Silyl Thioketones and Silylated Thiirans

By BIANCA F. BONINI,* GERMANA MAZZANTI, SAURO SARTI, and PAOLO ZANIRATO
(*Istituto di Chimica Organica, Università, Viale Risorgimento* 4, 40136 *Bologna, Italy*)

and GAETANO MACCAGNANI*
(*Istituto C.N.R. dei Composti del Carbonio contenenti Eteroatomi*, 40064 *Ozzano Emilia, Bologna, Italy*)

Summary The preparation of silyl thioketones, and their reactions leading to silylated thiirans and other hitherto unknown silylated heterocycles, are reported.

DESPITE the considerable and perhaps still underestimated synthetic utility of organosilicon compounds,[1] one of the most reactive class,[2] at least in principle, of such compounds, silylated thioketones, has never been described. We report here the preparation and properties of compounds of this type.

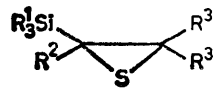
Anhydrous hydrogen chloride and hydrogen sulphide were bubbled for 10 min and 50 min, respectively, into a solution of phenyl trimethylsilyl ketone[3] in ether at −20 °C. The quantity of hydrogen chloride had to be carefully controlled in order to avoid loss of product. The reaction mixture gradually became blue and the conversion of the ketone into the thioketone was followed by t.l.c. The ether solution was washed with sodium hydrogen carbonate, dried, and chromatographed on Fluorisil under nitrogen. The thioketone (**1a**) was too unstable to allow its distillation or crystallisation and was therefore used as

$R^1_3Si–C(:S)–R^2$
(**1**)

	R^1	R^2
a	Me	Ph
b	Me	4-MeC_6H_4
c	Ph	Ph

crude material [n.m.r.: δ ($CDCl_3$) 0·4 ($SiMe_3$) and 6·7—8·2 (Ph); *m/e* 194 (M^+), 121 ($M^+ - Me_3Si$), and 73 (Me_3Si)]. Similar synthetic procedures were used for the thioketones (**1b**) and (**1c**).

The possibility of preparing, *via* silyl thioketones, some heterocyclic compounds which are otherwise difficult to obtain was explored. The reaction between the crude thioketones (**1**) and diphenyl- or di-*p*-methoxyphenyldiazomethane gave without difficulty the silylated thiirans (**2a—e**).[4] The overall yields for the conversion of the trimethylsilyl ketones into thiirans ranged between 70 and 90%. The triphenylsilyl ketone gave poorer yields. Structures (**2a—e**) were assigned on the basis of elemental analyses, and mass and n.m.r. spectra.

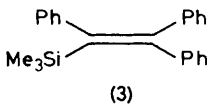


(**2**)

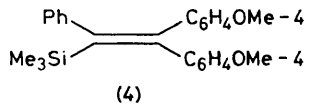
	R^1	R^2	R^3	M.p./°C
a	Me	Ph	Ph	104—105
b	Me	Ph	4-$MeOC_6H_4$	145—146
c	Me	4-MeC_6H_4	Ph	108—110
d	Me	4-MeC_6H_4	4-$MeOC_6H_4$	124
e	Ph	Ph	4-$MeOC_6H_4$	144

An independent proof of the structure of the silylthiirans (**2**) was provided by desulphurisation with triphenylphosphine to give the corresponding olefins. For instance (**2a**) and (**2b**) gave the hitherto unknown olefins (**3**) and (**4**) in 78% and quantitative yield, respectively.

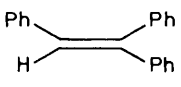
Desulphurisation of the thiiran (**2a**) by tetraethylammonium fluoride,[5] which can also lead to the cleavage of the carbon–silicon bond,[6] gave the known[7] olefin (**5**) in 60% yield. The olefin (**5**) was also obtained when (**3**) was desilylated with tetraethylammonium fluoride.



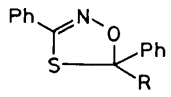
(**3**)



(**4**)

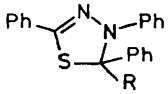


(**5**)



(**6**)

a; R = $SiMe_3$
b; R = H



(**7**)

a; R = $SiMe_3$
b; R = H

When phenyl trimethylsilyl thioketone (**1a**) was allowed to react with benzonitrile *N*-oxide (generated *in situ* from benzohydroximoyl chloride and triethylamine[8]) in ether at room temperature for 1 h, the 1 : 1 adduct (**6a**) was obtained (60% based on the ketone), m.p. 91—92 °C; *m/e* 313 (M^+), 298 (M^+ — Me), 240 ($M^+ - Me_3Si$), 210 (M^+ — PhCN), 135 (PhCNS), 121 (PhCS), 105 (PhCO), and 103 (PhCN).

The same thioketone (**1a**) with benzonitrile *N*-phenylimide generated *in situ*[9] gave the cycloadduct (**7a**) (55% based on the ketone), m.p. 146—148 °C; *m/e* 388 (M^+), 373 (M^+ — Me), 315 ($M^+ - Me_3Si$), 222 (PhCSNPh), 180 (PhCNPh), and 121 (PhCS).

Compounds (**6a**) and (**7a**) can be desilylated by tetraethylammonium fluoride to the heterocycles (**6b**) and (**7b**). Compound (**6b**) was unstable, and could be characterized only on the basis of its decomposition products benzonitrile and dibenzoyl disulphide. Compound (**7b**) could be isolated: m.p. 82—84 °C; δ ($CDCl_3$) 6·8 (**5-H**) and 7·0—8·3 (Ph); *m/e*[10]

316 (M^+), 239 (M^+ – Ph), 207 (M^+ – PhS), 194 (PhCNNPh), and 122 (PhCHS). It was slowly converted into *N*-phenylthiobenzamide and benzonitrile when kept.

All new compounds gave satisfactory analytical data.

(*Received, 6th March* 1981; *Com.* 251.)

[1] E. W. Colvin, *Chem. Soc. Rev.*, 1978, 15.
[2] F. Duus, 'Comprehensive Organic Chemistry,' ed. D. N. Jones, Pergamon, Oxford, 1979, Vol. 3, Part 11.22.
[3] E. J. Corey, D. Seebach, and R. Freedman, *J. Am. Chem. Soc.*, 1967, **89**, 434.
[4] Only 2-triphenylsilylthiiran is known: G. Barbieri, *J. Organomet. Chem.*, 1976, **117**, 157.
[5] Thiirans are desulphurized by fluoride ion in good yield, unpublished results.
[6] T. H. Chan, P. W. L. Lau, and M. P. Li, *Tetrahedron Lett.*, 1976, 2667.
[7] H. Adkins and W. Zartman, *Org. Synth.*, 1943, Coll. Vol. II, 606.
[8] R. Huisgen and W. Mack, *Chem. Ber.*, 1972, **105**, 2815.
[9] R. Huisgen, R. Gashey, M. Seidel, H. Kunpfer, and R. Schmidt, *Liebigs Ann. Chem.*, 1962, **658**, 169.
[10] S. Hammerum and P. Wolkoff, *J. Org. Chem.*, 1972, **37**, 3965.