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

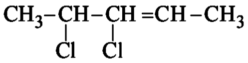
B **1.** F **2.** F **3.** F **4.** T

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)

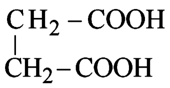
Section-A JEE Advanced/ IIT-JEE

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°.

$$d=\frac{1}{2}\left(109°28'-60°\right).$$

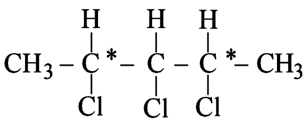
4. sp^3
5. **vicinal, adjacent** (or stable, different).
6. **non-superimposable, enantiomers;**
7. ***sp*;**
8. **Hyperconjugation;**
9. **Butane-1, 4-dioic acid;** Succinic acid has the formula.



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

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.

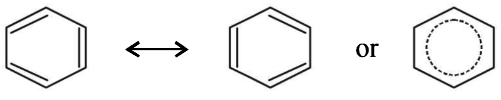


$$\mathrm{CH_3-\underset{Cl}{\overset{H}{C}}{}^{*}-\underset{Cl}{\overset{H}{C}}-\underset{Cl}{\overset{H}{C}}{}^{*}-CH_3}$$

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

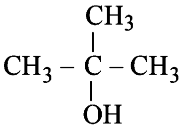
2. (a) **TIPS/Formulae :**
The bond length decreases in the order.

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

On the basis of the size of the hybrid orbitals, *sp* orbital should form the shortest and *sp³* orbital the longest bond with other atom.

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

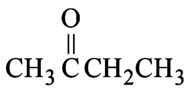
$n\text{-}C_3H_7OCH_3$, *n*-Propylmethylether ,



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

2-Methylpropan-2-ol

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



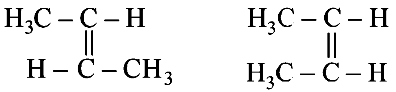
$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3}$$

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

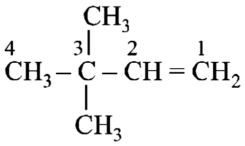
6. (a) **TIPS/Formulae :**
cis-trans – Isomerism is due to restricted rotation either due to carbon-carbon double bond or due to cyclic structure.
NOTE : Geometrical Isomerism : *The isomers which possess the same structural formula but differ in the spatial arrangement of the groups* **around the double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



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

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

7. (c)

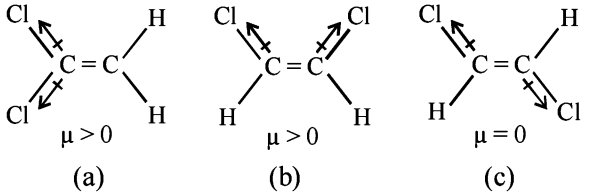


$$\overset{4}{\mathrm{CH_3}}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\overset{3}{\mathrm{C}}}}-\overset{2}{\mathrm{CH}}=\overset{1}{\mathrm{CH_2}}$$

3, 3-dimethylbut-1-ene

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

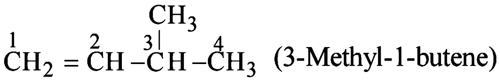
9. (c)



[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)

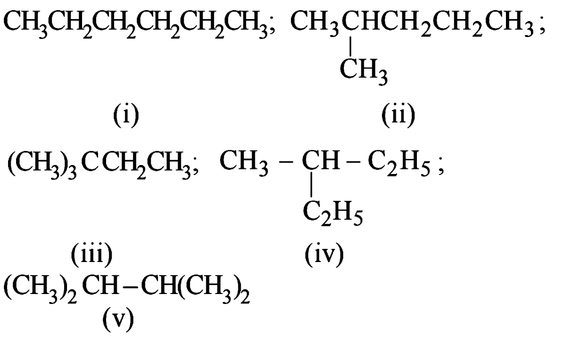
12. (b) **TIPS/Formulae :**

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}.



$CH_3CH_2CH_2CH_2CH_2CH_3$; $CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2CH_3$;
(i) (ii)

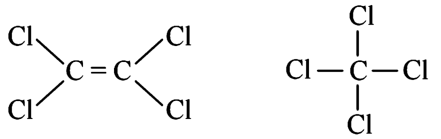
$(CH_3)_3CCH_2CH_3$; $CH_3-\underset{C_2H_5}{\underset{|}{C}}H-C_2H_5$;
(iii) (iv)

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

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

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

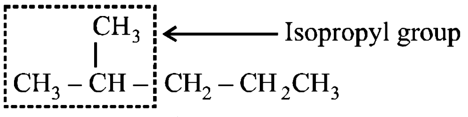
Tetrachloroethene being an alkene has sp^2 hybridised C-atoms and hence the Cl – C – Cl angle is 120°, whereas in tetrachloromethane, carbon is sp^3 hybridised, so the angle is 109°.28'.



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;

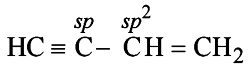
No of π bonds = 1 + 2 = 3

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:**

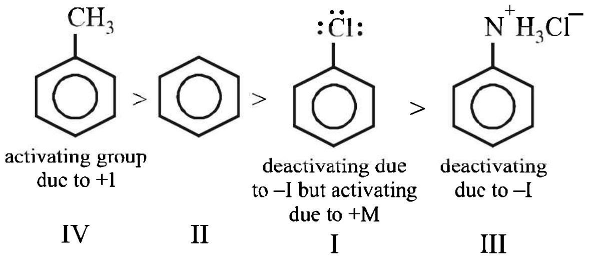
A compound which consists of at least one asymmetric carbon atom is capable of showing the phenomenon of optical isomerism.

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

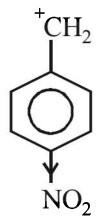
The above structure of allyl isocyanide clearly shows 5 C – H(σ), 2 C – C(σ), 1C – N(σ), 1N – C(σ), 1C – C(π), 2N– C (π) bonds, *i.e.*, 9σ and 3π bonds in all. There are 2 non-bonded electrons on the C-atom (co-ordinate bond between N and C, the electron pair of N is shifted towards C).

24. (c)

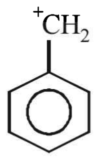


25. (d) TIPS/Formulae :

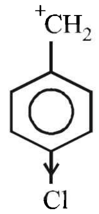
The stability of carbonium ion is influenced by both resonance and inductive effect.



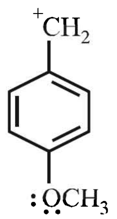
NO_2 intensifies +ve charge on benzyl cation due to –I and –M effects



Benzyl stable due to resonance



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

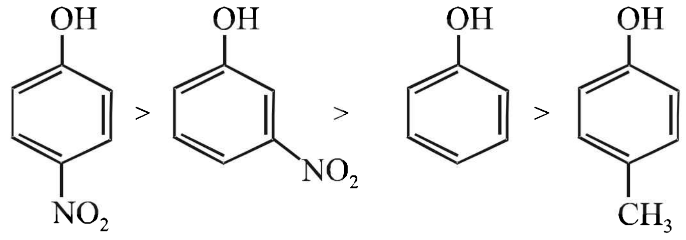


Positive charge of benzyl cation is more dispersed due to +M effect of the $-OCH_3$ group

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



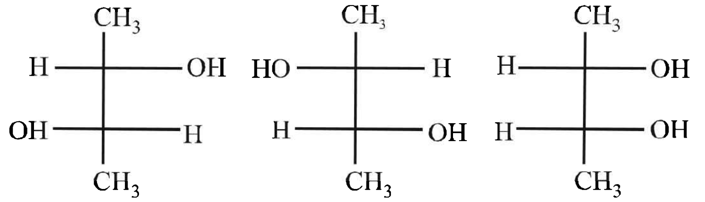
(IV) (III) (I) (II)

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) $\overset{1}{C}H_2 = \underset{sp^2}{\overset{2}{C}}H - \underset{sp^3}{\overset{3}{C}}H_2 - \overset{4}{C}H_2 - \overset{5}{C} \equiv \overset{6}{C}H$ (with sp^2 under C-1)

30. (c) TIPS/Formulae :

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

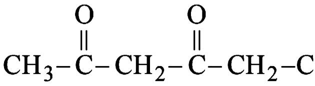
31. (a) $PhCH_2CH{=}CHCH_3$ will exhibit geometrical isomerism because in others one of the doubly bonded carbon atom has two similar groups.

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

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

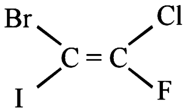
33. (d) Rate of reaction will be R – I > R – Br > R – Cl > R – F. because I^- is the best, while F^- is the poorest leaving groups among halide ions.

34. (b) In

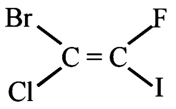


$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-CH_3$, $-CH_2-$ group is flanked on both sides by electron- withdrawing groups and hence its hydrogens are most acidic. Once a carbanion is formed, it is stabilised due to resonance.

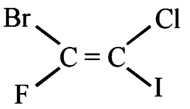
35. (d) Number of isomers (six) can be derived by keeping the position of any one halogen (say Br) fixed and changing the position of the other halogen one by one.



(Z and E)



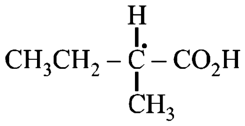
(Z and E)



(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



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

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

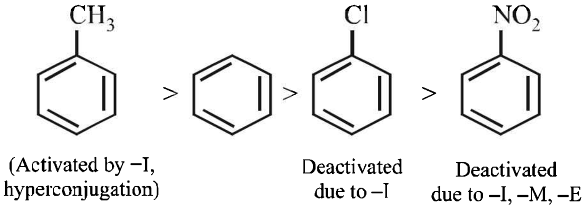
(i) The inductive effect decreases with increase in distance of halogen atom from the carboxylic group and hence the strength of acid proportionally decreases.

(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 $-COOH$.

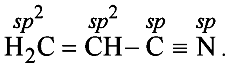
39. **(b)** In carboxylic acids, molecules are more strongly associated followed by alcohols.

40. **(c)**



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

42. **(a)**



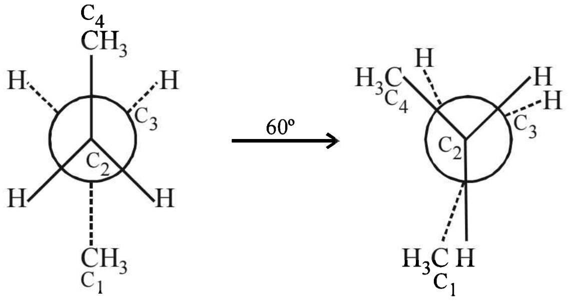
$\overset{sp^2}{H_2C} = \overset{sp^2}{CH} - \overset{sp}{C} \equiv \overset{sp}{N}$.

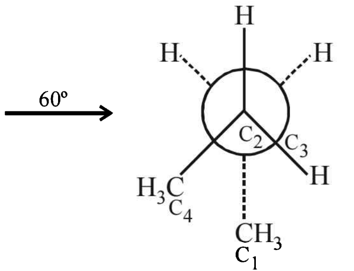
43. **(a)** **NOTE :** Dipole moment is a vector quantity.

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 :**

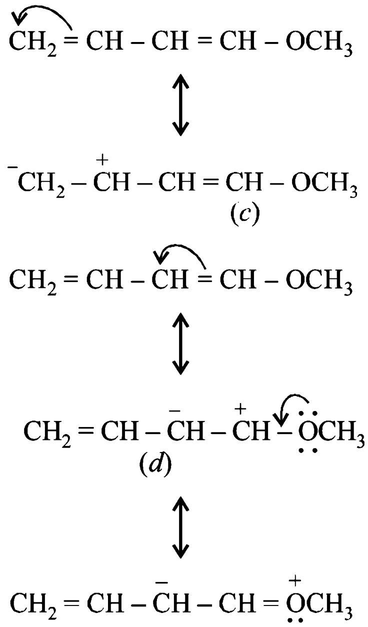
Any conformation between two extreme positions i.e. eclipsed and staggered is known as Gauche or Skew form.





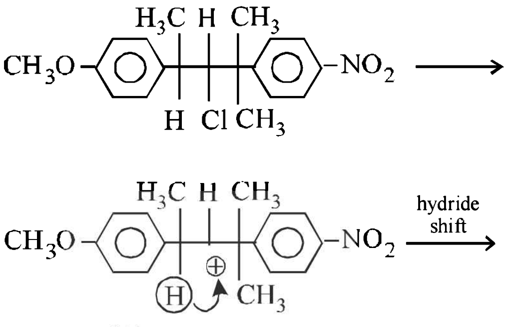
(Gauche conformation)

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.

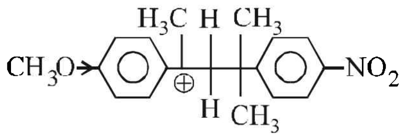


$$CH_2 = CH - CH = CH - OCH_3$$
$$\updownarrow$$
$${}^{-}CH_2 - \overset{+}{C}H - CH = CH - OCH_3$$
(*c*)
$$CH_2 = CH - CH = CH - OCH_3$$
$$\updownarrow$$
$$CH_2 = CH - \overset{-}{C}H - \overset{+}{C}H - \underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}CH_3$$
(*d*)
$$\updownarrow$$
$$CH_2 = CH - \overset{-}{C}H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

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

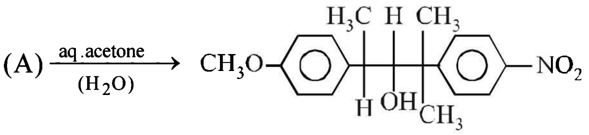


(A) 2° Carbocation

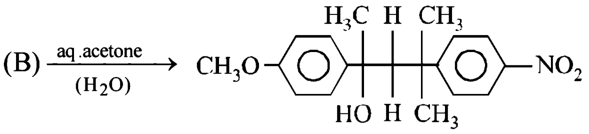


(B) 3° Carbocation; more stable; (positive charge is dispersed due to +M effect of $-OCH_3$)

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



(i)



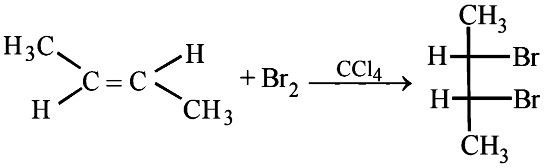
(ii)

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

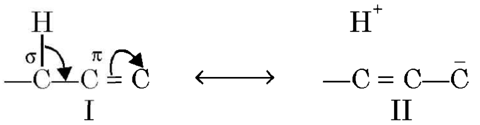
48. (b) The ring to which –NH group is attached is activated due to the lone pairs on N (+M and +E effects); while the ring to which –C = O is attached is deactivated. Hene, the electrophile would go to the *para*-position of the activated ring.

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.



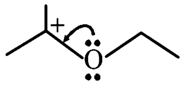
51. (b) Alkyl groups with at least one hydrogen atom on the α-carbon atom, attached to an unsaturated carbon atom, are able to release electrons in the following way.



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**

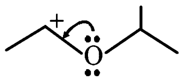
52. (d) The correct stability order is

I > III > II > IV



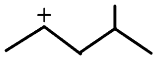
I

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



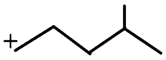
III

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



II

5 hyper conjugative CO – H's 2 R groups

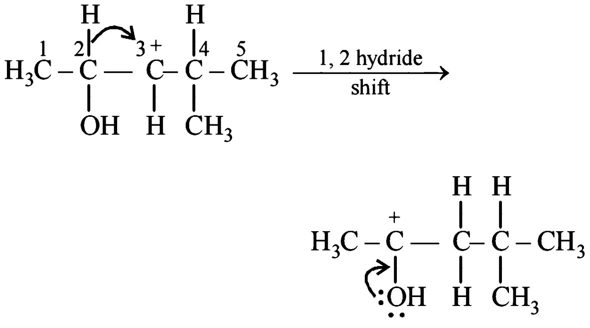


IV

5 hyperconjugative H's one R groups

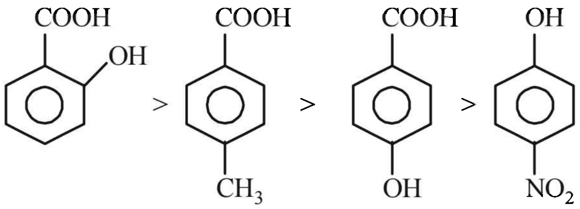
53. (b) – CN has highest priority. Further the sum of locants is 7 in (b) and 9 in (d).

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).

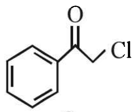
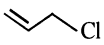
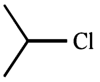


More stable carbocation

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



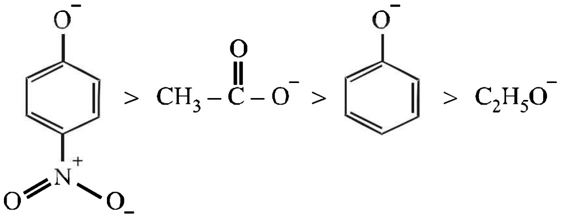
56. (b)

Compounds		: CH_3-Cl :	 :	
	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.

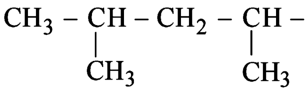
2. **(a, c)** Higher the stability of the corresponding anion, more will be the acidic character of the parent compound.



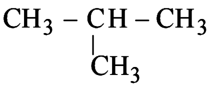
Higher stability of acetate ions than phenoxide ion is due to equivalent resonating structures in the former

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) :  $CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_2-\underset{CH_3}{\underset{|}{C}}H-CH_3$ 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) :  $CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_3$ 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.

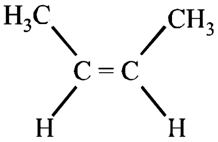
Acidic strength of acids,

$HOH > CH \equiv CH > NH_3 > CH_3.CH_3$

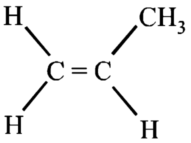
Hence the order of strength of bases,

$CH_3CH_2^- > NH_2^- > CH \equiv C^- > OH^-$

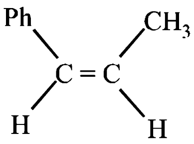
7. **(a, c)**



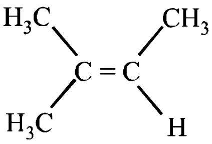
2-butene (*a*) ;



propene (*b*) ;



1-phenylpropene (*c*) ;



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

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

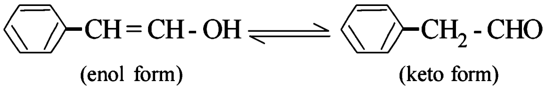
8. **(d)** Order of acidic strength

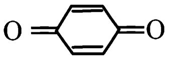
$CH_3OH > CH \equiv CH > C_6H_6 > C_2H_6$; CH_3OH is most acidic because O is more electronegative than C and capable of accommodating negative charge in CH_3O^- Although alcohols are neutral towards the litmus paper.

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

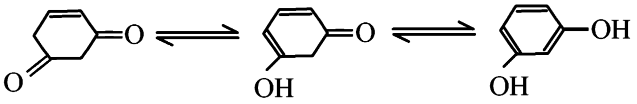
For a carbonyl compound to show tautomerism, it must have at least one H at the α – carbon atom.

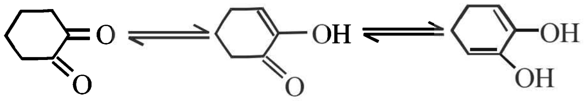
(a), (c) and (d) show tautomerism.





Tautomerism is not possible





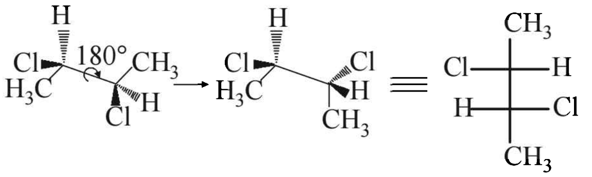
10. **(b,c,d)** **NOTE :** An aromatic species will have :

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

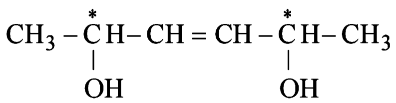
11. **(b,c,d)** E and F ; and also E and G differ in position of atom (H), so these are tautomers (not resonating structures. Geometrical isomers are also diastereomers).

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

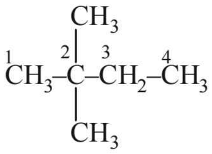
13. **(a,d)**  $CH_3-\underset{OH}{\underset{|}{\overset{*}{C}}}H-CH=CH-\underset{OH}{\underset{|}{\overset{*}{C}}}H-CH_3$

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*

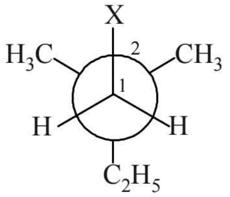
Enantiomers	I and II (*cis*); IV and V (*trans*)
Diastereomers	I (or II), III (or IV), V and VI
Meso	III and IV

14. **(b, d)**

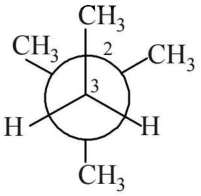
Structural formula of 2, 2-dimethylbutane is



(I) Newman projection using C_1–C_2 bond



(II) Newman projection using C_3–C_2 bond

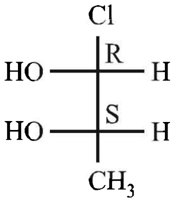


16. **(b, c)**

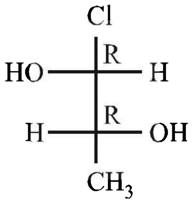
b and c, being antiaromatic, are unstable at room temperature.

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

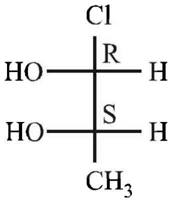
Converting all the structures in the Fischer projection



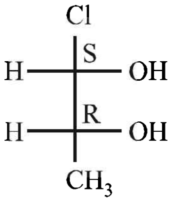
M



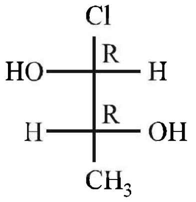
N



O



P



Q

M and N are diastereoisomers

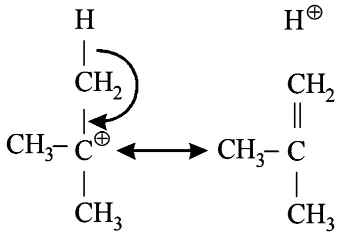
M and O are identical

M and P are enantiomers

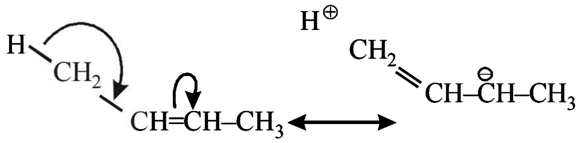
M and Q are diastereoisomers

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 $\sigma \rightarrow \pi^*$ bond.

E. Subjective Problems

1. (*i*) **TIPS/Formulae :**

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

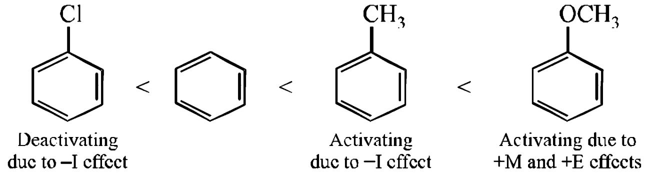
$C_2H_5COCH_3 < CH_3COCH_3 < CH_3CHO < HCHO$

(*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

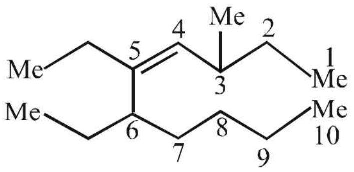
IV < II < V < III < I

(*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

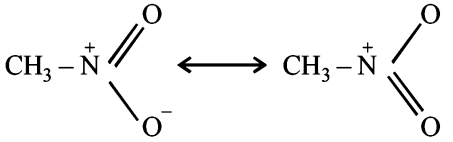
(*ii*)



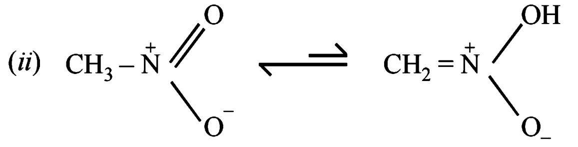
5, 6-diethyl-3-methyl-4-decene

(*iii*) IUPAC name is 3–(N, N-dimethylamino)–3–methylpentane.

3. (*i*)



(*ii*)

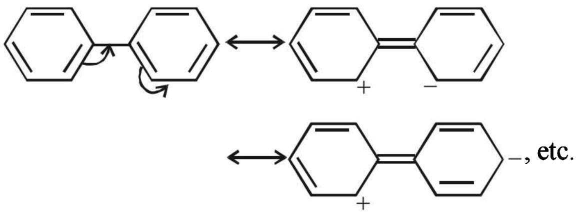


(*nitro* form) (*aci*-form)

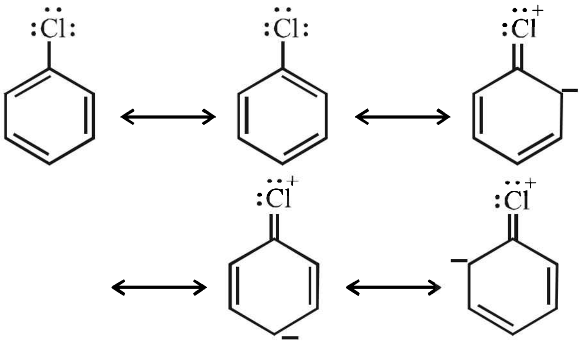
4. (*i*) In formic acid, resonance is not possible with the result there are two types of C – O bonds. In sodium formate, resonance is possible, so both of the C – O bonds have same bond length.

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.

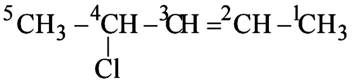


Resonating structures of chlorobenzene

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.*

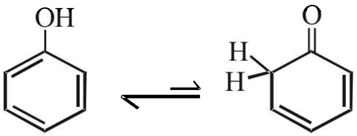
(*iv*) $CH \equiv C^-$, C^- is *sp* hybridised and more electronegative then the $\bar{C}H$ of $CH_2 = \bar{C}H$ which is sp^2 hybridised. Thus the former can better accomodate electron pair hence less basic.

(*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. 

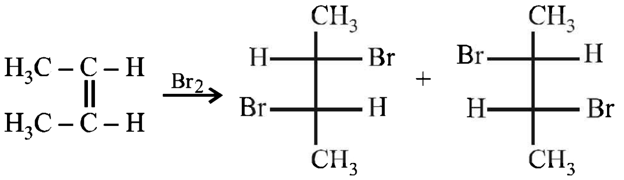
$$^5CH_3-\underset{\displaystyle Cl}{\overset{}{^4CH}}-{}^3CH={}^2CH-{}^1CH_3$$

6.



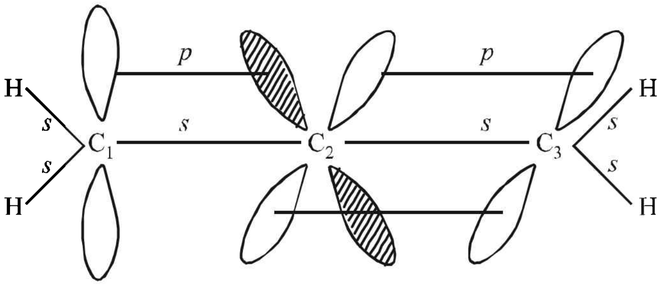
(keto) (enol)

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)

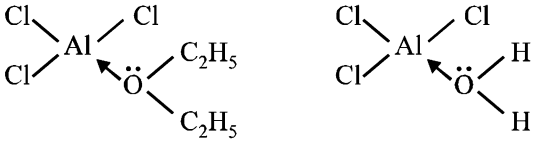


9. In order to convert a molecule with two stereogenic centres to its enantiomer, the confuguration at both centres must be reversed. Reversing the configuration at only one stereogenic centre converts it to a distereomeric structure. Thus structures I and III are enantiomers; while structures I and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

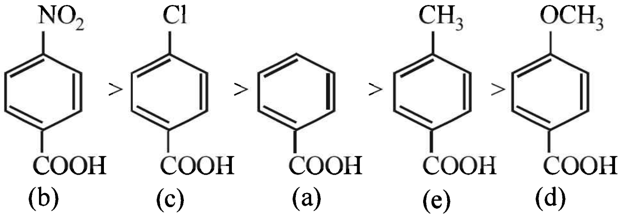
10. **TIPS/Formulae :**

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

Anyhydrous $AlCl_3$ 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.



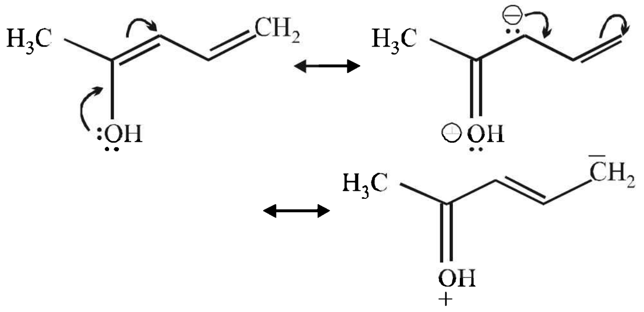
11. **NOTE :** Higher the K_a value, more stronger is the acid. Correct order of acidic strength of the given acids is



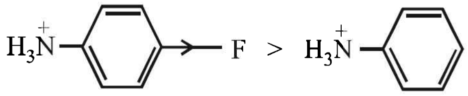
Hence the K_a values of the five acids will be in the order.

	(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}

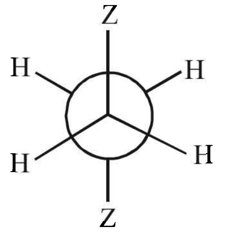
12.



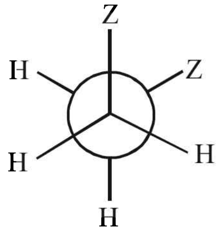
13. Presence of an electron-attracting group increases acidity of the compound. Thus



14. (*i*)



Anti conformer



Gauche conformer

Given, mole fraction of anti conformer = 0.82

$\therefore$ mole fraction of gauche conformer = 0.18

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

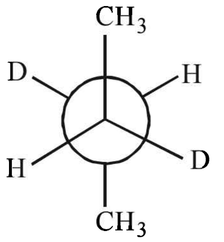
$$1=\mu_{(anti)}\times0.82+\mu_{(gauche)}\times0.18$$

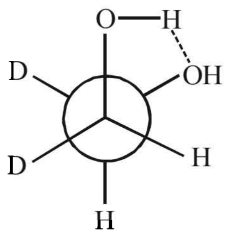
$$1=0\times0.82+\mu_{(gauche)}\times0.18\quad[\because\ \mu_{(anti)}=0]$$

$$\therefore\ 1=\mu_{(gauche)}\times0.18$$

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

(*ii*)





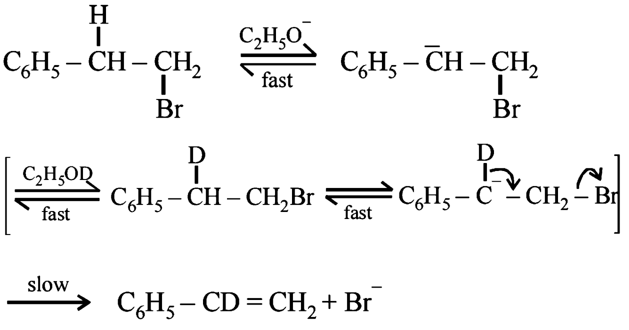
F. Match the Following

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 :



$$C_6H_5-\overset{H}{CH}-\underset{Br}{CH_2}\ \xrightleftharpoons[\text{fast}]{C_2H_5\bar{O}}\ C_6H_5-\bar{C}H-\underset{Br}{CH_2}$$

$$\left[\xleftarrow[\text{fast}]{C_2H_5OD}\ C_6H_5-\overset{D}{CH}-CH_2Br\ \xrightleftharpoons[\text{fast}]{}\ C_6H_5-\overset{D}{\bar{C}}-CH_2-Br\right]$$

$$\xrightarrow{\text{slow}}\ C_6H_5-CD=CH_2+Br^-$$

(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)**.

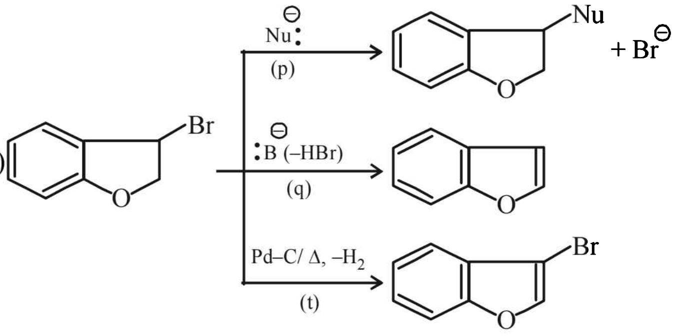
(B) $CH_3C\equiv CH$ gives ppt. with $AgNO_3$ **(q)**

(C) CN^- reacts with $AgNO_3$ to form ppt. of AgCN **(q)**, it is a nucleophile **(r)** and forms cyanohydrin **(s)**

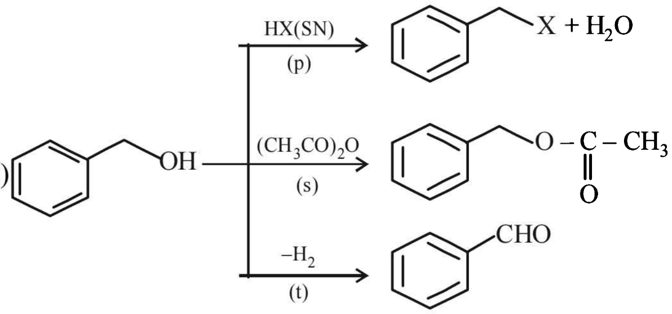
(D) I^- gives ppt. of AgI with $AgNO_3$ **(q)**, and it is a nucleophile **(r)**

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

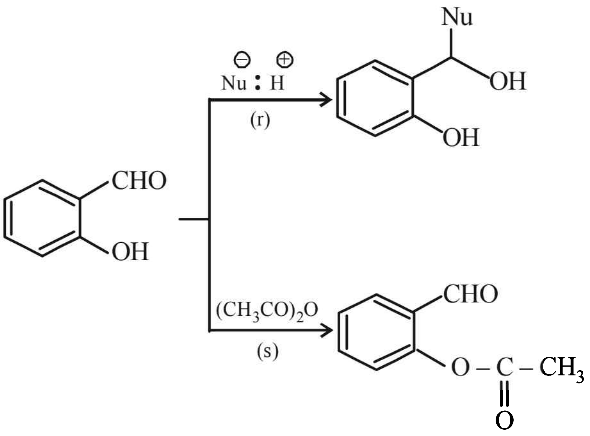
(A)



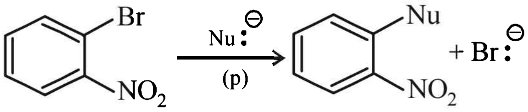
(B)



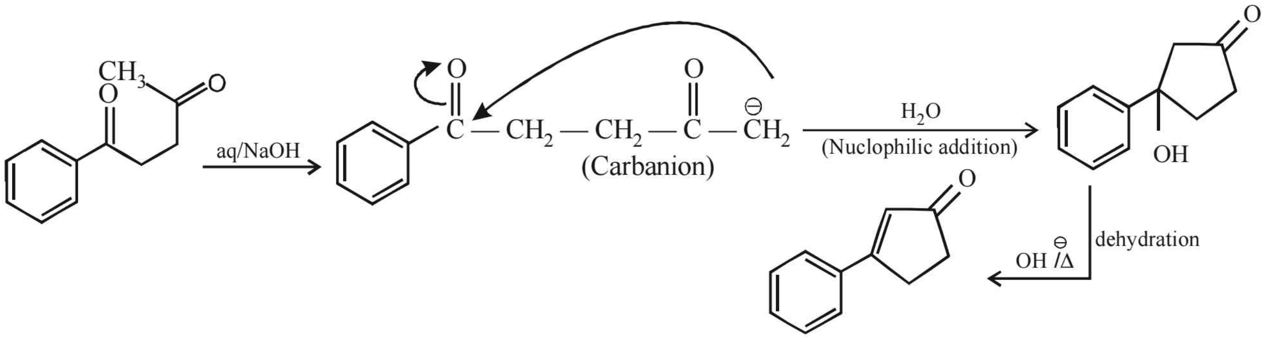
(C)



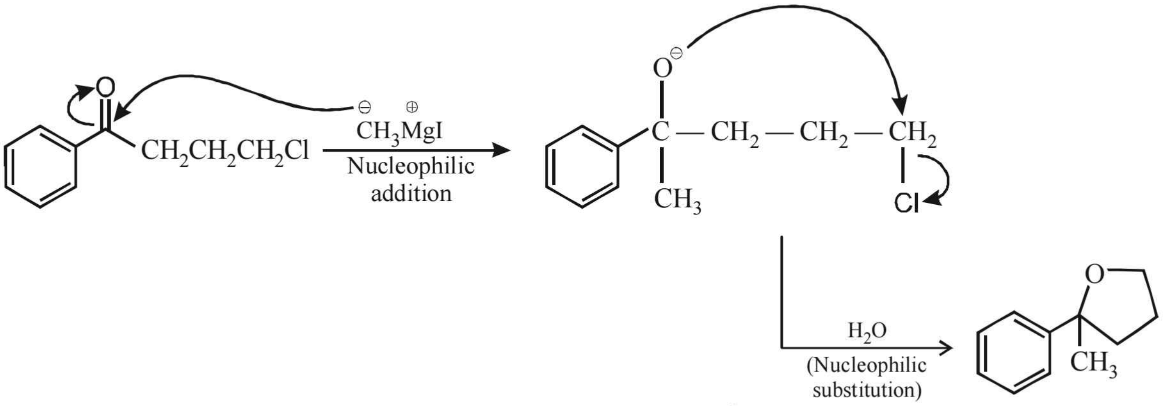
(D)



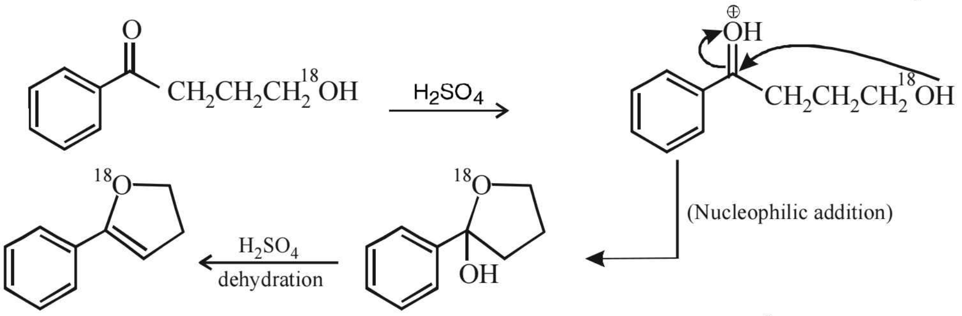
4. **A – r, s, t ; B – p, s ;C - r, s; D – q, r**



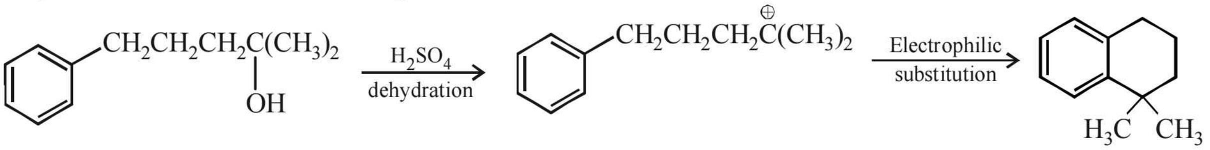
(B)



(C)



(D)



H. Assertion & Reason Type Questions

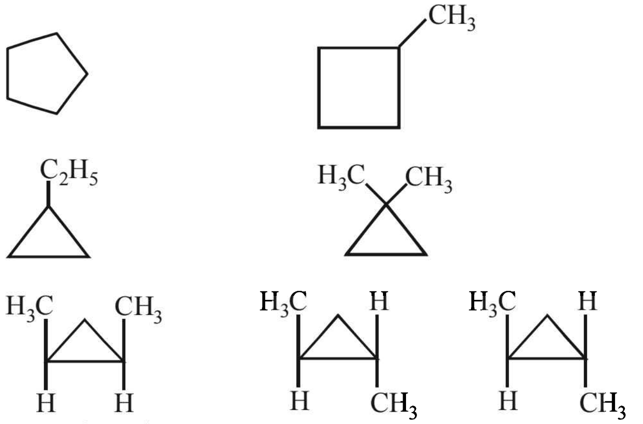
1. **(d)** Statement -1 is false because aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the carbon–chlorine bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles.

2. **(a)** Due to +M effect of $-\ddot{\underset{\cdot\cdot}{O}}H$, 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.

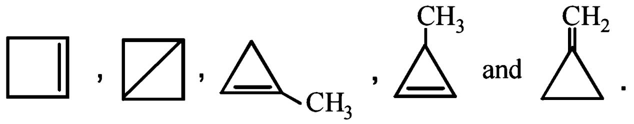
I. Integer Value Correct Type

1. The seven possible cyclic structural and stereoisomers are

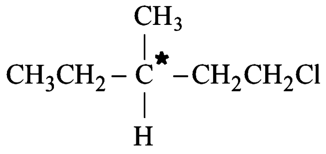


cis, (*meso*) *trans*, enantiomers

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

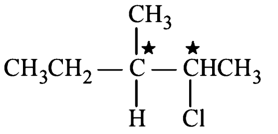


3. **8**



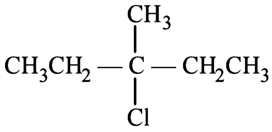
$$CH_3CH_2-\overset{CH_3}{\underset{H}{\overset{*}{C}}}-CH_2CH_2Cl$$

Enantiomeric pair = 2



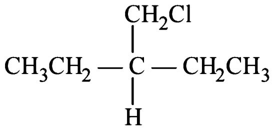
$$CH_3CH_2-\overset{CH_3}{\underset{H}{\overset{*}{C}}}-\underset{Cl}{\overset{*}{C}}HCH_3$$

Two enantiomeric pairs = 4



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

= 1

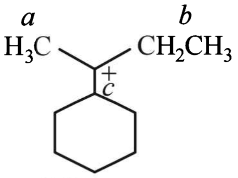


$$CH_3CH_2-\overset{CH_2Cl}{\underset{H}{C}}-CH_2CH_3$$

= 1

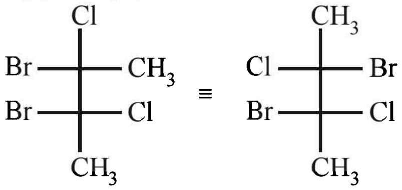
Total = 2 + 4 + 1 + 1 = 8

4. **6**

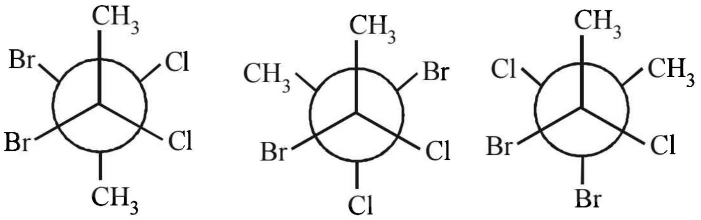


a = 3 Hyperconjugative H's
b = 2 Hyperconjugative H's
c = 1 Hyperconjugative H

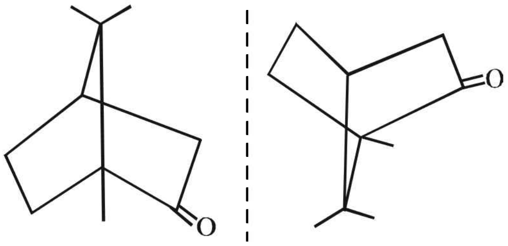
5. **(3)**



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



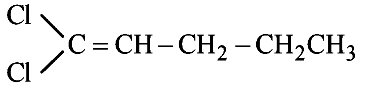
6. **(2)** The molecule cannot show geometrical isomerism, so only its mirror image will be the other stereoisomer.

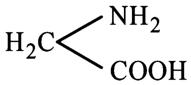


Section-B JEE Main/ AIEEE

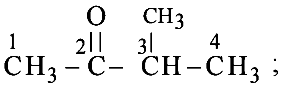
1. **(b)** $-CH_3$ group has +I effect, as number of $-CH_3$ group increases, the inductive effect increases. Therefore the correct order is
$CH_3-CH_2- < (CH_3)_2CH- < (CH_3)_3C-$

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)** 
$\genfrac{}{}{0pt}{}{Cl}{Cl}{>}C=CH-CH_2-CH_2CH_3$ 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 
$H_2C{<}^{NH_2}_{COOH}$

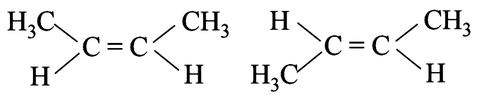
5. **(c)** The correct name is 3 - methylbut - 2 - ol

6. **(c)** 
$\overset{1}{C}H_3-\overset{O}{\underset{2}{\overset{\|}{C}}}-\overset{CH_3}{\underset{3}{\overset{|}{C}}}H-\overset{4}{C}H_3$;
3- methyl-2-butanone

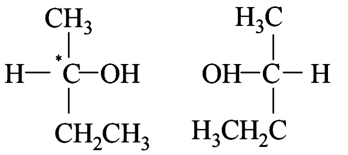
7. **(b)** In molecules (a), (c) and (d), the carbon atom has a multiple bond, only (b) has sp^3 hybridization.

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.

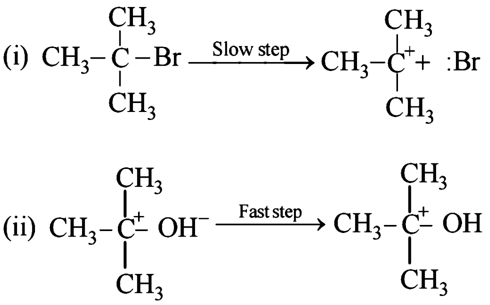
9. **(d)** **TIPS/Formulae :**
Stereoisomerism is of two types i.e., geometrical isomerism and optical isomerism
Both the structures shows sterioisomerism. Structure I shows geometrical isomerism as it contains two different atoms(H) and groups (CH_3) attached to each carbon containing double bond.


Cis butene *Trans* butene

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

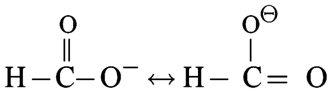

butyl alcohol (Two enantiomers)

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


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

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

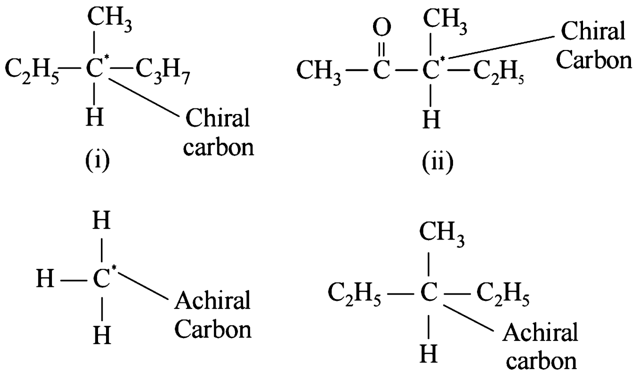
11. **(d)** $HCOO^-$ exists in following resonating structures


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

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

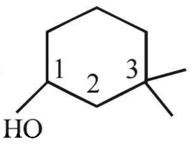
12. **(a)** $C_nH_{2n}O_2$ is general formula for carboxylic acid

13. **(a)**



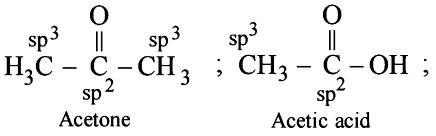
14. **(d)** **NOTE :** Among isomeric alkanes, the straight chain isomer has higher boiling point than the branched chain isomer. The greater the branching of the chain, the lower is the boiling point. Further due to the presence of π electrons, these moleculs are slightly polar and hence have higher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

15. **(a)**

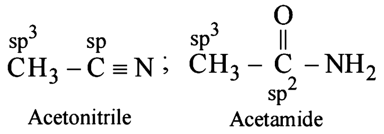


IUPAC name – 3, 3-Dimethyl -1 cyclohexanol

16. **(a)**

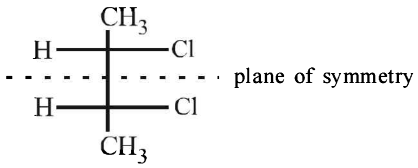


$\overset{sp^3}{H_3C} - \underset{sp^2}{\overset{\overset{O}{\|}}{C}} - \overset{sp^3}{CH_3}$; $\overset{sp^3}{CH_3} - \underset{sp^2}{\overset{\overset{O}{\|}}{C}} - OH$;



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

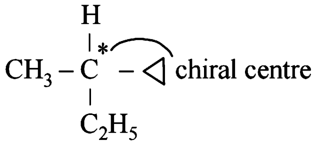
17. **(b)** **NOTE :** The compounds containing two similar assymmetric C-atoms have plane of symmetry and exist in Meso form.



Meso 2, 3 dichlorobutane

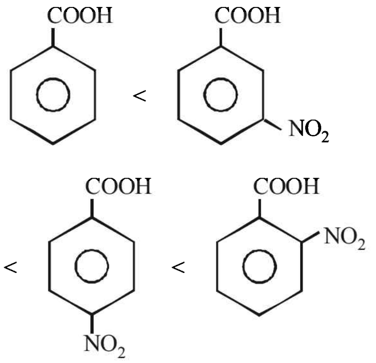
18. **(c)** Cl^- is the best leaving group among the given option.

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



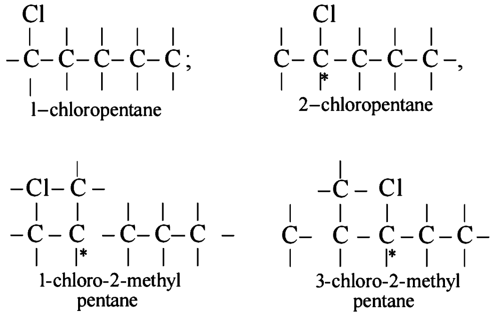
20. **(d)** In aromatic acids presence of electron withdrawing substituent e.g. $-NO_2$ disperses the negative charge of the anion and stablises it and hence increases the acidity of the parent benzoic acid.

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.



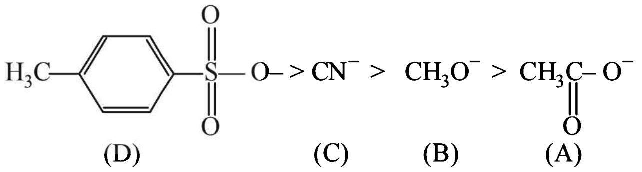
21. **(d)** Lone pair of electrons present on the nitrogen of benzyl amine is not involved in resonance.

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

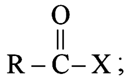


23. **(d)** Free radicals are electrically neutral, unstable and very reactive on account of the presence of odd electrons.

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

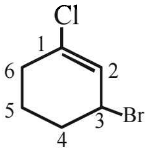


25. **(d)**



$R - \overset{\overset{O}{\|}}{C} - X$; 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.

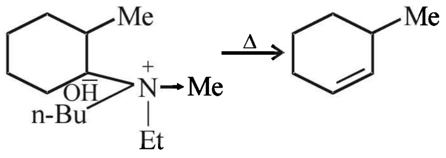
The acid character follows the order :

$$CH_3COOH > C_6H_5OH > H_2O > CH_3OH$$

The basic character will follow the order

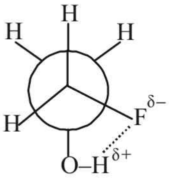
$$CH_3COO^- < C_6H_5O^- < O^-H < CH_3O^-$$

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

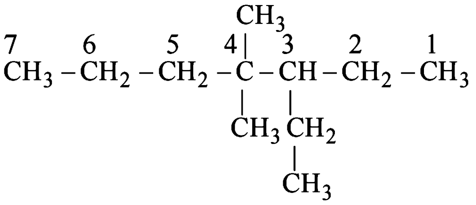
30. **(a)**



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

Eclipse, Anti, Gauche

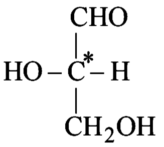
31. **(a)**



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

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.

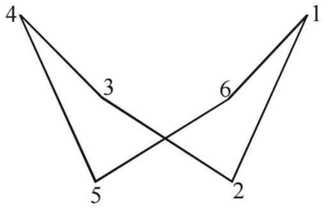


$$HO-\underset{CH_2OH}{\overset{CHO}{C^*}}-H$$

(* 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.

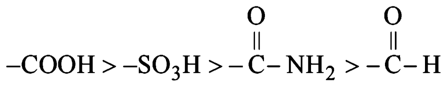


35. **(b)** The absolute configuration is (R, R)
(using priority rules to get the absolute configuration)
So the correct answer is (b)

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)

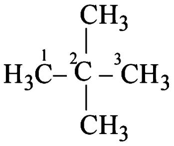
NOTE : The most stable complex has lowest energy.

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



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

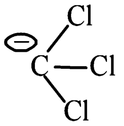
38. **(a)**



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

Neopentane
or 2,2- Dimethylpropane

39. **(b)**



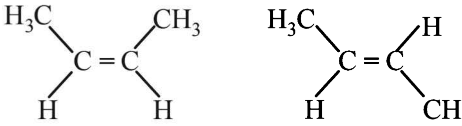
$> C_6H_5\bar{C}H_2 > (CH_3)_2CH^- > (CH_3)_3\bar{C}$

–ve charge highly dispersed due to – I effect

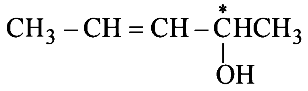
–M effect delocalises –ve charge

+I effect of CH_3 group intensifies the –ve charge

40. **(b)**



41. **(b)**



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

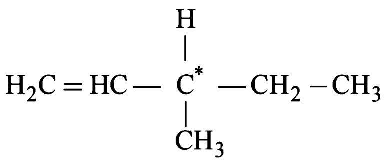
exhibits both geometrical as well as optical isomerism.

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

42. **(d)** The correct order of basicity is

$RCOO^- < CH\equiv C^- < NH_2 - < R^-$

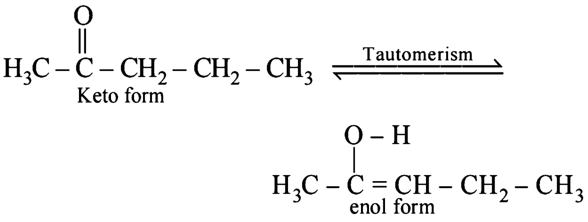
43. **(c)** For a compound to show optical isomerism, presence of chiral carbon atom is a necessary condition.



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

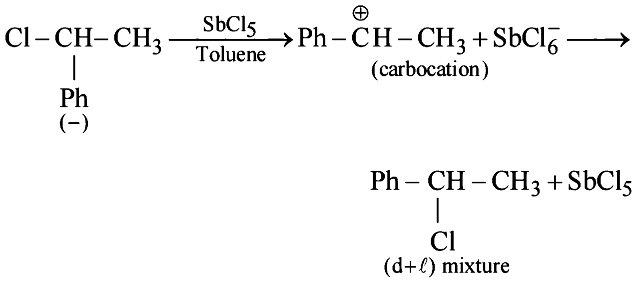
3- methyl-1-pentene

44. **(c)**



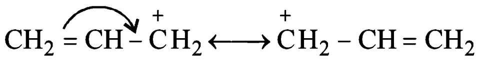
$$H_3C-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_3 \underset{\text{Keto form}}{} \xrightleftharpoons{\text{Tautomerism}} \underset{\text{enol form}}{H_3C-\overset{\overset{O-H}{|}}{C}=CH-CH_2-CH_3}$$

45. **(c)**



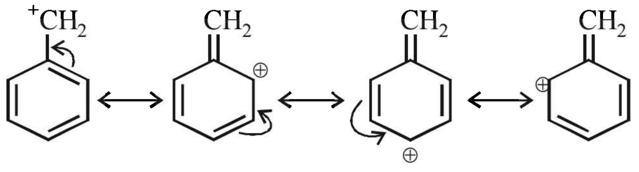
$$\underset{\underset{(-)}{\overset{|}{Ph}}}{Cl-CH-CH_3} \xrightarrow[\text{Toluene}]{SbCl_5} \underset{\text{(carbocation)}}{Ph-\overset{\oplus}{C}H-CH_3+SbCl_6^-} \longrightarrow \underset{(d+\ell)\text{ mixture}}{Ph-\underset{\underset{Cl}{|}}{CH}-CH_3+SbCl_5}$$

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



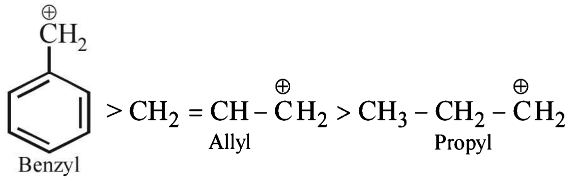
$$CH_2=CH-\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2-CH=CH_2$$

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

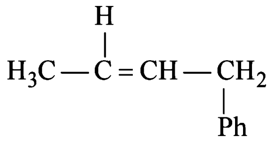
$$\text{meq. of } H_2SO_4 = 60\times\frac{M}{10}\times 2 = 12$$

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

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

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

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

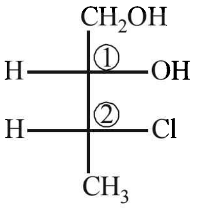
∴ 188 g of AgBr contain bromine = 80 g

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

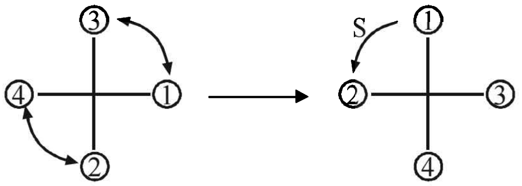
This much amount of bromine present in 0.250 g of organic compound

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

50. **(d)**

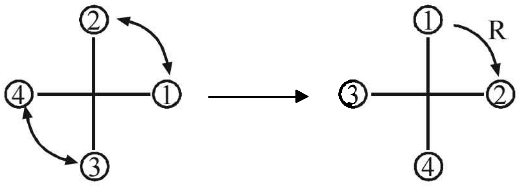


At (1),



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.