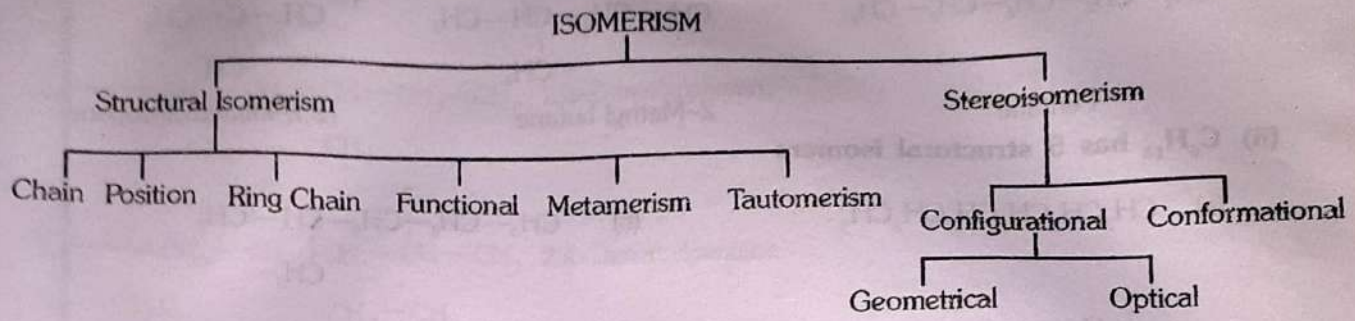
ISOMERISM

Two or more than two compounds having the same molecular formula but different physical/chemical or both properties are called isomers and the phenomenon is called isomerism.



2.1 Structural Isomerism

2.1.1 Chain Isomerism (C.I.)

The compounds which have same molecular formula, same functional group but different arrangement of carbon chain show chain isomerism.

Ex. $CH_3-CH_2-CH_2-CH_3$ $\qquad$ $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

Butane (4C) $\qquad$ 2–Methyl propane (3C)

Ex. $CH_3-CH_2-CH_2-CH_2-OH$ $\qquad$ $CH_3-\underset{\displaystyle CH_2}{\underset{|}{CH}}-CH_2-OH$

1–Butanol (4C) $\qquad$ 2–Methyl–1–propanol (3C)

Ex.  $\qquad$ 

Methylcyclobutane $\qquad$ Cyclopentane

2.1.2 Position Isomerism (P.I.)

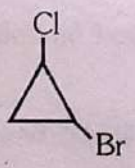
The compounds which have same molecular formula, same functional group, same parent carbon chain but different position of functional group or multiple bond or substituents, show position isomerism.

Ex. $CH_2=CH-CH_2-CH_3$ $\qquad$ $CH_3-CH=CH-CH_3$

But–1–ene $\qquad$ But–2–ene

Ex. $CH_3-CH_2-CH_2-CH_2-OH$ $\qquad$ $CH_3-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

1–Butanol $\qquad$ 2–Butanol

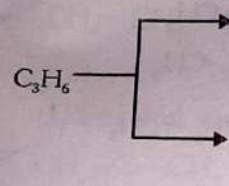
Ex. 

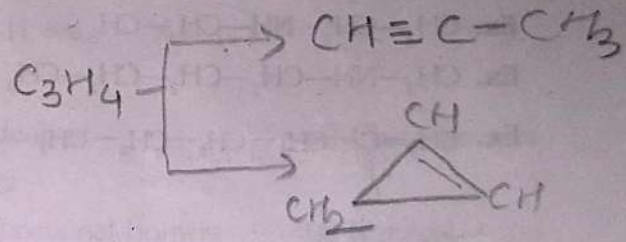
$\qquad$ 

1-Bromo-2-chlorocyclopropane $\qquad$ 1-Bromo-1-chlorocyclopropane

2.1.3 Ring chain isomerism (RCI)

Same molecular formula but different mode of linking (open chain & closed chain) of carbon atoms.





Priority : R T F M C P

- Alkenes with cycloalkane and alkynes and alkadienes with cycloalkenes show Ring-chain Isomerism.
- Ring-chain Isomers are also Functional Isomers but priority must be given to Ring-chain Isomers.

2.1.4 Functional Isomerism

Same molecular formula but different functional groups.

Following compounds show Functional isomerism, as they have same molecular formula and different functional group.

(i) Alcohol and Ether ⟶ CH_3-CH_2-OH and CH_3-O-CH_3

(ii) Aldehydes and Ketones ⟶ $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H$ and $CH_3-\underset{\underset{O}{\|}}{C}-CH_3$

(iii) Acids and Ester ⟶ $CH_3-\underset{\underset{O}{\|}}{C}-OH$ and $H-\underset{\underset{O}{\|}}{C}-O-CH_3$

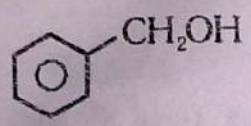
(iv) Cyanide and Isocyanide ⟶ $CH_3-CH_2-CH_2-CN$ and $CH_3-CH_2-CH_2-NC$

(v) Nitro and Nitrite ⟶ $CH_3-CH_2-N\begin{matrix}O\\ \diagdown\\ \diagup\\ O\end{matrix}$ and $CH_3-CH_2-O-N=O$

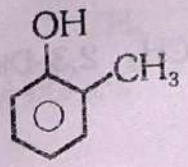
(vi) 1°, 2°, 3° Amines

(i) $CH_3—CH_2—CH_2—NH_2$ (ii) $CH_3—NH—CH_2—CH_3$ (iii) $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{N}}}}—CH_3$

(vii) Alcoholic and Phenolic compounds :



and

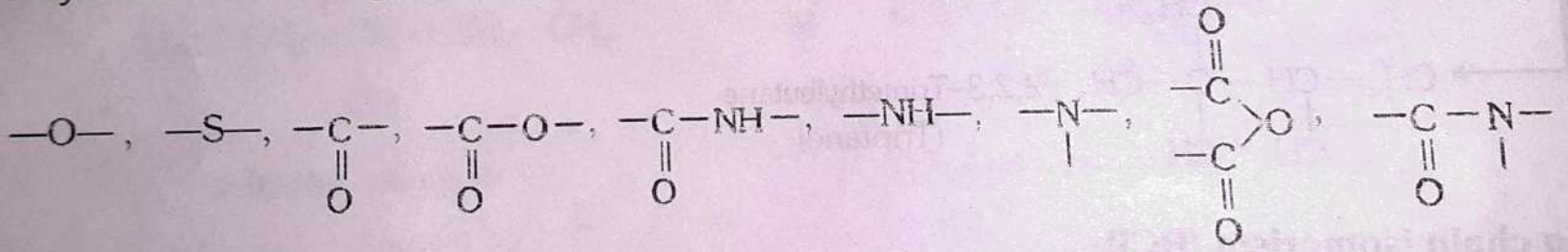


(viii) Alkyl halides do not show Functional isomerism.

2.1.5 Metamerism

Same molecular formula, same polyvalent Functional group but different alkyl groups attached to polyvalent Functional group.

Polyvalent Functional group [Which have more than one valency] are :



Ex. $CH_3—O—CH_2—CH_2—CH_3$; $H_3C–CH_2–O–CH_2–CH_3$

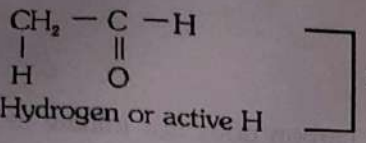
Ex. $CH_3—CH_2—NH—CH_2—CH_3$ $CH_3—NH—CH_2—CH_2—CH_3$

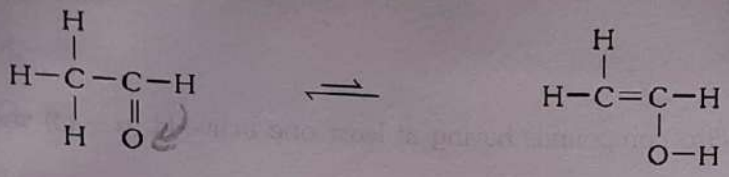
Ex. $CH_3—NH—CH_2—CH_2—CH_2—CH_3$ $H_3C–CH_2–NH–CH_2–CH_2–CH_3$

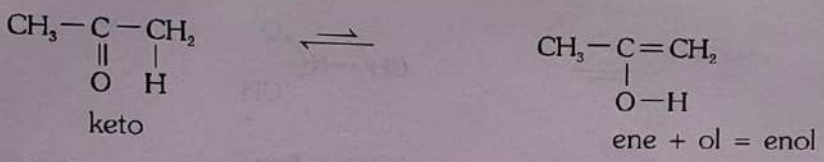
Ex. $CH_3—\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{||}{\underset{|}{C}}}}—CH_2—CH_2—CH_2—CH_3$ $CH_3—CH_2—\underset{\displaystyle O}{\overset{\displaystyle O}{\overset{||}{\underset{|}{C}}}}—CH_2—CH_2—CH_3$

3.5 TAUTOMERISM OR DESMOTROPISM

- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen between two atoms of a molecule.
- Desmotropism means bond turning. [Desmos = Bond ; Tropos = Turn]



Ex. 

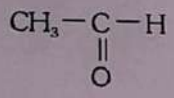
Ex. 

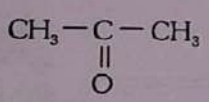
Note : **(1)** Tautomers are also F. I. and exist in dynamic equilibrium.

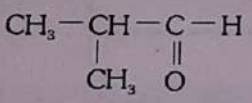
(2) By shifting of H–atom, π bond also changes its position.

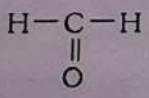
(I) Condition for Tautomerism :

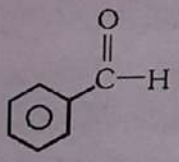
(a) For carbonyl compounds :- Carbonyl compounds having at least one active-H (α–H) show tautomerism

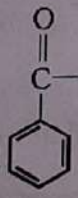
(i)  3 α H, shows tautomerism.

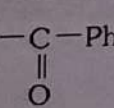
(ii)  6 α H, shows tautomerism

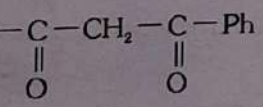
(iii)  1 α H, shows tautomerism

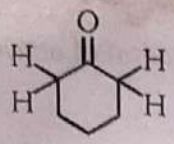
(iv)  No α H, No tautomerism

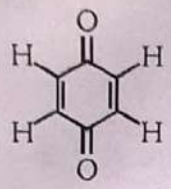
(v)  No α H, No Tautomerism

(vi)  (Acetophenone) 3 α H, shows tautomerism (Acetophenone)

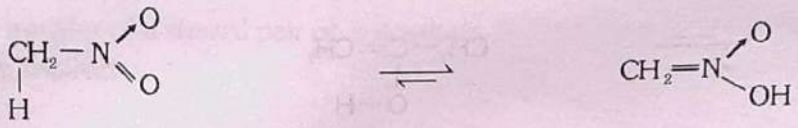
(vii)  (Benzophenone) No α H, No tautomerism (Benzophenone)

(viii)  2 α H, shows tautomerism

(ix)  4 α H, shows tautomerism

(x)  α–H, attached sp^2 carbon does not initiate in tautomerism

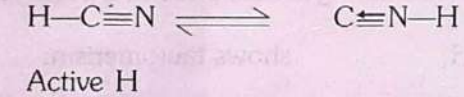
(b) For nitro compounds : Nitro compounds having at least one active-H (α – H) show tautomerism



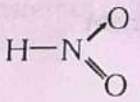
Nitro form Acinitro form

(acidic form so soluble in base)

(c) H—C≡N and H—N ≡ C are tautomers [also Functional isomers] while R—C≡N and R—N≡C are only Functional isomers.

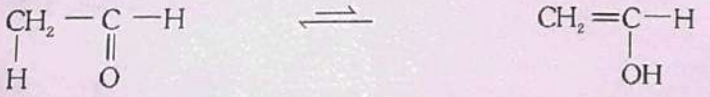


Active H

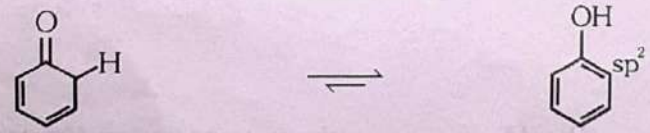
(d)  and H—O—N=O are tautomers.

Note : Nitro compounds with at least one α–H are soluble in NaOH.

(II) Enol Content :

1. 

"keto" (≈ 99%) "enol" (≈ 1%)

2. 

"keto" (≈ 1%) "enol" (stable by resonance and aromatic nature) (≈ 99%)

GOLDEN KEY POINTS

- More active the H, more will be its participation in tautomerism.
- Stability of enol form depends on (i) Resonance and (ii) H – Bond (iii) Aromaticity.

2.2 Stereo Isomerism

Two or more than two compounds having same molecular formula, same structural formula but different arrangements of atoms or groups in space.

(A) Configurational Isomerism : Stereo isomers which have following characteristics.

(a) Stereo isomer which cannot interconvert at room temperature due to restricted rotation known as Geometrical isomerism.

(b) Stereo isomers which have different behaviour towards plane polarised light are known as optical isomers.

(B) Conformational Isomerism

2.2.1 Geometrical isomerism (G. I) :

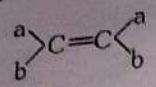
(i) Alkenes (>C=C<), oximes (>C= N—) and azo compounds [—N=N—] etc., show G. I. due to restricted rotation about double bond and (ii) cycloalkanes show G. I. due to restricted rotation about single bond in ring.

G. I. IN ALKENES :

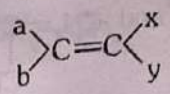
Reason : Restricted rotation about double bond :

Condition for Geometrical isomerism :

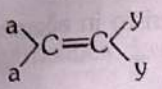
Only those alkenes show G. I. in which "Each sp^2 carbon individually have different atoms or groups"



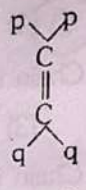
Geometrical isomerism possible



Geometrical isomerism possible



Geometrical isomerism not possible



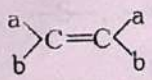
Geometrical isomerism not possible

GI → Cis trans (configuration) | E-Z configuration | Syn Anti configuration

Nomenclature Systems of Geometrical isomers

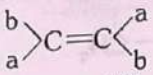
(a) Cis–Trans System

If same groups are at same side then cis and if same groups are at different side then trans.



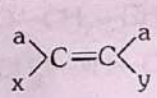
[Same groups, same side]

cis

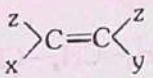


[Same groups different side]

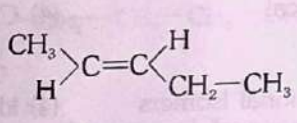
trans

Ex. 

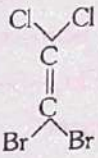
cis



cis

Ex. 

trans-2–pentene



It does not show Geometrical isomers

So no cis–trans

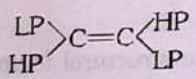
means opposite side when all four grp are diff. then we require E-Z nomenclature

(b) E – Z System:

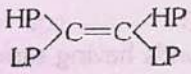
E (Entgegen) : When high priority groups are at opposite side.

Z (Zusamman) : When high priority groups are at same side.

same ← side



'E'

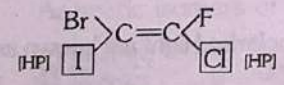


'Z'

HP – High priority and LP – Low priority

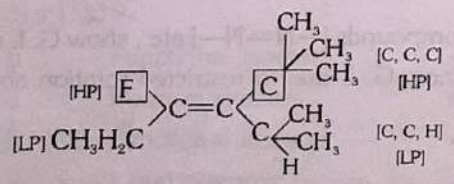
Priority Rules [CIP Sequence Rule] :

Rule I : Priority is proportional to atomic number of atom which is directly attached to sp^2 carbon.



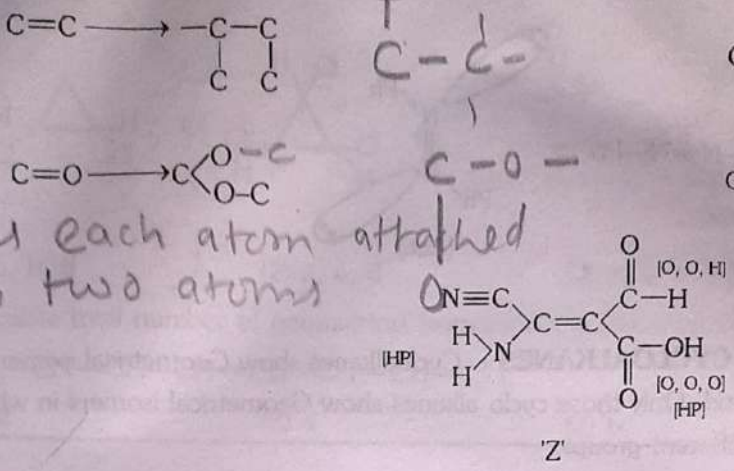
'Z'

Rule II : If rule-I is failed then consider the atomic number of next atom and so on.



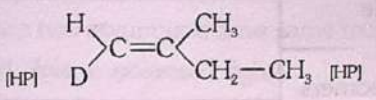
'Z'

Rule III :- If multiple bond is present then consider them as :-



'Z'

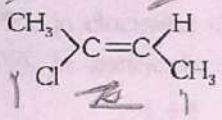
Rule IV : If isotopes are present then consider atomic weight.

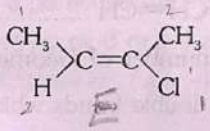


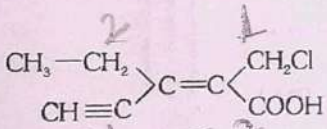
'Z'

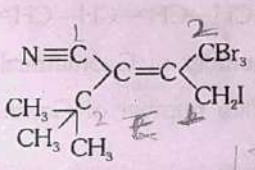
BEGINNER'S BOX-2

1. Assign correct E, Z configuration to following molecules :-

(1) 

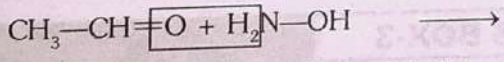
(2) 

(3) 

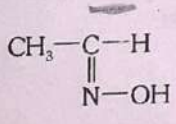
(4) 

GEOMETRICAL ISOMERS IN OXIMES [>C = N–] :

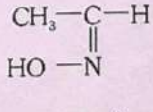
- Oximes show G. I. due to restricted rotation about double bond.
- Only those oximes show Geometrical isomerism in which sp^2 carbon have two different groups.



Ex. Acetaldoximes has two Geometrical isomers –



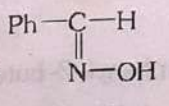
syn



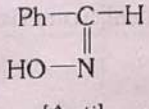
anti

When H and OH are on the same side. When H and OH are on the opposite side

Ex. Benzaldoxime

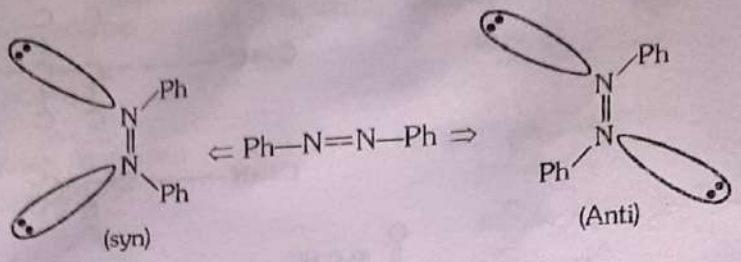


[Syn.]

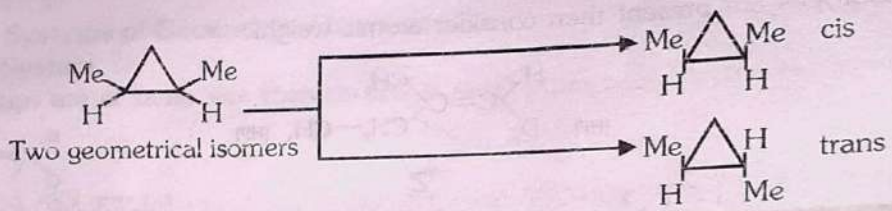


[Anti]

GEOMETRICAL ISOMERS IN AZO COMPOUNDS : (—N̈=N̈—)



GEOMETRICAL ISOMERS IN CYCLOALKANES : Cycloalkanes show Geometrical isomerism due to restricted rotation about single bond. Only those cyclo alkanes show Geometrical isomers in which atleast two different carbons have two different groups.



NUMBER OF GEOMETRICAL ISOMERS IN POLYENES :

$R_1—CH=CH—CH=CH$ ..... $CH=CH—R_2$

(a) If $R_1 \neq R_2$ then number of Geometrical isomers = 2^n

[n = number of double bonds which show G.I.]

Ex. $CH_3—CH=CH—CH=CH—CH=CH—CH_2CH_3$

As n = 3, number of Geometrical isomers = $2^3 = 8$

(b) If $R_1 = R_2$ then number of Geometrical isomers = $2^{n-1} + 2^{p-1}$

where $p = \frac{n}{2}$ (when n is even) and $p = \frac{n+1}{2}$ (n is odd)

Ex. $CH_3—CH=CH—CH=CH—CH=CH—CH_3$ [n = 3]

Number of Geometrical isomers = $2^2 + 2^1$

$= 4 + 2 = 6$

BEGINNER'S BOX-3

1. Which of the following shows Geometrical isomerism –

(a) $CH_3—CH_2—CH=\ddot{N}—OH$

(b) $H_2C=\ddot{N}—OH$

(c) $CH_3—\underset{\underset{N—OH}{\|}}{C}—CH_3$

(d) $CH_3—\underset{\underset{N—OH}{\|}}{C}—CH_2CH_3$

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

2. Which of the following show Geometrical isomerism –

(1) 1,1–Diphenyl–1–butene

(2) 1,1–Diphenyl–2–butene

(3) 2,3–Dimethyl–2–butene

(4) 3-Phenyl–1–butene