

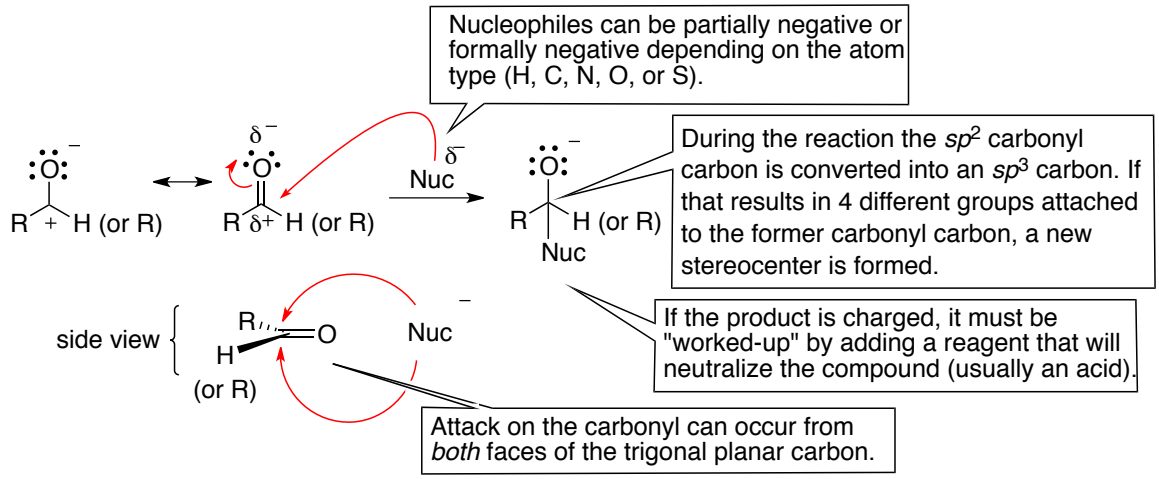
Ketones & Aldehydes
Learning Objectives

As we study this chapter, you should...

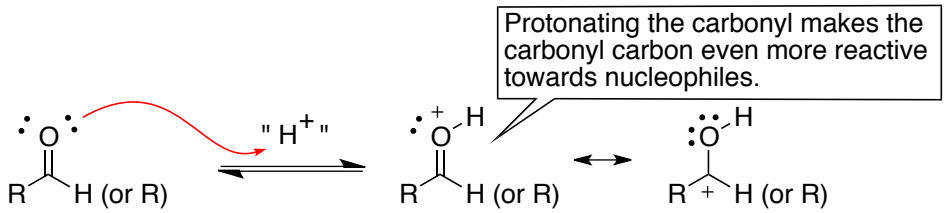
1) **Recall the methods we've used to synthesize ketones and aldehydes:**
   a) acid catalyzed hydration of internal alkynes (via enols and tautomerization) → ketones
   b) hydroboration of alkynes (via enols and tautomerization) → aldehydes
   c) chromic acid or PCC oxidation of 2° alcohols → ketones
   d) chromic acid oxidation of 1° alcohols → carboxylic acids
   e) PCC oxidation of 1° alcohols → aldehydes
   f) Friedel-Crafts acylation of benzene rings → ketones

2) **Be familiar with the physical properties of ketones & aldehydes**. Specifically, you should know that they can hydrogen bond with protic compounds and that their carbonyl groups possess dipoles.

3) **Understand that ketones & aldehydes can act as electrophiles.** They are attacked by nucleophiles in what are termed *Nucleophilic Addition Reactions*. This is their most common mode of reactivity and it arises from the partial positive charge on the carbonyl carbon. Several important points to this reaction are highlighted:



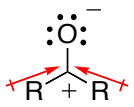
4) **Understand that ketones & aldehydes can act as Lewis bases.**



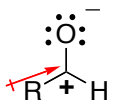
5) **Understand that reactions of the carbonyl functional group of ketones & aldehydes fall under two general categories; *irreversible* (when reacting with C or H nucs) and *reversible* (when reacting with O, S, or N nucs).** You should be able to predict the products of these reactions and provide their mechanisms.

6) **Know the Principle of Microscopic Reversibility.** It states that the mechanism of the reverse reaction constitutes the same steps as the forward reaction, only in the reverse order.

7) Know that aldehydes are more reactive than ketones towards nucleophilic addition. For 2 reasons...

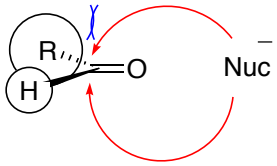


ketone



aldehyde

The aldehyde carbonyl carbon "feels" only 1 inductive effect, making it more positive and therefore more electrophilic.



Alkyl groups (R) take up more space than hydrogens. Therefore, a ketone, which has 2 R groups will be more sterically hindered than an aldehyde.

8) Understand when a nucleophile will undergo direct addition or conjugate addition. Hard nucleophiles undergo direct addition, soft nucleophiles undergo conjugate addition. While the theory behind what makes a nucleophile hard or soft is beyond the scope of this course, the following graphic places common nucleophiles under each category for your convenience...