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Palladium-Catalyzed Decarboxylative Aza-Michael Addition−Allylation Reactions between Allyl Carbamates and Activated Olefins. Generation of Quaternary Carbon Adjacent to Secondary Amine Carbon Center

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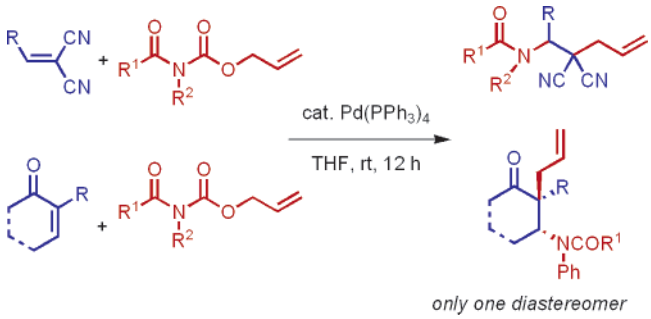

The reaction of allyl carbamates with activated olefins in the presence of $Pd(PPh_3)_4$ catalyst in THF proceeded smoothly at room temperature to give the corresponding β,α-bisadducts, β-amino-α-allylated products, in high yields. Not only highly activated olefins containing two cyano groups but also 2-cyano enones underwent facile aza-Michael addition−allylation with various allylic carbamates giving the corresponding products in high yields and with high diastereoselectivities. The stereochemistry of the singly formed product was confirmed with the help of X-ray crystallographic technique. It is an excellent method for creating β-amino α-allyl ketones having two contiguous stereocenters: quaternary carbon adjacent to secondary amine carbon center.

Introduction

The palladium-catalyzed C−C and C−N bond formation reactions via decarboxylative addition are one of the important areas in organic synthesis.[1] These reactions are synthetically very important because they can be performed under essentially neutral conditions; moreover, CO_2 gas is the only byproduct. Unfortunately, these catalytic reactions are strictly limited for allylic carbonates. The scope and utility of these types of reactions would be greatly expanded if the concept could be employed for the allylic carbamates.[2]

The generation of a quaternary carbon center is one of the important reactions in organic chemistry.[3] The palladium-catalyzed decarboxylative addition of enolates[4] as well as base-

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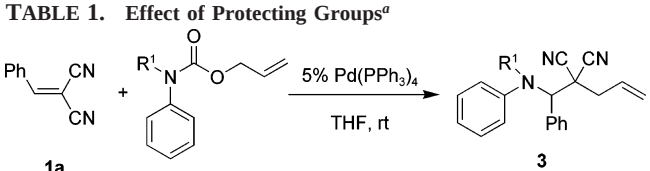
mediated allylation of carbonyl compounds[5] gives easy access to quaternary carbon centers. However, those reactions gave access to only α-allylated carbonyl compounds. In the course of a total synthesis investigation, we became interested in the synthesis of α-allyl β-amino enones having two contiguous stereocenters: quaternary carbon adjacent to secondary amine carbon center. We previously demonstrated that allylic carbonates reacted with highly activated olefins in the presence of palladium catalyst.[6] On the basis of this finding and the reports on the reactions of activated olefins in our laboratory,[7] we reasoned that benzylidenemalononitrile **1a** might react with allylic carbamates in a similar manner, and if successful, this methodology can be applicable to the enones which would give access to α-allyl β-amino enones.[8] To our pleasure, the hypothesis proved feasible, and the detailed results are reported herein.

Results and Discussion

Taking into consideration the potential of Pd(0) catalyst for the reaction of activated olefins,[7] we decided to use $Pd(PPh_3)_4$ catalyst and varied the protecting group on the amine nitrogen of allylic carbamates. The results are summarized in Table 1. At first, an equimolar mixture of *N*-phenyl carbamate **2a** and benzylidenemalononitrile **1a** in the presence of $Pd(PPh_3)_4$ (5 mol %) was stirred in THF at room temperature for 12 h. The desired product was not obtained at all, and the starting material was recovered (entry 1). The use of a methyl group on the carbamate nitrogen also did not lead to any product formation (entry 2). We envisaged that introduction of a −COR group on the amine would lead to the formation of an oxazabis-π-allylpalladium complex,[9] an analogue of the bis-π-allylpalladium complex. Since the amphiphilic[7a,b,10] nature of the bis-π-allylpalladium complex is known, the reaction was thought to proceed as expected. Accordingly, the carbamate **2c** was treated with **1a** in the presence of 5 mol % of palladium catalyst. Indeed, the starting materials completely disappeared, giving the amino allylation product **3c** in 87% isolated yield (entry 3). The use of a strong electron-withdrawing group, such as $-COCF_3$ on carbamate nitrogen, resulted in lower yield (entry 4). The substrate **2e**, wherein the ethyl ester group (−COOEt) bears on carbamate nitrogen, was found to be a good substrate for this amino allylation reaction, which gave **3e** in 91% isolated yield (entry 5). However, the benzyl ester group (−COOBn) resulted in lower yield as can be judged from the entry 6.

Next, we investigated the scope of the reaction with respect to various activated olefins. The results are summarized in Table 2. The treatment of the olefin **1a** with 1 equiv of the carbamate **2g** in the presence of 5 mol % of $Pd(PPh_3)_4$ in THF at room temperature gave the amino allylation product **3g** in 80% yield (entry 1). The reaction of the activated olefin **1b**, which has a methoxy group at the para position of the aromatic ring, with **2e** under the standard conditions gave the desired product **3h**

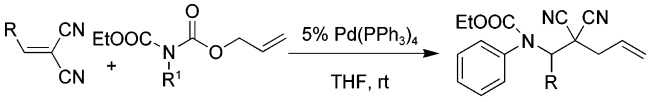
TABLE 1. Effect of Protecting Groups[a]



entry	R^1	product (**3**)	yield (%)[b]
1	**2a** H	**3a**	0
2	**2b** CH_3	**3b**	0
3	**2c** $COCH_3$	**3c**	87
4	**2d** $COCF_3$	**3d**	65[c]
5	**2e** COOEt	**3e**	94 (91)[d]
6	**2f** COOBn	**3f**	52[c]

[a] **2** was added to a solution of **1a** and 5% $Pd(PPh_3)_4$ in THF, and the mixture was stirred at room temperature for 12 h. [b] Yields were determined by ^1H NMR spectroscopy with dibromomethane as an internal standard. [c] The starting material was recovered in around 30% yield. [d] Isolated yield is shown in parentheses.

TABLE 2. Reactions of Various Activated Olefins with 2[a]



entry	1	2	product (**3**)	yield (%)[b]
1	**1a** R = Ph	**2g** R^1 = Cy	**3g**	80
2	**1b** *p*-OMe-C_6H_4	**2e** R^1 = Ph	**3h**	93
3	**1c** 2-furyl	**2e** R^1 = Ph	**3i**	86
4	**1d** OEt	**2e** R^1 = Ph	**3j**	88
5	**1e** ^{n}Bu	**2e** R^1 = Ph	**3k**	44
6	**1f** ^{i}Pr	**2e** R^1 = Ph	**3l**	80
7	**1g** ^{t}Bu	**2e** R^1 = Ph	**3m**	46

[a] **2** was added to a solution of **1** and 5% $Pd(PPh_3)_4$ in THF, and the mixture was stirred at room temperature for 12 h. [b] Isolated yields.

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(8) The palladium-catalyzed intramolecular Michael addition of the ketone enolates generated by the decarboxylation of allyl β-keto carboxylates is known; see: Nokami, J.; Watanabe, H.; Mandai, T.; Kawada, M.; Tsuji, J. *Tetrahedron Lett*. **1989**, *30*, 4829−4832.

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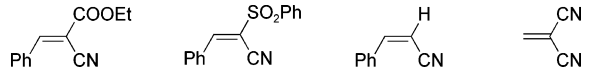


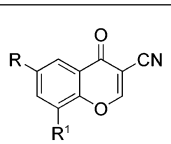
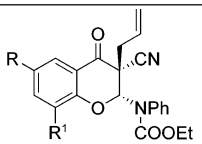
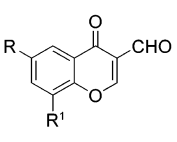
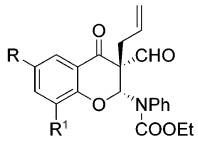
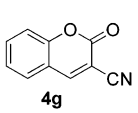
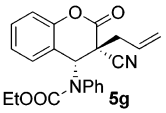
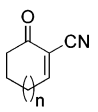
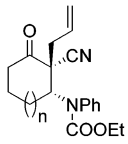
FIGURE 1. Structures of unreactive olefins.

in 93% yield (entry 2). The olefin **1c**, derived from 2-furaldehyde, also gave the desired product **3i** in 86% yield (entry 3). The ethoxy-substituted olefin **1d** also reacted well, giving the corresponding amino allylation product **3j** in 88% yield (entry 4). When the olefin **1e** was used, the corresponding allylated product **3k** was obtained in 44% yield (entry 5). The reaction of isopropyl- and *tert*-butyl-substituted olefins **1f** and **1g** proceeded well to give the corresponding products **3l** and **3m** in 80 and 46% yields, respectively (entries 6 and 7). It should be noted that, similar to our previous reports, the present reaction worked well only for the highly activated olefins containing two electron-withdrawing groups, such as nitrile. The other olefins shown in Figure 1 did not give any desired products under the standard conditions.[11]

It is clear that the scope and synthetic utility of this newly born process would be enhanced dramatically if the two contiguous stereocenters, quaternary carbon adjacent to secondary amine carbon center, could be generated. We envisioned that the 2-cyano enones **4** might be the ideal precursor to achieve this goal because the olefins' moiety is doubly activated by two electron-withdrawing groups, such as −CN and carbonyl. Indeed, the hypothesis proved realistic, and under simple standard experimental conditions, a wide range of substrates underwent smooth β-amino-α-allylation. The results are summarized in Table 2. The reactions of 3-cyanochromones **4a**−**d** with **2e** proceeded smoothly to give the corresponding products in high yields (entries 1−4). The reaction of 3-formylchromones **4e** and **4f** with **2e** also gave the desired products **5e** and **5f** in 72 and 90% yields, respectively (entries 5 and 6). 3-Cyanocoumarin **4g** was also found to be a good substrate for the reaction (entry 7). Not only chromones and coumarins but also the six-membered 2-cyano enone **4h** reacted well, giving the corresponding amino allylation product **5h** in 85% yield (entry 8). However, in the case of **4i**, decomposition was noticed (entry 9). It should be noted that the substrates bearing iodo substituents in the aromatic ring were not tolerated under the present reaction conditions presumably due to the oxidative insertion of Pd(0) to the aryl−iodide bond.

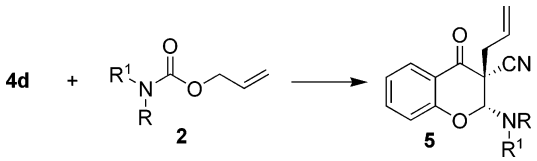
We next examined the scope of the reaction with respect to carbamates, and the results are summarized in Table 4. The cyclohexyl- and methyl-substituted carbamates **2g** and **2h** reacted smoothly with **4d** giving the corresponding products **5j** and **5k** in 93 and 84% yields, respectively (entries 1 and 2). However, in the case of the aryl-substituted carbamates **2i** and **2j**, having electron-donating groups, such as $-CH_3$ and $-OCH_3$, an excess amount of the carbamates was needed in order to obtain high yields of the desired products (entries 3 and 4). When 1 equiv of the carbamates was used, the yields of the desired products were low due to the formation of *N*-allyl carbamate as a side product. Due to the presence of the electron-donating substituent at the para position, the presumed oxazabis-π-allylpalladium complex may become unstable and immediately undergo a reductive elimination[12] reaction to give the *N*-allyl derivative. An acryloyl group on nitrogen also works equally, giving the product **5n** in 75% yield (entry 5).

TABLE 3. Reactions of 2e with Various Enones 4[a]

entry	enone (**4**)	product (**5**)	yield(%)[b]
			
1	**4a** R = Me, R^1 = H	**5a** R = Me, R^1 = H	84
2	**4b** R = Br, R^1 = H	**5b** R = Br, R^1 = H	96
3	**4c** R = R^1 = Cl	**5c** R = R^1 = Cl	78
4	**4d** R = R^1 = H	**5d** R = R^1 = H	80
			
5	**4e** R = R^1 = H	**5e** R = R^1 = H	72
6	**4f** R = F, R^1 = NO_2	**5f** R = F, R^1 = NO_2	90
7	 **4g**	 **5g**	79
			
8	**4h** n = 1	**5h** n = 1	85
9	**4i** n = 0	**5i** n = 0	0[c]

[a] The enones **4** were added to a solution of **2e** and 5% $Pd(PPh_3)_4$ in THF, and the mixture was stirred at room temperature for 12 h. [b] Isolated yield. [c] Decomposition noticed.

TABLE 4. Reactions of 4d with Various Carbamates 2[a]



entry	carbamate (**2**)	product (**5**)	yield[b]
1	R = cyclohexyl, R^1 = COOEt (**2g**)	**5j**	93
2	R = CH_3, R^1 = COOEt (**2h**)	**5k**	84
3	R = *p*-CH_3−C_6H_4, R^1 = COOEt (**2i**)	**5l**	88[c]
4	R = *p*-OCH_3−C_6H_4, R^1 = COOEt (**2j**)	**5m**	84[c]
5	R = Ph, R^1 = COCH=CH_2 (**2k**)	**5n**	75

[a] The carbamates **2** were added to a solution of **4d** and 5% $Pd(PPh_3)_4$ in THF, and the mixture was stirred at room temperature for 12 h. [b] Isolated yields. [c] 1.5 equiv of carbamate was used.

(11) As shown in Figure 1, when other activated olefins were used, the desired products were not obtained and the starting olefins were recovered quantitatively. Accordingly, a CN group in two electron-withdrawing groups is required to accomplish the present reaction. Complete coplanarity of two esters/SO_2Ph is difficult due to the steric repulsion of electron-withdrawing groups, although the small and linear cyano group leads to much less disruption than does the ester overlap. This phenomenon is in accord with Boeckman's and our previous results; see: (a) Boeckmann, R. K.; Ko, S. S. *J. Am. Chem. Soc.* **1982**, *104*, 1033. (b) Ref 7. It was believed that in the case of cyclic enones coplanarity is maintained, and that may be the reason for their high reactivity.

(12) Nakamura, H.; Bao, M.; Yamamoto, Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 3208−3210.

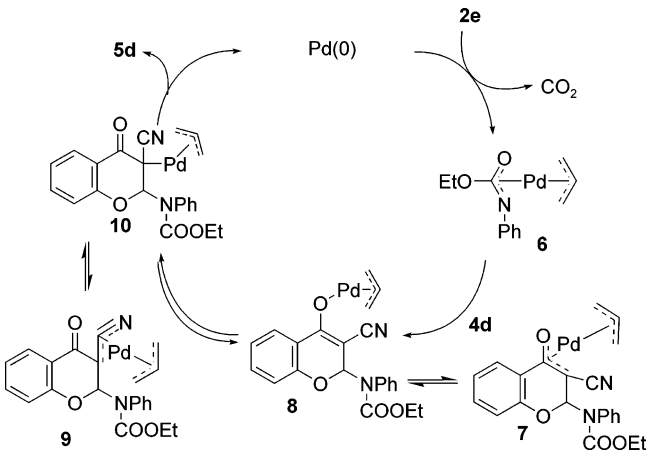


FIGURE 2. A plausible mechanism.

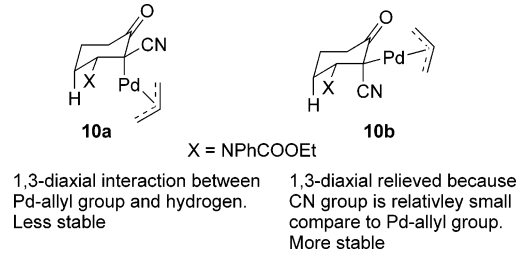


FIGURE 3. A proposed transition state for the formation of a single diastereomer.

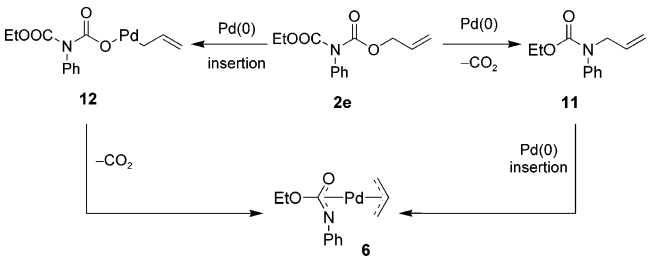
Fortunately, **5n** was obtained as a white solid, and its structure was unambiguously confirmed by X-ray crystallographic analysis.[13]

A proposed mechanism is shown in Figure 2. Initially, Pd(0) reacts with the carbamate **2e** to give the oxazabis-π-allylpalladium complex **6** with extrusion of CO_2. Then the insertion of the activated olefin **4d** into the complex **6** would form the π-allylpalladium intermediate **8**. This intermediate **8**, with Pd−O bonding, could be in equilibrium with the Pd−C bonded intermediate **10**. The intermediates **8** and **10** should most likely be represented as their bis-π-allylpalladium analogues **7** and **9**, respectively. The reductive elimination of Pd(0) from **10** gives the desired product **5d** with the regeneration of Pd(0).

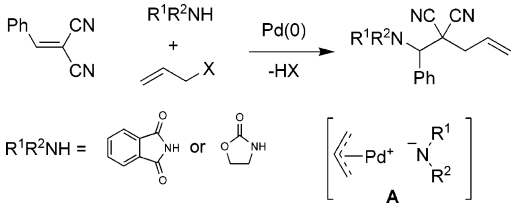
A plausible explanation for the observed diastereoselectivity in the intermolecular aminopalladation is made on the basis of 1,3-diaxial interactions. As depicted in Figure 3, the two transition states **10a** and **10b** are conceivable. In the model **10a**, the π-allylpalladium complex is in an axial position; therefore, it suffers from a severe 1,3-diaxial interaction. On the other hand, such a 1,3-diaxial interaction is not present in the transition state **10b**, as the π-allylpalladium complex is oriented at an equatorial position. There is an equilibrium between **10a** and **10b** through the π-allylpalladium complex **9**. This explains the exclusive formation of only one diastereomer. Another reason for the formation of anti-product can also be explained on the basis of steric interaction between first formed amino group and the Pd−allyl moiety.

To obtain some additional insight into the reaction mechanism, we conducted a few experiments (Scheme 1). There are

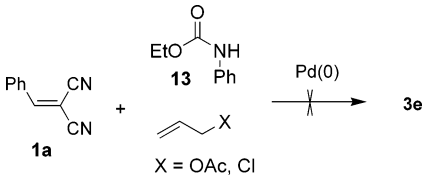
SCHEME 1. Two Possibilities for Production of 6



SCHEME 2



SCHEME 3



two possibilities for the formation of **6**: (i) the decarboxylative C−N bond[2] formation first takes place from **2e** to produce **11,** which after ionization of the N−C_{allyl} bond under the palladium catalysis generates the intermediate **6**; (ii) Pd(0) insertion into the O−C_{allyl} bond first takes place to form **12**, which immediately liberates CO_2 to give **6**. However, the reaction of **11** with **1a** under the standard conditions did not give **3a**, clearly ruling out the possibility for the pathway through **11**.

We previously reported the palladium-catalyzed three-component coupling reaction of activated olefins with allylic halide and phthalimide (Scheme 2).[7e] The reaction proceeds through the π-allylpalladium complex **A**, generated from amines and allylic substrates with concomitant removal of HX. The Michael addition of the nitrogen nucleophile of the intermediate **A** to the activated olefin followed by allylation gives the amino allylation product. To check the feasibility of this three-component coupling reaction for the present case, we performed the reaction between benzylidenemalononitrile **1a**, the carbamate **12**, and allyl acetate/chloride under the standard conditions (Scheme 3). However, no formation of the product **3e** was detected; the starting material was recovered. This observation indicated that the use of allylic carbamates is the key for the present reaction.

Summary

In conclusion, we have developed a new palladium-catalyzed highly stereoselective tandem α-allylation β-amination of enones via a decarboxylative aza-Michael addition−allylation cascade. This is the first example of excellent face selectivity of the palladium enolates in generating contiguous quaternary and tertiary carbon centers at the α- and β-position of enones, respectively. Due to the versatility of the cyano group, allowing for easy elaboration of the product, we believe that this process is expected to have broad synthetic utility.[14] It is noteworthy

(13) Efforts to determine the stereochemistry of **5n** were undertaken using nOe experiment. However, no satisfactory results could be obtained. For X-ray crystallographic analysis data, see Supporting Information.

that the process does not need any additives or bases and can be carried out at extremely mild conditions.[15] It is most probable that the oxazabis-π-allylpalladium complex is an intermediate for the present reaction. As the key for generating the oxazabis-π-allylpalladium complex in the presence of a −COR group on amines, we think that, similar to allylic carbonates, allylic carbamates also find extensive use in organic synthesis.

(14) Apart from the ability of the cyano group to undergo various structural manipulation depending on the reagents used, it can be used for various reactions; see: Liu, H.-J.; Zhu, J.-L.; Shia, K.-S. *Tetrahedron Lett*. **1998**, *39*, 4183−4186.

(15) Since the carbamates are weak nucleophiles, Michael addition of them to enones generally needs the use of promoters; see: (a) Xu, L.-W.; Xia, C.-G.; Hu, X.-X. *Chem. Commun*. **2003**, 2570−2571. (b) Gaunt, M. J.; Spencer, J. B. *Org. Lett*. **2001**, *3*, 25−28. (c) Wabnitz, T. C.; Spencer, J. B. *Tetrahedron Lett*. **2002**, *43*, 3891−3894. (d) Wabnitz, T. C.; Yu, J. Q.; Spencer, J. B. *Synlett* **2003**, 1070−1072. (e) Wabnitz, T. C.; Spencer, J. B. *Org. Lett*. **2003**, *5*, 2141−2144. (f) Kobayashi, S.; Kakumoto, K.; Sugiura, M. *Org. Lett*. **2002**, *4*, 1319−1322. (g) Xu, L.-W.; Xia, C.-G. *Tetrahedron Lett*. **2004**, *45*, 4507−4510.

Experimental Section

General Procedure for the Amino Allylation of Activated Olefins. To a 5 mL screw-capped vial equipped with a magnetic stirring bar were added the chromone **4a** (37.0 mg, 0.2 mmol), carbamate **2e** (49.8 mg, 0.2 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), and THF (4 mL). After the mixture was stirred for 12 h at room temperature, TLC was taken in order to confirm whole disappearance of the starting materials. The solvent was removed under reduced pressure, and the residue was purified by a short silica gel column with eluent (hexane:ethyl acetate, 9:1) to give **5a** (65.5 mg) in 84% yield.

Supporting Information Available: Experimental details, characterization data, including X-ray analysis, ^{1}H NMR spectra of newly synthesized compounds (27 pages), as well as a crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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