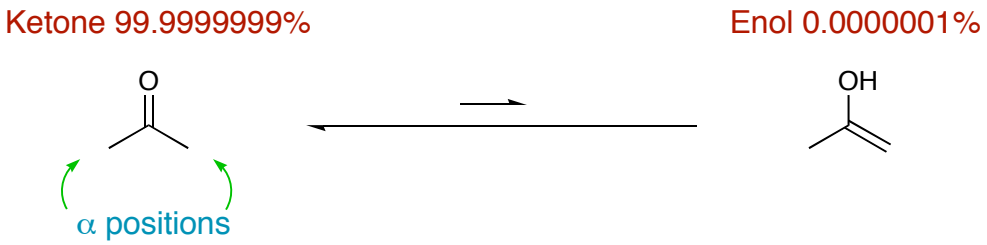
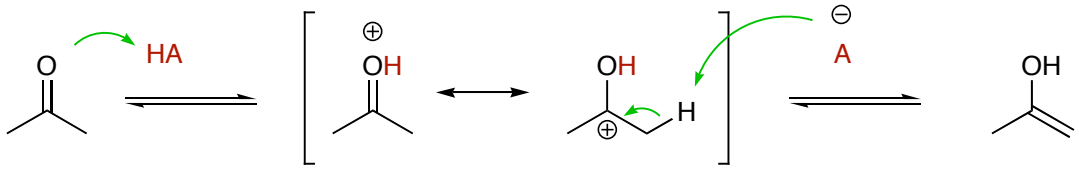
Chapter 22 - Carboxylic Alpha-Substitution Reactions

Enols

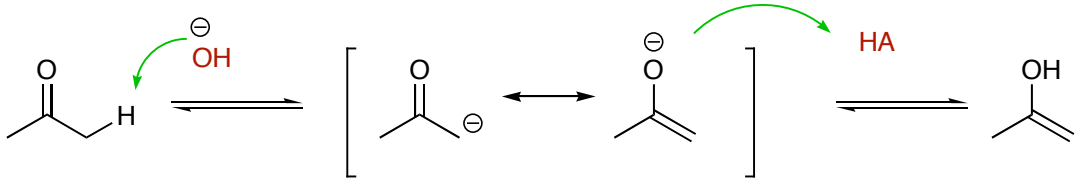
Ketoenol tautomerization lies far to the side of the ketone. The equilibrium is accelerated by the addition of acid or base catalysts.



Acid Catalyzed Enol Equilibrium

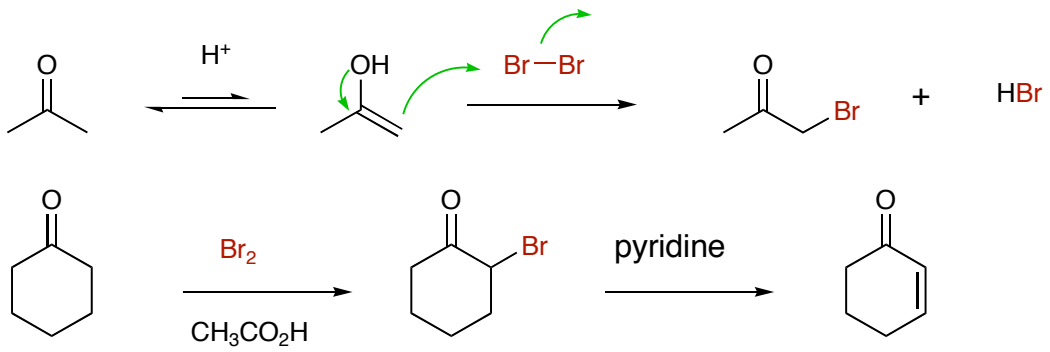


Base Catalyzed Enol Equilibrium



Alpha Halogenation

Enols are electron rich – more so than the typical alkenes – and they will react with reactive electrophiles like Br_2. Alpha bromo ketones can be eliminated easily with pyridine.



Acidity of Alpha Protons - Enolates

Enols will only react with very reactive electrophiles like bromine. In order to do alpha substitution with less reactive electrophiles, like alkyl halides, you need to deprotonate with a strong base to make an enolate. The hydrogen alpha to a ketone is less acidic than water, so hydroxide is not a strong enough base to completely form the enolate, though it will exist in a small amount in equilibrium with the ketone.