118. *Preparation and Properties of Dimethyliodosilane, 1 : 1′ : 2 : 2′-Tetramethyl-disiloxane and -disilthiane.*

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Dimethyliodosilane Me_2SiHI, 1 : 1′ : 2 : 2′-tetramethyldisiloxane $(Me_2SiH)_2O$, and 1 : 1′ : 2 : 2′-tetramethyldisilthiane $(Me_2SiH)_2S$ have been prepared and characterised. Preliminary experiments on the reaction of the disilthiane with typical acceptor compounds [Cu(I)Cl, $TiCl_4$, $PdCl_2$, and CH_3I] failed to show donor activity in the sulphur atom, though in some cases there were secondary reactions.

The donor properties of the sulphur and selenium atoms in disilthiane $(SiH_3)_2S$, and its selenium analogue have already been studied [1] and it was found that iodine did not give a sulphonium or selenonium compound, as it does with the methyl analogues. Both compounds were decomposed, silyl iodide SiH_3I being formed. Hydrogen iodide also caused decomposition and gave silyl iodide and hydrogen sulphide or selenide. Disilthiane did not react with silyl or methyl iodide, and with mercuric chloride it gave silyl chloride. These results showed that the silyl group had more powerful electron-attracting properties than had the methyl group. This investigation has now been extended to examine the effect of alkyl-substitution in the silyl group on the donor properties of oxygen and sulphur. Reactions with boron halides are reported separately [2] and attention is here concentrated on the reaction of 1 : 1′ : 2 : 2′-tetramethyldisilthiane with typical acceptors. The physical properties of the thiane have also been recorded, as have those of its hydrolysis product, 1 : 1′ : 2 : 2′-tetramethyldisiloxane.

Dimethylsilane was prepared by reduction of dimethyldichlorosilane or diethoxydimethylsilane with lithium aluminium hydride in ether.[3] It reacted with hydrogen iodide in the presence of aluminium iodide to give dimethyliodosilane, which was converted into 1 : 1′ : 2 : 2′-tetramethyldisiloxane by silver carbonate. The disilthiane was prepared by reaction of the iodo-compound with either black or red mercuric sulphide. Hydrolysis of 1 : 1′ : 2 : 2′-tetramethyldisilthiane to the siloxane occurred very readily and, since these two substances were difficult to separate, it was important to use dry mercuric sulphide. Disilthiane $(SiH_3)_2S$ is also readily hydrolysed.[1]

The preliminary study of the donor properties of the sulphur atom in 1 : 1′ : 2 : 2′-tetramethyldisilthiane was based on analogy with the sulphides, which form adducts with the halides of a small group of metals with relatively stable metallic sulphides. Among these are nickel, copper, silver, gold, titanium, and tin, the usual method of preparation being to add the sulphide to the metal halide in water or some other solvent. The addition compounds for which analogues were sought were $2CuCl,Me_2S$, $PdCl_2,2Me_2S$, $TiCl_4,Et_2S$, and $TiCl_4,2Et_2S$.[4] In addition, the reaction of the disilthiane with methyl iodide was

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[1] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.

[2] Emeléus and Onyszchuk, preceding paper.

[3] Eaborn, *J.*, 1950, 3077.

[4] Sidgwick, "Chemical Elements and their Compounds," Oxford Univ. Press, Vol. II, p. 884; Morgan and Ledbury, *J.*, 1922, **121**, 2882.

studied. The sulphur compound was added to the anhydrous metal halide, whereas many of the adducts between alkyl sulphides and metal salts were made in aqueous solution.

With cuprous chloride the recovery of pure 1 : 1′ : 2 : 2′-tetramethyldisilthiane varied from 81 to 95%. Palladous chloride reacted more extensively, giving hydrogen, hydrogen sulphide, and a mixture of dimethylchlorosilanes and unchanged disilthiane. With titanium tetrachloride the chief product was dimethyldichlorosilane. With methyl iodide there was no reaction. These results, though they relate to a limited range of compounds and conditions, afford no evidence of donor properties in the sulphur atom. It appears that the electron-attracting power of the alkyl-substituted group is still strong enough to prevent bond formation.

EXPERIMENTAL

Dimethylsilane was prepared by reducing dimethyldichlorosilane or dimethyldiethoxysilane with excess of lithium aluminium hydride in ether,[3] in ~85% yield (Found: *M*, 60·5. Calc. for C_2H_8Si: *M*, 60·1). The product was iodinated in the apparatus previously described,[5] a 2 : 1 mixture of dimethylsilane and hydrogen iodide being heated with freshly sublimed aluminium iodide for 12 hr. at 110°. *Dimethyliodosilane* was isolated by fractional condensation in a vacuum at −95° (Found: *Si*-H, 0·52; I, 68·4%; *M*, 186. C_2H_7ISi requires *Si*-H, 0·54; I, 68·2%; *M*, 186). Hydrogen was determined by hydrolysis with 10% aqueous alkali and measurement of the hydrogen evolved. Iodine was determined volumetrically in the hydrolysate. Carbon and hydrogen were not determined by microcombustion because of explosions. The v. p. was given in the range 0—50° by: $\log_{10} p$ (mm.) = 6·928 −1479/*T*. The extrapolated b. p. was 92° ± 1°, the latent heat of vaporisation 6760 cal./mole, Trouton's constant 18·5, the v. p. at 0° was 32 ± 0·5 mm., and the m. p. −88° ± 0·5°. In the fractionation a second product, which separated during the fractional condensation in a trap cooled at −22°, was probably dimethyldi-iodosilane but was not fully characterised.

Preparation of 1 : 1′ : 2 : 2′-*Tetramethyldisiloxane*.—Dimethyliodosilane (2—8 g.) was passed as vapour through a tube packed with dried silver carbonate (20 g.) and powdered glass. One passage gave a good conversion. Fractional condensation in a trap cooled to −95° gave a 70% yield of 1 : 1′ : 2 : 2′-*tetramethyldisiloxane* based on the equation $2Me_2SiHI + Ag_2CO_3 = (Me_2SiH)_2O + 2AgI + CO_2$. It was analysed by alkaline hydrolysis and measurement of the hydrogen liberated, followed by gravimetric estimation of silica in the hydrolysate (Found: *Si*-H, 1·46; Si, 41·5%; *M*, 133. $C_4H_{14}OSi_2$ requires *Si*-H, 1·46; Si, 41·5%; *M*, 134). The v. p. was given in the range 0—50° by $\log_{10} p$ (mm.) = 7·464 − 1585/*T*. The extrapolated b. p. was 73° ± 1°, the latent heat of vaporisation 7250 cal./mole, Trouton's constant 21, and the v. p. at 0° was 46 ± 0·5 mm. Samples were unchanged when stored in glass for 2—3 weeks, but later small amounts of hydrogen were liberated.

Preparation of 1 : 1′ : 2 : 2′-*Tetramethyldisilthiane*.—Dimethyliodosilane (2—8 g.) was passed as vapour through a tube closely packed with dry mercuric sulphide and a large excess of powdered glass. The yield did not depend on whether red or black mercuric sulphide was used. The product and unchanged reactant were condensed and then passed again through the tube. The desired product was separated by fractional condensation in traps cooled severally at −22°, −45°, and −95°. The first retained 70% of the total product, including most of the thiane. The other traps retained small amounts of unchanged iodide mixed with thiane; a small amount of hydrogen sulphide, formed by reaction of the thiane with traces of water, was condensed in liquid nitrogen. The product in the first trap, purified by fractional condensation at −22°, gave 1 : 1′ : 2 : 2′-*tetramethyldisilthiane* [65—70% based on the reaction $2Me_2SiHI + HgS = (Me_2SiH)_2S + HgI_2$ (Found: *Si*-H, 1·45; Si, 36·6; S, 20·8%; *M*, 150. $C_4H_{14}SSi_2$ requires *Si*-H, 1·33; Si, 37·4; S, 21·3%; *M*, 150)]. Sulphur was determined in the hydrolysate by oxidation with bromine water and precipitation as $BaSO_4$. The v. p. was given in the range 0—50° by $\log_{10} p$ (mm.) = 6·461 −1498/*T*. The extrapolated b. p. was 145° ± 1°, the latent heat of vaporisation 6850 cal./mole, and Trouton's constant 16·4, the v. p. at 0° was 9·0 ± 0·5 mm., and the m. p. −146° ± 0·1°.

The infrared spectra of the above new compounds will be reported elsewhere.

Reaction of 1 : 1′ : 2 : 2′-*Tetramethyldisilthiane with Metallic Salts*.—In three experiments

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[5] Emeléus, Onyszchuk, and Kuchen, *Z. anorg. Chem.*, 1956, **283**, 74.

in which dry cuprous chloride (0·350, 0·224, 0·140 g.) was treated in a sealed tube with 1 : 1′ : 2 : 2′-tetramethyldisilthiane (0·428, 0·970, 0·613 g.) the weights of the latter recovered were 0·407, 0·920, and 0·610 g. The purity of the recovered material was checked by the v. p. at 0° and the molecular weight. In the first experiment the tube was held for 12 hr. at 40° and in the other two it was shaken at room temperature.

Titanium tetrachloride (0·120 g.) and 1 : 1′ : 2 : 2′-tetramethyldisilthiane (0·680 g.) showed no sign of reaction at $-20°$ (1 hr.). At 0° a vigorous reaction occurred, the volatile products being unchanged 1 : 1′ : 2 : 2′-tetramethyldisilthiane (0·455 g.) (Found: *M*, 150; v. p. 9 mm. at 0°. Calc. for $C_4H_{14}SSi_2$: *M*, 150; v. p. 9 mm. at 0°) and dimethyldichlorosilane (Found: *M*, 129; v. p. 42 mm. at 0°. Calc. for $C_2H_6Cl_2Si$: *M*, 129; v. p. 40 mm. at 0°). A further fraction (0·047 g.) probably also contained dimethyldichlorosilane.

Palladous chloride (0·990 g.) and excess of 1 : 1′ : 2 : 2′-tetramethyldisilthiane reacted vigorously at room temperature, yielding a grey-black solid. The volatile products were hydrogen sulphide (0·029 g.) (Found: *M*, 34·1. Calc. for H_2S: *M*, 34·1) and a fraction (0·965 g.) of *M* 118 containing 39·6% of Cl, which was probably impure dimethyldichlorosilane (*M*, 128; Cl, 55%), but could not be further purified by vacuum-fractionation.

Methyl iodide (0·948 g.) was sealed with 1 : 1′ : 2 : 2′-tetramethyldisilthiane (0·581 g.) and kept at 40° (100 hr.). The liquids were miscible. Fractionation of the products gave only the tetramethyldisilthiane (0·560 g.) (Found: *M*, 149; v. p. 9 mm. at 0°) and methyl iodide (0·920 g.) (Found: *M*, 142; v. p. 134 mm. at 0°. Calc. for CH_3I: *M*, 142; v. p. 141 mm. at 0°).

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