CHAPTER 9

Organic Chemistry — Some Basic Principles and Techniques

Section-A JEE Advanced/ IIT-JEE

A Fill in the Blanks

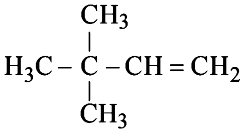
1. Among the given cations, ... is most stable. *(1981)* (*sec*-butyl carbonium ion; *tert*-butyl carbonium ion; *n*-butyl carbonium ion)
2. The compound having both *sp* and sp^2 hybridized carbon atoms is .... *(1981)* (propene, propane, propadiene)
3. .... ring is most strained. *(1981)* (Cyclopropane, 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 - ½ 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



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH=CH_2$$

   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 $N \equiv \underset{1}{C} - \underset{2}{CH} = CH_2$ involves the hybrids as *(1987)*

(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 *(1987)*

$CH_2=CH-CH(CH_3)_2$ 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 *(1987,2007)*

(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 *(1988)*

(a) 120° and 109.5° (b) 90° and 109.5°
(c) 109.5° and 90° (d) 109.5° and 120°

14. In CH_3CH_2OH, the bond that undergoes heterolytic cleavage most readily is *(1988)*

(a) C—C (b) C—O
(c) C—H (d) O—H

15. The compound which has one isopropyl group is : *(1989)*

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

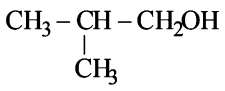
16. The C–H bond distance is the longest in : *(1989)*

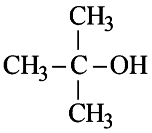
(a) C_2H_2 (b) C_2H_4
(c) C_2H_6 (d) $C_2H_2Br_2$

17. The number of sigma and pi-bonds in 1-butene-3-yne are : *(1989)*

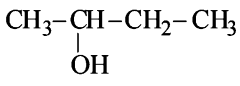
(a) 5 sigma and 5 pi (b) 7 sigma and 3 pi
(c) 8 sigma and 2 pi (d) 5 sigma and 4 pi

18. The compound which gives the most stable carbonium ion on dehydration is : *(1989)*

(a)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

(b)

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH$

(c) $CH_3-CH_2-CH_2-CH_2OH$

(d)

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_3$

19. The hybridization of carbon atoms in C–C single bond of $HC\equiv C-CH=CH_2$ is *(1991)*

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

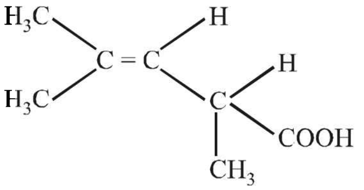
20. The products of combustion of an aliphatic thiol (RSH) at 298 K are *(1992)*

(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 *(1992)*

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

22. The structure



shows :

(a) geometrical isomersism *(1995S)*
(b) optical isomerism
(c) geometrical & optical isomerism
(d) tautomerism.

23. Allyl isocyanide has : *(1995S)*

(a) 9σ and 4π bonds
(b) 8σ and 5π bonds
(c) 9σ, 3π and 2 non-bonded electrons
(d) 8σ, 3π and 4 non-bonded electrons

24. Arrange in order of decreasing trend towards S_E reactions : *(1995S)*

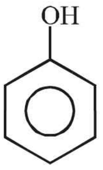
Chlorobenzene, benzene, anilinium chloride, toluene
I II III IV

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

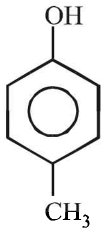
25. Most stable carbonium ion is : *(1995S)*

(a) p—NO_2—C_6H_4—CH_2^+
(b) $C_6H_5CH_2^+$
(c) p—Cl—C_6H_4—CH_2^+
(d) p—CH_3O—C_6H_4—CH_2^+

26. In the following compounds, *(1996)*



(I)



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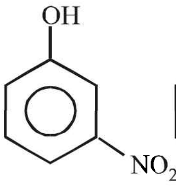

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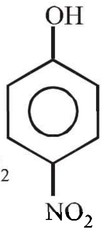


(IV)

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. *(1996)*

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? *(1997)*

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

29. In the compound $CH_2=CH–CH_2–CH_2–C\equiv CH$, the $C_2–C_3$ 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) F^- (b) OH^-
(c) CH_3^- (d) NH_2^-

33. The order of reactivities of the following alkyl halides for a S_N2 reaction is *(2000S)*
(a) RF > RCl > RBr > RI (b) RF > RBr > RCl > RI
(c) RCl > RBr > RF > RI (d) RI > RBr > RCl > 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 $C_2BrClFI$ is *(2001S)*
(a) 3 (b) 4
(c) 5 (d) 6

36. An S_N2 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

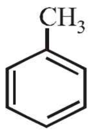
37. Which of the following compounds exhibits stereoisomerism? *(2002S)*
(a) 2-methylbutene-1 (b) 3-methylbutyne-1
(c) 3-methylbutanoic acid (d) 2-methylbutanoic acid

38. Which of the following acids has the smallest dissociation constant ? *(2002S)*
(a) $CH_3CHFCOOH$ (b) FCH_2CH_2COOH
(c) $BrCH_2CH_2COOH$ (d) $CH_3CHBrCOOH$

39. Identify the correct order of boiling points of the following compounds; *(2002S)*
$\underset{1}{CH_3CH_2CH_2CH_2OH}$, $\underset{2}{CH_3CH_2CH_2CHO}$, $\underset{3}{CH_3CH_2CH_2COOH}$
(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)*


1



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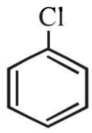

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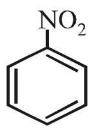
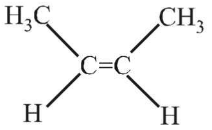
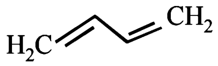


4

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

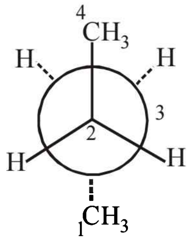
41. Which of the following hydrocarbons has the lowest dipole moment ? *(2002S)*
(a) 

(b) $CH_3C\equiv CCH_3$
(c) $CH_3CH_2C\equiv CH$ (d) $CH_2=CH-C\equiv CH$

42. Which of the following represents the given mode of hybridisation $sp^2-sp^2-sp-sp$ from left to right? *(2003S)*
(a) $H_2C=CH-C\equiv N$ (b) $HC\equiv C-C\equiv CH$
(c) $H_2C=C=C=CH_2$ (d) 

43. Among the following, the molecule with the highest dipole moment is: *(2003S)*
(a) CH_3Cl (b) CH_2Cl_2
(c) $CHCl_3$ (d) CCl_4

44. In the given conformation, if C_2 is rotated about C_2-C_3 bond anticlockwise by an angle of 120° then the conformation obtained is *(2004S)*



(a) fully eclipsed conformation
(b) partially eclipsed conformation
(c) gauche conformation
(d) staggered conformation

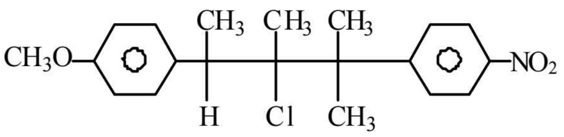
45. Which of the following resonating structures of 1–methoxy–1,3–butadiene is least stable? *(2005S)*

(a) $\overset{\ominus}{C}H_2-CH=CH-CH=\overset{\oplus}{O}-CH_3$

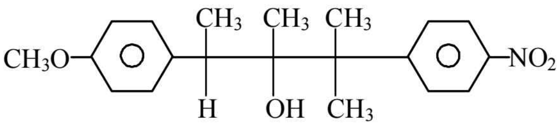
(b) $CH_2=CH-\overset{\ominus}{C}H-CH=\overset{\oplus}{O}-CH_3$

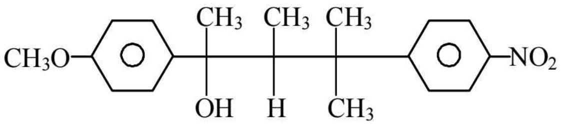
(c) $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-CH=CH-O-CH_3$

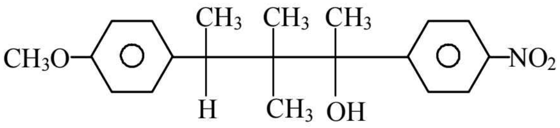
(d) $CH_2=CH-\overset{\ominus}{C}H-\overset{\oplus}{C}H-O-CH_3$

46. 

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

(i) 

(ii) 

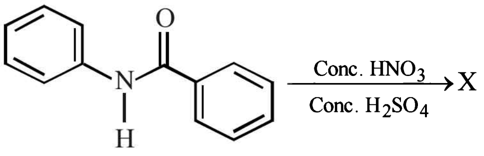
(iii) 

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

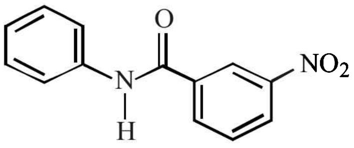
47. The IUPAC name of C_6H_5COCl is *(2006 - 3M, –1)*

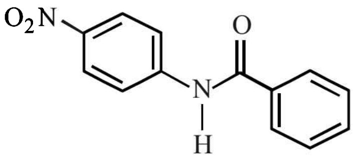
(a) Benzene chloro ketone
(b) Benzoyl chloride
(c) Chloro phenyl ketone
(d) Benzene carbonyl chloride

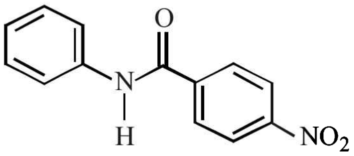
48. In the following reaction,

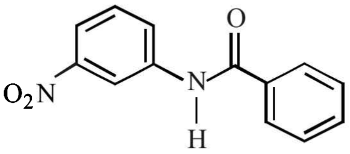


the structure of the major product 'X' is *(2007)*

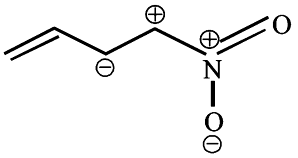
(a) 

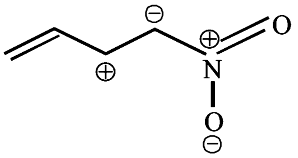
(b) 

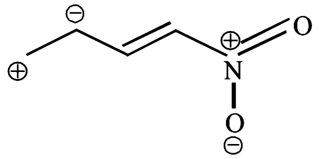
(c) 

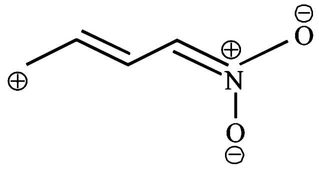
(d) 

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

(a) 

(b) 

(c) 

(d) 

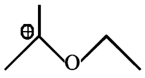
50. The number of stereoisomers obtained by bromination of *trans*-2-*butene* is *(2007)*

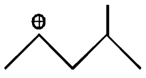
(a) 1 (b) 2
(c) 3 (d) 4

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

(a) σ-σ (b) σ - π
(c) p- p (d) π-π

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


(I)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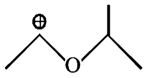
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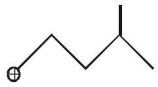
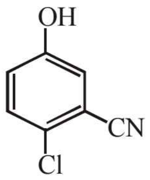

(IV)

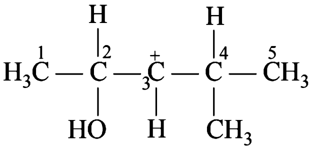
(a) (II) > (IV) > (I) > (III) (b) (I) > (II) > (III) > (IV)
(c) (II) > (I) > (IV) > (III) (d) (I) > (III) > (II) > (IV)

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_3 that is most likely to migrate to the positively charged carbon is *(2009)*

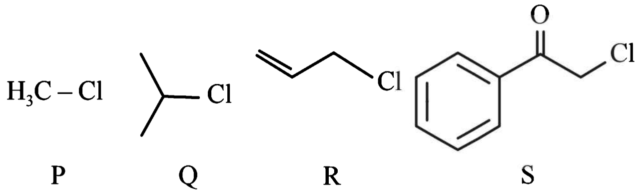


$$H_3\overset{1}{C}-\underset{HO}{\overset{H}{\overset{|2}{\underset{|}{C}}}}-\underset{H}{\underset{|}{\overset{+}{{}_3C}}}-\underset{CH_3}{\overset{H}{\overset{|4}{\underset{|}{C}}}}-\overset{5}{C}H_3$$

(a) CH_3 at C-4 (b) H at C-4
(c) CH_3 at C-2 (d) H at 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_N2 reaction with each of P, Q, R and S. The rates of the reaction vary as *(JEE Adv. 2013)*



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

D MCQs with One or More Than One Correct

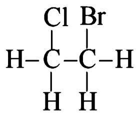
1. Resonance structures of a molecule should have : *(1984)*
(a) identical arrangement of atoms
(b) nearly the same energy content
(c) the same number of paired electrons
(d) identical bonding

2. Phenol is less acidic than : *(1986)*
(a) acetic acid (b) *p*-methoxyphenol
(c) *p*-nitrophenol (d) ethanol

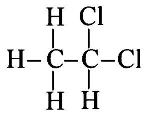
3. Dipole moment is shown by : *(1986)*
(a) 1, 4-dichlorobenzene
(b) *cis*- 1, 2-dichloroethane
(c) *trans* -1, 2-dichloroethene
(d) *trans*- 1, 2-dichloro-2-pentene

4. Only two isomeric monochloro derivatives are possible for: *(1986)*
(a) *n*-butane (b) 2, 4-dimethylpentane
(c) benzene (d) 2-methylpropane

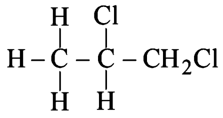
5. Which of the following have asymmetric carbon atom? *(1989)*

(a)


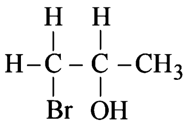
$$H-\underset{H}{\overset{Cl}{C}}-\underset{H}{\overset{Br}{C}}-H$$

(b)


$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-Cl$$

(c)


$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-CH_2Cl$$

(d)


$$H-\underset{Br}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-CH_3$$

6. What is the decreasing order of strength of the bases $OH^-, NH_2^-, HC\equiv C^-$ and $CH_3CH_2^-$? *(1993)*

(a) $CH_3-CH_2^- > NH_2^- > H-C\equiv C^- > OH^-$

(b) $H-C\equiv C^- > CH_3-CH_2^- > NH_2^- > OH^-$

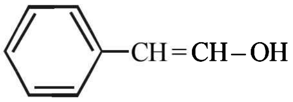
(c) $OH^- > NH_2^- > H-C\equiv C^- > CH_3-CH_2^-$

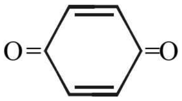
(d) $NH_2^- > H-C\equiv C^- > OH^- > CH_3-CH_2^-$

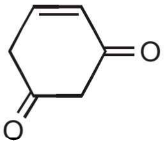
7. Which of the following compounds will show geometrical isomerism? *(1998)*
(a) 2–butene (b) propene
(c) 1–phenylpropene (d) 2–methyl–2–butene

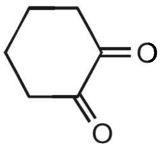
8. Among the following compounds, the strongest acid is *(1998)*
(a) $HC\equiv CH$ (b) C_6H_6
(c) C_2H_6 (d) CH_3OH

9. Tautomerism is exhibited by *(1998)*

(a)


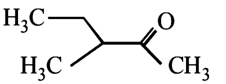
(b)


(c)


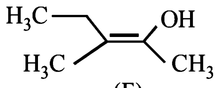
(d)


10. An aromatic molecule will *(1999)*
(a) have 4n π electrons (b) have (4n + 2) π electrons
(c) be planar (d) be cyclic

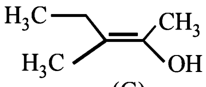
11. The correct statements(s) concerning the structures E,F and G is (are) – *(2008)*



(E)



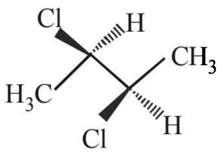
(F)



(G)

(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

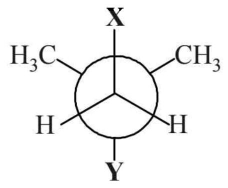
12. The correct statement(s) about the compound given below is (are) *(2008)*



(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

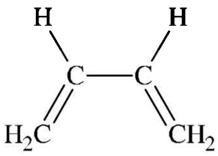
13. The correct statement(s) about the compound *(2009)*
$H_3C(HO)HC–CH=CH–CH(OH)CH_3$ (**X**) is(are)
(a) The total number of stereoisomers possible for **X** is 6
(b) The total number of diastereomers possible for **X** is 3
(c) If the stereochemistry about the double bond in **X** is *trans*, the 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

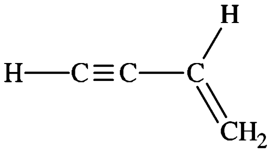
14. In the Newman projection for 2,2-dimethylbutane



X and **Y** can respectively be *(2010)*
(a) H and H
(b) H and C_2H_5
(c) C_2H_5 and H
(d) CH_3 and 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)*

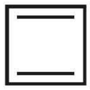
(a)


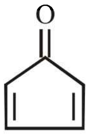
(b)


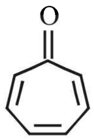
(c) $H_2C=C=O$
(d) $H_2C=C=CH_2$

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

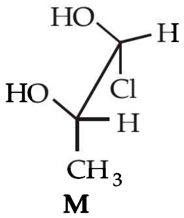
(a)


(b)


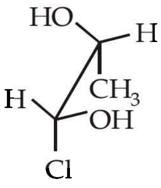
(c)


(d)


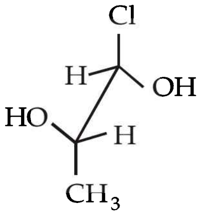
17. Which of the given statement(s) about **N, O, P** and **Q** with respect to **M** is (are) correct ? *(2012)*



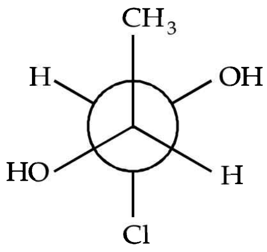
M



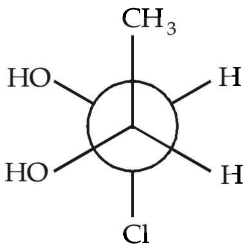
N



O



P



Q

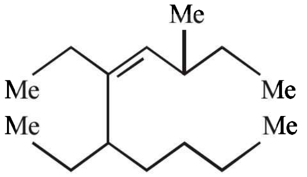
(a) **M** and **N** are non-mirror image stereoisomers
(b) **M** and **O** are identical
(c) **M** and **P** are enantiomers
(d) **M** and **Q** are identical

18. The hyperconjugative stabilities of tert-butyl cation and 2-butene, respectively, are due to *(JEE Adv. 2013)*
(a) $\sigma \to p$ (empty) and $\sigma \to \pi^*$ electron delocalisations
(b) $\sigma \to \sigma^*$ and $\sigma \to \pi$ electron delocalisations
(c) $\sigma \to p$ (filled) and $\sigma \to \pi$ electron delocalisations
(d) p (filled) $\to \sigma^*$ and $\sigma \to \pi^*$ electron delocalisations

E Subjective Problems

1. Arrange the following in :
(*i*) Increasing reactivity towards HCN *(1985)*
CH_3CHO, CH_3COCH_3, HCHO, $C_2H_5COCH_3$
(*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)*
$ClCH_2COOH$ (I), CH_3CH_2COOH (II), $ClCH_2CH_2COOH$ (III), $(CH_3)_2CHCOOH$ (IV), CH_3COOH (V)
(*v*) Increasing reactivity in nucleophilic substitution reactions *(1992)*
CH_3F, CH_3I, CH_3Br, CH_3Cl

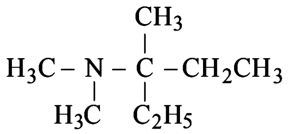
2. (*i*) Write the IUPAC name of : *(1986)*
$CH_3CH_2CH=CHCOOH$
(*ii*) Give the IUPAC name of the following compound : *(1990)*



(Me = Methyl)

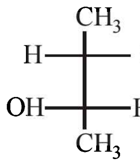
(*iii*) Write the IUPAC name for the following :

(1991)

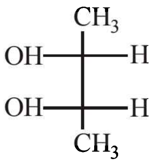


$$H_3C-\underset{\substack{|\\ H_3C}}{N}-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ C_2H_5}}{C}}-CH_2CH_3$$

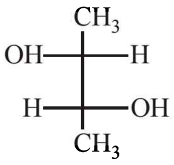
3. For nitromethane molecule, write structure(s).
   (*i*) showing significant resonance stabilisation. ***(1986)***
   (*ii*) indicating tautomerism. ***(1986)***
4. Give reasons for the following :
   (*i*) Carbon oxygen bond lengths in formic acid are 1.23Å and 1.36Å and both the carbon oxygen bonds in sodium formate have the same value i.e. 1.27Å. ***(1988)***
   (*ii*) Phenyl group is known to exert negative inductive effect. But each phenyl ring in biphenyl ($C_6H_5-C_6H_5$) is more reactive than benzene towards electrophilic substitution. ***(1992)***
   (*iii*) Aryl halides are less reactive than alkyl halides towards nucleophilic reagents ***(1994)***
   (*iv*) $CH_2{=}CH^-$ is more basic than $HC \equiv C^-$.
   (*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 (C_3H_4) and show the π-orbital overlaps. ***(1999)***
9. Identify the pairs of enantiomers and diastereomers from the following compounds I, II and III ***(2000)***



I



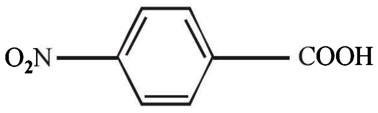
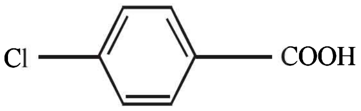
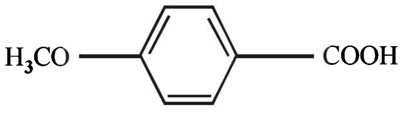
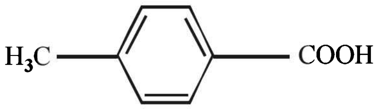
II



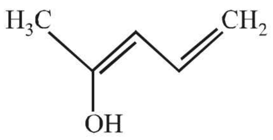
III

10. Which one is more soluble in diethyl ether - anhydrous $AlCl_3$ or hydrous $AlCl_3$? Explain in terms of bonding. ***(2003)***

11. Match the K_a values ***(2003)***

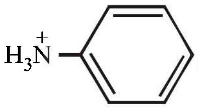
		K_a
(a)	Benzoic acid	6.4×10^{-5}
(b)		30.6×10^{-5}
(c)		10.2×10^{-5}
(d)		3.3×10^{-5}
(e)		4.2×10^{-5}

12. ***(2003)***

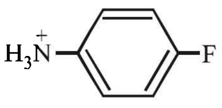


Write resonance structure of the given compound.

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



,



14. (*i*) $\mu_{obs} = \sum_i \mu_i x_i$, where μ_i is the dipole moment of a stable conformer of the molecule, $Z-CH_2-CH_2-Z$ and x_i is the mole fraction of the stable conformer.

    Given : $\mu_{obs} = 1.0\,D$ and $x_{(Anti)} = 0.82$

    Draw all the stable conformers of $Z-CH_2-CH_2-Z$ and calculate the value of $\mu_{(Gauche)}$.

    (*ii*) Draw the stable conformer of Y – CHD – CHD – Y (meso form), when Y = CH_3 (rotation about C_2-C_3) and Y = OH (rotation about C_1-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	●	ⓠ	ⓡ	●	●
B	ⓟ	●	●	ⓢ	ⓣ
C	●	●	ⓡ	ⓢ	ⓣ
D	ⓟ	ⓠ	ⓡ	●	ⓣ

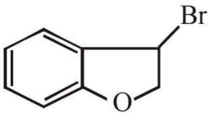
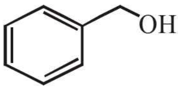
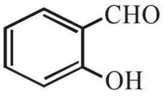
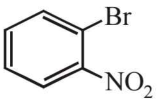
1. Given below are certain matching type questions, where two columns (each having 4 items) are given. Immediately after the columns the matching grid is given, where each item of Column I has to be matched with the items of Column II, by encircling the correct match(es). Note that an item of **Column 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

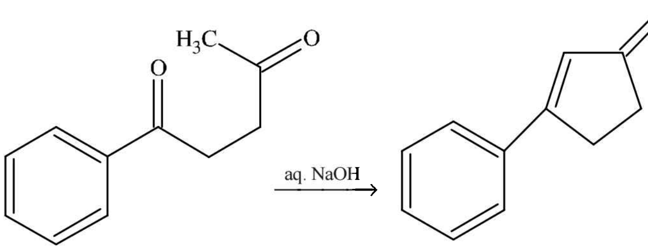
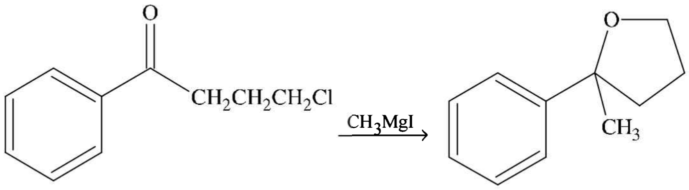
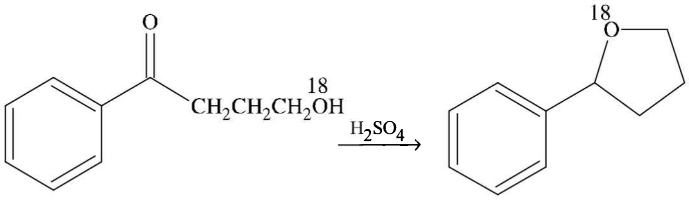
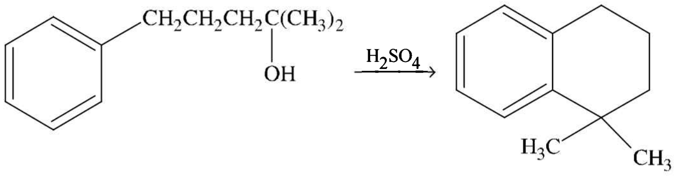
2. Match the compounds/ions in **Column I** with their properties/reactions in **Column II**. Indicate your answer by darkening the appropriate bubbles of the 4 × 4 matrix given in the ORS. *(2007)*

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**
(A) 	(p) Nucleophilic substitution
(B) 	(q) Electrophilic substitution
(C) 	(r) Dehydration
(D) 	(s) Nucleophilic addition
	(t) Carbanion

H Assertion & Reason Type Questions

Read the following Statement-1(Asseration) 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.

1. **Statement -1:** Aryl halides undergo nucleophilic substitution with ease.

   Statement -2: The carbon-halogen bond in aryl halides has partial double bond character. *(1991)*

2. **Statement -1:** Phenol is more reactive than benzene towards electrophilic substitution reactions.

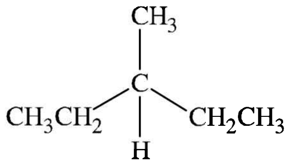
   Statement-2: In the case of phenol, the intermediate carbocation is more resonance stabilized. *(2000S)*

3. **Statement -1:** Molecules that are not superimpossable on their mirror images are chiral.

   Statement -2: All chiral molecules have chiral centres. *(2007)*

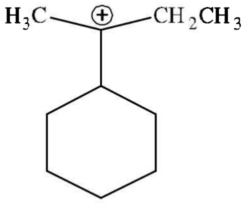
I Integer Value Correct Type

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

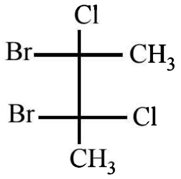


$$CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2CH_3$$

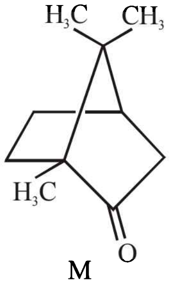
4. The total number of contributing structures showing hyperconjugation (involving C–H bonds) for the following carbocation is *(2011)*



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

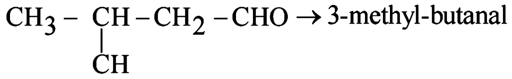
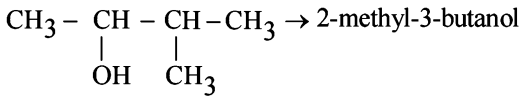
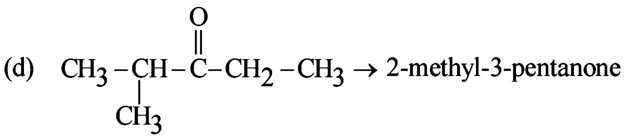


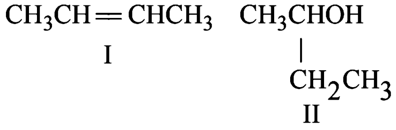
6. The total number of stereoisomers that can exist for M is *(JEE Adv. 2015)*



M

Section-B JEE Main / AIEEE

1. Arrangement of $(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3-CH_2- when attached to benzyl or an unsaturated group in increasing order of inductive effect is **[2002]**
   - (a) $(CH_3)_3C- < (CH_3)_2CH- < CH_3-CH_2$
   - (b) $CH_3-CH_2- < (CH_3)_2CH- < (CH_3)_3C-$
   - (c) $(CH_3)_2CH- < (CH_3)_3C- < CH_3, -CH_2$
   - (d) $(CH_3)_3C- < CH_3-CH_2-(CH_3)_2CH-$
2. A similarity between optical and geometrical isomerism is that **[2002]**
   - (a) each forms equal number of isomers for a given compound
   - (b) if in a compound one is present then so is the other
   - (c) both are included in stereoisomerism
   - (d) they have no similarity.
3. Which of the following does not show geometrical isomerism?
   - (a) 1,2-dichloro-1-pentene **[2002]**
   - (b) 1,3-dichloro-2-pentene
   - (c) 1,1-dichloro-1-pentene
   - (d) 1,4-dichloro-2-pentene
4. The functional group, which is found in amino acid is **[2002]**
   - (a) $-COOH$ group (b) $-NH_2$ group
   - (c) $-CH_3$ group (d) both (a) and (b).
5. Which of the following compounds has wrong IUPAC name? **[2002]**
   - (a) $CH_3-CH_2-CH_2-COO-CH_2CH_3$ → ethyl butanoate
   - (b) 
     $\underset{\displaystyle CH}{CH_3-\underset{|}{CH}}-CH_2-CHO \rightarrow$ 3-methyl-butanal
   - (c) 
     $CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3 \rightarrow$ 2-methyl-3-butanol
   - (d) 
     $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_3 \rightarrow$ 2-methyl-3-pentanone
6. The IUPAC name of $CH_3COCH(CH_3)_2$ is **[2003]**
   - (a) 2-methyl-3-butanone
   - (b) 4-methylisopropyl ketone
   - (c) 3-methyl-2-butanone
   - (d) Isopropylmethyl ketone
7. In which of the following species is the underlined carbon having sp^3 hybridisation? **[2002]**
   - (a) $CH_3\underline{C}OOH$ (b) $CH_3\underline{C}H_2OH$
   - (c) $CH_3\underline{C}OCH_3$ (d) $CH_2=\underline{C}H-CH_3$
8. Racemic mixture is formed by mixing two **[2002]**
   - (a) isomeric compounds
   - (b) chiral compounds
   - (c) meso compounds
   - (d) enantiomers with chiral carbon.
9. Following types of compounds (as I, II) **[2002]**

   
   $\underset{\text{I}}{CH_3CH=CHCH_3}$ $\quad$ $\underset{\text{II}}{\underset{\displaystyle CH_2CH_3}{\underset{|}{CH_3CHOH}}}$

   are studied in terms of isomerism in:
   - (a) chain isomerism (b) position isomerism
   - (c) conformers (d) stereoisomerism
10. The reaction: **[2002]**

    $(CH_3)_3C-Br \xrightarrow{H_2O} (CH_3)_3C-OH$
    - (a) elimination reaction
    - (b) substitution reaction
    - (c) free radical reaction
    - (d) displacement reaction.

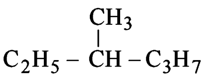
11. In the anion $HCOO^-$ the two carbon-oxygen bonds are found to be of equal length. what is the reason for it ? **[2003]**

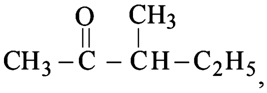
(a) The C = O bond is weaker than the C — O bond
(b) The anion $HCOO^-$ has two resonating structures
(c) The anion is obtained by removal of a proton from the acid molecule
(d) Electronic orbitals of carbon atom are hybridised

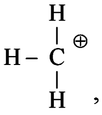
12. The general formula $C_nH_{2n}O_2$ could be for open chain **[2003]**

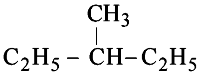
(a) carboxylic acids (b) diols
(c) dialdehydes (d) diketones

13. Among the following four structures I to IV, **[2003]**


$C_2H_5-\overset{CH_3}{\overset{|}{C}H}-C_3H_7$,
(I)


$CH_3-\overset{O}{\overset{||}{C}}-\overset{CH_3}{\overset{|}{C}H}-C_2H_5$,
(II)


(III)

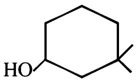

$C_2H_5-\overset{CH_3}{\overset{|}{C}H}-C_2H_5$
(IV)

it is true that

(a) only I and II are chiral compounds
(b) only III is a chiral compound
(c) only II and IV are chiral compounds
(d) all four are chiral compounds

14. Which one of the following has the minimum boiling point ? **[2004]**

(a) 1 - Butene (b) 1 - Butyne
(c) n- Butane (d) isobutane

15. The IUPAC name of the compound is 

(a) 3, 3-dimethyl - 1- cyclohexanol **[2004]**
(b) 1, 1-dimethyl-3-hydroxy cyclohexane
(c) 3, 3-dimethyl-1-hydroxy cyclohexane
(d) 1, 1-dimethyl-3-cyclohexanol

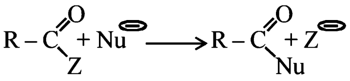
16. Which one of the following does not have sp^2 hybridized carbon ? **[2004]**

(a) Acetonitrile (b) Acetic acid
(c) Acetone (d) Acetamide

17. Which of the following will have a mesoisomer also?

(a) 2, 3- Dichloropentane **[2004]**
(b) 2, 3-Dichlorobutane
(c) 2-Chlorobutane
(d) 2-Hydroxypropanoic acid

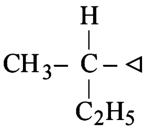
18. Rate of the reaction **[2004]**

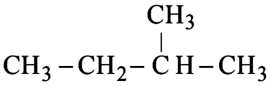


is fastest when Z is

(a) OC_2H_5 (b) NH_2
(c) Cl (d) $OCOCH_3$

19. Amongst the following compounds, the optically active alkane having lowest molecular mass is **[2004]**

(a) 

(b) 
$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_3$

(c) $CH_3-CH_2-CH_2-CH_3$

(d) $CH_3-CH_2-C\equiv CH$

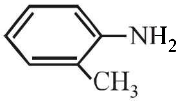
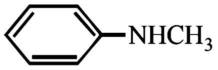
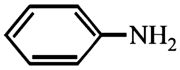
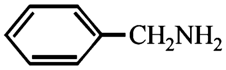
20. Consider the acidity of the carboxylic acids :

(a) PhCOOH (b) o-$NO_2C_6H_4COOH$
(c) p-$NO_2C_6H_4COOH$ (d) m-$NO_2C_6H_4COOH$

Which of the following order is correct ? **[2004]**

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

21. Which of the following is the strongest base ?

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

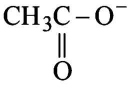
22. Which of the following compounds is not chiral? **[2004]**

(a) 1-chloro-2-methyl pentane
(b) 2-chloropentane
(c) 1-chloropentane
(d) 3-chloro-2-methyl pentane

23. Due to the presence of an unpaired electron, free radicals are: **[2005]**

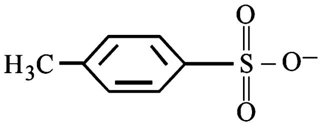
(a) cations (b) anions
(c) chemically inactive (d) chemically reactive

24. The decreasing order of nucleophilicity among the nucleophiles **[2005]**

(A) 
$CH_3\underset{O}{\underset{||}{C}}-O^-$

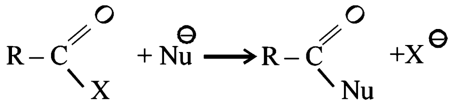
(B) CH_3O^-

(C) CN^-

(D)  is

(a) (C), (B), (A), (D) (b) (B), (C), (A), (D)
(c) (D), (C), (B), (A) (d) (A), (B), (C), (D)

25. The reaction **[2005]**

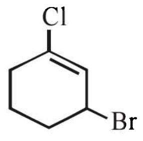


is fastest when X is

(a) OCOR (b) OC_2H_5

(c) NH_2 (d) Cl

26. The IUPAC name of the compound shown below is :



(a) 3-bromo-1-chlorocyclohexene **[2006]**

(b) 1-bromo-3-chlorocyclohexene

(c) 2-bromo-6-chlorocyclohex-1-ene

(d) 6-bromo-2-chlorocyclohexene

27. The increasing order of stability of the following free radicals is **[2006]**

(a) $(C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C} < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

(b) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

(c) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

(d) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

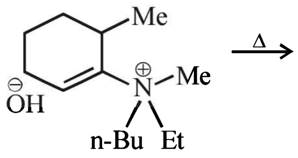
28. $CH_3Br + Nu^- \longrightarrow CH_3 - Nu + Br^-$ The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is **[2006]**

$[Nu^- = (A)\ PhO^-, (B)\ AcO^-, (C)\ HO^-, (D)\ CH_3O^-]$

(a) A > B > C > D (b) B > D > C > A

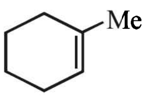
(c) D > C > A > B (d) D > C > B > A

29.

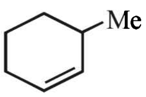


The alkene formed as a major product in the above elimination reaction is **[2006]**

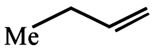
(a)



(b)



(c)



(d) $CH_2=CH_2$

30. Increasing order of stability among the three main conformations (i.e. Eclipse, Anti, Gauche) of 2-fluoroethanol is **[2006]**

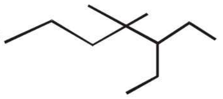
(a) Eclipse, Anti, Gauche

(b) Anti, Gauche, Eclipse

(c) Eclipse, Gauche, Anti

(d) Gauche, Eclipse, Anti

31. The IUPAC name of



is

(a) 3-ethyl-4-4-dimethylheptane **[2007]**

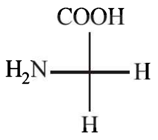
(b) 1, 1-diethyl-2,2-dimethylpentane

(c) 4, 4-dimethyl-5,5-diethylpentane

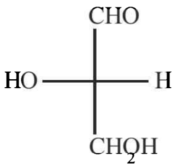
(d) 5, 5-diethyl-4,4-dimethylpentane.

32. Which of the following molecules is expected to rotate the plane of plane-polarised light? **[2007]**

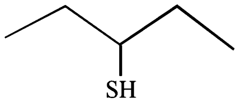
(a)



(b)



(c)



(d)

33. Presence of a nitro group in a benzene ring **[2007]**

(a) deactivates the ring towards electrophilic substitution

(b) activates the ring towards electrophilic substitution

(c) renders the ring basic

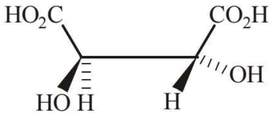
(d) deactivates the ring towards nucleophilic substitution.

34. Which one of the following conformations of cyclohexane is chiral? **[2007]**

(a) Boat (b) Twist boat

(c) Rigid (d) Chair.

35. The absolute configuration of **[2008]**

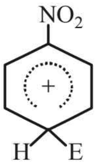


(a) S, S (b) R, R

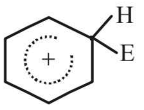
(b) R, S (c) S, R

36. The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ–complex. Of the following, which σ–complex is lowest energy? **[2008]**

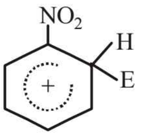
(a)



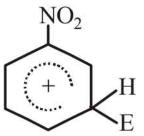
(b)



(c)



(d)



37. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is **[2008]**

(a) $-COOH, -SO_3H, -CONH_2, -CHO$

(b) $-SO_3H, -COOH, -CONH_2, -CHO$

(c) $-CHO, -COOH, -SO_3H, -CONH_2$

(d) $-CONH_2, -CHO, -SO_3H, -COOH$

38. The IUPAC name of neopentane is **[2009]**

(a) 2, 2 dimethylpropane

(b) 2 methylpropane

(c) 2, 2 dimethylbutane

(d) 2-methylbutane

39. Arrange the carbanions, **[2009]**

$(CH_3)_3\bar{C}, \bar{C}Cl_3, (CH_3)_2\bar{C}H, C_6H_5\bar{C}H_2$ in order of their decreasing stability :

(a) $(CH_3)_2\bar{C}H > \bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_3\bar{C}$

(b) $\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}$

(c) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$

(d) $C_6H_5\bar{C}H_2 > \bar{C}Cl_3 > (CH_3)_3\bar{C} > (CH_3)_2\bar{C}H$

40. The alkene that exhibits geometrical isomerism is:

(a) 2- methyl propene **[2009]**

(b) 2-butene

(c) 2- methyl -2- butene

(d) propene

41. The number of stereoisomers possible for a compound of the molecular formula

$CH_3-CH=CH-CH(OH)-Me$ is: **[2009]**

(b) 2 (c) 4

(d) 6 (d) 3

42. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is **[2010]**

(a) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$

(b) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$

(c) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$

(d) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

43. Out of the following, the alkene that exhibits optical isomerism is **[2010]**

(a) 3-methyl-2-pentene (b) 4-methyl-1-pentene

(c) 3-methyl-1-pentene (d) 2-methyl-2-pentene

44. Identify the compound that exhibits tautomerism : **[2011]**

(a) 2-Butene (b) Lactic acid

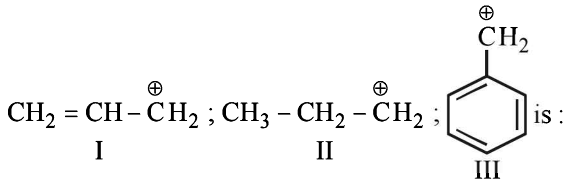
(c) 2-Pentanone (d) Phenol

45. A solution of $(-)-1-$chloro$-1-$phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of : **[JEE M 2013]**

(a) carbanion (b) carbene

(c) carbocation (d) free radical

46. The order of stability of the following carbocations :



$CH_2=CH-\overset{\oplus}{C}H_2$; $CH_3-CH_2-\overset{\oplus}{C}H_2$;

[JEE M 2013]

(a) III > II > I (b) II > III > I

(c) I > II > III (d) III > I > II

47. For the estimation of nitrogen, 1.4 g of an organic compound was digested by Kjeldahl method and the evolved ammonia was absorbed in 60 mL of $\frac{M}{10}$ sulphuric acid. The unreacted acid required 20 mL of $\frac{M}{10}$ sodium hydroxide for complete neutralization. The percentage of nitrogen in the compound is: **[JEE M 2014]**

(a) 6% (b) 10%

(c) 3% (d) 5%

48. Which of the following compounds will exhibit geometrical isomerism ? **[JEE M 2015]**

(a) 2 - Phenyl - 1 - butene

(b) 1, 1 - Diphenyl - 1 - propene

(c) 1 - Phenyl - 2 - butene

(d) 3 - Phenyl - 1 - butene

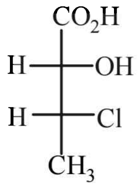
49. In Carius method of estimation of halogens, 250 mg of an organic compound gave 141 mg of AgBr. The percentage of bromine in the compound is : **[JEE M 2015]**

(at. mass Ag = 108; Br = 80)

(a) 48 (b) 60

(c) 24 (d) 36

50. The absolute configuration of **[JEE M 2016]**



is :

(a) (2S, 3S) (b) (2R, 3R)

(c) (2R, 3S) (d) (2S, 3R)

51. The distillation technique most suited for separating glycerol from spent-lye in the soap industry is : **[JEE M 2016]**

(a) Steam distillation.

(b) Distillation under reduced pressure.

(c) Simple distillation

(d) Fractional distillation

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

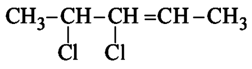
B **1.** F **2.** F **3.** F **4.** T

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. 
$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}=CH-CH_3$ **9.** enantionmers – I & III; diastereomers – I & II and II & III.

10. Anyhydrous $AlCl_3$ **14.** (i) $\mu_{(gauche)} = 5.55\,D$

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)

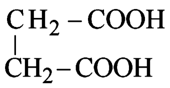
Section-A JEE Advanced/ IIT-JEE

A. Fill in the Blanks

1. ***tert*-butyl carbonium ion** is more stable due to hyperconjugation and +I effect of methyl groups.
2. **propadiene;** in it carbon-carbon is *sp* hybridised.
3. **cyclopropane,** because it has maximum deviation, from the normal bond angle of 109°28' present in alkanes. In it bond angle is 60°.

$$d = \frac{1}{2}(109°28' - 60°).$$

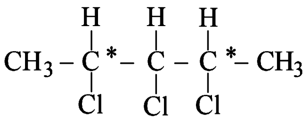
4. sp^3
5. **vicinal, adjacent** (or stable, different).
6. **non-superimposable, enantiomers;**
7. ***sp*;**
8. **Hyperconjugation;**
9. **Butane-1, 4-dioic acid;** Succinic acid has the formula.



$$\begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

B. True/False

1. **False :** Iodide is bigger in size than bromide, hence its electrons are more dispersed than that of bromide, with the result it is weaker nucleophile than bromide.
2. **False :** An electron-donating group increases the electron density in *o*- and *p*- positions due to +M, +E and/or +I effects and hence orients the new electrophile to *o*- and *p*- positions.
3. **False :** There are only two asymmetric (marked with *) carbon atoms.

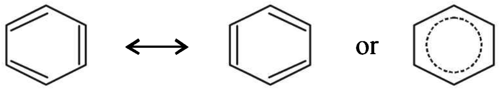


$$CH_3-\underset{Cl}{\overset{H}{C}}{}^{*}-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}{}^{*}-CH_3$$

4. **True :** In S_N1 (unimolecular nucleophilic substitution reaction), the leaving group leaves, thus producing a carbocation followed by the addition of the incoming group.

C. MCQs with One Correct Answer

1. (c) NOTE:
The phenomenon of resonance gives identical bonding and hence identical bond lengths.



C – C bond order in benzene = 1.5

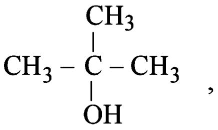
2. (a) **TIPS/Formulae :**
The bond length decreases in the order.

$$\underset{\text{alkane}}{sp^3-sp^3} > \underset{\text{alkene}}{sp^2-sp^2} > \underset{\text{alkyne}}{sp-sp}$$

On the basis of the size of the hybrid orbitals, *sp* orbital should form the shortest and sp^3 orbital the longest bond with other atom.

3. (d) The first three are isomers of diethyl ether, $C_2H_5OC_2H_5$ ($C_4H_{10}O$).

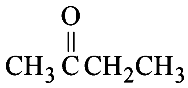
$\underset{n\text{-Propylmethylether}}{n\text{-}C_3H_7OCH_3}$,



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3$$

2-Methylpropan-2-ol

$\underset{\text{Butan-1-ol}}{n\text{-}C_4H_9OH}$,



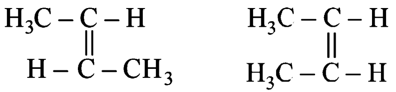
$$CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$$

Butanone (C_4H_8O)

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

5. (d) $\overset{4}{C}H_3-\overset{3}{C}H=\overset{2}{C}=\overset{1}{C}H_2$
Hybridisation in $C_1 = sp^2, C_2 = sp, C_3 = sp^2, C_4 = sp^3$.

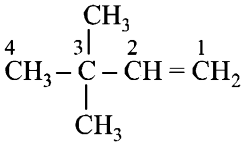
6. (a) **TIPS/Formulae :**
cis-trans – Isomerism is due to restricted rotation either due to carbon-carbon double bond or due to cyclic structure.
NOTE : Geometrical Isomerism : *The isomers which possess the same structural formula but differ in the spatial arrangement of the groups* **around the double bond** *are known as geometrical isomers.*



$$\begin{array}{c} H_3C-C-H \\ \| \\ H-C-CH_3 \end{array} \qquad \begin{array}{c} H_3C-C-H \\ \| \\ H_3C-C-H \end{array}$$

trans-butene-2 *cis*-butene-2

7. (c)

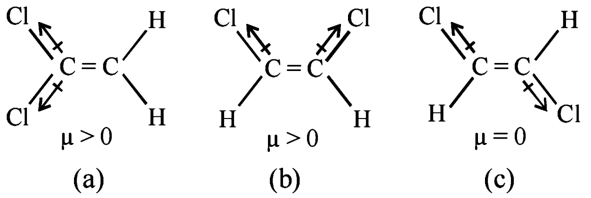


$$\overset{4}{C}H_3-\underset{CH_3}{\overset{CH_3}{\overset{3}{C}}}-\overset{2}{C}H=\overset{1}{C}H_2$$

3, 3-dimethylbut-1-ene

8. (d) $\underset{\text{dimethyl ether}}{CH_3-O-CH_3}$ is an isomer of $\underset{\text{ethanol}}{CH_3CH_2OH}$

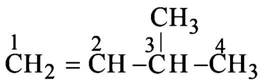
9. **(c)**



[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.

11. **(b)**



$\overset{1}{C}H_2 = \overset{2}{C}H - \overset{3}{C}H(CH_3) - \overset{4}{C}H_3$ (3-Methyl-1-butene)

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

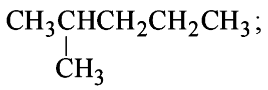
For knowing the possible isomers of the compound follow the following points.

(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.

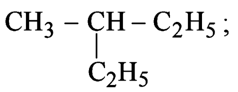
There are 5 isomers possible for C_6H_{14}.

$CH_3CH_2CH_2CH_2CH_2CH_3$; (i)



$CH_3CH(CH_3)CH_2CH_2CH_3$; (ii)

$(CH_3)_3CCH_2CH_3$; (iii)



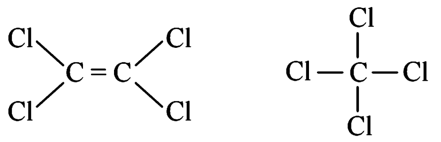
$CH_3 - CH(C_2H_5) - C_2H_5$; (iv)

$(CH_3)_2CH-CH(CH_3)_2$ (v)

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

The bond angle in sp^3, sp^2 and *sp* hybridization is respectively 109.28', 120° and 180°.

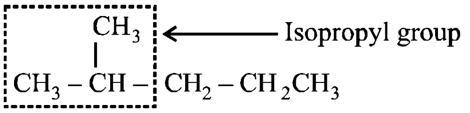
Tetrachloroethene being an alkene has sp^2 hybridised C-atoms and hence the Cl – C – Cl angle is 120°, whereas in tetrachloromethane, carbon is sp^3 hybridised, so the angle is 109°.28'.



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.

15. **(d)**



2-Methylpentane

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 akynes with the result C – H bond length will be maximum.

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

No of σ bonds = 2 + 1 + 1 + 1 + 1 + 1 = 7;

No of π 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)** $HC \equiv \overset{sp}{C} - \overset{sp^2}{C}H = CH_2$

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 *diasteromers*. **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 :**

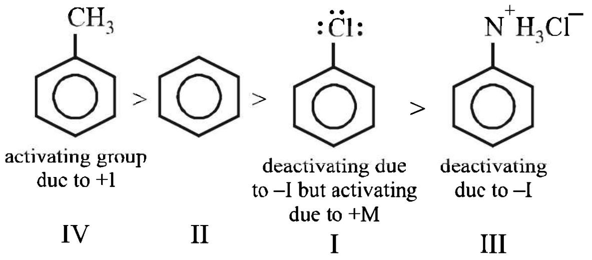
A compound which consists of at least one asymmetric carbon atom is capable of showing the phenomenon of optical isomerism.

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)** $CH_2 = CH - CH_2 - N \overset{\rightarrow}{=} C:$

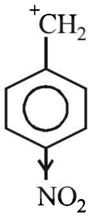
The above structure of allyl isocyanide clearly shows 5 C – H (σ), 2 C – C (σ), 1C – N (σ), 1N – C(σ), 1C – C (π), 2N – C (π) bonds, *i.e.*, 9σ and 3π bonds in all. There are 2 non-bonded electrons on the C-atom (co-ordinate bond between N and C, the electron pair of N is shifted towards C).

24. **(c)**

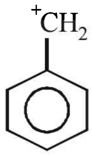


25. **(d)** **TIPS/Formulae :**

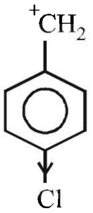
The stability of carbonium ion is influenced by both resonance and inductive effect.



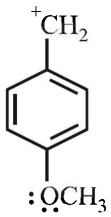
NO_2 intensifies +ve charge on benzyl cation due to –I and –M effects



Benzyl stable due to resonance



Cl intensifies +ve charge on C due to –I effect

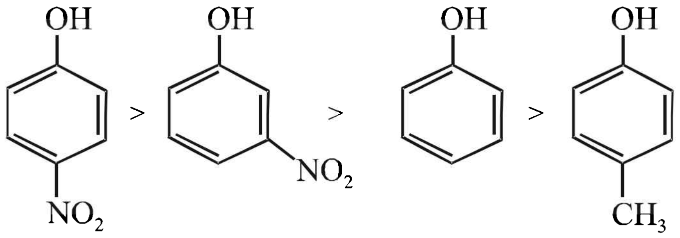


Positive charge of benzyl cation is more dispersed due to +M effect of the $–OCH_3$ group

26. **(d)** **NOTE :** $–NO_2$ is an electron-attracting group where as $–CH_3$ 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



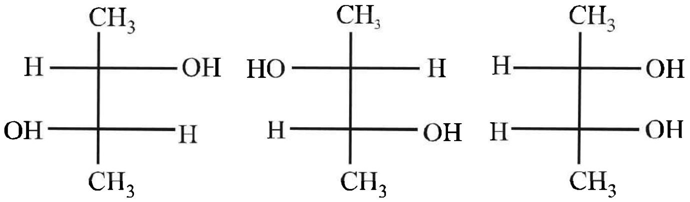
(IV) (III) (I) (II)

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 $–CH_3$ 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



Optically active enantiomers

meso-compound optically inactive

29. **(d)** $\overset{1}{\underset{sp^2}{CH_2}} = \overset{2}{\underset{sp^2}{CH}} - \overset{3}{\underset{sp^3}{CH_2}} - \overset{4}{CH_2} - \overset{5}{C} \equiv \overset{6}{CH}$

30. **(c)** **TIPS/Formulae :**

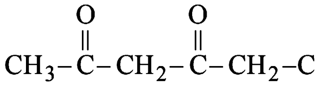
Glyceraldehyde is taken as arbitrary standard for D, L – nomenclature.

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

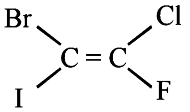
32. **(c)** $^-CH_3$ is the best nucleophile because carbon is least electronegative among the given options. The order is

$$H_3\bar{C} > \bar{N}H_2 > \bar{O}H > F^-$$

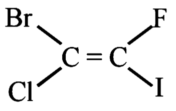
33. **(d)** Rate of reaction will be R – I > R – Br > R – Cl > R – F. because I^- is the best, while F^- is the poorest leaving groups among halide ions.

34. **(b)** In  $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$, $–CH_2–$ 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.

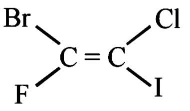
35. **(d)** Number of isomers (six) can be derived by keeping the position of any one halogen (say Br) fixed and changing the position of the other halogen one by one.



(Z and E)



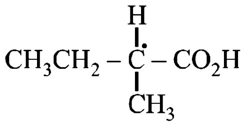
(Z and E)



(Z and E)

36. **(d)** S_N2 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



$$CH_3CH_2-\overset{H}{\underset{CH_3}{\overset{|}{\underset{|}{C^{\bullet}}}}}-CO_2H$$

38. (c) TIPS/Formulae :

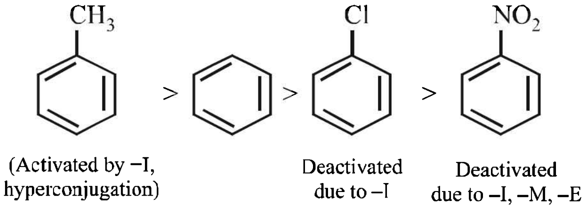
(i) The inductive effect decreases with increase in distance of halogen atom from the carboxylic group and hence the strength of acid proportionally decreases.

(ii) The acidity increases with the increase in electronegativity of the halogen present.

Smallest dissociation constant means weakest acid, which is $BrCH_2\ CH_2COOH$ because here Br (less electronegative than F) is two carbon atoms away from $-COOH$.

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

40. (c)



41. (b) $CH_3C\equiv CCH_3$ is linear and symmetrical ; thus it has lowest dipole moment.

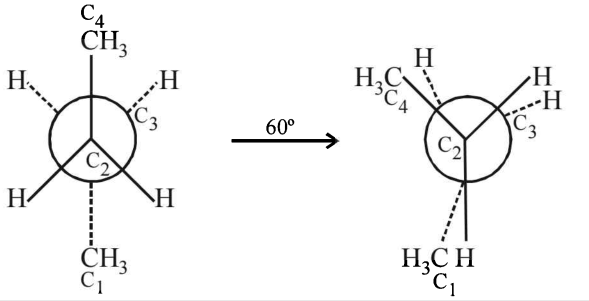
42. (a) $\overset{sp^2}{H_2C}=\overset{sp^2}{CH}-\overset{sp}{C}\equiv\overset{sp}{N}$.

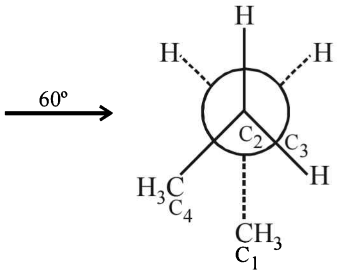
43. (a) NOTE : Dipole moment is a vector quantity.

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 (CCl_4) again becomes symmetrical and dipole moment reduces to zero. So, CH_3Cl will have the maximum dipole moment.

44. (c) TIPS/Formulae :

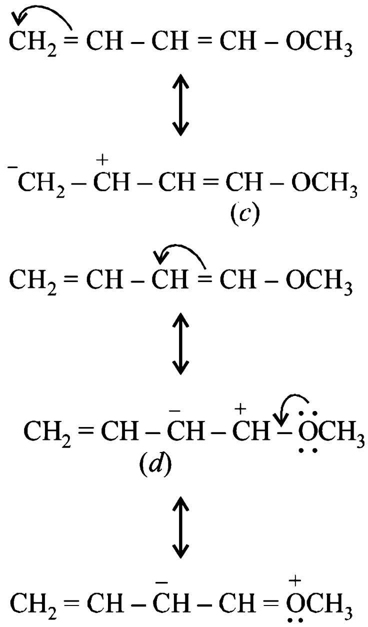
Any conformation between two extreme positions i.e. eclipsed and staggered is known as Gauche or Skew form.





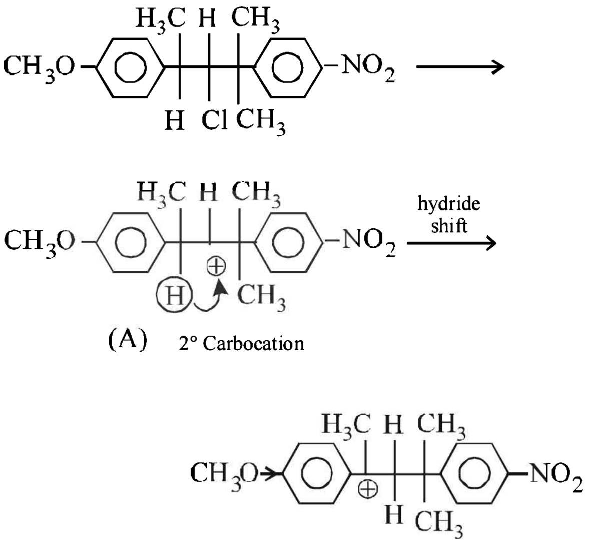
(Gauche conformation)

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.



$$CH_2=CH-CH=CH-OCH_3$$
$$\updownarrow$$
$$\overset{-}{C}H_2-\overset{+}{C}H-CH=CH-OCH_3$$
(*c*)
$$CH_2=CH-CH=CH-OCH_3$$
$$\updownarrow$$
$$CH_2=CH-\overset{-}{C}H-\overset{+}{C}H-\ddot{O}CH_3$$
(*d*)
$$\updownarrow$$
$$CH_2=CH-\overset{-}{C}H-CH=\overset{+}{O}CH_3$$

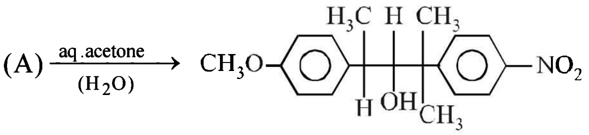
46. (a) NOTE : This is an example of S_N1 reaction involving carbocation as intermediate.



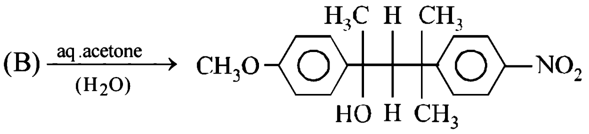
(A) 2° Carbocation

(B) 3° Carbocation; more stable; (positive charge is dispersed due to +M effect of $-OCH_3$)

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



(i)



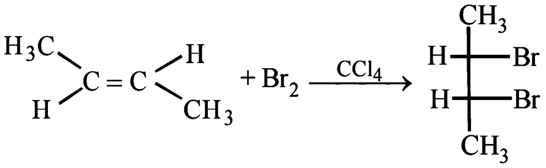
(ii)

47. **(b)** Carboxylic acids are named as *oyl chlorides*.

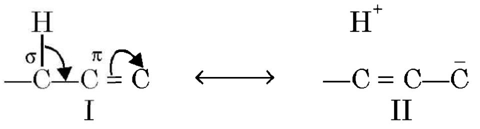
48. **(b)** The ring to which –NH group is attached is activated due to the lone pairs on N (+M and +E effects); while the ring to which –C = O is attached is deactivated. Hene, the electrophile would go to the *para*-position of the activated ring.

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.



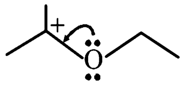
51. **(b)** Alkyl groups with at least one hydrogen atom on the α-carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.



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

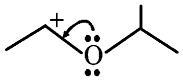
52. **(d)** The correct stability order is

I > III > II > IV



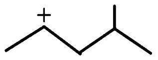
I

+ M effect, 6 hyper-conjugative H's, 2 CH_3 groups (+ I effect)



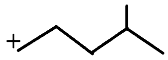
III

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



II

5 hyper conjugative CO – H's 2 R groups

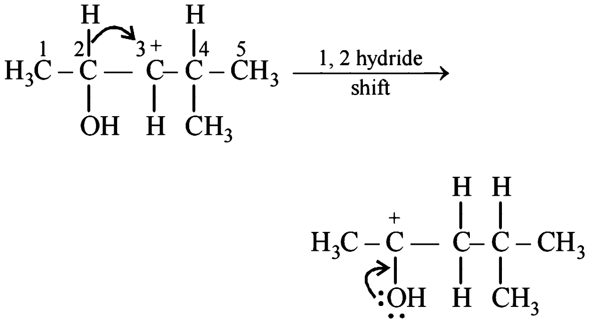


IV

5 hyperconjugative H's one R groups

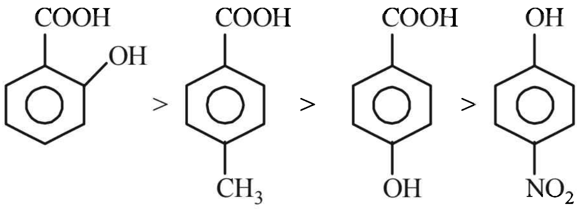
53. **(b)** – CN has highest priority. Further the sum of locants is 7 in (b) and 9 in (d).

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).

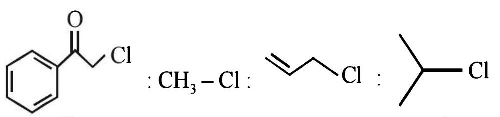


More stable carbocation

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



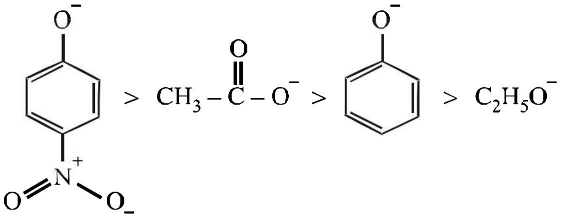
56. **(b)**



Compounds	S	P	R	Q
Relative reactivities towards S_{N^2} reaction	1,00,000 :	200 :	79 :	0.02

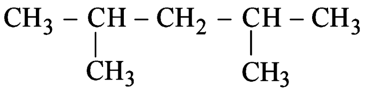
D. MCQs with One or More Than One Correct

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

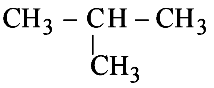


Higher stability of acetate ions than phenoxide ion is due to equivalent resonating structures in the former

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

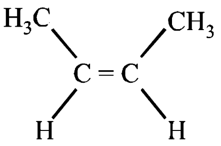


Option (b) : $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$ will give three isomers with Cl group at either of the CH_3 groups, second C-atom and 3rd C-atom.
Benzene forms only one single derivative.



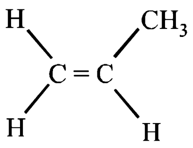
Option (d) : $CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3$ will again give two isomers with Cl at either one of the CH_3 groups or on the central C-atom.

5. **(c, d)** An asymmetric carbon atom is one which is attached with 4 different groups. Hence (c) & (d) are correct.
6. **(a)** **TIPS/Formulae :**
Conjugate base of strong acid is weak while conjugate base of a weak acid is stronger.
Acidic strength of acids,
$HOH > CH \equiv CH > NH_3 > CH_3.CH_3$
Hence the order of strength of bases,
$CH_3\,CH_2^- > NH_2^- > CH \equiv C^- > OH^-$
7. **(a, c)**



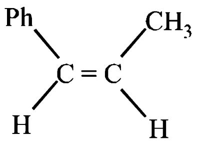
2-butene (*a*)

;



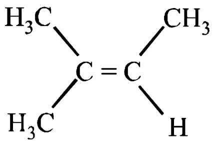
propene (*b*)

;



1-phenylpropene (*c*)

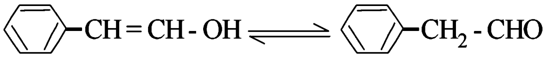
;



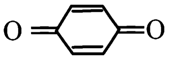
2-methyl-2-butene (*d*)

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

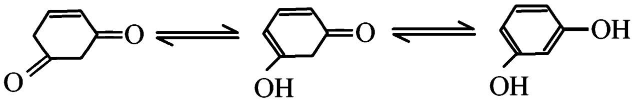
8. **(d)** Order of acidic strength
$CH_3OH > CH \equiv CH > C_6H_6 > C_2H_6$; CH_3OH is most acidic because O is more electronegative than C and capable of accommodating negative charge in CH_3O^-
Although alcohols are neutral towards the litmus paper.
9. **(a,c,d)** **TIPS/Formulae :**
For a carbonyl compound to show tautomerism, it must have at least one H at the α – carbon atom.
(a), (c) and (d) show tautomerism.

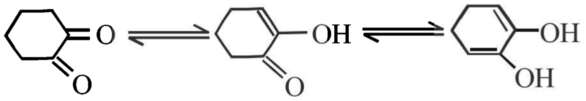


(enol form) (keto form)



Tautomerism is not possible

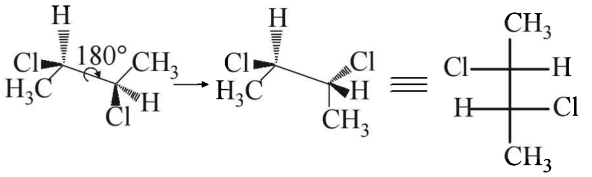




10. **(b,c,d)** **NOTE :** An aromatic species will have :

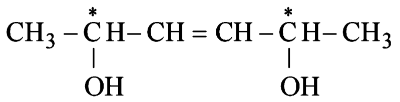
$(4n+2)$ π electrons	(by Huckel's Rule)
planar structure	(due to resonance)
cyclic structure	(due to presence of sp^2 - hybrid carbon atoms).

11. **(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).
12. **(a, d)** The given molecule although posseses 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°/n to produce a molecule indistinguishable from the original molecule.



Molecule has non-superimposable mirror image

13. **(a,d)**



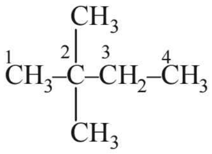
$CH_3-\overset{*}{\underset{\underset{OH}{|}}{C}}H-CH=CH-\overset{*}{\underset{\underset{OH}{|}}{C}}H-CH_3$

Stereoisomer	Configuration		
I	*d*	*cis*	*d*
II	*l*	*cis*	*l*
III	*d*	*cis*	*l*
IV	*d*	*trans*	*d*
V	*l*	*trans*	*l*
VI	*d*	*trans*	*l*

Enantiomers	$\underset{cis}{\text{I and II}}$; $\underset{trans}{\text{IV and V}}$
Diastereomers	I (or II), III (or IV), V and VI
Meso	III and IV

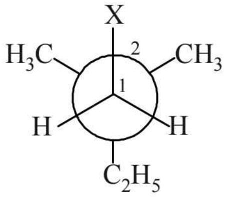
14. **(b, d)**

Structural formula of 2, 2-dimethylbutane is

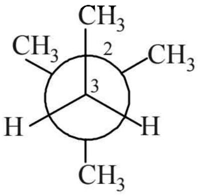


$\overset{1}{C}H_3-\overset{2}{C}(CH_3)_2-\overset{3}{C}H_2-\overset{4}{C}H_3$

(I) Newman projection using C_1-C_2 bond



(II) Newman projection using C_3-C_2 bond

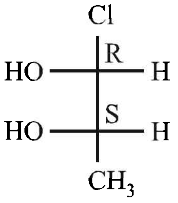


16. **(b, c)**

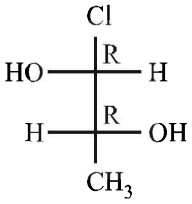
b and c, being antiaromatic, are unstable at room temperature.

17. **(a, b, c)**

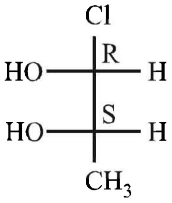
Converting all the structures in the Fischer projection



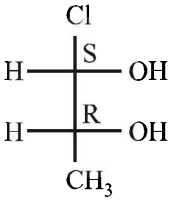
M



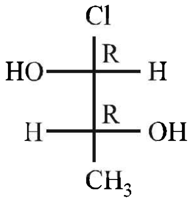
N



O



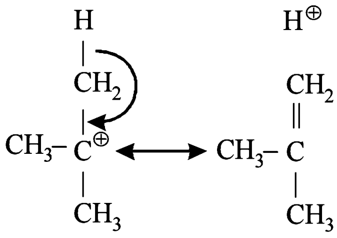
P



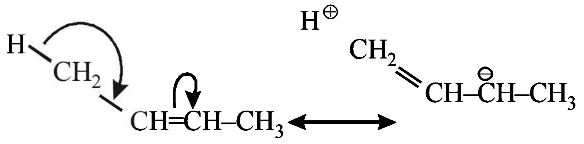
Q

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 σ–p (empty) conjugation or hyperconjugation.



In 2-butene, hyperconjugation is between σ→π* 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.

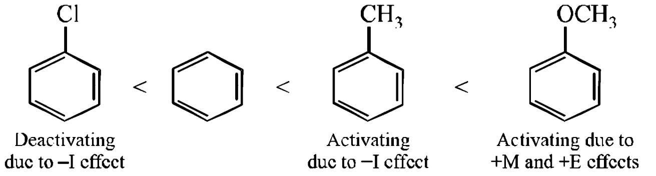
$C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

(*ii*) Isobutane < *n*-Butane < *n*-Butyl chloride < *n* - Butanol

van der Wall's 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 vander 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

IV < II < V < III < I

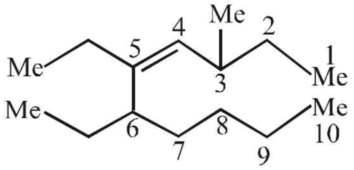
(*v*) **NOTE :** A weaker base is a better leaving group.

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*) $\overset{5}{C}H_3\overset{4}{C}H_2\overset{3}{C}H=\overset{2}{C}H\overset{1}{C}OOH$

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

(*ii*)

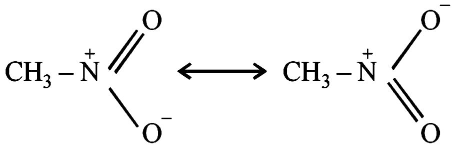


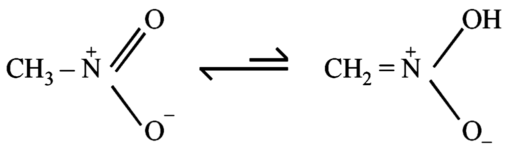
5, 6-diethyl-3-methyl-4-decene

(*iii*) IUPAC name is

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

3. (*i*)



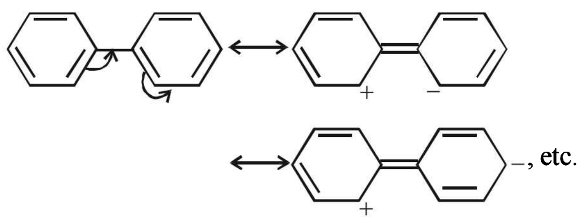
(*ii*) 

(*nitro* form) (*aci*-form)

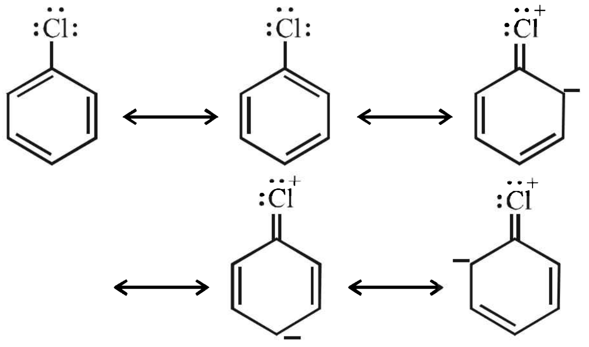
4. (*i*) In formic acid, resonance is not possible with the result there are two types of C – O bonds. In sodium formate, resonance is possible, so both of the C – O bonds have same bond length.

Formic acid Sodium formate (Resonating hybrid)

(*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.

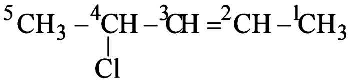


Resonating structures of chlorobenzene

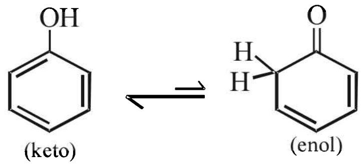
NOTE : *Due to resonance, carbon-chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be easily replaced by nucleophiles.*

(*iv*) $CH \equiv C^-$, C^- is *sp* hybridised and more electronegative then the $\bar{C}H$ of $CH_2 = \bar{C}H$ which is sp^2 hybridised. Thus the former can better accomodate 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.

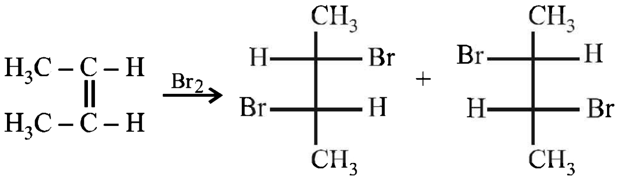
5. 

$${}^5CH_3-{}^4\underset{\underset{Cl}{|}}{C}H-{}^3CH={}^2CH-{}^1CH_3$$

6. 

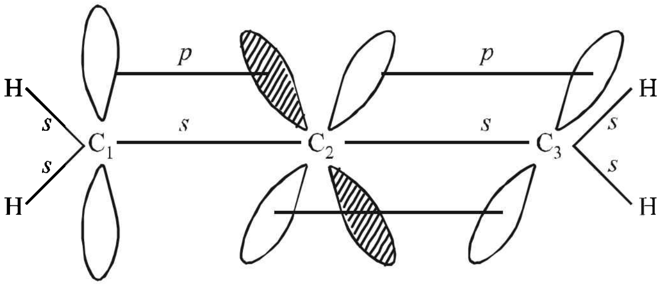
(keto) (enol)

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



cis-2-butene
2,3-dibromobutane
(Racemic mixture)

8. $\underset{sp^2}{CH_2} = \underset{sp}{C} = \underset{sp^2}{CH_2}$ (Allene)

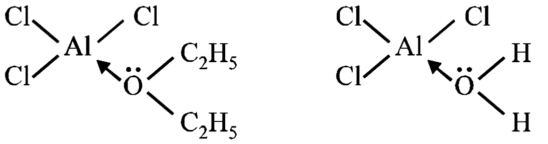


9. In order to convert a molecule with two stereogenic centres to its enantiomer, the confuguration at both centres must be reversed. Reversing the configuration at only one stereogenic centre converts it to a distereomeric structure. Thus structures I and III are enantiomers; while structures I and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

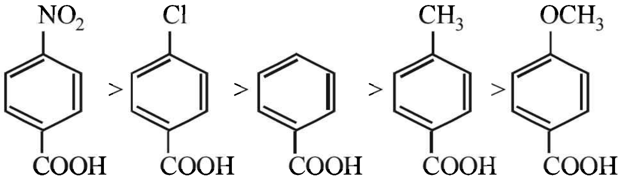
10. **TIPS/Formulae :**

Diethyl ether acts as a lewis base and anhydrous $AlCl_3$ as a lewis acid.

Anhydrous $AlCl_3$ 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 $AlCl_3$ through the formation of coordinate bond. In case of hydrated $AlCl_3$ 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

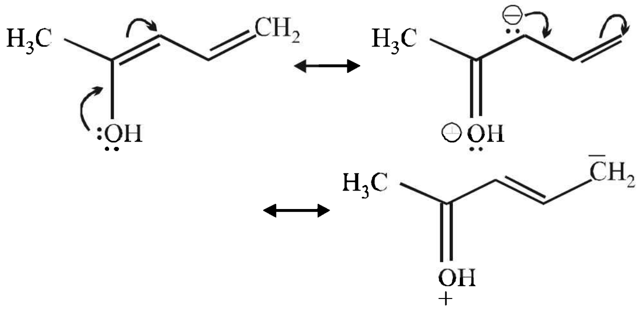


(b) (c) (a) (e) (d)

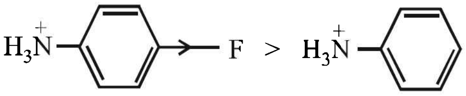
Hence the K_a values of the five acids will be in the order.

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

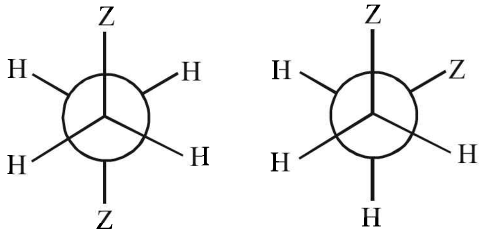
12.



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



14. (*i*)



Anti conformer Gauche conformer

Given, mole fraction of anti conformer = 0.82

∴ mole fraction of gauche conformer = 0.18

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

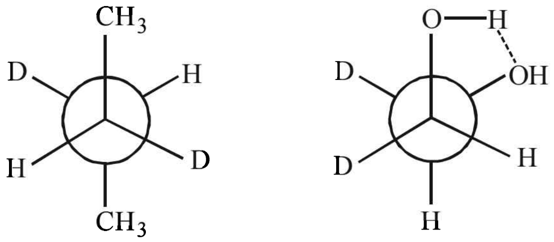
$$1 = \mu_{(anti)} \times 0.82 + \mu_{(gauche)} \times 0.18$$

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

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

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

(*ii*)

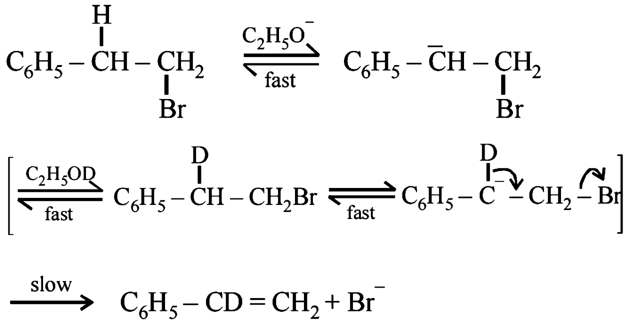


F. Match the Following

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) → E2 and (D) → 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)→E1 and first order reaction.

NOTE THIS STEP : Reaction of $C_6H_5CH_2CH_2Br$ on treatment with $C_2H_5O^-$ in presence of C_2H_5OD gives $C_6H_5CD{=}CH_2$. This reaction follows E1CB (Elimination unimolecular conjugate base) mechanism. This 2 step mechanism follows the following path :

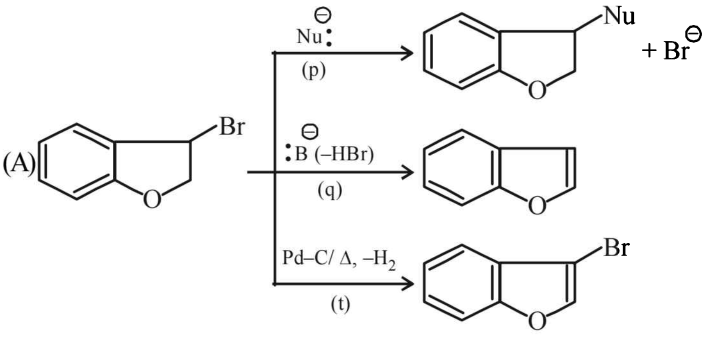


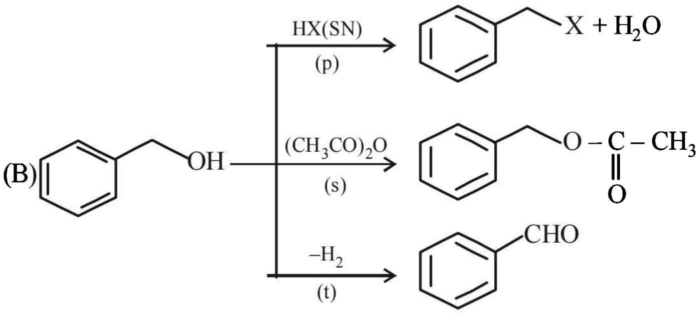
(formation of carbanion and elimination of Br from carbanion)

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) → (r), (s).

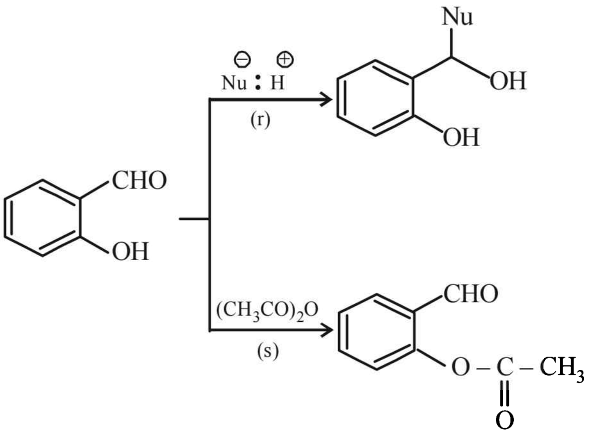
2. **(A) - p, q, s; (B) - q; (C) - q, r, s; (D) - q, r**
   - (A) C_6H_5CHO forms ppt. of 2, 4-dibromophenylhydrazone **(p)**, forms silver mirror with ammonical silver nitrate – Tollen's reagent **(q)**, forms cyanohydrin with CN^- **(s)**.
   - (B) $CH_3C \equiv CH$ gives ppt. with $AgNO_3$ **(q)**
   - (C) CN^- reacts with $AgNO_3$ to form ppt. of AgCN **(q)**, it is a nucleophile **(r)** and forms cyanohydrin **(s)**
   - (D) I^- gives ppt. of AgI with $AgNO_3$ **(q)**, and it is a nucleophile **(r)**

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

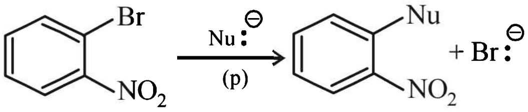




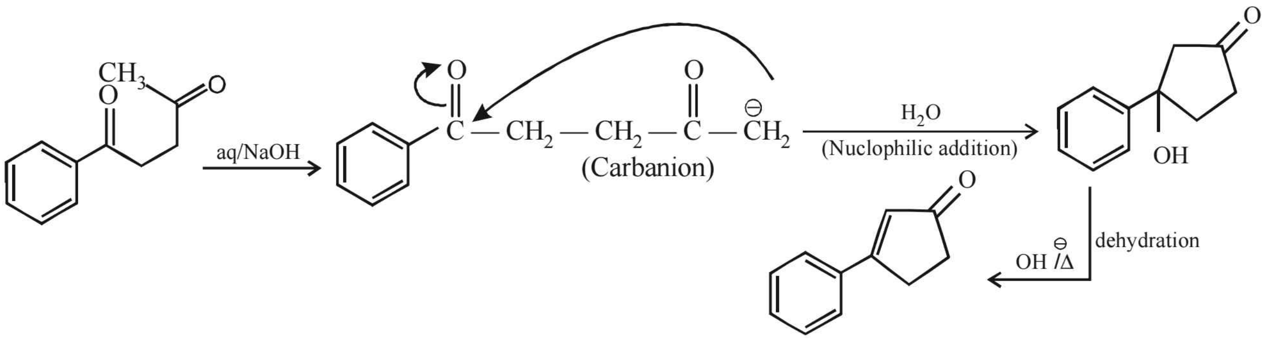
(C)



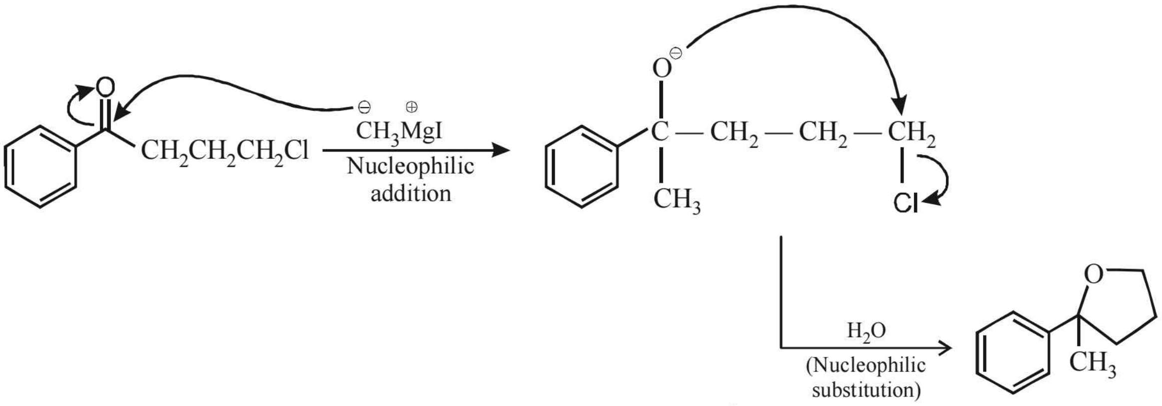
(D)



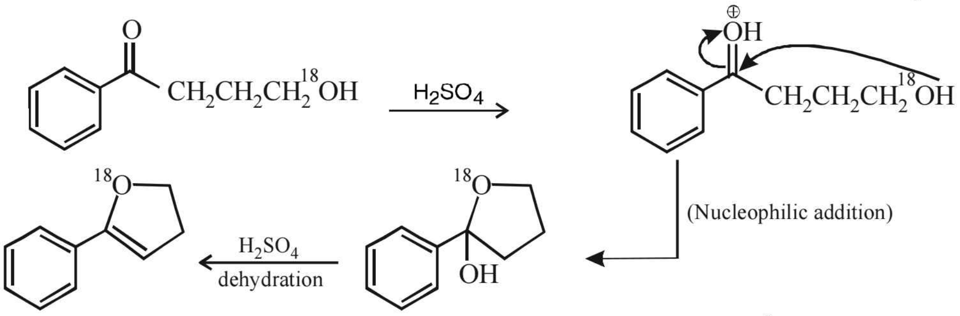
4. **A – r, s, t ; B – p, s ;C - r, s; D – q, r**



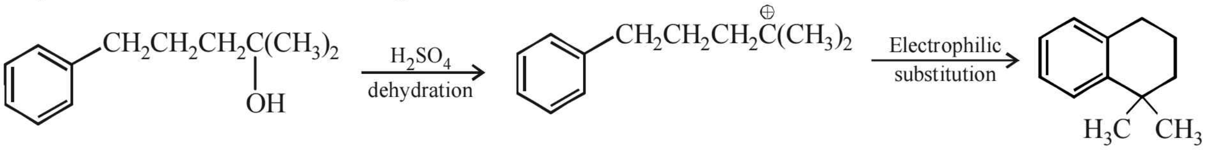
(B)



(C)



(D)

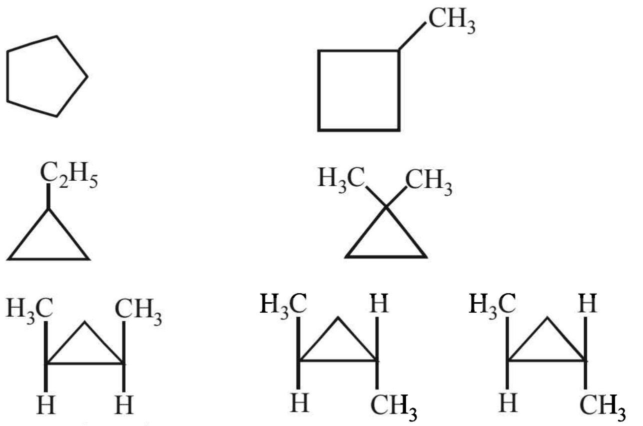


H. Assertion & Reason Type Questions

1. **(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.
2. **(a)** Due to +M effect of $-\ddot{O}H$, its intermediate carbocation is more stable than the one in benzene.
3. **(c)** Statement-1 is correct. Statement-2 is incorrect because compound can be chiral even in the absence of chiral atoms.

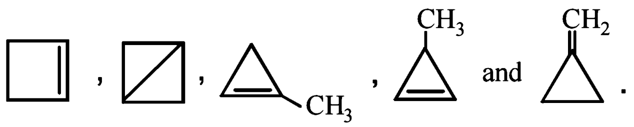
I. Integer Value Correct Type

1. The seven possible cyclic structural and stereoisomers are

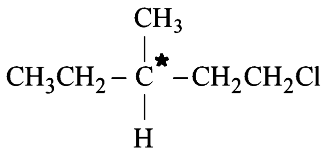


cis, (*meso*) *trans*, enantiomers

2. The number of cyclic isomers for a hydrocarbon with molecular formula C_4H_6 is 5.
The structures are

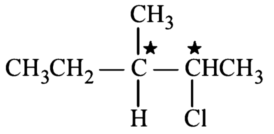


3. **8**



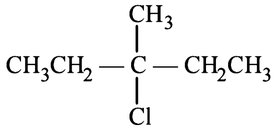
$$CH_3CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C^{\star}}}-CH_2CH_2Cl$$

Enantiomeric pair = 2



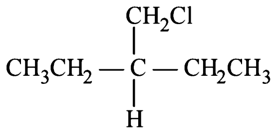
$$CH_3CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C^{\star}}}-\underset{\displaystyle Cl}{\overset{\star}{C}}HCH_3$$

Two enantiomeric pairs = 4



$$CH_3CH_2-\underset{\displaystyle Cl}{\overset{\displaystyle CH_3}{C}}-CH_2CH_3$$

= 1

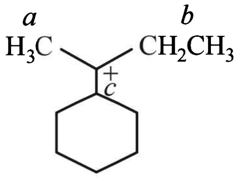


$$CH_3CH_2-\underset{\displaystyle H}{\overset{\displaystyle CH_2Cl}{C}}-CH_2CH_3$$

= 1

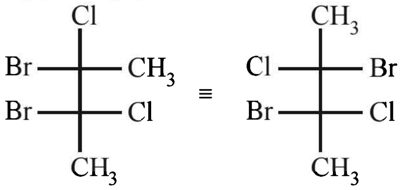
Total = 2 + 4 + 1 + 1 = 8

4. **6**

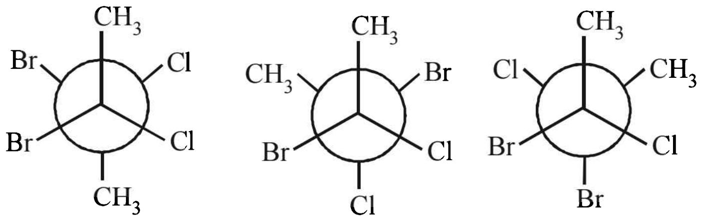


a = 3 Hyperconjugative H's
b = 2 Hyperconjugative H's
c = 1 Hyperconjugative H

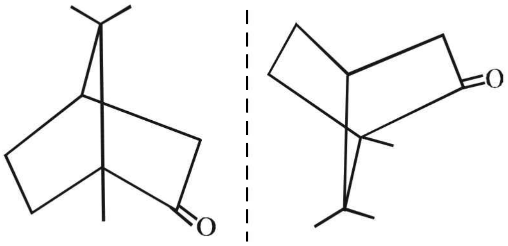
5. **(3)**



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



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



Section-B JEE Main/ AIEEE

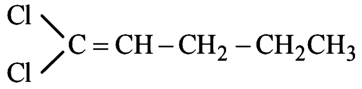
1. **(b)** $-CH_3$ group has $+I$ effect, as number of $-CH_3$ group increases, the inductive effect increases. Therefore the correct order is

$$CH_3-CH_2- < (CH_3)_2CH- < (CH_3)_3C-$$

2. **(c)** Sterioisomerism involve those isomers which contain same ligands in their co-ordination spheres but differ in the arrangement of these ligands in space. Stereo-isomerism is of two type geomerical isomerism and optical isomerism. In geomerical isomerism ligands occupy different positions around the central metal atom or ion.

NOTE : In optical isomerism isomers have same formula but differ in their ability to rotate directions of the plane of polarised light.

3. **(c)**

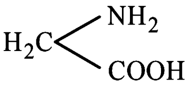


$$Cl_2C=CH-CH_2-CH_2CH_3$$

does not show geometrical isomerism due to presence of two similar Cl atoms on the same C-atom. Geometrical isomerism is shown by compounds in which the groups/atoms attached to $C=C$ are different.

4. **(d)** Amino acids contain $-NH_2$ and $-COOH$ groups e.g

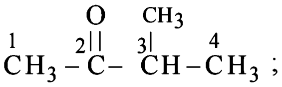
Glycine



$$H_2C(NH_2)COOH$$

5. **(c)** The correct name is 3 - methylbut - 2 - ol

6. **(c)**



$$\overset{1}{CH_3}-\overset{2}{C}(=O)-\overset{3}{CH}(CH_3)-\overset{4}{CH_3};$$

3- methyl-2-butanone

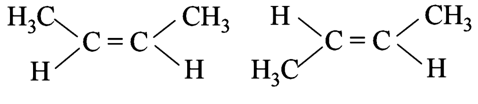
7. **(b)** In molecules (a), (c) and (d), the carbon atom has a multiple bond, only (b) has sp^3 hybridization.

8. **(d)** A mixture of equal amount of two enantiomers is called a racemic mixture. A racemic mixture does not rotate plane–polarized light. They are optically inactive because for every molecule in a racemic mixture that rotate plane of polarized light in one direction, there is a mirror image molecule that rotates the plane in oppsite direction.

9. **(d)** **TIPS/Formulae :**

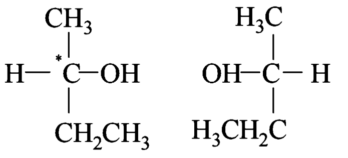
Stereoisomerism is of two types i.e., geometrical isomerism and optical isomerism

Both the structures shows sterioisomerism. Structure I shows geometrical isomerism as it contains two different atoms(H) and groups (CH_3) attached to each carbon containing double bond.



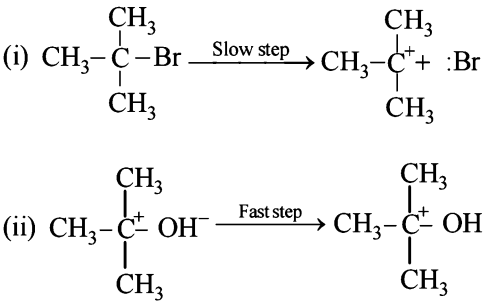
Cis butene *Trans* butene

Structure II shows optical isomerism as it contains a chiral carbon (attached to four different group) atom.



butyl alcohol (Two enantiomers)

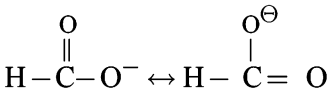
10. **(b)** The hydrolysis of t-butyl bromide is an example of S_N1 reaction. The reaction consists of two steps.



$$\text{(i)}\ CH_3-C(CH_3)_2-Br \xrightarrow{\text{Slow step}} CH_3-\overset{+}{C}(CH_3)_2 + :Br$$

$$\text{(ii)}\ CH_3-\overset{+}{C}(CH_3)_2\ OH^- \xrightarrow{\text{Fast step}} CH_3-C(CH_3)_2-OH$$

11. **(d)** $HCOO^-$ exists in following resonating structures

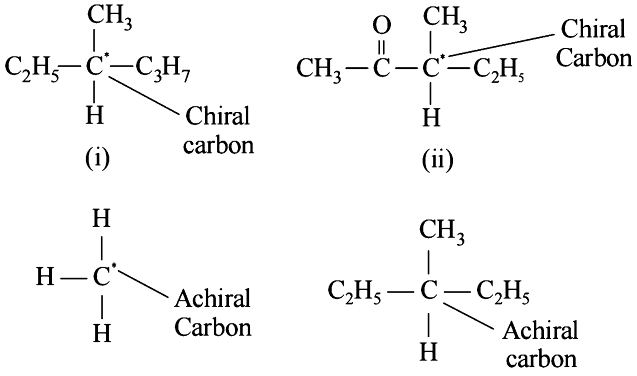


$$H-\overset{O}{\overset{\|}{C}}-O^- \leftrightarrow H-\overset{O^\ominus}{\overset{|}{C}}=O$$

Hence in it both the carbon oxygen bonds are found equal.

12. **(a)** $C_nH_{2n}O_2$ is general formula for carboxylic acid

13. **(a)**

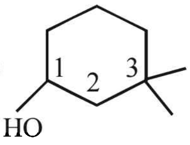


14. **(d)** **NOTE :** Among isomeric alkanes, the straight chain isomer has higher boiling point than the branched chain isomer. The greater the branching of the chain, the lower is the boiling point. Further due to the presence of π electrons, these moleculs are slightly polar and hence have higher boiling points than the corrosponding alkanes.

Thus B.pt. follows the order

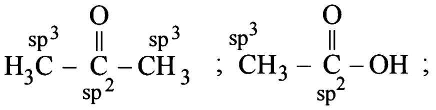
alkynes > alkene > alkanes (straight chain) > branched chain alkanes.

15. (a)



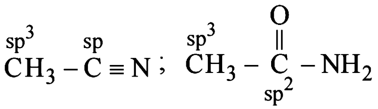
IUPAC name – 3, 3-Dimethyl -1 cyclohexanol

16. (a)



$$\overset{sp^3}{H_3C}-\overset{O}{\underset{sp^2}{\overset{\|}{C}}}-\overset{sp^3}{CH_3}\ ;\ \overset{sp^3}{CH_3}-\overset{O}{\underset{sp^2}{\overset{\|}{C}}}-OH\ ;$$

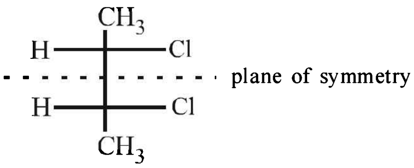
Acetone Acetic acid



$$\overset{sp^3}{CH_3}-\overset{sp}{C}\equiv N\ ;\ \overset{sp^3}{CH_3}-\overset{O}{\underset{sp^2}{\overset{\|}{C}}}-NH_2$$

Acetonitrile Acetamide

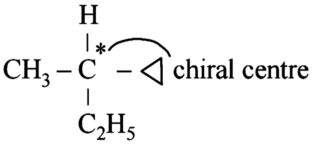
17. (b) **NOTE :** The compounds containing two similar assymmetric C-atoms have plane of symmetry and exist in Meso form.



Meso 2, 3 dichlorobutane

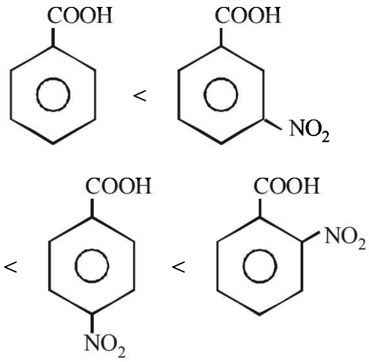
18. (c) Cl^- is the best leaving group among the given option.

19. (a) Only 2- cylcopropyl butane has a chiral centre.



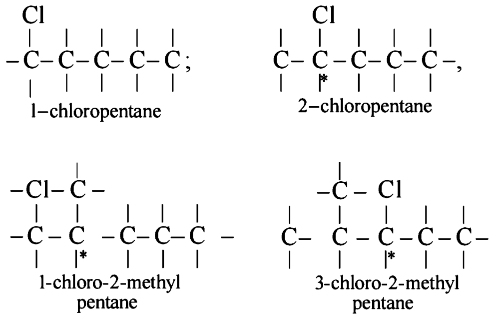
20. (d) In aromatic acids presence of electron withdrawing substituent e.g. $-NO_2$ disperses the negative charge of the anion and stablises it and hence increases the acidity of the parent benzoic acid.

Further *o*-isomer will have higher acidity than corresponding *m* and *p* isomers. Since nitro group at *p*-position have more pronounced electron withdrawing than $-NO_2$ group at *m*-position hence the correct order is the one given above.



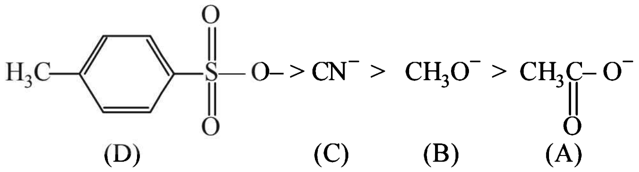
21. (d) Lone pair of electrons present on the nitrogen of benzyl amine is not involved in resonance.

22. (c) 1-chloropentane is not chiral while others are chiral in nature

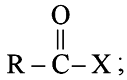


23. (d) Free radicals are electrically neutral, unstable and very reactive on account of the presence of odd electrons.

24. (a) In moving down a group, the basicity and nucleophilicity are inversely related, *i.e.* nucleophilicity increases while basicity decreases. In going from left to right across a period, the basicity and nucleophilicity are directly related. Both of the characteristics decrease as the electronegativity of the atom bearing lone pair of electrons increases. If the nucleophilic centre of two or more species is same, nucleophilicity parallels basicity, *i.e.* more basic the species, stronger is its nucleophilicity. Hence based on the above facts, the correct order of nucleophilicity will be

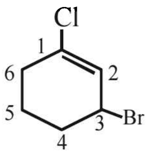


25. (d)



$R-\overset{O}{\overset{\|}{C}}-X$; when X is Cl the C–X bond is more polar and ionic which leaves the compound more reactive for nucleophilic substitution reaction.

26. (a)



3-bromo-1chlorocyclohexene

27. (b) The order of stability of free radicals

$$(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H$$

The stabilisation of first two is due to resonance and last two is due to inductive effect.

28. (c) **TIPS/Formulae :**

The stronger the acid, the weaker the conjugate base formed.

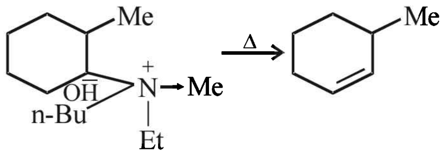
The acid character follows the order :

$$CH_3COOH > C_6H_5OH > H_2O > CH_3OH$$

The basic character will follow the order

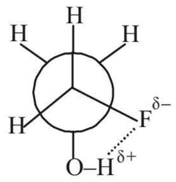
$$CH_3COO^- < C_6H_5O^- < O^-H < CH_3O^-$$

29. **(b)** **Hofmann's rule :** When theoretically more than one type of alkenes are possible in eliminations reaction, the alkene containing least alkylated double bond is formed as major product. Hence



NOTE : It is less stearically β-hydrogen is removed

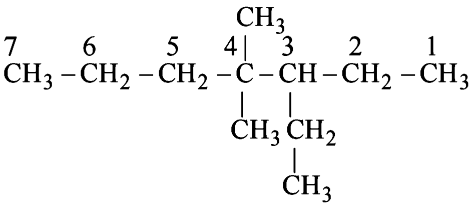
30. **(a)**



Due to hydrogen bonding between H & F gauche conformation is most stable hence the correct order is

Eclipse, Anti, Gauche

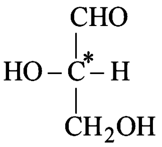
31. **(a)**



$$\overset{7}{CH_3}-\overset{6}{CH_2}-\overset{5}{CH_2}-\overset{4}{C}(CH_3)_2-\overset{3}{CH}(CH_2CH_3)-\overset{2}{CH_2}-\overset{1}{CH_3}$$

3–ethyl –4,4–dimethyl heptane

32. **(b)** **NOTE :** The organic compounds which have chiral carbon atom (a carbon atom attached to four different group or atoms and do not have plane of symmetry rotate plane polarised light.

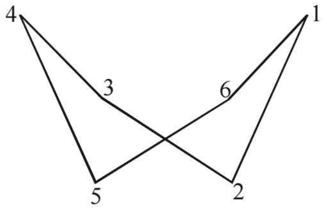


$$HO-\underset{CH_2OH}{\overset{CHO}{C^*}}-H$$

(* is asymmetric carbon)

33. **(a)** Nitro group is electron withdrawing group, so it deactivates the ring towards electrophilic substitution.

34. **(b)** Chiral conformation will not have plane of symmetry. Since twist boat does not have plane of symmetry it is chiral.

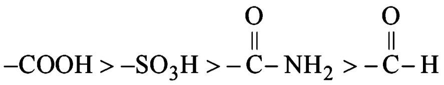


35. **(b)** The absolute configuration is (R, R)
(using priority rules to get the absolute configuration)
So the correct answer is (b)

36. **(b)** In option (b) the complex formed is with benzene where as in other cases it is formed with nitrobenzene with $-NO_2$ group in different position (o-, m-, p-). The complex formed with nitrobenzene in any position of $-NO_2$ group is less stable than the complex formed with benzene so the correct answer is (b)

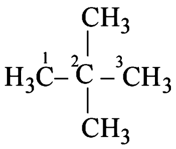
NOTE : The most stable complex has lowest energy.

37. **(a)** The correct order of priority for the given functional group is



$$-COOH > -SO_3H > -\overset{\overset{O}{\|}}{C}-NH_2 > -\overset{\overset{O}{\|}}{C}-H$$

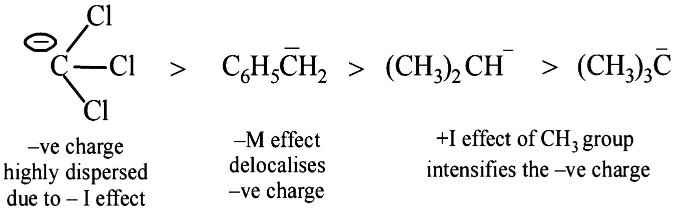
38. **(a)**



$$H_3\overset{1}{C}-\underset{CH_3}{\overset{CH_3}{\overset{2}{C}}}-\overset{3}{C}H_3$$

Neopentane
or 2,2- Dimethylpropane

39. **(b)**



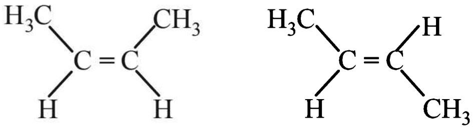
$$\overset{\ominus}{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2CH^- > (CH_3)_3\bar{C}$$

–ve charge highly dispersed due to – I effect

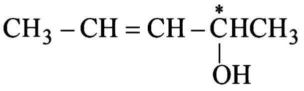
–M effect delocalises –ve charge

+I effect of CH_3 group intensifies the –ve charge

40. **(b)**



41. **(b)**



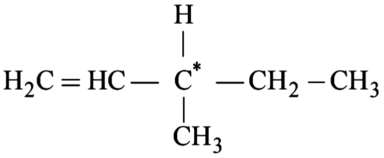
$$CH_3-CH=CH-\underset{OH}{\overset{*}{C}}HCH_3$$

exhibits both geometrical as well as optical isomerism.

cis - R	*cis* - S
trans - R	*trans* - S

42. **(d)** The correct order of basicity is
$RCOO^- < CH \equiv C^- < NH_2 - < R^-$

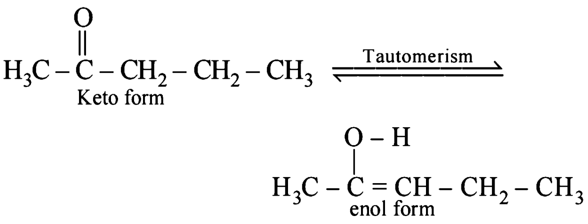
43. **(c)** For a compound to show optical isomerism, presence of chiral carbon atom is a necessary condition.



$$H_2C=HC-\underset{CH_3}{\overset{H}{C^*}}-CH_2-CH_3$$

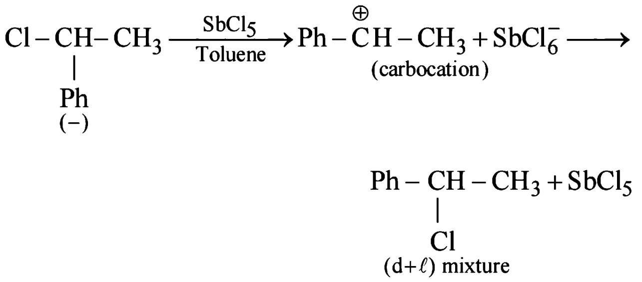
3- methyl-1-pentene

44. **(c)**



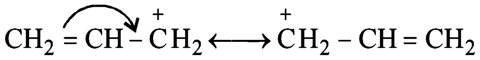
$$\underset{\text{Keto form}}{H_3C-\overset{\overset{\large O}{||}}{C}-CH_2-CH_2-CH_3} \xrightleftharpoons{\text{Tautomerism}} \underset{\text{enol form}}{H_3C-\overset{\overset{O-H}{|}}{C}=CH-CH_2-CH_3}$$

45. **(c)**



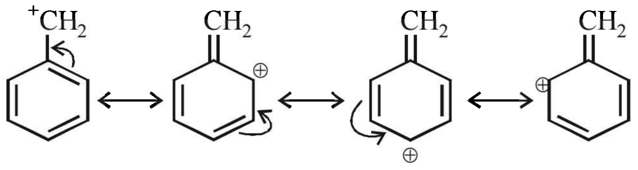
$$\underset{\underset{(-)}{Ph}}{Cl-\underset{|}{CH}-CH_3} \xrightarrow[\text{Toluene}]{SbCl_5} \underset{\text{(carbocation)}}{Ph-\overset{\oplus}{C}H-CH_3}+SbCl_6^- \longrightarrow \underset{(d+\ell)\text{ mixture}}{Ph-\underset{\underset{Cl}{|}}{CH}-CH_3}+SbCl_5$$

46. **(d)** Higher stability of allyl and aryl substituted methyl carbocation is due to dispersal of positive charge due to resonance



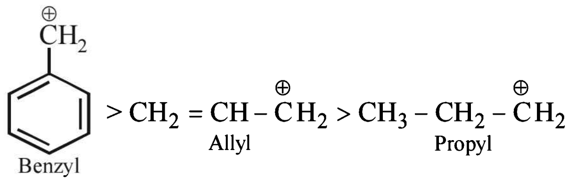
$$CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$$

Resonating structures of allyl carbocation



Resonating structures of benzyl carbocation

whereas in alkyl carbocations dispersal of positive charge on different hydrogen atoms is due to hyper conjugation hence the correct order of stability will be



$$\underset{\text{Benzyl}}{C_6H_5\overset{\oplus}{C}H_2} > \underset{\text{Allyl}}{CH_2=CH-\overset{\oplus}{C}H_2} > \underset{\text{Propyl}}{CH_3-CH_2-\overset{\oplus}{C}H_2}$$

47. **(b)** $\% \text{ of } N = \dfrac{1.4 \times \text{meq. of acid}}{\text{mass of organic compound}}$

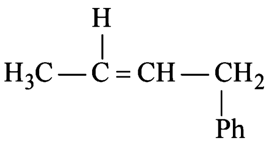
$$\text{meq. of } H_2SO_4 = 60 \times \frac{M}{10} \times 2 = 12$$

$$\text{meq. of NaOH} = 20 \times \frac{M}{10} = 2$$

$$\therefore \text{ meq. of acid consumed} = 12 - 2 = 10$$

$$\therefore \% \text{ of } N = \frac{1.4 \times 10}{1.4} = 10\%$$

48. **(c)**



$$H_3C-\overset{\overset{H}{|}}{C}=CH-\underset{\underset{Ph}{|}}{CH_2}$$

1- Phenyl-2-butene the two groups around each of the doubly bonded carbon

Because, all are different. This compound can show *cis*-and *trans*-isomerism.

49. **(c)** Mass of substance = 250 mg = 0.250 g

Mass of AgBr = 141 mg = 0.141 g

1 mole of AgBr = 1 g atom of Br

188 g of AgBr = 80 g of Br

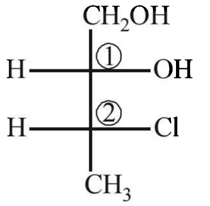
∴ 188 g of AgBr contain bromine = 80 g

$$0.141 \text{ g of AgBr contain bromine} = \frac{80}{188} \times 0.141$$

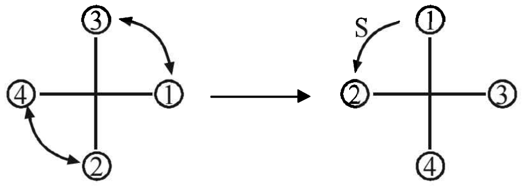
This much amount of bromine present in 0.250 g of organic compound

$$\therefore \% \text{ of bromine} = \frac{80}{188} \times \frac{0.414}{0.250} \times 100 = 24\%$$

50. **(d)**

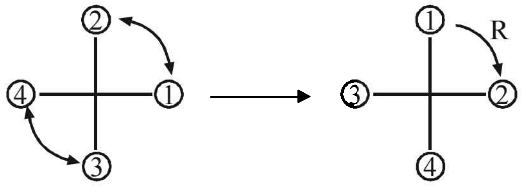


At (1),



It is 'S' configurated

At. (2),



It is 'R' configurated.

51. **(b)** Spent-lye and glycerol are separated by distillation under reduced pressure.

Under the reduced pressure the liquid boil at low temperature and the temperature of decomposition will not reach. e.g. glycerol boils at 290°C with decomposition but at reduced pressure it boils at 180° C without decomposition.