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Über eine Darstellungsweise des Benzylidenacetessigesters

Ber. Dtsch. Chem. Ges. **1896**, 29, 172–174.

Über den Chemismus der condensierenden Wirkung des Ammoniaks und organischer Amine bei Reactionen zwischen Aldehyden und Acetessigestern

Ber. Dtsch. Chem. Ges. **1898**, 31, 738–748.

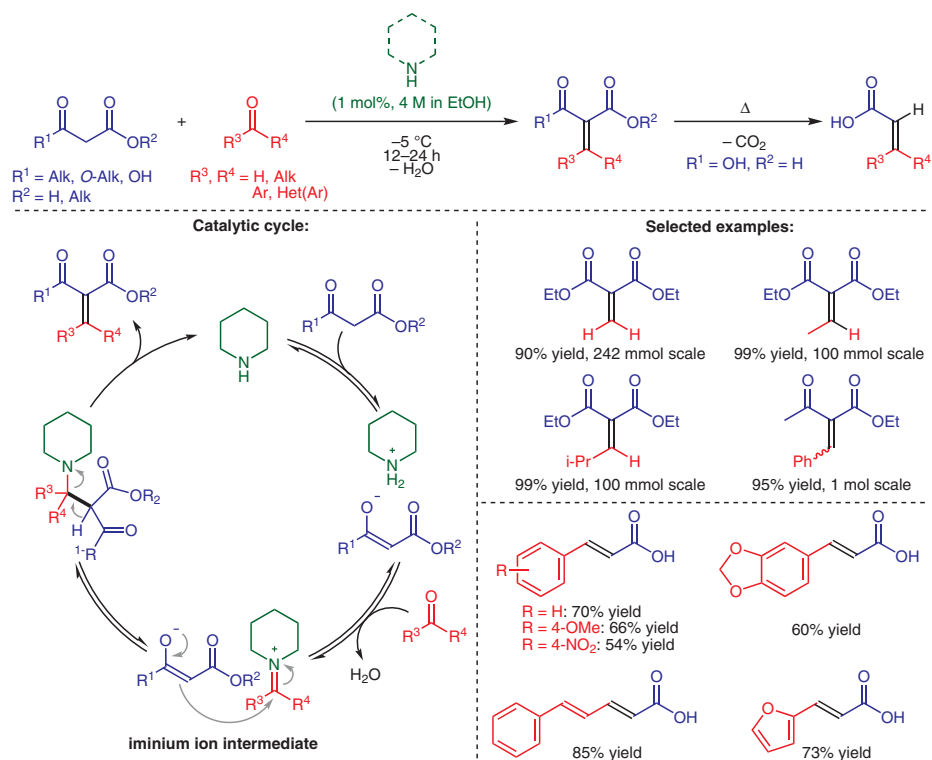
Condensation zwischen Malonester und Aldehyden unter dem Einfluss von Ammoniak und organischen Aminen

Ber. Dtsch. Chem. Ges. **1898**, 31, 2585–2595.

Condensation von Malonsäure mit aromatischen Aldehyden durch Ammoniak und Amine

Ber. Dtsch. Chem. Ges. **1898**, 31, 2596–2619.

The Knoevenagel Condensation



Significance: Between 1896 and 1898, Emil Knoevenagel reported that primary and secondary amines, their respective salts, and ammonia (but not tertiary amines) are efficient catalysts for the aldol condensation of β -keto esters or malonates with either aldehydes or ketones. The reaction proceeds under mild conditions, is scalable, tolerates a wide range of substrates, and delivers the corresponding α,β -unsaturated esters in good to excellent yields in an atom-economic fashion. Decarboxylation of malonic acid-derived products selectively provides (*E*)-cinnamic acid derivatives.

Comment: More than 120 years ago, Knoevenagel had already recognized the catalytic nature of the added amine. His discovery therefore arguably signifies the starting point of aminocatalysis. The proposal of iminium-type intermediates (*Schiff'sche Körper* or Schiff-type intermediates) had a great influence on later studies that ultimately led to the systematic development of aminocatalysis. As the Knoevenagel condensation is a reliable, efficient, and scalable method for the formation of C–C bonds, it is still widely used in both academia and industry.