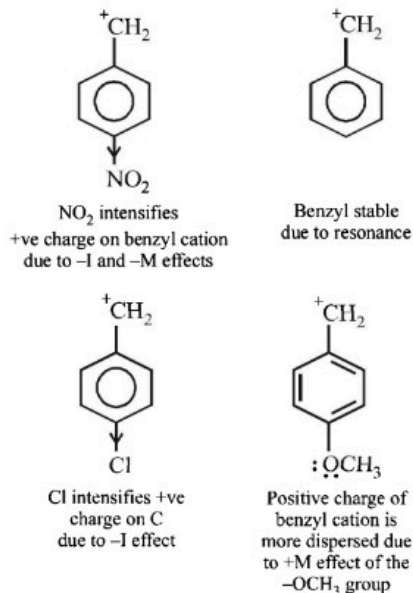
23. (c)  $CH_2 = CH - CH_2 - N \equiv C :$

The above structure of allyl isocyanide clearly shows 5 C-H ( $\sigma$ ), 2 C-C ( $\sigma$ ), 1 C-N ( $\sigma$ ), 1 N-C ( $\sigma$ ), 1 C-C ( $\pi$ ), 2 N-C ( $\pi$ ) bonds, i.e., 9  $\sigma$  and 3  $\pi$  bonds in all. There are 2 non-bonded electrons on the C-atom (co-ordinate bond between N and C, the electron pair of N is shifted towards C).



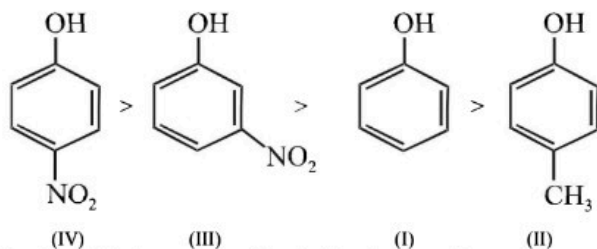
## 25. (d) TIPS/Formulae :

The stability of carbonium ion is influenced by both resonance and inductive effect.

26. (d) NOTE :  $-\text{NO}_2$  is an electron-attracting group where as  $-\text{CH}_3$  is an electron-releasing group.

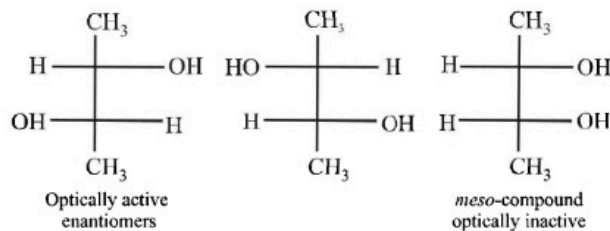
An **electron - attracting substituent** tends to disperse the negative charge of the phenoxide ion and thus, makes it more stable. This, in turn, **increases the acid strength of phenol**. The substituent in para position is more effective than in the meta position as the former involves a resonating structure bearing negative charge on the carbon attached to the electron - withdrawing substituent.

An **electron - releasing substituent** tends to intensify the negative charge of the phenoxide ion and thus makes it more unstable. This, in turn, **decreases the acid strength of phenol**. Hence, the order of acid strength is

27. (b) Dipole moment of *p*-dichlorobenzene is zero because of symmetrical structure. *o*- and *m*-dichlorobenzene have higher dipole moments than toluene due to high electronegativity of chlorine than  $-\text{CH}_3$  group. Further, the *o*-dichlorobenzene has higher dipole moment due to lower bond angle than the *m*-isomer. Hence, the order of increasing dipole moment is :

*p*-dichlorobenzene (IV) < toluene (I)  
< *m*-dichlorobenzene (II) < *o*-dichlorobenzene (III)

## 28. (b) The stereoisomers of butane -2,3-diol are

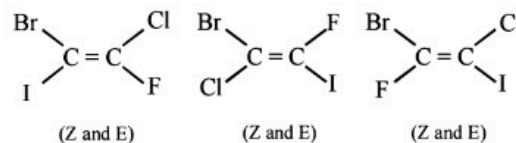
29. (d)  $\overset{1}{\text{CH}_2} = \overset{2}{\text{CH}} - \overset{3}{\text{CH}_2} - \overset{4}{\text{CH}_2} - \overset{5}{\text{C}} \equiv \overset{6}{\text{C}}$ 

## 30. (c) TIPS/Formulae :

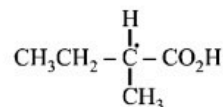
Glyceraldehyde is taken as arbitrary standard for D, L - nomenclature.

31. (a)  $\text{PhCH}_2\text{CH}=\text{CHCH}_3$  will exhibit geometrical isomerism because in others one of the doubly bonded carbon atom has two similar groups.32. (c)  $^-\text{CH}_3$  is the best nucleophile because carbon is least electronegative among the given options. The order is  $\text{H}_3\text{C}^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$ 33. (d) Rate of reaction will be  $\text{R} - \text{I} > \text{R} - \text{Br} > \text{R} - \text{Cl} > \text{R} - \text{F}$ . because  $\text{I}^-$  is the best, while  $\text{F}^-$  is the poorest leaving groups among halide ions.34. (b) In  $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_2 - \text{CH}_3$ ,  $-\text{CH}_2-$  group is flanked on both sides by electron- withdrawing groups and hence its hydrogens are most acidic. Once a carbanion is formed, it is stabilised due to resonance.

## 35. (d) Number of isomers (six) can be derived by keeping the position of any one halogen (say Br) fixed and changing the position of the other halogen one by one.

36. (d)  $\text{S}_{\text{N}}2$  reactions proceed with inversion of configuration. Since the attacking nucleophile is not necessarily the same as that of leaving group, the product cannot be enantiomer of the substrate and thus necessarily will not have opposite optical rotation. Moreover since only one product is obtained, we can not obtain diastereomers.

## 37. (d) 2-Methylbutanoic acid contains one asymmetric centre





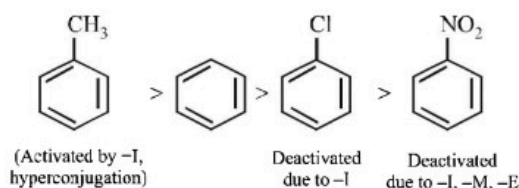
## 38. (c) TIPS/Formulae :

- (i) The inductive effect decreases with increase in distance of halogen atom from the carboxylic group and hence the strength of acid proportionally decreases.
- (ii) The acidity increases with the increase in electronegativity of the halogen present.

Smallest dissociation constant means weakest acid, which is  $\text{BrCH}_2\text{CH}_2\text{COOH}$  because here Br (less electronegative than F) is two carbon atoms away from  $-\text{COOH}$ .

## 39. (b) In carboxylic acids, molecules are more strongly associated followed by alcohols.

## 40. (c)

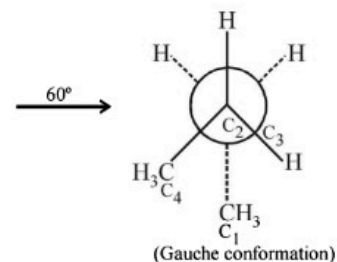
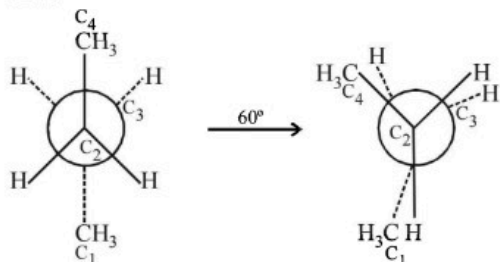
41. (b)  $\text{CH}_3\text{C}\equiv\text{CCH}_3$  is linear and symmetrical ; thus it has lowest dipole moment.42. (a)  $\text{H}_2\text{C}=\overset{sp^2}{\text{C}}-\overset{sp^2}{\text{C}}\equiv\overset{sp}{\text{N}}$ 

## 43. (a) NOTE : Dipole moment is a vector quantity.

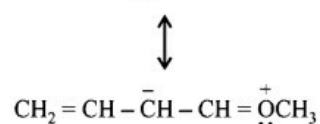
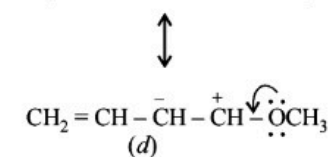
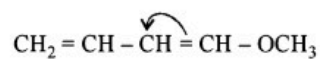
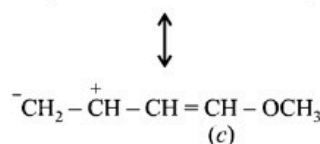
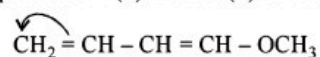
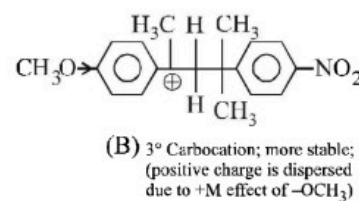
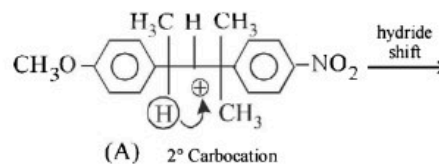
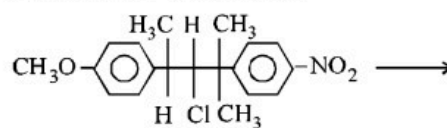
Methane molecule being symmetrical, has zero dipole moment. Replacement of one of the H-atoms by Cl atom increases the dipole moment. The increase in dipole moment is rather more than what can be expected because of the fact that the bond dipole moment of C-H bond and that of C-Cl bond reinforce one another. Replacement of another H atom by Cl increases the bond angle due to lone pair - lone pair repulsion between two Cl-atoms thereby reducing the dipole moment of the molecule. Increase in angle is again caused by the the introduction of the third Cl-atom. When the fourth Cl-atom is introduced, the molecule ( $\text{CCl}_4$ ) again becomes symmetrical and dipole moment reduces to zero. So,  $\text{CH}_3\text{Cl}$  will have the maximum dipole moment.

## 44. (c) TIPS/Formulae :

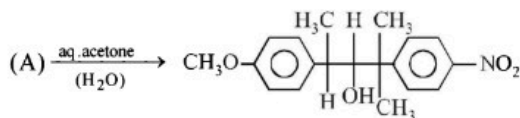
Any conformation between two extreme positions i.e. eclipsed and staggered is known as Gauche or Skew form.



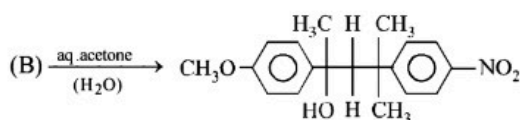
## 45. (c) Structures (a) and (b) are quite stable because here every atom has complete octet; in structures (c) and (d), every atom does not have complete octet; hence these are less stable than (a) and (b). However, structure (d) is stabilised by resonance, which is not possible in (c). Hence (c) is least stable.

46. (a) NOTE : This is an example of  $\text{S}_{\text{N}}1$  reaction involving carbocation as intermediate.

This carbocation is especially stabilised through resonance in which  $-\ddot{O}-CH_3$  group acts as a good electron donor.

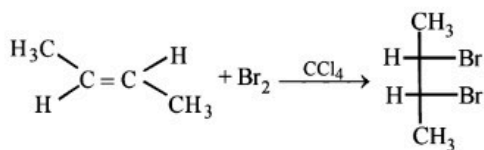


(i)

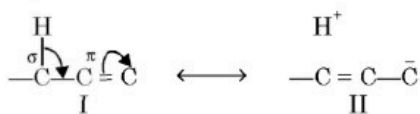


(ii)

47. (b) Carboxylic acids are named as *oyl chlorides*.
48. (b) The ring to which  $-NH$  group is attached is activated due to the lone pairs on N (+M and +E effects); while the ring to which  $-C=O$  is attached is deactivated. Hence, the electrophile would go to the *para*-position of the activated ring.
49. (a) Due to similar charges on adjacent atoms, the structure (a) is least stable.
50. (a) Anti addition of  $Br_2$  on *trans* alkene provides meso compound.

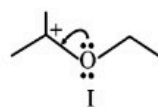


51. (b) Alkyl groups with at least one hydrogen atom on the  $\alpha$ -carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.

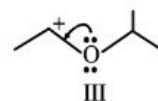


Note that the delocalisation involves  $\sigma$  and  $\pi$  bond orbitals (or  $p$  orbitals in case of free radicals); thus it is also known as  $\sigma-\pi$  conjugation. This type of *electron release due to the presence of the system  $H-C-C=C$*  is known as **hyperconjugation**

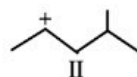
52. (d) The correct stability order is  
I > III > II > IV



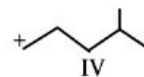
+ M effect, 6 hyperconjugative H's, 2  $CH_3$  groups (+ I effect)



+ M, 3 hyperconjugative H's, one  $CH_3$  group



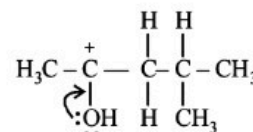
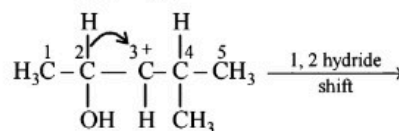
5 hyperconjugative CO-H's 2 R groups



5 hyperconjugative H's one R groups

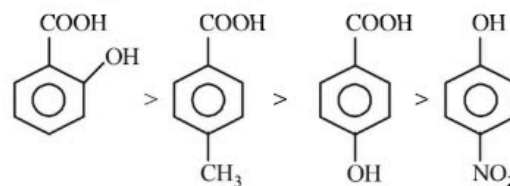
53. (b)  $-CN$  has highest priority. Further the sum of locants is 7 in (b) and 9 in (d).

54. (d) **NOTE**: Migrating tendency of hydride is greater than that of alkyl group. Further migration of hydride from C-2 gives more stable carbocation (stabilized by +R effect of OH group and +I and hyperconjugative effects of methyl group).

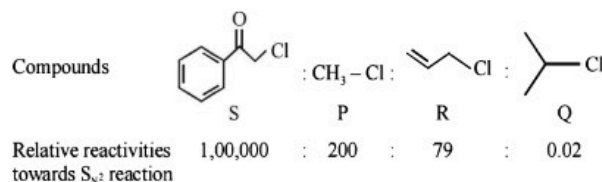


More stable carbocation

55. (c) *o*-Hydroxybenzoic acid is strongest acid and the decreasing order of acidity is

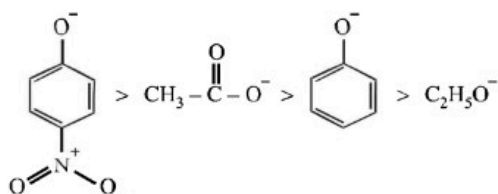


56. (b)



**D. MCQs with One or More Than One Correct**

- (a,b,c) Resonating structures differ in bonding pattern.
- (a, c) Higher the stability of the corresponding anion, more will be the acidic character of the parent compound.



Higher stability of acetate ions than phenoxide ion is due to equivalent resonating structures in the former.

- (b,d) 1,4-Dichlorobenzene (*p*-dichlorobenzene) and *trans*-1,2-dichloroethene have zero dipole moment because of their symmetrical structures.
- (a, d) In *n*-butane, Cl can add at either the first or second carbon giving two isomers.

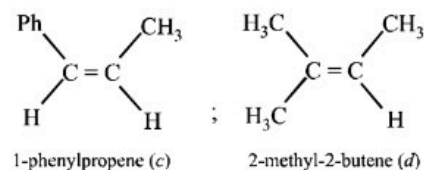
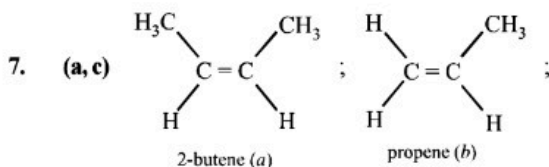
Option (b) :  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$  will

give three isomers with Cl group at either of the  $\text{CH}_3$  groups, second C-atom and 3rd C-atom. Benzene forms only one single derivative.

Option (d) :  $\text{CH}_3 - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$  will again give two

isomers with Cl at either one of the  $\text{CH}_3$  groups or on the central C-atom.

- (c, d) An asymmetric carbon atom is one which is attached with 4 different groups. Hence (c) & (d) are correct.
- (a) **TIPS/Formulae :**  
Conjugate base of strong acid is weak while conjugate base of a weak acid is stronger.  
Acidic strength of acids,  
 $\text{HOH} > \text{CH} \equiv \text{CH} > \text{NH}_3 > \text{CH}_3\text{CH}_3$   
Hence the order of strength of bases,  
 $\text{CH}_3\text{CH}_2^- > \text{NH}_2^- > \text{CH} \equiv \text{C}^- > \text{OH}^-$

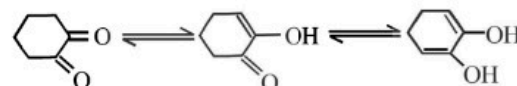
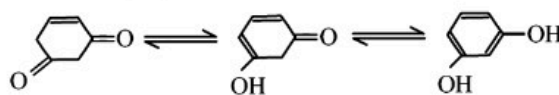
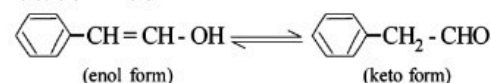


Only 2-butene and 1-phenylpropene can show geometrical isomerism (*cis*- and *trans*-isomers).

- (d) Order of acidic strength  
 $\text{CH}_3\text{OH} > \text{CH} \equiv \text{CH} > \text{C}_6\text{H}_6 > \text{C}_2\text{H}_6$ ;  $\text{CH}_3\text{OH}$  is most acidic because O is more electronegative than C and capable of accommodating negative charge in  $\text{CH}_3\text{O}^-$ . Although alcohols are neutral towards the litmus paper.

**9. (a,c,d) TIPS/Formulae :**

For a carbonyl compound to show tautomerism, it must have at least one H at the  $\alpha$ -carbon atom. (a), (c) and (d) show tautomerism.



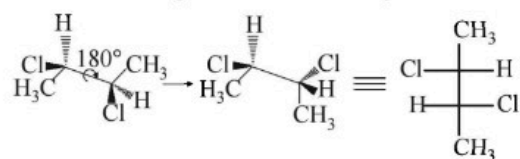
- (b,c,d) **NOTE :** An aromatic species will have :

|                          |   |
|--------------------------|---|
| $(4n + 2) \pi$ electrons | (by Huckel's Rule)                                |
| planar structure         | (due to resonance)                                |
| cyclic structure         | (due to presence of $sp^2$ -hybrid carbon atoms). |

- (b,c,d) E and F ; and also E and G differ in position of atom (H), so these are tautomers (not resonating structures). Geometrical isomers are also diastereomers.

- (a, d) The given molecule although possesses neither centre of symmetry nor a plane of symmetry (hence optically active) but it has an axis of symmetry ( $C_n$ ).

**NOTE :** A  $C_n$  axis of symmetry is an axis about which the molecule can be rotated by  $360^\circ/n$  to produce a molecule indistinguishable from the original molecule.



Molecule has non-superimposable mirror image

- (a,d)  $\text{CH}_3 - \overset{*}{\text{C}}\text{H}(\text{OH}) - \text{CH} = \text{CH} - \overset{*}{\text{C}}\text{H}(\text{OH}) - \text{CH}_3$

| Stereoisomer | Configuration |
|--------------|---------------|
|--------------|---------------|

|     |                  |
|-----|------------------|
| I   | <i>d cis d</i>   |
| II  | <i>l cis l</i>   |
| III | <i>d cis l</i>   |
| IV  | <i>d trans d</i> |
| V   | <i>l trans l</i> |
| VI  | <i>d trans l</i> |

Enantiomers I and II; IV and V  
*cis trans*

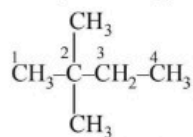
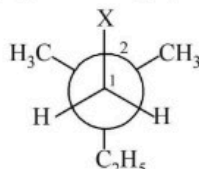
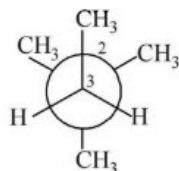
Diastereomers I (or II), III (or IV), V and VI  
III and IV

Meso



14. (b, d)

Structural formula of 2, 2-dimethylbutane is

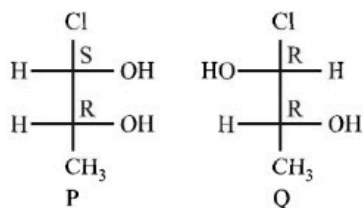
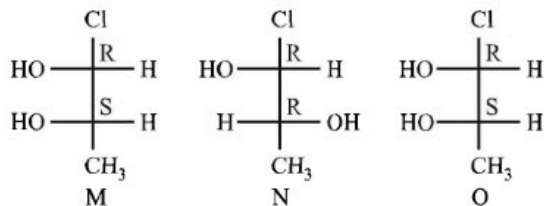
(I) Newman projection using  $C_1-C_2$  bond(II) Newman projection using  $C_3-C_2$  bond

16. (b, c)

b and c, being antiaromatic, are unstable at room temperature.

17. (a, b, c)

Converting all the structures in the Fischer projection



M and N are diastereoisomers

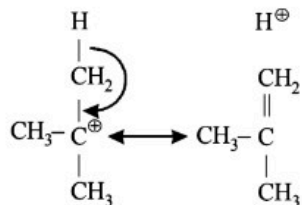
M and O are identical

M and P are enantiomers

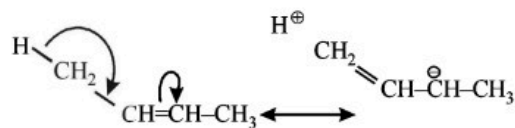
M and Q are diastereoisomers

Hence, the correct options are a, b, c.

18. (a)



In tert butyl cation, carbon bearing positive charge has one vacant  $p$ -orbital hence it is  $\sigma$ - $p$  (empty) conjugation or hyperconjugation.

In 2-butene, hyperconjugation is between  $\sigma \rightarrow \pi^*$  bond.

## E. Subjective Problems

1. (i) TIPS/Formulae :

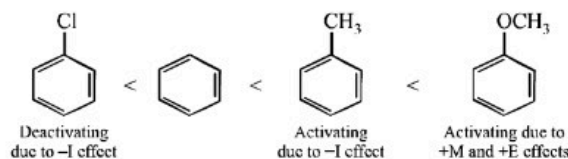
It is a case of nucleophilic addition reaction. More the electron deficiency of the carbonyl carbon, greater will be its reactivity towards nucleophilic addition.



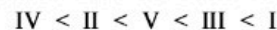
(ii) Isobutane <  $n$ -Butane <  $n$ -Butyl chloride <  $n$ -Butanol  
 van der Waals' forces      dipole-dipole attraction      H-bonding

Straight chain alkane isomer has higher boiling point than the isomeric branched chain isomer because the former isomer has larger surface area which leads to large van der Waals attractive forces.

(iii) NOTE :  $-OCH_3$  and  $-CH_3$  groups are activating group while  $-Cl$  is a deactivating group for electrophilic substitution.



(iv) Presence of electron withdrawing group increases the acidic character of the  $-COOH$  due to  $-I$  effect, while presence of electron-donating group (alkyl groups) decreases the acidic character due to  $+I$  effect. Thus

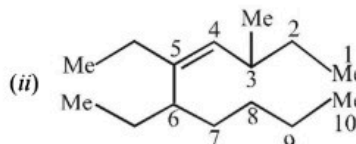


(v) NOTE : A weaker base is a better leaving group.

Rate of reaction will be  $R-I > R-Br > R-Cl > R-F$ . because  $I^-$  is the best, while  $F^-$  is the poorest leaving groups among halide ions.

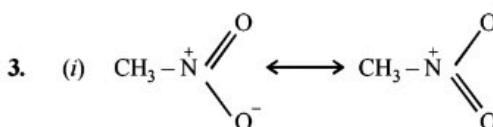
2. (i)  $CH_3CH_2CH=CHCOOH$ 

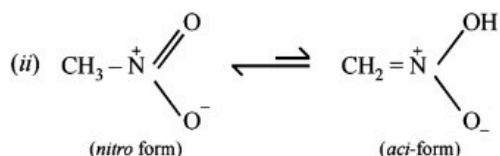
Pent-2-en-1-oic acid Or 2-Pentenoic acid



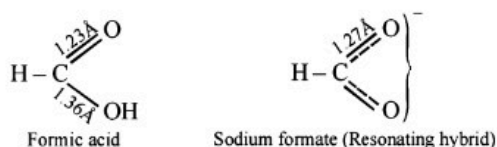
5, 6-diethyl-3-methyl-4-decene

(iii) IUPAC name is

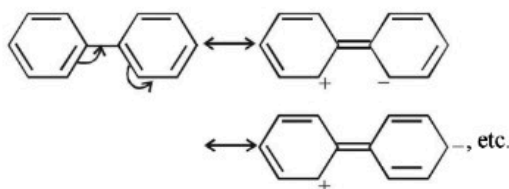
3-( $N,N$ -dimethylamino)-3-methylpentane.



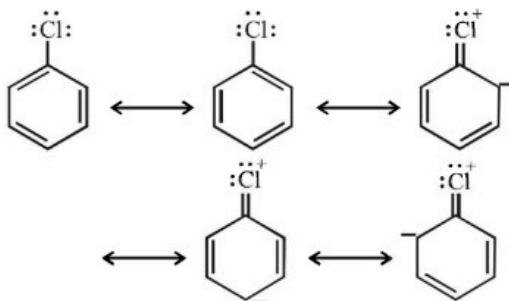
4. (i) In formic acid, resonance is not possible with the result there are two types of C–O bonds. In sodium formate, resonance is possible, so both of the C–O bonds have same bond length.



- (ii) In biphenyl, one of the phenyl groups acts as electron donor and the other electron acceptor due to mesomeric effect. This makes it more reactive than benzene.



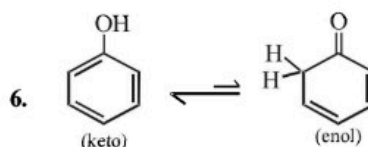
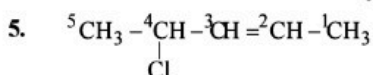
- (iii) The low reactivity of halogen atom in aryl and vinyl halides towards nucleophiles is due to resonance.



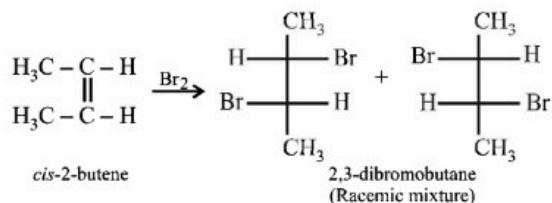
Resonating structures of chlorobenzene

**NOTE :** Due to resonance, carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be easily replaced by nucleophiles.

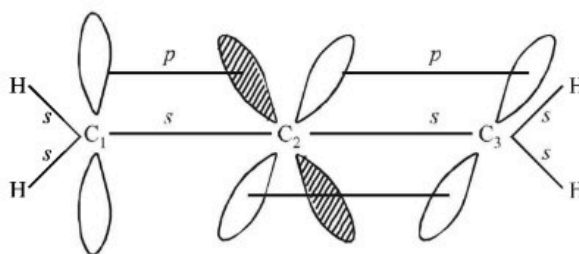
- (iv)  $\text{CH} \equiv \text{C}^-$ ,  $\text{C}^-$  is  $sp$  hybridised and more electronegative than the  $\bar{\text{C}}\text{H}$  of  $\text{CH}_2 = \bar{\text{C}}\text{H}$  which is  $sp^2$  hybridised. Thus the former can better accommodate electron pair hence less basic.
- (v) Benzene gives electrophilic substitution reaction rather than electrophilic addition reactions because it will have a stable benzene ring in the product, whereas electrophilic addition on benzene destroys the benzenoid ring.



7. *cis*-Alkenes add bromine to form racemic mixture.



8.  $\text{CH}_2 = \text{C} = \text{CH}_2$  (Allene)  
 $sp^2 \quad sp \quad sp^2$

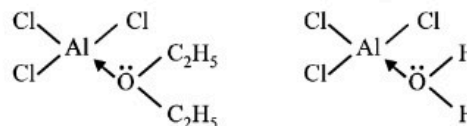


9. In order to convert a molecule with two stereogenic centres to its enantiomer, the configuration at both centres must be reversed. Reversing the configuration at only one stereogenic centre converts it to a diastereomeric structure. Thus structures I and III are enantiomers; while structures I and II as well as II and III are diastereomers.

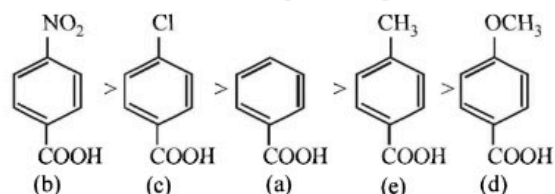
#### 10. TIPS/Formulae :

Diethyl ether acts as a lewis base and anhydrous  $\text{AlCl}_3$  as a lewis acid.

Anhydrous  $\text{AlCl}_3$  is more soluble in diethyl ether because the oxygen atom of ether donates its pair of electrons to the vacant orbital of electron deficient aluminium of  $\text{AlCl}_3$  through the formation of coordinate bond. In case of hydrated  $\text{AlCl}_3$  aluminium is not electron deficient as oxygen atom of water molecule has already donated its pair of electrons to meet the electron deficiency of aluminium.

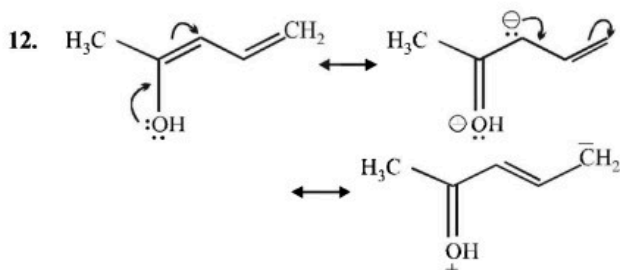


11. **NOTE :** Higher the  $K_a$  value, more stronger is the acid. Correct order of acidic strength of the given acids is

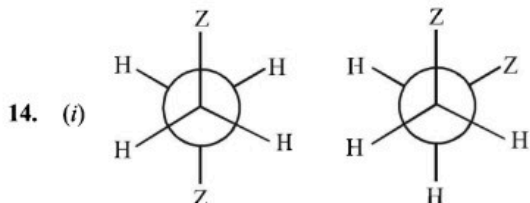
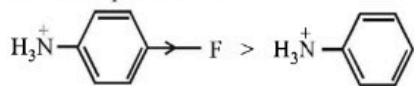


Hence the  $K_a$  values of the five acids will be in the order.

|             |                       |                       |                      |                      |                      |
|-------------|-----------------------|-----------------------|----------------------|----------------------|----------------------|
|             | (b)                   | (c)                   | (a)                  | (e)                  | (d)                  |
| $K_a$ value | $30.6 \times 10^{-5}$ | $10.2 \times 10^{-5}$ | $6.4 \times 10^{-5}$ | $4.2 \times 10^{-5}$ | $3.3 \times 10^{-5}$ |



13. Presence of an electron-attracting group increases acidity of the compound. Thus



Anti conformer                      Gauche conformer  
Given, mole fraction of anti conformer = 0.82  
 $\therefore$  mole fraction of gauche conformer = 0.18

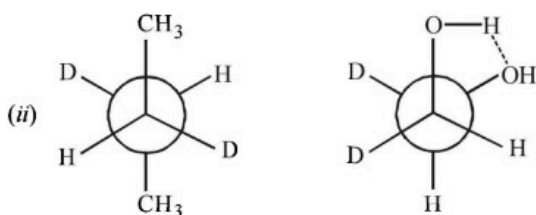
$$\mu_{\text{ob.}} = \mu_{\text{anti}} \times \chi_{\text{anti}} + \mu_{\text{gauche}} \times \chi_{\text{gauche}}$$

$$1 = \mu_{(\text{anti})} \times 0.82 + \mu_{(\text{gauche})} \times 0.18$$

$$1 = 0 \times 0.82 + \mu_{(\text{gauche})} \times 0.18 \quad [\because \mu_{(\text{anti})} = 0]$$

$$\therefore 1 = \mu_{(\text{gauche})} \times 0.18$$

$$\mu_{(\text{gauche})} = \frac{1}{0.18} = 5.55 \text{ D}$$



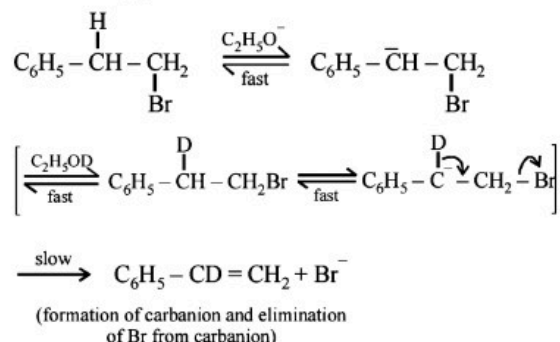
### F. Match the Following

1. (A) - q; (B) - p, s; (C) - r, s; (D) - q

E1 mechanisms are encountered only with tertiary or secondary substrates and in presence of either a weak base or a base in low concentration. So primary substrates will follow E2 mechanism, i.e. (A)  $\rightarrow$  E2 and (D)  $\rightarrow$  E2.

Further E1 mechanism (similar to  $S_N1$ ) proceeds by first order kinetics and is determined by the slower (first) step of the formation of carbocation. Hence (B)  $\rightarrow$  E1 and first order reaction.

**NOTE THIS STEP:** Reaction of  $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{Br}$  on treatment with  $\text{C}_2\text{H}_5\text{O}^-$  in presence of  $\text{C}_2\text{H}_5\text{OD}$  gives  $\text{C}_6\text{H}_5\text{CD}=\text{CH}_2$ . This reaction follows E1CB (Elimination unimolecular conjugate base) mechanism. This 2 step mechanism follows the following path:



Although this mechanism involves 2 steps the overall rate of the reaction is limited to the slower second step and hence the rate of reaction depends only on the concentration of the carbanion, i.e. first order reaction. Hence, (C)  $\rightarrow$  (r), (s).

2. (A) - p, q, s; (B) - q; (C) - q, r, s; (D) - q, r

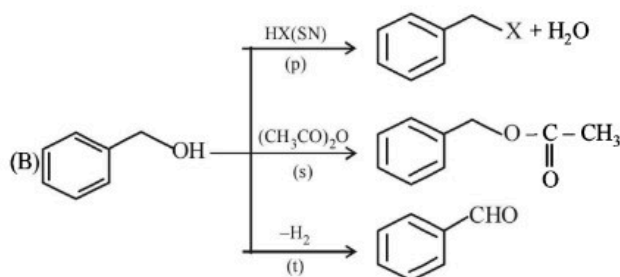
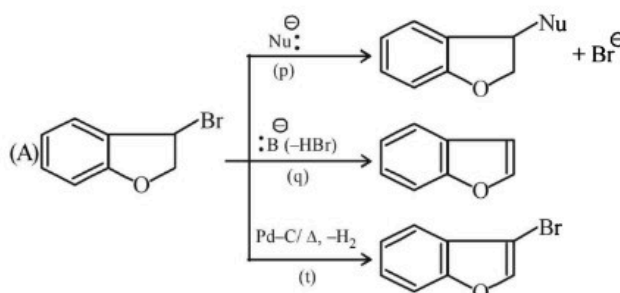
(A)  $\text{C}_6\text{H}_5\text{CHO}$  forms ppt. of 2, 4-dibromophenylhydrazine (p), forms silver mirror with ammonical silver nitrate - Tollen's reagent (q), forms cyanohydrin with  $\text{CN}^-$  (s).

(B)  $\text{CH}_3\text{C}\equiv\text{CH}$  gives ppt. with  $\text{AgNO}_3$  (q)

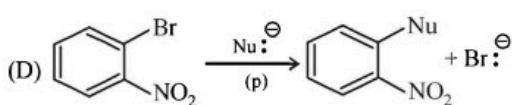
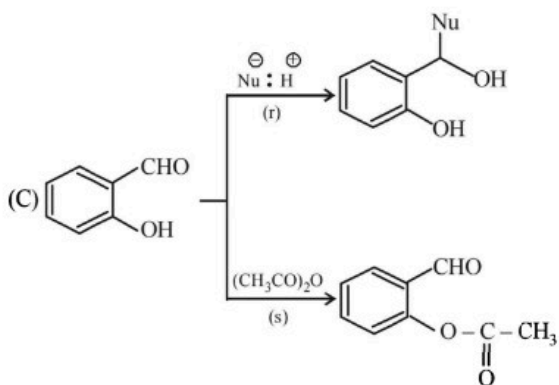
(C)  $\text{CN}^-$  reacts with  $\text{AgNO}_3$  to form ppt. of  $\text{AgCN}$  (q), it is a nucleophile (r) and forms cyanohydrin (s)

(D)  $\text{I}^-$  gives ppt. of  $\text{AgI}$  with  $\text{AgNO}_3$  (q), and it is a nucleophile (r)

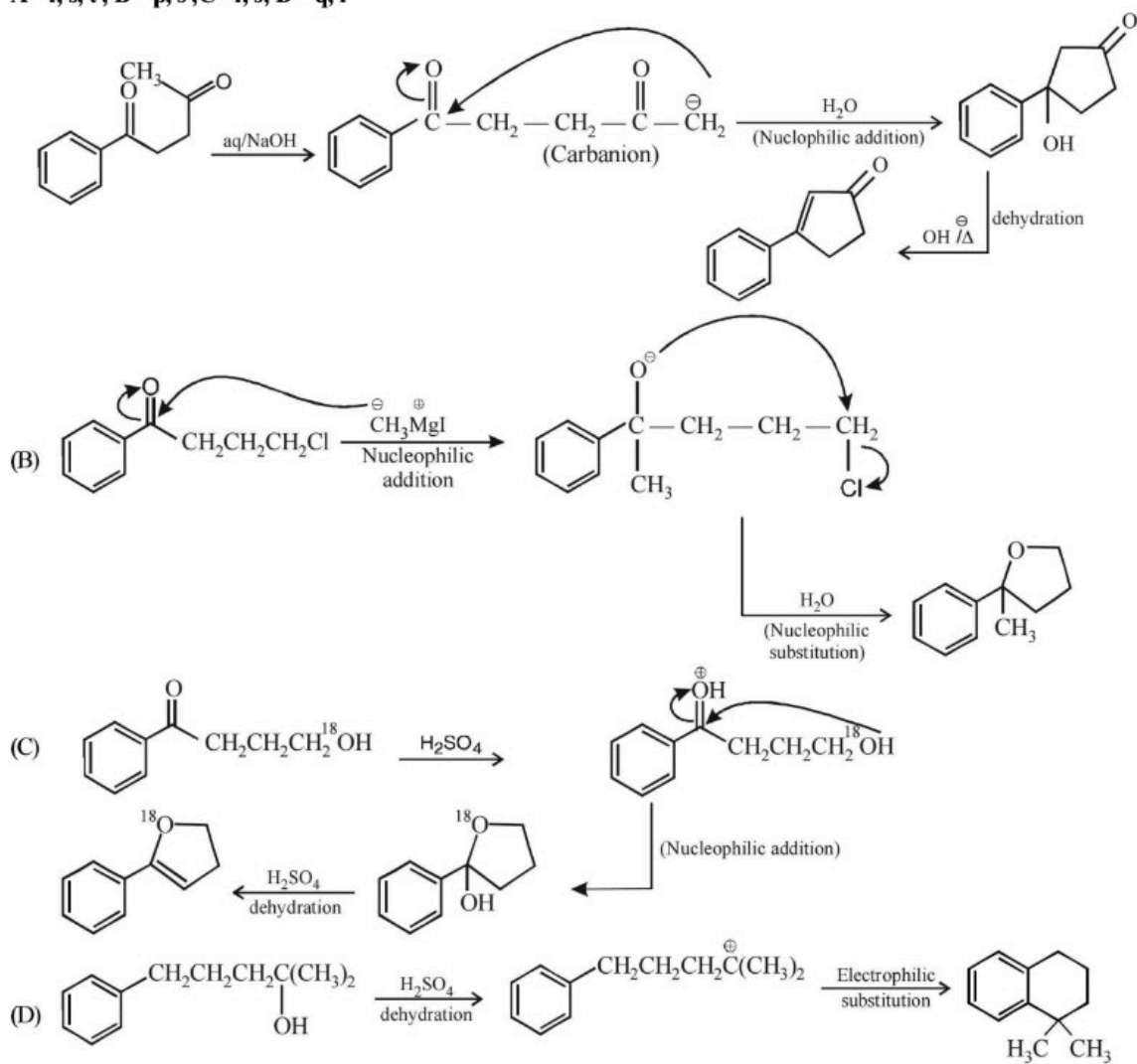
3. (A) - p, q, t; (B) - p, s, t; (C) - r, s; (D) - p







4. A - r, s, t; B - p, s; C - r, s; D - q, r

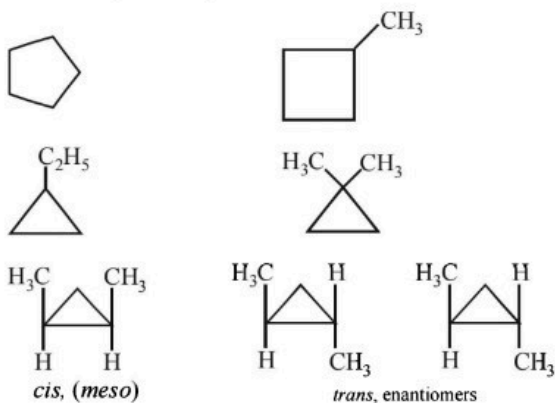


### H. Assertion & Reason Type Questions

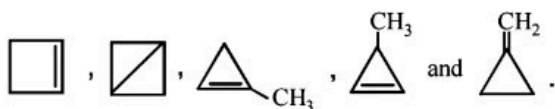
- (d) Statement -1 is false because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles.
- (a) Due to +M effect of  $-\ddot{O}H$ , its intermediate carbocation is more stable than the one in benzene.
- (c) Statement-1 is correct. Statement-2 is incorrect because compound can be chiral even in the absence of chiral atoms.

### I. Integer Value Correct Type

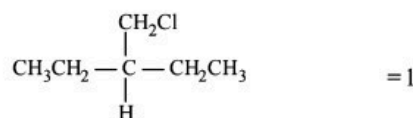
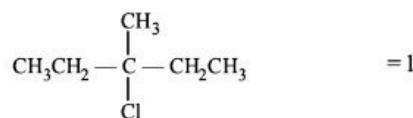
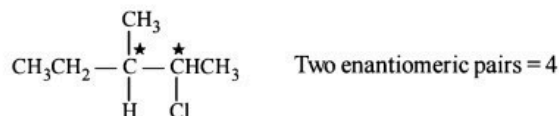
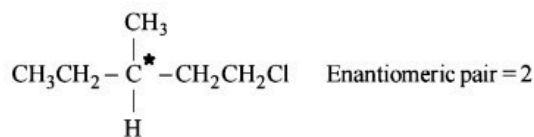
- The seven possible cyclic structural and stereoisomers are



- The number of cyclic isomers for a hydrocarbon with molecular formula  $\text{C}_4\text{H}_6$  is 5. The structures are

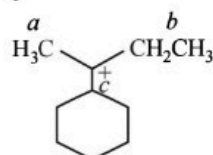


- 8



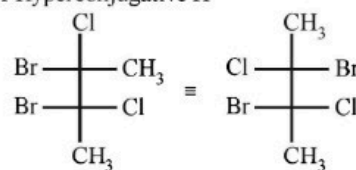
$$\text{Total} = 2 + 4 + 1 + 1 = 8$$

- 6

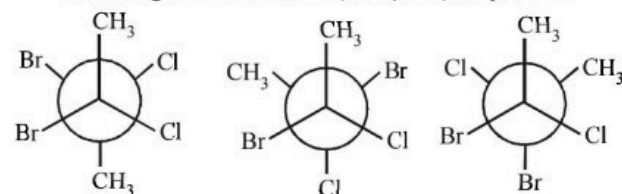


$a = 3$  Hyperconjugative H's  
 $b = 2$  Hyperconjugative H's  
 $c = 1$  Hyperconjugative H

- (3)



Following three conformers (with  $\mu \neq 0$ ) are possible



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

