CYCLIC POLYSILANES

IX *. THE REACTION OF CYCLOPERMETHYLPOLYSILANES AND α,ω-DICHLOROPERMETHYLPOLYSILANES WITH CHLORINE

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Summary

The reaction of Si_6Me_{12} and Si_5Me_{10} with chlorine gives $1,6\text{-}Cl_2Si_6Me_{12}$ and $1,5\text{-}Cl_2Si_5Me_{10}$, respectively, and these compounds are in turn cleaved by chlorine to give smaller α, ω-dichloropolysilanes. The terminal Si—Si bond in these linear chlorosilanes appears to be relatively unreactive towards chlorine, with chlorination occurring instead at the interior Si—Si bond positions in the chain. With larger amounts of chlorine, the methyl group in $1,2\text{-}Cl_2Si_2Me_4$ can also be chlorinated.

The relative reactivities toward chlorine were found to be: Si_5Me_{10} $>>> Si_6Me_{12} > 1,6 \geqslant 1,5 \geqslant 1,4 > 1,3 >> 1,2$.

Introduction

α,ω-Dichloropolysilanes are ideal compounds from which to synthesize higher ring and chain polysilanes and polysilane derivatives, for the silicon—chlorine bond in these compounds can react in both coupling and substitution reactions. Specific preparations for $1,2\text{-}Cl_2Si_2(CH_3)_4$ and $1,3\text{-}Cl_2Si_3(CH_3)_6$ have been reported [1], but these syntheses require several steps as well as troublesome separations of mono and dichloro products. Moreover, these methods are not applicable for the syntheses of higher chloropolysilanes.

The chlorination of cyclic permethylpolysilanes affords a better route to the preparation of α,ω-dichloropolysilanes. The cyclic starting materials can now be routinely prepared in over 90% yield [2], and by chlorinating them, higher α,ω-dichloropolysilanes can be produced. No monochloro derivatives are produced, making separation easier.

The reaction of dodecamethylcyclohexasilane with chlorine to give α,ω-di-
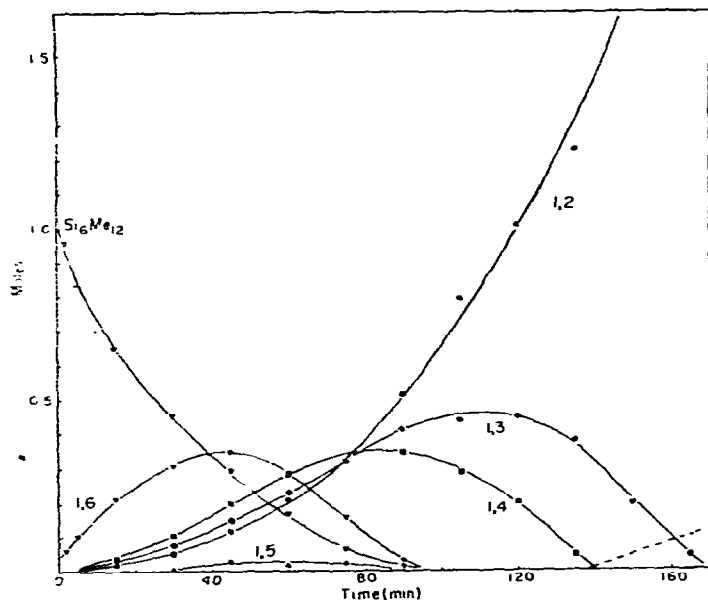
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Fig. 1. The reaction of Si_6Me_{12} with chlorine, yielding α,ω-dichloropermethylpolysilanes. The formation of the side product $ClSi(CH_3)(CH_2Cl)Si(CH_3)_2Cl$ is showed by the dashed line.

On this and all other graphs, the number of moles has been scaled to convenient, arbitrary units.

chloropolysilanes was first reported by Gilman [3], and a similar ring cleavage reaction with PCl_5 is also known [4]. We have investigated in more detail the chlorine cleavage of Si_6Me_{12} and have also studied the reactions of Si_5Me_{10} and the product α,ω-dichloropolysilanes with chlorine. The relative reactivities of these compounds and the preferred positions of bond cleavage have also been determined. Our results, summarized in Figs. 1 and 2, indicate the general course
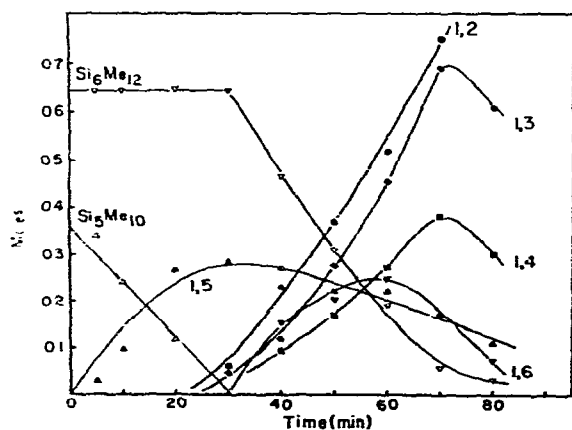

Fig. 2. The reaction of a mixture of Si_6Me_{12} and Si_5Me_{10} with chlorine.

of the chlorination reaction and can be used to maximize the yields of specific chlorosilanes and minimize sideproducts.

Results and discussion

The course of the reaction of Si_6Me_{12} with chlorine is shown in Fig. 1. The initial reaction appears to be the cleavage of Si_6Me_{12} to form 1,6-dichlorododecamethylhexasilane (1,6), followed by cleavage of 1,6 to give 1,4-dichlorooctamethyltetrasilane (1,4), 1,3-dichlorohexamethyltrisilane (1 3), and 1,2-dichlorotetramethyldisilane (1,2). The fact that only about 1% of 1,5-dichlorodecamethyl-pentasilane (1,5) is formed indicates that the Si–Si bonds in 1,6 are not cleaved by chlorine with equal probability, for if this were the case, 1,5, 1,4 and 1,3 would be initially formed from 1,6 in equal amounts. Although the amount of 1,5 formed is low, 1,3 and 1,4 are readily formed in approximately equimolar amounts. This indicates that while cleavage by Cl_2 at the terminal Si–Si bond is unfavorable, the three interior Si–Si bond positions are more easily cleaved, with about equal probability. However, when Si_5Me_{10} is reacted with chlorine (Fig. 2), 1,5 is the initial product. It should be noted that this is a new method of production for this compound giving 1,5 in high yield (80%).

Results of chlorination of other chlorosilanes similarly show that the attack of chlorine on the bond adjacent to the terminal $SiMe_2Cl$ group is extremely difficult. For example in Fig. 3, only 9% of 1,4 is cleaved by chlorine to form 1,3, with most of the cleavage taking place instead at the internal bond position to give 1,2. Also consistent with this is the fact that the Si–Si bond in 1,2 is very resistant to chlorination, leading to the formation of (chloromethyl)chlorosilanes.

In the chlorination of 1,2, we observed the formation of large amounts of side products, and observed that during the reaction chlorine was accumulating in sufficient concentration to turn the solution yellow. The side product formed first is $ClSi(CH_3)(CH_2Cl)Si(CH_3)_2Cl$, followed probably by $ClSi(CH_3)(CHCl_2)Si$-$(CH_3)_2Cl$, $ClSi(CH_3)(CH_2Cl)Si(CH_2)ClCH_3)Cl$ and $ClSi(CH_3)(CH_2Cl)Si(CHCl_2)$-$(CH_3)Cl$ and their isomers. These side products were eventually cleaved to mono-silanes. By reacting Si_6Me_{12} with a large excess * of chlorine, we also observed the formation of side products, this time early in the course of the reaction.

In order to find out why the terminal silicon–silicon bonds were resistant to chlorination, several other reactions were carried out. When 1-chloroundecameth-ylhexasilane was treated with chlorine, >95% of the cleavage took place at in-ternal silicon–silicon bonds (only about 3% of 1,5 was formed). Similarly, when linear decamethyltetrasilane was chlorinated, about 85% of the cleavage occurred at the central silicon–silicon bond to form Si_2Me_5Cl. These results show that a terminal $SiMe_3$ group also inhibits cleavage at the adjacent Si–Si bond, probably for steric reasons. However, a comparison of the rates of chlori-nation for Si_2Me_6 and 1,2 indicate that inhibition is much more pronounced when the terminal group is $SiMe_2Cl$. As previously noted, the reaction of 1,2 with chlorine proceeds very slowly whereas the corresponding reaction with Si_2Me_6 is quite rapid, with chlorine never building up in sufficient concentration to turn the reaction yellow.

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* 180 ml Cl_2 min^{-1}, as proposed by Inoue and Gilman [3].

274

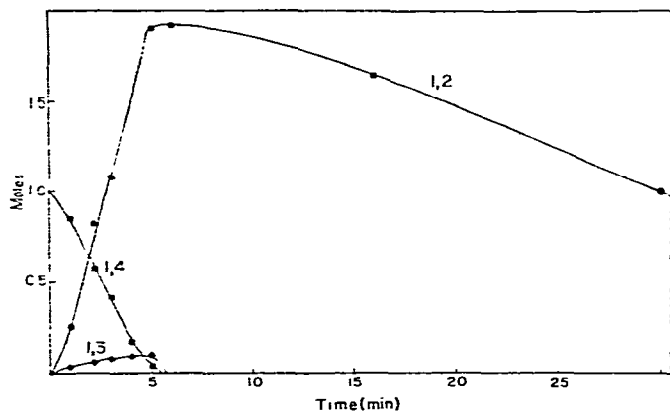
Fig. 3. The reaction of $1,4\text{-}Cl_2Si_4Me_8$ with chlorine.

As can be seen in Fig. 2, the reactivity of Si_5Me_{10} to chlorine is much greater than that of Si_6Me_{12}, such that essentially all of the Si_5Me_{10} is cleaved before the chlorination of Si_6Me_{12} begins. This is one of the first measures of the relative reactivities of these two compounds, with Si_5Me_{10} being more susceptible to cleavage presumably because of the less hindered approach of chlorine to the Si—Si bonds in the five-membered ring.

When an equimolar mixture of Si_6Me_{12} and 1,6 is reacted with chlorine (Fig. 4), Si_6Me_{12} reacts with chlorine at a slightly more rapid rate, as indicated by the slight increase in the amount of 1,6 during the initial stage of the reaction. Chlorine reacts with 1,6, 1 5, and 1,4 at approximately equal rates, but more slowly with 1,3, (Fig. 1). However, 1,2 reacts much more slowly, as clearly shown in Fig. 3.

To summarize, the rates of reaction with chlorine were found to decrease in the order:
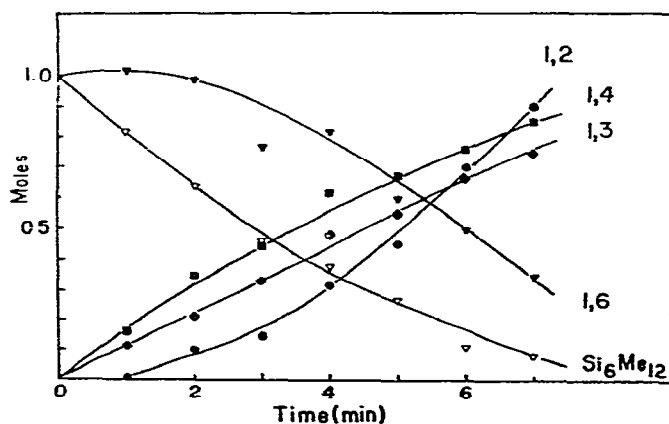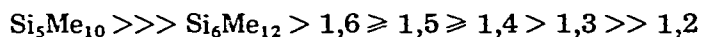
$Si_5Me_{10} >>> Si_6Me_{12} > 1,6 \geqslant 1,5 \geqslant 1,4 > 1,3 >> 1,2$

Fig. 4. The reaction of an equimolar mixture of Si_6Me_{12} and $1,6\text{-}Cl_2Si_6Me_{12}$ with chlorine.

From the course of the reactions shown in Figs. 1 and 2, it can be seen that it is only possible to obtain limited yields for each chlorosilane. The optimal reaction time to use for the preparation of a specific chlorosilane can be selected from these figures.

Experimental

All reactions were followed by VPC, using a Model 5340 Barber-Coleman gas chromatograph equipped with a thermal conductivity detector. A 15' × 1/4" QF-1 column (20% on Chromasorb W, 60—80 mesh) was used for analytical work with a helium flow of approximately 50 ml min⁻¹. Similarly a 7' × 3/8" column with a helium flow of 110 ml min⁻¹ was used for preparative work. The estimation peak area for 1,2 was difficult and subject to large error, for its peak lay very close to the solvent peak (see Fig. 6).

IR spectra were recorded on a Perkin-Elmer 457 grating spectrometer, using a sample film on CsI plates. ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard on a JEOL MH-100 spectrometer. Extensive mass spectral studies were carried out on the α,ω-dichloromethylpolysilanes [5], and will be reported in a later paper.

Chlorine (Matheson, 99.5%) was first diluted approximately 4 : 1 with nitrogen before being passed into the reaction mixture. A rate of approximately 40 ml min⁻¹ of this gas mixture was used for the kinetic studies, while for the larger scale reactions a rate of approximately 150 ml min⁻¹ was used. The exact rate of chlorine flow did not appear to be critical as long as it was kept low. With higher concentrations of chlorine, chlorination also occurred in the methyl group

Dodecamethylcyclohexasilane and decamethylcyclopentasilane were prepared using a modification of the procedure described by Carberry and West [2]. α,ω-Dichloropolysilanes were obtained from the chlorination of Si_6Me_{12}, as described below. 1-$ClSi_6Me_{11}$ was prepared from the reaction of MeMgI with 1,6-$Cl_2Si_6Me_{12}$. This reaction was carried out in dry ether, using a 1 : 1 ratio of reactants. The yield of this reaction was approximately 60%, as evidenced by VPC analysis, and the product was separated by preparative VPC.

Carbon tetrachloride was distilled from P_2O_5 whenever repeating literature reactions, and otherwise was used without further purification.

Reaction of Si₆Me₁₂ with chlorine

Expt. 1. A 100 ml three-necked flask equipped with a capillary inlet tube, column and thermometer was charged with 95 ml CCl₄ and 10 g Si_6Me_{12}. The flask was cooled with an ice bath and the flow of chlorine initiated, with rapid magnetic stirring throughout the reaction. Every 15 min, a one μl sample of the reaction mixture was withdrawn via syringe and analyzed by VPC. The reaction was stopped at the point at which only 1,2 remained, as shown by this analysis.

The results of this reaction are shown graphically in Fig. 1. Subsequent preparative chlorination reactions were based on these results, using this picture to predict product distributions and yields at specific points in the reaction.

Expt. 2. In an analogous manner, this reaction was carried out in a 1000 ml flask using 700 ml CCl₄ and 50 g Si_6Me_{12}. This reaction was stopped at the point at which all the Si_6Me_{12} had reacted. The solvent was removed by distillation,

and continued distillation at reduced pressure afforded the following fractions: 18 g (0.096 mol, 22%) 1,2, b.p. 68—69°C at 50 mmHg; 15 g (0.063 mol, 22%) 1,3, b.p. 97°C at 20 mmHg; 12 g (0.040 mol, 18.4%) 1,4, b.p. 56°C at 0.05 mmHg; 6 g (0.014 mol, 10%) 1,6 b.p. 130°C at 0.04 mmHg, for a total yield of 73%, based on available ($SiMe_2$) units. A nonvolatile viscous brown oil ($\sim$5 g) remained in the pot after distillation. This residue presumably contained Si—Cl linkages, as it evolved an acidic gas upon hydrolysis.

Reaction of Si_5Me_{10}/Si_6Me_{12} mixture with chlorine

Expt. 3. A mixture of Si_6Me_{12} and Si_5Me_{10} (1.8 : 1 molar ratio) was chlorinated in an analogous manner, using a 500 ml flask charged with 25 g of this mixture and 300 ml CCl_4. This mixture was immediately reacted with chlorine, because some decomposition of Si_5Me_{10} in CCl_4 was observed. Every 10 min, a 2 μl sample of the reaction mixture was withdrawn and analyzed by VPC. The reaction was continued until all the Si_6Me_{12} had undergone chlorination, as evidenced by VPC. The results are shown in Fig. 2.

Expt. 4. For isolation of 1,5-Dichlorodecamethylpentasilane, the reaction was run as described above, but stopped at the point at which all Si_5Me_{10} had
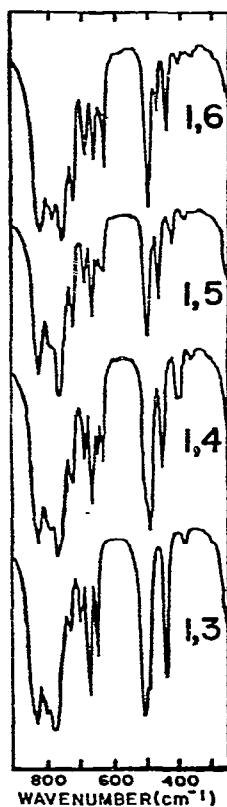

Fig. 5. IR spectra for α,ω-dichloropolysilanes (CsI, thin film).

reacted, for according to Fig. 2, this is the point at which a maximum amount of 1,5 is obtained.

The solvent was removed by distillation. Continued distillation under reduced pressure afforded fractions containing Si_6Me_{12} and 1,5-dichlorodecamethylpentasilane. However, distillation under these conditions (0.05 mmHg, 110—120°C) was extremely difficult because of the tendency of Si_6Me_{12} to solidify in the distillation head. Upon standing several days, this fraction partially crystallized, with the crystals being identified as Si_6Me_{12} by their IR spectrum. The fraction was centrifuged, and the resulting liquid was sufficiently enriched in 1,5-dichlorodecamethylpentasilane such that isolation of this compound by preparative VPC was feasible. The isolated product had $n_D^{22} = 1.5210$ (Lit [6] for 1,5-dichlorodecamethylpentasilane, $n_D^{20} = 1.5220$); Anal.:Found: Si, 38.78; C, 33.20; H, 8.51; Cl, 19.38. $Si_5C_{10}H_{30}Cl_2$ calcd.: Si, 38.83; C, 33.21; H, 8.35; Cl, 19.61%. The IR spectrum is shown in Fig. 5 together with the spectra of other α,ω-dichloropolysilanes for comparison.

General procedure for kinetic studies

Each reaction was carried out at 0°C in a 25 ml 3-necked flask equipped with a gas-inlet tube, condensor and rubber septum. The flask was charged with approximately 2 g of the polysilane to be chlorinated dissolved in 20 ml CCl_4 and was rapidly stirred with a magnetic stirrer. Every min a 2 μl sample of the reaction mixture was withdrawn through the septum with a Hamilton syringe for later analysis by VPC. In this manner, the chlorination of the following compounds and mixtures was carried out: Si_6Me_{12}, Si_6Me_{12}/Si_5Me_{10} (1.8 : 1), $Si_6Me_{12}/1,6$ (1 : 1), 1,6, 1-$ClSi_6Me_{13}$, n-Si_4Me_{10}, 1,4, 1,2 and Si_2Me_6. Fig. 6 shows one of the chromatograms obtained during the chlorination of Si_6Me_{12}. The chlorinations of 1,4 and of a mixture of Si_6Me_{12} and 1,6 are shown in Figs. 3 and 4, respectively.

Chlorination of 1,2 and isolation of chloromethyldisilanes

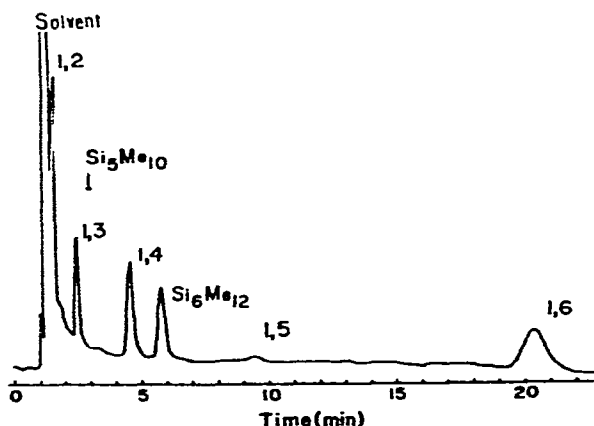In a 250 ml three-necked flask, 20 g of 1,2 in 180 ml CCl_4 were reacted with

Fig. 6. A typical chromatogram, showing the chlorination of Si_6Me_{12} (column temp. = 213°C). The position of Si_5Me_{10} is also indicated for reference.

chlorine, using a procedure similar to that described for Si_6Me_{12}. From VPC analysis, the sequential formation of four products was observed, with those with shorter retention times appearing first (1 earliest, 4 latest). The reaction was stopped at the point at which about 10% 1,2 remained, but with substantial amounts of all four products in the approximate ratios 10 : 3 : 4 : 1 (1 : 2 : 3 : 4). Mass balance calculation from VPC analyses of this reaction indicated that essentially no 1,2 was cleaved to form Me_3SiCl during the reaction.

The solvent was removed by distillation, and the four products separated by preparative VPC (column = 165°C). The products all showed chlorine substitution in the methyl groups, with no cleavage of the Si—Si bond. Tentative identifications were made on the basis of NMR data. These assignments are consistent with analyses by IR, GC and mass spectrometry. 1, $ClSi(CH_3)(CH_2Cl)Si(CH_3)_2Cl$, NMR: δ 0.65(s,6H), 0.67(s,3H), 3.11(s,2H); 2, $ClSi(CH_3)(CHCl_2)Si(CH_3)_2Cl$, NMR: δ 0.78(s,3H), 0.79(s,3H), 0.84(s,3H), 5.48(s,1H); 3 $[ClSi(CH_3)(CH_2Cl)]_2$ (plus isomer), NMR: δ 0.74(s,4H), 3.16(s,1H), 3.18(s,1H), 3.24(1/2H); 4, $ClSi(CH_3)(CH_2Cl)Si(CHCl_2)(CH_3)Cl$ (plus isomers), NMR: δ 0.80(s,3H), 0.84(s,3H), 3.18(s,1H), 3.22(s,1H), 5.50(s,1H).

Acknowledgement

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