9.

ISOMERISM

1. INTRODUCTION

Molecules with the same molecular formula, but different arrangements of atoms are called Isomers and the phenomenon is thus called Isomerism. They have different physical and chemical properties. They can be classified in the following manner.

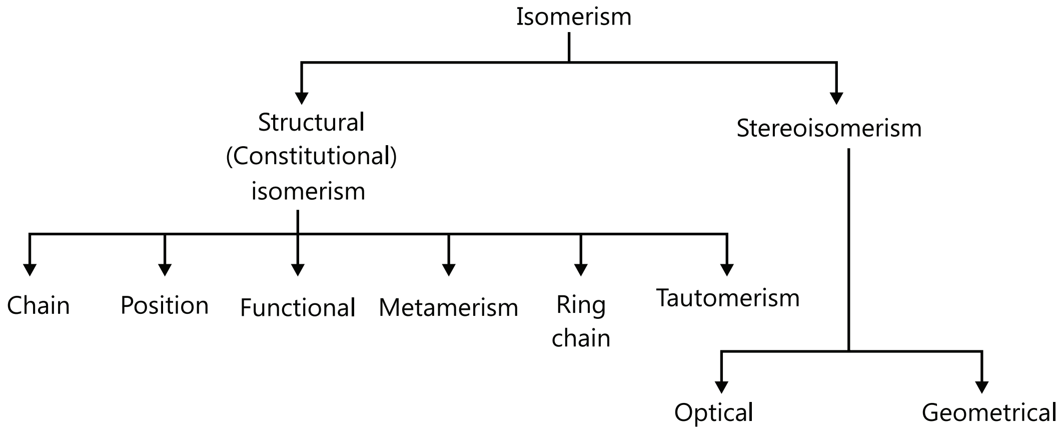


Figure 9.1: Types of isomerism – structural and stereoisomesrism

2. STRUCTURAL ISOMERISM

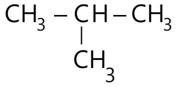
Compounds which have the same molecular formula but different structural formulas are called isomers and the phenomenon is known as isomerism.

Type of Structural Isomerism:

(a) **Chain Isomerism:** Chain isomers possess the same molecular formula, but different number of carbon in parent–chains (straight or branched).

(i) Butane: C_4H_{10}

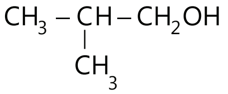
$CH_3-CH_2-CH_2-CH_3$ n – Butane



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$ Isobutane

(ii) Butyl alcohol: C_4H_9OH

$CH_3-CH_2-CH_2-CH_2OH$ n – Butyl alcohol

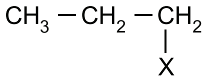


$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_2OH$ Isobutyl alcohol

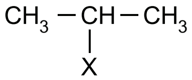
(b) Position Isomerism: Compounds having same molecular formula but the position of functional group, multiple bond or branches along the same chain length of carbon atoms varies.

(i) The same molecular formula
(ii) The same length of carbon chain
(iii) The same functional group

E.g. (i) Molecular formula; C_3H_7X(X=halogen, NH_2, OH or OR)



$CH_3-CH_2-\underset{|}{\underset{X}{CH_2}}$

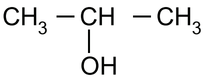


$CH_3-\underset{X}{\underset{|}{CH}}-CH_3$

In this structure three carbon atoms form a chain, and X is joined at the end in (I), while at the middle carbon in (II). To be specific.

(ii) $CH_3-CH_2-CH_2OH$ and

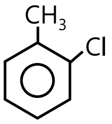
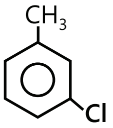
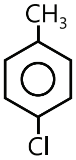
1—Propanol



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

2—Propanol

Note: In di–substituted derivatives, position isomerism also exists because of the relative positions occupied by the substituents on the benzene ring. Thus, Chlorotoluene, $C_6H_4(CH_3)Cl$ exists in three isomeric forms–ortho, meta and para.

 o-Chlorotoluene	 m-Chlorotoluene	 p-Chlorotoluene

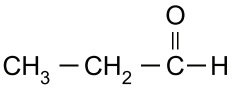
(c) Functional Group Isomerism: When isomers have the same molecular formula but different functional groups, these compounds are called functional group isomers. The following pairs of families show this isomerism.

E.g. (i) Molecular formula: C_2H_6O

$CH_3–CH_2–OH$ and $CH_3–O–CH_3$

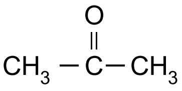
Ethyl alchol (Alcohol) — Dimethyl ether (Ether)

(ii) Molecular formula: C_3H_6O



$CH_3-CH_2-\overset{\overset{O}{||}}{C}-H$

and

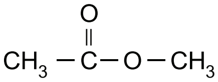


$CH_3-\overset{\overset{O}{||}}{C}-CH_3$

Propanal (Aldehyde) — Propanone (Ketone)

(iii) Molecular formula: $C_3H_6O_2$

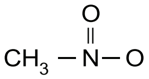
CH_3-CH_2-COOH and



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

Propanoic acid (Acid) — Methyl acetate (Ester)

(iv) Molecular formula: CH_3NO_2


$CH_3-\overset{O}{\overset{\|}{N}}-O$ and $CH_3-O-N=O$

Nitromethane Methyl nitrite

(d) **Metamerism:** This type of Isomerism is due to different position of poly valency functional group (like S, N, O, and CO,) in molecule, with alkyl groups around it. Members belong to the same homologous series.

E.g. **(i)** Diethyl ether and methyl propyl ether

$CH_3CH_2OCH_2CH_3$	Diethyl ether
$CH_3OCH_2CH_2CH_3$	Methyl propyl ether

(ii) Diethyl amine and methyl propylamine

$CH_3CH_2–NH–CH_2CH_3$	Diethyl amine
$CH_3CH_2CH_2–NH–CH_3$	Methyl propyl amine

(e) **Ring chain Isomerism:** Such isomerism arises due to difference of carbon–chain or ring. E.g. **(i)** Molecular formula: C_3H_6 $H_3C-CH=CH_2$ and

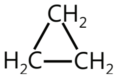
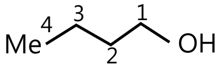


Illustration 1: Give various functional isomers of butanol and give their isomeric relations. **(JEE MAIN)**

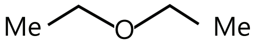
Sol: Functional Group Isomerism: These isomers have same molecular formula but different Functional groups. Alcohol show Functional group isomerism with ethers.

Alcohols:

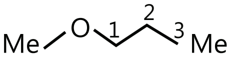
1. 

Butan-1-ol

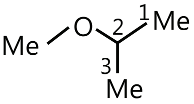
Ethers (R — O — R')

2. 

Ethoxy ethane
(Diethyl ether)

3. 

1-Methoxy propane
(Methyl propyl ether)

4. 

2-Methoxy propane
(Isorophy methyl ether)

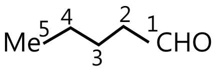
(1) and (2), (1) and (3), and (1) and (4) are functional isomers.

(2) and (3), and (2) and (4) are metamers.

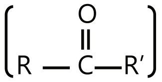
(3) and (4) are positional isomers.

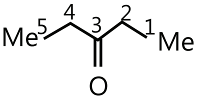
Illustration 2: Give various isomers of pentanal and give their isomeric relations. **(JEE MAIN)**

Sol: Aldehyde show Functional group isomerism with Ketone.

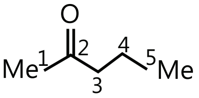
1. 

Pentanal

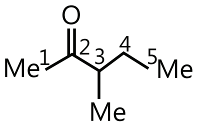
Ketones

$\left(R-\overset{O}{\overset{\|}{C}}-R'\right)$

2. 

Pentan-3-one
(Diethyl ketone)

3. 

Pentan-2-one
(Methyl propyl ketone)

4. 

3-Methyl butan-2-one
(Isopropyl methyl ketone)

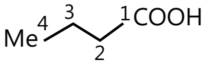
(1) and (2), (1) and (3), and (1) and (4) are functional isomers.

(2) and (3) are positional isomers.

(2) and (4) are position and chain isomers.

(3) and (4) are metamers.

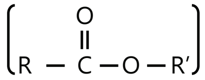
Illustration 3: Give various isomers of butanoic acid and give their isomeric relations. **(JEE ADVANCED)**

1. 

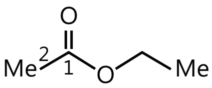
Butanoic acid

Sol: Acid show Functional group isomerism with Ester.

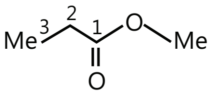
Acid:

Esters 

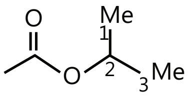
$\left(R-\overset{O}{\overset{\|}{C}}-O-R'\right)$

2. 

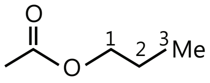
Ethyl ethanoate
(Ethyl acetate)

3. 

Methyl propanoate
(Methyl proplonate)

5. H 

Propyl-2-methanonate
(Isopropyl formate)

4. H 

Propyl methanote
(Propyl formate)

(1) and (2), (1) and (3), (1) and (4), and (1) and (5) are functional isomers.

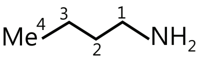
(2) and (3), (2) and (4), and (5) are metamers.

(3) and (4), and (3) and (5) are metamers.

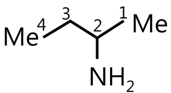
(4) and (5) are position isomers.

Illustration 4: Give various functional isomers of butan–1–amine and give their isomeric relations. **(JEE ADVANCED)**

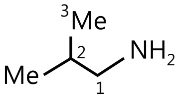
Sol: 1° amine (RNH_2)

1. 

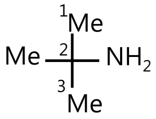
Butan-1-amine

2. 

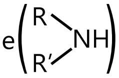
Butan-2-amine
(sec-Butyl amine)

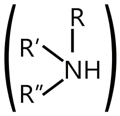
3. 

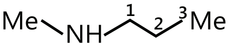
2-Methyl propan-1-amine
(Isobutyl amine)

4. 

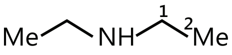
2-Methyl propan-2-amine
(t-Butyl amine)

2° amine 

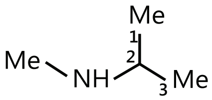
3° amine 

2. 

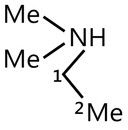
N-Methyl propan-1-amine
(Methyl propyl amine)

3. 

N-Ethyl ethan-1-amine
(Diethyl amine)

4. 

N-Methyl propan-2-amine
(Isopropyl methyl amine)

5. 

N,N-Dimethyl ethan-1-ami
(N,N-Dimethyl ethyl amin)

Note: (1° and 2° amine), (1° and 3° amine), and (2° and 3° amine) are functional isomers. 2° amine and other isomeric 2° amine are metamers. 3° amine and other isomeric 3° amine are metamers. But 1° amine and other isomeric 1° amine are position or chain isomers.

(2) and (2), (1) and (3), (1) and (4), and (1) and (5) as functional isomers.

(2) and (3), (2) and (4) and (4) are metamers.

(2) and (5), (3) and (5), and (4) and (5) are functional isomers.

Tautomerism: A phenomenon in which a single compound exists in two readily interconvertible structures that differ in the relative position of at least one atomic nucleus, generally hydrogen. Tautomeric structures are obtained by the simultaneous shift of H atom and a double bond (π–bond) at 1 and 3 positions. That is why it is also called 1, 3–shift, It is further called desmotropism (Greek: $\Rightarrow$ desmosbond, troops $\Rightarrow$ turn) or dynamic isomerism or kryptomerism or allelotropism or metrotropy or keto–enol tautomerism.

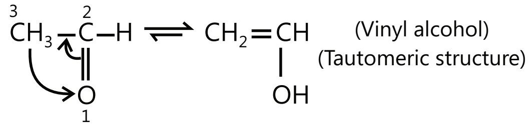
(a) Difference between resonance and tautomerism:

(i) Resonance is a hypothetical concept, whereas tautomerism is real.

(ii) Resonance–contributing structures (canonical structures) cannot be isolated, whereas tautomeric structures can be isolated.

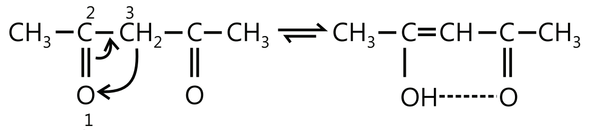
(iii) In resonance, position of atoms or nuclei are fixed; while in tautomerism there is a simultaneous shift of an H atom and π–bond takes place at 1, 3–positions (1, 3–shift).

E.g.



$$\overset{3}{CH_3}-\overset{2}{C}(=\underset{1}{O})-H \rightleftharpoons CH_2=CH(OH)$$

(Vinyl alcohol)
(Tautomeric structure)

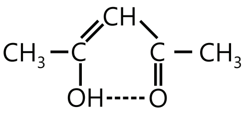


$$CH_3-\overset{2}{C}(=\underset{1}{O})-\overset{3}{C}H_2-C(=O)-CH_3 \rightleftharpoons CH_3-C(OH)=CH-C(=O)-CH_3$$

Acetyl acetone
or Pentane-2,4-dione

(Tautomeric structure with H-bonding)

or



(Chelation)

(iv) Tautomeric forms have different functional groups. Resonating structures have the same functional group.

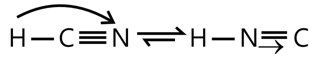
(v) Tautomeric forms have no effect on bond lengths, while resonance affects the bond length.

(vi) Resonance structures are obtained by the delocalisation of π or non–bonding e⁻'s or both, while tautomeric structures are obtained by delocalisation of σ–and π–bond.

(b) If the H atom oscillates between two polyvalent atoms linked together, the system is a dyad and if the H atom moves from the first to third atom in a chain, the system is a triad.

(c) Hydrocyanic acid is an example of dyad system in which the H atom oscillates between C and N atoms.

Therefore, (HCN) and ($HN\underset{\rightarrow}{\equiv}C$) are the examples of tautomerism.

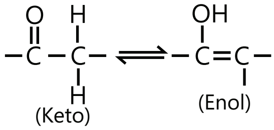


$$H-C\equiv N \rightleftharpoons H-N\underset{\rightarrow}{\equiv}C$$

Hydrocyanic acid   Isohydrocyanic acid

(d) **Triad System**

(i) Keto–enol system: Polyvalent atoms are O and two C atoms. It arises due to 1, 3–migration of a hydrogen atom from one polyvalent atom to the other within the same molecule. Isomers thus obtained exist in dynamic equilibrium with each other and are called tautomers and the phenomenon is called tautomerism.

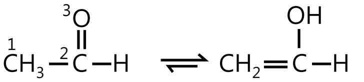


$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\underset{H}{C}}- \rightleftharpoons -\overset{OH}{C}=\underset{|}{C}-$$

(Keto)   (Enol)

There are several types of tautomerism but keto–enol tautomerism is most important. In this type of tautomerism, one form (tautomer) contains the keto group (>C=O) while the other contains the enolic (>C=C–OH) group. Two simplest examples of keto–enol tautomerism are acetaldehyde and acetone.

(ii)

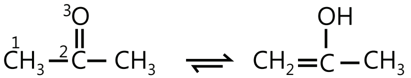


$$\overset{1}{CH_3}-\overset{2}{C}(=\overset{3}{O})-H \rightleftharpoons CH_2=C(OH)-H$$

(Acetaldehyde
(Keto form)

Vinyl alcohol
(Enolic form)
Negligible amount)

(c)



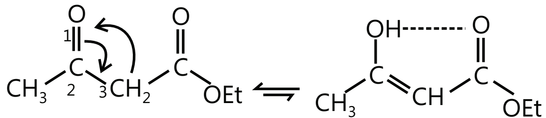
$$\overset{1}{CH_3}-\overset{2}{C}(=\overset{3}{O})-CH_3 \rightleftharpoons CH_2=C(OH)-CH_3$$

Acetone
(Keto form)

Prop-1-en-2-ol
(Enolic form)
Negligible amount)

In simple aldehydes and ketones (i.e., acetaldehyde, acetone, etc.), the amount of enolic form is stabilised by the intramolecular hydrogen–bonding (chelation), such as in 1, 3–dicarbonyl compounds, the amount of the enolic form is much greater than in acetaldehyde or acetone. For example, in acetoacetic ester, the amount of enolic form is 7%.

(iii)

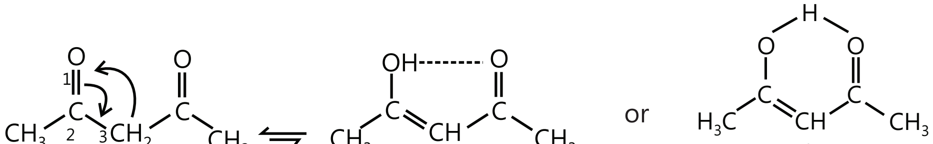


Acetoacetic ester
(Keto form 93%)

(Enolic form, 7%)

Similarly, acetyl acetone (i.e., a 1, 3–diketone) also exhibits keto–enol tautomerism but the amount of the enolic form here is much higher (76%) than even in acetoacetic ester. This is because the keto group is a much better electron–withdrawing group than the ester group.

(iv)



Acetyl acetone
(Keto form, 24%)

(Enolic form, 76%)
(More stable 5-membered ring)

(Not formed)
(Although 6-membered ring is more stable, H atomis so small that it dose not form a par of ring.)

Enol content of (I) is more stable because it has a conjugated (C=C–C=O) π–system and intramolecular H–bonding.

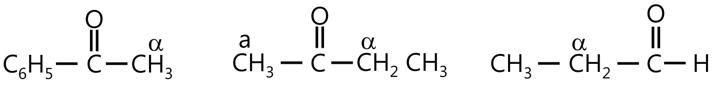
(v) Effect of solvent on enol content: Enol content of (I) is 15% in H_2O and 92% in hexane, since H_2O forms H–bonds with (C=O) of keto form, thereby inhibiting the intramolecular H–bonding of the enol form. Therefore, the enol content increases in the non–polar aprotic solvent (e.g., benzene or hexane) and decreases in polar protic or polar aprotic solvent (H_2O or acetone).

Order of enol content in different solvents:

Hexane> benzene> acetone > methanol> H_2O.

The enol content is more volatile and is separated by the careful distillation of the mixture in a fused quartz apparatus (eliminates base from glass).

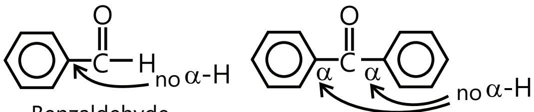
(e) **Essential conditions:** In order for an aldehyde or a ketone to exhibit keto–enol tautomerism, it is essential that it must have at least one α–hydrogen atom. Thus, acetophenone, butan–2–one, Tpresence of , is essentialan



$$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_3 \qquad \overset{a}{C}H_3-\overset{\overset{O}{\|}}{C}-\overset{\alpha}{C}H_2\,CH_3 \qquad CH_3-\overset{\alpha}{C}H_2-\overset{\overset{O}{\|}}{C}-H$$

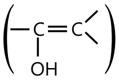
Acetopheone　　Butan-2-one　　Propanal

In contrast, benzaldehyde, benzophenone, etc., do not show keto–enol tautomerism because of the absence of α–hydrogen atoms.



Benzaldehyde　　Benzophenone

(i) Keto–form forms oximes, hydrazone, and gives DNP test which shows the presence of (C=O) group.

(ii) Enolic–form gives a colour with neutral $FeCl_3$ solution, a test of enolic  compounds

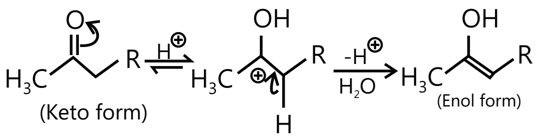
(iii) Enolic–form decolourises Br_2/CCl_4 solution –a test of unsaturation due to the presence of (C=C) bond.

(iv) Enolic–form also forms acetyl derivative, which shows the presence of (–OH) group.

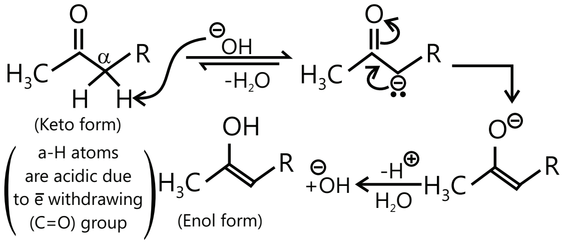
(v) Tautomerism occurs in both acidic and basic mediums.

(f) Mechanism of acid/base catalysed tautomerism:

(i) Acid–catalysed tautomerism:

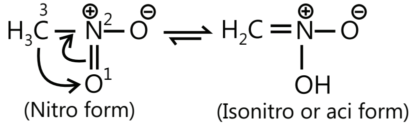


(ii) Base–catalysed tautomerism:

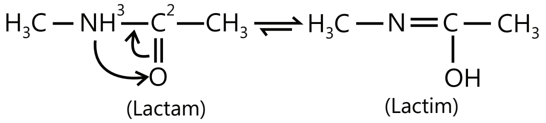


(b) Triad System Containing Nitrogen

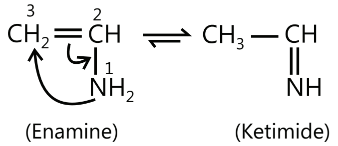
i) Nitro-isonitro tautomerism:



ii) Lactam-lactim tautomerism:

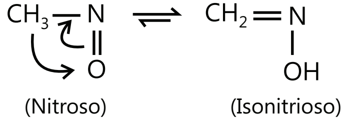


iii) Enamine-ketimide tautomerism:



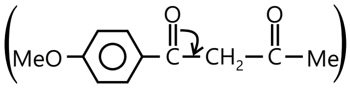
iv) Tautomerism of nitrous acid:

v)Nitroso-isonitroso tautomerism:

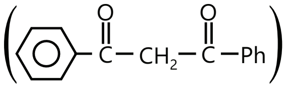


Increasing Order of Enol Content

Aldehyde (MeCHO) < ketone (MeCOMe) < ketoester ($CH_3COH_2COOC_2H_5$) < ketoester with (Ph) group ($PhCOCH_2COOC_2H_5$) < dial ($OHC–CH_2–CH_2–CHO$) < keto–aldehyde (CH_3COCH_2CHO) < diketone ($CH_3COCH_2COCH_3$) < (Ph) group containing e⁻ donating group with (C=O) group



< (Ph) group with (C=O)group



< (Ph) group containing e-withdrawing group with(C=O)group

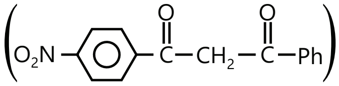


Illustration 5: Write more stable tautomerism structures of the following: **(JEE MAIN)**

(A) Phenol (B) Methyl–3–oxobutanoate (C) Cyclohexan–1, 3, 5–trione

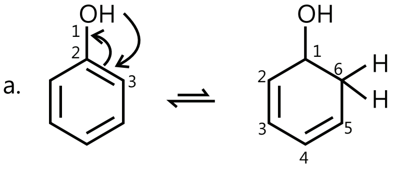
Sol:

(A) In case of phenol keto form is less stable due to loss of aromaticity.

(B) In case of Methyl–3–oxobutanoate Enol form is more stable as it involves hydrogen bonding between the OH group and carbonyl carbon.

(C) In case of Cyclohexan–1, 3, 5–trione Enol form is more due to gain of Aromatic structure.

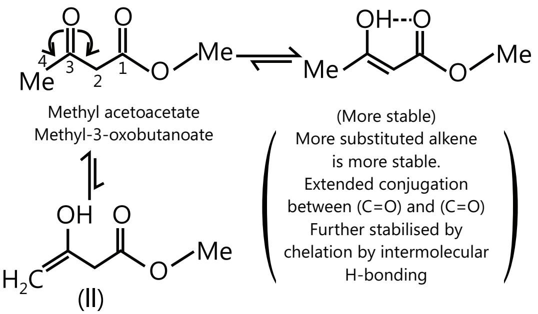
a.



Phenol
(More stable)
(Aromatic)

Cyclohexa-2,4-dine-1-one
(Less stable)
(non-aromatic)

b.

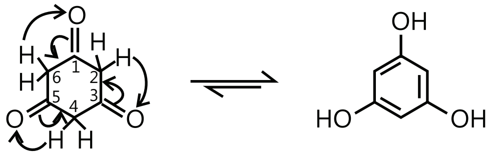


Methyl acetoacetate
Methyl-3-oxobutanoate

(More stable)
(More substituted alkene is more stable. Extended conjugation between (C=O) and (C=O) Further stabilised by chelation by intermolecular H-bonding)

(II)
(Less stable)
(Less substituted alkene and no extended conjugation)

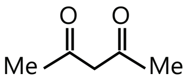
c.



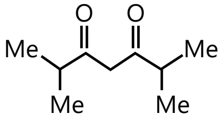
1,3,5-Trihydroxy benzene
(or) (Phloroglucinol)
(More stable due to aromatic character)

Illustration 6: Arrange the following in the decreasing order of enol content: **(JEE MAIN)**

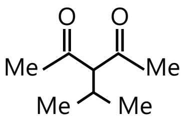
a.



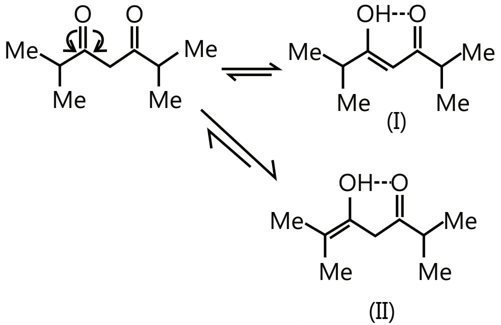
b.



c.



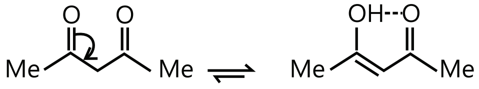
Sol: Both (B) and (A) are stabilised by intramolecular H–bonding. But (B) shows more enol content than (A) since (B) is more substituted alkene. In (C) there is only one α –H atom and its acidity is decreased by $\bar{e}$ donating (+I effect of) isopropyl group. It shows less enol form. b>a>c



(I)

(II)
(More substituted alkene; more stable)

(I) is more stable than (II), since (II) is more strained 5–membered ring joining the (C=C) bond.



Both (B) and (A) are stabilised by intramolecular H–bonding. But (B) shows more enol content than (A) since (B) is more substituted alkene.

In (C) there is only one α–H atom and its acidity is decreased by the e^- donating (+I effect of) isopropyl group. It shows a less enol form.

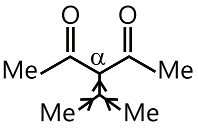
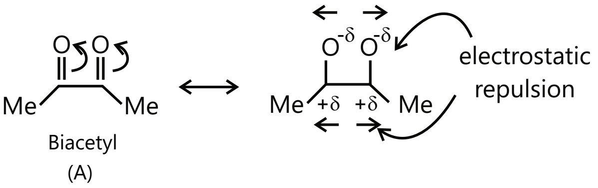
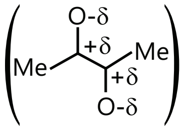
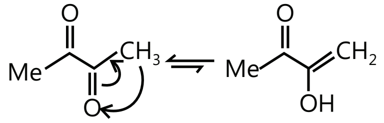
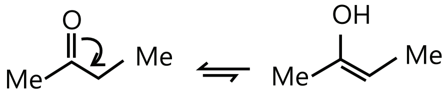
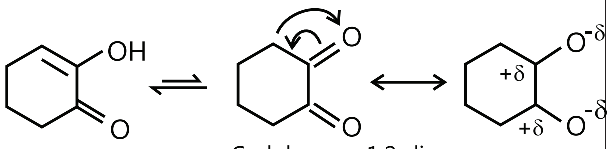
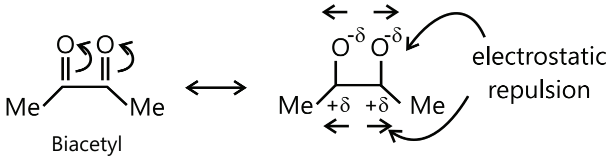


Illustration 7: Why is enol content of butane–2, 3–dione (biacetyl) (A) slightly higher than that of butan–2–one (B) and much less than that of cyclohexane–1, 2–dione (C)? **(JEE ADVANCED)**

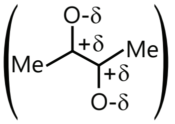
Sol:

(i)	In biacetyl (A), adjacent (C=O) groups destabilise the molecule due to the electrostatic repulsion of the similar charges on the O atom of (C=O), but the molecule relives some of this electrostatic repulsion by acquiring anti conformation. Some repulsion is further relieved in the enol form but enol content is still small because this relief occurs at the expenses of loss of (C=O) resonance energy.	 Biacetyl (A)   Keto form
(ii)	In butan–2–one (B), no other factor except the loss of resonance energy occurs during enolisation.	 Butan-2-one (B) Enol form
(iii)	In cyclohexane –1, 2–dione (C), the cyclohexane ring is rigid and the –σ charge on the adjacent (C=O) groups is in syn–position. Therefore, this molecule relieves its electrostatic repulsion only by the enolisation of one of the (C=O) groups.	 Enol form Cyclohexane-1,2-dione (C)

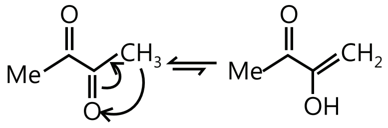


Biacetyl
(A)

In biacetyl (A), adjacent (C=O) groups destabilise the molecule due to the electrostatic repulsion of the similar charges on the O atom of (C=O), but the molecule relives some of this electrostatic repulsion by acquiring anti–conformation,

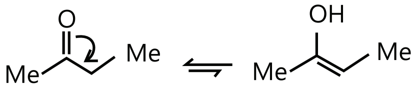


Some repulsion is further relieved in the enol form but enol content is still small because this relief occurs at the expenses of loss of (C=O) resonance energy.

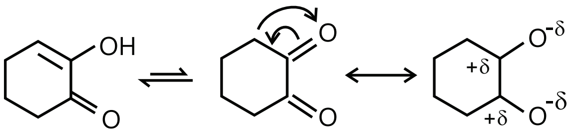


Keto form

In butan–2–one (B), no other factor except the loss of resonance energy occurs during enolisation.



Butan-2-one
(B)
Enol form



Enol form
Cyclohexane-1,2-dione
(C)

In cyclohexane –1, 2–dione (C), the cyclohexane ring is rigid and the–σ charge on the adjacent (C=O) groups is in syn–position. Therefore, this molecule relieves its electrostatic repulsion only by the enolisation of one of the (C=O) groups.

Thus, the enol content of (A) is slightly higher than that of (B) but much less than (C).

Illustration 8: Give the decreasing order of enol of ethyl acetoacetate in the following solvents: **(JEE ADVANCED)**

(A) Water (B) Methanol (C) Benzene (D) Acetone

Sol: Enol content increases in non–polar aprotic solvent (e.g., benzene or hexane) and decreases in polar protic or polar aprotic solvent.

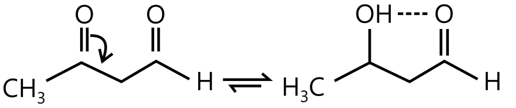
Effect of solvent on enol content c>d>b>a. Benzene (non–polar)>acetone (slightly polar)> methanol (polar, protic solvent)> H_2O (higher polar, protic solvent)

Illustration 9: Arrange the following in the decreasing order of enol content:

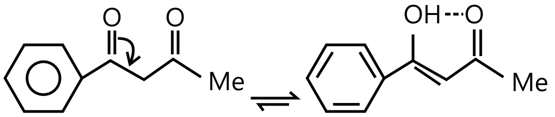
(A) $CH_2(COOEt)_2$ (Diethyl malonate) (B) CH_3COCH_2COOEt (EAA)

(C) $CH_3COCH_2COCH_3$ (D) $PhCOCH_2COCH_3$ **(JEE ADVANCED)**

Sol: d>c>b>a (89%>7.7%>1%) (diketone with (ph) group > diketone > keto ester> diester)

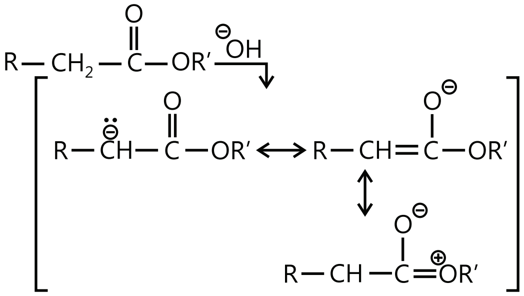


Enol is stabilised by intra-molecular H-bonding (Chelation)



(Ph group stabilises the enol by extending conjugation by p-bond delocalisation and also by chelation)

Esters do not show tautomerism due to the cross–conjugated resonance structures, which decreases the ability of (C=O) group of ester in stabilizing the enol from.



So, diethyl malonate does not show tautomerism.

3. STEREOISOMERISM

Those compounds having same molecular and structural formula but a different arrangement of group or atom in space is called stereo and phenomenon is termed as stereo isomerism.

It is divided into two parts:

(i) Configuration isomerism (ii) Conformational isomerism

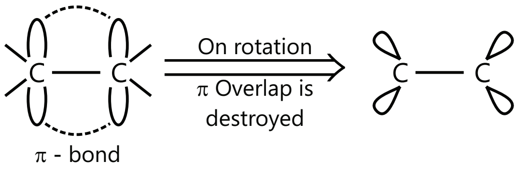
Configurational isomerism is further divided into two parts:

(i) Geometrical isomerism (ii) Optional isomerism

4. GEOMETRICAL ISOMERISM

The main criteria for geometrical isomerism is the restriction in rotation:

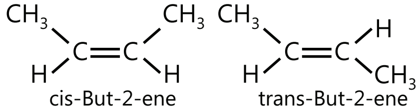
In alkenes, (C=C) bond is made of σ–and π–bonds. A π–bond is made by the sideways overlap of the un–hybridised π–orbitals of two C atoms above and below the plane of two C atoms. If one of the atoms is rotated through 90°, orbitals will no longer overlap and π–bond would break, which requires 25kJ/mol of energy. Hence, the rotation around (C=C) bond is not free but restricted. Due to this restricted rotation, the relative position of atoms or groups attached to the C atoms of the double bond gets fixed, which results in the formation of two distinct forms called geometrical isomers.



Types of geometrical isomerism: There are 3 types of geometrical isomerism on the basis of groups attached to double bond or the site of restricted rotation. They are mentioned below:

4.1 Cis–Trans Isomers

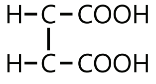
This kind of isomerism is used when there is at least a common group on both sides of the double bond or the site of restricted rotation (especially cycloalkane)



cis-But-2-ene (I) trans-But-2-ene (II)

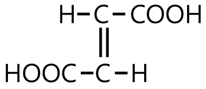
The isomer (I) in which similar groups or atoms lie on the same side of the double bond is called cis–isomer, whereas the isomer (II) in which the similar atoms or groups lie on the opposite side of the double bond is called the trans–isomer.

E.g. (I)



$$\begin{array}{c}H-C-COOH\\ \|\\ H-C-COOH\end{array}$$

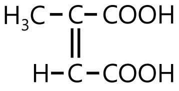
Maleric acid (cis)



$$\begin{array}{c}H-C-COOH\\ \|\\ HOOC-C-H\end{array}$$

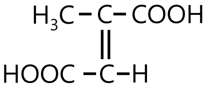
Fumatic acid (trans)

(II)



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

Crotonic acid (cis-isomer)



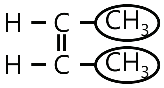
$$\begin{array}{c}H_3C-C-COOH\\ \|\\ HOOC-C-H\end{array}$$

Mesaconic acid (tran-isomer)

Properties of cis–trans isomer

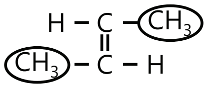
(i) Stability: Cis < Trans

Cis forms is less stable then trans because of the mutual repulsion between the same group e.g.



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

Cis form (more repulsion)



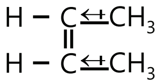
$$\begin{array}{c}H-C-CH_3\\ \|\\ CH_3-C-H\end{array}$$

Trans form (less repulsion)

(ii) Dipole moment: Asymmetrical trans molecule has zero dipole moment, even if trans molecule is not symmetrical than its dipole moment is less than that of the cis isomer.

μ(Sym trans)=0

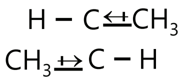
(unsym trans) μ < cis isomer



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

Cis form

μ=+ve



$$\begin{array}{c}H-C\leftarrow CH_3\\ CH_3\rightarrow C-H\end{array}$$

Trans form

μ=0

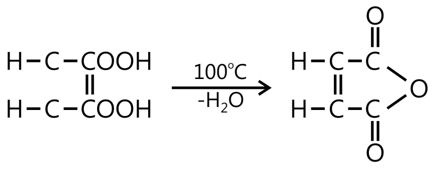
(iii) Polarity: Cis > Trans

(iv) Solubility: Soluble in a polar solvent. Cis > Trans

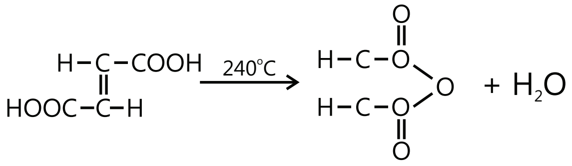
(v) Boiling point: Cis >Trans (due to high polarity)

(vi) Melting point: Cis < Trans. It is due to better packing in crystal due to symmetry. But heat of hydrogenation, heat of combination, density refractive index is higher in cis isomer than trans.

(vii) Heating effect: Maleic acid from anhydride at 100°C but fumaric acid forms anhydride at 250°C

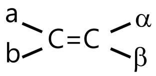


Maleic Acid



Fumaric Acid

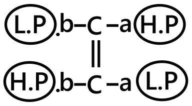
4.2 E–Z Isomerism



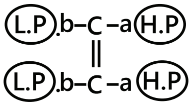
A better system E–Z, is applicable for those type of compounds which cannot be express by cis trans nomenclature.

E → Entegen (opposite) Z → Zusamann (same)

E–form: When two same priority groups present on the opposite side of the double bonded is known E–form and when the same priority group present on same side of the double bond is called Z–form.



E-Form



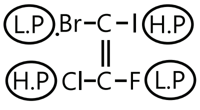
Z-Form

L.P=Low Priority group or atom

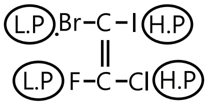
H.P.= High Priority group or atom

Priority rule: Chann, ingold & prelong proposed a sequence rule:

Rule 1: When an atom or group of atoms which are directly attached to the stereo genic centre have a higher atomic number, they will have higher priority. For example

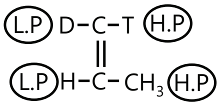


E-Form

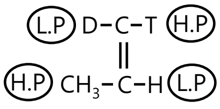


Z-Form

Rule 2: When the atomic number will be same, then higher atomic weight or group of atom have higher priority

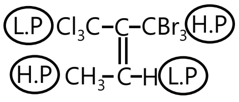


Z-Form

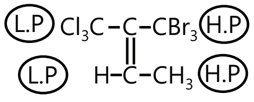


E-Form

Rule 3: When both atomic number and atomic weight are the same, then priority will be decided by the next joining atom.

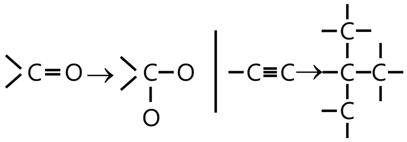


E-Form

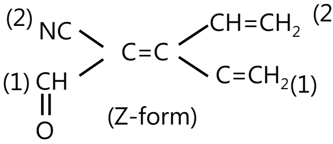


Z-Form

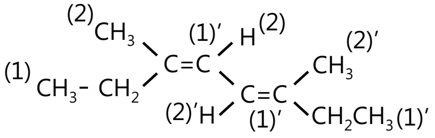
Rule 4: If multiple bonded group attach to the double bonded carbon, then they are considered in the following manner.



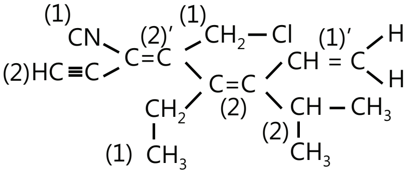
Some E–Z configuration of following compounds



(Z-form)

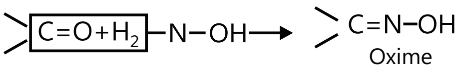


(3Z,5E)



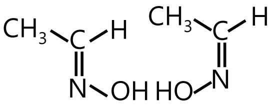
(2Z, 4E)′

4.3 Syn–Anti Isomerism



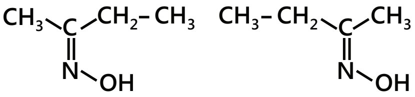
Oxime of aldehyde
and oxime of unsymmetrical
ketone also show
Geometrical Isomerism

Aldoximes



Syn form Anti form

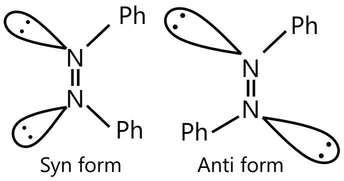
When the –OH group and H atom is on the same side of the double of C and N, then it is the syn form otherwise anti form



Syn form **Anti form**

In unsymmetrical Ketoxime, if –OH and the alphabetically alkyl present on the same side of double bond, then it is syn form and other isomer is anti form.

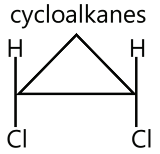
Geometrical isomerism in AZO compounds:



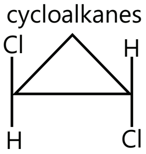
Syn form Anti form

4.4 Geometrical Isomerism in Cyclic Compounds

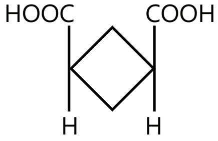
There is a restriction in rotation about the bonds in geometrical isomerism which is also seen in cycloalkanes.



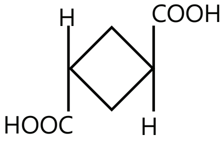
Cis form



Trans form



Cis form



Trans form

PLANCESS CONCEPTS

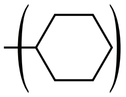
- In E–Z nomenclature, According to CIP rules priority is to be given to atomic numbers but in case they have same atomic number, i.e., isotopes, then priority is to be given to molecular weights.
- Misconception– it is not necessary that a compound having double bond must have geometrical isomers. In case if the 2 substituents on 1 side are the same, geometrical isomers are not possible.
- Geometrical isomers are diastereomers
- Misconception– in compounds having cumulative double bonds geometrical isomerism need not be defined. Those having an even number of double bonds can be optically active but doesn't have geometrical isomers while those having an odd number of double bonds cannot be chiral (unless chiral substituents) but can have geometrical isomers.
- Misconception– geometrical isomerism is not only restricted to double bonds but it can be extended to cyclic compounds and spiranes.

Nikhil Khandelwal (JEE 2009, AIR 94)

Illustration 10: Arrange the following ligands in the decreasing order of priority. **(JEE MAIN)**

(i) $-CH(CH_3)_2$

(ii)



Cyclohexyl

Sol: In cyclohexyl, (–CH) is joined to two (CH_2) groups and is further joined to another ring C atom. In (i), (–CH) is joined to two (CH_3) groups each having three H atoms.

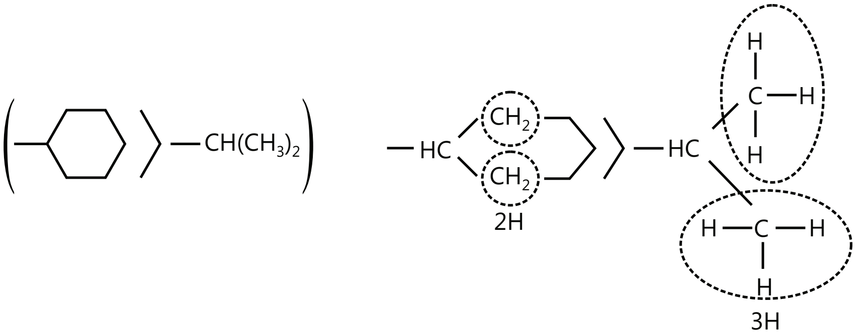
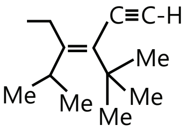
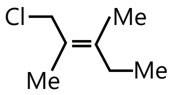


Illustration 11: Assign E–Z configuration to each of the following: **(JEE MAIN)**

a.



b.



Sol: If two higher priority groups are on same side we assign it Z–configuration.

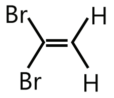
If two higher priority groups are on opposite sides we assign it E–configuration.

(i) (Z) Priority of $HC\equiv C\!-\!>\!-CMe_3$ and priority of $CH_2 = CH\!-\!>\!-CHMe_2$. So two higher priority groups on same side, hence Z–configuration.

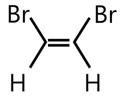
(ii) (E) Priority of $-CH_2Cl > Me$, and $CH_3\ CH_2\!-\!>Me$. So two higher priority groups on opposite sides, hence E–configuration.

Illustration 12: Give the decreasing order of net dipole moments of the following **(JEE ADVANCED)**

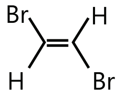
(I)



(II)

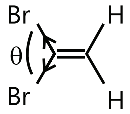


(III)

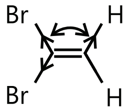


Sol: I>II>III

(I) has a smaller angle of separation between two Br atoms than in (II) and (III). Resulting in more net dipole moment (μ).



(II) Has a large angle of separation between two Br atoms; therefore, net (μ) is less than (I).



In (III), two Br atoms and two H atoms have equal and opposite bond moments; therefore, net μ is zero.

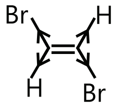
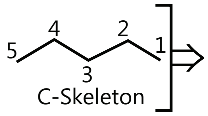
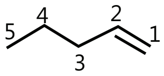


Illustration 13: Give the structural and diastereomers of pent–1–ene. **(JEE ADVANCED)**

Sol: Write the C–skeletons and introduce double bond. The possible structures are: (In Image II double bond is missing)

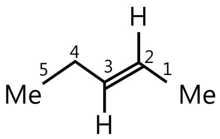


C-Skeleton



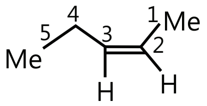
Pent-1-ene

(I)



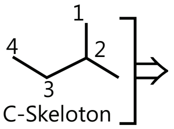
(E)-Pent-2-ene

(II)

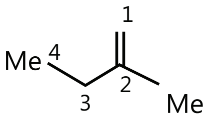


(Z)-Pent-2-ene

(III)

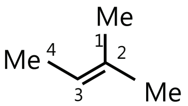


C-Skeloton



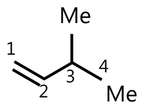
(IV)

2-Methyl but-1-ene



(V)

2-Methyl but-2-ene

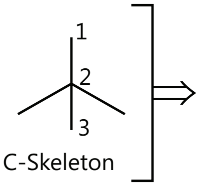


(VI)

3-Methyl but-1-ene

(II) and (III) are diastereomers (geometrical isomers).

C–2 is 4° C atom and cannot form a double bond to give an alkene.



C-Skeleton

5. OPTICAL ISOMERISM

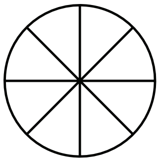
Compounds which can rotate plane polarised light, are called optically active compounds and this phenomenon is called optical activity. Plane polarised light can obtained by passing ordinary light through Nicol prism. Solution of an Optical active compound can rotate plane polarised light either left or to the right through the angle α. This property of a substance of rotating plane polarized light is called optical activity and the substance passing through it, is said to be optically active.

The observed rotation of the plane of polarised light produced by a solution depends upon–

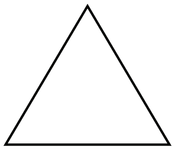
(i) The amounts of the substance in tube.

(ii) On the strength of the solution examined.

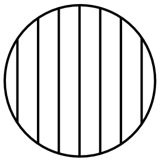
(iii) The temperature of the experiment and the wavelength of the light used.



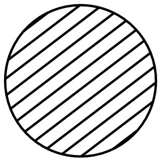
Ordinary light waves vibrating in all direction



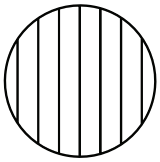
Nicol prism



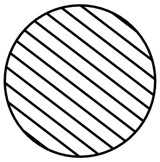
Plane polarizes waves vibrating in one direction



Plane Rotated to the right



Plane polarizes light



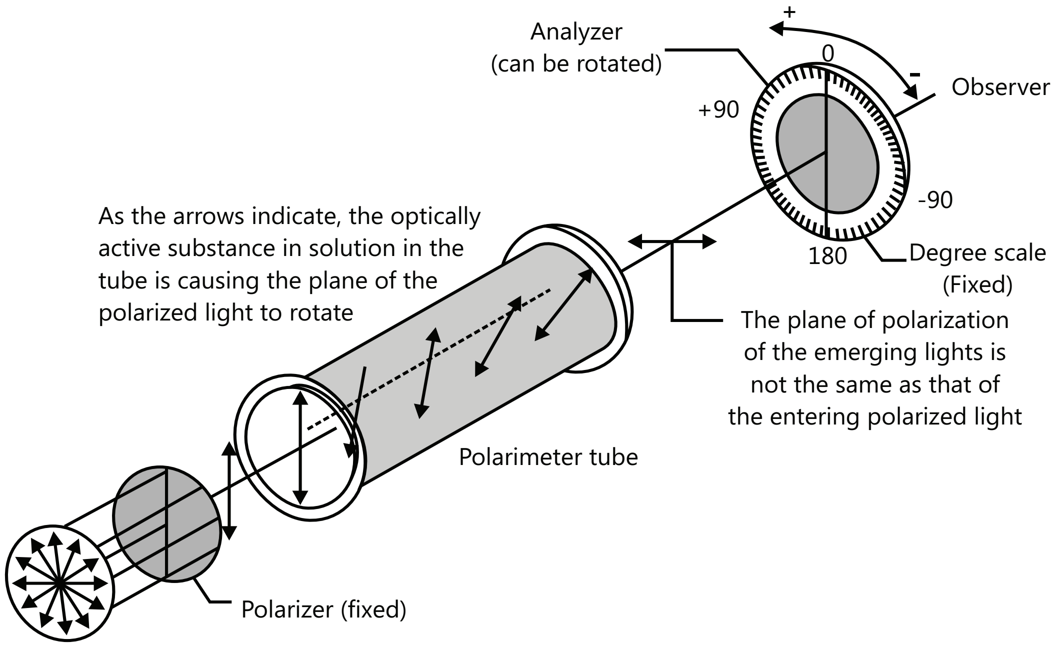
Plane Rotated to the left

All these substance are known to exist in three stages.

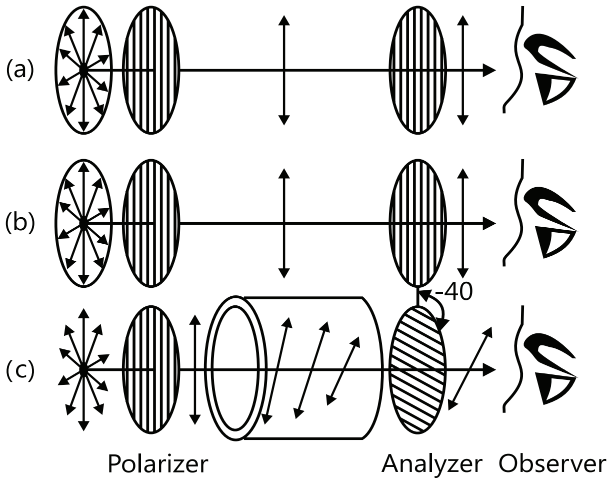
(i) One rotating the plane of polarised light to the left this forms is named laevorotatory.

(ii) One rotating the plane of polarized light exactly to the some extent but to the right. This form is named dextrorotatory.

(iii) An inactive form which does not rotate plane polarized light at all this is mixture of equal amounts of (+) and (–) forms and hence it is optical inactive. It is named (±)–mixture or Racemic mixture. (Latin, Racemic–mixture of equal compounds)



The principal working parts of a polar meter and the measurement of optical rotation.



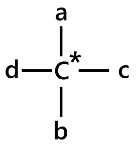
Polarizer and analyser are parallel. No optically active substance is present. Polarized light can get through the analyser.

- Polarizer and analyser are crossed.
- No optically active substance is present.
- No polarized light can emerge from the analyser.
- The substance between polarizer and analyser is optically active.
- Analyser has been rotated to the left (from observer's point of view) to permit rotated polarized light through (substance is levorotatory).
- Clockwise direction is also said to be dextrorotatory, and one that rotates plane–polarized light in a counterclockwise direction is said to be levorotatory (Latin: dexter, right, and leavus, left).

5.1 Specific Rotation

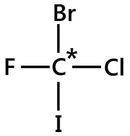
The number of degrees that the plane of polarization is rotated as the light passes through a solution of an enantiomer depends on the number of chiral molecules that it encounters. This, of course, depends on the length of the tube and the concentration of the enantiomer. In order to place measured rotations on a standard basis, chemicals calculate a quantity called the specific rotation, [α], by the following equation: $[\alpha] = \frac{\alpha}{c.l}$ where [α]= The specific rotation α = The observed rotation

Asymmetric carbon (or) Chiral Carbon: If all the four bonds of carbon are bounded by four different atoms / groups, it is chiral. Chiral carbon is denoted by star.



$$\mathrm{d{-}\overset{\displaystyle a}{\underset{\displaystyle b}{C^*}}{-}c}$$

Optical isomerism in bromochlorofluoroiodo methane: The structural formula of bromo chloroiodomethane is

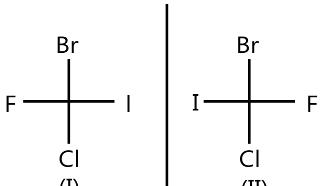


$$\mathrm{F{-}\overset{\displaystyle Br}{\underset{\displaystyle I}{C^*}}{-}Cl}$$

The molecule has one chiral carbon as designated by star. So, the molecule is chiral and is non–super imposable on its mirror image.

According to Van't Hoff rule, Total number of optical isomers should be = 2^n, where n is number of chiral centre(s).

The fischer projections of the two isomers are



(I) (II)

These are optically active, which are non–super imposable mirror images of each other and can rotate the plane of polarized light.

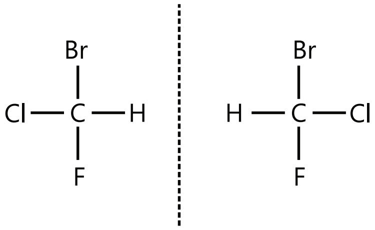
Stereoisomers which are mirror–images of each other can called enantiomers (or) Enantiomorphs. (i) and (ii) are enantiomers. All the physical and chemical properties of enantiomers are the same except two: They rotate PPL to the same extent but in opposite directions. One which rotates PPL in clockwise direction is called dextro–rotatory (dextro is Latin word meaning thereby right) and is designated by d (or) (+). One which rotates PPL in anti–clockwise direction is called laevo rotatory (means towards left) and designate by ℓ (or) (–).

5.2 Chirality

This term is been used to describe molecules without any elements of symmetry, thus unsymmetrical molecules are also called chiral molecules and optical activity is attributed to certain chiral centres in them. An asymmetrical carbon is a chiral center. Chirality is lost when two atoms bonded to an asymmetric carbon become similar, thus lactic acid is optically active but propionic acid is inactive.

Conditions for optical activity

(i) It must have an asymmetric C atom or the chiral C atom. C atom which is attached to four different atoms or groups is called an asymmetric C atom or the chiral centre or stereo genic or stereo centre.

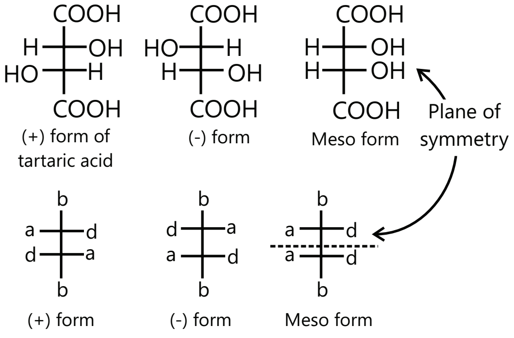


(ii) It must have a non–superimposable mirror image.

(iii) It should not contain any element of symmetry, i.e.,

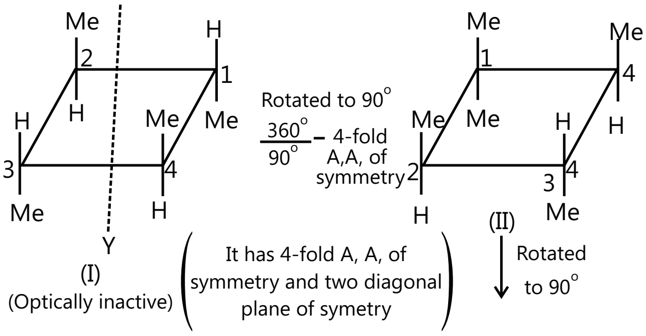
- Plane of symmetry or (mirror plane or σ –plane).
- Alternating axis of symmetry.
- Centre of symmetry or centre of inversion.

(i) **Plane of symmetry or mirror plane or σ –plane:** It is defined as an imaginary plane which divides the molecule into two equal parts such that one part of the molecule is a mirror image of the other part. For example:



(ii) **Alternating axis of symmetry:** A molecule possesses an n–fold alternating axis (A.A) of symmetry. When rotated through an angle of $360^\circ/n$ about this axis, followed by the reflection in a plane perpendicular to this axis, the molecule is identical to the original molecule. For example, 1,2,3,4–tetramethyl cyclobutane (I) contains four–fold alternating axis of symmetry. Rotation of (I) through 90° about axis XY, which passes through the centre of the ring perpendicular to its plane, gives (II) and reflection of (II) in the plane of the ring gives (I).

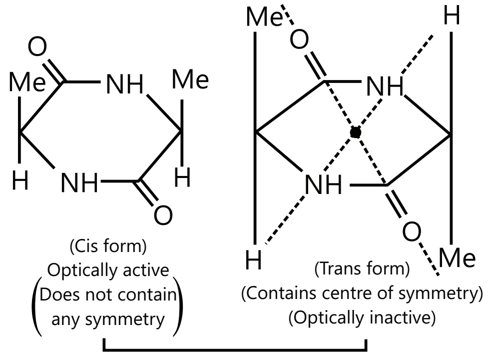
This situation arises n times in the molecule: (I) has two diagonal planes of symmetry.



(I)
(Optically inactive)

(It has 4-fold A, A, of symmetry and two diagonal plane of symetry)

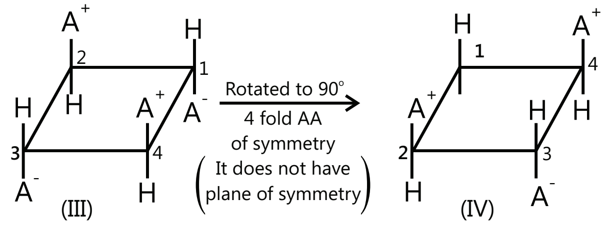
(II)



(Cis form)
Optically active
(Does not contain any symmetry)

(Trans form)
(Contains centre of symmetry)
(Optically inactive)

Dimethyl diketo piperzine



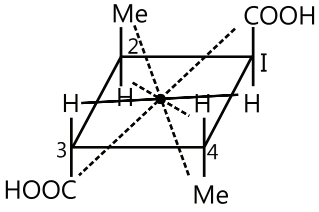
(III)
(Optically inactive)

(IV)

(iii) Centre of symmetry (or centre of inversion): It is defined as a point from which lines when drawn on one side and produced to an equal distance on the other side will meet identical points in the molecule. For example: (It possesses a centre of symmetry, which is the centre of the ring and is therefore optical inactive)

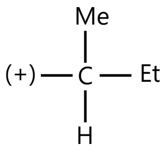
Fig. – Dimethyl cyclobutane–1.3 – dicarboxylic acid (It possess a centre of symmetry, which is the centre of the ring and is therefore optical inactive.

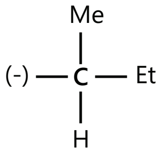
It may be noted that only an even–membered ring can possibly possess a centre of symmetry.



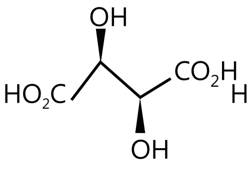
2,4–Dimethyl cyclobutane–1,3–dicarboxylic acid

A^+ and A^- are chiral group, e.g., $A^+ \Rightarrow$ $A^- \Rightarrow$

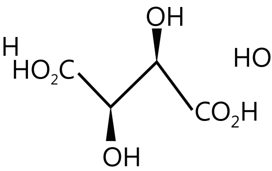




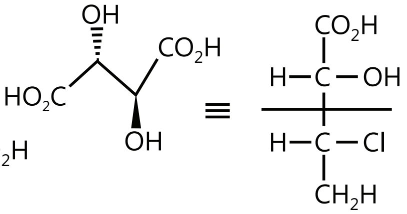
Stereoisomerism in Tartaric acid: Compounds which contain two asymmetric carbon atoms and are of the type Cabc–Cabc exist in only three isomeric forms. Two of these are non–superimposable mirror images of each other and are optically active and the third, a diastereomer of the first two, contains a plane of symmetry, is super imposable on its mirror image, and is not optically active.



I(-) tartaric acid



d(-) tartaric acid



Mesotartaric acid

The inactive diastereomer is usually described as a meso form. As with other examples of diastereomers, the properties of meso forms are different from those of the isomeric mirror–image pairs; for example, mesotartaric acid melts at a lower temperature [140° C] than the d and ℓ isomers [170° C], and is less dense, less soluble in water, and a weaker acid.

5.3 R–S System (Absolute Configuration)

R → Rectus (Right) S → Sinister (Left)

R → S nomenclature is assigned as follow:

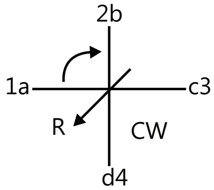
Step I: By the set of sequence rule, we give the priority order of atom or group connected through the chiral carbon.

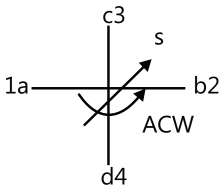
Step II: If atom/group of minimum priority is present on the vertical line, then

Movement of eyes in clockwise direction = R

Movement of eyes in anticlockwise =S

Movement of eyes taken from $1 \rightarrow 2 \rightarrow 3$ through low molecular weight group (if needed)

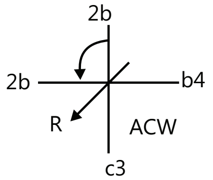


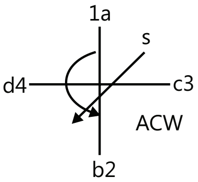


Step III: If minimum priority group present on the horizontal line, then

clockwise rotation ⇒ S

anticlockwise rotation ⇒ R





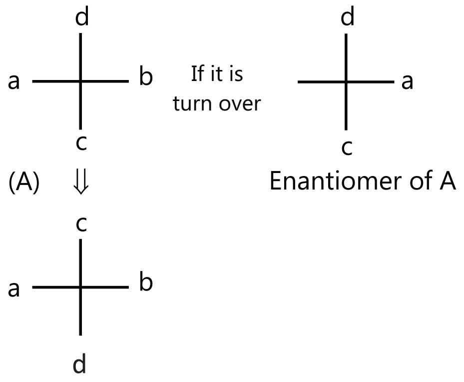
5.4 ENANTIOMERS

Those compounds which are nor superimposable on their mirror image, is called enantiomeric pairs.

Condition → same molecular formu, same structure formul, different configuration.

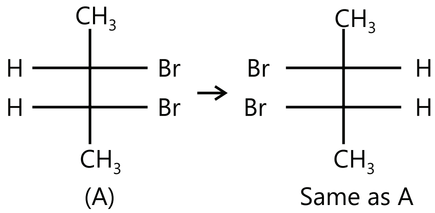
Some important facts about the fisher projection formulae.

(a) If the fisher projection of stereoisomers is lifted from the plane of paper & turned over, then such an operation will be result in enantiomers of the original compound.



i.e. if either vertical or Horizontal line groups are inverted, then enantiomers of the original compound result.

(b) If more than one chiral centre is present molecule have plane of symmetry



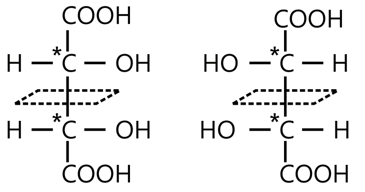
Properties of enantiomers:

(i) Enantiomers have a chiral molecule

(ii) Enantiomers have identical physical properties like b.p.,m.p., refractive index, density etc. They rotate the ppl in opposite direction but to equal extent.

(iii) They have identical chemical properties, However, their reactivity i.e. rate of reaction will be differ if they combine with other optically active reagents.

- All the optically active compounds exist in two or more isomeric forms, which differ from one another in the relative spatial arrangement of atoms or groups.
- These stereoisomers which resemble one another in their chemical reactions and most of the physical properties but differ only in their behaviour towards plane–polarised light are called optical isomers and the phenomenon is called optical isomerism.
- Optical isomers which are non–superimposable mirror images of each other are called enantiomers and the phenomenon is called enantiomerism. The enantiomers have identical physical and chemical properties but rotate the plane of polarised light in opposite directions but to the same extent.
- It may be noted that the necessary and sufficient condition for a molecule to exhibit enantiomerism (and hence optical activity) is chirality or dissymmetry of molecules, i.e., the molecule and its mirror image must be non–superimposable. It may or may not contain chiral or asymmetric carbon atoms.
- Usually, the presence of one or more chiral carbon atoms causes the molecule to show enantiomerism and hence the optical activity but certainly it is not the necessary and sufficient condition. For example, meso–tartaric acid contains two chiral carbon atoms (marked by asterisks) but does not show enantiomerism and is actually optically inactive.



Meso-tartaric acid Optically inactive

Plane of Symmetry (contains a plane of symmetry and hence does not show enantiomerism)

This is because it contains a plane of symmetry which divides the molecule into two equal halves so that one half of the molecule is a mirror image of the other. As a result, meso–tartaric acid and its mirror image are superimposable. In other words, meso–tartaric acid is an achiral or non–dissymmetric or symmetric molecule and hence it does not show enantiomerism or optical activity. Thus, the optical inactivity of meso–tartaric acid is due to internal compensation, i.e., the rotation caused by one half of the molecule is exactly cancelled by an equal and opposite rotation caused by the other half of the molecule.

5.5 Diastereomers

Those compounds which are neither mirror images nor are superimposable on each other, are called as diastereoisomers.

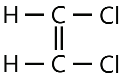
Ex: Cis–trans isomer are configurational isomers but they are not mirror images and are thus, they are said to be diastereomers.

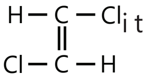
Characterstic of Diastereomers

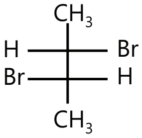
- Generally optical active, however geometrical isomers are an exception.
- Their physical properties are different like mpt, bpt, density, solubilities & values of specific rotation.
- They can be separated by fractional distillation, fractional crystallization & chromatography etc.
- They exhibit similar but not identical chemical behaviour.

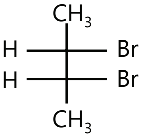
5.6 Meso Compounds

A meso compound is superimposed on its mirror image. It is optically inactive although contains two or more stereocenters. All meso compounds are achiral due to internal compensation.









5.7 Racemic Mixture and Optical Resolution

When equal amounts of two enantiomers are mixed together, it gives an optically inactive form called racemic mixture or modification. It is denoted by using the prefix ± or dl before the name of compound. For example, if equal amounts of (+) lactic acid and (–) lactic acid are mixed together, we get the racemic or (±) lactic acid, which is optically inactive. Evidently, the optical inactivity of a racemic mixture is due to external compensation i.e. the rotation caused by molecules of one enantiomer is exactly cancelled by an equal and opposite rotation caused by the same number of molecules of the other enantiomer.

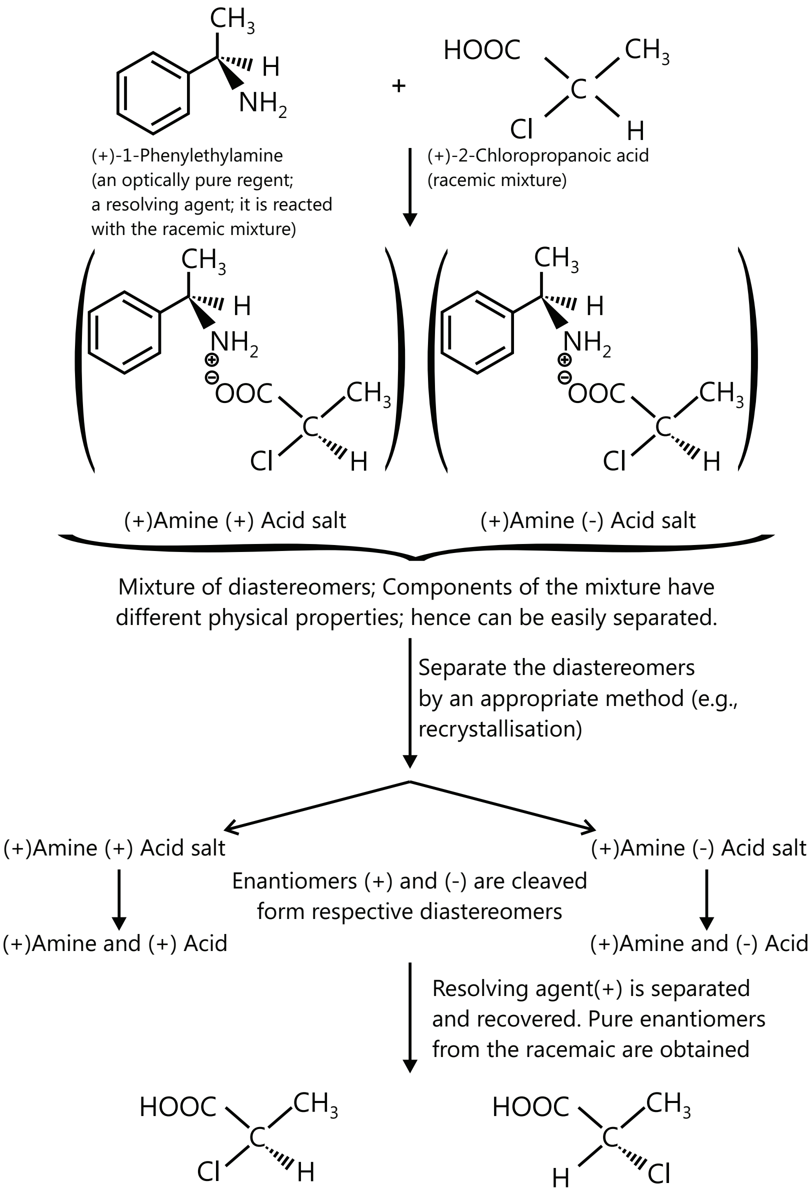
A racemic mixture can also be obtained chemically. The process by which one enantiomer (+or–) of an optically active compound is converted into a racemic mixture is called racemization. Racemisation can be carried out by heat, light, or chemical reagents. For example, lactic acid and tartaric acid undergo racemisation in the presence of a base.

Resolution of a Racemic Mixture

1. Since a racemic mixture contains equal amounts of two enantiomers, so they can be separated into (+) or (–) enantiomers by a number of methods. The process of separation of a racemic mixture into its (+) and (–) enantiomers is called resolution. Since, the enantiomers have identical physical and chemical properties except towards optically active reagents, they cannot be separated by the usual techniques such as fractional crystallization, fractional distillation, chromatography, etc. Therefore, special methods are used to achieve their separation. Some of these are listed below:

- Mechanical method.
- Biological method using enzymes.
- Chemical methods (by making their diastereomers).
- Chromatographic separation by using special adsorbents.

2. Diastereomeric method: One of the most common methods is to allow a racemic mixture to react with an enantiomer of some other compound. This changes a racemic form into a mixture of diastereomers which have different solubilitys as well as melting and boiling points. These can be separated from one another by conventional methods of separation of compounds. The separated diastereoisomer is then broken down to give pure enantiomers.



(+) Acid

(-) Acid

5.8 Racemic Forms and Enantiomeric Excess

A sample of an optically active substance that consists of a single enantiomer is said to be enantiomerically pure or to have an enantiomeric excess of 100%. (An enantiomerically pure sample of (S)–(+)–2–butanol shows a specific rotation of $+13.52^{o}\left[\alpha\right]_{D}^{25} = +13.52^{o}$). On the other hand, a sample of (S)–(+)–2–butanol that contains less than an equimolar amount of (R)–(–)–2–butanol will show a specific rotation that is less than +13.52° but greater than 0°. Such a sample is said to have an enantiomeric excess less than 100%. The enantiomeric excess (ee) is defined as follows:

$$\%\ \text{Enantiomeric excess} = \frac{\text{Moles of one enantiomer} - \text{Moles of other enantiomer}}{\text{Total moles of both enantiomers}} \times 100$$

The enantiomeric excess can be calculated from optical rotations:

$$\%\ \text{Enantiomeric excess}^{*} = \frac{\text{Observed specific rotation}}{\text{Specific rotation of the pure enantiomer}} \times 100$$

Let us suppose, for example, that a mixture of the 2–butanol enantiomers showed a specific rotation of +6.76°. We would then say that the enantiomeric excess of the (S)–(+)–2–butanol is 50%:

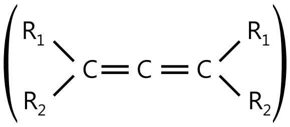
$$\text{Enantiomeric excess } = \frac{+6.76^{\circ}}{+13.52^{\circ}} \times 100 = 50\%$$

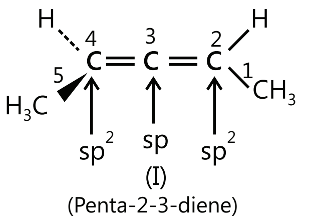
When we say that the enantiomeric excess of this mixture is 50%, we mean that 50% of the mixture consists of the (+) enantiomer (the excess) and the other 50% consists of the racemic form. Since for the 50% that is racemic the optical rotations cancel one another out, only the 50% of the mixture that consists of the (+) enantiomer contributes to the observed optical rotation. The observed rotation is, therefore, 50% (or one–half) of what it would have been if the mixture had consisted only of the (+) enantiomer.

5.9 Chirality in Compounds with No Optical Centres

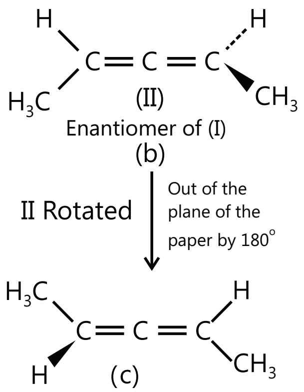
Stereochemistry of C Compounds Not Containing an Asymmetric C Atom (Allenes)

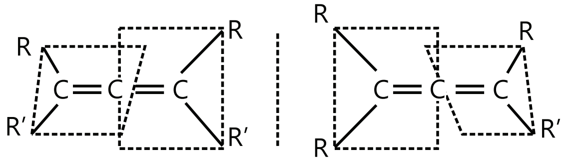
The presence of an asymmetric C atom is not essential for optical activity. The essential requirement is the asymmetry of a molecule as a whole.

Allenes of the type are  Asymmetric and are resolvable, e.g., penta–2,3–diene (I) has no chiral C atoms, yet it is a chiral molecule and has two enantiomers.



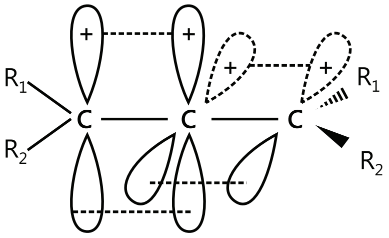
(I)
(Penta-2-3-diene)
(a)

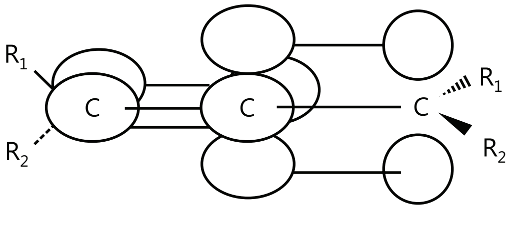




Non-superimposable minor images show cnantiomerism
(d)

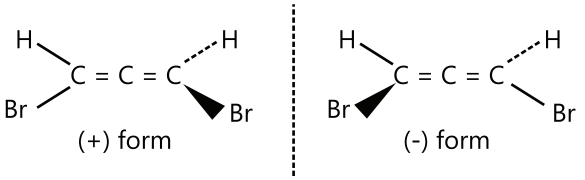
The planes of π– bonds of alkenes are perpendicular to each other. This geometry of π– bonds causes the groups attached to the end C atoms to lie in perpendicular planes. The allenes with different substituents on the end C atoms are chiral. Such allenes do not show cis–trans isomerism. This is an example of a chiral molecule which has two stereocentres at (C^2 and C^4) but no chiral centres.



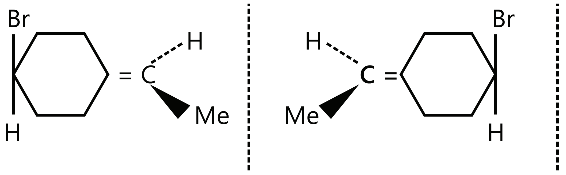


C^3 is sp–hybridised and has one p–orbital overlapping in the xy plane with the p–orbital of C^4, and the other p–orbital overlapping in the xz plane with the p–orbital of C^2 to form two double bonds. The two groups H and CH_3 attached to C^4 are, therefore, in the plane at right angles to the plane of two groups H and CH_3 attached to C^2. The mirror images are not identical as can be shown by rotating one of the structures, (II), 180° out of the plane of paper in order to superpose the H and Me groups in the plane of paper. The groups extending in the front and back of the plane of paper will not match.

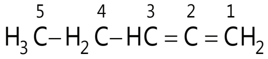
(A) 1,3–Dibromo allene also shows optical activity.



(B) 4–Bromoethenyl cyclohexane also shows enantiomers by considering the ring to be flat.



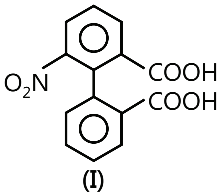
(C) Penta–1,2–diene does not show enantiomers, since terminal C has two H atoms.



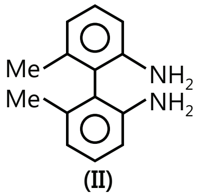
$\overset{5}{H_3C}-\overset{4}{H_2C}-\overset{3}{HC}=\overset{2}{C}=\overset{1}{CH_2}$

5.9.1 Optical Activity of Biphenyl Compounds

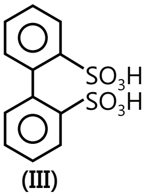
When at least three of the 2,2′,6, and 6′ positions are occupied by sufficiently large groups, free rotation about the single bond joining the two phenyl groups is no longer possible, provided each ring has no vertical plane of symmetry. This restricted rotation gives rise to optical activity due to the molecule being asymmetrical as a whole. Hence, 6–nitrobiphenyl–2, 2′–dicarboxylic acid (I) and 6, 6′–diamino–2, 2′–dimethyl biphenyl (II) have been resolved.



(I)



(II)

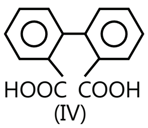


(III)

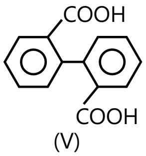
If the substituent groups are large enough, only two groups in the o and o′–positions will cause restricted rotation, e.g. biphenyl–2, 2′–disulphonic acid (III) has been shown to be optically active. So I, II, and III are resolvable.

The cause of restricted rotation is mainly due to the steric effects of groups in the o– and o′ positions (not at m and m′, and p and p′). This type of stereoisomerism arising from restricted rotation about a single bond (and where the stereoisomers can be isolated) is called ATROP ISOMERISM and the isomers are called ATROP ISOMERS.

Diphenic acid is not optically active. In configuration (IV), the molecule has a plane of symmetry, and in configuration (V), it has a centre of symmetry. Further, IV is less stable than (V) because of the repulsion between two (–COOH) groups.



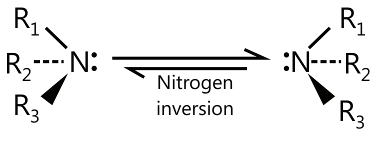
(IV)

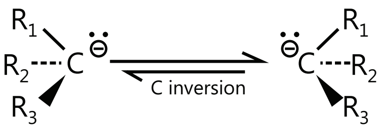


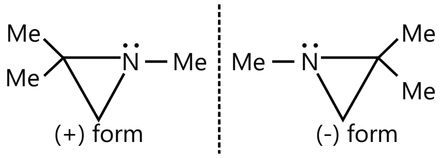
(V)

5.9.2 Optical Activity of t–Amines and t–Carbanion of the type ($R_1R_2R_3N$) and ($R_1R_2R_3C$)

Such an amine and carbanion with a lone pair of e⁻s (being considered a fourth different group) are chiral because of their pyramidal geometry, but they are optically inactive. A rapid" Umbrella" type inversion converts either of the enantiomers to a racemic mixture. The energy required for this inversion is very low bond breaking and bond formation. Thus, racemization occurs and enantiomers cannot be isolated. However amine salts are optically active. Nitrogen inversion is not possible e.r $R_1R_2R_3N^{\oplus}H]Cl^{\oplus}$





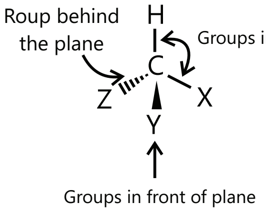


1,2,2-Trimethyl aziridine

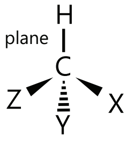
5.9.3 Projection Formulae

(a) Wedge–Dash formula: The configuration of organic molecules can be visualised by three–dimensional (3D) structures, which may be depicted by any of the following representations:

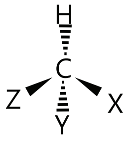
The thick solid (solid wedge) line indicates the bonds lying above the plane of paper (Projecting towards the viewer): thin lines indicate the bonds lying within the plane of paper; while the dotted lines indicate the bonds lying below the plane of paper. Such a representation is called Wedge–Dash formula.



(I)

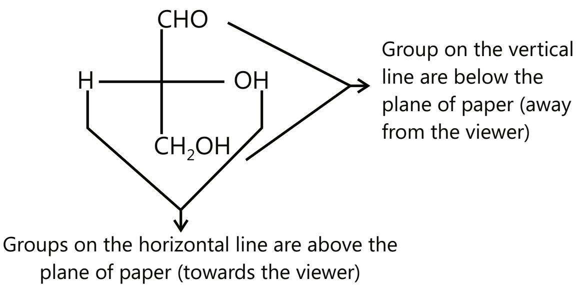


(II)



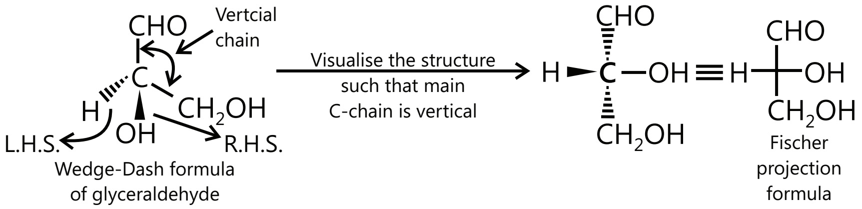
(III)

(b) Fischer projection formula: This formula is a standard way of depicting 3D structures in two dimensions (2D). It is useful for simpler representation of the stereochemistry of compounds that contain one or more chiral C atoms. In this formula, the molecule is drawn in the form of a cross with the chiral C atom at the intersection of the horizontal and vertical lines. The horizontal lines represent the bonds directed towards the viewer and the vertical lines away from the viewer. As far as possible, the vertical part of the projection formula thus obtained represents the longest chain of C atoms with the most–oxidised C atoms (mainly the principal functional group) at the top. For example, (–CHO) group in glyceraldehyde, (–COOH) group in lactic acid, etc. The C atoms are then numbered according to the IUPAC nomenclature.



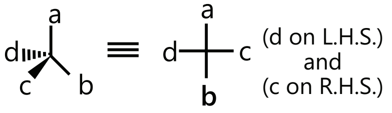
(c) Interconversion of Wedge–Dash formula to Fischer formula: For molecules containing several C atoms; it is customary to orient the molecule in such a way that the C–chain is vertical. Substituents which are at left and right of the viewer are written at left and right, respectively, and other two substituents which appear above and below are written at top and bottom positions.

E.g.

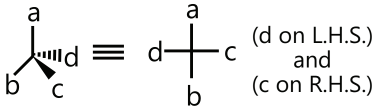


Although the Fischer projections are planar structures, these can be rotated end–for–end on the plane of paper only in multiples of 180° but not 90° at a time. Also, a Fischer projection formula may not be taken out of the plane of paper and flipped over.

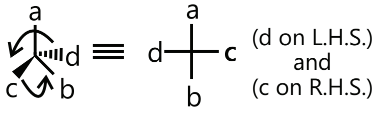
(i)



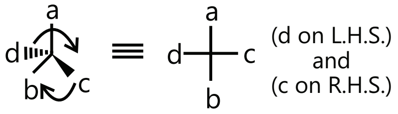
(ii)



(iii)

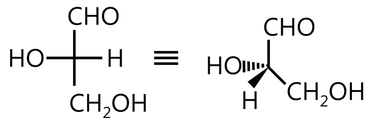


(iv)



(d) Interconversion of Fischer formula to Wedge–Dash formula

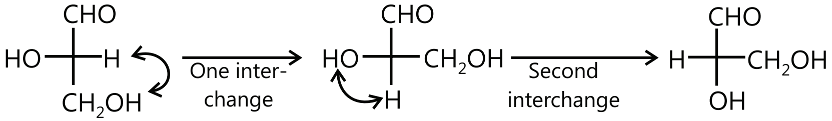
When drawing the 3D formulae from the corresponding Fischer formula, it is better to draw the group at the lower end of the vertical line towards R.H.S.



Fischer formula Wegde-Dash formula

Several Fischer projections can be drawn depending on the bonds drawn in the horizontal and vertical positions, respectively. It is, therefore, necessary to compare two different formulae to check whether they represent the same or different compounds. The following rules must be observed:

(i) A Fischer projection should not be taken out of the plane of paper and turned over. It would lead to the Fischer projection of the enantiomer, since it changes the configuration at the chiral centre.



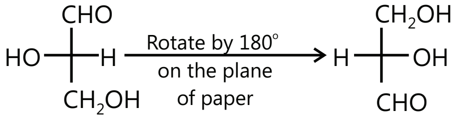
(I) (II) (III)

(ii) Even number of interchanges clockwise or anti–clockwise leads to the same stereoisomer, while odd number of interchanges results in an enantiomer. (I) and (III) are equivalent Fischer projections.

(iii) Rotation of Fischer projection by 180° on the plane of paper results in the equivalent Fischer projection.

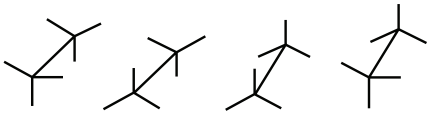
(I) and (II) are equivalent Fischer projections.

E.g. Sawhorse and Newman projection formulae.



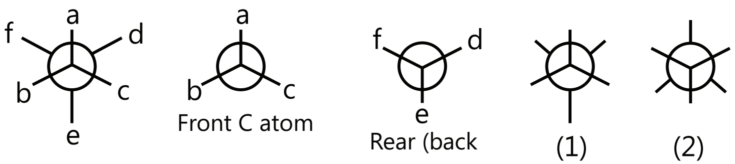
(I) (II)

- **Sawhorse projection formula:** This is a simple method of representing three–dimensional formula on paper. The molecule is viewed slightly from above and from the right and projected on the paper. The bond between the two carbon atoms is drawn diagonally and is slightly elongated for clarity. The lower left–hand carbon is considered to be towards the front and the upper right–hand carbon towards the back. It can be represented in various ways as shown, but structure (4) is the most convenient way of representing the Sawhorse projection formula.



(1) (2) (3) (4)

- **Newman projection formula:** Newman devised a simple and highly useful method of representing three–dimensional formula on paper. These are called Newman projections after his name. These projection formulae are obtained by viewing the molecule along the bonds joining two carbon atoms. The carbon atom near the eye is represented by a point and the three atoms or groups attached to it by three equally spaced (120o) radii. The carbon atom farther from the eye is designated by a circle and the three atoms or groups attached to it by three equally spaced radial extensions. It can be represented as shown in (1) or (2).

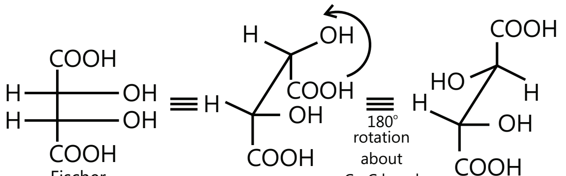


Front C atom

Rear (back C atom)

(1) (2)

Conversion of Sawhorse and Newman projection formulae in Fischer and vice versa: Groups on the horizontal line in Fischer projection are below the plane of paper and groups on the horizontal lines are above the plane of paper.

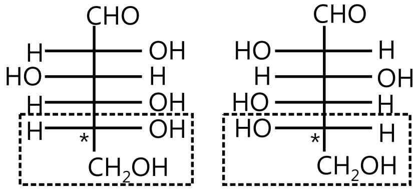


Fischer (20H; same side) (Erythrose form)

(Sawhorse) (20H; opposite side)

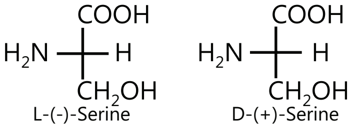
5.10 D–L Configuration (Relative Configuration)

D and L: Symbols D and L refer to the relative configuration of the (–OH) group at the penultimate carbon w.r.t. glyceraldehyde taken as a standard. D refers to the (–OH) group which lies on the right hand side and L refers to the (–OH) group which lies on the left hand side.



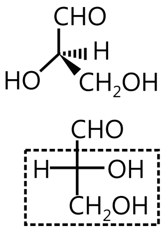
D-(+)-Glucose D-(+)-Glucose

Carbohydrates

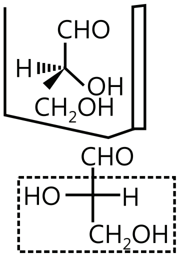


L-(-)-Serine D-(+)-Serine

Amino acids



D-(+)-Glyceraldehyde
–OH on right side
of chiral carbon



L-(-)-Glyceraldehyde
–OH on left side
of chiral carbon

All molecules which can be chemically related to D–glyceraldehyde are assigned the D configuration and those related to L–glyceraldehyde are all designated the L configuration. It may be noted that there is no direct relation between D and L configurations with d and l or (+) or (–) notations.

The DL system is commonly used in assigning the stereochemistry to carbohydrates and amino acids. For amino acid, (–)–serine has been used as a configurational reference compound, because there is a configurational similarity between L–glyceraldehyde and (–)–serine.

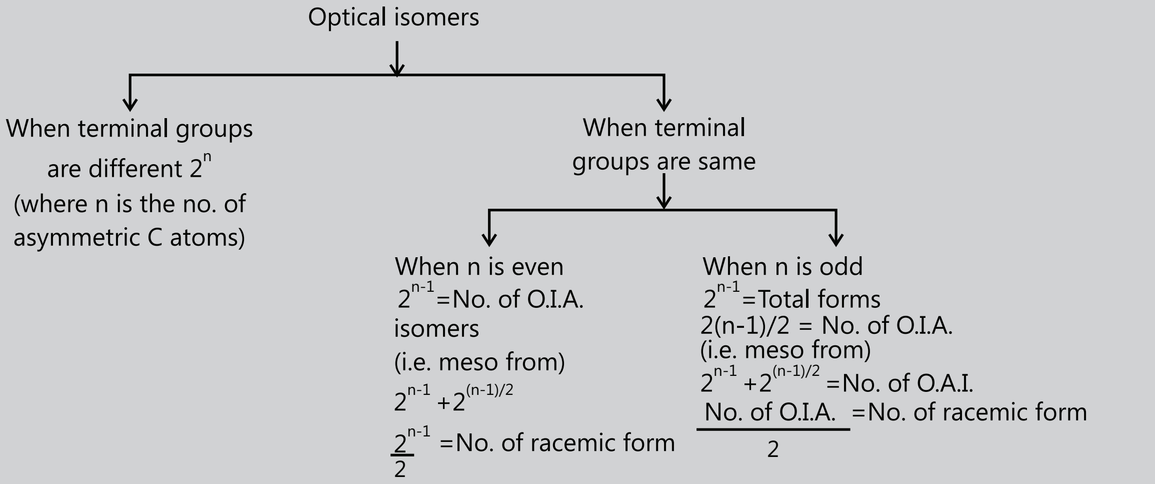
In drawing the Fischer projections while assigning D, L configuration, the Fischer projection of the molecule is drawn in such a way that the main longest chain becomes vertical with carbon–1, the most highly oxidised carbon at the top. For α –amino acids, the configurational arrangement of $–NH_2$, –COOH , R and H groups at the C_a atom is related to that of –OH, –CHO, $–CH_2OH$ and H groups, respectively, of glyceraldehyde (2,3–dihydroxy propanal). Thus, L–glyceraldehyde and $L-\alpha-$ amino acids are said to have the same relative configurations.

PLANCESS CONCEPTS

- The basic of deciding diastereomers is that the two compounds should be non–superimposable and non–mirror images of each other.
- Mesomers are optically inactive due to internal compensation while diastereomers are inactive due to external compensation.
- Generally anti conformation is the most stable conformation but if intramolecular hydrogen bonding is possible than in some cases the gauche form becomes the most stable.
- Diastereomers have different physical and chemical properties.
- In optical resolution of enantiomers, it is first converted to different diastereomers and then it is separated on the basis of difference in physical and chemical properties.
- If Sawhorse or Newman projection of two molecules are given and a relation is asked then convert it into fisher projection, assign R–S nomenclature and then compare the relation.

PLANCESS CONCEPTS

Formula for the number of optical isomers

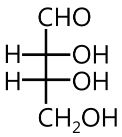


(O.A.I. ⇒ Optically active isomers. O.I.A. ⇒ Optically inactive isomers)

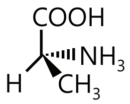
Vaibhav Krishnan (JEE 2009, AIR 22)

Illustration 14: Specify the configuration of following compounds in D or L. **(JEE MAIN)**

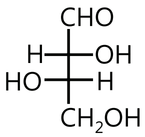
(i)



(ii)



(iii)



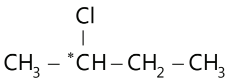
Sol: (a) D configuration, OH is at right.: (b) L– (Convert to fischer),–NH_2 is on the left) (c) L configuration (–OH on C–3 is on the left side).

Illustration 15: b. Which of the following are optically active compounds and why?

(i) Butan–1–ol (ii) 2–Chlorobutane (iii) Lactic acid (iv) 3–Chloropentane **(JEE MAIN)**

Sol: Compound containing chiral carbon (carbon bearing four different group is referred as chiral carbon) shows optical activity and are said to be optically active compound. From the given name write down the chemical structure of the compound and check whether the compound contains any chiral carbon and accordingly write down the answer.

The structural formulas of the given compounds are as under:

Butan–1–ol is not optically active since it does not contain any asymmetric carbon atom. Hence, the molecule is achiral.	$CH_3CH_2CH_2CH_2OH$ (Butan–1–ol)
Is a chiral molecule, since it contains an asymmetric carbon atom marked with an asterisk. Hence, it is optically active.	 $CH_3-\overset{\overset{Cl}{\vert}}{^{*}CH}-CH_2-CH_3$

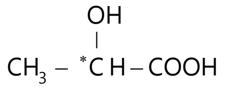
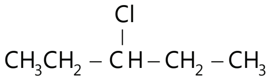
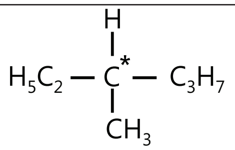
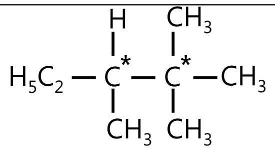
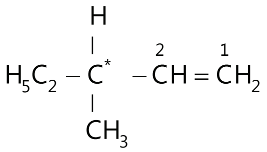
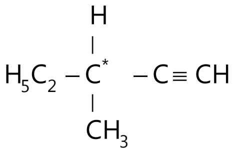
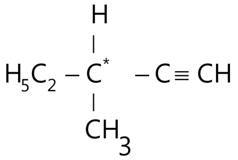
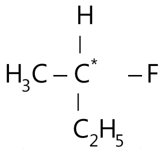
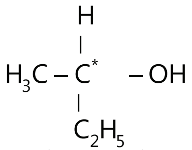
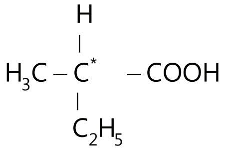
Contains one asymmetric carbon atom and its molecule is chiral. Thus, it shows optical activity.	 $CH_3-\overset{OH}{^{*}CH}-COOH$
Is a symmetrical molecule since it does not contain an asymmetric carbon atom. Hence, it does not show optical activity.	 $CH_3CH_2-\overset{Cl}{CH}-CH_2-CH_3$

Illustration 16: Write the name and structure of the following optically active compounds with lowest molecular weight.

(i) alkane (ii) alkene (iii) alkyne (iv) unsaturated hydrocarbon

(v) alkyl halide (vi) alcohol (vii) acid (viii) amine **(JEE ADVANCED)**

Sol:

i.	Optically active alkane with the lowest molecular weight:	 $H_5C_2-\underset{CH_3}{\overset{H}{C^*}}-C_3H_7$ and 3-Methyl hexna  $H_5C_2-\underset{CH_3}{\overset{H}{C^*}}-\underset{CH_3}{\overset{CH_3}{C^*}}-CH_3$ 2,3-Dimethyl pentane
ii.	Optically active alkene with lowest molecular weight:	 $H_5C_2-\underset{CH_3}{\overset{H}{C^*}}-\overset{2}{C}H=\overset{1}{C}H_2$ 3–Methyl hexane
iii.	Optically active alkyne with the lowest molecular weight:	 $H_5C_2-\underset{CH_3}{\overset{H}{C^*}}-C\equiv CH$ 3–Methyl hexane
iv.	Optically active unsaturated hydrocarbon with the lowest molecular weight:	 $H_5C_2-\underset{CH_3}{\overset{H}{C^*}}-C\equiv CH$ 3–Methyl hexane
v	Optically active alkyl halide with the lowest molecular weight:	 $H_3C-\underset{C_2H_5}{\overset{H}{C^*}}-F$ (2–Flurobutane)
vi	Optically active alcohol with the lowest molecular weight:	 $H_3C-\underset{C_2H_5}{\overset{H}{C^*}}-OH$ (Butan–2–ol)
vii	Optically active acid with the lowest molecular weight:	 $H_3C-\underset{C_2H_5}{\overset{H}{C^*}}-COOH$ (2–Methyl butanoic acid)

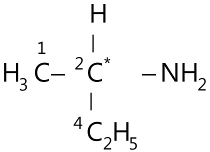
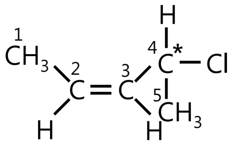
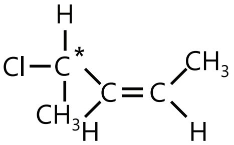
viii	Optically active amine with the lowest molecular weight:	 $\overset{1}{H_3C}-{}^{2}\overset{H}{\underset{{}^{4}C_2H_5}{C^*}}-NH_2$ (Butan–2–amine)

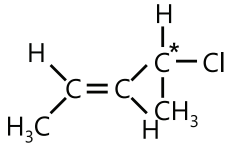
Illustration 17: How many stereoisomers are possible for the compound $CH_3CH = CHCHClCH_3$? **(JEE ADVANCED)**

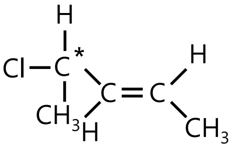
Sol: One double bond, two GI, and one asymmetric C atom, two optical isomers, total four.



(I) (+) cis-4-Chloro-pent-2-ene


(II) (-) cis-4-Chloro-pent-2-ene

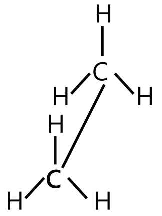

(III) (+) trans-4-Chloro-pent-2-ene

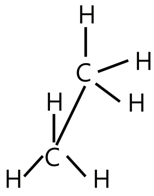

(IV) (-) trans-4-Chloro-pent-2-ene

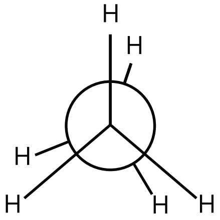
(I) and (II), and (III) and (IV) are enantiomers; (I) and (III), (II) and (IV), (I) and (IV), and (II) and (III) are diastereomers.

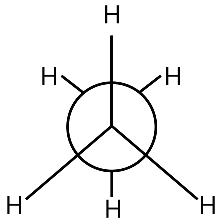
6. CONFORMATIONAL ISOMERISM

Different non–identical arrangement of atoms or group in a molecule that result by the rotation about a single bond and that can easily be reconverted at room temperature are known as conformational stereoisomers of conformers

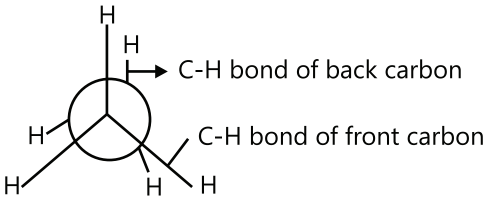

Eclipsed Sawhorse projection


Staggered Sawhorse projection

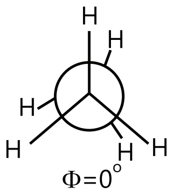

Eclipsed conformation

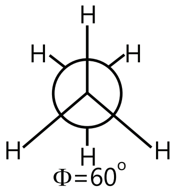

Staggered conformation

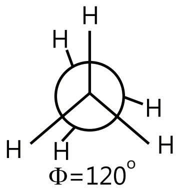
Note: In Newman projection of ethane both carbon atoms represented by circle but one behind the other so that only the front carbon is seen the C–H bond of the front carbon are depicted from the centre of the circle while C–H bonds of back carbon are drawn from the circumference of circle as

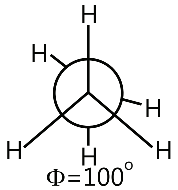


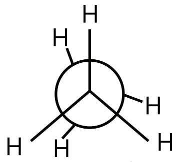
Conformation of ethane:


$\Phi=0^{o}$
(I)

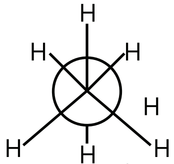

$\Phi=60^{o}$
(II)


$\Phi=120^{o}$
(III)

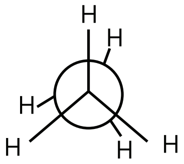

$\Phi=100^{o}$
(IV)



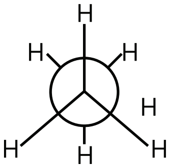
$\Phi=240^{\circ}$
(V)



$\Phi=300^{\circ}$
(VI)



Eclipsed conformation



Staggered conformation

(i) Ethane molecule contains an infinite number of conformers.

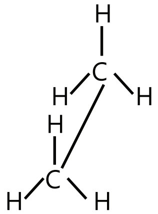
(ii) The extreme conformation of ethane molecules are staggered and eclipsed.

(iii) The energy of staggered conformation is lower than eclipsed conformation by 2.8kcal/mole(11.7kJ/mole).

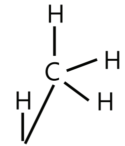
(iv) Staggered conformation is more stable than the eclipsed conformation.

(v) The mixture contains 99% staggered conformation and 1% eclipsed conformation.

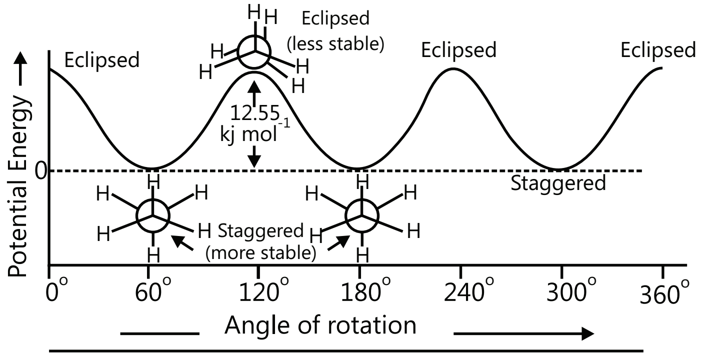
(vi) Eclipsed and staggered conformations are not isolated from the mixture.



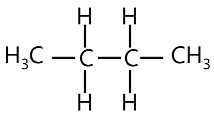
Eclipsed Sawhorse projection



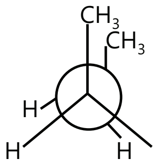
Staggered Sawhorse projection



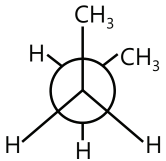
Conformation of Butane:



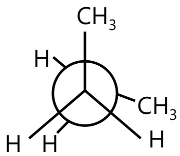
$$H_3C-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-CH_3$$



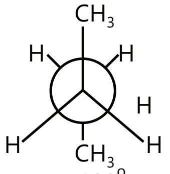
$\Phi=0^{\circ}$
(I)



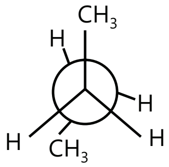
$\Phi=60^{\circ}$
(II)



$\Phi=120^{\circ}$
(III)



$\Phi=180^{\circ}$
(VI)



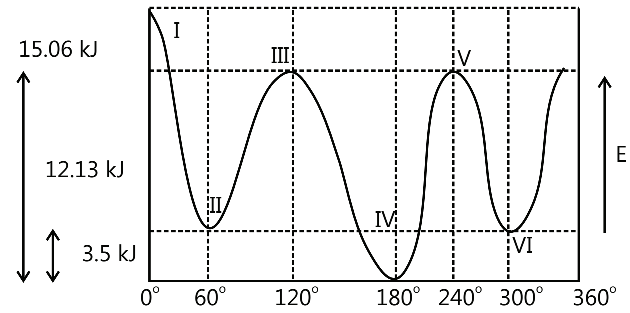
$\Phi=240^{\circ}$
(V)

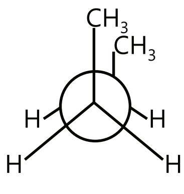
(I) = Fully eclipsed (CH, group eclipsed by CH, group)

(II) = (IV) = Gauche (Staggered)

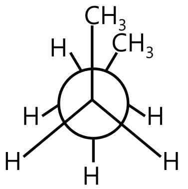
(IV) = Anti or trans (Staggered)

(V) = (V) = Partial eclipsed (CH, group eclipsed by H)

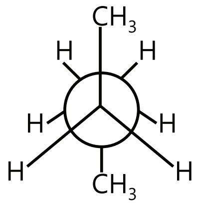




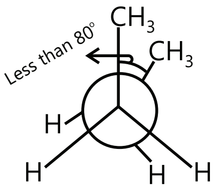
Eclipsed
(A)



Gauche
(B)



Staggered (anti)
(C)



Staggered (anti)
(D)

If the dihedral angle is less than 60, it is known as skew. Here stability of (C)>(B)>(D)>(A).

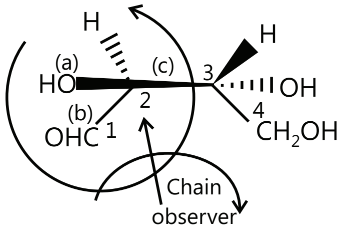
Partial eclipsed stability > Fully eclipsed stability.

PLANCESS CONCEPTS

- Two important factors that determine the stability of the conformers are– Torsional strain and Van der Waals strain.
- Generally, anti– conformation is the most stable conformation but if intramolecular hydrogen bonding is possible than in some cases the gauche form becomes the most stable.

Rohit Kumar (JEE 2012, AIR 79)

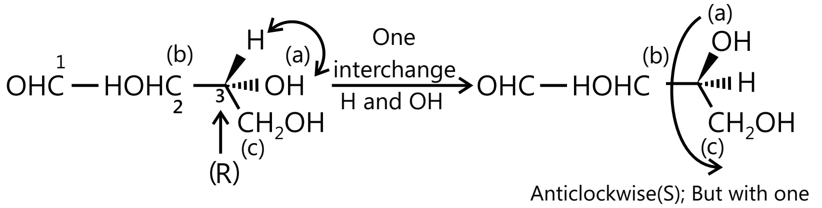
Illustration 18: Assign R and S configuration of the following compound.



Sol: Priority order at C–2: $\underset{a}{\underset{\downarrow}{-OH}} > \underset{b}{\underset{\downarrow}{CHO}} > \underset{c}{\underset{\downarrow}{-CH(OH)CH_2OH}} > \underset{d}{\underset{\downarrow}{-H}}$

First assign R/S at C–2, here, the lowest ligand is in the plane (i.e. on the dotted line). Priority sequence is anticlockwise, hence the configuration at C–2 is S.

Priority order at C – 3: –OH > –CHOHCHO. Here, H is not on the dotted line, so make one interchange of H and –OH so that –OH is projected away from the observer.



Anticlockwise(S); But with one interchange, the configuration changes from (S) to (R)

Illustration 19: Give the effect of the configuration of (S)–2–bromo butane on performing the following operations:

a. Exchanging ligands across the horizontal bond.

b. Exchanging ligands across the vertical bond.

c. Making both switches (A) and (B).

d. Exchanging a horizontal and vertical ligand.

e. A 180° vertical or horizontal rotation outside the plane of paper.

f. A 90° rotation on the plane of paper. **(JEE ADVANCED)**

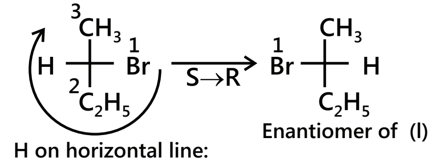
Sol: a. Priority order $-Br > -C_2H_5 > -CH_3 > -H$.

c. Thus, there is no change in the configuration when both switches (A) and (B) are made.

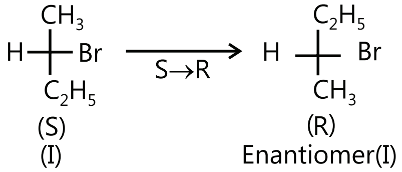
e. This type of operation is not allowed in Fischer projection because any flipping out of the plane of paper (side to side or top to bottom) would change the ligands formerly projecting behind the plane of paper to projecting towards the observer.

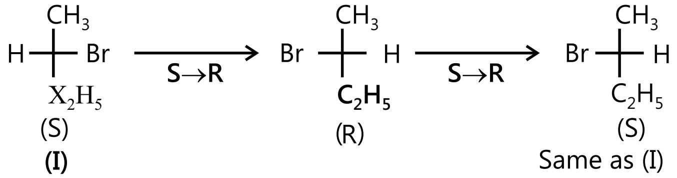
f. Those ligands formerly pointing towards the observer would change to behind the paper.

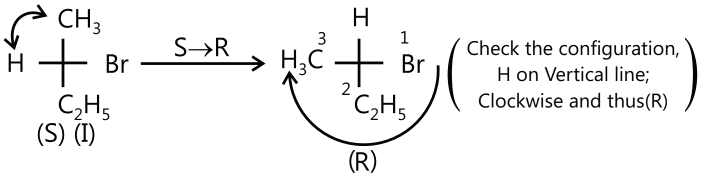
Priority order : $— Br > — C_2H_5 > — CH_3 > — H$.



H on horizontal line: Clockwise (R); Change (R) to (S); (S)-2-Bromobutane (I)





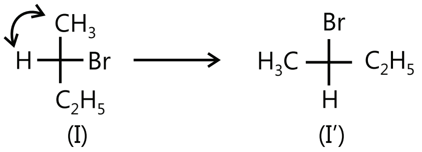


(Check the configuration, H on Vertical line; Clockwise and thus(R))

e. This type of operation is also not allowed in Fischer projection because any flipping out of the plane of paper (side to side or top to bottom) would change the ligands formerly projecting behind the plane of paper to projecting towards the observer.

Those ligands formerly pointing of paper to projecting towards the observer would change to behind the paper.

f. This type of operation is also not allowed in Fischer projection. F



POINTS TO REMEMBER

- **Chain Isomerism:** Chain isomers possess same but different number of carbon chains (straight or branched).
- **Position Isomerism:** Compounds having same molecular formula but the position of functional group, multiple bond or branches along the same chain length of carbon atoms varies.
- **Functional Group Isomerism:** These isomers have same molecular formula but different Functional groups. Such compounds are called functional group isomers.
- **Metamerism:** This type of Isomerism is due to different position of poly valency functional group in molecule Members belong to the same homologous series.
- **Ring chain Isomerism:** Such isomerism arises due to difference of carbon–chain or ring.
- **Cis–Trans Isomers:** The isomer (I) in which similar groups or atoms lie on the same side of the double bond is called cis–isomer, whereas the isomer (II) in which the similar atoms or groups lie on the opposite side of the double bond is called the trans–isomer.
- **E–Z Isomerism: E–Form:** When two same priority group present on the opposite side of double bonded is known Z–form and when same priority group present same side of double bond is called Z–form.
- **Racemic Forms and Enantiomeric Excess:**

$$\%\ \text{Enantiomeric excess} = \frac{\text{Moles of one enantiomer} - \text{Moles of other enantiomer}}{\text{Total moles of both enantiomers}} \times 100$$

$$\%\ \text{Enantiomeric excess}^{*} = \frac{\text{Observed specific rotation}}{\text{Specific rotation of the pure enantiomer}} \times 100$$

$$\text{Specific Rotation, } [\alpha]_D = \frac{\theta}{I \times C}$$

- **Optical activity in Allenes:** The planes of π–bonds of allenes are perpendicular to each other. This geometry of π–bonds causes the groups attached to the end C atoms to lie in perpendicular planes. The allenes with different substituents on the end C atoms are chiral.
- **Optical Activity of Biphenyl Compounds:** When at least three of the 2,2′,6, and 6′ positions are occupied by sufficiently large groups, free rotation about the single bond joining the two phenyl groups is no longer possible, provided each ring has no vertical plane of symmetry.

  This restricted rotation gives rise to optical activity due to the molecule being asymmetrical as a whole.

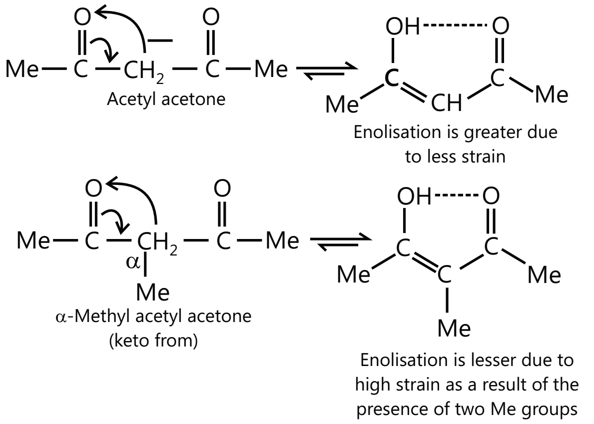
  If the substituent groups are large enough, only two groups in the o and o′–positions will cause restricted rotation.

Solved Examples

JEE Main/Boards

Example 1: Explain why α –methyl acetone enolises to a smaller extent than acetylacetone.

Sol:



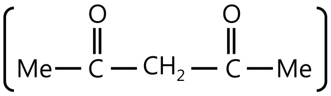
Acetyl acetone

Enolisation is greater due to less strain

α-Methyl acetyl acetone (keto from)

Enolisation is lesser due to high strain as a result of the presence of two Me groups

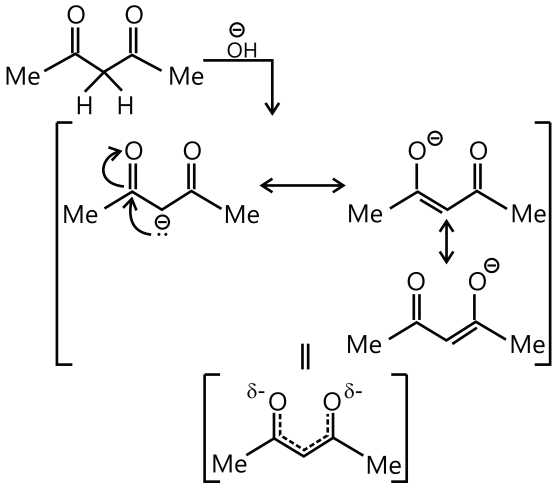
Example 2: Why is the $(-CH_2-)$ group in acetyl acetone called active methylene group?



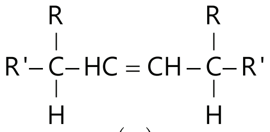
$$\left(Me-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Me\right)$$

Sol: The $(-CH_2-)$ group is acidic in nature because these H atoms can be easily lost as $H^{\ominus}$ with base, as the resulting carbanion is resonance stabilized.

The $(-CH_2-)$ group is acidic in nature because these H atoms can be easily lost as $H^{\ominus}$ with base, as the resulting carbanion is resonance stabilised.



Example 3: Consider the compound (A) given as:



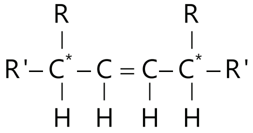
$$R'-\underset{H}{\overset{R}{C}}-HC=CH-\underset{H}{\overset{R}{C}}-R'$$

(A)

a. Give the total number of stereoisomers possible for (A).

b. If the stereochemistry about the double bond in (A) is cis, give the number of enantiomers possible for (A).

Sol: The compound (A) contains two asymmetric C atoms with the same terminal group.



$$R'-\underset{H}{\overset{R}{C^*}}-\underset{H}{C}=\underset{H}{C}-\underset{H}{\overset{R}{C^*}}-R'$$

Number of optically active isomers (O.I.A.) = $2^{n-1} = 2^{2-1} = 2$ (where, n is the number of asymmetric C atoms).

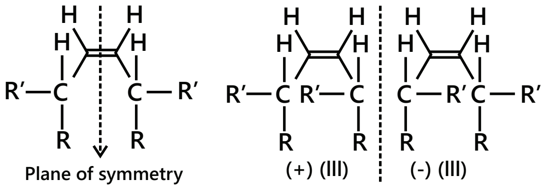
Number of meso form = $2^{(n-2)/2} = 2^0 = 1$

Total optical isomers = 2+1=3

Due to one double bond, the number of geometrical isomers = 2

Total number of stereoisomers = 3 × 2 = 6

If the stereochemistry about (C=C) bond is cis, Then two pairs of diastereomers (II) and (III) are possible. (II) is meso (O.I.A.) due to the presence of plane of symmetry. (III) is optically active (O.A) and two enantiomers are possible. Therefore, in total there are three diastereomers.



Plane of symmetry (meso) (O.I.O.) (II)

(+) (III) (-) (III)

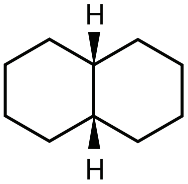
(III) (±) or racemate

II and (+) III, II and (–)III are diastereomers, whereas (+) III and (–) III are enantiomers.

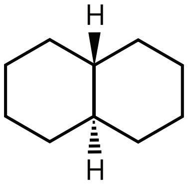
Example 4: How many geometrical isomers are possible for the following?

a. Decalin b. 1–Methyldecalin c. 9–Methyldecalin

Sol: a. Two geometrical isomers: cis and trans

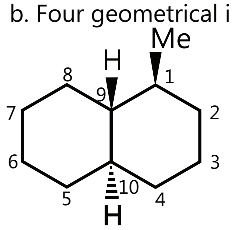


cis
(I)

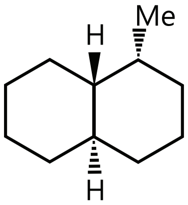


trans
(I)

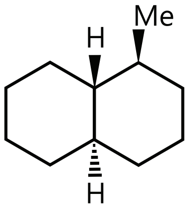
b. Four geometrical isomers



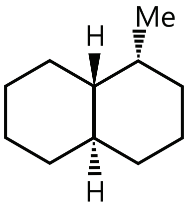
cis-1-Methyl-
cis-decalin
(I)



trans-1-Methyl-
cis-decalin
(II)

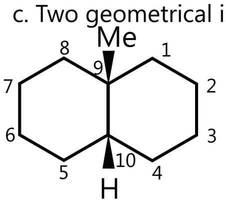


cis-1-Methyl-
trans-decalin
(III)

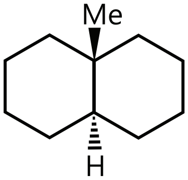


trans-1-Methyl-
trans-decalin
(IV)

c. Two geometrical isomers



cis-9-Methyl decalin
(I)



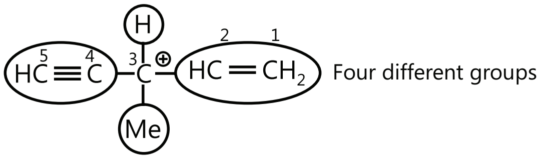
trans-9-Methyl decalin
(II)

Example 5: Give the structural formula of an unsaturated hydrocarbon with the lowest number of C atoms (or with lowest molecular mass) which shows:

a. Optical isomers b. Geometrical isomers

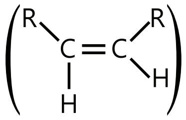
c. Both optical and geometrical isomers

Sol: a. An unsaturated hydrocarbon with the lowest molecular mass should have one $(C\equiv C)$, one $(C=C)$, one H atom, and finally one Me group.

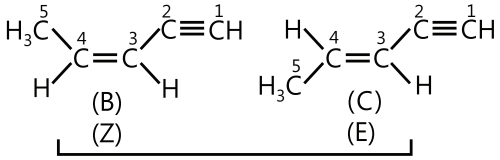


(3-Methyl pent-1-ene)
(A)

b. Geometrical isomerism is shown by the $(C\equiv C)$ only and not by $(C\equiv C)$, so we have an alkene of the type

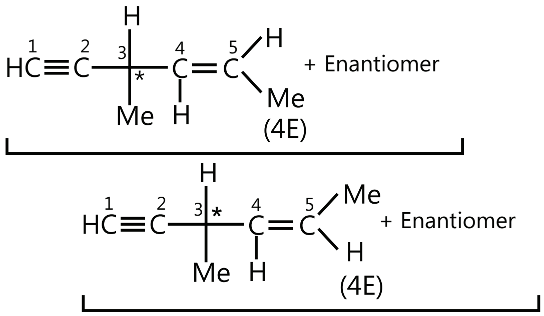


In this, one R group should have $(C\equiv C)$ and the other R should be a Me group so that the lowest number of C atoms is obtained.



Pent-3-en-1-yne

c. In compound (A) given in the solution to part (A), put one Me group at C–1 so that it can show both geometrical and optical isomerisms.



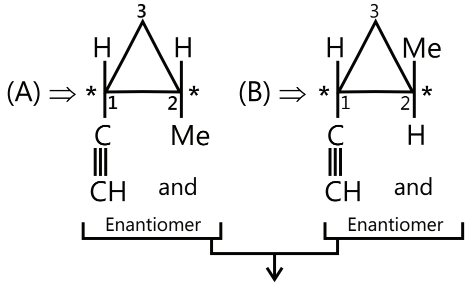
(4E and 4Z-3-Methyl hex-4-en-1-yne)

Example 6: Give the structural formula of a cyclic alkyne with the lowest number of C atoms and showing:

a. Both geometrical and optical isomerisms.

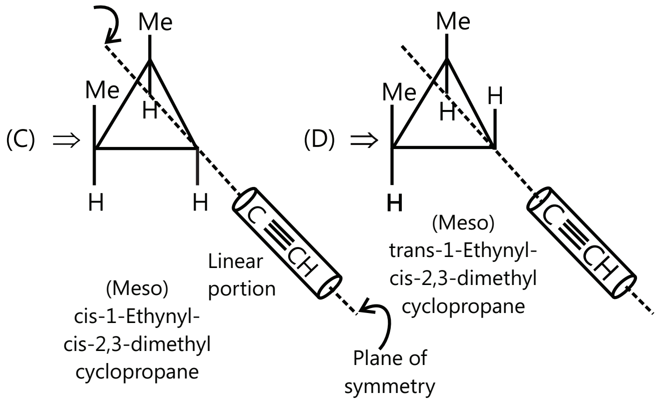
b. Geometrical isomerism with two meso stereo–isomers.

Sol: a. For the lowest number of C atoms, take disubstituted cyclopropane ring in which one group is (HC≡C)(ethynyl) and the other is (–Me) group.



1-Ethynyl-2-methyl cyclopropane

b. For the lowest number of C atoms, take the trisubstituted cyclopropane ring with one (HC≡C) ethyne group and two (–Me) groups, so that meso compound can be obtained to have the plane of symmetry in the molecule.

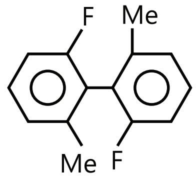


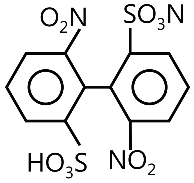
(Meso) cis-1-Ethynyl-cis-2,3-dimethyl cyclopropane

(Meso) trans-1-Ethynyl-cis-2,3-dimethyl cyclopropane

Example 7: 2, 2′–Difluoro–6,6′–dimethylbiphenyl is non–resolvable, whereas 2, 2′–dinitro–6, 6′–disulphonic acid biphenyl is resolvable. Account for this fact.

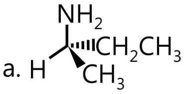
Sol: Presence of bulky group at ortho position causes ortho repulsion and due to this two ring becomes non planar and thus becomes resolvable.

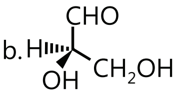


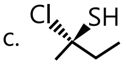


Steric crowding is not large enough to prevent free rotation about (C–C) single bond, so the energy of separation between various invertomers is low and consequently non–isoable. Due to the bulky group at ortho positions, free rotation is restricted as the two rings become nearly perpendicular and hence the energy of separation between the isomers is highly and consequently isolable.

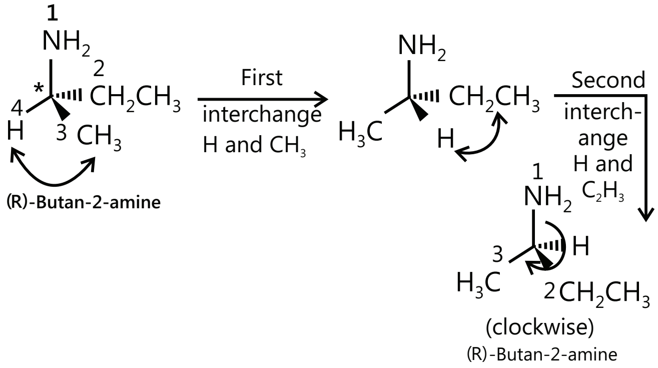
Example 8: Assign the R and S designations to the following compounds:







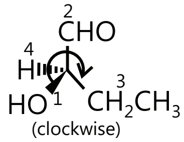
Sol: (A) The lowest priority ligand (H) is in the plane (i.e., not on the dotted line) so it makes two interchanges such that H is projected away from the observer.



Priority order:–NH_2>–CH_2CH_3>–CH_3>–H

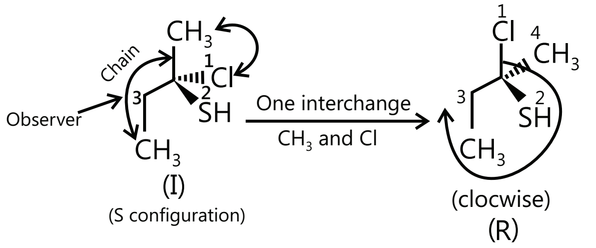
(B) The lowest priority ligand (H) is on the dotted line. R and S can be assigned directly from the priority rule.

(–OH>–CHO>–CH_2OH>–H).



(R)

(C) Lowest priority ligand (–CH_3) is in the plane (i.e., not on the dotted line). So make one interchange so that (–CH_3) is projected away from the observer. (Priority order. –Cl>–SH>–CH_2CH_3>–CH_3



(I)

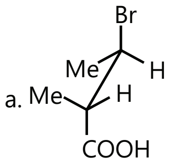
(S configuration)

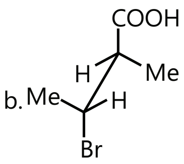
(clocwise)

(R)

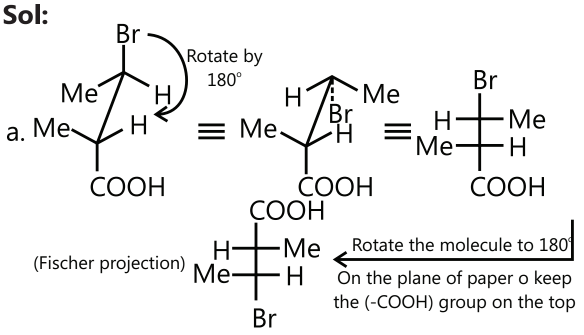
But with one interchange, the configuration changes from R to S.

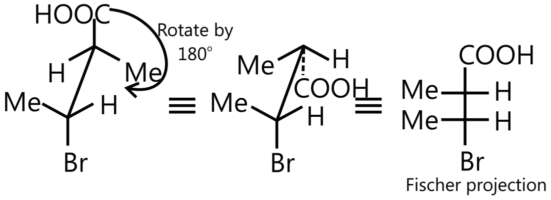
Example 9: Convert Sawhorse formula to Fischer formula.



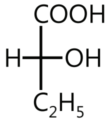


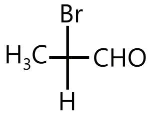
Sol:

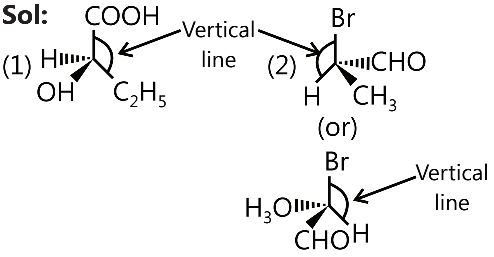


b.


Example 10: Convert Fischer formula to Wedge formula.

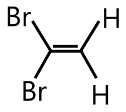
(1)


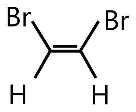
(2)


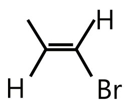
Sol:


JEE Advanced

Example 1: Give the decreasing order of net dipole moments of the following:

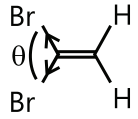
(I)


(II)


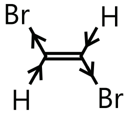
(III)


Sol: Dipole moment is inversely proportional to angle of separation. Thus smaller angle of separation will cause large dipole moment whereas large angle of separation causes less dipole moment. I>II>III

I. (I) has a smaller angle of separation between two Br atoms than in (II) and (III), resulting in more net dipole moment (μ).



II. (II) has a large angle of separation between two Br atoms; therefore, net (μ) is less than (I).



III. In (III), two Br atoms and two H atoms have equal and opposite bond moments; therefore, the net μ is zero.

Example 2: Write down the number of asymmetric carbon atoms in each optically active compound and report the number of isomers.

i. $CH_3(CHOH)_2COOH$ ii. $COOH(CHOH)_2COOH$

Sol: Since n is even in both the case,

Number of O.I.A = 2^n

Number of meso forms=$2^{(n-2)/2}$

Number of (O.I.A) racemic form=n/2

Total optical isomers=$2^{n-1} + 2^{(n-2)/2}$

i. Number of asymmetric C atoms = 2

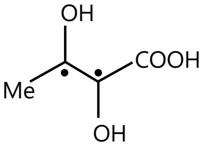
Different terminal groups : (–COOH) and (Me)

Number of O.I.A = $2^n=2^2=4$

Number of meso forms =0

Number of (O.I.A) racemic form = $\frac{4}{2}=2$

(racemate mixture)

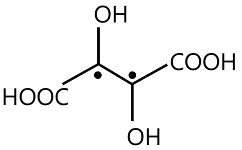


∴ Total optical isomers = 4

Optically inactive forms = 2.

ii. Number of asymmetric C atoms = 2.

Same terminal groups: (–COOH)



Number of O.I.A = $2^{n-1}=2^{2-t}=2$

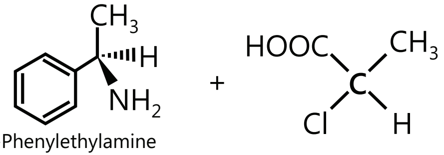
Number of meso forms = $2^{(n-2)/2}=2^{\circ}=1$

Number of (O.I.A) racemic form = $\frac{2}{2}=1$

Total optical isomers = 2+1=3

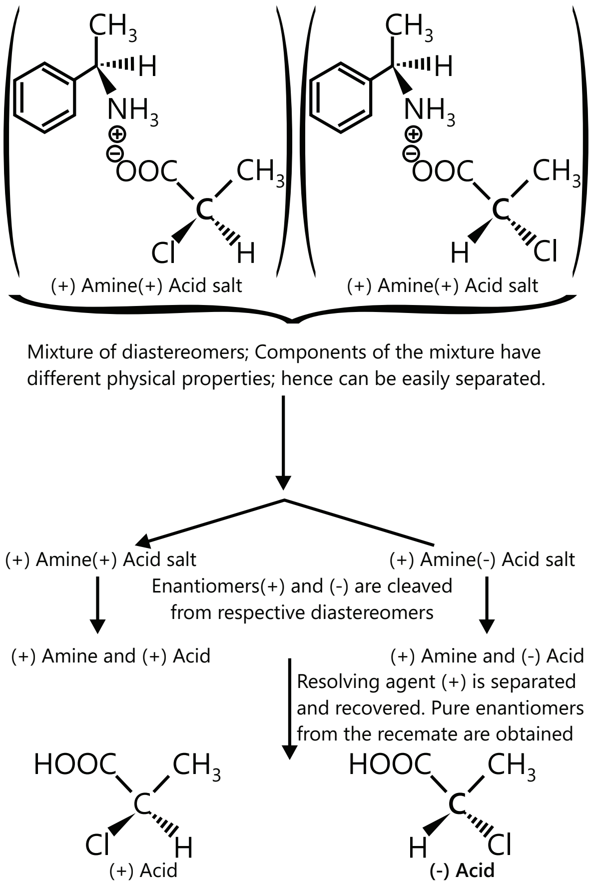
Example 3: Resolute the compounds from enantiometric mixture

Sol: First convert the pair of enantiomers into diastereomers by using proper resolving agent. The two diastereomers have different physical properties like solubility. By using a proper solvent two diastereomers can be separated and they are converted back into enantiomer.



(+)-1-Phenylethylamine
(an optically pure reagent;
a resolving agent; it is reacted
with the racemic mixture)

(+)-2-Chloropropanoic acid
(racemic mixture)



Example 4: An aqueous solution containing 10gm of optically pure fructose was diluted to 500 mL with water and placed in a polarimeter tube 20 cm long. The measured rotation was –5.0°. To this solution 500 mL of a solution containing 10 gm of racemic fructose is added. What will be the change in specific rotation?

Sol: Using the following equation, first calculate the specific rotation.

$$[\alpha]_D = \frac{\theta}{I \times C}$$

As we know, 20 cm = 2 dm.

$$[\alpha]_D = \frac{\theta}{I \times C} = \frac{-5.0^\circ}{2\text{dm} \times 10\text{gm}/500\text{ml}} = -125^\circ$$

Total volume of solution = 500+500=1000mL

Mass per mL of pure fructose = 10/1000 = 0.01 gm/mL^{-1}

Mass per mL of mixture = (10+10 = 2) = 20/1000

= 0.02 gm/mL^{-1}

OP (optical purity)

$$= \frac{[\alpha]_{obs.} \text{ of mixture}}{[\alpha]_D \text{ of pure form}} \alpha \frac{\text{Mass per ml of pure form}}{\text{Mass per ml of mixture}}$$

$$= \frac{0.01}{0.02} = 0.5\ (\because\ \text{l is constant})$$

New $[\alpha]_D = -125^\circ \times 0.5 = -62.5^\circ$

Change in specific rotation = 62.5–(–125)=+ 62.5°

Example 5: What is the optical purity of a sample having an $[\alpha]_{obs.} = +9.0$ if $[\alpha]_D = +12^\circ$

Sol Optical purity (OP) of sample = $\frac{+9^\circ}{+12^\circ} \times 100 = 75\%$

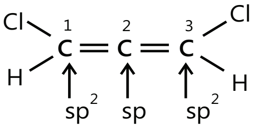
The mixture has 75% (+) and 25% racemic mixture [i.e.; 12.5%(+) and 12.5%(–) form.

Total percentage of (+) form= 75 % + $\frac{25\%}{2}$ =87.5%

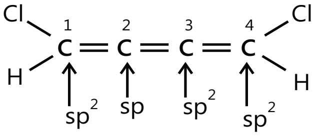
Total percentage of (–) form = 12.5%

Example 6: How many optically active and inactive isomers of 1, 2, 3 trimethylcyclohexane are possible?

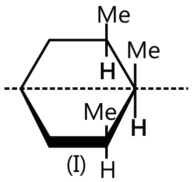
Sol:



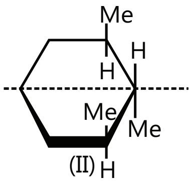
(C² is in different plane with C¹ and C³)
Optically active
and μ ≠ 0



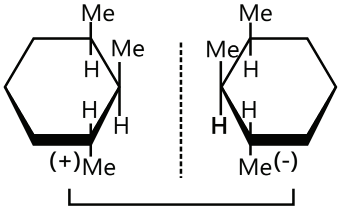
(All are in same plane)
optically inactive
and μ ≠ 0



(I)
(Meso)
(Plane of symmetry)

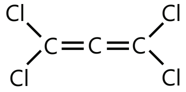


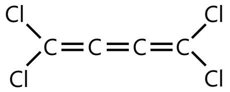
(II)
(Meso)
(Plane of symmetry)



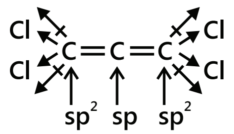
O.I.A.
(III) (IV)

Example 7: Which of the following will show dipole moment (μ)?

I.


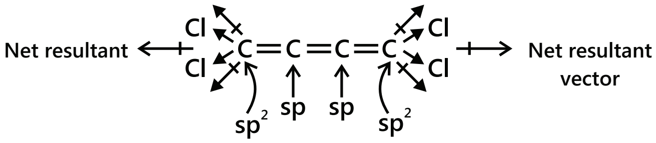
II.


Sol: (i) Will show dipole moment (μ). The terminal C atoms are not in plane with middle C atom.



So they have net resultant dipole moment.

(ii) Has zero dipole moment. All the C atoms are in one plane, so the net resultant bond moment is cancelled.



As a general rule, an even number of cumulative double bonds with all the same four groups will show a dipole moment and an odd number of cumulative double bonds with all the same four groups will not show dipole moment.

Similarly, an even number of cumulative double bonds with two different groups on terminal C atoms will be optically active and an odd number of cumulative double bonds with two different groups on terminal C atoms will be optically inactive.

Example 8: Give the effect of the configuration of (S)–2–bromo butane on performing the following operations:

(a) Exchanging ligands across the horizontal bond.

(b) Exchanging ligands across the vertical bond.

(c) Making both switches (A) and (B).

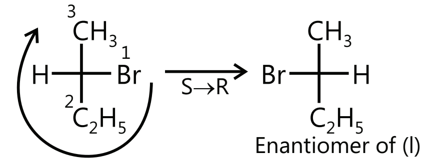
(d) Exchanging a horizontal and vertical ligand.

(e) A 180° vertical or horizontal rotation outside the plane of paper.

(f) A 90° rotation on the plane of paper.

Sol:

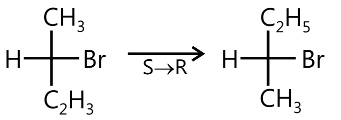
a.



Enantiomer of (I)

H on horizontal line:
Clockwise (R) ;
Change (R) to (S);
(S)-2-Bromobutane(I)

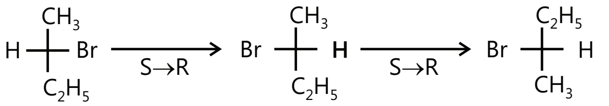
b.



(S)
(I)

(R)
Enantiomer of (I)

c.



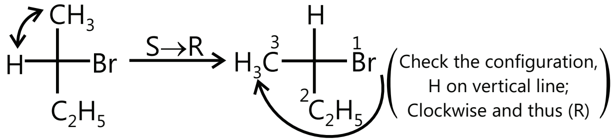
(S)
(I)

(R)

(S)
Same as (I)

Thus, there is no change in the configuration when both switches (A) and (B) are made.

d.

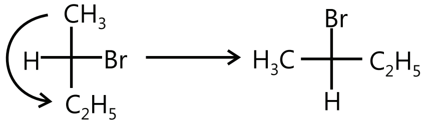


(S) (I)

(R)

e. This type of operation is not allowed in Fischer projection because any flipping out of the plane of paper (side to side or top to bottom) would change the ligands formerly projecting behind the plane of paper to projecting towards the observer. Those ligands formerly pointing towards the observer would change to behind the paper.

f. This type of operation is also not allowed in Fischer projection. For example,

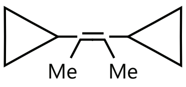


(I)

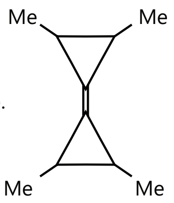
(I′)

Example 9: Some possible structures of a compound A ($C_{10}H_{16}$) are:

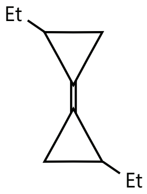
a.



b.



c.

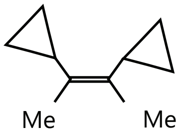


Write the possible stereoisomers of (A), (B) , and (C).

Sol: (A) Representations of geometrical isomers (diastereomers).

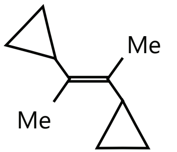
(B) Three geometrical isomers are shown; out of them one is optically active.

(C) The cis form is optically active.

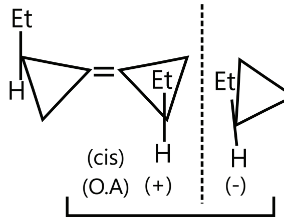


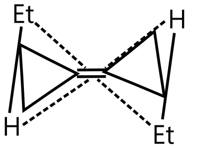
(Cis)
(I)

and

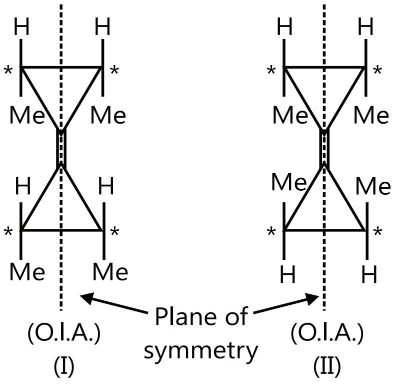


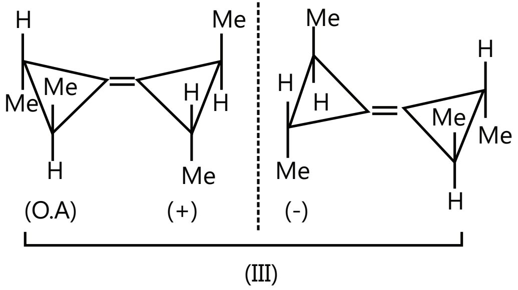
(Trans)
(II)





But the trans form is (O.I.A.) due to the presence of centre of symmetry.





Example 10: What is the observed rotation when 0.1 M solution of (R)–2 butanol is mixed with an equal volume of 0.05M solution of racemic 2– butanol and the resulting solution is taken in a cell of 5 cm long tube in a polarimeter? The specific rotation of (R)–2–butanol is +13.9°.

Sol: The racemic 2–butanol has no contribution to optical activity . So, the observed rotation will be due to (R)–2 butanol only. Racemic butanol helps in diluting after dilution is 0.05M. Molecular weight of 2– butanol is 74.

l=5 cm = 0.5 dm

$$\therefore \text{Concentration} = \frac{74 \times 0.05}{1000} = 3.7 \times 10^{-3} \text{gm ml}^{-1}$$

$$\therefore [\alpha]_{\text{obs.}} = [\alpha]_{\text{pure}} \times l \times c = 13.9 \times 0.5 \times 3.7 \times 10^{-3} = 0.26^{\circ}$$

JEE Main/Boards

Exercise 1

Q.1 0.90 gm of an organic compound $C_4H_{10}O_2$(A) when treated with sodium gives 224 mL of hydrogen at NTP. Compound (A) can be separated into fractions (B) and (C) , by crystallisation of which the fraction (B) is resolved into optical isomers (D) and (E). Write down the structural formula of (A) to (E) with proper reasoning.

Q.2 Write down the structures of close homologues of heptane having one quaternary C atom in their molecule and the other having two tertiary carbon atoms.

Q.3 An alkaline (A)C_5H_{12} on chlorination at 300°C gives a mixture of four different monochlorinated derivatives, (B), (C), (D), and (E). Two of these derivatives give the same stable alkene (F) on dehydrohalogenation. On oxidation with hot alkaline $KMnO_4$ followed by acidification, (F) gives two products (G) and (H). Give the structures of (A) to (H) with porper reasoning.

Q.4 Which alkane, having a molecular weight of 86, will form only two monobromo alkanes?

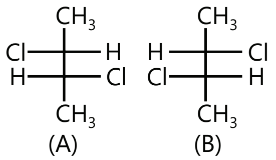
Q.5 A hydrocarbon (A) was found to have vapour density 36. It forms only a single monochloro substitution product. Suggest (A).

Q.6 Which of the following will not be able to show optical isomerism (enantiomerism)?

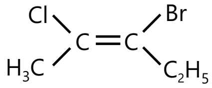
(A) 1,2–Propadiene (B) 2,3–Pentadiene

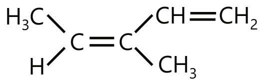
(C) Sec–Butyl alcohol (D) All exhibit enantiomerism

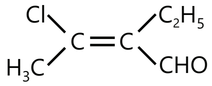
Q.7 If optical rotation produced by the compound (A) is +52°, the one produced by compound (B) is:

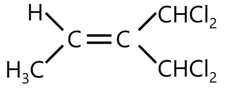


Q.8 The E–isomer among the following is:

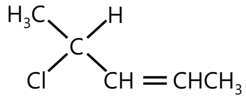
(A)


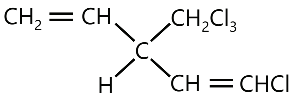
(C)


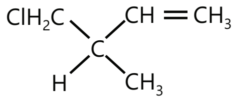
(B)


(D)


Q.9 Which of the following will not show geometrical isomerism?

(A)


(C)


(B)


(D) $CH_3CH=CHCH_2\,CH_3$

Q.10 The dihedral angle between the hydrogen atoms of two methyl groups in staggered conformation of ethane is:

(A) 120° (B) 180° (C) 90° (D) 60°

Q.11 Which of the following objects is chiral?

(A) Nail (B) Blade

(C) Tennis racket (D) Laced football

Q.12 Predict the number of stereoisomers for 2,5–heptadiene.

(A) 4 (B) 3 (C) 2 (D) 5

Q.13 Symbol D stands for:

(A) Dextrorotatory, which rotates P.P.L. towards right.

(B) Dextrorotary , which rotates P.P.L. towards left.

(C) Relative configuration with respect to lactic acid taken as standard.

(D) Relative configuration with respect to glyceraldehyde taken as standard and (OH) group is on the right side.

Q.14 Which of the following compounds will not show geometrical isomerism?

(A) 3–Phenyl–2–propenoic acid

(B) 2–Butene

(C) 3–Methyl–2–butenoic acid

(D) 3–Methyl–2–penteoic acid

Q.15 The enolic form of acetone contains:

(A) 9σ–bonds, 1π–bond, and 2 lone pairs

(B) 8σ–bonds, 2π–bond, and 2 lone pairs

(C) 10σ–bonds, 2π–bond, and 1 lone pairs

(D) 9σ–bonds, 2π–bond, and 2 lone pairs

Q.16 Arrange the following in the increasing order of expected enol content.

i. CH_3COCH_2CHO ii. CH_3COCH_3

iii. CH_3CHO iv. $CH_3COCH_2COCH_3$

(A) iii<i<ii<iv (B) iii<ii<i<iv

(C) i<iv<ii<iii (D) iv<i<ii<iii

Q.17 Hydrocarbon with formula C_8H_{18} gives one chloro derivative. The hydrocarbon can be:

(A) n–octane

(B) 2–methylheptane

(C) 2,2,4–trimethylpentane

(D) 2,2,3,3–tetramethylbutane

Q.18 The minimum number of carbon atoms an alkane should contain in order to exhibit optical activity is:

(A) 5 (B) 6 (C) 7 (D) 8

Q.19 A compound whose molecule is superimposable on its mirror image despite containing chiral carbon atoms is called:

(A) Threo isomer (B) Meso compound

(C) Enantiomer (D) No special name

Q.20 The IUPAC name of the compound with formula C_nH_{2n+2}, having the lowest possible molecular mass and capable of showing enantiomerism is:

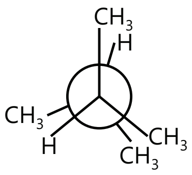
(A) 3–Methyl hexane (B) 2,3–Dimethyl pentane

(C) Methane (D) Both (A) and (B)

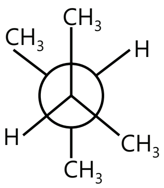
Exercise 2

Single Correct Choice Type

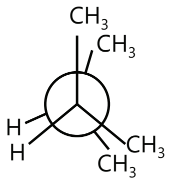
Q.1 In which of the following has minimum torsional strain and minimum Vander waal strain.



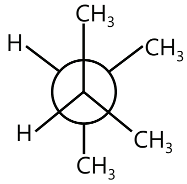
I



II



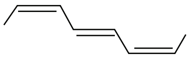
III



IV

(A) I (B) II (C) III (D) IV

Q.2 The IUPAC name of the compound:



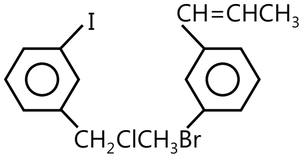
(A) (2E,4E,6Z)–octa–2,4,6–triene

(B) (2E,4E,6E)–octa–2,4,6–triene

(C) (2Z,4E,6Z)–octa–2,4,6–triene

(D) (2Z,4Z,6Z)–octa–2,4,6–triene

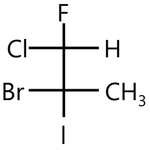
Q.3 How many spatial orientations are possible in the following compound?



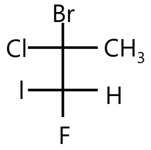
(A) 2 (B) 4 (C) 6 (D) 8

Q.4 How are compounds I and II are related?

(I)



(II)

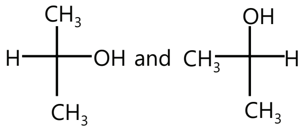


(A) Enantiomers (B) Diastereomers

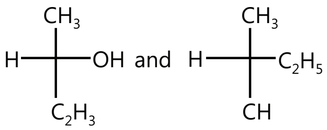
(C) Constitutional (D) Identical

Q.5 The non identical species are:

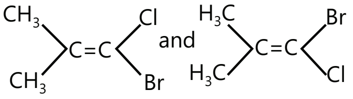
(A)



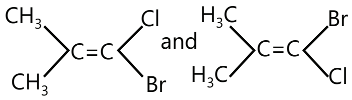
(B)



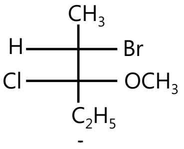
(C)

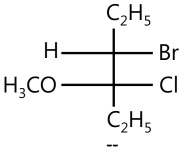


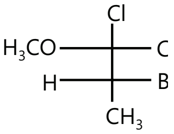
(C)



Q.6 Which statement is correct about the following structures







(A) I and II are structural isomers

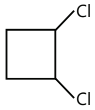
(B) I and II, I and III are enantiomers

(C) I, III are enantiomers and I, II are structural isomers

(D) I, II and III are stereoisomers.

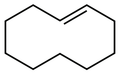
Q.7 Which will form geometrical isomers?

(A)



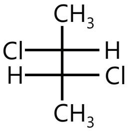
(B) $CH_3CH{=}NOH$

(C)

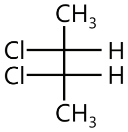


(D) All of these

Q.8 If optical rotation produced by (A) is +36° then optical rotation produced by (B) will be ?



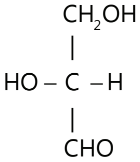
(A)



(B)

(A) +36° (B) 0° (C) +26° (D) Unpredictable

Q.9 What is the configuration of the given molecule?

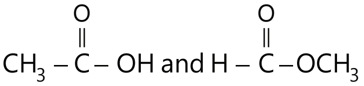


$$\begin{array}{c} CH_2OH \\ | \\ HO-C-H \\ | \\ CHO \end{array}$$

(A) D (B) L (C) d (D) 1

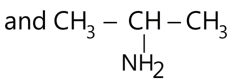
Q.10 Which of the following is/are correct matchings?

(A)



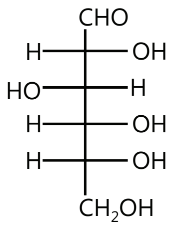
$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH \text{ and } H-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 \rightarrow \text{Metamers}$$

(B) $CH_3-CH_2-C\equiv CH$ and $\rightarrow$ Position isomers
$CH_3-C\equiv C-CH_3$

(C) $CH_3CH_2CH_2NH_2$ and 
$CH_3-\underset{NH_2}{\underset{|}{CH}}-CH_3$ → Tautomers

(D) Anisole ando-cresol → Metamers

Q.11 The correct IUPAC name of D–Glucose is:



(D-Glucose)

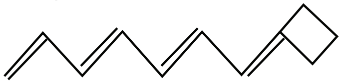
(A) (2D,3D,4L,5D) 2,3,4,5,6– penthahydroxyhexanal.

(B) D–2,3,4,5,6–pentahydroxyhexanal

(C) 6–oxo–(2D,3L,4D,5D)–2,3,4,5,6–pentahydroxyhexane.

(D) (2D,3L,4D,5D)–2,3,4,5,6–pentahydroxyhexanal.

Q.12 Total number of geometrical isomer of following compound.



(A) 2 (B) 4 (C) 8 (D) 16

Previous Years' Questions

Q.1 How many optically active stereoisomers are possible for butane–2,3–diol? ***(1997)***

(A) 1 (B) 2 (C) 3 (D) 4

Q.2 The optically active tartaric acid is named as D–(+)–tartaric acid because it has a positive ***(1999)***

(A) Optical rotation and is derived from D–glucose

(B) pH in organic solvent

(C) Optical rotation and is derived from D–(+)–glyceraldehydes

(D) Optical rotation when substituted by deuterium

Q.3 Which of the following compounds will exhibit geometrical isomerism? ***(2000)***

(A) 1–phenyl–2–butene (B) 3–phenyl–1–butene

(C) 2–phenyl–1–butene (D) 1,1–diphenyl–1–propene

Q.4 The number of isomers for the compound with molecular formula $C_2BrClFI$ is ***(2001)***

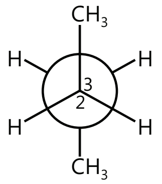
(A) 3 (B) 4 (C) 5 (D) 6

Q.5 Which of the following compounds exhibits, stereoisomerism? ***(2002)***

(A) 2–methylbutene–1 (B) 3–methylbutyne–1

(C) 3–methylbutanoic acid (D) 2–methylbutanoic acid

Q.6 C2 is rotated anti –clockwise 120^o about C2–C3 bond. The resulting conformer is ***(200)***



(A) Partially eclipsed

(B) Eclipsed

(C) Gauche

(D) Staggered

Q.7 The number of stereoisomers obtained by bromination of trans–2–butene is ***(2007)***

(A) 1 (B) 2 (C) 3 (D) 4

Q.8 Read the following questions and answer as per the direction given below: ***(2007)***

(A) Statement-I is true; statement-II is true; statement II is the correct explanation of statement-II.

(B) Statement: I is true; statement-II is true; statement-II is not the correct explanation of statement-I.

(C) Statement-I is true; statement-II is false

(D) Statement-I is false; statement-II is true

Statement-I : Molecules that are non–superimposable on their images are chiral.

Statement-II : All chiral molecules have chiral centres.

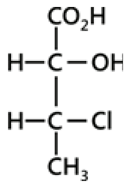
Q.9 Isomers which are .... mirror images are known as ....(superimposable, non–superimposable, enantiomers, diastereomers, epimers) ***(1988)***

Q.10 A solution of (–) 1–chloro–1–phenylethane in toluene racemises slowly in the presence of a small amount of $SbCl_5$, due to the formation of : ***(2013)***

(A) Carbanion (B) Carbene

(C) Carbocation (D) Free radical

Q.11 The absolute configuration of (figure) is ***(2016)***



(A) (2S, 3R)

(B) (2S, 3S)

(C) (2R, 3R)

(D) (2R, 3S)

JEE Advanced/Boards

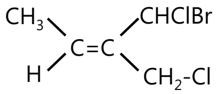
Exercise 1

Q.1 How many benzenoid isomer are possible for cresol?

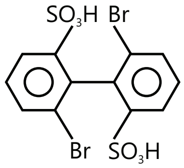
Q.2 Find out the total number of cyclic structural isomers of C_6H_{12}

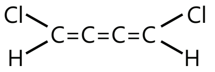
Q.3 How many pair(s) of geometrical isomers are possible with C_6H_{12} (with in open chain structures)

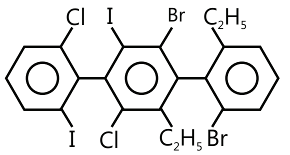
Q.4 Which of the following compounds can be optically active?

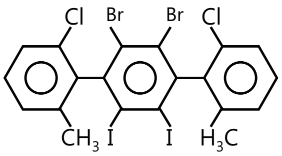
(A) 

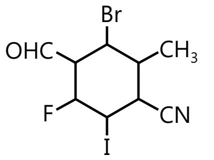
(B) $CH_3-CH=C$
$=CH-CH_3$

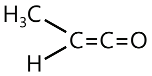
(C) 

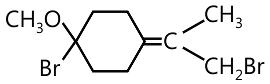
(D) 

(E) 

(F) 

(G) 

(H) 

(I) 

Q.5 Calculate the number of Benzenoid isomers possible for C_6H_3ClBrI.

Q.6 Calculate the total number of structural isomers of 3°– amines for the molecular formula $C_6H_{15}N$ are?

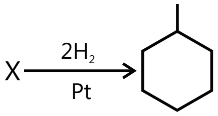
Q.7 Write the number of acyclic, optically active structural isomers having following molecular formula and write their structural formula also.

(A) C_7H_{16} (B) C_7H_{12} (C) C_7H_9Cl

(D) C_3H_4ClBr (E) $C_2H_2Cl_2F_2$

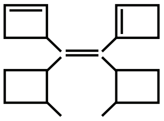
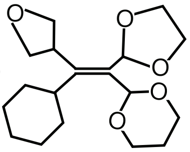
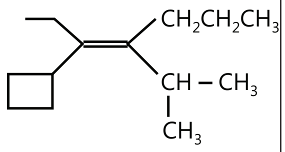
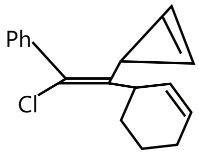
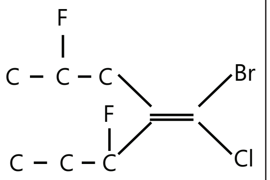
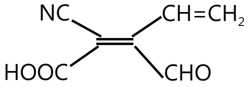
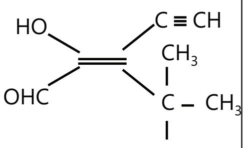
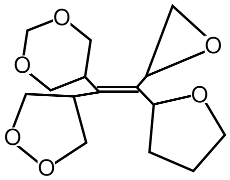
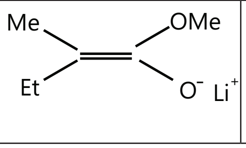
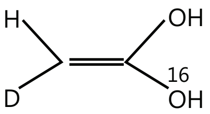
Q.8 How many cyclopentane structures (excluding stereo isomer) are possible for C_7H_{14}.

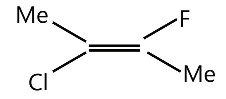
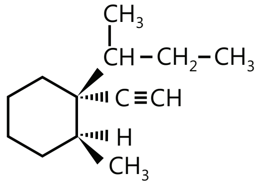
Q.9 Find out total number of structures of X.



Q.10 Calculate the total number of cyclic isomeric compounds of molecular formula C_5H_8O which can't show geometrical isomerism.

Q.11. Asssign E and Z configuration

(I) 	(II) 
(III) 	(IV) 
(V) 	(VI) 
(VII) 	(VIII) 
(IIX) 	(X) 

(XI) 	(XII) 

Q.12 Write the number of all possible acyclic compounds having molecular formula. Give their structural formula also.

(A) $C_2H_2Cl_2F_2$ (B) $C_2HClBrIF$ (C) $C_2ClBrIF$

Q.13 Mention the specific type of isomerism exhibited by each of the following pairs

(A) 1,2–dichloro ethane and 1,1–dichloro ethane

(B) Propanoic acid and methyl acetate

(C) Methyl acetate and ethyl formate

(D) o–Nitrophenol and P–nitrophenol.

(E) Anisole and o–cresol

(F) Phenol and Cyelohexa–2,4–dien–1–one.

Q.14 Draw the two chair conformers of each compound and indicate which conformer is more stable.

(A) Cis 1–ethyl–3–methylcyclohexane

(B) Trans–1–ethyl–3–isopropylcyclohexane

(C) Trans–1–ethyl–2–methylcyclohexane

(D) Trans–1–ethyl–3–methylcyclohexane

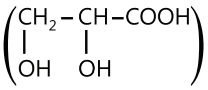
(E) Cis 1–ethyl–3– isopropylcyclohexane

(F) Cis 1–ethyl–4– isopropylcyclohexane

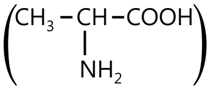
Q.15 Write stereochemical formula of the following compounds.

(A) D–2–Hexanol

(B) L–Lactic acid ($CH_3 - CHOH - COOH$)

(C) D-Glyceric acid 

$$\left(\begin{array}{c} CH_2 - CH - COOH \\ | \quad\quad | \\ OH \quad OH \end{array}\right)$$

(D) D-Alaninc 

$$\left(\begin{array}{c} CH_3 - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH \end{array}\right)$$

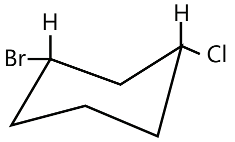
Q.16 Draw the most stable conformer of N–methylpiperidine.

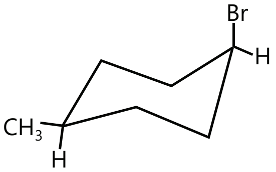
Q.17 Considering rotation about the C–3–C–4 bond of 2–methylhexane:

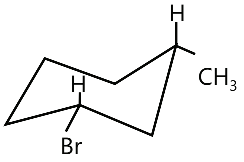
(A) Draw the Newman projection of the most stable conformer.

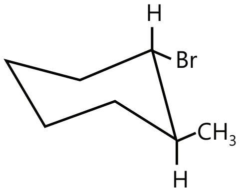
(B) Draw the Newman projection of the least stable conformer.

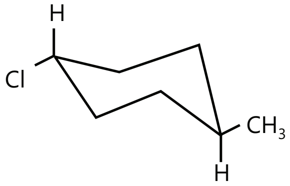
Q.18 Determine whether each of the following compounds is a cis isomer or a trans isomer.

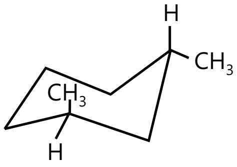
(A) 

(B) 

(C) 

(D) 

(E) 

(F) 

Q.19 Write down all the isomers of formula $C_7H_7O_2N$. What type of isomerism they show?

Q.20 Assign the priority order number to the following atoms or groups.

(A) $-CHO, -CH_2OH, -CH_3, -OH$

(B) $-Ph, -CH(Me)_2, -H, -NH_2$

(C) $-COOH, -Ph, -CHO, -CH=CH_2$

(D) $-CH(Me)_2, -CH=CH_2, -C\equiv CH_3 \ -Ph$

(E) $-CH_3, -CH_2Br, -CH_2OH, -CH_3Cl$

(F) $-H, -N(Me)_2, -Me, -OMe$

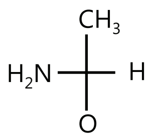
(G) $-CH=CH_2, -Me, -Ph, -Et$

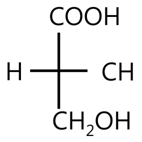
(H) $-CH-CH_2-Br, -Cl, -CH_2-CH_2$
$-CH_2-Br, (Me)_2CH-$

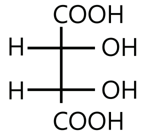
(I) $-Cl, -Br, -I, -NH_2$

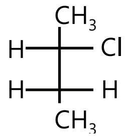
(J) $NH_2, NO_2, CH_2NH_2, C\equiv N$

Q.21 Allot R/S configurations to the following optical isomers.

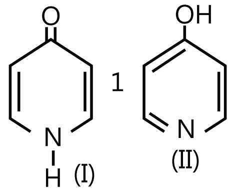
(A) 

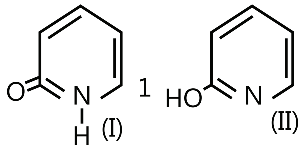
(B) 

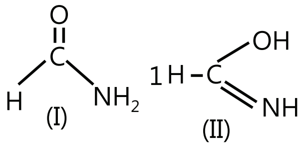
(C) 

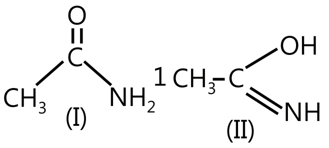
(D) 

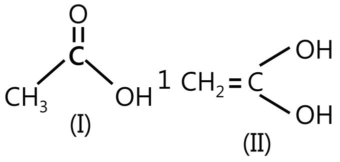
Q.22 In each of the following pairs which is more stable:

(A) 

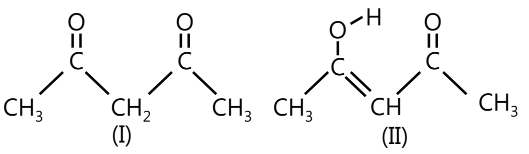
(B) 

(C) 

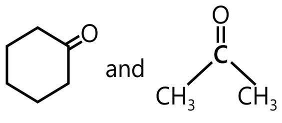
(D) 

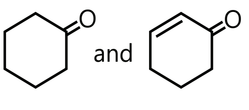
(E) 

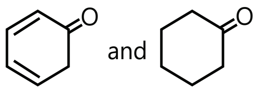
Q.23 In each of the following pairs which is more stable:

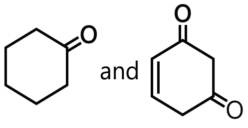
(A) 

Q.24 In each of the following pairs which will have less enol content:

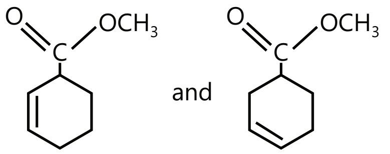
(A) 

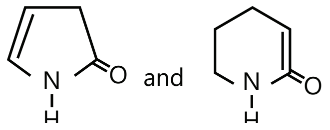
(B) 

(C) 

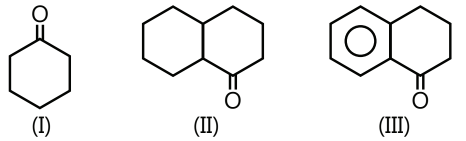
(D) 

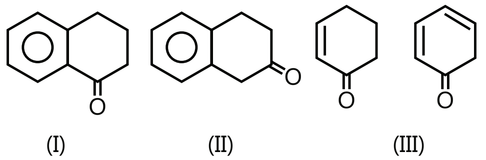
Q.25 In each of the following pairs which will have less enrol content:

(A) 

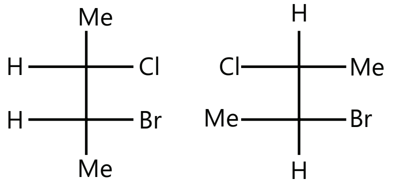
(B) 

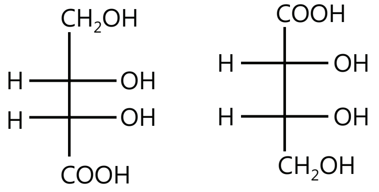
Q.26 In each of the following sets of compounds write the decreasing order of % enrol content.

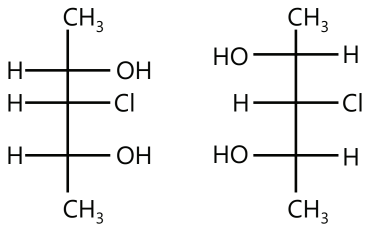
(A) 

(B) 

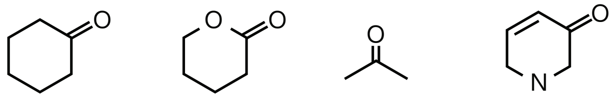
Q.27 Identify the following pairs as enantiomers, diastereomers or identicals.

(A) 

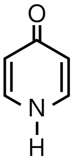
(B) 

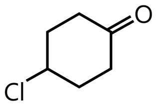
(C) 

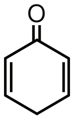
Q.28 In each of the following sets of compounds write the decreasing order of % enrol content.



Q.29 In each of the following sets of compounds write the decreasing order of % enrol content.


(A)


(B)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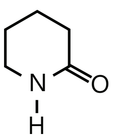
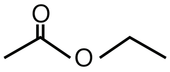
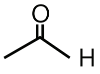

(D)

Q.30 In each of the following sets of compounds write the decreasing order of % enrol content.


(A)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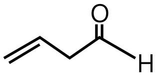
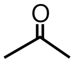
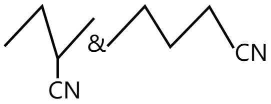

(C)

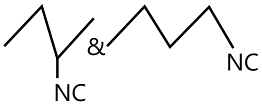

(D)

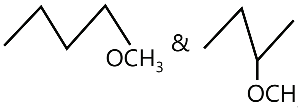
Exercise 2

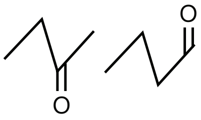
Single Correct Choice Type

Q.1 Identify the position isomer.

(A) 

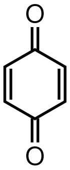
(B) 

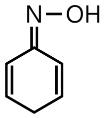
(C) 

(D) 

Q.2 Which compound show tautomerism

(A) Ph–NO

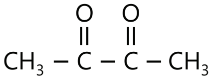
(B) 

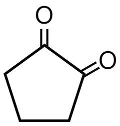
(C) 

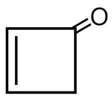
(D) HCHO

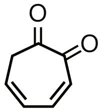
Multiple Correct Choice Type

Q.3 Which of the following compounds have higher enolic content than Keto content:

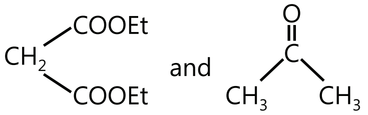
(A) 
$CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_3$

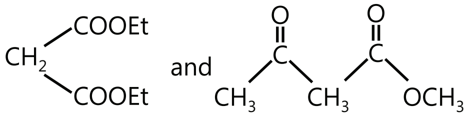
(B) 

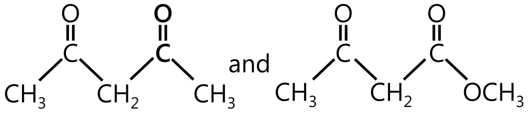
(C) 

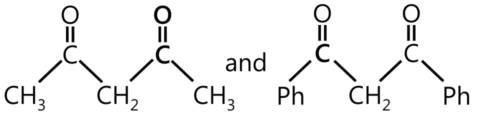
(D) 

Q.4 In which of the following pairs first will have higher enol content than second:

(A) 

(B) 

(C) 

(D) 

Q.5 What statement is correct for Keto – enol tautomerism?

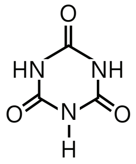
(A) Tautomerism is catalysed by acid and base.

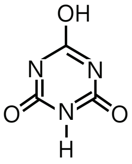
(B) Tautomers are present in dynamic equilibrium state.

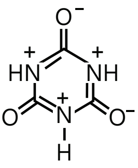
(C) Generally keto is more stable than enol from in mono Ketones

(D) Atomic arrangements are same in tautomerism.

Q.6 What is the relation between (I), (II) and (III)?

(I) 

(II) 

(III) 

(A) I and II are tautomers

(B) III is conjugate base of II

(C) III is resonance structure of I

(D) No relation exists.

Q.7 Which of the following have zero dipole moment?

(A) p–Dichlorobenzene

(B) Benzene–1,4–diol

(C) Fumaric acid

(D) Maleic acid

Q.8 Which of the following statements is/are not correct?

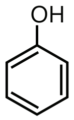
(A) Metamerism belongs to the category of structural isomerism

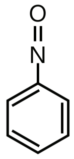
(B) Tautomeric structures are the resonating structures of a molecule.

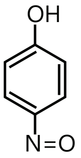
(C) Keto form is always more stable than the enol form

(D) Geometrical isomerism is shown only by alkanes

Q.9 Which compound show tautomerism:

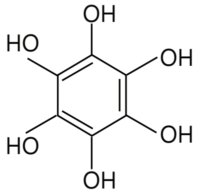
(A) 

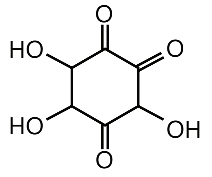
(B) 

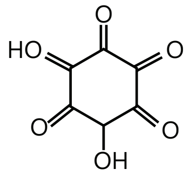
(C) 

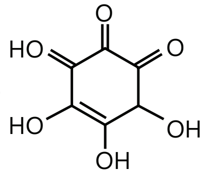
(D) None of these

Q.10 Tautomeric form of this compound is/are:



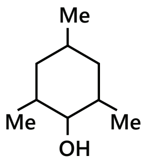
(A) 

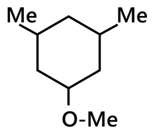
(B) 

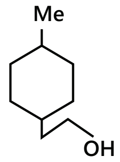
(C) 

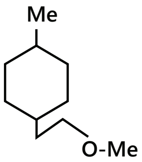
(D) All of these

Q.11 Which of the following is not the correct relationship.


I


II


III


IV

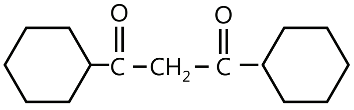
(A) II and TV are metamer

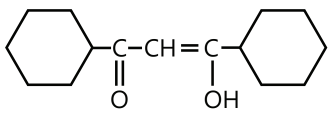
(B) I and II are functional isomer

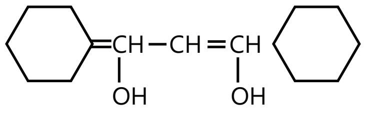
(C) I and III are chain isomer

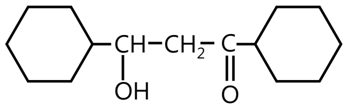
(D) I and IV are positional isomer.[as q 8]

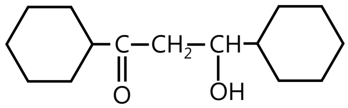
Q.12 Tautomer of following compound is:



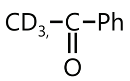
(A) 

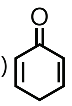
(C) 

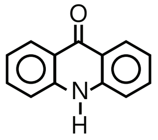
(B) 

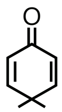
(D) 

Q.13 Which of the following can tautomerise:

(A) 
$CD_3-\underset{\underset{O}{\|}}{C}-Ph$

(B) 

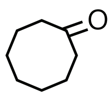
(C) 

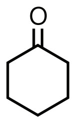
(D) 

Q.14 Tautomer of which of the following can show geometrical isomerism

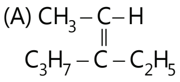
(A) CH_3-CHO

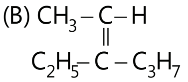
(B) CH_2CH_2-CHO

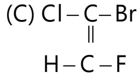
(C) 

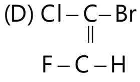
(D) 

Q.15 The Z–isomer among the following are:

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

Q.16 Which of the following is correctly matched?

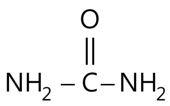
(A) $CH_3-CH=CH-CH=CH=C_2H_5 \rightarrow 4$

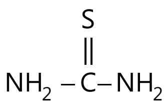
(B) $CH_3-(CH=CH)_4-CH_3 \rightarrow 2$

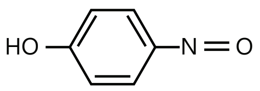
(C) $CH_3=CH-CH=CH_2 \rightarrow 2^3+2^1=10$

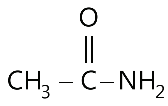
(D) $CH_3(-CH=CH)_5-CH_3 \rightarrow 2^4+2^2=20$

Q.17 Which of the following compounds show tautomerism?

(A) 
$NH_2-\overset{\overset{O}{\|}}{C}-NH_2$

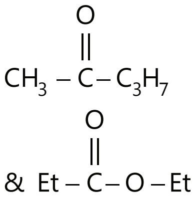
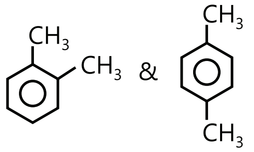
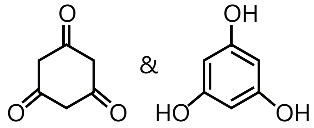
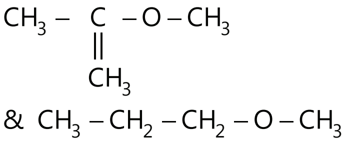
(B) 
$NH_2-\overset{\overset{S}{\|}}{C}-NH_2$

(C) 

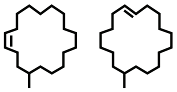
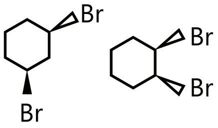
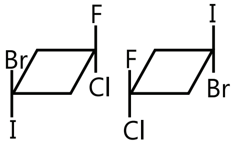
(D) 
$CH_3-\overset{\overset{O}{\|}}{C}-NH_2$

Match the Columns

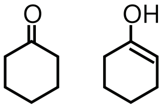
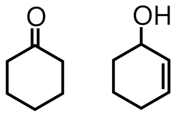
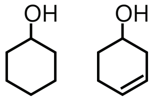
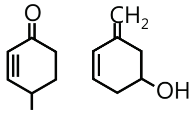
Q.18 Match Column I with Column II

Column I	Column II
(A)  $CH_3-\overset{\overset{O}{\|}}{C}-C_3H_7$ & $Et-\overset{\overset{O}{\|}}{C}-O-Et$	(p) Chain isomer
(B) 	(q) Positional isomers
(C) 	(r) Metamers
(D)  $CH_3-\underset{\underset{CH_3}{\|}}{C}-O-CH_3$ & $CH_3-CH_2-CH_2-O-CH_3$	(s) Tautomers

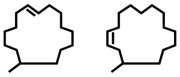
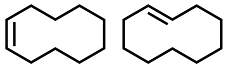
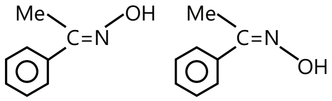
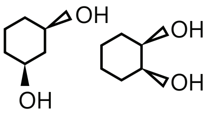
Q.19 Match Column I with Column II

Column I	Column II
(A) 	(p) Geometrical isomers
(B) 	(q) Structural isomer
(C) 	(r) Number of Geometrical isomer of first compound is even number
	(s) Number of geometrical isomer of second compound is even number

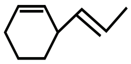
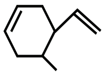
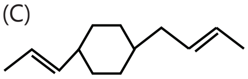
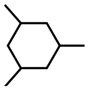
Q.20 Match Column I with Column II

Column I	Column II
(A) 	(p) Tautomers
(B) 	(q) Structural isomer
(C) 	(r) Positional isomers
(D) 	(s) Atleast one of the two structures is enol

Q.21 Match Column I with Column II

Column I	Column II
(A) 	(p) Positional isomers
(B) 	(q) Geometrical isomers
(C) 	(r) First is E and second is Z form
(D) 	(s) Structural isomer

Q.22 Match Column I with Column II

Column I Compound	Column II Number of geometrical isomers
(A) 	(p) 2
(B) 	(q) 4
(C) 	(r) 6
(D) 	(s) 8

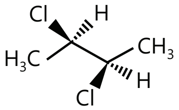
Previous Years' Questions

Q.1 Which of the following compounds will show geometrical isomerism? ***(1998)***

(A) 2–butene (B) Propene

(C) 1–phenyl propene (D) 2–methyl–2–butene

Q.2 The correct statement(s) about the compound given below is (are) ***(2008)***



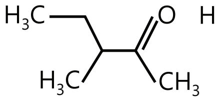
(A) The compound is optically active

(B) The compound possess centre of symmetry

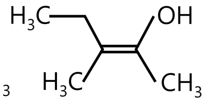
(C) The compound possess plane of symmetry

(D) The compound possess axis of symmetry

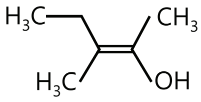
Q.3 The correct statement(s) concerning the structures E,F and G is (are) ***(2008)***



(E)



(F)



(G)

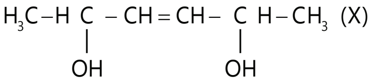
(A) E,F and G are resonance structures

(B) E,F and G are tautomers

(C) F and G are geometrical isomers

(D) F and G are diastereomers

Q.4 The correct statement(s) about the compound



$H_3C-\underset{|\atop OH}{CH}-CH=CH-\underset{|\atop OH}{CH}-CH_3$ (X) is (are) ***(2009)***

(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.

Q.5 M–chlorobromobenzene is an isomer of m–bromochlorobenzene. ***(1985)***

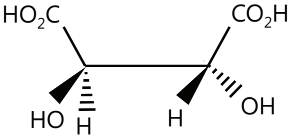
Q.6 2,3,4–trichloropentane has three asymmetric carbon atoms. ***(1990)***

Q.7 The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is ***(2008)***

(A) $(C_2H_5)_2CHCl$ (B) $(CH_3)_3CCl$

(C) $(CH_3)_2CHCl$ (D) CH3Cl

Q.8 The absolute configuration of is ***(2008)***



(A) S, S (B) R, R (C) R, S (D) S, R

Q.9 α–D–(+) glucose and β–D (+) – glucose are ***(2013)***

(A) Conformers (B) Epimers

(C) Anomers (D) Enantiomers

Q.10 Glycerine contain one ....hydroxy group. ***(2004)***

Q.11 (A) Draw Newman's projection for the less stable staggered form of butane.

(B) Relatively less stability of the staggered form is due to

(i) Torsional strain

(ii) van der waals' strain

(iii) Combination of the above two ***(2004)***

Q.12 $\mu obs = \sum \mu_i xi$ Where μ_i is the dipole moment of stable conformer and X_i is the mole fraction of that conformer.

(A) Write stable conformer for Z–CH_2– CH_2–Z in Newman's projection.

If $\mu_{solution}$ =1.0D and mole fraction of anti form = 0.82, find μ_{gauche}

(B) Write most stable meso conformer of $(CHDY)_2$ If

(i) Y = CH_3 about C2–C3 rotation and

(ii) Y = OH about C1–C2 rotation. ***(2005)***

Q.13 Give the total number of cyclic structural as well as stereo isomers possible for a compound with the molecular formula C_5H_{10} ***(2009)***

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.1 Q.3 Q.11 Q.15

Exercise 2

Q.2 Q.7 Q.11

Q.18 Q.22 Q.23

Previous Years' Questions

Q.4

JEE Advanced/Boards

Exercise 1

Q.4 Q.5 Q.11 (3,8,12)

Q.13 (E,B) Q.21 (C,D) Q.23 (D,E) Q.27

Exercise 2

Q.1 Q.3 Q.8 Q.20

Previous Years' Questions

Q.2 Q.4 Q.9

Answer Key

JEE Main/Boards

Exercise 1

Q.6 A **Q.7** –52° **Q.8** B **Q.9** B **Q.10** D **Q.11** D **Q.12** B

Q.13 B **Q.14** C **Q.15** A **Q.16** B **Q.17** A **Q.18** C **Q.19** B

Q.20 D

Exercise 2

Single Correct Chioce Type

Q.1 B **Q.2** C **Q.3** D **Q.4** C **Q.5** B **Q.6** C **Q.7** D

Q.8 C **Q.9** B **Q.10** A **Q.11** D **Q.12** B

Previous Years' Questions

Q.1 B **Q.2** C **Q.3** A **Q.4** D **Q.5** D **Q.6** C **Q.7** A

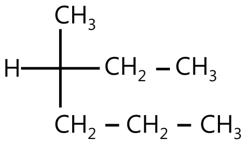
Q.8 C **Q.9** Non–superimposable; enantiomers **Q.10** C **Q.11** A

JEE Advanced/Boards

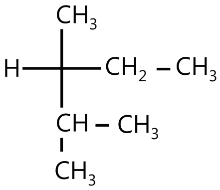
Exercise 1

Q.1 3 **Q.2** 6 **Q.3** 4 **Q.4** A,B,C,E,G **Q 5.** 10 **Q 6.** 7

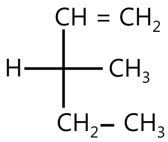
Q 7. (A) 2,



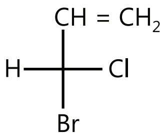
(B)



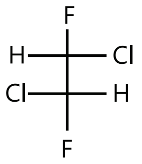
(C) 1,



(D) 1,



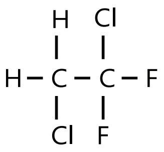
(E) 1,



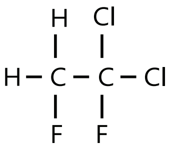
(d ,1)

Q.8 4 **Q.9** 7 **Q.10** 10 **Q.11** Z–I,II,III,VI,VII; E–IV,V,VIII,IX,X,XI,XII

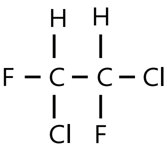
Q.12 (A) 6, structural isomers = 4, stereoisomers = 3



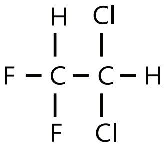
$\text{H}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{F}}{\text{C}}}-\text{F}$ (Optically inactive)



$\text{H}-\overset{\text{H}}{\underset{\text{F}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{F}}{\text{C}}}-\text{Cl}$ (Optically inactive)

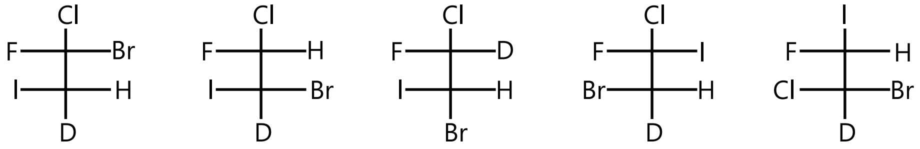


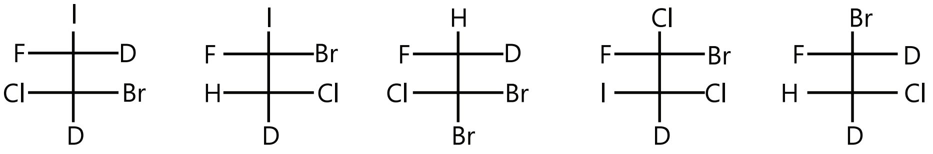
$\text{F}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{H}}{\underset{\text{F}}{\text{C}}}-\text{Cl}$ (d,1, meso)



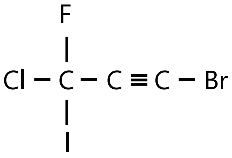
$\text{F}-\overset{\text{H}}{\underset{\text{F}}{\text{C}}}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}-\text{H}$ (Optically inactive)

(B) 10×4=40, structural (positional) isomers =10, stereoisomers = 40

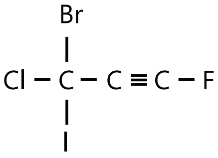




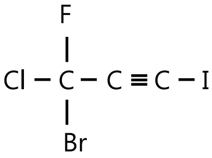
(C) 14, structural isomers = 7, Stereoisomers = 14



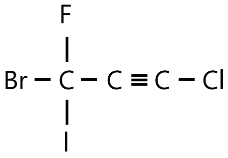
$\text{Cl}-\overset{\text{F}}{\underset{\text{I}}{\text{C}}}-\text{C}\equiv\text{C}-\text{Br}$



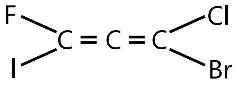
$\text{Cl}-\overset{\text{Br}}{\underset{\text{I}}{\text{C}}}-\text{C}\equiv\text{C}-\text{F}$

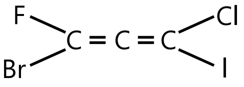


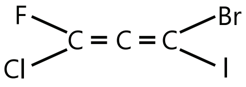
$\text{Cl}-\overset{\text{F}}{\underset{\text{Br}}{\text{C}}}-\text{C}\equiv\text{C}-\text{I}$



$\text{Br}-\overset{\text{F}}{\underset{\text{I}}{\text{C}}}-\text{C}\equiv\text{C}-\text{Cl}$



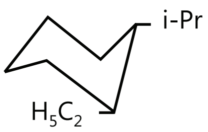




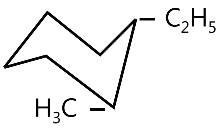
Q.13 (A) Positional (B) Functional (C) Metamerism (D) Positional
(E) Functional (F) Tautomerism

Q.14 Stable are : (A) diequatorial

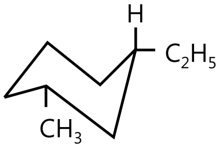
(B)



(C)

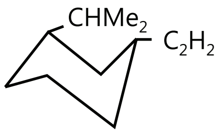


(D)

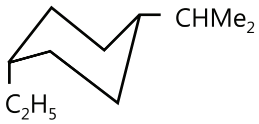


(trans)

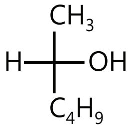
(E)



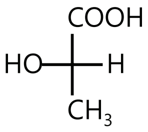
(F)



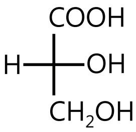
Q.15 (A)



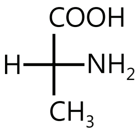
(B)



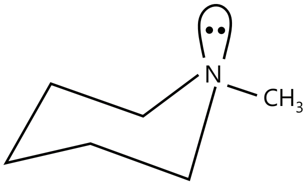
(C)



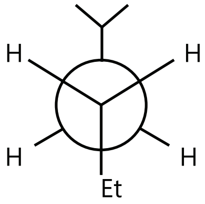
(D)



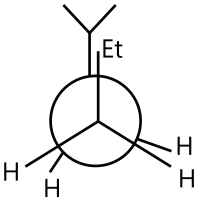
Q.16



Q.17 (A)

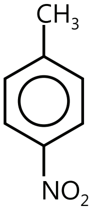


(B)



Q.18 (A) Cis (B) Cis (C) Cis (D) Trans (E) Trans (F) Trans

Q.19 Position isomers, Functional isomers, Tautomers, Geometrical isomers



Q.20 (A) 4,1,2,3 (B) 4,1,2,3 (C) 1,3,2,4 (D) 4,3,2,1 (E) 2,4,3,1 (F) 4,2,3,1

(G) 3,1,4,2 (H) 2,4,1,3 (I) 3,2,1,4 (J) 2,1,4,3

Q.21 (A) S (B) R (C) R, S (D) S , S

Q.22 (A) 1; (B) 1; (C) 1; (D) 1; (E) 1;

Q.23 (A) 2; (B) 2; (C) 1; (D) 2; (E) 1

Q.24 (A) 2; (B) 1; (C) 2; (D) 1; (E) 2

Q.25 (A) 2; (B) 2

Q.26 (A) 3>1>2 (B) 4>2>1>3

Q.27 (A) Diastereomer, (B) Enantiomer, (C) Diastereomer

Q.28 (D)>(B)>(A)>(C)

Q.29 (C)>(A)>(D)>(B)

Q.30 (C)>(D)>(B)>(A)

Exercise 2

Single Correct Chioce Type

Q.1 C **Q.2** C

Multiple Correct Choice Type

Q.3 B, D **Q.4** A, C **Q.5** A, B, C **Q.6** A,C **Q.7** A,B **Q.8** C,D

Q.9 (A) P,R,S (B) Q (C) Q **Q.10** A,B **Q.11** A,D **Q.12** A,C,D **Q.13** A,B,C **Q.14** B,C

Q.15 A,C **Q.16** A,B **Q.17** A,B,C,D

Match the Columns

Q.18 A → r; B → q; C → s; D → q **Q.19** A → q, r, s; B → q, r, s; C → p, r, s

Q.20 A → p, q, s; B → q, s, C → s; D → q, s **Q.21** A → p, r, s; B → q; C → q, r; D → p, r, s

Q.22 A → p; B → p; C → s; D → p

Previous Years' Questions

Q.1 A,C **Q.2** A,D **Q.3** B,C,D **Q.4** A,D **Q.7** D **Q.8** B **Q.9** C

Solutions

JEE Main/Boards

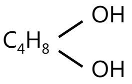
Exercise 1

Sol 1: i. (A) reacts with Na to give H_2 and thus it contains (–OH) group.

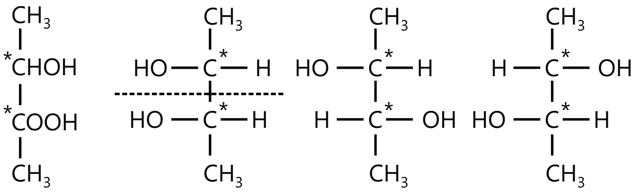
ii. The molecular weight of (A) ($C_4H_{10}O_2$) is 90. If one (OH) group, then 90 gm (A) with Na gives 11200 mL H_2 (i.e., half mole H_2).

0.90 gm of (A) gives $\frac{11200 \times 0.90}{90} = 112$ ml of H_2 at STP.

Since 0.90 Na gives 224 mL H_2 at STP, it contains two (–OH) groups.

iii. keeping in view the above facts, (A) is  $C_4H_8(OH)_2$

iv. (A) shows optical isomerism of which (B) form is optically active having two isomers (D) and (E); (C) being the inactive form; therefore, (A), (B), (C), and (D) are:



(A) (c) Meso form (D) 'l' form (E) 'd' form

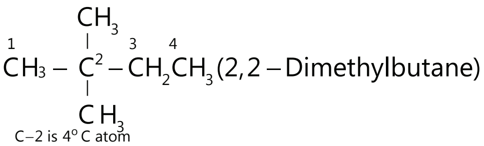
(B) 'd' 'l' forms

* Represents two asymmetric C atoms.

Sol 2: Heptane is C_7H_{16}.

The homologues of heptane are C_7H_{14} and C_8H_{18}.

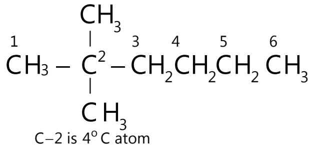
i. Molecule of hexane having one quaternary C atom:



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

C–2 is 4° C atom

ii. Molecule of octane having one quaternary C atom:



$$\overset{1}{C}H_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C^2}}-\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2\overset{6}{C}H_3$$

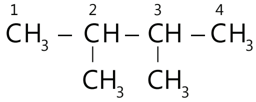
(2, 2–Dimethylhexane)

C–2 is 4° C atom

Note: Other structures with one quaternary may also be formed with octane.

ii. Molecule of hexane having two tertiary c atoms:

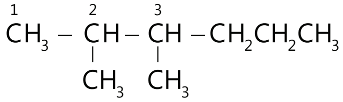
Where C–2 and C–3 are 3°C atoms.



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

(2, 3 – Dimethylbutane)

Molecule of octane having two tertiary C atoms:

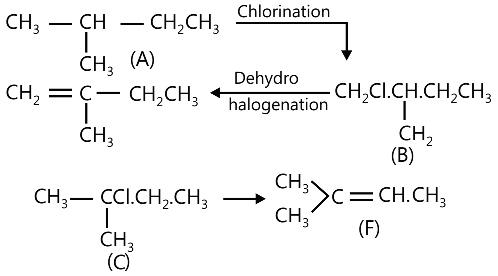


$$\overset{1}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{2}{C}H}-\underset{\underset{CH_3}{|}}{\overset{3}{C}H}-CH_2CH_2CH_3$$

(2, 3 – Dimethy hexane)

C–2 and C–3 are 3°C atoms.

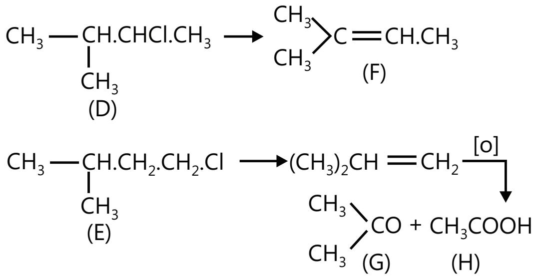
Sol 3: i. Alkane (A) C_5H_{12} on chlorination gives four monochlroro products and thus (A) is isopentane.



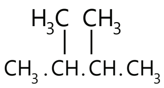
Sol 4: Alkane is C_nH_{2n+2}, Molecular weight =86

$\therefore 12n+2n+2=86 \Rightarrow n=6$

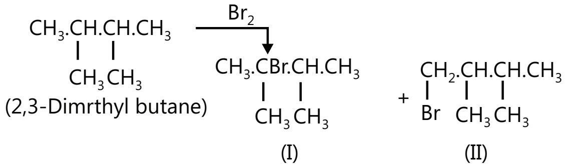
Therefore, alkane is $C_6H_{14.}$



The alkane with this formula on bromination giving two product may be written as



$$\underset{}{CH_3.}\overset{\overset{H_3C}{|}}{CH}.\overset{\overset{CH_3}{|}}{CH}.CH_3$$



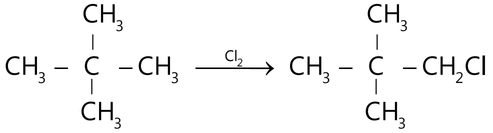
Sol 5: Vapour density = 36; Molecular weight = 2 × 36 = 72

Examination of molecular weight suggests it to be an alkane, i.e. $C_nH_{2n+2.}$

$12n+2n+2=72 \Rightarrow n=5$

Therefore, alkane (A) is $C_5H_{12.}$

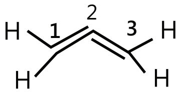
(A) Gives only one product on substitution, thus (A) is:



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xrightarrow{Cl_2} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Cl$$

(A) is $(CH_3)_4C$, i.e. 2, 2–dimethyl propane (neopentane).

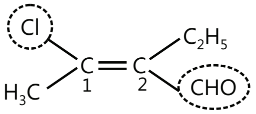
Sol 6:



Allenes of the type

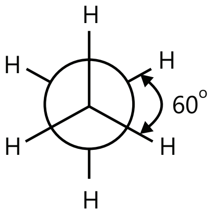
Sol 7: Since (A) and (B) are enantiomers, so specific rotation of B is –52° (because enantiomers have equal and opposite specific rotation).

Sol 8: Two higher priority groups (Cl and CHO) on C–1 and C–2 are in the opposite directions; so the and C–2 are in the opposite directions; so the configuration is E.



Sol 9: In (B), the two groups (two H atoms) are same around the double bond.

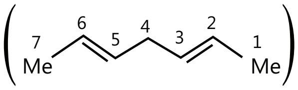
Sol 10:

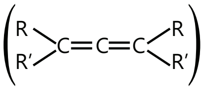


Staggered conformation

Sol 11: The mirror image of placed football is non–superimposable.

Sol 12:



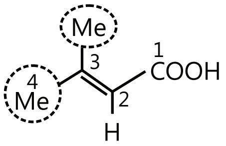


Terminal groups are same. The number of double bonds is two (even number).

∴ Number of GI= $2^{n-1} + 2^{(n-2)/2} = 2^1 + 2^0 = 2 + 1 = 3$

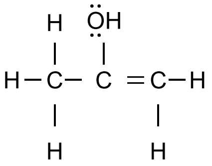
Where n is the number of double bonds.

Sol 14:



Two same groups (Me) on C–3; hence, do not show G.I.

Sol 15: 9σ Bonds, 1 π and 2 lone pairs.



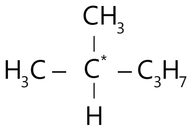
$$\begin{array}{ccccc} H & & \ddot{\underset{\cdot\cdot}{O}}H & & \\ | & & | & & \\ H-C- & & C & =C-H & \\ | & & & | & \\ H & & & H & \end{array}$$

Sol 16: Order of enol content:

Aldehyde < Ketone < Keto–aldehyde < Diketone.

(iii < ii < i < iv)

Sol 17:



$$H_3C-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C^*}}-C_3H_7$$

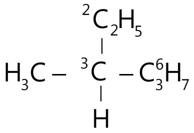
(Total C = 7)

(Optically active alkane)

Sol 18: Although the meso compounds contain asymmetric C atoms, but they are optically inactive due to superimposable mirror image or due to the presence of any element of symmetry.

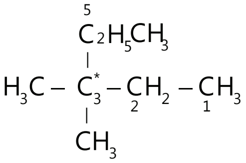
Sol 19: Meso compound

Sol 20:



$$H_3C-\underset{\underset{H}{|}}{\overset{\overset{{}^2C_2H_5}{|}}{{}^3C}}-C_3^6H_7$$

or



$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{\overset{5}{C}_2H_5CH_3}{|}}{C_3^*}}-\underset{2}{C}H_2-\underset{1}{C}H_3$$

2–Methyl hexane 2, 3–Dimethyl pentane

Both (I) and (II) are optically active alkanes.

Exercise 2

Single Correct Choice Type

Sol 1: (B) All groups are as far apart as possible.

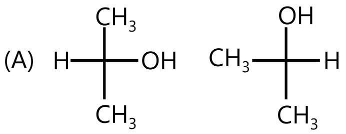
Sol 2: (C) (2Z,4E,6Z)–octa–2,4,6–triene

Sol 3: (D) 3– stereo centers and no POS in any compound

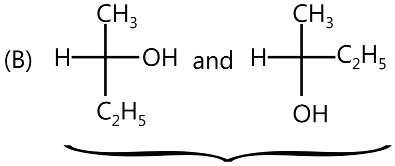
∴ Stereo isomers = $2^3 = 8$

Sol 4: (**C)** Compounds are (C) constitutional isomers

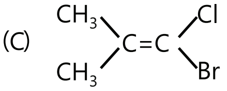
Sol 5: (B)



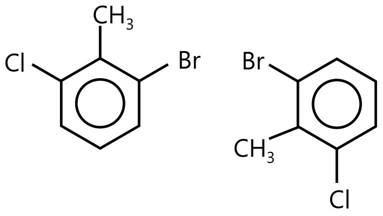
Achiral compounds hence identical



Enantiomers



Symmetric compound
(No isomers)

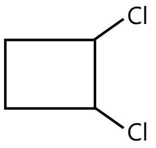


(Same compound)

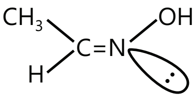
Sol 6: (C) I and II are enantiomers as they are non-superimposable mirror image of each other.

I, II and are all structural isomer as they have same molecular formula.

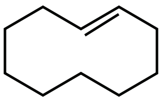
Sol 7: (D)



Forms G.I.



Forms G.I.

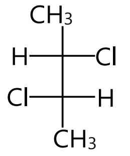


Forms geometric

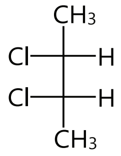
(Trans form)

As form of ring is also formed. Ans (D)

Sol 8: (C)



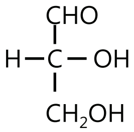
(A)



Meso-isomer
(Symmetric)

∴ Optically inactive optical rotation = 0

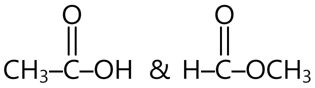
Sol 9: (B)



$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

Represent (D)

Since OH is on right side of the carbon chain, molecule acquires D configuration.



Sol 10: (A) $CH_3-\overset{\overset{O}{||}}{C}-OH$ & $H-\overset{\overset{O}{||}}{C}-OCH_3$ Are functional isomers

(B) $CH_3-CH_2-C\equiv H$ and $CH_3-C\equiv C-CH_3$ Are positional

(C) Are postional isomer

(D) Are funtional isomer

Sol 11: (D) Correct name

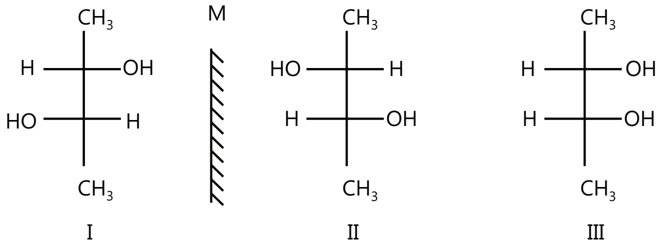
⇒ (2 D 3L 4D 5D) 2, 3, 4, 5, 6 – pentahydroxyhexanal

Sol 12: (B) 2 stereo centres and non symmetry

∴ $2^2 = 4$

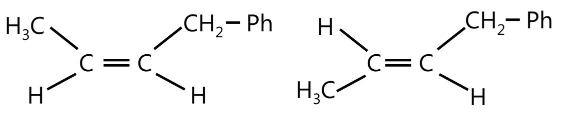
Previous Years' Questions

Sol 1: (B) I and II are optically active while III is optically inactive (meso form).



Sol 2: (C) The 'D' term in name is derived from D–glyceraldehyde.

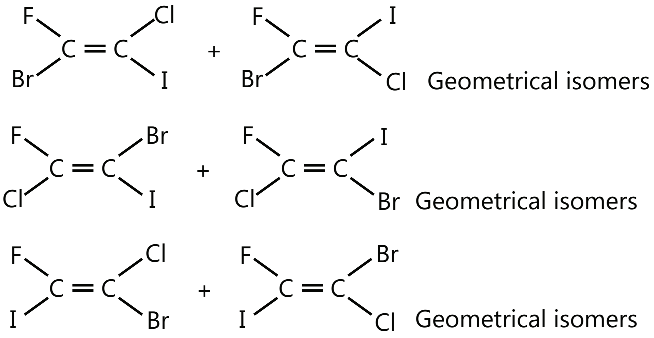
Sol 3: (A)



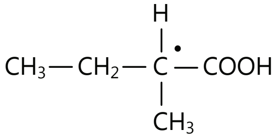
cis

trans
1-phenyl-2-butene

Sol 4: (D)



Sol 5: (D)

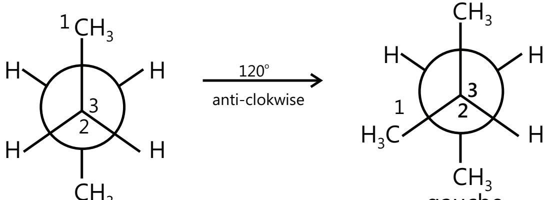


$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{\dot{C}}}-COOH$$

2-methyl butanoic acid

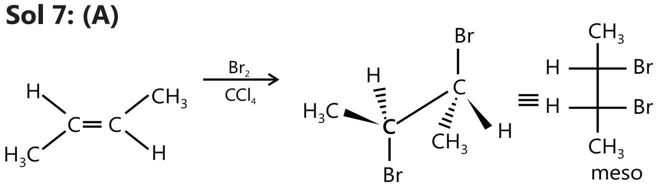
Has a chiral carbon, optically active.

Sol 6: (C)

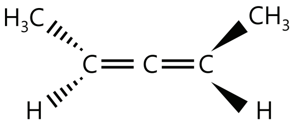


gauche

Sol 7: (A)



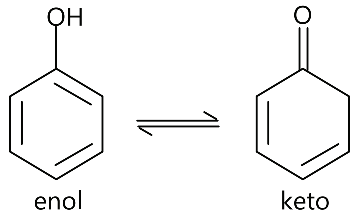
Sol 8: (C) Molecules that are non–super imposable on its mirror image are optically active and known as chiral molecule. However, for chirality of molecule, presence of chiral centre is not essential, eg.



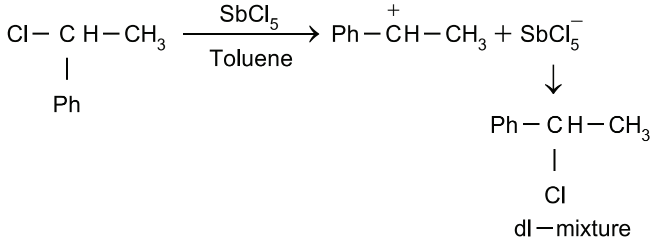
Molecule is chiral but does not possesses any chiral carbon.

Sol 9: Non–superimposable, Enantiomers.

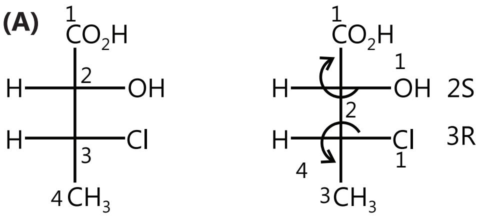
Sol 10: (C)



Sol 11: (C)



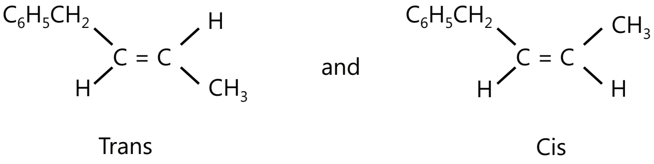
Sol 12: (A)



IUPAC numbering

Numbering according to CIP rules for R/S naming

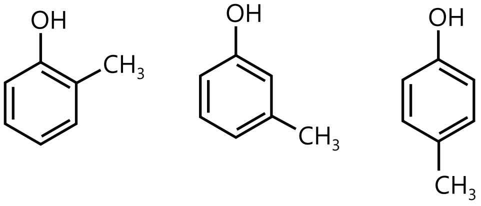
Sol 13: (A) $C_6H_5CH_2CH{=}CHCH_3$ has two geometrical isomers as



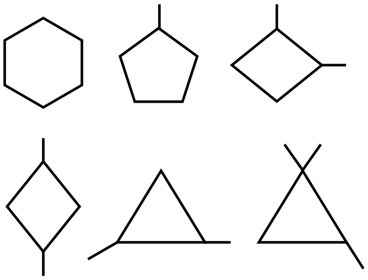
JEE Advanced/Boards

Exercise 1

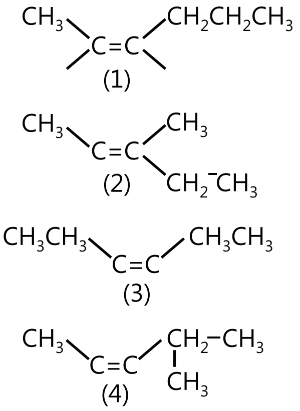
Sol 1: Three isomers are possible



Sol 2:



Sol 3: C_6H_{12}

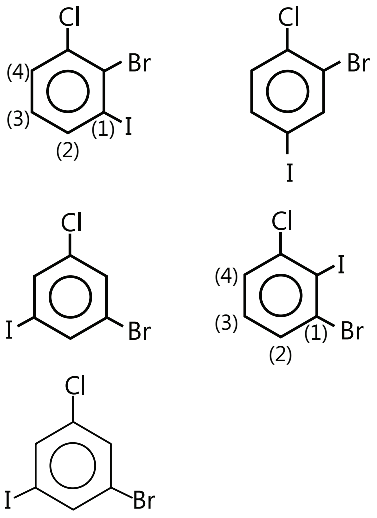


Total = 4 pair

Sol 4:

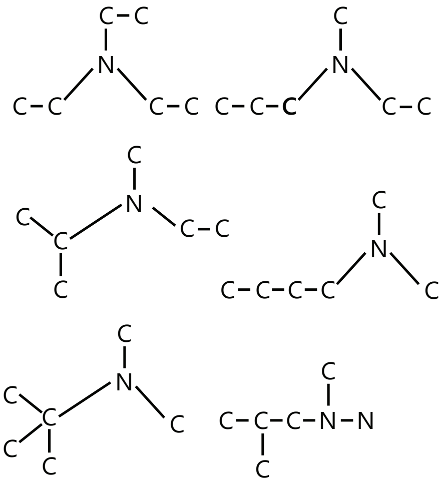
	Compound	Optical activity
(A)	Planar compound but CHClBr (group active)	Active due to CHCl–Br
(B)	Non–planar	Active
(C)	Non–planar	Active
(D)	Planar non symmetric	Inactive
(E)	Non–planar & asymmetric	Active
(F)	Non–symmetric but planar	Inactive
(G)	Non–planar (chain form)	Active
(H)	Planar	Inactive
(I)	Planar (no–chiral) side groups	Inactive

Sol 5:

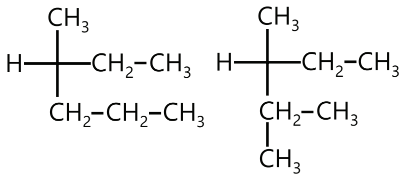


= 4 + 4 + 1 +2 − 1 = 10 isomers

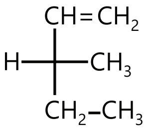
Sol 6: 7 isomers



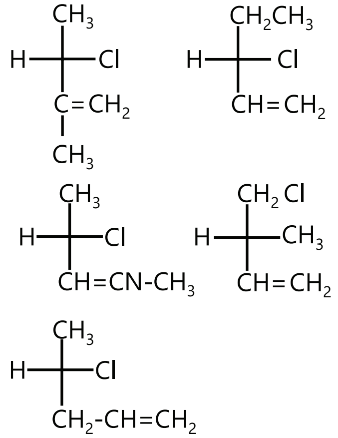
Sol 7: (A)



(B) C_6H_{12}

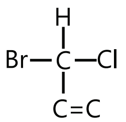


(C) C_5H_9Cl

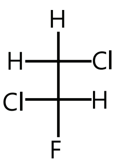


5 isomers

(D) C_2H_4ClBr

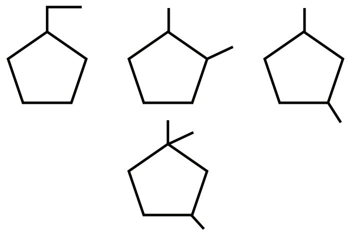


(e) $C_2H_2Cl_2F_2$



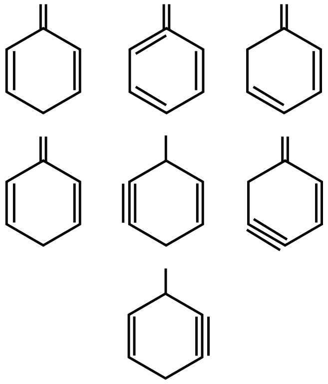
Optically active

Sol 8:



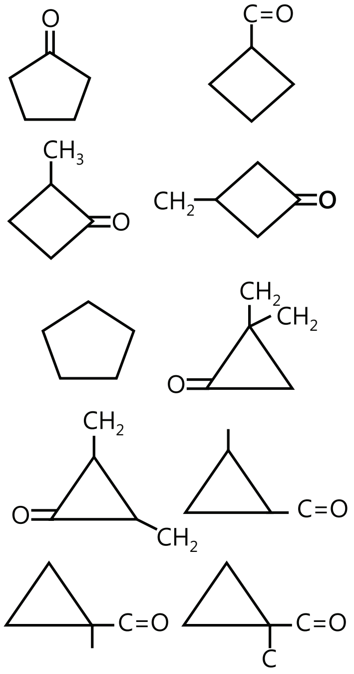
4 structure

Sol 9:

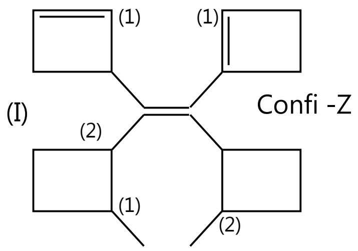


7 isomers

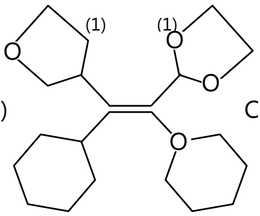
Sol 10: C_5H_8O



Sol 11:

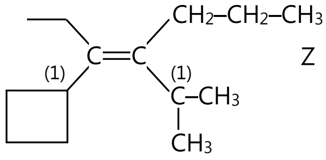


(II)



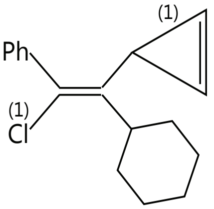
Confi = Z

(III)



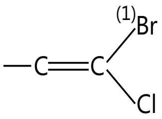
Z

(IV)



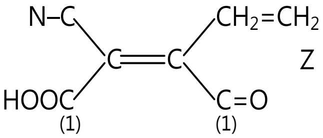
E

(V)



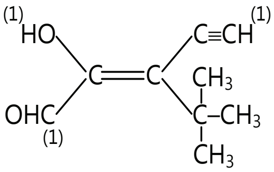
E

(VI)



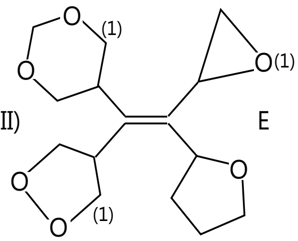
Z

(VII)



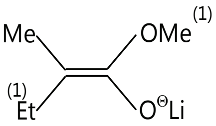
Z

(VIII)



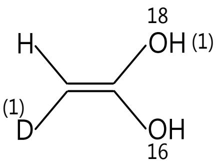
E

(IX)



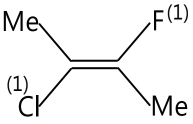
E

(X)



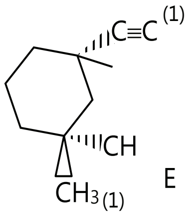
E

(XI)



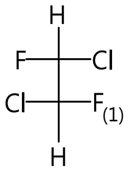
E

(XII)

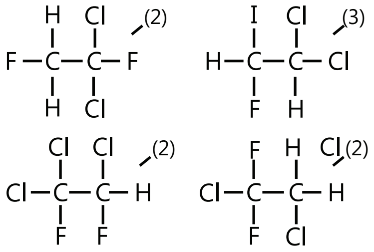


E

Sol 12: (A) $C_2H_2Cl_2F_2$ (3)



(optically active 2)

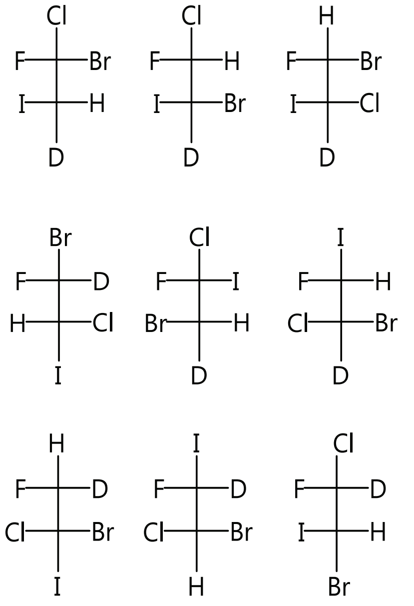


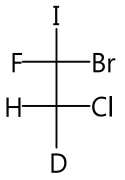
(B) C_2HClBr IFD

All isomers all active (no meso)

∴ Corresponding to each structural there all 4 stereo isomers

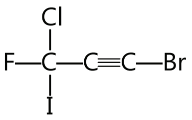
∴ Total number of isomers (structure all)





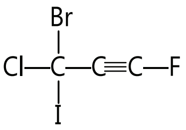
10 isomers

(C) Trans (2 isomers each)



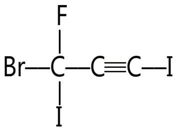
$F-\overset{Cl}{\underset{I}{C}}-C\equiv C-Br$

Chiral



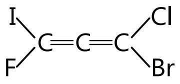
$Cl-\overset{Br}{\underset{I}{C}}-C\equiv C-F$

Chiral

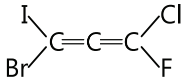


$Br-\overset{F}{\underset{I}{C}}-C\equiv C-I$

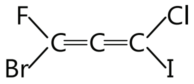
Chiral



Chiral



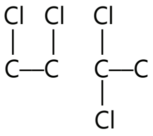
Chiral



Chiral

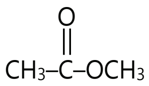
Sol 13:

(A)



Positional

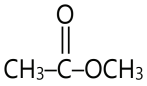
(B) C–C–COOH



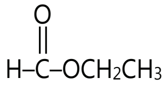
$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$

Functional

(C)



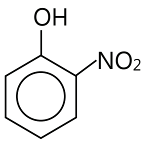
$CH_3-\overset{O}{\overset{\|}{C}}-OCH_3$

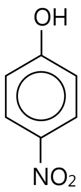


$H-\overset{O}{\overset{\|}{C}}-OCH_2CH_3$

Metamerism

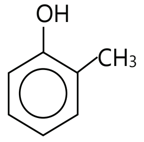
(D)

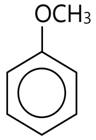




Positional

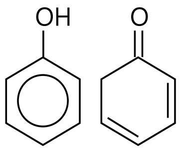
(E)





Functional

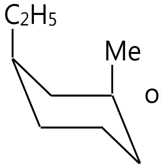
(F)



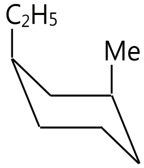
Tautamerism

Sol 14:

(A)

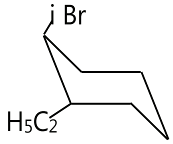


or



More stable (both in equatorial less repulsion**)**

(B)



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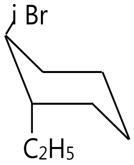
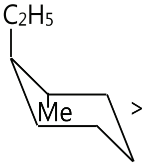


Both equatorial

(C)



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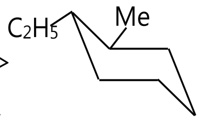
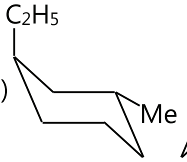
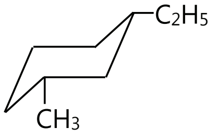


Morestable

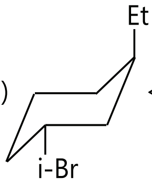
(D)





More stable

(E)



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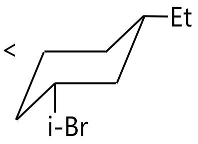
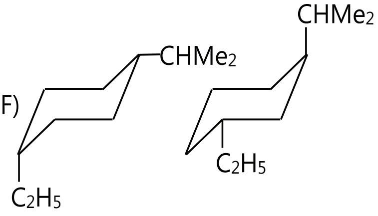
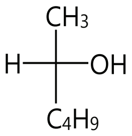


More stable

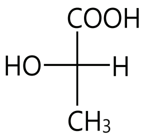
(F)



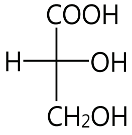
Sol 15: (A)



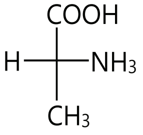
(B)



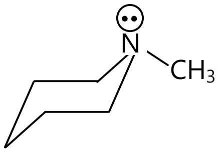
(C)



(D)

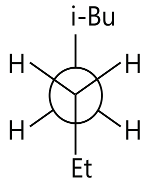


Sol 16:

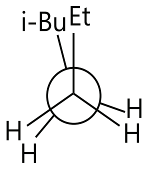


Sol 17:

(A)



(B)



According to hydrogen

Sol 18: (A) 1–3 axial–axia cis

(B) 1–4 axial–equitorial cis

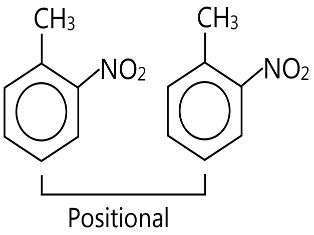
(C) 1–3 axial axial cis

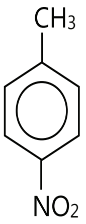
(D) 1–2 axial axial trans

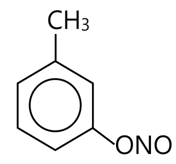
(E) 1–4 axial axial trans

(F) 1–3 axial equatorial trans

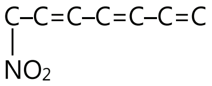
Sol 19: $C_7H_7O_2N$







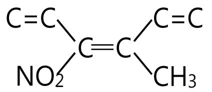
Functional



ONO–C–C=C–C=C–C=C

↓ Functional

C=C–C–C



Geometrical

Sol 20: (A) $OH > CHO > CH_2OH > CH_3$

4 > 1 > 2 > 3

(B) $NH_2 > -Ph > CH(Me)_2 > H$

4 > 1 > 2 > 3

(C) $COOH > CHO > Ph > C=CH_2$

1 > 3 > 2 > 4

(D) $Ph > C\equiv CH > CH=CH_2 > CHMe_2$

4 > 3 > 2 > 1

(E) $CH_2Br_3 > CH_3Cl > CH_2OH > CH_3$

2 > 4 > 3 > 1

(F) $OMe > -NMe_2 > Me > H$

4 > 2 > 3 > 1

(G) $Ph > CH=CH_2 > Et > Me$

3 > 1 > 4 > 2

(H) $Cl > CH(Me)_2 > CH_2(CH_2-Br) > CH_2-CH_2-CH_2-Br$

2 > 4 > 1 > 3

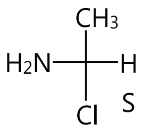
(I) $I > Br > Cl > NH_2$

3 > 2 > 1 > 4

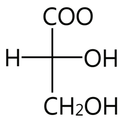
(J) $NO_2 > NH_2 > C\equiv N > CH_2NH_2$

2 > 1 > 4 > 3

Sol 21: (A)

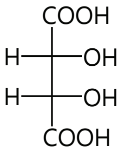


(B)



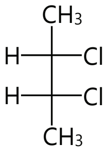
R

(C)

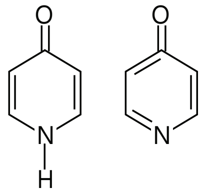


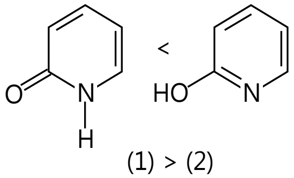
R₁S

(D)

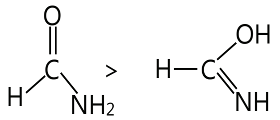


S₁S

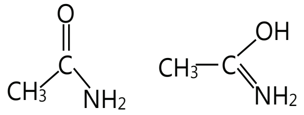
Sol 22: (A)  (1) > (2)

(B) 

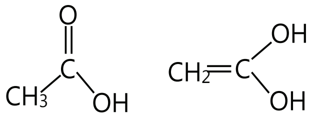
(1) > (2)

(C) 

(1) > (2)

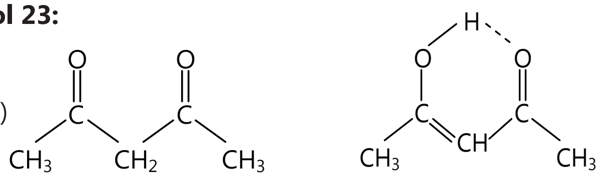
(D) 

(2) < (1)

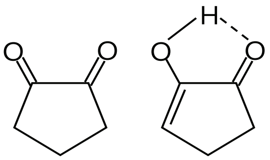
(E) 

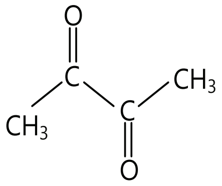
(1) > (2)

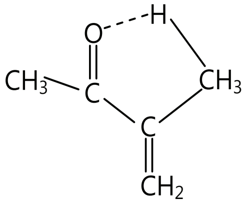
Sol 23:

(A) 

(2) > (1) due to H–O=C attraction and chelate formation

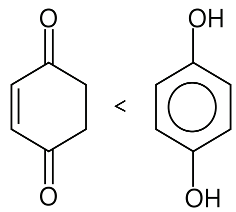
(B)  (2) >

(C) 

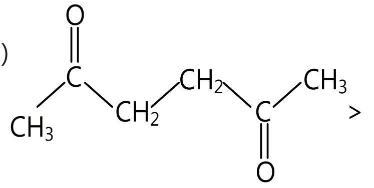


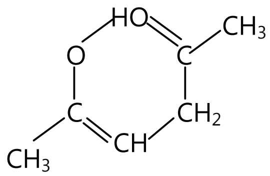
(1) > (2)

More e^- density is far on higher electro negative element only

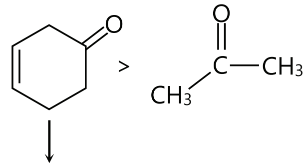
(D) 

Dislulented density but intramolecular attractive H–bonding

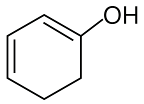
(E) 



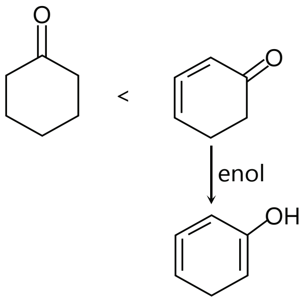
(7) membered chelates are very difficult

Sol 24: (A) 

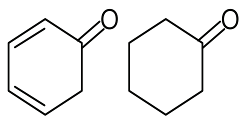
Enol for



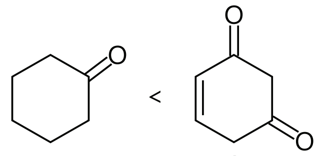
More stable due to resonance

(B) 

Resonance

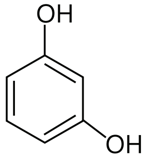
(C)  (1) > (2)

More stable due to extended resonance in enol–form

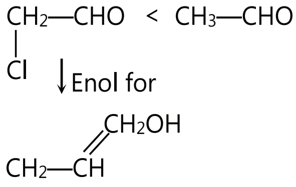
(D) 

(1) hass by

Enol for

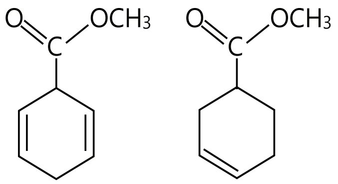


Extended Resonance

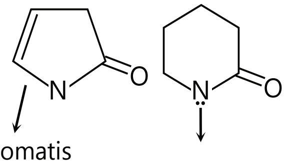


Stable due to –I effect

Sol 25:

(A) 

Less enol content as double bond not in conjugation

(B) 

Aromatis atom

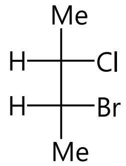
En enol formation

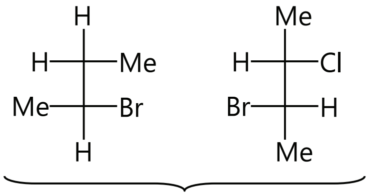
(2) < (1)

No aromatisation

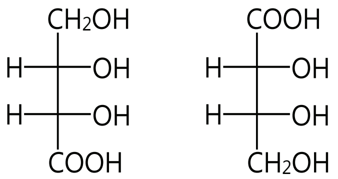
Sol 26: (A) 3 > 1 > 2 (B) 4 > 2 > 1 > 3

Sol 27:

(A) 

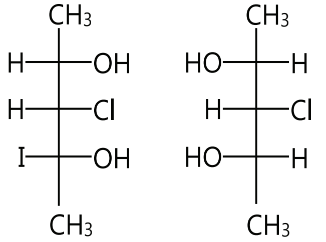


Distereomer

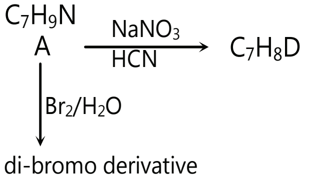
(B) 

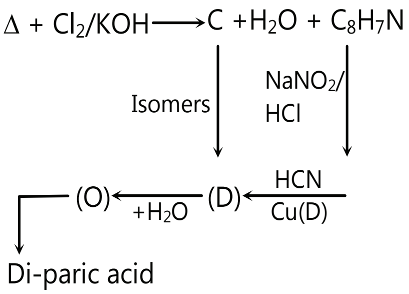
Enantiomer

(180° rotation and OH–H reversed)

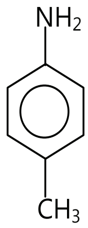
(C) 

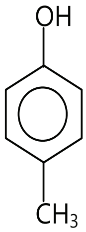
Diastereomer

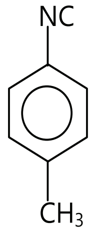


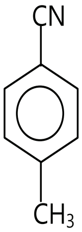


On halogenative forms one molecule direvative according to the following reactions compounds are

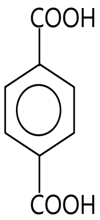
A= 

B= 

C= 

D= 

E=



Since D gives red colour with (A.N.)

∴ D is a pairing alcohol R–CH_2–OH

∴ C would be a primary amine

C = R–CH_2–NH_2

and A would be a R–CH_2–$CONH_2$

Mass of RCH_2CONH_2 = 135

∴ Mass of R = 135 – 2 × 12 – 16 – 14 – 4

= 135 – 24 – 16 – 18 = 77

∴ R–Phenyl group

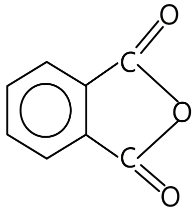
A = Ph–CH_2–$CONH_2$

B = Ph–CH_2–COOH

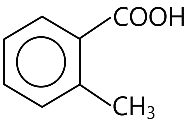
C = Ph–CH_2–NH_2

D = Ph–CH_2–OH

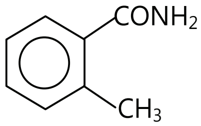
∴ Cr=



F =



E =



Sol 28: (D) > (B) > (A) > (C)

Sol 29: (C) > (A) > (D) > (B)

Sol 30: (C) > (D) > (B) > (A)

Exercise 2

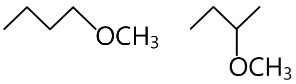
Single Correct Choice Type

Sol 1: (B)

(A) are chain isomers

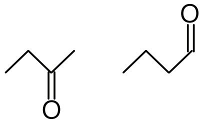
(B) position are isomers 1° ard.

(C)



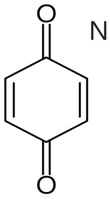
Positional isomers

(D)

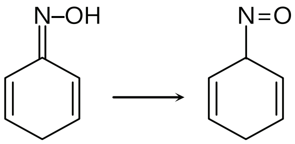


Functional isomers

Sol 2: (C) Ph–NO –No tautamerism

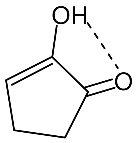


No – α –



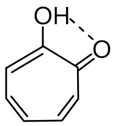
Multiple Correct Choice Type

Sol 3: (B,D) B → enol



chelation

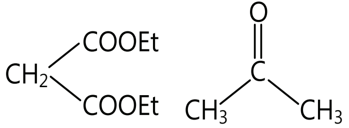
(D)



Chelation

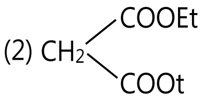
Sol 4: (A,C)

(A)

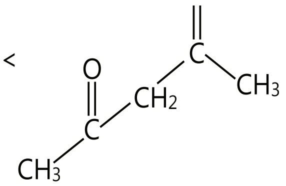


(1) > (2)

(B)

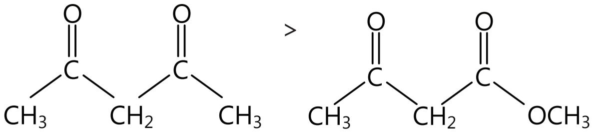


<

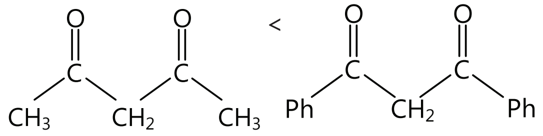


Carbanion in enol form more stable due to higher–I group.

(C)



(D)



Sol 5: (A,B,C)

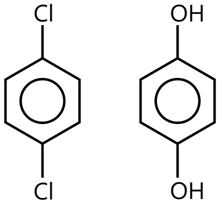
(A) Tautomers catalysed by acid/base

(B) Tautamers present in dynamic equilibrium continuous conversion form one form to other

(C) Generally mono ketones are more stable than enol.

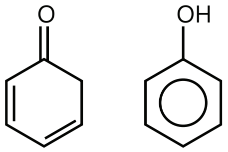
Sol 6: (A,C) I, II are tautamers and III and I are resonating structure

Sol 7: (A,B)

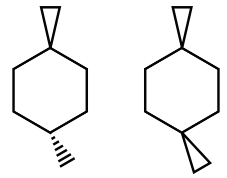


Sol 8: (C,D)

(D) Keto form is not always more stable than the

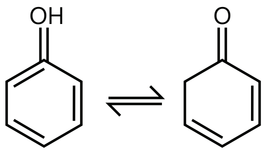


(D) For geometrical rotation can also be show in cyclic compound



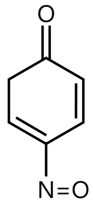
Sol 9: (A,C)

(A)



(B) No alpha–H

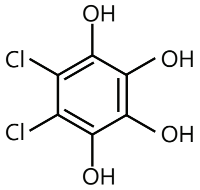
(C)

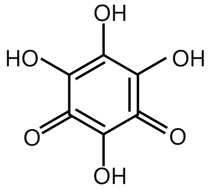


(enol form) tautamers

Sol 10: (A,B)

(B)



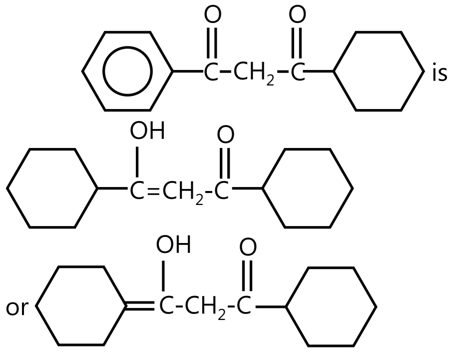


A can also be, but C is not possible

Sol 11: (A,D) (i) 2 and 4– are not metamers, they are chain isomer

(ii) I and V are not positional, they are structural isomers.

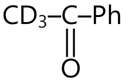
Sol 12: (A,C,D)



Similarly D

Similarly D

Sol 13: (A,B,C)



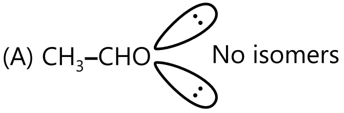
$CD_3-\underset{\underset{O}{\|}}{C}-Ph$ 3 – α –H can

(B) 2 – α – H can tautomerise

(C) 1 – α – H can tautomerise

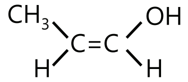
(D) No – α – H can not tautomerise

Sol 14: (B,C)

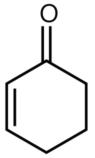


(A) $CH_3–CHO$ No isomers

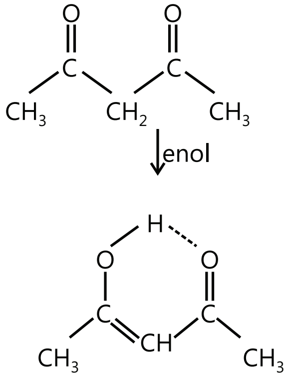
(B) $CH_3–CH_3–CHO$ No isomerism in keto for



(C) In enol form 2 geometrical isomers

(D)  No geometrical isomer

Sol 15: (A,C)



Resonance and chelate or due to a intramolecular H–bonds

Sol 16: (A,B)

(A) $CH_3–CH=CH–CH=CH–C_2H_5$

2–stereo centes $\Rightarrow 2 = 4$

$CH_2=CH–CH–CH_2$ (Planar symmetric compound)

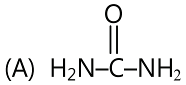
Isomer = 0

$CH_3–(CH=CH)_5–CH_3$

Total isomers

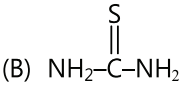
(B) $CH_3–(CH=CH)_4–CH_3$; Total isomers = 4

Sol 17: (A,B,C,D)



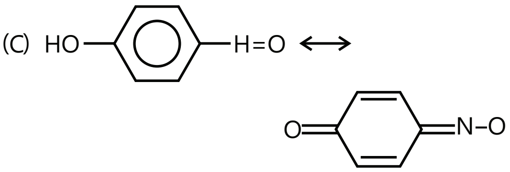
(A) $H_2N–\overset{\overset{O}{||}}{C}–NH_2$

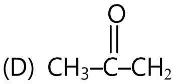
4–α–H will tautamerism



(B) $NH_2–\overset{\overset{S}{||}}{C}–NH_2$

4–α–H will show tautamerism

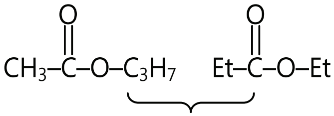




(D) $CH_3–\overset{\overset{O}{||}}{C}–CH_2$

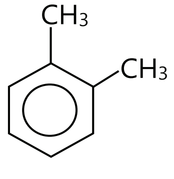
6–α–H will show tautamerism

Match the Columns

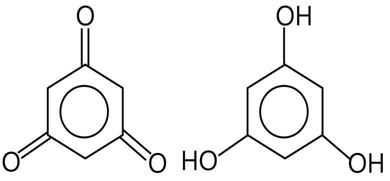
Sol 18: (A) 

$CH_3–\overset{\overset{O}{||}}{C}–O–C_3H_7 \quad Et–\overset{\overset{O}{||}}{C}–O–Et$

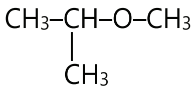
Metamers

(B) 

Positional isomers

(C) 

Tautomerism

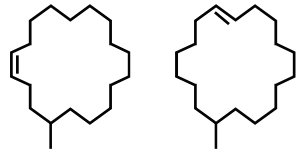
(D) 

$CH_3–\underset{\underset{CH_3}{|}}{CH}–O–CH_3$

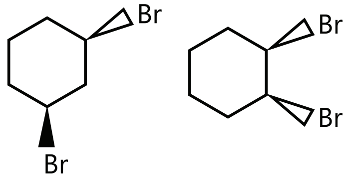
$CH_3–CH_2–CH_2–O–CH_3$

Chain isomers

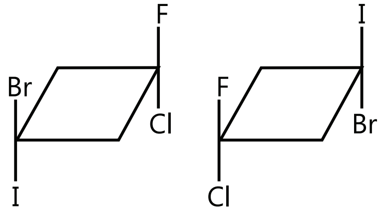
Sol 19 A → P, R, S B → Q C → Q



(A) Both are structural isomers of each other and both have even number of geometrical isomers.



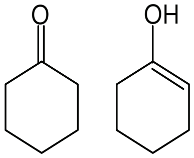
(B) Both are structural isomer of each other.



(C) Both are structural isomer of each other.

Sol 20:

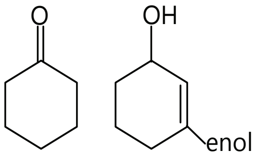
(A)



QPS

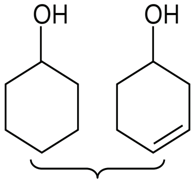
Tautomers and one is enol

(B)



Structural isomers (s)

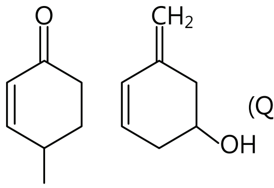
(C)



(S)

Not isomers

(D)



(Q) (S)

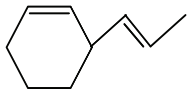
Sol 21: (A) Position isomers P, R, S structure

(B) GeometricQ

(C) Synand antiQ, R

(D) Position, structuralP, R, S

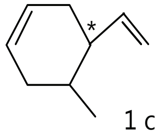
Sol 22: (A)



Isomer = $2^1 = 2$

No. of isomer

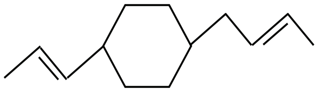
(B)



1 chiral $2^1 = 2$

center

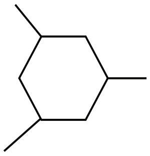
(C)



$2^3 = 8$

S-stereo centre

(D)

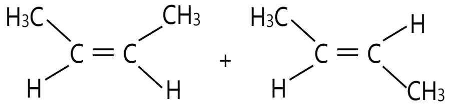


2-stereo isomers

Previous Years' Questions

Sol 1: (A,C) a and c will show geometrical isomerism as follow:

(A)



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

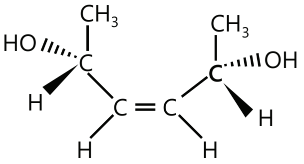
(C)

cis-1-phenylpropene *trans*-1-phenylpropene

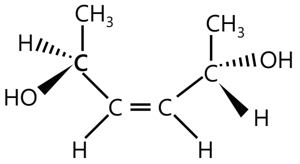
Sol 2: (A,D) The compound is optically active as well as it possesses a two–fold axis of symmetry.

Sol 3: (B,C,D) E, F and G are not resonance structures because movement of hydrogen between E and F are involved. E, F and E, G are tautomers in which E is keto form and both F and G are enol form of the same E.

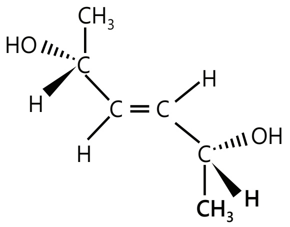
Sol 4: (A,D)



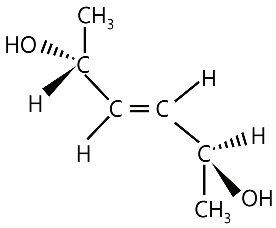
(I)
(meso)



(I+II)
(enantiomeric)



(IV + V)
(enantiomeric)

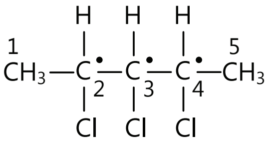


(VI)
(meso)

Total six isomers. In both *cis* and *trans* forms, there are two enantiomers each.

Sol 5: They are identical.

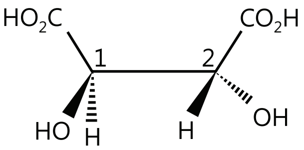
Sol 6: It has only two asymmetric carbon, carbon no.3 is not asymmetric.



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

Sol 7: (D) For S_N2 reaction, the C atom is least hindered towards the attack of nucleophile in the case of CH_3Cl
Hence, (D) is the correct answer.

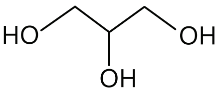
Sol 8: (B)



Both C_1 and C_2 have R – configuration.

Sol 9: (C) α–D–(+) glucose and β–D (+) – glucose are anomers.

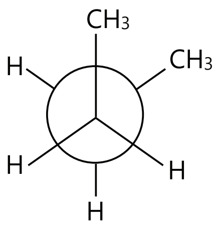
Sol 10:



glycerine

It contains a secondary (2°) hydroxy group.

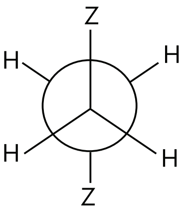
Sol 11: (A)



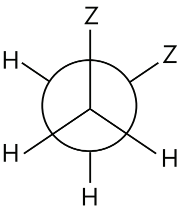
less stable staggered form of butane

(B) The less stability of above mentioned conformer is due to vander Waal's repulsion between the adjacent methyl groups.

Sol 12: (A)



anti



gauche

Mole–fraction of anti form = 0.82

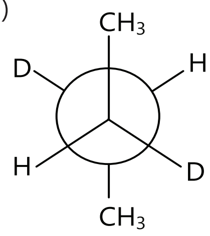
Mole–fraction of gauche form = 0.18

$\mu_{obs} = 1D$

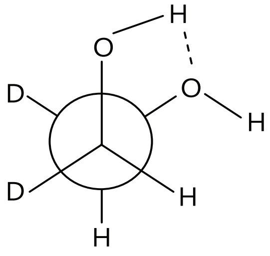
$\Rightarrow 1 = \mu_{anti} \times 0.82 + \mu_{gauche} \times 0.18 \qquad \therefore \ \mu_{anti} = 0$

$\Rightarrow 1 = \mu_{gauche} \times 0.18 \qquad \Rightarrow \mu_{gauche} = \frac{1}{0.18} = 5.55D$

(B)



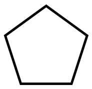
(i)

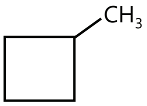


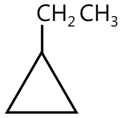
(ii)

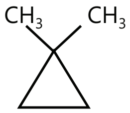
Structure (ii) is more stable than its anti conformer because of intra molecular H–bonding.

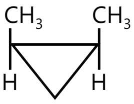
Sol 13:



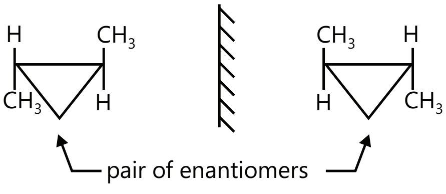








meso



$\Rightarrow$ Total seven isomers