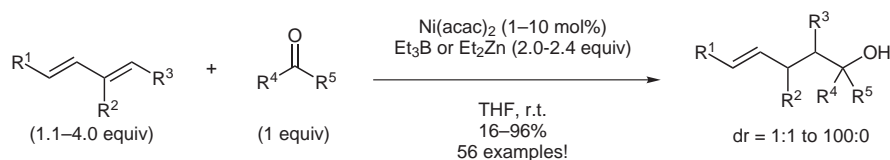


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Regio- and Stereoselective Nickel-Catalyzed Homoallylation of Aldehydes with 1,3-Dienes

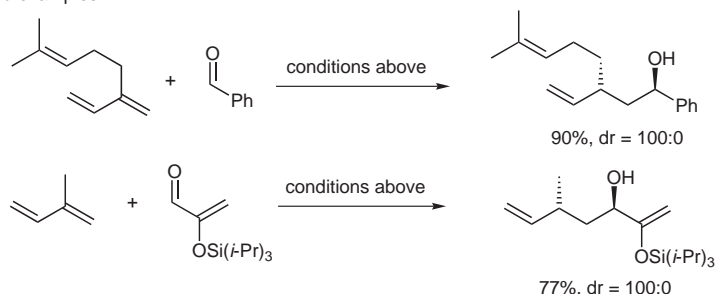
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## Stereoselective Homoallylation of Aldehydes and Ketones



$\text{R}^1 = \text{H, Alk, Ar, OMe, OSi}(i\text{-Pr)}_3$ ;  $\text{R}^2 = \text{H, Alk, OSi(Alk)}_3$   
 $\text{R}^3 = \text{H, Alk, OSi(Alk)}_3$ ;  $\text{R}^4 = \text{Alk, Ar}$ ;  $\text{R}^5 = \text{H, Alk}$

Selected examples:



**Significance:** In the presence of catalytic  $\text{Ni(acac)}_2$  and stoichiometric  $\text{Et}_3\text{B}$  or  $\text{Et}_2\text{Zn}$ , 1,3-dienes are added to aldehydes and ketones to stereoselectively afford homoallylation products. Aromatic aldehydes react in the presence of  $\text{Et}_3\text{B}$  with 1,3-*anti* selectivity whereas aliphatic aldehydes react in the presence of  $\text{Et}_2\text{Zn}$  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  $\text{Et}_2\text{Zn}$ , 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  $\text{Ni(II)-}\pi$ -allyl formation. Ethyl transfer from  $\text{Et}_3\text{B}$  or  $\text{Et}_2\text{Zn}$  forms an ethylnickel(II) species which undergoes  $\beta$ -hydride elimination followed by reductive elimination to generate  $\text{Ni(0)}$  and the product.

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homoallylation

nickel

aldehydes

ketones

**SYNFACTS**  
*of the month*

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