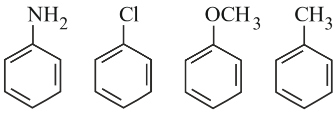
CHAPTER

21

Some Basic Principles of Organic Chemistry

1. The increasing order of nitration of the following compound is



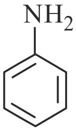
(A) (B) (C) (D)

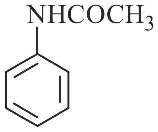
(a) (*B*) < (*A*) < (*C*) < (*D*) (b) (*B*) < (*A*) < (*D*) < (*C*)

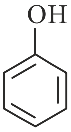
(c) (*A*) < (*B*) < (*C*) < (*D*) (d) (*A*) < (*B*) < (*D*) < (*C*)

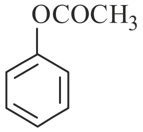
(Online 2018)

2. Which of the following compounds will form significant amount of *meta* product during mono-nitration reaction?

(a) 

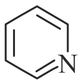
(b) 

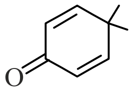
(c) 

(d) 

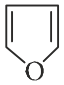
(2017)

3. Which of the following molecules is least resonance stabilised?

(a) 

(b) 

(c) 

(d) 

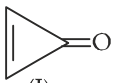
(2017)

4. 3-Methylpent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is

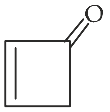
(a) two (b) four (c) six (d) zero.

(2017)

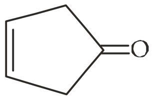
5. Which of the following compounds will show highest dipole moment?



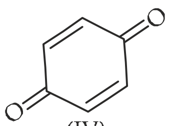
(I)



(II)



(III)



(IV)

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

(Online 2017)

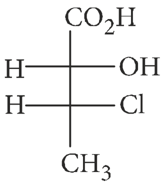
6. The increasing order of the boiling points for the following compounds is

C_2H_5OH (I) C_2H_5Cl (II) $C_2H_5CH_3$ (III) $C_2H_5OCH_3$ (IV)

(a) (IV) < (III) < (I) < (II) (b) (III) < (II) < (I) < (IV)

(c) (II) < (III) < (IV) < (I) (d) (III) < (IV) < (II) < (I)

(Online 2017)

7. The absolute configuration of  is

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

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

(2016)

8. Which of the following compounds will exhibit geometrical isomerism?

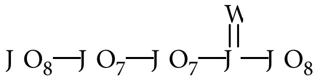
(a) 2-Phenyl-1-butene (b) 1, 1-Diphenyl-1-propane

(c) 1-Phenyl-2-butene (d) 3-Phenyl-1-butene

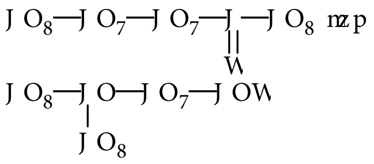
(2015)

9. Which of the following pairs of compounds are positional isomers?

(a) $CH_3CH_2CH_2CH_2CHO$ and

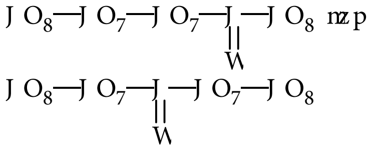


$J\,O_8-J\,O_7-J\,O_7-\overset{W}{\overset{\|}{J}}-J\,O_8$

(b) 

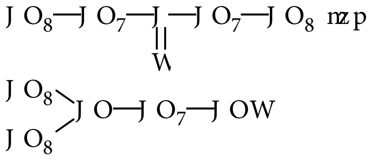
$J\,O_8-J\,O_7-J\,O_7-\underset{W}{\underset{\|}{J}}-J\,O_8$ mzp

$J\,O_8-\underset{J\,O_8}{\underset{|}{J}}\,O-J\,O_7-J\,OW$

(c) 

$J\,O_8-J\,O_7-J\,O_7-\underset{W}{\underset{\|}{J}}-J\,O_8$ mzp

$J\,O_8-J\,O_7-\underset{W}{\underset{\|}{J}}-J\,O_7-J\,O_8$

(d) 

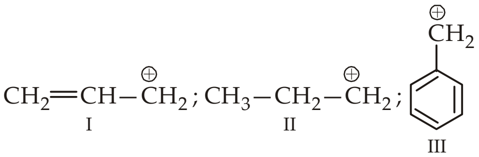
$J\,O_8-J\,O_7-\underset{W}{\underset{\|}{J}}-J\,O_7-J\,O_8$ mzp

$\begin{matrix}J\,O_8 \\ J\,O_8\end{matrix}\!\!>J\,O-J\,O_7-J\,OW$

(Online 2015)

10. The number of structural isomers for C_6H_{14} is
(a) 3 (b) 4
(c) 5 (d) 6 *(Online 2015)*

11. The order of stability of the following carbocations is



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

(a) III > I > II (b) III > II > I
(c) II > III > I (d) I > II > III *(2013)*

12. How many chiral compounds are possible on monochlorination of 2-methyl butane?
(a) 2 (b) 4
(c) 6 (d) 8 *(2012)*

13. Identify the compound that exhibits tautomerism.
(a) 2-Butene (b) Lactic acid
(c) 2-Pentanone (d) Phenol *(2011)*

14. Out of the following, the alkene that exhibits optical isomerism is
(a) 2-methyl-2-pentene (b) 3-methyl-2-pentene
(c) 4-methyl-1-pentene (d) 3-methyl-1-pentene
(2010)

15. The IUPAC name of *neo*-pentane is
(a) 2-methylbutane (b) 2,2-dimethylpropane
(c) 2-methylpropane (d) 2,2-dimethylbutane
(2009)

16. The number of stereoisomers possible for a compound of the molecular formula $CH_3 - CH = CH - CH(OH) - Me$ is
(a) 3 (b) 2
(c) 4 (d) 6 *(2009)*

17. The alkene that exhibits geometrical isomerism is
(a) propene (b) 2-methylpropene
(c) 2-butene (d) 2-methyl-2-butene
(2009)

18. Arrange the carbanions,

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

in order of their decreasing stability

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

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

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

(d) $(CH_3)_3\bar{C} > (CH_3)_2\bar{C}H > C_6H_5\bar{C}H_2 > \bar{C}Cl_3$ *(2009)*

19. The correct decreasing order of priority for the functional groups of organic compounds in the IUPAC system of nomenclature is

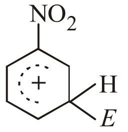
(a) $- CONH_2, - CHO, - SO_3H, - COOH$

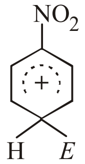
(b) $- COOH, - SO_3H, - CONH_2, - CHO$

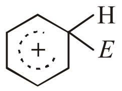
(c) $- SO_3H, -COOH, -CONH_2, - CHO$

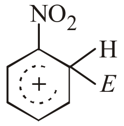
(d) $- CHO, -COOH, - SO_3H, -CONH_2$ *(2008)*

20. The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ-complex. Of the following, which σ-complex is of lowest energy?

(a)


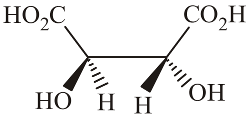
(b)


(c)


(d)


(2008)

21. The absolute configuration of



is

(a) *S*, *R* (b) *S*, *S* (c) *R*, *R* (d) *R*, *S*
(2008)

22. Which one of the following conformations of cyclohexane is chiral?
(a) Boat (b) Twist boat
(c) Rigid (d) Chair *(2007)*

23. Increasing order of stability among the three main conformations (*i.e.* eclipse, anti, gauche) of 2-fluoroethanol is
(a) eclipse, gauche, anti (b) gauche, eclipse, anti
(c) eclipse, anti, gauche (d) anti, gauche, eclipse.
(2006)

24. The increasing order of stability of the following free radicals is

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

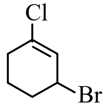
(b) $(C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H < (CH_3)_3\dot{C} < (CH_3)_2\dot{C}H$

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

(d) $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_3\dot{C} < (C_6H_5)_2\dot{C}H$ *(2006)*

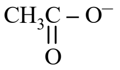
25. $CH_3Br + Nu^- \rightarrow CH_3 - Nu + Br^-$
The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) *A* to *D* is
[Nu^- = (*A*) PhO^-, (*B*) AcO^-, (*C*) HO^-, (*D*) CH_3O^-]
(a) *D* > *C* > *A* > *B* (b) *D* > *C* > *B* > *A*
(c) *A* > *B* > *C* > *D* (d) *B* > *D* > *C* > *A*.
(2006)

26. The IUPAC name of the compound shown below is



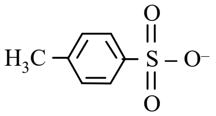
(a) 2-bromo-6-chlorocyclohex-1-ene
(b) 6-bromo-2-chlorocyclohexene
(c) 3-bromo-1-chlorocyclohexene
(d) 1-bromo-3-chlorocyclohexene. *(2006)*

27. The decreasing order of nucleophilicity among the nucleophiles is

(1) 
$CH_3C(=O)-O^-$

(2) CH_3O^-

(3) CN^-

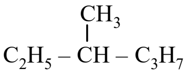
(4) 
$H_3C-C_6H_4-SO_2-O^-$

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

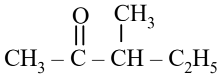
(2005)

28. Due to the presence of an unpaired electron, free radicals are
(a) chemically reactive
(b) chemically inactive
(c) anions
(d) cations. *(2005)*

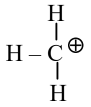
29. Among the following four structures I to IV,


$C_2H_5-CH(CH_3)-C_3H_7$

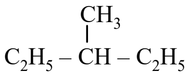
(I)


$CH_3-C(=O)-CH(CH_3)-C_2H_5$

(II)


$H-\overset{+}{C}H_2$

(III)


$C_2H_5-CH(CH_3)-C_2H_5$

(IV)

it is true that
(a) all four are chiral compounds
(b) only I and II are chiral compounds
(c) only III is a chiral compound
(d) only II and IV are chiral compounds. *(2003)*

30. The reaction :

$$(CH_3)_3C-Br \xrightarrow{H_2O} (CH_3)_3C-OH$$

(a) elimination reaction
(b) substitution reaction
(c) free radical reaction
(d) displacement reaction. *(2002)*

31. Which of the following does not show geometrical isomerism?
(a) 1,2-dichloro-1-pentene
(b) 1,3-dichloro-2-pentene
(c) 1,1-dichloro-1-pentene
(d) 1,4-dichloro-2-pentene. *(2002)*

32. A similarity between optical and geometrical isomerism is that
(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. *(2002)*

33. Racemic mixture is formed by mixing two
(a) isomeric compounds
(b) chiral compounds
(c) meso compounds
(d) optical isomers. *(2002)*

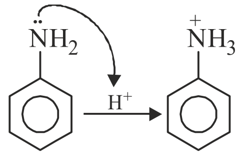
34. Arrangement of $(CH_3)_3C-$, $(CH_3)_2CH-$, CH_3CH_2- when attached to benzyl or an unsaturated group in increasing order of inductive effect is
(a) $(CH_3)_3C- < (CH_3)_2CH- < CH_3CH_2-$
(b) $CH_3CH_2- < (CH_3)_2CH- < (CH_3)_3C-$
(c) $(CH_3)_2CH- < (CH_3)_3C- < CH_3CH_2-$
(d) $(CH_3)_3C- < CH_3CH_2- < (CH_3)_2CH-$. *(2002)*

ANSWER KEY

1. (d)	**2.** (a)	**3.** (b)	**4.** (b)	**5.** (a)	**6.** (d)	**7.** (b)	**8.** (c)	**9.** (c)	**10.** (c)	**11.** (a)	**12.** (a)
13. (c)	**14.** (d)	**15.** (b)	**16.** (c)	**17.** (c)	**18.** (c)	**19.** (c)	**20.** (c)	**21.** (c)	**22.** (b)	**23.** (a)	**24.** (a)
25. (a)	**26.** (c)	**27.** (d)	**28.** (a)	**29.** (b)	**30.** (b)	**31.** (c)	**32.** (c)	**33.** (d)	**34.** (b)		

Explanations

1. **(d) :** Nitration is an electrophilic substitution reaction. Thus, groups which increase the electron density on benzene ring will have greater ease for nitration. — OCH_3 group shows + *R* effect but — CH_3 group shows inductive effect (+*I*). — Cl will have strong electron withdrawing effect (–*I*). In acidic medium, aniline undergoes protonation :

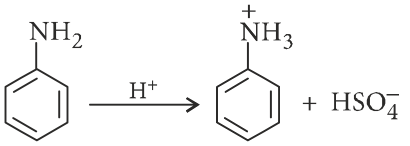


Aniline Anilinium ion

Thus, electron density on the benzene ring will be least in aniline. Therefore, aniline is least reactive.

Thus, increasing order of nitration is (*A*) < (*B*) < (*D*) < (*C*).

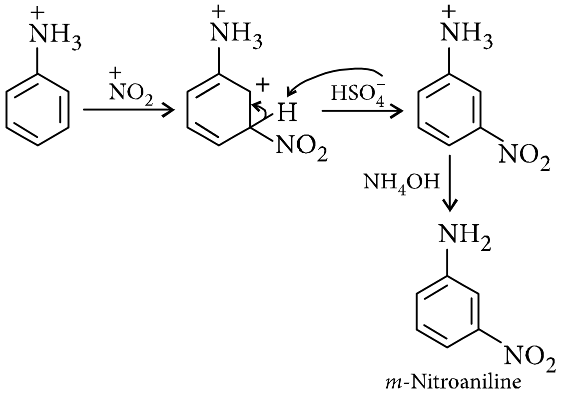
2. **(a) :** Conc. H_2SO_4 + conc. HNO_3 is a nitrating mixture. Aniline abstracts proton from sulphuric acid to give anilinium ion.



Anilinium ion

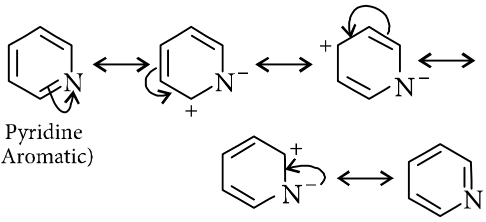
Due to electron withdrawing nature of anilinium ion, it acts as a *meta*-directing species in electrophilic aromatic substitution reactions.

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$



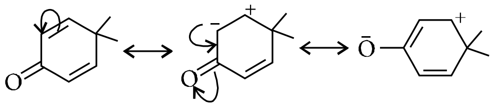
m-Nitroaniline
(51%)

3. **(b) :** (a)



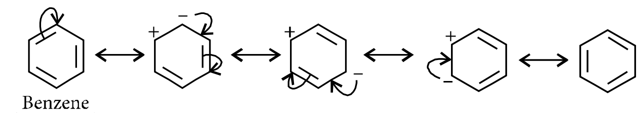
Pyridine
(Aromatic)

(b)



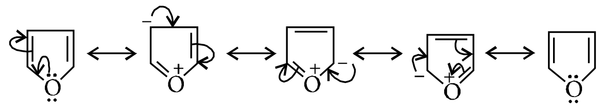
(Non-Aromatic)

(c)



Benzene
(Aromatic)

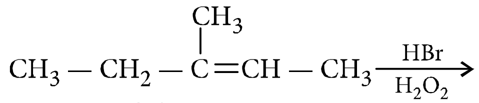
(d)



Furan
(Aromatic)

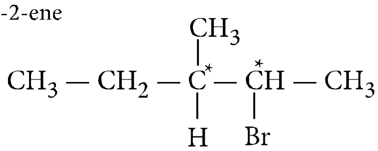
Greater the number of resonating structures, greater will be the stability of the compound. Aromatic compounds are resonance stabilised, hence, compound in option (b) is least resonance stabilised.

4. **(b) :**



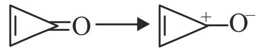
$$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \xrightarrow[H_2O_2]{HBr}$$

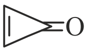
3-Methylpent-2-ene



$$CH_3-CH_2-\underset{H}{\underset{|}{\overset{CH_3}{\overset{|}{\overset{*}{C}}}}}-\underset{Br}{\underset{|}{\overset{*}{C}H}}-CH_3$$

There are two chiral carbon atoms present in the product. Therefore, total number of stereoisomers are = $2^n = 2^2 = 4$

5. **(a) :** 

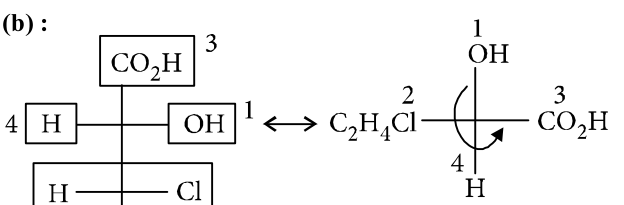
 gives most stable carbocation due to the formation of aromatic compound thus, shows highest dipole moment.

6. **(d) :** B.P. ∝ dipole moment ∝ O2n{zpuzs

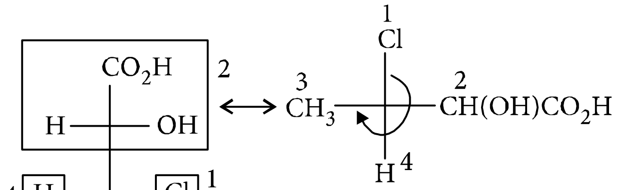
∴ The increasing order of boiling points will be :

$$C_2H_5CH_3 < C_2H_5OCH_3 < C_2H_5Cl < C_2H_5OH$$
(III) (IV) (II) (I)

7. **(b) :**



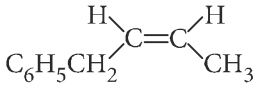
S-configuration

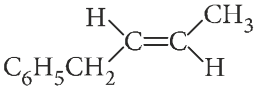


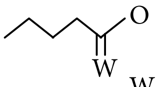
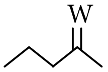
R-configuration

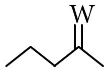
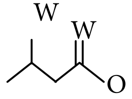
8. **(c) :** For geometrical isomerism, the molecule must contain a double bond and each of the two carbon atoms of the double bond must have different substituents which may be same or different. Thus, alkenes of the type $abC=Cab$ and $abC=Cde$ show geometrical isomerism.

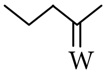
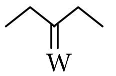
1-Phenyl-2-butene shows geometrical isomerism.

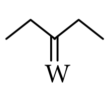
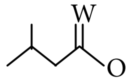

cis-form


trans-form

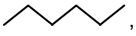
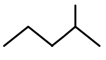
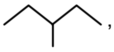
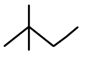
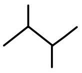
9. **(c) :** (a)  and  are functional isomers.

(b)  and  are functional isomers.

(c)  and  are positional isomers.

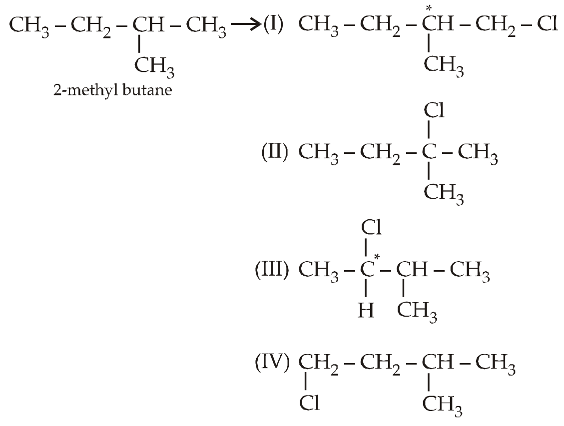
(d)  and  are functional isomers.

10. **(c) :** Structural isomers of C_6H_{14} are

, , , , 

11. **(a) :** Greater the number of resonating structures a carbocation possess, greater is its stability.

12. **(a) :**



$$\underset{\text{2-methyl butane}}{CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3} \rightarrow \text{(I) } CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{\overset{*}{C}H}}-CH_2-Cl$$

$$\text{(II) } CH_3-CH_2-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$$

$$\text{(III) } CH_3-\overset{\displaystyle Cl}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C^*}}}}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$$

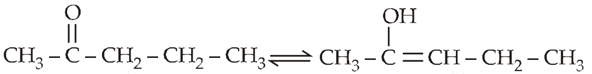
$$\text{(IV) } \underset{\displaystyle Cl}{\underset{|}{C}H_2}-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$$

Possible products on chlorination

Out of four possible isomers only I and III are chiral.

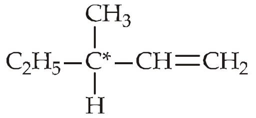
13. **(c) :** The type of isomerism in which a substance exists in two readily interconvertible different structures leading to a dynamic equilibrium is known as tautomerism.

2-pentanone exhibits tautomerism.



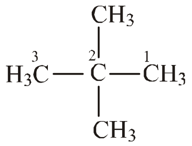
$$\underset{\text{Keto form}}{CH_3-\overset{\displaystyle O}{\overset{||}{C}}-CH_2-CH_2-CH_3} \rightleftharpoons \underset{\text{Enol form}}{CH_3-\overset{\displaystyle OH}{\overset{|}{C}}=CH-CH_2-CH_3}$$

14. **(d) :** 3-Methyl-1-pentene exhibits optical isomerism as it has an asymmetric C-atom in the molecule.



$$C_2H_5-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C^*}}}}-CH=CH_2$$

3-methyl-1-pentene

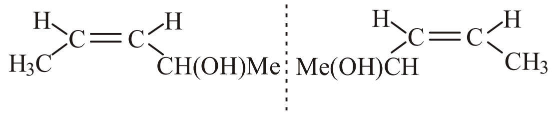
15. **(b) :** 

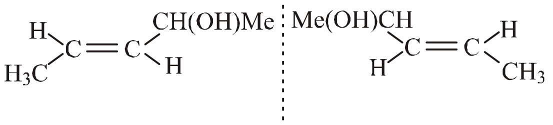
$$\overset{3}{H_3C}-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{\overset{2}{C}}}}}-\overset{1}{CH_3}$$

neo-pentane or 2,2-dimethylpropane

16. **(c) :** The given compound has a C $=$ C group and one chiral (*) carbon,

$H_3C-HC=CH-\overset{*}{C}H(OH)-Me$

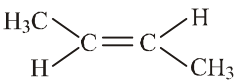

d, *l* isomers of *cis*-form

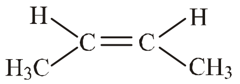

d, *l* isomers of *trans*-form

∴ Total stereoisomers = 4.

17. **(c) :** When two groups attached to a double bonded carbon atom are same, the compound does not exhibit geometrical isomerism.

Compounds in which the two groups attached to a double bonded carbon are different, exhibit geometrical isomerism, thus, only 2-butene exhibits *cis-trans* isomerism.


trans-2-butene


cis-2-butene

18. **(c) :** The groups having +*I* effect decrease the stability while groups having –*I* effect increase the stability of carbanions. Benzyl carbanion is stabilized due to resonance. Also, out of 2° and 3° carbanions, 2° carbanions are more stable, thus the decreasing order of stability is :

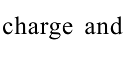
$$\bar{C}Cl_3 > C_6H_5\bar{C}H_2 > (CH_3)_2\bar{C}H > (CH_3)_3\bar{C}.$$

19. **(c) :** The order of preference of functional groups is as follows:

$$-SO_3H > -COOH > -COOR > -COX > -COCl > -CONH_2$$

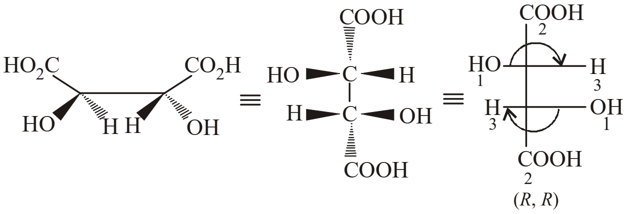
$$> -CHO > -CN > \;\rangle C=O > -OH > -SH > -NH_2$$

$$> \;\rangle C=C\langle\; > -C\equiv C- > -NO_2 > -NO > -X$$

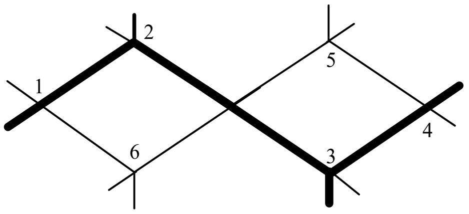
20. **(c) :** 

This structure will be of lowest energy due to resonance stabilisation of +ve charge. In all other three structures, the presence of electron-withdrawing NO_2 group will destabilize the +ve charge and hence they will have greater energy.

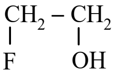
21. (c) :



22. (b) : The twist boat conformation of cyclohexane is optically active as it does not have any plane of symmetry.

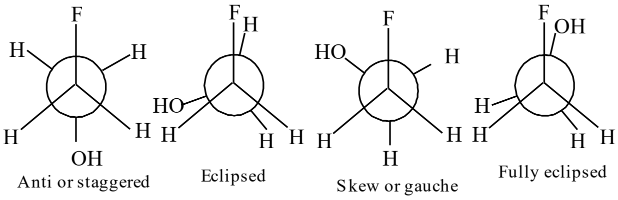


23. (a) :



$$\underset{F}{CH_2} - \underset{OH}{CH_2}$$

2-fluoroethanol



Anti or staggered · Eclipsed · Skew or gauche · Fully eclipsed

The anti conformation is most stable in which F and OH groups are far apart as possible and minimum repulsion between two groups occurs.

In fully eclipsed conformation F and OH groups are so close that the steric strain is maximum, hence this conformation is most unstable. The order of stability of these conformations is anti > gauche > partially eclipsed > fully eclipsed

24. (a) : On the basis of hyperconjugation effect of the alkyl groups, the order of stability of free radical is as follows: tertiary > secondary > primary.

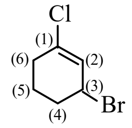
Benzyl free radicals are stabilised by resonance and hence are more stable than alkyl free radicals. Further as the number of phenyl group attached to the carbon atom holding the odd electron increases, the stability of a free radical increases accordingly. *i.e.* $(CH_3)_2\dot{C}H < (CH_3)_3\dot{C} < (C_6H_5)_2\dot{C}H < (C_6H_5)_3\dot{C}$

25. (a) : If the nucleophilic atom or the centre is same, nucleophilicity parallels basicity, *i.e.* more basic the species stronger is the nucleophile.

$CH_3O^- > HO^- > PhO^- > AcO^-$

Here, the nucleophilic atom *i.e.* O is the same in all these species. This order can be easily explained on the general concept that a weaker acid has a stronger conjugate base.

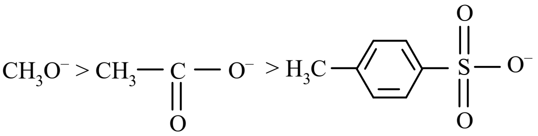
26. (c) :



3-bromo-1-chlorocyclohexene

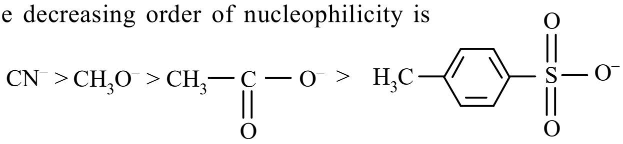
27. (d) : Strong bases are generally good nucleophile.

If the nucleophilic atom or the centre is the same, nucleophilicity parallels basicity, *i.e.*, more basic the species, stronger is the nucleophile. Hence basicity as well as nucleophilicity order is



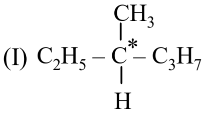
Now CN^- is a better nucleophile than CH_3O^-.

Hence decreasing order of nucleophilicity is

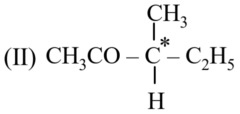


28. (a) : Free radicals are highly reactive due to presence of an unpaired electron. They readily try to pair-up the odd electrons.

29. (b) : A chiral object or compound can be defined as the one that is not superimposable on its mirror image, or we can say that all the four groups attached to a carbon atom must be different. Only I and II are chiral compounds.



$$\text{(I) } C_2H_5 - \overset{CH_3}{\underset{H}{C^*}} - C_3H_7$$

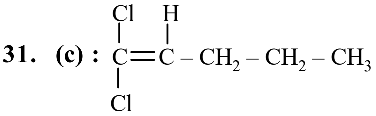


$$\text{(II) } CH_3CO - \overset{CH_3}{\underset{H}{C^*}} - C_2H_5$$

30. (b) : This is an example of nucleophilic substitution reaction.

$$\underset{\text{Substrate}}{(CH_3)_3C - Br} + \underset{\text{Nucleophile}}{OH^-} \longrightarrow (CH_3)_3C - OH + \underset{\text{Leaving group}}{Br^-}$$

31. (c) :



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

Condition for geometrical isomerism is presence of two different atoms of groups attached to each carbon atom containing double bond.

Identical groups (Cl) on C - 1 will give only one compound. Hence it does not show geometrical isomerism.

32. (c) : Both involves compounds having the same molecular and structural formulae, but different spatial arrangement of atoms or groups.

33. (d) : An equimolar mixture of two *i.e.* dextro and laevorotatory optical isomers is termed as racemic mixture or *dl* form or (±) mixture.

34. (b) : $-CH_3$ group has $+I$ effect, as number of $-CH_3$ group increases the inductive effect increases.