4, N^6CH_3), 4.26 (t, J = 6.6 Hz, 4, N^9CH_2), 6.1 (br s, 2, NH), 7.92 (s, 2, H8), 8.40 (s, 2, H2). Anal. Calcd for $C_{15}H_{18}N_{10}$: C, 53.24; H, 5.37; N, 41.39. Found: C, 53.29; H, 5.41; N, 40.84.

6,6′-Bis(methylthio)-9,9′-trimethylenebis(purine) (34). To a stirred mixture of 6-methylthiopurine (2.0 g, 12.4 mmol) in DMSO (20 mL) was added at 30 °C 1,3-dibromopropane (0.65 mL, 6.2 mmol). Stirring was continued at 30 °C for 16 h. After the reaction was over, water (50 mL) was added to the mixture, and yielded precipitates were collected, washed successively with water and acetone, and then recrystallized from ethyl acetate to give 1.1 g (47%) of **34** as colorless prisms: mp 236–237 °C; ^1H NMR (100 MHz, $CDCl_3$) δ 2.59 (q, J = 6.8 Hz, 2, $CH_2CH_2CH_2$), 2.74 (s, 6, SCH_3), 4.32 (t, J = 6.8 Hz, 2, N^9CH_2), 8.12 (s, 2, H8), 8.73 (s, 2, H2); MS, 372 (M^+). Anal. Calcd for $C_{15}H_{16}N_8S_2$: C, 48.37; H, 4.33; N, 30.08; S, 17.22. Found: C, 48.38; H, 4.36; N, 29.82; S, 17.04.

1,4-Bis(N^6,9-dimethyladenin-2-yl)butane (35). Under a nitrogen atmosphere was added 60% NaH (132 mg, 3.3 mmol) to a stirred solution of **30** (500 mg, 1.4 mmol) in DMF (10 mL). After being stirred for 10 min, methyl iodide (0.26 mL, 4.1 mmol) was added to the solution, and stirring was continued at room temperature for 3 h. After the reaction was over, the mixture was chromatographed on silica gel with methanol–chloroform (1:3) and purified with preparative TLC (silica gel) with methanol–chloroform (1:9) to give the N^9,$N^{9\prime}$-dimethyl derivative of **30** in 54% yield. Recrystallization from 2-propanol gave the pure compound as white microcrystals: mp 223 °C; ^1H NMR (100 MHz, $CDCl_3$) δ 1.89–2.06 (m, 4, $ArCH_2CH_2$), 2.96–3.17 (m, 4, $ArCH_2$), 3.89 (s, 5, CH_3), 8.01 (s, 2, ArH); MS, 394, 392, 390 (M^+), 357, 355 (M^+ − Cl).

To a solution of the above described compound (210 mg, 0.54 mmol) in 1-butanol was added a 40% aqueous solution of monomethylamine (0.46 mL) and triethylamine (0.18 mL, 1.3 mmol), and the mixture was gently refluxed for 5.5 h. During the reaction, each 0.46 mL of monomethylamine aqueous solution was added five times to the reaction mixture. After the reaction was over, the solvent was removed and crude product was purified by preparative TLC (silica gel) with methanol–chloroform (1:5) to give 61 mg (30%) of **35**. Further purification from 1-butanol gave pure **35** as white microcrystals: mp 262–265 °C; ^1H NMR (100 MHz, $CDCl_3$) δ 1.88–2.03 (m, 4, $ArCH_2CH_2$), 2.82–2.91 (m, 4, $ArCH_2$), 3.22 (d, J = 4.9 Hz, 6, $NHCH_3$), 3.77 (s, 6, NCH_3), 5.54 (br s, 2, $NHCH_3$), 7.62 (s, 2, ArH); MS, 380 (M^+). Anal. Calcd for $C_{18}H_{24}N_{10}$: C, 56.83; H, 6.36; N, 36.81. Found: C, 56.59; H, 6.64; N, 36.53.

N^6,9-Dimethyladenine (36). A mixture of **37** (0.2 g, 1.1 mmol), 40% monomethylamine (0.5 mL, 6.4 mmol), and water (0.5 mL) in an ampule was heated at 130 °C for 20 h. After being cooled, the solvent was removed and the residue was chromatographed on silica gel with methanol. Recrystallization from benzene gave 0.10 g (55%) of **36** as colorless prisms: mp 181.5–182.5 °C; ^1H NMR (100 MHz, $CDCl_3$) δ 3.23 (d, J = 5.1 Hz, 3, N^6CH_3), 3.82 (s, 3, N^9CH_3), 5.80 (br s, 1, NH), 7.71 (s, 1, H8), 8.43 (s, 1, H2); MS, 163 (M^+). Anal. Calcd for $C_7H_9N_5$: C, 51.52; H, 5.56; N, 42.92. Found: C, 51.57; H, 5.39; N, 42.67.

9-Methyl-6-(methylthio)purine (37). A mixture of 6-methylthiopurine (1.0 g, 6.2 mmol), potassium carbonate (0.6 g, 4.3 mmol), and methyl iodide (0.4 mL, 7.4 mmol) in DMSO (10 mL) was stirred at 30 °C for 16 h. The solvent was removed under reduced pressure, and the residue was extracted with chloroform. Crude product was passed through a short column of silica gel with methanol and then purified by column chromatography on alumina with benzene–chloroform, followed by recrystallization from benzene to give 0.65 g (58%) of **37** as colorless prisms: mp 167–167.5 °C; ^1H NMR (100 MHz, $CDCl_3$) δ 2.74 (s, 3, SCH_3), 3.88 (s, 3, NCH_3), 7.93 (s, 1, H8), 8.74 (s, 1, H2); MS, 180 (M^+). Anal. Calcd for $C_7H_8N_4S$: C, 46.65; H, 4.47; N, 31.09; S, 17.79. Found: C, 46.94; H, 4.38; N, 31.19; S, 17.73.

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The First Silylenium Ions in Solution

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Abstract: The first silylenium ions (R_3Si^+) have been produced in solution. They are generated in polar solvents of low nucleophilicity, including CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, and sulfolane. Tris(alkylthio)silyl cations [$(R'S)_3Si^+$, R′ = Me, Et, *i*-Pr] are produced by treatment of the corresponding silane with trityl perchlorate. The covalent form is unambiguously eliminated as the structure in dilute solution by the conductance and molecular weight. A dicationic bridged dimer is eliminated by the molecular weight and by crossover experiments. Complexation with solvent is inconsistent with the ^1H and ^{13}C resonance positions. Similar treatment of triphenylsilane yields a solution of low conductance in CH_2Cl_2 and $ClCH_2CH_2Cl$ and of high conductance in CH_3CN and sulfolane. Molecular weight measurements show that triphenylsilyl perchlorate in dilute sulfolane is unambiguously in the two-particle ionic form, whereas the azide is in a one-particle covalent or ion-paired form. Carbon-13 analysis of the phenyl resonances in all solvents substantiates an ionic or ion-paired form. Conductance and ^{35}Cl experiments demonstrate that the ionic form is favored at low concentrations but that association occurs at high concentrations. The ^{13}C and ^{15}N resonance positions of CH_3CN and sulfolane eliminate the possibility that they are forming tetravalent complexes in CH_2Cl_2 and $ClCH_2CH_2Cl$.

Silylenium ions[2] have been known and studied in the gas phase for over 20 years. Electron impact mass spectrometry gave values of the appearance potential of Me_3Si^+ in the early 1960s.[3] Fragmentation studies indicated reasonable stability for silylenium ions,[4-6] which were found to be more stable than analogous carbenium ions, as judged from the fragment intensities. The ion Me_2PhSi^+ represented 50% of the total ion current in the mass spectrum of (trimethylsilyl)benzene.[5] Several ion cyclotron resonance studies have been carried out on silylenium ions,[7-9] with

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[2] Even the nomenclature for trivalent, positive silicon (R_3Si^+) has been controversial. The earliest term was *siliconium*, but, like its strict analogue *carbonium*, it denotes hypervalency and is best reserved for pentacoordinate silicon, R_5Si^+. We and others have used the term *silicenium*, by loose analogue to *carbenium*. This term, however, seems to have no linguistic basis. The term *carbenium* is derived from the divalent species *carbene*. Thus, since the divalent silicon species is *silylene*, the trivalent, positive form should be *silylenium*. The general term *carbocation* finds analogy with *silyl* cation. Pronunciation of all these terms varies according to the side of the Atlantic, with Americans preferring the initial *i* long (except in *siliconium* because of the close analogy to *silicon*). Individual species are best named as derivatives of silanes, so that Me_3Si^+ becomes trimethylsilylenium or trimethylsilyl.

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some attention to substituent effects.

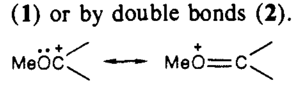
Theory predicts that a silylenium ion is more stable than the analogous carbenium ion.[10] Apeloig and Schleyer[11] studied the isodesmic reaction of eq 1 and found that the left side, with the

$$SiH_2X^+ + CH_3X \rightleftarrows CH_2X^+ + SiH_3X \qquad (1)$$

silylenium ion, was favored for a wide variety of X (by 73.5 kcal/mol for H, by 55.3 for CH_3, and by 28.7 for OH). Later theoretical studies found stabilization of silylenium ions by heteroatoms[12,13] and by double bonds[14] (in trivinylsilyl: $(CH_2{=}CH)_3Si^+$). The larger size, polarizability, and electropositivity of silicon apparently make it better able to stabilize positive charge than carbon. Because of better overlap with the empty carbenium 2p orbital, however, substituents reduce the difference in stability. Nonetheless, there clearly is no thermodynamic reason why silylenium ions cannot be observed in solution. Their inherent stability is comparable to or better than that of analogous carbenium ions.

Despite the thermodynamic stability of silylenium ions, they have firmly resisted preparation in solution until recently. Early attempts at their preparation were thoroughly reviewed in 1974 by Corriu and Henner.[15] Since then, unsuccessful attempts have been reported by solvolysis of silyl-substituted substrates,[16,17] reaction of Lewis acids with halosilanes,[18] and hydride abstraction from silanes.[19] It is possible that some of these methods actually produced silylenium ions, but proof was lacking. Only covalent or ion-paired materials, pentavalent siliconium ions, or bridged species were proved by the observations.

The difficulty in producing silylenium ions in solution appears to result from a number of causes. (1) Most important probably is the high bond strength between silicon and strongly electronegative elements such as oxygen, nitrogen, and the halogens. Traditional leaving groups in carbocation production have been oxygen functionalities such as tosylate, as well as halogens. The barrier to the departure would therefore be higher for silicon than for carbon, unless the higher polarizability of silicon could be reflected in better solvation of the transition state. (2) A clear kinetic result of the oxa- and halophilicity of silicon is expected to be lower barriers to reactions of such materials with the silyl cation than with carbocations. Thus, even if silylenium ions are produced in solution, internal return of the leaving group or reaction with a nucleophilic solvent could lead to unobservably short lifetimes. (3) In carbocation chemistry, stabilization has been obtained by donation of π electrons from a substituent to the empty 2p orbital on sextet carbon, as by lone pairs on oxygen (**1**) or by double bonds (**2**). Silicon is well-known for its poor ability to support such π overlap, because bonds to silicon are longer than those to carbon and because 2p–π donors have a poor fit with the empty silicon 3p orbital. (4) Finally, it is noted that the substituents that are associated with good π donation to carbocations are usually electron withdrawing by induction, e.g., oxygen (**1**), nitrogen, halogens, double bonds (**2**), and phenyl rings. Because 2p–2p overlap in carbocations is very strong, the inductive effect is of less importance. The weaker 2p–3p overlap in silyl cations may be unable to compensate for inductive destabilization.



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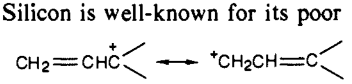

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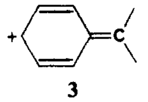
In order to overcome these difficulties, we have combined several strategies.[19] (1) We utilize the procedure of J. Y. Corey,[20] which involves hydride as the leaving group. In this way, the high bond strengths of traditional organic leaving groups are avoided. Because the Si–H bond is weaker than an analogous C–H bond, a carbocation should be able to abstract hydride from a silane in the manner of the Bartlett–Condon–Schneider reaction (eq 2).

$$Ph_3C^+ + R_3SiH \rightarrow R_3Si^+ + Ph_3CH \qquad (2)$$

This reaction moreover generates no new anion capable of internal return, and the only byproduct is the nonreactive hydrocarbon triphenylmethane. (2) Conditions of generation must be as nonnucleophilic as possible if the ion is to have long-term stability. Thus, both the gegenion and the solvent must be chosen appropriately. For the anion, we have used perchlorate, tetrafluoroborate, and triflate, with varying degrees of success. The solvent must have low nucleophilicity but good ionizing power. Hydroxylic solvents were rejected in favor of a series of dipolar solvents: dichloromethane, 1,2-dichloroethane, sulfolane, acetonitrile, nitroalkanes. These materials are sufficiently polar to generate ions or ion pairs while still being poorly nucleophilic. (3) Because π overlap by silicon is expected to be poor, we have selected alternative methods of stabilization.[19] Sulfur is a highly polarizable substituent capable of stabilizing negative charge for example in the 1,3-dithiane anion. Sulfur attached directly to positive silicon thus may be able to stabilize charge by induced dipoles. It is also possible that the 3p lone pairs on sulfur may have a better orbital fit with the empty 3p orbital of silicon than would 2p donors, although bond distances are still long. Consequently, our first target was the tris(alkylthio)silyl cation $(RS)_3Si^+$. In a second approach, the phenyl group is capable of stabilization of charge not only through resonance but also through π polarization. The principal difference between the two mechanisms is that resonance transfers charge into or out of the phenyl ring whereas π polarization involves no net charge transfer (cp., **3** and **4**). The π polarization mechanism has been suggested for stabilization of the triphenylsilyl anion.[21] Consequently, our second target was the triphenylsilyl or sityl cation Ph_3Si^+. (4) Both substituents were chosen for their low electronegativity. In carbon systems, the best electron donors by resonance (Me_2N, MeO, F) often are highly electronegative. Since resonance effects are weak for silicon, inductive effects can counterbalance them entirely. Sulfur is nearly isoelectronegative with carbon, and phenyl is only slightly electron withdrawing by reason of the sp^2 carbon atoms. Thus, inductive effects are small or negligible, so that induced dipoles have the opportunity to exert an optimal effect.



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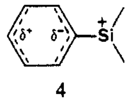

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Stability by σ Polarization

Synthesis. For polarizable substituents, we considered both sulfur and phosphorus. On the basis of ease of synthesis, we chose the sulfur system. The choice was fortunate, as Godleski later pointed out that phosphorus is less effective than sulfur in stabilizing a silylenium ion, possibly because the energy to planarize phosphorus is larger.[13] Thus, 3p–3p overlap, as well as polarization, may be important.

Tris(alkylthio)silicon hydrides are easily but unpleasantly available from the reaction of trichlorosilane with alkanethiols (eq 3).[22] We prepared the silane of eq 3 with R′ = Me, Et, *i*-Pr.

$$3R'SH + 3py + HSiCl_3 \rightarrow (R'S)_3SiH + 3py{\cdot}HCl \qquad (3)$$

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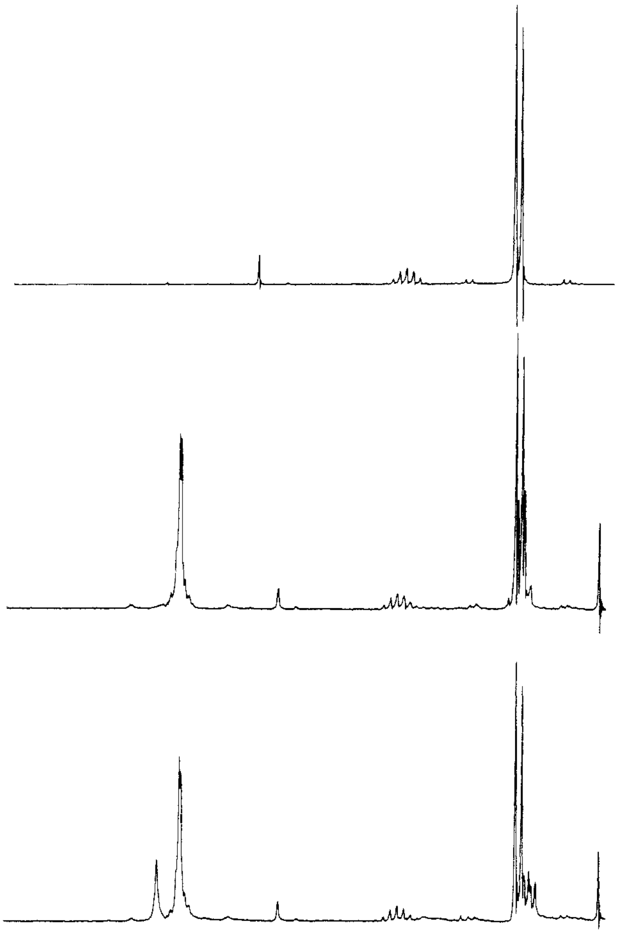
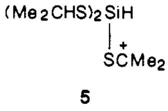


Figure 1. 60-MHz ^1H spectrum of (top) tris(2-propylthio)silane in CD_2Cl_2, (middle) the same material after the addition of 0.80 equiv of trityl perchlorate, and (bottom) the same material after the addition of a total of 1.2 equiv of trityl perchlorate.

Silyl Cation Preparation and ^1H Spectra. According to the method of J. Y. Corey,[20] we dissolved the silane in CD_2Cl_2 and added 1 equiv of solid trityl perchlorate under nitrogen (eq 2). Originally we did these manipulations at −78 °C but found no differences if carried out at ambient temperature. The solution was allowed to warm slowly to room temperature, and the disappearance of solid material indicated that the reaction was complete.

Progress of the reaction was conveniently monitored by ^1H NMR spectroscopy. The disappearance of the silyl hydride resonance at δ 5.67, the absence of any resonances from trityl, and the appearance of triphenylmethane resonances (CH at δ 5.37) showed that the reaction occurred very cleanly. Figure 1 shows a series of additions of trityl perchlorate for the case of tris(2-propylthio)silane in CD_2Cl_2. The top spectrum shows pure starting material. After 0.80 equiv of trityl perchlorate is added (middle), the SiH resonance is almost replaced by the CH resonance, and two isopropyl methyl resonances are visible. After an excess of trityl is added (bottom), there is essentially a single species, and the excess trityl resonances are clearly visible as the lowest field peak.



$$\begin{array}{c}(Me_2CHS)_2SiH\\ |_{+}\\ SCMe_2\end{array}$$

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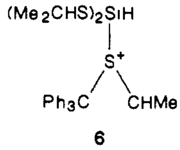

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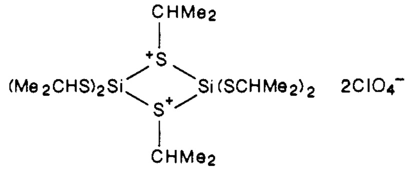
These spectra immediately eliminate a number of alternative pathways. (1) Trityl did not abstract a hydride from carbon, for example to give species **5**, since this molecule retains SiH and possesses methyls (Me_2C^+) that would have an unsplit proton resonance. (2) Trityl did not attack sulfur to form a sulfonium ion **6**, as this species retains SiH, does not give Ph_3CH, and has two types of isopropyl groups in the ratio 2/1. This side reaction probably was responsible for the presence of several small peaks in the CH/SiH region for the case of methylthio (eq 2, R = SCH_3). It was this presumed side reaction (more precisely, these extra resonances) that made us decide to concentrate on the isopropylthio system, in which the larger alkyl group provides steric hindrance to sulfonium ion formation. The isopropyl group also probably provides greater polarizability. Indeed, the additional resonances were very small (Figure 1). Moreover, the resonances attributable to the sulfonium ion of isopropylthio disappeared over time, giving the resonances of the silylenium ion. Thus, the sulfonium ion is the first formed, kinetic product, but the silylenium ion is the thermodynamic product. Ethylthio also was examined briefly and was found to resemble isopropylthio, but the latter provided simpler resonances to follow in the methyl region. (3) The dimer of the silylenium ion **7** is a reasonable species[23] but is not in agreement with the ^1H spectrum, which contains only a single type of isopropyl resonance. This dimer, however, might be in dynamic equilibrium with the monomeric silylenium ion, thereby interconverting the two types of isopropyl groups, so that the evidence presented thus far does not eliminate **7**. The ^1H spectra demonstrate that a single species is formed cleanly and that it possesses only a single type of isopropyl group, unless there is dynamic interconversion of forms.



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Similar experiments were carried out with trityl tetrafluoroborate in an attempt to form the silylenium ion with a different anion. The CH_2Cl_2 solution of trityl tetrafluoroborate and tris(2-propylthio)silane, after momentary stability, gave up a gas (presumably BF_3). The silylenium ion, if formed, probably abstracted fluorine from the anion to form fluorotris(2-propylthio)silane.

Conductance. The ^1H NMR spectra do not distinguish covalent, ion-paired, and free ionic forms of the perchlorate. One way of doing so is by conductance. We carried out these experiments in the same solvent (CH_2Cl_2) as for the NMR work. Figure 2 depicts a plot of specific conductance vs amount of added trityl perchlorate, a species well-known to be ionic under these conditions (no silane present). The specific conductance increases monotonically to about 120 μmho cm^{-1} for the concentration range illustrated. An extension of this experiment to the silyl perchlorate was carried out in the form of a titration, as shown in Figure 3 for tris(2-propylthio)silyl perchlorate. A solution of tris(2-propylthio)silane was prepared in CH_2Cl_2, and aliquots of trityl perchlorate were added, with specific conductance measured after each addition. Reaction occurred immediately between the two materials to form the silyl perchlorate. If this species were covalent, negligible conductance should be observed, since neither covalent silyl perchlorate nor triphenylmethane should conduct. Contrary to this scenario, a very large conductance was observed (Figure 3). After 1 equiv of trityl perchlorate is used, additional conductance comes from trityl rather than from tris(2-propylthio)silyl. Indeed, a slight inflection is observed at this point, but the similarity in slope indicates a similarity in specific conductances. The equivalent conductance (Λ) of trityl perchlorate was measured to be 43.5 mho cm^2 equiv^{-1} at about 1 mM and that of tris(2-propylthio)silyl 33.4 at the same concentration. Thus, the ionic nature of the silyl cation is very similar to that of trityl under these conditions. The specific conductance L (mho cm^{-1}) is converted to equivalent conductance Λ according to the rela-

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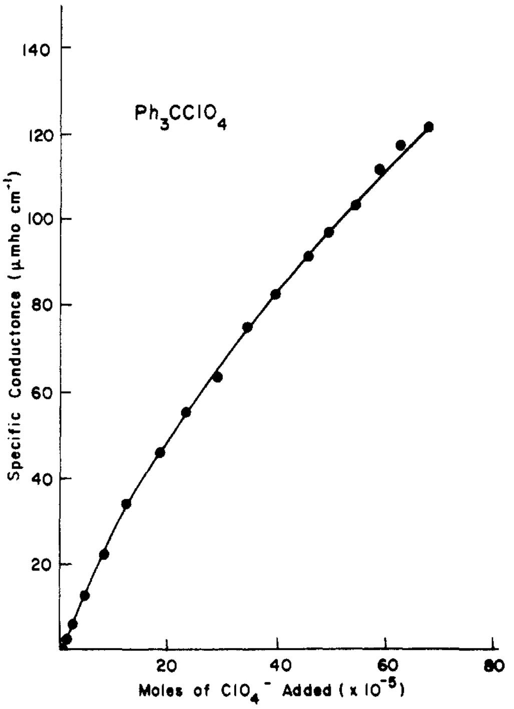


Figure 2. Plot of specific conductance vs the amount of trityl perchlorate added to CH_2Cl_2.

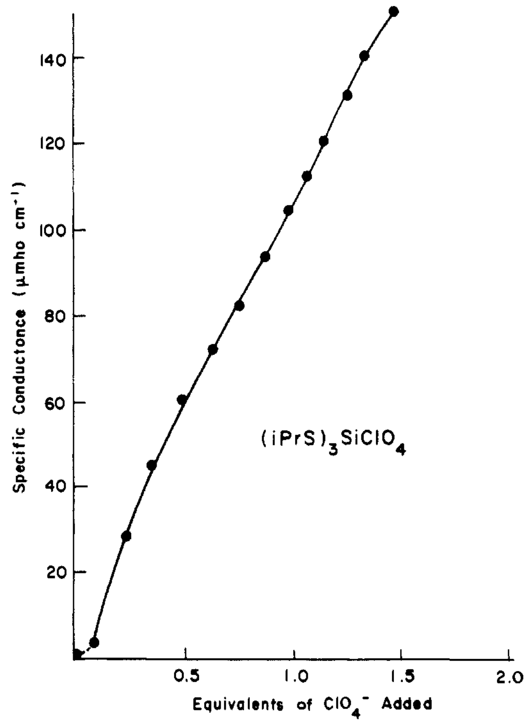


Figure 3. Plot of specific conductance as trityl perchlorate is added to a solution of tris(2-propylthio)silane in CH_2Cl_2.

tionship $\Lambda = 1000L/M$, in which M is the concentration in equiv L^{-1}. Similar observations were made with tris(methylthio)silyl perchlorate, although some of the conductance may derive from the sulfonium ion.

If a hydrolysis reaction occurred (eq 4), the perchlorate would be converted to the silanol, with perchloric acid as a byproduct.

$$R_3Si\text{-}OClO_4 + H_2O \rightarrow R_3Si\text{-}OH + HOClO_3 \qquad (4)$$

We can eliminate this possibility by two observations. First, neither the ^1H nor the ^{13}C (vide infra) NMR spectra provided evidence for the presence of the silanol. Resonances expected from model systems were not observed. Second, and more important, *perchlorate acid has a negligible conductance in CH_2Cl_2*. In a control experiment, we added $HClO_4$ (70% aqueous solution) to CH_2Cl_2 under analogous conditions and measured Λ to be 0.01 mho cm^2 equiv^{-1}. Apparently, $HClO_4$ is predominantly covalent or ion paired in CH_2Cl_2. Thus, not more than 0.03% of the observed conductance of tris(2-propylthio)silyl perchlorate can be due to hydrolysis and conductance of $HClO_4$. A covalent species therefore is clearly eliminated at these concentrations.

Table I. Molecular Weights in Sulfolane

solute	no. of runs	no. of particles (ν)	MW calcd	MW exptl	diff, %
Ph_3CH	1	1	244.3	232	+5.0
Ph_3CClO_4	1	2	342.8	325	−5.2
Ph_3CClO_4[a]	1	2	342.8	367	+7.1
$(Me_2CHS)_3SiClO_4$[a]	3	2 (ionic)	353.0	377	+6.8
$(Me_2CHS)_3SiClO_4$[a]	3	1 (covalent)	353.0	188	−46.7
$(Me_2CHS)_3SiClO_4$[a]	3	3 (dimer)	706.0	565	−20.0
sulfonium **6**[a]	3	2	597.3	411	−31.2
complex **8**[a]	3	2	473.2	506	+6.9

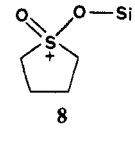
[a] Determined in the presence of an equimolar amount of triphenylmethane.

Product Recovery. In order to ensure that the entire structural integrity of the molecule had been retained, we carried out a product recovery experiment. Although lithium aluminum hydride apparently caused decomposition (the sulfur–silicon bonds are reactive), we found that diisobutylaluminum hydride (DIBAL-H) reacted smoothly at −78 °C to regenerate tris(2-propylthio)silane. This material was isolated from the reaction mixture by distillation. (CAUTION: explosion of the perchlorate-containing residue may occur.) No silicon products other than the silane were observed.

Molecular Weight. Determination of molecular weight provides an independent proof of the ionic, monomeric nature of the perchlorate. We chose freezing point depression in sulfolane as the method for determination of molecular weight, because sulfolane is a nonhydroxylic, dipolar solvent with an extremely large cryoscopic constant. The molecular weight is obtained from the expression $m = \Delta T_f/\nu K_f$, in which m is the molality (whence the molecular weight), ΔT_f is the difference in freezing point between pure solvent and solvent with solute, ν is the number of particles of which the solute is composed, and K is the molal freezing point depression constant (65–66 deg m^{-1} for sulfolane). The procedure is given in the Experimental Section, with details recorded elsewhere.[24]

Preliminary measurements were carried out on triphenylmethane, trityl perchlorate, and a mixture of these two solutes and were quite satisfactory. As seen from Table I, errors were 5–7%. Under the assumption of two particles, for the ionic form, tris(2-propylthio)silyl perchlorate was found to have a molecular weight within 7% of the calculated value. These measurements were made necessarily in the presence of triphenylmethane. The molecular weight of trityl perchlorate in the presence of an equimolar amount of triphenylmethane also was 7% high. Although this error may be statistical, it is also possible that the assumed additivity of effects is not quite valid, that is, the independent effect of each solute is not quite the same when both are present. Under any circumstance, the 7% error is quite convincing that the species is ionic and two particles. Table I contains calculations for several alternative representations. If the one particle, covalent form is assumed, the observed molecular weight is 47% off. If the three particle dimer is assumed (7), the error is 20%, and if the sulfonium ion **6** is assumed, the error is 31%.

The only other species consistent with the molecular weight measurement is the solvent complex **8**, which also possesses two particles and gives a comparable error of 7%. No new peaks were



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[24] Schulz, W. J., Jr. Ph.D. Dissertation, Northwestern University, 1983.

Table II. Carbon-13 Chemical Shifts[a]

compd	δ(CH)	δ(CH$_3$)	Δδ(CH)[b]	Δδ(CH$_3$)[b]
$(Me_2CH)_2S$	33.70 33.37[c]	23.8		
$(Me_2CH)_2S^+MeI^-$	44.91	18.58	11.21	−5.26
$(Me_2CH)_2S^+HFSO_3^-$	42.43[c]	18.66[c]	9.06	−5.18
$(Me_2CHS)_3SiH$	36.52	27.08		
$(Me_2CHS)_3SiClO_4$	37.46	27.08	0.94	0.00

[a] In CH_2Cl_2. [b] δ(ionic) − δ(neutral). [c] Neat samples.

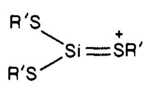
observed in the ^1H NMR spectrum for complexed solvent. Moreover, sulfolane's low basicity is well-known ($pK_B = -12.88$); it is not even protonated by concentrated sulfuric acid ($H_o = -10.60$).

The ability of sulfolane to form a complex was tested by making a solution of the silyl perchlorate in CD_2Cl_2 and adding an equivalent of sulfolane. The ^1H resonances of sulfolane under these conditions were identical with those of free sulfolane, indicating no interaction of the type depicted in **8**.

The molecular weight experiments were carried out on solutions with a concentration of 0.033 M silyl perchlorate, considerably more dilute than the NMR experiments. To ensure that hydrolysis was not important, the amount of water in the sulfolane was measured by the Karl Fischer method and found to be 0.00105 M or only 3% compared with solute. This small amount could have no palpable effect on the molecular weight measurements.

The molecular weight data clearly eliminate species with one or three particles. Thus, the model of a dynamic dimer, in equilibrium with the monomer to explain the single isopropyl ^1H resonances is not tenable. The molecular weight data are in clear accord with the conductance results in rejecting the covalent form in these concentration ranges.

Carbon-13 Spectra. In addition to confirming the ^1H observation of a single species, the ^{13}C NMR spectra can provide some indication of the location of positive charge within the silyl cation. If there is comparable 2p–3p overlap, the species may more properly be written as a sulfonium ion **9**, by analogy with 2p–2p stabilized carbenium ions, which are best written in the oxonium ion form **1**. For comparison, sulfonium ions were prepared by both protonation and methylation of diisopropyl sulfide. The ^{13}C results are given in Table II. The normal effect of converting the sulfur from neutral to positive state is a downfield shift of about 10 ppm for the methinyl carbon of isopropyl and an upfield shift of about 5 ppm for the methyl carbon. In contrast, conversion of tris(2-propylthio)silane to the silyl perchlorate results in a downfield shift of about 1 ppm for the methyl carbon and no shift for the methyl carbon. These data support the major contribution from the form with positive charge on silicon rather than sulfur. Even if the 1 ppm shift is tripled to allow for the effect of three isopropylthio groups, the resulting 3 ppm shift still admits a sulfonium ion contribution of only about one-third.



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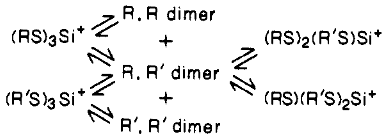
Crossover Experiments. As an additional way to eliminate the possibility that the observed ionic species is the dimer **7** in dynamic equilibrium with the monomeric silylenium ion, we carried out a crossover experiment. If two silylenium ions carrying different substituents on sulfur are generated in solution, dimer formation would result in scrambling of substituents, Scheme I. The two monomers can form three different dimers. Of these, the mixed dimer can break the opposite bonds to those originally formed, to give the mixed monomers. Thus, a crossover experiment actually tests two hypotheses. (1) If the predominant species in solution is dimeric, rapid equilibration with monomer will lead to spectra from all three dimers in Scheme I. (2) If the predominant species in solution is monomeric, equilibration with dimer will lead to a mixture of four monomers.

Separate samples were prepared of tris(2-propylthio)silyl perchlorate and of tris(ethylthio)silyl perchlorate. The ^1H spectra of the separate samples in CD_2Cl_2 showed that each system consisted primarily of the respective desired silyl salt. Each solution was appropriately conducting. The two samples were mixed. The ^1H spectrum of the mixed samples contained only resonances identical with those of the separate species, and the conductance of the mixed sample was unchanged. Consequently, it appears that there is no exchange through a dimer and hence no dynamic process.

Scheme I



Other Spectroscopic Measurements. All the above measurements were made on fresh solutions. After several hours, the solution turned to a highly viscous gel. Thus, no long-term averaging experiments were possible, for example to observe a ^{29}Si resonance. Whereas the starting material, tris(2-propylthio)silane, gave a sharp ^{29}Si signal 0.96 ppm downfield of Me_4Si, no signal was observed after treatment with trityl perchlorate for conversion to the silylenium ion. After 16–40 h, a signal associated with the gel developed at about δ 18. The likelihood of obtaining ^{29}Si signals of the *free* silyl cations is poor, because they are available only in dilute solution (vide infra). We have applied several polarization transfer experiments to highly concentrated samples (up to 1.0 M) of tris(ethylthio)silyl perchlorate and obtained broad signals in the regions δ 23–30, presumably from associated materials.

The infrared spectrum of tris(2-propylthio)silyl perchlorate in CH_2Cl_2 contained bands associated with tetrahedral perchlorate at 1095 and 625 cm^{-1}, as did trityl perchlorate. The spectrum, however, was not clean, and other bands were present at 1240 and 1030 cm^{-1}.

The solutions of the silyl perchlorate were a characteristic light to deep yellow, depending on the concentration. At about 10^{-5} M, tris(2-propylthio)silyl perchlorate showed a λ_{max} at 352 nm. Trityl phosphate gave a characteristic pair of maxima at 410 and 435 nm.

No ESR spectrum was observed for a 10^{-2} M solution of tris(2-propylthio)silyl perchlorate in CH_2Cl_2, so the concentration of radicals must be less than about 10^{-8} M. Thus, the observed material is not a radical pair or a cation radical.

Summary. The species produced by treatment of tris(2-propylthio)silane with trityl perchlorate gives all indications of being the monomeric, trivalent tris(2-propylthio)silyl perchlorate. The four main competing structures are eliminated in the following fashion. (1) The sulfonium ion **6** is in disagreement with the ^1H and ^{13}C spectra (one type of isopropyl, absence of a SiH resonance) and the molecular weight (31% off). (2) The dimer **7** is in disagreement with the ^1H and ^{13}C spectra (one type of isopropyl), the molecular weight (20% off), and the crossover experiments (no crossover). (3) The covalent representation is in disagreement with the conducting nature of the solution and the molecular weight (47% off). (4) The complex with solvent (**8**) is in disagreement with the observation that the sulfolane resonances are identical in the presence or absence of the silyl perchlorate in CH_2Cl_2.

Stabilization by π Polarization

^1H Spectra. Preparation of the triphenylsilyl cation has been a long-standing problem in silicon chemistry.[15] Our initial efforts with this material[25] in fact simply assumed, essentially for historical reasons, that it was covalent in its interaction with perchlorate. Because of our success with the sulfur substrate, we reexamined the situation with triphenylsilyl,[19] which we call *sityl*, and report herein those results.

The perchlorate may be prepared free of halogen by the Corey reaction of eq 2 (R = Ph). Reaction of triphenylsilane with trityl

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[25] Lambert, J. B., Sun, H.-n. *J. Am. Chem. Soc.* **1976**, *98*, 5611–5615.

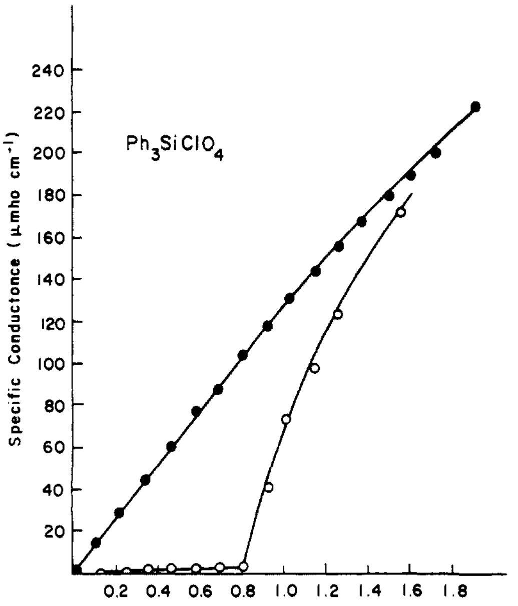


Figure 4. Plot of specific conductance as trityl perchlorate added to a solution of triphenylsilane in CH_2Cl_2 (○) or sulfolane (●).

perchlorate in CD_2Cl_2, either as a transition experiment or by equivalent addition, resulted in the complete loss of the SiH and trityl resonances and the appearance of new phenyl resonances, as well as that of CH in triphenylmethane. The simplicity of the spectrum indicated that no side reactions had occurred and that sityl perchlorate was formed cleanly. The addition of 1 equiv of acetonitrile to sityl perchlorate produced in CD_2Cl_2 had no effect on the sityl resonances, and the CH_3CN resonance was unchanged from that of CH_3CN in CD_2Cl_2. Further addition of up to 6 equiv of CH_3CN also had no effect.

Conductance. Conductance titrations were carried out as for tris(2-propylthio)silane above. Figure 4 shows the results in CH_2Cl_2 and in sulfolane. Studies also were carried out in acetonitrile. In CH_2Cl_2, there is very little conductance until the amount of trityl perchlorate exceeds 1 equiv, at which point trityl conductance is evident. The equivalent conductance (Λ) of sityl perchlorate is 1.13 mho cm^2 equiv^{-1}, a value that is considerably larger than the value expected if all the sityl perchlorate had hydrolyzed to silanol and perchloric acid (0.01, or 1% of the observed sityl conductance). Consequently, the material does have significant conductance, but only about 3% that of trityl or tris(2-propylthio)silyl perchlorates.

If sityl perchlorate exists as an ion pair in CH_2Cl_2, use of a more highly ionizing solvent may result in conversion to free ions. Therefore, we also examined the reaction of eq 2 in sulfolane and acetonitrile. Sulfolane was dried to the millimolar level, and acetonitrile to below 0.22 mM, as determined by Karl Fischer titration. Figure 4 shows that reaction of triphenylsilane with trityl perchlorate in sulfolane gives a highly conducting solution, Λ = 12.0 mho cm^2 equiv^{-1}. (For comparison of conductance between solvents, viscosity differences must be taken into consideration by multiplication of Λ by η; since sulfolane is some 10 times more viscous than CH_2Cl_2, sityl is actually more than 100 times more conducting in sulfolane than in CH_2Cl_2.) We observed that, unlike in CH_2Cl_2, perchloric acid is a conducting material in sulfolane and CH_3CN, in fact more so than sityl perchlorate. Addition of water to a solution of sityl perchlorate (formed from equivalent amounts of trityl perchlorate and triphenylsilane) did in fact increase the conductance, as the perchlorate was converted to perchloric acid. Prior hydrolysis would have resulted in little or no change.

A conductance titration also was carried out by stepwise addition of trityl perchlorate to a solution of triphenylsilane in CH_2Cl_2 containing 0.5 equiv of CH_3CN or pyridine. If sityl perchlorate forms a complex with the additive, the conductance should increase rapidly up to 0.5 equiv of added trityl perchlorate.

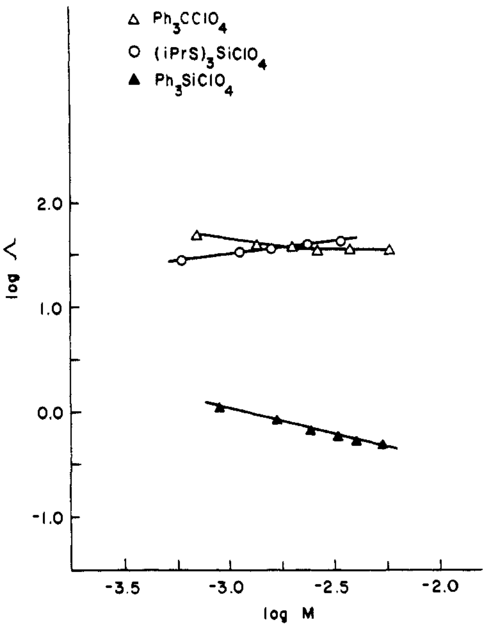
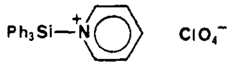


Figure 5. Logarithmic plot of equivalent conductance vs concentration in CH_2Cl_2 for trityl perchlorate (△), tris(2-propylthio)silyl perchlorate (○), and sityl perchlorate (▲).

As more trityl perchlorate is added, however, the conductance should nearly level off as the ion-paired species is formed with the addition of the second 0.5 equiv. When 0.5 equiv of CH_3CN was present, no such observation was made; the conductance increased slowly and monotonically, as in the absence of CH_3CN. No complex formed in this case. In contrast, in the presence of pyridine, the conductance increased dramatically up to 0.5 equiv, then decreased, and finally almost leveled off. This behavior is consistent with formation of a complex between pyridine and triphenylsilyl, **10**. The decrease in conductance after 0.5 equiv is probably caused by precipitation of **10** in CH_2Cl_2.



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Plots of log Λ vs log M are useful in determining the identity of the conducting species. Because the equivalent conductance already contains a division by concentration, such a plot should be level for a simple ionic species. Covalent and ion-paired species of course would show no conductance. Covalent or ion-paired species in equilibrium with a free ion, however, produce a distinctive pattern in which the slope is negative. As the concentration of the solute is reduced, the equilibrium moves further to the side of the free ion and hence shows increased conduction on a molar basis.

Figure 5 shows such a plot for trityl, tris(2-propylthio)silyl, and sityl perchlorate in CH_2Cl_2. Both trityl and tris(2-propylthio)silyl show high conductance with a nearly level slope, as expected for free ions. Sityl, on the other hand, shows low conduction with a pronounced negative slope. We reiterate that perchloric acid, formed by a possible hydrolysis reaction, under these conditions has a log of −2, well below the range of Figure 5. These observations are consistent with a model for sityl in which an ion pair or a covalent species is in equilibrium with a free ion in this concentration range.

Molecular Weight. Freezing point depression studies were carried out for sityl perchlorate, sityl triflate, and sityl azide in sulfolane. Table III gives these results. Sityl perchlorate is seen to be a free ion with two particles. The experiments does not distinguish between the free ion Ph_3Si^+ and a complex like **8** or **10**. Calculations with one particle (covalent or ion-paired form) or three particles (dimer, like **7**, with phenyl bridging) excluded these alternatives. In particular, the assumption of a covalent model gives a 50% error, in variance with a description of sityl

Table III. Molecular Weights in Sulfolane

solute	no. of particles (ν)	MW calcd	MW exptl	diff, %
Ph_3SiClO_4[a]	2 (ionic)	358.5	380	+6.0
Ph_3SiClO_4[a]	1 (covalent)	358.5	191	−46.7
Ph_3SiClO_4[a]	3 (dimer)	717.0	572	−20.2
Ph_3SiClO_4:sulfolane[a]	2 (complex)	478.5	511	+6.8
$Ph_3SiSO_3CF_3$	2 (ionic)	408	813	+99.3
$Ph_3SiSO_3CF_3$	1 (covalent)	408	407	−0.2
$Ph_3SiSO_3CF_3$	3 (dimer)	816	1220	+49.5
Ph_3SiN_3	2 (ionic)	301	560	+86.0
Ph_3SiN_3	1 (covalent)	301	280	−7.0
Ph_3SiN_3	3 (dimer)	602	840	+39.5

[a] Determined in the presence of an equimolar amount of triphenylmethane.

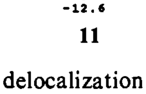
perchlorate as covalent in solution.

In contrast, both sityl triflate and sityl azide were found to give only one particle in solution. Thus, at these concentration ranges in sulfolane, these species are covalent or ion paired. The azide measurements were carried out at 0.099 M and the triflate measurements at 0.038 M. In agreement with this conclusion, we observed three ^{15}N resonances for sityl azide, whereas a free ion should have given only two.

A picture begins to emerge of sityl as a species that varies with concentration, solvent, and gegenion. In CH_2Cl_2, the perchlorate is covalent or ion paired at high concentrations, but free ions persist below 10^{-3} M. In sulfolane the perchlorate is clearly a free ion, but the azide and triflate are covalent or ion paired. The concentration dependence of the perchlorate in CH_2Cl_2 indicates that ^1H and ^{13}C NMR studies do not give straightforward conclusions, since they normally are carried out in more concentrated solutions.

To complement the molecular weight measurements, conductance experiments were carried out on the azide and triflate. The azide gave no observable conductance ($\Lambda \ll 0.1$). The triflate gave some conductance that was concentration dependent in CH_2Cl_2 and $ClCH_2CH_2Cl$, around 0.2 at the millimolar point. These results indicate that triflate interacts with sityl more strongly than does perchlorate, in agreement with the observations of Bassindale with trimethylsilyl.[26]

Carbon-13 NMR Spectroscopy. This method is particularly useful with sityl because it can probe the possibility of charge delocalization within the phenyl ring. Transmission of electronic effects has previously been studied in this manner for the triphenylsilyl anion.[21] These authors found that (triphenylmethyl)potassium produced a typical pattern for resonance delocalization (3, with sign reversed). One measure of delocalization is the difference between the chemical shift at a given phenyl position in neutral triphenylmethane subtracted from that in the anion, $\delta(Ph_3CK) - \delta(Ph_3CH)$. Structure 11 shows the result:



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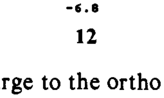

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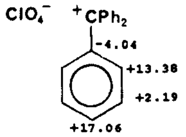
greater delocalization of negative charge to the ortho and para positions is shown by large negative numbers, and little movement of charge to the meta position is shown by the small value. In contrast, (triphenylsilyl)potassium gives the result in structure **12**. Here both the meta and para positions show some buildup of negative charge (but much less than in the carbon case **11**), and little charge is on the ortho position. (The ipso shifts do not directly reflect charge delocalization because of the standard α effect of silicon vs carbon; similarly, the ortho positions are not entirely reflective of charge because of β effects; thus, reliable electronic effects are best found at the meta and para positions, at which γ and δ effects are small.) This pattern closely follows that suggested by π polarization, i.e., **4** with the signs reversed.[27]

Table IV. Carbon-13 Chemical Shifts in CD_2Cl_2[a]

compd	δ_{ipso}	δ_{ortho}	δ_{meta}	δ_{para}
Ph_3CH	144.47	129.83	128.78	126.78
Ph_3CClO_4	140.43	143.21	130.97	143.84
Ph_3SiH	133.73	136.03	128.38	130.16
Ph_3SiClO_4	128.70	136.37	128.92	132.43

[a] In δ downfield from Me_4Si, as measured with the solvent as reference (δ 53.80); assignments were based on coupling patterns; the APT pulse sequence was used to assign the ipso carbon in some cases.

Similar experiments may be carried out for the cationic species under current study. The relevant data are given in Table IV. Structures **13** and **14** show the values for $\delta(Ph_3MClO_4) - \delta(Ph_3MH)$ in CD_2Cl_2, where M is C or Si.



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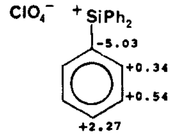

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The values for trityl (M = C) shown in **13** are characteristic of resonance delocalization (**3**) of positive charge to the ortho and para positions, the opposite charge to **11**. The values for sityl (M = Si) shown in **14** are characteristic of π polarization (**4**) with the opposite charge to **12**.

The positive charge at the para position in **14** is about 40% as large as the negative charge in **12**, as judged by the shift differences. Ion pairing at the concentrations required for ^{13}C spectra may substantially reduce the amount of charge polarization. Still, the value of 2.27 in **14** is substantially larger than observed for any other substituent. An electron-withdrawing group also may perturb charge by π polarization. Values of $\delta(Ph_3SiX) - \delta(Ph_3SiH)$ include 0.17 for X = OEt, 0.11 for $OSiPh_3$, 0.33 for OH, 1.11 for Cl, and 1.16 for F. Thus, the ^{13}C values are inconsistent with a covalent perchlorate, for example, since it is doubtful that $OClO_3$ could produce an effect twice as large as that for F.

The value of $\delta(Ph_3SiClO_4) - \delta(Ph_3SiH)$ is solvent dependent, changing from 2.27 in CD_2Cl_2 to 2.41 in sulfolane, as expected for opening of the ion pair.[27] We do not view these ^{13}C results as conclusive by themselves, but they are entirely consistent with the conductance and molecular weight experiments.

Chlorine-35 NMR Spectroscopy. G. A. Olah has suggested (private communication) that ^{35}Cl is a useful probe for determining the nature of silyl perchlorates in solution. Whereas the tetrahedral perchlorate ion should give a sharp ^{35}Cl resonance, a covalent or tightly ion-paired perchlorate should give a broad resonance. The normal quadrupolar interaction of ^{35}Cl is ineffective in the tetrahedral environment. We observed a sharp ^{35}Cl resonance (line width at half-height 18 Hz) for sityl perchlorate at 0.002 M concentration in sulfolane, in agreement with the ionic formulation of the material. As the concentration is increased, the peak broadens and disappears (220 Hz at 0.0042 M, 380 Hz at 0.0088 M), as expected for an equilibrium with a covalent or ion-paired species. The sharp ^{35}Cl resonance at 0.002 M cannot be due to a small amount of hydrolyzed material, or else it should have appeared as a low-intensity, sharp peak at all concentrations. Instead, the peak is entirely absent at much higher concentrations. The chemical shift of the ClO_4^- peak also is sharply concentration dependendent (δ 4.51, 0.13, −17.47 from lowest to highest concentrations; the reference is external aqueous ClO_4^-). Trityl perchlorate gives a sharp peak at δ 4.94 at normal NMR concentrations (~0.1–1 M) in CH_2Cl_2, in agreement with an ionic formulation. For these experiments, sulfolane was specially dried

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(26) Bassindale, A. R.; Stout, T. *J. Organomet. Chem.* **1982**, *238*, C41–C45. *Tetrahedron Lett.* **1985**, *26*, 3403–3406. *J. Chem. Soc. Perkin Trans. 2* **1986**, 221–225.

(27) More complete data are given in: McConnell, J. A. Ph.D. Dissertation, Northwestern University, 1986.

Table V. Carbon-13 Chemical Shifts of Ph_3SiClO_4

solvent	nucleophile	equiv	δ_{ortho}	δ_{meta}	δ_{para}
CH_2Cl_2	none		136.37	128.92	132.43
	CH_3CN	1	136.32	128.87	132.41
		3	136.30	128.87	132.41
	sulfolane	1	136.32	128.89	132.43
		3	136.19	128.81	132.35
	DMF[a]	1	136.11	129.30	132.71
	DMI[a]	1	136.22	129.70	132.78
	DMAP[a]	1	136.54	129.62	132.87
	NMI[a]	1	136.46	129.57	132.95
	pyridine	1	136.86	129.99	133.64
$ClCH_2CH_2Cl$	none		136.01	128.60	132.11
	CH_3CN	1	136.01	128.63	132.14
	pyridine	1	136.41	129.60	133.25

[a] DMF, dimethylformamide; DMI, 1,2-dimethylimidazole; DMAP, 4-(*N*,*N*-dimethylamino)pyridine; NMI, *N*-methylimidazole.

with CaH_2 to the 0.1 mM level.

The effect of added based on the ^{35}Cl NMR spectrum is very interesting. Addition of pyridine (1 equiv) to sityl perchlorate in CH_2Cl_2 at 0.219 M immediately brings out a sharp resonance at δ 4.14, in agreement with formation of the complex **10**. In contrast, addition of 1 equiv of acetonitrile does not result in such a peak. Observations in sulfolane are essentially identical. Thus, it appears that pyridine but not acetonitrile or sulfolane can form the complex, as a result of their considerable differences in nucleophilicity.

Carbon-13 NMR Studies of Complex Formation. Bassindale and Stout have obtained evidence for complexation formation in the case of Me_3SiX.[26] Their experiments were carried out in CD_2Cl_2 and CD_3CN with the assumption that these materials did not form complexes. Table V contains ^{13}C data for sityl perchlorate in CH_2Cl_2, sulfolane, and CH_3CN with various added nucleophiles. The addition of CH_3CN or sulfolane causes little or no change in the resonance positions of the phenyl carbons (<0.1 ppm), in agreement with absence of complex formation. The same result is obtained for the addition of up to 5 equiv of either material. Moreover, the ^{13}C positions for the nucleophiles themselves were essentially the same as for the free nucleophile.[28] In contrast, addition of a wide variety of stronger nucleophiles caused large changes in the phenyl resonances (0.4–1.2 ppm). These included dimethylformamide, 1,2-dimethylimidazole, 4-(*N*,*N*-dimethylamino)pyridine, *N*-methylimidazole, and pyridine. These materials appear to form complexes of the type **10**. The ^{13}C resonances of the nucleophiles reflect these events. The chemical shifts for the ring carbons are δ 147.16, 147.86, and 128.95 for the complex **10**, in comparison with 150.29, 136.11, and 124.03 for free pyridine in CH_2Cl_2.[28] When the second or third equivalents of the nucleophile were added, additional peaks did not appear in the ^{13}C spectrum, indicative of a rapid exchange on the NMR time scale between free and complexed nucleophile.

It is noteworthy that the slightly yellow solutions of sityl perchlorate instantly decolorized on the addition of all the above nucleophiles except sulfolane and CH_3CN. Apparently, complexes of the type **10** do not absorb in the visible, whereas the species formed in the presence of CH_2Cl_2, CH_3CN, or sulfolane shows such absorption. It is highly unlikely that a covalent form would absorb in the visible, but a free ion or ion-paired material is expected to.

These ^{13}C studies give strong evidence that CH_3CN and sulfolane do not form complexes with sityl perchlorate. These solvents have very low nucleophilicities for dipolar molecules. On the Gutmann scale,[28] CH_2Cl_2 and $ClCH_2CH_2Cl$ are very low (<0.1), CH_3CN is 14.1, sulfolane is 14.8, dimethylformamide is 26.6, and pyridine is 33.1. There is the formal possibility that even CH_2Cl_2 could form a complex via a bridged chlorine ($Ph_3Si–Cl^+–CH_2Cl$). Such a possibility is highly unlikely for 1,2-dichloroethane, so we have also studied sityl perchlorate in this solvent. The conductance of sityl perchlorate in $ClCH_2CH_2Cl$ paralleled that in CH_2Cl_2. The equivalent conductance was 0.28 mho cm^2 mol^{-1} at 1 mM, and a plot of log M vs log Λ exhibited a negative slope,[26] in agreement with the presence of ion pairs. The ^{13}C data in $ClCH_2CH_2Cl$ were quite analogous to those in CH_2Cl_2 (Table V). Again, addition of CH_3CN caused little change in the resonance position, whereas addition of pyridine caused large changes.[27] The absence of evidence that $ClCH_2CH_2Cl$ complexes with sityl supports the conclusion that CH_2Cl_2 does not form a bridged complex.

Nitrogen-15 NMR Spectroscopy. Although the ^{13}C shifts of the phenyl resonances of sityl perchlorate gave clear evidence for complex formation in the presence of good nucleophiles such as pyridine, the shifts were up to only about 1 ppm. The argument that poor nucleophiles such as sulfolane or acetonitrile do not form complexes is only as good as the negative observation of little or no such shift. A far more sensitive probe is provided by the ^{15}N nucleus in the case of acetonitrile. Quaternization of nitrogen is attended by very large shifts of the ^{15}N resonance. The paramagnetic shift is dominated by the $n \rightarrow \pi^*$ transition, which is eliminated on quaternization. Thus, the resonance position of CH_3CN in CD_2Cl_2 is at 244.2 ppm downfield of anhydrous liquid ammonia. Protonation leads to a resonance position of δ 141 and methylation of 132, in both cases a change of about 100 ppm.[29]

A solution of sityl perchlorate was prepared in the usual fashion in CD_2Cl_2, and 1 equiv of [^{15}N]acetonitrile was added. The chemical shift of CH_3CN in the presence of sityl perchlorate was found to be δ 245.7, essentially unchanged from that of free CH_3CN. This result is totally inconsistent with the possibility of complex formation. Thus, acetonitrile moves some 1% of the possible shift on quaternization, so that very little interaction between the lone pair on nitrogen and the silicon atom is admissible. The experiment was repeated with 6 equiv of CH_3CN in the presence of sityl perchlorate, and the observed chemical shift was δ 244.8. Thus, even an excess of CH_3CN does not bring about complexation. The experiment with 1 equiv of CH_3CN was also carried out in $ClCH_2CH_2Cl$ with the same result: CH_3CN resonated at δ 246.1.

To ensure that the observations were not some failure to bring about complexation under any circumstance, we carried out the same set of experiments with added pyridine. Free [^{15}N]pyridine resonates at δ 314.0 in CD_2Cl_2. Protonation leads to a position of δ 204.8 and methylation to 200.1, shifts of over 100 ppm.[29] Addition of 1 equiv of pyridine to sityl perchlorate in CH_2Cl_2 led to an ^{15}N shift of δ 216.8; in $ClCH_2CH_2Cl$ the position was 232.8. Thus, very clearly, pyridine forms a full complex (**10**) with sityl perchlorate that can be documented by ^{15}N NMR spectroscopy. Such structures have been isolated and characterized by X-ray diffraction.[30]

These results indicate that CH_3CN does not form a complex with sityl perchlorate in CD_2Cl_2 or $ClCH_2CH_2Cl$, whereas pyridine does. They are in accord with the ^{13}C results.

Other Spectroscopic Measurements. Silicon-29 experiments using a variety of spin polarization procedures led only to negative results. Silicon-29 has low sensitivity, low natural abundance, and long relaxation times. At high concentrations, at which previous evidence had indicated formation of a covalent or ion-paired structure, a weak resonance was observed for sityl perchlorate at δ 2.00 in CH_2Cl_2. This resonance moved to δ 7.27 on addition of pyridine but was unchanged on addition of CH_3CN. In sulfolane, a weak resonance was observed at δ 3.13, which moved to 5.94 on addition of pyridine. These resonance positions are not consistent with the expectations based on the models of carbenium ions.[18] The associated species (covalent or ion paired) must give rise to the signals at δ 2–3. These signals disappeared on slight dilution, so that unfortunately no observations could be made at the concentration used for molecular weight and conductance measurements (<0.03 M). Observation of signals may

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[28] Gutmann, V. CHEMTECH **1977**, *7*, 255–263.

[29] Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley-Interscience: New York, 1979; pp 67, 79, 80.

[30] Hansen, K.; Zengerly, T.; Pickel, P.; Klebe, G. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 725–726.

be further hampered by the dynamic exchange of free and associate sityl perchlorate with vastly different chemical shifts, which may broaden signals at certain concentration ranges. Thus, ^{29}Si does not provide assistance. Moreover, the resonance position of a tightly ion-paired species is not known, so that the signal at δ 3 cannot be firmly assigned as being from a covalent or an ion-paired species.

Although infrared spectroscopy can characterize a free, tetrahedral perchlorate ion, it is not useful in distinguishing between covalent and ion-paired forms. A study by Goel and Prasad[31] on $(Ph_3Sb)_2(ClO_4)_2$ in CH_2Cl_2 found similar conductance to sityl perchlorate and ambiguous infrared bands, interpreted as either from covalent or ion-paired materials. For trityl perchlorate in CH_2Cl_2, we observed bands at 1250, 1100, and 620 cm^{-1}, in sulfolane at 1230, 1070, and 620 cm^{-1}. For sityl perchlorate in CH_2Cl_2 we observed bands at 1235, 1110–1030, and 620 cm^{-1}, in sulfolane at 1250, 1050, and 620 cm^{-1}. Similar species are indicated for both compounds. The expectations from the solid state[32] are 1110 and 626 cm^{-1} for the ionic (T_d) form and 1122, 1040, 632, and 616 cm^{-1} for the covalent (C_{3v}) form. Although our results are consistent with an ionic form, they do not unambiguously eliminate ion pairs or covalency.

Sityl perchlorate is light yellow in all noncoordinating solvents. Upon addition of a strong nucleophile such as pyridine, this color dissipates as the complex **10** is formed. In CD_2Cl_2, maxima were observed at 360, 405, 433, and 560, tailing to 780 nm. In CH_3CN, maxima were at 340, 410, and 430, tailing to 540 nm. In sulfolane, maxima were at 340 and 390, tailing to 640 nm. The visible absorptions are not expected for covalent materials but may be observed for free ions or ion pairs. Thus, the UV/vis spectra are consistent with ionic formulations but are not clear-cut.

Summary. Reaction of triphenylsilane with trityl perchlorate forms a single species in several nonnucleophilic solvents, according to the ^{1}H and ^{13}C spectra. Molecular weight measurements in sulfolane indicate very clearly that sityl perchlorate at 0.02–0.03 M is composed of two particles. Covalent or ion-paired forms are eliminated under these conditions. In contrast, sityl azide and sityl triflate produce only one particle in sulfolane, either the covalent or ion-paired species. Sityl perchlorate is highly conducting in sulfolane. In CH_2Cl_2 and $ClCH_2CH_2Cl$ the conductance is very low but the profile of equivalent conductance vs concentration is indicative of ion pairs in equilibrium with free ions. The ^{13}C resonance positions of the phenyl carbons do not agree with a mechanism of resonance delocalization but are consistent with movement of charge by π polarization. Such a mechanism is expected for phenyl attached to a charged center such as a sityl cation, ion pair, or complex with sovlent but is inconsistent with a covalent structure. The ^{35}Cl resonance is sharp at low concentrations in sulfolane, in accord with the ionic structure, but disappears at higher concentrations. Also, at high concentrations the ^{29}Si resonance occurs near δ 3. These observations are consistent with an equilibrium between a free ion and a covalent or ion-paired species.

All the evidence may be explained by the presence of free ions in dilute sulfolane and an equilibrium among ion-paired, freely ionic, and possibly covalent species in CH_2Cl_2, in $ClCH_2CH_2Cl$, and in concentrated sulfolane. The question as to whether the ionic species is a trivalent silylenium ion or a tetravalent complex with solvent is answered by other experiments. Addition of 1 equiv of CH_3CN or sulfolane to sityl perchlorate in CH_2Cl_2 results in ^{13}C and ^{15}N resonance positions that are characteristic of free CH_3CN and sulfolane: sityl does not complex with these materials. In contrast, similar experiments with pyridine and other strong nucleophiles give clear evidence for complex formation (**10**). Conductance experiments corroborate these conclusions. Thus, we may conclude that sityl does not form complexes with the solvents of low nucleophilicity with which we are dealing, $ClCH_2CH_2Cl$, CH_2Cl_2, CH_3CN, and sulfolane, so that the ionic species demonstrated by the conductance and molecular weight experiments must be the silylenium ion. This is not to say that these solvents do not interact with the sityl cation. Polar solvents interact with any ionic solute, whether it be sodium or sityl cation. Our evidence, however, indicates that the interactions are nonspecific.

Experimental Section

Conductance experiments were peformed with a cell of homemade design with Pt electrodes. Conductance was measured with an Industrial Instruments conductivity bridge, Model RC16. Water content was determined for solvents just before usage by the Karl Fischer titration method with a Beckman Aquameter, Model KF4B. Elemental analyses were carried out by Micro-Tech Laboratories, Inc., Skokie, IL. Proton NMR spectra were obtained at 90 MHz on a Varian EM390 spectrometer. The ^{13}C and ^{15}N spectra were obtained at 67.8 and 27.28 MHz, respectively, on a JEOL FX270 spectrometer. The ^{29}Si and ^{35}Cl measurements and some ^{1}H and ^{13}C measurements were carried out on a Varian XLR-400 spectrometer. The ^{1}H, ^{13}C, and ^{29}Si chemical shifts (δ) are reported in parts per million (ppm) downfield from Me_4Si (δ = 0.00 ppm). The ^{15}N chemical shifts are reported in ppm downfield from anhydrous liquid ammonia at 25 °C and ^{35}Cl from external aqueous ClO_4^-. Infrared spectra were obtained on a Perkin-Elmer 283 instrument. Ultraviolet-visible spectra were obtained on a Perkin-Elmer 330 spectrometer. All liquid transfers were made with syringe techniques under N_2 or Ar.

Tris(alkylthio)silanes[22] were synthesized as described by Wolinski et al. through the addition of thiols to trichlorosilane. Trichlorosilane (44.7 g, 0.33 mol) was dissolved in 600 mL of dry benzene, and the system was cooled to ca. 5 °C under N_2. Pyridine (79.1 g, 1.0 mol) was then added dropwise with vigorous stirring. The addition of the alkanethiol (1.0 mol) was then made over a 1-h period, while the temperature of the system was maintained at ca. 5 °C. The system was stirred for an additional 1 h in the ice bath and then was allowed to warm slowly to room temperature and to stir overnight. The solid pyridinium hydrochloride was filtered in a Büchner funnel and washed well with dry benzene. The benzene fractions were combined, and the solvent was removed by distillation at atmospheric pressure. The nonvolatile products were then distilled under high vacuum and stored in a desiccator. *CAUTION*: These compounds are very unpleasant, they may have a toxic effect, and they can cause severe headaches. They should be handled carefully and used with adequate ventilation.

Tris(methylthio)silane: yield 19.7 g (35%); bp 59–61 °C (0.9 mmHg) [lit.[22] bp 66.5–69 °C (1.5 mmHg)]. Anal. Calcd for $C_3H_{10}S_3Si$: C, 21.15; H, 5.92; S, 56.45; Si, 16.48. Found: C, 21.03; H, 5.92; S, 56.69; Si, 16.48.

Tris(ethylthio)silane: yield 42.8 g (61%); bp 60–62 °C (0.07 mmHg) [lit.[22] bp 88 °C (1.0 mmHg)]. Anal. Calcd for $C_6H_{16}S_3Si$: C, 33.92; H, 7.59. Found: C, 33.39; H, 7.85.

Tris(2-propylthio)silane: yield 59.6 g (71%); bp 70–72 °C (0.5 mmHg) [lit.[22] bp 100 °C (2.5 mmHg)]. Anal. Calcd for $C_9H_{22}S_3Si$: C, 42.47; H, 8.71; S, 37.79; Si, 11.03. Found: C, 41.98; H, 8.56; S, 37.35; Si, 10.91.

Triphenylmethyl Perchlorate (Trityl Perchlorate).[33] Triphenylcarbinol (1.0 g, 0.003 84 mol) was reacted with 70% $HClO_4$ (1.25 mL, 0.015 mol) in 15 mL of acetic anhydride. The acid was added dropwise from an addition funnel to the alcohol, which had been dissolved in the anhydride by gentle warming with a heat gun. The mixture was stirred rapidly with a magnetic stirrer and cooled in ice water during the addition to maintain the reaction temperature between 10 and 20 °C. After addition was complete, the mixture was stirred for an additional 1 h in the ice bath to assure complete precipitation of the product. The stirring was ended, and the product was allowed to settle. The supernatant liquid was drawn off with a pipet, and the yellow solid was washed with 20-mL portions of anhydrous diethyl ether until the ether washing was colorless. After each washing, the ether was decanted. The remaining solid was then placed under high vacuum for 24 h to rid the solid of residual ether, acetic anhydride, and acetic acid. The product was stored in a light-tight desiccator at ca. −10 °C: 1.26 g (95%); NMR (CD_3COCD_3) δ 7.28 (s); IR (CH_2Cl_2) 1095 (s), 625 (m) (Cl–O) cm^{-1}.

Spectroscopic Measurements (CH_2Cl_2). Samples of the tris(alkylthio)silyl perchlorates that were used for spectroscopic measurements were all prepared in the same manner. The desired amount of trityl salt was weighted into a flask and covered with CH_2Cl_2 (or CD_2Cl_2), a septum cap was added, and the system was stirred under N_2. The flask was then immersed in a dry ice/2-propanol bath and cooled. The cold bath was removed, and the appropriate silane was syringed into the

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(32) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331–335.

(33) Dauben, H. J., Jr.; Honnen, L. R.; Harmon, K. M. *J. Org. Chem.* **1960**, *25*, 1442–1445.

slurry. As the sample warmed to room temperature, the reaction was complete. The samples were then manipulated in either a N_2 or Ar atmosphere or by syringe techniques.

Conductance Measurements (CH_2Cl_2). Approximately 0.1 g of the desired silane was syringed into a 200-mL, three-necked flask that had been dried, flushed with N_2 or Ar, and fitted with three rubber septa. The flask also contained a magnetic stirring bar. The silane was dissolved in 125 mL of freshly distilled CH_2Cl_2, and the system was placed under heavy N_2 (Ar) back-pressure. The tip of a buret containing CH_2Cl_2 solution of the desired trityl salt was pushed through one of the septa, and a pipet-type conductance cell was pushed through a second septum and into the silane solution. Addition of the trityl salt was performed in small aliquots, allowing 10 min after each addition for the reaction to take place. After this waiting period, some of the reaction mixture was drawn into the conductance cell, the measurement was taken, and the solution was forced back into the reaction vessel with a stream of N_2 or Ar. Measurements were continued until more than 1 equiv of the trityl salt had been added to the silane. Measured conductances were converted to absolute conductances by employing the cell constant, which had been determined by measuring the conductance of a standard KCl solution.

Conductance of $HClO_4$. Perchloric acid (70%) was added via microsyringe to a 100-mL flask that was equipped with a magnetic stirring bar and the pipet-type conductance cell and that contained approximately 50 mL of solvent. The solution was stirred for 10 min and then drawn into the conductance cell. A measurement was taken, and the solution was drained back into the flask.

Reduction of tris(2-propylthio)silyl perchlorate with diisobutylaluminum hydride (DIBAL-H) was performed under N_2 by cooling a CH_2Cl_2 solution of the silyl perchlorate to −78 °C in a dry ice/2-propanol bath, and adding 1 equiv of DIBAL-H (in diethyl ether) dropwise over a 15-min period. After being stirred at −78 °C for an additional 1 h, the colorless solution was allowed to warm slowly to room temperature. The solvent was removed under vacuum, and the residue was *carefully* distilled under high vacuum (*CAUTION*: explosion may occur). The boiling point, proton NMR spectrum, and IR spectrum of the material recovered were identical with those of a known sample of tris(2-propylthio)silane.

Spectroscopic Measurements (Sulfolane). Samples of the silyl perchlorates were produced in the same fashion as in CH_2Cl_2, except that the reactions were necessarily performed at ca. 30 °C rather than at −78 °C. The reaction temperatures were maintained by employing warm water baths.

Molecular Weight Determinations. A sample of freshly purified[34] sulfolane (vide infra) was syringed into a dry flask and weighed. This flask was placed under N_2 or Ar and immersed in a water bath at ca. 35 °C. Ice was added to the bath, and the temperature of the sulfolane was monitored and recorded every 30 s. Temperature readings were taken from a thermometer calibrated in 0.2 °C increments and certified by the National Bureau of Standards. From these data a cooling curve was made and the freezing point of the sulfolane was determined. Next, a weighed sample of the desired solute was added, and the experiment was repeated. In trials that required production of a silyl perchlorate, the freezing point depression was measured first on a weighed sample of trityl perchlorate, and then the silane was added and allowed to react. The freezing point of the sulfolane was then measured again to determine the depression caused by the silyl perchlorate and the triphenylmethane formed in the reaction. To determine the depression caused by the silyl perchlorate, the theoretical amount of Ph_3CH that should be formed in the reaction was calculated, and the freezing point depression that would be caused by this amount of material was determined and subtracted from the overall freezing point depression.

Sulfolane-*2,2,5,5-d*$_4$. Sulfolane (15.0 g, 0.125 mol) was added to 15 mL of D_2O (99.5% D) and 0.15 g of K_2CO_3. The system was heated to reflux under N_2 for 24 h, and the solution was frozen and lyophilized to remove the water. This procedure was repeated seven more times, and the four α positions in the sulfolane were shown to be 98% deuteriated at this point by ^1H NMR spectroscopy. The sulfolane-d_4 was then distilled from K_2CO_3 under vacuum: 12.8 g (85%); NMR ($CDCl_3$) δ 2.22 (br s).

Conductance Measurements (Sulfolane). Since the viscosity of sulfolane is very high, and the freezing point is ca. 28 °C, a conductance cell other than the pipet-type previously described was used. This cell was a cylindrical glass container with Pt electrodes, into which could be poured sulfolane solutions of the silyl perchlorates. The solutions were maintained in the liquid phase by employing a water bath at ca. 30 °C, and the cell constant was determined as previously described.

Dichloromethane and 1,2-Dichloroethane. The solvent was shaken with portions of concentrated H_2SO_4 until the acid was colorless. The solvent was then washed with H_2O, 5% $NaHCO_3$, and H_2O again. After having been predried over $CaCl_2$, the solvent was stirred over CaH_2 at ca. 30 °C for 2 h. The solvent was then distilled through a Vigreux column and collected in a flask containing 4A molecular sieves. The solvent was stored over 4A molecular sieves in a brown bottle out of direct sunlight.

Sulfolane was stirred over CaH_2 for 48 h and then distilled through a Vigreux column. The middle, constant-boiling fraction was collected in a flask containing 4A molecular sieves and stored in a brown bottle over 4A molecular sieves.

Acetonitrile was shaken with 4A molecular sieves and then stirred over CaH_2 until the evolution of H_2 ceased. The solvent was then fractionally distilled at very high reflux through a Vigreux column and collected in a flask containing 4A molecular sieves. This material was then slowly passed through a column (2 × 35 cm) containing 4A molecular sieves, collected, and stored in a brown bottle over 4A molecular sieves.[35]

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(34) Perrin, P. D.; Armarigo, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

(35) After submission of this paper, another paper appeared on the subject of triphenylsilyl perchlorate.[36] Their observation of covalency in the solid has no direct bearing on our studies in solution but is consistent with our observation of association with increased concentration. Our ^{35}Cl studies at the dilute concentrations of the conductance and cryoscopic experiments support the ionic formulation. The ^{35}Cl and ^{29}Si spectra of Prakash et al.[36] were at high concentrations (>0.1 M) and correspond to the associated form; we had made these same observations and described them herein.

(36) Prakash, G. K. S.; Keyaniyan, S.; Aniszfeld, R.; Heibiger, L.; Olah, G. A.; Stevens, R. C.; Choi, H.-K.; Ban, R. *J. Am. Chem. Soc.* **1987**, *109*, 5123-5126.

Intramolecular Radical Cyclization of Phenolic Enolates

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Abstract: Phenol rings bearing three- or four-carbon chains terminated by enolic or enolizable groups have been subjected to oxidation at alkaline pH using aqueous potassium ferricyanide or potassium hexachloroiridate. Substrates in which the enolizable system is an indandione, a 1,3-cyclohexanedione, a malononitrile, a barbituric acid, a pyrazolinedione, an oxindole, or a benzopyrandione undergo such oxidative cyclization in moderate to good yields when a new five-membered ring can be formed. Cyclization was not observed for several acyclic enolizable end groups. Dienone–phenol rearrangements of several spirocyclic dienones derived from these oxidations were carried out in CH_2Cl_2–CF_3SO_3H. A hypothesis regarding the possible course of the oxidation sequence is presented.

Formation of carbon rings by free-radical cyclizations is exhibiting a renaissance in modern organic synthetic methodology.[1] We have recently described a novel intramolecular radical cyclization whereby the phenolic indandione **1** reacts with K_3Fe-

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