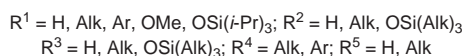
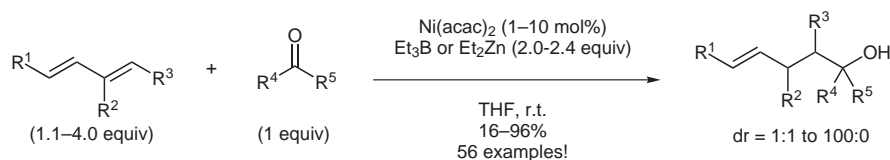


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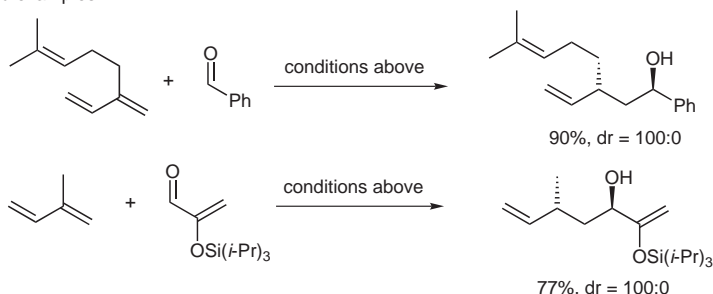
Regio- and Stereoselective Nickel-Catalyzed Homoallylation of Aldehydes with 1,3-Dienes

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Stereoselective Homoallylation of Aldehydes and Ketones



Selected examples:



Significance: In the presence of catalytic $\text{Ni}(\text{acac})_2$ 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 homoallylation 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 $\text{Ni}(0)$ coordinates to the diene and aldehyde, promoting aldehyde addition and $\text{Ni}(\text{II})$ - 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 $\text{Ni}(0)$ and the product.

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Reactions

Key words

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nickel

aldehydes

ketones

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of the month

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