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The behaviour of medium-sized permethylated cyclosilanes towards $SOCl_2$ and $SOCl_2$–$HC(OCH_3)_3$ *

P.K. Jenkner, A. Spielberger and E. Hengge
Institute of Inorganic Chemistry, Technical University of Graz (Austria)

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Abstract

Treatment of Si_6Me_{12} with $SOCl_2$ in various solvents gives α,ω-dichloropermethylpolysilanes (n_{Si} = 2,3,4,6) at temperatures above 80°C. In contrast to an earlier report, treatment of the α,ω-dichloropermethylpolysilanes with $HC(OCH_3)_3$ in the presence of $SOCl_2$ does not give Si_6Me_{12}.

Introduction

Considerable effort has gone into the search for simple and convenient methods for formation of silicon–silicon bonds but only a very few satisfactory preparative methods have resulted. Thus there is much interest in possible new methods.

Recently, Oka *et al.* obtained α,ω-dichloropermethylpolysilanes by cleavage of dodecamethylcyclohexasilane (Si_6Me_{12}) with thionyl chloride ($SOCl_2$) [1]:

$$Si_6Me_{12} + SOCl_2 \xrightarrow[RT]{CCl_4} Cl(SiMe_2)_nCl \quad (n = 2, 3, 4, 6) \qquad (1)$$

The reaction took place at room temperature and was monitored by GLC–MS analysis. Quantitative regeneration to Si_6Me_{12} was reported to take place upon addition of orthoformic acid trimethyl ester $HC(OCH_3)_3$ to the product mixture, and since such a process would have to involve a Si–Si bond formation step [2,3] it seemed to make available a new and very valuable route to species containing Si–Si bonds. We thus decided to explore this possibility.

Results

α,ω-Dichlorosilanes from Si_6Me_{12} and Si_5Me_{10}

As described by Oka and Nakao, the reaction of Si_6Me_{12} with $SOCl_2$ diluted in CCl_4 (eq. 1) was followed by GLC–MS analysis, and the results were in agreement

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Correspondence to: Professor E. Hengge, Institute of Inorganic Chemistry, Technical University of Graz, Graz, Austria.

* Dedicated to Professor Peter Sartori on the occasion of his 60th birthday.

Table 1

Product distribution in reactions of Si_6Me_{12} with $SOCl_2$

Solvent	Time (h)	T (°C)	$Cl(SiMe_2)_nCl$ (%)			
			$n=2$	$n=3$	$n=4$	$n=6$
CCl_4	8	RT	–	–	–	–
CCl_4	8	76	–	–	2	12
$C_2H_2Cl_4$	4	146	20	24	18	28

with those previously reported [1,2]. The data obtained were used for identification purposes in subsequent experiments. Similar results have been obtained by treatment of Si_6Me_{12} with PCl_5 [4] or $SnCl_4$ [5].

We then examined the ring-opening of Si_6Me_{12} in greater detail. We confirmed that, as reported by Gilman and Inoue [4], treatment of Si_6Me_{12} with PCl_5 in a refluxing solution of CCl_4 gives a mixture of α,ω-dichloropermethylpolysilanes. The nature and yield of the products obtained varied with the duration of the reaction and significantly with the amount of reagent. Initially, the higher homologues (n = 4,6) are formed, and these subsequently degrade to give lower α,ω-dichloropermethylpolysilanes (n = 2,3) (eq. 2).

$$Si_6Me_{12} + PCl_5 \rightarrow Cl(SiMe_2)_nCl \quad (n = 2,3,4,6) \qquad (2)$$

Reactions were carried out under various conditions using freshly distilled PCl_5 and in all cases the results agreed with those previously reported [4].

Treatment of Si_6Me_{12} with $SOCl_2$ in *sym*-tetrachloroethane under reflux (146°C) gave the same products; the amount of $SOCl_2$ used determined the yield of α,ω-dichloropermethylpolysilanes. Stirring of a solution of Si_6Me_{12} and $SOCl_2$ (tenfold molar excess) in CCl_4 under reflux (76°C) for 40 h also produced a small amount of the α,ω-dichloropermethylpolysilanes with n = 4 or 6. (eq. 3), as shown in Table 1.

$$Si_6Me_{12} + SOCl_2 \xrightarrow[CCl_4,\ C_2H_2Cl_4]{\text{reflux}} Cl(SiMe_2)_nCl \qquad (3)$$

Mixtures obtained by reaction of Si_6Me_{12} with PCl_5 or with $SOCl_2$ were separated by distillation *in vacuo*. Comparison of the physical and ^{29}Si NMR data for the products with those for authentic samples confirmed their identities. The solvents CCl_4 and $C_2H_2Cl_4$ were found to be completely inert towards either $SOCl_2$ or Si_6Me_{12}.

When the reaction was carried out at room temperature (RT) the Si_6Me_{12} was recovered quantitatively by distillation and subsequent sublimation *in vacuo* (90°C). The absence of any reaction was also shown by GLC analysis at a fixed column temperature not higher than 70°C. However, when column temperatures above 140°C were used, various α,ω-dichlorosilanes were detected, even when the $SOCl_2$ was added to the solution of Si_6Me_{12} immediately before a sample was taken for analysis. This showed that the cleavage of the ring was taking place only during the GLC analysis.

Evolution of gas was observed in the course of the reactions at the reflux temperature, and this was identified as SO_2 ($BaCl_2$ solution). It is known that $SOCl_2$ decomposes at 76°C as shown in eq. 4.

$$4\ SOCl_2 \rightarrow S_2Cl_2 + 2SO_2 + 3Cl_2 \qquad (4)$$

Chlorine is commonly used for synthesis of α,ω-dichloropermethylpolysilanes by scission of Si_6Me_{12} [6] and so was probably responsible for some of the cleavage observed. However, treatment of Si_6Me_{12} with S_2Cl_2 caused ring cleavage in much the same way as $SOCl_2$, but only in $C_2H_2Cl_4$ under reflux. Variation of the amount of $SOCl_2$ used resulted in different product distributions. Reactions of S_2Cl_2 or Cl_2 with Si_6Me_{12} both yield α,ω-dichloropermethylpolysilanes; and since both of these reagents are formed during thermal decomposition of $SOCl_2$ they are presumably both involved in the reaction taking place on the GLC column.

In contrast to Si_6Me_{12}, decamethylcyclopentasilane (Si_5Me_{10}) underwent reaction with $SOCl_2$, S_2Cl_2, or PCl_5 in $C_2H_2Cl_4$, to give 1,5-dichlorodecamethylpentasilane selectively, even at room temperature (eq. 5). This product decomposes readily at the reflux temperature to give 1,3-dichlorohexamethyltrisilane and 1,2-dichlorotetramethyldisilane.

$$Si_5Me_{10} + SOCl_2\ (S_2Cl_2, PCl_5) \xrightarrow[C_2H_2Cl_4]{RT} Cl(SiMe_2)_5Cl \xrightarrow[C_2H_2Cl_4]{146^\circ C} Cl(SiMe_2)_nCl \qquad (5)$$

$(n = 2,3)$

Addition of $HC(OCH_3)_3$ to the system $Si_6Me_{12}/SOCl_2$

As stated above, we found no evidence of a reaction leading to α,ω-dichloropermethylpolysilanes in the system $Si_6Me_{12}/SOCl_2$ at room temperature. When a molar excess of $HC(OCH_3)_3$ is added to this mixture, $SOCl_2$ is rapidly consumed, and subsequent GLC analysis at a range of temperatures (80–250°C) showed only starting Si_6Me_{12} to be present; *i.e.* no conversion into α,ω-dichloropermethylpolysilanes occurred in the GLC column. As expected, addition of $HC(OCH_3)_3$ to a mixture of α,ω-dichloropermethylpolysilanes (generated in refluxing $C_2H_2Cl_4$) did not produce Si_6Me_{12}.

Mixtures of α,ω-dichloropermethylpolysilanes were reacted with various other nucleophiles, *e.g.* alcohols, water, or acetic acid [2,3]. Treatment with $HC(OCH_3)_3$ yielded the corresponding α,ω-dimethoxy homologues [7] (eq. 6); the compounds were identified by linked GLC–MS analysis; no degradation took place in the GLC.

$$Cl(SiMe_2)_nCl + HC(OCH_3)_3 \rightarrow CH_3O(SiMe_2)_nOCH_3 \qquad (6)$$

Pure α,ω-dichloro compounds ($n = 2$–6), as well as mixtures of them showed the same behaviour towards $HC(OCH_3)_3$ and no linear or cyclic polysilanes were detected in reactions in various solvents at several temperatures. No formation of polysilanes from $SiMe_2Cl_2$ was detected under these conditions.

It is clear that no reaction takes place between Si_6Me_{12} and $SOCl_2$ in CCl_4, C_6H_6, $C_2H_2Cl_4$, THF or cyclo-C_6H_{12} at room temperature. Our results suggest that $HC(OCH_3)_3$ reacts immediately with $SOCl_2$. There is clear evidence of ring cleavage at temperatures above 80°C in solution (at the relevant boiling point) or on a non-polar GLC column, and that is due mainly to reaction with decomposition products from $SOCl_2$ (namely S_2Cl_2 and Cl_2). Thus the observations of Oka *et al.* do not provide the basis of a new route to formation of Si–Si bonds.

Experimental

GLC analysis was carried out with a HP 5890 II/ HP3396 chromatograph (single FID, column HP 1 (12 m, diameter 0.53 mm), temperature range 80–250°C).

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker MSL 300 (300 MHz) instrument in C_6D_6 solutions with TMS as internal standard. For GLC–MS analysis a Finnigan-MAT-212 spectrometer was used.

Dodecamethylcyclohexasilane [8], decamethylcyclopentasilane [9] and the pure α,ω-dichloropermethylpolysilanes [4] were made by literature procedures. 1,5-Dichlorodecamethylpentasilane was prepared by selective cleavage of Si_5Me_{10} with PCl_5. CCl_4 and *sym*-$C_2H_2Cl_4$ were dried over P_4O_{10} and freshly distilled.

All reactions were carried out in oven-dried 50 ml glassware in an atmosphere of oxygen-free, dry nitrogen. A 0.2 g sample of Si_6Me_{12} or Si_5Me_{10} was dissolved in 5 ml of the chosen solvent and $SOCl_2$ or S_2Cl_2 was added from a syringe. The reactions were monitored continuously by GLC. Reliable analysis was possible only after removal of low boiling species by distillation *in vacuo* (5×10^{-5} bar), since reactions can occur in the GLC column.

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