7122 *J. Am. Chem. Soc.* **2000,** *122,* 7122−7123

Highly Regio- and Stereoselective Acylboration of Allenes Catalyzed by Palladium Complexes: An Efficient Route to a New Class of 2-Acylallylboronates

Feng-Yu Yang, Ming-Yuan Wu, and Chien-Hong Cheng*

Department of Chemistry
National Tsing Hua University
Hsinchu, Taiwan, 30043

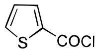
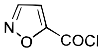
Received March 28, 2000

Construction of chemical bonds via addition of an electrophile and a nucleophile to an unsaturated carbon−carbon bond is an ideal method in organic synthesis.[1] However, it is extremely difficult to achieve this three-component assembling by the classical synthetic route due to the facile direct coupling of the electrophile and nucleophile. With the assistance of palladium complexes, allenes are capable of undergoing this type of addition.[2] Several types of electrophiles[3] including aryl and vinyl halides and nucleophiles[4] such as amines, alkoxides, and stable carbon anions are known in this palladium-catalyzed addition to allenes, but low stereo- and regioselectivity were encountered in most cases[4] and no report using acyl halides as the electrophiles was found.

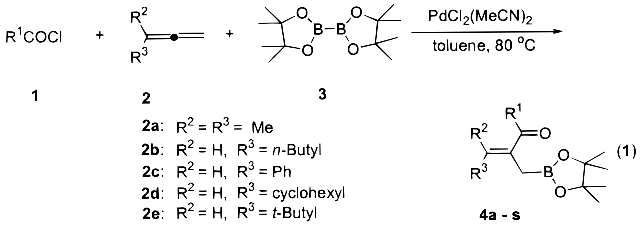
Our continuous interest in the metal-mediated three-component assembling reaction[2] led us to explore the reaction of acyl chlorides, allenes, and diborons. In this paper, we report for the first time a palladium-catalyzed addition of acyl and boryl groups to allenes to give a new class of substituted allylboronates with high regioselectivity and *E* stereoselectivity. In addition, a mechanism accounting for the origin of *E* stereochemistry is proposed. Allylboronates are highly important synthetic reagents used in the Suzuki reaction[5] and regioselective allylic coupling with aldehydes,[6] but they are relatively difficult to prepare. The present catalytic reaction provides a convenient synthetic method for a wide range of allylboronates from easily available materials.

The results of the three-component assembling reaction of acyl chlorides **1**, allenes **2**, and diboron **3** are listed in Table 1 and eq 1. Treatment of 1,1-dimethylallene (**2a**) with *p*-toluoyl chloride and **3** in the presence of Pd(MeCN)$_2$Cl$_2$ in toluene at 80 °C gave 2-acylallylboronate **4a** in good yield (entry 1). This palladium-catalyzed reaction is believed to proceed via the well-established steps: oxidative addition of toluoyl chloride to Pd(0) species,[7,8] insertion of the allene into the Pd−acyl bond,[9] and borylation of the resulting allyl species with **3**.[10,11] The aroyl and boryl groups are added to the middle and to the unsubstituted terminal carbons, respectively, of the allene moiety. No other regioisomer in the reaction mixture was detected, indicating that the catalytic reaction is completely regioselective. The presence of a carbonyl group in **4a** is evidenced by the observation of a resonance at 201.2 ppm in the ^{13}C NMR spectrum and a strong absorption at 1655 cm^{-1} (conjugated ketone) in the IR spectrum.

Table 1. Palladium-Catalyzed Assembling of Acyl Chlorides, Diboron **3**, and Allenes[a]

entry	R^{1}COCl	allene	product	*E*/*Z*	yield (%)[b,c]
1	*p*-MeC$_6$H$_4$COCl	**2a**	**4a**		72 (82)
2	C$_6$H$_5$COCl	**2a**	**4b**		68 (74)
3	C$_6$H$_5$COBr	**2a**	**4b**		67 (74)
4	*p*-MeO$_2$CC$_6$H$_4$COCl	**2a**	**4c**		67 (81)
5	*p*-NO$_2$C$_6$H$_4$COCl	**2a**	**4d**		77 (88)
6	*p*-MeOC$_6$H$_4$COCl	**2a**	**4e**		61 (76)
7	*m*-MeOC$_6$H$_4$COCl	**2a**	**4f**		75 (85)
8	*o*-MeOC$_6$H$_4$COCl	**2a**	**4g**		57 (72)
9	1-C$_{10}$H$_7$COCl	**2a**	**4h**		92 (99)
10		**2a**	**4i**		71 (85)
11		**2a**	**4j**		62 (83)
12	*t*-BuCH$_2$COCl	**2a**	**4k**		80 (88)
13	*i*-PrCH$_2$COCl	**2a**	**4l**		63
14	C$_6$H$_5$CH$_2$COCl	**2a**	**4m**		57 (72)
15	*t*-BuCH$_2$COCl	**2b**	**4n**	99/1	91
16	*t*-BuCH$_2$COCl	**2c**	**4o**	93/7	77
17	*t*-BuCH$_2$COCl	**2d**	**4p**	93/7	88
18	*p*-MeOC$_6$H$_4$COCl	**2b**	**4q**	98/2	70 (93)
19	1-C$_{10}$H$_7$COCl	**2b**	**4r**	99/1	71 (96)
20	*p*-MeC$_6$H$_4$COCl	**2e**	**4s**	98/2	50 (48)

[a] Reaction conditions: acyl chloride (0.55 mmol), Pd(CH$_3$CN)$_2$Cl$_2$ (0.025 mmol, 5 mol %), **3** (0.50 mmol), allene (1.00 mmol), and toluene (2.0 mL); temperature, 80 °C; reaction time, for aroyl chloride 10 h and for alkanoyl chloride 2 h. [b] Isolated yield. [c] Yields determined by ^{1}H NMR integration method using mesitylene as an internal standard are shown in parentheses.



2a: R^2 = R^3 = Me
2b: R^2 = H, R^3 = *n*-Butyl
2c: R^2 = H, R^3 = Ph
2d: R^2 = H, R^3 = cyclohexyl
2e: R^2 = H, R^3 = *t*-Butyl

There are two intriguing aspects of the present catalytic reaction. First, the acyl group adds to the allene moiety without decarbonylation, in contrast to many transition metal-mediated addition reactions of acid chlorides.[12] For example, Tsuji and co-workers[7] reported that in the palladium-catalyzed carbosilylation of 1,3-dienes by acid chlorides (RCOCl) and disilanes, decarbo-

---

(1) (a) Wang, Z.; Lu, X.; Lei, A.; Zhang, Z. *J. Org. Chem.* **1998**, *63*, 3806−3807. (b) Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991**, *113*, 7778−7780. (c) Ikeda, S. I.; Cui, D. M.; Sato, Y. *J. Am. Chem. Soc*. **1999**, *121*, 4712−4713. (d) Nakamura, H.; Shim, J. G.; Yamamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 8113−8114.

(2) (a) Wu, M. Y.; Yang, F. Y.; Cheng, C. H. *J. Org. Chem.* **1999**, *64*, 2471−2474. (b) Yang, F. Y.; Wu, M. Y.; Cheng, C. H. *Tetrahedron Lett.* **1999**, *40*, 6055−6058.

(3) (a) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: New York, 1980. (b) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994.

(4) (a) Larock, R. C.; Tu, C.; Pace, P. *J. Org. Chem.* **1998**, *63*, 6859−6866. (b) Larock, R. C.; He, Y.; Leng, W. W.; Han, X.; refvik, M. D.; Zenner, J. M. *J. Org. Chem.* **1998**, *63*, 2154−2160. (c) Ma, S.; Negishi, E. I. *J. Am. Chem. Soc.* **1995**, *117*, 6345−6357. (d) Gamex, P.; Ariente, C.; Gore, J.; Cazes, B. *Tetrahedron* **1998**, *54*, 14825−14834. (e) Al-Masum, M.; Yamamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 3809−3810. (f) Jonasson, C. Backvall, J. E. *Tetrahedron Lett.* **1998**, *39*, 3601−3604.

(5) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483.

(6) (a) Vaultier, M.; Carboni, B.*Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: Oxford, 1995; Vol. 11, p 191−276. (b) Roush, W. R.; Grover, P. T. *J. Org. Chem.* **1995**, *60*, 3806−3813. (c) Brown, H. C.; Ramachandran, P. V. *Pure Appl. Chem.* **1991**, *63*, 307−316.

(7) (a) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc*. **1993**, *115*, 10414−10415. (b) Obara, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc*. **1995**, *115*, 9814−9821.

(8) Yamamoto, K.; Hayashi, A.; Suzuki, S.; Tsuji, J.*Organometallics* **1987**, *6*, 974−979.

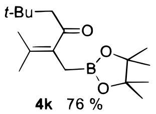
(9) (a) Grigg, R.; Brown, S.; Sridharan, V.; Uttley, M. D. *Tetrahedron Lett.* **1997**, *38*, 5031−5034. (b) Okuro, K.; Alper, H. *J. Org. Chem.* **1997**, *62*, 1566−1567.

(10) (a) Ishiyama, T.; Itoh, Y.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1997**, *38*, 3447−3450. (b) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508−7510.

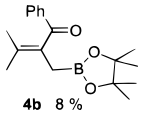
(11) (a) Ahiko, T. A.; Ishiyama, T.; Miyaura, N. *Chem. Lett*. **1997**, 811−812. (b) Ishiyama, T.; Ahiko, T.; Miyaura, N. *Tetrahedron Lett.* **1996**, *37*, 6889−6892.

10.1021/ja001082u CCC: $19.00 © 2000 American Chemical Society
Published on Web 07/08/2000

Chart 1



4k 76 %



4b 8 %

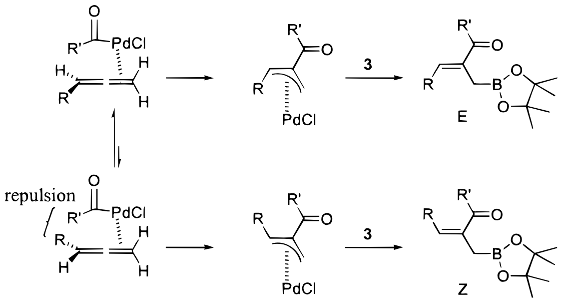
nylation occurs prior to insertion of 1,3-dienes into the RCO−Pd bond. Second, in contrast to most transmetalation processes of diborons,[10] borylation in the present catalytic reaction occurs smoothly without the assistance of a base.

Under similar reaction conditions, other aroyl chlorides, where R = p-MeOC$_6$H$_4$, p-NO$_2$C$_6$H$_4$, C$_6$H$_5$, p-MeO$_2$CC$_6$H$_4$, 1-naphthyl, and heterocyclic carbonyl chlorides (R = 2-thienyl and 5-isoxazolyl), also undergo three-component assembling with **2a** and **3** to afford the corresponding 2-acylallylboronates (Table 1) in good to excellent yields (entries 2−11). The substituent on the aryl group shows little effect on the product yield. Aroyl chlorides with either an electron-withdrawing or -donating substituent at the ortho, meta, or para position of the aryl group all react smoothly to afford the products in high yields (entries 6−8). Again, no corresponding decarbonylative products were observed in these reactions.

Several alkanoyl chlorides (R = t-BuCH$_2$, i-Bu, Bn) were tested for the reaction with **2a** and **3**. All these reactions proceed efficiently to give the corresponding allylboronates. Surprisingly, alkanoyl chlorides react much faster than aroyl chlorides under similar reaction conditions. The reaction time required for completion is 1−2 h for alkanoyl chlorides and about 10 h for aroyl chlorides. The reactivity difference is further demonstrated by an interesting competition between *tert*-butylacetyl chloride and benzoyl chloride for allene **2a**. When the same amounts of these two acid chlorides were treated with **2a** and **3** in toluene in the presence of Pd(MeCN)$_2$Cl$_2$ for 10 h (60 °C), the yields of allylboronate **4k** and **4b** were 76 and 8%, respectively (Chart 1). The exact reason for the reactivity difference is not clear. A possibility is that the insertion of allene into the Pd−COR bond is slower for benzoyl chloride than for *tert*-butylacetyl chloride.[7] Further studies to unravel the detailed mechanistic pathways are underway.

Monosubstituted allenes RCHCCH$_2$ (R = n-Bu, **2b**; Ph, **2c**; cyclohexyl, **2d,** *tert*-butyl, **2e)** also react with acyl chlorides and **3** to give the corresponding allylboronates in good to excellent yields. These monosubstituted allenes are in general more reactive than disubstituted allene **2a** and show extremely high stereoselectivity and regioselectivity. The *E* isomer was observed as the major product for each reaction (entries 15−20, Table 1). The stereochemistry of these products was determined using the typical ^{1}H NMR NOE technique. Under similar conditions, the reaction of **1**, **3**, and 1,3-substituted allenes PhCHCCHMe or Me$_2$CCCMe$_2$ is extremely slow, and no desired product was observed.

Scheme 1



The formation of *E* isomers from monosubstituted allenes is remarkable in view of the fact that most carbopalladation reactions of monosubstituted allenes reported gave *E* and *Z* isomeric products with low selectivity.[4] To account for the present stereoselectivity, a mechanism based on face-selective coordination of allenes to the palladium center is proposed. The terminal double bond of allene is bonded to the palladium moiety at the face opposite to the substituents R favorably to avoid steric congestion (Scheme 1). Coordination of the terminal double bond at the other face or of internal double bond to the palladium center will lead to a great increase of steric repulsion and is unlikely. As shown in Scheme 1, the face-selective coordination results in a π-allylpalladium species with the R group anti to the acyl moiety. Further reaction with **3** affords allylboronate with *E* stereochemistry. Clearly, the latter step is faster than the syn−anti rearrangement of the π-allylpalladium species to obtain high *E* selectivity.

We have successfully developed a method for the preparation of a new class of organic compounds, 2-acylallylboronates, from allenes, acid chlorides, and a diboron. It is the first time that acyl chlorides are used in the addition reaction of allenes. No decarbonylation of the acyl group occurs in the addition to allenes, and no base is required for this three-component assembling. The reaction shows excellent *E* stereoselectivity for mono-substituted allenes and is explained in terms of face-selective coordination of mono-substituted allenes to the palladium center.

Acknowledgment. We thank the National Science Council of Republic of China for support of this research.

Supporting Information Available: Preparation details, characterization data, and ^{1}H NMR spectra of **4a**−**4s** and NOE experimental data of **4n**−**4s** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001082U

---

(12) (a) Ohno, K.; Tsuji, J. *J. Am. Chem. Soc.* **1968**, *90*, 99−107. (b) Lau, K. S. Y.; Becker, Y.; Huang, F.; Baenziger, N.; Still, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 5664−5672. (c) Krafft, T. E.; Rich, J. D.; McDermott, P. J. *J. Org. Chem.* **1990**, *55*, 5430−5432. (d) Rich, J. D. *J. Am. Chem. Soc.* **1989**, *111*, 5886−5893.