gaseous $CO_2$ was introduced into the reaction mixture for 20 min. Subsequent addition of 10 mL of a 1.0 M solution of HCl was followed by allowing the reaction mixture to stir for 15 additional min. Aqueous extraction with three 35-mL portions of $CH_2Cl_2$, treatment of the organic layers with 30 mL of a saturated solution of $NaHCO_3$, drying of the resultant $CH_2Cl_2$ solution over $MgSO_4$, and removal of solvent in vacuo afforded a light yellow oil. Purification of this residue by silica gel chromatography (10:1, hexanes/EtOAc) afforded 116 mg (0.69 mmol, 98% yield) of the desired product as a clear viscous oil: IR (NaCl) 2960 (s), 2940 (s), 2860 (s), 2850 (m), 1780 (s), 1720 (s), 1480 (m), 1440 (m), 1380 (s), 1310 (m), 1180 (s) $cm^{-1}$; $^1H$ NMR $\delta$ 4.73 (dd, 1 H, $J$ = 7.8, 4.8 Hz, $C\mathit{H}(OCO)$), 3.10 (dt, 1 H, $J$ = 4.9, 1.2 Hz, $C\mathit{H}C(O)$), 2.25 (s, 1 H, bridge CH), 2.13 (d, 1 H, $J$ = 4.4 Hz, bridge CH), 1.76 (m, 3 H, $CH(OCO)C\mathit{H}_2$ and $C\mathit{H}CH_2CH_3$), 1.14 (m, 2 H, bridgehead $C\mathit{H}_2$), 1.34 (dt, 2 H, $J$ = 7.3, 6.3 Hz, $C\mathit{H}_2CH_3$), 0.94 (t, 3 H, $J$ = 7.3 Hz, $C\mathit{H}_3$); $^{13}C$ NMR $\delta$ 180.7, 80.4, 49.7, 45.9 (2C), 40.6, 38.8, 34.8, 27.5, 11.7. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.18; H, 8.52.

***exo*-5-Isopropyl *endo*-2,6-lactone 15**: IR (NaCl) 3560 (w), 2950 (s), 2850 (s), 1780 (s), 1720 (s), 1640 (m), 1480 (s), 1440 (m), 1380 (m), 1360 (m), 1350 (s), 1320 (m), 1300 (s), 1270 (m), 1180 (s), 1115 (s), 1090 (s), 1020 (s), 990 (s) $cm^{-1}$; $^1H$ NMR $\delta$ 4.75 (dd, 1 H, $J$ = 7.8, 5.1 Hz, $C\mathit{H}(OCO)$), 3.11 (t, 1 H, $J$ = 4.8 Hz, $C\mathit{H}C(O)$), 2.44 (d, 1 H, $J$ = 2.7 Hz, bridge CH), 2.28 (d, 1 H, $J$ = 4.9 Hz, $OCHCH_2C\mathit{H}$), 1.50 (m, 6 H, $C\mathit{H}_2CHO$, bridgehead $CH_2$, $C\mathit{H}(CH_3)_2$, $C\mathit{H}CH(CH_3)_2$), 0.99 (d, 3 H, $J$ = 6.1 Hz, $C\mathit{H}_3CH$), 0.94 (d, 3 H, $J$ = 6.3 Hz, $C\mathit{H}_3CH$); $^{13}C$ NMR $\delta$ 180.0, 80.5, 55.9, 46.1, 44.8, 39.1, 39.0, 34.7, 30.9, 20.7, 20.4; HR CIMS $C_{11}H_{16}O_2 + 1$ requires $m/z$ 181.1228, found 181.1225.

**Ketone I.** Alcohol **1a** (150 mg, 1.36 mmol) was dissolved in THF (5.0 mL), and *n*-PrMgCl (1.10 mL, 1.63 mmol) was added to the solution. $Cp_2Zr(n\text{-}Pr)_2$ (1.36 mmol, prepared at −78 °C according to the procedure mentioned above) was added to the original mixture at 25 °C. The solution was allowed to stir for 5 h, cooled to 0 °C, and treated with gaseous CO. The mixture was allowed to warm to 25 °C under CO atmosphere for 2 h. The reaction was quenched upon addition of a 5-mL portion of a 2.0 M solution of HCl. Subsequent extraction with three 100-mL portions of $CH_2Cl_2$, drying of organic layers over anhydrous $MgSO_4$, and removal of solvent in vacuo afforded a yellow oily residue. Silica gel chromatography (3:1, hexanes/EtOAc) yielded 147 mg of ketone I (0.82 mmol, 60% yield): IR (NaCl) 3434 (brm), 3426 (m), 3419 (m), 3408 (m), 1731 (s) $cm^{-1}$; $^1H$ NMR $\delta$ 4.24 (dt, 1 H, $J$ = 9.8, 3.9 Hz, $C\mathit{H}OH$), 2.92 (d, 1 H, $J$ = 9.3 Hz, $C\mathit{H}C(O)$), 2.55 (d, 1 H, $J$ = 3.9 Hz, $CH(OH)C\mathit{H}$ (bridge CH)), 2.29 (dd, 1 H, $J$ = 17.0, 7.3 Hz, exo $C\mathit{H}_2C(O)$), 2.15 (d, 1 H, $J$ = 6.3 Hz, bridge CH), 2.01 (m, 2 H, endo $C\mathit{H}_2C(O)$, exo $C\mathit{H}_2CH(OH)$), 1.94 (dd, 1 H, $J$ = 8.8, 7.3 Hz, $CH_3CHC\mathit{H}$), 1.71 (m, 1 H, $C\mathit{H}(CH_3)$), 1.19 (d, 3 H, $J$ = 6.9 Hz, $CH_3$), 1.12 (dp, 1 H, $J$ = 3.9, 1.9, 11.2 Hz, bridgehead CH anti to ketone), 0.85 (dt, 1 H, $J$ = 13.2, 3.4 Hz, bridgehead CH syn to ketone); $^{13}C$ NMR $\delta$ 222.9, 71.0, 52.3, 47.9 (2C), 45.7, 41.9, 38.0, 34.1, 33.6, 21.6; HR EIMS $C_{11}H_{16}O_2$ requires $m/z$ 180.1150, found 180.1150.

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**Supplementary Material Available:** Spectra of deuterium labeling experiments in reactions of **1a** and the corresponding exo alcohol (5 pages). Ordering information is given on any current masthead page.

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# An NMR Study of the Formation of Silyloxonium Ions by Using Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate as Counteranion[1]

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**Abstract:** The capability of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) as a counteranion for organosilicenium ions was investigated by NMR spectroscopy. Although reactions of hydrosilanes with trityl-TFPB did not give the corresponding silicenium ions as long-lived species in dichloromethane-$d_2$, the reactions produced rather stable silyloxonium ions in the presence of ethers at low temperatures. The evidence for the formation of cyclic silyloxonium ions was obtained by monitoring the reaction of 3-ethoxypropylsilanes with trityl-TFPB by NMR spectroscopy. The use of TFPB as a non-nucleophilic counteranion was crucial for the formation of the silyloxonium ions; silyl perchlorates did not show significant interaction with ethers.

## Introduction

The question of the existence of silicenium ions[2] in solution or in the solid state has received much attention in recent years. Lambert et al.[3] have claimed by means of conductance, cryoscopic molecular weight, and $^1H$, $^{13}C$, and $^{15}N$ NMR spectroscopy that triphenylsilyl and trimethylsilyl perchlorates are ionic species in sulfolane and acetonitrile as well as in highly diluted dichloromethane. On the other hand, Olah et al.[4,5] have argued against this conclusion; they have concluded that these silyl perchlorates exist as covalent esters both in solution and in the solid state by $^{29}Si$ and $^{35}Cl$ NMR spectroscopy and X-ray crystallography.

Perchlorate ion used in the previous studies would not be suitable for a counteranion of silicenium ions, because of the high oxo-

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(1) Chemistry of Organosilicon Compounds. 292.

(2) The nomenclature for trivalent silico cation has been controversial. Lambert, Barton, and some others have used the term *silylenium*, since the divalent species corresponding to *carbene* is *silylene*. However, *silylene* should have a logical relationship to *methylene* rather than *carbene*; the term corresponding to *carbene* should be *silicene*. On this basis, we prefer here to use *silicenium* as the general term for trivalent silicocations after Olah et al.

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(4) (a) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485. (b) Olah, G. A.; Laali, K.; Farooq, O. *Organometallics* **1984**, *3*, 1337. (c) Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heiliger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Bau, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123. (d) Olah, G. A.; Mo, Y. K. *J. Am. Chem. Soc.* **1971**, *93*, 4942. (e) Olah, G. A.; Heiliger, L.; Li. X.-Y.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1990**, *112*, 5991.

(5) See also following papers for other studies on this topic: (a) Eaborn, C. *J. Organomet. Chem.* **1991**, *405*, 173 and references cited therein. (b) Chojnowski, J.; Fortuniak, W.; Stanczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776. (c) Apeloig, Y.; Stanger, A. *J. Am. Chem. Soc.* **1987**, *109*, 272. (d) Cowley, A. H.; Cushner, M. C.; Riley, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 624.

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philicity of silicon making a strong Si–O covalent bond. We have investigated the capability of tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB)[7] as a counteranion for preparation of organosilicenium ions in dichloromethane-$d_2$.[6] TFPB is nonnucleophilic and much more stable and soluble in organic solvents than tetraphenylborate, which has recently been used by Lambert et al.[3g] as an anion for phenyldimethylsilicenium ion but no experimental details have been described.

The attempted preparation of the silicenium ions in the presence of an ether gave rather stable silyloxonium ions at low temperatures, although silicenium TFPBs were not long-lived species in dichloromethane, even if they were generated. Whereas adducts of silyl-based Lewis acids with bases such as pyridines and imidazoles are well established by using NMR spectroscopy[8a–d] and X-ray crystallography,[8e] no direct spectroscopic evidence for the addition of silicenium ions or equivalents to ether in solution has yet been obtained.[9] The use of TFPB as a nonnucleophilic counteranion was crucial for the formation of the silyloxonium ions; silyl perchlorates did not show significant interaction with ethers. It is suggested that the silicenium ions can be attacked even by ether, which is a weaker nucleophile than perchlorate ion, giving tetracoordinate silicon species.

## Results and Discussion

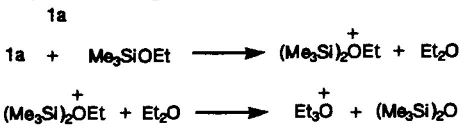
**Attempted Detection of Silicenium Ions in Dichloromethane.** Generation of silicenium TFPBs in dichloromethane-$d_2$ was examined by using the following two methods: (i) the hydride abstraction from a silane[14] by trityl-TFPB which was pregenerated by the reaction of trityl chloride and NaTFPB and (ii) the direct reaction of a chlorosilane with NaTFPB. All experiments were performed in carefully dried dichloromethane-$d_2$ by the use of vacuum-line techniques. When trimethylsilane was introduced to a solution of trityl-TFPB in dichloromethane-$d_2$ or toluene-$d_8$, the yellow color of trityl-TFPB disappeared immediately and the quantitative formation of triphenylmethane was indicated by $^1$H NMR spectroscopy. However, the $^{29}$Si NMR resonance due to the silicenium ion was not observed in the 0–400-ppm range; only the signals due to trimethylchlorosilane and trimethylfluorosilane were observed. Trimethylchlorosilane would be produced by the reaction of the silicenium ion with chloride ions in the system. Trimethylfluorosilane may be produced by the reaction of trimethylsilicenium ion with TFPB moiety, where the fluorines on TFPB may serve as nucleophiles. Alternatively, trimethylfluorosilane may be produced by a radical process. Thus, electron transfer from TFPB anion to silicenium ion may give a pair consisting of a silyl radical and a TFPB radical, the latter of which will decompose to give 3,5-bis(trifluoromethyl)phenyl radical and tris(3,5-bis(trifluoromethyl)phenyl)borane. Fluorine atom abstraction by the silyl radical may afford trimethylfluorosilane. As minor byproducts, 1,3-bis(trifluoromethyl)benzene and 3,3′,5,5′-tetrakis(trifluoromethyl)biphenyl were detected by GC-MS spectrometry. Tetraarylborates have been known to decompose via electron transfer.[15]

**Table I.** Summary of NMR Data for Diethylsilyloxonium Ions in $CD_2Cl_2$

| | chemical shift/ppm | | |
|---|---|---|---|
| compd | $^{29}$Si | $^{13}$C (Si$CH_3$) | $^1$H (SiC$H_3$) |
| $[Me_3SiOEt_2]^+TFPB^-$ | $66.9^a$ | $-1.1^a$ | $0.61^c$ |
| $Me_3SiH$ | $-15.5^a$ | $-3.4^a$ | $0.04^c$ |
| $[Ph_2MeSiOEt_2]^+TFPB^-$ | $38.0^b$ | $-4.5^c$ | $1.23^b$ |
| $Ph_2MeSiH$ | $-17.4^b$ | $-5.3^c$ | $0.61^b$ |
| $[(2\text{-thienyl})_2MeSiOEt_2]^+TFPB^-$ | $21.4^b$ | $-2.9^b$ | $1.28^c$ |
| $(2\text{-thienyl})_2MeSiH$ | $-31.5^b$ | $-3.2^b$ | $0.81^c$ |

[a] At −70 °C. [b] At −40 °C. [c] At −30 °C.

Scheme I



$$Me_3Si\overset{+}{O}Et_2 \underset{\mathbf{1a}}{} + Et_2O \longrightarrow Et_3\overset{+}{O} + Me_3SiOEt$$

$$\mathbf{1a} + Me_3SiOEt \longrightarrow (Me_3Si)_2\overset{+}{O}Et + Et_2O$$

$$(Me_3Si)_2\overset{+}{O}Et + Et_2O \longrightarrow Et_3\overset{+}{O} + (Me_3Si)_2O$$

**Formation of Silyloxonium Ions in the Presence of Diethyl Ether.** When the hydride abstraction from silanes by trityl-TFPB was applied in the presence of diethyl ether (10–20 equiv), diethylsilyloxonium ions (**1**) were produced at −70 °C (eqs 1 and 2).[16]

Method 1.

$$Ph_3CCl + Na^+TFPB^- \xrightarrow[rt]{CD_2Cl_2/Et_2O} Ph_3C^+TFPB^- \quad (1)$$

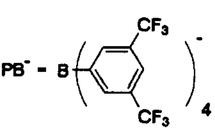
$$R_2MeSiH + Ph_3C^+TFPB^- \xrightarrow[-70\ °C]{CD_2Cl_2/Et_2O} R_2MeSi{-}\overset{+}{O}Et_2\ TFPB^- + Ph_3CH \quad (2)$$

**1a**, R = Me
**1b**, R = Ph
**1c**, R = 2-Thienyl

Method 2.

$$Me_3SiCl + Na^+TFPB^- \xrightarrow[-70\ °C]{CD_2Cl_2/Et_2O} \underset{\mathbf{1a}}{Me_3Si{-}\overset{+}{O}Et_2}\ TFPB^- + NaCl \quad (3)$$

TFPB$^-$ =



The formation of diethyl(trimethylsilyl)oxonium ion (**1a**) together with triphenylmethane, trimethylfluorosilane, trimethylchlorosilane, and hexamethyldisiloxane was evidenced by $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy. The yield of **1a** was determined by $^1$H NMR spectroscopy to be 44% based on the produced triphenylmethane. The $^1$H, $^{13}$C, and $^{29}$Si resonances for the tri-

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(6) Although acetonitrile has been taken as a nonnucleophilic solvent for silyl perchlorates by Lambert et al.,[3g] attempted preparation of silicenium TFPBs in a mixture of dichloromethane and acetonitrile gave the corresponding acetonitrile adducts; the $^{29}$Si resonances depended on the amount of acetonitrile and typically appeared at 38.5 ppm during the reaction of trimethylhydrosilane with trityl-TFPB in the presence of 2 equiv of acetonitrile in dichloromethane-$d_2$. Therefore, we did not use acetonitrile as a solvent in this study. Details will be reported elsewhere.

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(9) Silyloxonium ions have often been proposed as important intermediates in the reactions of ethereal substrates with iodosilanes,[10] silyl triflates,[11] and silyl perchlorates.[12] Convincing kinetic evidence for the formation of intramolecular silyloxonium ions has been provided by Eaborn et al.[13a] Silyloxonium ions generated in solution by the protonation of the corresponding silyl ether have been observed by NMR spectroscopy.[13b] For silyloxonium ions generated in the gas phase, see refs 13c and 13d.

(10) For a review, see: Olah, G. A.; Narang, S. C. *Tetrahedron* **1982**, *38*, 2225.

(11) For a review, see: Noyori, R.; Murata, S.; Suzuki, M. *Tetrahedron* **1981**, *37*, 3899.

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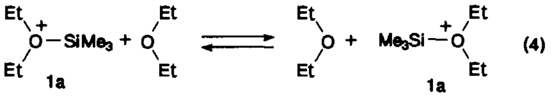
(15) (a) Eisch, J. J.; Wilcsek, R. J. *J. Organomet. Chem.* **1974**, *71*, C21. (b) Geske, D. H. *J. Phys. Chem.* **1959**, *63*, 1062 and references cited therein. (c) Geske, D. H. *J. Phys. Chem.* **1962**, *66*, 1743.

(16) Although the quantitative formation of triphenylmethane even in the absence of diethyl ether may suggest the intermediacy of the silicenium ions during the reaction in eq 2, the breaking of the Si–H bonds may accompany the simultaneous formation of the Si–O bond, as suggested by a referee. The detailed mechanisms for the formation of **1** remain open.

methylsilyl group of **1a** appeared at 0.61, −1.1, and 66.9 ppm, respectively, as shown in Table I. Significant line broadening was found in both the $^{1}H$ and $^{13}C$ resonances for methylene and methyl groups of the ether in the reaction mixture; the α- and β-$^{13}C$ resonances were found at 68 and 15 ppm with broad half line widths of 100 and 18 Hz, respectively. The line broadening may be ascribed to the facile degenerate nucleophilic substitution of **1a** by diethyl ether (eq 4). The line shape did not change



(4)

significantly from −70 to −30 °C. Whereas an extensive study of the temperature dependence of the line shape is required for the detailed analysis of the dynamic process, the low solubility of the ions prevented the NMR measurements at temperatures lower than −70 °C.

The formation of **1a** was also shown in an independent experiment, the direct reaction of NaTFPB with trimethylchlorosilane in the presence of diethyl ether at −70 °C (eq 3).

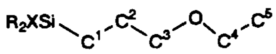
Although the NMR spectra of the reaction mixture did not change at temperatures lower than −30 °C, the signals due to **1a** disappeared rapidly at room temperature, by accompanying appearance of the signals due to triethyloxonium ion,[17] which would be formed by the reaction sequences shown in Scheme I. The fact that no signals due to an expected product, ethoxytrimethylsilane, were observed in the $^{1}H$, $^{13}C$, and $^{29}Si$ NMR spectra may suggest that even ethoxytrimethylsilane works as a nucleophile for trapping the trimethylsilicenium ion equivalent. Actually, an independent reaction of trimethylsilane with trityl-TFPB in the presence of ethoxytrimethylsilane showed a signal at 59.0 ppm in the $^{29}Si$ NMR spectrum, being indicative of the formation of ethylbis(trimethylsilyl)oxonium ion.

The $^{29}Si$ resonance for **1a** is even lower than that for trimethylsilyl triflate (46 ppm),[7b] thus suggesting the significant development of the positive charge on silicon, while much lower field resonances have been reported for trimethylsilyl triflate–$BCl_3$ (72.4 ppm)[4b] and trimethylfluorosilane–$SbF_5$ (102 ppm).[4e] The $^{29}Si$ resonance for "free" trimethylsilicenium ion has been predicted to be 225–275 ppm by comparing the $^{29}Si$ to $^{13}C$ NMR chemical shifts in $Me_3MX$ (M = Si and C)[4a] and 324 ppm by IGLO calculations.[18]

Similarly, diphenylmethylsilane and methyldi(2-thienyl)silane formed the corresponding (diethyl)silyloxonium ions, **1b** and **1c**, respectively, whose NMR data are also shown in Table I. All the $^{29}Si$ NMR chemical shifts for **1** appeared at more than 50 ppm lower field than those for the corresponding hydrosilanes. Formation of the corresponding (trimethylsilyl)oxonium ions from several polyethers such as 1,2-dimethoxyethane and 18-crown-6 ether were evidenced by the $^{29}Si$ resonances which appeared at 73.7 and 70.6, respectively.

It is noteworthy that the reaction of trimethylchlorosilane with silver perchlorate in the presence of 15 equiv of diethyl ether in dichloromethane–$d_2$ gave trimethylsilyl perchlorate quantitatively but no evidence for the formation of diethyl(trimethylsilyl)oxonium perchlorate. Thus, a sharp singlet resonance in the $^{29}Si$ NMR spectrum appeared at 46.4 ppm, which was in good agreement with the reported value for $Me_3SiClO_4$ (45.1 ppm) in dichloromethane-$d_2$.[7c] Although Lambert et al. have recently reported as the evidence for uncomplexed silicenium ions in acetonitrile that the $^{15}N$ NMR signal of acetonitrile was not affected even if the enriched acetonitrile-$^{15}N$ was added to trimethylsilyl perchlorate in dichloromethane,[3g] these results would be better taken as the other evidence indicating that trimethylsilyl perchlorate is covalent in nature and resists nucleophilic displacement by a weak nucleophile like ether or acetonitrile.[6]

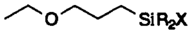
Table II. $^{13}C$ and $^{29}Si$ NMR Data for 3-Ethoxypropylsilyl Derivatives in $CD_2Cl_2$



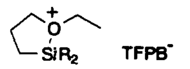
| compd | chemical shift/ppm | | | | | | |
|---|---|---|---|---|---|---|---|
| | C(Me) | $C^1$ | $C^2$ | $C^3$ | $C^4$ | $C^5$ | Si |
| **3a**[a] | −2.1 | 10.0 | 20.9 | 81.3 | 75.0 | 13.4 | 67.1 |
| **4**[b] | −1.6 | 11.9 | 22.8 | 71.4 | 66.7 | 14.3 | 38.6 |
| **2a**[c] | −4.3 | 10.8 | 25.2 | 73.5 | 66.4 | 15.6 | −12.9 |
| **3b**[d] | | 8.8 | 25.1 | 73.0 | 66.3 | 15.5 | 36.5 |
| **2b**[c] | | 8.9 | 21.7 | 81.7 | 76.9 | 13.0 | −13.3 |

[a] At −43 °C. [b] At −10 °C. [c] At room temperature. [d] At −40 °C.

**Formation of Cyclic Silyloxonium Ions from 3-Ethoxypropylsilanes .** Striking difference between TFPB and perchlorate as a possible counteranion for silicenium ions has been indicated by monitoring the reactions of 3-ethoxypropylsilanes (**2a** and **2b**) with trityl-TFPB and trityl perchlorate. Thus, the reactions of **2a** and **2b** with trityl-TFPB gave the corresponding cyclic silyloxonium TFPBs (**3a** and **3b**) in $CD_2Cl_2$, while a similar reaction of **2a** with trityl perchlorate gave the open-chain silyl perchlorate **4**. NMR spectra corresponding to **3a** were also observed during the reaction of **5** with NaTFPB in dichloromethane-$d_2$. The NMR data for **3a**, **3b**, **4**, and related compounds are summarized in Table II. The $^{29}Si$ resonances for **3a** and **3b** were found at 67.1 and 38.6 ppm, respectively, but as rather broad singlets, which values are comparable to that for **1a** and **1b**. Interestingly, the average deshielding of $C^4$ and $C^5$ from **2a** to **3b** (Δδ, 8.2 ppm) was about a half the corresponding difference between the values for diethyl ether and triethyloxonium ion (Δδ, 16.8 ppm);[17] the positive charge in **3** is suggested to develop significantly at silicon. The structure of ion **3** would be described as a cyclic silyloxonium ion; the cyclic form is suggested to be in equilibrium with the extended ion since the line widths of the $^{1}H$, $^{13}C$, and $^{29}Si$ NMR signals were rather broad.



**2a**, R = Me, X = H; **2b**, R = Ph, X = H; **4**, R = Me, X = $ClO_4$; **5**, R = Me, X = Cl.



**3a**, R = Me; **3b**, R = Ph

On the other hand, $^{13}C$ NMR resonances for **4** demonstrated close similarity to those for **2a**, being clearly indicative of the covalent nature in the silyl perchlorate. The $^{29}Si$ resonance for **4** which appeared even at higher field than that for trimethylsilyl perchlorate may suggest that the intramolecular ethereal oxygen can attack the silicon of **4** without displacement of perchlorate ion, forming a pentacoordinate silicon as a minor component in the equilibrium. In this context, it is interesting to note that the reaction of 3- and 4-(triphenylmethoxy)alkylsilyl hydrides occurs effectively in the presence of a catalytic amount of trityl perchlorate to give the corresponding cyclic ethers.[12]

## Experimental Section

All NMR spectra were recorded on a Bruker AC-300P NMR spectrometer ($^{1}H$ at 300 MHz, $^{13}C$ at 75.4 MHz, and $^{29}Si$ at 59.6 MHz).

NaTFPB was obtained as a hydrate either by preparation following a literature method[7] or by purchase from Dojin Chemicals, Co. Ltd., Japan.

**Methyldi-2-thienylsilane.**[19] Reaction of methyldichlorosilane (2.1 g, 18 mmol), 2-bromothiophene (6.7 g, 41 mmol), and magnesium (2.9 g, 119 mmol) in diethyl ether (20 mL) gave the title compound in 53% yield: $^{1}H$ NMR ($CD_2Cl_2$) δ 0.80 (d, $J$ = 3.7 Hz, 3), 5.30 (q, $J$ = 3.7 Hz, 1), 7.31 (dd, $J$ = 4.6, 3.5 Hz, 2), 7.50 (d, $J$ = 3.5 Hz, 2), 7.76 (d, $J$ = 4.6 Hz, 2); $^{13}C$ NMR ($CD_2Cl_2$) δ −2.6, 128.8, 132.5, 137.0; $^{29}Si$ NMR ($CD_2Cl_2$) δ −31.5.

**(3-Ethoxypropyl)dimethylchlorosilane (5).** A mixture of allyl ethyl ether (2.31 g, 26.8 mmol), excess dimethylchlorosilane, and a catalytic

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[17] The resonances at 84.1 and 12.1 ppm have been reported for triethyloxonium tetrafluoroborate: Breitmair, E.; Voelter, W. In *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: Weinheim, 1987; p 215.

[18] Cited in ref 4e. It was recently reported by Prof. Y. Apeloig, Technion Israel Institute of Technology, that the $^{29}Si$ resonance for $Me_3SiO^+H_2$ was calculated to be at 94 ppm by the IGLO method.

[19] (a) Lukevics, E.; Sturkovich, R. Y.; Pudova, O. A. *J. Organomet. Chem.* **1985**, *292*, 151. (b) Lukevics, E.; Germane, S.; Pudova, O. A.; Erchak, N. P. *Khim.-Farm. Zh.* **1979**, *13*, 52.

amount of $H_2PtCl_6$ was heated for 12 h at 60 °C. A fraction boiling at about 150 °C was collected to give **5** (2.41 g, 13.3 mmol) in 50% yield: $^1H$ NMR ($CDCl_3$) δ 0.37 (s, 6), 0.78–0.84 (m, 2), 1.16 (t, *J* = 7.0 Hz, 3), 1.60–1.70 (m, 2), 3.37 (t, *J* = 6.7 Hz, 2), 3.43 (q, *J* = 7.0 Hz, 2); $^{13}C$ NMR ($CDCl_3$) δ 1.5, 15.1, 15.3, 23.3, 66.0, 72.5; $^{29}Si$ NMR ($CDCl_3$) δ 32.2. Anal. Calcd for $C_7H_{17}SiOCl$: C, 46.51; H, 9.48. Found: C, 46.49; H, 9.14.

**(3-Ethoxypropyl)dimethylsilane (2a).** To a suspension of $LiAlH_4$ (0.23 g, 6.2 mmol) in ether (8 mL) was added **5** (2.24 g, 12.4 mmol) at 0 °C, and then the mixture was stirred at room temperature for 12 h and under reflux for 2 h. The usual workup gave **2a** (1.29 g, 8.8 mmol) in 71% yield: bp 122 °C (400 mmHg); $^1H$ NMR ($CD_2Cl_2$) δ 0.11 (d, *J* = 3.7 Hz, 6), 0.58–0.65 (m, 2), 1.18 (t, *J* = 7.1 Hz, 3), 1.56–1.66 (m, 2), 3.38 (t, *J* = 6.8 Hz, 2), 3.46 (q, *J* = 7.1 Hz, 2), 3.88 (sept, *J* = 3.7 Hz, 1); $^{13}C$ NMR ($CD_2Cl_2$) δ −4.3, 10.8, 15.6, 25.2, 66.4, 73.5; $^{29}Si$ NMR ($CD_2Cl_2$) δ −12.9. Anal. Calcd for $C_7H_{18}SiO$: C, 57.47; H, 12.40. Found: C, 57.29; H, 12.15.

**(3-Ethoxypropyl)diphenylsilane (2b).** To a mixture of allyl ethyl ether (1.46 g, 17.0 mmol) and a catalytic amount of $H_2PtCl_6$ was added diphenylsilane (2.80 g, 15.2 mmol) and the solution was allowed to react for 12 h at temperatures from 80 to 160 °C. Distillation at a reduced pressure gave **2b** (2.44 g, 9.0 mmol) in 59% yield, bp 101–110 °C (0.05 mmHg): $^1H$ NMR ($CD_2Cl_2$) δ 1.27–1.35 (m, 5), 1.82–1.92 (m, 2), 3.52 (t, *J* = 6.7 Hz, 2), 3.53 (q, *J* = 6.7 Hz, 2), 5.04 (t, *J* = 3.7 Hz, 1), 7.40–7.50 (m, 6), 7.60–7.80 (m, 4, $^1J_{Si-H}$ = 193 Hz); $^{13}C$ NMR ($CD_2Cl_2$) δ 8.4, 15.1, 24.6, 65.9, 72.7, 127.9, 129.4, 134.2, 135.0; $^{29}Si$ NMR ($CD_2Cl_2$) δ −13.3. Anal. Found: C, 75.41; H, 7.98%. Calcd for $C_{17}H_{22}OSi$: C, 75.50; H, 8.20.

**Sample Preparation for NMR Measurements. (a) Reaction of Hydrosilanes with trityl-TFPB.** An apparatus having two side arms was used for the preparation and sampling of the silyloxonium TFPBs for NMR spectroscopy. Typically, NaTFPB was treated with trityl chloride without solvent in a side arm at highly reduced pressure ($<10^{-6}$ mmHg) yielding yellow solids; $H_2O$ of hydrate NaTFPB was removed during this procedure. Then, $CD_2Cl_2$ was introduced to the mixture by trap-to-trap distillation; the resulting suspension was filtered through a sintered glass filter into a central tube giving a yellow solution of trityl-TFPB at ambient temperature. Trimethylsilane and diethyl ether were transferred to the frozen solution of trityl-TFPB and then the sample tube was sealed off at −196 °C. The mixture was warmed with a methanol bath to −70 °C to start the reaction; the characteristic yellow color of trityl ions disappeared immediately. For NMR spectroscopic measurements, the mixture was transferred into another side arm having an NMR tube, which was sealed off without raising the temperature higher than −50 °C.

**(b) Reaction of Chlorosilanes with NaTFPB.** A similar apparatus and procedure as described above was applied for the sample preparation. NaTFPB was dehydrated and pulverized by magnetic stirring under high vacuum for 2 h before use.

**Preparation of Trimethylsilyl Perchlorate in the Presence of Diethyl Ether.** By using a similar procedure as described above, the reaction of trimethylchlorosilane with silver perchlorate in the presence of 15 equiv of diethyl ether in $CD_2Cl_2$ at ambient temperature gave a solution of trimethylsilyl perchlorate together with the precipitate of AgCl. For NMR measurements, the solution was transferred into an NMR tube after removal of AgCl by decantation and sealed off.

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**Supplementary Material Available:** $^1H$, $^{13}C$, and $^{29}Si$ NMR spectra for the reaction mixture of trityl-TFPB with $Me_3SiH$ and $^{29}Si$ NMR spectrum for **3a** (4 pages). Ordering information is given on any current masthead page.

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# Arylsilsesquioxane Gels and Related Materials. New Hybrids of Organic and Inorganic Networks

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**Abstract:** Molecular building blocks for the preparation of amorphous hybrid organic–inorganic network materials have been synthesized. Hydrolysis and condensation of bis(triethoxysilyl)aryl **1–4** and -ethynyl **5** monomers results in formation of aryl- and ethynyl-bridged polysilsequioxanes in the form of xerogels. The gels were glasslike materials composed of uniform aggregates of particles between 50 and 80 nm in diameter. Atomic force microscopy was used to examine the fine grained aggregate characteristics of phenyl-bridged polysilsesquioxanes. The aryl-bridged materials were microporous with surface areas as high as 1000 $m^2/g$ and thermally stable to 400 °C in air. Solid state $^{13}C$ and $^{29}Si$ NMR spectroscopies were used evaluate the integrity of the aryl and ethynyl bridges and to determine the degrees of hydrolysis (semiquantitative) and condensation in the network materials.

## Introduction

Silicates comprise the earth's most abundant mineral form.[1] A remarkable diversity of morphologies exist within the simple pattern of alternating silicon and oxygen atoms. Synthetic glasses, prepared by sol–gel processing of alkoxysilanes (eq 1), allows for the preparation of amorphous materials (xerogels) that can serve as precursors to high purity glasses, ceramics, coatings, and fibers.[2]

$$n\,Si(OEt)_4 \;+\; 2n\,H_2O \;\rightleftharpoons\; (SiO_2)_n \;+\; 4n\,EtOH \qquad (1)$$

The importance of synthetic silicates arises from the diversity of physical properties of the resulting materials. These properties can be influenced by changes in sol–gel reaction conditions or in the subsequent processing of the gel. Sol–gel chemistry allows for the fabrication of silicates with morphologies distinctly different from, and often more useful than, naturally occurring silicates. While the manipulation of polymerization and processing conditions allows for the preparation of a variety of silicates, an alternative strategy for designing new silicate-like materials is to

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