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PRELIMINARY NOTE

Aluminum chloride-catalyzed reactions of organosilicon compounds
IV. Preparation of tetrakis(chlorodimethylsilyl)-silane and -methane

In the previous papers of this series[1,2,3], we have shown that the reaction of alkylsilanes, germanes and stannanes with acetyl chloride in the presence of anhydrous aluminum chloride gives rise to the corresponding alkylchloro compounds, affording a convenient method of synthesis of a wide variety of alkylchlorosilanes.

In the present communication, we wish to report the application of the method to a highly branched-chain polysilane, tetrakis(trimethylsilyl)silane (I)[4], and to an analogous carbon compound, tetrakis(trimethylsilyl)methane (II)[5], to give novel symmetrical tetrakis(chlorodimethylsilyl)-silane (III) and -methane (IV) respectively.

$$[(CH_3)_3Si]_4E + 4\,CH_3COCl \xrightarrow[\text{solvent}]{AlCl_3} [Cl(CH_3)_2Si]_4E + (CH_3)_2CO$$

$$E = C, Si$$

Since (I) and (II) are crystalline, a suitable solvent was required to carry out the reaction smoothly. We have examined a number of solvent and found that petroleum ether has been the most satisfactory for this purpose. In petroleum ether, the reaction proceeded at a moderate rate heterogeneously, the product being separated from acetone-aluminum chloride complex simply by decantation. In methylene chloride or 1,2-dichloroethane, the homogeneous reaction took place rapidly and the yield was fair examined by vapor phase chromatography, however, a considerable decrease of yield was always accompanied in the step of separation of the product.

In a typical run, 39 ml (*ca.* 0.55 mole) of acetyl chloride in 50 ml of petroleum ether was added to the mixture of 10 g (0.031 mole) of (I) and 65 g (0.52 mole) of anhydrous aluminum chloride in 60 ml of petroleum ether over a period of 2.5 h with vigorous stirring. A moderate exothermic reaction with gentle reflux of petroleum ether took place. Inspections with periodic removal of aliquots which were analyzed by vapor phase chromatography showed that the reaction proceeded stepwise. When the addition was complete, however, only the final product was found in the solution. The upper layer was then decanted and the residue was extracted twice with petroleum ether. Evaporation of the solvent from the combined solution gave white crystalline material. After recrystallization from carbon tetrachloride followed by sublimation (about 150° at 6 mm), 10 g (0.025 mole, yield 80%) of pure (III) was obtained as white crystals. (Found: C, 24.08; H, 6.00; Cl, 35.24. $C_8H_{24}Cl_4Si_5$ calcd.: C, 23.87; H, 6.01; Cl, 35.23%.) The melting point could not be measured because of a high tendency of sublimation of this compound. The NMR spectrum of (III) (in deuterochloroform) showed a singlet at 0.68 ppm upfield from internal cyclohexane.

Essentially by the same procedure, (IV) was prepared from (II). However in this case, the reaction took place far more slowly than in the case of (I), and required a large excess of reagents with heating. Thus, 5 g (0.016 mole) of (II) was subjected to react with 52 ml (0.73 mole) of acetyl chloride and 86 g (0.64 mole) of aluminum chloride in 160 ml of petroleum ether. After work-up as above, recrystallization from carbon tetrachloride and sublimation (about 170° at 6 mm) gave 5.5 g (0.014 mole, yield 88 %) of pure IV, m.p. $>300°$, NMR; singlet at 0.56 ppm upfield from internal cyclohexane (in deuterochloroform). (Found: C, 27.85; H, 6.40; Cl, 36.96. $C_5H_{24}Si_4$ calcd.: C, 27.97; H, 6.26; Cl, 36.70%.)

It seems reasonable that the low reactivity of (II) might be due to steric crowding of atoms in this molecule. Interestingly (IV) was fairly stable toward hydrolysis. In (I) and (III), however, the steric requirement is presumably decreased to some extent because of a longer bond length of Si–Si than of Si–C; in agreement, (III) was found to react gradually with atmospheric moisture.

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