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Regio- and Stereoselective Nickel-Catalyzed Homoallylation of Aldehydes with 1,3-Dienes
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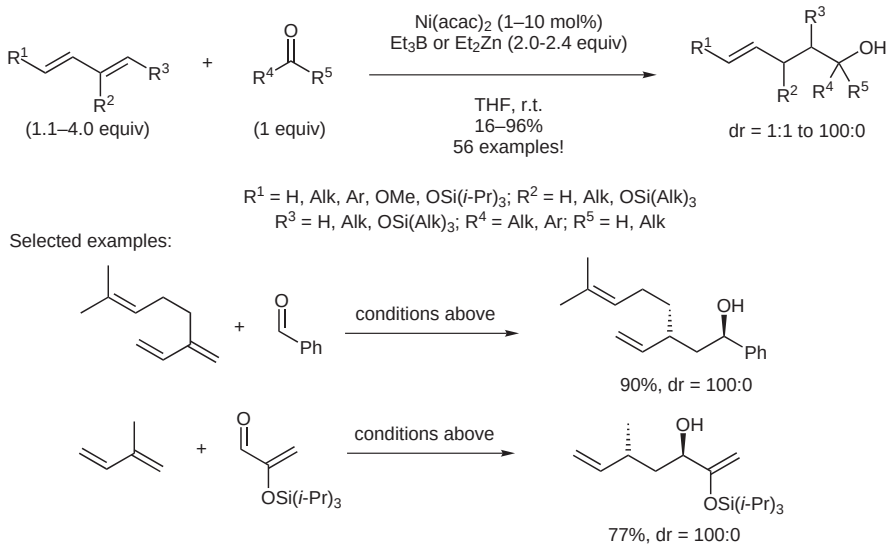
Stereoselective Homoallylation of Aldehydes and Ketones



Significance: In the presence of catalytic $Ni(acac)_2$ and stoichiometric Et_3B or Et_2Zn, 1,3-dienes are added to aldehydes and ketones to stereoselectively afford homoallylation products. Aromatic aldehydes react in the presence of Et_3B with 1,3-*anti* selectivity whereas aliphatic aldehydes react in the presence of Et_2Zn to give exclusively 1,3-*anti* products. Terminally substituted dienes generally afford 1,2-*anti* products, except hydroxyterminal dienes which afford 1,2-*syn* products. Less reactive moieties such as ketones and cyclohexadiene required Et_2Zn, and afforded the product in moderate yields, with cyclohexadiene affording allylation, not homallylation products. Catalyst loadings as low as 1 mol% were used on a 50-mmol scale and the diene loading was decreased to 1.1 equivalents. The method was applied to a 10-g scale reaction of isoprene and dehydrocinnamaldehyde, affording product in 80% yield.

Comment: This report is a thorough examination of the Ni-catalyzed homoallylation of aldehydes and ketones, which explored nearly all of the factors affecting the reaction. Mechanistically, it is proposed that Ni(0) coordinates to the diene and aldehyde, promoting aldehyde addition and Ni(II)-π-allyl formation. Ethyl transfer from Et_3B or Et_2Zn forms an ethylnickel(II) species which undergoes β-hydride elimination followed by reductive elimination to generate Ni(0) and the product.

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