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[1,2-Benzenediolato(2-)-O,O']oxotitanium. A Mild and Efficient Catalyst for the Michael Reaction of Ketene Silyl Acetals with α,β-Unsaturated Ketones

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In the presence of a catalytic amount of [1,2-benzenediolato(2-)-O,O']oxotitanium, ketene silyl acetals smoothly react with α,β-unsaturated ketones to afford the corresponding Michael adducts in high yields.

Ketene silyl acetals have been attracted much attention as useful carbon nucleophiles in synthetic reactions.1) It was already shown that the ketene silyl acetals react with α,β-unsaturated ketones to give the corresponding Michael adducts by the promotion of typical Lewis acids such as $TiCl_4$, $SnCl_4$, etc.,2) or thermally in acetonitrile.3) Although several examples have been reported that reactions are carried out under mild conditions by the use of tris-(dimethylamino)sulfonium difluorotrimethylsiliconate (TASF)4) or a catalytic amount of trityl salts,5) it is strongly desired to explore a new catalyst which promotes the reaction under almost neutral conditions.

In the course of our investigations to search for a novel and mild catalyst, we focused on titanium tetraalkoxides. Although titanium tetraalkoxides are frequently employed in transesterifications as "neutral" Lewis acid catalyst,6) there has been no report on their possible use in carbon-carbon bond forming reactions. Here, we would like to describe the first example, as far as we know, that [1,2-benzenediolato(2-)-O,O']oxotitanium behaves as such an extremely mild and efficient catalyst to promote the above-mentioned Michael reaction at low temperature.

First, various titanate derivatives were screened taking the reaction of t-butyldimethylsiloxy-1-methoxyethene and chalcone as a model (Table 1).

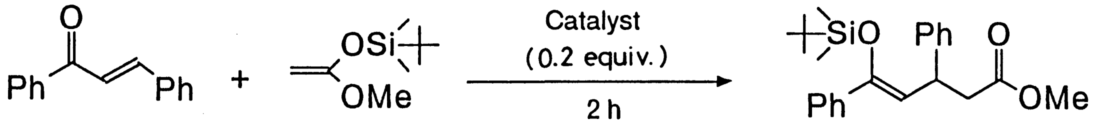
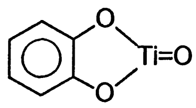


Table 1. Effect of catalyst and solvent

Entry	Catalyst		Solvent	Temperature	Yield / %
1	$(i\text{-}PrO)_4Ti$	1	CH_2Cl_2	-78 °C → r.t.	0
2	$(i\text{-}PrO)_2Ti{=}O$	2	CH_2Cl_2	-78 °C → r.t.	0
3	$(PhO)_2Ti{=}O$	3	CH_2Cl_2	-78 °C	88
4		4	CH_2Cl_2	-78 °C	95
5	4		Toluene	-78 °C	90
6	4		Et_2O	-78 °C	90
7	4		THF	-78 °C	92
8	4		CH_3CN	-23 °C	91

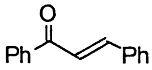
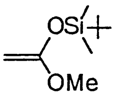
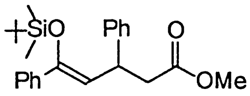
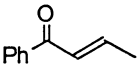
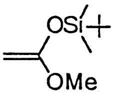
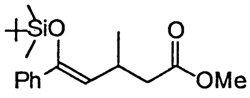
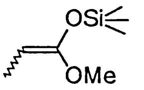
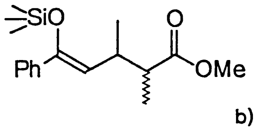
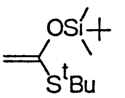
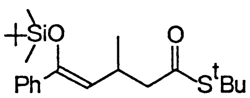
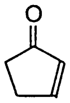
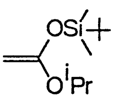
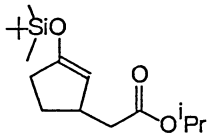
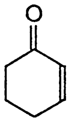
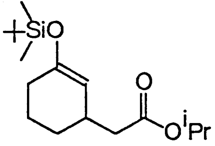
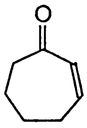
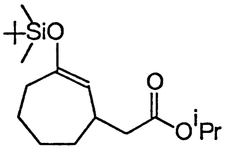
In case of titanium tetraisopropoxide 1, no reaction took place even at room temperature. Bis(2-propanolato)oxotitanium 2 was also ineffective, however, both phenolato oxides 3 and 4 were turned out to be operative.7) Catalyst 4 with a rigid ring structure gave somewhat better result compared with 3.

Moreover, in the presence of 4 (0.2eq), the reaction proceeded smoothly at -78 °C not only in CH_2Cl_2 but also in toluene, Et_2O and THF, different from the same reaction promoted by typical acid catalysts. Acetonitrile also served as an efficient solvent at -23 °C.8)

Several examples of the Michael reactions are demonstrated in Table 2. In every case, the reactions proceeded at -78 °C and the adducts were isolated as silyl enol ethers in high yields.

A typical procedure is described for the reaction of t-butyldimethylsiloxy-1-methoxyethene with chalcone; [1,2-benzenediolato(2-)-O,O']oxotitanium (19 mg; 0.1 mmol) was dissolved in dichloromethane (2 cm^3) and cooled to -78 °C. t-Butyldimethylsiloxy-1-methoxyethene (113 mg; 0.6 mmol), chalcone (104 mg; 0.5

Table 2. The Michael reaction catalyzed by 4

α, β - Unsaturated ketone	Ketene silyl acetal	Product	Yield / %
			95
			83
	 (E/Z=89/11)$^{b)}$	 (ul/lk=54/46)$^{b)}$	79
			87
			87
			93
			75

a) All products gave satisfactory NMR and IR spectral data.
b) Determined by GC.

mmol) in dichloromethane (3 cm^3) were added dropwise and a mixture was stirred for 2 h. The reaction was quenched with phosphate buffer(PH=7). After removal of insoluble materials by filtration, the aqueous layer was extracted with dichloromethane. The organic layer was dried and the solvent was removed under reduced pressure. The residue was purified by preparative thin layer chromatography on silica gel (20:1=hexane:ethyl acetate as a developing solvent) to give the product (187 mg; 95%).

Thus, [1,2-benzenediolato(2-)-O,O']oxotitanium is shown to be an efficient catalyst in the Michael reaction of ketene silyl acetals with α,β-unsaturated ketones. It should be noted that the present catalyst can be used in various solvents and the reactions proceed under extremely mild conditions to afford the corresponding adducts in their silyl enol ether forms.

Currently we are investigating further possibilities of this mild catalyst in synthetic reactions.

References

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7) Catalyst 2 was synthesized by the procedure similar to that described for $(EtO)_2Ti=O$.[9] 3 and 4 were prepared by mixing a stoichiometric amount of phenol or catechol with 2 in benzene, followed by azeotropic removal of resulting 2-propanol. V. V. Lukachina, Ukr. Khim. Zh. (Russ. Ed.), 53, 382 (1987); Chem. Abstr., 108, 176209n (1987).

8) No reaction occurred at this temperature without 4.

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