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THE METHOXYCARBONYLALKYLATION AND METHOXYCARBONYLALKYLIDENATION OF SILYL ENOL ETHERS[1]

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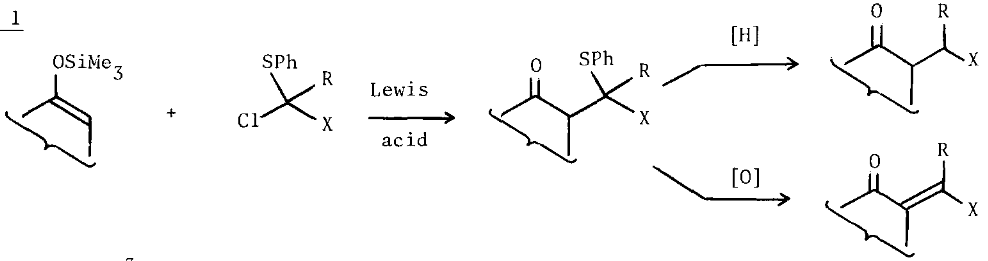
Summary—Silyl enol ethers (**1**) react with the phenylthio(methoxycarbonyl)alkyl chlorides (**2**) in the presence of Lewis acids to give good yields of the γ-ketoesters (**3**); oxidative and reductive desulphurisations give the saturated (**4**) and unsaturated (**5** or **6**) γ-keto esters, respectively.

We reported earlier[2] that phenylthioalkylation of silyl enol ethers, using phenylthioalkyl chlorides and Lewis acid catalysis, was a powerful method for the regiocontrolled primary alkylation and alkylidenation of ketones and esters (Scheme 1). In our work so far the group X has been hydrogen.[3] We now report that the group X may be methoxycarbonyl, making the synthesis of saturated (**4**) and unsaturated (**5** or **6**) γ-ketoesters particularly easy (Scheme 2).[4] The reaction is regiocontrolled (entries 5 and 6 in the Table) and the starting materials (**2**) are easy to make by chlorination (NCS, CCl_4, r.t., 10 h) of the corresponding α-phenylthioesters. The reaction conditions are closely similar to those used by us earlier.[2] The oxidative desulphurisation (**3** → **5** or **6**) usually gave the fully conjugated product (**5**), but when R^2 was not hydrogen and R^3 was a methyl group, the cycloelimination of phenylsulphenic acid took place towards the methyl group, and gave the α-methylene ester (**6**). The alkylation step was not successful with silyl enol ethers derived from aldehydes or lactones.

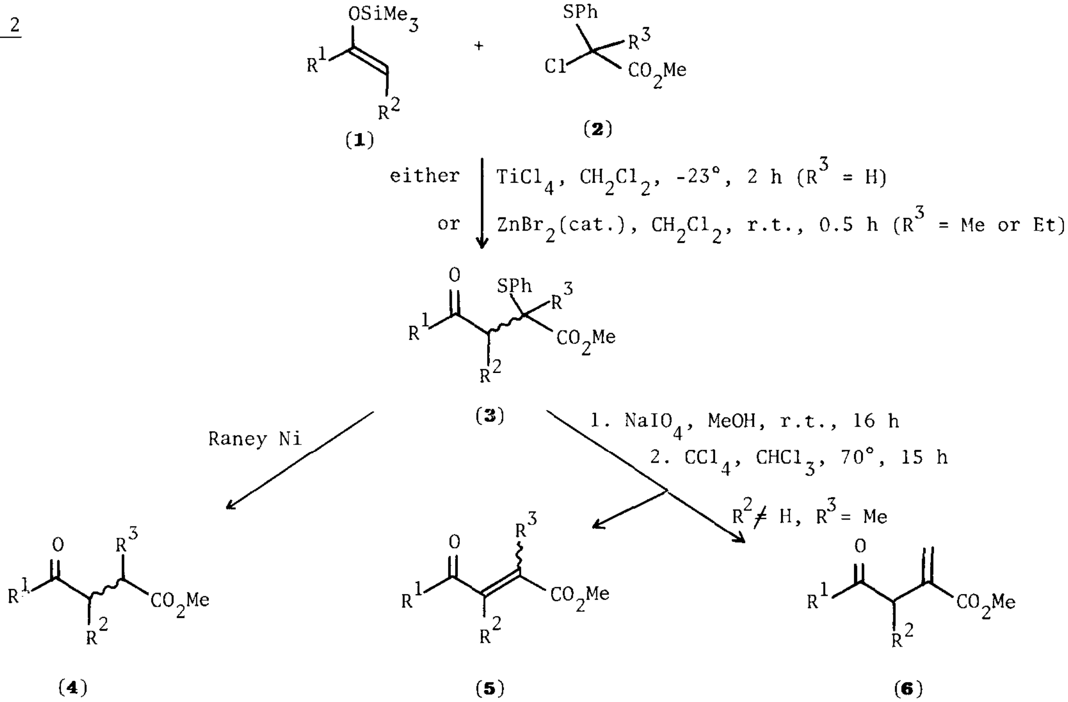
Scheme 1



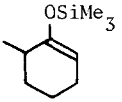
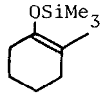
NOTES and REFERENCES

1. No reprints available.
2. I. Paterson and I. Fleming, *Tetrahedron Lett.*, 995 and 2179 (1979); I. Fleming, J. Goldhill, and I. Paterson, *ibid.*, 3209; I. Fleming and T. V. Lee, *ibid.*, **22**, 705 (1981); I. Fleming and D. A. Perry, *Tetrahedron*, **37**, 4027 (1981); H. A. Khan and I. Paterson, *Tetrahedron Lett.*, **23**, 2399 (1982). See also, N. Ono, H. Miyake, and A. Kaji, *Synthesis*, 1003 (1981).
3. For secondary thioalkylation, see, M. T. Reetz and A. Giannis, *Synth. Commun.*, **11**, 315 (1981).
4. The combination of an α-chloro-α-phenylthio*ketone* and a silyl enol ether has been shown to give furans: R. Tanikaga, K. Miyashita, H. Sugihara, and A. Kaji, *J. Chem. Soc. Chem. Commun.*, 1106 (1981).

Scheme 2



Table

Silyl enol ether (**1**) R^1	 R^2	Phenylthioalkyl chloride (**2**) R^3	Yield % (**3**)	Yield % (**4**)	Yield % (**5**)	Yield % (**6**)
Ph	H	H	79	92	83	
Ph	Me	H	88	83	91	
Et	Me	H	78	81	90	
(CH$_2$)$_4$		H	88	91	85	
		H	69	93	81	
		H	78	83	-	
Ph	H	Me	83	77	78	
Ph	Me	Me	78	69		81
Et	Me	Me	90	83		81
(CH$_2$)$_4$		Me	90	87		81
EtO	Me	Me	77	73		76
Ph	H	Et	83		77	

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