Organosilicon Chemistry in Synthesis: Silylcyclopropanation

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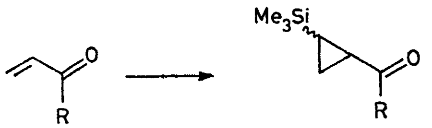
Summary αβ-Unsaturated ketones have been shown to react with trimethylsilylmethylene-sulphurane (**2**; X = SMe_2) to give silylcyclopropyl ketones.

As part of a programme concerned with using organosilicon chemistry in carbon–carbon bond-forming reactions,[1] we required a method of converting αβ-unsaturated carbonyl systems into the silylcyclopropyl ketones (**1**) (Scheme 1).

Whilst a few silylcyclopropanes are known no silylcyclopropyl ketones have been prepared previously.[2]



(1)

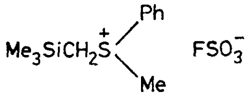
Scheme 1

A number of silylated ylides (**2**) have been described[3] although virtually no details of their reactions with organic substrates were disclosed.[3] Recently the reactions of a species presumed to be the ylide (**2**; X = SMe_2) were described, but the products obtained from reactions with saturated ketones and aldehydes indicated that desilylation had taken place to give the dimethylsulphonium methylide.[4]

$Me_3SiCH{=}X$

(2)

X = SMe_2, $S(O)Me_2$, $S(O)R{\cdot}NR_2$, SMePh, or PPh_3



$Me_3SiCH_2\overset{+}{S}(Ph)(Me)\ FSO_3^-$

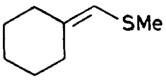
(3)

$Me_3SiCH_2\overset{+}{S}Me_2I^-$

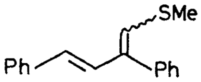
(4)

p-$MeC_6H_4CH{=}CHSMe$

(5)



(6)

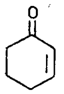
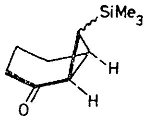
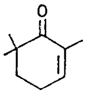
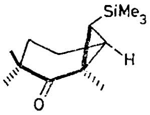
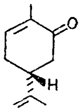
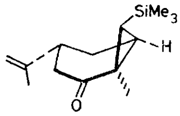
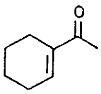
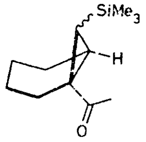
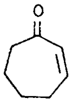
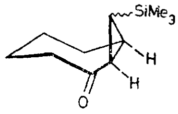
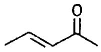
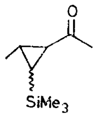
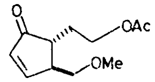
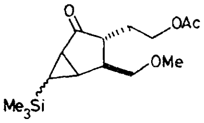
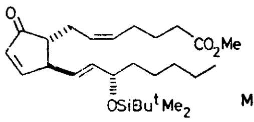
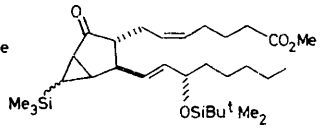


(7)

The ylide [**2**; X = $S(O)Me_2$] did not react with cyclohexenone under forcing conditions (tetrahydrofuran at reflux).[5] Phenylthiomethyltrimethylsilane was converted into the sulphonium salt (**3**), m.p. 84 °C (decomp.), which was deprotonated (Bu^sLi in tetrahydrofuran) to give the ylide (**2**; X = SPhMe). Treatment of this ylide with cyclohexenone under a variety of conditions gave complicated mixtures, although thioanisole was formed. Methylthiomethyltrimethylsilane was converted into the methiodide (**4**), and deprotonated (Bu^sLi in tetrahydrofuran; other bases gave unsatisfactory results). Treatment of the resulting ylide (**2**; X = SMe_2) with cyclohexenone gave 7-*exo*- and 7-*endo*-trimethylsilylbicyclo[4.1.0]heptan-2-one (7 : 1); other unsaturated ketones gave similar results (Table). The conditions described in the footnotes to the Table are the only ones that work adequately. In particular if Bu^tLi or Bu^nLi are used, no silylcyclopropanation results. The ylide (**2**; X = SMe_2), reacts with p-tolualdehyde and cyclohexanone to give the vinyl sulphides (**5**) and (**6**), respectively.

No trace of the corresponding $\alpha\beta$-epoxysilanes[1,4] could be detected, and neither could epoxides that would have resulted from the reaction of dimethylsulphonium methylide

Table

Substrate	Product	Yield (%)
		55[a]
		61
		36
		40[b]
		40
		65
		44
		40

[a] Bu^sLi (1·2 M in cyclohexane; 9·5 ml) was added slowly to a suspension of (**4**) (3·04 g) in dry tetrahydrofuran (20 ml) at −55 °C. The mixture was warmed to +10 °C, then cooled to −30 °C. Cyclohexenone (0·96 g) was added and the mixture allowed to warm to 15 °C. Work-up with sat. aqueous ammonium chloride, extraction (CH_2Cl_2), *etc.* gave 7-*exo*- and 7-*endo*-trimethylsilylbicyclo[4·1·0]heptan-2-one (55%), b.p. 68—69 °C at 0·3 mmHg; ν_{max} 1695, 1250, 970, 860, 840, 760, 690, and 645 cm^{-1}; τ 7·75—8·4 (8H, m), 9·6—9·7 (1H, m), and 9·92—9·98 (9H, d, in the ratio of 7 : 1 for the 7-*exo*- and 7-*endo*-epimers); 2,4-dinitrophenylhydrazone, m.p. 174—176 °C (C, H, and N analyses were satisfactory). [b] Requires 12 h at 40 °C for complete reaction.

with the above substrates. Surprisingly, chalcone, normally an excellent 1,4-acceptor, gave the vinyl sulphide (**7**) as the only product.

The method described here provides access to the new class of compounds, silylcyclopropyl ketones, that can be used in synthesis by exploiting the ability of the silicon atom to stabilize a β-carbonium ion (Scheme 2).

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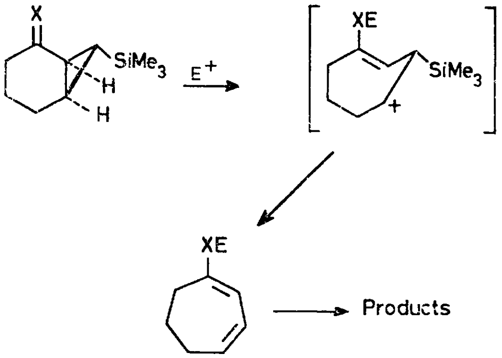

Scheme 2

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[1] C. Burford, F. Cooke, E. Ehlinger, and P. D. Magnus, *J. Amer. Chem. Soc.*, 1977, **99**, 4536; F. Cooke and P. D. Magnus, *J.C.S. Chem. Comm.*, 1977, 513; D. Ayalon-Chass, E. Ehlinger, and P. D. Magnus, *ibid.*, p. 772; P. D. Magnus and G. Roy, *ibid.*, 1978, 297.

[2] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, 1968, **90**, 1081; this paper describes 7-*exo*- and -*endo*-trimethylsilylbicyclo[4·1·0]heptane. Other unfunctionalized trimethylsilylcyclopropanes have been described: A. J. Ashe, *J. Amer. Chem. Soc.*, 1973, **95**, 818; H. Sakurai, A. Hosomi, and M. Kumada, *Tetrahedron Letters*, 1968, 2469; R. A. Olofson, D. H. Hoskin, and K. D. Lotts, *ibid.*, 1978, 1677;R. N. Haszeldine, D. L. Scott, and A. E. Tipping, *J.C.S. Perkin I*, 1974, 1440.

[3] For references to silylated ylides see: X = SMe$_2$, N. E. Miller, *Inorg. Chem.*, 1965, **4**, 1458; X = S(O)Me$_2$, H. Schmidbaur and W. Kapp, *Chem. Ber.*, 1972, **105**, 1203; X = PPh$_3$, H. Gilman and R. Tomasi, *J. Org. Chem.*, 1962, **27**, 3647; N. E. Miller, *J. Amer. Chem. Soc.*, 1965, **87**, 390; X = S(O)R·NR$_2$, H. Schmidbaur and G. Kammel, *Chem. Ber.*, 1971, **104**, 3252; H. Schmidbaur and H. Stühler, *Angew. Chem. Internat. Edn.*, 1973, **12**, 321.

[4] C. Fleischmann and E. Zbiral, *Tetrahedron*, 1978, 317. These authors describe the deprotonation of (**4**) using potassium t-butoxide in dimethyl sulphoxide. The supposed ylide (**2**; X = SMe$_2$) was treated with ketones to give mixtures of vinyl sulphides and epoxides. The epoxides would result from the reaction of dimethylsulphonium methylide with the carbonyl component. It should be noted that the electropositive silicon atom in (**4**) is readily attacked by bases (proton analogy in silicon chemistry) giving the desilylated ylide. In this work and our previous publications[1] the correct choice of base is crucial to the clean preparation of the desired reactive intermediates.

[5] Dimethylsulphoxonium methylide reacts with cyclohexenone to give 1,4-addition products, *i.e.* cyclopropanation, whereas dimethylsulphonium methylide only undergoes 1,2-addition, *i.e.* epoxidation; E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.