The Double Michael Reaction of  $\alpha$ , $\beta$ -Unsaturated Ketones with Siloxydienes Catalyzed by Trityl Perchlorate Forming Six-Membered Ring Systems

> Teruaki MUKAIYAMA, Yukihiro SAGAWA, and Shū KOBAYASHI Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

In the presence of a catalytic amount of trityl perchlorate, the double Michael reaction of  $\alpha$ , $\beta$ -unsaturated ketones with siloxydienes smoothly proceeds to afford six-membered ring systems stereoselectively in good yields. Decalin derivatives are also obtained according to this procedure.

In the previous papers,<sup>1,2)</sup> we have shown that the tandem reaction of the conjugate addition of silyl enol ethers to  $\alpha$ , $\beta$ -unsaturated ketones and the sequential aldol addition is carried out in one-pot to afford  $\gamma$ -acyl-substituted  $\delta$ -hydroxy ketone derivatives in high yields. This reaction is applied to the stereoselective synthesis of acyl-substituted dihydropyrans,<sup>1)</sup> tetrahydropyrans,<sup>1)</sup> and  $\delta$ -valerolactones.<sup>2)</sup> In the course of our investigations on the development of the trityl salts-catalyzed Michael reaction under non-basic conditions,<sup>3)</sup> it was assumed that the successive inter- and intramolecular Michael reactions would provide a useful method for the construction of the cyclic systems. In this communication, we wish to describe the trityl perchlorate catalyzed double Michael reaction of  $\alpha$ ,  $\beta$ -unsaturated ketones with siloxydienes leading to six-membered ring compounds.

In the first place, the reaction of benzalacetone with 2-trimethylsiloxy-1,3butadiene was chosen as a model and the reaction parameters such as solvent, reaction time, reaction temperature, the amounts and the kinds of trityl salts, siloxy groups, the order of addition, and addition time etc. were examined. It was found that the best result was obtained when benzalacetone and the siloxydiene were simultaneously added to the dichloromethane solution of trityl perchlorate<sup>4</sup> (5 - 10 mol\$) at -78 °C. The desired 3,4-disubstituted cyclohexanone derivative  $(\underline{1})$  was obtained in 62% yield, and the stereochemistry of this adduct was assigned as trans on the basis of its <sup>1</sup>H NMR spectra<sup>5</sup> and no cis adduct was detected in this reaction.

Several examples are demonstrated in Table 1. In every case, cyclohexanone derivatives are obtained in good yields. Since only a single isomer was isolated, the remarkable stereocontrol could be achievable in the present reaction. Concerning the relative stereochemical relationship between two or three contiguous chiral centers on six-membered rings, corresponding trans or trans-cis isomers were obtained respectively. Furthermore, this procedure is easily applied to cyclic enone systems, for example, decalin structure, which are versatile intermediates for the syntheses of various sesquiterpenes, diterpenes, steroids etc., are also obtained in good yields, while the Diels-Alder reaction to give the corresponding compounds requires drastic conditions and prolonged reaction times giving the adducts in rather low yields.<sup>5)</sup>



Table 1. Double Michael reaction of  $\alpha$ , $\beta$ -unsaturated ketones with siloxydienes

Entry	α,β-Unsaturated ketone	Siloxydiene	Product <sup>a)</sup>	Yield/%
1	O Ph	OSIĘ	Ph ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	62
2	Ph	OSi	Ph Do	68
3	Ph	OSIĘ Ph	Ph Ph	72
4	Ph	OSIĘ Ph	Ph	78
5	Ů	OSI = Ph	O Ph +isomer <sup>b</sup> )	74
6	Ů	OSi		55

a) Only one isomer was obtained except for entry 5.

b) Though the minor product was confirmed to be a single isomer, its stereostructure was not assigned.

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A typical procedure for the reaction of siloxydienes with  $\alpha,\beta$ -unsaturated ketones is as follows: a mixture of an  $\alpha,\beta$ -unsaturated ketone (0.4 mmol), a siloxydiene (0.52 mmol), and trityl perchlorate (5 - 10 mol%) in dichloromethane (3 ml) was stirred at -78 °C for 2 - 3 h. Aqueous sodium hydrogencarbonate was added and the aqueous layer was extracted with dichloromethane. Then the solvent was removed under reduced pressure and the residue was treated with the solution of THF and 1 mol dm<sup>-3</sup> HCl aq. (5:1) at room temperature. After usual work-up, the crude cyclohexanone derivative was purified by silica gel column chromatography.

Although the regio- and stereoselectivity of the present reaction are the same as those of the Diels-Alder reaction, accumulated experimental data suggest otherwise. We now assume the stepwise mechanism of the successive inter- and intramolecular Michael reactions. Namely, siloxydienes react with  $\alpha$ , $\beta$ unsaturated ketones, in the first step, to afford the corresponding silyl enol ethers, which contain the functionality of  $\alpha$ ,  $\beta$ -unsaturated ketone in their molecules. In the second step, the intramolecular Michael additions take place in these silyl enol ethers to produce cyclohexanone derivative. It is noteworthy to point out that the activation of  $\alpha$ ,  $\beta$ -unsaturated ketones by a catalytic amount of trityl perchlorate is essential in this reaction. Actually, when the competition reaction of each 1 equivalent of benzalacetone and diethyl fumarate with 2trimethylsiloxy-4-phenyl-1,3-butadiene was carried out in the presence of a catalytic amount of trityl perchlorate, only the adduct of the former reaction was obtained and diethyl fumarate was recovered almost completely. This result is in marked contrast to that of the corresponding thermal reaction, in which the conventional Diels-Alder adduct of the latter reaction was obtained.



The present reaction has the advantage over the similar double Michael type reaction of Li enolates<sup>7)</sup> and the Diels-Alder reaction,<sup>8)</sup> in the extreme mildness of the reaction conditions. It smoothly proceeds even at -78 °C under almost neutral conditions and the products were obtained with high stereoselectivity. On the other hand, the reactions of Li enolates was carried out under strongly basic conditions, and the conventional Diels-Alder reactions often require high reaction temperature, prolonged reaction time, or a stoichiometric amount of Lewis acids. Recently there have been reported the improved Diels-Alder reaction of cyclic enone systems.<sup>9)</sup> However, even in this case, the reaction proceeds at the temperature range of 20 - 70 °C in the presence of a stoichiometric amount of aluminium chloride, and the side reaction, acid-induced isomerization of the

product, was accompanied. On the contrary, the present reaction proceeds at -78 °C in the presence of a catalytic amount of trityl perchlorate, no isomerization of the adducts are observed, and the products may be obtained under kinetic control.

Further progress leading to natural products by the use of this reaction is now in progress.

## References

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