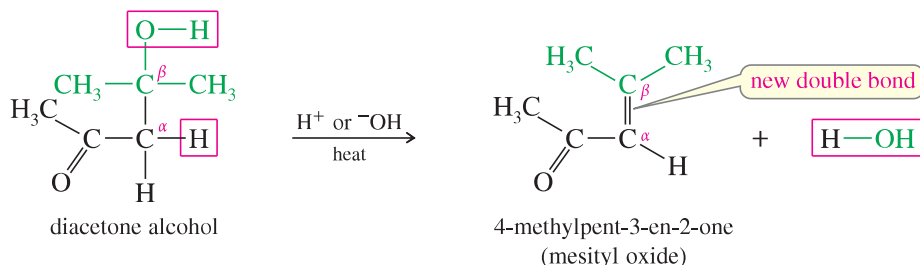


22-8 Dehydration of Aldol Products

Heating a basic or acidic mixture of an aldol product leads to dehydration of the alcohol functional group. The product is a conjugated α,β -unsaturated aldehyde or ketone. Thus, an aldol condensation, followed by dehydration, forms a *new carbon-carbon double bond*. Before the Wittig reaction was discovered (Section 18-18), the aldol with dehydration was probably the best method for joining two molecules with a double bond. It is still often the cheapest and easiest method.



Under acidic conditions, dehydration follows a mechanism similar to those of other acid-catalyzed alcohol dehydrations (Section 11-10). We have not previously seen a base-catalyzed dehydration, however. Base-catalyzed dehydration depends on the acidity of the α proton of the aldol product. Abstraction of an α proton gives an enolate that can expel hydroxide ion to give a more stable product. Hydroxide is not a good leaving group in an E2 elimination, but it can serve as a leaving group in a strongly exothermic step like this one, which stabilizes a negatively charged intermediate. The following mechanism shows the base-catalyzed dehydration of 3-hydroxybutanal.

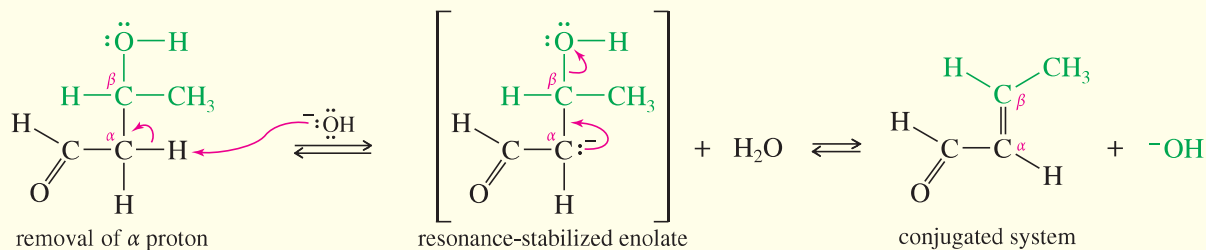


KEY MECHANISM 22-11 Base-Catalyzed Dehydration of an Aldol

Unlike most alcohols, aldols undergo dehydration in base. Abstraction of an α proton gives an enolate that can expel hydroxide ion to give a conjugated product.

Step 1: Formation of the enolate ion.

Step 2: Elimination of hydroxide.



Even when the aldol equilibrium is unfavorable for formation of a β -hydroxy ketone or aldehyde, the dehydration product may be obtained in good yield by heating the reaction mixture. Dehydration is usually exothermic because it leads to a conjugated system. In effect, the exothermic dehydration drives the aldol equilibrium to the right.

PROBLEM 22-22

Propose a mechanism for the dehydration of diacetone alcohol to mesityl oxide
 (a) in acid. (b) in base.