

* Isomerism

Structural Isomerism

- Chain Isomerism
- Position Isomerism
- Ring chain Isomerism
- Functional Isomerism
- Metamerism
- Tautomerism.

Configuration Isomerism

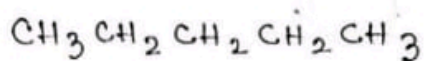
Geometrical Isomerism

• Chain or Nuclear Isomerism:

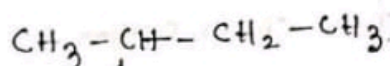
(due to difference in the arrangement of carbon atoms constituting the chain i.e. straight or branched chain)

Isomers showing chain isomerism belong to same homologous series.

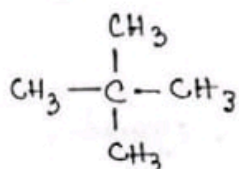
eg. i) Pentane (C_5H_{12}).



n-Pentane

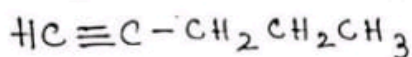


Isopentane

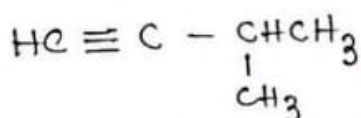


Neopentane.

ii) C_5H_8

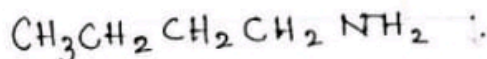


Pent-1-yne

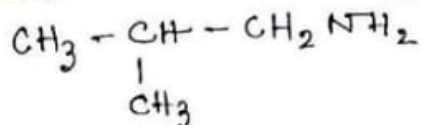


3-Methylbut-1-yne.

iii) $C_4H_{11}N$



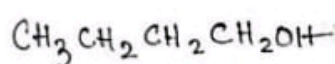
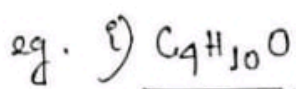
Butan-1-amine



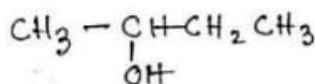
2-Methylpropan-1-amine.

● Position Isomerism :

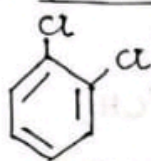
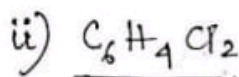
(due to the difference in the positions occupied by the particular atom or group in the same carbon chain or due to different positions of double or triple bonds in alkenes & alkynes). [NB - Aldehydes, Carboxylic acids (& their derivatives) & cyanides do not exhibit position isomerism].



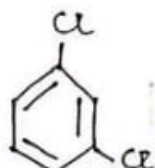
Butan-1-ol



Butan-2-ol.



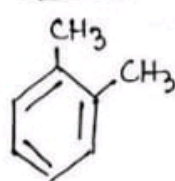
o-Dichlorobenzene



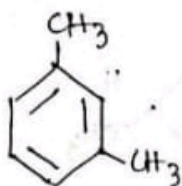
m-Dichlorobenzene



p-Dichlorobenzene



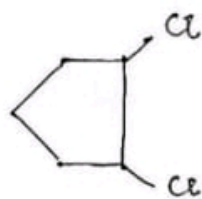
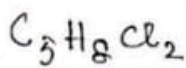
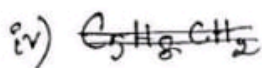
o-Xylene



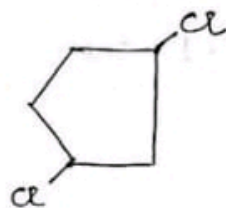
m-Xylene



p-Xylene



1,2-Dichlorocyclopentane



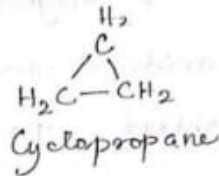
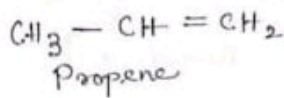
1,3-Dichlorocyclopentane.



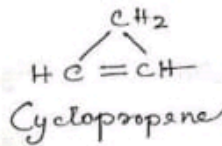
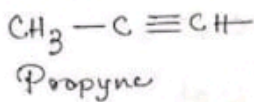
• Ring-Chain Isomerism:

(due to different kinds of linking of carbon atoms, i.e. the isomers possess either open chain or closed chain structures.)

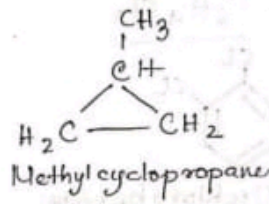
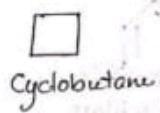
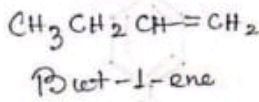
eg. i) C_3H_6



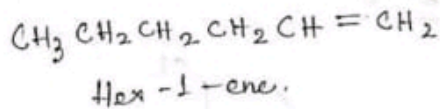
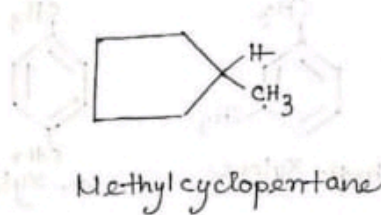
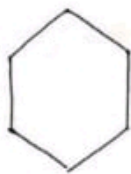
ii) C_3H_4



iii) C_4H_8



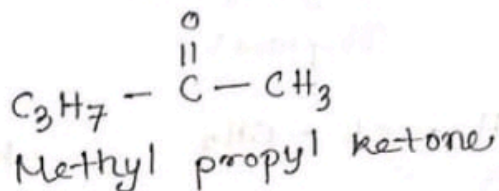
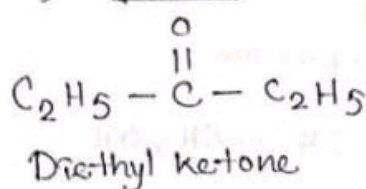
iv) C_6H_{12}



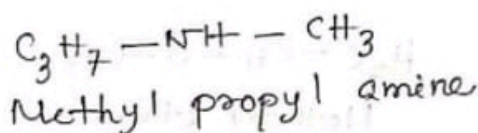
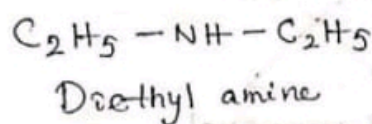
Metamerism:

(due to the presence of different alkyl groups attached to the same polyvalent functional group or atom)

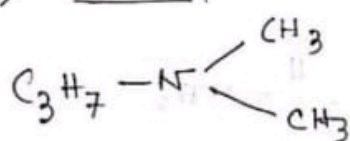
eg. i) $C_5H_{10}O$



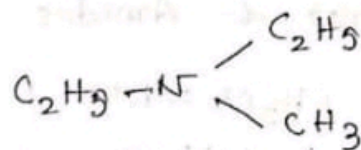
ii) $C_4H_{11}N$



iii) $C_5H_{13}N$

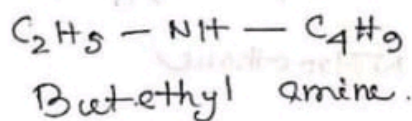
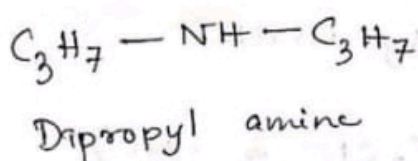


Dimethyl propyl amine



N-Ethyl - N-methyl ethanamine

iv) $C_6H_{15}N$

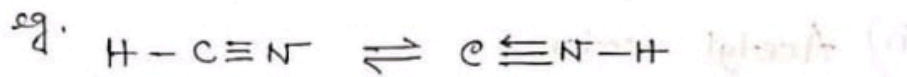


[NB - If same polyvalent functional group is there in two or more organic compounds, they are not supposed to be chain or position isomer, they are metamers.]

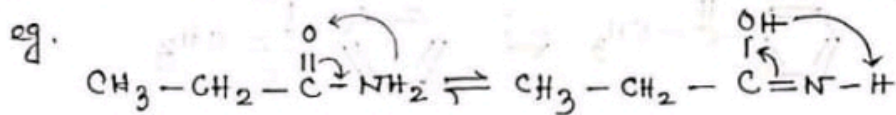
• Tautomerism:

(The type of isomerism in which a substance exists as two readily interconvertible different structures leading to dynamic equilibrium is known as Tautomerism. It is caused by the wandering nature (1,2 or mainly 1,3-migration) of mobile hydrogen atom between two polyvalent atoms within the same molecule.)

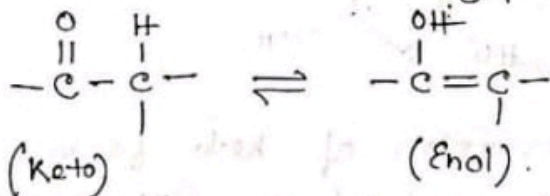
Dyad: If the hydrogen atom oscillates between two polyvalent atoms within the same molecule, the system is a dyad.



Triad: If the hydrogen atom travels from first to third on a chain, the system is triad.

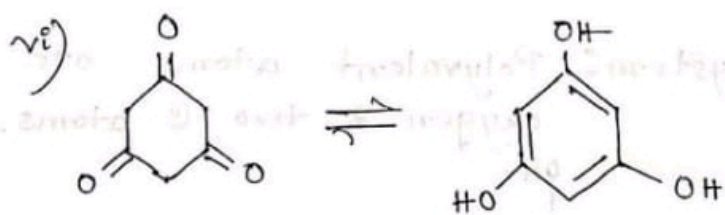
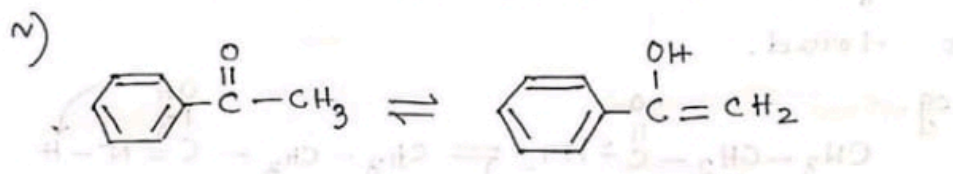
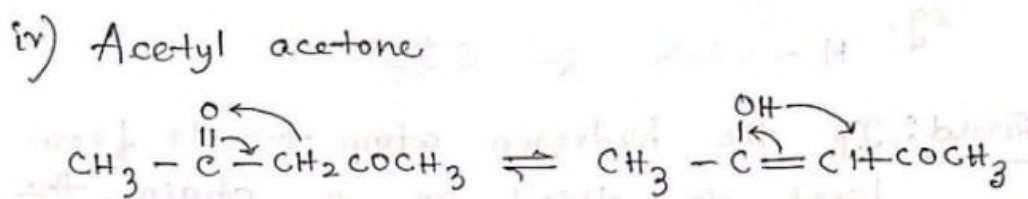
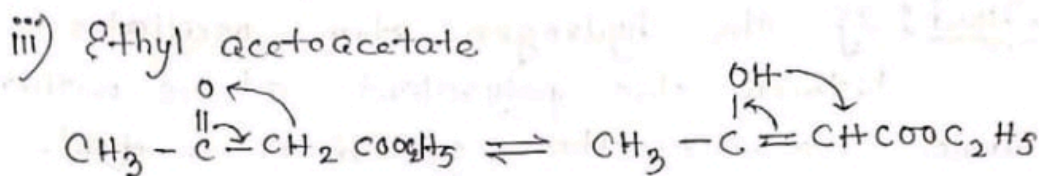
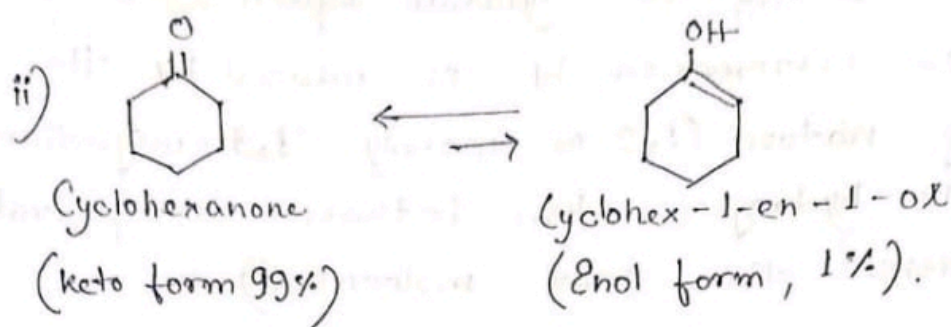
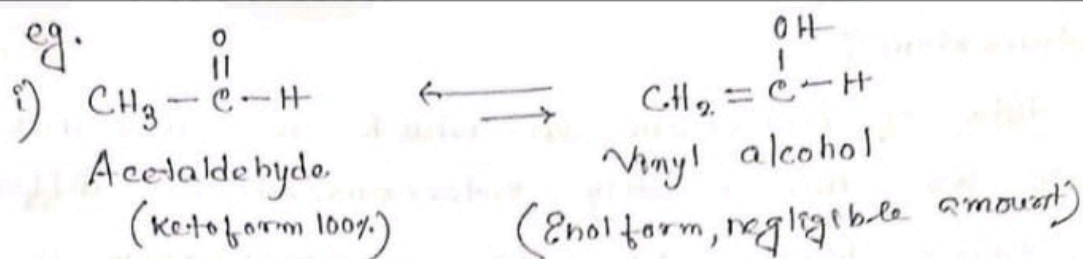


1) Keto-enol System: Polyvalent atoms are oxygen & two C atoms.



(Bond energy - 361 kcal) (BE - 313 kcal).

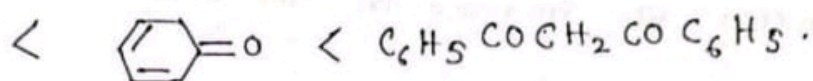
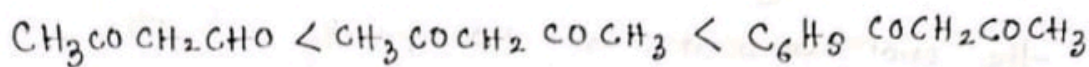
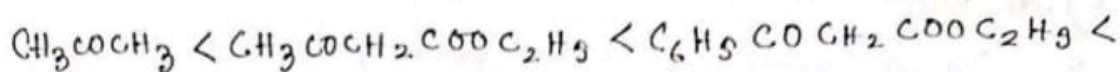
Keto form is more stable than enol form due to greater strength of C-O π bond as compared to C-C π bond.



Enolisation: Conversion of keto form into enol form. Experimentally, the percentage of enol form has been found to increase in the order:

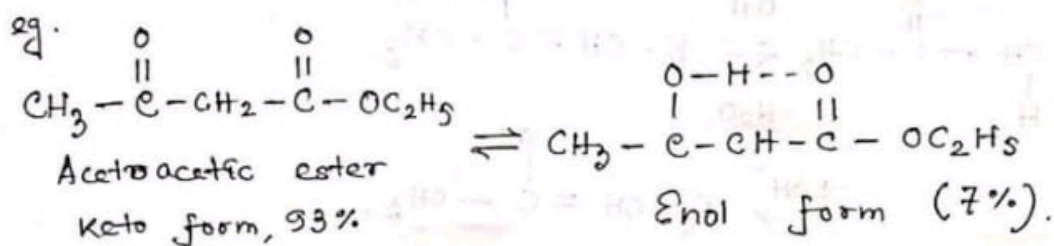
Simple aldehydes & ketone < β -keto ester < β -diketones having phenyl group < phenols.

Enolisation is in order:

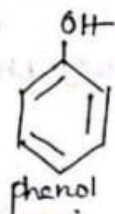
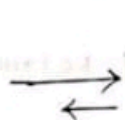
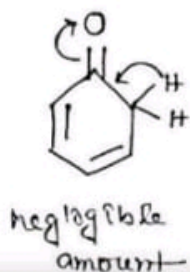
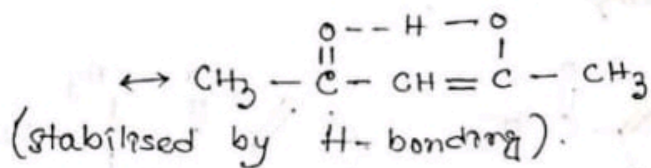
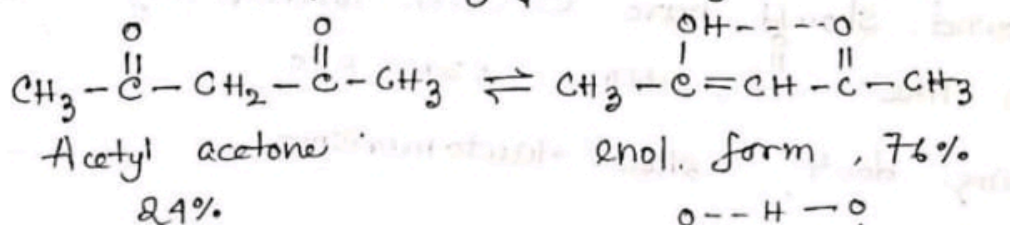


Stability of keto & enol form:

A) If the two keto groups of a compound are separated by methylene group, then enolic form becomes more stable by intramolecular hydrogen bonding (Chelation).



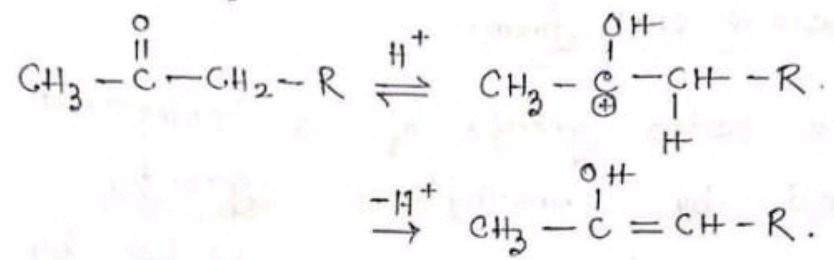
B) Some enol tautomers are more stable than corresponding keto tautomers because of intramolecular H-bonding, aromatic nature, formation of conjugated system.



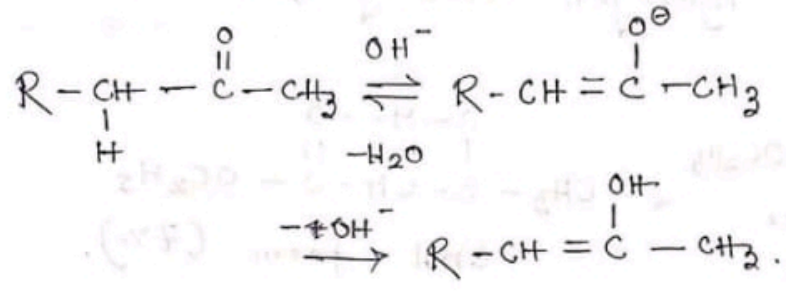
(stabilised by conjugation, conjugated with aromatic ring).

c) In polar solvents, which form H-bonds with the $>C=O$ group of keto form, decrease the enol content. In non-polar solvents, there occurs an increase in the enol content.

Acid catalysed interconversion:



Base catalysed interconversion:

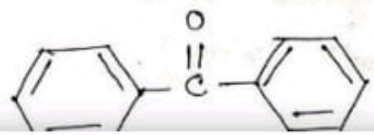
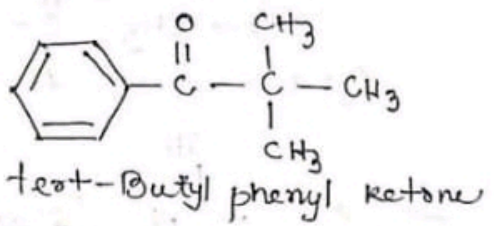
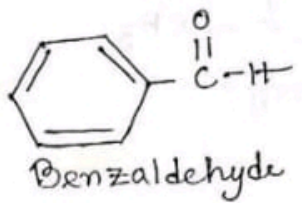


* Essential condition for (keto-enol)

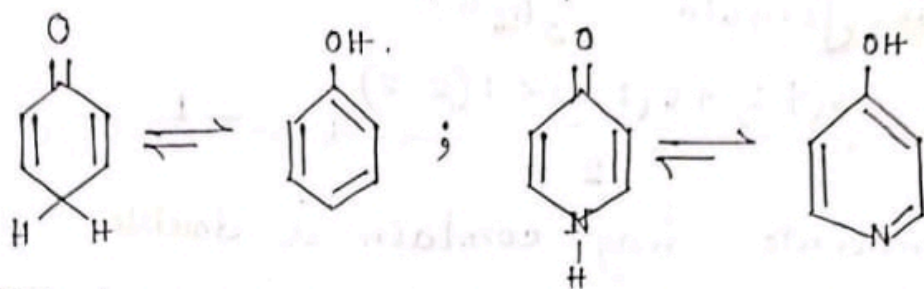
tautomerism: Aldehydes & ketones having at least one acidic α -hydrogen atom show keto-enol tautomerism.

Compound should have electron withdrawing groups like $-\overset{\text{O}}{\parallel}{\text{C}}-$, $-\text{NO}_2$, $-\text{C}\equiv\text{N}$ etc.

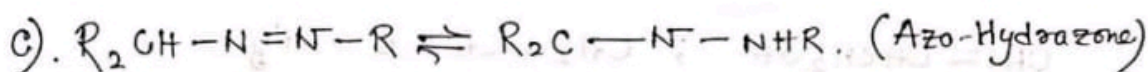
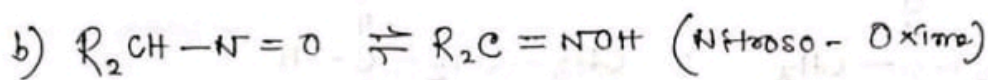
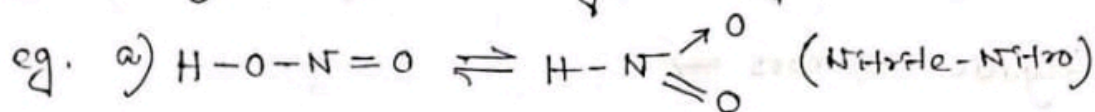
Following don't show tautomerism-



2. Para-tautomerism: H atom migrates from para position.



3. Triad system containing Nitrogen:



• Double Bond Equivalent (DBE):

$$\text{DBE} = \frac{\sum n(v-2)}{2} + 1.$$

n = no. of different kinds of atoms present in molecule.

v = valency of each atom.

eg. C_4H_6 $\text{DBE} = \frac{4(4-2) + 6(1-2)}{2} + 1 = 2.$

Thus the compound may contain i) two double bonds or a triple bond,
 ii) one ring & one double bond,
 iii) two rings.