

A FACILE SYNTHESIS OF HOMOALLYL ETHERS.  
THE REACTION OF ACETALS WITH ALLYLTRIMETHYLSILANES  
PROMOTED BY TRITYL PERCHLORATE OR DIPHENYLBORYL TRIFLATE

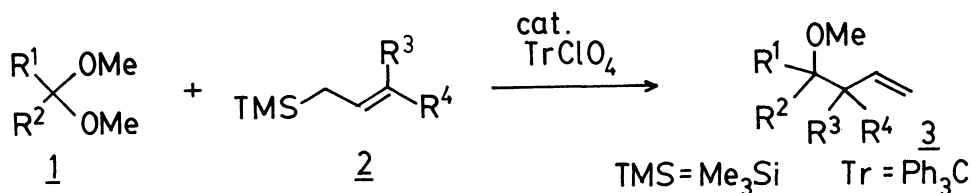
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In the presence of a catalytic amount of trityl perchlorate or diphenylboryl triflate, acetals react smoothly with allyltrimethylsilanes to give the corresponding homoallyl ethers in good yields with good regio- and stereoselectivities.

The addition of allylmetal compounds to carbonyl compounds or their equivalents is one of the most useful synthetic reactions and many organometallic reagents have been developed. Of these reagents, allylsilanes are known as useful reagents because of their stability and selectivity in the reaction, and the reactions with carbonyl compounds or acetals promoted by Lewis acids have been reported. Concerning the reactions of acetals with allylsilanes, a stoichiometric amount of  $\text{TiCl}_4$ <sup>1)</sup> or a catalytic amount of  $\text{TMSOTf}$ <sup>2)</sup> or  $\text{TMSI}$ <sup>3)</sup> is generally employed as a promoter.

In our recent reports, it was shown that trityl perchlorate effectively catalyzed the reactions of acetals and aldehydes with silyl enol ethers to form the corresponding aldol-type products in excellent yields.<sup>4)</sup>

Based on the fact, we investigated the allylation of acetals with allylsilanes promoted by trityl perchlorate, and it was found that acetals (1) reacted with allyltrimethylsilanes (2) to afford the corresponding homoallyl ethers (3) (Scheme 1).



Scheme 1.

After screening the reaction conditions, such as solvent and reaction temperature, it was observed that the reaction proceeded smoothly at -23 °C in  $\text{CH}_2\text{Cl}_2$  to give the corresponding homoallyl ethers. The allylation of acetals (1) with various allyltrimethylsilanes (2) afforded the homoallyl ethers (3) in good to excellent yields as shown in Table 1.

Table 1. The reaction of acetals with allyltrimethylsilanes catalyzed by  $\text{TrClO}_4$ 

Entry	Acetals	Allylsilane	Conditions		Yield/%	Diastereomer ratio <sup>a)</sup>
			Temp/°C	Time/h		
1	$\text{PhCH(OMe)}_2$	$\text{CH}_2=\text{CHCH}_2\text{TMS}$ <u>4</u>	-23	, 3	82	
2	$\text{PhCH}_2\text{CH}_2\text{CH(OMe)}_2$	<u>4</u>	-23	, 4.5	90	
3	$\text{PhCH}_2\text{CH}_2\text{C(OMe)}_2\text{CH}_3$	<u>4</u>	-23	, 9.5	82	
4	$\text{PhCH=CHCH(OMe)}_2$	<u>4</u>	-23	, 0.25	80	
5	$\text{PhCH(OMe)}_2$	$\text{CH}_3\text{CH=CHCH}_2\text{TMS}^{\text{b)}$	-23	, 1	62	(71:29) <sup>d)</sup>
6			-78	, 24	85	(64:36) <sup>d)</sup>
7	$\text{PhCH(OMe)}_2$	$\text{PhCH=CHCH}_2\text{TMS}^{\text{c)}$	-23	, 24	64	(67:33) <sup>e)</sup>
8	$\text{PhCH}_2\text{CH}_2\text{CH(OMe)}_2$	$\text{Me}_2\text{C=CHCH}_2\text{TMS}$	-23	, 20	57	

a) The ratios were determined by  $^1\text{H-NMR}$ .

b) This allylsilane was prepared from 1-bromo-1-propene (E/Z=20:80) and chloromethyltrimethylsilane.<sup>5)</sup>

c) This allylsilane was prepared from (E)-cinnamyl chloride and chlorotrimethylsilane,<sup>6)</sup> and the product was found to be a single isomer by  $^{13}\text{C-NMR}$  spectrum.

d) The major product was assigned to a threo-isomer by comparing its NMR spectrum with those of the authentic sample.<sup>8)</sup>

e) The relative configuration was not assigned.

The reaction took place regioselectively at the  $\gamma$ -carbon of allylsilanes similar to previously reported results.<sup>3,7)</sup> In the cases of crotyltrimethylsilane and cinnamyltrimethylsilane (entries 5, 6, 7), the moderate diastereoselectivity was observed.<sup>8)</sup> Further, it was found that ( $\gamma,\gamma$ -dimethylallyl)trimethylsilane reacted with an acetal to give the corresponding homoallyl ether (entry 8), which was not obtained in the presence of a catalytic amount of activators such as  $\text{TMSI}$ .<sup>3)</sup>

A typical procedure is described for the reaction of benzaldehyde dimethylacetal with allyltrimethylsilane (entry 1): To a  $\text{CH}_2\text{Cl}_2$  (1 ml) solution of trityl perchlorate (0.035 mmol) was added a mixture of benzaldehyde dimethylacetal (0.70 mmol) and allyltrimethylsilane (0.90 mmol) in  $\text{CH}_2\text{Cl}_2$  (4 ml) at  $-23^\circ\text{C}$  (dry ice -  $\text{CCl}_4$ ) under argon atmosphere, and the reaction mixture was stirred for 3 h. The reaction was quenched with aqueous  $\text{NaHCO}_3$ , and organic materials were extracted with  $\text{CH}_2\text{Cl}_2$ . The combined extracts were dried over  $\text{Na}_2\text{SO}_4$ , and then the solvent was evaporated. The residue was purified by preparative TLC to afford 4-methoxy-4-phenyl-1-butene (0.57 mmol, 82%).

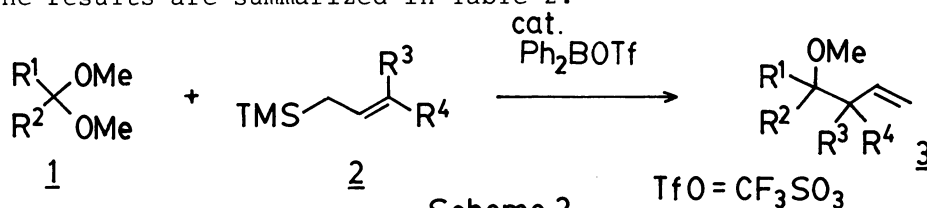
In the above mentioned trityl perchlorate promoted reaction, triphenylmethyl carbenium ion plays an important role as an activator of acetals. Then we were interested in this unique character of the cation stabilized by phenyl groups, and investigated the other metal cations containing phenyl groups. It is well-known

that boron has a strong affinity for oxygen, so we expected that the boron cation stabilized by phenyl groups could promote the allylation of acetals more effectively than trityl cation.

It was reported that diphenylboryl perchlorate was prepared from diphenylboryl chloride and silver perchlorate, and the boron atom had a cationic character.<sup>9)</sup> Instead of diphenylboryl perchlorate, we chose diphenylboryl triflate and investigated the allylation of acetals. It was found that in the presence of a catalytic amount of diphenylboryl triflate prepared from diphenylboryl chloride and silver triflate in situ, acetals (1) reacted with allyltrimethylsilanes (2) smoothly to afford the homoallyl ethers (3) in good yields (Scheme 2).

In this reaction, neither diphenylboryl chloride nor silver triflate catalyzed the allylation of acetals, and dibutylboryl triflate was also not an effective catalyst. So it was presumed that the boron cation stabilized by two phenyl groups played an important role as an activator in this reaction, although the reaction mechanism was not clear in detail.

The reaction of acetals (1) with various allyltrimethylsilanes (2) in the presence of a catalytic amount of Ph<sub>2</sub>BOTf gave the homoallyl ethers (3) in good yields. The results are summarized in Table 2.



Scheme 2.

Table 2. The reaction of acetals with allyltrimethylsilanes catalyzed by Ph<sub>2</sub>BOTf

Entry	Acetal	Allylsilane	Conditions		Yield/%	Diastereomer ratio <sup>a)</sup>
			Temp/°C	Time/h		
1	PhCH(OMe) <sub>2</sub>	CH <sub>2</sub> =CHCH <sub>2</sub> TMS <u>4</u>	-78	, 12	71	
2	PhCH <sub>2</sub> CH <sub>2</sub> CH(OMe) <sub>2</sub>	<u>4</u>	-78	, 24	77	
3	PhCH(OMe) <sub>2</sub>	CH <sub>3</sub> CH=CHCH <sub>2</sub> TMS	-78	, 24	69	(76:24) <sup>b)</sup>
4	PhCH(OMe) <sub>2</sub>	PhCH=CHCH <sub>2</sub> TMS	-78	, 48	73	(82:18) <sup>c)</sup>

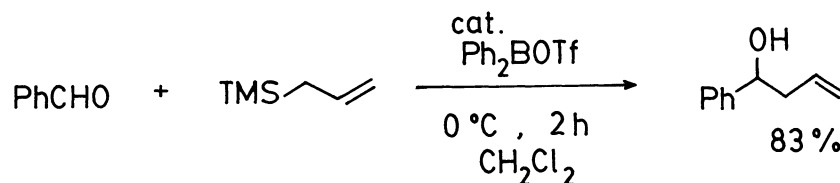
a) The ratios were determined by <sup>1</sup>H-NMR.

b) The major product was assigned to be a threo-isomer by comparing its NMR spectrum with those of authentic sample.<sup>8)</sup>

c) The relative configuration was not assigned.

It was observed that the reaction could be carried out at lower temperature than the same reaction promoted by trityl perchlorate, and the diastereoselectivity was improved (entries 3,4). Further, in the presence of a catalytic amount of Ph<sub>2</sub>BOTf, benzaldehyde also reacted with allyltrimethylsilane to afford

the homoallyl alcohol in good yield (Scheme 3).<sup>10)</sup>



Scheme 3.

Thus, it is noted that trityl perchlorate and diphenylboryl triflate effectively catalyze the reaction of acetals with allyltrimethylsilanes to afford the homoallyl ethers in good to excellent yields under mild conditions.

#### References

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- 9) J. M. Davidson and C. M. French, *Chem. Ind. (London)*, 1959, 750.
- 10) When trityl perchlorate was used as a catalyst, the allylation of benzaldehyde with allyltrimethylsilane did not proceed.

(Received April 19, 1985)