



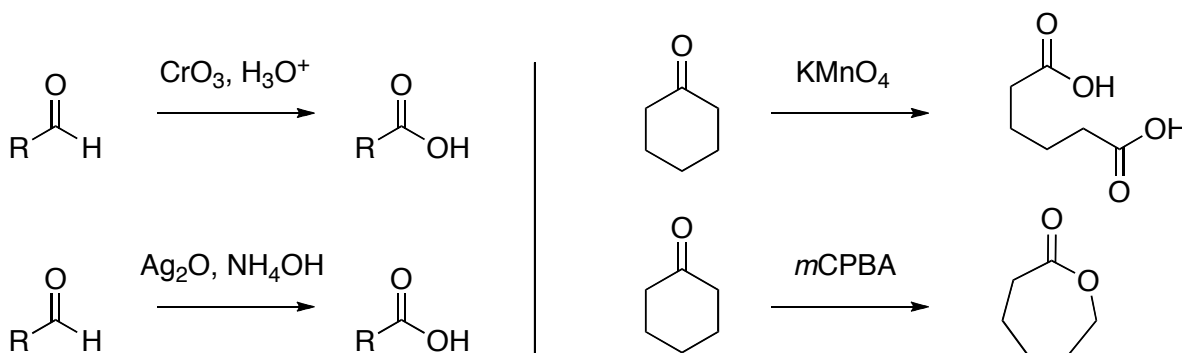
Chem 342 • Organic Chemistry II

Lecture Summary 20 - 06 Mar 2009

Chapter 19 - Aldehydes and Ketones: Nucleophilic Addition Reactions

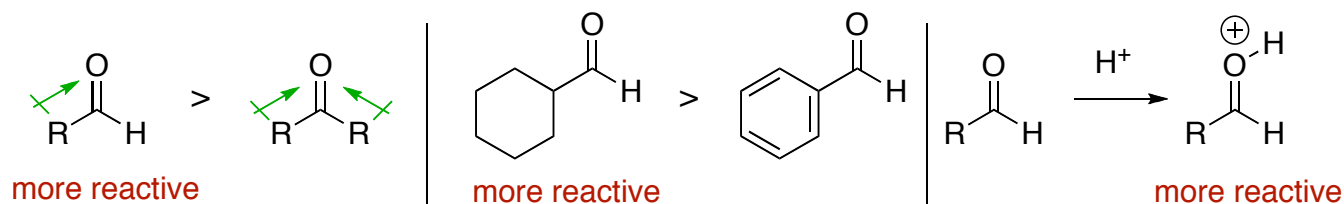
Oxidation of Carbonyls

Aldehydes can be oxidized to carboxylic acids using Jones Reagent (CrO_3/H^+). A milder method under slightly basic conditions utilizes silver oxide and ammonium hydroxide. Ketones are relatively inert to oxidation and Jones Reagent will not affect ketones. However potassium permanganate will oxidize the C-C bond next to a ketone. A C-C bond next to a carbonyl can be broken and an oxygen inserted in between using mCPBA as an oxidant.



Reactivity of Aldehydes and Ketones

Aldehydes are more reactive than ketones toward nucleophilic attack because they are less hindered and the plus charge on the carbonyl carbon is more stabilized with more alkyl groups. Conjugation also stabilizes carbonyls and makes them less reactive. Carbonyl compounds are more reactive electrophiles if they are activated by protonation or coordination to a Lewis acid.



Carbonyl compounds generally react with nucleophiles. These can be strong nucleophiles that are negatively charged, or neutral nucleophiles - usually under acid or base catalysis.

Strong Nucleophiles

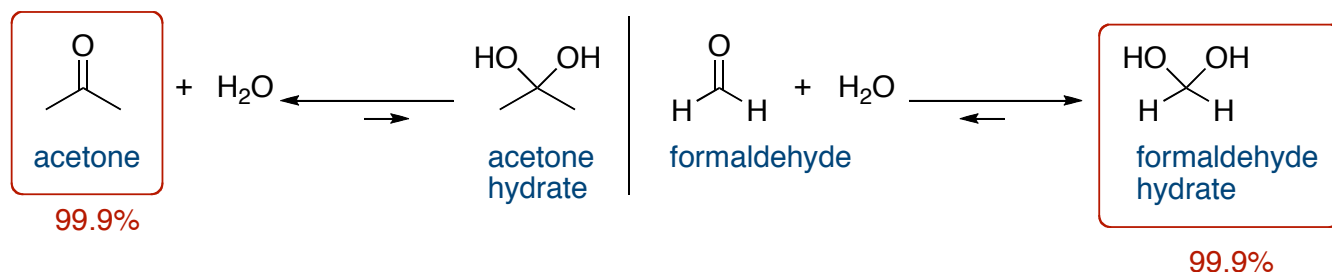


Weak Nucleophiles



Hydration of Aldehydes and Ketones

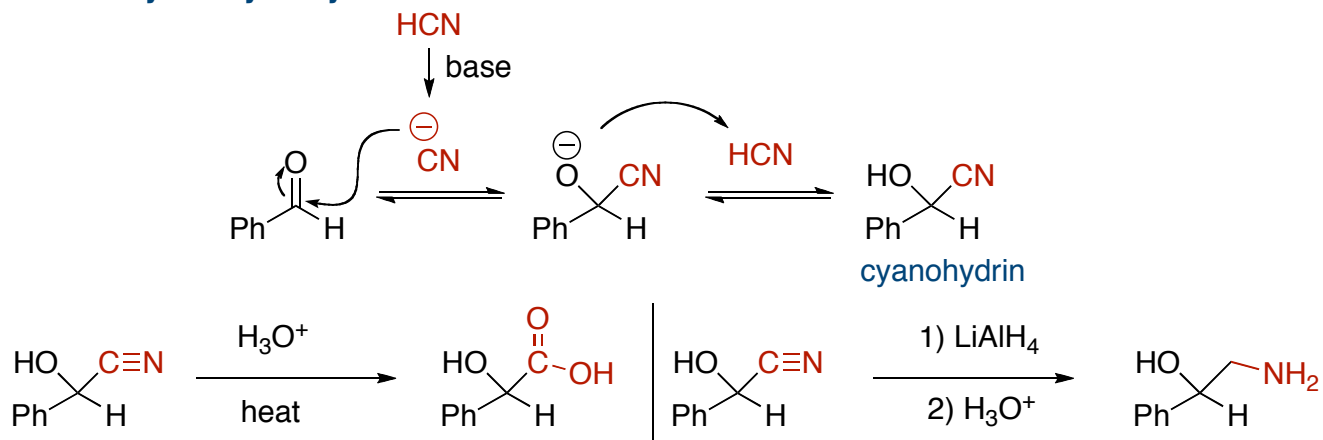
In water, aldehydes and ketones are in equilibrium with the hydrated form. Most carbonyls largely favor the ketone form. Some examples, e.g. formaldehyde, favor the hydrated form but this is rare.



Hydrocyanation of Aldehydes and Ketones

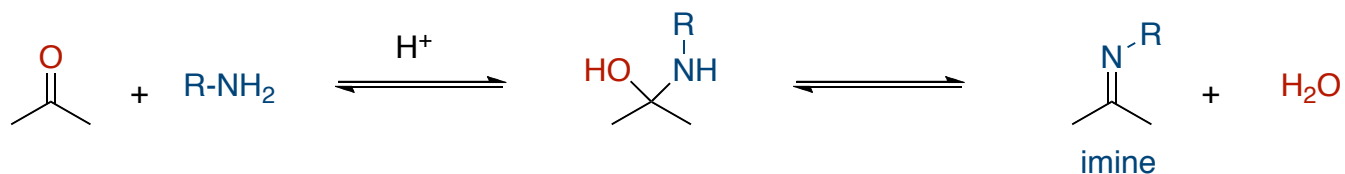
HCN adds to aldehydes and ketones to afford cyanohydrins. This reaction is best when catalyzed by base. The base could be KCN or NaOH . The products can be further manipulated by hydrolysis or reduction. This is a useful method for forming a new carbon-carbon bond.

Base Catalyzed Hydrocyanation



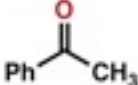
Addition of Amines

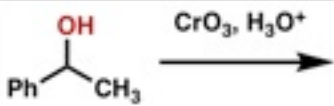
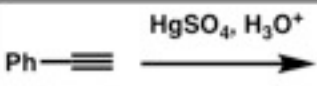
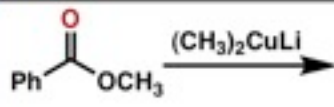
Primary amines (RNH_2) will react with aldehydes and ketones to form imines. This reaction is acid catalyzed.



Daily Quiz

Q: Which of the four reactions shown on the right will NOT work to prepare the ketone, acetophenone?



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<input type="checkbox"/> 2:	
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