Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

Aluminum chloride-catalyzed reactions of organosilicon compounds
Part III. Synthesis of some polychloro-substituted methylpolysilanes*

In a recent communication[1] from this laboratory we reported that dealkylation of alkylsilanes with acetyl chloride and aluminum chloride affords a preferred, one-step procedure for synthesis of the corresponding alkylchlorosilanes, and that the reaction is also applicable to the preparation of alkylchloro-germanes and -stannanes.

$$R_4M + n\,CH_3COCl \xrightarrow{AlCl_3} R_{4-n}MCl_n + n\,CH_3COR$$

$$M = Si, Ge, Sn;\ R = \text{alkyl}$$

As an extention of this work it was desirable to determine the applicability of the method for the preparation of polychloro-substituted methylpolysilanes.

We now report the preparation of 1,1,2-trichlorotrimethyldislane (I), 1,1,2,2-tetrachlorodimethyldisilane (II) and 1,2,3-trichloropentamethyltrisilane (III). Although these compounds are potentially important as intermediates in polysilane chemistry, there has been no satisfactory method for the preparation.

In a typical experiment 24 ml (*ca.* 0.34 mole) of acetyl chloride was added to 14.5 g (0.99 mole) of hexamethyldisilane and 40 g (0.30 mole) of anhydrous aluminum chloride contained in a three-necked flask equipped with an air-tight stirrer, a reflux condenser and a dropping funnel. An exothermic reaction took place and the reaction mixture became homogeneous. After the addition was completed, the mixture was heated to 125° with stirring for 14 h. The product, (I), was removed from the mixture by distillation under reduced pressure. Redistillation gave 15.2 g (74% yield) of (I), which was essentially homogeneous on vapor phase chromatography, b.p. 144–146° (Found: C, 17.53; H, 4.57; Cl, 50.80. $C_3H_9Cl_3Si_2$ calcd.: C, 17.35; H, 4.37; Cl, 51.12%) The NMR spectrum of (I) (in carbon tetrachloride) showed singlets at 0.50 ppm (1H) and at 0.77 ppm (2H) upfield from internal cyclohexane.

Similarly, the reaction of hexamethyldisilane (14.5 g, 0.099 mole) with acetyl chloride (32 ml, *ca.* 0.45 mole) and aluminum chloride (55 g, 0.41 mole) gave (II) (13.0 g, 0.057 mole, 58% yield), b.p. 152–153°. (Found: C, 10.68; H, 2.86; Cl, 62.30. $C_2H_6Cl_4Si_2$ calcd.: C, 10.53; H, 2.65; Cl, 62.18%) The NMR spectrum of (II) (in carbon tetrachloride) showed a singlet at 0.39 ppm upfield from internal cyclohexane.

It has already been shown that the fraction boiling over the range about 150–160° from the distillation residue of the direct synthesis of methylchlorosilanes, consists essentially of a mixture of (I) and (II)[2]. Accordingly, (II) can be obtained conveniently from this mixture.

The mixture of (I) and (II) (425 g, 2.00 mole) whose average chlorine content was 52.54% ($Si_2Me_{2.89}Cl_{3.11}$) was stirred with 223 g of acetyl chloride and 317 g of aluminum chloride at 125° for 20 h. (II) was simply isolated in pure state from the mixture by distillation under reduced pressure, yield was 415 g (91%).

Finally was prepared, (III) in 54% yield, b.p. 55–57°/2, (Found: C, 22.80; H, 5.82; Cl, 40.47. $C_5H_{15}Cl_3Si_3$ calcd.: C, 22.60; H, 5.69; Cl, 40.01%) from octamethyltrisilane. The NMR spectrum of (III) (in carbon tetrachloride) showed singlets at 0.73 ppm (1H) and at 0.89 ppm (4H) *upfield* from internal cyclohexane.

Further work is in progress and will be reported fully later.

The authors are indebted to the Tokyo Shibaura Electric Co., Ltd. for a generous gift of methylchlorosilanes. The research was supported in part by the Kawakami Memorial Foundation to which the authors' thanks are due.

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Received November 29th, 1966

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* For Part II, see ref. 1.