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$B(C_6F_5)_3$-Catalyzed Allylation of Secondary Benzyl Acetates with Allylsilanes

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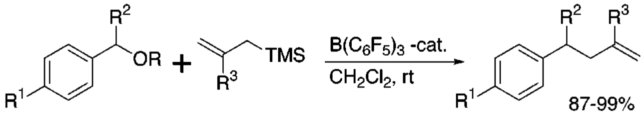
ABSTRACT



A highly effective protocol for allylation of secondary benzylic alcohol derivatives with allylsilanes in the presence of catalytic amounts of $B(C_6F_5)_3$ has been developed. Some additional functionalities, such as bromo, acetoxy, and primary benzyloxy groups, were tolerated under these conditions.

Lewis acid mediated nucleophilic allylation of various substrates with allylsilanes is a powerful protocol for the formation of a carbon−carbon bond. Besides the well-known reaction with carbonyl compounds and acetals (Sakurai reaction),[1] the allylations of other electrophilic substrates, such as benzylic, allylic, and propargylic halides, with allylsilanes have been extensively investigated and well documented.[2] However, similar transformations with more synthetically attractive alcohols and their derivatives are far less developed.[3] Most known protocols of this type require at least stoichiometric amounts of Lewis acid. There are only a few scattered reports on catalytic versions of this reaction: allylation of allylic and benzylic alcohols with $HN(SO_2F)_2$,[4] allyl silyl ethers with $ZnCl_2$,[5] alkyl allyl ethers with $TrClO_4$,[6] and alkyl propargyl ethers with the $SnCl_4-ZnCl_2$ binary system.[7] However, the reactions reported are not general and are incompatible with most functional groups, often providing moderate yields of the products. Accordingly, development of more general, efficient, and environmentally benign catalytic methodology for allylation of alcohols and their derivatives is exceedingly desired. Herein we wish to report a very simple procedure for allylation of secondary benzylic alcohols and their derivatives with allylsilanes in the presence of a catalytic amount of tris(pentafluorophenyl) borane, $B(C_6F_5)_3$.[8]

We have recently reported a novel procedure for exhaustive reduction of alcohols and reductive cleavage of ethers,[9] as well as direct exhaustive reduction of carboxylic acids and their derivatives[10] with hydrosilanes in the presence of catalytic amounts of $B(C_6F_5)_3$. In continuation of our study on catalytic applications of this unusual Lewis acid in organic

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(1) For reviews, see: (a) Sakurai, H. *Pure Appl. Chem.* **1982**, *54*, 1. (b) Sakurai, H. *Pure Appl. Chem.* **1989**, *57*, 1759.

(2) (a) Dau-Schmidt, J.-P.; Mayr, H. *Chem. Ber.* **1994**, *127*, 205. (b) Mayr, H.; Pock, R. *Tetrahedron* **1986**, *42*, 4211. (c) Mayr, H.; Gorath, G.; Bauer, B. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 788.

(3) See, for example: Cella, J. A. *J. Org. Chem.* **1982**, *47*, *2125*.

(4) Kaur, G.; Kaushik, M.; Trehan, S. *Tetrahedron Lett.* **1997**, *38*, 2521.

(5) Yokozawa, T.; Furuhashi, K.; Natsume, H. *Tetrahedron Lett.* **1995**, *36*, 5243.

(6) Murakami, M.; Kato, T.; Mukaiyama, T. *Chem. Lett.* **1987**, 1167.

(7) Hayashi, M.; Inubushi, A.; Mukaiyama, T. *Chem. Lett.* **1987**, 1975.

(8) For recent review on use of $B(C_6F_5)_3$ and analogues as cocatalysts in the metal-catalyzed olefins polymerization, see: (a) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391. For the use of $B(C_6F_5)_3$ as a catalyst for 1,3-isomerization of allylstannanes, see: (b) Marshall, J. A.; Gill, K. *J. Organomet. Chem.* **2001**, *624*, 294. For hydrosilylation of carbonyl compounds and imines, see: (c) Blackwell, J. M.; Sonmor, E. R.; Scoccitti, T.; Piers, W. E. *Org. Lett.* **2000**, *2*, 3921. (d) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090. For allylstannylation of aldehydes, see: (e) Blackwell, J. M.; Piers, W. E. *Org. Lett.* **2000**, *2*, 695. For silylation of alcohols, see: (f) Blackwell, J. M.; Foster, K. L.; Beck, V. H.; Piers, W. E. *J. Org. Chem.* **1999**, *64*, 4887.

(9) (a) Gevorgyan, V.; Liu, J.-X.; Rubin, M.; Benson, S.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 8918. (b) Gevorgyan, V.; Rubin, M.; Benson, S.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2000**, *65*, 6179.

(10) Gevorgyan, V.; Rubin, M.; Liu, J.-X.; Yamamoto, Y. *J. Org. Chem.* **2001**, *66*, 1672.

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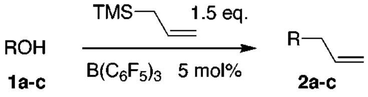
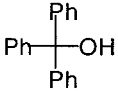
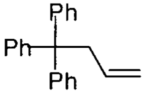
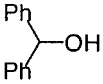
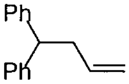
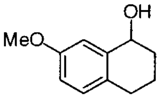
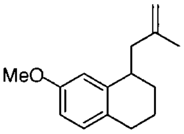
synthesis, we attempted $B(C_6F_5)_3$-catalyzed allylation of benzylic alcohols with allylsilanes.

In test experiments, both trityl alcohol (**1a**) and benzhydrol (**1b**) smoothly underwent allylation with allyltrimethylsilane in the presence of 5 mol % of $B(C_6F_5)_3$ to give the corresponding alkenes **2a** and **2b** in high yields (eq 1, Table 1, entries 1 and 2). However, allylation of secondary or tertiary benzylic alcohols possessing β-hydrogen atoms did not proceed smoothly: the competing elimination process took place to produce inseparable mixtures of the corresponding styrenes, their oligomers, and polymers along with the allylation products. However, in certain cases employment of slightly more nucleophilic methallylsilane made the allylation reaction favorable (Table 1, entry 3).The observed elimination process could be rationalized as follows. Allylation of secondary benzylic alcohol **3a** with allyltrimethylsilane produces **4a** and silanol **5a** (X = OH) as a byproduct (eq 2). Silanol **5a**, in turn, undergoes dehydrocondensation to give siloxane[11] and eliminates a molecule of water, which is immediately caught by $B(C_6F_5)_3$. The hydrates produced by this means, $B(C_6F_5)_3 \cdot xH_2O$, are known to ionize in solution to form $H_3O^+[B(C_6F_5)_3OH]^-$, a Brönsted acid which is nearly as strong as H_2SO_4.[12] The presence of such a strong Brönsted acid could be responsible for induction of both undesired processes, elimination of water from benzylic alcohols and oligomerization of forming styrenes.[13] Thus, we decided to search for a suitable leaving group, one that would allow for easier formation of benzylic cation and byproduct **5** (X ≠ OH), which would not liberate water under these conditions and thus will not initiate the above-mentioned undesired side reactions (eq 2, Table 2).

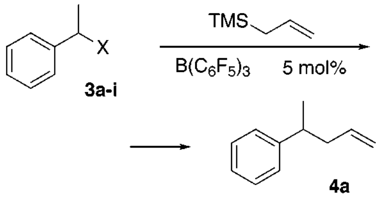


(1)

Table 1. Allylation of Benzylic Alcohols

	Alcohol		Product		Yield,[a] %
1		**1 a**		**2 a**	90
2		**1 b**		**2 b**	80
3		**1 c**		**2 c**	82[b]

[a] Isolated yield. [b] Methallyltrimethylsilane was used in this reaction.



(2)

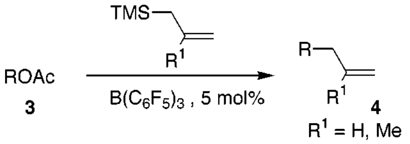
Table 2. Optimization of Leaving Group

	leaving group (X)		**4a**, yield,[a] %
1	OH	(**3a**)	15–20
2	OTMS	(**3b**)	NR
3	OMe	(**3c**)	98
4	OBn	(**3d**)	85
5	OMOM	(**3e**)	92
6	$OCOCH_3$	(**3f**)	96
7	OCOPh	(**3g**)	74
8	$OCOCMe_3$	(**3h**)	69
9	$OCOCF_3$	(**3i**)	99

[a] NMR yields.

As discussed above, unprotected *sec*-phenethyl alcohol **3a** gave allylation product **4a** in very low yields (Table 2, entry 1). TMS-protected alcohol **3b**, probably due to steric reasons, did not undergo allylation at all (entry 2). In contrast, all of the alkyl- (**3c**–**e**) and acyl-protected (**3f**–**i**) benzylic substrates tested smoothly underwent the allylation reaction to give the allylation product **4a** in good to very high yields (entries 3–9).

Although methyl- (**3c**) and TFA-protected (**3i**) alcohols provided the highest yields of **4a**, the acetate derivatives, for obvious synthetic reasons (being cheapest and easiest for preparation and purification), were chosen for further investigation. Thus, a series of secondary benzylic acetates were prepared and tested in the $B(C_6F_5)_3$-catalyzed allylation reaction (eq 3, Table 3).[14] The acetate of *sec*-phenethyl alcohol **3f** gave allylation product **4a**[15] in 91% isolated yield (entry 1). Allylation of **3f** with methallylsilane allowed for



(3)

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[11] The formation of hexamethyldisiloxane was detected by ^1H NMR analyses of the crude reaction mixtures.

[12] Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Perkin, G. *J. Am. Chem. Soc.* **2000**, *122*, 10581.

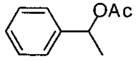
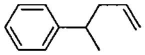
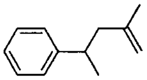
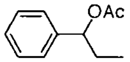
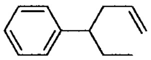
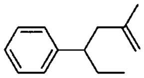
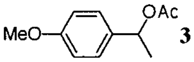
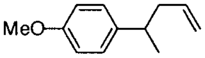
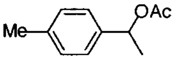
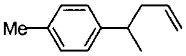
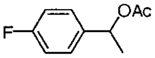
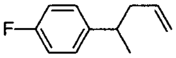
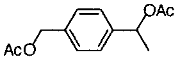
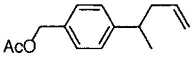
[13] Independent experiments demonstrated that treatment of certain secondary alcohols with $B(C_6F_5)_3$, preliminarily exposed to wet air, led to the formation of notable amounts of alkenes.

[14] All reactions were carried out in the presence of 5 mol % of $B(C_6F_5)_3$. Reactions in the presence of lesser amount of $B(C_6F_5)_3$ were sluggish and incomplete.

[15] The preparation of **4a** is representative. To a stirred solution of $B(C_6F_5)_3$ (26 mg, 5 mol %) in anhydrous CH_2Cl_2 (1 mL) was added **3f** (1 mmol, 164 mg), followed by the addition of allyltrimethylsilane (1.5 mmol, 240 μL). The mixture was stirred at room temperature, and the reaction

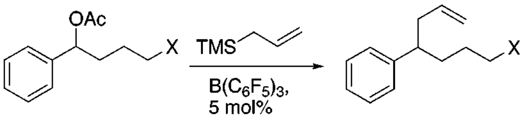
obtaining compound **4b** in 94% yield (entry 2). A somewhat more hindered acetate **3j** gave allylation products **4c** and **4d** in 92% and 94% yields with allyltrimethylsilane and methallyltrimethylsilane, respectively (entries 3 and 4). As expected, introduction of electron-donating groups, stabilizing the forming benzylic cation, essentially accelerated the reaction:[16] *p*-methoxy-, *p*-methyl-, and *p*-fluoro-substituted *sec*-phenethyl acetates **3k**, **3l**, and **3m** readily gave the corresponding allylation products **4e**, **4f**, and **4g** in excellent yields (entries 5−7). Our test experiments indicated that primary benzylic acetates, in contrast to secondary ones, in the presence of catalytic amounts of $B(C_6F_5)_3$ did not undergo allylation at all.[17] Accordingly, we were able to selectively substitute a secondary benzylic acetate group in the presence of a primary one in the diacetate **3n** to produce the monoallylation product **4h** in a virtually quantitative yield (entry 8).

Table 3. Allylation of Secondary Benzylic Acetates

	Acetate **3**		R1	Product **4**		Yield,[a] %
1		**3 f**	H		**4 a**	91
2	"	**3 f**	Me		**4 b**	94
3		**3 j**	H		**4 c**	92
4	"	**3 j**	Me		**4 d**	94
5		**3 k**	H		**4 e**	90
6		**3 l**	H		**4 f**	96
7		**3 m**	H		**4 g**	95
8		**3 n**	H		**4 h**	99

[a] Isolated yield.

We found the last result especially interesting since the presence of an additional Lewis basic group such as primary acetate did not deactivate $B(C_6F_5)_3$ catalyst. Encouraged by this fact we performed initial experiments on functional group tolerance (eq 4). As expected, secondary benzylic acetates possessing an unprotected alcohol group (**6d**, X = OH) and nitrile function (**6e**, X = CN) did not undergo the allylation reaction (eq 4).[18] In contrast, diacetate **6a** (X = OAc) smoothly underwent mono-allylation to give **7a** in 91% yield. Similarly, substrates possessing a bromide group (**6b**, X = Br) or benzyl ether moiety (**6c**, X = OBn) provided the corresponding allylation products **7b** and **7c** in 87% and 96% yields, respectively (eq 4).



6a-e

X = OH, CN - NR
7a, X = OAc, 91%
7b, X = Br, 87%
7c, X = OBn, 96%

(4)

In summary, we developed an effective protocol for allylation of secondary benzylic alcohol derivatives with allylsilanes in the presence of catalytic amounts of $B(C_6F_5)_3$. Various secondary benzylic acetates smoothly underwent the allylation reaction under mild conditions to give the corresponding allylation products in very high yields. Initial experiments on functional group tolerance demonstrated that bromo, acetoxy, and benzyloxy groups are tolerated under these reaction conditions.

Acknowledgment. The support of the Petroleum Research Fund (AC1-36370), administrated by American Chemical Society, is gratefully acknowledged.

Supporting Information Available: Detailed experimental procedures for preparation and spectroscopic data for compounds **6a−e**. Spectroscopic and analytical data for compounds **2c**, **4d**,**e**,**g**,**h**, and **7a−c**. This material is available free of charge via Internet at http://pubs.acs.org.

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course was monitored by capillary GLC analysis. After the reaction was complete (12 h for **4a**), the mixture was filtered through a short column (silica gel) and concentrated. Purification by column chromatography (silica gel, hexane as an eluent) gave 133 mg (91%) of **4a**.

[16] Reactions, in these cases, were finished in 5−6 h, whereas normally the reaction needed 12−48 h for completion.

[17] Conversion of primary benzylic acetate in the presence of a stoichiometric amount of $B(C_6F_5)_3$ did not exeed 20%.

[18] Lewis acid was passivated by complexation with these functional groups. For binding of $B(C_6F_5)_3$ with alcohols and nitriles see ref 12.