The reductive cocondensation of chlorotrimethylsilane and dichlorodimethylsilane

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Linear and cyclic permethyloligosilanes were prepared by the Wurtz-type cocondensation of chlorotrimethylsilane and dichlorodimethylsilane in the presence of sodium metal or samarium iodide as reducing agents. The yields and composition of the reaction products depend on the cocondensation conditions.

Key words: permethyloligosilanes, cocondensation, chlorosilanes; sodium metal, samarium iodide.

Linear permethyloligosilanes $Me(SiMe_2)_nMe$ (**1a**), where $n \geq 3$, are usually obtained by a stepwise synthesis, *i.e.*, by the elongation of the silane chain, using the reaction of reductive coupling of chlorosilanes in the presence of alkaline metal (Na or K—Na alloy) as the reducing agent in the Wurtz-type reaction.[1—4] The particular members of the homologous series of linear oligosilanes (up to heptasilane) were also obtained by one-step cocondensation of chlorotrimethylsilane (**2**) and dichlorodimethylsilane (**3**) with sodium metal at 230—250 °C.[2] Unexpectedly, the formation of oligocyclosilanes $(Me_2Si)_m$ (**1b**) did not occur. It is known[5] that in the condensation of dichlorodiorganosilanes with Na in the presence of a solvent, **1b** are usually formed (mainly, $m = 6$) along with linear oligo- and polysilanes. Recently,[6] we have demonstrated for the first time that the Si—Si bonds can be formed in the coupling of chlorotriorganosilanes or dichlorodiorganosilanes when Sm (II) salts, in particular, SmI_2 are used instead of Na as the reducing agent.

In this paper, we report the results of a study of cocondensation of chlorosilanes **2** and **3** using sodium metal, which is traditionally employed in this reaction, and SmI_2 suggested by us, as the reducing agents.

Results and Discussion

Cocondensation of chlorosilanes **2** and **3** with Na was carried out in refluxing *o*-xylene at different molar ratios of the initial chlorosilanes (**2** : **3** = 3 : 1, 2 : 1 and 1 : 1). According to GLC analysis (Fig. 1), linear (**1a**, $n = 2—10$), as well as cyclic (**1b**, $m = 5—10$) oligosilanes were present in the reaction products in all cases (Scheme 1).

Scheme 1

$$\underset{\mathbf{2}}{Me_3SiCl} + \underset{\mathbf{3}}{Me_2SiCl_2} \xrightarrow[-NaCl]{Na} \underset{\mathbf{1a}}{Me(SiMe_2)_nMe} + \underset{\mathbf{1b}}{(Me_2Si)_m}$$

The content of **1b** depends on the ratio of chlorosilanes and increases with the increase in the molar percentage of **3** in the mixture (Table 1); the total yield of

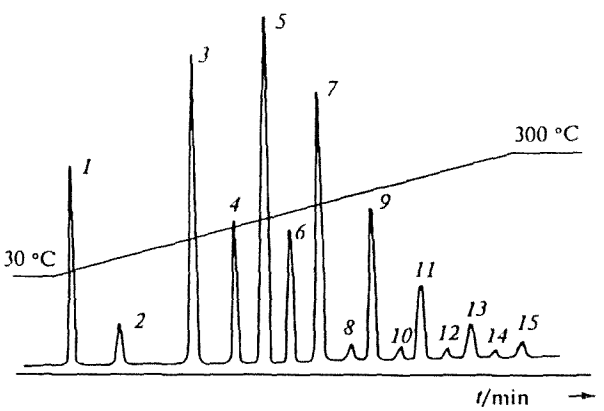

Fig. 1. Chromatogram of the cocondensation products of **2** and **3** (2 : 1) with Na: *1, 2, 3, 5, 7, 9, 11, 13, 15*; **1a**, n = 2—10 respectively; *4, 6, 8, 10, 12, 14*; **1b**, m = 5—10, respectively.

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Table 1. Effect of the ratio of the initial chlorosilanes on the composition of the cocondensation products

Entry	2 : 3	Reducing agent	Product composition (%)			Total yield (%)
			1a	**1b**	**1c**	
1	3 : 1	Na	80.5	19.5	—	77
2	2 : 1	Na	77.3	22.7	—	80
3	2 : 1	SmI_2	76.7	23.3	—	83
4	1 : 1	Na	65.5	23.5	11.0	72

1a and **1b** is 70—80 %. High-molecular-weight polydimethylsilane (**1c**) was also isolated in a ratio of **2** : **3** = 1 : 1.

In addition to the change in the composition of the reaction products, in the cocondensation in *o*-xylene, a striking difference in the distribution pattern of oligosilanes according to the chain length (n) was also observed. The results differ from those reported earlier[2] (Fig. 2). When the cocondensation was performed in an autoclave in the absence of a solvent, **1a** (n = 2) was formed in the highest yield, and the distribution pattern was of an asymptotic character (see Fig. 2, *a*), whereas in *o*-xylene, oligosilanes **1a** (n = 4—6, see Fig. 2, *b*) were the major products. As for oligomers of **1b**, cyclopenta- and cyclohexasilanes were formed predominantly (see Fig. 2, *c*). Thus, the conditions of cocondensation affect

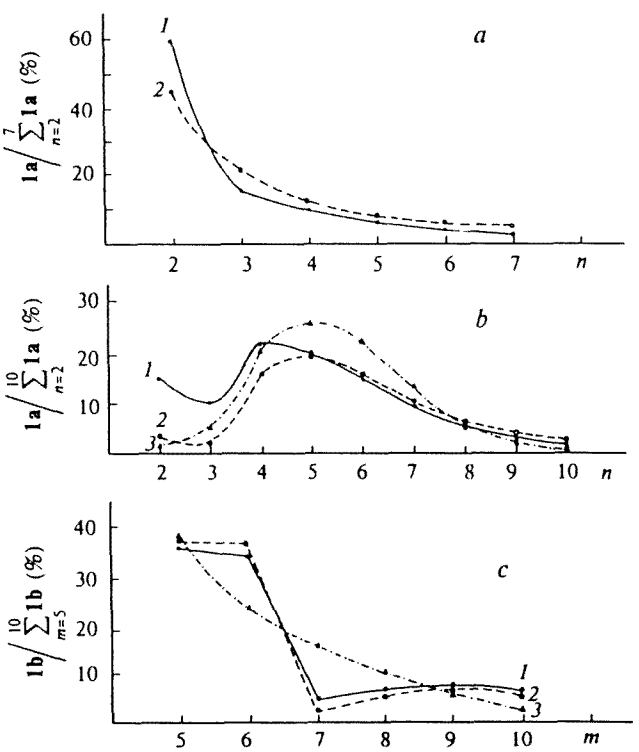

Fig. 2. Distribution patterns according to the chain length (n) of **1a** (*a*, *b*) and the cycle size (m) of **1b** (*c*) as a function of the **2** : **3** ratio: 3 : 1 (*1*); 2 : 1 (*2*); 1 : 1 (*3*) (*a*), the published data[2](*a*).

substantially the composition and the yields of the reaction products.

Previously,[6] we have demonstrated that in the reaction of **2** with SmI_2, disilane **1a** (n = 2) was obtained only in a negligible amount. At the same time, **3** reacts rapidly with SmI_2 at ambient temperature affording a mixture of permethyl-α,ω-dichlorooligosilanes along with a small amount of **1b**. In a continuation of our investigation of the reductive coupling of organochlorosilanes, we studied the cocondensation of **2** and **3** with SmI_2 (0.1 *M* solution in THF). It was established that this reaction proceeds in a boiling solvent (THF) affording oligosilanes **1a** and **1b**, and in a ratio of **2** : **3** equal to 2 : 1 the ratio of **1a** : **1b** is almost the same as that for cocondensation in the presence of Na (see Table 1). However, the use of SmI_2 as a reducing agent in this reaction instead of alkaline metal has some advantages: the cocondensation may be carried out in a homogeneous medium (in THF) at lower temperature (at 66 °C instead of 144 °C) and the reaction time is shortened from 30 to 5 h.

Experimental

The GLC analysis was carried out with an LKhM-8MD chromatograph on a stainless steel column (100×0.3 cm, 5 % SE-30 on Chromaton N-AW-DMCS), equipped with a katharometer, using a temperature range from 30 to 300 °C programmed with 12 deg min^{-1}, and He as the carrier gas.

The reaction products were identified by comparison with authentic samples of **1a** and **1b** synthesized according to the known procedures from Refs. 2, 3, 7, and 8.

All reactions were carried out under dry Ar.

Cocondensation of 2 and 3 (1 : 1) in the presence of Na. A mixture of **2** (108.5 g, 1 mol) and **3** (129.0 g, 1 mol) was added dropwise to a dispersion of Na (69.0 g, 3 g-at.) in boiling, anhydrous *o*-xylene (400 mL) for 3 h, and the mixture was refluxed for 30 h with intense stirring; the reaction was monitored by GLC. The reaction mixture was cooled and filtered. Volatile substances (the fraction with b.p. 105—120 °C) and the solvent were removed from the filtrate. The residue was combined with the collected fraction, treated with cold, concentrated H_2SO_4 to remove siloxanes, washed with water to the neutral reaction, dried with Na_2SO_4, and analyzed by GLC. Fractionation of the residue (73.4 g) on a rectification column afforded **1a** (95—98 % purity according to GLC) with n up to 5 (from n = 6, **1a** contained 15—20 % of **1b** as an admixture): n = 2, b.p. 113—114 °C, n_D^{20} 1.4225 (*cf.* Ref. 2: b.p. 112—113 °C, n_D^{25} 1.4200); n = 3, b.p. 177—178 °C, n_D^{20} 1.4638 (*cf.* Ref. 2: b.p. 176—177 °C, n_D^{25} 1.4572); n = 4, b.p. 125—126 °C (34 Torr), n_D^{20} 1.4875 (*cf.* Ref. 2: b.p. 121—122 °C (35 Torr), n_D^{30} 1.4810); n = 5, b.p. 115—116 °C (5 Torr), n_D^{20} 1.5055 (*cf.* Ref. 2: b.p. 162—163 °C (33 Torr), n_D^{30} 1.5010).

The precipitate after filtration of the reaction mixture was washed subsequently with anhydrous *o*-xylene, ethanol, and water, and the insoluble residue was washed with an ethanol—water mixture (1 : 1) until the reaction for the presence of Cl^- was negative. The residue was dried in a vacuum oven (70 °C), yielding **1c** (4.6 g, 7.9 % from **3**) as a white powder. UV, λ_{max}/nm: 345. IR (KBr), ν/cm^{-1}: 2990, 2940 (C—H), 1245, 835 (Si—Me).

Cocondensation of **2** and **3** in the ratios of 3 : 1 and 2 : 1 was carried out in a similar manner.

Cocondensation of 2 and 3 (2 : 1) in the presence of SmI_2. A mixture of **2** (0.5 g, 0.0046 mol) and **3** (0.3 g, 0.0023 mol) in anhydrous THF (5 mL) was added dropwise over 5 min to a stirred 0.1 *M* solution of SmI_2 in anhydrous THF (110 mL) prepared from Sm (3.32 g, 0.022 g-at.) and diiodomethane (2.95 g, 0.011 mol). The mixture was refluxed for 5 h until a yellow-brown coloration appeared. The reaction mixture was cooled and treated with 0.1 *N* HCl to dissolve the precipitate of SmI_2Cl; the organic layer was extracted with ether, washed with water, aqueous sodium thiosulfate, and water, and dried with Na_2SO_4. Ether and THF were removed; according to GLC, the residue (0.31 g) contained mainly a mixture of **1a** and **1b**.

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