# Bistrimethylsilylthioketen: a Versatile Reagent for Thioketen-based Syntheses

By Stephen J. Harris and David R. M. Walton
(*School of Molecular Sciences, University of Sussex, Brighton, Sussex* BN1 9QJ)

*Summary* The stable thioketen, $(Me_3Si)_2C{=}C{=}S$ (**1**), reacts with alcohols and amines to give *O*-alkyl thio-esters $Me_3SiCH_2C(S)OR$ (**2**), and thioamides, $Me_3SiCH_2C(S)NR_2$ (**3**), which can be desilylated or metallated for further use in synthesis; the isomeric $Me_3SiC{\equiv}CSSiMe_3$ (**8**) thermally rearranges to (**1**).

THE instability of thioketen[1] and its simpler derivatives[2] has confined the use of such compounds to syntheses based upon *in situ* generation and trapping techniques.[3] Stable molecules such as $Bu^t_2C{=}C{=}S$[4] and $(CF_3)_2C{=}C{=}S$[5] are known but contain substituents which are virtually impossible to transform or to remove.

We describe here the preparation and some reactions of bistrimethylsilylthioketen (**1**), a useful reagent which overcomes these limitations.

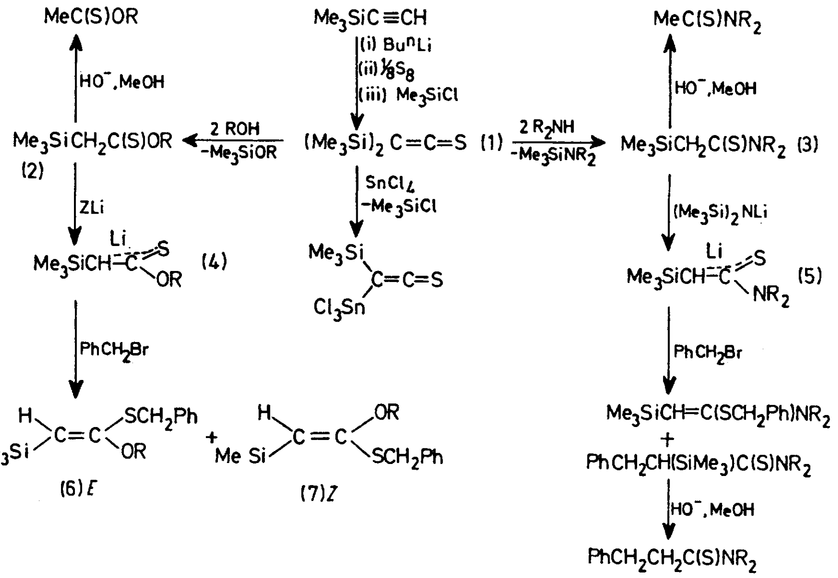
Trimethylsilylethynyl-lithium, when treated successively with sulphur and $Me_3SiCl$ in ether at −45 °C, gives pure (**1**) in 90% yield as a distillable yellow oil† which, unlike most thioketens,[2-4] does not dimerise or polymerise even upon

TABLE. Products from metallation–benzylation of *O*-ethyl *C*-trimethylsilylthioacetate.

| Metallating agent Z in ZLi | Temp. °C | Solvent | Product (%) (**6**)*E* | (**7**)*Z* |
|---|---|---|---|---|
| $Bu^n$ | −40 | Ether | 95 | 5 |
| $(Cyclohexyl)_2N$ | −80 | Ether | 84 | 16 |
| $Pr^i_2N$ | −10 to 0 | Tetrahydrofuran | 78 | 22 |
| $(Me_3Si)_2N$ | −80 | Ether | 8 | 92 |

---

† B.p. 45 °C at 1 mmHg; $n_D^{20}$ 1·5000; $\nu_{max}$ (film) 1757s (C=C=S) cm$^{-1}$; $\lambda_{max}$ (hexane) 218 (log ε 4·40), 263 (3·06), and 413 (1·04) nm; n.m.r.: $^1$H, δ($CCl_4$) 0·25 (s, $Me_3Si$); $^{13}$C, δ($CDCl_3$) +214·4 (C=S), +52·0 ($Si_2C$), and +0·8 ($Me_3Si$) p.p.m. (relative to $Me_4Si$).

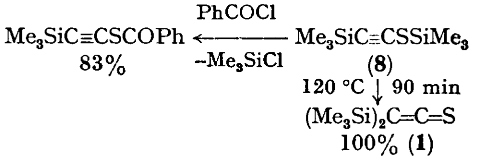


**Scheme.** R = Me, Et, or $Pr^i$. Addition of $Pr^i_2NH$ (but not $Pr^iOH$) to (**1**) requires acid catalysis which results in partial displacement of the second $Me_3Si$ group to give $MeC(S)NPr^i_2$.

prolonged heating (8 h, 140 °C). Compound (**1**) reacts exothermally with alcohols and with secondary amines at ambient temperatures to give *C*-trimethylsilyl *O*-alkyl thioesters (**2**) and thioamides (**3**), respectively, one $Me_3Si$ group always being displaced in the process.[‡] The products may be desilylated directly by treatment with slightly alkaline methanol,[§] or metallated to give the species (**4**) and (**5**) which can be alkylated. Thus, with benzyl bromide, (**4**), for example, yields keten monothioacetals [(**6**) and (**7**)] in accord with hard and soft acid and base principles.[6] The *E*(**6**) : *Z*(**7**) isomer ratio is strongly dependent upon the metallating agent used[7] (Table), and can be shifted subsequently (in favour of the *E* isomer) by treating the mixture with $Me_3SiBr$ and $HgBr_2$.[8] The intermediate (**5**) on the other hand, upon alkylation with benzyl bromide yields equimolar quantities of *C*-alkylated product and α-thioenamine (single isomer, see Scheme).

Removal of one $Me_3Si$ group from (**1**) by direct displacement (or by an addition–elimination sequence) is feasible as exemplified by the reaction with $SnCl_4$.

Interestingly, $Me_3SiBr$ with $Me_3SiC{\equiv}CSLi$ reacts at −45 °C to give the isomeric silylated alkynethiol, $Me_3SiC{\equiv}CSSiMe_3$ (**8**)[¶] in 80% yield. Compound (**8**), which may also be used in synthesis, is converted by heat into (**1**).



$$\begin{tikzcd}[column sep=large] \underset{83\%}{Me_3SiC{\equiv}CSCOPh} & \underset{(\mathbf{8})}{Me_3SiC{\equiv}CSSiMe_3} \arrow[l, "PhCOCl", "-Me_3SiCl"'] \arrow[d, "120\,^{\circ}C"', "90\ min"] \\ & \underset{100\%\ (\mathbf{1})}{(Me_3Si)_2C{=}C{=}S} \end{tikzcd}$$

The conversion (**8**) → (**1**) is not accelerated in solution by reagents (or products) involved in the preparation of (**1**). We believe that the production of (**1**) [or (**8**)] clearly represents discrimination by $Me_3SiCl$ or $Me_3SiBr$ for the two possible sites of attack upon the ambident species, $[R{\equiv}C\;C{=}S]^-Li^+$, present in solutions of alkynethiolate salts,[9] rather than initial generation of (**8**), followed by rearrangement to the thermodynamically more stable thioketen (**1**).

We thank Ciba-Geigy (U.K.) Ltd. for a maintenance award (to S.J.H.).

(*Received*, 28*th September* 1976; *Com.* 1100.)

---

[‡] Intermediates $(Me_3Si)_2CHC(S)OR$ and $(Me_3Si)_2CHC(S)NR_2$ cannot be detected. The latter may be prepared by treating (**5**) with $Me_3SiCl$; the resulting α-thioenamine $Me_3SiCH{=}C(SSiMe_3)NR_2$ rearranges slowly to the thioamide $(Me_3Si)_2CHC(S)NR_2$; see I. F. Lutsenko, Yu. I. Baukov, A. S. Kostyuk, N. I. Savelyeva, and V. K. Krysina, *J. Organometallic Chem.*, 1969, **17**, 241.

[§] These and subsequent steps in the synthetic sequence are high-yield (>80%) processes. Desilylations are quantitative and can be monitored by u.v. spectroscopy.

[¶] B.p. 42 °C at 2 mmHg; $n_D^{18}$ 1·4765; $\nu_{max}$ (film) 2082s (C≡C) $cm^{-1}$; n.m.r.: $^1H$, δ($CCl_4$) 0·44 (s, $SSiMe_3$) and 0·17 (s, $CSiMe_3$).

[1] E. G. Howard, Jr., U.S.P. 3,035,030 (1962) (*Chem. Abs.*, 1962, **57**, P13617f); K. Georgiou, H. W. Kroto, and B. M. Landsberg, *J.C.S. Chem. Comm.*, 1974, 739; A. Krantz and J. Laureni, *J. Amer. Chem. Soc.*, 1974, **96**, 6768.
[2] D. Borrmann, 'Methoden der Organischen Chemie,' (Houben-Weyl-Muller), Thieme Verlag, Stuttgart, Band VII/4, Oxygen Compounds II, 1968, 312.
[3] G. Seybold, *Tetrahedron Letters*, 1974, 555; G. Seybold and C. Heibl, *Angew. Chem. Internat. Edn.*, 1975, **14**, 248.
[4] E. U. Elam, F. H. Rash, J. T. Dougherty, V. W. Goodlett, and K. C. Brannock, *J. Org. Chem.*, 1968, **33**, 2738.
[5] M. S. Raasch, *J. Org. Chem.*, 1970, **35**, 3470; *ibid.*, 1972, **37**, 1347.
[6] Tse-Lok Ho, *Chem. Rev.*, 1975, **75**, 1.
[7] R. A. Olofson and C. M. Dougherty, *J. Amer. Chem. Soc.*, 1973, **95**, 582.
[8] G. S. Burlachenko, Yu. I. Buakov, T. G. Dzherayan, and I. F. Lutsenko, *Zhur. obshchei Khim.*, 1975, **45**, 81.
[9] J. F. Arens, L. Brandsma, P. J. W. Schuijl, and H. E. Wijers, *Quart. Reports Sulphur Chem.*, 1970, **5**, 1.