LETTER

Hexamethoxy Disilane

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Among the alkoxyds of disilane, hexaethoxy-[1,2] and hexapropoxy[2]- disilane only have been studied. Now we wish to report on the preparation and properties of hexamethoxy disilane $(CH_3O)_3SiSi(OCH_3)_3$, the lowest member of the alkoxyds of disilane.

Hexachlorodisilane (b.p. 69.8° C./49 mm. Hg. m.p. $-1.2° \sim -0.8°$C., *Anal.* Calcd. for Si_2Cl_6: Cl, 79.18, Found: Cl, 79.05) (36 g., 0.134 mol.) was placed in a 300 cc. three-necked flask, equipped with an efficient stirrer, a dropping funnel and a reflux condenser, and was cooled with an ice-salt bath. The outlet tube from the upper end of the condenser was led above the surface of the alkali solution which was placed to absorb the hydrogen chloride gas. After the hexachlorodisilane was completely solidified, the purified and dehydrated methanol (0.05% H_2O, determined

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[1] G. Martin, *J. Chem. Soc.*, **105**, 2860 (1914).

[2] E. W. Abrahamson, I. Joffe and H. W. Post, *J. Org. Chem.*, **13**, 275 (1948).

by the Kahr-Fischer reagent) (26.5 g., 0.83 mol.) was added drop by drop to the solid. When the solid was made to disappear by the reaction, the temperature of the mixture was gradually raised to 30°C. with vigorous stirring. If the temperature was raised to 40°C., the floating white mass was suddenly increased on the surface of alkali solution under the outlet tube. Since this mass may be regarded as a decomposition product appearing from the fission of Si-Si bond, the dehydrochlorination of the mixture was carried out by bubbling nitrogen slowly through the mixture at the temperature not over 30°C. After bubbling for five hours, 28 g. of the mixture was obtained, of which the chlorine content was 3%. Repeated addition of methanol, followed by aeration with nitrogen could not markedly reduce the chlorine content.

When the product was fractionated adding a small amount of methanol, there was obtained impure hexamethoxy disilane contaminated by a trace of methoxy chlorodisilane, which fumes in air and causes the hexamethoxy disilane to decompose when the product is exposed to air. To prepare the pure hexamethoxy disilane, a trace of methoxy chlorodisilane should be completely expelled before the fractionation.

For this purpose the following ammonia treatment was found to be effective. A small amount of methanol (3 g.) was added to the mixture (28 g.) and dry ammonia gas was slowly bubbled through the mixture, until the odor of hydrogen chloride disappeared. After filtration, the precipitate was washed with a small quantity of dehydrated ethyl ether. The filtrate was repeatedly evacuated until the odor of ammonia practically disappeared.

The product was rigorously fractionated through a semi-micro Stedman column of about 15 plates under reduced pressure. The constant boiling fraction (I): 63°∼4°C./86 mm.Hg (6 g.), (II): 100°∼101°C./20 mm.Hg (8 g., yield: 25%) and the residue (6 g.) were obtained.

Judging from the boiling point, fraction (I) may be methyl orthosilicate. The fraction (II), which was analysed, was a transparent liquid having a faint odor and did not decompose in air. n_D^{20} 1.4070, d_4^{20} 1.095. *Anal.* Calcd. for $C_6H_{18}O_6Si_2$ (mol. wt. 242), C: 29.73. H: 7.49, Si: 23.18, Found for (II), C: 29.48, H: 7.60, Si: 23.0, mol. wt. 235 (in benzene).

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