PROBLEM 22-20

A student wanted to dry some diacetone alcohol and allowed it to stand over anhydrous potassium carbonate for a week. At the end of the week, the sample was found to contain nearly pure acetone. Propose a mechanism for the reaction that took place.

22-7B Acid-Catalyzed Aldol Condensations

Aldol condensations also take place under acidic conditions. The enol serves as a weak nucleophile to attack an activated (protonated) carbonyl group. As an example, consider the acid-catalyzed aldol condensation of acetaldehyde. The first step is formation of the enol by the acid-catalyzed keto—enol tautomerism, as discussed earlier. The enol attacks the protonated carbonyl of another acetaldehyde molecule. Loss of the enol proton gives the aldol product.

MECHANISM 22-10 Acid-Catalyzed Aldol Condensation

The acid-catalyzed aldol involves nucleophilic addition of an enol to a protonated carbonyl group.

Step 1: Formation of the enol, by protonation on O followed by deprotonation on C.

Step 2: Addition of the enol to the protonated carbonyl.

attack by enol

resonance-stabilized intermediate

Step 3: Deprotonation to give the aldol product.

$$\begin{bmatrix} : \ddot{O} - H & : \ddot{O} - H \\ H - C - CH_3 & H - C - CH_3 \\ H & \downarrow \alpha & H - \dot{\Omega} \\ H & \downarrow \alpha & H - \dot{\Omega} \\ R \ddot{O} H & H & \downarrow \alpha \\ H & \downarrow \alpha & H - \dot{\Omega} \\ \end{bmatrix} \xrightarrow{|\beta|} H + C - CH_3$$

$$\downarrow O - H +$$

resonance-stabilized intermediate

aldol product

PROBLEM 22-21

Propose a complete mechanism for the acid-catalyzed aldol condensation of acetone.

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.