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Palladium-Catalyzed Aminocarbonylation of Cinnamyl *N,N*-Dialkylcarbamates. An Intriguing Crossover with *p*-Methylcinnamylamines

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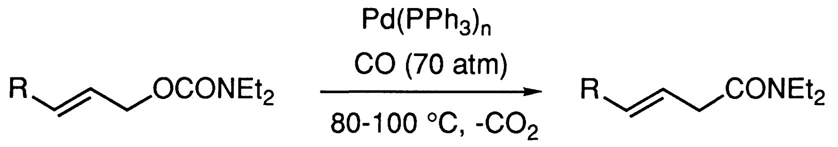
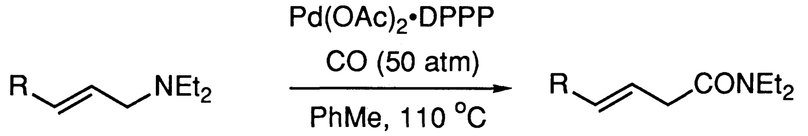
Competition experiments in the palladium-catalyzed aminocarbonylation of cinnamyl *N,N*-dialkylcarbamates with *p*-methylcinnamylamines revealed that the allylamine did not undergo oxidative addition but attacked extensively a π-allylpalladium which arose from the allyl carbamate under the conditions employed, forming a mixture of the corresponding amides containing either cinnamyl moiety that incorporates a dialkylamino component *originated only from the carbamate*.

Aiming at the aminocarbonylation of certain substrate of allyl alcohol origin, we have recently reported the Pd(0)-catalyzed decarboxylative carbonylation of allyl *N,N*-diethylcarbamates to give β,γ-unsaturated amides (Eq. 1).1) There has been a closely related Pd(0)-catalyzed carbonylation of allylamines to give also β,γ-unsaturated amides (Eq. 2).2)



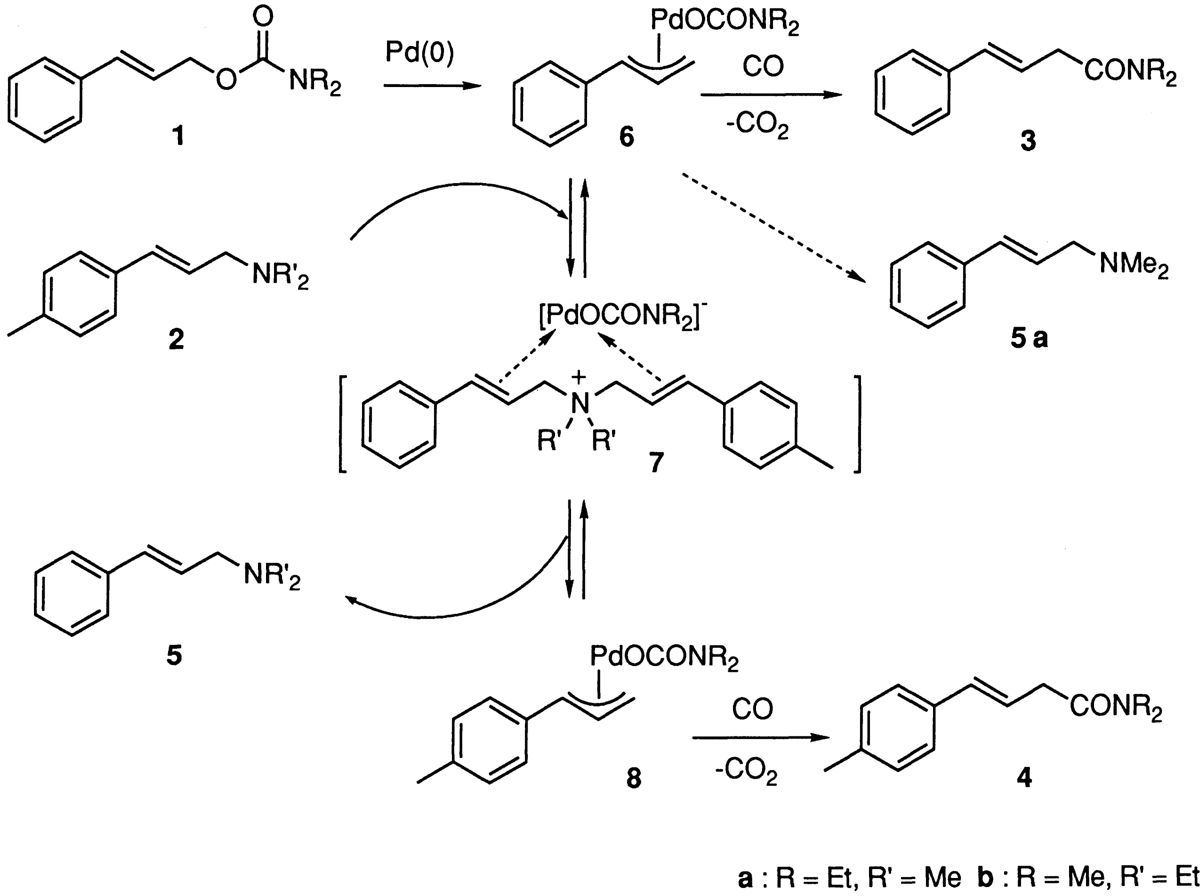
(1)



(2)

Although the former reaction does not appear to proceed under forcing conditions compared with those of allylamines, the difference between these two reactions is rather ambiguous. For instance, 2,7-octadienyl *N,N*-diethylcarbamate gave *N,N*-diethyl-3,8-nonadienamide in 60% yield under a carbon monoxide pressure (70 atom) at 100 °C in the presence of $Pd_2(dba)_3 \cdot CHCl_3$3) and PPh_3 (1:4) (5 mol%), whereas the carbamate afforded *N,N*-diethyl-2,7-octadienylamine as a simple decarboxylation product (40% yield) along with the amide (28%) under CO (50 atm) at 110 °C in toluene in the presence of $Pd(OAc)_2$ and DPPP3) (5 mol%) in exactly the same manner as reported for allylamines.2) Consequently, it seems necessary to distinguish whether an allylamine participates as an intermediate in the decarboxylative carbonylation of allyl carbamates. In order to elucidate these issues, we have carried out a competition experiment between allyl carbamates and related allylamines in the Pd(0)-catalyzed carbonylation, which is the subject of this paper.

A mixture of cinnamyl *N*,*N*-diethylcarbamate (**1a**) (1.0 mmol), *N*,*N*-dimethyl-*p*-methylcinnamylamine (**2a**) (1.0 mmol) and $Pd(PPh_3)_3$ prepared in-situ (5 mol%)[4] was heated at 80 °C under CO (80 atm) for 60 h in a glass-lined micro autoclave (50 mL). An aliquot of the reaction mixture was analyzed by GLC (Silicone DC-550 3m, at 180 °C). The starting carbamate **1a** was found to be completely consumed and there were four components consisting of two carbonylation products **3a** and **4a** (in a ratio 46 : 54)[5] as well as two dimethylamine derivatives **2a** and **5a** (50 : 50)[5] (see, Scheme 1 and Table 1 Entry 1). It was found that **4a** formed rather exceedingly as compared with **3a**. However, it is noteworthy that, while the allylic moiety did exhibit an extensive crossover in both amides and amines, neither *N*,*N*-dimethylamide (**3b** or **4b**) nor diethylamine (**2b** or **5b** in Scheme 1) was detected within the accuracy of GLC analysis of the reaction mixture. A puzzling result may be understood by considering the second competition experiment that is given below: An equimolar mixture of cinnamyl *N*,*N*-dimethylcarbamate (**1b**) and *N*,*N*-diethyl-*p*-methylcinnamylamine (**2b**) in the presence of $Pd(PPh_3)_3$[4] (5 mol%) was heated at 80 °C under CO (70 atm) for 60 h in order to consume **1b** completely, giving two different amides **3b** and **4b** (82 : 18)[5] and diethylamines **2b** and **5b** as well as *N*,*N*-dimethylcinnamylamine (**5a**) in a ratio 60 : 21 : 19[5] (see also, Scheme 1 and Table 1 Entry 3). It is again obvious that the crossover, observed in the amides heavily biased to the carbamate **1b** origin, was restricted within the allyl moiety, and no *N*,*N*-diethylamino group was incorporated into amides. These results indicate



a : R = Et, R' = Me **b** : R = Me, R' = Et

Scheme 1.

that *p*-methylcinnamylamines, **2a** and **2b**, *do not* participate in the present Pd(0)-catalyzed carbonylation by way of an oxidative addition to form π-1-(*p*-tolyl)allylpalladium, but rather react, as a nucleophile, with the π-1-phenylallylpalladium **6** formed from the carbamate **1**. So that, it would also be rationalized that the extent of the crossover in product amides (3/4) depends markedly on the conversion of the competition experiments (cf. Table 1 Entries 1 and 2).

Table 1. Competition experiment in the Pd(0)-catalyzed carbonylation[a)]

Entry	R	R'	Conv./%	Amides		Amines	
				Yield[b)]/%	**3 / 4**	Yield[c)]/%	**2 / 5a / 5b**
1	Et	Me	100	-	46 / 54	-	50 / 50 / 0
2	Et	Me	66	81	37 / 63	100	59 / 41 / 0
3	Me	Et	100	84	82 / 18	120	60 / 19 / 21

a) Reaction conditions : CO 70-80 atm, temp 80 °C, reaction time 60 h, carbamate / amine = 1 / 1, $Pd_2(dba)_3{\bullet}CHCl_3$ 2.5 mol% and Ph_3P 15 mol%. b) Isolated yield. c) Combined yield of **2** with **5**.

Although Pd(0)-catalyzed amination of allylic esters with secondary amines has extensively been studied to exhibit an efficient synthesis of tertiary allylamines,6) few papers are reported concerning the amine exchange of allylic amines. Trost and Keinan7) have reported that Pd(0)-catalyzed amine exchange is realized between an allylamine and benzylamine in the presence of an acid, implying that allyl ammonium salts are substrates for an oxidative addition to the Pd(0) complex. Hirao et al.8) have shown that reactions of allylic triethylammonium bromides with carbon nucleophiles are catalyzed by $Pd(PPh_3)_4$, indicative of a π-allylpalladium as a key intermediate. Furthermore, there is a report on the Pd(0)-catalyzed reaction of allyl *N,N*-dialkylcarbamates with carbon nucleophiles,9) where the *N*-allylation is often competitive with the *C*-allylation, because the dialkylamine component formed by decarboxylation that follows an oxidative addition of the starting carbamate may well be a good nucleophile.

Thus, all results obtained in the present competition experiments may be fully explained by Scheme 1 (phosphine ligands on palladium are omitted for simplicity): A key intermediate π-1-phenylallylpalladium **6a** (R = Et), which arises from the carbamate **1a**, can undergo either decarboxylative carbonylation to give the amide **3a** or an attack of the added amine **2a** (R' = Me) to form *unsymmetric bisallylammonium palladate* **7a**.10) The crucial crossover must take place exclusively by way of the oxidative addition of the latter to form both **6a** and **8a** presumably in an equal amount, because of no steric discrimination between cinnamyl and *p*-methylcinnamyl group in the intermediate **7a**.10) At the same time, two dimethylamines **2a** and **5a** are necessarily liberated. Decarboxylative carbonylation of both **6a** and **8a** affords eventually the amides **3a** and **4a**, respectively in comparable yields in this particular case. When the amine **2b** (R' = Et) is used, the amine attack to **6b** (R = Me) would become less favored owing to the steric demand of **2b**, forming **7b** to a lesser extent. Consequently, most diethylamine **2b** would remain unchanged and only one fourth of **2b** participates in the crossover to form another diethylamine **5b** as well as π-1-(*p*-tolyl)allylpalladium **8b**, an immediate precursor to **4b**. As a result, the ratio of amides **3b** to **4b** becomes ca. 5 : 1, the former arising mainly from the direct decarboxylative carbonylation of **6b**. Formation of a significant amount of **5a** in this case is the result of internal competitive reactions between aminocarbonylation and simple decarboxylative amination of **6b** as exemplified in the Pd(0)-catalyzed allylation using allyl *N,N*-dimethylcarbamates,[9] a dimethylamino group being particularly a good nucleophile.

In conclusion, we have confirmed that allyl *N,N*-dialkylcarbamates **1** are better substrates for a Pd(0) complex to undergo oxidative addition than tertiary allylamines **2**, and that an intriguing crossover observed between these two compounds in the Pd(0)-catalyzed aminocarbonylation is most certainly explained by their proceeding to an amine exchange by way of unsymmetric bisallylammonium palladate **7** as a key intermediate.

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2) S. -I. Murahashi, Y.Imada, and K.Nishimura, *J. Chem. Soc., Chem. Commun.,* **1988**, 1578.
3) Dba = dibenzylideneacetone. DPPP = diphenylphosphinopropane.
4) Prepared in-situ from $Pd_2(dba)_3 \cdot CHCl_3$ and PPh_3 (6 equiv).
5) The amides (94% combined yield) were easily separable from amines (96% combined yield) by acid treatment and recovery. Each component (**2**, **3**, **4**, and **5**) was characterized by the exact GC-MS measurements and % ratio was determined by GLC peak areas and by peak ratio of ^1H NMR.
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10) However, cinnamyl-*p*-nitrocinnamyldimethylammonium bromide was found to undergo oxidative addition of $Pd(PPh_3)_4$ as catalyst in MeCN at 0 °C, reacting preferably at a *p*-nitrocinnamyl moiety with the added nucleophiles such as trimethylamine or methyl methylpropionylacetate anion. Significant substituent effects on these reactions will be reported elsewhere.

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