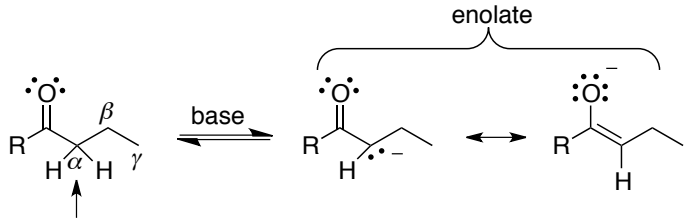


Reactions at the α-Carbon of Carbonyl Compounds (Enolate Ions)
Learning Objectives

As we study this chapter, you should...

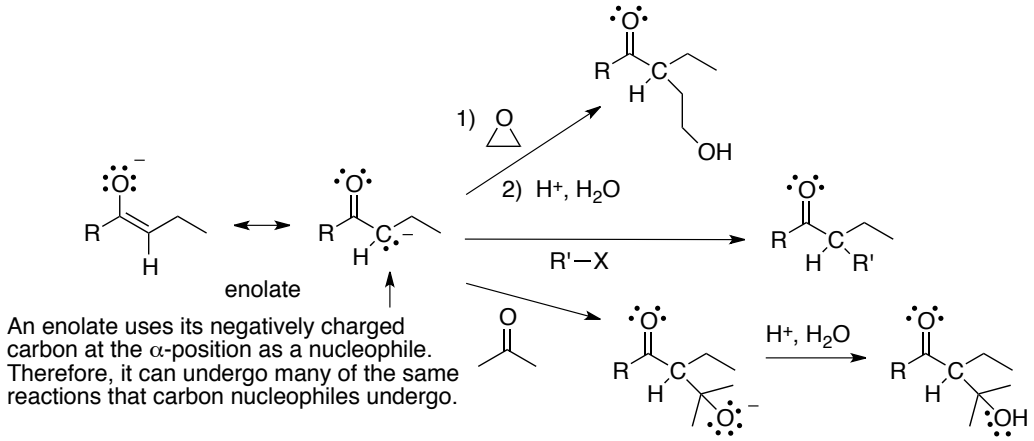
1) Know that **α-protons** of ketones, aldehydes and esters have enhanced acidity.



Type of carbonyl	pK_a
ketones & aldehydes	19-21
esters	22-25

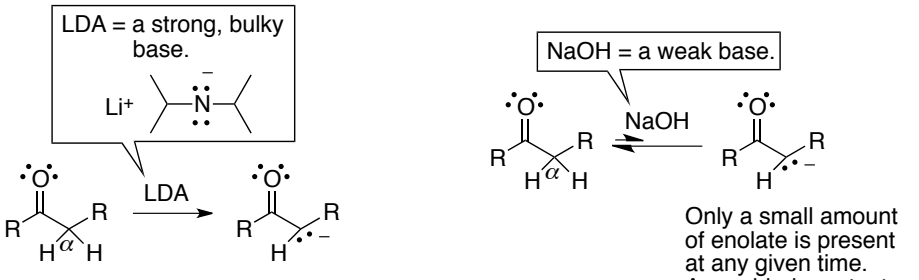
Protons at the α-position exhibit enhanced acidity because their conjugate bases (known as enolates) are stabilized by resonance.

2) Understand how an **enolate**, because it possesses a negatively charged carbon, can act as a nucleophile.



An enolate uses its negatively charged carbon at the α-position as a nucleophile. Therefore, it can undergo many of the same reactions that carbon nucleophiles undergo.

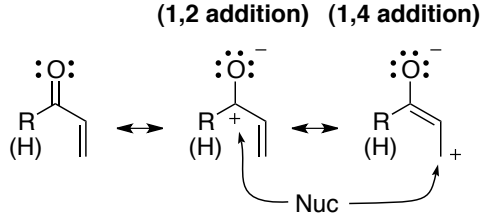
3) Be able to generate enolates **quantitatively** (using a strong base) or **under equilibrium** (using a weak base), and know when to use each scenario.



Enolate is formed quantitatively. Other reactants can be added to it.

Only a small amount of enolate is present at any given time. Any added reactants can react with all three species present.

4) Understand that α,β-unsaturated carbonyls can be attacked at the carbonyl (1,2-addition or direct addition) or at the β carbon of the alkene (1,4 addition or conjugate addition).



Hard Nucleophiles Undergo 1,2-Addition	Soft Nucleophiles Undergo 1,2-Addition
R–MgX	$K^+ CN^-$
R–Li	R_2CuLi
R—≡ Na^+	** enolates **
	oxygen nucleophiles
	sulfur nucleophiles
	nitrogen nucleophiles