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Über eine Darstellungsweise des Benzylidenacetessigesters

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

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

Condensation von Malonsäure mit aromatischen Aldehyden durch Ammoniak und Amine

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.