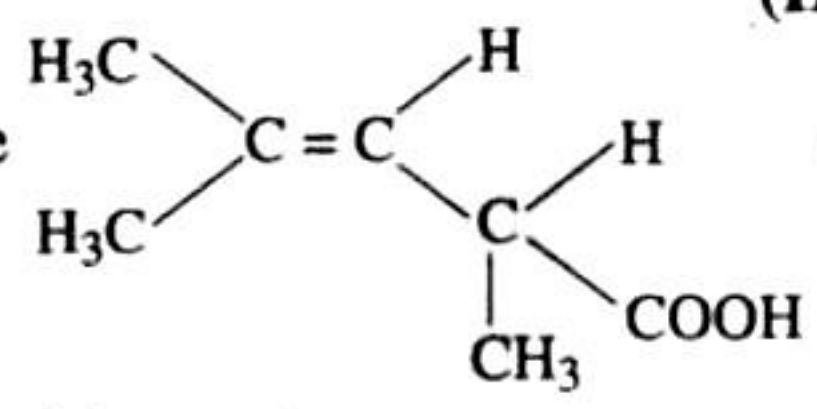


## ISOMERISM IN ORGANIC COMPOUNDS

### [JEE ADVANCED PREVIOUS YEAR SOLVED PAPERS]

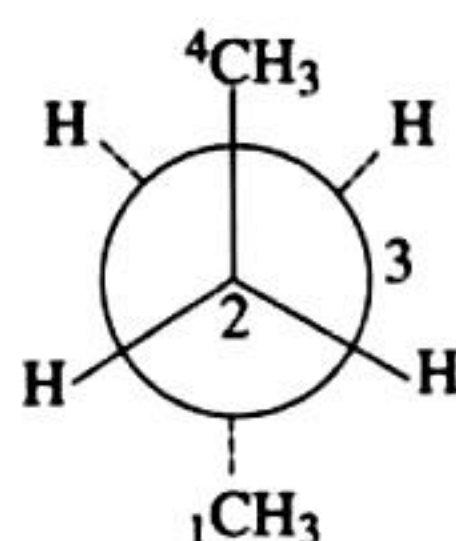
#### JEE Advanced

##### Single Correct Answer Type

- The compound which is not isomeric with diethyl ether is  
 a. *n*-propyl methyl ether    b. butan-1-ol  
 c. 2-methylpropan-2-ol    d. butanone  
 (IIT-JEE 1981)
- Which of the following will have the least hindered rotation about carbon-carbon bond?  
 a. Ethane    b. Ethylene  
 c. Acetylene    d. Hexachloroethane  
 (IIT-JEE 1981)
- How many optically active stereoisomers are possible for butane-2,3-diol?  
 a. 1    b. 2    c. 3    d. 4  
 (IIT-JEE 1981)
- Which of the following compounds will exhibit *cis-trans* (geometrical) isomerism?  
 a. 2-butene    b. 2-butyne  
 c. 2-butanol    d. butanal  
 (IIT-JEE 1983)
- An isomer of ethanol is  
 a. methanol    b. diethyl ether  
 c. acetone    d. dimethyl ether  
 (IIT-JEE 1986)
- The number of isomers of  $C_6H_{14}$  is  
 a. 4    b. 5    c. 6    d. 7  
 (IIT-JEE 1987, 2007)
- The enolic form of acetone contains:  
 a. 9  $\sigma$ -bonds, 1  $\pi$ -bond, and 2 lone pairs  
 b. 8  $\sigma$ -bonds, 2  $\pi$ -bond, and 2 lone pairs  
 c. 10  $\sigma$ -bonds, 1  $\pi$ -bond, and 1 lone pairs  
 d. 9  $\sigma$ -bonds, 2  $\pi$ -bond, and 1 lone pairs  
 (IIT-JEE 1990)
- The optically active tartaric acid is named as D-(+)-tartaric acid because it has a positive  
 a. Optical rotation and is derived from D-glucose  
 b. pH in organic solvent  
 c. Optical rotation and is derived from D-(+)-glyceraldehyde  
 d. Optical rotation when substituted by deuterium.  
 (IIT-JEE 1992)
- Isomers which can be interconverted through rotation around a single bond are  
 a. Conformers    b. Diastereomers  
 c. Enantiomers    d. Positional isomers  
 (IIT-JEE 1992)
- The structure  shows:  
 a. geometrical isomerism  
 b. optical isomerism  
 c. geometrical and optical isomerism  
 d. tautomerism  
 (IIT-JEE 1995)
- How many optically active stereoisomers are possible for butane-2,3-diol?  
 a. 1    b. 2    c. 3    d. 4  
 (IIT-JEE 1997)
- Which of the following will exhibit geometrical isomerism?  
 a. 1-Phenyl-2-butene    b. 3-Phenyl-1-butene  
 c. 2-Phenyl-1-butene    d. 1,1-Diphenyl-1-propene  
 (IIT-JEE 2000)
- The number of isomers for the compound with molecular formula  $C_2BrClFI$  is  
 a. 3    b. 4    c. 5    d. 6  
 (IIT-JEE 2001)
- Which of the following compounds exhibits stereoisomerism?  
 a. 2-methylbutene-1    b. 3-methylbutyne-1  
 c. 3-methylbutanoic acid    d. 2-methylbutanoic acid  
 (IIT-JEE 2002)



15. In the given conformation, if  $C_2$  is rotated about  $C_2 - C_3$  bond anticlockwise by an angle of  $120^\circ$  then the conformation obtained is



- a. fully eclipsed conformation  
b. partially eclipsed conformation  
c. gauche conformation  
d. staggered conformation

(IIT-JEE 2004)

16. The number of stereoisomers obtained by bromination of *trans*-2-butene is

- a. 1      b. 2      c. 3      d. 4

(IIT-JEE 2007)

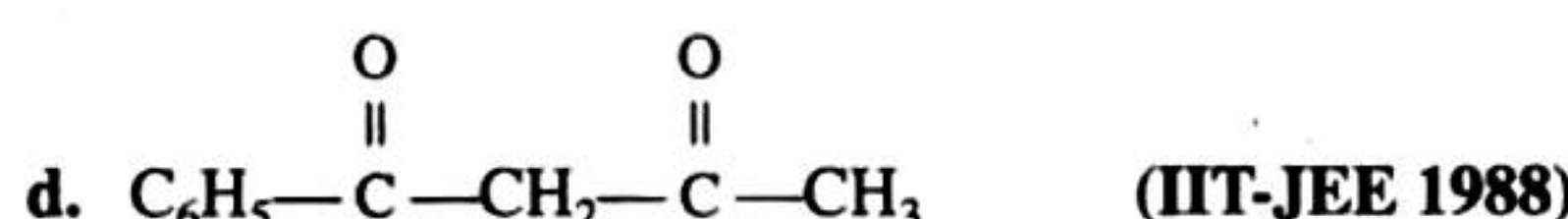
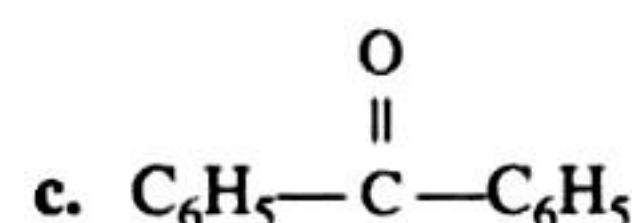
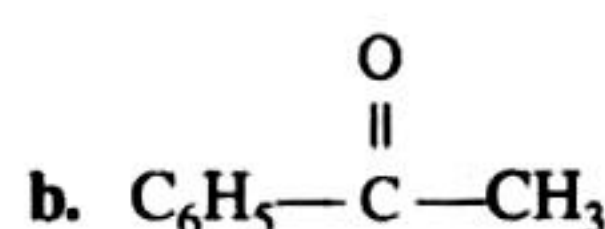
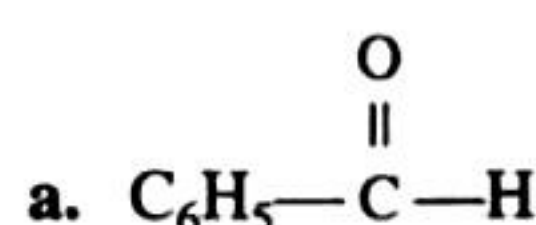
### Multiple Correct Answers Type

1. Only two isomeric monochloro derivatives are possible for:

- a. *n*-butane      b. 2, 4-dimethylpentane  
c. benzene      d. 2-methylpropane

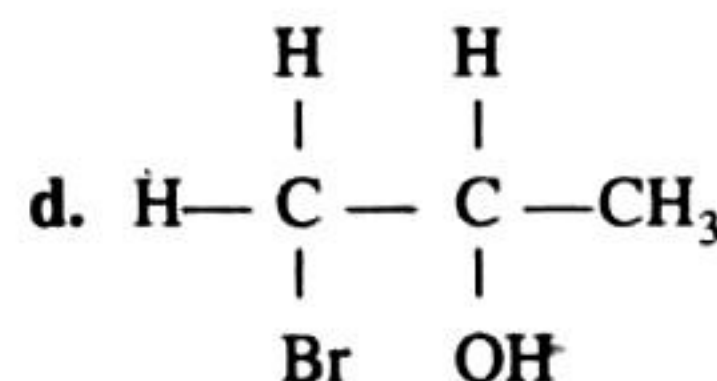
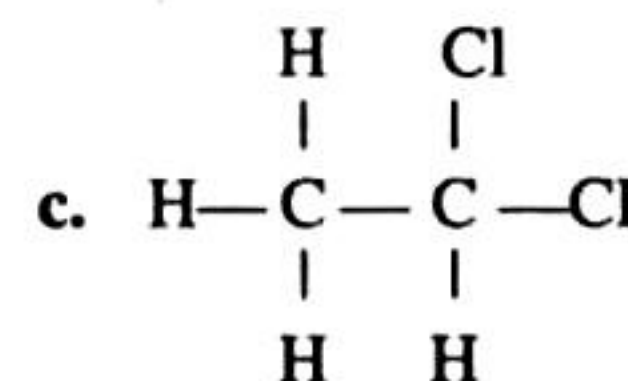
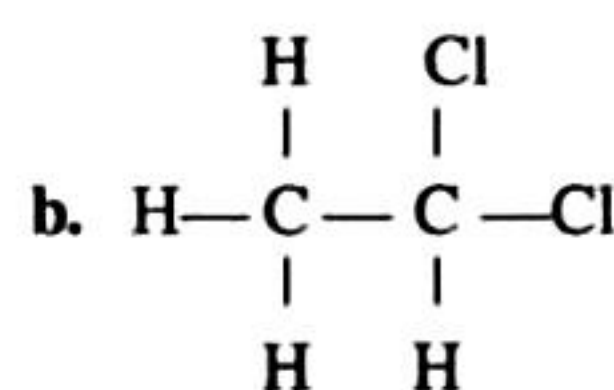
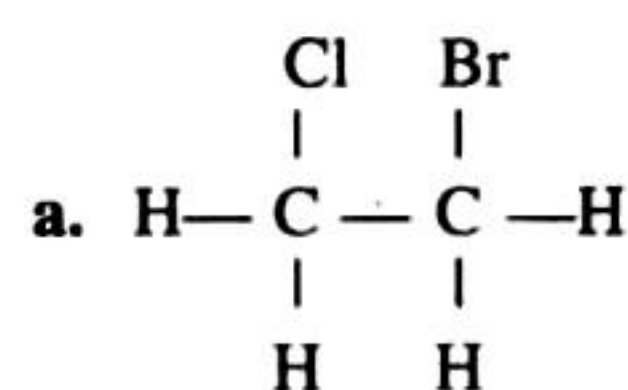
(IIT-JEE 1986)

2. *Keto-enol* tautomerism is observed in



(IIT-JEE 1988)

3. Which of the following have asymmetric carbon atom?



(IIT-JEE 1989)

4. The molecule(s) that will have dipole moment is/are

- a. 2,2-Dimethyl propane      b. *trans*-2-Pentene  
c. *cis*-3-Hexene      d. 2,2,3,3-Tetramethyl butane

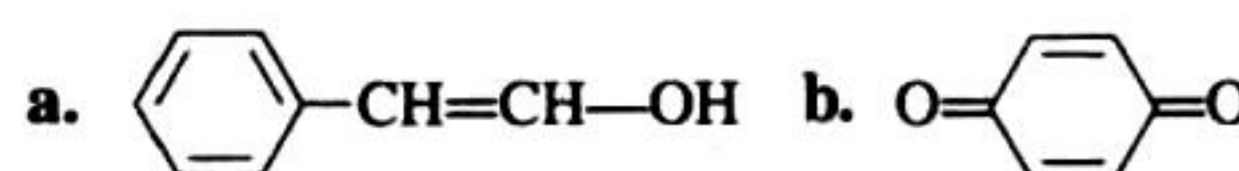
(IIT-JEE 1992)

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

- a. 2-butene      b. propene  
c. 1-phenylpropene      d. 2-methyl-2-butene

(IIT-JEE 1998)

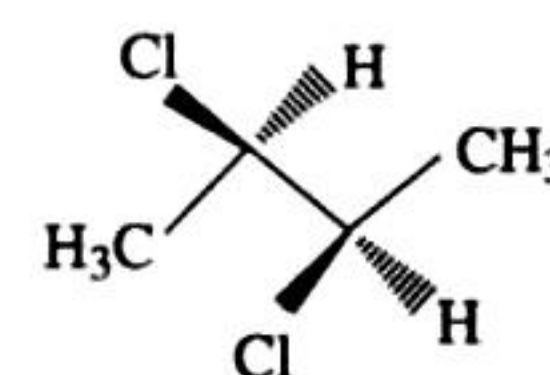
6. Tautomerism is exhibited by



(IIT-JEE 1998)

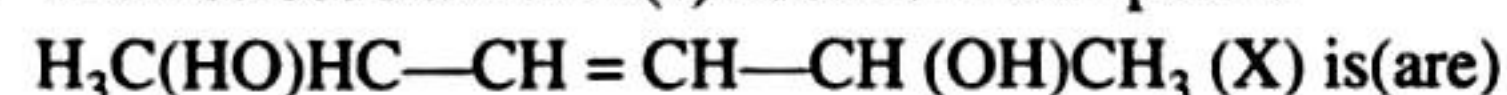
7. The correct statement(s) about the compound given below is (are)

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



(IIT-JEE 2008)

8. The correct statement(s) about the compound

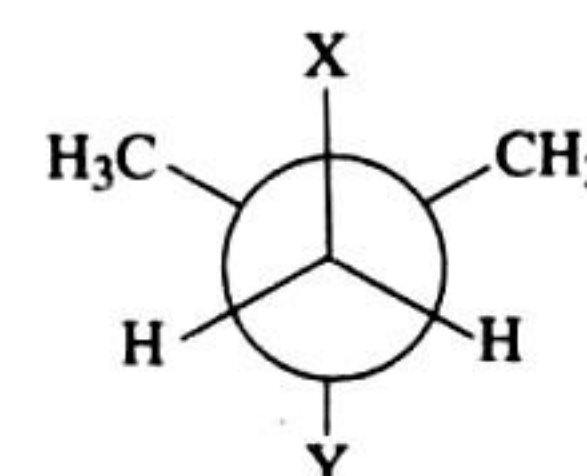


- a. The total number of stereoisomers possible for X is 6  
b. The total number of diastereomers possible for X is 3  
c. If the stereochemistry about the double bond in X is *trans*, the number of enantiomers possible for X is 4  
d. If the stereochemistry about the double bond in X is *cis*, the number of enantiomers possible for X is 2

(IIT-JEE 2009)

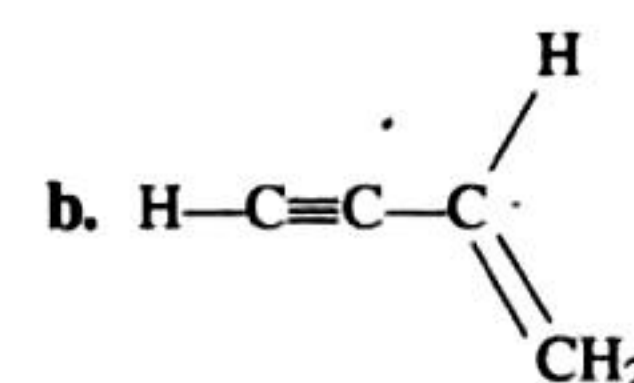
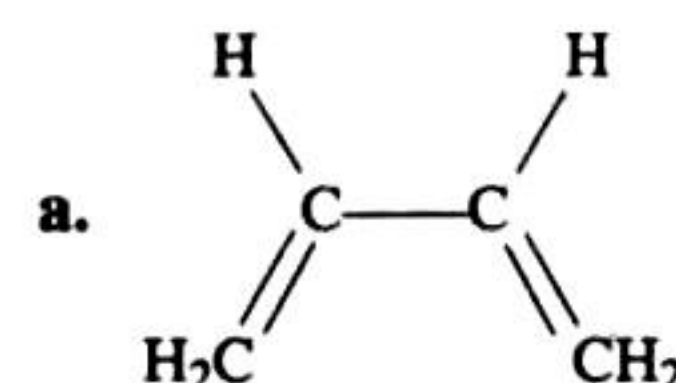
9. In the Newman projection for 2, 2-dimethylbutane X and Y can respectively be

- a. H and H  
b. H and  $\text{C}_2\text{H}_5$   
c.  $\text{C}_2\text{H}_5$  and H  
d.  $\text{CH}_3$  and  $\text{CH}_3$



(IIT-JEE 2010)

10. Amongst the given options, the compound(s) in which all the atoms are in one plane in all the possible conformations (if any), is (are)



(IIT-JEE 2011)

# Answer Key

## JEE Advanced

### Single Correct Answer Type

- |        |        |        |        |        |
|--------|--------|--------|--------|--------|
| 1. d.  | 2. a.  | 3. b.  | 4. a.  | 5. d.  |
| 6. b.  | 7. a.  | 8. c.  | 9. a.  | 10. b. |
| 11. b. | 12. a. | 13. d. | 14. d. | 15. c. |
| 16. a. |        |        |        |        |

### Multiple Correct Answers Type

- |                |           |           |           |            |
|----------------|-----------|-----------|-----------|------------|
| 1. a., d.      | 2. b., d. | 3. c., d. | 4. b., c. | 5. a., c.  |
| 6. a., c., d.  | 7. a., d. | 8. a., d. | 9. b., d. | 10. b., c. |
| 11. a., b., c. |           |           |           |            |

### Integer Answer Type

- |        |        |        |        |
|--------|--------|--------|--------|
| 1. (7) | 2. (5) | 3. (8) | 4. (2) |
|--------|--------|--------|--------|

### Assertion–Reasoning Type

1. c.

### Fill in the Blanks Type

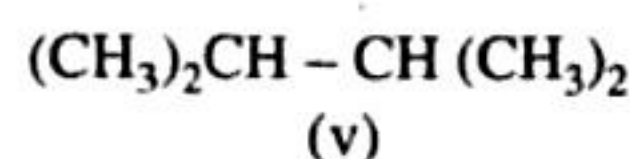
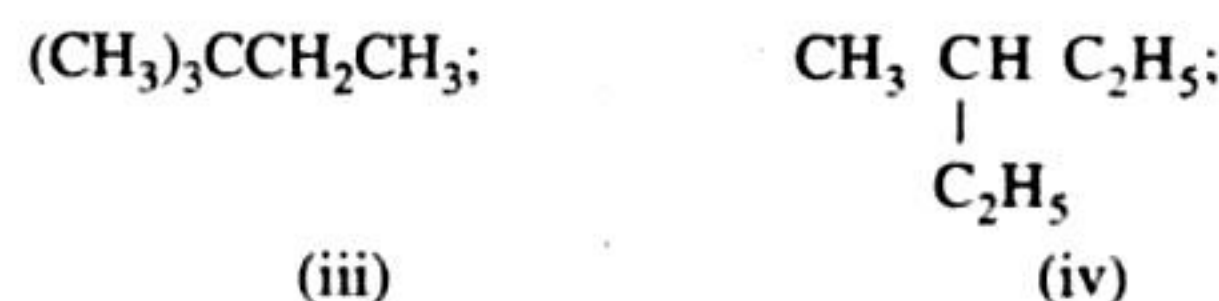
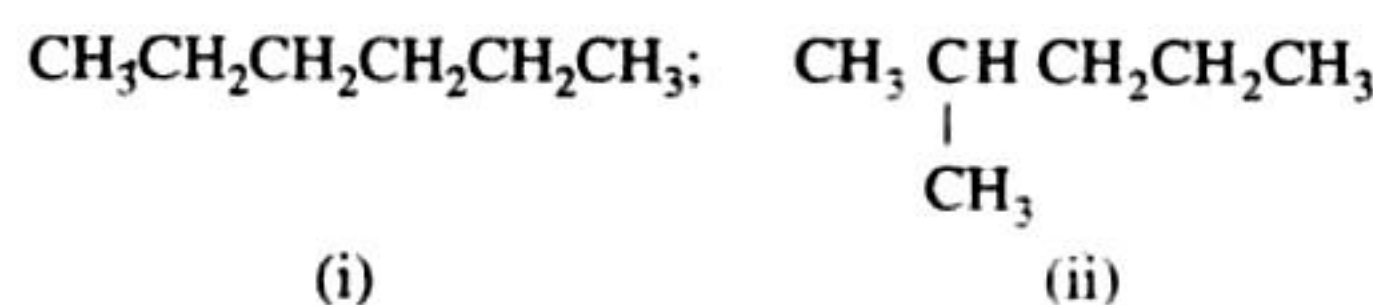
1. non-superimposable, enantiomers

### True/False Type

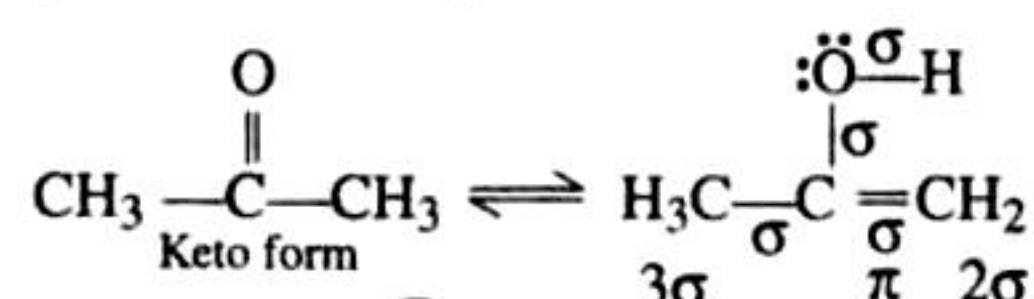
- |          |          |
|----------|----------|
| 1. False | 2. False |
|----------|----------|



## Hints and Solutions



7. a. (9σ, 1π, 2LP e<sup>-</sup>'s)

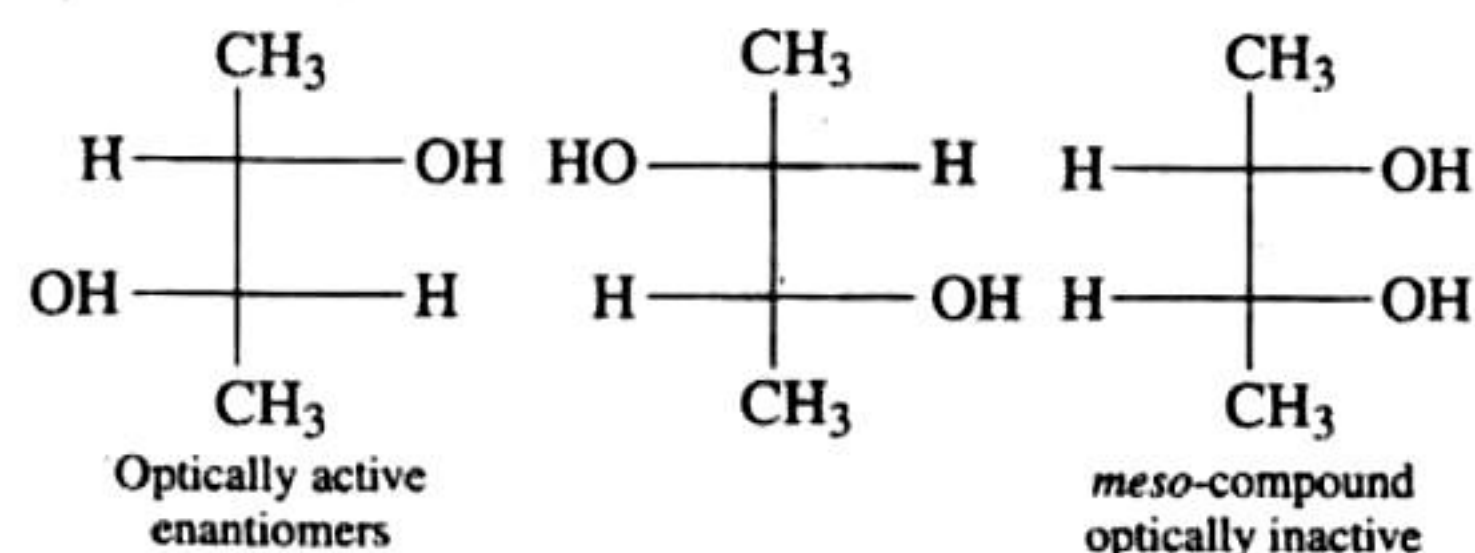


8. c. The symbol D denotes the relative configuration of (OH) group w.r.t. glyceraldehydes taken as standard. Also, (+) sign refers to optical rotation and is dextrorotatory.

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

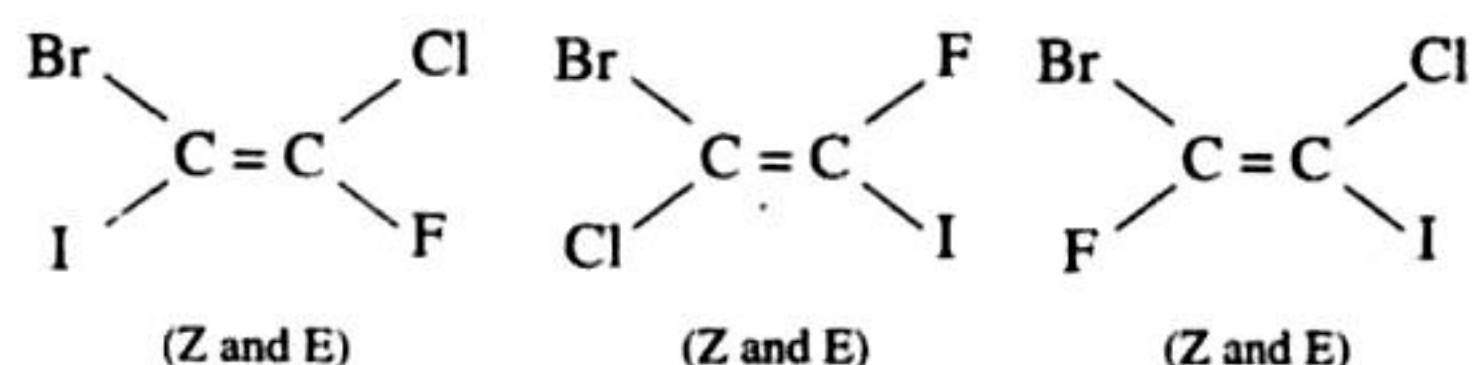
10. b. In the given structure one of the carbons along the double bond has identical group (methyl), so it cannot show geometrical isomerism. Tautomerism is not possible because of the absence of -CO group. It shows optical isomerism because it has chiral C atom with four different groups, H, CH<sub>3</sub>, COOH and (CH<sub>3</sub>)<sub>2</sub>C=CH. A compound which consists of at least one asymmetric carbon atom is capable of showing the phenomenon of optical isomerism.

11. b. The stereoisomers of butane 2, 3-diol are

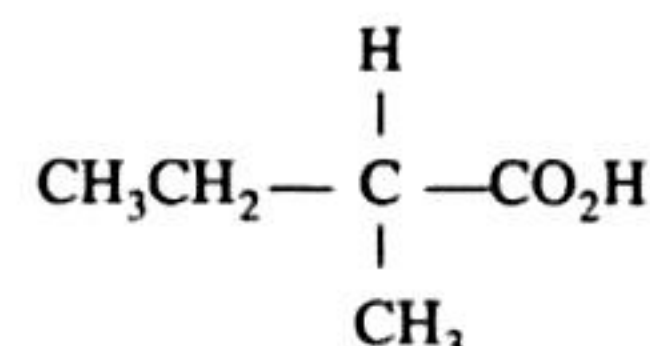


12. a. PhCH<sub>2</sub>CH=CHCH<sub>3</sub> will exhibit geometrical isomerism because in others one of the doubly bonded carbon atom has two similar groups.

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



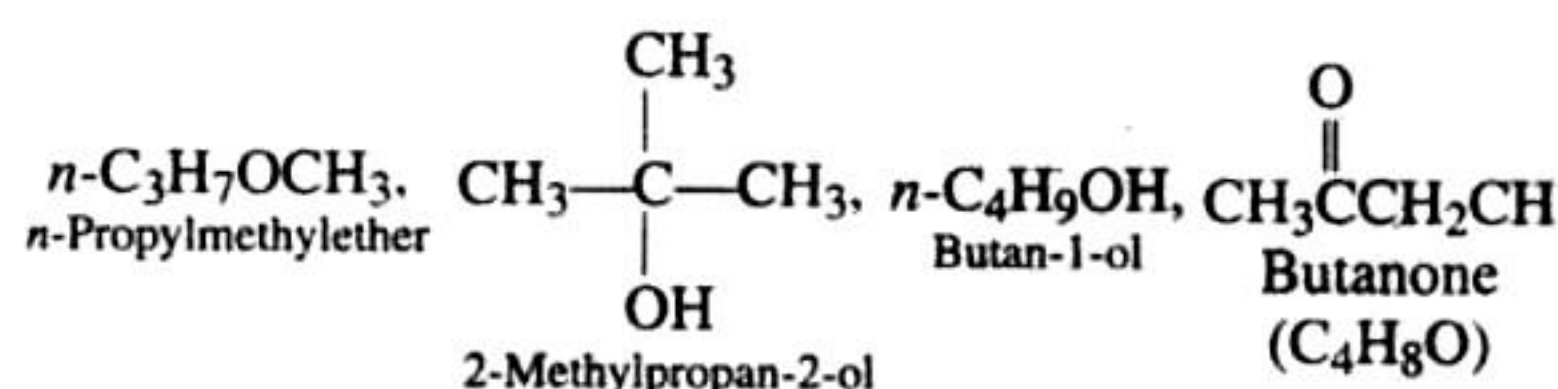
14. d. 2-Methylbutanoic acid contains one asymmetric centre



## JEE Advanced

### Single Correct Answer Type

1. d. The first three are isomers of diethyl ether, C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub> (C<sub>4</sub>H<sub>10</sub>O).



Note: Functional isomer of ether is alcohol (a) is metamer, (b) and (c) are functional isomers.

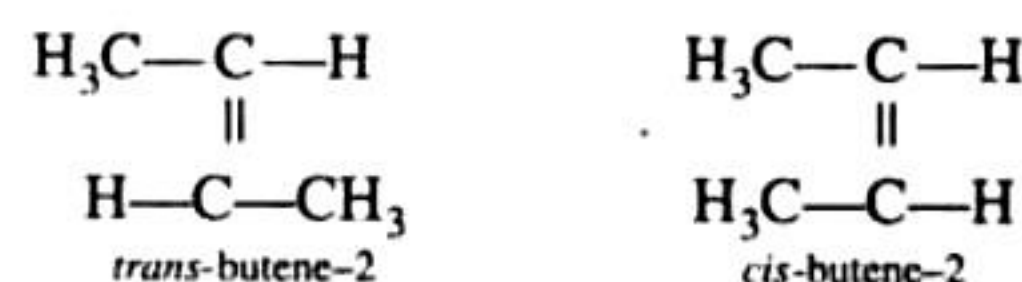
2. a. Ethane (CH<sub>3</sub>-CH<sub>3</sub>) has the least hindered rotation about (C-C) bond.

3. b.  $\begin{array}{c} \text{OH} \\ | \\ \text{Me}-\text{C}^*-\text{C}^*-\text{Me} \\ | \quad | \\ \text{OH} \end{array}$  (Number of asymmetric C atoms = 2)  
Terminal groups are the same.

Number of O.A. isomers = 2<sup>n-1</sup> = 2<sup>2-1</sup> = 2<sup>1</sup> = 2

Number of meso forms = 2<sup>(n-2)/2</sup> = 2<sup>0</sup> = 1

4. a. Shown by >C=C<, >C=N<, -N=N- due to restricted rotation.

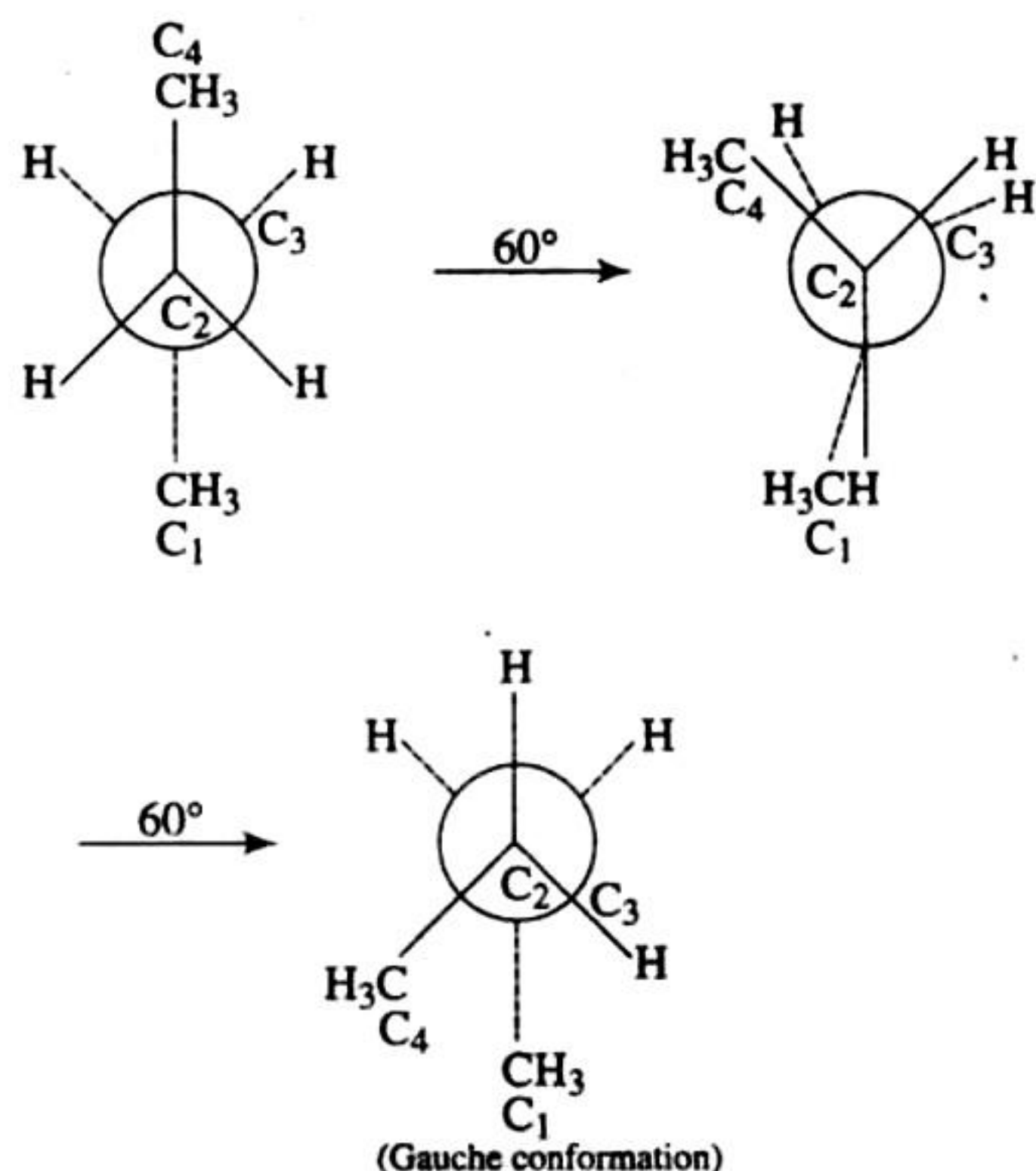


5. d. CH<sub>3</sub>-O-CH<sub>3</sub> is an isomer of CH<sub>3</sub>CH<sub>2</sub>OH  
dimethylether ethanol

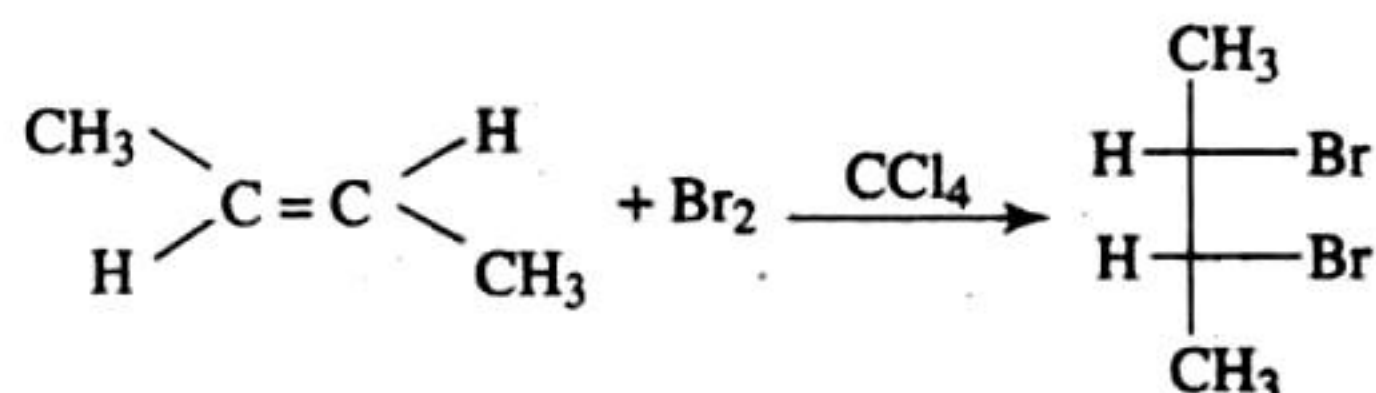
6. b. As C<sub>6</sub>H<sub>14</sub> is alkane so it shows chain isomerism  
There are 5 isomers possible for C<sub>6</sub>H<sub>14</sub>.



15. c. Any conformation between two extreme positions, i.e., eclipsed and staggered is known as gauche or skew form.



16. a. Anti addition of  $\text{Br}_2$  on *trans*-alkene provides meso compound.



### Multiple Correct Answers Type

1. a., d.

In (a), i.e., in *n*-butane, Cl can add at either the first or the second carbon giving two isomers.

In (d), i.e., in 2-methylpropane ( $\text{CH}_3-\text{CH}(\text{CH}_3)_2$ ) will again

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

In (b), i.e., in 2, 4-dimethylpentane

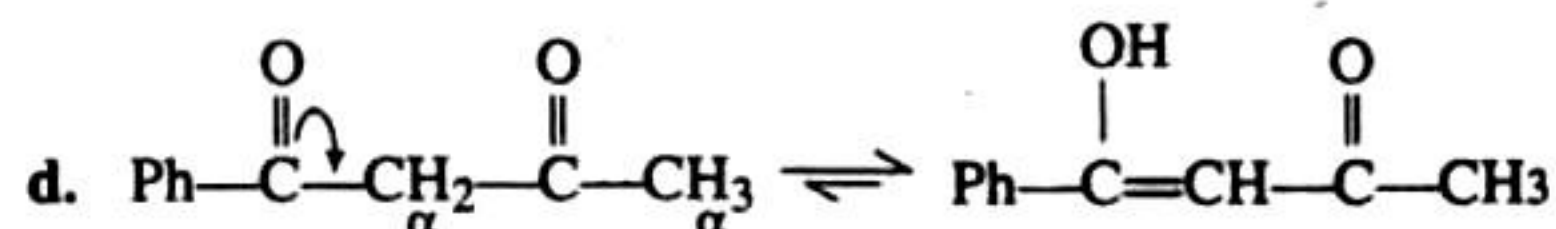
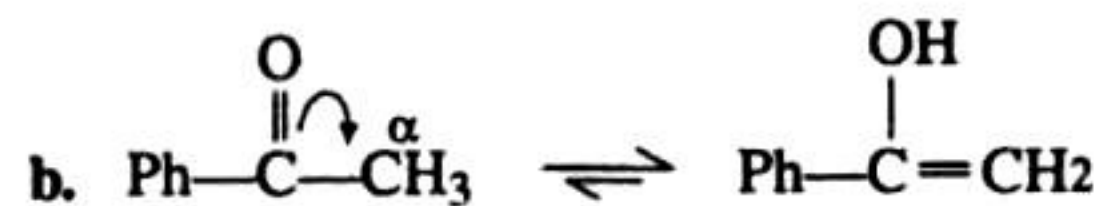
( $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{CH}_3$ ) will give three isomers

with Cl group at either of the  $\text{CH}_3$  groups, second C-atom and third C-atom.

And in (c) benzene forms only one single derivative.

2. b., d.

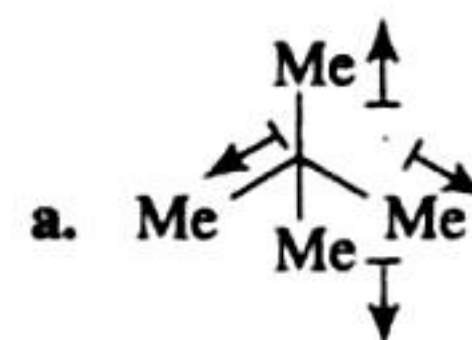
Tautomerism is possible in the compounds which have  $\alpha$ -H atom, i.e., (b) and (d).



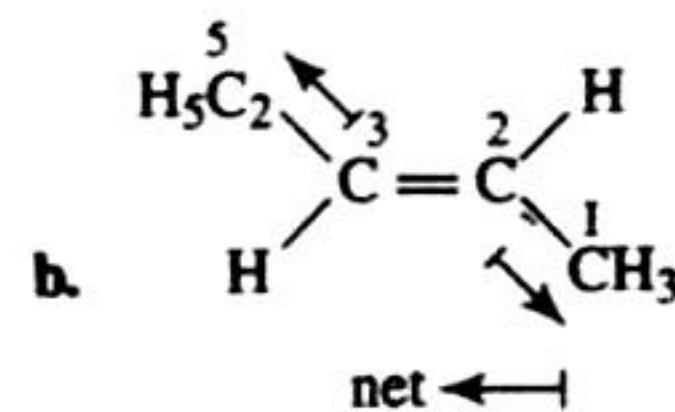
3. c., d.

As in (c) and (d) carbon atom is attached with 4 different groups (asymmetric carbon).

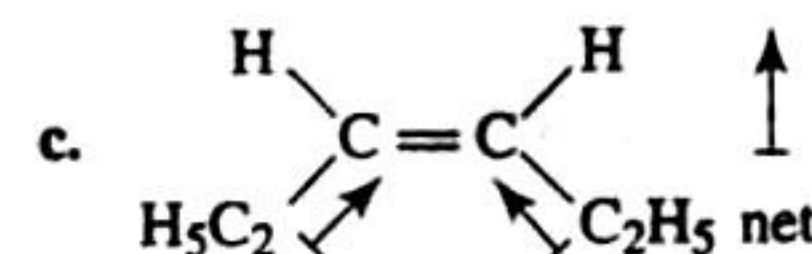
4. b, c.



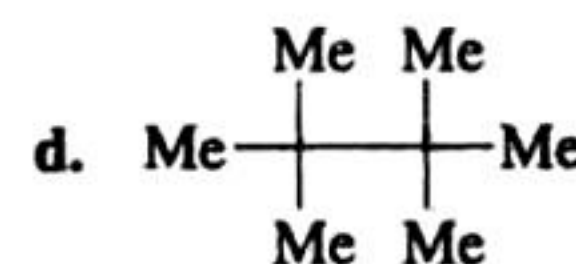
All vectors cancel each other, so  $\mu = 0$ .



Vectors due to Me and ethyl do not cancel each other, so have net vector. Thus  $\mu > 0$ .



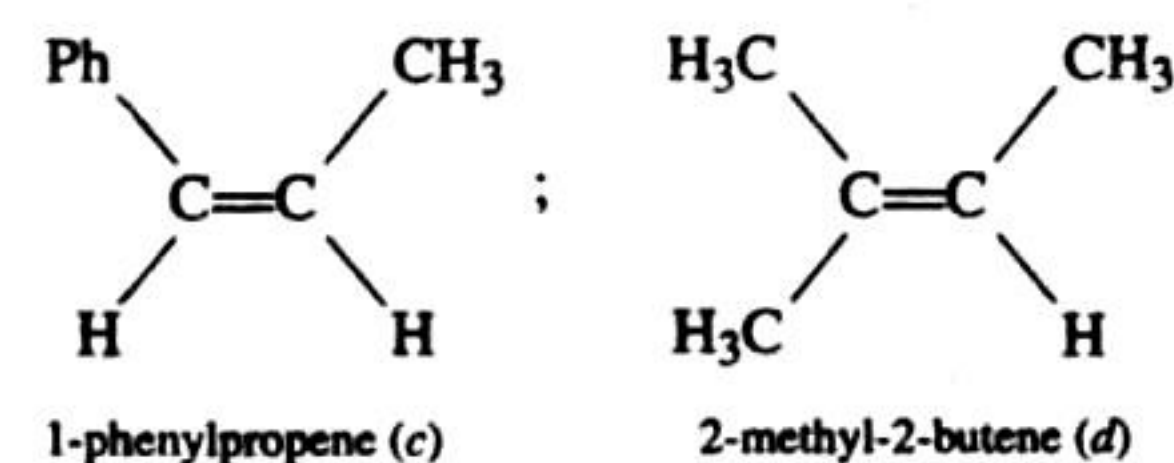
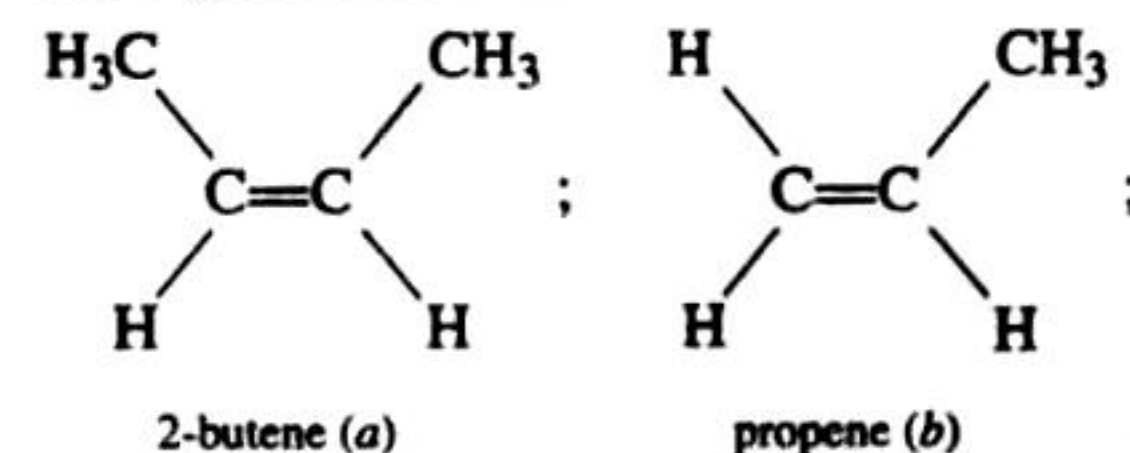
Two vectors do not cancel and give net resultant vector. So,  $\mu > 0$ .



All vectors cancel each other, so  $\mu = 0$ .

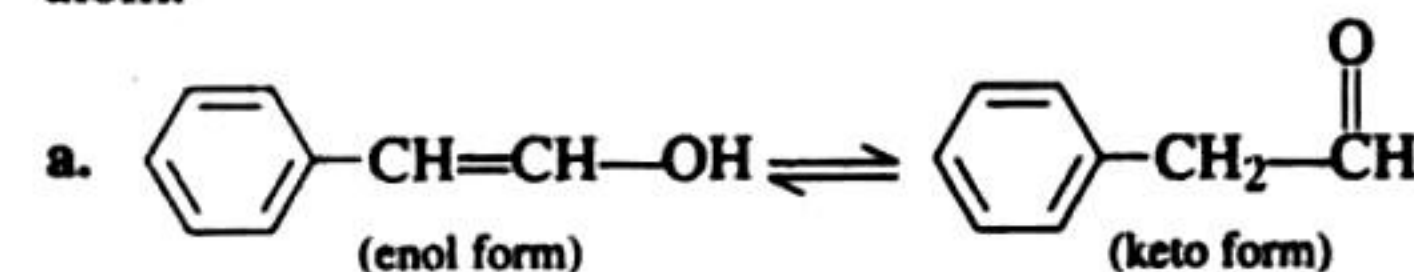
5. a., c.

Only 2-butene and 1-phenylpropene can show geometrical isomerism (*cis*- and *trans*-isomers). In (b) and (c) doubly bonded carbon has two same groups attached to it so it doesn't show geometrical isomerism.



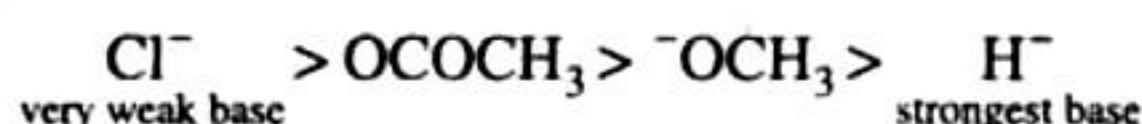
6. a., c., d.

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

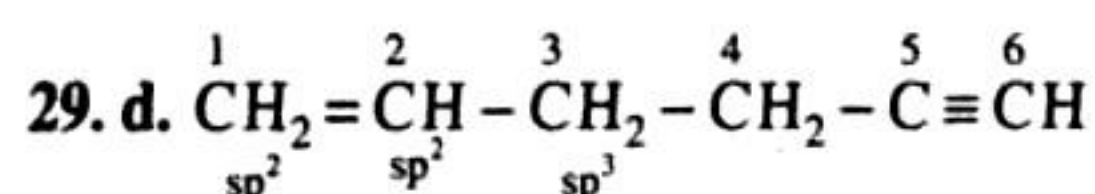




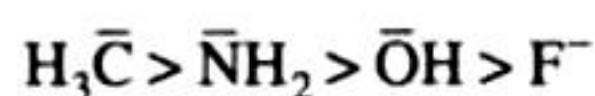
Weaker the base, the better is its leaving characteristic which lies in the following order.



Hence  $\text{CH}_3\text{COCl}$  will be most reactive for nucleophilic substitution at acyl carbon.



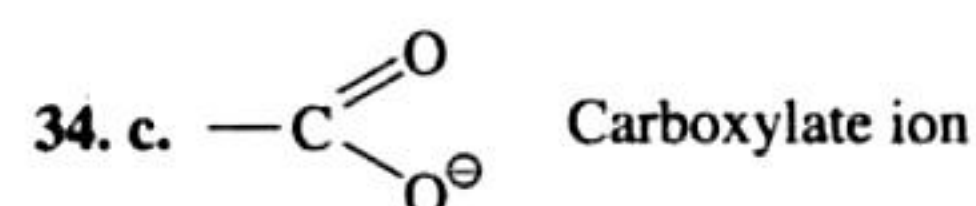
30. c.  $-\text{CH}_3$  is the best nucleophile because carbon is least electronegative among the given options. The order is



31. d. As  $\text{I}^-$  is the best, while  $\text{F}^-$  is the poorest leaving groups among halide ions. Therefore, rate of reaction will be  $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$ .

32. b.  $\text{CH}_3-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{CH}_2-\text{CH}_3$ ,  $(-\text{CH}_2-)$  group is flanked on both sides by electron-withdrawing groups and hence its hydrogens are most acidic. Once a carbanion is formed, it is stabilised due to resonance.

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



Charge dispersal stabilizes and charge intensification destabilizes.

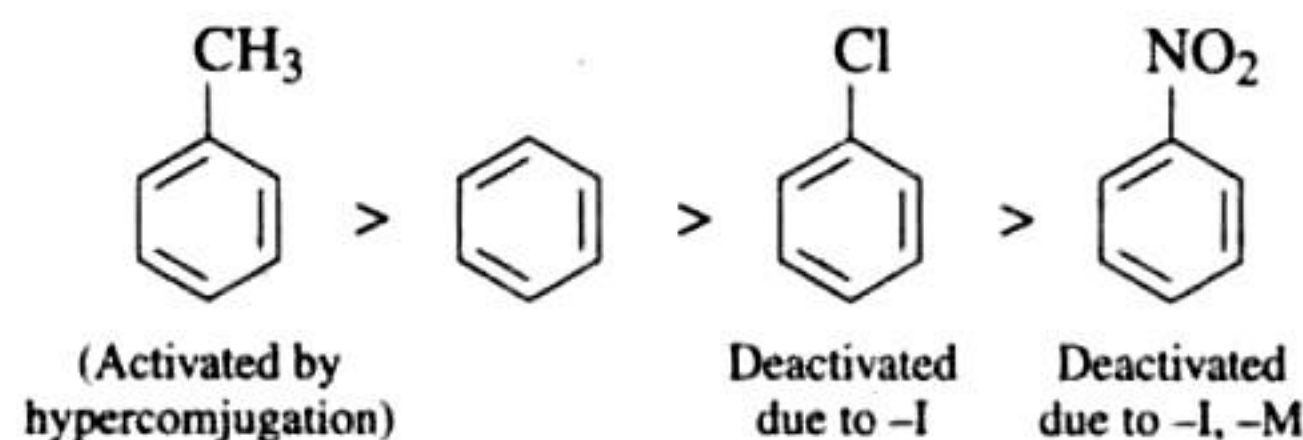
i. The inductive effect decreases with increase in distance of halogen atom from the carboxylate ion and hence the strength of acid proportionally decreases due to decrease in stability of carboxylate ion.

ii. The acidity increases with the increase in electronegativity of the halogen present due to  $-I$  effect of stronger electronegative group.

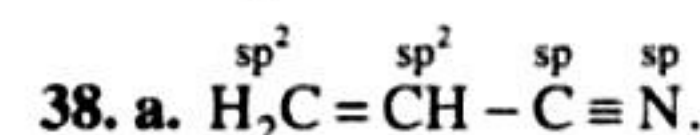
Smallest dissociation constant means weakest acid, which is  $\text{BrCH}_2\text{CH}_2\text{COOH}$  because here Br (less electronegative than F) is two carbon atoms away from  $-\text{COOH}$ .

35. b. In carboxylic acids, molecules are more strongly associated followed by alcohols due to H-bonding and in aldehydes the dipole interactions.

36. c.



37. b.  $\text{CH}_3\text{C}\equiv\text{CCH}_3$  is linear and symmetrical; thus, it has lowest dipole moment.



39. a. Methane molecule being symmetrical, has zero dipole moment. Replacement of one of the H-atoms by Cl atom increases the dipole moment. The increase in dipole moment is more because the bond dipole moment of  $\text{C}-\text{H}$  bond and that of  $\text{C}-\text{Cl}$  bond reinforce one another.

Replacement of another H atom by Cl increases the bond angle due to lone pair – lone pair repulsion between two Cl – atoms thereby reducing the dipole moment of the molecule.

Increase in angle is again caused by the introduction of the third Cl – atom.

When the fourth Cl – atom is introduced, the molecule ( $\text{CCl}_4$ ) again becomes symmetrical and dipole moment reduces to zero.

So,  $\text{CH}_3\text{Cl}$  will have the maximum dipole moment.

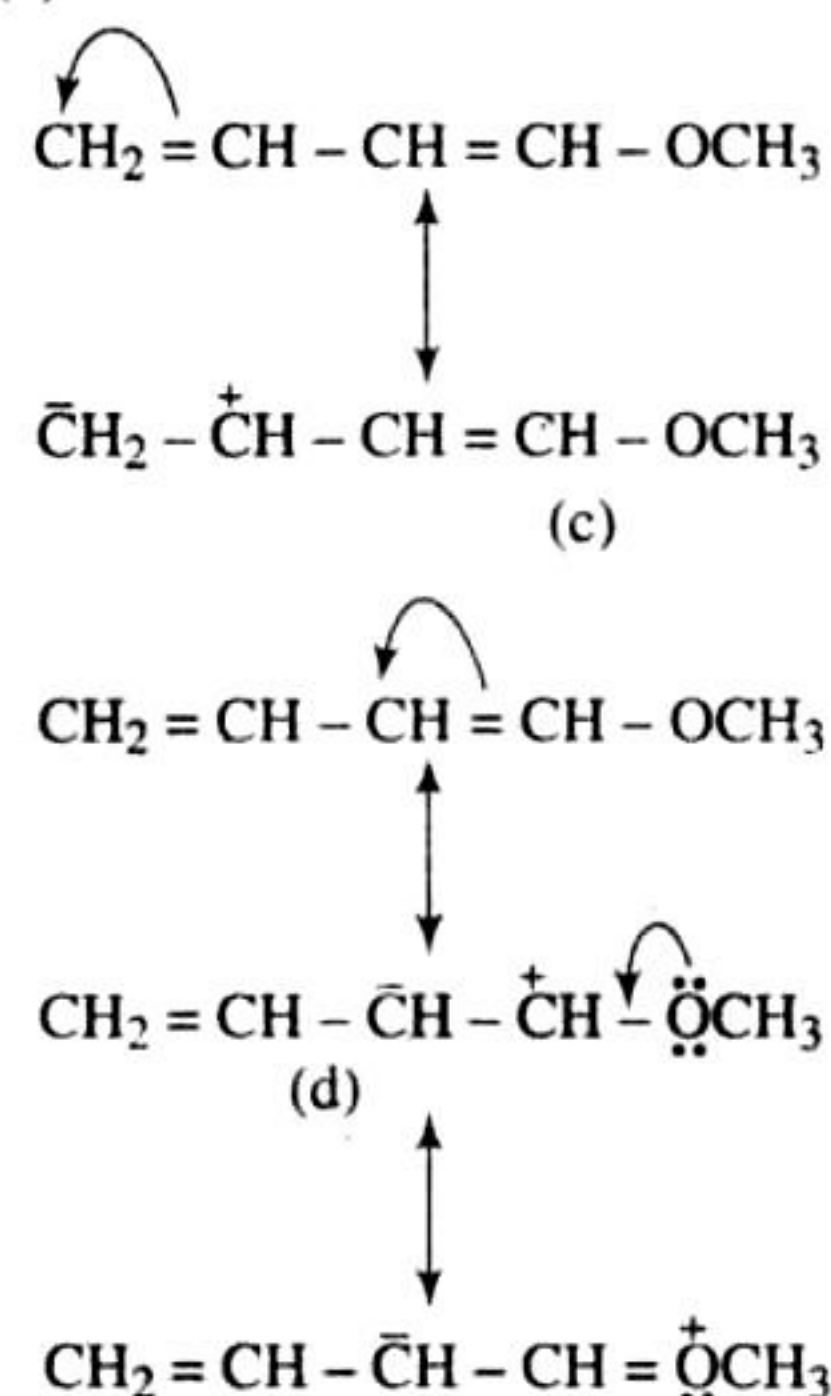
40. a. Carboxylic acids are stronger acid than  $\text{NH}_3^+$  in amino acid and  $-\text{NH}_3^+$  (Y). (Z) is more acidic than (Y) due to  $-I$  effect of  $(-\text{COOH})$  group which is nearer to (Z) than (Y). Hence, the acidic order:  $\text{X} > \text{Z} > \text{Y}$ .

41. c. Structures (a) and (b) are quite stable because every atom has complete octet

Structures (c) and (d) are less stable than (a) and (b), because in these every atom does not have complete octet.

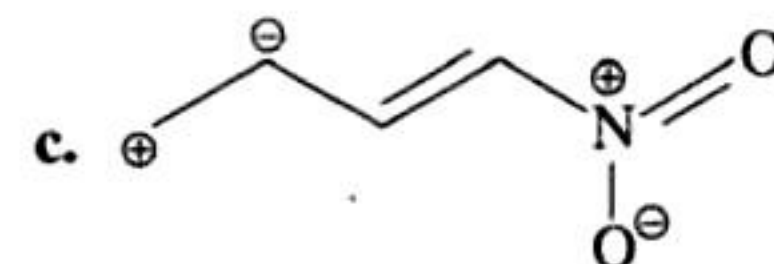
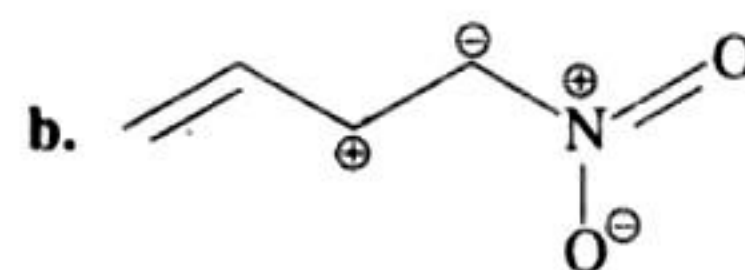
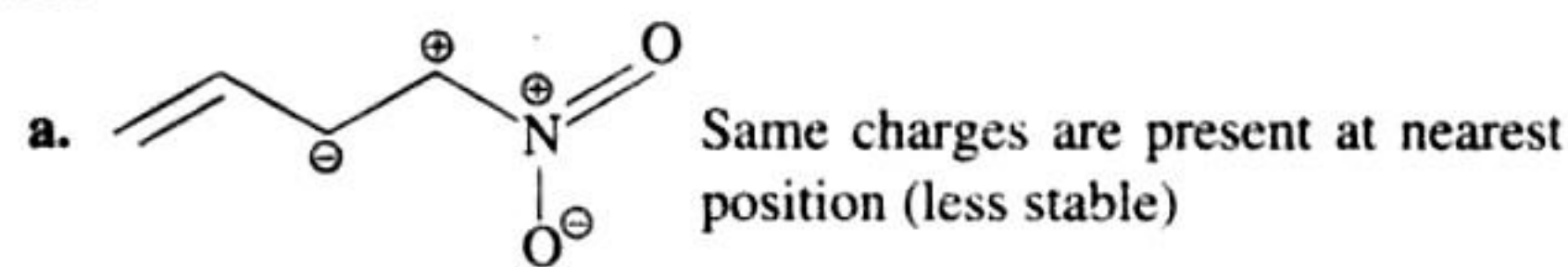
Structure (d) is stabilised by resonance, which is not possible in (c).

Therefore (c) is least stable.

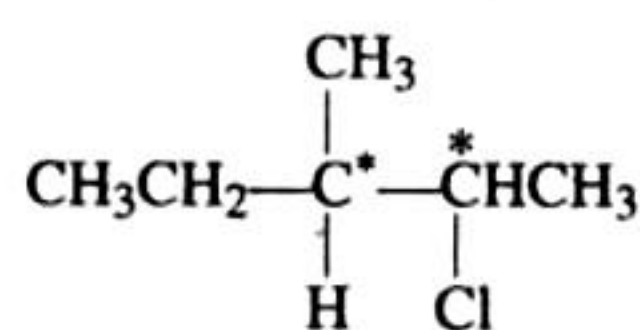


42. b. General IUPAC name is alkanoyl halide.

43. a.

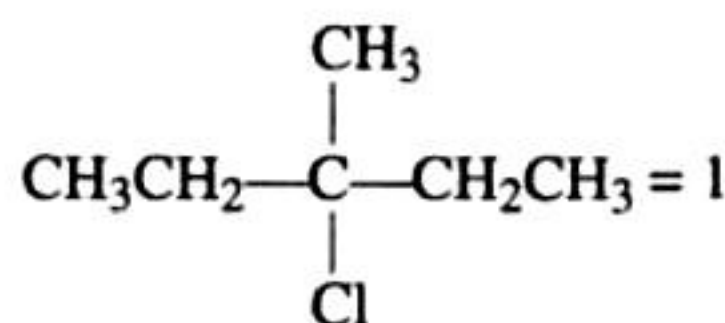




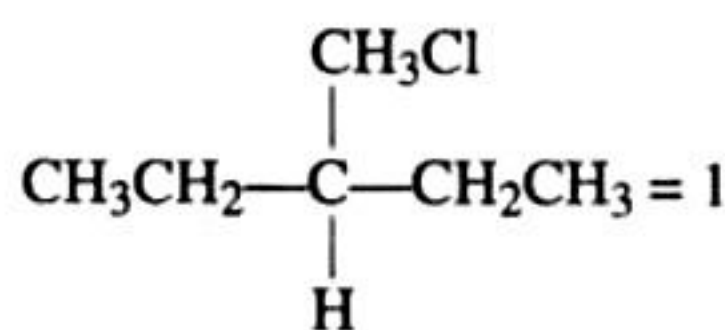


Two enantiomeric pairs = 4

(Isomer due to replacement of H on C - b)



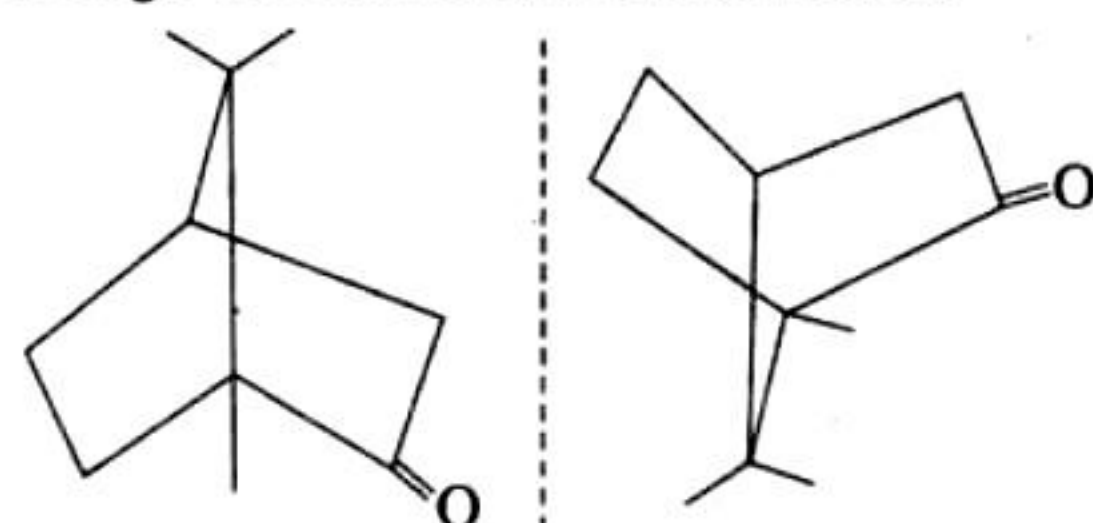
(Isomer due to replacement of H on C - d)



(Isomer due to replacement of H on C - c)

Total 2 + 4 + 1 + 1 = 8

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

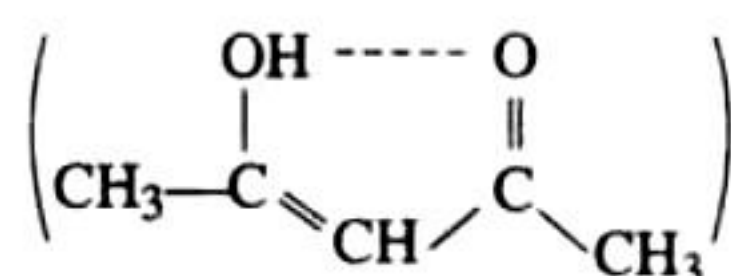


### Assertion-Reasoning Type

1. c. Statement 1 is correct. Statement 2 is incorrect because compound can be chiral even in the absence of chiral atoms.

### Fill in the Blanks Type

- nonsuperimposable, enantiomers
- Chelation

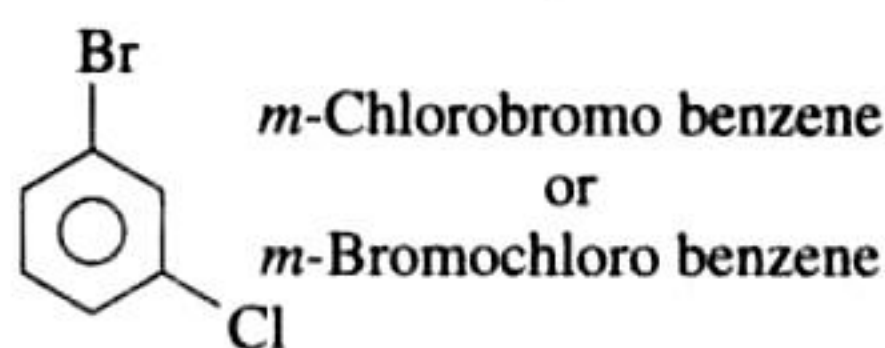


3. (5) In  $\text{C}_4\text{H}_6$ , possible cyclic isomers are



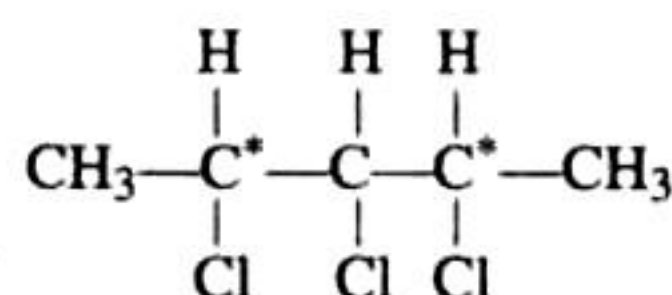
### True / False Type

1. False: Both identical,



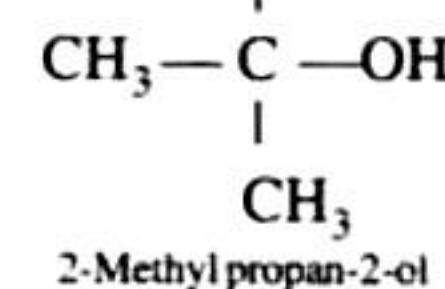
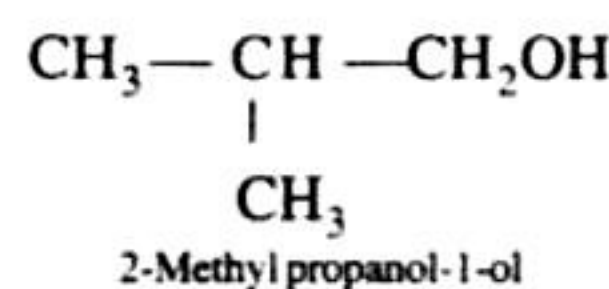
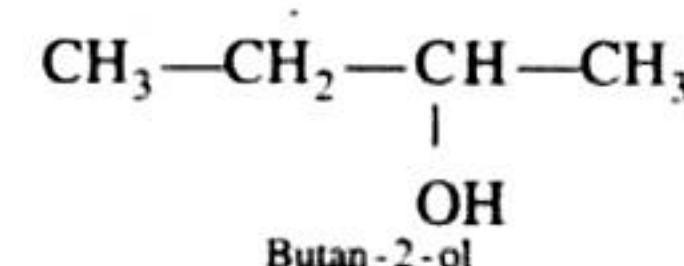
2. False: There are only two asymmetric (marked with\*) carbon atoms.

Asymmetric carbon is the carbon attached to four different groups.

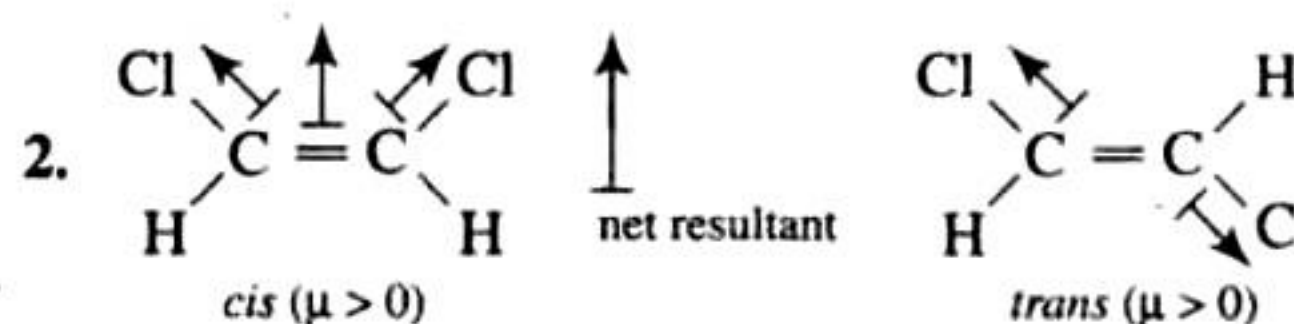
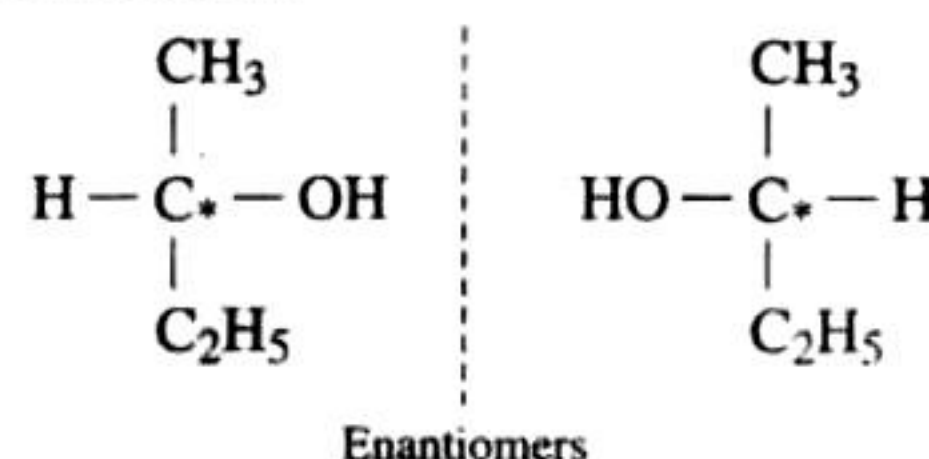


### Subjective Type

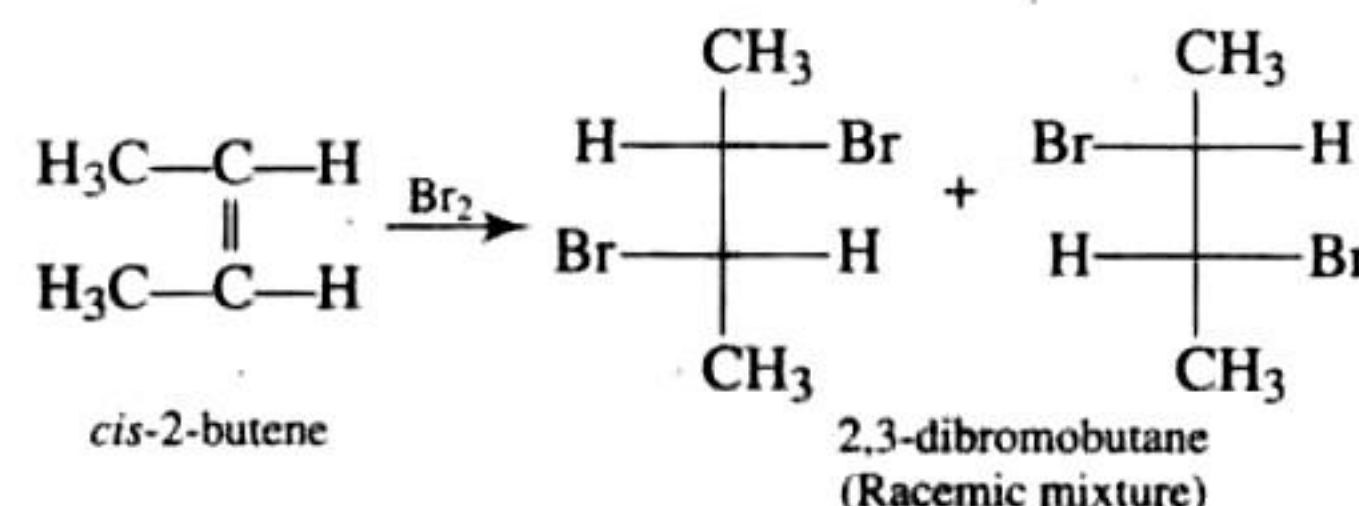
1.  $\text{C}_4\text{H}_{10}\text{O}$  represents 4-isomeric alcohols:



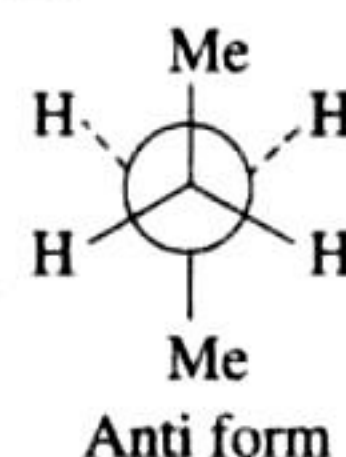
Further, butan-2-ol shows optical isomerism, as it has one asymmetric carbon atom and exists into two optically active forms shown below:



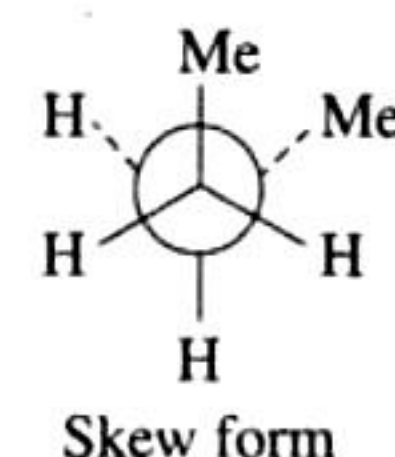
4. *cis*-Alkenes add bromine to form racemic mixture.



5. a. Two Newman projections for the staggered form of butane are

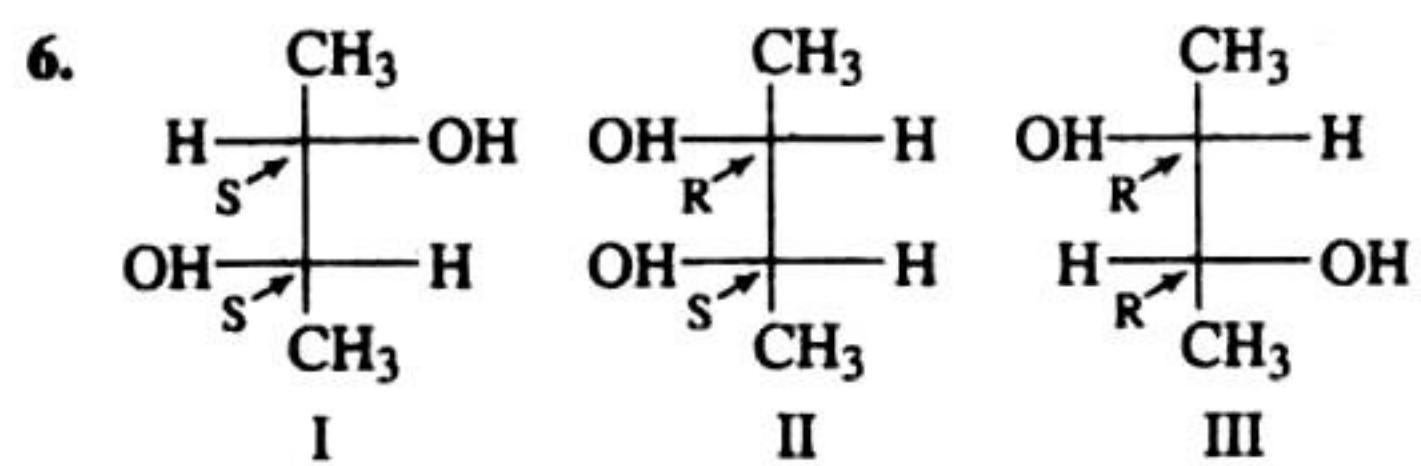


Here, two ( $-\text{Me}$ ) groups are at the maximum possible distance from each other. Hence, this is the condition for maximum stability because of less repulsion.



Here, although two ( $-\text{Me}$ ) groups are separated from each other, this is not the situation of maximum distance. Hence, this form is relatively less stable due to more repulsion.

- b. The less stability of such a form can be explained on the basis of van der Waals strain because the groups are not at the maximum distance from each other. Thus, the repulsive forces between them are more than in anti form.



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