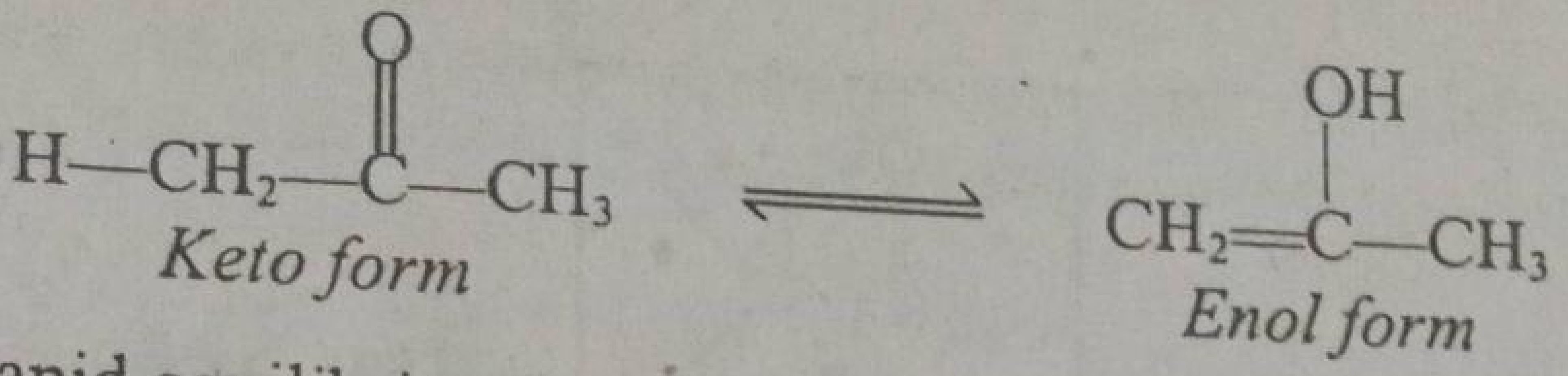
Tautomerism

While writing the resonance structures to describe the actual structure of a compou it was observed that the relative positions of the atomic nuclei remained unchanged. T structures which differ in the relative positions of their atoms are not resonance forms represent different compounds which are isomeric with each other and are capable independent existence. If two isomers differ in the placement of a proton on one atom another (mostly hetero atom such as oxygen or nitrogen) with the correspond adjustment of a double bond, the phenomenon is referred to as **tautomerism** and isomers are known as **tautomers.** The most common examples of tautomerism provided by the carbonyl compounds containing α-hydrogen, in which the proton fr the α-carbon atom shifts to the carbonyl oxygen, associated with the appropr movement of electron pair, to form an enol (from *ene* + *ol*, i.e., unsaturated alcohol). T process is called **enolization.** The proton then moves back to convert the enol form b to the keto for

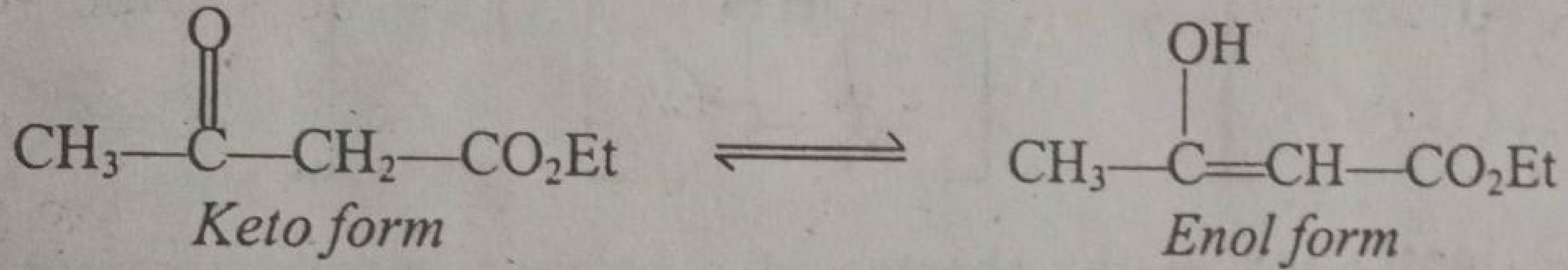


$$H-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \rightleftharpoons CH_2=\overset{\overset{OH}{|}}{C}-CH_3$$

Keto form *Enol form*

Thus, there is a rapid equilibrium between the keto and the enol forms. It is therefore also commonly known as **keto-enol tautomerism.** That both forms exist simultaneously is evident from the behaviour of acetoacetic ester.

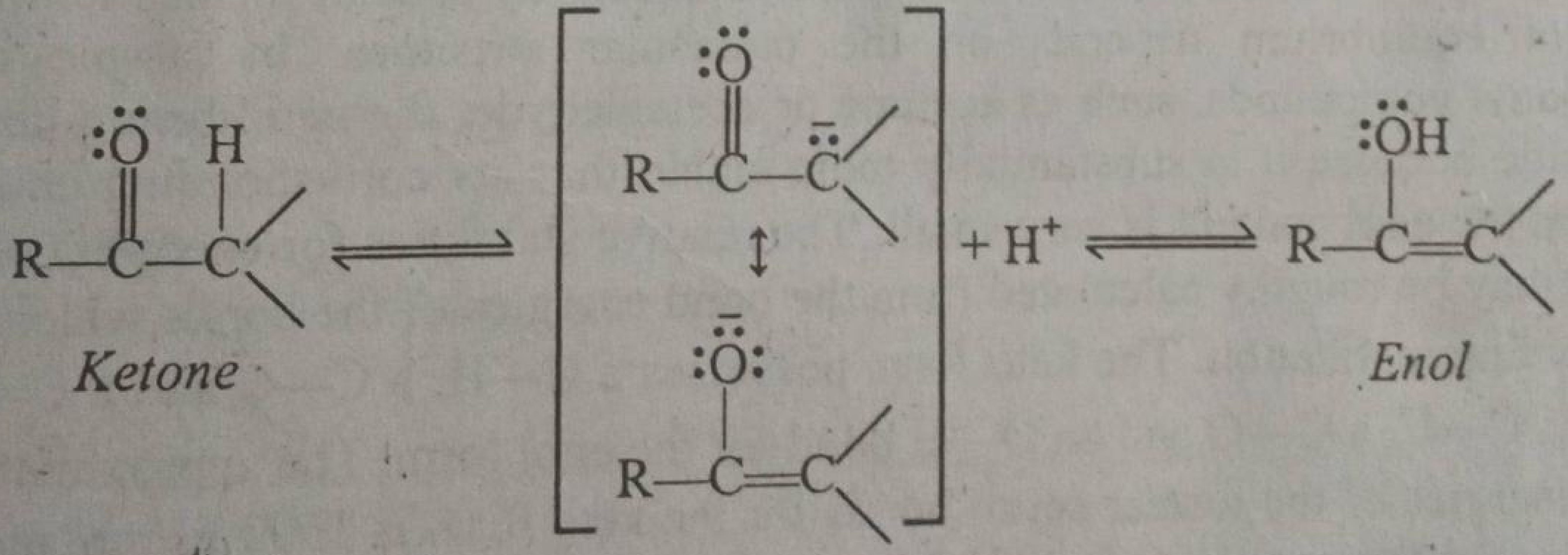
Acetoacetic ester forms oxime with hydroxylamine and cyanohydrin with hydrogen cyanide, indicating the presence of a keto group. On treatment with sodium it evolves hydrogen and forms sodium salt, indicating the presence of a hydroxyl group. It discharges the colour of ethanolic solution of bromine, indicating the presence of an olefinic double bond. It produces a reddish-violet colour on treatment with neutral ferric chloride, which is a characteristic test for enolic group $(-\overset{|}{C}=\overset{|}{C}-OH)$. Thus, acetoacetic ester is, in fact, a mixture of keto and enol forms which are always in equilibrium with each other.



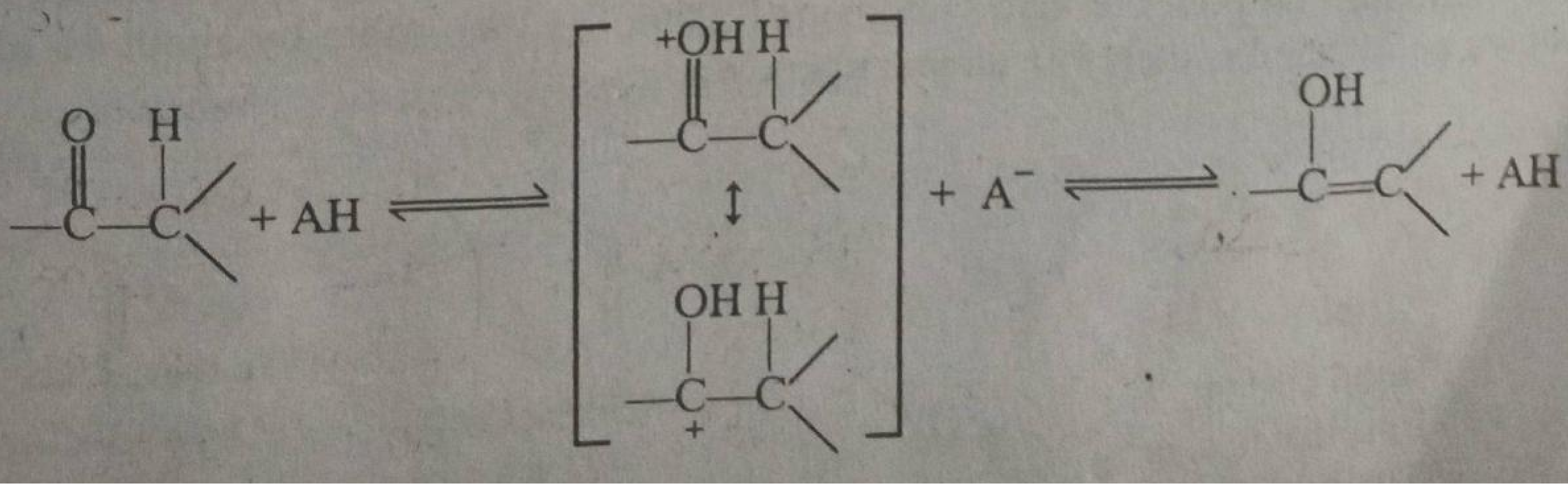
$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CO_2Et \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH-CO_2Et$$

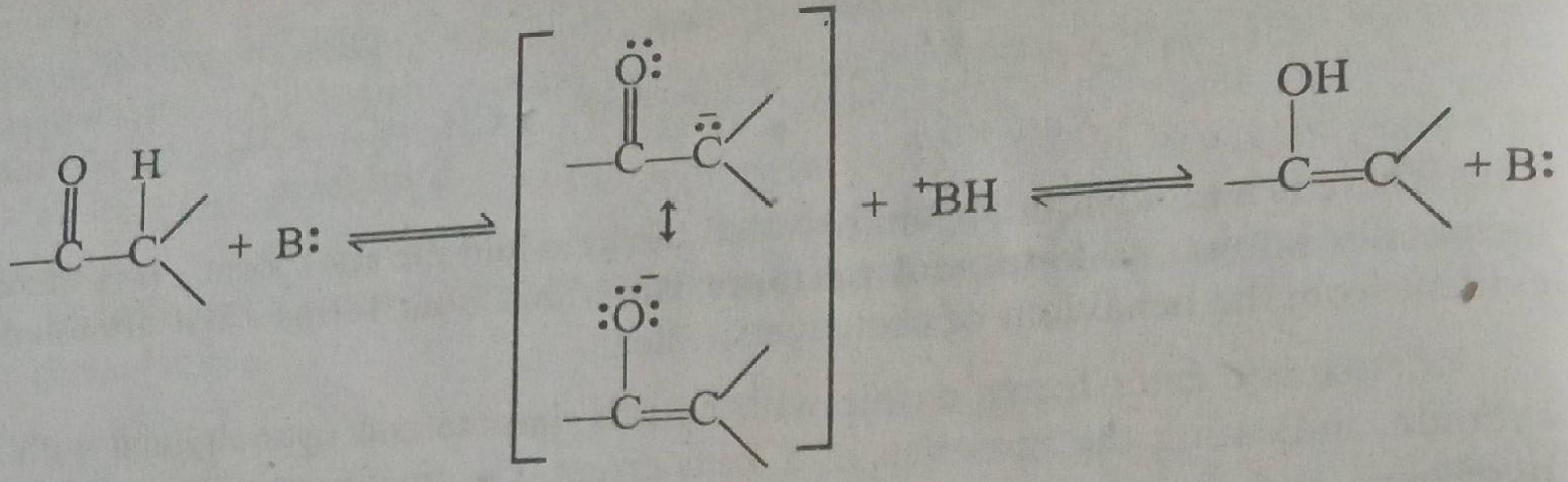
Keto form *Enol form*

Either the ketone or its tautomeric enol may lose a proton and form a single intermediate, **enolate ion** (described by two resonance forms), which may recombine with the proton to yield either tautomer.

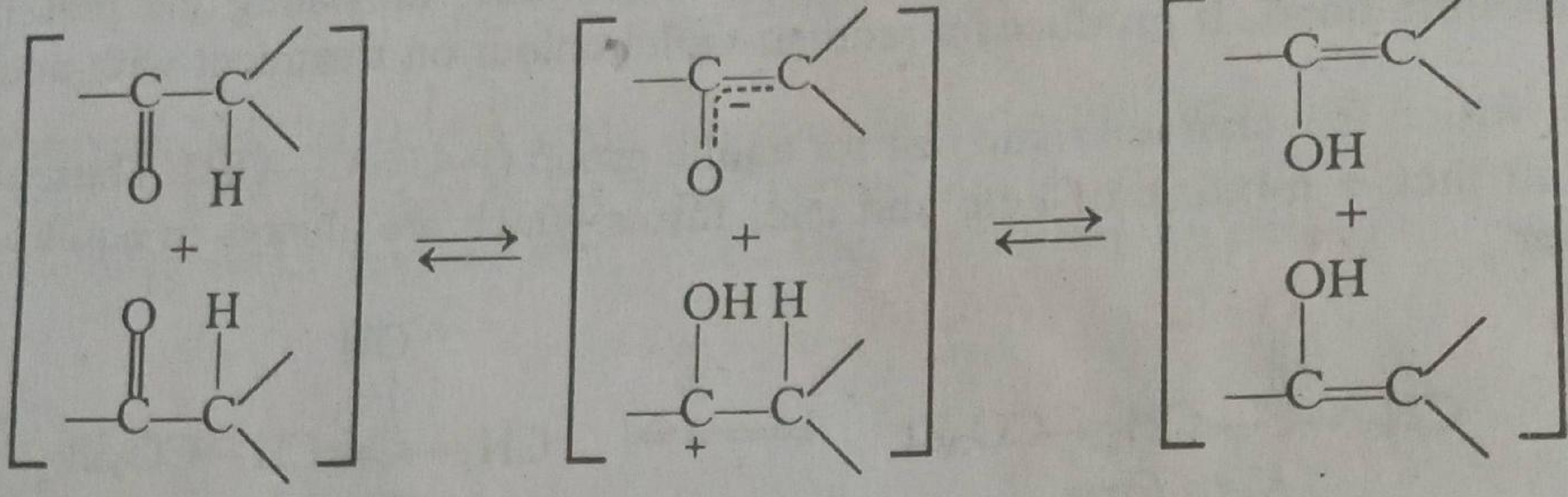


Since tautomerization (*interconversion of the tautomers*) involves the transfer of a proton, it is catalysed by both acids and bases.





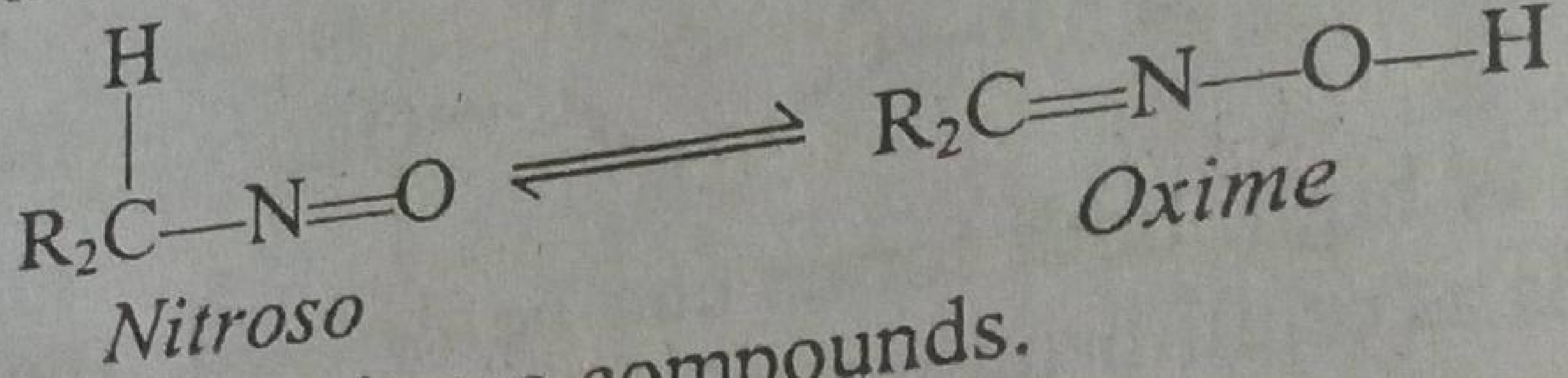
In the absence of a catalyst, tautomerization occurs by autoprotolysis.



However, at –80°C and in the absence of a catalyst, either tautomer can be kept indefinitely.

There are certain other systems that involve a rapid shift of proton to show tautomerism, similar to the keto-enol tautomerism. For example,

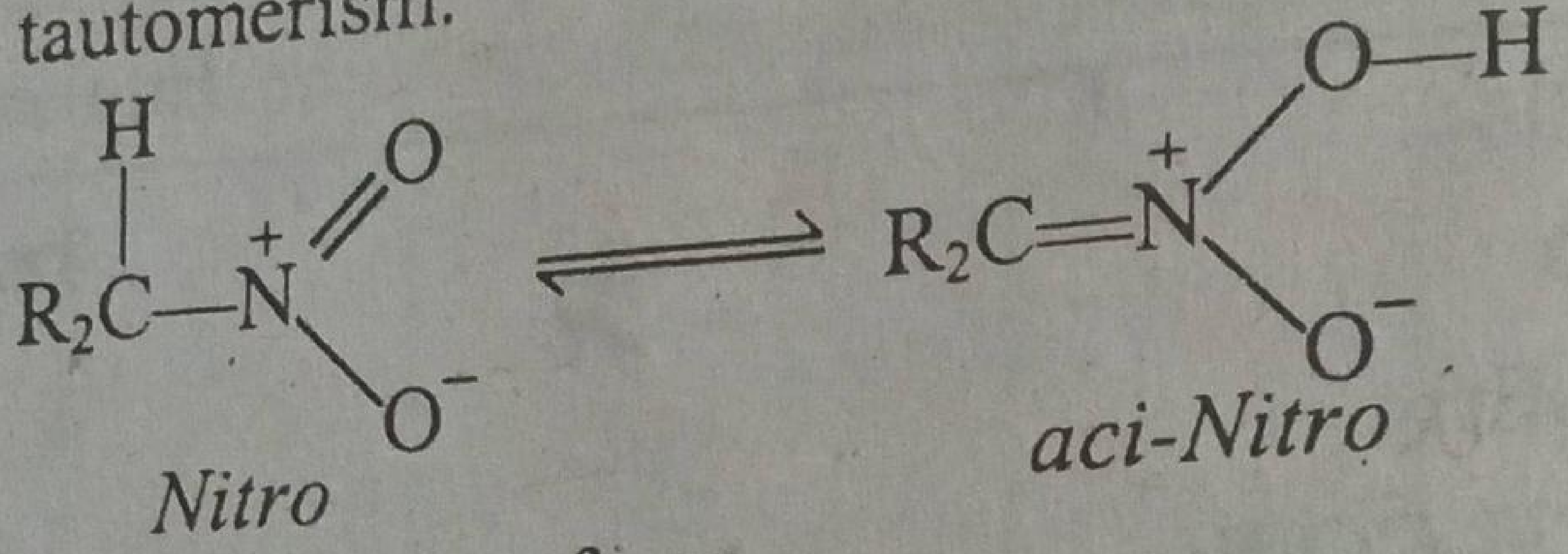
1. Nitroso–oxime tautomerism.



$$R_2\overset{H}{C}-N=O \rightleftharpoons R_2C=N-O-H$$

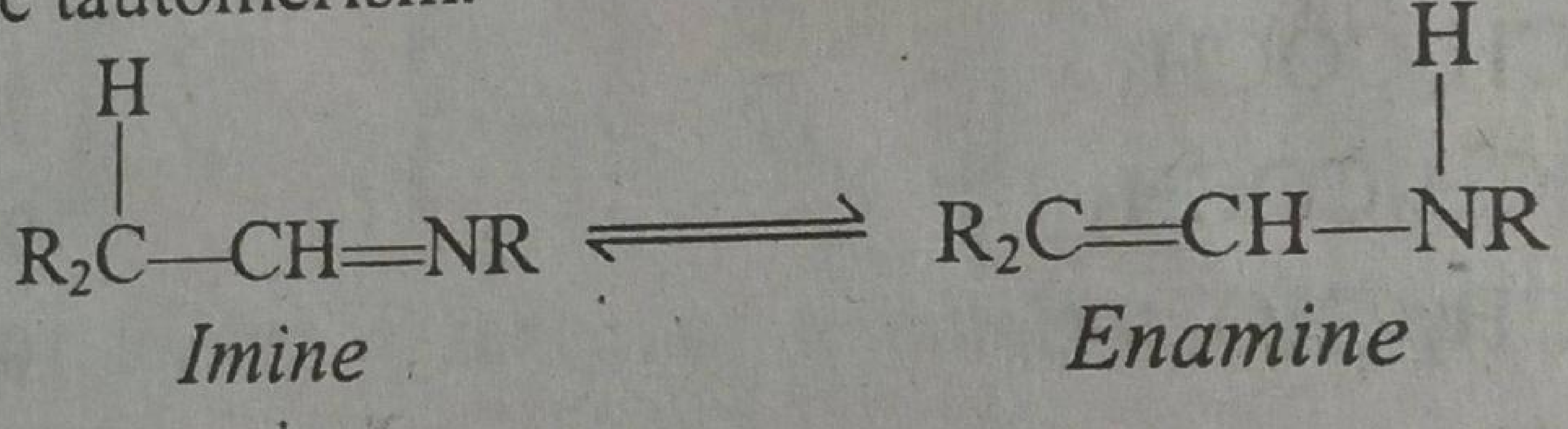
Oximes are more stable than the nitroso compounds.

2. Nitro–*aci*-nitro tautomerism.



Nitro form is more stable than *aci*-nitro form.

3. Imine–enamine tautomerism.



$$R_2\overset{H}{C}-CH=NR \rightleftharpoons R_2C=CH-\overset{H}{N}R$$

Imine is more stable than enamine.