# SOME REACTIONS OF DISILYL SULPHIDE

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Abstract — The reactions of disilyl sulphide with some protonic acids, covalent halides and salts are described. A convenient preparation of disilyl sulphide from silyl bromide is described and the existence of silyl mercaptan is confirmed.

IN THE heavy metal salt "conversion series" [1] for silyl compounds, disilyl sulphide lies above silyl bromide. This is shown by the reaction of the sulphide with mercuric bromide which gives silyl bromide almost quantitatively and by the failure of silyl bromide to react with mercuric sulphide. Seeking a method of converting silyl bromide to disilyl sulphide without going via trisilylamine and silyl iodide, we have attempted to silylate the SH<sup>-</sup> ion. When silyl bromide and KSH are kept together for 50 hr at  $-96^{\circ}$ C in dimethyl ether, no reaction occurs. Under similar conditions, Me<sub>3</sub>NH<sup>+</sup> SH<sup>-</sup> gives disilyl sulphide in 58 per cent yield after 24 hr. This, and similar results with the SeH<sup>-</sup> ion[2], can probably be attributed to the greater solubility in dimethyl ether of the trimethylammonium salts compared with the potassium salts. Better conversions, however, are obtained using lithium sulphide: *ca.* 90 per cent after only 6 hr.

Since silylisothiocyanate, SiH<sub>3</sub>NCS, is thought to lie below silyl bromide in the conversion series, silver thiocyanate should react with disilyl sulphide. When the disilyl sulphide was distilled through a column of the silver salt, silylisothiocyanate was obtained in 86 per cent yield, a considerable improvement on the 66 per cent yield obtained using silyl iodide[3]. Disilylcarbodiimide lies below silyl bromide in the conversion series[4]: in an attempt to improve on the 60 per cent yield obtained using silyl iodide, disilyl sulphide was streamed over silver cyanamide. The silver salt blackened rapidly, but there were no volatile products: possibly the silver is reduced with formation of  $(-SiH_2-N=C=N-)_n$  polymer.

If KPH<sub>2</sub> is treated with excess disilyl sulphide in dimethyl ether at  $-96^{\circ}$ C, trisilylphosphine is obtained along with unreacted sulphide. With the KPH<sub>2</sub> in excess, no silylphosphines are found in the volatile products, but on acidification of the involatile products with hydrogen sulphide, disilylphosphine is produced. This is similar to the results of the silylation of PH<sub>2</sub><sup>-</sup> with silyl bromide[5].

Onyszchuk[6] found that there is no reaction between disilyl sulphide and boron trifluoride but did not try its reaction with boron trichloride. We have found

5. C. Glidewell and G. M. Sheldrick, To be published.

<sup>1.</sup> C. Eaborn, J. chem. Soc. 3077 (1950).

<sup>2.</sup> C. Glidewell, Unpublished observations.

<sup>3.</sup> A. G. MacDiarmid, Ph.D. Thesis, Cambridge (1955).

<sup>4.</sup> M. J. Mays, Ph.D. Thesis, Cambridge (1963).

<sup>6.</sup> M. Onyszchuk, Can. J. Chem. 39, 808 (1961).

a rapid reaction at  $-96^{\circ}$ C, which yields silyl chloride and boron trisulphide. This is consistent with boron trichloride's being a better electron acceptor than boron trifluoride: a similar contrast has been found in phenyl silyl sulphide[7], which does not react with boron trifluoride but reversibly forms a 1:1 adduct with the trichloride. In view of the failure of disilyl sulphide to react with either methyl iodide[8] or silyl iodide[8], the ease of reaction and so presumably of adduct formation with boron trichloride is surprising.

The reaction of disilyl sulphide with cyanogen chloride yields silyl cyanide, silylisothiocyanate and sulphur. Possibly silyl-n-thiocyanate is formed initially, followed rapidly by either rearrangement to silylisothiocyanate or by loss of sulphur to give silyl cyanide. In view of this loss of sulphur, reactions with nitrosyl chloride and acetyl chloride were studied. The former gave silyl chloride, nitric oxide and sulphur only, while with the latter no loss of sulphur occurred, the products being silyl chloride and a liquid whose i.r. spectrum was not inconsistent with its being diacetyl sulphide.

Disilyl sulphide is cleaved by hydrogen iodide[8], water[8] and methanol[9], giving hydrogen sulphide and silyl iodide, disiloxane and methyl silyl ether respectively. We have examined the reactions of disilyl sulphide with some other protonic acids. With phenol, a rapid reaction occurs to give phenyl silyl ether[7] in almost quantitative yield. No reaction is found with either pyrrole or thiophenol under the conditions used: this is probably a reflection of their weakness as acids. The reaction with hypophosphorous acid is very rapid to give only decomposition products; no silyl hypophosphite was found. The reaction with aqueous hydrogen peroxide yields no disilyl peroxide, but only disiloxane and a solid assumed to be silica.

It has been reported that reaction of disilyl sulphide with hydrogen sulphide gives silyl mercaptan[8], but this compound is not well characterised. We have repeated this reaction and have measured the i.r. and NMR spectra of the mercaptan; the NMR spectrum is first order at 100 Mc/s and was measured relative to the solvent chloroform. We find  $\delta(SiH_3) = +2.935 \pm 0.001$  ppm,  $\delta$  SH' =  $+7.364 \pm 0.001$  ppm, J HH' =  $4.7 \pm 0.1$  c/s,  $J(^{29}SiH) = 224.2 \pm 0.2$  c/s. The spectrum was recorded in the presence of excess hydrogen sulphide to reduce the extent of redistribution and it was apparent that no exchange of hydrogen atoms bound to sulphur was occurring. The principal i.r. absorptions are found at: 2196s, 2190s, 2180s, 964s, 941vs, 916vs, 761w, 524m, 514m: this spectrum was also recorded in the presence of excess hydrogen sulphide. The absence of any band assignable to  $\nu(S-H)$  is not surprising in view of the extreme weakness of this band in methyl mercaptan[10].

# **EXPERIMENTAL**

All manipulations were carried out in a conventional pyrex vacuum system with rigorous exclusion of air and moisture. Silyl bromide was prepared by reduction of phenyltrichlorosilane with LiAlH<sub>4</sub> in di-isoamyl ether, followed by cleavage with liquid HBr[11]. All other compounds were commercially

- 7. C. Glidewell and D. W. H. Rankin, J. chem. Soc. (A). In press.
- 8. H. J. Emeleus, A. G. MacDiarmid and A. G. Maddock, J. inorg. nucl. Chem. 1, 194 (1955).
- 9. G. S. Weiss and E. R. Nixon, Spectrochim. Acta. 21, 903 (1965).
- 10. H. W. Thompson and N. P. Skerrett, Trans. Faraday. Soc. 36, 812 (1940).
- 11. G. Fritz and D. Kummer, Z. anorg. allg. Chem. 308, 105 (1961).

obtained or were prepared by standard methods. Pyrrole was twice pumped through a flamed-out molecular sieve: phenol was twice sublimed *in vacuo*: all covalent halides were purified by fractionation in the vacuum system. Known volatile compounds were identified spectroscopically and by their distillation properties in the vacuum system. Infra-red spectra were recorded on a Perkin-Elmer 457 spectrometer: NMR spectra were recorded at 100 Mc/s on a Varian Associates HA 100 instrument.

#### Reactions

HgS and  $SiH_3Br$ . 2.0 m-mole of silv bromide was twice passed over a column of dry mercuric sulphide: the i.r. spectrum of the products showed only silv bromide and a trace of disiloxane.

KSH and  $SiH_3Br$ . 24.5 m-mole of KSH and 25.0 m-mole of SiH<sub>3</sub>Br in *ca.* 10 ml of dimethyl ether were held at -96 for 50 hr with occasional shaking. On fractionation, only dimethyl ether, silyl bromide and a trace of monosilane were found. 20.0 m-mole of hydrogen chloride were added to the solid residue and left at room temperature for 20 min. On fractionation, no silyl compound was found.

 $Me_3NH^+SH^-$  and  $SiH_3Br$ . 7.3 m-mole of  $Me_3NH^+SH^-$  and 8.0 m-mole of silyl bromide were kept in *ca*. 5 ml of dimethyl ether for 24 hr at -96 with occasional shaking. On fractionation, 0.200 g (2.13 m-mole, 58 per cent) of disilyl sulphide was obtained, together with dimethyl ether and some silyl bromide.

 $Li_2S$  and  $SiH_3Br$ . Typically, 11.4 m-mole of lithium sulphide and 24.0 m-mole of silyl bromide were kept in ca. 20 ml of dimethyl ether for 6 hr at -96. On fractionation, 0.957 g (10.2 m-mole, 89.5 per cent) of disilyl sulphide were obtained, together with dimethyl ether and some silyl bromide.

 $(SiH_3)_2S$  and  $HgBr_2$ . 0.050 g (0.53 m-mole) of disilyl sulphide was distilled three times through a column of mercuric bromide. The volatile products consisted of silyl bromide (1.03 m-mole) containing a trace of disiloxane.

 $(SiH_3)_2S$  and AgNCS. 0.524 g (5.70 m-mole) of disilylsulphide was pumped out of a trap held at -64 through a short column of AgNCS and glass wool and the products were collected in a trap held at -196. After fractionation 0.872 g (9.80 m-mole: 86.0 per cent) of silylisothiocyanate were obtained.

 $(SiH_3)_2S$  and  $Ag_2CN_2$ . When disilyl sulphide was pumped out of a trap held at -45 through a short column of silver cyanamide and glass wool in a water condenser, the silver salt turned black rapidly but no volatile products were obtained. If the sulphide was diluted with a rapid stream of dry nitrogen, again no condensible volatiles were found.

 $(SiH_3)_2S$  and  $KPH_2$ . (i) 0.132 g (14.0 m-mole) of disilyl sulphide and 0.93 m-mole of  $KPH_2$  were kept in ca. 5 ml of dimethyl ether at -96 for 3 hr. On fractionating the volatile products, 8.4 mg (0.068 m-mole: 22 per cent based on  $KPH_2$ ) of trisilylphosphine and 1.20 m-mole of disilyl sulphide were obtained, together with dimethyl ether, phosphine and a trace of monosilane. (ii) 0.094 g (1.0 m-mole) of disilyl sulphide and 2.13 m-mole of  $KPH_2$  were kept in ca. 5 ml of dimethyl ether at -96 for 4 hr. The volatile products gave on fractionation only dimethyl ether, phosphine and a trace of monosilane. 2.0 m-mole of hydrogen sulphide was added to the remaining solid and left at -96 for 2 hr. The products were 0.049 g (0.52 m-mole) of disilylphosphine and a mixture of phosphine and hydrogen sulphide. There was no evidence for the formation of silylmercaptan.

 $(SiH_3)_2S$  and  $BCl_3$ . 0.0989 g (1.05 m-mole) of disilylsulphide and 1.80 m-mole of boron trichloride were sealed together and held at -96. A white solid was formed as soon as the mixture melted. Fractionation gave 1.11 m-mole of boron trichloride, 2.10 m-mole of silyl chloride and 0.0400 g of a white involatile solid. On treatment with 4.20 m-mole of methanol[12] for 2 hr at room temperature, 0.98 m-mole of hydrogen sulphide and 0.67 m-mole of trimethyl borate were obtained, together with excess methanol; this corresponds to B = 18.1%, S = 78.7\%: B<sub>2</sub>S<sub>3</sub> requires B = 18.4\%, S = 81.4\%.

 $(SiH_3)_2S$  and NOCl. 0.085 g (0.90 m-mole) of disilylsulphide and 0.90 m-mole of nitrosyl chloride were frozen together and warmed to -96 for 5 min. The red colour turned rapidly to yellow-green giving 0.0426 g (0.45 m-mole) of disilyl sulphide, 0.89 m-mole of nitric oxide, 0.90 m-mole of silyl chloride and a trace of nitrous oxide. 0.0144 g of a yellow solid, shown by its mass spectrum to be sulphur, remained.

 $(SiH_3)_2S$  and ClCN. 0.0797 g (0.85 m-mole) of disilylsulphide and 0.50 m-mole of cyanogen chloride were kept together overnight at room temperature: 0.30 m-mole of silyl chloride were formed together with an inseparable mixture of cyanogen chloride, disilyl sulphide, silyl chloride and silylisothiocyanate, and some yellow solid. All the products were sealed up again and left for 4 days at room

12. J. M. Lalancette, Can. J. Chem. 42, 2356 (1964).

temperature. On fractionation, 0.50 m-mole of silyl chloride, 0.83 m-mole of a mixture of disilyl sulphide, silyl cyanide and silylisothiocyanate and 0.0126 g (0.393 m-mole) of sulphur, identified mass spectrometrically, were found.

 $(SiH_3)_2S$  and  $CH_3COCl$ . 0.0843 g (0.896 m-mole) of disilyl sulphide and 0.0667 g (0.850 m-mole) of acetyl chloride were kept together at room temperature for 24 hr. 0.0561 g (0.844 m-mole) of silyl chloride and 0.0450 g (0.478 m-mole) of disilyl sulphide were found, together with 0.0499 g of a barely volatile liquid, whose i.r. spectrum showed the following principal absorptions: 2915m, 2840mw, 1760s, 1700vs, 1410ms, 1350s, 1005s, 950s, 915s, 855ms, 835s, 630mw, 690m, 665m, 600s, 520w, 505w, 435w, 350w. No sulphur was deposited.

 $(SiH_3)_2S$  and  $C_6H_5OH$ . 0.804 g (8.55 m-mole) of phenol and 4.25 m-mole of disilyl sulphide were kept together at room temperature for 30 min. The products were hydrogen sulphide and phenyl silyl ether (involatile at -23) and traces of monosilane and disiloxane. The yield of the ether was almost quantitative: it will be more fully described elsewhere[7].

 $(SiH_3)_2S$  and  $C_8H_5SH$ . 0.960 g (8.73 m-mole) of thiophenol and 4.37 m-mole of disilyl sulphide were kept together at room temperature for 2 weeks. Unchanged starting materials were recovered almost quantitatively.

 $(SiH_3)_2S$  and  $C_4H_5N$ . 0.126 g (1.87 m-mole) of pyrrole was added, diluted with dry nitrogen, in portions to 0.166 g (1.77 m-mole) of disilyl sulphide in the gas phase. No solid was formed and on fractionation only unchanged starting materials were found, with traces of disiloxane, hydrogen cvanide and an unidentified liquid.

 $(SiH_3)_2S$  and  $H_3PO_2$ . 4.17 m-mole of disilyl sulphide were frozen onto 0.567 g (8.34 m-mole) of hypophosphorous acid: as the sulphide was frozen down a white solid formed and permanent gas was evolved. After *ca*. 10 min at -64, the mixture was fractionated giving hydrogen, hydrogen sulphide, monosilane and traces of phosphine and disiloxane. A white air-stable solid remained which was too involatile to give a mass spectrum and whose i.r. spectrum showed the absence of P—H and Si—H bonds, but the presence of Si—O bonds. Analysis showed H = 2.54%, P = 17.4%. This value for hydrogen may be too low because of absorption of water by the phosphorous pentoxide formed in combustion.

 $(SiH_3)_2S$  and  $H_2O_2$ . 0.0231 g of 100 vol. hydrogen peroxide (containing *ca*. 0.20 m-mole of hydrogen peroxide and *ca*. 0.90 m-mole of water) and 0.1035 g (1.10 m-mole) of disilyl sulphide were frozen together. As soon as the sulphide melted, a white solid was deposited and gas was evolved. The products were 1.07 m-mole of hydrogen sulphide, 0.90 m-mole of disiloxane and 9.7 mg. of white involatile solid.

 $(SiH_3)_2S$  and  $H_2S$ . 2.00 m-mole of disilyl sulphide and 6.00 m-mole of hydrogen sulphide were left together at room temperature for 2 months. In addition to unchanged reactants, silyl mercaptan (M = 64.4, calcd. 64.2) was obtained, volatile at -96°C and involatile at -120°C. No attempt was made to determine the amount of mercaptan formed in order to keep the extent of redistribution to a minimum.

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