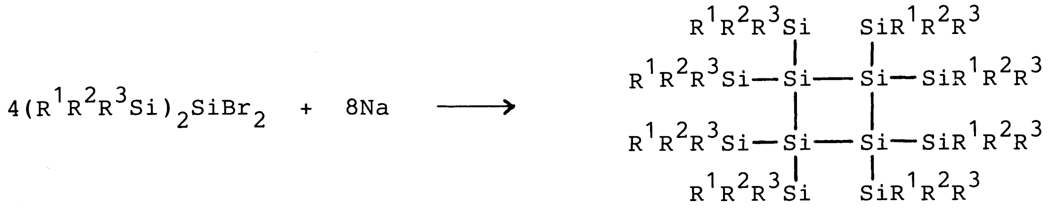
CHEMISTRY LETTERS, pp. 1643-1646, 1986.

Reductive Coupling of 2,2-Dibromo-1,1,1,3,3,3-hexaalkyltrisilanes. A Novel Route to Persilylcyclotetrasilanes of the Type $[(R^1R^2R^3Si)_2Si]_4$

Hideyuki MATSUMOTO,* Noriyasu YOKOYAMA, Atsushi SAKAMOTO, Yumiko ARAMAKI,
Reiko ENDO, and Yoichiro NAGAI*
Department of Chemistry, Gunma University, Kiryu, Gunma 376

Persilylcyclotetrasilanes of the type $[(R^1R^2R^3Si)_2Si]_4$ ($R^1 = R^2 = R^3 = Me$; $R^1 = Et$, $R^2 = R^3 = Me$) were readily obtained by the reductive coupling of the corresponding 2,2-dibromo-1,1,1,3,3,3-hexaalkyltrisilanes using sodium; the Si_4 frameworks of these persilyl compounds act as much more intense chromophore than those of peralkyl analogues.

Organopolysilanes whose Si_n frameworks are fully substituted by silyl groups are of interest, since such compounds are expected to exhibit some unique properties arising from the persilylsilicon frameworks. As a convenient example of persilylpolysilanes, we became particularly interested in octakis(trimethylsilyl)cyclotetrasilane which had been prepared by Chen and Gaspar$^{1)}$ from thermolysis of 2-methoxy-2-(trimethylsilyl)-1,1,1,3,3,3-hexamethyltrisilane, an efficient precursor of bis(trimethylsilyl)silylene. Taking advantage of our recent investigation on the chemistry of small-membered cyclopolysilanes bearing bulky substituents,$^{2)}$ we have thus commenced an investigation on the synthesis and properties of persilylcyclopolysilanes. Now we would like to report our finding that persilylcyclopolysilanes of the type $[(R^1R^2R^3Si)_2Si]_4$ were readily obtained by the reductive coupling of the corresponding 2,2-dibromo-1,1,1,3,3,3-hexaalkyltrisilanes $[(R^1R^2R^3Si)_2SiBr_2]$ using sodium (Scheme 1). Although the reductive coupling of dihalosilanes has been extensively investigated and sometimes provides cyclotetrasilanes in variable yields, the structures of cyclotetrasilanes so far prepared are limited to peralkyl, peraryl, and alkylaryl derivatives.$^{2,3)}$



1, $R^1 = R^2 = R^3 = Me$

2, $R^1 = Et$, $R^2 = R^3 = Me$

Scheme 1.

The dibromotrisilane $[(Me_3Si)_2SiBr_2]$ (**3**)4) (3.90 g, 11.2 mmol) was allowed to react with sodium (0.60 g, 26.0 mg-atom) in toluene (37 ml) at 110 °C under nitrogen. The reaction reached completion in 3 h to give octakis(trimethylsilyl)cyclotetrasilane5) in 46% yield, as shown by GLC analysis.6) The compound **1** was isolated by recrystallization from benzene (0.50 g, 25% yield). For comparison, the reaction of the dibromotrisilane **3** with lithium was also examined (THF, r.t.), but no trace of the desired compound was obtained.

It was further found that the reductive tetramerization of 2,2-dibromo-1,3-diethyl-1,1,3,3-tetramethyltrisilane (**4**)4) could be also effected by sodium. Thus, treatment of **4** with 2.4 equiv. of sodium at 110 °C for 2 h led to the formation of octakis(ethyldimethylsilyl)cyclotetrasilane (**2**)7) in 29% yield.

Unlike the peralkyl analogues which are subject to oxidation with m-chloroperbenzoic acid (MCPBA),3a, 8) both **1** and **2** were virtually inert to MCPBA oxidation. For instance, **1** remained intact after treatment with 2 equiv. of MCPBA at 30 °C for 30 h in benzene, while $({}^iPr_2Si)_4$ afforded a 8:2 mixture of ${}^iPr_8Si_4O_2$ and ${}^iPr_8Si_4O_3$ under nearly the same conditions. The observed kinetic stability could arise from the strong steric shielding of the Si_4 frameworks by the trialkylsilyl groups.9)

In the U.V. absorptions of these persilylcyclotetrasilanes the lowest energy-transitions occur at about 300 nm with the extinction coefficients of 1300 and 1900 for **1** and **2**, respectively (in cyclohexane).10) Figure 1 shows the U.V. spectra of **1** and **2** together with those of peralkylcyclotetrasilanes $({}^iPr_2Si)_4$ (λ_{max} 290 nm, 200)11) and $[({}^tBuCH_2)_2Si]_4$ (λ_{max} 286 nm, 440),2a) demonstrating that the persilyl Si_4 frameworks act as much more intense chromophore than the peralkyl Si_4.
The bathochromic shifts observed for **1** and **2** relative to the peralkyl derivatives

and the marked intensification of absorption bands for **1** and **2** may be attributable to the electronic perturbation to the Si_4 rings by the full silyl substitution[12)] as well as the large steric congestion caused by the bulkiness of the substituents.

Finally, it is noted that the 0.15-mol scale reaction of the dibromotrisilane **3** with sodium led to isolation of 8.0 g (27% yield) of pure **1**. Hence, the present recipe offers a direct and convenient route to the persilylcyclotetrasilanes.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

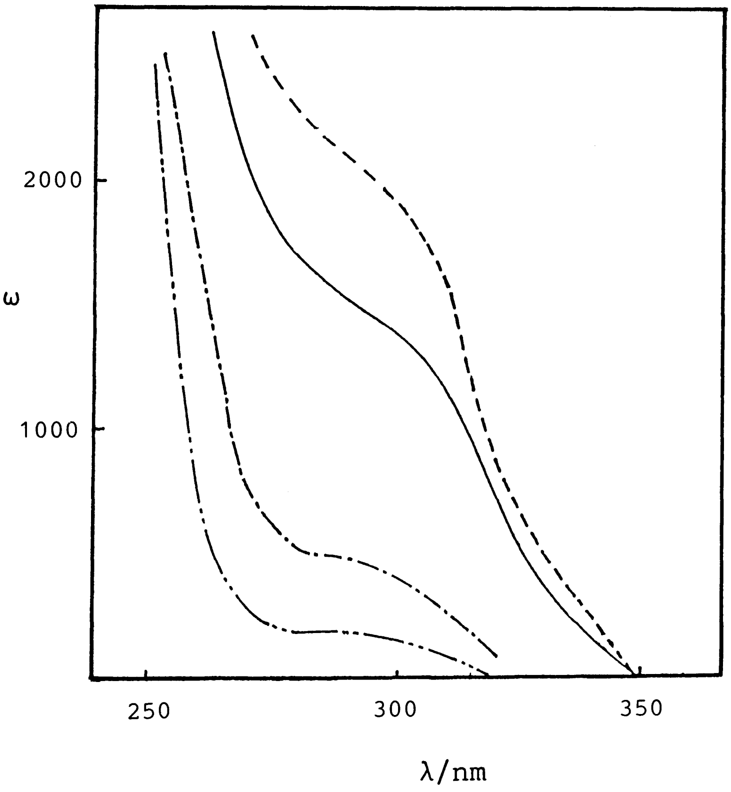


Fig. 1. UV spectra of the persilyl- and peralkyl-cyclotetrasilanes.

----: $[(EtMe_2Si)_2Si]_4$, **2**,

——: $[(Me_3Si)_2Si]_4$, **1**,

-·-·: $[(^tBuCH_2)_2Si]_4$,

··—··: $(^iPr_2Si)_4$.

References

1) Y.-S. Chen and P. P. Gaspar, Organometallics, 1, 1410 (1982).

2) a) H. Matsumoto, M. Minemura, T. Takatsuna, Y. Nagai, and M. Goto, Chem. Lett., 1985, 1005; b) H. Matsumoto, T. Takatsuna, M. Minemura, Y. Nagai, and M. Goto, J. Chem. Soc., Chem. Commun., 1985, 1366; c) H. Matsumoto, M. Minemura, A. Sakamoto, and Y. Nagai, Bull. Chem. Soc. Jpn., in press.

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4) We found that the 2,2-dibromohexaalkyltrisilanes can be readily prepared by the following reactions.

$$\mathrm{Ph_2SiCl_2} \xrightarrow[\mathrm{THF/HMPA}]{\mathrm{R^1R^2R^3SiCl/Mg}} \mathrm{(R^1R^2R^3Si)_2SiPh_2}$$

$\mathrm{R^1 = R^2 = R^3 = Me}$, 85%

$\mathrm{R^1 = Et,\ R^2 = R^3 = Me}$, 74%

$$\xrightarrow{\mathrm{HBr/AlBr_3(cat.)}} \mathrm{(R^1R^2R^3Si)_2SiBr_2}$$

3, $\mathrm{R^1 = R^2 = R^3 = Me}$, 80%

4, $\mathrm{R^1 = Et,\ R^2 = R^3 = Me}$, 85%

3: bp 92 °C/2.93 x 10^3 Pa; ^{1}H NMR (CCl_4) δ 0.30 (s, Me); Anal. Found: C, 21.80; H, 5.38%. Calcd for $C_6H_{18}Si_3Br_2$: C, 21.57; H, 5.37%. 4: bp 115 °C/6.67 x 10^2 Pa; ^{1}H NMR (CCl_4) δ 0.26 (s, 6H, Me) and 1.06 (m, 5H, Et); Anal. Found: C, 26.50; H, 6.02%. Calcd for $C_8H_{22}Si_3Br_2$: C, 26.52; H, 6.12%.

5) Structural assignment for the compound was based on a comparison of its physical properties with those reported previously.$^{1)}$

6) Also formed were $(Me_3Si)_4Si$ (1%), $(Me_3Si)_3SiSi(SiMe_3)_3$ (9%), and higher oligomers whose structures were not further examined.

7) Colorless crystals (triclinic): mp 335-347 °C (dec). The compound 2 exhibited physical properties fully consistent with cyclotetrameric structure: MS (field desorption) m/z 808-815 (parent clusters); Found: 808.4117. Calcd for $C_{32}H_{88}Si_{12}$: M, 808.4118; ^{29}Si NMR (C_6D_6, Me_4Si) δ -5.12 ($EtMe_2Si$) and -89.77 [$(EtMe_2Si)_2\underline{Si}$]. It is further noted that 2 is much more soluble in hydrocarbons than 1.

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9) For steric effects of trialkylsilyl groups, see: C. F. Shaw, III and A. L. Allred, Organomet. Rev. A, 5, 95 (1970); H. Sakurai, Kagaku, 12, 888 (1983).

10) The UV spectrum of the cyclotetrasilane 1 was not recorded previously.$^{1)}$

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(Received August 11, 1986)