

BIS (TRIMETHYLSILYL) THIOKETONE

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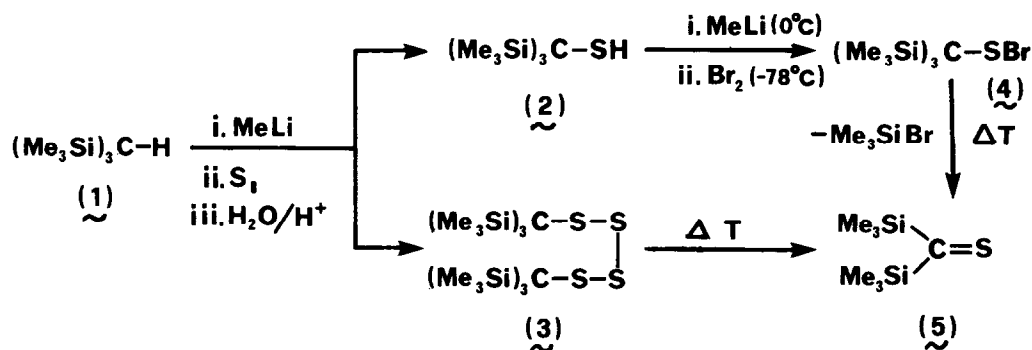
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Summary: Tris(trimethylsilyl)methylsulphenylbromide undergoes facile Me₃SiBr
 elimination to give bis(trimethylsilyl)thioketone.

Many methods are available for the synthesis of acylsilanes¹ and their
 reactional features have been extensively studied² and applied to organic syn-
 thesis³, whereas only one report has recently appeared on the corresponding
 thioketones⁴. On the other hand the chemistry of (Me₃Si)₂C=X (X=O,S), appears
 almost completely unexplored⁵, in spite of the high theoretical interest and
 synthetic potential.

We describe below the first synthesis of bis(trimethylsilyl)thioketone (5),
 a potential and novel synthon of the thioformyl carbanion. Our route to (5)
 shown in the Scheme, is based on the α,β elimination which occurs easily in
 many sterically hindered organosilicon compounds⁶.



Reaction of tris(trimethylsilyl)methane (TsiH) (1) with 1 equiv. of MeLi
 followed by addition of elemental sulfur (1.5 equiv.) in light petroleum gave,
 after acidic hydrolysis and column chromatography (n-hexane eluent), TsiSH (2),
 (60%; m.p. 175°C)⁷. A solution of (2) in light petroleum after treatment with

1 equiv. of MeLi at 0°C, was cooled to -78°C and bromine (10% molar excess) was added slowly. The reaction mixture was then warmed to room temperature and the solvent removed. Vacuum distillation of the brown crude reaction mixture led, after elimination of Me₃SiBr, to (5) as a reddish-violet oil (50%; b.p. 89-90°C at 2 mmHg), which from GC/MS analysis, appeared to be contaminated by a small amount of the dimer of (5) (M⁺ 380)^{8,9}. Further attempts to purify (5) by distillation or by chromatography on florisil, failed due to the instability of this compound. The structure of (5) was confirmed by IR, UV, ¹³C-NMR and Chemical Ionisation Mass Spectrometry (C.I.M.S.): IR (neat) 1425, 1250, 1070, 1010, 840 cm⁻¹; UV λ_{max} 530, 320, 230 nm (n-hexane); ¹³C-NMR (C₆D₆) 4.04 (9C), 267.0 (1C) ppm from TMS; MS, m/z 190 (M⁺), 175, 148, 97, 73.

Vacuum pyrolysis of (2) and (3) was also investigated as an alternative route to (5): heating (2) at 150°C in vacuo (2 mmHg) resulted in a quite complex mixture containing as the major component, (Me₃Si)₂CHSSiMe₃ resulting from rearrangement of the starting material; on the other hand pyrolysis of (3) under the same conditions afforded (5) in good yields together with Me₃SiSSiMe₃ and other unidentified organothiosilanes.

References and footnotes

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2. A.G.Brook, *Acc. Chem. Res.*, **7**, 77 (1974).
3. A.Degl'Innocenti, S.Pike, D.R.M.Walton, G.Seconi, A.Ricci and M.Fiorenza, *J. Chem. Soc. Chem. Commun.*, 1201 (1980); A.Ricci, A.Degl'Innocenti, S.Chimichi, M.Fiorenza, G.Rossini and H.J.Bestmann, *J. Org. Chem.* in press; H.J. Reich, M.J.Kelly, R.E.Olson and C.R.Holtan, *Tetrahedron*, **39**, 949 (1983) and references cited therein.
4. B.F.Bonini, G.Mazzanti, S.Sarti, P.Zanirato and G.Maccagnani, *J. Chem. Soc. Chem. Commun.*, 822 (1981).
5. The only attempt of synthesizing a (Me₃M)₂C=X type compound (M=Si and Ge; X=O) was based on the dithiane Corey method and proved to be not satisfactory, see: A.G.Brook, J.M.Duff, P.F.Jones and N.R.Davis, *J. Am. Chem. Soc.*, **89**, 431 (1967).
6. For the synthesis of unsaturated compounds through α,β elimination of sterically hindered organosilanes, see also: M.van der Leij, P.A.T.W.Porskamp, B.H.M.Lammerink and B.Zwanenburg, *Tetrahedron Lett.* **19**, 811 (1978); I.Kuwajima, T.Abe and N.Minami, *Chem. Lett.*, 993 (1976).
7. The crude reaction mixture appeared contaminated by sizeable amounts (20% ca.) of Tsi(S)Tsi(3) (m.p. 154°C, MS, m/z 591 (M⁺), 559, 295, 263, 249, 233, 217, 201, 190.) separated in the column chromatography; minor amounts of TsiSMe were also detected by GC/MS analysis.
8. The synthesis of (5) through bromination of (2) with N-bromosuccinimide in CCl₄, resulted in somewhat lower yields.
9. The synthetic route depicted in the Scheme was also applied to the preparation of the previously reported Ph(CS)SiMe₃, thus outlining the quite general application of this route.

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