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A Tertiary Phosphine-Catalyzed Reaction of Acrylic Compounds with Aldehydes

Bull. Chem. Soc. Jpn. **1968**, *41*, 2815.

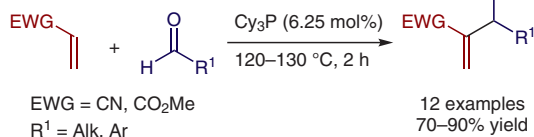
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Verfahren zur Herstellung von Acrylverbindungen

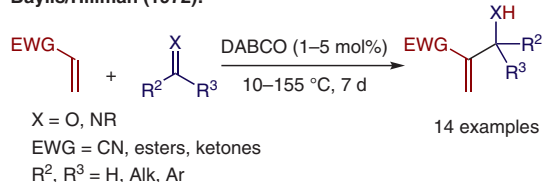
German Patent 2155113, 1972.

The Morita–Baylis–Hillman Reaction

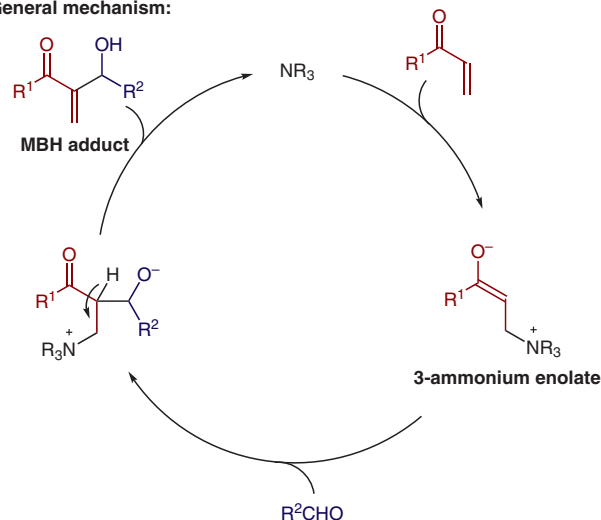
Morita (1968):



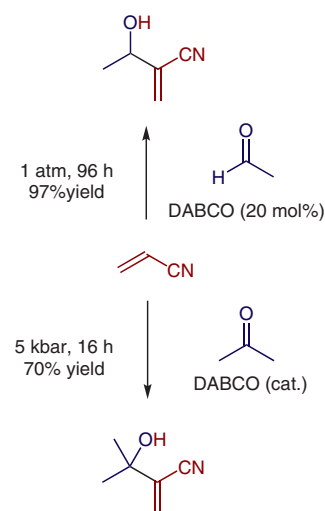
Baylis/Hillman (1972):



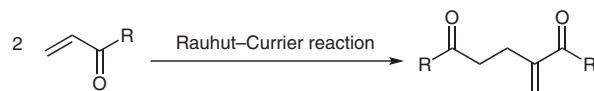
General mechanism:



Comparison of aldehyde and ketone electrophiles:



In absence of a good electrophile:



Significance: In 1968, Morita and co-workers reported the first Lewis base catalyzed acrylic α -substitution of activated vinyl compounds by using Cy₃P as catalyst. Additionally, in 1972, Baylis and Hillman patented the reaction between α,β -unsaturated carboxylic acid derivatives and aldehydes in the presence of a tertiary amine catalyst. This reaction, nowadays called the Morita–Baylis–Hillman (MBH) reaction, is highly versatile and atom economical.

Comment: The MBH reaction typically requires an activated alkene, an electrophile, and a Lewis base catalyst. The mechanism starts with the conjugate addition of the catalyst to the activated alkene, thus forming a zwitterionic adduct, typically a 3-ammonium enolate, which reacts with the electrophile. After proton transfer and elimination of the catalyst, the product is obtained in typically good yields, sometimes after long reaction times. To use ketones as electrophiles, high pressures are required.

SYNFACTS Contributors: Benjamin List, Oleg Grossmann
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Category

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Key words

Morita–Baylis–Hillman reaction

aldehydes

phosphines

acrylic compounds

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Classic