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Synthesis of the Cyclotetrasilanes of the Type[$(PhRSi)_4$] (R=*t*-Bu; *t*-$BuCH_2$)

Hideyuki Matsumoto,* Atsushi Sakamoto, Masahiko Minemura, Kenji Sugaya, and Yoichiro Nagai*
Department of Chemistry, Gunma University, Kiryu, Gunma 376

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Synopsis. The cyclotetrasilanes of the type [$(PhRSi)_4$] (R=*t*-Bu; *t*-$BuCH_2$) were prepared by the reductive coupling of the corresponding dichlorosilanes ($PhRSiCl_2$) with lithium.

As part of our continuing study of the chemistry of small-membered cyclopolysilanes bearing bulky alkyl substituents, we attempted to prepare alkylphenylcyclotetrasilanes of the type [$(PhRSi)_4$]. The cyclotetrasilanes so far obtained are limited to rings such as $(Me_2Si)_4$,[1] $(Et_2Si)_4$,[2] (i-$Pr_2Si)_4$,[3–5] (s-$Bu_2Si)_4$,[5] (i-$Bu_2Si)_4$,[5] [(t-$BuCH_2)_2Si]_4$,[6] [$(Me_3SiCH_2)_2Si]_4$,[7] [$(Me_3Si)_2Si]_4$,[8] (t-$BuMeSi)_4$,[9] $(EtMeSi)_4$,[10] [t-Bu(n-Pr)Si$]_4$,[5] [(t-$BuCH_2)_2Si]_2$(i-$Pr_2Si)_2$,[11] [(t-$BuCH_2)_2Si]_2$ (t-$BuMeSi)_2$,[11] $(Ph_2Si)_4$,[12] and [(p-$MeC_6H_4)_2Si]_4$.[13] We report here the synthesis of the novel cyclotetrasilanes, (t-$BuPhSi)_4$, **1**, and [(t-$BuCH_2)PhSi]_4$, **2**.

The cyclotetrasilane **1** was prepared by the reaction of t-$BuPhSiCl_2$, **3**, with lithium (Eq. 1). The yield of the

$$4\,t\text{-BuPhSiCl}_2(\mathbf{3}) + 8\,\text{Li} \longrightarrow (t\text{-BuPhSi})_4(\mathbf{1}) + 8\,\text{LiCl} \qquad (1)$$

cyclotetrasilane strongly depended upon the choice of reaction conditions. Optimum conditions involve the treatment of **3** with 3 equiv of lithium at 0 °C for 0.5 h in THF. Under these conditions, the cyclotetrasilane **1** was formed in 45% yield, as shown by a GLC analysis. The usual workup and recrystallization from MeOH/EtOH (1/1) led to the isolation of **1** in 36% yield. The reaction of the dichlorosilane **3** with sodium was also examined (toluene, 60—70 °C, 3h), but no trace of the desired compound was obtained.

The first step in the reductive coupling of the dichlorosilane **3** seems to be the formation of Cl(t-Bu)PhSiSiPh(Bu-t)Cl, **4**, which would then react with lithium to give the cyclic tetramer **1**. The formation of peralkylcyclotetrasilanes from 1,2-dichloro-1,1,2,2-tetraalkyldisilanes has been reported previously.[5,6,10] The observation that if the dichlorosilane **3** is treated with a deficiency of lithium, the reaction mixture contains the dichlorodisilane **4** as its major component, is in agreement with this view.

To explore the scope of the present approach further, (t-$BuCH_2$)$PhSiCl_2$, **5**, was also allowed to react with lithium. In this case, the use of a 1:1 mixture of THF and benzene as the solvent led to a higher yield of the tetraneopentyltetraphenylcyclotetrasilane **2** than did the use of THF alone. Thus, stirring a mixture of the dichlorosilane **5** with 2.4 equiv. of lithium at 0 °C for 2 h in the mixed solvent resulted in the formation of the cyclic tetramer **2** in 54% yield, as shown by the GLC analysis. The same cyclotetrasilane was also prepared by the reaction of Cl(t-$BuCH_2$)PhSiSiPh(CH_2Bu-t)Cl, **6**, with lithium (a slight excess) in 57% yield under nearly the same conditions.

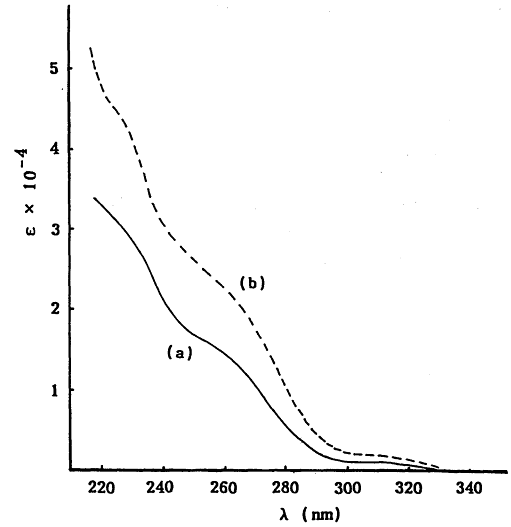

Fig. 1. UV absorption spectra for 1,2,3,4-tetraalkyl-1,2,3,4-tetraphenylcyclotetrasilane: (a): **1**, (b): **2**.

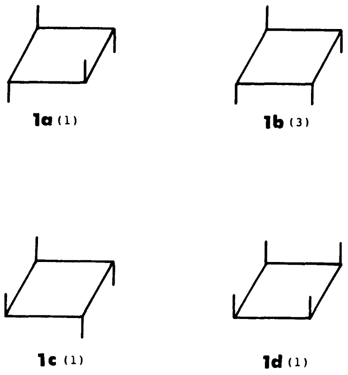
1a (1) **1b** (3)
1c (1) **1d** (1)

Fig. 2. The possible geometrical isomers of the cyclotetrasilane **1** in planer conformations and the number of expected β-methyl NMR resonances of the t-butyl substituents.

Both **1** and **2** are air-stable, evidently owing to a steric protection by the t-butyl and neopentyl substituents, respectively. The UV absorption spectra of these four-membered rings are shown in Fig. 1. The longest wavelength bands for these rings at ca. 315 nm are slightly lower in energy than the corresponding absorptions for peralkylcyclotetrasilanes [e.g., 300 nm for (t-$BuMeSi)_4$[9] and 286 nm for [(t-$BuCH_2)_2Si]_4$[6]], presumably due to perturbation of the electronic structures of the Si_4 frameworks by the phenyl substituents.[14] In the mass spectra, good agreement is found between the observed isotope ratios for the parent clusters and those calculated, in support of the assignments for **1** and **2**.

The presence of the two different substituents on each silicon atom should give rise to the four isomers. For example, the possible isomers for **1** and the number of expected β-methyl resonaces of the t-butyl groups in the NMR are shown in Fig. 2.[9,10] Both ^1H and

^{13}C{^{1}H}NMR show six β-methyl signals, respectively, suggesting the presence of all four isomers **1a**—**d**. Further work to determine the isomeric distribution of the products is in progress.

In short, the present reductive couplings can provide a useful route to the novel 1,2,3,4-tetraalkyl-1,2,3,4-tetraphenylcyclotetrasilanes **1** and **2**, which might be latent sila-functional cyclotetrasilanes since it has been shown by Hengge and coworkers that phenylcyclopolysilanes can be converted to the corresponding halocyclopolysilanes via the dephenylation with hydrogen halides.[15]

Experimental

Melting and boiling points were uncorrected. ^{1}H (90 MHz) and ^{13}C (22.64 MHz) NMR spectra were recorded on a Hitachi R-90H spectrometer. IR spectra were recorded on a JASCO A102 spectrometer. UV spectra were taken on a Hitachi 200-10 spectrometer. Mass spectra were recorded on a JEOL DX-300 spectrometer. GLC analyses were carried out using an Ohkura 103 gas chromatograph equipped with 1 m×0.4 cm Pyrex glass columns packed with 10% Silicone SE-30 and 10% Silicone KF-96 on Celite 545 SK (60—80 mesh).

Benzene and THF were distilled from sodium benzophenone ketyl prior to use. All reactions were carried out under an atmosphere of dried nitrogen.

The dichlorosilane **3** was prepared according to literature direction.[16] (*t*-BuCH$_2$)PhSiCl$_2$, **5**, and Cl(*t*-BuCH$_2$)PhSiSiPh(CH$_2$Bu-*t*)Cl, **6**, were prepared by the methods shown (Eqs. 2 and 3).[17,18]

$$\text{PhSiCl}_3 \xrightarrow{t\text{-BuCH}_2\text{Li}} \mathbf{5}\ (73\%) \tag{2}$$

$$\begin{gathered}\text{PhHSiCl}_2 \xrightarrow{t\text{-BuCH}_2\text{Li}} (t\text{-BuCH}_2)\text{PhHSiCl}\ (69\%) \xrightarrow{\text{Li}} \\ \text{H}(t\text{-BuCH}_2)\text{PhSiSiPh}(\text{CH}_2\text{Bu-}t)\text{H}\ (\mathbf{7})\ (56\%) \xrightarrow[\text{PdCl}_2]{\text{CCl}_4} \mathbf{6}\ (77\%)\end{gathered} \tag{3}$$

For **5**: Bp 113—115 °C (32 mmHg); ^{1}H NMR (CCl$_4$) δ=1.03 (s, 9H, *t*-Bu), 1.21 (s, 2H, -CH$_2$-), and 7.3—7.7 (m, 5H, Ph). Found: C, 53.50; H, 6.53%. Calcd for C$_{11}$H$_{16}$SiCl$_2$: C, 53.44; H, 6.52%.

For **7**: Bp 135—138 °C (0.20 mm Hg); IR (neat) principal absorptions, 2130, 1420, 1260, and 1110 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=0.88 (s, 9H, *t*-Bu), 0.93 (s, 9H, *t*-Bu), 1.23 (s, 4H, -CH$_2$-), 4.41 (m, 2H, SiH), and 7.25 (m, 10H, Ph); Found: C, 74.28; H, 9.76%. Calcd for C$_{22}$H$_{34}$Si$_2$: C,74.50; H, 9.66%.

For **6**: Bp 149—155 °C (0.15 mmHg); IR (neat) principal absorptions, 1425, 1260, 1230, 1115, and 1100 cm^{-1}; ^{1}H NMR (CCl$_4$) δ=0.80 (s, 9H, *t*-Bu), 0.94 (s, 9H, *t*-Bu), 1.21 (s, 2H, -CH$_2$-), 1.38 (s, 2H, -CH$_2$-), and 7.2—7.8 (m, 10H, Ph); Found: C, 62.41; H, 7.54%. Calcd for C$_{22}$H$_{32}$Si$_2$Cl$_2$: C, 62.38; H, 7.62%.

Reaction of *t*-BuPhSiCl$_2$, 3, with Lithium: A 200 ml flask equipped with a magnetic stirrer and a nitrogen inlet was charged with lithium cut (0.60 g, 87 mg-atom) and THF (60 ml). The flask was cooled to 0 °C by an ice-water bath, and the dichlorosilane **3** (7.0 g, 30 mmol) was added dropwise over 5 min. The mixture was stirred for an additional 0.5 h and filtered. A GLC analysis showed that (*t*-BuPhSi)$_4$, **1**, had been produced in 45% yield. Approximately 100 ml of cyclohexane was added, and the solution was washed with water and dried over anhydrous MgSO$_4$. Evaporation of the solvents yielded a half-solid that was recrystallized from MeOH/EtOH (1/1) to give 1.9 g (36% yield) of **1** as fine colorless powders.

In another run, a mixture of **3** (4.63 g, 20 mmol), lithium (0.14 g, 20 mg-atom), and THF (48 ml) was stirred at 0 °C for 7 h. A GLC analysis showed that 68% of **3** had been consumed and that Cl(*t*-Bu)PhSiSiPh(Bu-*t*)Cl, **4**, had been produced in 27% yield together with a trace amount of **1**.

For **1**: Mp 280—310 °C; IR (KBr disk) principal absorptions, 1415, 1260, and 1095 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.77 (s, 4.5H, *t*-Bu), 0.81 (s, 3.1H, *t*-Bu), 0.98 (s, 5.2H, *t*-Bu), 1.03 (s, 11.4H, *t*-Bu), 1.42 (s, 8.9H, *t*-Bu), 1.51 (s, 2.9H, *t*-Bu), and 6.74—7.89 (m, 20H, Ph); ^{13}C{^{1}H}NMR (CDCl$_3$) δ=21.13, 21.56, 22.62, 23.20, 23.63, 24.42 (Me$_3\underline{\text{C}}$), 30.21, 30.58, 31.07, 31.28, 32.07, 32.44 ($\underline{\text{C}}$H$_3$), 125.98—123.39 (phenyl carbons), and 135.57—139.12 (phenyl carbons); MS (70 eV) *m/z* (isotope ratios for parent clusters) Obsd: 696 (100), 697 (67), 698 (41), 699 (21). Calcd: 696 (100), 697 (67), 698 (34), 699 (16); UV$_{\text{max}}$ (cyclohexane) 233 (ε 28000), 263 (ε 14200), and 317 nm (ε 522). Found: C, 73.95; H, 9.02%. Calcd for C$_{24}$H$_{72}$Si$_4$: C, 74.03; H, 8.70%.

For **4**: ^{1}H NMR (CCl$_4$) δ=0.85 (s, 18H, *t*-Bu) and 7.28—7.75 (m, 10H, Ph); exact mass for M$^+$ measd 394.1101. Calcd 394.1106, dev 0.5 mmu.

Reaction of (*t*-BuCH$_2$)PhSiCl$_2$, 6, with Lithium: A 300 ml flask was charged with lithium cut (0.94 g, 135 mg-atom), THF (65 ml), and benzene (65 ml). The flask was cooled to 0 °C by ice-water bath, and **5** (14.5 g, 59 mmol) in THF (10 ml) and benzene (10 ml) was added dropwise over 1 h. The mixture was stirred for an additional 1 h and filtered. A GLC analysis showed that the cyclotetrasilane **2** had been produced in 54% yield. The filtrate was washed with water and dried over anhydrous MgSO$_4$. Evaporation of the solvents and recrystallization from MeOH/EtOH (3/1) afforded 1.12 g (28% yield) of **2** as colorless powders.

For **2**: IR (KBr disk) principal absorptions, 1420, 1355, 1250, 1090, 720, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=0.70 (s, 2.0H, *t*-Bu), 0.74 (s, 4.7H, *t*-Bu), 0.79 (s, 16.0H, *t*-Bu), 0.81 (s, 2.0H, *t*-Bu), 0.90 (s, 7.7H, *t*-Bu), 0.99 (s, 3.6H, *t*-Bu), 1.35—1.58 (m, 8H, -CH$_2$-), and 6.70—7.90 (m, 20H, Ph); ^{13}C{^{1}H}NMR (CDCl$_3$) δ=30.73—31.97 (Me$_3\underline{\text{C}}$ and -CH$_2$-), 32.07, 32.14, 32.99, 33.10, 33.26, 33.32 ($\underline{\text{C}}$H$_3$), 126.7—128.2 (phenyl carbons), and 136.8—137.4 (phenyl carbons); MS (70 eV) *m/z* (isotope ratios for the parent clusters) Obsd: 704 (100), 705 (71), 706 (40), 707 (16). Calcd: 704 (100), 705 (71), 706 (38), 707 (14); UV$_{\text{max}}$ (cyclohexane) 230 (ε 42600), 264 (ε 22500), 313 nm (ε 1900). Found: C, 74.86; H, 9.14%. Calcd for C$_{44}$H$_{64}$Si$_4$: C, 74.93; H, 9.14%.

Reaction of the Dichlorodineopentyldiphenyldisilane 6 with Lithium: A mixture of **6** (0.25 g, 0.55 mmol), lithium cut (9.0 mg, 1.3 mg-atom), THF (1.4 ml), and benzene (1.4 ml) was stirred at 0 °C for 2 h. A GLC analysis showed that the cyclotetrasilane 2 had been produced in 57% yield together with a trace amount of the dihydrodisilane **7**.

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