Pergamon

Tetrahedron Letters 40 (1999) 6795–6798

TETRAHEDRON
LETTERS

Allylation of aldehydes via Umpolung of π-allylpalladium(II) with triethylborane

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Received 21 May 1999; revised 2 July 1999; accepted 9 July 1999

Abstract

Triethylborane induces allylic substrates (benzoates, phenyl ethers, benzyl ethers, but not halides) to undergo allylation of aldehydes in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0). The reaction proceeds via Umpolung of π-allylpalladium. © 1999 Elsevier Science Ltd. All rights reserved.

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

In previous papers,[1] we have demonstrated that diethylzinc promotes a novel allylation of carbonyl compounds with π-allylpalladium(II) complexes, which are generated in situ from a catalytic amount of a palladium(0) complex and a wide range of allylic substrates. The reaction involves ethyl group transfer from diethylzinc to π-allylpalladium(II) complexes as a key step, whereby the electrophilic nature of π-allylpalladiums is altered into a nucleophilic one (Umpolung).[2] On the other hand, recently, we have uncovered that both diethylzinc and triethylborane induce a variety of conjugated dienes to undergo nickel-catalyzed regio- and stereoselective homoallylation of aldehydes and ketones.[3] Mechanistic considerations suggested to us that the homoallylation was also triggered by ethyl group transfer from these organometallics to π-allylnickel(II) intermediates. The ethyl-π-allylnickel(II) intermediates thus formed, however, in this case, are subjected to β-hydrogen elimination and reductive elimination to finally produce bishomoallyl alcohols and Ni(0) species.

Bearing in mind the idea that triethylborane might be capable of donating an ethyl group even to π-allylpalladium(II) complexes,[4] and hence might induce Umpolung of the complexes, we examined palladium-catalyzed allylation of aldehydes with allylic benzoates in the presence of triethylborane and found that the expected allylation did proceed nicely at room temperature. To the best of our knowledge, this is the first example that demonstrates that triethylborane efficiently promotes Umpolung of π-allylpalladium complexes.[2,4]

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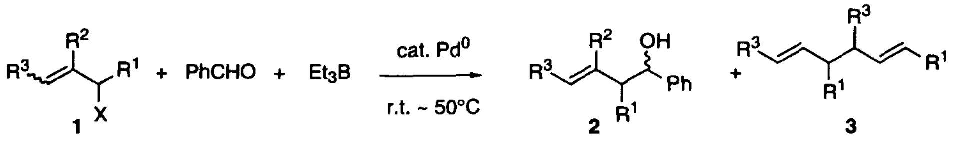
PII: S0040-4039(99)01359-3

Table 1
Palladium-catalyzed allylation of benzaldehyde with allylic substrates **1** (R^1=R^2=R^3=H) bearing various leaving groups (X): formation of homoallyl alcohol **2a** (R^1=R^2=R^3=H)[a]

run	**1** (R^1 = R^2 = R^3 = H)	organometal	reaction conditions	% isolated yield of **2a**
1	X = OCOPh	Et_3B	r.t., 4 h	68
2	X = OCOPh	Bu_3B	r.t., 16 h; 40°C, 4 h	74
3	X = OCOPh	Ph_3B	r.t., 46 h; 40 °C, 5 h	0[b]
4	X = OCOPh	Bu_4Sn	r.t., 12 h	0[c]
5	X = OPh	Et_3B	r.t., 6 h	59
6	X = OCH_2Ph	Et_3B	r.t., 45 h; 50 °C, 17 h	47
7	X = Cl	Et_3B	r.t., 24 h	0[c]
8	X = Br	Et_3B	r.t., 38 h	0[c]

[a] Allylic substrate **1** (1.0 mmol), benzaldehyde (1.1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), oraganometal (2.4 mmol) in 5 mL of dry THF under N_2. [b] Allyl benzoate disappears completely; however **2a** is not formed at all. [c] No reaction takes place and benzaldehyde is recovered.



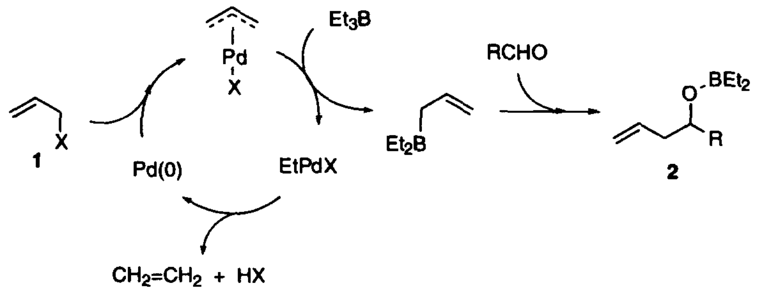
(1)

When a mixture of allyl benzoate (**1a**: R^1=R^2=R^3=H, 1.0 mmol), benzaldehyde (1.1 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.05 mmol) in dry THF (5 mL) was treated with triethylborane (2.4 mmol, 1 M in hexane) at ambient temperature for 4 h, **1a** disappeared completely and homoallyl alcohol **2a** (R^1=R^2=R^3=H) was produced in 68% isolated yield (Eq. 1 and run 1, Table 1). Tributylborane worked similarly and furnished **2a** in a slightly better isolated yield (run 2, Table 1). Triphenylborane, on the other hand, turned out to be useless for the reaction (run 3, Table 1): it consumed allyl benzoate for some unidentified reactions and **2a** was not formed in any detectable amount (TLC monitoring). Tributyltin was ineffective for the reaction and allyl benzoate was completely recovered (run 4, Table 1).

We next examined the scope of the leaving group of allylic substrates. The reactivity of phenyl ether and benzyl ether was in line with our previous observation regarding the reaction with diethylzinc (runs 5 and 6, Table 1);[1] however, to our surprise, neither chloride nor bromide was reactive toward allylation (runs 7 and 8, Table 1). In accord with this, when allyl benzoate was subjected to the reaction in the presence of LiCl (1.0 mmol) under conditions similar to those of run 1 in Table 1, only a negligibly small amount of **2a** was detected by TLC (at room temperature for 17 h).

In Scheme 1 is outlined our working hypothesis for the present palladium-catalyzed allylation reaction, which invokes an allyl–ethyl exchange between π-allylpalladium(II) and Et_3B as a key step. The allylborane thus formed would readily react with aldehydes to give homoallyl alcohols **2**,[5] and ethylpalladium(II) complexes might undergo β-hydrogen elimination thereby regenerating a Pd(0) species. The observations that: (1) there was no reaction with allylic halides; and (2) the reaction was inhibited by LiCl as an additive; suggest that the kind of counter-ions X of π-allylpalladium(II) intermediates are crucial to the allyl–ethyl exchange process.

Allylic benzoates with some typical substitution patterns were examined under the conditions of run 1 in Table 1. Results are summarized in Table 2. As is generally observed, compounds **2** were obtained



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

Table 2
Palladium-catalyzed allylation of benzaldehyde with allylic benzoates **1** and triethylborane[a]

run	allylic benzoate **1** (X = OCOPh)				reaction conditions[b]	% isolated yield of **2** and **3**[c]	
		R^1	R^2	R^3	(additive, if applied)	**2** [*anti*:*syn*]	**3**
1	**1a**:	H	H	H	r.t., 4 h	**2a**: 68	
2	**1b**:	Ph	H	H	r.t., 14 h	**2b**: 77 [2.3:1]	**3b**: 6
3	**1c**:	Me	H	H	r.t., 24 h, + Pd, 40 °C, 2 h	**2c**: 60 [2.2:1]	
4	**1d**:	$PhCH_2CH_2$	H	H	r.t., 5 h, 45 °C, 21 h	**2d**: 76 [1.6:1],	**3d**: 21
5	(*E*)-**1e**:	H	H	Ph	r.t., 18 h, + Pd, r.t., 5 h	**2b**: 74 [2.3:1],	**3b**: 6
6	(*Z*)-**1e**:	H	H	Ph	r.t., 14 h	**2b**: 83 [2.2:1],	**3b**: 0
7	(*E*)-**1f**:	H	H	Me	r.t., 24 h	**2c**: 64 [2.6:1]	
8	**1g**:	H	Me	H	r.t., 9 h, + Pd, 40 °C, 4 h	**2g**: 60	
9	**1g**:	H	Me	H	r.t., 20 h (Et_3N, 1.0 mmol)	**2g**: 63	

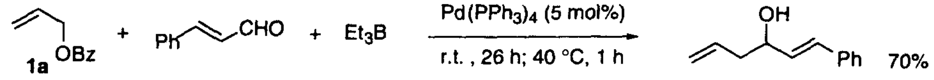
[a] Allylic benzoate **1** (1.0 mmol), benzaldehyde (1.1 mmol), $Pd(PPh_3)_4$ (0.05 mmol), Et_3B (2.4 mmol, 1 M in hexane) in 5 mL of dry THF under N_2. [b] The sign, + Pd, indicates that an additional 0.05 mmol of $Pd(PPh_3)_4$ is applied to complete reaction. [c] Yields based on **1**.

in only moderate to good yields. One main reason for this is the formation of 1,5-hexadienes **3** as side products, which might be formed via homo-coupling of the allylic moieties of π-allylpalladium(II) intermediates. In fact, in run 4, the combined isolated yield of **2d** and **3d** reaches as high as 97% based on **1d**. In runs 1, 3, and 7–9, we must have missed **3** owing to their high volatility. Indeed, when the reaction was undertaken with use of a slight excess of allyl benzoate (**1a**) with respect to benzaldehyde, **2a** was obtained in 98% isolated yield (based on PhCHO), with recovery of **1a** in 10% yield (0.15 mmol); reaction conditions: **1a** (1.5 mmol), PhCHO (1.0 mmol), Et_3B (2.4 mmol), $Pd(PPh_3)_4$ (0.05 mmol) in THF (5 mL) at room temperature for 5 h.

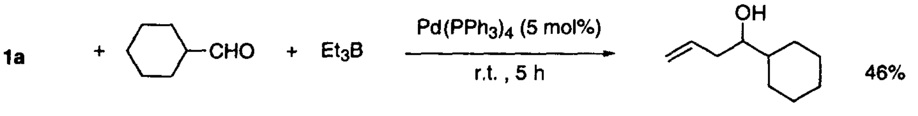
In some instances, it was necessary to use an additional 5 mol% of the catalyst to complete the reaction (runs 3, 5, and 8). For such sluggish reactions, application of 1 equivalent of triethylamine (or 1 equivalent of phenol, with respect to PhCHO) turned out to be very effective (cf. runs 8 and 9, Table 2); with these additives, the reaction was completed at room temperature within a reasonable reaction time without using the additional catalyst.

In Eqs. 2 and 3 are shown examples of reactions of unsaturated and saturated aldehydes, respectively, undertaken under standard conditions.[6] For unsaturated aldehydes, selective 1,2-addition takes place to provide the corresponding homoallyl alcohols in good yields. No 1,4-addition products are detected. For saturated aldehydes, the yields are not satisfactory at this stage of study, and optimization of reaction conditions is a subject to be pursued further.

In conclusion, we have demonstrated for the first time that triethylborane and tributylborane nicely promote the palladium-catalyzed allylation of aldehydes with allylic substrates (benzoates, phenyl ethers, and benzyl ethers, but not chlorides or bromides) via Umpolung of π-allylpalladium intermediates.



(2)



(3)

Acknowledgements

Financial support from the Ministry of Education, Science, Sports and Culture, the Japanese Government, is acknowledged.

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6. Typical reaction procedure (run 1, Table 1): Into an N_2 purged flask containing $Pd(PPh_3)_4$ (0.05 mmol), are added successively THF (5 mL), benzaldehyde (1.1 mmol), allyl benzoate (**1a**, 1.0 mmol), and Et_3B (2.4 mmol, 1 M in hexane) via syringe. The homogeneous mixture is stirred at ambient temperature for 4 h, during which the reaction is monitored by means of TLC. The mixture is subjected to thorough stirring with 2 M HCl (2.5 mL) for 1 h and then 2 M NaOH (5 mL) for 1 h, and extracted with ethyl acetate (2×20 mL). The combined organic extracts are dried ($MgSO_4$) and concentrated in vacuo and the residue is purified by column chromatography over silica gel hexane–ethyl acetate 16/1, v/v) to provide **2a** in 68% yield.