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An Efficient and Convenient Method for the Asymmetric Allylation of Aldehydes with Allyltrimethylsilane Catalyzed by Diphenylboryl Triflate

Teruaki MUKAIYAMA, Masahiro OHSHIMA, and Norikazu MIYOSHI
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

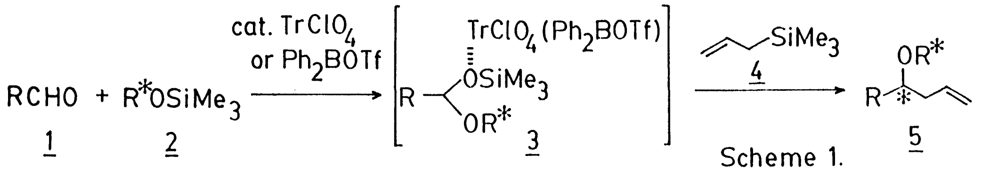
In the presence of a catalytic amount of diphenylboryl triflate, aldehydes smoothly react with (S)-1-phenyl-1-trimethylsilyloxyethane and allyltrimethylsilane to afford the chiral homoallyl ethers in good yields with high stereoselectivities.

In recent years, much attention has been paid to asymmetric allylation of aldehydes, since optically active homoallyl alcohol units constitute a characteristic structural feature of numerous macrolides and polyether antibiotics. Therefore, a number of methods have been developed using various allylmetal reagents, such as allylborane,1) allylboronate,2) allyltitanium,3) allylaluminum,4) allylstannane,5) and allylsilane.6-9)

Concerning the asymmetric allylation of aldehydes with allylsilane, chiral cyclic acetals are generally employed as chiral templates.6) However, these methods require the tedious steps for synthesis and purification of the chiral acetals and removal of the chiral sources, and the reaction was promoted by a stoichiometric amount of Lewis acid. So it is desirable to develop a one-pot procedure for asymmetric allylation of aldehydes with allylsilane without isolation of the intermediate chiral acetals.

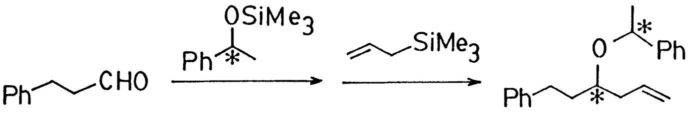
In the previous paper, it was reported that trityl perchlorate ($TrClO_4$) and diphenylboryl triflate (Ph_2BOTf) are effective catalysts for allylation of acetals with allylsilanes.10) In an extension of this study, an application of this allylation reaction to asymmetric synthesis was attempted. And here, we wish to disclose that, in the presence of a catalytic amount of diphenylboryl triflate, the one-pot asymmetric allylation of aldehydes with allyltrimethylsilane is successfully achieved, and chiral homoallyl ethers are obtained in good yields with high stereoselectivities. Recently, the one-step procedure for the asymmetric allylation of aldehydes with allyltrimethylsilane by the use of dialkoxydichlorotitanium as a promoter has been reported.8) In this reaction, desired chiral homoallyl alcohols are obtained by using two molar amount of the chiral source and a stoichiometric amount of Lewis acid in 40-50% chemical yields. So the present method reported in this communication is of synthetic value in terms of the efficiency and the mildness of reaction conditions.

The strategy of the present study is depicted in Scheme 1, and the reaction involves two stages. Firstly, silylated hemiacetal (3) is formed by the addition of trimethylsilyl ether of chiral alcohol (2) to aldehyde (1). Then, the trimethylsilyloxy group of the silylated hemiacetal (3) is coordinated to $TrClO_4$ or Ph_2BOTf, and the activated silylated hemiacetal (3) is attacked by nucleophile, allylsilane (4), with chiral induction to yield optically active homoallyl ether (5).[11,12] Since both of the reactions are catalyzed by $TrClO_4$ or Ph_2BOTf, the one-pot synthesis of chiral homoallyl ether (5) becomes possible without isolation of the intermediate acetal (3).



Scheme 1.

Based on this consideration, the reaction of 3-phenylpropanal and allyltrimethylsilane was tried by the use of 1-phenyl-1-trimethylsilyloxyethane as a chiral source.[13] And it was found that, in the presence of a catalytic amount of $TrClO_4$, the highest yield was achieved when the reaction was carried out in CH_2Cl_2 at -23 °C (Table 1, entry 2), though the stereoselectivity was unsatisfactory. It is considered that, in order to increase the stereoselectivity, the reaction should be carried out at a lower temperature by the use of more effective catalyst than $TrClO_4$. It has been reported that Ph_2BOTf is more effective catalyst for the allylation of acetals with allyltrimethylsilanes and the reaction proceeds even at -78 °C.[10] So we next tried the same allylation reaction by the use of Ph_2BOTf as a promoter, and it was found that the reaction proceeded smoothly at -78 °C to give the chiral homoallyl ether in good yield with good stereoselectivity, as expected (entry 5). Moreover, it is noted that the selectivity was enhanced when toluene was used as a solvent (entry 6).



Scheme 2.

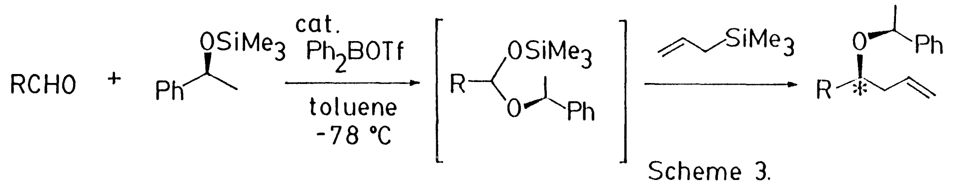
Table 1. The screening of the reaction conditions[a)]

Entry	Catalyst	Solvent	Temp/°C	Yield/%	Diastereomer ratio[b)]
1	$TrClO_4$	CH_2Cl_2	-45	24	82:18
2			-23	92	78:22
3			0	63	75:25
4		CH_3CN	-23	35	58:42
5	Ph_2BOTf	CH_2Cl_2	-78	74	86:14
6		toluene	-78	72	96: 4

a) Racemic 1-phenyl-1-trimethylsilyloxyethane was used in the reaction.
b) Determined by GC.

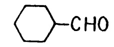
It became apparent that, in the presence of Ph_2BOTf, the one-pot asymmetric allylation of aldehydes with allyltrimethylsilane proceeded in a highly stereoselective manner. Then the application of this method to various aldehydes was tried, and the results are shown in Table 2. In the case of aliphatic aldehydes, high stereoselectivities were realized (Table 2, entries 1-5), however, in the case of benzaldehyde, the selectivity was decreased (entry 6). This is explained by considering the easiness of formation of the benzylic oxocarbenium ion which prefers the S_N1 transition state to diminish effective chiral induction. It was assumed that bulky silyloxy group should favor the stereoselective S_N2 process, because the coordination of the silyloxy group to Ph_2BOTf is weakened and the displacement requires greater assistance from the nucleophile. Indeed, the selectivity was increased to 56% d.e. by the use of (S)-1-phenyl-1-triethylsilyloxyethane as a chiral source (entry 7).

The chiral sources of the homoallyl ethers were easily removed by catalytic hydrogenation or cleavage of the benzylic ether bond with iodotrimethylsilane$^{15)}$ to give the optically active alcohols or homoallyl alcohols.



Scheme 3.

Table 2. The synthesis of chiral homoallyl ether$^{a)}$

Entry	Aldehyde	Yield/%	Diastereomer excess/%$^{b)}$	Absolute configuration$^{c)}$
1	$PhCH_2CH_2CHO$	71	93	$\mathrm{R}^{16)}$
2	$(CH_3)_2CHCHO$	66	99	$\mathrm{S}^{2d)}$
3		74	85	$\mathrm{S}^{6a,b)}$
4	$CH_2{=}CH(CH_2)_8CHO$	79	84	e)
5	$PhCH_2O(CH_2)_2CHO$	81	90	$\mathrm{S}^{17)}$
6	PhCHO	77	48	$\mathrm{S}^{2d)}$
7	PhCHO	$77^{d)}$	56	$\mathrm{S}^{2d)}$

a) Molar ratio of Ph_2BOTf:aldehyde:(S)-1-phenyl-1-trimethylsilyloxyethane:allyltrimethylsilane=0.2-0.3:1.0:1.1-1.2:1.6-2.0.
b) Determined by GC.
c) Determined by comparison of the optical rotation values with the known alcohols after the removal of the chiral source.
d) (S)-1-phenyl-1-triethylsilyloxyethane was used as a chiral source.
e) Not determined.

A typical procedure is described for the synthesis of (R)-6-phenyl-4-[(S)-1-phenylethoxy]-1-hexene; under argon atmosphere, to a toluene (2 ml) solution of silver triflate (65 mg, 0.25 mmol)$^{18)}$ was added chlorodiphenylborane (50 mg, 0.25 mmol) in toluene (2 ml) at 0 °C. After stirring for 1 h, the resulting mixture was cooled to -78 °C, and a toluene (3 ml) solution of (S)-1-phenyl-1-trimethylsilyloxyethane (192 mg, 0.99 mmol) and allyltrimethylsilane (168 mg, 1.47 mmol) was added. Then 3-phenylpropanal (115 mg, 0.86 mmol) in toluene (2 ml) was added over 30 min, and stirring was continued for 22 h at -78 °C. The reaction was quenched with pH 7 phosphate buffer, and insoluble materials were filtered off through celite pad. The organic materials were extracted with ether, and the combined extracts were washed with brine. After drying over Na_2SO_4, the solvent was evaporated. The residue was purified by preparative TLC (silica gel) to afford the title compound [171 mg, 71%, $[\alpha]_D^{24}$ -61.0°(c 2.11, CH_2Cl_2)].

It is noted that, according to the present method, the chiral homoallyl ethers are synthesized in good yields with high stereoselectivities by one-pot procedure in the presence of a catalytic amount of promoter, diphenylboryl triflate.

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