# TAUTOMERISM

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## What is Tautomerism?

Tautomerism is a phenomenon where a single chemical compound tends to exist in two or more interconvertible structures that are different in terms of the relative position of one atomic nucleus which is generally the hydrogen. The two structures are called tautomers and these type of isomer compounds usually differ only in the number of electrons and protons. They also exist in dynamic equilibrium.
When a reaction occurs between these compounds there is only transfer of protons. Tautomerism is also termed as desmotropism.

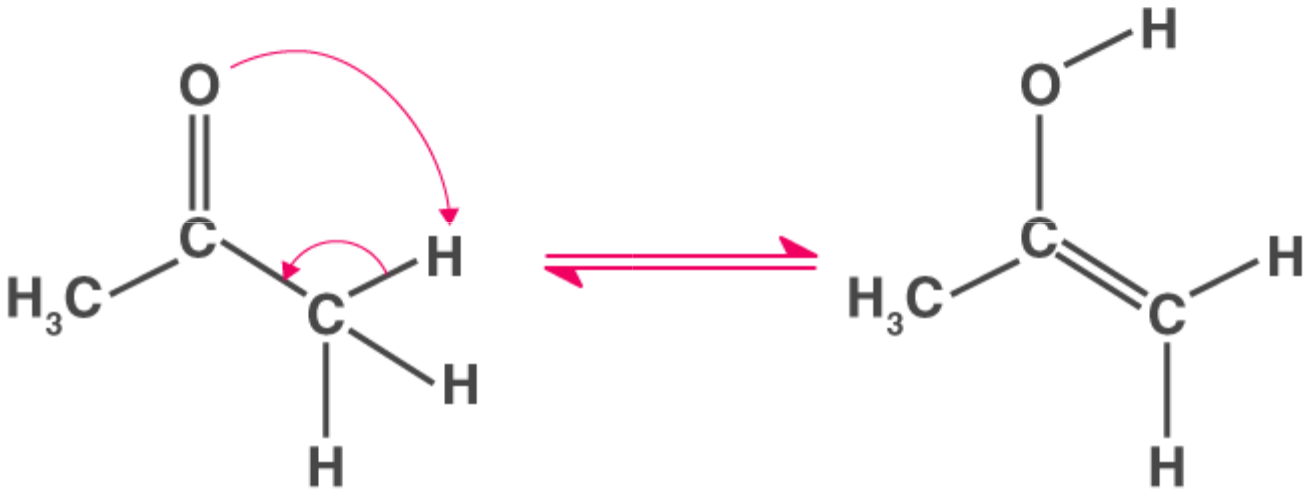
Tautomerism basically happens in the presence of a catalyst.

•Acid-catalyst: Here firstly the protonation occurs, cation will be delocalized. Then, deprotonation will occur in the adjacent position of the cation.

•For base catalysts, deprotonation is the first step. Here, instead of cation delocalization, anion delocalization occurs and finally protonation to the different position of the anion.

## automerism Example

we consider the simple definition of tautomerism then it is described as a f isomerism wherein the isomers interchange into or between one another very easily in orde xist together in equilibrium. During the reaction, there is proton transfer occurs in an intramolec ashion. Consider an example of tautomerism given below,




Keto form more stable 99.9%

Enol form less stable 0.001%

etone-enol, enamine-imine,lactam-lactim, etc are some of the examples of tautomers

## Structural Requirement of Tautomerism

- Compounds contain polar molecules and weakly acidic group functional groups.
- It involves the change in position of an atom.
- It has no effects on bond length or such features.
- Generally, it occurs in planar or non-planar molecules.

## automerism Types

the 1880's a scientist named Emil Erlenmeyer developed rule for the utomerism. He is one of the first one to have studied about the keto-enol utomerism. This rule states that hydroxyl group in all alcohols is attached with ouble-bonded carbon atom directly, and forms ketones or aldehydes. This ccurred due to the more stability of the keto form.

here are different types of tautomerism but among them, keto-enol utomerism is the most important one. In this form, one structure is a ketone nd the other is in enol form. Both of the tautomeric forms are interconvertible o each other by use of acid or base catalysts. This process of conversion of the etone to enol is known as enolization.

## rototropy

is a type of tautomerism that occurs due to the acid-base behaviour of the compound. Her
wo forms differ only in the position of a proton. This structure will have the same empirica
ormula and the number of charges.

## nnular Tautomerism

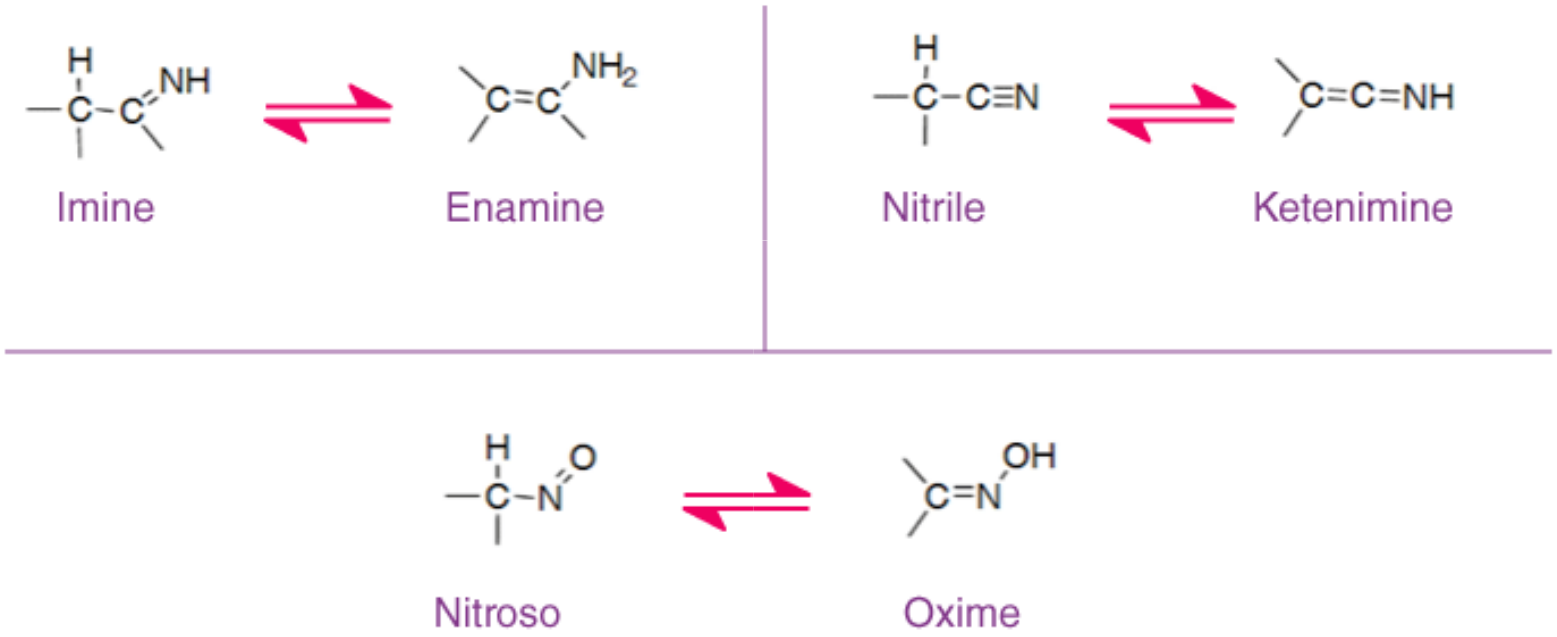
a proton occupies two or more position of a heterocyclic system, then such process is calle
nnular tautomerism. In tautomerism, due to the delocalization of proton, if an open structure i
hanged to a ring structure, then such tautomer is called as ring-chain tautomers. Glucose is a
xample of ring-chain tautomers.

## alence Tautomerism

alence tautomerism is a type of tautomerism where there is continuous formation and breakin
f single and double bonds in the compound without any migration of groups or atoms. It i
ifferent from the previous type of tautomerism, and it is a rapid process.
this tautomerism, there is a change in geometrical structure but no change for canonica
esonance structure or mesomers.

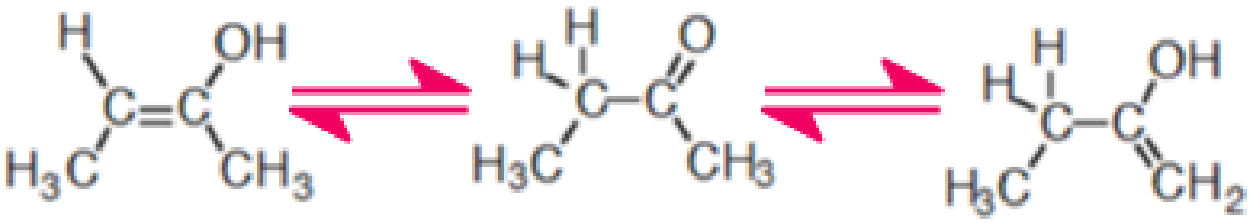
## automerism in Non-Carbonyl Compounds

ost of the non-carbonyl systems are available as a mixture of tautomers. Some of the examples e given below;



## automeric Form of Unsymmetrical Ketones

n symmetric form, there is only one form of tautomer. But for an unsymmetrical form, there can be two. Let'
ave a look to the example given



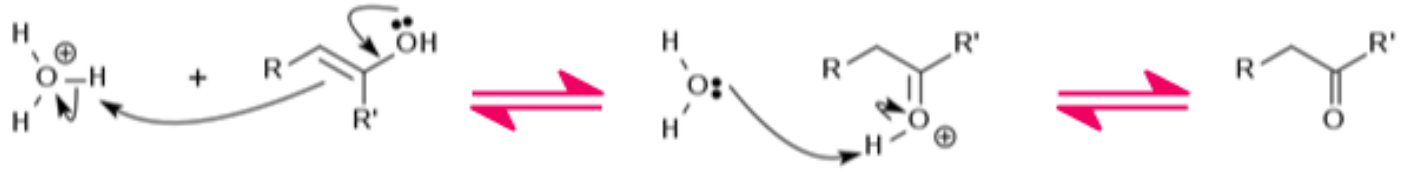
## automerism Reaction Mechanism

et's discuss the acid catalyzation of keto-enol tautomerization. It is a two-step process in an aqueou olution of acid. The carbon atom closest to the functional group is called the alpha carbon atom. So, for th echanism to happen at least one hydrogen atom should be with the alpha carbon atom. It can also b alled an alpha hydrogen atom.

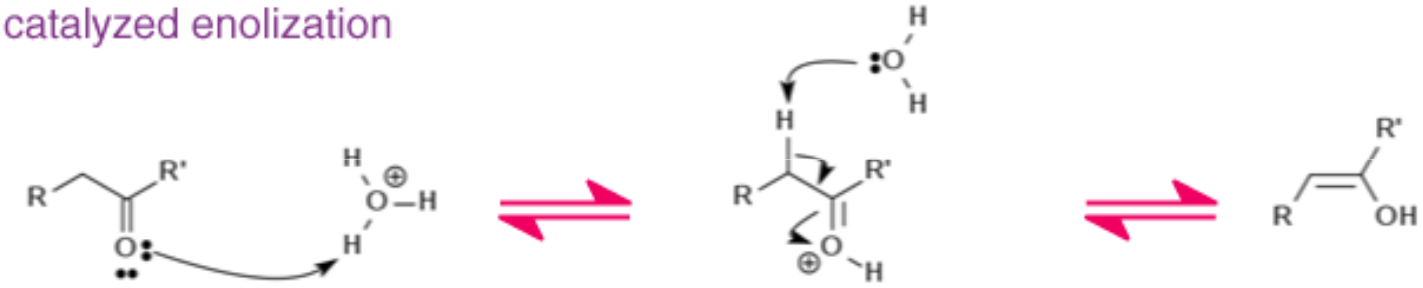
his hydrogen atom is added parallelly to the anti-bonding pi-orbital of the carbonyl group. This bond w ndergo hyperconjugation with the C-H bond and reduces the electron density at the alpha carbon ator here the alpha hydrogen atom will become more acidic than before. If the position of alpha hydrogen is n o, the process of tautomerism will be very slow. Adamatanone is an example of this slow process.

this process, we should follow Markovnikov's rule for addition. Firstly, in the mechanism, there is ydronium ion ($H_3O^{+)}$ is present which is an electrophile, so the electrons exposed near the C=C bond will b onated. If the no. of hydrogen atom present in the compound is more, the addition of protons als creases.

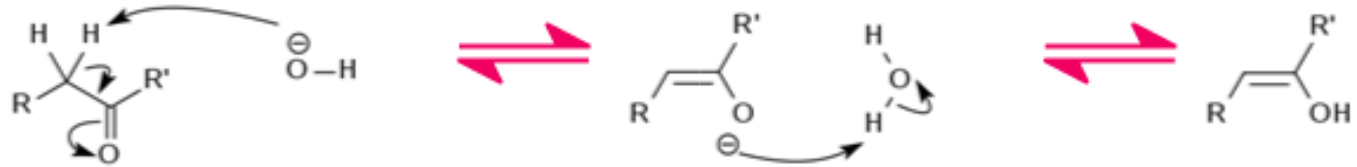
## Reaction mechanism



## Acid catalyzed enolization



## Base catalyzed enolization



## Important Questions On Tautomerism

1.What do you mean by the term tautomer?
2.Explain the process of tautomerization.
3.What are the structural requirements of a compound to possess tautomerization?
4.Explain the mechanism of tautomerism with examples step by step procedure.
5.Which are the different types of tautomerism? How they are classified? Explain.
6.What is meant by annular tautomerism?
7.How a ring- chain tautomerism is obtained?
8.Protonation and deprotonation are the two-essential processes in tautomerism. Justify.
9.What is valence tautomerism?
10.Explain the tautomerism related to acid-base behaviour of the molecule.
11.Write some examples for tautomerism, ring- chain tautomerism, annular tautomerism.
12.How tautomerism is depending on the catalyzation process? Which is the type of such process? Explai briefly.
13.Write the importance of alpha carbon atom in tautomerism.
14.List the applications of tautomerism in various fields.
15.Explain the stability of keto-enol form of tautomer?


THANK
YOU