Palladium-Catalyzed Allylic Amination of Allylic Alcohols with Tin(II) Chloride and Triethylamine

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Allylic alcohols caused allylic amination with primary or secondary amines in the presence of a catalytic amount of $Pd(PPh_3)_4$ and a stoichiometric amount of tin(II) chloride in THF at 50 °C to produce the corresponding allylic amines regioselectively.

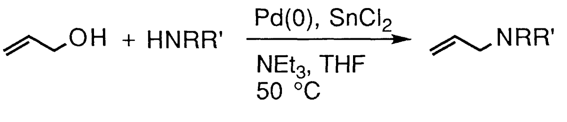
Allylic alcohols are less effective substrates than allylic esters for formation of π-allylpalladium complexes.[1] The direct formation of π-allylpalladium complexes from allylic alcohols is one of the important themes in palladium-catalyzed allylation in terms of saving in resources and energy, because allylic esters are usually prepared from stable and tractable allylic alcohols. We have found that tin(II) chloride probably promotes the formation of π-allylpalladium complex from allylic alcohol in palladium-catalyzed carbonyl allylation.[2] We here report allylic amination via the formation of π-allylpalladium complexes from allylic alcohols with tin(II) chloride.[1a,1f,3]

A palladium-catalyzed allylic amination of 2-propen-1-ol and dibenzylamine was investigated with tin(II) halides under various conditions (Table 1). Using tin(II) chloride and triethylamine in the presence of a catalytic amount of $Pd(PPh_3)_4$ in dry THF at 50 °C under a nitrogen atmosphere led to efficient allylic amination to afford *N,N*-dibenzyl-2-propenylamine in a high yield (Entry 2, eq. 1; R, R'=$PhCH_2$). No reaction proceeded without either palladium catalyst or tin(II) chloride. The reaction without triethylamine exhibited a low yield (entry 5).[4] Catalysts such as $Pd(OAc)_2/4PPh_3$ (Entry 6), $Pd(OAc)_2/2bpy$ (90 h, 46%) and $PdCl_2(PPh_3)_2$ (Entry 8) were also effective for the allylic amination. $Pd(OAc)_2$, $PdCl_2(PhCN)_2$, $Pd(OAc)_2/2dppe$ (Entry 7), and $Pd(OAc)_2/2dppp$ did not so much catalyze the reaction. Tin(II) chloride was more effective than tin(II) bromide (50 °C, 41 h, 48%). No reaction occurred with tin(II) fluoride or tin(II) acetate. The reaction quite slowly proceeded at 25 °C (Entry 1). Higher reaction temperature lowered the yield (Entry 3). Polar DMF is also a good solvent (Entry 9), and nonpolar 1,2-dichloroethane is not so good (Entry 11). A slight amount of water inhibited the reaction.

Table 1. Allylation of dibenzylamine by 2-propen-1-ol[a]

Entry	Catalyst	Solvent	Temp/°C	Yield/%[b]
1	$Pd(PPh_3)_4$	THF	r.t.	24
2	$Pd(PPh_3)_4$	THF	50	78
3	$Pd(PPh_3)_4$	THF	reflux	41
4	$Pd(PPh_3)_4$	THF	50	67[c]
5	$Pd(PPh_3)_4$	THF	50	43[d]
6	$Pd(OAc)_2/4PPh_3$	THF	50	42
7	$Pd(OAc)_2/2dppe$	THF	50	trace
8	$PdCl_2(PPh_3)_2$	THF	50	55
9	$Pd(PPh_3)_4$	DMF	50	83
10	$Pd(PPh_3)_4$	DMI	50	47
11	$Pd(PPh_3)_4$	$ClCH_2CH_2Cl$	50	48

[a] The reaction of 2-propen-1-ol (2 mmol) and dibenzylamine (1 mmol) was carried out with tin(II) chloride (2 mmol) and triethylamine (2 mmol) in the presence of $Pd(PPh_3)_4$ (0.02 mmol) in solvent (4 ml) for 45 h. [b] Isolated yields based on dibenzylamine. [c] 2-Propen-1-ol:dibenzylamine:$SnCl_2$:Et_3N=1:2:1:1. The yield was based on 2-propen-1-ol. [d] The reaction was carried out without Et_3N.



(1)

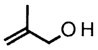
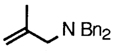
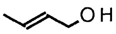
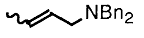
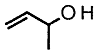
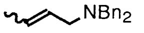
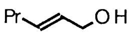
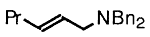
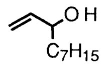
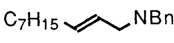
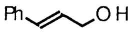
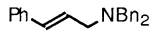
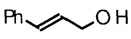
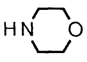
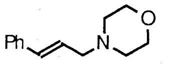
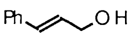
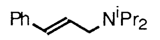
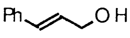
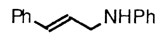
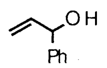
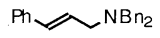
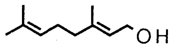
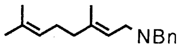
The results of the allylic amination of 2-propen-1-ol and various amines under the same conditions as those of Entry 2 in Table 1 are summarized in Table 2 (eq. 1). Reactivity of aliphatic amines is better than that of aromatic amines. Less nucleophilic amines such as diphenylamine did not react under the same conditions as those of dibenzylamine. The allylic amination with a primary aliphatic amine such as benzylamine only produced diallylated *N,N*-di-2-propenylbenzylamine, even if less than one equimolar amount of 2-propen-1-ol was used to that of benzylamine (Entry

Table 2. Allylic amination of 2-propen-1-ol[a]

Entry	Amine	Time/h	Yield/%[b]
1	*N*-Benzylethylamine	43	46
2	Di-*n*-butylamine	43	69
3	*N*-Methylaniline	43	31
4	1,2,3,4-Tetrahydroquinoline	69	32
5	1,2,3,4-Tetrahydroisoquinoline	71	75
6	Benzylamine	45	73[c]
7	Aniline	47	70[d]

[a] The reaction of 2-propen-1-ol (2 mmol) and amines (1 mmol) was carried out with tin(II) chloride (2 mmol) and triethylamine (2 mmol) in the presence of $Pd(PPh_3)_4$ (0.02 mmol) at 50 °C in THF (4 ml). [b] Isolated yields based on amines. [c] Diallylated product was only obtained. [d] 2-Propen-1-ol:aniline:$SnCl_2$:Et_3N=1:2:1:1. The yield was based on 2-propen-1-ol.

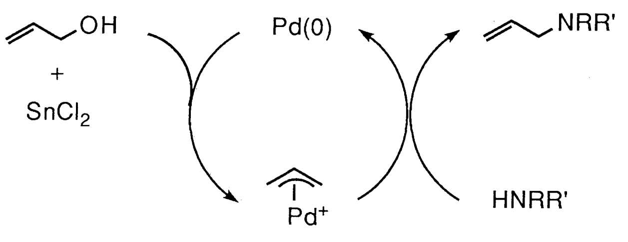
Table 3. Allylic amination of allylic alcohols[a]

Entry	Allylic Alcohol	Amine[b]	Time/h	Product (Yield/%)[c]	
1		$HNBn_2$	42		(70)
2		$HNBn_2$	42	 E:Z=8:1	(64)
3		$HNBn_2$	46	 E:Z=7:1	(55)
4		$HNBn_2$	46		(42)
5		$HNBn_2$	44		(38)
6		$HNBn_2$	45		(51)
7			34		(61)
8		HN^iPr_2	45		(22)
9		H_2NPh	42		(51)[d]
10		$HNBn_2$	47		(42)
11		$HNBn_2$	45		(15)

[a] The reaction of allylic alcohols (2 mmol) and amines (1 mmol) was carried out with tin(II) chloride (2 mmol) and triethylamine (2 mmol) in the presence of $Pd(PPh_3)_4$ (0.02 mmol) at 50 °C in THF (4 ml). [b] Bn: benzyl. [c] Isolated yields based on amines. [d] Cinnamyl alcohol:aniline:$SnCl_2$:Et_3N=1:2:1:1. The yield was based on cinnamyl alcohol.

6). The use of a primary aromatic amine such as aniline led to monoallylation selectively (Entry 7).[5]

The results of the allylic amination of allylic alcohols with amines under the same conditions as those of Entry 2 in Table 1 are summarized in Table 3. (*E*)-Allylic alcohols caused allylic amination regioselectively and stereoselectively to produce the corresponding (*E*)-allylic amines (Entries 2, 4, 6-9, and 11). The allylic amination of 1-substituted allylic alcohols also produced 3-substituted (*E*)-allylic amines regioselectively and stereoselectively (Entries 3, 5, and 10).



Scheme 1.

This reaction probably proceeded via the formation of π-allylpalladium complex from allylic alcohol with tin(II) chloride, as illustrated in Scheme 1.[6-8]

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References and Notes

1 For formation of π-allylpalladium complexes from allylic alcohols, see: a) K. E. Atkins, W. E. Walker, and R. M. Manyik, *Tetrahedron Lett.*, **1970**, 3821; b) J.-P. Haudegond, Y. Chauvin, and D. Commereuc, *J. Org. Chem.*, **44**, 3063 (1979); c) X. Lu, L. Lu, and J. Sun, *J. Mol. Catal.*, **41**, 245 (1987); d) X. Lu, X. Jiang, and X. Tao, *J. Organomet. Chem.*, **344**, 109 (1988); e) D. E. Bergbreiter and D. A. Weatherford, *J. Chem. Soc., Chem. Commun.*, **1989**, 883; f) M. Sakamoto, I. Shimizu, and A. Yamamoto, *Abstracts of 41st Symposium on Organometallic Chemistry, Japan,* Osaka, **1994**, PB214.

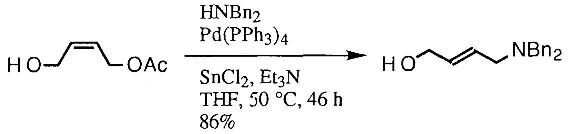
2 Y. Masuyama, in "Advances in Metal-Organic Chemistry," ed by L. S. Liebeskind, JAI Press Inc., Greenwich, Connecticut (1994), Vol. 3, pp 255-303.

3 For palladium-catalyzed allylic amination of allylic esters, see: a) Y. Tanigawa, K. Nishimura, A. Kawasaki, and S.-I. Murahashi, *Tetrahedron Lett.*, **23**, 5549 (1982); b) R. Jumnah and J. M. J. Williams, *Tetrahedron Lett.*, **34**, 6619 (1993); c) P. v. Matt, O. Loiseleur, G. Koch, A. Pfaltz, C. Lefeber, T. Feucht, and G. Helmchen, *Tetrahedron: Asymmetry,* **5**, 573 (1994) and references cited therein.

4 Since dibenzylamine was almost consumed, a half amount of dibenzylamine was supposed to serve as a base for the proton abstraction from the amine. Thus, triethylamine, which functioned as a base, was added.

5 Y. Tsuji, R. Takeuchi, H. Ogawa, and Y. Watanabe, *Chem. Lett.*, **1986**, 293.

6 The chemoselectivity between an allylic alcohol and an allylic acetate in this palladium-catalyzed allylic amination of 4-acetoxy-(Z)-2-buten-1-ol with tin(II) chloride was examined to demonstrate the high reactivity of allylic acetate, which is the inverse of that in the palladium-catalyzed carbonyl allylation with tin(II) chloride. See: J. P. Takahara, Y. Masuyama, and Y. Kurusu, *J. Am. Chem. Soc.*, **114**, 2577 (1992).



7 No by-products were detected in cases of relatively low yields, and the starting allylic alcohols such as 1-decen-3-ol, cinnamyl alcohol, and 3,7-dimethylocta-2,6-dien-1-ol were almost recovered.

8 Carbon nucleophiles, such as dimethyl malonate and ethyl cyanoacetate, instead of amines did not cause allylic alkylation under the same conditions as those of the allylic amination.