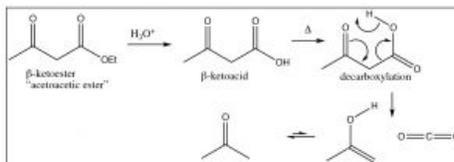
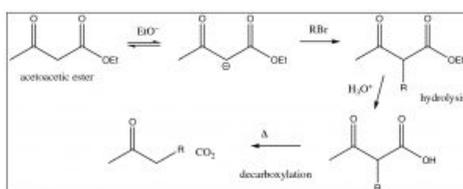


## 9.4: $\beta$ -Ketoacids Decarboxylate

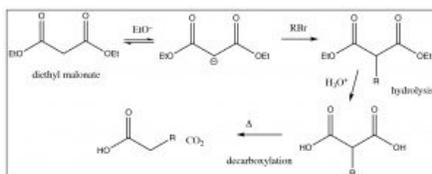
All of these Claisen condensation reactions produce a difunctional compound in which a carbonyl group is located on the beta position of an ester. There is a useful reaction that can be carried out if the ester is hydrolyzed to the corresponding acid. If the resulting  $\beta$ -keto acid is heated, it decarboxylates (loses  $\text{CO}_2$ ) in a pericyclic reaction that involves the cyclic rearrangement of six electrons as shown below.



The  $\beta$ -ketoester here is known as acetoacetic ester. The  $\text{CH}_2$  group between the two carbonyls is easily deprotonated, and the resulting anion can do a nucleophilic attack on any susceptible substrate: for example, an alkyl halide. A subsequent hydrolysis and decarboxylation results in a compound that has three more carbons in it than the original alkyl halide, as shown below.



The “acetoacetic ester” synthesis is a powerful way of adding a 3-carbon unit. A similar reaction involves malonic ester (below), which can be used to add a 2-carbon unit.



In the decarboxylation step, only one of the carboxylic acids decarboxylates and the alkyl group is extended by two carbon atoms. Interestingly, fatty acids (long chain carboxylic acids) are synthesized by a mechanism that is analogous to this malonic ester synthesis.

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