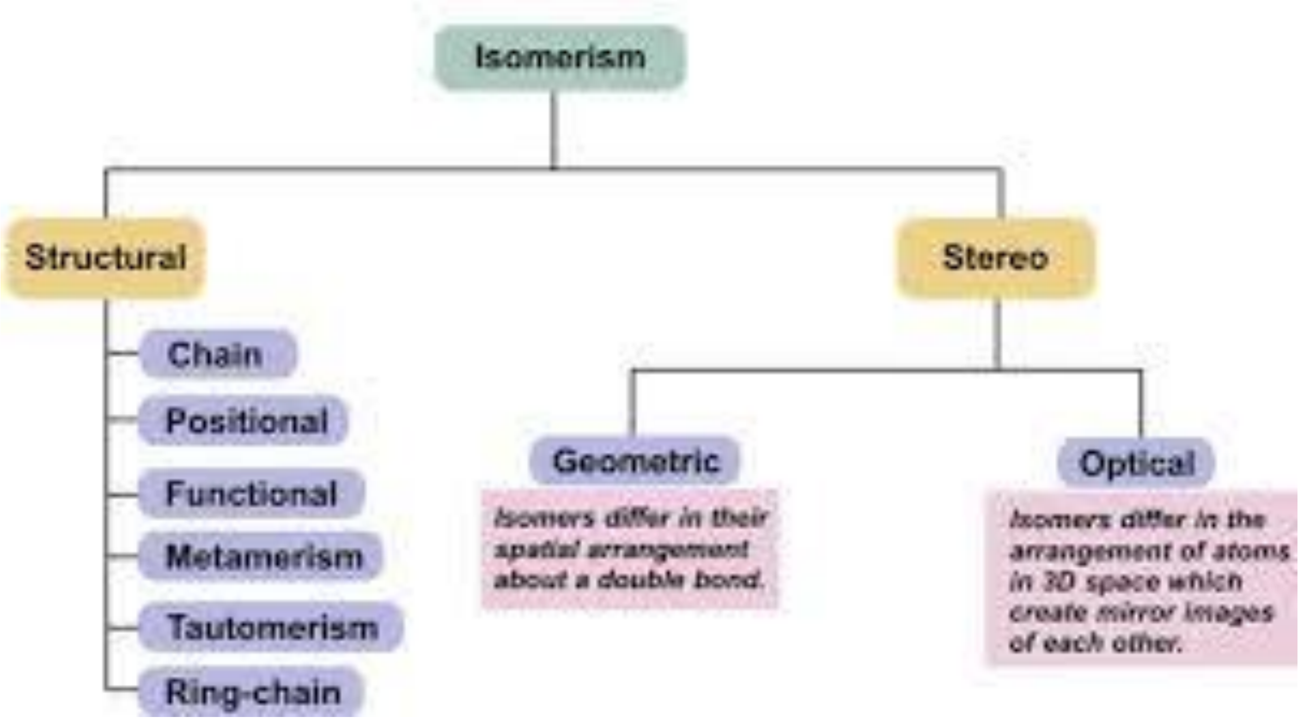
What is Tautomerism?

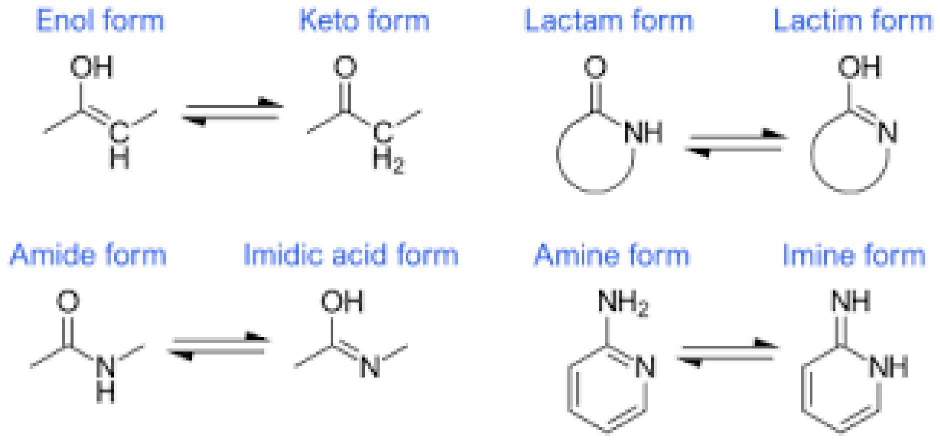
Tautomerism is a phenomenon where a single chemical compound tends to exist in two or more interconvertible structures that are different in terms of the relative position of one atomic nucleus which is generally the hydrogen. The two structures are called tautomers and these type of isomer compounds 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.



Examples of Tautomerism

If we consider the simple definition of tautomerism then it is described as a type of isomerism wherein the isomers interchange into or between one another very easily in order to exist together in equilibrium. During the reaction, there is proton transfer occurs in an intramolecular fashion. Consider few examples of tautomerism given below:



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

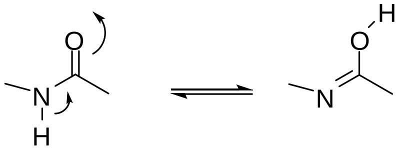
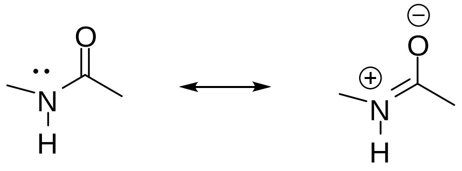
In this phenomenon, there is an exchange of a hydrogen atom between two other atoms while forming a covalent bond to either one. Tautomerism is a reversible process.

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.**

What are the Differences Between Resonance and Tautomerism?

Resonance and Tautomerism are important chemical concepts. Resonance is used to determine the actual structure of a chemical compound. Tautomerism determines the chemical structure of a compound, which is most stable at given conditions. There are many differences between two terms. The difference between resonance and tautomerism is that resonance occurs due to the interaction between lone electron pairs and bond electron pairs whereas tautomerism occurs due to the interconversion of organic compounds by relocating a **proton.**

Tautomerism	Resonance
Tautomerism is the effect of having several compounds that are capable of interconversion via relocating a **proton**.	Resonance is a chemical concept that describes the interaction between **lone pair of electrons and bond pair of electrons** of a compound.
Tautomerism is the presence of two (or more) forms of the same compound that are capable of interconversion.	Resonance is the presence of several forms (of the same chemical compound) which determines the actual structure of a compound.
Tautomers exist in equilibrium with each other.	Resonance structures do not exist in equilibrium
Tautomers can be obtained by relocation a proton (and electrons).	Resonance structures can be obtained by the relocation of bond electrons and lone pair electrons.
Tautomerism has no effect on the stability of the molecule	Resonance has a profound effect on the stability of the molecule
Tautomerism has no effect on bond length	Resonance affects the bond length (single bond is shortened while the double bond becomes longer).
Tautomeism is a real phenomenon ie tautomers exist in reality	Resonance is a hypothetical phenomenon ie resonating structures are non-existence
example  amide imidol	example 

Types of Tautomerism

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

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

Prototropy

It is a type of tautomerism that occurs due to the acid-base behaviour of the compound. Here two forms differ only in the **position of a proton**. This structure will have the same empirical formula and the number of charges.

Annular Tautomerism

If a proton occupies two or more position of a heterocyclic system, then such process is called annular tautomerism. In tautomerism, due to the delocalization of proton, if an open structure is changed to a ring structure, then such tautomer is called as ring-chain tautomers. Glucose is an example of ring-chain tautomers.

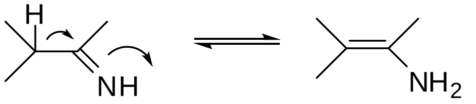
Valence Tautomerism

Valence tautomerism is a type of tautomerism where there is continuous formation and breaking of single and double bonds in the compound without any migration of groups or atoms. It is different from the previous type of tautomerism, and it is a rapid process.

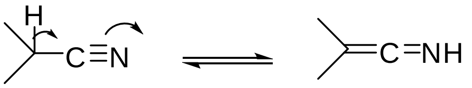
In this tautomerism, there is a change in geometrical structure but no change for canonical resonance structure or mesomers.

Tautomerism in Non-Carbonyl Compounds

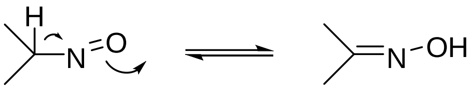
Most of the non-carbonyl systems are available as a mixture of tautomers. Some of the examples are given below;



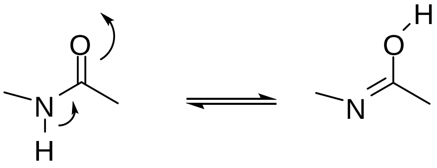
Imine Enamine



Nitrile Ketenimine



Nitroso Oxime

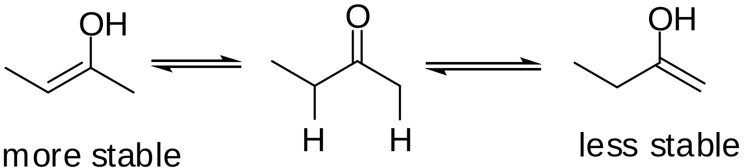


amide imidol

Tautomerism can have a huge impact on the chemical properties of the compound.

Tautomeric Form of Unsymmetrical Ketones

In symmetric form, there is only one form of tautomer. But for an unsymmetrical form, there can be two. Let’s have a look to the example given below;



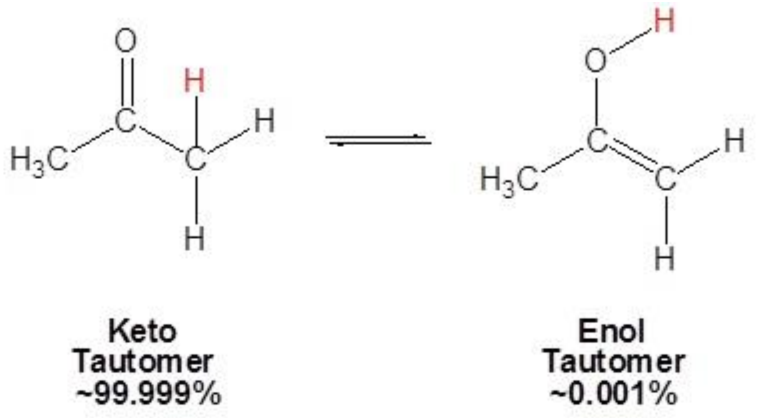
more stable enol

unsymm Ketone

less stable enol

Keto-Enol Tautomerism

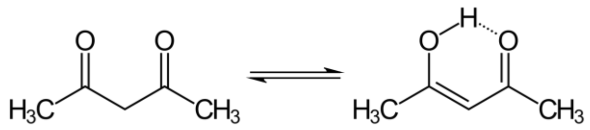
Because of the acidity of α hydrogens carbonyls undergo keto-enol tautomerism. Tautomers are rapidly interconverted constitutional isomers, usually distinguished by a different bonding location for a labile hydrogen atom and a differently located double bond. The equilibrium between tautomers is not only rapid under normal conditions, but it often strongly favors one of the isomers (acetone, for example, is 99.999% keto tautomer). Even in such one-sided equilibria, evidence for the presence of the minor tautomer comes from the chemical behavior of the compound. Tautomeric equilibria are catalyzed by traces of acids or bases that are generally present in most chemical samples.



A compound containing a carbonyl group (C=O) is normally in rapid equilibrium with an enol tautomer, which contains a pair of doubly bonded carbon atoms adjacent to a hydroxyl (−OH) group, C=C-OH. The keto form predominates at equilibrium for most ketones. Nonetheless, the enol form is important for some reactions.

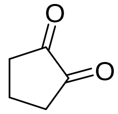
Case 1: Intramolecular H-bonding

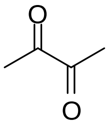
An example is the 1,3-diketones, such as acetylacetone (2,4-pentanedione), which favor the enol form.



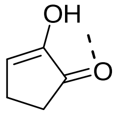
Intramolecular H-bonding forms the 6-membered cyclic structure that stabilizes the enol form over the keto.

Which diketone will form enol more, A or B?


A

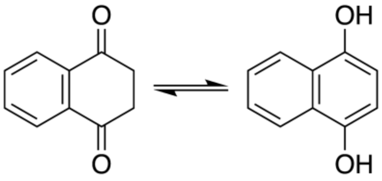

B

In A, two C=O grp locked in *syn* conformation, suffering from severe dipolar repulsion and the enol form gets relief from dipolar repulsion and stabilized by intramolecular H-bonding.

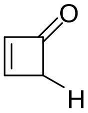

intrmolecular H-bonding

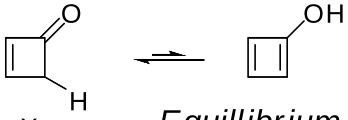
Case 2: Aromaticity

In certain aromatic compounds such as phenol, the enol is more stable due to the aromatic character of the enol but not the keto form.



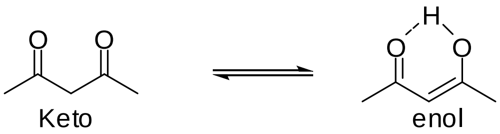
The compound 'X' exists entirely in keto form (100%).


X


X

Equillibrium is totally shifted towards keto as enol form gets antiaromatic

Case 3: Solvent



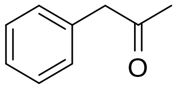
Polar solvent (capable of forming H-bonding) will make lone pairs less available for intramolecular H-bonding, hence % of keto increases

6 : 94 (wheh benzene is used as sovent)

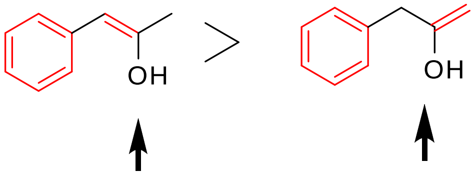
81:19 (when water is used as solvent)

Case 4: Conjugation

Example Which enol is favoured for the ketone



?

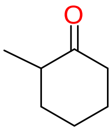


here the double bond is in conjugation of the phenyl ring

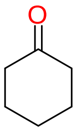
here double bond not in conjugation with the phenyl ring

Case 5: Substitution

Example Which ketone will favour to form enol more, **A** or **B**?



A



B

Remember that enols are nothing but alkenes, and the stability of alkenes are as follows: tetrasubstituted>trisubstituted>disubstituted> monosubstituted

Questions

Q1.1

Draw the enol forms of the following molecules

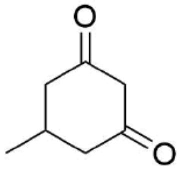
a. 4-methylcyclohexanone
b. Ethyl thioactetate
c. Methyl acetate
d. Butanal
e. Propionic Acid
f. 1-phenyl-2-butanone

Q1.2

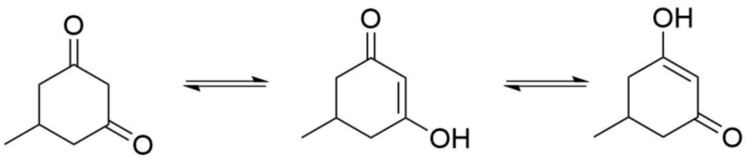
How many acid protons do each of the molecules from the previous question have? Label them.

Q1.3

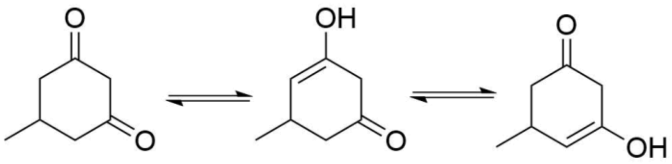
Draw all of the monoenol forms for the following molecule. Which ones are most stable? Why?



Ans:

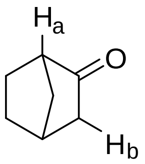


Ability to resonate stabilizes the above enol form.



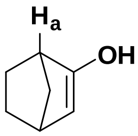
This enol has no resonance form, hence less stable.

Q1.4



Which of the hydrogen (H_a or H_b) will enolize for this ketone?

Ans:



H_b will enolise at a much faster rate than H_a as no double bond can be formed at bridgehead position of a bicyclic system according to the Bredt's Rule.