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PREPARATION OF DIMETHYLTETRAMETHOXYDISILANE FROM THE DISILANE FRACTION

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Summary

Reaction of *sym*-dimethyltetrachlorodisilane, obtained by chlorination with hydrogen chloride of the higher-boiling residue produced in the Direct Synthesis of methylchlorosilanes, with methyl orthoformate or methanol/methyl orthoformate gave rise to *sym*-dimethyltetramethoxydisilane.

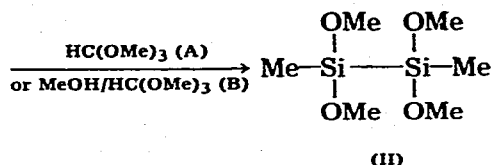
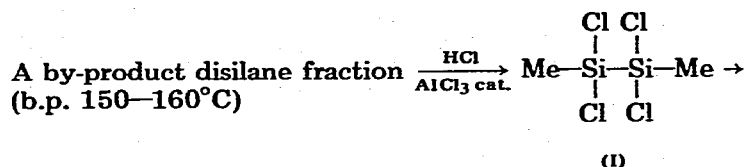
Results and discussion

sym-Dimethyltetramethoxydisilane is a very useful silicon compound, since it serves as a methoxymethylsilylene precursor [1–5]. Our interest in the large scale preparation of this disilane and the related compounds led us to try to utilize the by-product disilane fraction produced industrially in the Direct Synthesis of methylchlorosilanes as a starting material.

Three methods of preparing *sym*-dimethyltetramethoxydisilane have been reported: direct methoxylation of the disilane fraction via methanolysis followed by fractional distillation [6,7]; methoxylation [6,8] of *sym*-dimethyltetrachlorodisilane obtained by chlorination of the disilane fraction with acetyl chloride and aluminum chloride [9] or by a similar chlorination of hexamethyldisilane with acetyl chloride [9]; and photochemical coupling of dimethoxymethylsilane with loss of hydrogen [10]. The separation of the product in high purity by simple distillation is difficult using the first method [6]. The second method requires an uneconomically large amount of the catalyst. The last method is only suitable on a small scale.

We should like to report a convenient method for large scale production of the compound in good yield. The method consists of two steps: the chlorination of the disilane fraction (an 1 : 1 mixture of 1,1,2-trichloro-1,2,2-trimethyldisilane and *sym*-dimethyltetrachlorodisilane) with hydrogen chloride in the presence of a catalytic amount of aluminum chloride and the subsequent treatment of the resulting *sym*-dimethyltetrachlorodisilane with methyl ortho-

formate or methanol/methyl orthoformate to form the product. The first step involves the conversion of one Si—C bond of 1,1,2-trichloro-1,2,2-trimethyldisilane into a Si—Cl bond to give *sym*-dimethyltetrachlorodisilane. The second involves the conversion of the four Si—Cl bonds of *sym*-dimethyltetrachlorodisilane (I) to Si—OMe bonds employing methyl orthoformate (Method A). The required amount of the methyl orthoformate can be reduced considerably by pre-treatment of the chlorodisilane with methanol (Method B) [6].



Experimental

All the boiling points are uncorrected. IR spectra were recorded as neat liquids with a Hitachi EPI-G3 spectrometer, and NMR spectra were measured in CCl_4 solution using a Varian A-60D spectrometer. GLC analyses were conducted using an Ohkura Model 1700 gas chromatograph.

Preparation of *sym*-dimethyltetrachlorodisilane (I)

A disilane fraction, 920 g, boiling at 150–160°C, obtained from the Direct Synthesis (reaction of methyl chloride with copper/silicon), which was shown by NMR analysis to contain mainly *sym*-dimethyltetrachlorodisilane and 1,1,2-trichloro-1,2,2-trimethyldisilane in 1 : 1 ratio, was placed in a three-necked two liter flask fitted with an air-tight stirrer, a reflux condenser and a gas-inlet tube the end of which was extended into the liquid nearly to the bottom of the flask. To this, 67 g of aluminium chloride (7% for the amount of the disilane fraction) was added and dry hydrogen chloride was introduced through the gas-inlet tube while the mixture was stirred and heated to 150°C (oil bath). After stirring for ca. 15 h, the complete consumption of 1,1,2-trichloro-1,2,2-trimethyldisilane was confirmed by GLC analysis (2 m × 4 mm, 20% silicone SF-96 on Celite 545-AW; column temp. 110–135°C). The mixture was distilled to give the crude product (751 g) boiling at 155–160°C. In order to decompose aluminum chloride remaining in the product fraction, it was mixed well with a small amount of anhydrous acetone (ca. 30 ml) * and then redistilled to give a pure sample of *sym*-dimethyltetrachlorodisilane (I), b.p. 153–154°C (lit. [9] b.p. 152–153°C); 685 g (conversion yield, 75%); NMR (CCl_4 solution): δ 3.52 (s) ppm.

* Freshly distilled from phosphorus pentoxide.

Methoxylation of I.

Method A. In a one liter dry flask fitted with a reflux condenser and a dropping funnel, 228 g (1.0 mol) of I was placed and heated to ca. 70°C. Methyl orthoformate, 466 g (4.4 mol), was added over a period of 6 h while stirring at this temperature. After the addition of methyl orthoformate was completed, the mixture was heated at 100–115°C for 40 h, after which time gas evolution of methyl chloride ceased*. The reaction mixture was distilled through a 15 cm Vigreux column under reduced pressure. After recovery of 45 g (yield, 42%) of methyl formate, which was collected in a dry-ice/acetone trap, there was obtained *sym*-dimethyltetramethoxydisilane (II): b.p. 80–84°C/27–30 mmHg, n_D^{25} 1.4168 (lit. [6] b.p. 86.2–87°C/30 mmHg, n_D^{25} 1.4166); 190 g (yield, 90%; purity > 99.5%).

Method B. In a dry three-necked two liter flask equipped with an air-tight stirrer, an addition funnel and a Dimroth condenser the top of which was connected to an aspirator through a calcium chloride tube, was placed 456 g (2.0 mol) of I. Absolute methanol, 256 g (8 mol), was added dropwise with stirring over a period of 2.5 h while the hydrogen chloride which evolved was removed under reduced pressure. After completion of the addition of methanol, the solution was heated to 90°C for 4 h under reduced pressure (up to 65 mmHg) and 225 g (2.1 mol) of methyl orthoformate was added dropwise in a 4 h period of time. The mixture was stirred at 95°C for 4 h until the gas evolution of methyl chloride had ceased* and then fractionally distilled as described above. After recovery of methyl formate and then unidentified materials (5 g) boiling up to 82°C at 30 mmHg, 285 g (yield, 68%) of II was obtained: b.p. 82–83°C/30 mmHg, n_D^{25} 1.4166.

Identification of the products was accomplished by the comparison of the spectral data (NMR and IR) with those of the literature [8,10]. The physical constants and GLC analysis (see the previous section) confirmed the purity of the products to be at least 99.5%.

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References

- 1 W.H. Atwell and D.R. Weyenberg, *J. Organometal. Chem.*, **5** (1966) 594.
- 2 E.G. Janzen, J.B. Pickett and W.H. Atwell, *J. Amer. Chem. Soc.*, **90** (1968) 2721.
- 3 W.H. Atwell and D.R. Weyenberg, *J. Amer. Chem. Soc.* **90** (1968) 3438.
- 4 W.H. Atwell and D.R. Weyenberg, *Angew. Chem., Int. Ed.*, **8** (1969) 469.
- 5 D.R. Weyenberg and W.H. Atwell, *Pure Appl. Chem.*, **19** (1969) 343.
- 6 J.W. Ryan, *J. Amer. Chem. Soc.*, **84** (1962) 4762 and the literature cited therein.
- 7 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, *J. Org. Chem.*, **21** (1956) 1264.
- 8 E. Henge and N. Holdschmidt, *Monatsh. Chem.*, **99** (1968) 340.
- 9 H. Sakurai, T. Watanabe and K. Kumada, *J. Organometal. Chem.*, **7** (1967) P15.
- 10 M.E. Childs and W.P. Weber, *J. Organometal. Chem.* **86** (1975) 169.

* The more definite method of establishing the completion of the reaction is the spot test that no white turbidity, due to the formation of quaternary ammonium salt, was observed by adding triethylamine to a small amount of the reaction mixture.