

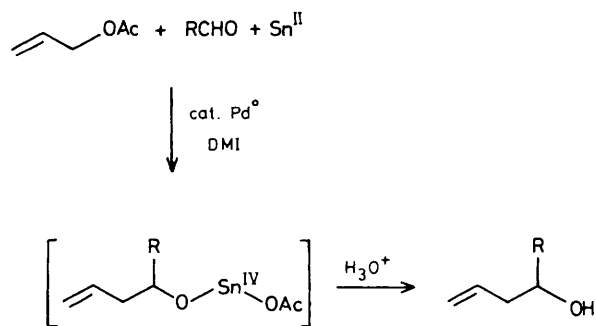
Charge Reversal of Electrophilic π -Allylpalladium Intermediates; Carbonyl Allylation by Allylic Acetates with $\text{PdCl}_2(\text{PhCN})_2\text{-SnCl}_2$

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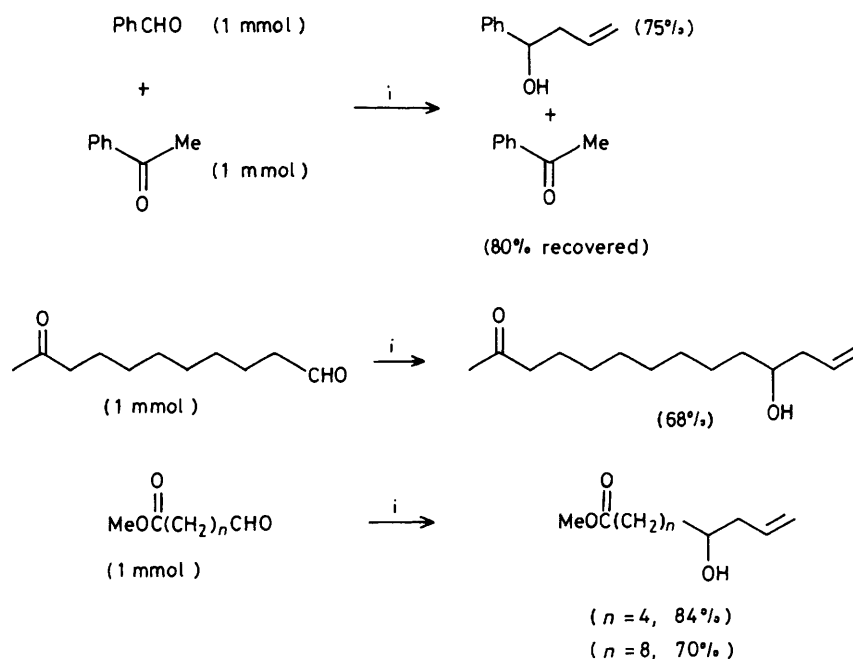
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Carbonyl allylation by stable allylic acetates with $\text{Pd}^0\text{-SnCl}_2$ occurred regio-, chemo-, and diastereoselectively to afford the corresponding homoallylic alcohols.

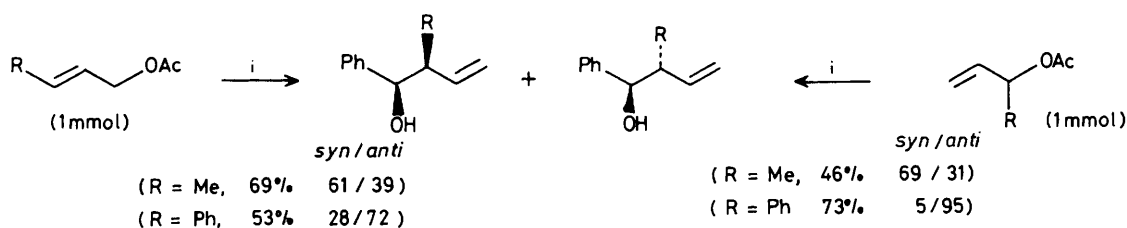
The addition reaction of allylic organometallic reagents with aldehydes is one of the most synthetically useful methods for acyclic stereoselection.¹ Allylic halides or alkenes, from which the allylic organometallic reagents are generally prepared, are often unstable or intractable. We have recently reported that stable allylic acetates, easily derived from available allylic alcohols, serve as the allylic organometallic reagents for carbonyl allylation using the $\text{Pd}(\text{PPh}_3)_4\text{-Zn}$ system.² However, the reaction was slow (taking 5–6 days at room temperature), and required excess of allylic acetates (5–10 equiv.) since homocoupling of the allylic acetates also occurred under these conditions. We now report that the $\text{PdCl}_2(\text{PhCN})_2\text{-SnCl}_2$ system in 1,3-dimethylimidazolidin-2-one (DMI)³ promotes the carbonyl allylation *via* an apparent



Scheme 1



Scheme 2. Reagents and conditions: i, allyl acetate (3 mmol), 50 °C, 20 h.



Scheme 3. Reagents and conditions: i, PhCHO (1 mmol), 50 °C, 20 h.

Table 1. Carbonyl allylation by allyl acetate with Pd⁰-SnCl₂.^a

Aldehyde	Temp./°C	Time/h	Yield (%) ^b
Hexanal	60	19	54
Undec-10-enal	60	17	76
Benzaldehyde	60	15(25) ^c	82(75) ^c
Piperonal	25	60	63
Cinnamaldehyde	25	57	60
Citral	25	59	50

^a Addition reaction of allyl acetate (3 mmol) to aldehydes (1 mmol) with PdCl₂(PhCN)₂ (0.02 mmol) and SnCl₂ (3 mmol) was carried out in DMI (5 ml). ^b The yields of isolated pure products were based on the aldehydes. ^c One equivalent of allyl acetate was used.

charge reversal of π -allylpalladium intermediates which occurs without homocoupling (Scheme 1).

The results of representative experiments using allyl acetate are summarised in Table 1. Aromatic and α,β -unsaturated aldehydes can be used in this Pd⁰-SnCl₂ system without pinacol type self-coupling reactions occurring.⁴ The allylation of an aldehyde was chemoselectively performed in the presence of a ketone group or an ester group (Scheme 2). In

the cases of crotyl, 1-methylallyl, cinnamyl, and 1-phenylallyl acetates, benzaldehyde regioselectively attacked the more substituted allylic position of the π -allylpalladium intermediates to give a single regioisomer (Scheme 3). The diastereoselectivity (*anti* selectivity) of (*E*)-cinnamyl acetate was the reverse of that (*syn* selectivity) found for (*E*)-crotyl acetate, similar to the selectivity observed for allyltins.⁵ It is noteworthy that 1-substituted allyl acetates have exhibited diastereoselectivity values the same as, or higher than, those of (*E*)-3-substituted allyl acetates, since various 1-substituted allyl acetates are easily prepared from aldehydes and vinyl-magnesium halide *via* acetylation.

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