13 Chapter

ORGANIC CHEMISTRY Some Basic Principles-2 (Stereochemistry)

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. $CH_3CH_2C \equiv CCH_2CH_3 \xrightarrow{\text{Na, liq. } NH_3} [X] \xrightarrow{Br_2}$ Product. Here the product is

(a) Optically active

(b) Optically inactive due to formation of racemate mixture

(c) Optically inactive due to formation of *meso* compound

(d) Optically inactive due to absence of chiral carbon

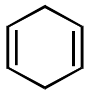
2. *rac* $-$ $CH_3CHBrCH_2COOH \xrightarrow{\text{1 mole P, } Br_2}$ Product is

(a) a racemic mixture

(b) a mixture of two racemic mixtures

(c) optically active mixture

(d) *meso*

3.  $\xrightarrow[\text{ter}-\text{BuOK}]{CHBr_3} [X] \xrightarrow{KMnO_4} [Y]$

The compound [Y] is

(a) dextrorotatory (b) laevorotatory

(c) racemic mixture (d) meso

4. Addition of bromine to *cis*-but-2-ene is a

(a) Stereospecific reaction

(b) Stereoselective reaction

(c) Both

(d) None

5. Addition of bromine to *trans*-but-2-ene is

(a) *syn*-addition (b) *anti*-addition

(c) both (d) none

6. Addition of bromonium ion to the top and bottom face of *cis*-but-2-ene will give intermediates which

(a) are different and achiral

(b) are different and chiral

(c) are identical and achiral

(d) are identical and chiral

7. Addition of bromine to *trans*-2-pentene and *cis*-2-pentene give respectively.

(a) Racemic mixture and meso

(b) Meso and racemic mixture

(c) Racemic mixture in both cases

(d) Meso isomer in both cases

8. *trans*-2-Pentene + $Br_2 \longrightarrow$ Enantiomeric pair (I + II)

cis-2-Pentene + $Br_2 \longrightarrow$ Enantiomeric pair (III + IV)

What is the relation between the constituents of the two enantiomeric pairs?

(a) All the four compounds are identical

(b) They represent two diastereomeric pairs

(c) They represent three diastereomeric pairs

(d) They represent four diastereomeric pairs

9. Dehydrogenation of 1-bromo-1, 2-diphenylpropane proceeds through E-2 mechanism to form 1,2-diphenylpropene; what do you expect about this reaction?

(a) It is a stereoselective reaction

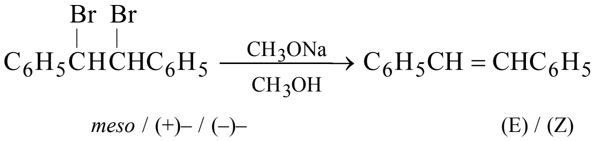
(b) It is a stereospecific reaction

(c) Both (a) and (b)

(d) None of the two

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	

10. 1, 2-Dibromo-1,2-diphenylethane has two similar chiral carbon atoms, hence it exists as a *meso-*, (+) – and (–) – form. What product do you expect from the following dehydrohalogenation of each of the two diastereomers?

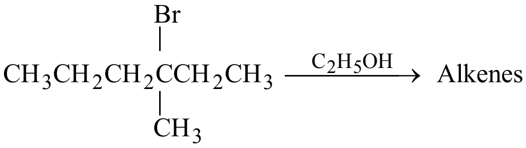


$$\overset{\text{Br}}{\underset{}{C_6H_5CH}}\overset{\text{Br}}{CHC_6H_5} \xrightarrow[CH_3OH]{CH_3ONa} C_6H_5CH = CHC_6H_5$$

meso / (+)– / (–)– (E) / (Z)

(a) *meso*-isomer will give (E) – alkene, while (+) – or (–) – isomer will give (Z)-alkene
(b) *meso*-isomer will give (Z) – alkene, while (+) – or (–) – isomer will give (E)-alkene
(c) (E)-as well as (Z)-alkenes will be formed in both reactions
(d) (Z)-alkene will be formed in both reactions

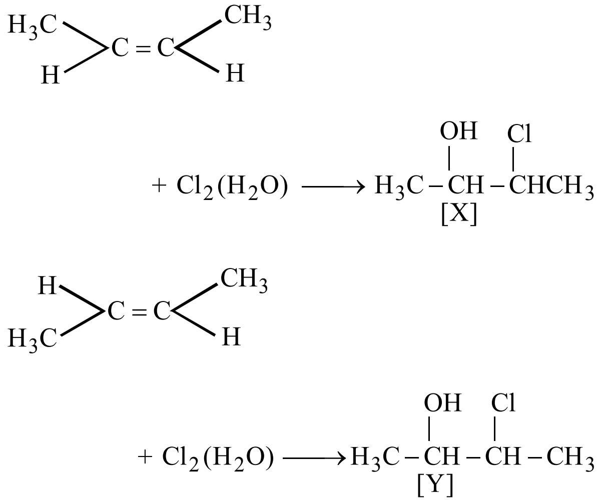
11. What do you expect about the stereochemistry of the following reaction which follows E1 path ?



$$CH_3CH_2CH_2\underset{CH_3}{\overset{Br}{C}}CH_2CH_3 \xrightarrow{C_2H_5OH} \text{Alkenes}$$

(a) It is stereoselective (b) It is stereospecific
(c) Both of the two (d) None of the two

12.



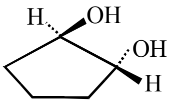
$$+ Cl_2(H_2O) \longrightarrow \underset{[X]}{H_3C-\overset{OH}{CH}-\overset{Cl}{C}HCH_3}$$

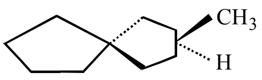
$$+ Cl_2(H_2O) \longrightarrow \underset{[Y]}{H_3C-\overset{OH}{CH}-\overset{Cl}{CH}-CH_3}$$

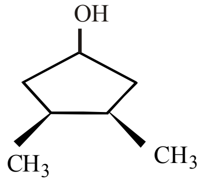
Products X and Y respectively are
(a) Racemic-threo-chlorohydrin
(b) Racemic-erythro-chlorohydrin
(c) Racemic-threo-chlorohydrin and racemic-erythro-chlorohydrin
(d) Racemic-erythro-chlorohydrin and racemic-threo-chlorohydrin

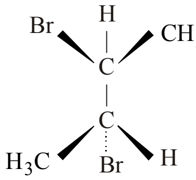
13. Which of the following reaction of alkenes take place in *syn*-manner?
(a) Halohydrin formation
(b) Hydroxylation with permanganate
(c) Hydroxylation with peroxy acids
(d) Addition of bromine

14. Which of the following structure represent *meso*-compounds?

(i)


(ii)


(iii)


(iv)


(a) (i) and (ii) (b) (iii) and (iv)
(c) (i) , (ii) and (iii) (d) All the four

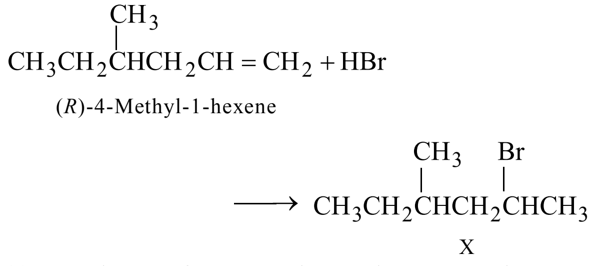
15. $CH_3(CH_2)_5CH = CH_2 \xrightarrow[\text{Oxidation}]{\text{Hydroboration}}$

$\cdot CH_3(CH_2)_5CH_2CH_2OH$

The above reaction is
(a) Stereoselective (b) Stereospecific
(c) Both (a) and (b) (d) Regioselective

16. The addition product of Br_2 on *cis* -and *trans*-2- hexenes, respectively are
(a) Racemic mixture and meso
(b) Meso and racemic mixture
(c) A racemic mixture containing equal amount of each enantiomer (i.e. 50 : 50 mixture) in both cases.
(d) A non-50 : 50 mixture (i.e. racemic mixture containing unequal amounts of the two enantiomers).

17.



$$CH_3CH_2\overset{CH_3}{C}HCH_2CH = CH_2 + HBr$$

(*R*)-4-Methyl-1-hexene

$$\longrightarrow \underset{X}{CH_3CH_2\overset{CH_3}{C}HCH_2\overset{Br}{C}HCH_3}$$

(a) A mixture of two enantiomers in 50 : 50 ratio
(b) A mixture of two enantiomers in non - 50 : 50 ratio
(c) A mixture of two diastereomers in 50 : 50 ratio
(d) A mixture of two diastereomers in non - 50 : 50 ratio

MARK YOUR RESPONSE	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ
	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ		

18. 1-Methylcyclohexene + $Br_2 \longrightarrow$ 1, 2-Dibromo-1-methylcyclohexane

The product is

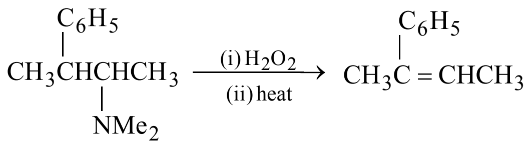
(a) A 50 : 50 racemic mixture

(b) A non - 50 : 50 racemic mixture

(c) A mixture of two diastereomers

(d) Only a single compound is formed

19.



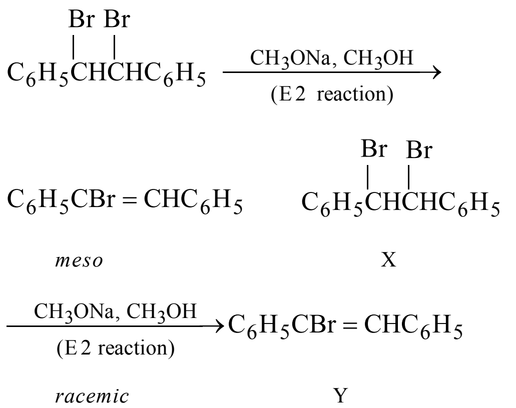
$$CH_3\overset{C_6H_5}{\overset{|}{C}}H\underset{\underset{NMe_2}{|}}{C}HCH_3 \xrightarrow[\text{(ii) heat}]{\text{(i) } H_2O_2} CH_3\overset{C_6H_5}{\overset{|}{C}}=CHCH_3$$

If the starting amine is 2*R*, 3*S*, or 2*S*, 3*R,* the alkene formed should respectively be

(a) *E* and *Z* (b) *Z* and E

(c) *E* in both cases (d) *Z* in both cases

20.



$$C_6H_5\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}HC_6H_5 \xrightarrow[\text{(E 2 reaction)}]{CH_3ONa,\ CH_3OH}$$

$C_6H_5CBr = CHC_6H_5$ $C_6H_5\overset{Br}{\overset{|}{C}}H\overset{Br}{\overset{|}{C}}HC_6H_5$

meso X

$\xrightarrow[\text{(E 2 reaction)}]{CH_3ONa,\ CH_3OH} C_6H_5CBr = CHC_6H_5$

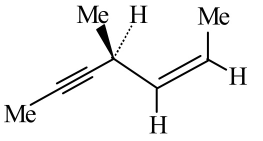
racemic Y

The alkenes X and Y respectively are

(a) Z and E (b) E and Z

(c) Z in both cases (d) E in both cases

21.



Hydrogenation of the above compound in the presence of poisoned palladium catalyst gives

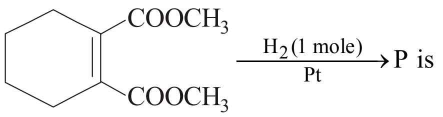
(a) an optically active compound

(b) an optically inactive compound

(c) a racemic mixture

(d) a diastereomeric mixture

22.



$\xrightarrow[Pt]{H_2\text{(1 mole)}}$ P is

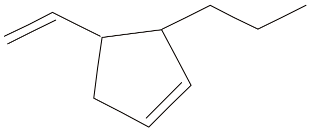
(a) optically active

(b) optically inactive due to internal compensation

(c) optically inactive due to external compensation

(d) diastereomeric mixture

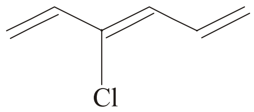
23. Total number of stereoisomers for the following compound is



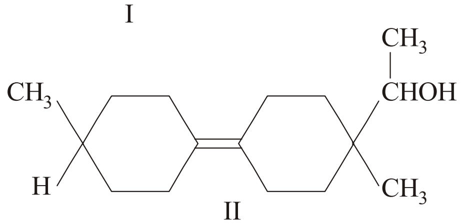
(a) 4 (b) 8

(c) 16 (d) 32

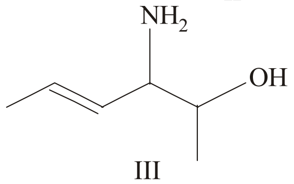
24. Arrange the following compounds in decreasing order of stereogenic centres.



I



II

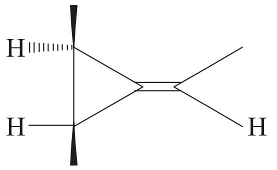


III

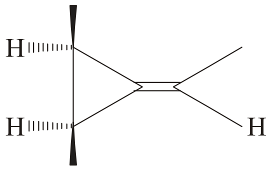
(a) I > II > III (b) III > II > I

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

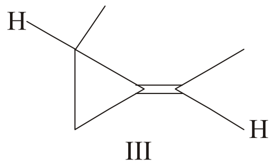
25. Arrange the following compounds in increasing order of the number of their stereocenters.



I



II



III

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

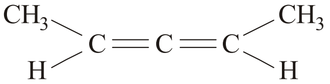
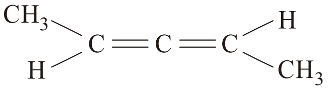
(c) II < I < III (d) II < III < I

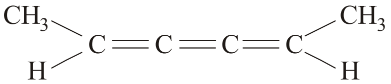
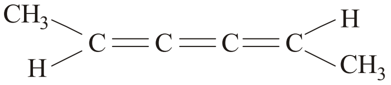
MARK YOUR RESPONSE					
	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ
	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ		

26. Reduction of but-2-yne with Na in liq. NH_3 gives an alkene, *A* which upon catalytic hydrogenation with D_2 in presence of Pt gives an alkane, *B*. Here *A* and *B* respectively are

(a) *cis*-but-2-ene and racemic-2, 3-dideuterobutane
(b) *cis*-but-2-ene and meso-2, 3-dideuterobutane
(c) *trans*-but-2-ene and meso-2, 3-dideuterobutane
(d) *trans*-but-2-ene and racemic-2, 3-dideuterobutane

27. Which of the following pairs are geometrical isomers ?

(a)  and 

(b)  and 

(c) Both (a) and (b)
(d) none of the two

MARK YOUR RESPONSE	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ			

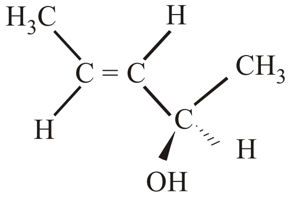
B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

Broadly speaking, there are three types of stereoisomers, namely conformational, geometrical and enantiomers. Although conformational isomers, have same configuration, geometrical isomers have different atoms attached to each of the doubly bonded carbon atom and enantiomers are due to chirality in the molecule. Enantiomers are also known as optical isomers. Those stereoisomers which are not enantiomers are known as diastereomers. In simple compounds, number of stereoisomers in a chiral molecule is given by the relation 2^n, where *n* is the number of dissimilar chiral carbon.

Observe the following structure and answer the questions given below :



The priority order of the four groups is : $OH > C = C > CH_3 > H$

1. How many stereoisomers are possible in 3-penten-2-ol, $CH_3CH{=}CHCHOHCH_3$

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

2. The correct name for the above structure is :

(a) (2S, 3E)-3-penten-2-ol (b) (2R, 3E)-3-penten-2-ol
(c) (2R, 3Z)-3-penten-2-ol (d) (2S, 3Z)-3-penten-2-ol

3. Enantiomer of (2R, 3E)-3-penten-2-ol will be :

(a) 2 R, 3 Z (b) 2 S, 3 Z
(c) 2 S, 3 E (d) 2 S, 3 R

4. The structure can have how many other diastereomers?

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

PASSAGE-2

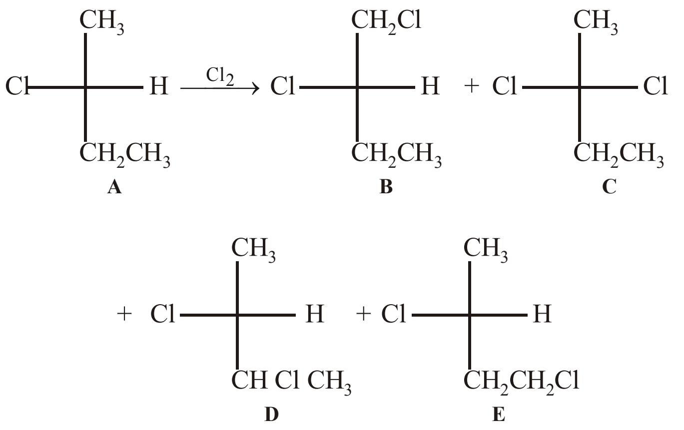
The D, L system of relative configuration is not 100% correct; and hence R, S system was adopted as a defect proof system for assigning absolute configuration. The R, S system involves the following steps :

Step I : The four atoms or groups attached to the chiral carbon atom are assigned a sequence of priorities according to sequence rules.

Step II : The arrangement of these four atoms is observed by drawing a curved arrow from the atom with the highest priority (1) to the atom with next highest priority (2) and if the direction of this arrow is clockwise it indicates R configuration, while the anticlockwise direction from group (1) to group (2) indicates **S** configuration. However, this convention is true only when the atom with the lowest priority (4) is present on the vertical bond, in case of Fischer projection. In case, the atom (4) lies on the horizontal bond opposite configuration is assigned.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	

Now observe the monochlorination of 2-chlorobutane and answer the questions given below :



Priority order of some groups :

$Cl > CH_2CH_3 > CH_3 > H; CH_2Cl > CH_2CH_3 ; CH_2CH_2Cl > CH_3$

5. Which of the above compounds have **S** configuration?

(a) only A (b) A and B
(c) A and E (d) B and E

6. Which of the above structures can exist as enantiomers?

(a) only A and B (b) A, B and E
(c) A, B, D and E (d) All the five

7. Which of the following structures can exist as *meso*-isomer?

(a) B (b) D
(c) E (d) None

8. Which of the following can represent diastereomeric pairs?

(a) B and E (b) B and D
(c) D and E (d) only D

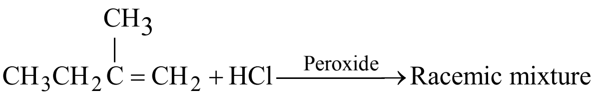
PASSAGE-3

When $CH_3CH = CH_2$ is treated with Br_2 it forms an optically inactive product, further the same compound when treated with HBr also forms optically inactive product.

$$CH_3CH = CH_2 + Br_2 \longrightarrow \text{Product}$$

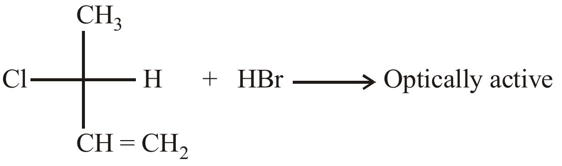
$$CH_3CH = CH_2 + HBr \longrightarrow \text{Product}$$

When HCl adds to 2-methyl-1-butene in the presence of benzoyl peroxide, the product is racemic mixture.



$$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2 + HCl \xrightarrow{\text{Peroxide}} \text{Racemic mixture}$$

However, when HBr adds on 3-chloro-1-butene, the product is found to be optically active.



9. Formation of optically inactive product by the additions of Br_2 and HBr on $CH_3CH = CH_2$ is

(a) of same type
(b) of different types
(c) due to formation of carbocation in I reaction and free-radical in II reaction
(d) due to formation of carbocation in both reactions.

10. The type of intermediate formed in the addition of HCl on 2-methyl-1-butene in presence of peroxide is

(a) carbocation (b) free radical
(c) carbanion (d) carbene

11. Optical activity in the product of the reaction of (+)-3-chloro-1-butene is due to

(a) formation of the (+)– enantiomer
(b) formation of the (–)– enantiomer
(c) formation of non-50 : 50 racemic mixture
(d) formation of diastereomeric pair

12. When an alkene having one chiral center on reaction with a reagent creates another chiral center, a diastereomeric pair is formed in which

(a) two components of the diastereomeric pair are formed in equal amounts
(b) two components of the diastereomeric pair are formed in different amounts
(c) either of the two is true
(d) none of the two is true

PASSAGE-4

In the S_N1 reaction of (**S**)-2-bromobutane with water, two substitution products are formed, one has the same relative configuration as the reactant and the other has the inverted configuration. This is because in such reactions, the leaving group departs before the nucleophile attacks.

In most of S_N1 reactions, the racemic product is non-50 : 50 mixture, i.e. partial racemization takes place, the inverted product is more than 50%. The formation of different composition of the product is due to following steps involved in S_N reactions.

$$\underset{\substack{\text{Undissociated}\\ \text{molecule}\\ \text{I}}}{R-X} \longrightarrow \underset{\substack{\text{Intimate}\\ \text{ion pair}\\ \text{II}}}{R^+X^-} \longrightarrow \underset{\substack{\text{Solvent−separated}\\ \text{ion pair}\\ \text{III}}}{R^+\text{solvent}\ X^-} \longrightarrow \underset{\substack{\text{Dissociated}\\ \text{ions}\\ \text{IV}}}{R^+ \quad X^-}$$

MARK YOUR RESPONSE	5. ⓐⓑⓒⓓ	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ
	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ		

13. Which type of intermediate is formed in the reaction of (**S**)-2-bromobutane with water?

(a) sp^3 hybridised (b) sp^2 hybridised
(c) sp hybridised (d) a transition state

14. 50 : 50 racemic mixture is due to attack of the nucleophile on which intermediate species of the reaction

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

15. The non-50 : 50 racemic mixture during S_N reaction of an alkyl halide is due to attack of the nucleophile on species

(a) I (b) II
(c) III (d) Both II or III

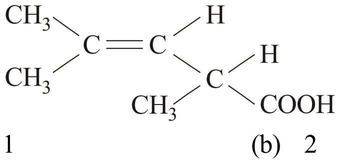
16. In the above reaction, the non-5 : 50 racemic contains more amount of

(a) original configuration (b) inverted configuration
(c) either of the two (d) None

PASSAGE-5

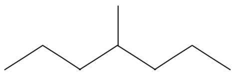
When all the atoms attached to a carbon are different, the carbon is said to be stereogenic carbon. Stereogenic centre is important in predicting the geometrical and optical isomerism. In optical isomerism, also known as enantiomerism, the four atoms or groups attached to a carbon should be different. Such carbon and molecule are respectively known as chiral carbon and chiral molecule. Chirality of a molecule is best described in terms of symmetry; a molecule having plane of symmetry is said to be achiral. In most cases (but not all) if no plane of symmetry is present, then the molecule is chiral.

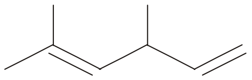
17. How many stereogenic centres are present in the following compound ?

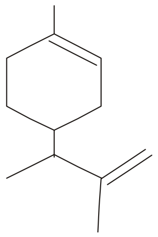


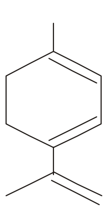
(a) 1 (b) 2
(c) 3 (d) 4

18. Which of the following compound has chiral carbon ?

(i)


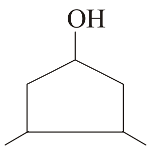
(ii)


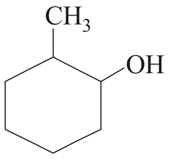
(iii)


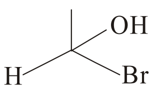
(iv)


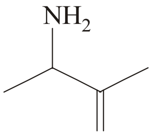
(a) (ii) (b) (ii) and (iii)
(c) (ii), (iii) and (iv) (d) All the four

19. Observe the following structures and pick up the correct option among those given below.

I.


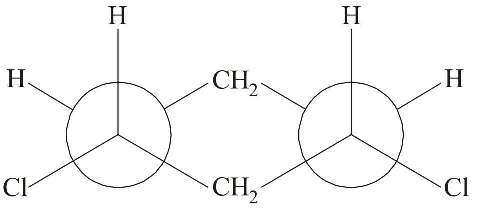
II.


III.


IV.


(a) All have stereogenic centre
(b) All but I have stereogenic centre
(c) All have plane of symmetry
(d) Only I is optically active

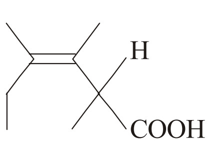
20.



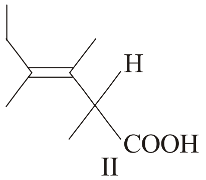
Above molecule has

(a) no chiral carbon and thus optically inactive
(b) one chiral carbon and thus optically active
(c) two chiral carbon atoms and optically active
(d) two chiral carbon atoms and optically inactive

21.



I



II

(i) I and II are same structures
(ii) I and II are enantiomers
(iii) I and II are diastereomers
(iv) I and II are geometrical isomers

Pick up the correct statement about above compounds.

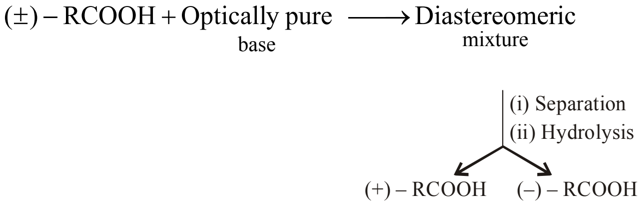
(a) (i) (b) (iii)
(c) (iv) (d) (iii) and (iv)

PASSAGE-6

The process of separation of a racemic modification into its enantiomers is known as resolution. Of the several methods of resolution, diastereomeric formation is considered to be the best. Diastereomers are stereoisomers which are not enantiomers. These are formed by treating racemic mixture of a compound with a pure enantiomer of another proper compound.

MARK YOUR RESPONSE	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ
	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	

Various types of organic compounds have been resolved by diastereomeric formation. The most common is the resolution of racemic mixture of an organic acid or organic base with optically active base or acid respectively. For example,



$$\underset{}{(\pm)-\text{RCOOH}} + \underset{\text{base}}{\text{Optically pure}} \longrightarrow \underset{\text{mixture}}{\text{Diastereomeric}}$$

On basis of the above facts, answer the following questions

22. The base used in the above reaction is
(a) (+) – base (b) (–) – base
(c) either (a) or (b) (d) (±) – base

23. The number of diastereomers formed in the above reaction is
(a) 1 (b) 2
(c) 3 (d) 4

24. The diastereomers formed in the above reaction can best be separated by
(a) distillation (b) fractional crystallisation
(c) reaction with base (d) hydrolysis with acid

25. The diastereomeric mixture formed in the above reaction when $(+)-\text{RNH}_2$ is used is

(i) $(+)-\text{RCOO}^{-}(-)-\overset{+}{\text{N}}\text{H}_3\text{R}$

(ii) $(+)-\text{RCOO}^{-}(+)-\overset{+}{\text{N}}\text{H}_3\text{R}$

(iii) $(-)-\text{RCOO}^{-}(-)-\overset{+}{\text{N}}\text{H}_3\text{R}$

(iv) $(-)-\text{RCOO}^{-}(+)-\overset{+}{\text{N}}\text{H}_3\text{R}$

(v) $(\pm)-\text{RCOO}^{-}(+)\overset{+}{\text{N}}\text{H}_3\text{R}$

(a) (i) and (ii) (b) (i) and (iii)
(c) (ii) and (iv) (d) (ii), (iv) and (v)

26. Diastereomeric method for resolution is applicable to racemic mixture of
(i) acids (ii) bases
(iii) hydrocarbons (iv) alcohols
(a) (i) and (ii) (b) (i), (ii) and (iv)
(c) (i) and (iii) (d) (i) to (iv)

MARK YOUR RESPONSE	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. Statement-1 : Addition of bromine to *trans*-2-butene yields *meso*-2, 3-dibromobutane.
Statement-2 : Bromine addition to an alkene is an electrophilic addition.

2. Statement-1 : Reduction of but-2-yne with H_2 in presence of Lindlar's catalyst gives *cis*-2-butene.
Statement-2 : Both alkyne and H_2 get absorbed over the surface of the catalyst and the two H-atoms are then transferred to the triple bond from the same face.

3. Statement-1 : Treatment of fumaric acid with OsO_4 followed by hydrolysis with an aqueous solution of $NaHSO_3$ gives a mixture of (+) and (–)-tartaric acids.
Statement-2 : OsO_4 brings about *trans*-addition of hydroxyl groups to the double bond.

4. Statement-1 : Benzaldehyde forms two oximes on reacting with NH_2OH.
Statement-2 : The two oximes arise due to geometrical isomerism around C=N bond.

5. Statement-1 : Diastereomers have different solubilities in the same solvent.
Statement-2 : Diastereomers may or may not be optically active.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. **Statement-1** : Nucleophilic substitution reaction of an optically active alkyl halide gives a mixture of enantiomers.

Statement-2 : The reaction occurs by S_N1 mechanism.

7. **Statement-1** : Organic compounds which do not contain chiral carbon atoms cannot be optically active.

Statement-2 : An organic compound is optically active only when its mirror image is non-superimposable irrespective of the fact whether it contains a chiral carbon atom or not.

8. **Statement-1** : Trihydroxyglutaric acid (HO_2C–CHOH–CHOH–CHOH–CO_2H) exists in four stereoisomeric forms; two of which are optically active while the other two are *meso*-forms.

Statement-2 : It contains two asymmetric and pseudo-asymmetric carbon atom.

9. **Statement-1** : The styrene molecule does not exhibit geometrical isomerism.

Statement-2 : All the carbon atoms of styrene molecule lie in a plane.

10. **Statement-1** : Addition of HCN to benzaldehyde gives racemic cyanohydrin.

Statement-2 : Attack of CN^- ion from the upper face of C=O group of benzaldehyde is favoured while from the lower face is retarded due to steric hindrance.

11. **Statement-1** : Addition of Br_2 to 1-butene gives two optical isomers.

Statement-2 : The product contains one asymmetric carbon.

12. **Statement-1** : Optically active 2-iodobutane on treatment with NaI in acetone undergoes racemization.

Statement-2 : Reaction involves multiple Walden inversion forming mixture of dextro and laevo isomers.

13. **Statement-1** : Addition of H_2O_2/OsO_4 to *cis*-alkene forms optically inactive product.

Statement-2 : *d*- and *l*-isomers are formed in equal amounts.

14. **Statement-1** : 2-Butyne when reduced with Na/NH_3 gives *trans*-2-butene.

Statement-2 : 2-Butene has *cis*- and *trans*-isomers.

15. **Statement-1** : β-Dehydrohalogenation of alkyl halides is *anti* elimination in which bond breaking and bond forming occur simultaneously.

Statement-2 : β-Dehydrohalogenation of alkyl halides gives Saytzeff product.

16. **Statement-1** : The rate enhancement by neighbouring group participation is called anchimeric assistance.

Statement-2 : The neighbouring group acting as nucleophile is present in the same molecule.

17. **Statement-1** : Molecules that are not superimposable on their mirror images are chiral.

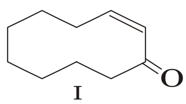
Statement-2 : All molecules containing chiral centre are optically active.

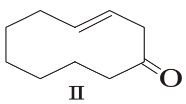
MARK YOUR RESPONSE	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ
	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ			

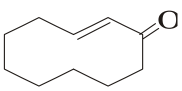
D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. Which of the following statement is true?

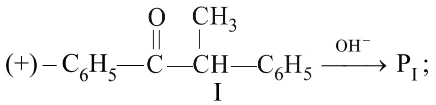

I

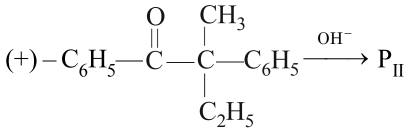

II


III

(a) I and III are diastereomers.
(b) I and II are constitutional isomers.
(c) I and III are constitutional isomers.
(d) All are same.

2. Each of the following two ketones is treated with a base (KOH)


$$(+)-C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-C_6H_5 \xrightarrow{OH^-} P_I;$$
I


$$(+)-C_6H_5-\overset{\overset{O}{\|}}{C}-\underset{\underset{C_2H_5}{|}}{\overset{\overset{CH_3}{|}}{C}}-C_6H_5 \xrightarrow{OH^-} P_{II}$$
II

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ				

Which of the following statement is *false* regarding above reactions ?

(a) Both P_I as well as P_{II} are racemic mixtures
(b) Both P_I as well as P_{II} are optically pure enantiomers
(c) P_I is optically pure while P_{II} is a racemic mixture
(d) P_I is a racemic mixture while P_{II} is optically pure.

3. Which of the following pairs represent stereoisomerism?

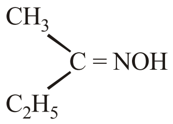
(a) Geometrical isomerism, position isomerism
(b) Geometrical isomerism, conformational isomerism
(c) Optical isomerism, geometrical isomerism
(d) Optical isomerism, metamerism

4. Which of the following compounds will show geometrical isomerism?

(a) 1-Phenylpropene (b) 2-Methyl-2-butene
(c) Acetaldoxine (d) Acetone oxime

5. Which of the following can exist in *syn* and *anti* forms?

(a) $C_6H_5N=NOH$ (b) $C_6H_5CH=NOH$

(c) 

(d) $C_6H_5N=NC_6H_5$

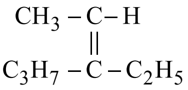
6. Which of the following can show geometrical isomerism?

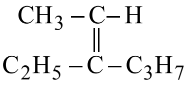
(a) 2-Butene (b) 1-Butene
(c) 1,3-Butadiene (d) Isobutene

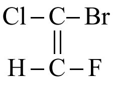
7. *cis*-2-Butene and *trans*-2-butene are

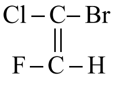
(a) geometrical isomers (b) diastereomers
(c) enantiomers (d) position isomers

8. Which of the following is/are Z isomer?

(a) 
$\begin{array}{c} CH_3-C-H \\ \| \\ C_3H_7-C-C_2H_5 \end{array}$

(b) 
$\begin{array}{c} CH_3-C-H \\ \| \\ C_2H_5-C-C_3H_7 \end{array}$

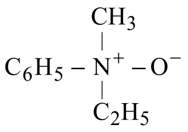
(c) 
$\begin{array}{c} Cl-C-Br \\ \| \\ H-C-F \end{array}$

(d) 
$\begin{array}{c} Cl-C-Br \\ \| \\ F-C-H \end{array}$

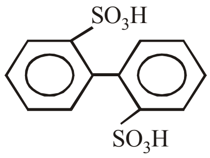
9. The lowest molecular weight alkanes which are optically active are

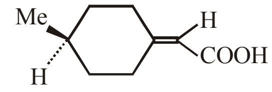
(a) 3-Methylhexane (b) 2,3-Dimethylpentane
(c) 2,3,3-Trimethylbutane (d) 2-Methylhexane

10. Which of the following are optically active?

(a) 
$C_6H_5-\overset{\overset{CH_3}{|}}{\underset{\underset{C_2H_5}{|}}{N^+}}-O^-$

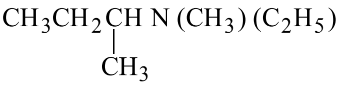
(b) $CH_3CH=C=CH_2$

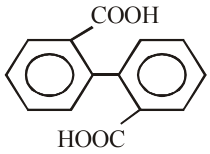
(c) 

(d) 

11. Which of the following compounds are chiral and resolvable?

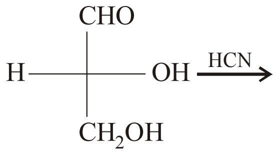
(a) $[C_6H_5N^+(CH_2CH_2CH_3)(C_2H_5)(CH_3)]Br^-$
(b) $C_6H_5N(CH_3)(C_2H_5)$

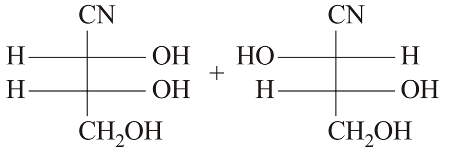
(c) 
$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}N(CH_3)(C_2H_5)$

(d) 

12. In which of the following cases, addition to 2-butene is stereoselective ?

(a) HCOOOH (b) MnO_4^-/OH^-
(c) D_2 (d) Br_2

13. 



I II

Compounds I and II are

(a) optical isomers (b) epimers
(c) enantiomers (d) diastereomers

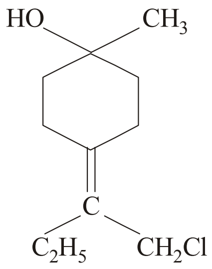
14. Fructose, on reduction gives a mixture of two alcohols which are

(a) enantiomers (b) diastereomers
(c) epimers (d) anomers

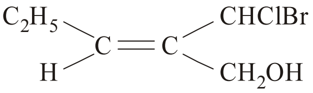
MARK YOUR RESPONSE	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ	6. ⓐⓑⓒⓓ
	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ
	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ		

15. Which of the following is/are optically active ?

(a)

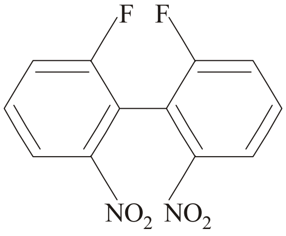


(b)

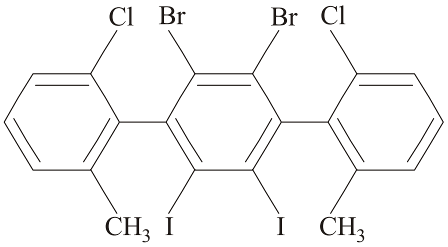


$$\mathrm{C_2H_5(H)C{=}C(CHClBr)(CH_2OH)}$$

(c)



(d)



16. D-(+)-Tartaric acid is named so because

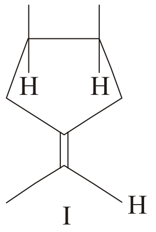
(a) it has positive optical rotation and is derived from D-(+)-glyceraldehyde

(b) it has positive optical rotation and is derived from D-glucose

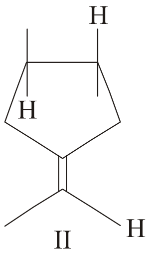
(c) it is dextro-rotatory

(d) none of the above is correct

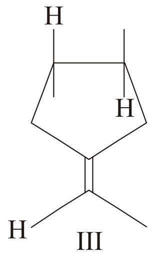
17. Which of the following represents enantiomeric pair ?



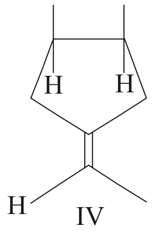
I



II



III



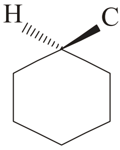
IV

(a) I and IV (b) I and II

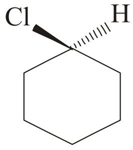
(c) II and III (d) II and IV

18. Which of the following pairs is/are example of achiral-identical mirror images ?

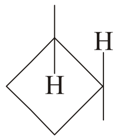
(a)



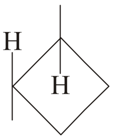
and



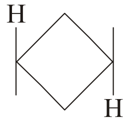
(b)



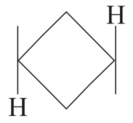
and



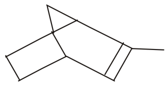
(c)



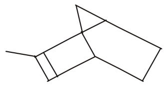
and



(d)

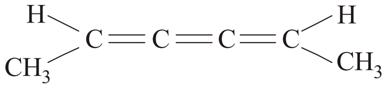


and



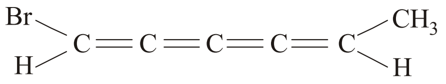
19. Which is optically active ?

(a)



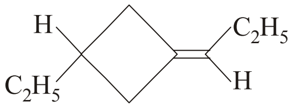
$$\mathrm{H(CH_3)C{=}C{=}C{=}C(H)(CH_3)}$$

(b)

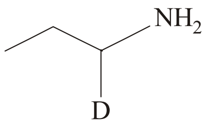


$$\mathrm{Br(H)C{=}C{=}C{=}C{=}C(CH_3)(H)}$$

(c)



(d)



Mark Your Response	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ

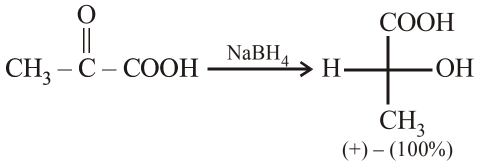
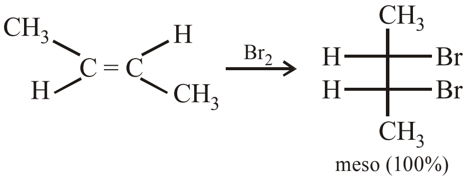
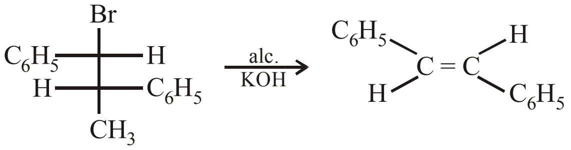
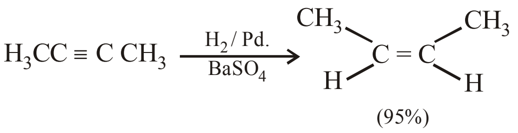
E

MATRIX-MATCH TYPE

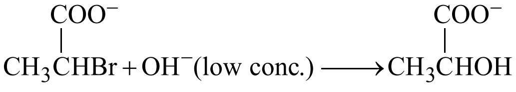
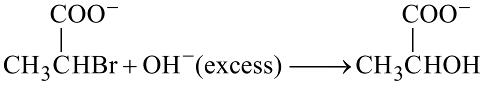
Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II.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

	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

1.

	Column-I		Column-II
A.		p.	Stereospecific
B.		q.	Stereoselective
C.		r.	*anti*-Addition
D.		s.	*anti*-Elimination

2.

	Column-I		Column-II
A.	$CH_3CH_2MgBr + HBr \longrightarrow CH_3CH_3$	p.	SE1
B.	$CH_3COOAg + Br_2 \longrightarrow CH_3Br$	q.	Configuration retained
C.	 $CH_3\overset{\overset{COO^-}{\mid}}{C}HBr + OH^-(\text{low conc.}) \longrightarrow CH_3\overset{\overset{COO^-}{\mid}}{C}HOH$	r.	SE2
D.	 $CH_3\overset{\overset{COO^-}{\mid}}{C}HBr + OH^-(\text{excess}) \longrightarrow CH_3\overset{\overset{COO^-}{\mid}}{C}HOH$	s.	Configuration inverted

MARK YOUR RESPONSE

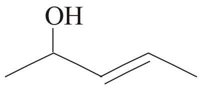
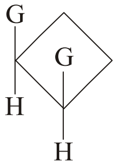
1.

	p	q	r	s
A	○	○	○	○
B	○	○	○	○
C	○	○	○	○
D	○	○	○	○

2.

	p	q	r	s
A	○	○	○	○
B	○	○	○	○
C	○	○	○	○
D	○	○	○	○

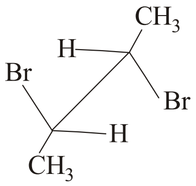
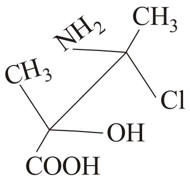
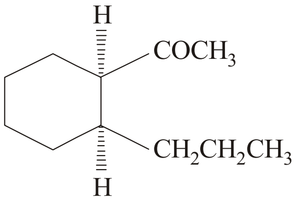
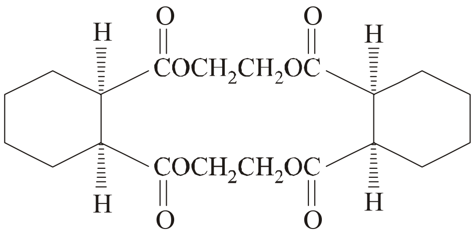
3.

Column - I	**Column - II**
A. $CH_3CH=CH_2 > CH_2=CH_2$	p. Configurational isomerism
B. $CH_3CH=CHCH_3 > (CH_3)_2C=CH_2$	q. Conformational isomerism
C. 	r. Reactivity with HBr
D. 	s. Heat of hydrogenation

4.

Column - I	**Column - II**
A. Asymmetric synthesis reaction	p. Carbocation intermediate is not formed
B. Stereospecific reaction	q. Two stereoisomers are formed in unequal amounts
C. Stereoselective reaction	r. Product has inverted configuration
D. Pericyclic reaction	s. A transition state is formed

5.

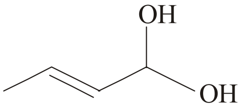
Column - I	**Column - II**
A. 	p. Achiral
B. 	q. Compound having even number of chiral centres
C. 	r. Chiral
D. 	s. Meso

MARK YOUR RESPONSE

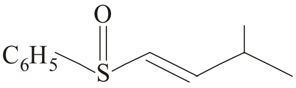
	3. p	q	r	s	4. p	q	r	s	5. p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ	ⓟ	ⓠ	ⓡ	ⓢ

6. **Column - I**

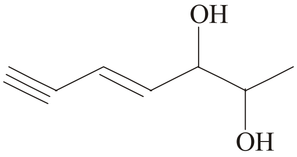
A.



B.



C.



Column - II

p. Two stereocentres

q. Three stereocentres

r. Four stereocentres

s. Enantiomerism

MARK YOUR RESPONSE

6.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

Answerkey

A SINGLE CORRECT CHOICE TYPE

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

B COMPREHENSION TYPE

1	(d)	**6**	(c)	**11**	(d)	**16**	(b)	**21**	(b)	**26**	(b)
2	(b)	**7**	(b)	**12**	(c)	**17**	(a)	**22**	(c)		
3	(c)	**8**	(d)	**13**	(b)	**18**	(b)	**23**	(b)		
4	(c)	**9**	(b)	**14**	(d)	**19**	(b)	**24**	(c)		
5	(c)	**10**	(a)	**15**	(d)	**20**	(d)	**25**	(c)		

C REASONING TYPE

1	(b)	**4**	(a)	**7**	(d)	**10**	(c)	**13**	(c)	**16**	(b)
2	(a)	**5**	(b)	**8**	(a)	**11**	(a)	**14**	(b)	**17**	(c)
3	(c)	**6**	(a)	**9**	(b)	**12**	(a)	**15**	(c)		

D MULTIPLE CORRECT CHOICE TYPE

1.	a,b	**2.**	a,b,c	**3.**	b,c	**4.**	a,c	**5.**	a,b,c	**6.**	a,c	**7.**	a,b	**8.**	a,c	**9.**	a,b	**10.**	a,c,d
11.	a,c	**12**	a,b,c,d	**13**	a,b,d	**14**	b,c	**15**	a,b,c	**16**	b	**17**	a,c	**18**	a,b,c	**19**	b,c,d		

E MATRIX-MATCH TYPE

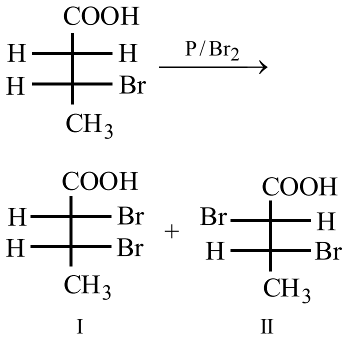
1. **A-q; B-p, q, r; C-p, q, s; D-q**
2. **A-p, q; B-q, r; C-q; D-s**
3. **A-r; B-s; C-p, q; D-p**
4. **A-q, r; B-q, r, s; C-q, r, s; D-p, q, r, s**
5. **A-p, q, s; B-q, r; C-q, r; D-p, q, s**
6. **A-p; B-q, s; C-r, s**

Solutions

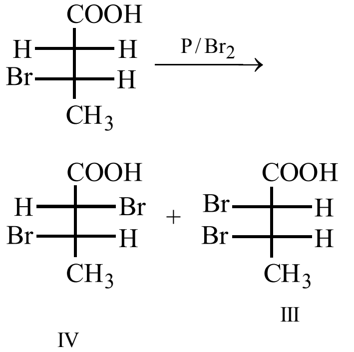
A SINGLE CORRECT CHOICE TYPE

1. **(c)** Reduction of alkyne by Na in liq. NH_3 produces *trans*-alkene on which bromine adds forming *meso* product.

2. **(b)**

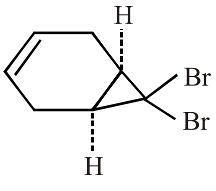


or

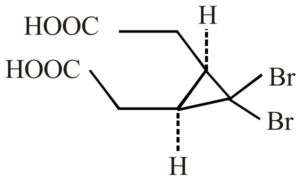


Note that I and IV are enantiomers, hence they represent one racemic mixture; similarly II and III are enantiomers and hence represent a different racemic mixture.

3. **(d)**



[X]

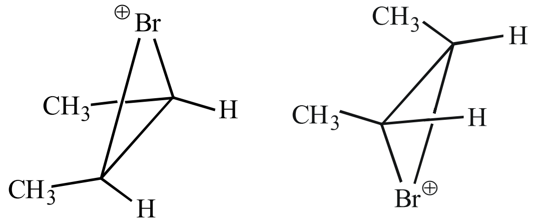


[Y] *meso*

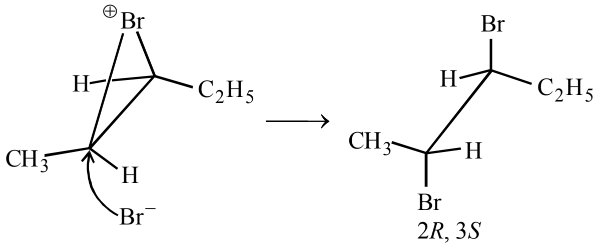
4. **(c)** A reaction that yields predominantly one stereoisomer (or one pair of enantiomers) of several possible diastereomers is called a *stereoselective reaction*, viz. addition of Br_2 on but-2-ene either gives *meso* or a pair of enantiomers, but not both products. A reaction in which stereochemically different reactants react differently is called a *stereospecific reaction*, viz. *cis*-but-2-ene gives racemic mixture, while *trans*-but-2-ene gives *meso* diastereoisomer. Note that every stereospecific reaction is stereoselective but the reverse is not true.

5. **(b)** A cyclic bromonium ion is formed as an intermediate which is attacked from the opposite side to give *anti* addition product.

6. **(c)**

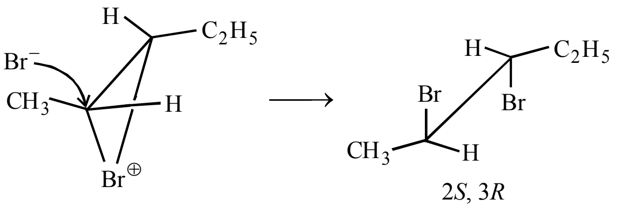


7. **(c)** Even though attacks by the two paths – at the methyl end and at the ethyl end – are not equally likely, the products is racemic : (2*R*, 3*S*)- and (2*S*, 3*R*)-2, 3-dibromopentane.There are equal amounts of the enantiomeric cyclic bromonium ions undergoing attack. The product from one bromonium ion undoubtedly consists of unequal amounts of the two possible enantiomeric dibromides; if, say, attack at the methyl end were preferred, then *R, S* > *S, R*.



+ some 2*S*, 3*R*

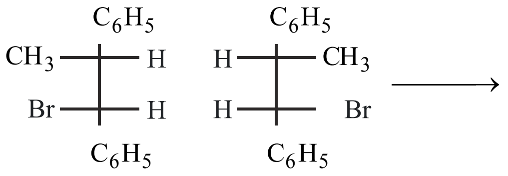
But this would be exactly balanced by the same preference for attack at the methyl end of the other (enantiomeric) bromonium ion, to give *S, R* > *R, S*.



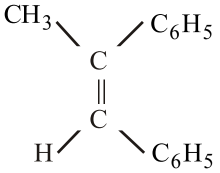
+ some 2*R*, 3*S*

8. **(d)** I and III, I and IV, II and III, II and IV are diastereomeric pairs.

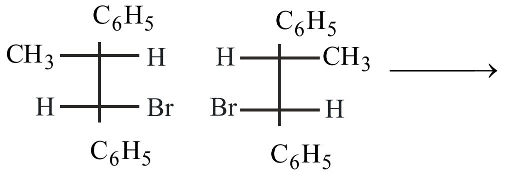
9. **(c)**



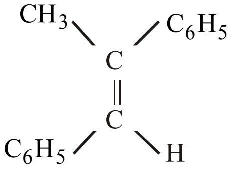
erythro



(Z) -1, 2-Diphenyl-1-propene (100%)



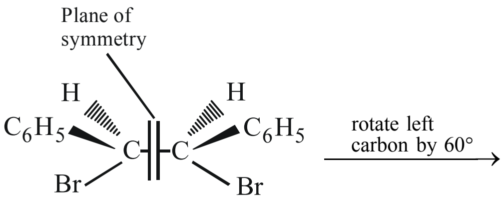
threo



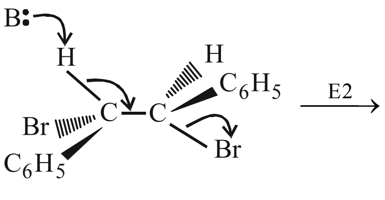
(E)-1, 2-Diphenyl-1-propene (100%)

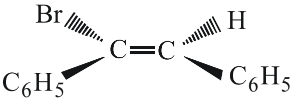
Thus the reaction is stereoselective as well as stereospecific.

10. **(a)** The necessary condition for an E2 reaction is that the –H and –X must be anti and coplanar. The required conformation of the *meso* structure-I can be achieved by rotating the left carbon by 60°; the new *meso* structure II on E 2 reaction gives E-alkene.



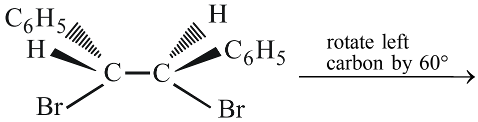
Meso isomer



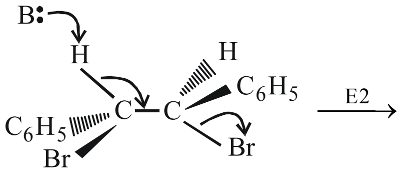


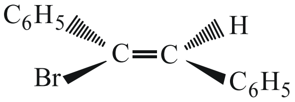
(E)-1-Bromo-1, 2-diphenylethene

The E2 reaction of the proper conformation of either enantiomer of the racemic mixture gives Z-alkene.



One enantiomer of the racemic mixture

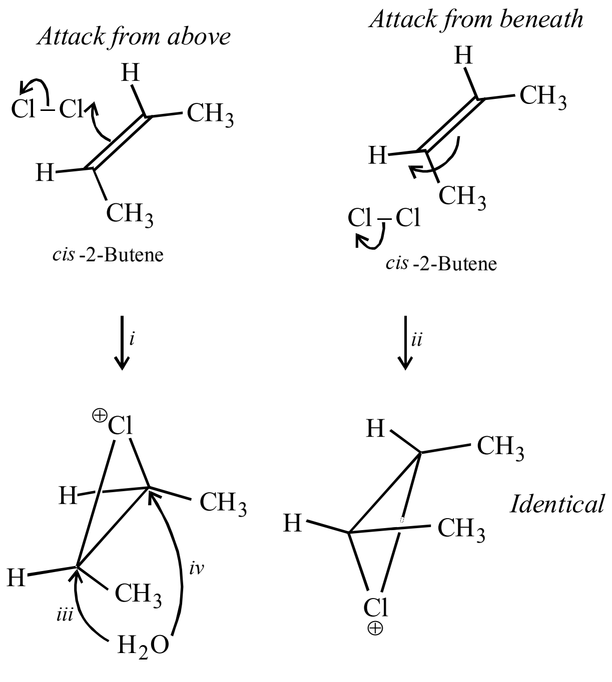


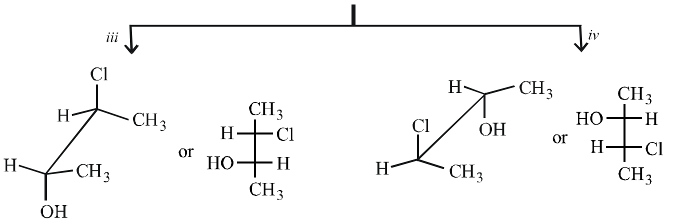


(Z)-1-Bromo-1, 2-diphenylethene

11. **(d)** E1 eliminations are non-stereoselective and non-stereospecific since the leaving groups are lost in different steps. The carbocation formed in the first step could exist in various conformations-either as initially formed or through subsequent rotation about a carbon-carbon bond, from which a β-proton could be lost.

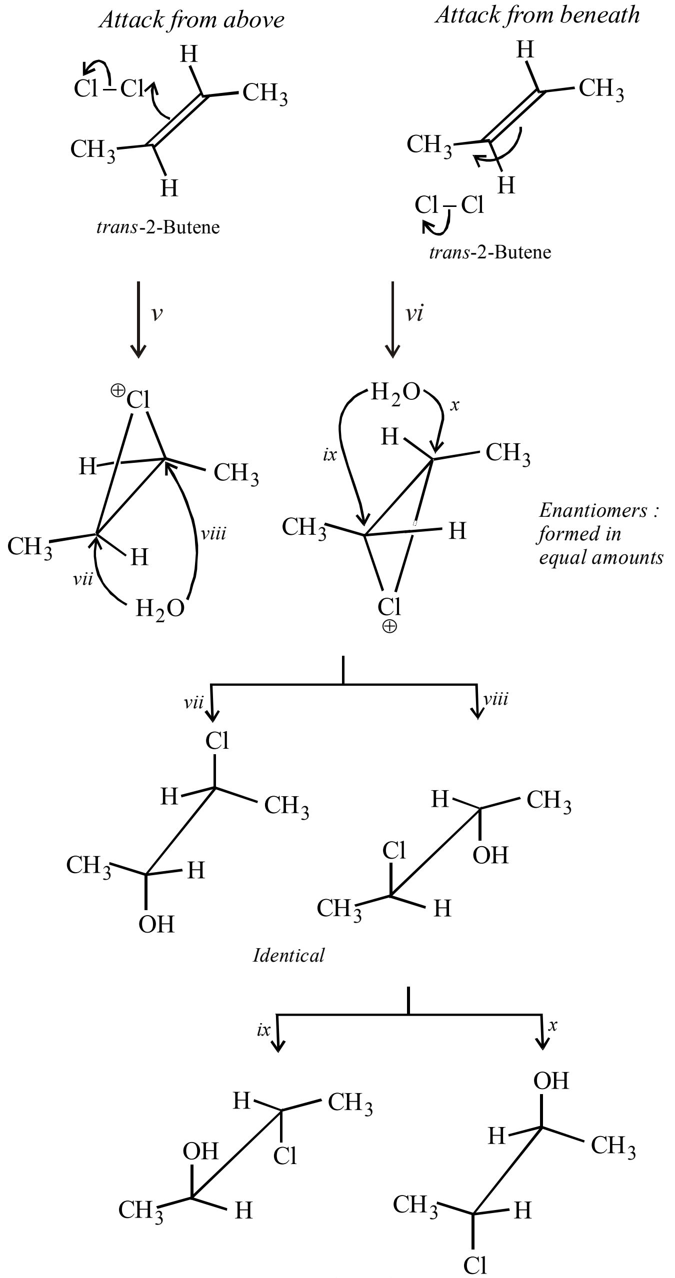
12. **(c)** Halohydrin formation is an *anti*-addition reaction in which same cyclic chloronium ion is formed in *cis*-but-2-ene whether Cl_2 attacks from the top side or from the bottom side of the molecule. Nucleophile now adds on this chloromium ion from the opposite side forming *threo* halohydrin.

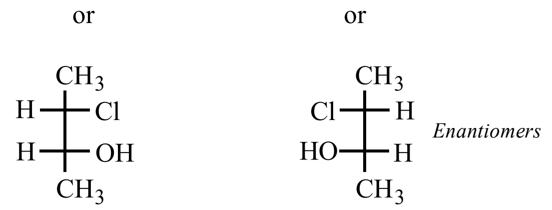




threo-3-Chloro-2-butanol (enantiomers formed in equal amounts, hence racemic modification)

However in *trans*-2-butene two different (an enantiomeric pair) cyclic chloromium ions will be formed, one due to attack from above and another due to attack from below. However, each enantiomer gives only one chlorohydrin on reaction with nucleophile (H_2O) leading to two enantiomeric chlorohydrins.





erythro-3-Chloro-2-butanol
Racemic modification

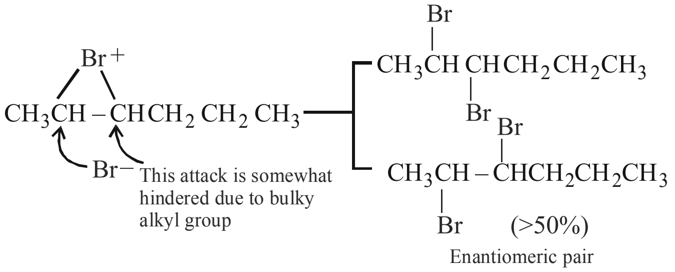
13. **(b)** Conceptual question.

14. **(b)** Conceptual question.

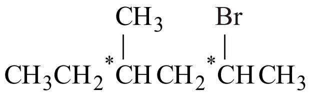
15. **(d)** A regioselective reaction is that in which bond making and bond breaking occur on one location in preference to all other possible locations.

16. **(d)** $CH_3CH = CHCH_2CH_2CH_3 \xrightarrow{Br_2}$

cis–/*trans*–2–Hexene



17. **(d)** The product, 2-bromo-4 methylhexane, has two chirality centers

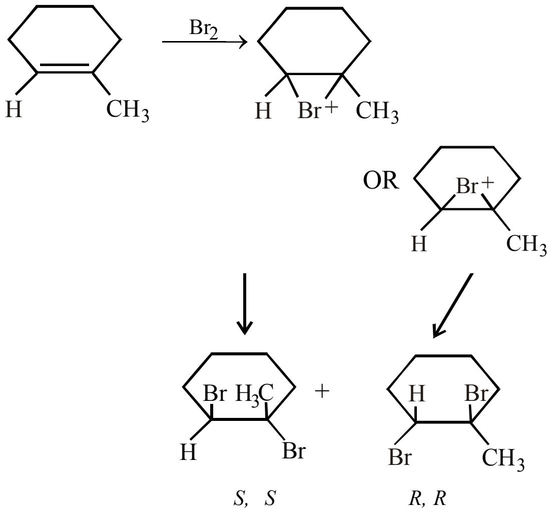


$$CH_3CH_2\overset{*}{C}H(CH_3)CH_2\overset{*}{C}H(Br)CH_3$$

Since C_4 of the product has *R* configuration in the reactant, and since this chirality center is unaffected by the reaction, its configuration is unaffected (assuming that the relative priorities of the four group are not changed by the reaction); i.e. the configuration at C_4 in the product is also *R*.

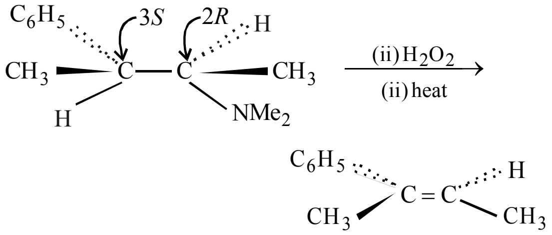
Addition of HBr involves the formation of carbocation, it is attacked by Br^- form top as well as bottom face leading to configuration at C_2 as *R* as well as *S*. However, the carbocation does not have a plane of symmetry, it is chiral because of the chirality center at C_4, *hence it will not be attacked equally from the two faces,* leading to a mixture of 2*R* and 2*S* products in a ratio other than 50 : 50. Thus the net result is the formation of two diastereomeric products [2*R*, 4*R*]– and [2*S*, 4*R*]– in unequal amounts.

18. **(a)**



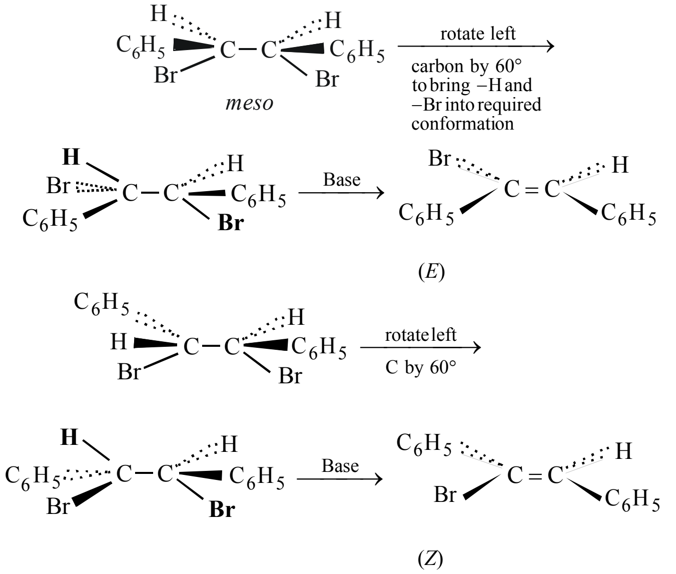
Since both bromonium ions do not have symmetry planes, so an unequal attack from right and left sides will take place leading to an unequal mixture of *R,* R and S, S products in each case. However, the minor product from [say*R, R or S, S*] will be major product from the other bromonium ion, so overall a 50 : 50 racemic mixture of *R,* R and *S, S* will be formed.

19. **(c)**

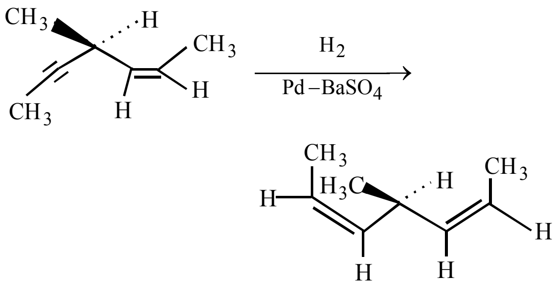


Cope elimination
(*syn*- elimination) (*E*)

20. **(b)** For an E 2 reaction, – H and –X must be oriented anti and coplanar (at a dihedral angle of 180°) to one another



21. **(b)**



Due to *cis* - addition of hydrogen to the triple bond, the reduced product has a plane of symmetry and hence is optically inactive.

B COMPREHENSION TYPE

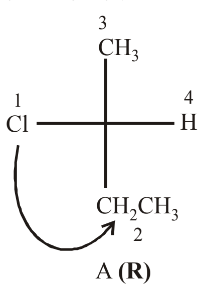
1.(d) The compound has one chiral carbon, so two enantiomers (**R** and **S**) are possible. Further, each enantiomer can exist in **E** and **Z** isomeric forms.

2.(b) The arrangement of the highest priority group (OH) to the next highest priority group (C=C) is in clockwise direction, hence it is **R**. Further the group of higher priority on each of the doubly bonded carbon lies in the opposite direction, it should be **E**.

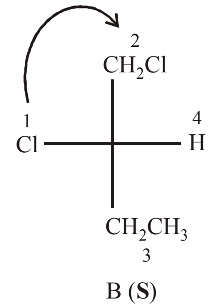
3.(c) The enantiomer of 2**R**, 3**E** will be 2**S**, 3**E**.

4.(c) Of the four possible stereoisomers, two are enantiomers and the rest two will be diastereomer of each of the enantiomer.

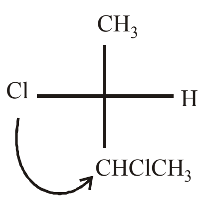
5.(c)



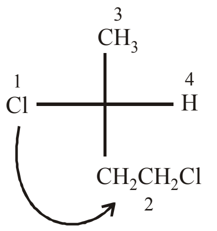
A (**R**)



B (**S**)



D(R)



E (**R**)

Note the lowest priority group (4) lies on horizontal bond, hence opposite convention should be adopted, i.e. R to anticlockwise and S to clockwise.

6.(c) Compound C is achiral, hence it does not show enantiomerism.

7–8.(b–d)

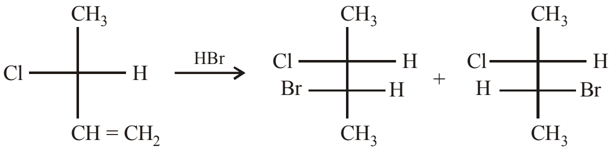
In D, a new chiral carbon is introduced, hence it can exist as 2**R**, 3**R** (optically active) and 2**R**, 3**S** (*meso*); the two structures are examples of diastereomers.

9.(b) $CH_3CH = CH_2 + Br_2 \longrightarrow \underset{\text{racemic mixture (optically inactive)}}{CH_3CHBrCH_2Br}$

$CH_3CH = CH_2 + HBr \longrightarrow \underset{\text{Achiral molecule (optically inactive)}}{CH_3CHBrCH_3}$

10.(a) Addition of HCl on an alkene involves the formation of carbocation as an intermediate. Remember that peroxide effect, i.e. formation of free radical as an intermediate, takes place only when hydrogen halide is HBr.

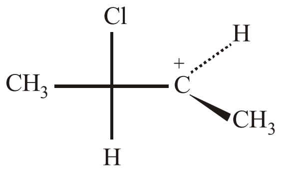
11.(d)



(+)-3-chloro-1-butene

A pair of diastereomers

12.(c) If the existing chirality center is near the positively charged carbon, one face of the intermediate carbocation will be more sterically hindered than the other and the incoming nucleophile will have greater access to the less sterically hindered face. Thus one diastereomer will be formed in greater amount than the other **(a stereoselective reaction)**.



One face of carbocation is more sterically hindered than the other.

13.(b) Since the leaving group (Br) is departing before the attack of the nucleophile, the intermediate formed must be carbocation which is *sp*^{2} hybridised.

14.(d) When the nucleophile attacks the completely dissociated carbocation (IV), there is no steric hindrance on either side of the carbocation with the result a 50 : 50 racemic mixture is obtained.

15–16.(d–b)

When the nucleophile attacks the carbocation of either the intimate ion pair (II) or the solvent-separated ion pair (III), the leaving group will partially block the approach of the nucleophile to that side of the carbocation; with the result a non-50 : 50 racemic mixture is obtained in which inverted configuration is in greater amount.

C REASONING TYPE

1.(b) Even though, both assertion and reason are correct, the correct reason for the formation of *meso*–2,3–dibromobutane from *trans*–2–butene is *anti* addition of Br_2.

2.(a) **R** is the correct explanation of **A**.

3.(c) **Correct R :** OsO_4 brings about *cis*-addition of hydroxyl groups.

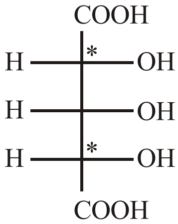
4.(a) **R** is the correct explanation of **A**.

5.(b) **Correct explanation :** Diastereomers are not mirror images of each other and hence have different solubilities in the same solvent.

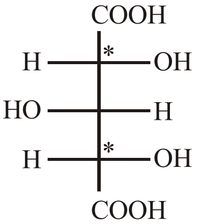
6.(a) **R** is the correct explanation of **A**.

7.(d) **Correct A :** Optically active compounds may or may not contain chiral carbon atom.

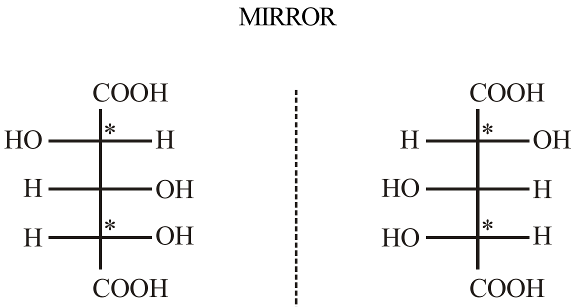
8.(a) **R** is the correct explanation of **A**.



meso-form



meso-form



(+)-form

(–)-form

The central carbon atom is pseudochiral carbon atom.

9.(b) **Correct explanation -** In styrene ($C_6H_5CH = CH_2$) the terminal carbon atom has two identical groups i.e. H-atoms.

10.(c) **Correct R :** Attack of CN^- ion from upper and lower faces occur with equal ease.

11.(a) $CH_3CH_2–CH{=}CH_2 + Br_2 \longrightarrow CH_3CH_2\overset{*}{C}H\,Br.CH_2Br$

C* is an asymmetric C-atom.

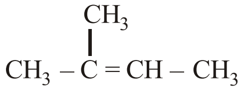
D MULTIPLE CORRECT CHOICE TYPE

1. **(a,b)** Structures I and II differ only in the position of the double bond, hence constitutional isomers; while structures I and III are stereoisomers but not optically active, hence diastereomers.

2. **(a,b,c)** Carbonyl compounds having αH form carbanion on treatment with a base, carbanion being flat can be attacked by proton on either side of the face forming racemic mixture. Only ketone I has α H, so it will form carbanion while ketone II does not form such carbanion.

3. **(b,c)** Geometrical isomers, optical isomers and conformational isomers differ in the relative arrangement of atoms in space.

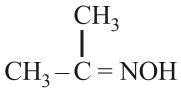
4. **(a,c)** $C_6H_5CH = CHCH_3$



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

(a) *(b)*

$CH_3CH = NOH$



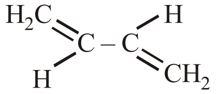
$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = NOH$

(c) *(d)*

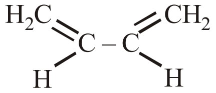
5. **(a,b,c)** In (d) each N has identical group.

6. **(a,c)** $CH_3CH = CHCH_3$

2-Butene



s-trans-1,3-Butadiene



s-cis-1,3-Butadiene

In (*c*), *s*-stands for single bond.

7. **(a,b)** Geometrical isomers are also diastereomers.

8. **(a,c)** In (a) and (c) groups of higher priority, i.e. CH_3 and C_3H_7 in (a) and Br and F in (c) are on the same side.

9. **(a,b)** Only (a) and (b) have chiral carbon.

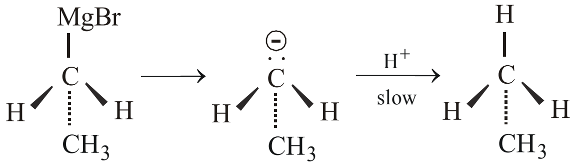
10. **(a,c,d)** Except (b), all have non-superimposable mirror image.

11. **(a,c)** (a) has chiral N and also resolvable because it has a resolvable mirror image.
(b) has chiral N but not resolvable because of rapid N-inversion
(c) has chiral N and chiral C and also resolvable because of presence of bulky alkyl groups.
(d) –COOH groups are small, hence do not provide sufficient steric hindrance to prevent rotation about C–C single bond, hence compound is non-resolvable.

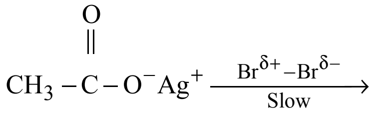
E MATRIX-MATCH TYPE

1. **A-q; B-p, q, r; C-p, q, s; D-q**
   (A) Here although two products are possible, only one is formed, the reaction is 100% stereoselective.
   (B) The reaction involves the addition of Br_2 on *trans*-alkene to form 100% *meso* product. It is **stereospecific** in the sense that it involves the addition on a stereoisomer (*trans*) and forms a stereoisomeric product (*meso*). Further every stereospecific reaction is **stereoselective**. Since here cyclic bromonium ion is formed as an intermediate, the two bromine atoms add in *anti*-manner.
   (C) This reaction is just the reverse of the above one, i.e. it involves the conversion of an optical isomer to geometrical isomer through elimination reaction, it is stereospecific, stereoselective and involves *anti* elimination.
   (D) Here one of the stereoisomeric product (95%) is formed from compound having no stereoisomerism, it is **highly stereoselective**.

2. **A-p, q; B-q, r; C-q; D-s**
   (A) $CH_3CH_2MgBr + HBr \longrightarrow CH_3CH_3 + MgBr_2$
   It is an example of S_E1. However, here carbanion is formed as an intermediate, which being tetrahedral, will be attacked only from one side leading to retention of configuration.



(B)

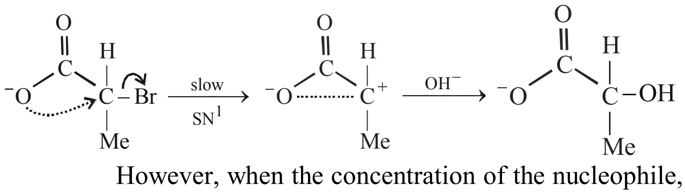


$CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - O^- Ag^+ \xrightarrow[\text{Slow}]{Br^{\delta+}-Br^{\delta-}}$

$CH_3 - Br + CO_2 + AgBr$

It is S_E2 reaction and proceeds with retention in configuration.

(C) When the carbon atom undergoing nucleophilic attack has an atom or group with unused electron pair, the group participates by using its electron pair and thus prevents the backside attack of carbon by nucleophile. Hence nucleophilic substitution takes place with retention of configuration.



However, when the concentration of the nucleophile, OH^- is increased the reaction undergoes S_N2 path.