

THE TRITYL PERCHLORATE CATALYZED MICHAEL REACTION

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In the presence of a catalytic amount of trityl perchlorate, 1,5-dicarbonyl compounds, the Michael adducts, are obtained in high yields by the reaction of silyl enol ethers with α,β -unsaturated ketones. The intermediate adducts, the synthetically valuable silyl enol ethers, are also isolated in high yields.

Recently, we have demonstrated that trityl perchlorate effectively catalyzes the glycosylation reactions¹⁾ and the aldol reactions.²⁾ We also found that various trityl salts (such as TrOTf , TrSbCl_6 , TrSnCl_5 , TrPF_6 , etc.) are also effective and the counter anions of these trityl salts have an influence on the stereochemistry in the aldol reaction.³⁾ In the course of our continuous investigations to explore useful synthetic reactions by utilizing trityl salts, we have now found that it also activates α,β -unsaturated ketones. In this communication, we wish to describe the trityl perchlorate catalyzed Michael reaction, and also the isolation of the intermediate adduct, the synthetically valuable silyl enol ether.

In the first place, the reaction of trimethyl silyl enol ether of acetophenone with 2-cyclohexene-1-one was tried in the presence of a catalytic amount of trityl salts (5 mol %) such as TrClO_4 , TrOTf , TrSbCl_6 , TrSnCl_5 , etc. In each case, the Michael reaction proceeded smoothly at -78°C to give the corresponding 1,5-dicarbonyl compound in good yields, and no 1,2 addition product was detected.⁴⁾ Among various trityl salts screened, trityl perchlorate gave the best yield. Other examples are shown in the Table 1.

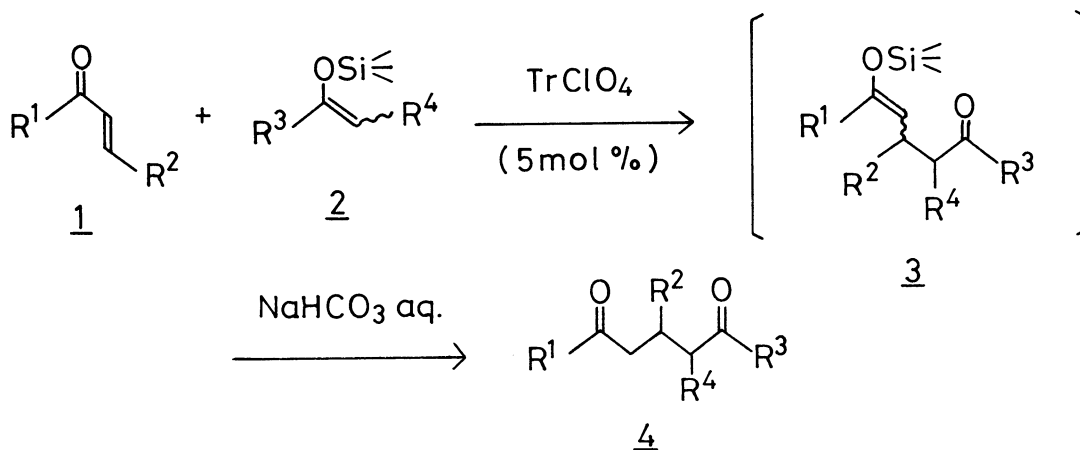


Table 1. The reaction of silyl enol ethers with α, β -unsaturated ketones^{a)}

Entry	α, β -Unsaturated ketone	Silyl enol ether	Yield/%
1			91
2			89
3			73 ^{b)}
4			87
5			92
6			78
7			90

a) All products gave satisfactory NMR and IR spectra.

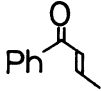
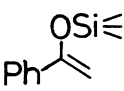
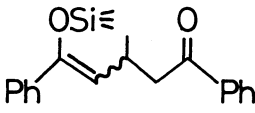
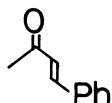
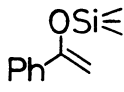
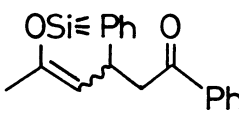
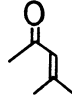
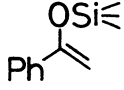
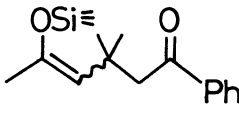
b) A mixture of diastereomers.

A typical procedure for the reaction of a silyl enol ether with an α, β -unsaturated ketone is as follows; the mixture of a silyl enol ether (0.55 mmol), an α, β -unsaturated ketone (0.5 mmol), and trityl perchlorate (0.025 mmol, 5 mol %) in dichloromethane (4 ml) was stirred at -78°C . After the reaction was completed, aqueous sodium hydrogen carbonate was added and extracted with dichloromethane. The organic layer was dried and the solvent was removed under reduced pressure. The residue was separated by silica gel column chromatography.

Next, we tried to isolate the synthetically useful intermediate, silyl enol ether (3).⁵⁾ It was detected by thin layer chromatography in the reaction mixture, and the addition of aqueous sodium hydrogen carbonate resulted in the formation of (4). After examination of various conditions of quenching the reaction mixture, we found that the use of pyridine instead of aqueous sodium

hydrogen carbonate gave the satisfactory yield of the intermediate silyl enol ether (Table 2). In each case, single isomers were obtained exclusively.⁶⁾

Table 2. Isolation of the silyl enol ethers

Entry	α,β -Unsaturated ketones	Silyl enol ether	Product	Yield/%
a				85
b				88
c				87

Concerning the Michael reaction using silyl enol ethers, the first example was reported from our laboratory by using titanium tetrachloride as a promoter.⁷⁾ After that, a heterogeneous CsF-catalyzed addition was also reported.⁸⁾ In these reactions, however, the synthetically valuable intermediate, the silyl enol ether (3) cannot be isolated.

It is noted that, according to the present method, both the Michael adducts, 1,5-dicarbonyl compounds, and the intermediate silyl enol ethers are obtained in high yields by treating silyl enol ethers with α,β -unsaturated ketones in the presence of a catalytic amount of trityl perchlorate.

Further investigations leading to the tandem reactions using the intermediate adduct, the silyl enol ether (3), are now in progress.

References

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- 2) T. Mukaiyama, S. Kobayashi, and M. Murakami, Chem. Lett., 1984, 1759; 1985, 443.
- 3) Unpublished results.
- 4) In the case of the reaction of silyl enol ethers with α,β -unsaturated aldehydes, both 1,2 and 1,4 addition products were produced.
- 5) In the reaction between ketene silyl acetals and α,β -unsaturated ketones, the intermediate silyl enol ether has been isolated. Y. Kita, J. Segawa, J. Haruta, H. Yasuda, and Y. Tamura, J. Chem. Soc., Perkin Trans. 1, 1982, 1099; T. V. RajanBabu, J. Org. Chem., 49, 2083 (1984).
- 6) These products are presumed to be cis forms. See, C. H. Heathcock, C. T. Buse, W. A. Kleschick, M. C. Pirrung, J. E. Sohn, J. Lampe, J. Org. Chem., 45, 1066 (1980).

Physical data of the silyl enol ethers 3a, 3b, 3c are as follows.

3a: ^1H NMR (CCl_4) 0.9 (d, $J=7$ Hz, 3H), 2.7 (m, 2H), 3.0 (m, 1H), 4.8 (d, $J=9$ Hz, 1H); ^{13}C NMR (CDCl_3) 20.8, 27.8, 46.0, 116.0, 148.8, 199.3; IR (neat) 1685cm^{-1} .

3b: ^1H NMR (CCl_4) 1.5 (s, 3H), 3.0 (d, $J=6$ Hz, 2H), 4.2 (m, 1H), 4.5 (d, $J=9$ Hz, 1H); ^{13}C NMR (CDCl_3) 22.4, 38.0, 46.0, 111.1, 147.0, 198.4; IR (neat) 1690cm^{-1} .

3c: ^1H NMR (CDCl_3) 0.9 (s, 6H), 1.4 (s, 3H) 2.9 (s, 2H), 4.1 (s, 1H); ^{13}C NMR (CDCl_3) 23.4, 29.2, 33.9, 49.0, 145.8, 200.1; IR (neat) 1670cm^{-1} .

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