ISOMERISM

Definition:

The different organic compounds having same molecular formula but different physical or chemical or both the properties are called isomers and the phenomenon is called Isomerism.

Isomerism

- Structural isomerism
  - Chain isomerism
  - Positional
  - Functional
  - Metamerism
  - Ringchain
  - Tautomerism
- Stereo isomerism or space isomerism
  - Configurational
    - Geometrical or Cis-trans isomerism
    - Optical
  - Conformational

A. STRUCTURAL ISOMERISM

Arises due to the difference in the manner of linkage of atom to atom.

1. **Chain isomerism/Skeleton/Nuclear :**

   The structural isomerism which arises due to the difference in the length of C-chain is called chain isomerism.

   (a) $H_3C - CH_2 - CH_2 - CH_3$ & $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_3$

   n-Butane   iso-Butane

   (b) $CH_3CH_2CH_2CH_2CH_3$, $CH_3 - \underset{\underset{CH_3}{|}}{CH} - CH_2CH_3$ & $CH_3 - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$

   n-Pentane   iso-Pentane   neo-Pentane

2. **Positional Isomerism :**

   The structural isomerism which arises due to the difference in the position of

   (a) Double bond   (b) Triple bond

   (c) Same functional groups

   e.g. $\Rightarrow CH_3 - CH = CH - CH_3, CH_3 - CH - CH = CH_2$

   But $-2-$ene   But $-1-$ene

   $\Rightarrow CH_3 - CH_2 - CH_2OH, CH_3 - \underset{\underset{OH}{|}}{CH} - CH_3$

   $1 - $Propanol

   $2 - $Propanol

$$1,2/1,6 = \text{ortho}$$
$$1,5/1,3 = \text{meta}$$
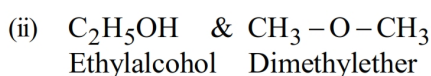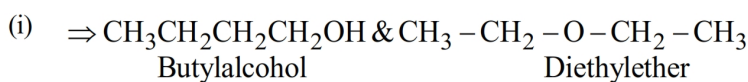$$1,4 = \text{para}$$

ortho   meta   para

3. Functional Isomerism :

The isomerism which arises due to the difference in their functional group is called as functional isomerism.
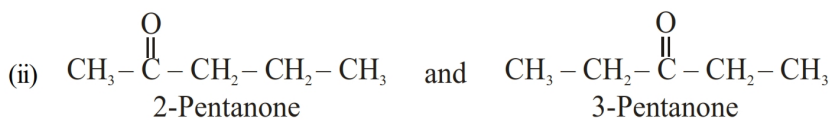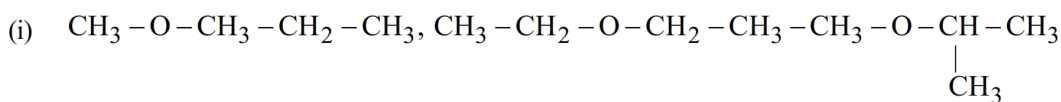
General Formula	Homologous Series	Homologous Series
$C_nH_{2n+2}O$	Alcohol	Ether
C_nH_{2n+2}	Aldehyde	Ketone
$C_nH_{2n}O$	Acid	Ester
$C_{n+1}H_{2n+1}N$	Cyanide	Isocyanide (carbylamine)

(i) $\Rightarrow CH_3CH_2CH_2CH_2OH \ \& \ CH_3-CH_2-O-CH_2-CH_3$
          Butylalcohol   Diethylether

(ii) $C_2H_5OH \ \ \& \ CH_3-O-CH_3$
   Ethylalcohol   Dimethylether

4. Metamerism :

- The structural isomerism which arises due to the difference in the distribution of C-atom on the either or both sides of same functional group.
- Metamers can also be chain and position isomers.

Some examples of Metamerism

(i) $CH_3-O-CH_3-CH_2-CH_3, \ CH_3-CH_2-O-CH_2-CH_3-CH_3-O-\overset{\displaystyle |}{\underset{\displaystyle CH_3}{CH}}-CH_3$

(ii) $CH_3-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-CH_2-CH_2-CH_3$ and $CH_3-CH_2-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-CH_2-CH_3$
        2-Pentanone   3-Pentanone

5. Ring Chain Isomerism

Shown by unsaturated hydrocarbons and alicyclic compounds.

e.g. $CH_3CH_2CH = CH_2$

$CH_3CH_2-CH = CH_2$ &   ☐
     But-1-ene   Cyclobutane
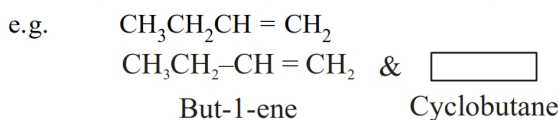
* Ring chain isomers are actually a type of functional isomers.

6. **Tautomerism :**

- It is special type of functional isomerism in which two functional isomers interconvert due to the movement of an acidic H-atom between two poly valent atoms. Here two isomers exist in dynamic equilibrium and hence it is also known as desmotropism/kryptomerism/Alleotropism.

Shown by the compounds having $-\overset{\overset{O}{\|}}{C}-$, $-\overset{\overset{O}{\uparrow}}{N}=O$, $-N=O$, $-CN$ groups attached with $-\overset{|}{\underset{|}{C}}-$ group.
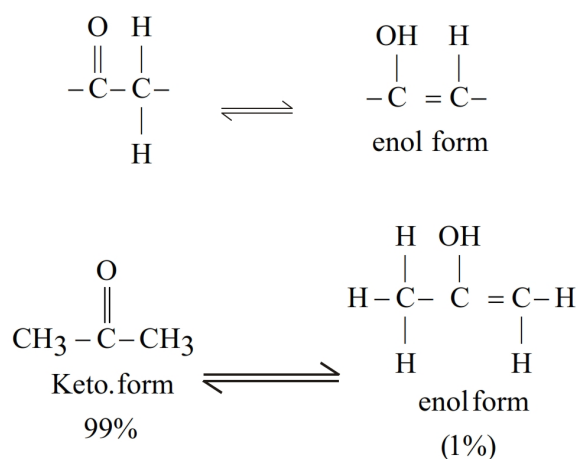
- Tautomerism arises due to shift of an atom from one site in the molecule to another equivalent site in the same molecule.

SOME EXAMPLES OF TAUTOMERISM :

(i) **Keto-enol tautamerism :**

- Aldehydes and ketones containing $-\overset{\overset{O}{\|}}{C}-CH_2-$ group shows tautomerism.

- Enol containing $-\overset{\overset{OH}{|}}{C}=\overset{|}{C}-$ group shows tautomerism.

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

$$\underset{\underset{99\%}{\text{Keto.form}}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} \rightleftharpoons \underset{\underset{(1\%)}{\text{enol form}}}{H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{OH}{|}}{C}=\overset{|}{\underset{\underset{H}{|}}{C}}-H}$$

- β-diketones have more enolic content due to the formation of chelation.

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{C}H-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH=\overset{\overset{\displaystyle OH}{}}{C}-CH_3$$

<div align="center">enol form</div>

$$CH_3-C\overset{O------HO}{\diagdown \diagup}C-CH_3$$
$$\diagup \qquad \diagdown$$
$$CH$$
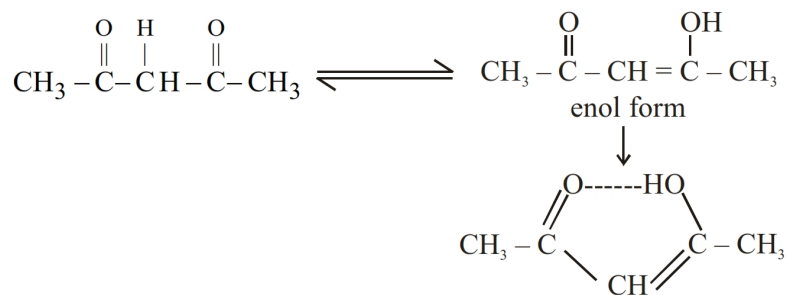
Order of enol-content of some molecule :

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 > CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-H > CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 > CH_3CHO$$

(ii) Nitro-aci tautomerism :

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\overset{\curvearrowright}{N=O} \rightleftharpoons \overset{H}{\underset{H}{\diagup}}C=N-OH$$
$$\overset{}{\underset{\displaystyle O}{\downarrow}} \qquad\qquad\qquad \overset{}{\underset{\displaystyle O}{\downarrow}}$$

<div align="center">Nitro form   aci form</div>

(iii) Nitroso-oximino form :

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\overset{\curvearrowright}{N=O} \rightleftharpoons \overset{H}{\underset{H}{\diagup}}C=N-O-H$$

<div align="center">Nitroso form   Oximino-form</div>