

## Evidence for the Formation of Chloromethoxy(trimethyl)silane

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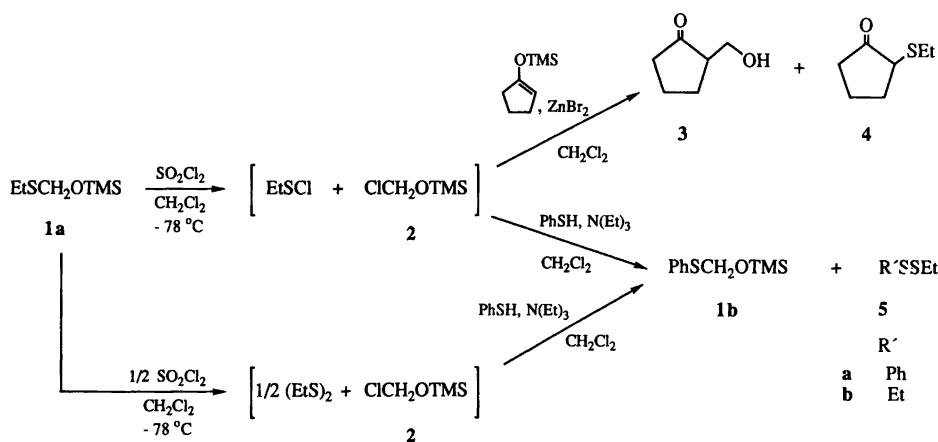
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We have previously reported the synthesis and utility of several chloromethoxysilanes.<sup>1</sup> The simplest member of this class of compounds, chloromethoxy(trimethyl)silane (**2**), was not prepared as it was expected to be of low stability.<sup>2</sup> Although the synthesis of **2** by a different route has been reported in the literature,<sup>3</sup> the NMR data are inconsistent: the <sup>1</sup>H NMR value<sup>3</sup> given for the chloromethoxy protons ( $\delta$  2.72) are not in accordance with corresponding data for other chloromethoxysilanes ( $\delta$  5.54–5.61).<sup>1</sup> The observed <sup>1</sup>H NMR values for the methylene group in a number of chloromethoxy ethers, also lie in the range  $\delta$  5–6.<sup>4</sup> The <sup>13</sup>C NMR data<sup>5a</sup> for the methylene carbon ( $\delta$  76.29) fit well, however, with other chloromethoxysilanes.<sup>1</sup> Another surprising feature of this compound, is its stability towards hydrolysis.<sup>3</sup> Similar compounds have been reported to decompose when treated with water.<sup>6</sup> In order to clarify the points mentioned above, we decided to try and synthesize chloromethoxy(trimethyl)silane. In earlier papers we have shown that *O,S*-acetals can be cleaved with sulfuryl chloride to give an  $\alpha$ -chloro ether and a sulfonyl chloride.<sup>1,4d,7</sup> Thus we find that treatment of the *O,S*-acetal **1a** with sulfuryl chloride at  $-78^\circ\text{C}$  for a short period,

followed by addition of 1-(trimethylsilyloxy)cyclopentene and a catalytic amount of zinc bromide, gives 2-hydroxy-methylcyclopentanone (**3**) and 2-ethylthiocyclopentanone (**4**) in 71 and 62 % yield, respectively (Scheme 1).

The above procedure using triethylammonium benzenethiolate in place of 1-(trimethylsilyloxy)cyclopentene, gives a mixture of the *O,S*-acetal **1b**<sup>8</sup> and ethyl phenyl disulfide (**5a**, Scheme 1). In accordance with earlier observations,<sup>7c</sup> addition of 0.5 equiv. of sulfuryl chloride relative to the *O,S*-acetal is sufficient to bring about complete cleavage the *O,S*-acetal **1a**. Half of the *O,S*-acetal is cleaved by sulfuryl chloride and the remaining by ethanesulfonyl chloride. The chloromethoxy(trimethyl)silane thus formed, was trapped with benzenethiolate to give the *O,S*-acetal **1b** (Scheme 1).

Low-temperature <sup>1</sup>H NMR ( $-50^\circ\text{C}$ ) spectroscopy of the mixture of the *O,S*-acetal **1a** and sulfuryl chloride, showed a value of  $\delta$  5.58 for the methylene protons, which corresponds to the value expected for chloromethoxy(trimethyl)silane (**2**) (*vide supra*). Warming of the sample to ambient temperature gradually caused decomposition of the product. The experiments quoted above lead us to propose



Scheme 1.

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chloromethoxy(trimethyl)silane (**2**) as one of the products in the cleavage of the *O,S*-acetal **1a** with sulfonyl chloride. Moreover, under these conditions **2** is stable only at low temperatures.

### Experimental

NMR spectra were recorded on a Varian Gemini-200 or a Varian XL-300 spectrometer operating at 200 and 300 (<sup>1</sup>H) and 50 and 75 MHz (<sup>13</sup>C), respectively. The solvent was deuteriochloroform and Me<sub>4</sub>Si was used as an internal reference. The mass spectra, under electron impact conditions (EI), were recorded at 70 eV ionizing energy. Ammonia was used for chemical ionization (CI) unless otherwise stated; the spectra are presented as *m/z* (% rel. int.).

**Phenylthiomethanol.**<sup>9</sup> A mixture of thiophenol (11.0 g, 0.1 mol), paraformaldehyde (3.0 g, 0.1 mol) and a 30% solution of sodium methoxide in methanol (0.03 ml) was heated at 110 °C for 30 min and cooled; yield 13.6 g (97%). Found: C 59.54; H 5.81. Calc. for C<sub>7</sub>H<sub>8</sub>OS: 59.97; H 5.75. <sup>1</sup>H NMR: δ 2.70 (br s, OH), 4.93 (CH<sub>2</sub>), 7.2–7.5 (m, Ph). MS (EI): 140 (5, *M*<sup>+</sup>), 110 (100), 77 (15), 69 (14), 66 (15), 65 (32), 51 (15).

**Ethyl (trimethylsilyloxy)methyl sulfide 1a.** 4-(*N,N*-dimethylamino)pyridine (342 mg, 2.8 mmol), triethylamine (24 ml, 175 mmol) and chlorotrimethylsilane (17.7 ml, 140 mmol) were added to a stirred solution of ethylthiomethanol<sup>1a</sup> (6.44 g, 70 mmol) in dry dichloromethane (100 ml) at 0 °C under N<sub>2</sub>. The mixture was stirred for 14 h at ambient temperature and then evaporated. Hexane was added to the residue, the mixture was filtered and the filtrate evaporated. The product was purified by distillation; yield 6.89 g (60%). B.p. 61–62 °C/19 mmHg. Anal. C<sub>6</sub>H<sub>16</sub>OSSi: C, H. <sup>1</sup>H NMR: δ 0.17 (SiMe<sub>3</sub>), 1.20 (t, *J* 7.4 Hz, Me), 2.66 (q, *J* 7.4 Hz, CH<sub>2</sub>), 4.79 (OCH<sub>2</sub>S). <sup>13</sup>C NMR: δ -0.1 (SiMe<sub>3</sub>), 14.9 (Me), 24.6 (CH<sub>2</sub>), 65.7 (OCH<sub>2</sub>S). MS (CI): 164 (9, *M*<sup>+</sup>), 149 (1), 134 (7), 119 (7), 103 (64), 92 (48), 90 (100), 75 (55), 74 (30), 73 (59).

**Phenyl (trimethylsilyloxy)methyl sulfide 1b.**<sup>8</sup> **Method A.** Compound **1b** was prepared as for **1a** above. The product was contaminated with (phenylthio)trimethylsilane (ca. 10%), which was difficult to remove by distillation. Yield 76%. B.p. 60–62 °C/0.5 mmHg.<sup>8</sup> <sup>13</sup>C NMR: δ 0.6 (SiMe<sub>3</sub>), 68.6 (SCH<sub>2</sub>O), 126.1, 128.3 and 129.7 (CH in Ph), 135.6 (C in Ph). MS (CI, CH<sub>4</sub>): 213 (83, *M*<sup>+</sup>+1), 182 (9), 169 (11), 151 (6), 141 (57), 123 (100), 111 (25), 109 (28), 103 (36), 91 (9).

**Method B.** Sulfonyl chloride (1.60 ml, 20 mmol) in dry dichloromethane (10 ml) was added to a stirred solution of ethyl (trimethylsilyloxy)methyl sulfide (**1a**) (3.24 g, 20 mmol) in dichloromethane (20 ml) under N<sub>2</sub> at -78 °C. After 30 min, a solution of thiophenol (4.20 ml, 40 mmol) and triethylamine (5.60 ml, 40 mmol) in dichloromethane (50 ml) was added. The mixture was stirred for 1 h at

-78 °C and 1.5 h at ambient temperature before the solvent was evaporated. Hexane was added to the residue, the mixture was filtered and the filtrate evaporated. The residue was distilled. The fraction boiling in the range 58–60 °C/0.3 mmHg contained 3.68 g **1b** and **5a**<sup>10</sup> (1:1.9 from the <sup>1</sup>H NMR spectrum). <sup>1</sup>H NMR: δ 0.16 (SiMe<sub>3</sub>), 1.31 (t, *J* 7.3 Hz, Me), 2.75 (q, *J* 7.3 Hz, CH<sub>2</sub>), 5.12 (SCH<sub>2</sub>O), 7.2–7.6 (m, Ph). GC-MS (CI): **1b**: 230 (3, *M*<sup>+</sup> + 18), 212 (15, *M*<sup>+</sup>), 182 (15), 167 (5), 151 (4), 140 (27), 123 (38), 103 (79), 90 (100), 73 (88). GC-MS (CI): **5a**: 170 (1, *M*<sup>+</sup>), 138 (11), 111 (35), 110 (100), 109 (29), 83 (38), 78 (75), 66 (17), 65 (20), 62 (53).

**Method C:** Sulfonyl chloride (0.53 ml, 6.6 mmol) in dry dichloromethane (10 ml) was added to a stirred solution of ethyl (trimethylsilyloxy)methyl sulfide (**1a**) (2.17 g, 13.2 mmol) in dichloromethane (10 ml) under N<sub>2</sub> at -78 °C. After 40 min, a solution of thiophenol (1.39 ml, 13.2 mmol) and triethylamine (1.85 ml, 13.2 mmol) in dichloromethane (20 ml) was added. The mixture was stirred for 1 h at -78 °C and 1.5 h at ambient temperature before the solvent was evaporated. Hexane was added to the residue, the mixture filtered and the filtrate evaporated. Diethyl disulfide (**5b**) was removed under reduced pressure and the residue distilled; yield 1.18 g (56%).

**Chloromethoxy(trimethyl)silane 2.** A solution of ethyl (trimethylsilyloxy)methyl sulfide (**1a**) (20 mg, 0.12 mmol) in deuteriochloroform (0.6 ml) was cooled to -50 °C in an NMR tube. The tube was removed from the probe, sulfonyl chloride (0.01 ml, 0.12 mmol) added and the <sup>1</sup>H NMR spectrum recorded immediately at -50 °C. <sup>1</sup>H NMR: δ 0.23 (SiMe<sub>3</sub>), 1.44 (t, *J* 7.1 Hz, Me in EtSCl<sup>11</sup>), 3.13 (q, *J* 7.1 Hz, CH<sub>2</sub> in EtSCl), 5.58 (ClCH<sub>2</sub>O). <sup>13</sup>C NMR: δ -0.4 (SiMe<sub>3</sub>), 13.9 (Me in EtSCl), 35.4 (CH<sub>2</sub> in EtSCl), 76.3 (ClCH<sub>2</sub>O).

**2-Hydroxymethylcyclopentanone 3**<sup>12</sup> and **2-ethylthiocyclopentanone 4**.<sup>13</sup> Sulfonyl chloride (0.16 ml, 2.0 mmol) in dry dichloromethane (2 ml) was added to a stirred solution of ethyl (trimethylsilyloxy)methyl sulfide (**1a**) (328 mg, 2.0 mmol) in dichloromethane (2 ml) under N<sub>2</sub> at -78 °C. After 15 min, 1-(trimethylsilyloxy)cyclopentene (1.07 ml, 6.0 mmol) in dichloromethane (2 ml) and zinc bromide (45 mg, 0.2 mmol) were added. The mixture was stirred at -78 °C for 4 h and diluted with diethyl ether and the ether layer was washed with saturated aqueous sodium hydrogen carbonate and saturated aqueous sodium chloride. The combined water solutions were extracted with ethyl acetate (×3), the combined organic solutions were dried (MgSO<sub>4</sub>) and evaporated. The products were separated by flash chromatography using EtOAc–hexane (1:1). Compound **5** was purified by flash chromatography using EtOAc–hexane (1:20).

**3:** Yield 163 mg (71%). <sup>13</sup>C NMR: δ 20.9, 26.3 and 38.8 (CH<sub>2</sub>), 51.0 (CH), 62.0 (CH<sub>2</sub>OH), 222.6 (CO). MS (CI): 114 (19, *M*<sup>+</sup>), 96 (12), 83 (11), 73 (10), 69 (11), 68 (36), 67 (18), 60 (50), 57 (62), 55 (100).

**4:** Yield 179 mg (62%). <sup>1</sup>H NMR: δ 1.01 (t, *J* 7.4 Hz,

Me), 1.7–2.7 (m, 8 H, CH<sub>2</sub>), 3.0–3.1 (m, CHS). <sup>13</sup>C NMR: δ 14.3 (Me), 20.5, 25.0, 30.4 and 36.0 (CH<sub>2</sub>), 47.1 (CH), 214.4 (CO). MS (EI): 144 (55, M<sup>+</sup>), 88 (45), 87 (40), 85 (10), 84 (100), 73 (11), 61 (8), 60 (83), 58 (8), 55 (44).

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