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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 Si₄ frameworks of these persilyl compounds act as much more intense chromophore than those of peralkyl analogues.

Organopolysilanes whose Sin 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 Gaspar¹⁾ from thermolysis of 2-methoxy-2-(trimethylsilyl)-1,1,1,3,3,3-hexamethyltrisilane, an efficient precursor of bis-Taking advantage of our recent investigation on the (trimethylsilyl)silylene. chemistry of small-membered cyclopolysilanes bearing bulky substituents,²⁾ we have thus commenced an investigation on the synthesis and properties of persilylcyclo-Now we would like to report our finding that persilylcyclopolypolysilanes. silanes 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 $[(R^{1}R^{2}R^{3}Si)_{2}SiBr_{2}]$ 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)}

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-1,3diethyl-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 (${}^{i}Pr_{2}Si$)₄ afforded a 8:2 mixture of ${}^{i}Pr_{8}Si_{4}O_{2}$ and ${}^{i}Pr_{8}Si_{4}O_{3}$ under nearly the same conditions. The observed kinetic stability could arise from the strong steric shielding of the Si₄ frameworks by the trialkylsilyl groups.⁹

In the U.V. absorptions of these persilylcyclotetrasilanes the lowest energytransitions 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 (${}^{i}\text{Pr}_{2}\text{Si}$)₄ (λ_{max} 290 nm, 200)¹¹⁾ and [(${}^{t}\text{BuCH}_{2}$)₂Si]₄ (λ_{max} 286 nm, 440),^{2a)} demonstrating that the persilyl Si₄ frameworks act as much more intense chromophore than the peralkyl Si₄. 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 Si₄ rings by the full silyl substitution¹²⁾ 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.

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

$$Ph_{2}SiCl_{2} \xrightarrow{R^{1}R^{2}R^{3}SiCl/Mg} (R^{1}R^{2}R^{3}Si)_{2}SiPh_{2} \\ R^{1} = R^{2} = R^{3} = Me, 85\% \\ R^{1} = Et, R^{2} = R^{3} = Me, 74\% \\ \xrightarrow{HBr/AlBr_{3}(cat.)} (R^{1}R^{2}R^{3}Si)_{2}SiBr_{2} \\ 3, R^{1} = R^{2} = R^{3} = Me, 80\% \\ 4, R^{1} = Et, R^{2} = R^{3} = Me, 85\% \end{cases}$$

3: bp 92 °C/2.93 x 10³ Pa; ¹H NMR (CCl₄) δ 0.30 (s, Me); Anal. Found: C, 21.80; H, 5.38%. Calcd for C₆H₁₈Si₃Br₂: C, 21.57; H, 5.37%. 4: bp 115 °C/ 6.67 x 10² Pa; ¹H NMR (CCl₄) δ 0.26 (s, 6H, Me) and 1.06 (m, 5H, Et); Anal. Found: C, 26.50; H, 6.02%. Calcd for C₈H₂₂Si₃Br₂: 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; ²⁹Si NMR (C_6D_6 , Me₄Si) δ -5.12 (EtMe₂Si) and -89.77 [(EtMe₂Si)₂Si]. It is further noted that 2 is much more soluble in hydrocarbons than 1.
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