These notes can be obtained at: http://www.ndsu.nodak.edu/instruct/grcook/chem342/notes.shtml

Chapter 19: Aldehydes and Ketones: Nucleophilic Addition Reactions

Cannizzaro Reaction

The Cannizzaro reaction is a rare example of a hydride (H⁻) leaving group which attacks another carbonyl. Only a few carbonyl compounds will do this reaction (benzaldehyde and formaldehyde). The mechanism is a good model for the biological reducing agent, NADH.

2
 Ph $^{\odot}$ OH $^{\odot}$ Ph OH $^{+}$ Ph OH $^{-}$ Ph

α,β-Unsaturated Carbonyls

Carbonyl compounds which are conjugated with a double bond are called α,β -unsaturated carbonyls. Note from the resonance structures that there is electrophilic character (positive charge) on the carbonyl carbon AND the beta carbon.

$$\bigcap_{\alpha} \beta \qquad \bigoplus_{\beta} \beta \qquad \bigoplus_{\alpha} \beta \qquad \bigoplus_{\beta} \beta \qquad \bigoplus_{\beta$$

Using a hydration reaction as an example, you can see that addition of the H⁺ and ⁻OH can occur in a 1,2-fashion or a 1,4-fashion.

Amines and Gilman reagents are very good at generating 1,4-addition products with unsaturated carbonyls. Many other strong nucleophiles (hydride reagents, Grignard reagents, Lithium reagents) afford the 1,2-addition products.

