

Journal of Organometallic Chemistry, 427 (1992) 161–164
 Elsevier Sequoia S.A., Lausanne
 JOM 22383

The behaviour of medium-sized permethylated cyclosilanes towards SOCl_2 and $\text{SOCl}_2\text{-HC(OCH}_3)_3$ *

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(Received June 10, 1991)

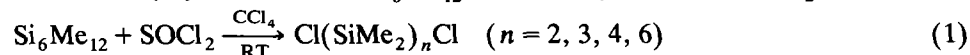
Abstract

Treatment of $\text{Si}_6\text{Me}_{12}$ with SOCl_2 in various solvents gives α,ω -dichloropermethylpolysilanes ($n_{\text{Si}} = 2,3,4,6$) at temperatures above 80°C . In contrast to an earlier report, treatment of the α,ω -dichloropermethylpolysilanes with $\text{HC(OCH}_3)_3$ in the presence of SOCl_2 does not give $\text{Si}_6\text{Me}_{12}$.

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 ($\text{Si}_6\text{Me}_{12}$) with thionyl chloride (SOCl_2) [1]:



The reaction took place at room temperature and was monitored by GLC–MS analysis. Quantitative regeneration to $\text{Si}_6\text{Me}_{12}$ was reported to take place upon addition of orthoformic acid trimethyl ester $\text{HC(OCH}_3)_3$ 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 $\text{Si}_6\text{Me}_{12}$ and $\text{Si}_5\text{Me}_{10}$

As described by Oka and Nakao, the reaction of $\text{Si}_6\text{Me}_{12}$ 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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* Dedicated to Professor Peter Sartori on the occasion of his 60th birthday.

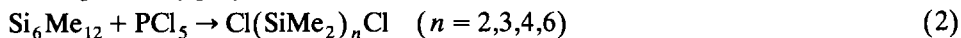
Table 1

Product distribution in reactions of $\text{Si}_6\text{Me}_{12}$ with SOCl_2

Solvent	Time (h)	T ($^{\circ}\text{C}$)	$\text{Cl}(\text{SiMe}_2)_n\text{Cl}$ (%)			
			$n = 2$	$n = 3$	$n = 4$	$n = 6$
CCl_4	8	RT	–	–	–	–
CCl_4	8	76	–	–	2	12
$\text{C}_2\text{H}_2\text{Cl}_4$	4	146	20	24	18	28

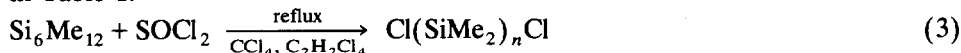
with those previously reported [1,2]. The data obtained were used for identification purposes in subsequent experiments. Similar results have been obtained by treatment of $\text{Si}_6\text{Me}_{12}$ with PCl_5 [4] or SnCl_4 [5].

We then examined the ring-opening of $\text{Si}_6\text{Me}_{12}$ in greater detail. We confirmed that, as reported by Gilman and Inoue [4], treatment of $\text{Si}_6\text{Me}_{12}$ with PCl_5 in a refluxing solution of CCl_4 gives a mixture of α,ω -dichloropermethylopolysilanes. 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 -dichloropermethylopolysilanes ($n = 2,3$) (eq. 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 $\text{Si}_6\text{Me}_{12}$ 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 -dichloropermethylopolysilanes. Stirring of a solution of $\text{Si}_6\text{Me}_{12}$ 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 -dichloropermethylopolysilanes with $n = 4$ or 6. (eq. 3), as shown in Table 1.



Mixtures obtained by reaction of $\text{Si}_6\text{Me}_{12}$ 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 $\text{C}_2\text{H}_2\text{Cl}_4$ were found to be completely inert towards either SOCl_2 or $\text{Si}_6\text{Me}_{12}$.

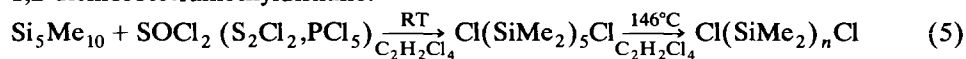
When the reaction was carried out at room temperature (RT) the $\text{Si}_6\text{Me}_{12}$ was recovered quantitatively by distillation and subsequent sublimation *in vacuo* (90°C). The absence of any reaction was also shown by GLC analysis at a fixed column temperature not higher than 70°C . However, 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 $\text{Si}_6\text{Me}_{12}$ 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.



Chlorine is commonly used for synthesis of α,ω -dichloropermethylpolysilanes by scission of $\text{Si}_6\text{Me}_{12}$ [6] and so was probably responsible for some of the cleavage observed. However, treatment of $\text{Si}_6\text{Me}_{12}$ with S_2Cl_2 caused ring cleavage in much the same way as SOCl_2 , but only in $\text{C}_2\text{H}_2\text{Cl}_4$ under reflux. Variation of the amount of SOCl_2 used resulted in different product distributions. Reactions of S_2Cl_2 or Cl_2 with $\text{Si}_6\text{Me}_{12}$ 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 $\text{Si}_6\text{Me}_{12}$, decamethylcyclopentasilane ($\text{Si}_5\text{Me}_{10}$) underwent reaction with SOCl_2 , S_2Cl_2 , or PCl_5 in $\text{C}_2\text{H}_2\text{Cl}_4$, 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.

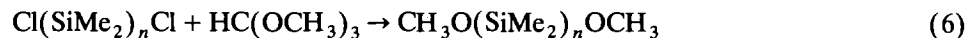


$$(n = 2,3)$$

Addition of $\text{HC}(\text{OCH}_3)_3$ to the system $\text{Si}_6\text{Me}_{12}/\text{SOCl}_2$

As stated above, we found no evidence of a reaction leading to α,ω -dichloropermethylpolysilanes in the system $\text{Si}_6\text{Me}_{12}/\text{SOCl}_2$ at room temperature. When a molar excess of $\text{HC}(\text{OCH}_3)_3$ 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 $\text{Si}_6\text{Me}_{12}$ to be present; *i.e.* no conversion into α,ω -dichloropermethylpolysilanes occurred in the GLC column. As expected, addition of $\text{HC}(\text{OCH}_3)_3$ to a mixture of α,ω -dichloropermethylpolysilanes (generated in refluxing $\text{C}_2\text{H}_2\text{Cl}_4$) did not produce $\text{Si}_6\text{Me}_{12}$.

Mixtures of α,ω -dichloropermethylpolysilanes were reacted with various other nucleophiles, *e.g.* alcohols, water, or acetic acid [2,3]. Treatment with $\text{HC}(\text{OCH}_3)_3$ 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.



Pure α,ω -dichloro compounds ($n = 2-6$), as well as mixtures of them showed the same behaviour towards $\text{HC}(\text{OCH}_3)_3$ 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 $\text{Si}_6\text{Me}_{12}$ and SOCl_2 in CCl_4 , C_6H_6 , $\text{C}_2\text{H}_2\text{Cl}_4$, THF or cyclo- C_6H_{12} at room temperature. Our results suggest that $\text{HC}(\text{OCH}_3)_3$ 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).

^1H 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-Dichlorododecamethylpentasilane was prepared by selective cleavage of $\text{Si}_5\text{Me}_{10}$ with PCl_5 . CCl_4 and *sym*- $\text{C}_2\text{H}_2\text{Cl}_4$ 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 $\text{Si}_6\text{Me}_{12}$ or $\text{Si}_5\text{Me}_{10}$ 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.

Acknowledgments

Financial support from the Fonds zur Förderung der wissenschaftlichen Forschung and a gift of silanes from Wacker A.G. (Burghausen/Germany) are gratefully acknowledged.

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