

The Rauhut-Currier reaction: Why are phosphines catalytically active but amines are not?

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The Rauhut-Currier (RC) reaction describes the coupling of two Michael acceptors under nucleophilic catalysis and is closely related to the Morita-Baylis-Hillman (MBH) reaction in which a Michael acceptor is coupled with an aldehyde.¹ While only the mechanism of the MBH reaction has been studied experimentally, it is generally assumed that both reactions proceed through similar reaction mechanisms.² However, this does not explain why a phosphine catalyst is required in RC reactions, while both amines and phosphines are suitable catalysts for MBH reactions.¹ This difference in catalyst reactivity is illustrated by two competition experiments in which ethyl acrylate, in the presence of a nucleophilic catalyst, can react both with benzaldehyde *via* a MBH reaction and diethyl fumarate *via* a RC reaction. While the phosphine catalyst gives the RC product, only the MBH product is observed in the presence of an amine catalyst, thus giving opposite product selectivity in these two reactions. Here, we present a mechanistic model for the RC reaction which explains the necessity for *phosphine catalysts* in the RC reaction. Our proposal is supported by kinetic analysis and modelling as well as isotope labelling and computational studies.

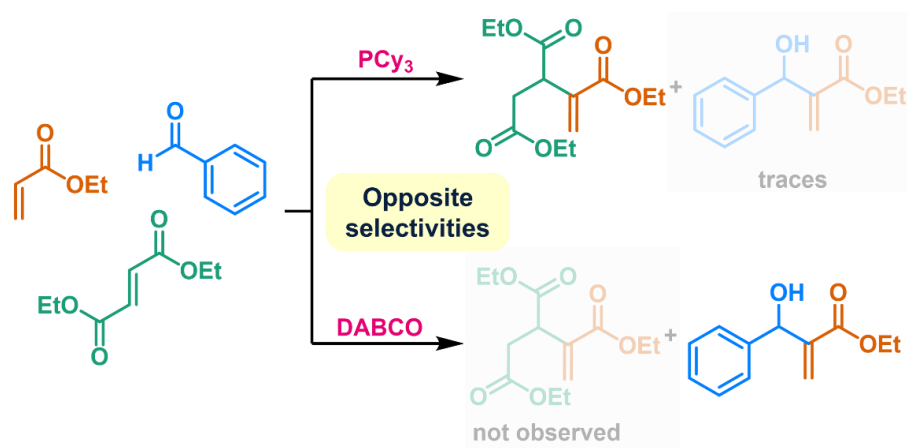


Figure 1. Competition of a RC and a MBH reaction with an amine and a phosphine catalyst.

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