Tetrahedron Letters, Vol. 34, No. 47, pp. 7611-7614, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Pd^{2+}-catalyzed Oxidative Aminocarbonylation of *O*-2,3-Butadienyl and *O*-3,4-Pentadienyl *N*-Tosylcarbamates

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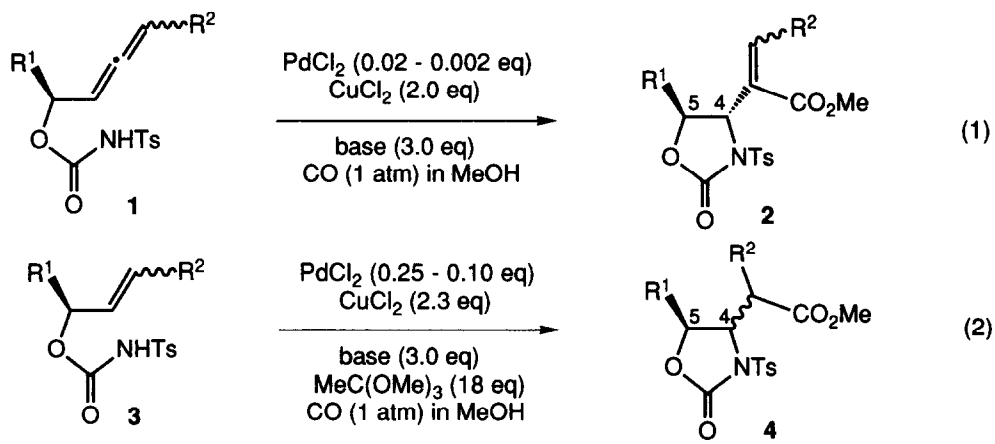
Abstract: Pd^{2+}-catalyzed aminocarbonylation of *O*-2,3-butadienyl **1** and *O*-3,4-pentadienyl carbamates **5** stereoselectively provides 4-(1-methoxycarbonylvinyl)-1,3-oxazolidin-2-ones **2** and 4-(1-methoxycarbonylvinyl)-1,3-oxazin-2-ones **6**, respectively, in high yields.

Recently we have reported that *O*-allyl carbamates **3** undergo a Pd^{2+}-catalyzed aminocarbonylation to provide 1,3-oxazolidin-2-one-4-acetic acids **4** (eq 2)[1] through a different reaction mechanism from those for *N*-4-pentenyl carbamates, forming *N*-alkoxycarbonylpyrrolidine-2-acetic acids, and the corresponding urea derivatives.[2] The reaction is useful for the preparation of β-amino acids, however, plagued with the low turnover number (4 - 10) of the catalyst and the moderate stereoselectivity. Furthermore, the reaction suffers from the low structural flexibility. For example, neither carbamates with an internal olefins, e.g., **3** (R^1= H, R^2= Me), nor most of the one-carbon higher homologues of **3**, e.g., *O*-3-butenyl *N*-tosylcarbamate, can participate in the aminocarbonylation.



In order to surmount these drawbacks associated with **3**, we focused on the aminocarbonylation of an allenic double bond, since many precedents suggest that allenic double bonds are very reactive toward transition metal-catalyzed aminations.[3]

Indeed, *O*-2,3-butadienyl **1**[4] (eq 1) and its one-carbon higher homologues, *O*-3,4-pentadienyl *N*-tosylcarbamates **5**[5] (eq 3), irrespective of their substitution pattern (R^1-R^3), nicely undergo a Pd^{2+}-catalyzed aminocarbonylation and provide 4-(1-methoxycarbonyl)vinyl substituted 1,3-oxazolidin-2-ones **2** and 1,3-oxazin-2-ones **6**, respectively, in high yields (Tables 1 and 2). The utility of the present reaction may be fur-

ther augmented by the high stereoselectivity, giving *trans*-4,5-disubstituted **2** and **6** exclusively, and also by the high catalytic turn-over number, ranging 50-500.

Table 1. Pd^{2+}-catalyzed Aminocarbonylation of *O*-2,3-Butadienyl *N*-Tosylcarbamates **1**[a]

run	**1**			$PdCl_2$ (equiv)	$CuCl_2$ (equiv)	$ClCH_2CO_2Na$ (equiv)	time (h)	% isolated yield of **2**
		R^1	R^2					
1	**1a**:	H	H	0.02	2.0	3.0	2.5	**2a**: 90
2	**1b**:	Me	H	0.02	2.0	3.0	2.0	**2b**: 88
3	**1c**:	Et	H	0.1	2.3	3.0	2.0	**2c**: 68
4	**1c**:	Et	H[b]	0.1	2.3	3.0	3.0	**2c**: 88
5	**1c**:	Et	H	0.1	2.3	0	9.0	**2c**: 9
6	**1c**:	Et	H	0.02	2.0	3.0	2.0	**2c**: 99
7	**1c**:	Et	H	0.002	2.0	3.0	49	**2c**: 86
8	**1d**:	*n*-Pr	H	0.02	2.0	3.0	2.0	**2d**: 94
9	**1e**:	*t*-Bu	H[b]	0.1	2.3	3.0	2.0	**2e**: 59
10	**1e**:	*t*-Bu	H	0.02	2.0	3.0	2.0	**2e**: 73
11	**1f**:	Ph	H[c]	0.02	2.0	1.0	2.5	**2f**: 59
12	**1g**:	H	Me	0.02	2.0	3.0	2.5	**2g**: 41[d]
13	**1h**:	Me	Me[e]	0.02	2.0	3.0	2.0	**2h**: 65[f]

a) A mixture of **1** (1 mmol), $PdCl_2$, $CuCl_2$, and $ClCH_2CO_2Na$ (all in given amounts) in 8 mL of anhydrous methanol was stirred under CO (1 atm, a balloon) at 30 °C.

b) The reaction contains 18 equiv of methyl orthoacetate.

c) The carbamate **1f** was used as the triethylamine salt. The yield of **2f** refers to an overall yield from the corresponding alcohol.

d) A mixture of *N*-tosyl-(*E*)- and (*Z*)-4-(1-methoxycarbonyl-1-propenyl)oxazolidin-2-ones (**2g**) was obtained in a ratio of 1:1.

e) A diastereomeric mixture of **1h** (1:0.9) was used.

f) A mixture of *N*-tosyl-(*E*)-5-methyl-4-[(*Z*)-1-methoxycarbonyl-1-propenyl]- and *N*-tosyl-(*E*)-5-methyl-4-[(*E*)-1-methoxycarbonyl-1-propenyl]oxazolidin-2-ones (**2h**) was obtained in a ratio of 1:0.7.

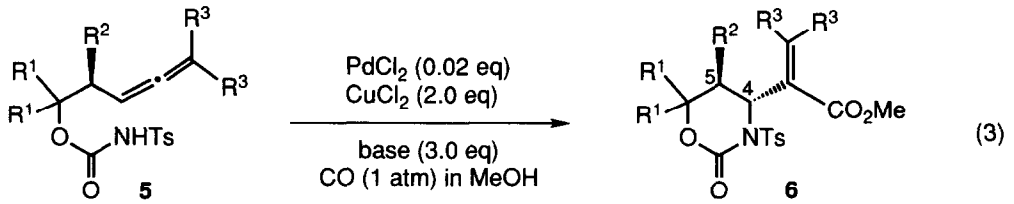
The reaction of **1** was thoroughly examined using **1c** as a representative (runs 3-7, Table 1). Like the reaction of **3** (eq 2),[1] the aminocarbonylation of **1c** is only successful under a basic buffer condition. Under a neutral or acidic condition, the cyclization was very slow and **2c** was isolated in a low yield in addition to an intractable mixture of products (run 5). Interestingly, although the conditions optimized for **3** (eq 2) could be successfully applied to **1** (run 4), the better results were obtained by reducing the amount of $PdCl_2$ (run 6). The similar improvement in yields by reduction of the amounts of $PdCl_2$ was generally noted for the other

derivatives of **1** (e.g., runs 9 and 10). The amounts of $PdCl_2$ may be further cut back as small as 0.002 equiv without significantly deteriorating the isolated yields (run 7), however, we mostly applied the reaction condition of run 6 in Table 1 to the other derivatives of **1**.

As judged from the reaction times and the isolated yields, the present reaction is insusceptible to the steric bulk of R^1 substituents, ranging widely from H to *t*-Bu. The moderate yield of **2f** (run 11) may primarily be attributed to instability of **1f**.[6] The carbamate **1f**, however, turned out rather stable as the triethylamine salt and this salt was subjected to the aminocarbonylation.

Making sharp contrast to **3** (eq 2),[1] **1** undergo cyclization highly stereoselectively. Only the *trans*-4,5 disubstituted isomers of **2b-f** were detected from the ^1H NMR spectra (400 MHz) of their crude samples. On the other hand, the reaction was non-stereoselective with respect to the olefin geometry and furnished **2g** and **2h** as mixtures of olefinic geometric isomers (runs 12-13).[7]

To our pleasing surprise, the aminocarbonylation of *O*-3,4-pentadienyl carbamates **5** (eq 3, Table 2) proceeded smoothly without any difficulties associated with the cyclization of *O*-3-butenyl carbamates (*vide supra*).[1] As apparent from runs 1-3 (Table 2), the kind of the bases enormously affects the yields. Sodium acetate turned out best among the other bases examined (e.g., sodium chloroacetate, sodium benzoate). Here again the stereoselectivity is very high, providing *trans*-**6b** as a single diastereomer (run 4).



(3)

Table 2. Pd^{2+}-catalyzed Aminocarbonylation of *O*-3,4-Pentadienyl *N*-Tosylcarbamates **5**[a]

run	**5**	R^1	R^2	R^3	base	time (h)	% isolated yield of **6**
1	**5a**:	H	H	H	$ClCH_2CO_2Na$	5.0	**6a**: 53
2	**5a**:	H	H	H[b]	$ClCH_2CO_2Na$	5.0	**6a**: 48
3	**5a**:	H	H	H	CH_3CO_2Na	3.0	**6a**: 90
4	**5b**:	H	Me	H	CH_3CO_2Na	4.0	**6b**: 45[c]
5	**5c**:	Me	H	H	CH_3CO_2Na	0.5	**6c**: 77
6	**5c**:	Me	H	H[b]	CH_3CO_2Na	2.0	**6c**: 72
7	**5d**:	Me	H	Me	CH_3CO_2Na	7.0	**6d**: 73

a) A mixture of **5** (1 mmol), $PdCl_2$ (0.02 mmol), $CuCl_2$ (2.0 mmol), and a given base (3 mmol) in 8 mL of anhydrous methanol was stirred under CO (1 atm, a balloon) at room temperature.

b) The reaction contains 18 equiv of methyl orthoacetate.

c) Only (*E*)-*N*-tosyl-4-(1-methoxycarbonylvinyl)-5-methyl-1,3-oxazin-2-one (**6b**) was obtained.

Methyl orthoacetate, being essential for the aminocarbonylation of **3** (eq 2),[1] is not necessarily required for the cyclization of **1** and **5** [cf. runs 3 and 4, 9 and 10 (Table 1), 1 and 2, and 5 and 6 (Table 2)].

The reactions in Tables 1 and 2 were undertaken according to the similar procedure as follows (run 3, Table 2): a flask containing **5a** (281 mg, 1 mmol), $PdCl_2$ (3.5 mg, 0.02 mmol), $CuCl_2$ (269 mg, 2 mmol), CH_3CO_2Na (246 mg, 3 mmol), and a stirring bar was purged with CO (a balloon) and into this was added anhydrous methanol (8 mL, distilled from $Mg(OMe)_2$) via a syringe. A homogeneous deep green solution was stirred at room temperature for 3 h, during which a white solid precipitated. The reaction was monitored with TLC (Merck Kieselgel $60F_{254}$; R_f = 0.66 and 0.51 for **5a** and **6a**, respectively, with benzene/ethyl acetate = 4:1 vol.). The reaction mixture was diluted with ethyl acetate (30 mL) and washed with 1:1 mixture of 10%-$NH_4^+ OH^-$ and 10%-$NH_4^+ Cl^-$ twice and then with water. The organic layer was dried ($MgSO_4$) and concentrated to give a faint-yellow oil, which was purified by column chromatography (silica gel 60, benzene/ethyl acetate = 16:1 vol.) to give **6a** (306 mg, 90% yield) as a white solid: mp 118.2-118.6 °C (dichloromethane-hexane). IR (KBr disk) 1725 (s), 1345 (s), 1270 (s), 1160 (s), 1135 (s), 1085 (s) cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz) δ 2.17 (dq, *J* = 15.8, 3.1 Hz, 1 H), 2.28 (ddt, *J* = 15.8, 11.4, 5.5 Hz, 1 H), 2.43 (s, 3 H), 3.80 (s, 3 H), 4.21 (dt, *J* = 3.1, 11.4 Hz, 1 H), 4.25 (m, 1 H), 5.61 (br. s, 1 H), 5.83 (d, *J* = 0.7 Hz, 1 H), 6.95 (s, 1 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.90 (d, *J* = 8.4 Hz, 2 H). Anal. Calcd for $C_{15}H_{17}NO_6S$: C, 53.09; H, 5.05; N, 4.13; S, 9.45. Found: C, 52.85; H, 4.98; N, 4.19; S, 9.42.

Acknowledgment: We thank Mr. Y. Ohhama, NMR Facility, for his splendid assistance. Support from the Ministry of Education, Science and Culture, Japanese Government is gratefully acknowledged.

References and Notes

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4) For the preparation of 2,3-butadienyl alcohols, see: a) J. S. Cowie, P. D. Landor, S. R. Landor, *J. Chem. Soc. Perkin I*, **1973**, 720-724. b) J. A. Marshall, X. Wang, *J. Org. Chem.* **1991**, *56*, 960-969.

5) For the preparation of 3,4-pentadienyl alcohols, see: J. K. Crandall, G. L. Tindall, *J. Chem. Soc. Chem. Commun.* **1970**, 1411-1412.

6) R. W. Friesen, A. E. Kolaczewska, N. Khazanovich, *Tetrahedron Lett.* **1992**, *33*, 6715-6718.

7) The stereochemical outcome of the present reaction makes sharp contrast to that observed for the Ag^+-catalyzed amination of **1**, being *E*-selective with regard to olefin geometry and non-stereoselective with respect to the C_4 and C_5 substituents.[3b] A mechanistic rationale for these results will be reported in due course.

(Received in Japan 1 July 1993; accepted 16 August 1993)