14

Isomerism in Organic Compounds

IN THIS CHAPTER ....

Isomerism

Compounds having the same molecular formula but differ in properties due to difference in their structural formula and spatial arrangement of atoms are called **isomers** and the phenomenon is called **isomerism.**

Usually chemical compounds show different properties due to the presence of different atoms in them. Hence, presence of similar atoms, i.e. same molecular formula with dissimilar properties makes this phenomenon extraordinary. Also, this clearly indicates that the properties of isomers are attributed to their structures or arrangement of atoms in them.

Isomerism can be of the following two types

1. Structural Isomerism

Those isomers which show differences in properties due to the difference in their 2D structures are called structural isomers and this phenomenon is called **structural isomerism**. This isomerism is also called **constitutional isomerism** and categorised in to following sub-types

(i) Chain isomerism
(ii) Position isomerism
(iii) Functional isomerism
(iv) Metamerism
(v) Tautomerism
(vi) Ring-chain isomerism
(vii) Isotopic isomerism

Out of these, tautomerism and ring-chain isomerism are considered as the specialised sub-types of functional isomerism.

2. Stereoisomerism

Those isomers which have the same structural formula along with same molecular formula but differ in their 3D arrangement of atoms or configuration are called stereoisomers and this phonomenon is called stereoisomerism.

Due to difference in configuration this isomerism is also called **configurational isomerism** and can be categorised to

(i) Geometrical or *cis-trans* isomerism,

(ii) Optical isomerism

Remember Neither resonating forms nor-conformations are considered as isomers.

Chain or Nuclear Isomerism

The difference in properties of chain isomers is due to the difference in the order in which their carbon atoms are bonded to each other, e.g. C_5H_{12} have *n*-pentane (normal chain), 2-methyl butane (*iso*-chain) and 2,2-dimethyl propane (*neo*-chain). This isomerism is also called **nuclear** or **skeletal isomerism** as different isomers differ in carbon skeleton.

Important Points Related to Chain Isomerism

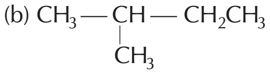
- This isomerism is seen mainly in hydrocarbons. A member with minimum 4C-atoms can show this isomerism.
- Chain isomers may show similar or dissimilar chemical properties but definitely differ in physical properties.

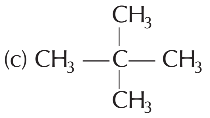
Difference in properties of chain isomers can be explored through following example.

Example 1. *Which isomer of* C_5H_{12} *gives mono-halogenated product in following reaction ?*

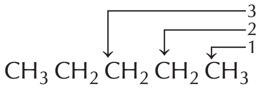
$$C_5H_{12} + X_2 \text{ (1 mole)} \longrightarrow ?$$

(a) $CH_3CH_2CH_2CH_2CH_3$

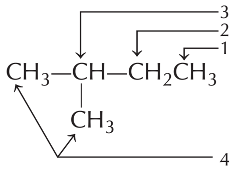
(b)

$CH_3—\underset{\large CH_3}{\underset{|}{CH}}—CH_2CH_3$

(c)

$CH_3—\overset{\large CH_3}{\overset{|}{\underset{\large CH_3}{\underset{|}{C}}}}—CH_3$

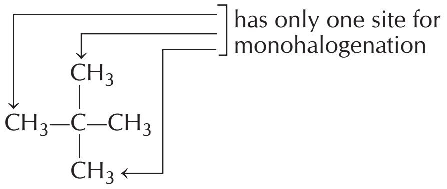
(d) None of these

Sol. (c)


$CH_3CH_2CH_2CH_2CH_3$ has 3 sites at which mono-halogenation can be done. Thus, in this case 3 products are possible.



Similarly, 2-methyl butane have following 4 sites at which mono-halogenation can be done. Thus, in this case 4 products are possible.



However, in 2, 2-dimethyl propane only one site is available in the following way

So, only this can give one product on mono-halogenation.

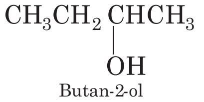
Differences in such a property of given isomers is basically due to the differences in their carbon skeletons.

Position Isomerism

In position isomers, the properties differ due to difference in the position of substituent/functional group or atom in the same chain.

Principally, the phenomenon of position isomerism is visible in those compounds which have **monovalent substituent functional groups** in them.

e.g. **C_4H_9O have**


$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \text{ and } \underset{\text{Butan-2-ol}}{CH_3CH_2\underset{\large OH}{\underset{|}{C}}HCH_3}$$

as their position isomers.

Remember, monovalent functional groups have only one free valency, e.g.

$$—OH, —CHO, —CN, —COOH, —X$$

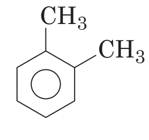
Position of double and triple bond also considered as an example of position isomerism.

e.g. **C_4H_8 have**

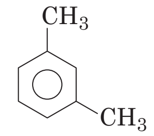
$$\underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} \text{ and } \underset{\text{But-2-ene}}{CH_3CH=CHCH_3}$$

as their positional isomers

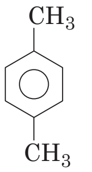
C_8H_{10} have the following positional isomers.



1, 2-dimethyl benzene



1, 3-dimethyl benzene



1, 4-dimethyl benzene

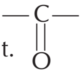
Here, position of one $—CH_3$ differ with respect to other.

Important Points Related to Position Isomerism

- The cyanides, aldehydes, carboxylic acids and their derivatives do not exhibit position isomerism when present singly as these never be considered as branch in such cases.
- Chain and position isomerism cannot exist together, i.e. if two compounds are chain isomers then these will not be considered as position isomers and *vice-versa.*
- Due to difference in the position of groups or atoms, these isomers show difference in physical as well as chemical properties.
- Monosubstituted alicyclic compounds and aromatic compounds do not exhibit positional isomerism.

Example 2. *Which of the following compounds does not show position isomerism ?*

(a) $CH_3CH_2CH_2CH_2CHO$
(b) $CH_3CH_2COCH_2CH_3$
(c) $CH_3CH_2OCH_2CH_2CH_3$
(d) All of the above

Sol. (*d*) $CH_3CH_2CH_2CH_2CHO$ does not show position isomerism as single —CHO group can never be considered as a branch  $-\underset{\underset{O}{\|}}{C}-$ and —O—functional groups are or better to say polyvalent. Hence, $CH_3CH_2COCH_2CH_3$ and $CH_3CH_2OCH_2CH_2CH_3$ also do not show position isomerism.

Functional Isomerism

Isomers which show difference in properties due to difference in functional group attached to them are called functional isomers. e.g.

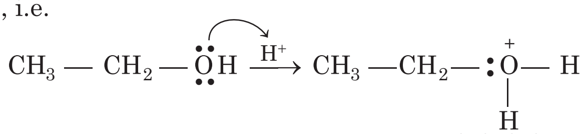
- C_2H_6O have two functional isomers, i.e. C_2H_5OH (ethyl alcohol) and CH_3OCH_3 (dimethyl ether)
- Similarly, $C_2H_4O_2$ have CH_3COOH (acetic acid) and $HCOOCH_3$ (methyl formate) as functional isomers.

Important Facts Related to Functional Isomerism

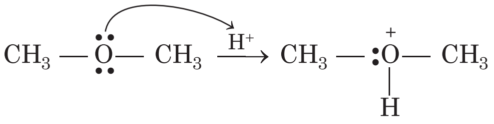
- If two compounds with same molecular formula contain different functional groups, never write chain or position isomerism, there will always be functional isomerism.
- Functional isomers show similar approach towards a reagent (due to the presence of similar atoms) as distribution of electron cloud remains more or less same in their molecules.

  e.g. CH_3CH_2OH and CH_3OCH_3 have similar approach towards H^+ as both have oxygen as central atom with high electron density around itself.

  So, H^+ attacks on the electron cloud of O in both the cases, i.e.



Protonated alcohol



Oxonium ion

Similarly, just like aldehydes and ketones, oxiranes also show nucleophilic additions reactions.

Other examples which show functional isomerism are CH_3CN (cyanide) and CH_3NC (isocyanide)
CH_3NO_2 (nitro) and CH_3ONO (nitrite)

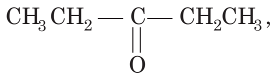
Metamerism

Metamers show difference in properties due to the difference in the nature of same alkyl group attached to the polyvalent functional group.

Here, the word *meta* signifies **middle** e.g.

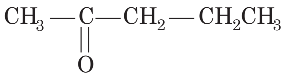
- For $\rangle C{=}O$ group (carbonyl group)

  $C_5H_{10}O$ has three metamers, i.e.



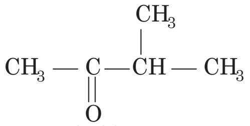
$CH_3CH_2-\underset{\underset{O}{\|}}{C}-CH_2CH_3$,

Pentan-3-one



$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2CH_3$

Pentan- 2-one

and 

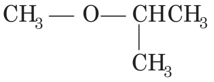
$CH_3-\underset{\underset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{C}H-CH_3$

3-methyl butan-2-one

- For —O— (ether group)

  $C_4H_{10}O$ has four metamersic i.e. $CH_3CH_2-O-CH_2CH_3$ Diethyl ether

  with $CH_3CH_2CH_2-O-CH_3$ Methyl propyl ether and

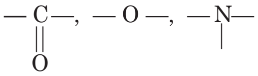


$CH_3-O-\underset{\underset{CH_3}{|}}{C}HCH_3$

Methyl iso- propyl ether

Important Points Related to Metamerism

- Polyvalent functional groups are those functional groups which have more than one free valency. e.g.



$-\underset{\underset{O}{\|}}{C}-,\ -O-,\ -\underset{|}{N}-$

- If two molecules contain same functional group (polyvalent) never write chain or position isomerism for them, it will always be metamerism.
- Metamerism is never shown by alkenes or alkynes.

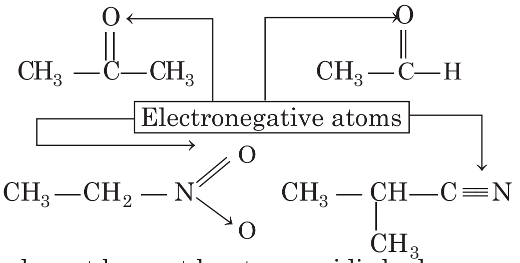
Tautomerism

It is a special type of functional isomerism. Tautomerism is defined as the isomerism in which the molecules have same molecular formulae but different structural formulae due to wandering nature of hydrogen atom in between two polyvalent atoms. The isomers here, are called **tautomers**.

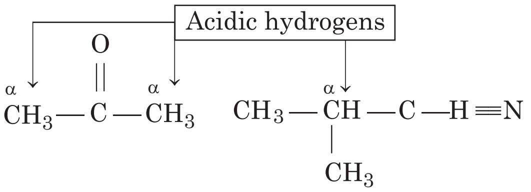
The tautomerism is also called **kryptomerism** or **allelotropism** or **desmotropism** or **dynamic isomerism.**

The structural requirements for tautomerism include

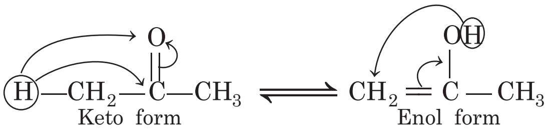
- The compound must have at least one highly electronegative atom (e.g. F, O and N) bonded with a multiple bond.



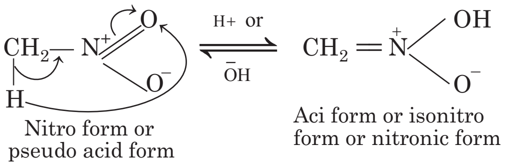
- Compound must have at least one acidic hydrogen present on α-carbon atom of the molecule. e.g.



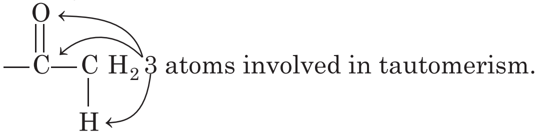
The basic cause of tautomerism is the migration of acidic hydrogen from carbon to multiple bonded electronegative atom, e.g. In acetone tautomerism will be seen as



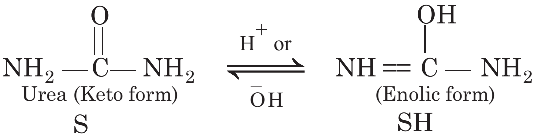
Similarly, nitroalkanes containing α-hydrogen show tautomerism as



The above examples of tautomerism comes under **triad system** as these involve three molecules in tautomeric system, i.e.

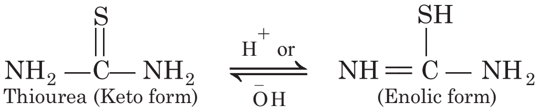


Other examples of such triad system are

(i) 

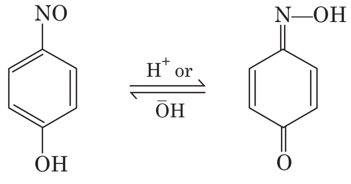
$NH_2-\overset{\overset{O}{\|}}{C}-NH_2 \xrightleftharpoons[\bar{O}H]{H^+\text{ or}} NH=\overset{\overset{OH}{|}}{C}-NH_2$

Urea (Keto form) (Enolic form)

(ii) 

$NH_2-\overset{\overset{S}{\|}}{C}-NH_2 \xrightleftharpoons[\bar{O}H]{H^+\text{ or}} NH=\overset{\overset{SH}{|}}{C}-NH_2$

Thiourea (Keto form) (Enolic form)

(iii) 

p-nitrosophenol
(Enol form)

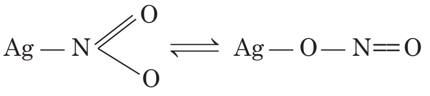
(Keto form)

The other system of tautomers is called dyad system which involves only two atoms along with acidic hydrogen, e.g.

$$H-C\equiv N \rightleftharpoons H-N\overset{\rightarrow}{=}C$$

Hydrocyanic acid Isohydrocyanic acid

Remember Silver nitrate or silver nitrite is the only compound in which tautomerism is shown by the migration of silver instead of hydrogen.



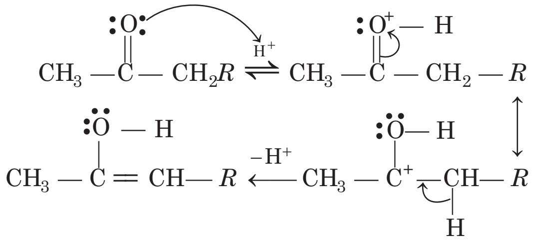
1,2-tautomerism

Important Facts Related to Tautomerism

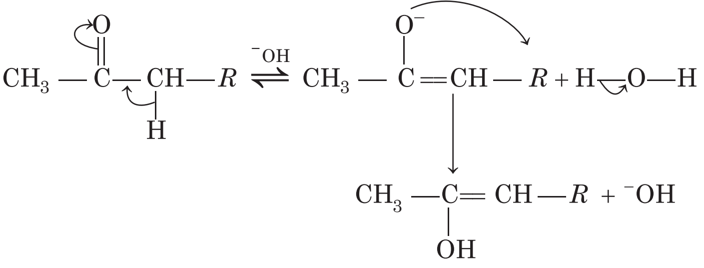
- Tautomers always exist in **dynamic equillibrium.**
- Number of sigma bonds, pi bonds and lone pair of electrons are always same in both the tautomers.
- It is a chemical phenomenon which takes place in liquid and gaseous phase only. It never takes place in solid state.

The process can be catalysed by the acid as well as bases as shown below.

(i) **Acid catalysed conversion**



(ii) **Base catalysed conversion**

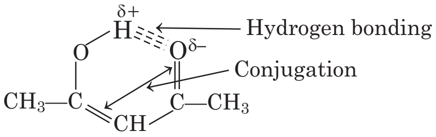


- The conversion of keto form into enol form is called **enolisation** and depends upon various factors such as (i) structure-especially from resonance and hydrogen bonding point of view (ii) temperature and (iii) the nature of solvent.

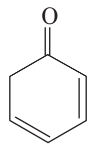
Among these the most important aspect is the structural aspect, e.g.

(i) Ketonic form predominates in simple monocarbonyl compounds like CH_3CHO, CH_3COCH_3 etc., (due to greater bond strength of $\gt C=O$ bond in comparison to $\gt C=C\lt$ bond.

(ii) Similarly enolic forms predominate in β-diketones due to intramolecular hydrogen bonding and resonance, e.g. the $CH_3COCH_2COCH_3$ will have



- In most of the cases of keto enol tautomerism, the quantity of keto form is always greater than the enol form, i.e. keto form is more stable than the enol form. But in certain cases enol form also predominates.The percentage of enolic contents of some common compounds in decreasing order is given below.

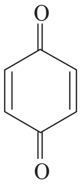


$> C_6H_5COCH_2COCH_3 > CH_3COCH_2COCH_3 >$

(Maximum enolic content)

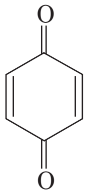
$CH_3COCH_2COOC_2H_5 > CH_3COCH_2CHO > CH_3COCH_3 >$

$CH_3CHO >$



(Least enolic content)

- Compound having quinonoid structure does not show tautomerism because of the absence of free α–H atoms. e.g.



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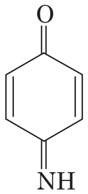


- **Enol content** is also affected by solvents. It increases in non-polar aprotic solvents and decreases in polar protic or polar aprotic solvents. Enol content order in different solvents is

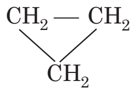
  Hexane > benzene > acetone > methanol > H_2O
  (Max.) (Min.)
- Enol content being more volatile is separated by careful distillation of the mixture in a fused quartz apparatus.
- Enol content is reduced due to steric factor as well e.g. the enol content of α-methyl acetyl acetones is much lower (44% in gaseous state) as compared to that of acetyl acetone (92% in gaseous state) due to greater internal strain in the former case.

Ring Chain Isomerism

If one isomer has open chain structure and the other has cyclic structure then isomers are known as **ring chain isomers** and isomerism is called **ring chain isomerism**. Ring chain isomers are also specialised functional isomers. e.g.

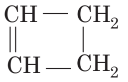
(i) Alkene and cycloalkane

C_3H_6, i.e. $CH_3 — CH = CH_2$ and



(ii) Cycloalkene and alkyne

C_4H_6, i.e.

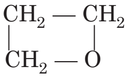


$$\begin{matrix} CH — CH_2 \\ \| \quad\quad | \\ CH — CH_2 \end{matrix}$$

and $CH_3 — CH_2 — C \equiv CH$

(iii) Alkenol and cyclic ether

C_3H_6O, i.e. $CH_2 = CH — CH_2OH$ and



$$\begin{matrix} CH_2 — CH_2 \\ | \quad\quad | \\ CH_2 — O \end{matrix}$$

Isotopic Isomerism

In this isomerism, isomers show difference in their properties due to the presence of different isotopes of an element with in the compound. e.g.

H_2O and D_2O; $^{12}CH_4$ and $^{14}CH_4$

Geometrical Isomerism

When a π-bond is present or we observe a cyclic hydrocarbon the restriction for the free rotation of atoms around their axis is visible. This give rise to two different structural formulae or forms :

The properties of these forms differ due to different arrangement of atoms about double bonds in alkenes or about single bonds in cyclic compounds their.

So, this isomerism which arises due to difference in spatial arrangement of groups about the

- doubly bonded C-atoms in **alkenes,**
- single bonded C-atoms in **cyclic compounds,**
- doubly bonded C and N-atoms in **oximes,**
- doubly bonded N-atoms in **diazo compounds,** is called **geometrical isomerism.**

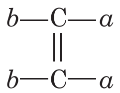
Conditions for Exhibiting Geometrical Isomerism

The conditions for exhibiting geometrical isomerism include following two elaborations

- There should be frozen rotation about two atoms in the molecules, e.g.
  (i) $>C=C<$, i.e. alkenes there is frozen rotation about C— C double bond.
  (ii)  , i.e. cycloalkanes there is frozen rotation about carbon-carbon single bond.
  (iii) $>C=N$, i.e. there is oximes and imines frozen rotation about carbon-nitrogen double bond.
  (iv) $—N=N—$, i.e. azo compounds there is frozen rotation about nitrogen-nitrogen double bond.
- Both the atoms of above written bonds should contain different substituents.

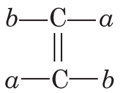
Geometrical Isomerism in Alkenes

Among the forms which are associated with an alkene, the forms in which similar groups are present on the same side of double bond are called ***cis* forms** [Latin *cis* = same side] and the forms, in which similar groups are present on the different sides are called ***trans* forms** [Latin *trans* = across]. e.g.



$$\begin{array}{c} b\text{—C—}a \\ \| \\ b\text{—C—}a \end{array}$$

cis-form

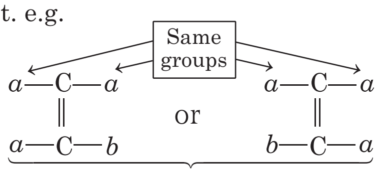


$$\begin{array}{c} b\text{—C—}a \\ \| \\ a\text{—C—}b \end{array}$$

trans-form

These forms show usually similar chemical but different physical properties. However some of these forms may show difference in chemical properties as well.

Geometrical isomerism is not seen in those forms in which the doubly bonded carbon atom have same groups attached to it. e.g.



$$\underbrace{\begin{array}{c} a\text{—C—}a \\ \| \\ a\text{—C—}b \end{array} \quad \text{or} \quad \begin{array}{c} a\text{—C—}a \\ \| \\ b\text{—C—}a \end{array}}$$

Both the structures are identical

Above written geometrical figures are identical, hence, no geometrical isomers are possible for such compund.

The conversion of *cis* isomer into *trans* isomer or *vice-versa* is possible only if either of the isomer is heated to a high temperature or absorbs light. The heat supplies the energy to break the π-bond.

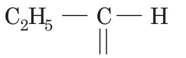
Some examples of geometrical isomers are as

- Two geometrical isomers are possible for **hex-3-ene** ($CH_3CH_2CH = CHCH_2CH_3$). This is because each doubly bonded carbon atom is attached to two different groups, i.e. —CH_2CH_3 and H.

  The *cis* and *trans* isomers of hex-3-ene are shown below.

$$\begin{array}{c} C_2H_5\text{ — C — H} \\ \| \\ C_2H_5\text{ — C — H} \end{array}$$

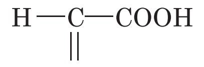
cis-hex-3-ene



$$\begin{array}{c} C_2H_5\text{ — C — H} \\ \| \\ \text{H — C — }C_2H_5 \end{array}$$

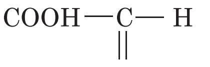
trans-hex-3-ene

- Both **fumaric** and **maleic acids** have the same molecular formula, $C_4H_4O_4$. They differ in most of their physical properties and in some of their chemical properties.
- Originally they were thought as structural isomers and assigned different names. Later on van't Hoff suggested them as geometrical isomers. Maleic acid, which gives anhydride at lower temperatures, is infact the *cis* acid, while fumaric acid is its *trans* isomer.



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

Maleic acid [*cis*]



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

Fumaric acid [*trans*]

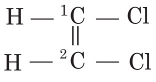
These isomers are

- differ in physical properties such as melting point, dipole moment and acidities. The *trans* isomer has no dipole moment since it is symmetrical, unlike the *cis* isomer. The *cis* isomer is stronger acid than the *trans* isomer.
- differ even in chemical properties, as well e.g. *cis* acid undergo dehydration at 100°C and form an anhydride. However the *trans* acid does not form an anhydride until heated to 240°C.
- at that temperature there is sufficient thermal energy to break the double bond, so that the *cis* acid changes to *trans* and then anhydride is formed in sucession. They can be separated by conventional techniques like fractional distillations, gas chromatography etc.

General Points of Distinction Between *cis* and *trans* Isomers

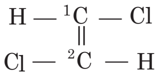
- The *trans* forms are more stable than the corresponding *cis* isomer. This is because, in the *cis* isomer, the bulky groups are on the same side of double bond. Their steric repulsion is maximum thus making the *cis* isomer less stable.
- The condition is reverse in *trans* isomers in which the bulky groups are far apart.
- Melting point of *trans* form is higher than the melting point of *cis* form because of symmetrical packing of *trans*-compounds in its crystal lattice.
- Boiling point of *cis* form is higher than that of the *trans* form because of steric hindrance and high polarity of *cis*- compound.
- Solubility of *cis*-isomer is higher as compared to *trans*-isomer, because molecules of *trans*- isomer are more tightly held in the crystal lattice than the corresponding *cis*-isomer.

  So, it is easier to break the crystal lattice of *cis*-isomer as compared to *trans*- isomer.
- Generally, a *cis*-isomer cyclises on heating to form the corresponding anhydride at lower temperatures, while a *trans*-isomer forms its anhydride at higher temperatures with difficulty.
- The *cis*-isomer of a **symmetrical** alkene has a definite dipole moment, while the *trans*- isomer has zero dipole moment. e.g.



$$\begin{array}{c} \text{H — }{}^1\text{C — Cl} \\ \| \\ \text{H — }{}^2\text{C — Cl} \end{array}$$

cis-dichloroethene
($\mu = 1.9D$)

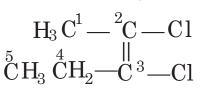


$$\begin{array}{c} \text{H — }{}^1\text{C — Cl} \\ \| \\ \text{Cl — }{}^2\text{C — H} \end{array}$$

trans-dichloroethene
($\mu = 0.0D$)

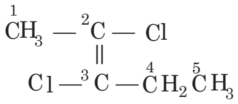
In *trans* isomer shown above, the effect produced in one half of the molecule is cancelled by that in the other half of the molecule.

- In case of **unsymmetrical** alkenes, the *cis*- isomer has higher dipole moment than the corresponding *trans*-isomer. e.g.



$$\begin{array}{l} H_3\overset{1}{C}-\overset{2}{C}-Cl \\ \qquad\quad \| \\ \overset{5}{C}H_3\overset{4}{C}H_2-\overset{3}{C}-Cl \end{array}$$

cis-2,3-dichloropent-2-ene
(high dipole moment)



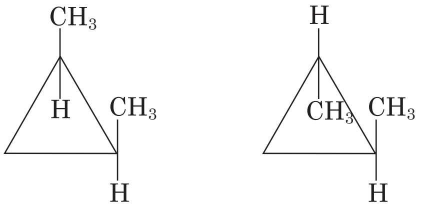
$$\begin{array}{l} \overset{1}{C}H_3-\overset{2}{C}-Cl \\ \qquad\quad \| \\ Cl-\overset{3}{C}-\overset{4}{C}H_2\overset{5}{C}H_3 \end{array}$$

trans -2,3 dichloropent-2-ene
(low dipole moment)

Geometrical Isomerism in Cyclic Compounds

Geometrical isomerism is also possible in cyclic compounds as no free rotation is possible about carbon-carbon single bonds in such compounds.

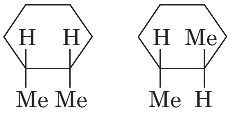
Thus, for rotation, bond breaking is required which results in the ring cleavage. e.g. **1,2-dimethyl cyclopropane** exists in the following two isomeric forms



cis-form *trans*-form
1,2-dimethyl cyclopropane

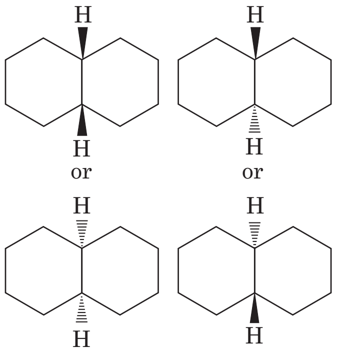
Other examples of cyclic compounds exhibiting geometrical (*cis-trans*) isomerism are as follows

(i)



cis *trans*
1,2-dimethyl cyclohexane

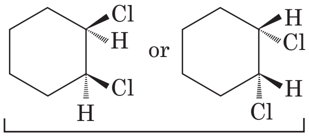
(ii)



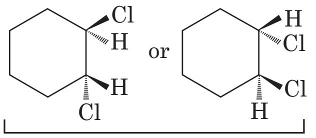
cis *trans*

decalin or bicyclo (4. 4. 0)
decane or decahydro naphthalene

(iii)



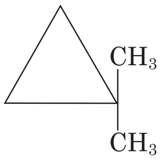
cis-1,2-dichloro cyclohexane



trans-1,2-dichloro cyclohexane

A requirement for geometrical isomerism in cyclic compounds is that there must be at least two other groups besides hydrogen on the ring and these must be on different C-atoms of the ring.

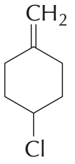
For example no geometrical isomers are possible for 1, 1-dimethylcyclopropane.



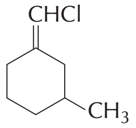
1,1-dimethyl cyclopropane (no isomers possible)

Example 3. *Among the following compounds, geometrical isomerism is exhibited by* ***(JEE Main 2020)***

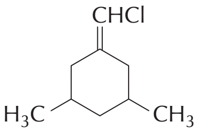
(a)



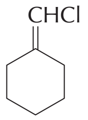
(b)



(c)

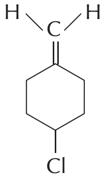


(d)



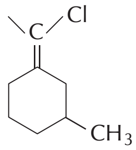
Sol. (*b*) Look for the condition two different groups must be attached to any two carbon atoms of restricted rotation.

(a)

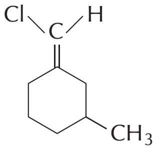


Does not show geometrical isormerism

(b)

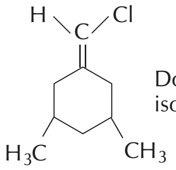


and



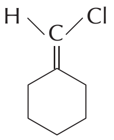
show geometrical or possible *cis* and *trans* isomers

(c)



Does not show geometrical isomerism

(d)



Does not show geometrical isomerism

Geometrical Isomerism in Nitrogen Compounds

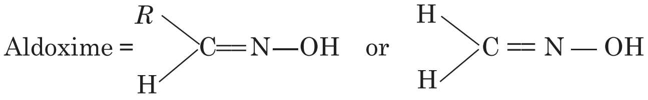
Geometrical isomerism is also seen in oximes, imines and azo compounds. All of them are nitrogen compounds.

The oximes are formed by the reaction of carbonyl compounds, i.e. $>C=O$ compounds or aldehydes and ketones with NH_2OH (hydroxyl amine) as

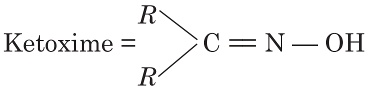
$$>C=\boxed{O + H_2}N-OH \longrightarrow >C=\underset{\text{Oxime}}{N}-OH + H_2O$$

If $>C=O$ is aldehyde then oxime is called aldoxime.

If $>C=O$ is ketone then oxime is called ketoxime.Hence,



$$\text{Aldoxime} = \begin{matrix}R\\ H\end{matrix}\!\!>C=N-OH \quad \text{or} \quad \begin{matrix}H\\ H\end{matrix}\!\!>C=N-OH$$



$$\text{Ketoxime} = \begin{matrix}R\\ R\end{matrix}\!\!>C=N-OH$$

In nitrogen compounds, the steric repulsion occurs

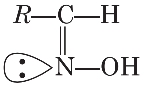
(a) between the lone pair of nitrogen with bond pair of larger group in oximes and imine

(b) between the two lone pairs of two nitrogens, e.g. of azo compounds resulting to *syn* (corresponding to *cis*) and *anti* (corresponding to *trans*) forms.

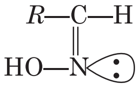
Some examples of these are given below

1. **In oximes** There are two oximes aldoximes and ketoximes. Their geometrical isomers are discussed below.

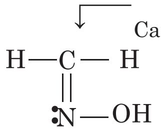
   (i) **In aldoximes**



syn oxime



anti oxime

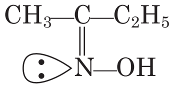


Carbon atom attached with same groups

No geometrical isomer

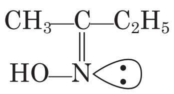
Thus, the first member of aldoximes does not show any geometrical isomer.

   (ii) **In ketoximes**



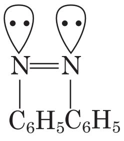
This compound is *syn* for ethyl group and *anti* for methyl group or this can be called *anti* compound.

Similarly,



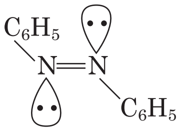
This compound is *anti* for ethyl group and *syn* for methyl group or this can be called *syn* compound.

2. **In azo compounds** Azo compounds also show *syn* and *anti* geometrical isomers.



syn azo

and



anti azo

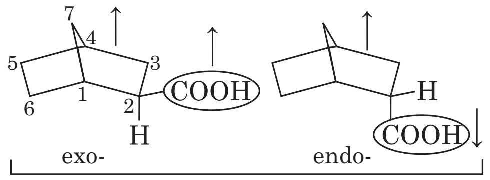
Exo and Endo forms in Bicyclic Compounds

Exo and endo forms are seen in the case of bicyclic compounds.

When two rings or a ring and a group are in *cis*-position, it is called **exo-stereoisomer**, when two rings or a ring and a group are in *trans*-position, it is called **endo-stereoisomer**,

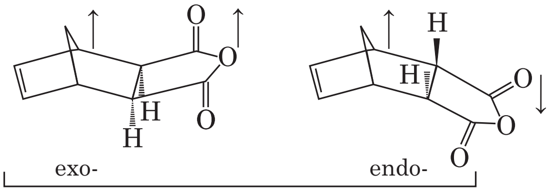
e.g.

(i)



Bicyclo [2. 2. 1] heptane-2-carboxylic acid

(ii)

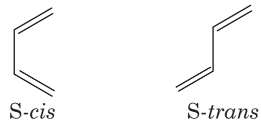


Bicyclo-2. 2. 1 hept-5-ene-2, 3-dicarboxylic anhydride

It is quite obvious that endo-stereoisomer is more stable than exo-stereoisomer.

Geometrical Isomerism Across a Single Bond

cis-and *trans*-isomerism is also possible across a single bond, e.g. in buta-1,3-diene.



S-*cis* S-*trans*

S-cis form of butadiene undergoes Diels Alder reaction very easily with dienophile while *S-trans* does not.

Calculation of Number of Geometrical Isomers

The number of geometrical isomers of a compound can be calculated with the help of following formulae.

(i) In **compounds with *n* number of π-bonds and different ends**, number of geometrical isomers = 2^n.

(ii) In **compounds with *n* number of π-bonds and similar ends**.

***Case* I** When n = even number

Then, number of geometrical isomers

$$= 2^{(n-1)} + 2^{\left(\frac{n}{2}-1\right)}$$

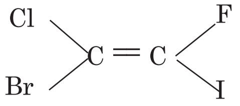
***Case* II** When n = odd number

Then, number of geometrical isomers

$$= 2^{(n-1)} + 2^{\left(\frac{n+1}{2}-1\right)}$$

E, Z-System of Geometrical Isomers

cis and *trans* system of geometrical isomerism cannot work in compounds which do not have identical groups on both the sides of double bond, e.g.



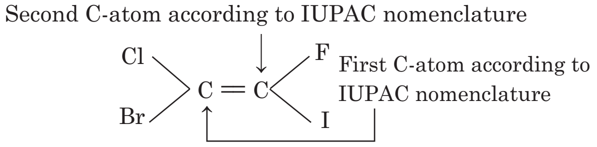
1-bromo-1-chloro-2-fluoro-2-iodoethene

The configuration of these kind of compounds can be specified by using the notations *E* (from German *Entgegen* = opposite) and *Z* (from German *Zusammen* = together). Out of these *E* forms are analogous to *cis* forms while *Z* forms are analogous to *trans* forms.

For determining *E* and *Z* configurations, we have to assign priority to the groups attached to the doubly bonded C-atoms. The rules for assigning the priority are as follows

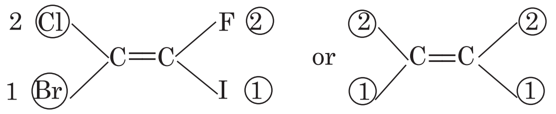
I. The priority can be assigned on the basis of the atomic number of the atom or group attached. In fact the atomic number of that atom of the group is considered which is attached directly to the C-atom.

The group with higher atomic number will get the first priority, e.g. For the compound 1-*bromo*-1-*chloro*-2-*fluoro*-2-*iodo*-*eth*-1-ene as shown below



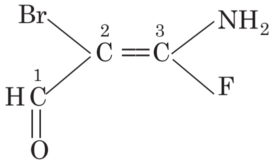
Out of chlorine and bromine attached to first C-atom, the atomic number of Br is higher, thus, Br gets priority over Cl.

Similarly out of fluorine and iodine attached, the atomic number of iodine is greater thus it will get priority over F. Thus, the compound looks like



Now as it is very clear that the bulky groups are at the same side of double bond, hence the above form is ***Z*-form**.

II. Similarly, in the compound 3-amino-2-bromo-3-fluoroprop-2-en-1-al



The priorities are given as

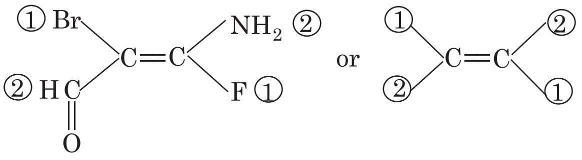
(i) It is written earlier that if the functional group contains more than one atom then the atomic number of that atom is considered which is attached directly to the doubly bonded C-atom.

So, out of two groups, i.e. Br and — CHO attached to the C-atom number 2, the atomic number of Br is greater than the C-atom of — CHO group.

Hence, in this case Br gets priority over —CHO group.

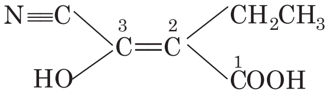
(ii) Out of the two groups attached to the C-atom number 3, i.e. F and —NH_2, the atomic number of F is greater than that of the N of —NH_2 group, thus F gets priority over —NH_2 .

Hence, the compound will looks like



Now, as it is very clear that the bulky groups are at the opposite side of double bond, hence the above form is called ***E*-form**.

III. Now, if two or more atoms are attached to doubly bonded C-atoms with the same atomic number, then the priority is given according to the atomic number of next connected atom. It is shown in the compound written below



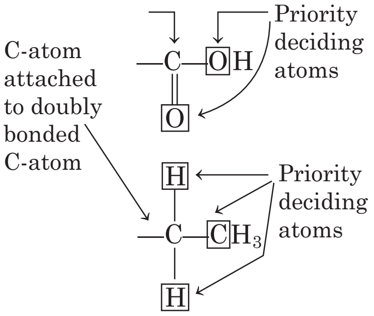
2-ethyl-3-cyano-3-hydroxy prop-2-en-1-oic acid

Here,

(i) Out of the — OH and — CN groups which are attached to the 3rd C-atom, the atomic number of oxygen of — OH group is greater than the atomic number of C-atom of —CN group. Hence, — OH gets priority over — C≡N.

(ii) On the other hand, out of the two groups attached to C-atom number 2, each one begins with C-atom.

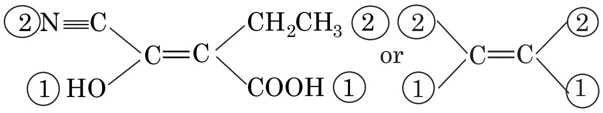
Here, the — COOH group is given priority over — CH_2CH_3 group due to following reason.



In —COOH all the three remaining valencies of C-atom are satisfied with oxygen atoms as shown.

In —CH_2CH_3 out of remaining 3 valencies of C-atom, two are satisfied with H-atom and one with C-atom as shown.

Thus, oxygen of first case is preferred over C or H of second case and the compound looks like



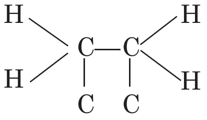
i.e. the compound is in ***Z*-form.**

From the above point (3) the two things are clear

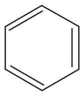
(i) If atoms attached to doubly bonded C-atoms are same, the priority is determined by going towards next connected.

(ii) Multiple bonds are treated as if each atom of the multiple bond is attached to similar multiple atoms.

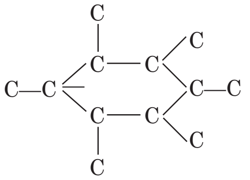
e.g. $H_2C{=}CH_2$ will be treated as



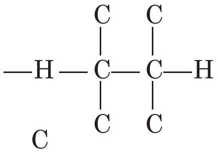
or



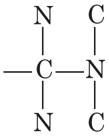
will be as



or $HC{\equiv}CH$ will be as



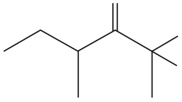
Similarly, — $C{\equiv}N$ as



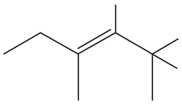
and so on.

Example 4. *Which of the following alkenes shown below has the Z-configuration of its double bond?*

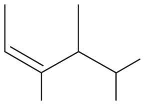
(a)



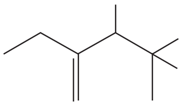
(b)



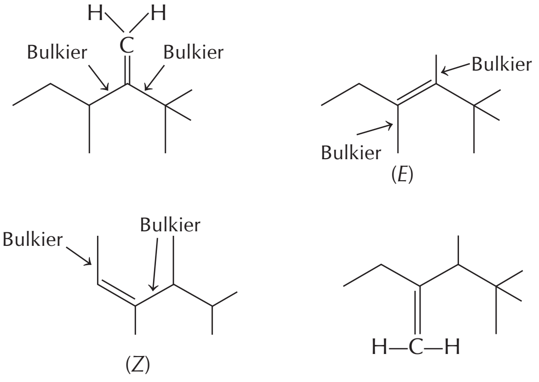
(c)



(d)



Sol. (c) *Z*-configuration shows the presence of bulkier groups at the same side of double bond.



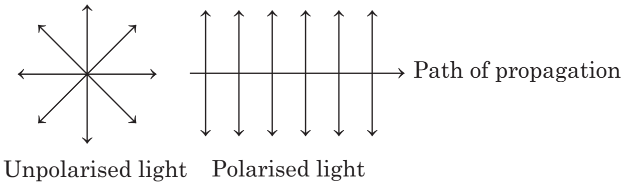
Optical Isomerism

Compounds with similar or dissimilar physical as well as chemical properties and with marked difference in their behaviour towards plane polarised light are called optical isomers and their this property is called optical isomerism. Before going in detail it is better to understand some terms related to this isomerism.

Important Terms Related to Optical Isomerism

(i) **Polarised light** According to wave theory, an ordinary ray of light is considered to have particulate vibrations in all possible planes perpendicular to its path of propagation.

However, in polarised light the particulate vibrations occur in any one plane only.



Polarised light is produced when ordinary light is passed through *Nicol Prism* or *polarising filters*.

(ii) **Optical activity** The property of a compound by virtue of which it can rotate the plane of polarised light, is called optical activity and such a compound is called optically active.

(iii) **Asymmetric C-atom** The C-atom which have 4 different groups or atoms attached separately to its four valencies is called asymmetric carbon atom.

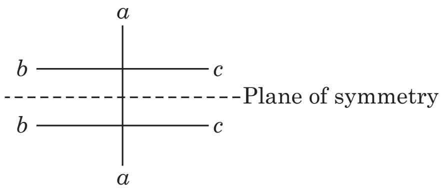
(iv) **Chiral molecule** A molecule completely lacking plane of symmetry is called chiral molecule. In other words, it can also be defined as the molecule which is not superimposable on its mirror reflection or the molecule in which line of symmetrisation is lacking.

As “asymmetric” and “chiral” words are synonymons hence asymmetric C-atom will generally be considered as chiral.

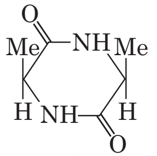
(v) **Achiral molecule** A molecule which is superimposable on its mirror image is called achiral.

(vi) **Elements of symmetry** The terms related to following elements of symmetry are frequently used in optical isomerism.

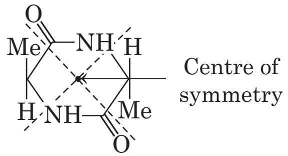
(a) **Plane of symmetry**



(b) **Centre of symmetry**

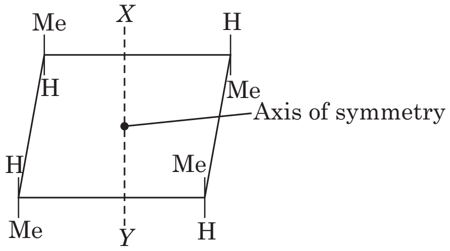


no centre of symmetry
(*cis*-form)



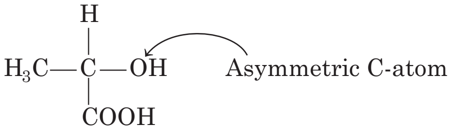
trans-form
(has centre of symmetry)

(c) **Axis of symmetry**



Categories of Optical Isomers

Usually the compounds having atleast one asymmetric C-atom are capable of exhibiting optical isomerism, e.g. **lactic acid**.



$$H_3C-\overset{H}{\underset{COOH}{C}}-OH$$

Optically active

On the basis of functionality the optical isomers can be categorised into the following two types

1. Optically Active

Those isomers which have the ability to rotate the plane of polarised light are called **optically active isomers.** These isomers are infact chiral, i.e. don't have elements of symmetry.

Among the optically active isomers following two types are included.

(i) **Dextrorotatory or *d*-or** (+) **forms** which rotate the plane of polarised light to the right hand side or in clockwise direction.

(ii) **Laevorotatory or *l* or** (–) **forms** which rotate the plane of polarised light to the left hand side or anti-clockwise.

2. Optically Inactive

Those isomers which do not have such an ability, i.e. which do not rotate the plane of polarised light are called **optically inactive isomers.**

The reasons for the inactivity of these isomers may be one of the following

(i) presence of element of symmetry

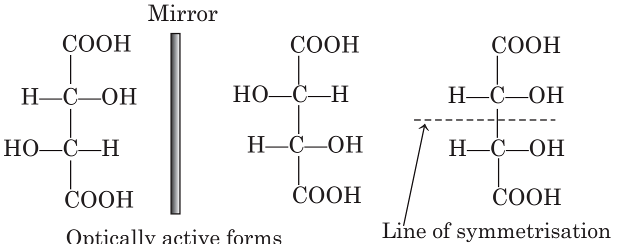
(ii) presence of *d* and *l*-forms in equal amounts.

On the basis of above reasons, optically inactive isomers can be further, categorised to following two types

(i) ***Meso* form** It has the plane of symmetry within the molecule, i.e. **the one half of the molecule is dextrorotatory** and **rest half is laevorotatory.** Thus, within the molecule both halves show equal and opposite optical activity.

As a result, the net molecule becomes optically inactive. This phenomenon of optical inactivation in which the rotation produced by one half of the molecule is cancelled by its another half is called **internal compensation**.

This simply means *meso* forms are said to be optically inactive due to the phenomenon of internal compensation. e.g. The optically active and inactive forms of tartaric acid are given below.



Optically active forms

meso tartaric acid

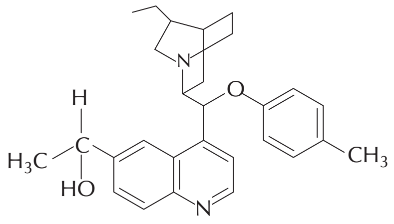
(ii) **Racemic mixture** The equimolar mixture of two optically active forms (*d* and *l*-forms) of a compound is called racemic mixture. This mixture is optically inactive as both the forms cancel out the optical activity of one another.

Such a cancelling effect is called **external compensation.** This simply means racemic mixtures are optically inactive due to the process of external compensation.

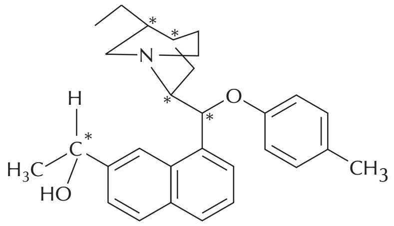
The process of formation of racemic mixture is called **racemisation** while separation of these forms from the mixture is called **resolution.**

Resolution can be achieved by mechanical methods, biological methods using enzymes, chemical methods (by making their diastereomers) or by chromatographic separation (by using special adsorbents).

Example 5. *The number of chiral carbons present in the molecule given below is …… .* ***(JEE Main 2020)***



Sol. (5)



The molecule contains five chiral carbon (C*) atoms.

On the basis of structural aspect, the optical isomers can be categorised into following types

1. Enantiomers

Optically active compounds which are non-superimposable mirror images of each other are called enantiomers. e.g. In tartaric acid shown above first two figures written are called enantiomers.

Remember, an asymmetrical object can have only single mirror image, thus an optically active compound (being asymmetrical) can have only one enantiomer always. Secondly this mirror image is always non-superimposable.

The properties of the enantiomers include

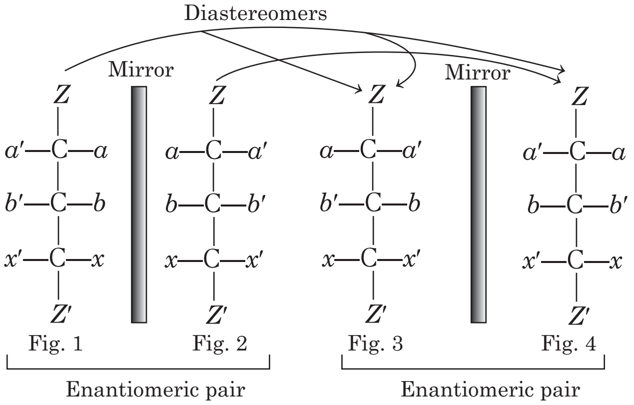
(i) These are stable compounds that differ from one another in three dimensional spatial arrangements.

(ii) These cannot be interconverted under ordinary conditions.

(iii) These have many identical properties but certainly differ in their interaction with plane of polarised light.

2. Diastereomers

Optical isomers which are not the mirror images of each other are called diastereomers, e.g. in the following compounds



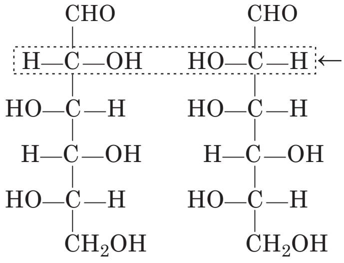
The outline structure of all the four given figures is same as their IUPAC names are same. However, spatial arrangement of their groups differ as fig. (1) and (2) are enantiomeric, similarly fig. (3) and (4) are enantiomeric.

But fig. (1) is diastereomeric with fig. (3) and (4) because all of them have same molecular formula, different optical behaviour and no mirror image relationship. Similarly fig. (2) is diastereomeric with fig. (3) and (4).

Contrary to enantiomers, two diastereomers have different melting points, boiling points and solubilities. They will have different chemical reactivities towards most reagents. It means overall they show significant differences in physical as well as in chemical properties both.

The diastereomers are further categorised to following two types

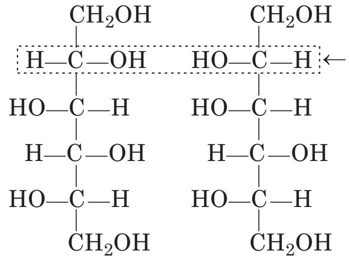
(i) **Epimers** The pair of diastereomers which differ in configuration about a single interstitial C-atom are called epimers. e.g.



L-(+)-glucose L-(+)-mannose

←**Epimeric C-atom showing enantiomeric condition;** note rest of the structure of both the compound is exactly same

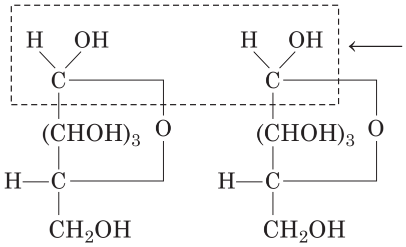
Similarly,



←Epimeric C-atom

Sorbitol Mannitol

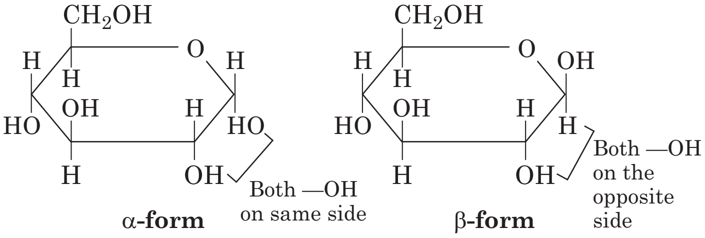
(ii) **Anomers** The pair of diastereomers that differ only in configuration about a **single terminal C-atom**, are called **anomers**, i.e. the ring forms of sugars are anomeric, i.e.



α-glucose β-glucose

←**Anomeric terminal C-atoms** with rest of the structures are exactly same.

In Howarth configuration, the α and β forms of glucose are identified as



Remember, ring forms of sugars are formed when powdered sugars are dissolved to make solutions.

Calculation of Number of Optical Isomers

The number of optical isomers depends upon the number of asymmetric centres and can be calculated with the help of following general relations

1. In molecules **which are not divisible into two equal halves** and **have *n* number of asymmetric C-atoms**
   - (i) Number of optically active forms $= 2^n = a$
   - (ii) Number of enantiomeric pairs $= a/2$
   - (iii) Number of racemic mixtures $= a/2$
   - (iv) Number of *meso* forms = 0
2. In molecules **which are divisible into two equal halves**.

   ***Case* I** When $n =$ even number,
   - (i) Number of optically active forms $= (a) = 2^{n-1}$
   - (ii) Number of enantiomeric forms $= a/2$
   - (iii) Number of racemic mixtures $= a/2$
   - (iv) Number of *meso* forms $= (m) = 2^{\left(\frac{n}{2}-1\right)}$
   - (v) Total number of configurational isomers $= a + m$

   ***Case* II** When $n =$ odd number,
   - (i) Number of optically active forms $= (a) = 2^{(n-1)} - 2^{\left(\frac{n-1}{2}\right)}$
   - (ii) Number of enantiomeric pairs $= a/2$
   - (iii) Number of racemic mixtures $= a/2$
   - (iv) Number of *meso* forms $= (m) = 2^{\left(\frac{n-1}{2}\right)}$
   - (v) Total number of configurational isomers $= a + m$

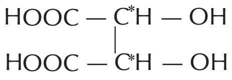
Remember

- Geometrical isomers may also be considered as diastereomers as they have different physical properties.
- Stereoisomers that are not the mirror images of each other are also called diastereomers.

Example 6. *The number of opitcal isomers for the compound* $(CH(OH)COOH)_2$ *is*

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

Sol. (c) The structure of the compound can also be written as



$$\begin{array}{l} HOOC - \overset{*}{C}H - OH \\ \qquad\quad\;\; | \\ HOOC - \overset{*}{C}H - OH \end{array}$$

∴ No. of asymmetric C atoms $(C^*) = 2$ but the two ends are similar or the molecule is divisible into equal values.

Hence, $a = 2^{n-1} = 2^{2-1} = 2$

$$m = 2^{\frac{n}{2}-1} = 2^{\frac{2}{2}-1} = 2^\circ = 1$$

No. of optical isomers = 2 + 1 = 3

Optical Isomerism in Compounds having no Asymmetric C-atom

Besides such compounds which have asymmetrical C-atoms, there are certain other compounds also which show optical activity but lack any asymmetric C-atom.

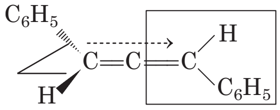
These compounds show optical activity just because of the fact that their molecule is chiral, means lack symmetrisation completely. e.g.

1. Allene Derivatives

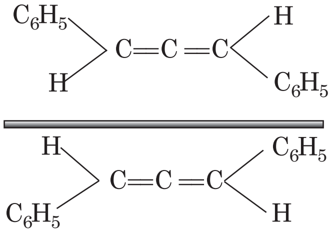
Some of the allene derivatives show optical activity as 1, 3-diphenyl propadiene. In this compound the central atom forms two $sp - sp^2$ σ-bonds.

The central atom also has two π orbitals, which are mutually perpendicular to each other and form π-bonds with the *p*-orbitals of other C-atoms.

As a result the substituents at one end of the molecule are in a plane which is perpendicular to that of the substituents at the other end as shwon below.

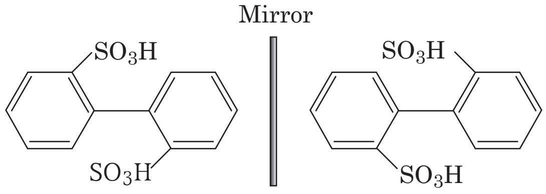


Thus, the compound exists in two forms which are non-superimposable mirror images and are optically active.



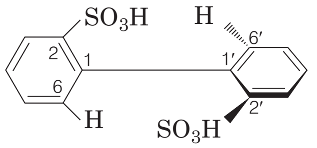
2. Biphenyl Derivatives

Substituted biphenyls also show optical isomerism. It is seen when substituent in the 2-positions are large enough to prevent rotation about the bond joining the two benzene rings, e.g. biphenyl-2, 2′ -disulphonic acid exists in following two forms.



These two forms are non-superimposable mirror images. They do not interconvert at room temperature because the energy required to twist one ring through 180° relative to the other is too high.

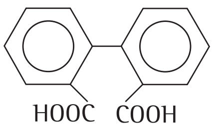
This is so because during the twisting process, the two $-SO_3H$ groups must come into very close proximity when the two benzene rings become coplanar and strong repulsive forces are introduced. In spatial arrangement the molecule show following arrangement.



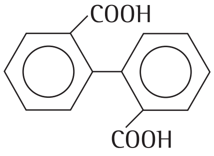
Remember This type of stereoisomerism arising from restricted rotation about a single bond (and where the stereoisomers can be isolated) is called **atrop isomerism** and the isomers are called **atrop isomers**.

Optical Inactivity of Diphenic Acid

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



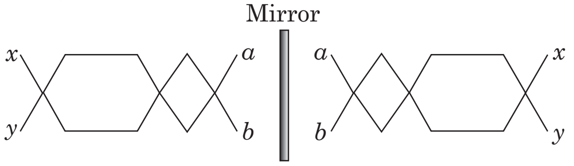
(I)



(II)

3. Spiranes

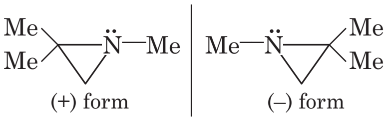
When two double bonds in allenes are replaced by two cycloalkane rings, the resulting system also show optical isomerism, as shown below



4. *t*-amines, Amine Salts and *t*-carbanion

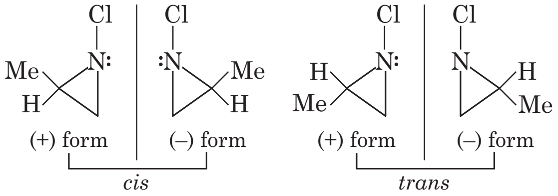
Amine and carbanion with a lone pair of electrons are chiral as they have pyramidal geometry, but they are optically inactive. Their lone pair is considered as the 4th group. However, amine salts are optically active, e.g. $[R_1R_2R_3N^{\oplus}H]Cl^{\ominus}$.

Some more examples of optically active N-containing compounds are



1,2,2-trimethyl aziridine

Similarly, 1-chloro-2-methyl aziridine shows four stereoisomers



Systems of Nomenclature of Optical Isomers

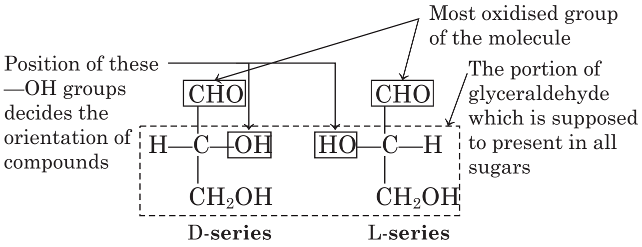
The nomenclature of optical isomers can be done in accordance with following three systems.

1. Dee-Eel (D,L) system of nomenclature
2. *Erythro* and *threo* system of nomenclature
3. The *R,S* (*Rectus*, *sinister*) system of nomenclature or system of absolute configuration.

1. D, L System of Nomenclature or Partial Configuration

The D, L system of nomenclature is used for optically active polyhydroxy carbonyl compounds, i.e. carbohydrates mainly. This nomenclature was given by **Emil Fischer** who considered glyceraldehyde as the parental sugar.

In this system when a molecule is visualised with keeping its most oxidised group at the top, then the position of —OH group at the second last C-atom decides the configuration as shown below.



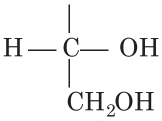
Glyceraldehyde

This configuration is based on the fact that 2-lower most C-atoms of every molecule represent glyceraldehyde as shown.

All sugars whose Fischer projection formula shows the —OH group on the right hand side on second last chiral C-atom adjacent to the terminal $—CH_2OH$ group are called the sugars of D-series.

Hence, all sugars having below written structure at their terminus will belong to the **D-series.**

Position of this —OH decides configuration.



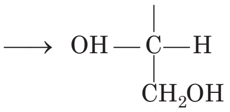
$$\begin{array}{c} | \\ H—C—OH \\ | \\ CH_2OH \end{array}$$

D-series

Remember Here, D stands for dextro, i.e. right hand side and not dextrorotatory.

Similarly, if the —OH group is positioned left then it belongs to **L-series**.

Position of this OH decides the configuration



L-series

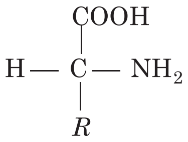
Here, L stands for laevo, i.e. left hand side and not laevo rotatory.

As a whole we can say that any compound that can be prepared from or converted into D-glyceraldehyde will belong to D-series.

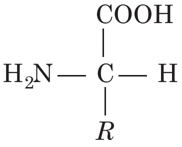
Similarly any compound that can be prepared from or converted into L-glyceraldehyde will belong to the L-series.

It must be noted that there is no relation between the sign of rotation (i.e. +, − or d, l) and the configuration (D and L) of the enantiomer.

This nomenclature is also used for α-amino acids. e.g.



D-amino acid



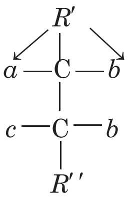
L-amino acid

Here, the position of $—NH_2$ at second last C-atom decides configuration.

2. *Erythro* and *Threo* System

The *erythro* and *threo* system of nomenclature is used in those compounds which have

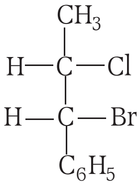
(i) only two chiral carbons and
(ii) the following structure



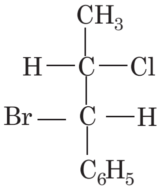
i.e. out of the 6 substituents on two asymmetric carbons at least two should be same.

When two like groups in Fischer projection formulae are drawn on the same side of vertical line, the isomer is called ***erythro* form** while if these are placed on the opposite sides, the isomer is said to be ***threo* form**.

e.g.

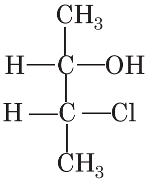


erythro form

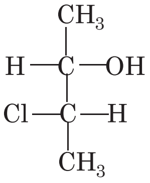


threo form

Similarly,

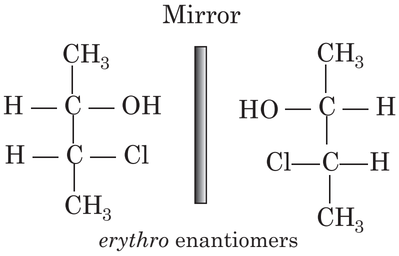


erythro form

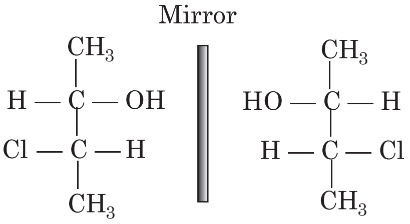


threo form

These *threo* and *erythero* forms are diastereomers and each one have their own enantiomers as shown below



erythro enantiomers



threo enantiomers

3. *R, S* System or Absolute Configuration

This *R,S* system of nomenclature is more important as compared to the previous two. The actual three dimensional arrangement of groups in an asymmetrical molecule is called its **absolute configuration.**

We can specify its configuration by using the *R,S* system, i.e. *rectus* and *sinister* system. Here, rectus stands for right hand side, sinister stands for left hand side.
This nomenclature was proposed by **Cahn, Ingold** *and* **Prelog** and involves following two steps in it.

***Step* I** Following a set of sequence rules, a sequence of priority is assigned to four different groups or atoms attached to a chiral C-atom. The most acceptable criterion of priority is based on atomic numbers, i.e. **atom with higher atomic number will get higher priority.**

e.g. In the case of bromochloroiodomethane the sequence of priority is I, Br, Cl, and H. This system of priortising was explained in details within *E-Z* system of nomenclature for geometrical isomers.

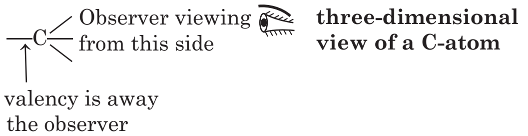
***Step* II** The molecule is next visualised so oriented that the group of lowest priority is directed away from you and the arrangement of remaining groups is observed. While observing you have to proceed from the group of highest priority to the group of second priority and then to the third.

(i) If your eye travels in a clockwise direction, the configuration is called *R* [Latin *rectus* = right].

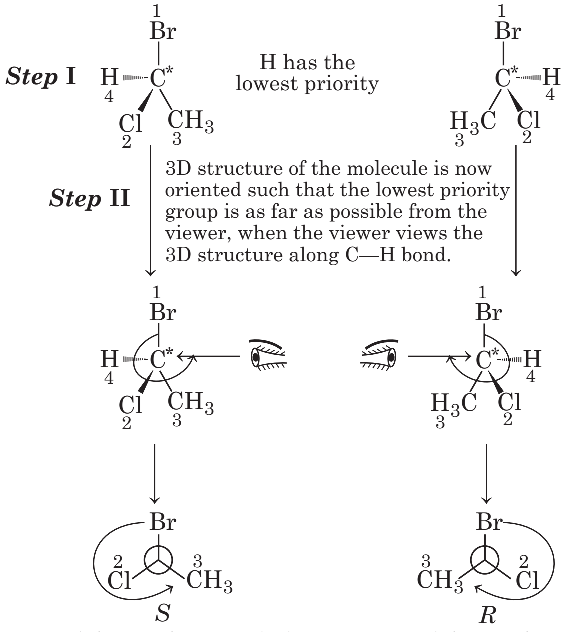
(ii) If your eye travels anticlockwise, the configuration is called *S* [Latin *sinister* = left].

Assigning *R, S* Configuration in 3D

One can easily position the group of lowest priority away from you if you see the C-atom three dimensionally



Above both the steps are shown below



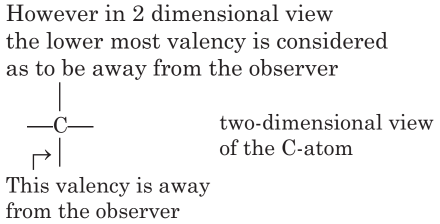
Highest to lowest priority is counter clockwise, hence, ***S* configuration**

Highest to lowest priority is clockwise, hence, ***R* configuration**

Assigning *R, S* Configuration in 2D

The positioning of the lowest priority group down and away from the observer can be assumed easily in three dimensions but difficult a bit in two dimensions.

e.g.



***Step* I** Remains same is 3D and 2D both.

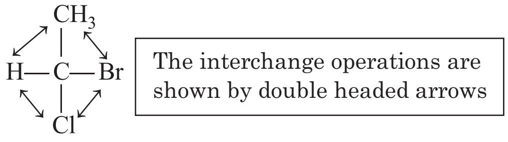
***Step* II** In 2D view is discussed below.

For positioning the group of lowest priority on this valency one has to perform pair inter changes among the groups attached to asymmetric C-atom

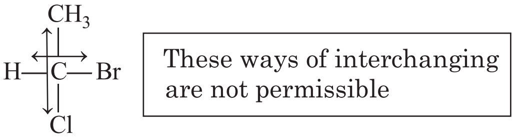
While studying, it is not possible always to keep the three dimensional view of C-atom, so we perform and learn the complete exercise in accordance with two dimensional view. Thus, we have to learn the pair interchanging in detail which can be done easily if we keep following four points in our mind.

(i) Our target is to position the group with lowest priority to the valency away from the observer.

(ii) This target can be achieved by pair interchanges that will always be diagonal. That means

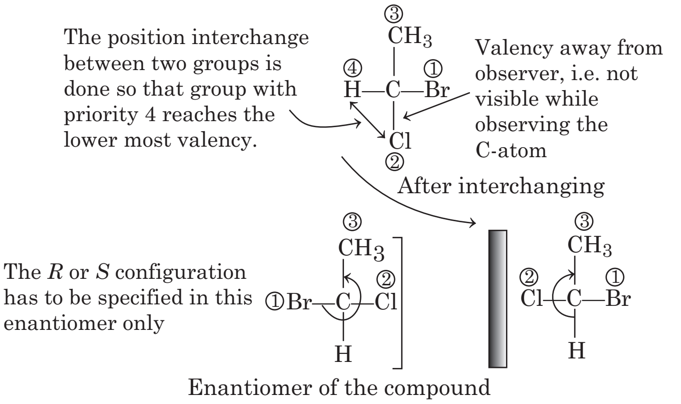


The possible ways of pair interchanging



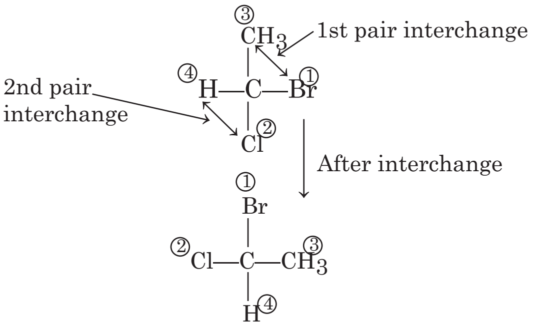
(iii) The single pair (or odd number) interchanging in Fischer projection inverts the configuration.

This means, in single pair inter change the enantiomer of the compound formed will give the absolute configuration of compound, e.g.



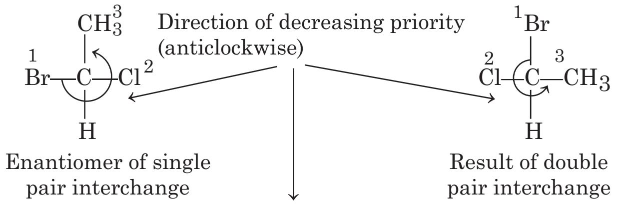
(iv) The two pair interchanges (or even number interchanges) retains the original configuration.

This means if we perform 2 pair exchanges then there is no need of enantiomer formation as seen above, e.g. Consider the same compound written above



Step III Specify the direction of decreasing priority of the three groups (1 → 2 → 3) after ignoring 4th one.

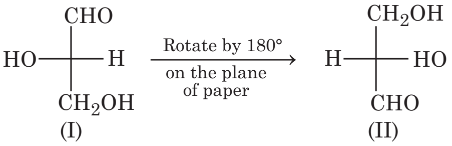
If the groups are arranged in clockwise fashion then the configuration is R and if these occur in anticlockwise manner, the configuration is S. e.g. If we look at the result of single pair and double pair interchanges, i.e.



Hence, the configuration of the C-atom in compound is S.

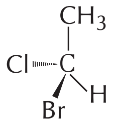
Thus, in the above example the configuration is S because the groups 1, 2 and 3 are arranged in anticlockwise fashion and shown by circular arc.

Remember Rotation of Fischer projection by 180° on the plane of paper results in the equivalent Fischer projection.



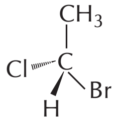
(I) and (II) are equivalent Fischer projections.

Example 7. *In which of the following representations given below, spatial arrangement of group/atom is same as that given in structure 'A' ?* ***(NCERT Exemplar)***

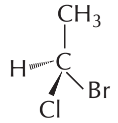


(A)

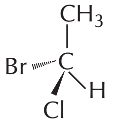
(a)



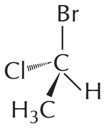
(b)



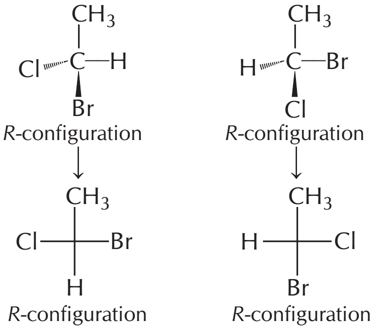
(c)



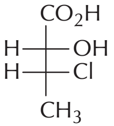
(d)



Sol. (b)



Example 8. *The absolute configuration of*

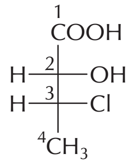


$$H-\overset{\displaystyle CO_2H}{C}-OH,\ H-\underset{\displaystyle CH_3}{C}-Cl$$

is ***(JEE Main 2016)***

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

Sol. (a)



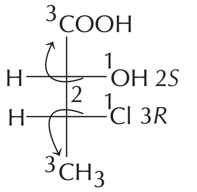
For C-2, order of priority of substituents is

$$OH > CH(Cl)(CH_3) > COOH$$

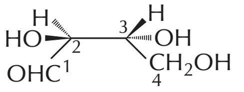
For C-3, order of priority of substituents is

$$Cl > CH(OH)COOH > CH_3$$

Hence, according to CIP rules,



Example 9. *Assign R-S configuration to the following compound*



(a) C – 2 (R), C – 3 (S)
(b) C – 2 (S), C – 3 (R)
(c) C – 2 (S), C – 3 (S)
(d) C – 2 (R), C – 3 (R)

Sol. (b) Priority order at C2

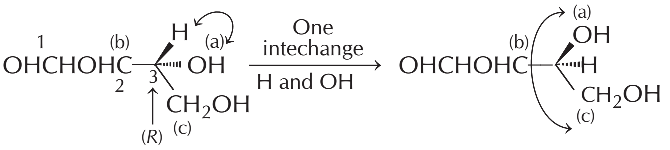
$$\underset{\displaystyle a}{\underset{\downarrow}{-OH}} > \underset{\displaystyle b}{\underset{\downarrow}{-CHO}} > \underset{\displaystyle c}{\underset{\downarrow}{CH(OH)CH_2OH}} > \underset{\displaystyle d}{\underset{\downarrow}{-H}}$$

Written as $a > b > c > d$

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 : $—OH > —CHOHCHO > CH_2OH > H$.

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*)

So, the configuration is (2*S*, 3*R*).

Remember *R* and *S* are the only configurations assigned to a particular three dimensional arrangement and these are not related to the optical rotation of the compound.

If the absolute configuration about an asymmetric carbon is *R* then it is not necessary that it will rotate the plane of polarised like clockwise, it may rotate it anticlockwise also.

Measurement of Optical Activity and Specific Rotation

The optical activity of a compound can be detected and measured by means of a **polarimeter.**

When a solution of a known concentration of an optically active compound is placed in a polarimeter, the beam of polarised light is rotated through a certain number of degrees either to the right (clockwise) or to the left (anticlockwise). This degree is measured and called **rotation** produced by the solution.

The degree of rotation depends upon the number of molecules of the compound encountered by light along its path. This degree of rotation, if measured under specific conditions is called *specific rotation and can be defined as the rotation produced by a solution of 10 cm length and unit concentration* (1g/mL) *for the given* λ *of light at the given temperature.*

Thus, for a system in which plane of polarised light is rotated through α degrees at a temperature of t°C and using the sodium-D lines as the source, the specific rotation $[\alpha]_D^t$ is given by

$$[\alpha]_D^t = 100\,\alpha / l \times c$$

Here, l = length of the fluid filled tube in decimeters (10 cm = 1 decimetre)

c = number of grams per 100 mL of solution

The specific rotation varies both with light wavelength and temperature.

Example 10. *The specific rotation of a pure enantiomer is* $+10°$. *Its observed rotation if it is isolated from a reaction with*

(*i*) *30% racemisation and 70% retention,*

(*ii*) *70% racemisation and 30% inversion are respectively*

(a) 7, 3 (b) 3, 7 (c) +7, −3 (d) −7, −3

Sol. (*c*) (i) $[\alpha]_{obs} = 0.70 \times +(10^\circ) = +7.0^\circ$

(ii) 30% inversion, with inversion specific rotation is (−10°)

$$\therefore \qquad [\alpha]_{obs} = 0.30 \times (-10^\circ) = -3.0^\circ$$

Example 11. *What is the percentage composition of (–) form in a mixture of two enantiomers whose rotation is* $-10°$? *The specific rotation of pure enantiomers is* $-20°$.

(a) 25% (b) 10%

(c) 50% (d) 15%

Sol. (*d*) Optical purity (OP) of sample $= \dfrac{[\alpha]_{obs}}{[\alpha]_D}$

$$= \frac{-10^\circ \times 100}{-20^\circ} = 50\%$$

So, 50% of the mixture consists of (–) enantiomer and 50% is the racemate [i.e. *25% (+) and 25% (–) form].*

Total percentage of (–) form = 50% + 25% = 75%

Total percentage of (+) form = 25%

Example 11. *An aqueous solution containing* 10 g *of optically pure fructose was diluted to* 500 mL *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 g of racemic fructose is added. What will be the change in specific rotation?

(a) −62.5° (b) +62.5°

(c) −12.5° (d) +12.5°

Sol. (*b*) As we know, 20 cm = 2 dm

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

Total volume of solution = 500 + 500 = 1000 mL

Mass per mL of pure fructose $= 10/1000 = 0.01\text{ g mL}^{-1}$

Mass per mL of mixture $= (10 + 10 = 20) = 20/1000 = 0.02\text{ g mL}^{-1}$

$$\text{OP (optical purity)} = \frac{[\alpha]_{obs}\text{ of mixture}}{[\alpha]_D\text{ of pure form}} \propto \frac{\text{Mass per mL of pure form}}{\text{Mass per mL of mixture}}$$

$$= \frac{0.01}{0.02} = 0.5$$

($\therefore l$ is constant)

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

Change in specific rotation $= -62.5 - (-125) = 62.5^\circ$

Practice Exercise

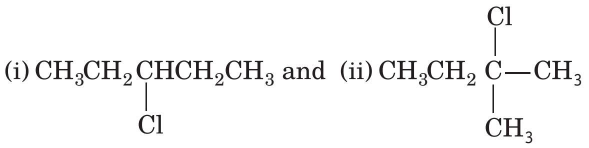
ROUND I Topically Divided Problems

Chain, Position Isomerism and Metameresm

1. The isomerism observed in alkanes is

(a) metamerism (b) chain isomerism
(c) position isomerism (d) geometrical isomerism

2. Compounds with following formula will show



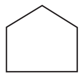
(i) $CH_3CH_2\underset{\underset{\displaystyle Cl}{|}}{C}HCH_2CH_3$ and (ii) $CH_3CH_2\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—CH_3$

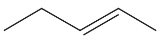
(a) position and functional isomerism
(b) only chain
(c) chain and functional isomerism
(d) None of the above combinations

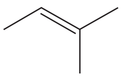
3. Number of chain isomers of C_5H_{12} is

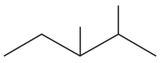
(a) 2 (b) 3
(c) 4 (d) 5

4. Select pair of chain isomers from the following.

I. 

II. 

III. 

IV. 

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

5. 2-pentanone and 3-methyl 2-butanone are a pair of ………isomers

(a) functional (b) chain
(c) positional (d) stereo

6. The structures $(CH_3)_3CBr$ and $CH_3(CH_2)_3Br$ represent

(a) chain isomerism (b) position isomerism
(c) functional (d) metamerism

7. The molecular formula of a saturated compound is $C_2H_4Cl_2$. The formula permits the existence of two

(a) functional isomers (b) position isomers
(c) optical isomers (d) *cis-trans* isomers

8. Propan-1-ol and propan-2-ol are ……… isomers

(a) chain (b) position
(c) functional (d) metamerism

9. The compounds, $CH_3CH = CHCH_3$ and $CH_3CH_2CH{=}CH_2$

(a) are tautomers
(b) are position isomers
(c) contain same number of sp^3 - sp^3 , sp^3 - sp^2 and sp^2- sp^2 carbon- carbon bond
(d) exist together in dynamic equilibrium

10. Which of the following pairs of compounds are position isomers?

(a) Ethylene dichloride and ethylidene dichloride
(b) Propylene glycol and trimethylene glycol
(c) Isobutylamine and *tert*-butylamine
(d) All of the above

11. Which among the following compounds will show metamerism?

(a) $CH_3COC_3H_7$ (b) $CH_3OC_2H_5$
(c) $CH_3SC_2H_5$ (d) CH_3OCH_3

12. Metamerism is not found in

(a) ethers (b) dialkyl sulphides
(c) alkenes (d) 2° amines

13. Which of the following are metamers ?

(a) $CH_3—CO—OCH_2CH_3$ and $CH_3CH_2—CO—OCH_3$
(b) $CH_3CH_2—CO—CH_2CH_3$ and $CH_3CH_2—CO—OCH_3$
(c) $CH_3—CO—OCH_2CH_3$ and $CH_3—CO—O—CH(CH_3)_2$
(d) $CH_3—CO—OC_2H_5$ and $C_2H_5—CO—O—C_2H_5$

14. 1-methoxypropane and ethoxyethane are

(a) position isomers (b) metamers
(c) functional isomers (d) chain isomers

15. The number of ether metamers represented by the formula $C_4H_{10}O$

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

16. The number of acyclic ether metamers of the compound with molecular formula $C_4H_{10}O$ is

(a) 1 (b) 3 (c) 4 (d) 6

Functional Isomerism, Tautomerism and Ring Chain Isomerism

17. The compounds $R—NO_2$ and R—ONO are
(a) geometrical isomers
(b) functional isomers
(c) metamers
(d) optical isomers

18. Which of the following represent isomerism ?
(a) Nitroalkanes and alkyl nitrites
(b) Alkanenitriles and carbylamines
(c) Alcohols and ethers
(d) All above are functional isomers

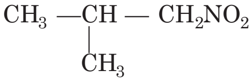
19. Ammonium cyanate (NH_4CNO) and urea (NH_2CONH_2) are
(a) chain isomers
(b) functional isomers
(c) position isomers
(d) metamers

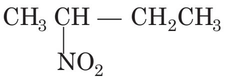
20. Which of the following pairs of compounds are not functional isomers ?
(a) Glucose and fructose
(b) Methyl cyanide and methyl isocyanide
(c) 2-pentanone and 3-pentanone
(d) Nitromethane and methyl nitrite

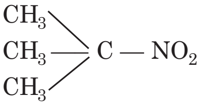
21. Methoxymethane and ethanol are
(a) position isomers
(b) chain isomers
(c) functional isomers
(d) optical isomers

22. Which of the following nitroalkane will not show tautomerism?

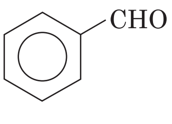
(a) $CH_3CH_2CH_2CH_2NO_2$

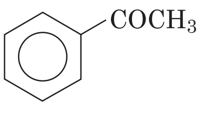
(b) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2NO_2$

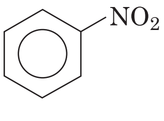
(c) 
$CH_3\,\underset{\displaystyle NO_2}{\underset{|}{CH}}-CH_2CH_3$

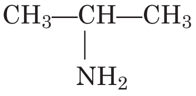
(d) 
$\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\!\!\!>C-NO_2$

23. Which of the following compounds can exhibit tautomerism?

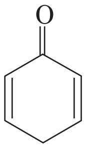
(a) 

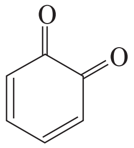
(b) 

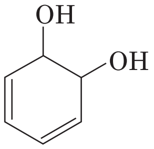
(c) 

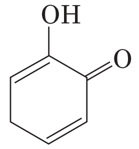
(d) 
$CH_3-\underset{\displaystyle NH_2}{\underset{|}{CH}}-CH_3$

24. Which of the following has maximum probability of showing tautomerism?

(a) 

(b) 

(c) 

(d) 

25. The type of isomerism in the molecule of compounds $CH_3CH_2COCH_2CH_3$ and $CH_3CHC(OH)CH_2CH_3$ is referred as
(a) metamerism (b) chain isomerism
(c) functional isomerism (d) tautomerism

26. Which of the following isomerism is shown by ethyl acetoacetate?
(a) Geometrical isomerism (b) Keto-enol tautomerism
(c) Enantiomerism (d) Diastereoisomerism

27. Nitroethane can exhibit one of the following kind of isomerism
(a) metamerism (b) optical activity
(c) tautomerism (d) position isomerism

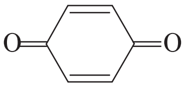
28. Keto-enol isomerism is exhibited by
(a) acetone (b) benzaldehyde
(c) benzene (d) formaldehyde

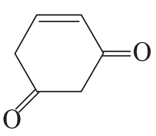
29. Acetophenone can exhibit
(a) functional isomerism
(b) chain isomerism
(c) tautomerism
(d) chain and position isomerism

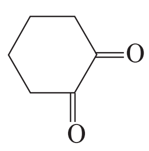
30. Identify the compound that exhibits tautomerism
(a) 2-butene (b) lactic acid ***(AIEEE 2011)***
(c) 2-pentanone (d) phenol

31. Tautomerism is not exhibited by

(a) $C_6H_5—CH{=}CH—OH$

(b) 

(c) 

(d) 

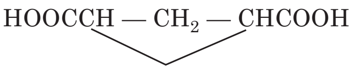
32. The type of isomerism found in urea molecule is
(a) chain (b) position
(c) tautomerism (d) None of these

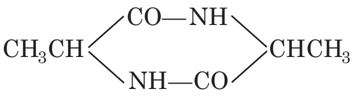
33. Which pair of isomerism is not possible together?
(a) Chain and position
(b) Functional and position
(c) Tautomerism and functional
(d) All of the above

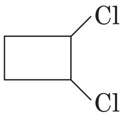
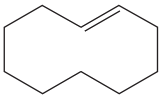
34. But-1-ene and cyclobutane exhibit
(a) ring chain isomerism
(b) position isomerism
(c) tautomerism
(d) functional isomerism

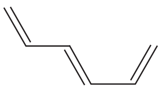
35. Which of the following is/are cyclic isomer/s of cyclohexane ?
(a) Methylcyclobutane
(b) 1, 3-dimethylcyclobutane
(c) 1, 2, 3-trimethylcyclopropane
(d) All the above three

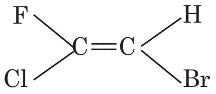
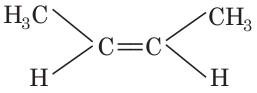
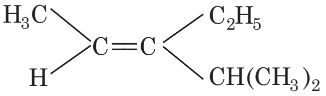
Geometrical Isomerism

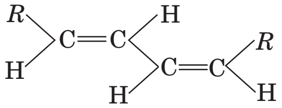
36. Which class of compounds can exhibit geometrical isomerism?
(a) $C_6H_5CH = NOH$
(b) $CH_3CH = CHCH_3$
(c)

$HOOCCH - CH_2 - CHCOOH$
(d) All of the above

37. Which of the following shows geometrical isomerism?
(a) 1, 2-dichloroethene
(b) 1,2-dimethylcyclopropane
(c)

(d) All of the above

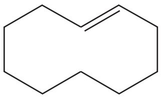
38. Which will form geometrical isomers?
(a)

(b) $CH_3CH{=}NOH$
(c)

(d) All of these

39. In

the double bonds are
(a) *cis, cis*
(b) *cis, trans*
(c) *trans, cis*
(d) *trans, trans*

40. The '*E*'-isomer is
(a)

(b)

(c)

(d) None of the above

41. Number of geometrical isomers for the molecule

are
(a) 2
(b) 3
(c) 6
(d) 5

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

43. Which of the following will show geometrical isomerism?
(a) Methyl cyclohexane
(b)

(b) $(CH_3)_2C{=}NOH$
(d) $CH_3CH{=}NOH$

44. Which of the following compounds shows geometrical isomerism? **(JEE Main 2020)**
(a) 2-methylpent-2-ene
(b) 4-methylpent-2-ene
(c) 4-methylpent-1-ene
(d) 2-methylpent-1-ene

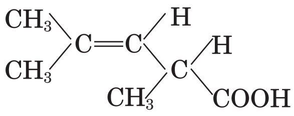
Optical Isomerism

45. The property by virtue of which a compound can rotate the plane of polarised light is known as
(a) polarisability
(b) phosphorescense
(c) optical activity
(d) polarisation

46. Chiral molecules are those which are
(a) superimposable on their mirror images
(b) non-superimposable on their mirror images
(c) unstable molecules
(d) capable of showing geometrical isomerism

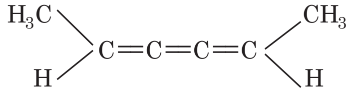
47. (+) and (–) forms of optically active compounds are different in
(a) boiling points
(b) melting points
(c) specific gravity
(d) specific rotation

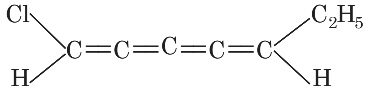
48. The following compound can exhibits

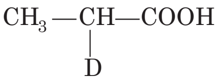


(a) tautomerism
(b) optical isomerism
(c) geometrical isomerism
(d) geometrical and optical isomerism

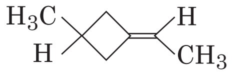
49. Which is/are optically in active?

(a) 

(b) 

(c) 

$CH_3-\underset{\substack{| \\ D}}{CH}-COOH$

(d) 

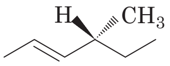
50. Out of the following, the alkene that exhibits optical isomerism is *(AIEEE 2010)*

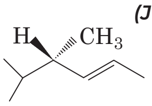
(a) 3-methyl-2-pentene
(b) 4-methyl-1-pentene
(c) 3-methyl-1-pentene
(d) 2-methyl-2-pentene

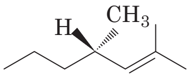
51. Which types of isomerism is shown by 2,3-dichlorobutane? *(AIEEE 2005)*

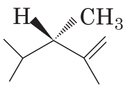
(a) Structural
(b) Geometric
(c) Optical
(d) Diastereo

52. Which of the following compounds produces an optically inactive compound on hydrogenation? *(JEE Main 2020)*

(a) 

(b) 

(c) 

(d) 

53. A compound contains 2 dissimilar asymmetric C-atoms. The number of optical isomers are

(a) 2
(b) 3
(c) 4
(d) 5

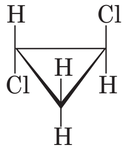
54. Which of the following statements is not correct ?

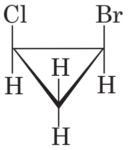
(a) A *meso* compound has chiral centres but it does not exhibits no optical activity
(b) A *meso* compound has no chiral centres and thus is optically inactive
(c) A *meso* compound has molecules in which one half of molecule is superimposable on the other even though chiral centre is present in them
(d) A *meso* compound is optically inactive because the rotation caused by one half of molecule is cancelled by the rotation produced by another half

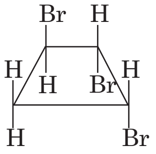
55. An enantiomerically pure acid is treated with racemic mixture of an alcohol having one chiral carbon. The ester formed will be

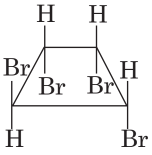
(a) optically active mixture
(b) pure enantiomer
(c) *meso* compound
(d) racemic mixture

56. Which of the following compounds is not optically active?

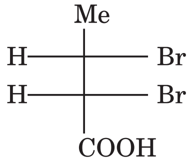
(a) 

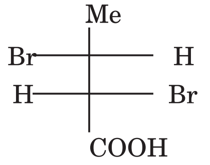
(b) 

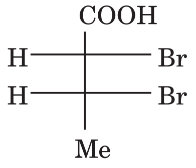
(c) 

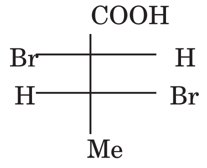
(d) 

57. Which of the following are diastereomers?

I. 

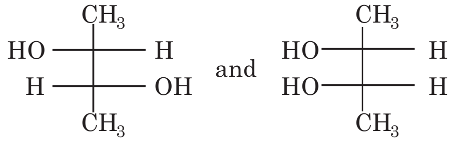
II. 

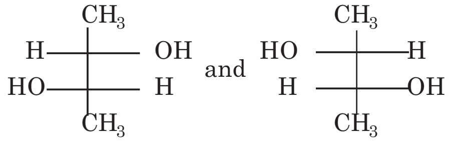
III. 

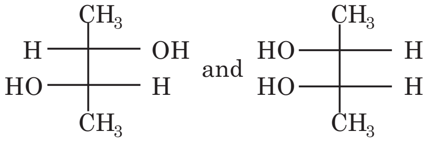
IV. 

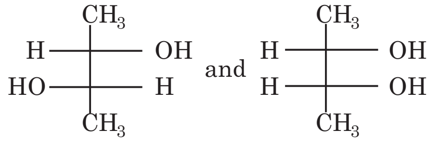
(a) I and III
(b) II and IV
(c) I and II
(d) None of the above

58. Which of the following pairs of compounds are enantiomers?

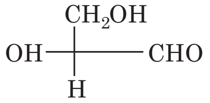
(a) 

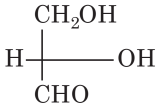
(b) 

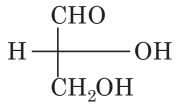
(c) 

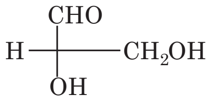
(d) 

59. Which of the following Fischer projection formula is same as D-glyceraldehyde?

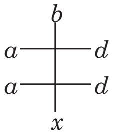
(a) 

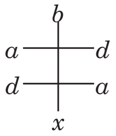
(b) 

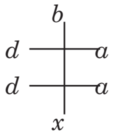
(c) 

(d) 

60. Which of the following is/are *threo* isomers?

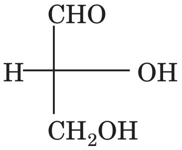

(i)

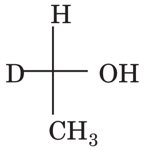

(ii)

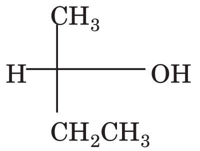

(iii)

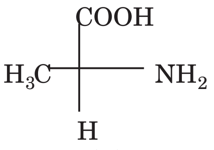
(a) Only (i)
(b) Only (ii)
(c) Only (iiii)
(d) All (i), (ii) and (iii)

61. The *R*-isomer among the following are


(i)


(ii)


(iii)

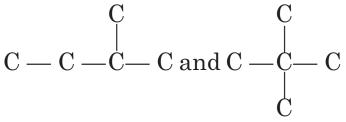

(iv)

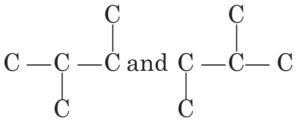
(a) (i) and (ii)
(b) (ii) and (iii)
(c) (iii) and (iv)
(d) (i) and (iii)

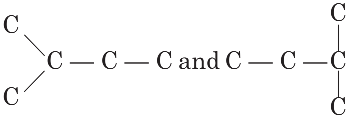
ROUND II Mixed Bag

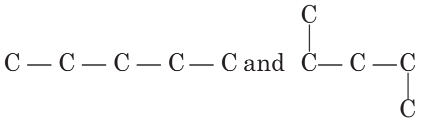
1. Compounds having the same molecular formula but different properties are called
(a) isotopes
(b) isobars
(c) isomers
(d) isomorphs

2. Which pair of carbon skeleton is an example of isomerism?

(a) 

(b) 

(c) 

(d) 

3. Isomers have essentially identical
(a) structural formula
(b) chemical properties
(c) physical properties
(d) molecular formula

4. Which of the following is not isomeric with diethyl ether?
(a) Methyl *n*-propyl ether
(b) Butan-1-ol
(c) 2-methyl propan-2-ol
(d) Butan-2-one

5. Which of the following is not an isomer of but-1-yne ?
(a) But-2-yne
(b) Buta-1,3-diene
(c) Methyl cyclopropene
(d) But-2-ene

6. Enol form is more stable in
(a) CH_3CHO
(b) CH_3COCH_3
(c) $CH_3COCH_2COOC_2H_5$
(d) cyclohexanone

7. Keto form is more stable in
(a) $CH_3COCH_2COOC_2H_5$
(b) $CH_3COCH_2COCH_3$
(c) CH_3COCH_3
(d) $CH_3COCH_2COC_2H_5$

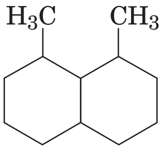
8. Stereoisomers have different
(a) molecular formula (b) structural formula
(c) configuration (d) molecular mass

9. The number of isomers of the compound $C_2FClBrI$ is
(a) 3 (b) 4 (c) 5 (d) 6

10. Racemic tartaric acid is optically inactive due to
(a) external compensation
(b) internal compensation
(c) presence of plane of symmetry
(d) All of the above

11. How many carbon atoms in the molecule $HOOC—(CHOH)_2—COOH$ are asymmetric?
(a) 1 (b) 2
(c) 3 (d) None of these

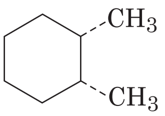
12. Number of chiral centres in

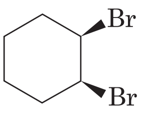


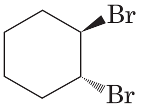
is/are

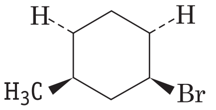
(a) 1 (b) 2 (c) 3 (d) 4

13. Mark the unidentical compound

(a)


(b)


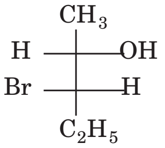
(c)


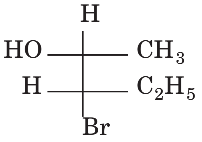
(d)


14. Which statement is true?
(a) A compound with *R* configuration is the (+) enantiomer
(b) If configuration changes from + to –, that essentially means inversion of configuration takes place
(c) An achiral molecule reacts always with racemic forms, to give a chiral molecule,
(d) By breaking two bonds on the chiral centre configuration changes

15. The terms stereoisomers, enantiomers and diastereomers will refer
(a) only to configurational isomers including geometrical isomers
(b) only to configurational isomers
(c) to both configurational as well as conformational isomers
(d) to neither configurational nor conformational isomers

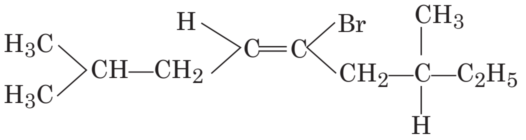
16. The molecules represented by the following two structures are

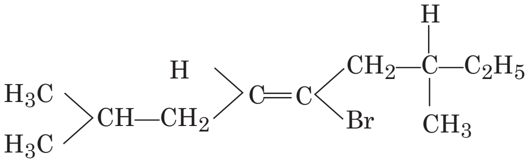


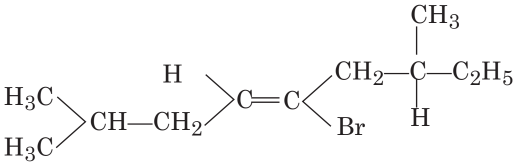


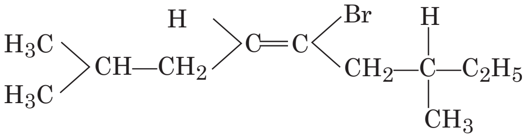
(a) epimers (b) diastereomers
(c) enantiomers (d) identical

17. Correct structures of [*E*][*S*]-5-bromo-2,7-dimethyl, non-4-ene is

(a)


(b)


(c)


(d)


18. Consider the following statements.
I. Chain and position isomerism are not possible together between two isomers.
II. Tautomerism is a chemical phenomenon which is catalysed by acid as well as base.
III. Tautomers are always metamers.
IV. Tautomers are always functional isomers.

Select the correct answer by using the codes given below.
(a) only III is correct (b) III and IV are correct
(c) I, II and III are correct (d) I ,II and IV are correct

19. Increasing order of expected enol contentis
(a) $CH_3COCH_2CHO > CH_3COCH_3 > CH_3CHO > CH_3COCH_2COCH_3$
(b) $CH_3COCH_2COCH_3 > CH_3COCH_2CHO > CH_3COCH_3 > CH_3CHO$
(c) $CH_3CHO > CH_3COCH_3 > CH_3COCH_2CHO > CH_3COCH_2COCH_3$
(d) $CH_3COCH_3 > CH_3COCH_2COCH_3 > CH_3CHO > CH_3COCH_2CHO$

20. Increasing order of expected keto content

(a) $CH_3COC_2H_5 > CH_3CHO > CH_3COCH_3 > CH_3COCH_2COCH_3$

(b) $CH_3COCH_3 > CH_3CHO > CH_3COC_2H_5 > CH_3COCH_2COCH_3$

(c) $CH_3CHO > CH_3COC_2H_5 > CH_3COCH_3 > CH_3COCH_2COCH_3$

(d) $CH_3COCH_2COCH_3 > CH_3CHO > CH_3COCH_3 > CH_3COC_2H_5$

21. *Meso*-tartaric acid is optically inactive due to the presence of

(a) molecular symmetry

(b) molecular asymmetry

(c) external compensation

(d) two asymmetric C-atoms

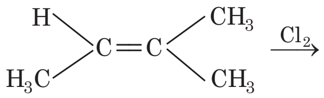
22. Which will give chiral molecule?

(a) $CH_3COCl \xrightarrow{LiAlH_4}$

(b) $C_2H_5CHO \xrightarrow[H^+/H_2O]{CH_3MgBr}$

(c) $(CH_3)_2CHC_2H_5 \xrightarrow{Cu}$

(d)



Numeric Value Questions

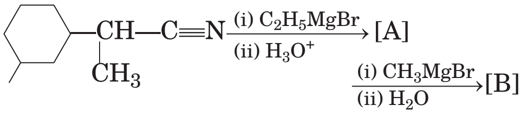
23. Number of isomers represented by molecular formula $C_4H_{10}O$ is …… .

24. Maximum number of open chain isomers that an alkene can have with the molecular formula C_4H_8 is ……… .

25. The number of stereoisomers for pent-3-en-2-ol is …… .

26. The number of enantiomers and meso forms for the compound, HOOC—CH(CH_3)—CHOH—CHBr —CHOHCH(CH_3)—COOH are respectively, x and y. Sum of the $x + y$ is ……… .

27. The number of chiral centres present in [B] is .... **(JEE Main 2020)**

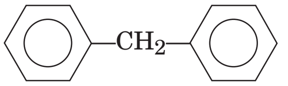


28. The number of chiral centres present in threonine is ……… . **(JEE Main 2020)**

29. The number of isomeric pentyl alcohols possible is ……… .

30. Total number of isomeric alcohols with formula $C_4H_{10}O$ are ……… .

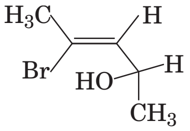
31. The molecular formula of diphenyl methane.



is $C_{13}H_{12}$.

How many structural isomers are possible when one of the hydrogen is replaced by a chlorine atom?

32. The compound, whose stereo chemical formula is written below, exhibits x-geometrical isomers and y-optical isomers. The value of x and y are ……… .



Answers

Round I

1. (b)	**2.** (b)	**3.** (b)	**4.** (d)	**5.** (b)	**6.** (a)	**7.** (b)	**8.** (b)	**9.** (b)	**10.** (d)
11. (a)	**12.** (c)	**13.** (a)	**14.** (b)	**15.** (b)	**16.** (c)	**17.** (b)	**18.** (d)	**19.** (b)	**20.** (c)
21. (c)	**22.** (d)	**23.** (b)	**24.** (d)	**25.** (d)	**26.** (b)	**27.** (c)	**28.** (a)	**29.** (c)	**30.** (c)
31. (d)	**32.** (c)	**33.** (c)	**34.** (a)	**35.** (d)	**36.** (d)	**37.** (d)	**38.** (d)	**39.** (c)	**40.** (c)
41. (b)	**42.** (c)	**43.** (d)	**44.** (b)	**45.** (c)	**46.** (b)	**47.** (d)	**48.** (b)	**49.** (a)	**50.** (c)
51. (c)	**52.** (d)	**53.** (c)	**54.** (b)	**55.** (a)	**56.** (d)	**57.** (c)	**58.** (b)	**59.** (c)	**60.** (b)
61. (a)									

Round II

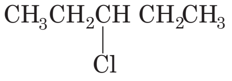
1. (c)	**2.** (a)	**3.** (d)	**4.** (d)	**5.** (d)	**6.** (c)	**7.** (c)	**8.** (c)	**9.** (d)	**10.** (a)
11. (b)	**12.** (b)	**13.** (c)	**14.** (d)	**15.** (a)	**16.** (d)	**17.** (a)	**18.** (d)	**19.** (b)	**20.** (c)
21. (a)	**22.** (b)	**23.** (7)	**24.** (5)	**25.** (4)	**26.** (4)	**27.** (2)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

Solutions

Round I

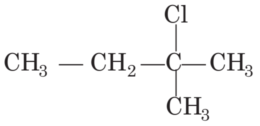
1. Alkanes are saturated hydrocarbons without any functional group, hence can show chain isomerism only.

2. Isomeric substances that differ only in the arrangement of carbon atoms forming the base chain are known as chain isomers.

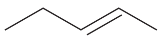
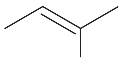


$$CH_3CH_2\underset{\underset{Cl}{|}}{C}H\;CH_2CH_3$$

and



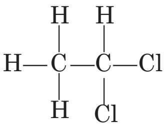
$$CH_3-CH_2-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

4.  and  are chain isomers.

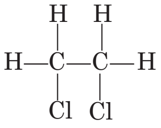
5. $\overset{1}{C}H_3\,\overset{2}{C}O\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_3$ (2-pentanone) $CH_3COCH(CH_3)_2$ (3-methyl-2-butanone)

They are chain isomers.

6. Because of difference in the structure of carbon skeleton, $CH_3CH_2CH_2CH_2-Br$ and $(CH_3)_3C-Br$ are chain isomers.

7. (i)  (1,1-dichloroethane)

$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-Cl$$

(ii)  (1,2-dichloroethane)

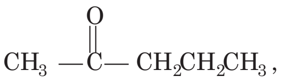
$$H-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{Cl}{|}}{C}}-H$$

Both are position isomers.

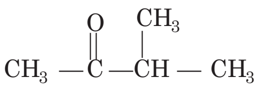
9. $CH_3CH{=}CHCH_3$ (2-butene) and $CH_3CH_2CH{=}CH_2$ (1-butene) are position isomers.

They have different number of sp^3 - sp^3 (2-butene has no sp^3 - sp^3 bond while 1-butene has one sp^3 - sp^3 bond) and sp^3 - sp^2 (2-butene has 2 sp^3 - sp^2 bonds while 1 butene has only one sp^3 - sp^2 bond) bonds while both have same number (2) of sp^2-sp^2 bonds.

11. $CH_3COC_3H_7$ can exhibit metamerism.

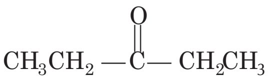


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CH_3,$$



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

and



$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3$$

14. $CH_3O-CH_2CH_2CH_3$ (1-methoxypropane) $CH_3CH_2O-CH_2CH_3$ (Ethoxyethane)

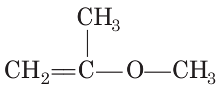
are metamers since they have substituents with different number of carbon atoms one either side of the functional group, i.e. oxygen atom.

15. There are three ether metamers with molecular formula $C_4H_{10}O$.

$CH_3CH_2OCH_2CH_3$, $CH_3-O-CH_2CH_2CH_3$ and $CH_3-O-CH(CH_3)_2$

16. The following four ether metamers are possible :

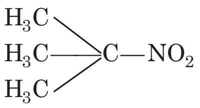
$CH_2{=}CH-O-CH_2CH_3$ or
$CH_2{=}CH-CH_2-O-CH_3$

or  or $CH_3-CH{=}CH-O-CH_3$

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

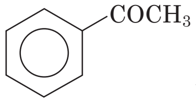
19. $$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{\Delta} \underset{\text{Urea}}{NH_2CONH_2}$$

Ammonium cyanate and urea have different functional groups and hence are functional isomers.

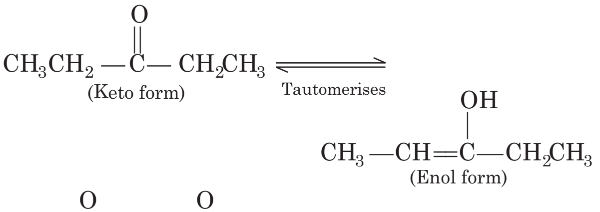
22. 

has no α-hydrogen. Hence, it will not show tautomerism.

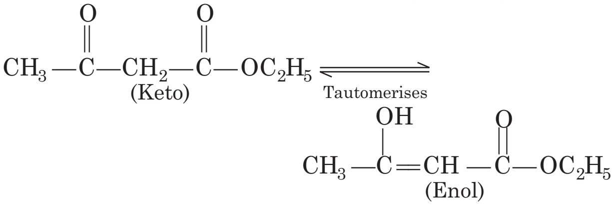
23. Presence of α-H atom along with a multi bonded functional group is an essential condition for exhibiting tautomerism.



satisfies this condition, so exhibits tautomerism.

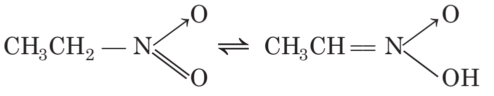
25. 

$$\underset{\text{(Keto form)}}{CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_2CH_3} \underset{\text{Tautomerises}}{\rightleftharpoons} \underset{\text{(Enol form)}}{CH_3-CH{=}\overset{\overset{OH}{|}}{C}-CH_2CH_3}$$

26. 

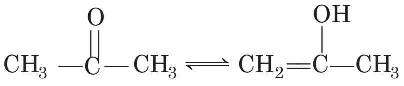
$$CH_3-\overset{\overset{O}{\|}}{C}-\underset{\text{(Keto)}}{CH_2}-\overset{\overset{O}{\|}}{C}-OC_2H_5 \underset{\text{Tautomerises}}{\rightleftharpoons} \underset{\text{(Enol)}}{CH_3-\overset{\overset{OH}{|}}{C}{=}CH-\overset{\overset{O}{\|}}{C}-OC_2H_5}$$

27. Nitroethane exhibits tautomerism.



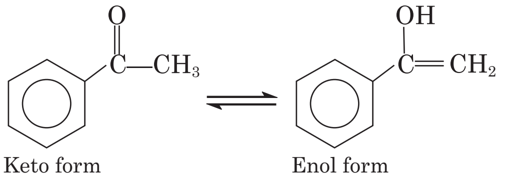
Nitro form Aci form

28. Acetone exhibits keto-enol tautomerism.

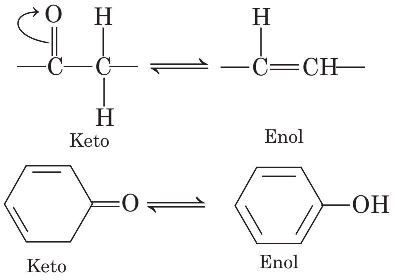


$$\underset{\text{(Keto form)}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \rightleftharpoons \underset{\text{(Enol form)}}{CH_2{=}\overset{\overset{OH}{|}}{C}-CH_3}$$

29. Tautomerism in acetophenone can be represented as



30. Tautomerism is due to spontaneous interconversion of two isomeric forms with different functional groups into each other. The term tautomer means constitutional isomers that undergo such rapid interconversion that can't be independently isolated.



Thus, (c) 2-pentanone and (d) phenol exhibit tautomerism.

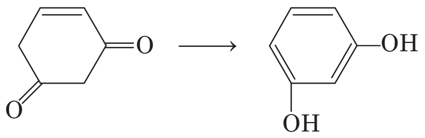
Here, (c) may be considered as answer because keto form of phenol is highly unstable.

31. (a) shows tautomerism since aldehydes are more stable than vinyl alcohols.

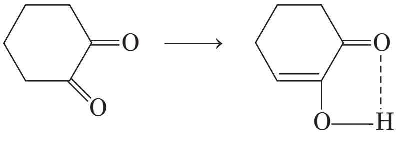
$$C_6H_5-CH=CHOH \longleftrightarrow C_6H_5CH_2CH=O$$

(b) does not show tautomerism because it does not have hydrogens at α-positions.

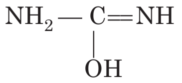
(c) shows tautomerism because enol form is stabilised by aromatic character



(d) shows tautomerism because enol form is stabilised by H-bonding.

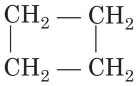


32. Urea, $NH_2-\underset{\underset{O}{\|}}{C}-NH_2$ shows tautomerism as



$$NH_2-\underset{\underset{OH}{|}}{C}=NH$$

34. $CH_3-CH_2-CH=CH_2$ and

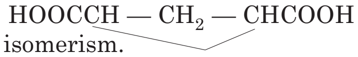


$$\begin{array}{c}CH_2-CH_2\\ |\qquad\quad |\\ CH_2-CH_2\end{array}$$

exhibit ring chain isomerism.

35. All the three have the same molecular formula as that of cyclohexane (C_6H_{12}) and hence are cyclic isomers of cyclohexane.

36. All the compounds in which there should be restricted rotation about a bond in the molecule, show geometrical isomerism. Oximes of the type $R-CH=N-OH$, $C_6H_5-\underset{\underset{CH_3}{|}}{C}=N-OH$ and cyclic compound like

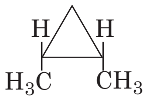


$HOOCCH-CH_2-CHCOOH$ show geometrical isomerism.

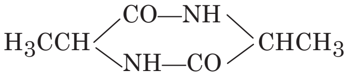
37. Disubstituted cyclic compounds and disubstituted alkenes show geometrical isomerism.

$$\begin{array}{c}CHCl\\ \|\\ CHCl\end{array}$$

(Non-cyclic, but have ═ bond so exhibits geometrical isomerism).

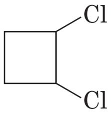


(Cyclic, two different groups at adjacent positions, so exhibits geometrical isomerism).

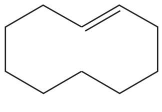


(Cyclic)

38. The isomerism which arises due to restricted rotation about a bond in a molecule is known as geometrical isomerism.

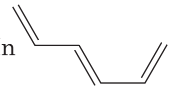


, $CH_3-CH=NOH$ and



All of these form geometrical isomers.

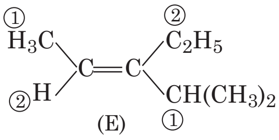
39. In



the double bonds are *trans* and *cis*.

The first and third bonds are identical.

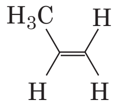
40. If the highest priority groups of two carbon atoms of the double bond are on the opposite sides, the configuration is *E*. (*Entgegen*).



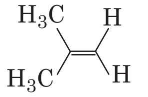
41. When n = even number then for two identical ends, number of geometrical isomers

$$= 2^{n-1} + 2^{n/2-1}$$
$$= 2^1 + 2^0 = 3$$

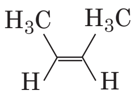
42.



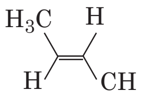
Propene



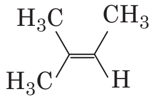
2-methyl propene



cis-2-butene



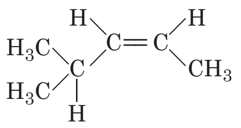
trans-2-butene



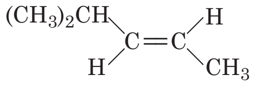
2-methyl-2-butene

43. Since, the molecules given in option (a), (b) and (c) are symmetrical, they do not exhibit geometrical isomerism.

44. Only 4-methylpent-2-ene shows geometrical isomerism.



(*cis*-4-methylpent-2-ene)

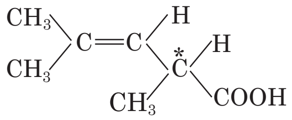


(*trans*-4-methylpent-2-ene)

Hence, the correct option is (b).

47. If a substance rotates the plane polarised light in clockwise direction, it is dextrorotatory (+). If it rotates the plane polarised light in anticlockwise direction then it is laevorotatory (–). Thus, +I– form differ in specific rotation.

48.



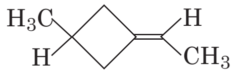
The above compound has chiral centre.

Hence, it can exhibit optical isomerism while geometrical isomerism is not possible due to the presence of identical groups on double bonded carbon atoms.

49. (b) Alkene with odd number of carbon atoms are non-planar so, these are optically active.

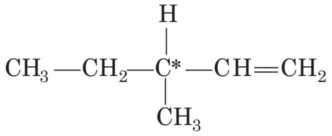
(c) CH_3 — CH(*D*) — COOH molecule contains one chiral carbon atom thus, it is optically active.

(d)



is non-planar and does not contain any symmetry element thus, optically active.

50.

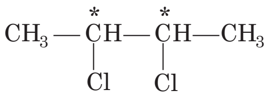


$$\mathrm{CH_3{-}CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle H}{C^*}}{-}CH{=}CH_2}$$

3-methyl-1-pentene

(It has one chiral centre.)

51.

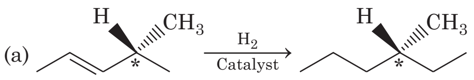


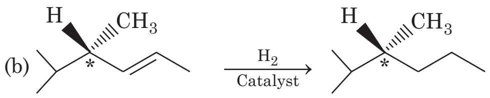
$$\mathrm{CH_3{-}\underset{\displaystyle Cl}{\overset{*}{C}H}{-}\underset{\displaystyle Cl}{\overset{*}{C}H}{-}CH_3}$$

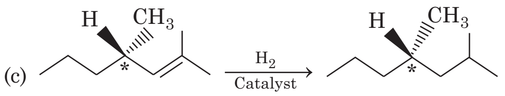
There are two chiral C-atoms (*).

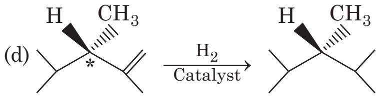
Thus, optical isomerism is possible.

52. Reaction of all options are as follows



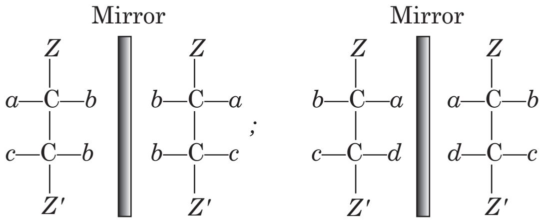






No change in chirality or optical activity due to hydrogenation of (a), (b) and (c) but in (d) the substrate (alkene) on hydrogenation becomes optically inactive as the product obtained does not have any chiral atom.

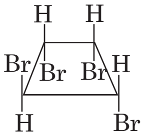
53. The minimum possible isomers of compounds will be



Alternative No. of optical isomers = $Z^n = 2^2 = 4$, here n = No. of dissimilar asymmetric C-atoms.

54. Compounds which do not show optical activity inspite of the presence of chiral carbon atoms are called *meso*-compounds.

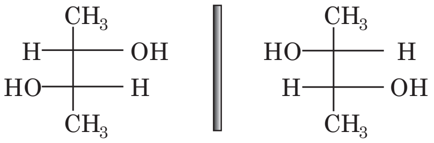
56. The compound



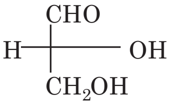
is symmetrical with respect tocentre of the molecule.

57. Superimposable compounds which are also not the mirror images of each other are called diastereomers. Thus, I and II are diastereomers.

58. Optical isomers of a compound which are non-superimposable but releated to each other as an object and its mirror image are called enantiomers.



59. The configuration in the Fischer projection of which —OH group is on right hand side, H-atom is on left hand side, —CHO group is on upper side and CH_2OH is on lower side is known as D-configuration.

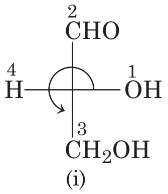


D-glyceraldehyde

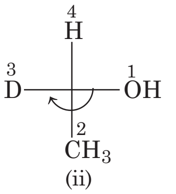
60. The prefixes *erythro* and *threo* are used in systems containing two asymmetric carbons when two of the groups are the same and the third is different.

The *erythro-isomer* has identical groups on the same side when drawn in Fischer projection and *threo*-isomer has them on opposite side.

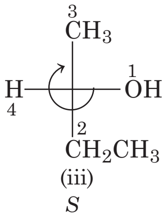
61.



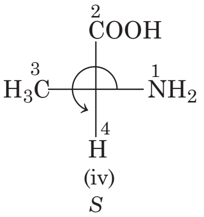
(i)
R



(ii)
R



(iii)
S



(iv)
S

Note If H is on vertical line *R* represents clockwise and *S* represents anticlock wise rotation. Opposite is true when H or lower priority group is present on horizontal line.

Round II

4. Butan-2-one $CH_3—\overset{\overset{O}{\|}}{C}—CH_2—CH_3$ is not isomeric with diethyl ether $CH_3CH_2 — O — CH_2 — CH_3$. Because both are differing in molecular formula.

5. But-2-ene and but-1-yne do not have same molecular formula, thus are not isomers.

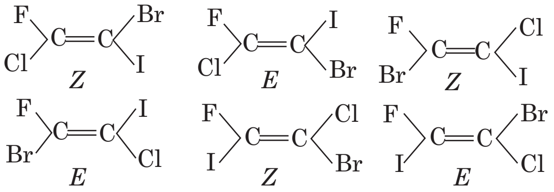
$$\underset{\substack{\text{But-1-yne}\\(C_4H_6)}}{CH_3 — CH_2 — C \equiv CH} \quad \underset{\substack{\text{But-2-ene}\\(C_4H_8)}}{CH_3 — CH = CH — CH_3}$$

6. The stabilising effect of enolic form is the intramolecular hydrogen bond present in enols. This provides another source of increasing bonding and hence, increased stabilisation.

Thus, $CH_3COCH_2\overset{\overset{O}{\|}}{C}—OC_2H_5$ is more stable.

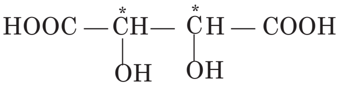
7. C$=$O double bond of a carbonyl group is a stronger bond (C$=$O, 364 kJ/mol) than the C$=$C bond (strength 250 kJ/mol) of the enol. Thus, CH_3COCH_3 is more stable keto form.

9.



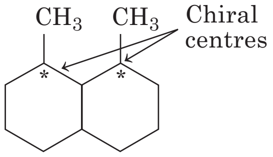
10. Racemic tartaric acid is optically inactive due to external compensation. Racemic tartaric acid is an equimolar mixture of optically active *d*- and *l*- forms.

11. A carbon atom which is attached to four different group is called an asymmetric carbon atom or chiral centre. $HOOC(CHOH)_2COOH$ has two asymmetric carbon (C^*) atoms.



$$HOOC — \underset{\underset{OH}{|}}{\overset{*}{C}H} — \underset{\underset{OH}{|}}{\overset{*}{C}H} — COOH$$

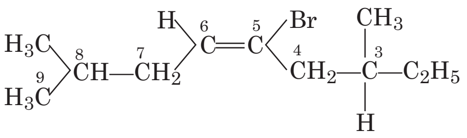
12.



(* asymmetric C atom)

13. Compound given in option (c) is *trans* while all other have *cis* configuration.

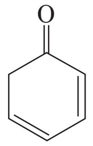
17.



[*E*][*S*]-5-bromo-2,7-dimethylnon-4-ene

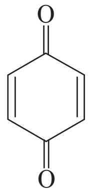
18. Tautomers may or may not be metamers. These are infact functional isomers. Tautomerism is catalysed by acid as well as base. Chain and position isomerism do not exist together.

19. The percentage of enolic contents of some common compounds in decreasing order will be



$> C_6H_5COCH_2COCH_3 > CH_3COCH_2COCH_3$
$> CH_3COCH_2COOC_2H_5 > CH_3COCH_2CHO$

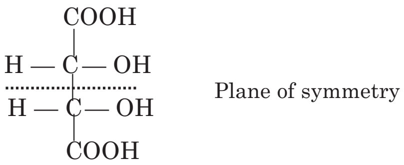
$> CH_3COCH_3 > CH_3CHO >$



20. ~~The reverse~~ of enolic contents of compound is ketonic contents. Thus, the correct order of ketonic contents are

$CH_3CHO > CH_3COC_2H_5 > CH_3COCH_3$
$> CH_3COCH_2COCH_3$

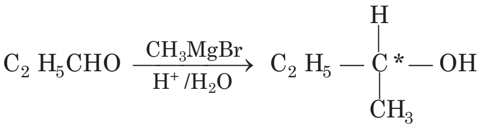
21.



Meso tartaric acid is optically inactive due to the presence of molecular symmetry.

It is optically inactive due to internal compensation, i.e. the effect of one half of the molecule is neutralised by other.

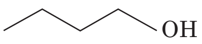
22.

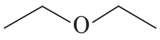


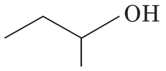
$$C_2H_5CHO \xrightarrow[H^+/H_2O]{CH_3MgBr} C_2H_5-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}{}^*-OH$$

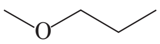
(For these reactions read successive chapters.)

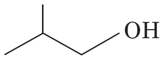
23. The following structures are possible for the molecular formula $C_4H_{10}O$.

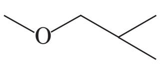
(i) 

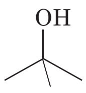
(ii) 

(iii) 

(iv) 

(v) 

(vi) 

(vii) 

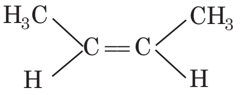
Out of these, four are alcohols and three are ethers.

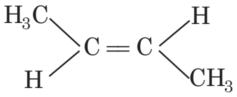
An alkene with molecules formula C_4H_8 will have the following isomers.

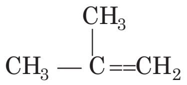
24. An alkene with molecular formula C_4H_8 will have the following isomers

(i) $CH_3-CH_2-CH=CH_2$

(ii) $CH_3-CH=CH-CH_3$

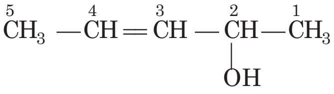
(iii) 

(iv) 

(v) 

$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2$$

25.



$$\overset{5}{C}H_3-\overset{4}{C}H=\overset{3}{C}H-\underset{\underset{OH}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$$

The number of stereoisomers = number of optical isomers + number of geometrical isomers

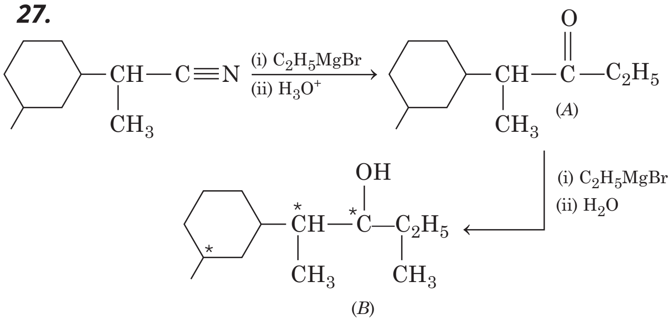
In this compound,
the number of optical isomers $= 2^1 = 2$
the number of geometrical isomers $= 2^1 = 2$
Thus, the number of stereoisomers $= 2 + 2 = 4$

26. Since, the compound can be divided into two equal halves and has five asymmetric carbon atoms, the

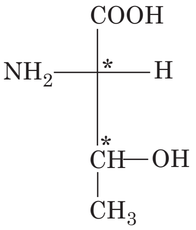
$$\text{number of enantiomers } (x) = 2^{n-1} - 2^{\left(\frac{n-1}{2}\right)}$$
$$= 2^{5-1} - 2^2 = 2^4 - 2^2 = 16 - 4 = 12$$

$$\text{Number of } meso \text{ forms } (y) = 2^{\left(\frac{n-1}{2}\right)} = 2^2 = 4$$

27.



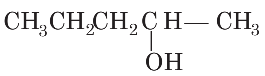
28. Structure of threonine is



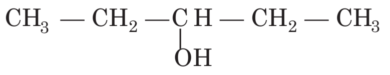
Threonine have 2 chiral carbon atoms.

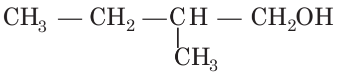
29. The number of possible isomeric pentyl alcohols is eight which are as

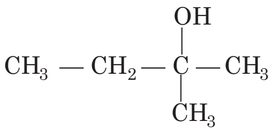
(i) $CH_3CH_2CH_2CH_2CH_2OH$ *n*-pentanol

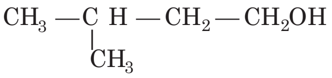
(ii)  2-pentanol

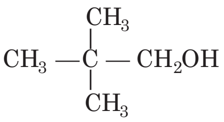
$$CH_3CH_2CH_2\underset{\underset{OH}{|}}{C}H-CH_3$$

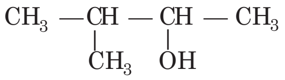
(iii) 
$CH_3-CH_2-\underset{OH}{\underset{|}{C}H}-CH_2-CH_3$ 3-pentanol

(iv) 
$CH_3-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_2OH$ 2-methyl butanol

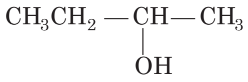
(v) 
$CH_3-CH_2-\overset{OH}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3$ 2-methyl butan-2-ol

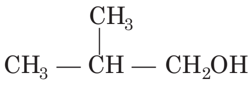
(vi) 
$CH_3-\underset{CH_3}{\underset{|}{C}H}-CH_2-CH_2OH$ 3-methyl butanol

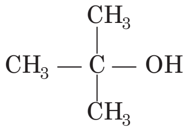
(vii) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_2OH$ 2,2-dimethyl propanol

(viii) 
$CH_3-\underset{CH_3}{\underset{|}{C}H}-\underset{OH}{\underset{|}{C}H}-CH_3$ 3-methyl butan-2-ol

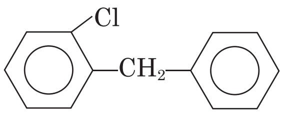
30. (i) $CH_3CH_2CH_2CH_2OH$

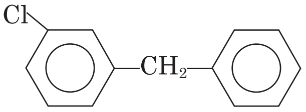
(ii) 
$CH_3CH_2-\underset{OH}{\underset{|}{C}H}-CH_3$

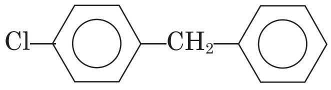
(iii) 
$CH_3-\overset{CH_3}{\overset{|}{C}H}-CH_2OH$

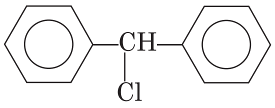
(iv) 
$CH_3-\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-OH$

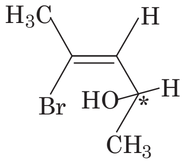
31. Four structural isomers are possible for diphenyl methane when one H-atom is replaced by a Cl-atom.

I. 

II. 

III. 

IV. 

32. Compound  has one chiral carbon atom and one double bond thus, it has two geometrical (*x*) (*cis* and *trans*) and two optical (*y*) isomers.