

A Conjugate Addition of Allylsilanes to
 α,β -Unsaturated Ketones Catalyzed by Trityl Perchlorate

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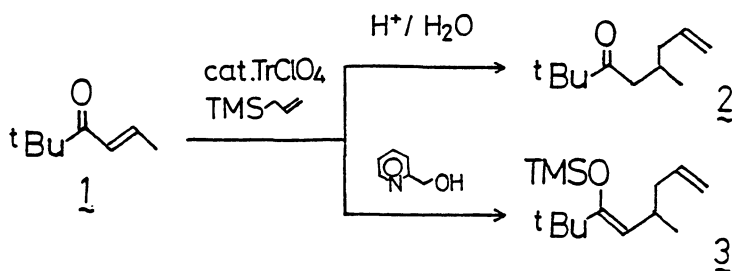
A conjugate addition of allylsilanes to α,β -unsaturated ketones was effectively promoted by a catalytic amount of trityl perchlorate to give the corresponding Michael adducts in good yields.

Allylsilanes are versatile reagents for the allylation of a variety of electrophiles with regiospecific transposition of the allylic part.¹⁾ It has been reported that Lewis acids, such as TiCl_4 , $\text{BF}_3 \cdot \text{OEt}_2$ and SnCl_4 ,²⁾ or a fluoride ion³⁾ effectively promotes the conjugate addition of allylsilanes to α,β -unsaturated carbonyl compounds. However, a stoichiometric amount of Lewis acid is generally required for the completion of this reaction.²⁾ And, a mixture of 1,2- and 1,4-addition products is obtained when the fluoride ion is employed in the reaction with α,β -unsaturated ketones.⁴⁾

Recently, new possibilities in synthetic reactions have been widely exploited in our laboratory by employing a catalytic amount of triphenylmethyl (trityl) perchlorate as a promoter. It has been shown that a conjugate addition of silyl enol ethers to α,β -unsaturated ketones is effectively catalyzed by trityl perchlorate.^{5,6)}

In this communication, we wish to describe a trityl perchlorate catalyzed conjugate allylation and also the further reaction of the intermediates, silyl enol ethers, with carbonyl compounds or their derivatives, such as aldehydes or dimethyl acetals.

In the first place, 2,2-dimethyl-4-hexen-3-one (**1**) was treated with allyl-



Scheme 1.

trimethylsilane in the presence of 2 mol% of trityl perchlorate in CH_2Cl_2 at 0°C . And the conjugate allylation proceeded to afford solely the δ,ϵ -unsaturated ketone (2) (11%) with no accompanying of the 1,2-addition product, and most of the starting material (1) was recovered. Subsequent screening of solvents showed that the highest yield was realized when acetonitrile was employed (92%). Further, it was found that the silyl enol ether, an intermediate adduct, could be isolated when the reaction mixture was quenched with a small amount of 2-pyridine-methanol.^{5a)}

Having attained the best reaction conditions, the reactions of several α,β -unsaturated ketones with allyltrimethylsilane were tried and the corresponding conjugate adducts were obtained in good yields except for Entries 6 and 8.⁷⁾

A typical procedure for the preparation of 4,7,7-trimethyl-6-trimethylsilyloxy-1,5-octadiene (Entry 1) is as follows: Under an argon atmosphere, to an CH_3CN solution (3 ml) of TrClO_4 (0.04 mmol) were added successively allyltrimethylsilane (1.93 mmol) in CH_3CN (1.5 ml) and 2,2-dimethyl-4-hexen-3-one

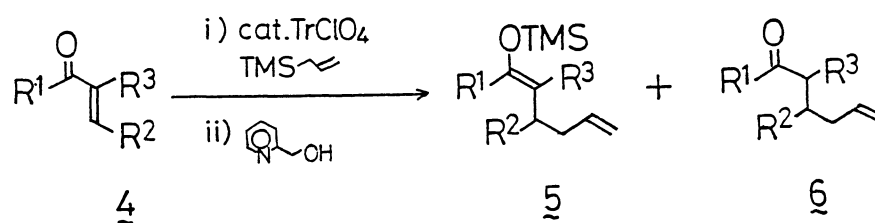


Table 1. The Reaction of α,β -Unsaturated Ketones with Allyltrimethylsilane^{a)}

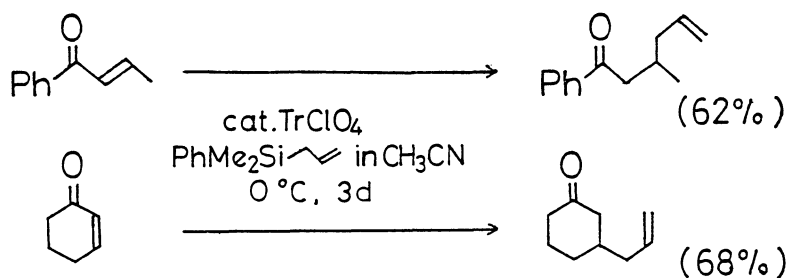
Entry	R ¹	<u>4</u> R ²	R ³	Temp/ $^\circ\text{C}$	Time/d	Yield/% ^{b)}	
						<u>5</u>	<u>6</u>
1	<i>t</i> Bu	H	H	-20	1	47	16
2	<i>t</i> Bu	H	Me	0	1	88	10
3	<i>t</i> Bu	H	Ph	0	2	89	10
4	<i>i</i> Pr	H	Me	-20	3	73	7
5	<i>i</i> Pr	H	Ph	-20	3	48	27
6	Ph	H	Me	-20	0.1	—	29 ⁷⁾
7	Ph	H	<i>t</i> Bu	0	2	19	63
8	-(CH ₂) ₃ -	H	H	-20	0.1	—	— ⁷⁾
9	-(CH ₂) ₃ -	H	Me	0	1	79	19
10	-(CH ₂) ₂ -	H	Me	0	1	62	32
11	-(CH ₂) ₂ -	H	Br	0	1	7	54

a) Reaction was carried out in CH_3CN with 1.5 equiv. of allyltrimethylsilane in the presence of 2 mol% trityl perchlorate.

b) Isolated yields. All the products gave satisfactory NMR and IR spectra.

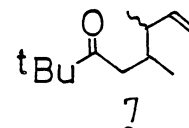
(1.28 mmol) in CH_3CN (1.5 ml) at 0°C . The reaction mixture was stirred for 1 d at the same temperature, then quenched with 2-pyridinemethanol (0.03 mmol). After concentration of the mixture, the resulted residue was purified by preparative TLC (silica gel) to afford 4,7,7-trimethyl-6-trimethylsilyloxy-1,5-octadiene (1.13 mmol, 88%) along with a small amount of 2,2,5-trimethyl-7-octen-3-one (0.13 mmol, 10%).

When allyldimethylphenylsilane instead of allyltrimethylsilane was used in the above reaction, α,β -unsaturated ketones, as shown in Scheme 2, were converted into the corresponding Michael adducts in moderate yields.

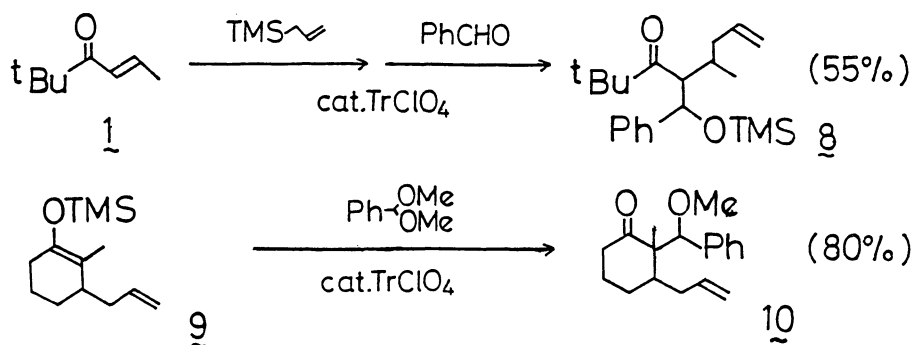


Scheme 2.

Although the detailed mechanism is not yet clear, it is most probable that trityl cation firstly interacts with the carbonyl oxygen to activate the carbonyl carbon to accept the nucleophilic attack of allylsilane in a regio-controlled manner. That is, the γ -carbon of allylsilane nucleophilically attacks the α,β -unsaturated ketone to induce positive charge development at the β -carbon, and then the β -silyl carbonium ion undergoes rapid loss of the silyl group. In result, the product has the substitution with a net shift of the double bond, which is confirmed by the formation of 7⁸⁾ by the reaction of crotylsilane with the α,β -unsaturated ketone (1).



Further, it became possible to obtain the aldol products by the sequential reaction of the intermediate, silyl enol ether (5), with various aldehydes or acetals. That is, as shown in Scheme 3, the conjugate addition of allyltrimethylsilane to α,β -unsaturated ketone (1) and the sequential aldol reaction



Scheme 3.

with benzaldehyde was carried out smoothly to afford 8⁸⁾ by a one pot procedure. Also, the isolated silyl enol ether (9) reacted with benzaldehyde dimethyl acetal in the presence of a catalytic amount of trityl perchlorate to afford 10.⁸⁾

It is noted that a catalytic amount of trityl perchlorate effectively promotes the conjugate allylation of α,β -unsaturated ketones with allyltrimethylsilane to afford the corresponding adducts in good yields, and that two carbon-carbon bonds formation is achieved in a single operation by further treatment of the intermediates with aldehydes or dimethyl acetals.

References

- 1) E. Colvin, "Silicon in Organic Synthesis," Butterworths (1981), Chap.9, p.97; W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag (1983), Chap.11, p.173.
- 2) A. Hosomi and H. Sakurai, *Tetrahedron Lett.*, 1976, 1296; *J. Am. Chem. Soc.*, 99, 1673 (1977) and references cited therein.
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- 4) G. Majetich, A. Casares, D. Chapman, and M. Behnke, *J. Org. Chem.*, 51, 1745 (1986).
- 5) a) T. Mukaiyama, M. Tamura, and S. Kobayashi, *Chem. Lett.*, 1986, 1017.
b) S. Kobayashi and T. Mukaiyama, *Chem. Lett.*, 1986, 221.
- 6) It was reported that trityl perchlorate is an effective catalyst for the allylation of acetals with allyltrimethylsilanes. T. Mukaiyama, H. Nagaoka, M. Murakami, and M. Ohshima, *Chem. Lett.*, 1985, 977.
- 7) In each case, the main product was the self-condensation product between α,β -unsaturated ketone and the silyl enol ether (5), because 5, the initial product, is more reactive toward the ketone than allyltrimethylsilane. Based on these observations, it was assumed that the above self-condensation reaction could be depressed by employing α,β -unsaturated ketones with moderately bulky substituents.
- 8) The stereochemistry was not determined.

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