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Isomerism (isos = same, merias = form)

The compounds having same molecular formula but different properties are called isomers and this phenomenon is called isomerism.

Isomerism may be of following two types-

(A) Structural isomerism

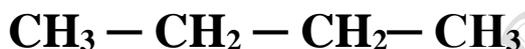
(B) Stereo isomerism

(A) Structural isomerism

The compounds having same molecular formula but different structural formula and therefore, different properties are called structural isomers and this phenomenon is called structural isomerism.

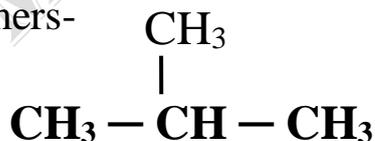
Structural isomerism may be of following types-

(1) **Chain Isomerism-** Such structural isomers which differ in size of longest continuous carbon chain are called chain isomers and this phenomenon is called chain isomerism. This isomerism is specially exhibited by alkanes. For example, butane (C_4H_{10}) has following two chain isomers-



n-Butane

(Butane)



Iso-butane

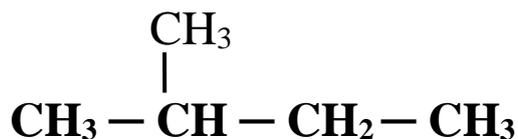
(2-Methylpropane)

Similarly, pentane (C_5H_{12}) has following three chain isomers-



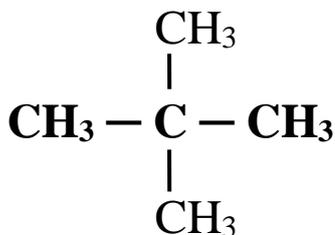
n-Pentane

(Pentane)



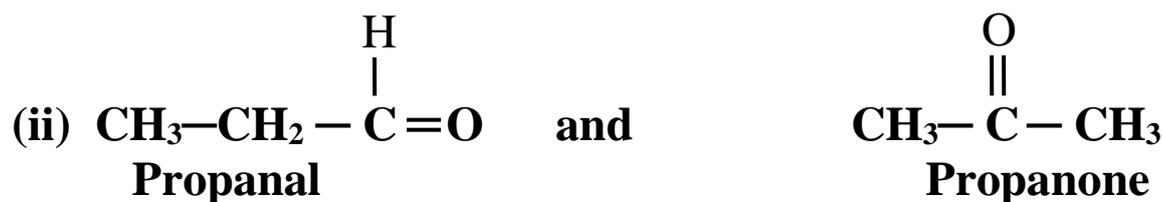
Iso-pentane

(2-methylbutane)



Neo-pentane

(2,2-dimethylpropane)

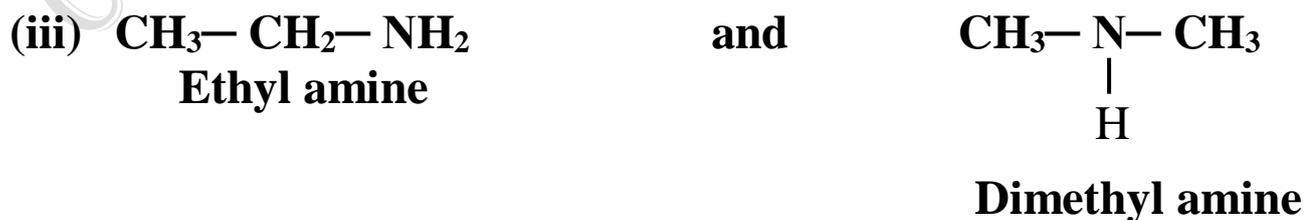
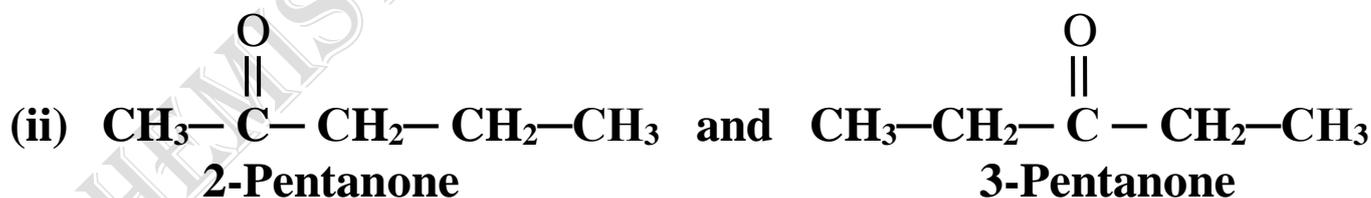
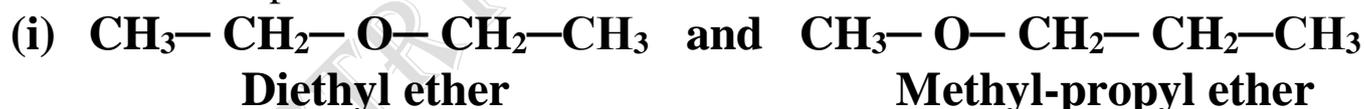


It is clear that, functional isomers belong to different organic families.

➤ Following pairs of compounds are functional isomers of each other-

- (1) Alcohols and Ethers
- (2) Aldehydes and Ketones
- (3) Carboxylic acids and Esters
- (4) Alkyl cyanides and Alkyl isocyanides

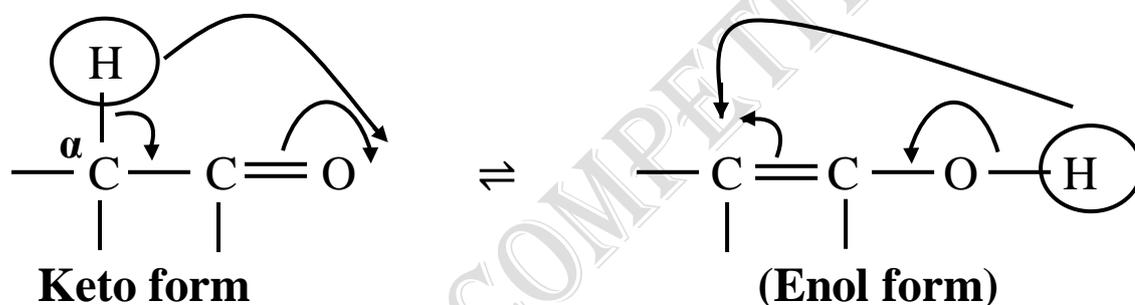
(4) Metamerism- It is a special type of position isomerism, where different isomers called metamers differ in size of alkyl groups attached to a polyvalent atom. For example-



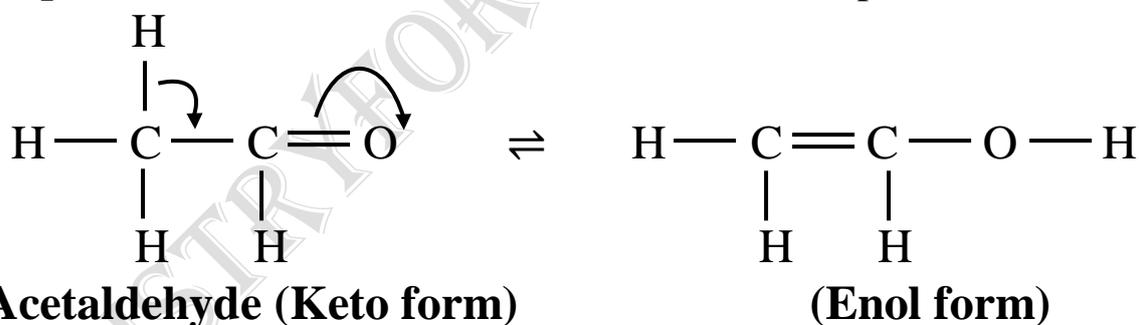
It is clear that, metamers belong to the same organic family.

(5) Tautomerism- It is a special type of functional isomerism where, the isomers called tautomers exist in dynamic equilibrium and frequently interconvert by migration of a proton (prototropy or cationotropy) or a group or an anion from one polyvalent atom to another polyvalent atom. This phenomenon of tautomerism is also called desmotropism, allelotropism, cryptotropy or merotropy. For example,

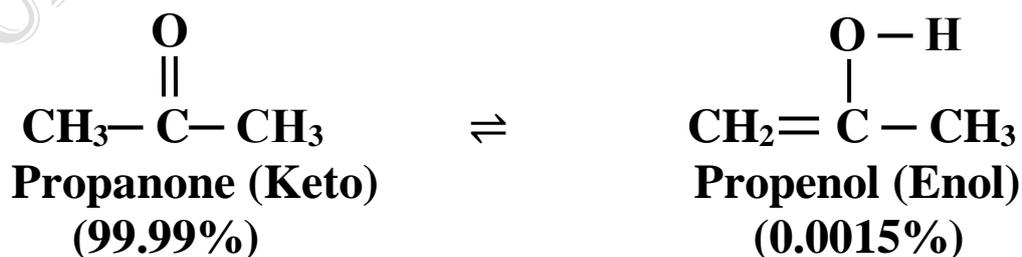
(i) Keto-Enol Tautomerism- It is most common type of tautomerism where, keto and enol forms of carbonyl compounds exist in dynamic equilibrium. In fact, α -hydrogen atoms of carbonyl compounds are acidic in nature and migrates as proton from α -carbon to carbonyl oxygen and vice versa with simultaneous change of bond structure of the molecules. Thus, the compound is a mixture of keto and enol forms.



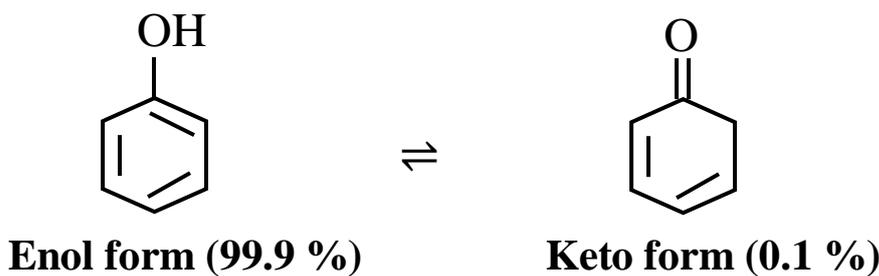
For example, keto and enol forms of ethanal can be represented as under-



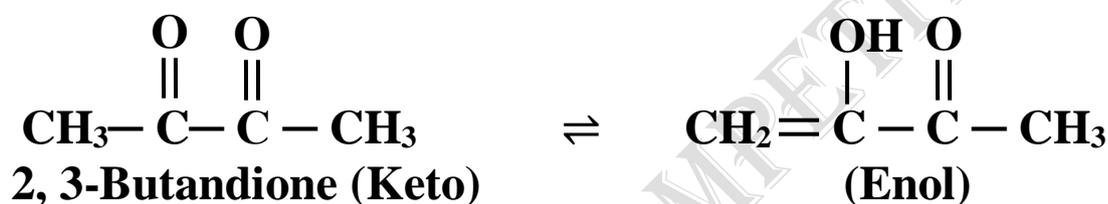
Here, since C=O is more stronger than C=C bond, for mono ketones, in general, keto form is more stable than enol form and therefore, enolization is not preferred. For example, for acetone, keto form is more stable than enol form and predominates in equilibrium mixture.



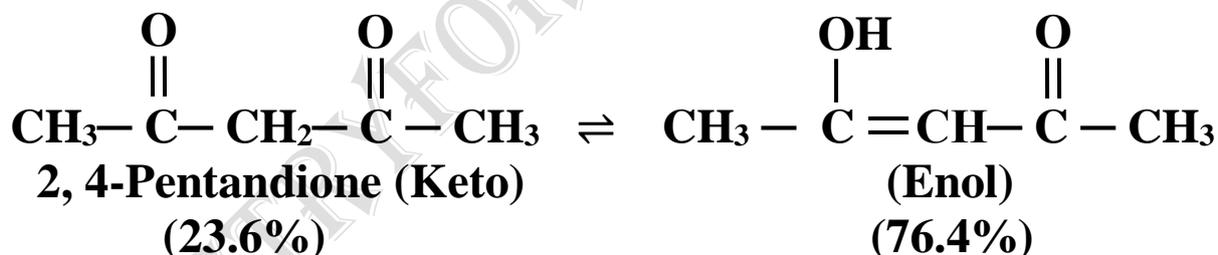
However, for phenol, enol form (99.9 %) is more stable than keto form. Here, aromatic character of benzene ring stabilizes enol form.



Also for di-ketones, where carbonyl group remain present on adjacent carbon atoms, keto form is more stable than enol form. For example, for 2,3-butandione, keto form is more stable than enol form and predominates in equilibrium mixture.

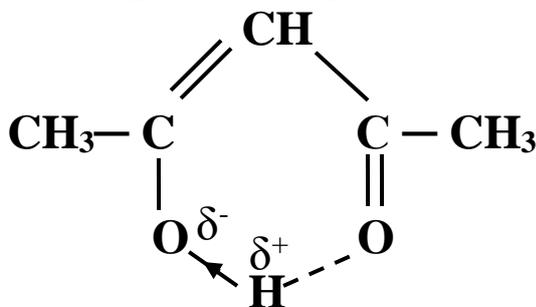


However, for 2,4-pentandione (acetopropanone) enol form is more stable and predominates in the equilibrium mixture.



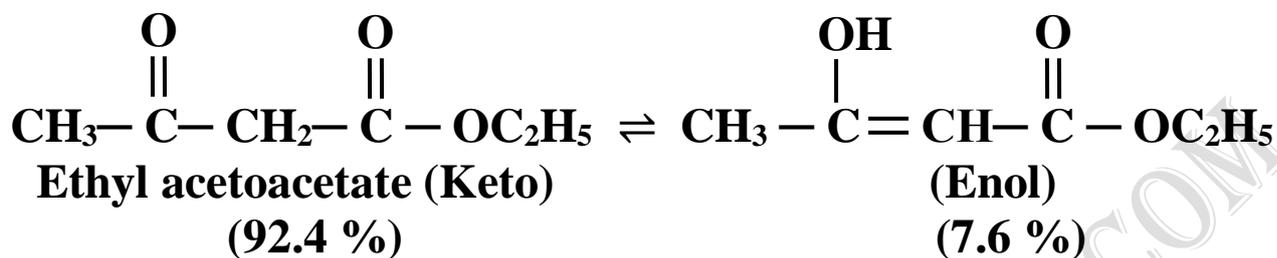
The stability of enol form of 2,4-pentandione is due to following reasons-

- (1) More acidic nature of the hydrogen of active methylene group
- (2) Intramolecular hydrogen bonding in enol form



- (3) Resonance stabilization of enol form due to presence of conjugation

Ethyl acetoacetate (Acetoacetic ester) contains 92.4 % keto form and 7.6 % enol form at room temperature. Here, also enol form is stabilized by intramolecular hydrogen bonding and resonance.



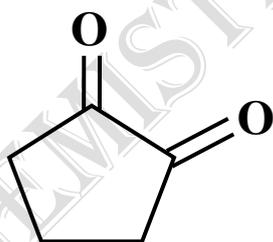
At -78°C interconversion of keto and enol forms is relatively slow and therefore, they can be isolated easily.

Enolization of a compound is directly proportional to the acidity of α -hydrogen and stability of enol form. For example, Extent of enolization for cis diketone is more than that for trans diketone. Here, enol form of cis diketone is stabilized by intramolecular hydrogen bonding.

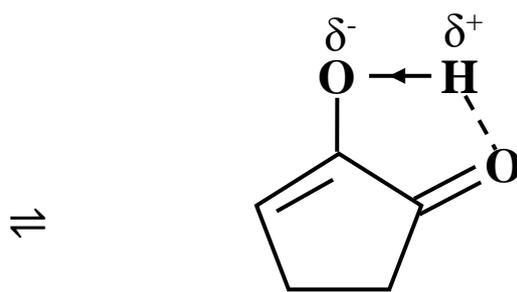


2, 3-Butandione (Keto)
Trans diketone

Enol form
(No intramolecular H-bonding)

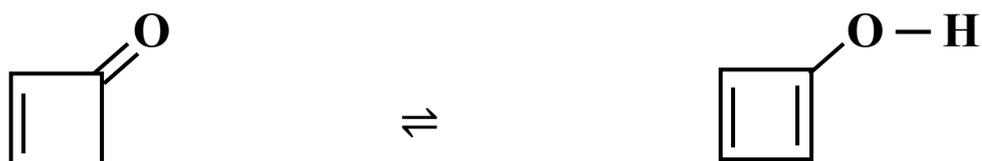


Cis diketone



Enol form
(Stabilized by intramolecular H-bonding)

Similarly, in following compound enolization is not preferred due to the presence of highly unstable anti-aromatic ring in enol form.



**Highly unstable due to presence of
Anti-aromatic ring**

Mechanism of Enolization- Enolization is in general base catalysed and involves the formation of resonance stabilized enolate ion which takes a proton from medium to form enol.

