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THE MICHAEL TYPE REACTION OF O-SILYLATED KETENE ACETALS WITH α,β-UNSATURATED CARBONYL COMPOUNDS PROMOTED BY TITANIUM TETRACHLORIDE

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O-Silylated ketene acetals reacted with α,β-unsaturated carbonyl compounds at -78°C in the presence of $TiCl_4$ or in the coexistence of $TiCl_4$ and $Ti(OPr\text{-}i)_4$ to afford the corresponding δ-ketoesters in good yields.

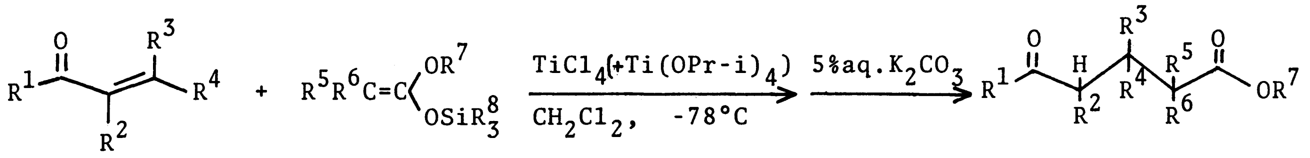
In the previous paper,[1] it was shown that β-hydroxyesters are obtained in good yields by the $TiCl_4$-promoted reaction of O-silylated ketene acetals with various carbonyl compounds. Recently, it was reported from our laboratory that silyl enol ethers react with α,β-unsaturated carbonyl compounds or their acetals in the presence of $TiCl_4$ or in the coexistence of $TiCl_4$ and $Ti(OPr\text{-}i)_4$ to afford the corresponding 1,5-dicarbonyl compounds or their mono acetals in good yields.[2] In this communication, we wish to report a convenient method for the preparation of δ-ketoesters by the Michael type reactions of O-silylated ketene acetals with α,β-unsaturated carbonyl compounds.

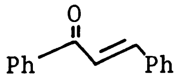
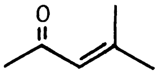
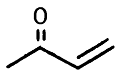
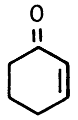
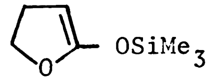
In a typical experiment, to a dichloromethane (5 ml) solution of benzalacetophenone (208 mg, 1 mmol) was added a dichloromethane (2 ml) solution of $TiCl_4$ (209 mg, 1.1 mmol) at -78°C under an argon atmosphere. After stirring for 15 min, a dichloromethane (1 ml) solution of benzylketene methyl trimethylsilyl acetal (260 mg, 1.1 mmol) was added dropwise to the solution, and the mixture was stirred for 3 hr. The reaction mixture was quenched with 5% aq. K_2CO_3, filtered and extracted with ethyl acetate. After concentration of the organic layer, thin layer chromatography (silica gel) afforded methyl 2-benzyl-3,5-diphenyl-5-oxopentanoate in 90% yield.

In a similar manner, several δ-ketoesters were obtained in good yields by the reaction of benzalacetophenone or mesityl oxide with several O-silylated ketene acetals as shown in the Table.

On the other hand, when methyl vinyl ketone or cyclohexenone, which is very sensitive toward $TiCl_4$, was employed as a Michael acceptor, the desired product was obtained in a low yield and polymeric substance resulted exclusively. This problem was overcome by using $TiCl_4$ and $Ti(OPr\text{-}i)_4$ together for the promotion of the present reaction to yield the corresponding adduct in excellent yields (see the Table).

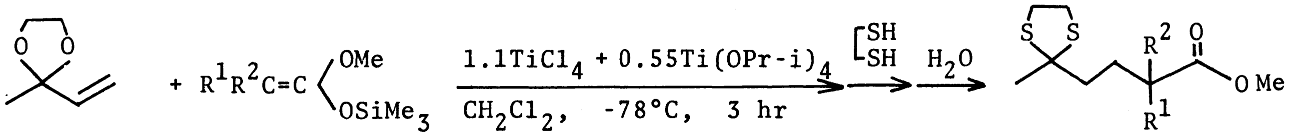
Moreover, it was found that the present $TiCl_4$-promoted Michael reaction was applicable to the reaction of acetals of α,β-unsaturated carbonyl compounds with O-silylated ketene acetals. For instance, in the case of the reaction of methyl vinyl ketone ethylene acetal with benzylketene methyl trimethylsilyl acetal or dimethylketene methyl trimethylsilyl acetal, δ-ketoester ethylene thioacetal[3]



Michael Acceptor (1.0 mmol)	O-Silylated Ketene Acetal (1.1 mmol)	$TiCl_4$ (mmol)	$Ti(OPr\text{-}i)_4$ (mmol)	Reaction Time (hr)	δ-Ketoester[3] Yield (%)
	$PhCH_2CH{=}C(OMe)OSiMe_3$	1.1	——	3	90
	$Me_2C{=}C(OMe)OSiMe_3$	1.1	——	5	quant
	$CH_2{=}C(OEt)OSiMe_2Bu\text{-}t$	1.1	——	3	98
	$PhCH_2CH{=}C(OMe)OSiMe_3$	1.1	——	3	79
	$Me_2C{=}C(OMe)OSiMe_3$	1.1	——	3	72
	$PhCH_2CH{=}C(OMe)OSiMe_3$	1.1	——	3	0*
		1.1	0.55	3	38
	$PhCH_2CH{=}C(OMe)OSiMe_3$	1.1	0.55	3	81
	$Me_2C{=}C(OMe)OSiMe_3$	1.1	0.55	3	74
		1.1	0.55	3	82

* Only unknown polymeric substance resulted.

was obtained in 62% or 90% yield, respectively, by quenching successively with ethanedithiol and 5% aq. K_2CO_3.



$R^1 = PhCH_2,\ R^2 = H$

$R^1 = R^2 = Me$

Concerning the preparation of δ-ketoester, it is usually performed by the reaction of carbonyl compound with α,β-unsaturated ester under basic and rather drastic conditions, but, there is no report about the reaction of ester enolates with α,β-unsaturated carbonyl compounds except for the case of malonate.

It should be noted that the present Michael type reaction of O-silylated ketene acetals with α,β-unsaturated carbonyl compounds provides a convenient and useful method for the preparation of δ-ketoesters.

References

1) K. Saigo, M. Osaki, and T. Mukaiyama, Chem. Lett., 989 (1975). 2) K. Narasaka, K. Soai, and T. Mukaiyama, Chem. Lett., 1223 (1974). K. Narasaka, K. Soai, Y. Aikawa, and T. Mukaiyama, Bull. Chem. Soc. Japan, submitted for publication.
3) All compounds exhibited ir and nmr spectrum data in accordance with assigned structures.

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