



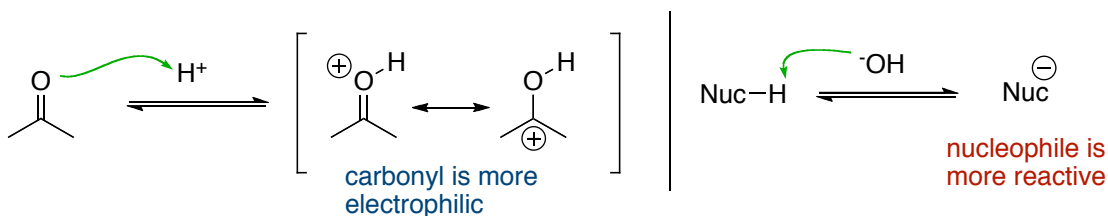
# Chem 342 • Organic Chemistry II

Lecture Summary 21 - 09 Mar 2009

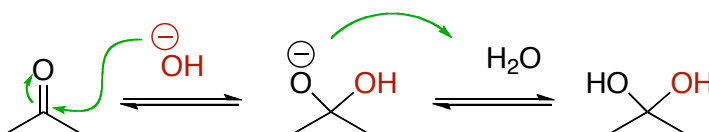
## Chapter 19 - Aldehydes and Ketones: Nucleophilic Addition Reactions

### Mechanism for Hydration

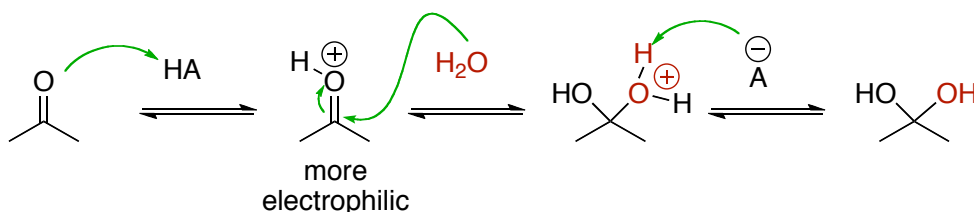
The reaction of a carbonyl with water is very slow. It can be catalyzed by either acid or base. It is useful to understand the mechanism for this process because it relates to many reactions of carbonyl compounds. These mechanisms are worth learning as most of the catalyzed carbonyl chemistry is very similar. Strong nucleophiles like Hydride reagents ( $\text{NaBH}_4$  or  $\text{LiAlH}_4$ ) or Grignard reagents add to carbonyls without any activation. For weaker nucleophiles ( $\text{H}_2\text{O}$ ,  $\text{ROH}$ ,  $\text{RNH}_2$ ,  $\text{R}_2\text{NH}$ , etc) either the carbonyl needs to be made electrophilic by protonation (acid catalysis) or the nucleophile needs to be made stronger by deprotonation (base catalysis).



**Base Catalyzed Hydration** hydroxide is a more reactive nucleophile than water and can add more readily to the carbonyl

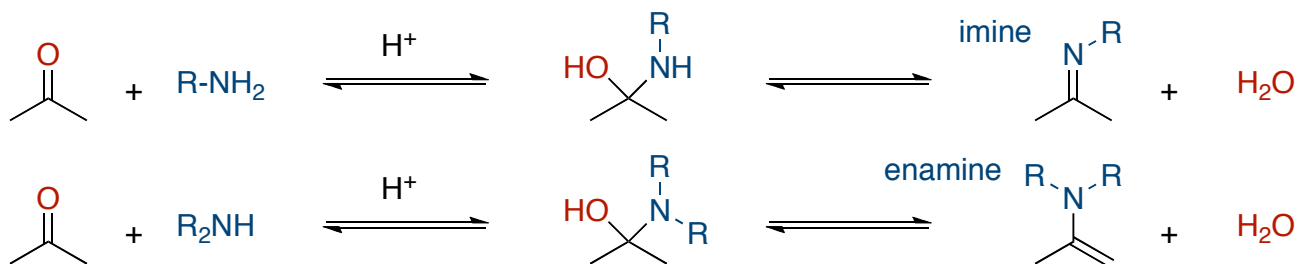


**Acid Catalyzed Hydration** acid activates the carbonyl making it more reactive (more electrophilic) so water can add



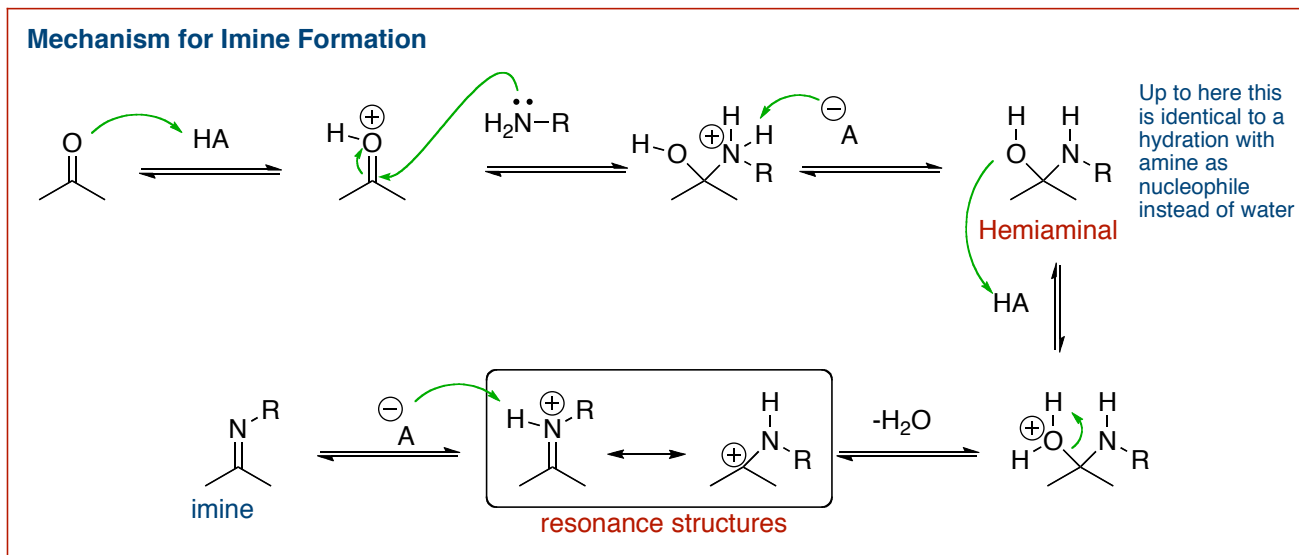
### Addition of Amines - Imine and enamine formation

Primary amines ( $\text{RNH}_2$ ) will react with aldehydes and ketones to form Imines. If the amine is a secondary amine ( $\text{R}_2\text{NH}$ ) then enamines are formed. This is an acid-catalyzed reaction very similar to acid catalyzed hydration.



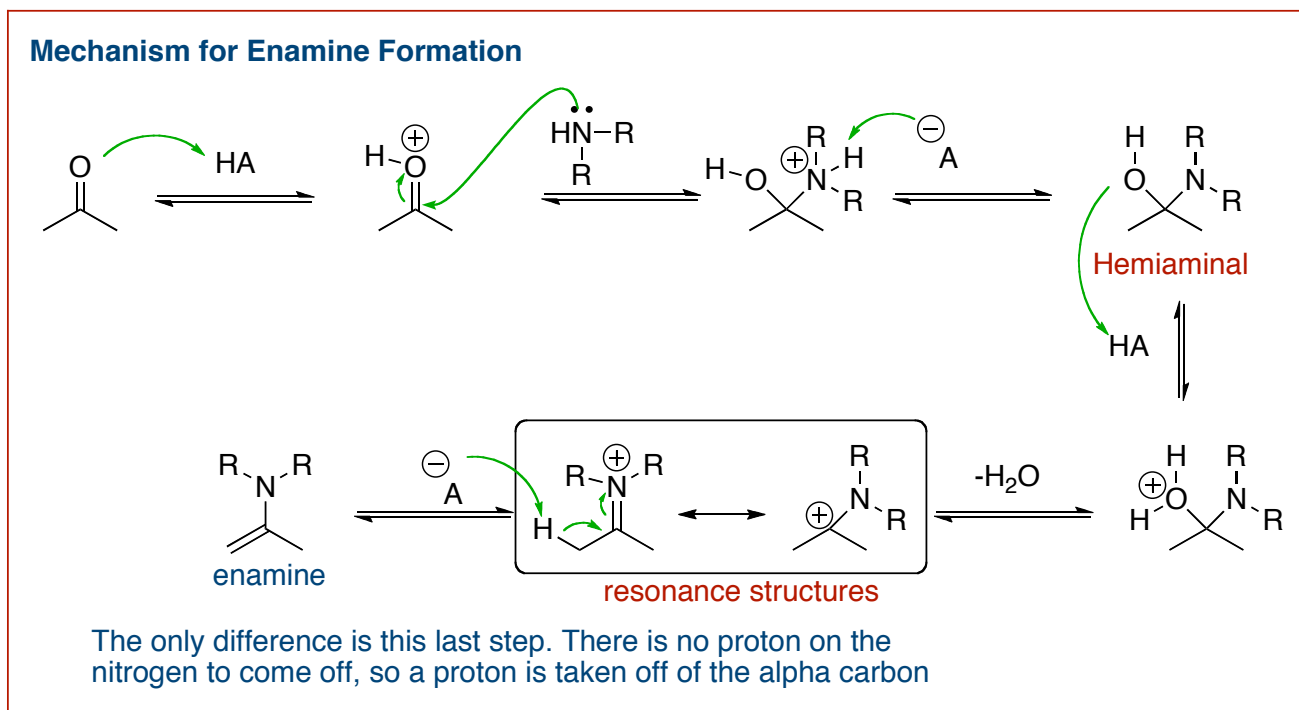
Imine formation begins just like the hydration of ketones. The acid protonates the carbonyl making it more electrophilic. The amine attacks the carbonyl carbon and the conjugate base takes the proton off of the nitrogen. This generates a hemiaminal. This is not very stable. If the acid protonates the OH group, it can leave, facilitated by the lone pair on nitrogen. The conjugate base then deprotonates the nitrogen to form the imine.

### NEED TO KNOW MECHANISM



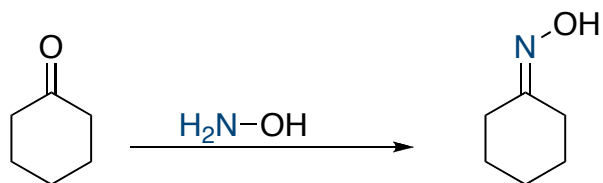
The mechanism for the formation of an enamine from a secondary amine is exactly the same up to the last deprotonation step. As there is no hydrogen on the nitrogen, the conjugate base deprotonates the alpha carbon instead, neutralizing the intermediate and forming the carbon-carbon double bond.

### NEED TO KNOW MECHANISM

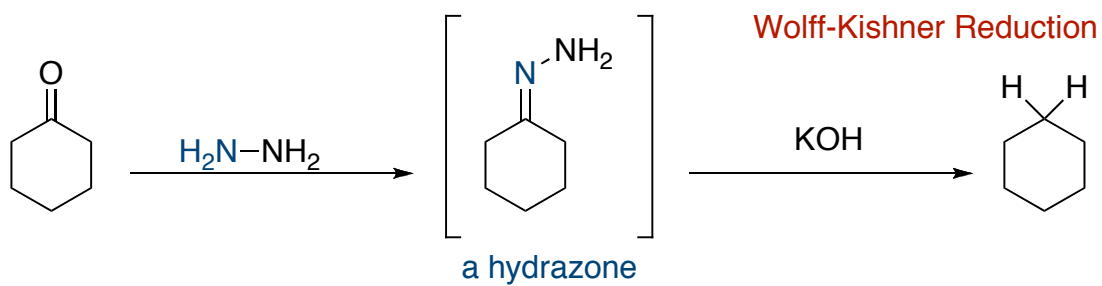


## Oximes and Hydrazines

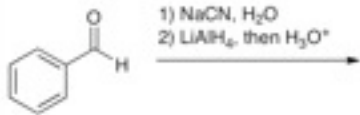
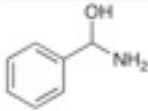
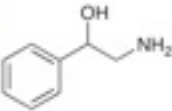
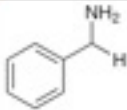
Many kinds of amines participate in imine formation reactions including hydroxyl amine and hydrazine.



an oxime



## Daily Quiz

<p>Q: What is the product of the following sequence of reactions?</p> <p></p>	<input type="checkbox"/> 1:	
	<input checked="" type="checkbox"/> 2:	
	<input type="checkbox"/> 3:	
	<input type="checkbox"/> 4:	