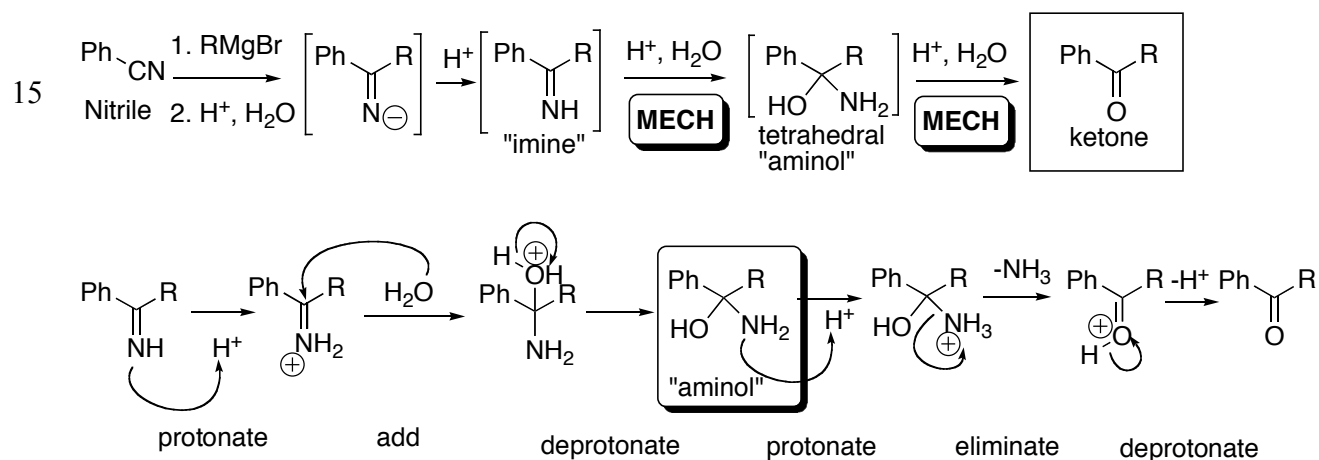
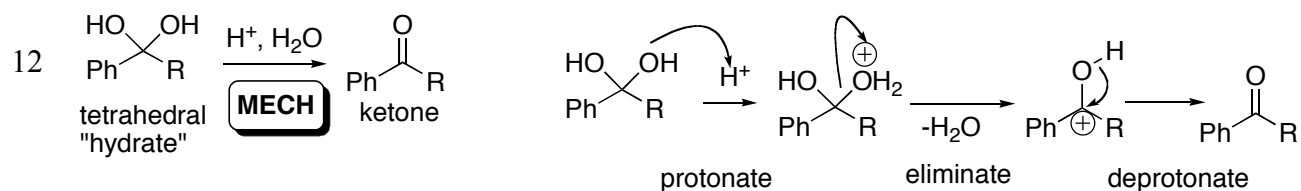
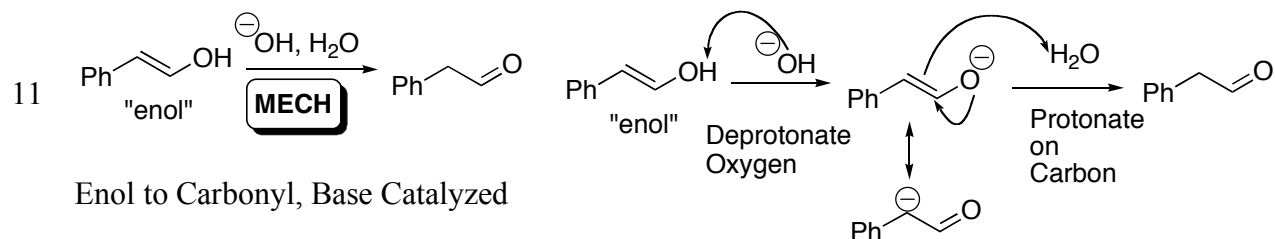
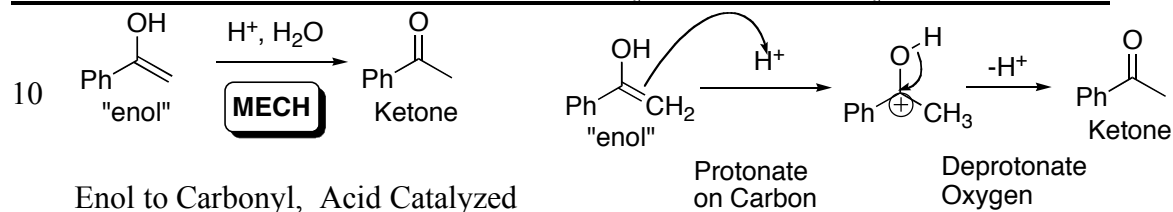
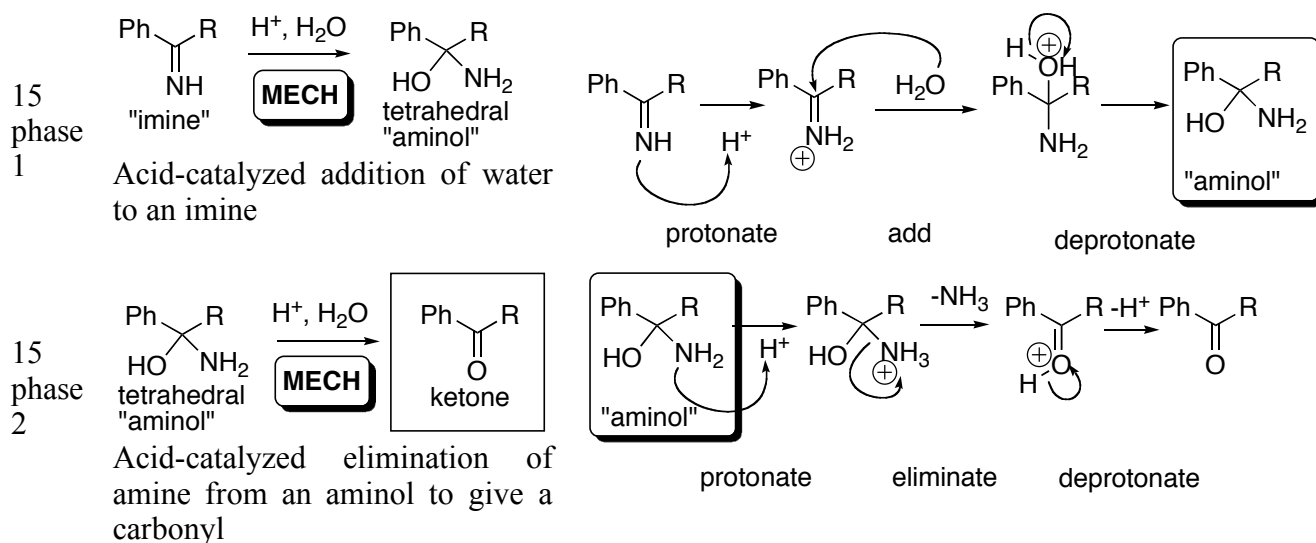
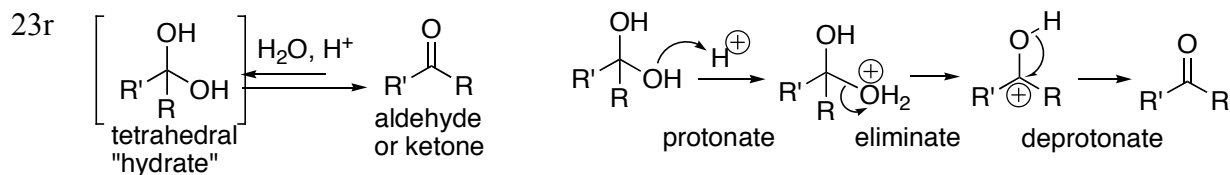
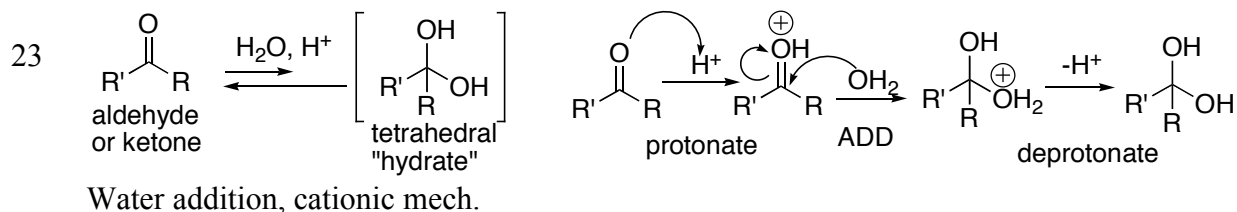
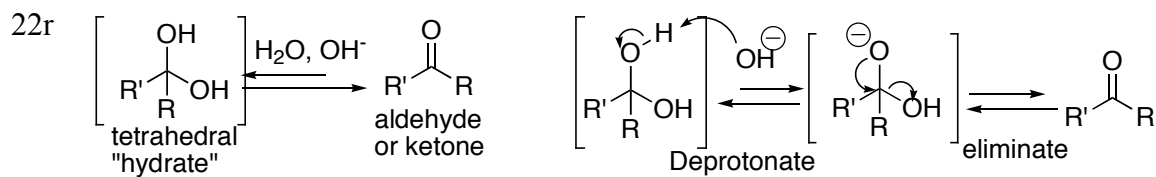
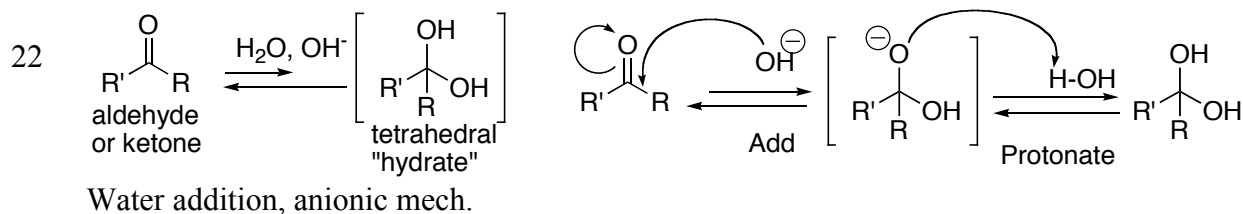
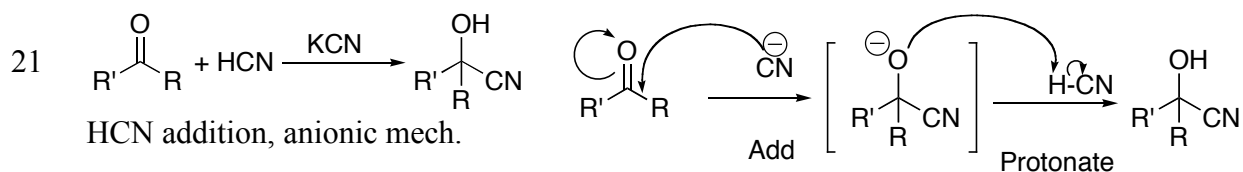
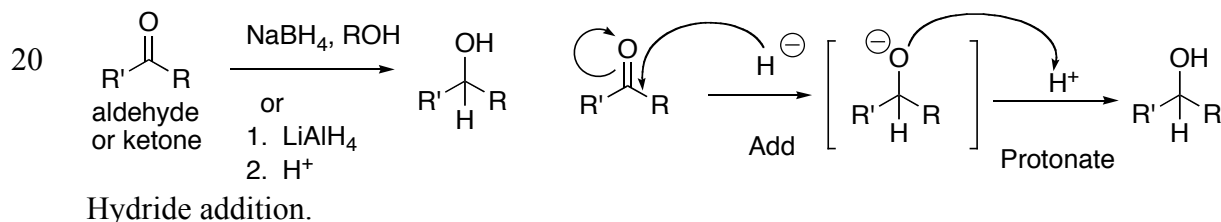
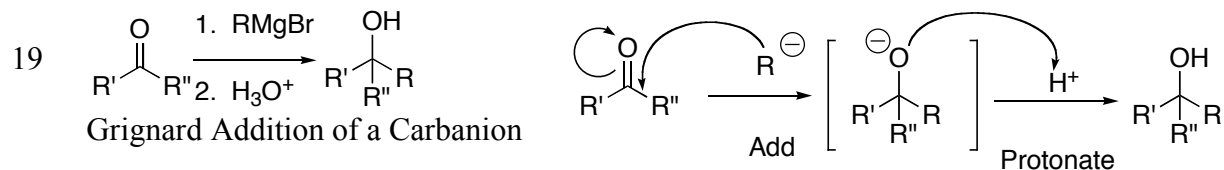


Ch. 18 Mechanisms**Some New Mechanisms Associated with the Syntheses of Aldehydes and Ketones**

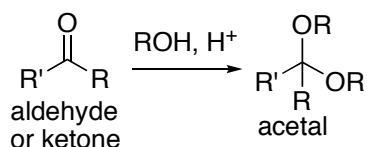


Review: Several Pertinent Mechanistic Principles

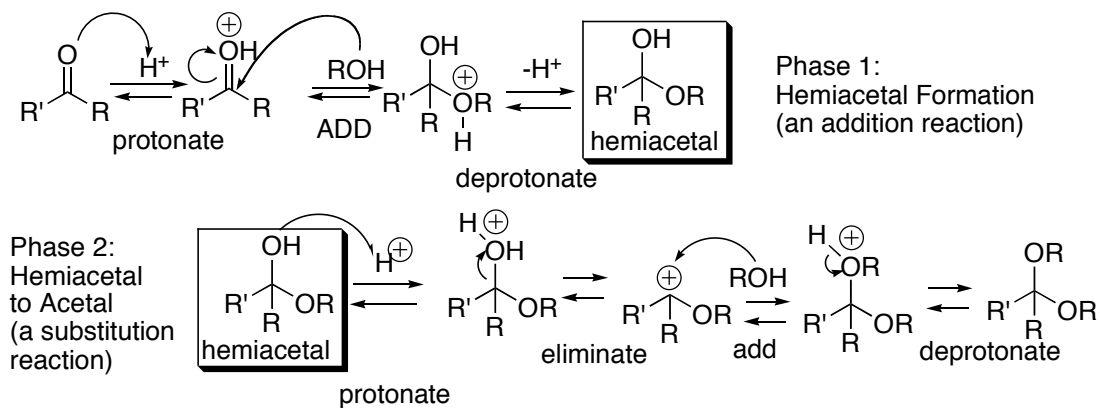
- 1. Recognize anionic mechanisms** (when a strong anion is involved)
 - In an anionic mechanism, a strong anion will drive the first step
 - In an anionic mechanism, intermediates should avoid positive charges
 - Recognize anionic species even when they are disguised by a cationic metal counterion.
- 2. Recognize cationic mechanisms**
 - Recipes that involve acid will be cationic
 - In a cationic mechanism, the first step will routinely involve protonation
 - In a cationic mechanism, the last step will frequently involve deprotonation to return to neutral
 - Normally the main step or steps are sandwiched in between the protonation and deprotonation events
3. Focus on bonds made and broken
4. Draw in hydrogens on carbons whose bonding changes
5. Keep track of lone pairs on reacting centers (in your head if not on paper)
6. Always draw in formal charges where appropriate
7. Arrows show electron flow, from giver to receiver
8. A good mechanism illustrates not only where electrons go as bonds change, but also the timing of bond changes. Avoid drawing bond changes that occur at different times as if they occur in the same step, i.e. as if they were concerted.

Some Mechanisms Associated with the Reactions of Aldehydes and Ketones

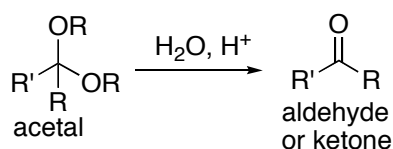
24



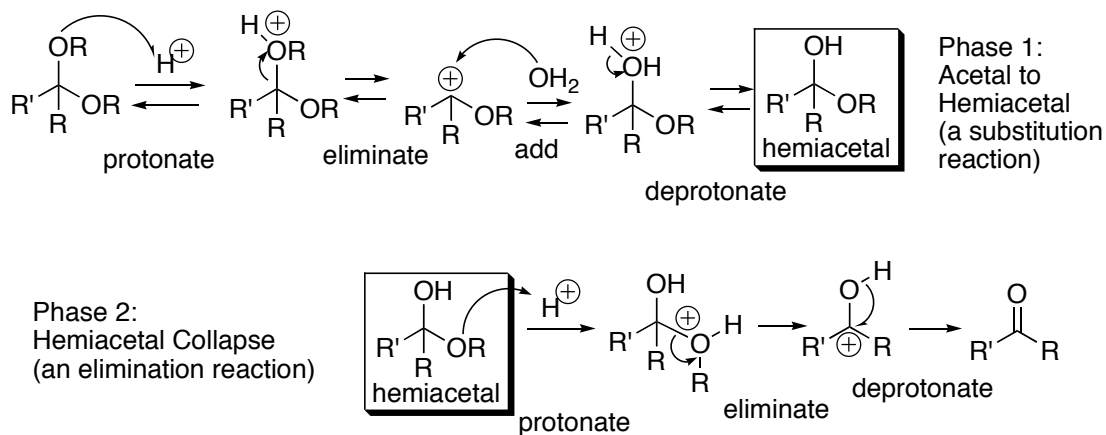
Acetal formation

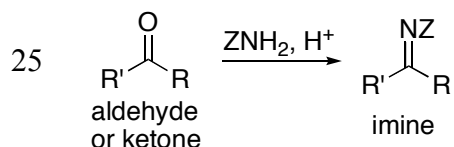


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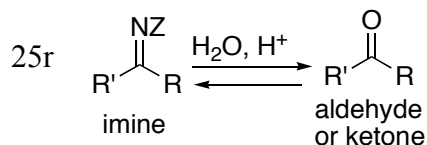
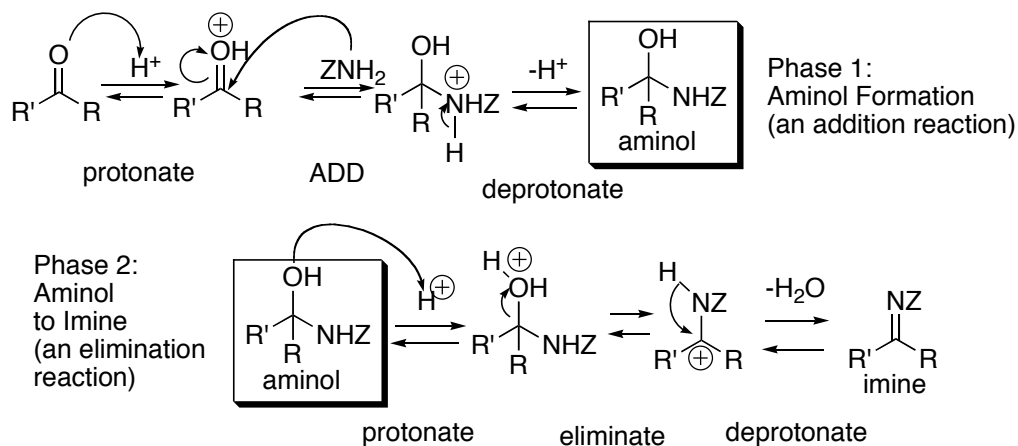


Acetal hydrolysis.

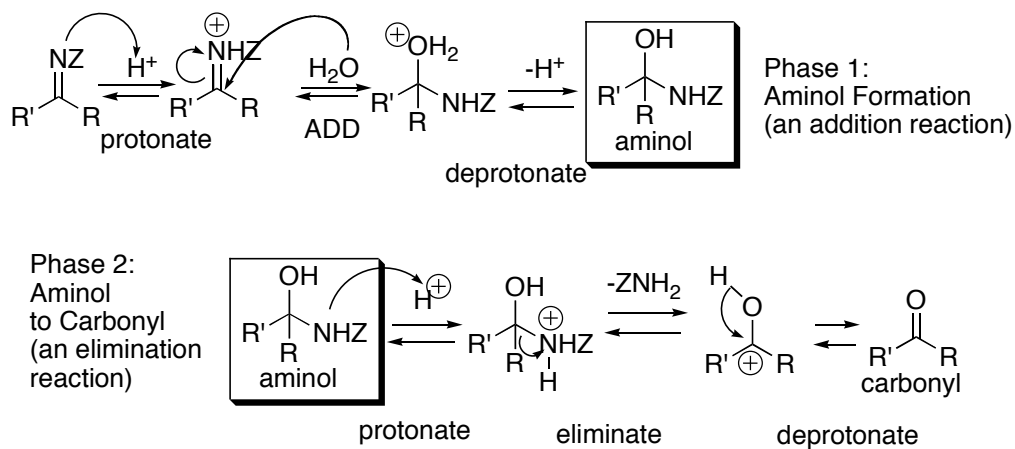




Imine Formation

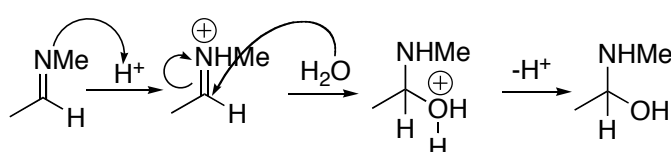
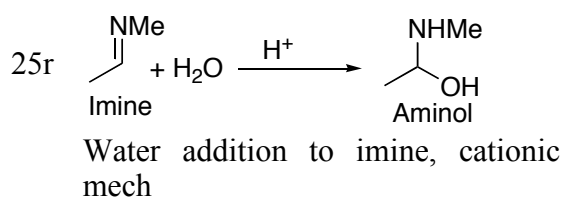
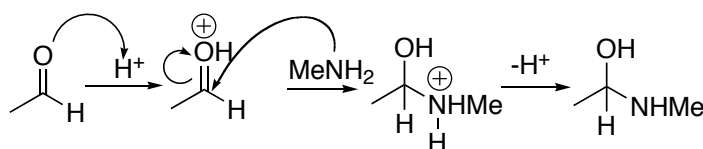
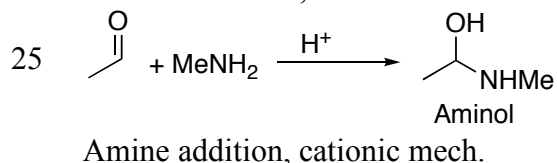
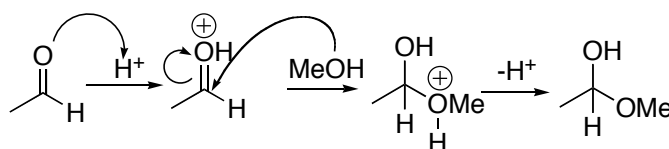
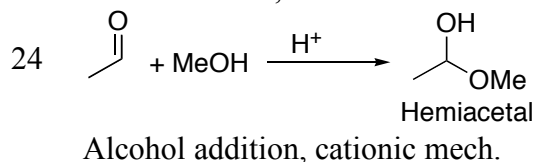
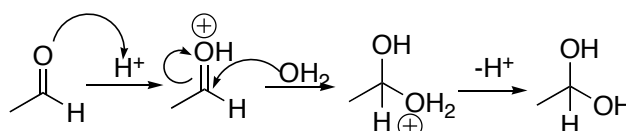
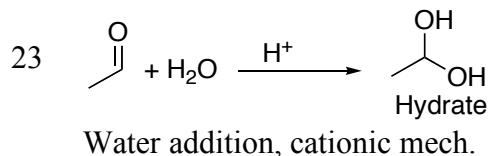
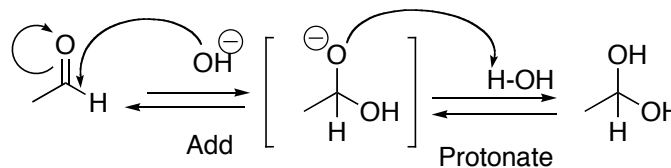
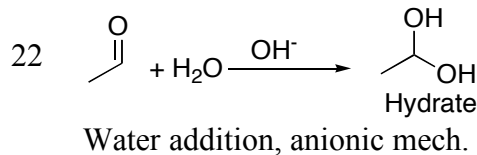
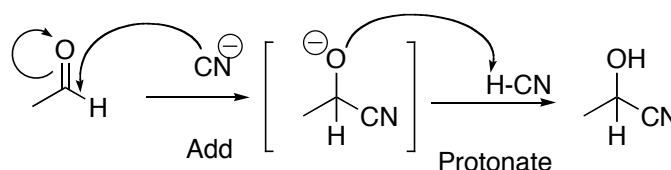
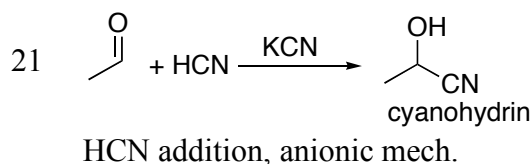
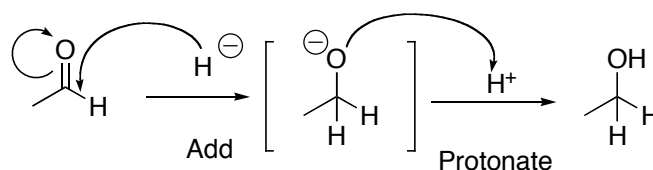
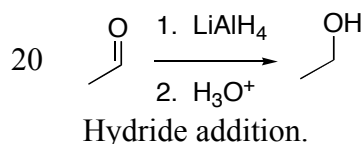
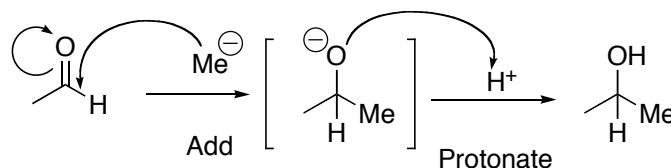
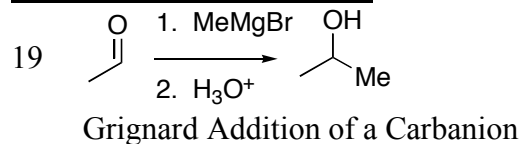


Imine Hydrolysis



Classification of Mechanisms Associated With Ketone/Aldehyde Reactions.

- There may seem to be a dizzying number of mechanisms this chapter. But all of them simplify into some combination of acid- or base-catalyzed **addition reaction**, **elimination reaction** and/or **substitution reaction**.
- To predict what product forms that can be isolated, you will need to know when an addition is all that happens, and when an addition is followed by elimination or substitution.
- Many reactions are reversible, and are controlled by equilibrium principles, so you ought to be able to go in either direction.
- The sequencing of many of the mechanistic steps is dependent on whether you are under acidic (cationic) conditions or basic (anionic) conditions.

ADDITION REACTIONS.

Elimination Reactions.

22r	$\left[\begin{array}{c} \text{OH} \\ \\ \text{R}'-\text{C}-\text{OH} \\ \\ \text{R} \end{array} \right] \xrightleftharpoons{\text{H}_2\text{O}, \text{OH}^-} \begin{array}{c} \text{O} \\ \\ \text{R}'-\text{C}-\text{R} \end{array}$ <p>tetrahedral "hydrate" aldehyde or ketone</p>	<p>Deprotonate eliminate</p>
23r	$\left[\begin{array}{c} \text{OH} \\ \\ \text{R}'-\text{C}-\text{OH} \\ \\ \text{R} \end{array} \right] \xrightleftharpoons{\text{H}_2\text{O}, \text{H}^+} \begin{array}{c} \text{O} \\ \\ \text{R}'-\text{C}-\text{R} \end{array}$ <p>tetrahedral "hydrate" aldehyde or ketone</p>	<p>protonate eliminate deprotonate</p>
24r	$\left[\begin{array}{c} \text{OH} \\ \\ \text{R}'-\text{C}-\text{OR} \\ \\ \text{R} \end{array} \right] \xrightleftharpoons{\text{H}_2\text{O}, \text{H}^+} \begin{array}{c} \text{O} \\ \\ \text{R}'-\text{C}-\text{R} \end{array}$ <p>tetrahedral "hemiacetal" aldehyde or ketone</p>	<p>protonate eliminate deprotonate</p>
25r	$\left[\begin{array}{c} \text{OH} \\ \\ \text{R}'-\text{C}-\text{NHZ} \\ \\ \text{R} \end{array} \right] \xrightleftharpoons{\text{H}_2\text{O}, \text{H}^+} \begin{array}{c} \text{O} \\ \\ \text{R}'-\text{C}-\text{R} \end{array}$ <p>tetrahedral "aminol" aldehyde or ketone</p>	<p>protonate eliminate deprotonate</p>
25b	$\left[\begin{array}{c} \text{OH} \\ \\ \text{R}'-\text{C}-\text{NHZ} \\ \\ \text{R} \end{array} \right] \xrightleftharpoons{\text{H}_2\text{O}, \text{H}^+} \begin{array}{c} \text{NZ} \\ \\ \text{R}'-\text{C}-\text{R} \end{array}$ <p>tetrahedral "aminol" imine</p>	<p>protonate eliminate deprotonate</p>

Substitution Reactions.

24b	$\begin{array}{c} \text{OH} \\ \\ \text{R}'-\text{C}-\text{OR} \\ \\ \text{R} \end{array} \xrightleftharpoons{\text{ROH}, \text{H}^+} \begin{array}{c} \text{OR} \\ \\ \text{R}'-\text{C}-\text{OR} \\ \\ \text{R} \end{array}$ <p>"hemiacetal" "acetal"</p>	<p>protonate eliminate add deprotonate</p>
24r	$\begin{array}{c} \text{OR} \\ \\ \text{R}'-\text{C}-\text{OR} \\ \\ \text{R} \end{array} \xrightleftharpoons{\text{HOH}, \text{H}^+} \begin{array}{c} \text{OH} \\ \\ \text{R}'-\text{C}-\text{OR} \\ \\ \text{R} \end{array}$ <p>"acetal" "hemiacetal"</p>	<p>protonate eliminate add deprotonate</p>