

Clay Montmorillonite-catalysed Michael Reactions of Silyl Ketene Acetals and a Silyl Enol Ether with α,β -Unsaturated Carbonyl Compounds

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In the presence of the clay montmorillonite, silyl ketene acetals and a silyl ether react with α,β -unsaturated esters and ketones to afford the corresponding Michael adducts in the form of the silyl ketene acetals and silyl enol ethers in good yields.

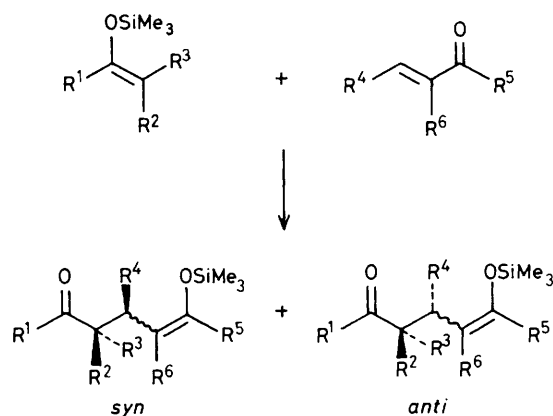
There has been extensive investigation recently on conjugate addition of silyl ketene acetals and silyl enol ethers to α,β -unsaturated ketones. The reaction is generally performed with the aid of a stoichiometric amount of a Lewis acid to afford 1,5-dicarbonyl compounds.¹ The intermediate adducts

are also isolable in the form of synthetically valuable silyl enol ethers when the reaction is accomplished thermally in acetonitrile,² under high pressure,³ or by use of $(\text{Me}_2\text{N})_3\text{S}^+\text{Me}_3\text{SiF}_2^-$ ⁴ or Ph_3CClO_4 .⁵ However, the only example of the Michael reaction of silyl ketene acetals with

Table 1. The reactions of silyl ketene acetals and a silyl enol ether with Michael acceptors (Scheme 1).^a

Entry	Nucleophile			Michael acceptor			Temp./°C (Time/h)	Product	
	R ¹	R ²	R ³	R ⁴	R ⁵	R ⁶		% Yield	syn : anti ^b
1	MeO ^c	Me	H	Me	OMe	H	-78 (0.5)	84	27 : 73
2	MeO ^d	H	H	Me	OMe	H	-50 (1)	86	—
3	MeO	Me	Me	Me	OMe	H	-10 (1)	52 ^e	—
4	MeO ^c	Me	H	Ph	OMe	H	-50 (0.5)	91	61 : 39
5	MeO ^c	Me	H	H	OMe	Me	-50 (1)	79	—
6	MeO ^c	Me	H	MeCH=CH ^f	OMe	H	-50 (0.5)	96 ^g	39 : 61
7	EtO ^h	Me	H	EtO ₂ C	OEt	H	-78 (0.5)	85	42 : 58
8	EtO ^h	Me	H	-[CH ₂] ₃ -		H	-78 (0.5)	91	57 : 43
9	Et ⁱ	Me	H	Ph	Me	H	-78 (1)	98	29 : 71
10	Et ⁱ	Me	H	Ph	Me	H	-30 (0.8)	81 ^j	21 : 79

^a Nucleophile (1 mmol), Michael acceptor (1 mmol), Al-Mont (0.2 g), CH₂Cl₂ (4 ml). ^b Relative stereochemistry of the two newly created chiral carbon centres. Ratios were determined after hydrolysis of the parent products with dilute HCl to the 1,5-dicarbonyl compounds. The stereostructures were assigned by comparison with authentic samples prepared according to the literature.^{1c,5b,9} ^c *E/Z* = 61 : 39. ^d OSiMe₂Bu^t instead of OSiMe₃. ^e 0.5 g of Al-Mont was used. A hydrolysed product, dimethyl 2,2,3-trimethylglutarate, was also obtained (18% yield). ^f *trans*. ^g The ratio of 1,4-adduct to 1,6-adduct was 98 : 2. ^h *E/Z* = 80 : 20. ⁱ *E/Z* = 83 : 17. ^j 1,2-Dimethoxyethane was used as solvent.

**Scheme 1**

ketene acetals or silyl enol ethers in good yields and with moderate diastereoselectivity. Especially in the case of methyl sorbate (entry 6), the preferential 1,4-addition (98%) over 1,6-addition is notable because the lithium enolate-mediated reaction gave a mixture (70 : 30) of 1,4- and 1,6-adducts.⁹

In the present method the Al-Mont catalyst is easily separable from the organic products by filtration, so that simple distillation is all that is required to furnish pure products. Al-Mont thus enables silyl ketene acetals to react with α,β -unsaturated esters to create new silyl ketene acetals effectively.

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α,β -unsaturated esters was reported in the study of group-transfer polymerization by use of (Me₂N)₃S⁺Me₃SiF₂⁻⁶ or Lewis acids.⁷

Previously we have shown that the clay montmorillonite is an efficient, heterogeneous catalyst for the aldol reaction between silyl enol ethers and aldehydes or acetals.⁸ Here we describe the Michael reactions of silyl ketene acetals with enoates and enones catalysed by aluminium cation-exchanged montmorillonite (Al-Mont).[†]

The results are listed in Table 1. The Michael reactions were promoted by Al-Mont at low temperatures to give the corresponding adducts (1,4 exclusively) in the form of silyl

[†] The following procedure is typical (Table 1, entry 4). Al-Mont (0.2 g) was dried at 120 °C and 0.5 Torr for 3 h, and then cooled to -78 °C under nitrogen. A solution of methyl cinnamate (1 mmol) in CH₂Cl₂ (4 ml) was added. After stirring for 1 min, a solution of 1-methoxy-1-trimethylsiloxypropene (1 mmol) in CH₂Cl₂ (1 ml) was added. The temperature was then raised to -50 °C, the mixture was stirred for 0.5 h, and cold ether (5 ml) was added. The Al-Mont catalyst was filtered off through a Celite pad and washed with ether. The organic layer was evaporated and distilled on a Kugelrohr apparatus to yield methyl 5-methoxy-2-methyl-3-phenyl-5-trimethylsiloxy-pent-4-enoate (91% yield).

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- A control experiment resulted in 37% yield of 1,4- and 1,6-addition products in a ratio of 70 (*syn* : *anti* = 95 : 5) : 30; procedure as in M. Yamaguchi, M. Tsukamoto, S. Tanaka, and I. Hirao, *Tetrahedron Lett.*, 1984, **25**, 5661.