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Bistrimethylsilylthioketen: a Versatile Reagent for Thioketen-based Syntheses

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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 $Me_3SiC=CSSiMe_3$ (8) thermally rearranges to (1).

THE instability of thioketen¹ and its simpler derivatives² has confined the use of such compounds to syntheses based upon *in situ* generation and trapping techniques.³ Stable molecules such as $Bu_2^tC=C=S^4$ 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 Me₃SiCl 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 Ctrimethylsilylthioacetate.

Metallating agent	Temp.		Product (%)	
Z in ZLi	°C	Solvent	(6)E	$(\tilde{7})\tilde{Z}$
Bun	-40	Ether	95	5
Cyclohexyl),N	-80	Ether	84	16
Pr ⁱ ,N	-10 to 0	Tetrahydrofuran	78	22
Me ₃ Si) ₂ N	-80	Ether	8	92

⁺ B.p. 45 °C at 1 mmHg; $n_{\rm p}^{20}$ 1-5000; $\nu_{\rm max}$ (film) 1757s (C=C=S) cm⁻¹; $\lambda_{\rm max}$ (hexane) 218 (log ϵ 4·40), 263 (3·06), and 413 (1·04) nm; n.m.r.: ¹H, δ(CCl₄) 0·25 (s, Me₃Si); ¹³C, δ(CDCl₃) + 214·4 (C=S), +52·0 (Si₂C), and +0·8 (Me₃Si) p.p.m. (relative to Me₄Si).



SCHEME. R = Me, Et, or Prⁱ. Addition of Prⁱ₂NH (but not PrⁱOH) to (1) requires acid catalysis which results in partial displacement of the second MeaSi group to give MeC(S)NPris.

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 Me₃Si 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 used7 (Table), and can be shifted subsequently (in favour of the E isomer) by treating the mixture with Me₃SiBr and HgBr₂.⁸ 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 Me₃Si group from (1) by direct displacement (or by an addition-elimination sequence) is feasible as exemplified by the reaction with SnCl₄.

Interestingly, Me₃SiBr with Me₃SiC≡CSLi reacts at -45 °C to give the isomeric silvlated alkynethiol, Me_sSiC=CSSiMe_s

(8) I in 80% yield. Compound (8), which may also be used in synthesis, is converted by heat into (1).



The conversion $(8) \rightarrow (1)$ 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 Me₃SiCl or Me₃SiBr for the two possible sites of attack upon the ambident species, [R=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 thicketen (1).

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[‡] 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_{13}^{18} 1·4765; ν_{max} (film) 2082s (C=C) cm⁻¹; n.m.r.: ¹H, δ (CCl₄) 0·44 (s, SSiMe₃) and 0·17 (s, CSiMe₃).

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.

- ^a 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.