

## SOME REACTIONS OF SILYL- AND GERMYL-SULPHUR COMPOUNDS WITH THE S<sup>II</sup>-N BOND

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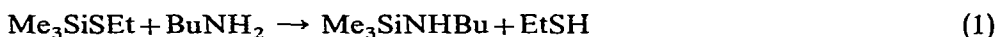
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### SUMMARY

Though the reaction of S<sup>II</sup>-N compounds with thiosilanes is of little use in synthesising disulphides, it does provide a convenient preparative route to silyl- and germylsulphinylamines, R<sub>3</sub>M-NSO.

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(Ethylthio)trimethylsilane reacts with primary and secondary amines on warming, yielding the aminosilane and ethanethiol<sup>1</sup>. This reaction is a specific case



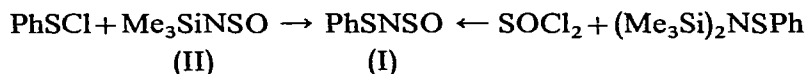
of a more general metathetical reaction involving the Si-S and N-X bonds and this paper considers the case where X is bivalent sulphur.



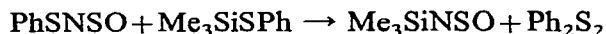
We have found that *N,N*-dimethylbenzenesulphenamide reacts with (phenylthio)trimethylsilane on heating to give good yields of diphenyl disulphide and the aminosilane. The (ethylthio)silane gave only a 19% yield of ethyl phenyl disulphide however, so the reaction seems of little use as a synthetic method for unsymmetrical disulphides.



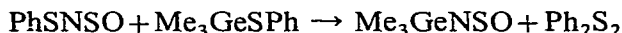
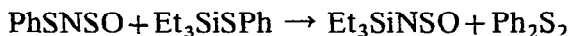
Sulphinylamine derivatives of silicon and germanium have been successfully prepared using reaction (2). The starting material for this work, *N*-(phenylthio)sulphinylamine PhSNSO, (I), has been synthesised by the method of Scherer<sup>2</sup>, and also from *N*-(trimethylsilyl)sulphinylamine (II) and benzenesulphenyl chloride. (I) is an



orange liquid characterised by strong infrared absorptions at 1000 and 1195 cm<sup>-1</sup> ascribed to  $\nu_{\text{sym}}(\text{NSO})$  and  $\nu_{\text{asym}}(\text{NSO})$ . It reacts exothermically with (phenylthio)trimethylsilane giving (II) in high yield. Both *N*-(triethylsilyl)sulphinylamine and



*N*-(trimethylgermyl)sulphinylamine can be prepared by the same method, though the reactants had to be heated. The products show strong infrared absorptions at



about 1100 and 1300  $\text{cm}^{-1}$ , as does (II)<sup>3</sup>, while *N*-(trimethylgermyl)sulphinylamine also shows a single peak in its PMR spectrum at  $\tau$  value 9.40.

#### EXPERIMENTAL

The thiotrimethylsilanes and the thiogermane<sup>4</sup>, benzenesulphenyl chloride and *N,N*-dimethylbenzenesulphenamide<sup>5</sup>, *N*-(trimethylsilyl)sulphinylamine<sup>3</sup> and *N*-(phenylthio)hexamethyldisilazane<sup>6</sup> were all prepared by standard methods. (Phenylthio)triethylsilane was prepared from  $\text{Et}_3\text{SiBr}$  and  $\text{NaSPh}$  in 42% yield, b.p. 80°/0.1 mm,  $n_D^{25}$  1.5320. (Found: C, 65.3; H, 8.88; S, 14.1.  $\text{C}_{12}\text{H}_{20}\text{SSi}$  calcd.: C, 65.3; H, 8.93; S, 14.3%.)

#### *Reaction of N,N-dimethylbenzenesulphenamide with (phenylthio)trimethylsilane*

The sulphenamide (3.7 g, 1 mol.) and thiosilane (4.4 g, 1 mol.) were heated to 190°. (Dimethylamino)trimethylsilane (1.9 g, 67%), b.p. 84°,  $n_D^{25}$  1.3943, was slowly evolved and recrystallisation of the residue from ethanol gave diphenyl disulphide (3.3 g, 63%), m.p. 62–63°. (Found: C, 66.0; H, 5.1; S, 29.6.  $\text{C}_{12}\text{H}_{10}\text{S}_2$  calcd.: C, 66.1; H, 4.6; S, 29.3%.) No depression of the mixture m.p. was observed.

#### *Reaction of N,N-dimethylbenzenesulphenamide with (ethylthio)trimethylsilane*

The procedure of the last experiment was employed, yielding (dimethylamino)-trimethylsilane (1.0 g, 35%), b.p. 83°,  $n_D^{25}$  1.3945, and ethyl phenyl disulphide (0.8 g, 19%), b.p., 82°/1.5 mm,  $n_D^{25}$  1.5973. (Found: C, 56.1; H, 5.9; S, 37.8.  $\text{C}_8\text{H}_{10}\text{S}_2$  calcd.: C, 56.5; H, 5.9; S, 37.6%.)

#### *Reaction of benzenesulphenyl chloride with N-(trimethylsilyl)sulphinylamine*

The chloride (5.13 g, 1 mol.) was slowly added to the sulphinylamine (4.80 g, 1 mol.) with cooling and the mixture heated to 130°. Trimethylchlorosilane (3.2 g, 84%), b.p. 58°,  $n_D^{25}$  1.3863, was isolated and vacuum distillation of the residual red oil gave *N*-(phenylthio)sulphinylamine (5.17 g, 85%), b.p. 80°/0.2 mm, as an orange distillate. (Found: C, 42.1; H, 2.8; N, 8.2.  $\text{C}_6\text{H}_5\text{NS}_2\text{O}$  calcd.: C, 42.0; H, 2.9; N, 8.2%.)

#### *Reaction of N-(phenylthio)sulphinylamine and (phenylthio)trimethylsilane*

The thiosilane (3.82 g, 1 mol.) was added to the sulphinylamine (3.6 g, 1 mol.). The liquids were immiscible but warming occurred at the interface and thorough shaking, with cooling produced discoloration. Warming at 100° for 1 h followed by distillation gave *N*-(trimethylsilyl)sulphinylamine (2.7 g, 96%), b.p. 106°,  $n_D^{25}$  1.4258. (Found: C, 26.7; H, 6.6; N, 10.6; S, 23.5.  $\text{C}_3\text{H}_9\text{SiNSO}$  calcd.: C, 26.7; H, 6.7; N, 10.4; S, 23.7%.) The peaks in the infrared and PMR spectra corresponded with those previously reported<sup>3</sup>.

#### *Reaction of N-(phenylthio)sulphinylamine and (phenylthio)triethylsilane*

Mixing the thiosilane (5.75 g, 1 mol.) and sulphinylamine (4.4 g, 1 mol.)

produced discoloration and after heating at 170° for 2 days, vacuum distillation gave *N*-(triethylsilyl)sulphinylamine (2.0 g, 44%), b.p. 40°/0.2 mm,  $n_D^{25}$  1.4540. (Found: C, 40.3; H, 8.3; N, 7.4; S, 18.0. C<sub>6</sub>H<sub>15</sub>SiNSO calcd.: C, 40.6; H, 8.5; N, 7.9; S, 18.1 %.)  $\nu_{\text{asym}}(\text{NSO})$  and  $\nu_{\text{sym}}(\text{NSO})$  at 1300 and 1125 cm<sup>-1</sup>. Recrystallisation of the residue gave diphenyl disulphide (3.0 g, 52%), m.p. 62–63°.

*Reaction of N-(phenylthio)sulphinylamine with (phenylthio)trimethylgermane*

The germane (7.6 g, 1 mol.) and sulphinylamine (5.6 g, 1 mol.) were heated at 90° till the mixture no longer smelled of phenylthio compounds. Subsequent distillation yielded *N*-(trimethylgermyl)sulphinylamine (4.9 g, 83%), b.p. 131°,  $n_D^{25}$  1.4555. (Found: C, 20.3; H, 5.2; N, 8.4. C<sub>3</sub>H<sub>9</sub>GeNSO calcd.: C, 20.1; H, 5.0; N, 7.9 %.)  $\nu_{\text{asym}}(\text{NSO})$  and  $\nu_{\text{sym}}(\text{NSO})$  at 1270 and 1100 cm<sup>-1</sup> and a singlet in the PMR spectrum at  $\tau$  value 9.40.

ACKNOWLEDGEMENT

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