Pergamon

Tetrahedron Letters 41 (2000) 3627–3629

TETRAHEDRON
LETTERS

Et_3B–Pd-promoted allylation of benzaldehyde with allylic alcohols

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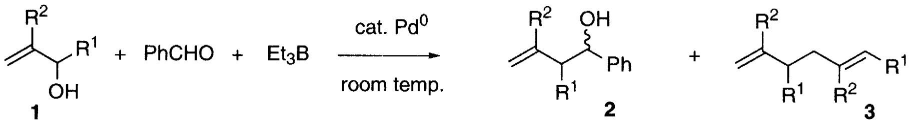
Received 15 February 2000; revised 9 March 2000; accepted 10 March 2000

Abstract

In the presence of $Pd(OAc)_2$ (0.05 equiv.) and PPh_3 (0.1 equiv.), triethylborane promotes a variety of allyl alcohols to undergo allylation of benzaldehyde to provide homoallyl alcohols in good yield. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: aldehydes; allylation; boron and compounds; palladium and compounds.

Nucleophilic allylation of carbonyl compounds with allyl metal reagents is among the most useful methods for the construction of desired molecules and has been studied extensively.[1] Most of the allyl metals have been prepared from allylic halides, acetates, carbonates, or ethers, which are in turn derived from allylic alcohols. Therefore, if allylic alcohols themselves could be utilized directly as an allylating agent, the synthetic efficiency might be enormously improved. Masuyama et al.[2] achieved for the first time the palladium-catalyzed allylation of carbonyl compounds with allylic alcohols, where $SnCl_2$ reduced a π-allylpalladium intermediate and bestowed it nucleophilic ability (umpolung).



(1)

Here we would like to report that triethylborane is also capable of promoting palladium-catalyzed direct allylation of benzaldehyde with allylic alcohols via the umpolung of π-allylpalladium (Eq. (1)). Thus, when a mixture of allyl alcohol (**1a**, 1 mmol), benzaldehyde (1.2 mmol), $Pd(OAc)_2$ (0.05 mmol), PPh_3 (0.1 mmol), and Et_3B (2.4 mmol, 1 M hexane) in THF was stirred for 28 h at room temperature under N_2, 1-phenyl-3-buten-1-ol (**2a**) was produced in 64% isolated yield (run 1, Table 1). The ratio $PPh_3/Pd(OAc)_2=2$ turned out to be the best; a higher (runs 3 and 4) or a lower ratio (run 2) was

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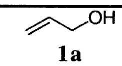
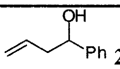
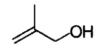
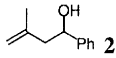
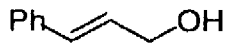
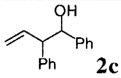
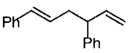
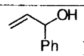
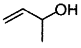
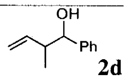
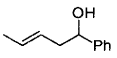
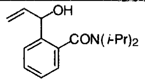
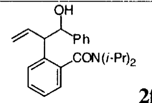
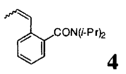
PII: S0040-4039(00)00429-9

less efficient. With this catalytic system, other allylic alcohols (**1b–f**) underwent allylation with similar efficiency (Table 1).

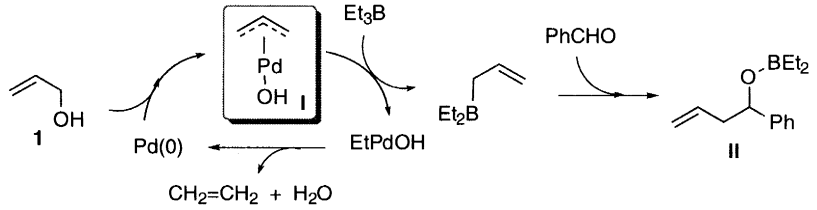
Table 1
Palladium-catalyzed allylation of benzaldehyde with allylic alcohols promoted by triethylborane[a]

run	allylic alcohol **1**	Pd salt	PPh_3 (mmol)	PhOH (mmol)	temp (°C); time (h)	product (% isolated yield)
1	 **1a**	$Pd(OAc)_2$	0.10	0	25; 28	 **2a** (64)
2		$Pd(OAc)_2$	0	0	25; 22	**2a** (0); no reaction
3		$Pd(OAc)_2$	0.15	0	25; 19	**2a** (52)
4		$Pd(OAc)_2$	0.20	0	25; 22	**2a** (17)
5		$PdCl_2$	0.10	0	25; 28	**2a** (0); no reaction
6		*$Pd(OAc)_2$*	*0.10*	*0*	*25; 35*	***2a*** *(73)*[b]
7	 **1b**	$Pd(OAc)_2$	0.10	0	25; 16	 **2b** (69)
8		$Pd(OAc)_2$	0.10	1.0	25; 27	**1b** (78)
9	 **1c**	$Pd(OAc)_2$	0.10	0	25; 15	 **2c** (58)  **3** (18)
10	 **1d**	$Pd(OAc)_2$	0.10	0	25; 7	**2c** (42), **3** (5)
11		*$Pd(OAc)_2$*	*0.10*	*0*	*25; 23*	***2c*** *(81),* ***3*** *(18)*
12	 **1e**	$Pd(OAc)_2$	0.10	0	40; 20	 **2d** (42)  **2e** (14)
13		*$Pd(OAc)_2$*	*0.10*	*0*	*35; 50*	***2d*** *(73)*
14		$Pd(OAc)_2$	0.10	1.0	25; 24	**2d** (64)
15	 **1f**	$Pd(OAc)_2$	0.10	0	25; 21	 **2f** (57)  **4** (27)

a) Reaction conditions: **1** (1.0 mmol), benzaldehyde (1.2 mmol), Et_3B (2.4 mmol, 1M in hexane), Pd(II) salt (0.05 mmol), PPh_3 (indicated amount), with or without phenol (1.0 mmol) in dry THF under N_2. In the runs shown in italics (runs 6, 11, and 13), **1** (2.0 mmol) and benzaldehyde (1.0 mmol) were used under otherwise the same conditions. b) In addition to **2a**, 1-phenyl-2-buten-1-ol was isolated in 8% yield.

In accord with our previous observation of the BEt_3–Pd promoted allylation with allylic benzoates,[3] the chloride ion was detrimental (run 5) and phenol (1 equiv.) significantly helped improve the yield of **2** (runs 8 and 14). Apparently, side reactions, giving rise to 1,5-hexadienes (e.g. **3**, run 9) or alkene (e.g. **4**, run 15), reduced the yield of **2**. Indeed, the use of an excess amount of **1** (2 equiv., relative to aldehyde) brought about a significant improvement of the yield of **2** (runs 6, 11 and 13).

In Scheme 1 is outlined our working hypothesis, which invokes an allyl–ethyl exchange between π-allylpalladium **I** and Et_3B as the key step, producing allylborane and ethylpalladium. Allylborane would readily react with aldehyde to give homoallyl diethylborate **II**,[1b] and ethylpalladium might undergo β-hydrogen elimination thereby regenerating a Pd(0) species. The facile generation of **I**[4] was evidenced by quantitative formation of 5,5-bis(cinnamyl)-2,2-dimethyl-1,3-dioxane-4,6-dione (82% isolated yield) on replacing aldehyde with Meldrum's acid: cinnamyl alcohol (2.2 mmol), Meldrum's acid (1.0 mmol), Et_3B (2.4 mmol), $Pd(OAc)_2$ (0.1 mmol), and PPh_3 (0.2 mmol) in THF at room temperature for 2 h.[5,6]



Scheme 1. A plausible catalytic cycle for allylation of benzaldehyde via umpolung of π-allylpalladium with Et_3B

References

1. (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207; (b) Brown, H. C.; Racherla, U. S.; Pellechia, P. J. *J. Org. Chem.* **1990**, *55*, 1868.
2. Takahara, J. P.; Masuyama, Y.; Kurusu, Y. *J. Am. Chem. Soc.* **1992**, *114*, 2577.
3. Kimura, M.; Kiyama, I.; Tomizawa, T.; Horino, Y.; Tanaka, S.; Tamaru, Y. *Tetrahedron Lett.* **1999**, *40*, 6795.
4. Coordination of Et_3B to the oxygen of allyl alcohol might be responsible for the facile generation of **I**. For palladium-catalyzed α-allylation of diethyl malonate with $Ph_3B^-OCH_2CH{=}CH_2$, see: Stary, I.; Stara, I. G.; Kocovsky, P. *Tetrahedron Lett.* **1993**, *34*, 179.
5. Details of the palladium-catalyzed direct allylation of soft nucleophiles with allyl alcohols will be reported in due course.
6. Financial support from the Ministry of Education, Science, Sports and Culture, Japanese Government, Grant-in-Aid for Scientific Research B, is acknowledged. We also thank Mr. Y. Ohhama (NMR Facility) for his splendid assistance.