Cyclic Polysilanes. III.[1] The Preparation of Permethylcyclopolysilanes by Coupling, Pyrolysis, and Redistribution Reactions[2]

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Abstract: A study of reaction variables in the coupling of dimethyldichlorosilane with sodium–potassium alloy to form cyclic permethylpolysilanes has been carried out. Recommended procedures are given for the preparation of $Me_{12}Si_6$ and for obtaining maximum amounts of $Me_{10}Si_5$ and $Me_{14}Si_7$. The isolation of $Me_{16}Si_8$ is also described. Permethylpolysilanes have also been obtained by thermal cracking of linear $(Me_2Si)_x$ polymer, and by base-catalyzed redistribution of linear and cyclic polysilanes. Possible mechanisms for the condensation and redistribution reactions are discussed.

Permethylcyclopolysilanes have been known since 1949, when Burkhard found that the reaction of dimethyldichlorosilane with sodium metal in a steel autoclave at 115–200°, 220 psi, yielded large quantities of polymeric material and also a very small amount of dodecamethylcyclohexasilane.[4] No further work on this substance was published for over 10 years, but in the early 1960's other workers reported methods of producing the cyclic hexamer in higher yields. Hengge and Reuter found in 1962 that the reaction of dimethyldichlorosilane with lithium in tetrahydrofuran at 250° and 50 atm produced the cyclic hexamer in yields of about 2.5%.[5] Low yields of the hexamer were also obtained by Anderson from the treatment of dimethyldichlorosilane with sodium upon extended refluxing in tetrahydrofuran.[6] Similar results were obtained with lithium by Gilman and Schwebke.[7]

The first preparations of the cyclic hexamer in good yields were reported in 1963. Gilman and Tomasi found that adding a small amount of triphenylsilyllithium in the reaction of dimethyldichlorosilane with lithium in tetrahydrofuran greatly improved the yields of $Me_{12}Si_6$ to 60–70%.[8] Simultaneously Stolberg reported a remarkably high 81% yield of $Me_{12}Si_6$ from dimethyldichlorosilane and sodium–potassium alloy in refluxing tetrahydrofuran.[9]

Other members of the $(Me_2Si)_n$ series were unknown until 1966, when we attempted to repeat Stolberg's synthesis of dodecamethylcyclohexasilane. Although we never obtained yields of $Me_{12}Si_6$ as high as those reported, we were able to isolate small amounts of the analogous five- and seven-membered ring compounds by gas chromatographic separation from crude $Me_{12}Si_6$.[1] Subsequently Kumada obtained $Me_{10}Si_5$ by the reaction of linear permethylpolysilanes with triphenylsilyllithium.[10]

This paper reports our further study of the synthesis of permethylcyclopolysilanes by three different methods: (1) the reaction of dimethyldihalosilanes with sodium–potassium alloy; (2) the pyrolysis of linear polymeric permethylpolysilane; and (3) the base-catalyzed redistribution of linear and cyclic permethylpolysilanes.

Coupling Reactions. Following the discovery of $Me_{10}Si_5$ and $Me_{14}Si_7$, we carried out a detailed study of the Stolberg coupling reaction with a view toward maximizing the amounts of these new cyclic compounds. The reaction between dimethyldichlorosilane and sodium–potassium alloy in tetrahydrofuran was carried out more than 50 times, with changes in selected variables in each reaction. In many reactions, samples from the reaction mixture were withdrawn and examined periodically as the reaction proceeded, so that the amounts of each cyclic compound present could be followed as a function of time.

Table I lists the reaction conditions and the results obtained in representative experiments. The following is a summary of the results of this study.

1. The highest proportions of $Me_{10}Si_5$ and $Me_{14}Si_7$ relative to $Me_{12}Si_6$ were present in the reaction mixtures immediately after the addition of the dimethyldichlorosilane to the alloy in tetrahydrofuran was completed. In this way yields of 13–19% $Me_{10}Si_5$ and 6–8% $Me_{14}Si_7$ were observed consistently. The reactions at this point, however, were less than 20% complete so the yield of cyclic compounds was very low indeed, making work-up difficult.

2. Refluxing for short periods of time did not greatly decrease the relative amounts of $Me_{10}Si_5$ or $Me_{14}Si_7$, but increased the yield of all crystalline (cyclic) products substantially; for example, yields of combined cyclic products were increased from about 20% after 0.5 hr of refluxing to about 40–50% after 1 hr of refluxing.

3. Refluxing for long periods of time decreased the amounts of $Me_{10}Si_5$ and $Me_{14}Si_7$ relative to $Me_{12}Si_6$.

4. Stirring for long periods of time without additional refluxing also greatly reduced the amounts of $Me_{10}Si_5$ and $Me_{14}Si_7$, to about 2–3 and 3–4% of the total

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[1] Previous paper in this series: E. Carberry and R. West, *J. Organometal. Chem.*, **6**, 582 (1966).

[2] Research sponsored by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. AF-AFOSR-1061-66.

[3] Author to whom correspondence should be addressed.

[4] C. A. Burkhard, *J. Am. Chem. Soc.*, **71**, 963 (1949). No yield was reported in this paper, but independent repetition as well as private communication with Dr. Burkhard indicate tha tthe yield must have been less than 0.1%.

[5] E. Hengge and H. Reuter, *Naturwissenshaften*, **49**, 514 (1962).

[6] R. P. Anderson, unpublished studies.

[7] H. Gilman and G. L. Schwebke, unpublished studies.

[8] H. Gilman and R. A. Tomasi, *J. Org. Chem.*, **28**, 1651 (1963).

[9] U. G. Stolberg, *Angew. Chem. Intern. Ed. Engl.*, **2**, 150 (1963). Stolberg also reports preparation of $(Me_2Si)_6$ from 1,2-dichlorotetramethyldisilane, but in much lower yield.

[10] M. Kumada, M. Ishikawa, S. Sakamoto, and S. Maeda, *J. Organometal. Chem.*, **17**, 223 (1969).

Table I. Summary of Representative Reactions Involving Dimethyldichlorosilane and Sodium–Potassium Alloy in Tetrahydrofuran

Na–K,[a] moles	Me_2Si-Cl_2, mole	Excess alloy, %	THF, ml	Addition time, min	Reflux,[b] min	Remarks	% yields Polym[c]	Cryst[d]	Total[e]	% of cryst[f] Si_5	Si_6	Si_7	Other[g] compds noted
2.16	1.00	8	250	240	0	20 hr of stirring	60	40	100	3	94	3	. . .
1.13	0.50	13	200	20	60	Partial work-up	. . .	. . .	. . .	19	72	9	D
0.59	0.25	18	150	20	0	Solvent removed; baked 130°, 16 hr	60–75	24	85–100	7	89	4	. . .
0.54	0.25	8	150	25	120	Standing 36 hr before work-up	40–45	36	75–80	3	96	1	. . .
0.50	0.25	0	150	2	0	Reaction at 0°; stir 4.5 hr	<5	<5	<10	6	93	1	. . .
0.55	0.25	10	150	25	30	Filtration work-up	15–20	15–20	30–40	12	76	12	D
0.55	0.25	10	150	25	30	Hydrolysis work-up	15–20	15–20	30–40	14	77	9	. . .
0.55	0.25	10	150	20	30	Immediate work-up	24	20	44	14	78	8	D + Si_8
0.55	0.25	10	150	60	0	Immediate work-up	15	<5	<20	19	73	8	D
1.00	0.50	0	300	60	60	Immediate work-up	37	40	77	14	78	8	D
1.10	0.50	10	300	60	60	Immediate work-up	28	47	75	18	76	6	D

[a] In all cases the alloy was the eutectic mixture of sodium and potassium which contains 78% potassium. [b] Indicates hours reflux after addition was completed. [c] Per cent yield of polymeric product obtained after work-up. [d] Per cent yield of crystalline products obtained after work-up; this is the solvent-soluble portion which contains the three cyclics. [e] Indicates per cent completion of the reaction. [f] Indicates the gram-percentage of the cyclic in the crystalline product. [g] D = decomposition products from compound T (probably the cyclic tetramer). Si_8 = $Me_{16}Si_8$.

cyclics, respectively. The coupling reaction, however, proceeds nearly to completion after about 20 hr of stirring.

5. Allowing the reactions to stand without stirring or refluxing for long periods of time before work-up likewise greatly reduced the relative yields of $Me_{10}Si_5$ and $Me_{14}Si_7$.

6. Once the reactions were worked up and the products separated from excess alkali metal, the ratio of cyclic species did not change upon standing or stirring in tetrahydrofuran.

7. Removal of the solvent after addition was completed and baking of the reaction mixtures at 130–150° for about 12 hr decreased the relative yields of $Me_{10}Si_5$ and $Me_{14}Si_7$ considerably to about 4–6 and 3–4%, respectively.

8. Reaction at low temperatures decreased the relative amounts of $Me_{10}Si_5$ and $Me_{14}Si_7$. Yields of only about 6 and 0–1%, respectively, were obtained at 0°.

9. An excess of alloy appeared to favor cyclic formation to some degree and also aided completion of the reaction upon refluxing.

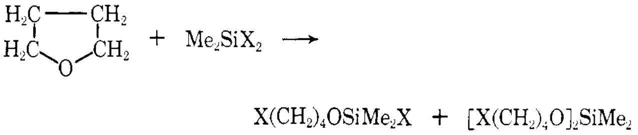
10. It did not seem to matter whether the work-up of the reaction was done by filtration or by hydrolysis; the proportions of the desired cyclics were not affected.

11. Traces of other products were detected in small quantities in many of the reactions.

From the above study we found that the reaction of dimethyldichlorosilane with sodium–potassium alloy in tetrahydrofuran can be performed in such a way as to produce consistent yields of 40–50% of cyclic materials containing about 20% $Me_{10}Si_5$, 72% $Me_{12}Si_6$, and 8% $Me_{14}Si_7$. These maximum amounts of $Me_{10}Si_5$ and $Me_{14}Si_7$ were obtained when the dimethyldichlorosilane was added to about a 10% excess of sodium–potassium alloy in dry, purified tetrahydrofuran over a period of about 1 hr; the reaction mixture was stirred and refluxed for about another hour and then immediately worked up either by filtration in a glove-bag or hydrolysis directly in the reaction flask. These reaction conditions are more specifically described in the Experimental Section.

Immediately after the addition of the chlorosilane had been completed, the yields of pentamer and heptamer were quite high, but upon continued refluxing, stirring, or even standing in contact with the reactants, the amounts of these cyclics were substantially reduced while the amount of the hexamer was increased. Thus it appears that the formation of pentamer and heptamer is kinetically favored whereas the formation of hexamer is favored thermodynamically. This observation prompted the study of the reaction of other dimethyldihalosilanes with sodium–potassium alloy, in the hope that more reactive halosilanes might serve to increase the amounts of the kinetically favored cyclics. However, reactions involving dimethyldibromosilane produced very low yields of cyclic products even after extended periods of refluxing. The amounts of decamethylcyclopentasilane and tetradecamethylcycloheptasilane were not substantially increased as anticipated. The reactions instead proceeded very slowly and were unusual in that none of the polymer usually formed was produced.

It was even more striking that reactions involving the most reactive halosilane, dimethyldiiodosilane, produced little or no polymer and no trace of the cyclic compounds when the usual tetrahydrofuran solvent was employed. Instead yellow viscous liquid products resulting from cleavage of the tetrahydrofuran by the halosilane were obtained. Reactions of this kind have been noted previously.[11-13]



In the presence of sodium–potassium alloy, these products then underwent coupling to yield complex reaction products. Some possible reactions are shown below.

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(11) R. P. Anderson, U. S. Patent 3,083,219; *Chem. Abstr.*, **59**, P8789*g* (1963).

(12) M. G. Voronkov and Yu. P. Romadan, *Khim. Geterosikl. Soedin., Akad. Nauk Latv. SSR*, **2**, 470 (1966); Faraday translation, *Chem. Heterocyclic Compds.*, **2**, 349 (1966).

(13) U. Kruerke, *Chem. Ber.*, **95**, 174 (1962).

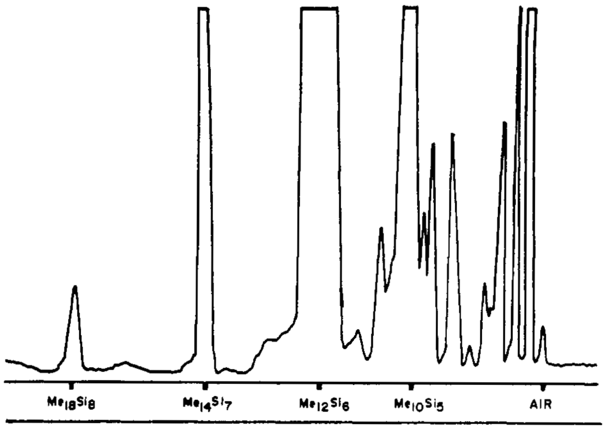

Figure 1. Temperature-programmed gas chromatographic trace of the cyclopolysilanes showing the presence of the component believed to be hexadecamethylcyclooctasilane.

$$2[X(CH_2)_4O]_2SiMe_2 \xrightarrow{\text{Na–K}} X(CH_2)_4OSiMe_2O(CH_2)_8OSiMe_2O(CH_2)_4X$$

$$X(CH_2)_4OSiMe_2X \xrightarrow[n\text{Me}_2\text{SiCl}_2]{\text{Na–K}} X\,(CH_2)_4O(SiMe_2)_nX, \text{ etc.}$$

When the yellow viscous products obtained from these reactions were treated with an excess of phenyllithium and then hydrolyzed, the major products were 1,8-octanediol and diphenyldimethylsilane.

$$(Me_2SiO(CH_2)_8OSiMe_2O(CH_2)_8OSiMe_2)_n \xrightarrow[2.\ \text{H}_2\text{O}]{1.\ \text{PhLi}} HO(CH_2)_8OH + Ph_2SiMe_2$$

Because Me_2SiBr_2 and Me_2SiI_2 reacted so rapidly with ethers, similar reactions were attempted in a less reactive solvent, cyclohexane. In all such reactions the amount of cyclic pentamer was found to be *greater* than the amount of cyclic hexamer. Little cyclic heptamer was detected. Dimethyldichlorosilane appeared to be by far the least reactive of the three halosilanes in cyclohexane. Increased refluxing did not decrease the amount of cyclic pentamer in the reactions in cyclohexane as it did in tetrahydrofuran. But in each case work-up gave considerable polymeric material and only very low yields (~5%) of cyclic material.

These results indicate that the mechanism necessary for conversion of the pentamer to hexamer is not available in a very nonpolar, poorly solvating solvent. And in fact, cyclic formation itself is suppressed to an extensive degree.

Hexadecamethylcyclooctasilane

In several reactions between dimethyldichlorosilane and sodium–potassium alloy in tetrahydrofuran, a peak was observed beyond tetradecamethylcycloheptasilane on the gas chromatographic trace, making up about 1% of the total crystalline material. The retention time suggested that it might be the cyclic octamer, hexadecamethylcyclooctasilane (see Figure 1). A few milligrams of this compound, a white crystalline solid like the other permethylcyclopolysilanes, was isolated by preparative gas chromatography. The amount obtained was insufficient for elemental analysis, but the compound was characterized spectroscopically. The infrared spectrum was essentially identical with that for the other cyclic permethylpolysilanes. The compound showed a singlet absorption in the proton nmr at τ 9.86, with a possible small upfield shoulder, and an ultraviolet absorption maximum at 235 nm. Most important was the mass spectrum, which showed a parent peak at 464, the calculated molecular weight for $Me_{16}Si_8$. The P + 1 peak was found to be 60% of the parent peak, which is well within experimental error of the calculated value of 58.9% for $Me_{16}Si_8$.[14] All of the data are consistent with the proposed hexadecamethylcyclooctasilane structure.

Possible Detection of Octamethylcyclotetrasilane

In several of our later experiments we also noted that if oxygen was carefully excluded during the work-up, a component could be detected by analytical gas chromatography which had a retention time suggesting that it might be the cyclic tetramer, octamethylcyclotetrasilane. Many preparative reactions were found to contain considerable amounts of this compound before the actual work-up was performed, but even the slightest air oxidation during work-up caused the component to disappear, and two new peaks, very close in retention time, were then detected in the gas chromatographic trace, appearing just before the cyclic pentamer. Infrared analysis of these components showed that there were oxidized polysilanes probably formed from decomposition of the tetramer.

It would be expected that the cyclic tetramer would be even less stable to air oxidation than the cyclic pentamer because of its much greater ring strain and the fact that the more widely separated methyl groups provide less steric hindrance to attacking oxygen molecules. This rapid oxidation of the tetramer explains why these oxidation products were detected in many of the reactions worked up by hydrolysis or filtration techniques.

Several attempts to isolate the tetramer directly were unsuccessful. Even when the reaction mixture was worked up using syringe technique in an argon atmosphere, decomposition took place. We were unable to perform the lengthy concentration steps under conditions completely free from traces of oxygen. Moreover, absolute identification of the oxidation products proved to be impossible since these were unstable to further oxidation and polymerization. Ultraviolet spectral evidence, however, indicated that probably four silicon atoms were present in each compound.

Preparation of the Cyclics by Redistribution Reactions from Polymer

In most of the reactions described previously, a rather large percentage of what was designated as polymeric product was obtained. This material is a white powder which is insoluble in almost all organic solvents. The infrared spectrum shows the presence only of dimethylsilene groups. The structure is thus believed to be linear of the form $(Me_2Si)_x$.

The polymer is thermally unstable. If heated in air at 150–200° it ignites and forms a very light, sponge-like white powder which shows the presence of siloxane bands in the infrared. If instead the polymer is heated in the absence of oxygen or under greatly reduced pressures, decomposition is found to occur beginning at

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(14) Similar calculations for $Me_{12}Si_6$ predict a P + 1 of 44.2%. An intensity of 48% is actually observed, showing that this method of analysis is consistent.

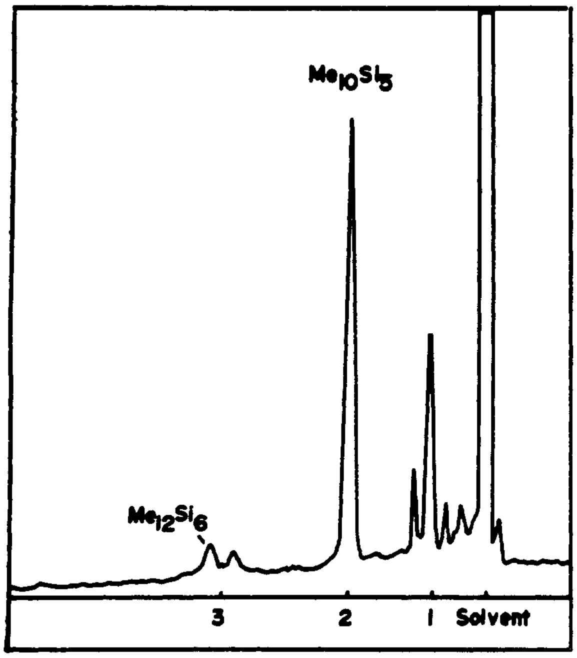


Figure 2. Unresolved gas chromatographic trace of the volatile pyrolysis products.

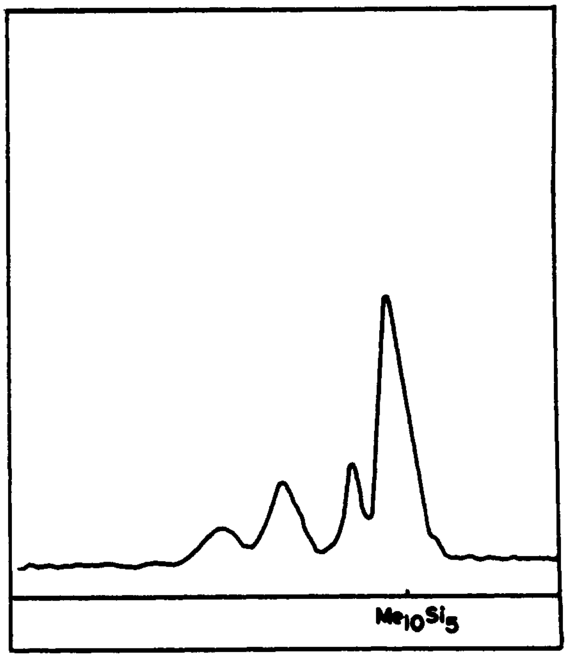


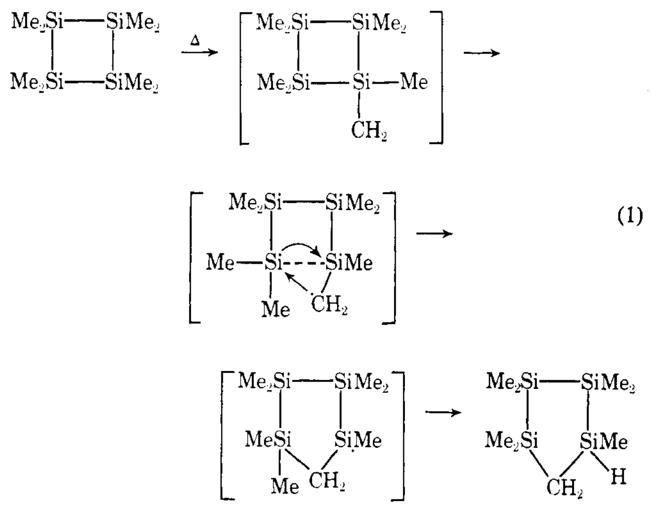
Figure 3. Resolved gas chromatographic trace showing the second area of the pyrolysis products in detail.

about 250°. However, no extensive pyrolysis occurs until temperatures of about 350–400°.

Many such pyrolyses were performed in a number of different types of apparatus. Early experiments included pyrolysis of polymer under high vacuum in a tube heated with an electrical oven. The volatile products were collected in cold traps. Later experiments were carried out at atmospheric pressure under argon by passing the finely powdered polymer through a short pyrolysis tower. Sealed tube reactions were also investigated.

Polymer pyrolyses carried out in the first two types of apparatus gave excellent yields of liquid products which were syringed from the cold traps and distilled. The gas chromatographic traces of the distilled products indicated the presence of many volatile species, but in general these fell into three areas (Figure 2).

The first area was made up of several small peaks, the largest of which was identified by elemental and spectroscopic analysis as 2,2,3,3,4,4,5-heptamethyl-2,3,4,5-silacyclopentane. This compound could easily arise from the rearrangement of the cyclic tetramer $(Me_2Si)_4$ formed during the pyrolysis experiments (eq 1).[15]



(1)

The largest component of the pyrolysis was always found in the second area of peaks and was identified as the cyclic pentamer, decamethylcyclopentasilane. It is estimated that this product makes up about 20–30% of the total liquid product. Unfortunately, several impurities with almost the same retention time made isolation of pure cyclic pentamer by preparative gas chromatography very difficult indeed (Figure 3). For this reason, pyrolysis does not appear to be a satisfactory method for the preparation of the cyclic pentamer.

The very similar peaks were tentatively assigned to pyrolysis products of the pentamer similar to that identified for the tetramer. Both Si–H and $Si–CH_2–Si$ linkages were detected by infrared analysis.

The third area was composed of only a very small amount of cyclic hexamer (<5%) along with several other unidentified compounds. No cyclic heptamer was detected in these products.

Similar pyrolysis experiments were conducted simultaneously by Russian workers.[16] They reported a very similar gas chromatographic analysis at this same temperature.but did not characterize any of the products obtained other than the cyclic pentamer and hexamer.

Permethylpolysilane polymer was also found to undergo redistribution to cyclic compounds by reaction with catalytic amounts of base or sodium naphthalide in tetrahydrofuran or 1,2-dimethoxyethane. It was found that when purified polymer was added to a small amount of naphthalene radical anion in 1,2-dimethoxyethane and refluxed for a few moments, the polymer quickly dissolved and upon work-up showed a 65% conversion to $Me_{10}Si_5$, $Me_{12}Si_6$, and $Me_{14}Si_7$ in a ratio of about

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[15] Similar rearrangement involving insertion of a CH_2 fragment into a silicon–silicon bond has previously been observed in the pyrolysis of hexamethyldisilane: H. Sakurai, R. Koh, A. Hosomi, and M. Kumada, *Bull. Chem. Soc. Japan*, **39**, 2050 (1966).

[16] T. Szekely, O. M. Nefedov, G. Garzo, V. I. Shiryayev, and D. Fritz, *Acta Chim. Acad. Sci. Hung.*, **54**, 241 (1967).

6:93:1. Shiina has recently found similar results and reported a 60% conversion to the cyclic hexamer with either naphthalide radical anion or potassium hydroxide.[17] Our attempts to repeat these experiments using potassium hydroxide in tetrahydrofuran or diglyme, however, produced only about 35% conversion to cyclic materials, but again about 5% cyclic pentamer and 1% cyclic heptamer were also detected.

The conversion of polymer to cyclic hexamer by naphthalene radical anion is very useful, because large amounts of undesirable polymer are usually obtained in the preparation of the cyclic materials. Moreover, we find that if a small amount of naphthalene is added to the reaction mixture in the condensation of Me_2SiCl_2, naphthalide radical anions are formed from the excess sodium–potassium alloy. These attack the polymer after it is formed and thus greatly increase the yield of cyclic hexamer. Refluxing for 15 hr caused the percentage of polymer found upon work-up to decrease from an average of about 40% to about 14% of the total product. Similar reactions refluxed for 20 hr decreased the polymeric yield to only 4% while 95% of crystalline product was obtained. The crystalline product was shown to be 94% cyclic hexamer; therefore the yield of dodecamethylcyclohexasilane was about 90%, considerably higher than any previously reported yield by any preparative method.

From Lower Membered Linear Polysilanes. Just as linear polymers can be converted to the cyclic polysilanes, so can linear polysilanes of lower molecular weight. For example, the linear hexasilane, tetradecamethylhexasilane, underwent redistribution in the presence of naphthalene radical anion to yield not only the cyclic pentamer and cyclic hexamer in a 1:9 ratio, but also the lower membered linear species $Me(-Me_2Si-)_nMe$, where $n = 2–6$. The distribution between cyclic and linear products was about equal. Therefore this reaction would find little preparative value.

From Other Cyclic Polysilanes. From the comprehensive study of the preparation of the cyclic polysilanes by coupling techniques as previously described, it is obvious that the cyclic compounds themselves undergo redistribution reactions very readily. These redistributions observed in the many preparative reaction mixtures prompted us to study the redistribution of highly purified cyclic compounds under controlled conditions.

Pure decamethylcyclopentasilane was refluxed in a dilute solution of naphthalene radical anion in tetrahydrofuran. The reaction was followed by analytical gas chromatography. Almost immediately, the formation of dodecamethylcyclohexasilane was detected. After 2 hr all but 10% of the cyclic pentamer had been converted to cyclic hexamer. Even after over 75 hr of continued refluxing, the conversion proceeded no further. Little or no cyclic heptamer was detected.

Likewise, pure dodecamethylcyclohexasilane was refluxed in a similar radical-anion solution. Surprisingly, the reaction mixture showed the formation of a small amount of cyclic pentamer after only a few minutes of refluxing. After 2 hr, the gas chromatographic trace showed the presence of about 10% of the pentamer. Continued refluxing, as in the previous case, did not affect the product ratios. Again, little or no heptamer was detected.

Similar experiments using pure tetradecamethylcycloheptasilane again showed conversion to about 10% pentamer and about 90% hexamer. Only a very small amount of heptamer was left unrearranged.

Thus in pure tetrahydrofuran, naphthalene radical anion causes the cyclics to redistribute such that an apparent equilibrium is established between the three cyclic species which greatly favors the pentamer and hexamer. The equilibrium constant for the equilibrium between pentamer and hexamer can be calculated to be about 7.5.

Although many of the reactions considered in the first section of this paper showed a somewhat similar distribution of cyclic products, it should be remembered that the preparative reaction mixtures were much more complex in nature and so cannot be compared directly to those considered here.

Mechanistic Considerations. It appears that polymer formation may be the first step in the preparative reactions. The polymer may then be attacked by radical-anion species present in the reaction mixture to cause redistribution of the polymer into the cyclic compounds. In this way many of the desired cyclics may be initially formed in somewhat high percentages, but further reaction causes redistribution of these cyclics by a similar radical-anion mechanism into the more thermodynamically stable species, dodecamethylcyclohexasilane.

This would explain why in the poorly solvating solvents which do not favor radical-anion formation the yields of polymer were so high while the cyclic yields were so poor. The pentamer formed in these reactions was likewise not rearranged to the more stable hexamer product even after extended refluxing. This mechanism would also explain why in tetrahydrofuran, a favorable solvent for radical-anion formation, the cyclic pentamer and heptamer are largely rearranged to hexamer upon continued refluxing. The addition of naphthalene radical anion probably aids in the above radical-anion attacks on polymer and other cyclic species by providing a more stable source of radical anions for further attack and rearrangements.

Thus it seems likely that radical anions are involved in both the cyclic formation and the cyclic redistribution reactions. The dark color of the solutions during the reactions is consistent with this view. The complete mechanism for such reactions, however, is undoubtedly complex.

Experimental Section

Recommended Procedure for the Preparation of Decamethylcyclopentasilane and Tetradecamethylcycloheptasilane A 500-ml three-necked reaction flask was fitted with a reflux condenser, a Tru-bore mechanical stirrer, and a 125-ml pressure equalized addition funnel. The apparatus was thoroughly dried and provided with a nitrogen atmosphere. About 300 ml of tetrahydrofuran was distilled directly into the reaction flask from lithium aluminum hydride. Then 8.1 g of sodium and 29.0 g of potassium (1.1 moles of sodium–potassium alloy) were added. (*Caution!* Sodium–potassium alloy will inflame spontaneously in air. Adequate measures should be taken so that a vigorous fire can be controlled if the flask should break.) Upon stirring for a short time, a finely dispersed alloy was formed. At this point 64.5 g (0.50 mole) of freshly distilled dimethyldichlorosilane[18] was added dropwise over 1 hr with refluxing. The refluxing

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[17] K. Shiina and Y. Minoura, quoted by M. Kumada and K. Tamao, *Advan. Organometal. Chem.*, 6, 19 (1968).

[18] All chlorosilanes used in this research were obtained from Dow Corning Corp., Midland, Mich., unless noted otherwise.

was then continued for another hour. The solution was then cooled and filtered through a sintered-glass funnel in a dry glove-bag. The filtrate was hydrolyzed with a small amount of ethanol, and then the solvent was removed by rotary evaporation. The resulting crystalline material was sublimed once to give a 45–50% yield of the cyclic polysilanes. This was then dissolved in a minimum of hydrocarbon solvent. The cyclic compounds were then isolated by preparative gas chromatography giving 15–20% $\mathrm{Me_{10}Si_5}$, mp 186–189°; 70–75% $\mathrm{Me_{12}Si_6}$, mp 252–255°; and 5–10% $\mathrm{Me_{14}Si_7}$, mp 278–232°. Good separations were obtained using a $^3/_8$ in. × 20 ft column packed with 30% SE-30 silicone on Chromosorb W, and a helium flow of 150 ml/min.

The solid from the filtration was carefully added to ethanol to destroy the excess sodium–potassium alloy. Water was then added, dissolving the salts and leaving a white residue. This was washed repeatedly to remove all traces of salts and then dried to give 30–35% of a hydrocarbon- and water-insoluble white powder whose infrared spectrum showed only absorptions for $\mathrm{Si{-}CH_2}$, identified as permethylpolysilane polymer.

Improved Preparation of Dodecamethylcyclohexasilane. Using an apparatus and procedure as described above, 64.5 g (0.5 mole) of dimethyldichlorosilane was added dropwise to 1.1 moles of sodium–potassium alloy in 300 ml of tetrahydrofuran containing 1.0 g of naphthalene. The reaction was refluxed for 20 hr. Work-up by filtration and hydrolysis in the usual manner gave 27.6 g (95%) of crystalline products made up of 94% $\mathrm{Me_{12}Si_6}$ along with 4% $\mathrm{Me_{10}Si_5}$ and 2% $\mathrm{Me_{14}Si_7}$; 1.2 g (4%) of polymer was also obtained.

Reaction of Dimethyldibromosilane with Sodium–Potassium Alloy in Tetrahydrofuran. In a similar reaction apparatus using a 100-ml reaction flask, 0.08 mole of sodium–potassium alloy was prepared in 50 ml of dry tetrahydrofuran. To this, 8.5 g (0.039 mole) of dimethyldibromosilane was added with stirring over a 1-hr period of time. Refluxing was continued overnight. Work-up by the usual filtration technique gave about 0.23 g (10%) of crystalline product consisting of 20% $\mathrm{Me_{10}Si_5}$, 79% $\mathrm{Me_{12}Si_6}$, and 1% $\mathrm{Me_{14}Si_7}$. No polymer was detected, but about 2 g of a viscous liquid product remained.

Reaction of Dimethyldiiodosilane with Sodium–Potassium Alloy in Tetrahydrofuran. In a similar apparatus, 0.77 mole of sodium–potassium alloy was prepared in 300 ml of dry tetrahydrofuran. To this, 110 g (0.35 mole) of dimethyldiiodosilane was added over 1 hr, and the mixture was stirred for 15 hr. Work-up by filtration gave 53 g of a yellowish liquid product. No cyclic polysilanes or polymers were found. The nmr and infrared spectra of the liquid product showed the presence of rather large hydrocarbon chains as well as siloxane linkages.

Reaction of Dimethyldihalosilanes with Sodium–Potassium Alloy in Cyclohexane. In a similar 100-ml reaction apparatus, 0.08 mole of sodium–potassium alloy was prepared in 50 ml of dry cyclohexane. To this, 5.0 g (0.039 mole) of dimethyldichlorosilane was added over 1 hr. The reaction was refluxed for about 12 hr. Work-up gave 54% of polymer and about 5–10% crystalline products consisting of 80% $\mathrm{Me_{10}Si_5}$, 19% $\mathrm{Me_{12}Si_6}$, and 1% $\mathrm{Me_{14}Si_7}$.

Similar reactions were carried out using dimethyldibromosilanes and dimethyldiiodosilane, except that refluxing was continued only for 4 hr. From $\mathrm{Me_2SiBr_2}$ was obtained 30% of polymer and 5–10% of crystalline material consisting of 60% $\mathrm{(Me_2Si)_5}$, 39% $\mathrm{(Me_2Si)_6}$, and 1% $\mathrm{(Me_2Si)_7}$. $\mathrm{Me_2SiI_2}$ produced 60% polymer and 5–10% crystalline products containing 55% $\mathrm{(Me_2Si)_5}$, 44% $\mathrm{(Me_2Si)_6}$, and 1% $\mathrm{(Me_2Si)_7}$.

Reaction of Dimethyldiiodosilane with Tetrahydrofuran. A 100-ml two-necked flask was fitted with a rubber septum and a reflux condenser with an argon gas inlet tube. Using syringe technique, 50 ml of dry tetrahydrofuran was added to the flask along with 22.0 g of dimethyldiiodosilane. A very exothermic reaction occurred and the solution became yellowish in color. Proton nmr showed that no $\mathrm{Me_2SiI_2}$ remained. After several hours of reflux, the excess tetrahydrofuran was removed leaving 24.0 g of a viscous yellowish liquid. About 10 g of the liquid product was added dropwise to an excess of phenyllithium in an ether–benzene solvent. After 10 hr of refluxing, the mixture was hydrolyzed and the solvents were removed by distillation. Further distillation gave about 6 g of diphenyldimethylsilane and about 2 g of 1,8-octanediol. The nmr and infrared spectrum of the residue (8.6 g) indicated that it consisted of hydrocarbon chains with small amounts of phenyl- and methylsilyl substituents attached.

Reaction of Dimethyldibromosilane with Tetrahydrofuran. In a similar apparatus, 8.5 g of dimethyldibromosilane was added to 25 ml of dry tetrahydrofuran. A slight exothermic reaction occurred. The reaction was refluxed for 12 hr. After this time, the proton nmr of the solution mixture showed no trace of $\mathrm{Me_2SiBr_2}$. New peaks indicating the presence of Si–O–C and $\mathrm{CH_2{-}Br}$ were detected. The excess tetrahydrofuran was then removed leaving about 10.0 g of a viscous liquid.

Attempted Reaction of Dimethyldichlorosilane with Tetrahydrofuran. In a similar apparatus, 10.0 g of dimethyldichlorosilane was added to 50 ml of dry tetrahydrofuran. No apparent reaction was noted. Even after refluxing for 12 hr, the proton nmr spectrum of the solution showed only the presence of $\mathrm{Me_2SiCl_2}$.

Polymer Redistributions. Vertical Column Method. A 125-cc pressure-equalized powder addition funnel fitted with an argon gas inlet tube was attached to a 6-in. pyrolysis tower filled with glass beads and heated externally with a high resistance heating coil. The tower was connected to a Dry Ice cooled trap with a gas exit port and a rubber septum to allow easy removal of the liquid products. A second cold trap was added. Temperatures were measured by a precalibrated iron–constantin thermocouple.

The column was heated to 350° as the apparatus was flushed with dry argon. Then 17.7 g of purified permethylpolysilane polymer was placed into the addition funnel and slowly added over a period of 8 hr; 15.39 g (87% yield) of liquid products was obtained from the traps along with 2.18 g of residue polymer. Many other similar experiments were run.

Tube Furnace Method. A horizontal pyrolysis tube 3 cm in diameter and about 20 cm in length was fitted into a cold trap and attached to a vacuum system. A tube furnace was used to heat the pyrolysis tube. The temperature was measured with a thermocouple.

Purified polymer 6.5 g was placed in the pyrolysis tube and the pressure reduced to 0.05 mm. The furnace was heated to 422° for about 2 hr. From the cold trap 2.62 g (39%) of liquid products was obtained; 1.6 g of residue polymer was also recovered. Many other similar experiments were run.

Sealed-Tube Method. A. A 0.20-g sample of polymer was sealed in a glass tube under argon. The tube was heated at 325° for about 19 hr. It was then cooled in Dry Ice and opened, and the residue was extracted with dry ether. Gas chromatographic analysis of the ether solution showed the presence of about 5–10% $\mathrm{Me_{10}Si_5}$ and other unidentified more volatile products. A small amount of insoluble residue remained.

B. Similarly, 0.15 g of polymer along with a sliver of pure sodium metal was sealed in a glass tube under argon and heated at 325° for about 19 hr. Gas chromatographic analysis of the ether soluble products showed fewer peaks than did sample A, with a small amount of $\mathrm{Me_{12}Si_6}$ present and a much larger amount of $\mathrm{Me_{10}Si_5}$. Insoluble residue was also found.

Isolation and Characterization of 2,2,3,3,4,4,5-Heptamethyl-2,3,4,5-silacyclopentane. The liquid products obtained by pyrolysis of permethylpolysilane polymer were fractionated under vacuum. The largest component of the first fraction, boiling below 105° at 50 Torr, was isolated by preparative gas chromatography using a $^3/_8$ in. × 20 ft column packed with 30% SE-30 silicone on Chromosorb W. It was a colorless liquid having an infrared spectrum showing the presence of Si–Me as well as $\mathrm{Si{-}CH_2{-}Si}$ (1050 $\mathrm{cm^{-1}}$) and Si–H (2100 $\mathrm{cm^{-1}}$)[19] bonds. The proton nmr of a weak sample showed the presence of about seven poorly resolved peaks in the Si–Me region.

Anal. Calcd for $\mathrm{C_8H_{24}Si_4}$: C, 41.30; H, 10.40; Si, 48.30; mol wt, 232. Found: C, 41.49; H, 10.42; Si, 48.10; mol wt 232 by mass spectroscopy.

Chemical Redistributions. Naphthalene Radical-Anion Method. A 50-ml flask was fitted with a reflux condenser with a nitrogen gas inlet tube. One gram of purified polymer was placed in the flask along with 25 ml of dried 1,2-diethoxyethane, a trace of naphthalene, and a drop of sodium–potassium alloy. The solution was stirred with a magnetic stirrer and refluxed for about 1 hr. After this time the polymer was completely dissolved. Work-up produced 0.65 g (65%) of crystalline material made up of the three cyclics, $\mathrm{Me_{10}Si_5}$, $\mathrm{Me_{10}Si_6}$, and $\mathrm{Me_{14}Si_7}$, in the ratio of about 6:93:1. About 0.1 g of residual polymer was also recovered.

Potassium Hydroxide Method. Using a similar apparatus and procedure as outlined above, 1.0 g of polymer, 25 ml of dried 1,2-dimethoxyethane, and 0.2 g of potassium hydroxide were stirred with refluxing for several minutes. Work-up gave 0.35 g (35%) of crystalline products made up of the three cyclics, $\mathrm{Me_{10}Si_5}$, $\mathrm{Me_{12}Si_6}$, and $\mathrm{Me_{14}Si_7}$, in the ratio 5:94:1. About 0.35 g of polymeric residue was also recovered.

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Redistribution of Linear Tetradecamethylhexasilane with Naphthalene Radical Anion. Using an apparatus and procedure similar to that for the naphthalene radical-anion redistribution of polymer, 40 ml of highly purified tetradecamethylhexasilane[20] was added to a dilute naphthalene radical-anion solution which was refluxed for 20 hr. Gas chromatographic analysis showed the presence of the linear compounds Me_6Si_2, Me_8Si_3, $Me_{10}Si_4$, $Me_{12}Si_5$, and $Me_{14}Si_6$, along with the cyclics $Me_{10}Si_5$, $Me_{12}Si_6$, and $Me_{14}Si_7$.

Redistribution of Decamethylcyclopentasilane with Naphthalene Radical Anion. Using an apparatus and procedure similar to that used for the naphthalene radical-anion redistribution of polymer, 0.05 g of pure decamethylcyclopentasilane was added to a dilute naphthalene radical-anion solution in tetrahydrofuran. The reaction was followed by analytical gas chromatography. After 2 hr, the reaction mixture was composed of 10% $Me_{10}Si_5$ and 90% $Me_{12}Si_6$. No $Me_{14}Si_7$ was detected.

Similar reactions and similar results were obtained from the redistribution of dodecamethylcyclohexasilane and also of tetradecamethylcycloheptasilane.

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Cyclic Polysilanes. IV.[1] Anion Radicals and Spectroscopic Properties of the Permethylcyclopolysilanes[2]

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Abstract: Cyclic permethylpolysilanes, $(Me_2Si)_n$, where $n = 5$, 6, and 7, undergo reduction to anion radicals at low temperatures. The compounds with $n = 5$ and 6 give $(Me_2Si)_5\cdot^-$ and $(Me_2Si)_6\cdot^-$, respectively, upon electrolytic reduction, but all three compounds give only $(Me_2Si)_5\cdot^-$ upon reduction with alkali metals. The esr spectra of the anion radicals show that the unpaired electron contacts equally all of the methyl protons and so is delocalized equally over all of the silicon atoms in the ring. The order of electron affinities $(Me_2Si)_5 >$ benzene $> (Me_2Si)_6 > (Me_2Si)_7$ was established. The ultraviolet, nmr, and infrared spectra of the $(Me_2Si)_n$ compounds are also described. The compounds have absorption bands in the near-ultraviolet which shift to shorter wavelength as ring size is increased. The proton nmr spectrum for each compound shows only a single line from −95° to room temperature, indicating that conformational equilibration is rapid.

Anion radicals in which unpaired electrons occupy low-lying antibonding π molecular orbitals are well known, but formation of anion radicals by species lacking unsaturation and hence available antibonding π levels is not normally observed. However, the polysilanes,[3] and other catenated polymetal compounds,[4] are exceptional among formally saturated compounds in that they show strong absorption bands in the accessible region of the ultraviolet. This observation suggested that relatively low-energy orbitals are available in the polymetal compounds which might accommodate an additional electron, and in 1965 we reported the reduction of dodecamethylcyclohexasilane, $(Me_2Si)_6$, to an anion radical.[5] In this paper, a more complete study of the electrolyic and chemical reduction is reported for the cyclic permethylpolysilanes, $(Me_2Si)_n$, where $n = 5$, 6, and 7, whose syntheses are described in the accompanying paper.[1] The esr and ultraviolet spectra of the resulting anion radicals are discussed, and other spectral properties of the neutral $(Me_2Si)_n$ compounds, particularly those bearing on the nature of bonding in these species, are also presented.

Reduction of Decamethylcyclopentasilane. Upon electrolytic reduction at −100 to −120° in complexing ether solvents (normally 3:1 by volume dimethyl ether–1,2-dimethoxyethane), $(Me_2Si)_5$ was reversibly transformed to an anion radical. The radical was dark blue in color and gave an esr spectrum at low gain consisting of about 15 equally spaced lines at intervals of 0.53 G (Figure 1). These lines fit the binomial intensity pattern expected for the center lines of a 31-line pattern due to splitting by 30 equivalent protons on the 10 methyl groups in $(Me_2Si)_5\cdot^-$ (Table I). The spectrum therefore indicates that the unpaired electron contacts each proton equally, and so is equally delocalized over each of the five ring atoms, as in a typical aromatic anion radical. In the sense that it is a completely delocalized species which should show a ring current, $(Me_2Si)_5\cdot^-$ can also be regarded as an aromatic anion radical.

At higher gain and higher resolution, a greater number of lines was observed in the esr spectrum of $(Me_2Si)_5\cdot^-$, but the pattern was complicated by the appearance of two doublet satellite spectra replicating the central spectrum (Figure 2). The outer doublet, which had a principal splitting of 16.03 G, consisted of about 11 lines with the same spacings, line widths, and relative intensities as the central spectrum. The inner, more intense doublet had a splitting of 6.13 G, and again consisted of about 11 lines with the same spacing and line width as the main spectrum.

The satellite spectra are attributed to splitting by the natural carbon-13 and silicon-29 present in the mole-

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(1) Previous paper in this series: E. Carberry and R. West, *J. Am. Chem. Soc.*, **91**, 5440 (1969).

(2) Research sponsored by the Air Force Office of Scientific Research (SRC), Office of Aerospace Research, U. S. Air Force, Grant No. AF-AFOSR-1061-66.

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