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SOME REACTIONS OF SILYL- AND GERMYL-SULPHUR COMPOUNDS WITH THE S^{II}–N BOND

D. A. ARMITAGE AND M. J. CLARK

Department of Chemistry, Queen Elizabeth College, Atkins Building, Campden Hill, Kensington, London, W.8 (Great Britain)

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SUMMARY

Though the reaction of S^{II}–N compounds with thiosilanes is of little use in synthesising disulphides, it does provide a convenient preparative route to silyl- and germylsulphinylamines, $R_3M{-}NSO$.

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

$$Me_3SiSEt + BuNH_2 \rightarrow Me_3SiNHBu + EtSH \qquad (1)$$

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.

$$Si{-}S + N{-}X \rightarrow Si{-}N + S{-}X \qquad (2)$$

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.

$$Me_3SiSR + PhSNMe_2 \rightarrow Me_3SiNMe_2 + PhSSR \qquad (R = Et\ \text{or}\ Ph)$$

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[2], and also from *N*-(trimethylsilyl)suphinylamine (II) and benzenesulphenyl chloride. (I) is an

$$PhCl + \underset{(II)}{Me_3SiNSO} \rightarrow \underset{(I)}{PhSNSO} \leftarrow SOCl_2 + (Me_3Si)_2NSPh$$

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

$$PhSNSO + Me_3SiSPh \rightarrow Me_3SiNSO + Ph_2S_2$$

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 cm^{-1}, as does (II)[3], while *N*-(trimethylgermyl)sulphinylamine also shows a single peak in its PMR spectrum at τ value 9.40.

$$PhSNSO + Et_3SiSPh \rightarrow Et_3SiNSO + Ph_2S_2$$

$$PhSNSO + Me_3GeSPh \rightarrow Me_3GeNSO + Ph_2S_2$$

EXPERIMENTAL

The thiotrimethylsilanes and the thiogermane[4], benzenesulphenyl chloride and *N,N*-dimethylbenzenesulphenamide[5], *N*-(trimethylsilyl)sulphinylamine[3] and *N*-(phenylthio)hexamethyldisilazane[6] were all prepared by standard methods. (Phenylthio)triethylsilane was prepared from Et_3SiBr and 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. $C_{12}H_{20}SSi$ 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. $C_{12}H_{10}S_2$ 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. $C_8H_{10}S_2$ 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. $C_6H_5NS_2O$ 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. C_3H_9SiNSO 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[3].

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. $C_6H_{15}SiNSO$ calcd.: C, 40.6; H, 8.5; N, 7.9; S, 18.1%.) ν_{asym}(NSO) and ν_{sym}(NSO) at 1300 and 1125 cm^{-1}. 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_3H_9GeNSO calcd.: C, 20.1; H, 5.0; N, 7.9%.) ν_{asym}(NSO) and ν_{sym}(NSO) at 1270 and 1100 cm^{-1} and a singlet in the PMR spectrum at τ value 9.40.

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