

Class Topic → Tautomerism.

①

When a compound has constitutional isomers which is interconvertible by a low energy barrier and isomerisation of that compound involves migration of one atom or group from one position to another then this type of isomerism is known as tautomerism and the isomers arises due this called tautomers.

Tautomers of a compound exist in equilibrium which is influenced by various thermodynamic condition like Pressure, temperature, solvent, pH etc.

Tautomerism is generally exhibited by liquid and gaseous form of a molecule.

Depending on the functional group nature of tautomers these are various type.

- 1) Keto-enol tautomerism
- 2) Phenol-Keto " 8) Amidine-Imidine tautomerism
- 3) Amido-imidol " 9) Azo-hydrazone "
- 4) Nitroso-Oxime " 10) Diazo-nitrosoamine "
- 5) Nitro-acinitro " 11) Ring-chain "
- 6) Imine-enamine " 12) " "
- 7) Diazo-amine

## Another classification

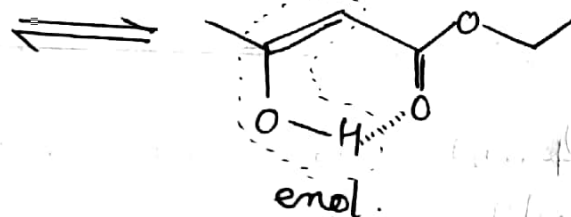
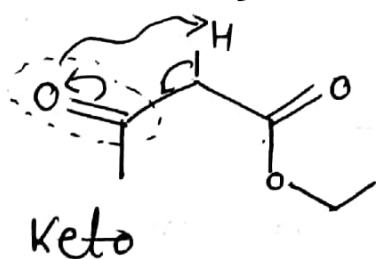
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- 1) Cationotropy tautomerism      2) Anionotropy tautomerism      3) Valence tautomerism

### examples of various tautomerism

Prototropy → Keto-enol, aci-nitro, nitroso-oxime, diazo-amino and enamine-imine, (as per your CBCS syllabus)

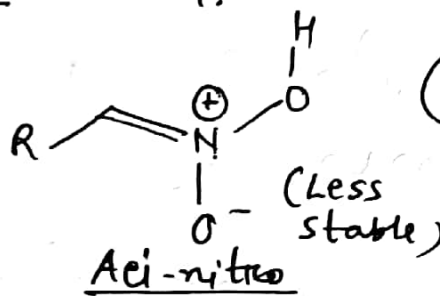
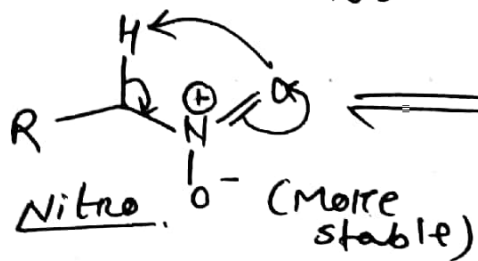
#### 1) Keto enol tautomerism



This is a Prototropy type as here H<sup>+</sup> is shifted from Carbon to oxygen.

#### 2) Acid-nitro or Nitro-acid tautomerism

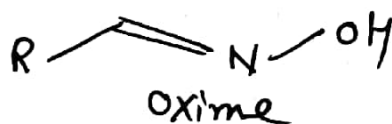
Condition ⇒ there should be at least one α-H w.r.t NO<sub>2</sub> group.



(Prototropy) shift of H<sup>+</sup> from Carbon to oxygen.

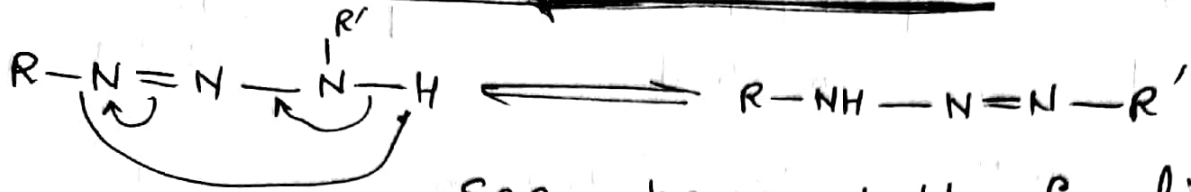
#### 3) Nitroso-oxime tautomerism

Condition ⇒ α-H atom w.r.t nitroso group. (Just as before). (Prototropy)

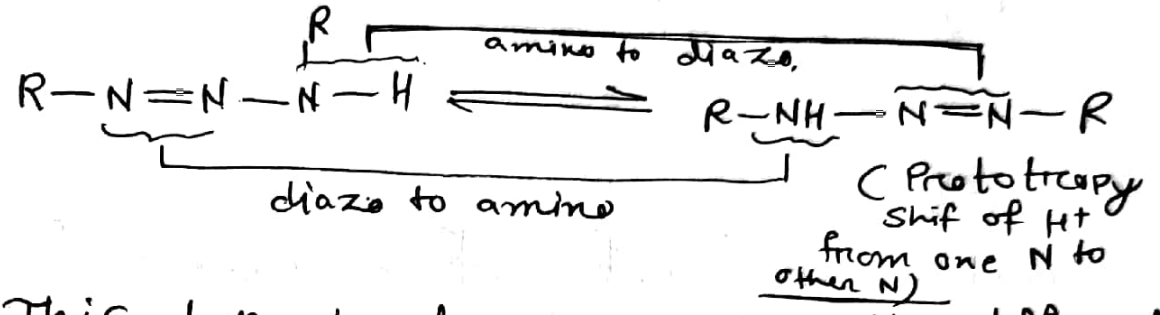


Note! Nitroso form is only stable when there is no α-H's.

4) Diazo-amino tautomerism

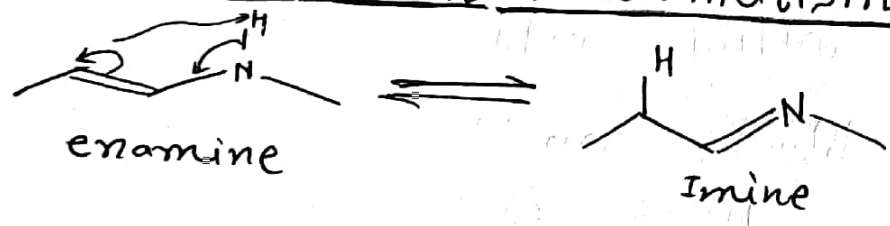


See here both functionality has same structure. Unlike R/R', when R=R' → called degenerate diazo-amino tautomerism.



\* Note - This type tautomerism is little different than other type tautomerism.

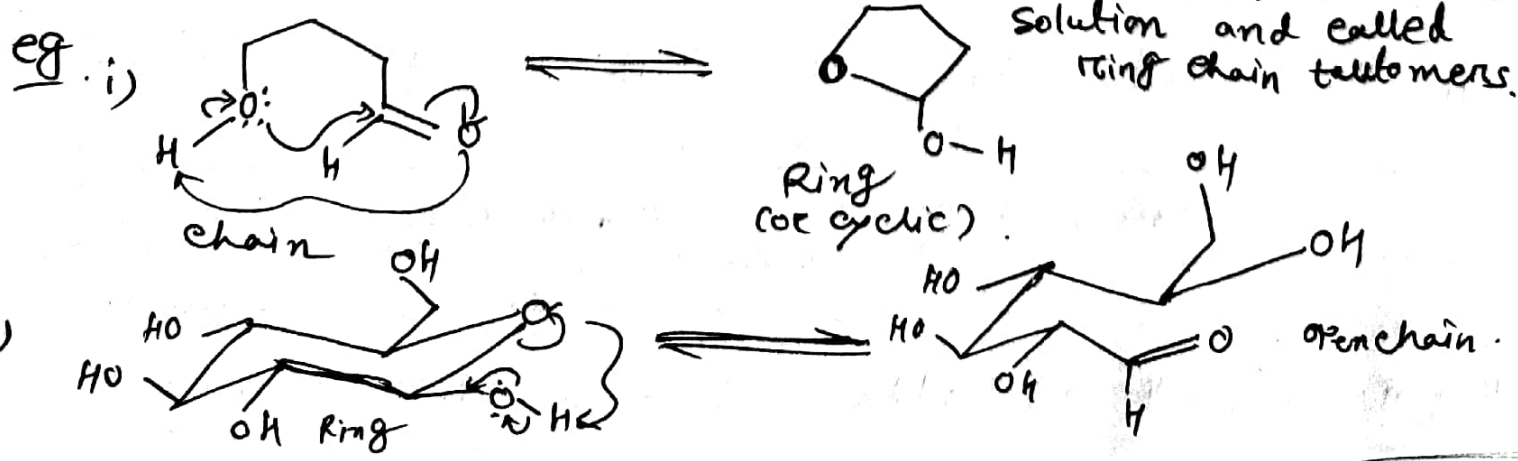
5) Enamine-Imine tautomerism



Protropic (shift of H<sup>+</sup> from N to carbon).

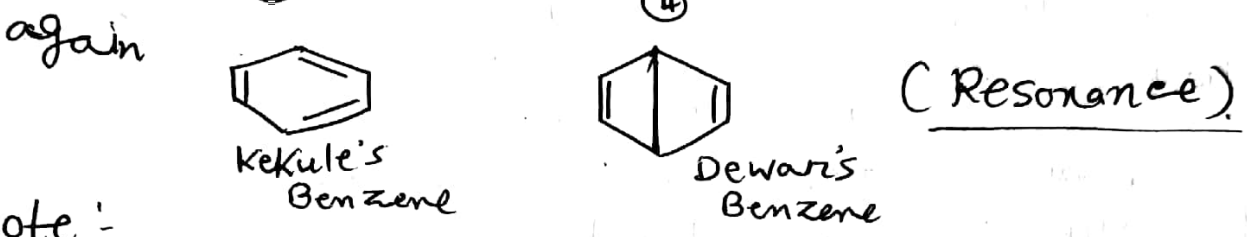
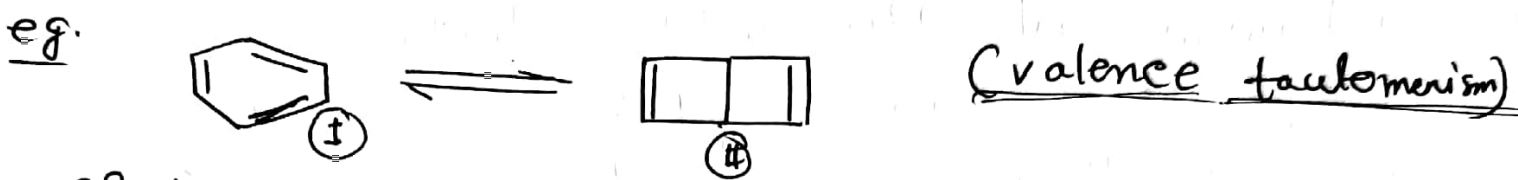
Ring-chain tautomerism

Here the equilibrium structures contain one cyclic structure and one open chain structure. These are in rapid equilibrium in liquid or in solution and called ring chain tautomers.



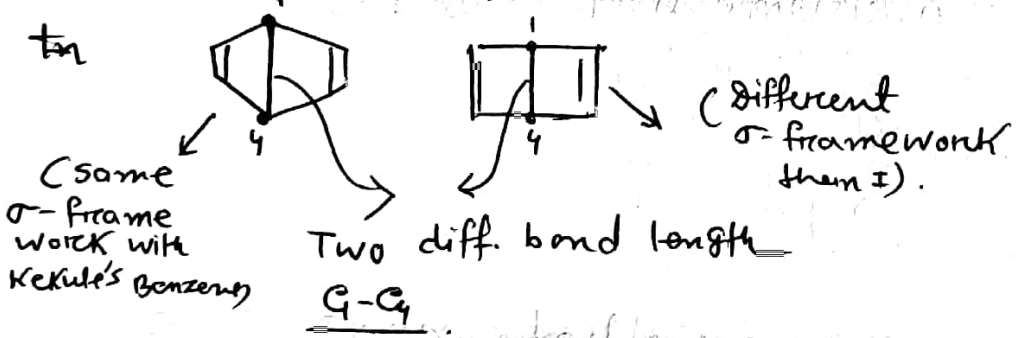
# Valence tautomerism

In this type of tautomerism valence electrons undergo redistribution and new structural isomers are generated upon migration of atomic nuclei



## Note:

Apparently structure II and Dewar's Benzene looks same, but there is difference.



Str's I and II are different structures, because of different  $\sigma$ -framework and no shift of atomic nuclei.

But in Kekule's and Dewar's benzene. (they are resonating str's). the valence e's. are redistributed. in the same  $\sigma$ -frameworks (both are hexagonal str's unlike valence tautomerism where hexagonal str's changes to square type structure) to form different structures. whereas in VT, shift of valence e's is accompanied with the change in basic structure, but not involving change in position.