A one-step synthesis of some substituted trisilanes

As an extension of our studies of organopolysilanes it was desirable to determine the applicability of the *in situ* type reaction used for the preparation of tetrakis-(trimethylsilyl)silane¹ to the synthesis of other polysilanes. This type of reaction has already proven useful with polyhalides of carbon².

We now report the results of the reactions of a few dichlorosilanes (RCH₃SiCl₂, $R = CH_3$, C_2H_5 and C_6H_5) with lithium and chlorotrimethylsilane (I). The reaction of dichlorodimethylsilane (II) in the presence of a large excess of (I) gave 60–70 % yields of octamethyltrisilane (III) along with small amounts of the next two higher homologues.

$$2 (CH_3)_3 SiCl + (CH_3)_2 SiCl_2 + 4 Li \xrightarrow{THF} (CH_3)_3 Si[(CH_3)_2 Si]_n Si(CH_3)_3$$

$$(I) \qquad n = 1-3$$

The most widely used procedures³⁻⁷ for the preparation of (III) involves a three step synthesis as shown below. The highest yield reported was 72% for the third step³.

$$\begin{array}{cccc} (CH_3)_3 SiCl & \xrightarrow{Na} & (CH_3)_6 Si_2 \\ (I) & & (IV) & (IV) \end{array}$$

$$(IV) & \xrightarrow{(V,H_4SO_2)} & (CH_3)_3 SiSi(CH_3)_2 CI \\ (V) & + (I^{\dagger} & \xrightarrow{Na} & (III) \end{array}$$

Kumada and Ishikawa³ also isolated, from their attractive general procedures, low yields of (III) from the reaction of (I), (II) and sodium. An important advantage of the procedure now being reported is that it is a one-step synthesis employing commercially available materials*.

In a typical procedure 5.0 g of (II) was added to 15.0 g (2.2 g-atom) of finely cut lithium wire in 180 g (1.66 mole) of (I) and 300 ml of tetrahydrofuran (THF) contained in a three-necked flask equipped with a Hershberg stirrer and reflux condenser. An exothermic reaction started in about 10 min, and after 0.5 h of stirring a solution of 60 g (0.45 mole) of (II) in 170 ml of THF was added dropwise in 8 h. After 24 h of stirring the excess lithium and lithium chloride were filtered off. Most of the solvent and excess (I) were then distilled off together for re-use. Subsequent to acid hydrolysis and the usual work-up, distillation gave 67.2 g (64.6%) of (III). The physical properties were the same as those of an authentic sample**.

When a smaller ratio of (I) to (II) was used and the reagents were added to the lithium simultaneously we were able to isolate and identify a series of compounds of the type $Me_3Si(Me_2Si)_nSiMe_3$, with n=1-6 and 8 along with some dodecamethyl-cyclohexasilane. In addition, there were isolated small amounts of material that have not been fully characterized which appear to have values of n greater than 10. The

The methylphenyldichlorosilane was purchased from the Dow Corning Corp. All other chlorosilanes were supplied by the Union Carbide Corp.

[&]quot;We are grateful to Dr. Kunada for supplying us with samples of compounds $(CH_3)_3$ Si- $[(CH_3)_2$ Si- $_n$ Si($CH_3)_3$ (n = o-10) for comparison of physical properties.

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ultraviolet properties of polysilanes⁶⁻¹¹ are useful in characterizing these compounds because the λ_{max} has been found to increase with chain length. A compound which has a λ_{max} (288 m μ) and melting point (205-207°), both of which are greater than those of Kumada's compound (CH₃)₃Si[(CH₃)₂Si]₁₀Si(CH₃)₃, has been isolated from a reaction of (II) with lithium and (I). The infrared of this sample shows only the presence of methyl on silicon.

The reaction with methylethyldichlorosilane, carried out similarly to the preparation of (III), except that this reaction was heated to reflux, gave a 65.6% yield of a product that has not been rigorously identified but appears to be 2-ethylheptamethyltrisilane, b.p. $67^{\circ}/5$ mm, $n_D^{20.3}$ 1.4679, $d^{20.3}$ 0.7984 (Found: MR_D 76.70. Calcd.: MR_D 76.93). The infrared spectrum is consistent with the assigned structure.

Surprisingly, the reaction with methylphenyldichlorosilane, under the same conditions, afforded only 25% of the known^{12,13} heptamethyl-2-phenyltrisilane. Kumada *et al.*¹² obtained a 32% yield of this compound from the sodium coupling of these same reactants. In addition, our reaction gave a crystalline product, m.p. 120–121°, which has not been identified as yet. The infrared of this solid does not show the presence of a phenyl group.

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