01 Structural Isomerism

Isomerism name was given by Berzilius. Two or more than two organic compounds having the same molecular formula and molecular weight but different physical and chemical properties are called isomers and the phenomenon is called isomerism.

ISOMERISM

- Structural Isomerism
  - Chain
  - Position
  - Ring Chain
  - Functional
  - Metameris
  - Tautomeris
- Stereoisomerism
  - Conformation
  - Configuration
    - Geometric
    - Optical

Structural Isomerism:

When two or more number of organic compounds have same molecular formula but different structural formula these are called structural isomers.

S.No.	Isomers	Characteristics	Conditions
1	Chain Isomers	They have different size of main chain or side chain	They have same functional group
2	Positional Isomers	They have different position of locant	They should have same carbon skeleton and same functional group
3	Ring Chain Isomers	They have difference in open & close chain structure	Different mode of linkage (open chain or closed chain)
4	Functional Isomers	Different functional group	Chain and positional isomerism is not considered
5	Metamerism	Different nature of alkyl group along a polyvalent functional group on either side	They should have same nature of functional group; chain & positional isomerism is ignored
6	Tautomerism	Different position of an atom usually hydrogen atom	The two isomers remains in dynamics equilibrium with each other

1. Chain Isomerism (CI) :

The compounds which have same molecular formula, same functional group, same position of functional group or multiple bond or substituent but different arrangement of carbon chain (main chain or side chain) shows chain isomerism.

Example : $CH_3-CH_2-CH_2-CH_3$

Butane (4C)

$$\begin{array}{l} CH_3-\underset{|}{C}H-CH_3 \\ \quad\;\;\, CH_3 \end{array}$$

2-Methyl propane(3C)

Example : $CH_3-CH_2-CH_2-CH_2-OH$

1-Butanol (4C)

$$\begin{array}{l} CH_3-\underset{|}{C}H-CH_2-OH \\ \quad\;\;\, CH_3 \end{array}$$

2-Methyl-1-propanol(3C)

Example : $CH_3-CH_2-CH_2-CH_2-\overset{\overset{O}{||}}{C}-OH$

Pentanoic acid (5C)

$$\begin{array}{l} CH_3-\underset{|}{C}H-CH_2-\overset{\overset{O}{||}}{C}-OH \\ \quad\;\;\, CH_3 \end{array}$$

2-Methyl butanoic acid

$$\begin{array}{l} \quad\;\;\, H_3C \\ CH_3-\overset{|}{\underset{|}{C}}-\overset{\overset{O}{||}}{C}-OH \\ \quad\;\;\, CH_3 \end{array}$$

2,2-Dimethyl propanoic acid

2. Position Isomerism (PI) :

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, are position isomers.

Example : $CH_2=CH-CH_2-CH_3$ $\qquad$ $CH_3-CH=CH-CH_3$

But–1–ene $\qquad$ But–2–ene

Example : $CH_3-CH_2-CH_2-CH_2-OH$

$$\begin{array}{l} CH_3-CH_2-\underset{|}{C}H-CH_3 \\ \qquad\qquad\;\;\, OH \end{array}$$

1–Butanol $\qquad$ 2–Butanol

Example : $CH_3-CH_2-CH_2-CH_2-Cl$

$$\begin{array}{l} CH_3-CH_2-\underset{|}{C}H-CH_3 \\ \qquad\qquad\;\;\, Cl \end{array}$$

1–Chlorobutane $\qquad$ 2–Chlorobutane

Illustration 1:

How many structural isomers are possible for molecular formula C_6H_{14}

Solution:

C_6H_{14} has 5 isomers :

(a) $CH_3CH_2CH_2CH_2CH_2CH_3$

Hexane

(b) $CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

2–Methyl pentane

(c) $CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

3–Methyl pentane

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

2,3–Dimethyl butane

(e) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{CH}}-CH_2-CH_3$

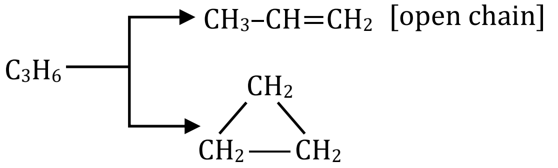
2,2–Dimethyl butane

a & b, b & d, a & c, c & d $\longrightarrow$ Chain Isomers

b & c, d & e $\longrightarrow$ Position Isomers

3. Ring chain isomerism (RCI) :

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



[closed chain or ring]

They have same molecular formula so they are Ring chain isomers.

Illustration 2:

How many minimum carbons required for Chain isomerism and Position isomerism in alkenes?

Solution:

4, 4

Illustration 3:

How many minimum carbons required for Chain isomerism and Position isomerism in alkynes?

Solution:

5, 4

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 $\longrightarrow$ CH_3-CH_2-OH and CH_3-O-CH_3

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

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

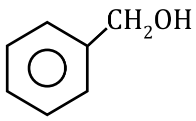
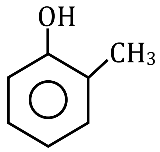
(iv) Cyanide and isocyanide $\longrightarrow$ $CH_3-CH_2-CH_2-CN$ and $CH_3-CH_2-CH_2-NC$

(v) Nitro and Nitrite $\longrightarrow$ $CH_3-CH_2-N\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix}$ and CH_3-CH_2-O-NO

(vi) Amide and Oxime $\longrightarrow$ $CH_3-\underset{\underset{O}{\|}}{C}-NH_2$ and $CH_3-CHNOH$ and $CH_3CH_2-N=O$

(vii) 1°, 2°, 3° amines

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

(viii) Alcoholic and phenolic compounds :  and 

(ix) 1°, 2°, 3° amide

$MeCH_2CH_2-\overset{\overset{O}{\|}}{C}-NH_2$, $MeCH_2-\overset{\overset{O}{\|}}{C}-NH-Me$, $Me-\overset{\overset{O}{\|}}{C}-\underset{\underset{Me}{|}}{N}-Me$

5. Metamerism:

Same molecular formula, same polyvalent Functional goup but different alkyl groups attached to polyvalent Functional group on either side.

Polyvalent Functional group [More than one valency] are :

$-O-$, $-S-$, $-\underset{\underset{O}{\|}}{C}-$, $-\underset{\underset{O}{\|}}{C}-O-$, $-\underset{\underset{O}{\|}}{C}-NH-$, $-NH-$, $-\underset{|}{N}-$, $\begin{matrix}-\overset{\overset{O}{\|}}{C} \\ -\underset{\underset{O}{\|}}{C}\end{matrix}\!\!>O$, $-\underset{\underset{O}{\|}}{C}-\underset{|}{N}-$

Example : $CH_3-O-CH_2-CH_2-CH_3$; $CH_3-CH_2-O-CH_2-CH_3$

Both are metamers

Example : $CH_3-CH_2-NH-CH_2-CH_3$ $CH_3-NH-CH_2-CH_2-CH_3$

N–Ethyl ethanamine N–Methyl propanamine

They are only metamers not CI

Example : $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_3$ $CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_3$

2–Hexanone 3–Hexanone

Both are metamers and Position isomer

Example : $CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-CH_3$ $H_3C-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-O-CH_3$

Propyl ethanoate Methyl–2–methyl propanoate

Both are Metamers

KEY POINTS

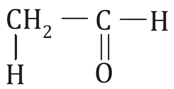
1. Parent carbon chain and functional group must be same in chain isomers.
2. Polyvalent functional group must be present for metamerism.
3. 1°, 2° and 3° amines are considered as different type of functional group.
4. 1°, 2° and 3° alcohols are considered as same functional group.

6. Tautomerism or Desmotropism:

Tautomerism was introduced by "Laar". It's also called desmotropism.

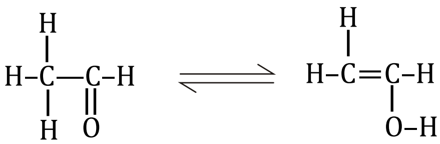
Defination of tautomerism → Arises due to rapid oscillation of an atom usually hydrogen between 2 polyvalent atoms in a molecule.

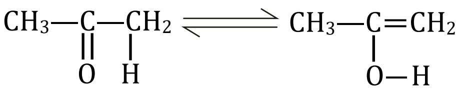
The tautomerism is also called **kryptomerism or allotropism or desmotropism or dynamic isomerism.**



α–Hydrogen or active

α–H attached to carbonyl compound is active H

Example : 

Example : 

keto ene + ol = enol

→ It involves σ–bond shifting

desmotropism → desmo (σ bond) → tropism (Shifting)

→ Tautomers remain in dynamic equilibrium with each other

→ More stable isomer is present in higher concentration.

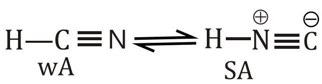
→ Tautomerism Involve intramolecular acid-base reaction.

→ The process can be catalysed by acid as well as base

Type of tautomerism:

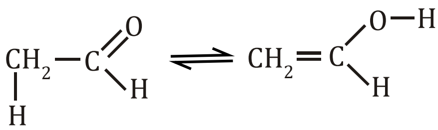
(1) Diad tautomerism :-

If the migration take place in between adjacent atoms then system is known as diad tautomerism.



(2) Triad tautomerism :-

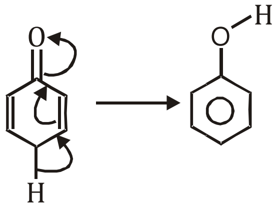
If migration take place between first atom to third atom.



Ket enol

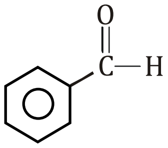
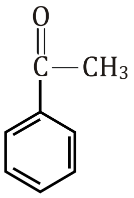
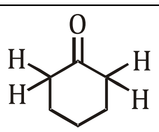
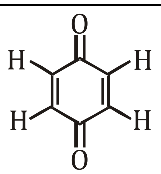
(3) Space tautomerism :

If distance of migration is more than 3 atom then it is known as space tautomerism.

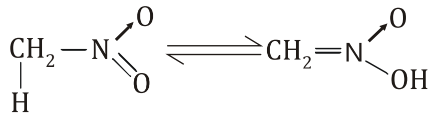


Condition for Tautomerism :

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

(i)	$CH_3-\underset{\underset{O}{\Vert}}{C}-H$	3 α H	show tautomerism.
(ii)	$CH_3-\underset{\underset{O}{\Vert}}{C}-CH_3$	6 α H,	show tautomerism
(iii)	$CH_3-\underset{\underset{CH_3}{\vert}}{CH}-\underset{\underset{O}{\Vert}}{C}-H$	1 α H,	show tautomerism
(iv)	$H-\underset{\underset{O}{\Vert}}{C}-H$	No α H,	No tautomerism
(v)		No α H,	No Tautomerism
(vi)		3 α H,	shows tautomerism (Acetophenone)
(vii)	$Ph-\underset{\underset{O}{\Vert}}{C}-Ph$	No α H,	No tautomerism (Benzophenone)
(viii)	$Ph-\underset{\underset{O}{\Vert}}{C}-CH_2-\underset{\underset{O}{\Vert}}{C}-Ph$	2 α H,	shows tautomerism
(ix)		4 α H,	shows tautomerism
(x)		α–H,	attached sp^2 carbon does not take part in tautomerism

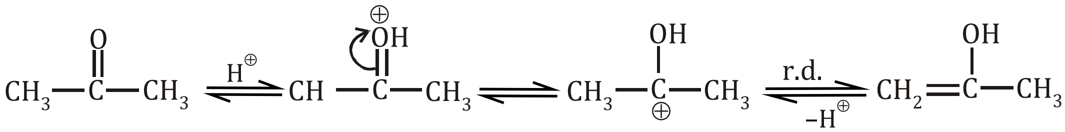
(b) For nitro compounds : Nitro compounds having atleast one α – H show tautomerism



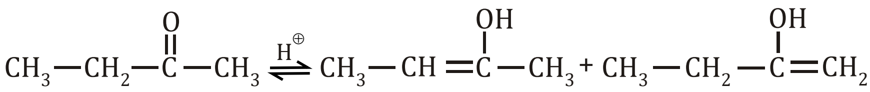
Nitro form　　　　Aci nitro form

Mechanism:

(I) Acid catalysed Mechanism:-

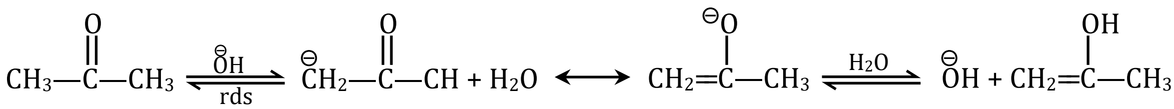


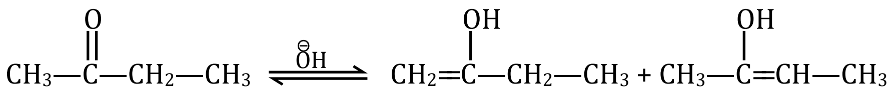
→ More stable product is major product in case of more than one enol



(major)　　　　(Minor)

(II) Base catalysed mechanism :





(major)　　　　(minor)

Enol Content : Generally keto form is more stable than enol form

→ % amount of enol at equilibrium is known as enol content.

→ enol content $\propto$ stability of enol

$\propto$ aromatization of enol

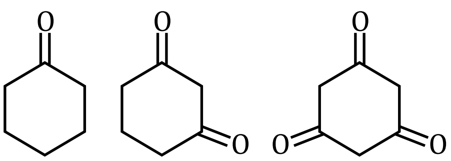
$\propto$ stability of enolate ion

$\propto$ Intramolecular H-bonding

$\propto$ Stability of anion

Illustration 4:

Arrange following in decreasing order of enol content.



Ans. |||>||>|

Solution:

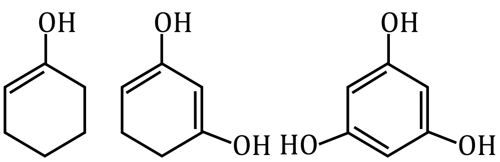
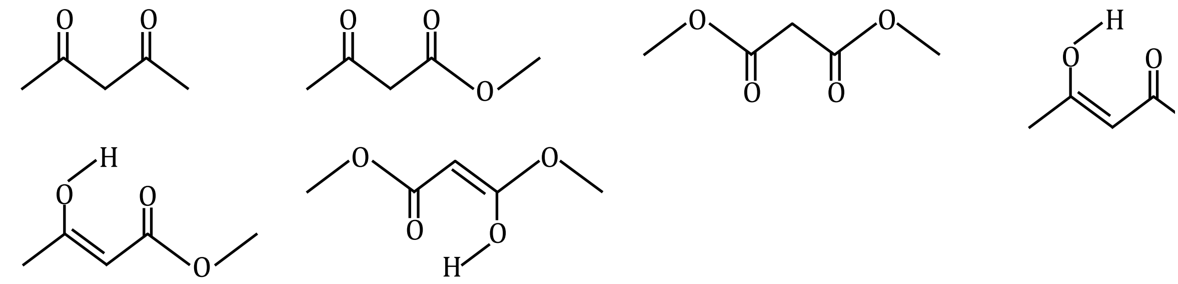


Illustration 5:

Arrange following in decreasing order of enol content.



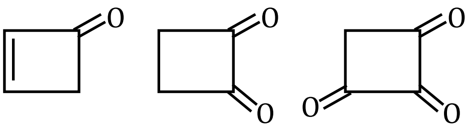
Ans. I > II > III

Solution:

Due to strong chelate in I

Illustration 6:

Arrange following in decreasing order of enol content.



Ans.

Aromatic

↑

III > II > I → Ant

↓

Non aromatic

Solution:

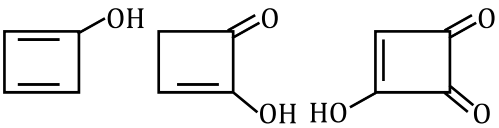
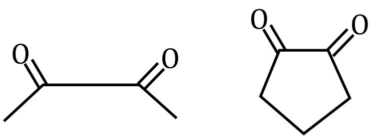


Illustration 7:

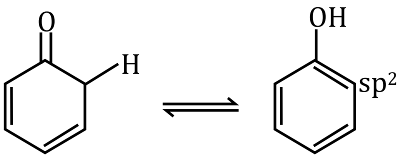
Arrange following in decreasing order of enol content.



Ans. I < II

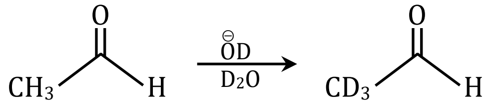
Illustration 8:

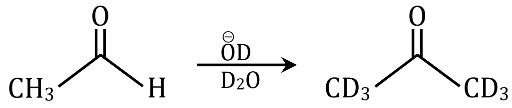
Arrange following in decreasing order of enol content.

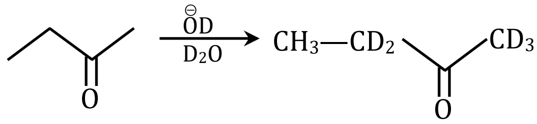


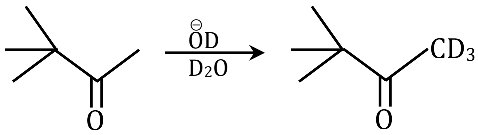
"keto" (≈1%) "enol" (stable by resonance and aromatic nature)(≈99%)

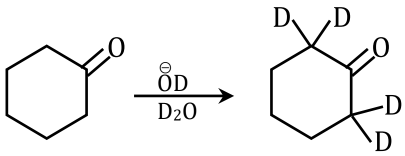
Kinetic isotopic exchange :

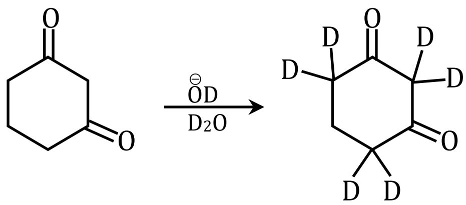
1. 

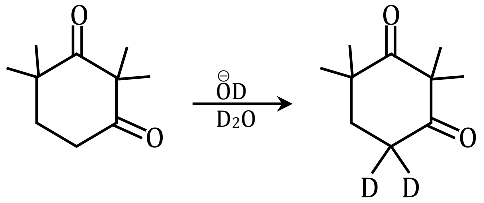
2. 

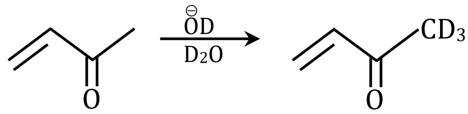
3. 

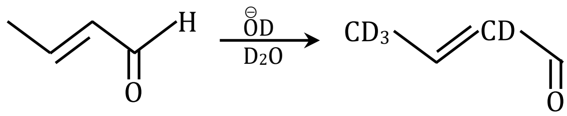
4. 

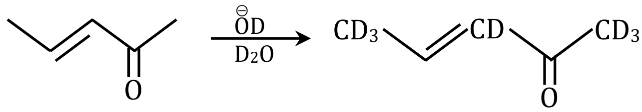
5. 

6. 

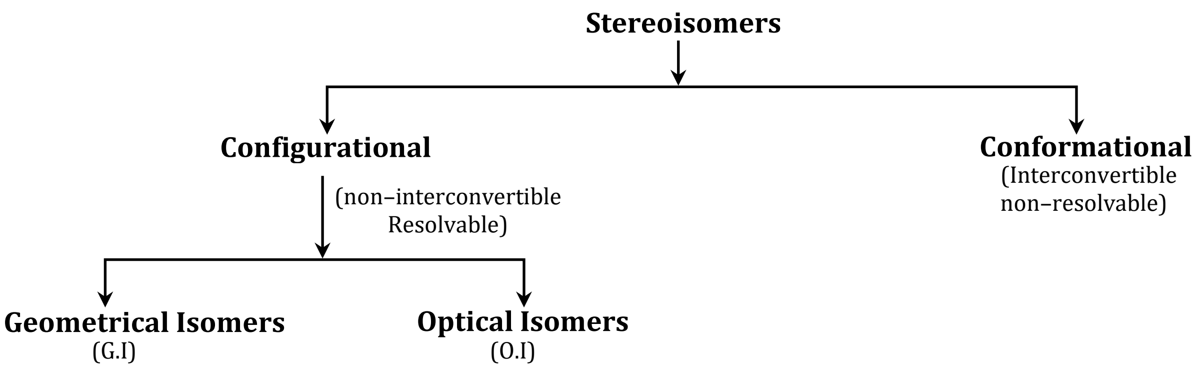
7. 

8. 

9. 

10. 

Stereoisomerism:



Stereoisomerism :-

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