

## Trimethylsilyl and Related Cations in Solution

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The silicon analogue of the *tert*-butyl cation, Me<sub>3</sub>Si<sup>+</sup> (the trimethylsilyl cation), has been produced as its perchlorate in high-polarity, low-nucleophilicity solvents such as sulfolane and dichloromethane. Generation is carried out by treatment of trimethylsilane with trityl perchlorate. Ionicity is demonstrated (and covalency excluded) in dilute sulfolane by conductance, cryoscopic molecular weight, and multinuclear NMR experiments. The level of hydrolysis from residual water is established by direct observation of the <sup>1</sup>H resonances of Me<sub>3</sub>SiClO<sub>4</sub> and of the hydrolysis product Me<sub>3</sub>SiOSiMe<sub>3</sub>. The water level is about 1 order of magnitude lower than that of substrate. Although the ions are free in dilute sulfolane, they are associated with the perchlorate anion in more concentrated solutions of sulfolane and at all concentrations in dichloromethane. Analogous experiments were carried out for the phenyldimethylsilyl (Me<sub>2</sub>PhSi<sup>+</sup>) and methyl-diphenylsilyl (MePh<sub>2</sub>Si<sup>+</sup>) cations. The phenyldimethylsilyl cation also was prepared with the tetraphenylborate anion, which cannot be covalently bound to the cation.

Although the *tert*-butyl cation (Me<sub>3</sub>C<sup>+</sup>) has been known for some time to be stable in solution, its silicon analogue (Me<sub>3</sub>Si<sup>+</sup>) has only recently been reported.<sup>2</sup> The gas-phase chemistry of the trimethylsilyl cation has been studied extensively,<sup>3</sup> and trimethylsilyl in solution as its triflate has become an important synthetic reagent. Development of the chemistry of trivalent organosilicon cations has been inhibited by difficulties in identifying proper anions, solvents, and procedures for generation. Resolution of these difficulties was recently reported for two examples, tris(alkylthio)silyl ((RS)<sub>3</sub>Si<sup>+</sup>) and triphenylsilyl or silyl (Ph<sub>3</sub>Si<sup>+</sup>).<sup>4</sup> As a result chemists have become more comfortable in suggesting silylenium (a term preferred to *silicenium*) ions as intermediates.<sup>5,6</sup>

Because of the important role of the trimethylsilyl cation as a reactive intermediate and potentially in synthesis, we have carried out studies to characterize it as a perchlorate under stable conditions. We report those experiments herein. Moreover, we address in detail the issue of hydrolysis, which is key to the demonstration of long-term stability of all silylenium ions.<sup>7</sup> Our control experiments show that hydrolysis has no significant effect under our conditions. We also report some parallel experiments on the related phenyldimethylsilyl (Me<sub>2</sub>PhSi<sup>+</sup>) and methyl-diphenylsilyl (MePh<sub>2</sub>Si<sup>+</sup>) cations. Finally, we report the successful use of tetraphenylborate as the anion with Me<sub>2</sub>PhSi<sup>+</sup>. This anion, in contrast to perchlorate, cannot be bound covalently.

### Preparation

Trimethylsilyl perchlorate was generated by the reaction of trimethylsilane with triphenylmethyl (trityl) perchlorate (eq 1) in rigorously dried, polar, nonnucleophilic solvents.<sup>2</sup>

$$\text{Me}_3\text{SiH} + \text{Ph}_3\text{C}^+\text{ClO}_4^- \rightarrow \text{Me}_3\text{Si}^+\text{ClO}_4^- + \text{Ph}_3\text{CH} \quad (1)$$

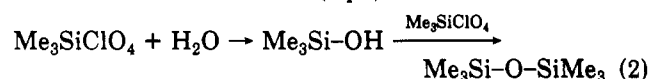
For experiments in dilute solutions all operations were carried out in closed, sealed vessels under nitrogen to ex-

clude additional moisture. In sulfolane (0.27 M), the doublet at  $\delta$  0.09 and the multiplet at  $\delta$  3.91 in the <sup>1</sup>H spectrum of the starting material were replaced cleanly by a singlet at  $\delta$  0.5 from Me<sub>3</sub>SiClO<sub>4</sub>, plus the triphenylmethane resonances. In the <sup>13</sup>C spectrum under the same conditions, the methyl resonance of Me<sub>3</sub>SiH at  $\delta$  -2.62 was replaced with the methyl resonance of Me<sub>3</sub>SiClO<sub>4</sub> at  $\delta$  -0.55. The infrared spectrum in dichloromethane contained medium-intensity peaks at 1245, 1030, and 620 cm<sup>-1</sup>. The light yellow solution in sulfolane exhibited UV maxima at 375 and 435 nm, tailing to 760 nm. Phenyldimethylsilyl and methyl-diphenyl perchlorates were prepared in an analogous fashion.

As an alternative anion, we examined tetraphenylborate (BPh<sub>4</sub><sup>-</sup>). Phenyldimethylsilyl tetraphenylborate was prepared by the reaction of the silane with trityl tetraphenylborate, which had been prepared by the procedure of Tilley and co-workers.<sup>8</sup> The starting trityl compound was not stable in either dichloromethane or sulfolane, so that experiments in these solvents and hence cryoscopic measurements were excluded. Although it is light- and air-sensitive,<sup>8</sup> trityl tetraphenylborate was sufficiently stable in acetonitrile to permit clean reaction with phenyldimethylsilane. Progress of the reaction was monitored by <sup>1</sup>H NMR spectroscopy, and the reaction involved simple loss of the resonances of starting material and replacement with the resonances of phenyldimethylsilyl tetraphenylborate. These solutions were stable at room temperature for about 24 h. Isolation of a solvent-free salt was hindered by the presence of the byproduct, triphenylmethane. Decomposition or polymerization occurred before purification could be carried out.

### Extent of Hydrolysis

Many of the important measurements on these ions are made in dilute solution, down to 0.01 M or lower. Therefore it is imperative to demonstrate that our conditions are sufficiently anhydrous to permit survival of the perchlorate under the conditions of observation. The solvents were dried rigorously in multiple stages, as described in the Experimental Section. The process of hydrolysis would convert the perchlorate first to the silanol and then to the disiloxane (eq 2). The resonance of the



(1) (a) Supported by the National Science Foundation (Grant CHE-8910841). (b) On leave from the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw.

(2) Lambert, J. B.; McConnell, J. A.; Schilf, W.; Schulz, W. J., Jr. *J. Chem. Soc., Chem. Commun.* 1988, 455-456.

(3) For example, see: Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* 1982, 104, 4329-4332.

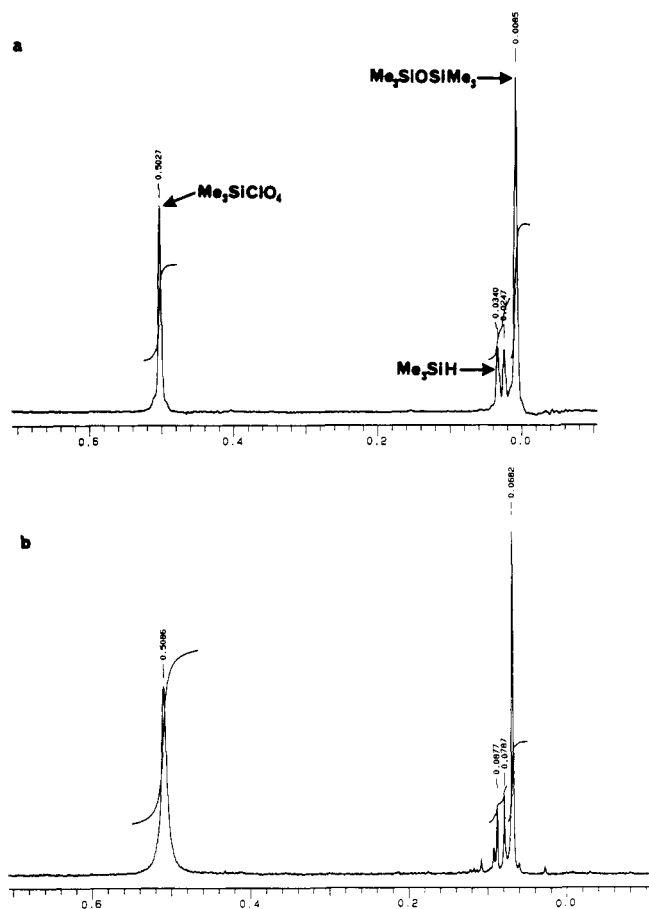
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**Figure 1.** (a)  $^1\text{H}$  spectrum of trimethylsilyl perchlorate at 0.007 M in sulfolane, showing resonances for  $\text{Me}_3\text{SiClO}_4$  ( $\delta$  0.503),  $\text{Me}_3\text{SiH}$  ( $\delta$  0.034 and 0.025), and  $\text{Me}_3\text{SiOSiMe}_3$  ( $\delta$  0.008). (b)  $^1\text{H}$  spectrum of trimethylsilyl perchlorate at 0.003 M in  $\text{CH}_2\text{Cl}_2$ , showing resonances for  $\text{Me}_3\text{SiClO}_4$  ( $\delta$  0.509),  $\text{Me}_3\text{SiH}$  ( $\delta$  0.088 and 0.079), and  $\text{Me}_3\text{SiOSiMe}_3$  ( $\delta$  0.068).

methyl protons of trimethylsilyl perchlorate at  $\delta$  0.5 can be followed to low concentrations, and the resonance of the hydrolysis product disiloxane at about  $\delta$  0.01 can be observed as it forms. That this resonance was from the disiloxane was confirmed by peak enhancement with authentic material. In all samples, the hydrolysis product did not increase with time, so that the samples are clearly protected from absorbing any moisture after formulation.

Figure 1a shows the  $^1\text{H}$  spectrum of a sample of trimethylsilyl perchlorate in sulfolane at a starting solute concentration of 0.007 M. Singlets are present for the unhydrolyzed perchlorate and for the disiloxane product of hydrolysis, as well as the small doublet at  $\delta$  0.03 from unreacted (excess) starting material. The absolute level of water may be calculated from the NMR intensities in the following manner.<sup>7</sup> For the general case, the initial level of  $\text{Me}_3\text{SiClO}_4$  is  $a$  (0.007 M for the example of Figure 1a) and the unknown level of water is  $b$ . Because one molecule of water converts two molecules of  $\text{Me}_3\text{SiClO}_4$  to one molecule of disiloxane (eq 2), the final concentration of disiloxane equals that of water originally present ( $b$ ) and the residual concentration of  $\text{Me}_3\text{SiClO}_4$  then is  $(a - 2b)$ , as in eq 3. Thus the molar ratio of residual perchlorate



to disiloxane is  $(a - 2b)/b$ . Because the disiloxane has twice the number of protons as the perchlorate, the ratio of the intensity of the  $\delta$  0.5 peak to that of the  $\delta$  0.01 peak then is  $(a - 2b)/2b$ . When  $a = 0.007$  M (Figure 1a), the

**Table I. Level of Water in Perchlorate Solutions**

solvent	solute conc, <sup>a</sup> M (a)	H <sub>2</sub> O conc, M (b)	peak ratio, <sup>b</sup> (a - 2b)/2b	peak ratio, obs
sulfolane	0.0070	0.0020	0.75	0.72
sulfolane	0.0080	0.0019	1.1	1.08
sulfolane	0.050	0.0034	6.3	6.25
$\text{CH}_2\text{Cl}_2$	0.0030	0.00044	2.3	2.4

<sup>a</sup> Starting concentration of  $\text{Me}_3\text{SiClO}_4$ . <sup>b</sup> Ratio of peaks from unhydrolyzed and hydrolyzed materials, calculated from  $a$  and  $b$  in the second and third columns.

observed intensity ratio is 0.72, so the level of water  $b$  then is 0.0020 M.

Table I shows the data for four such experiments. The water concentrations calculated for the three experiments in sulfolane are 0.0020, 0.0019, and 0.0034 M, for an average of 0.0024 M. The single experiment in dichloromethane (Figure 1b) indicates a water level of 0.00044 M. The fourth column of Table I gives the peak ratio as calculated from  $a$  and  $b$ . The last column is the observed ratio. The solutions for determining molecular weight and conductance were prepared in a similar fashion, so that the figures in Table I should represent an upper limit to hydrolysis for these experiments as well.

Previous measurements by the Karl Fischer method<sup>4</sup> indicated that water was present at the 0.001 M level in both sulfolane and dichloromethane. We are not certain that this procedure gives accurate results. Moreover, the level of water in freshly dried solvent may not be the same as the level during an operation such as a conductance titration. The values determined by  $^1\text{H}$  NMR spectroscopy are within a factor of 2 or 3 of the Karl Fischer values,<sup>4</sup> which therefore were approximately correct. The NMR values moreover correspond to the real conditions of an experiment.

In two recent papers,<sup>9,10</sup> Olah and co-workers have suggested that our solutions were partially or entirely hydrolyzed, that "The claimed water concentration of 0.001–0.003 M thus may be an inaccurate measurement of the actual water content of the sulfolane used" and that "the concentrations of solute 'silyl cation' and the water content of the solvent are at least comparable". We show herein that the "actual" water concentration in sulfolane is about 0.0024 M, within the range previously claimed. Moreover, contrary to the allegation that the concentrations of substrate and water are comparable, the water level is at most 10% of the substrate in a 0.05 M sulfolane solution or a 0.01 M dichloromethane solution. (The percentage hydrolysis is  $1002b/a$ , in which  $a$  and  $b$  are defined in eq 3.) Although use of proper drying procedures and anhydrous conditions, as was done, is critical to our conclusions, the question of hydrolysis is not relevant to the fundamental problem of the nature of these silyl perchlorates in solution.

### Ionicity from Conductance Measurements

The observation that triphenylsilyl perchlorate is covalent in the solid state<sup>9</sup> has no bearing on the situation in solution. A change in form from the solution to the solid state is quite common, e.g., trityl iodide. We have found<sup>4,11</sup> that silyl cations exist in equilibrium with an associated

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Table II. Conductance of Silyl Derivatives (0.01 M)

system	solvent	additive	molar conductance ( $\Lambda$ ), $\Omega \text{ cm}^2$ equiv <sup>-1</sup>	$\eta\Lambda^a$
Ph <sub>3</sub> CClO <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>		420	165
		CH <sub>3</sub> CN	2020	656
		sulfolane	130	1290
Ph <sub>3</sub> SiClO <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>		0.46	0.18
		CH <sub>3</sub> CN	690	224
		sulfolane	105	1040
PhMe <sub>2</sub> SiCl- O <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>		0.46	0.18
		CH <sub>3</sub> CN	836	272
Me <sub>3</sub> SiClO <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>		150	1480
		CH <sub>3</sub> CN	0.38	0.15
		sulfolane	932	303
Ph <sub>3</sub> CBPh <sub>4</sub>	CH <sub>3</sub> CN		104	1030
		CH <sub>3</sub> CN	1930	628
PhMe <sub>2</sub> SiB- Ph <sub>4</sub>	CH <sub>3</sub> CN		2120	689
		CH <sub>2</sub> Cl <sub>2</sub>	0.57	0.22
		CH <sub>3</sub> CN	660	214
Me <sub>3</sub> SiOTf	sulfolane		57	563
		CH <sub>2</sub> Cl <sub>2</sub>	0	0
		CH <sub>3</sub> CN	1.1	0.36
Me <sub>3</sub> SiN <sub>3</sub>	sulfolane		0.70	7.2
		CH <sub>2</sub> Cl <sub>2</sub>	0.74	0.29
		CH <sub>3</sub> CN	25.4	9.8
Me <sub>3</sub> SiClO <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN	71	28
		<i>N</i> -methylpyrrole	0.65	0.25
		pyridine	32	13
Ph <sub>3</sub> SiClO <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN	124	49
		<i>N</i> -methylpyrrole	0.52	0.21
		pyridine	25	9.8
PhMe <sub>2</sub> SiCl- O <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	<i>N</i> -methylpyrrole	100	39
		pyridine	0.57	0.22
		sulfolane	0.57	0.22

<sup>a</sup>The product of viscosity and molar conductance.

form, so that it is necessary to examine dilute solutions in order to obtain the ionic form. Direct observations can be made for dilute solutions by conductance, cryoscopy, and magnetic resonance spectroscopy of more receptive nuclei than <sup>29</sup>Si. We have utilized all three methods in order to assess the ionicity of these silyl perchlorates.

Ionicity was examined first through conductance titrations, whereby the conductance was measured as a function of concentration. Table II gives data extracted from these experiments arbitrarily at 0.01 M, for the perchlorates of trityl, of several silyl cations, of one triflate, and of one azide in several solvents, and of the tetraphenylborate of trityl and one silyl cation in acetonitrile. The majority of our experiments were carried out in dichloromethane, in which water is present at the upper limit of 0.00044 M (Table I). At 0.01 M substrate, no more than about 9% of the solute perchlorate has hydrolyzed (calculated as 1002*b/a* from Table I).

At 0.01 M, trimethylsilyl azide has no conductance, as expected for a covalent species. Trimethylsilyl perchlorate, trimethylsilyl triflate, triphenylsilyl perchlorate, and phenyldimethylsilyl perchlorate have relatively similar molar conductances in the vicinity of 0.5  $\Omega \text{ cm}^2 \text{ equiv}^{-1}$ . Trityl perchlorate and tris(2-propylthio)silyl perchlorate have conductances about 2 orders of magnitude higher.<sup>4</sup> These last materials clearly are ionic even in this poorly ionizing solvent at these concentrations. The range of behavior, from covalent trimethylsilyl azide to ion-paired trimethylsilyl perchlorate (and its congeners) to freely ionic tris(2-propylthio)silyl perchlorate shows that this method can characterize all types of species. The product of hydrolysis, HClO<sub>4</sub>, showed negligible conductance in dichloromethane (it is probably covalent), so that the small

levels of hydrolysis could not be contributing to these results.

Measurements also were made in sulfolane in the range 0.01–0.1 M. It should be kept in mind that values in sulfolane are artificially low because of its very high viscosity. For this reason, Table II contains the product of molar conductance and viscosity ( $\eta\Lambda$ ), which is a better figure for comparison between solvents. The conductance of trimethylsilyl azide, though nonzero in this solvent, still is very low, 0.70  $\Omega \text{ cm}^2 \text{ equiv}^{-1}$ . The triflate shows much higher molar conductance (57), and trimethylsilyl, triphenylsilyl, phenyldimethylsilyl, and triphenylmethyl perchlorates all show yet higher values, about 130 (Table II). Again, this range of observations shows that we are distinguishing levels of ionicity. Hydrolysis is higher in this solvent. According to the NMR measurements, up to 50% of a 0.01 M solution would be hydrolyzed. Therefore we also calculated conductance values at 0.05 M, at which less than 10% hydrolysis should occur, and all the results were parallel. These observations indicate that in sulfolane the silyl perchlorates are highly ionic, although we cannot say whether a maximum value has been reached or whether there is association at the higher concentrations. The ionicity is at least comparable to that of trityl perchlorate, which is widely accepted as an ionic species.

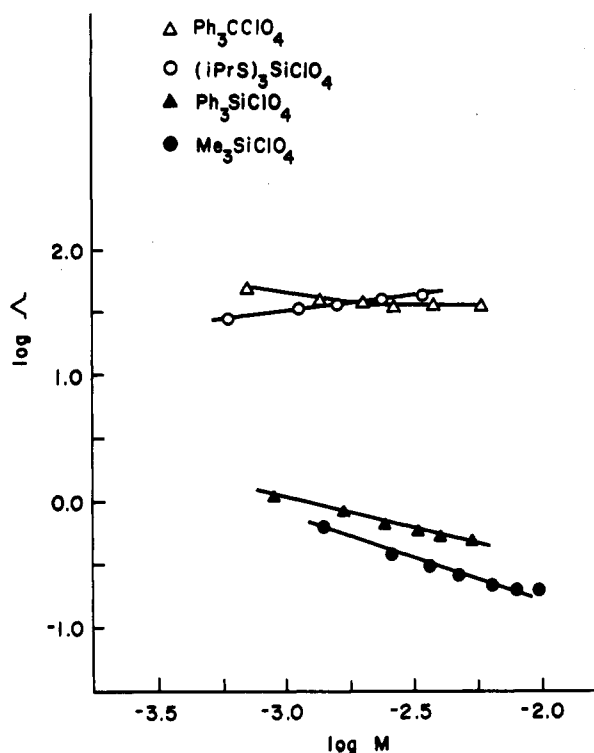
Measurements also were made in acetonitrile, and the situation was found to be similar to that in sulfolane. The molar conductances in acetonitrile in Table II are much higher than those in sulfolane, but this observation is an artifact of the differences in viscosity.

The tetraphenylborate of trityl was found not to be stable in sulfolane or dichloromethane, but conductances could be measured in acetonitrile. Trityl had about the same conductance in acetonitrile for its perchlorate and its tetraphenylborate. In contrast, the conductance of phenyldimethylsilyl tetraphenylborate was about 3 times higher than that of the perchlorate. This observation indicates that the silyl perchlorates may not be entirely free ions in sulfolane at these concentrations. In acetonitrile trimethylsilyl azide still is essentially nonconducting and trimethylsilyl triflate is substantially less conducting than trimethylsilyl perchlorate.

Logarithmic plots of molar conductance vs concentration are useful in determining the nature of ionic species.<sup>4</sup> A horizontal line is expected for free ions, and a line with negative slope for ion pairs (as the concentration decreases, the conductance decreases proportionately less, because ion pairs dissociate to form free ions). Such a plot for trimethylsilyl perchlorate in dichloromethane has a negative slope, indicative of ion pairs. Figure 2 shows this plot, along with those for related ions. The same plots for sulfolane were level, as expected for free ions.

#### Ionicity from Cryoscopic Measurements

Molecular weight measurements were carried out in dilute sulfolane (0.02–0.05 M).<sup>4</sup> According to the data obtained by NMR spectroscopy, the level of water in sulfolane is about 0.0024 M (Table I). Since each mole of water hydrolyzes 2 mol of substrate, this level corresponds to hydrolysis of a maximum of 9% (1002*b/a*) of the solute at 0.05 M or 22% at 0.02 M. The cryoscopic results are given in Table III for trimethylsilyl perchlorate and several related systems. The second column contains the theoretical monomeric molecular weight. Conversion of the melting point depression to an observed molecular weight requires the assignment of the number of particles  $\nu$ . If the perchlorate is covalent or ion paired, it exists as one particle ( $\nu = 1$ ). The third column of Table III gives the



**Figure 2.** Equivalent conductance of trimethylsilyl perchlorate vs concentration in  $\text{CH}_2\text{Cl}_2$  as a double logarithmic plot (filled circles). For comparison the same plots are given for triphenylsilyl perchlorate (filled triangles), tris(2-propylthio)silyl perchlorate (open circles), and trityl perchlorate (open triangles).

**Table III.** Cryoscopic Molecular Weights

molecule	MW	MW <sup>a</sup> $\nu = 1$	error, % $\nu = 1$	MW <sup>b</sup> $\nu = 2$	error, % $\nu = 2$
$\text{Me}_3\text{SiClO}_4$	173.0	84.9	-51	169.8	-1.8
$\text{PhMe}_2\text{SiClO}_4$	234.6	120.9	-49	241.8	+3.1
$\text{Me}_3\text{SiN}_3$	115.2	114.2	-0.1	228.4	+98
$\text{Ph}_3\text{SiN}_3$	301.4	299.2	-0.7	598.4	+99
$\text{Me}_3\text{SiOTf}$	222.3	220.0	-1.0	444.0	+100
$\text{Ph}_3\text{SiOTf}$	408.5	406.6	-0.5	813.2	+99

<sup>a</sup> Observed value if  $\text{R}_3\text{SiX}$  is one particle (covalent or ion paired).

<sup>b</sup> Observed value if  $\text{R}_3\text{SiX}$  is two particles (ionic).

observed molecular weights for this model, and the fourth column gives the percentage deviation of observed from calculated. If the perchlorate is ionic (as is the case for the silylenium ion structure), it exists as two particles ( $\nu = 2$ ). The fifth column of Table III gives the observed molecular weight for the ionic model, and the last column gives the percentage deviation of observed from calculated. The two perchlorates clearly agree with the ionic model, whereas the four azides and triflates just as clearly agree with the one-particle model.

The cryoscopic experiment involves fewer manipulations than the NMR experiments, so the levels of water may be lower here than those indicated in Table I. The likelihood of much lower levels of water is supported by the accuracy of the measured molecular weights (Table III). We find that trimethylsilyl perchlorate and phenyldimethylsilyl perchlorate exist as two particles in sulfolane at this concentration, with respective errors on the measured molecular weights of 1.8 and 3.1%. We have previously reported similar results<sup>4</sup> with tris(2-propylthio)silyl perchlorate (two-particle, ionic model, deviating 6.8% from the calculated value) and triphenylsilyl perchlorate (two-particle, ionic model, 6.0% from calculated). In all four cases the one-particle, covalent (or tight ion-paired) model gives half the calculated value (error about -50%) and

**Table IV.** Nuclear Magnetic Resonance Chemical Shifts of Silyl Perchlorates<sup>a</sup>

system	nucleus	conc, M	$\delta(\text{CH}_3)$	$\delta(\text{Ph})$	$\delta(\text{CH})^b$
$\text{MePh}_2\text{SiClO}_4$	$^1\text{H}$	0.27	1.026	7.61 <sup>c</sup>	5.58
				7.43 <sup>d</sup>	
		0.09	1.048	7.41 <sup>e</sup>	5.58
				7.61 <sup>c</sup>	
		0.03	1.121	7.43 <sup>d</sup>	5.58
				7.42 <sup>e</sup>	
	0.009	1.127	7.71 <sup>c</sup>	5.57	
			7.53 <sup>d</sup>		
	$^{13}\text{C}$	0.27	-3.71	128.97 <sup>f</sup>	56.74
				135.00 <sup>c</sup>	
		0.09	-3.71	129.73 <sup>d</sup>	56.62
				132.45 <sup>e</sup>	
0.03		-3.66	128.96 <sup>f</sup>	56.52	
			134.96 <sup>c</sup>		
0.01	-3.60	129.64 <sup>d</sup>	56.50		
		132.47 <sup>e</sup>			
$\text{PhMe}_2\text{SiClO}_4$	$^1\text{H}$	0.27	0.793	5.57	5.57
				0.796	
		0.09	0.800	5.56	5.56
				0.808	
		0.009	0.808	5.57	5.57
				0.808	
	$^{13}\text{C}$	0.27	0.494	5.57	5.57
				0.499	
		0.09	0.503	5.57	5.57
				0.503	
		0.007	0.503	5.57	5.57
				0.503	
0.27	-0.55	5.57	5.57		
		-0.53			
0.09	-0.53	5.57	5.57		
		-0.53			
0.03	-0.34	5.57	5.57		
		-0.34			
0.01	-0.3	5.57	5.57		
		-0.3			

<sup>a</sup> Measured in sulfolane ( $\delta$  2.08 for  $^1\text{H}$ ) containing 10%  $\text{CD}_2\text{Cl}_2$  ( $\delta$  54.48 for  $^{13}\text{C}$ ). <sup>b</sup> Methine proton or carbon of triphenylmethane. <sup>c</sup> Ortho proton or carbon. <sup>d</sup> Meta proton or carbon. <sup>e</sup> Para proton or carbon. <sup>f</sup> Ipso carbon.

consequently is excluded. The Olah covalent model<sup>9,10</sup> therefore again is not supported by the evidence. The azides and the triflates in Table III, on the other hand, give precise results in all four cases for one-particle structures. From these observations alone, one cannot determine whether the single particle is a covalent species or a tight ion pair.

Other models also may be considered. If two molecules of  $\text{R}_3\text{SiClO}_4$  form a bridged dimer, the result contains three particles (dicationic dimer and two perchlorates). For the case of trimethylsilyl perchlorate, the calculated dimer molecular weight is 346.0 and the observed value for this model is 253.8, a deviation of 27%. For phenyldimethylsilyl perchlorate, the calculated dimer molecular weight is 469.2 and the observed value for this model is 358.3, a deviation of 24%.

### Ionicity from NMR Measurements

The conductance experiments indicate that trimethylsilyl, phenyldimethylsilyl, and methyldiphenyl perchlorate are associated in dichloromethane and are freely ionic at low concentrations in sulfolane. The possibility of two forms suggests that nuclear magnetic resonance spectra could exhibit concentration-dependent chemical shifts. Consequently, we have examined  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{29}\text{Si}$  resonances over a range of concentrations in sulfolane. Table

IV shows the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts as a function of concentration. For methylphenylsilyl perchlorate the methyl protons and carbon show a decided shift with concentration, as do the phenyl protons. The  $^1\text{H}$  resonances for triphenylmethane remained unchanged. For trimethylsilyl perchlorate, also in Table IV, the  $^{13}\text{C}$  spectrum of the methyl carbons shows a decided change. Although we could go to below 0.005 M in the  $^1\text{H}$  spectrum, sensitivity problems prevented examination of the  $^{13}\text{C}$  spectrum below about 0.02 M.

Silicon-29 has even poorer receptivity than  $^{13}\text{C}$  by a factor of about 2, and in the present cases the absence of magnetically active nuclei directly bonded to silicon results in long relaxation times and makes polarization transfer experiments difficult. With a Bruker AM 500 spectrometer, we attempted to observe  $^{29}\text{Si}$  resonances at dilute concentrations but unfortunately lost visible resonances by 0.1 M. The only observed peak for trimethylsilyl perchlorate was that of the associated form at about  $\delta$  47, which (like  $^1\text{H}$  and  $^{13}\text{C}$ ) did not change position down to about 0.1 M.

The best NMR probe as a function of concentration was  $^{35}\text{Cl}$ , on which we have reported previously.<sup>11</sup> Measurements on trimethylsilyl perchlorate in sulfolane could be made to the 0.005 M level, at which the  $^{35}\text{Cl}$  resonance became extremely sharp (half-width 15–30 Hz) and showed a resonance position ( $\delta$  4.6) typical of free, ionic perchlorate. As the concentration was increased, the resonance broadened enormously (to 1400 Hz at 0.1 M), and the chemical shift moved upfield to  $\delta$  -33. At higher concentrations still (up to 0.584 M), the peak broadened to the point of disappearance. Not previously reported, 1 equiv of water was added to a 0.146 M solution of trimethylsilyl perchlorate in sulfolane and the  $^{35}\text{Cl}$  spectrum recorded. A relatively sharp peak (half-width 312 Hz) was observed at  $\delta$  -7.1. For comparison, the same sample before addition of water gave a signal of width 1500 Hz, 70%  $\text{HClO}_4$  in sulfolane gave a signal of width 25 Hz, and 100%  $\text{HClO}_4$  in sulfolane gave a signal of width 300 Hz. Clearly, the sample of trimethylsilyl perchlorate had not been subject to prior hydrolysis. Olah et al.<sup>10</sup> have suggested to the contrary that the  $^{35}\text{Cl}$  observations resulted from exchange between covalent trimethylsilyl perchlorate and ionic perchloric acid freed by hydrolysis. This mechanism, however, is excluded because the measured levels of hydrolysis are too small. For example, at 0.073 M there is only about 6.5% hydrolysis (Table I). This very low level of water could not explain a chemical shift of 6 ppm or a line width change of 600 Hz (from the observation at 0.584 M).

Comparison of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  line widths demonstrated that the exchange is fast on the NMR time scale,<sup>11</sup> in agreement with the observation of only a single peak for all nuclei. Although the chlorine isotope line width ratios are consistent with fast exchange in sulfolane, it is interesting that the  $^1\text{H}$  line width in dichloromethane may be showing some effects of exchange. In Figure 1b, the line width of the protons from trimethylsilyl perchlorate at 0.003 M clearly is broader than that of the hydrolysis product, bis(trimethylsilyl) ether. At this low concentration in this solvent, we may be reaching the slow-exchange limit between the free and associated perchlorates.

The  $^{29}\text{Si}$  resonance of trimethylsilyl triflate was found at  $\delta$  44.0 in dichloromethane ( $\delta$  46.5 in sulfolane), and that of trimethylsilyl azide at  $\delta$  16.2 in dichloromethane ( $\delta$  17.4 in sulfolane). The  $^{15}\text{N}$  spectrum of the azide in 1,2-dichloroethane contained three peaks at  $\delta$  319.9, 145.3, and 209.1 (in sulfolane at  $\delta$  332.7, 147.6, and 211.8), in agree-

ment with a covalent species.

### NMR Tests for Complexation

It is possible for the silyl cation to complex with the solvent to form another two-particle, ionic species, in which silicon is tetravalent (eq 4). Various NMR tests were carried out to assess this possibility. In dichloromethane,



the structure of the complex would be something like  $\text{Me}_3\text{Si}\cdots\text{Cl}^+\cdots\text{CH}_2\text{Cl}$  (bridging chlorine). If a better nucleophile Y were introduced, the complex would then become  $\text{Me}_3\text{Si}-\text{Y}^+$ , as in eq 4. In dichloromethane solutions of trimethylsilyl perchlorate at 0.219 M, the addition of 1 equiv of acetonitrile had no effect on the  $^{29}\text{Si}$  resonance at  $\delta$  45.6, but addition of 1 equiv of pyridine moved it to  $\delta$  42.6. Introduction of 1 equiv of sulfolane or acetonitrile did not alter the  $^1\text{H}$  or  $^{13}\text{C}$  positions of the methyl resonance, but these probes are relatively insensitive.

Similar experiments were carried out with the more sensitive  $^{35}\text{Cl}$  nucleus. Upon addition of 1 equiv of pyridine to a sulfolane solution of trimethylsilyl perchlorate at 0.219 M, whose  $^{35}\text{Cl}$  resonance was extremely broad and located at  $\delta$  -33, the signal immediately became sharp and moved to  $\delta$  4-5, indicative of ionic perchlorate. Addition of 1 equiv of acetonitrile under the same conditions had little effect; the peak remained broad (half-width 500 Hz; chemical shift at  $\delta$  -29).

The  $^{15}\text{N}$  nucleus serves as an excellent probe for complexation. Coordination of acetonitrile or pyridine at nitrogen results in an upfield shift of about 100 ppm.<sup>12</sup> Free acetonitrile resonates at about  $\delta$  244. When enriched acetonitrile- $^{15}\text{N}$  was added to trimethylsilyl perchlorate in dichloromethane (circa 0.2 M), the  $^{15}\text{N}$  position was essentially the same ( $\delta$  244) as that of free acetonitrile. Under these conditions, acetonitrile is not able to displace perchlorate from its association with  $\text{Me}_3\text{Si}^+$ , so no nitrilium ion ( $\text{Me}_3\text{Si}-\text{N}^+\equiv\text{CCH}_3$ ) was formed. Since the nitrile should easily have displaced coordinating bridged chlorine, we conclude that complexation between the trimethylsilyl cation and dichloromethane (as well as acetonitrile) is negligible. For comparison, we carried out the same experiments with the more nucleophilic pyridine, which resonates at about  $\delta$  314 in its uncomplexed state. When labeled pyridine- $^{15}\text{N}$  was added to trimethylsilyl perchlorate (circa 0.2 M), its resonance moved to  $\delta$  219. Clearly, pyridine is able to displace perchlorate to form a complex,  $\text{Me}_3\text{Si}-\text{pyr}^+$ .

### Conductance Tests for Complexation

Attachment of the solvent to silicon should have a major influence on solution conductance, particularly if the complex is ionic and the silyl perchlorate is ion-paired or even covalent. There is a standard conductance test for complexation involving titration of a solution containing 1.0 equiv of silane and 0.5 equiv of a complexing agent Y in dichloromethane. If the additive Y reacts with  $\text{Me}_3\text{Si}^+$  as the latter is formed (eq 4) by stepwise addition of trityl perchlorate, the ionic complex  $\text{R}_3\text{Si}-\text{Y}^+$  should produce an increasing conductance up to 0.5 equiv, at which point all of the additive is consumed. Between 0.5 and 1.0 equiv, the conductance curve should flatten out to resemble that of the poorly conducting trimethylsilyl perchlorate. Such a break in the curve would be diagnostic for complexation. In the absence of complexation, Y should have no effect

(12) Levy, G. C.; Lichter, R. L. *Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy*; Wiley-Interscience: New York, NY, 1979; pp 67, 79, 80.

on the conductance, and the curve would be essentially the same as in the absence of Y (there may be a small effect of the bulk dielectric).

We carried out such experiments for  $\text{Me}_3\text{SiClO}_4$ ,  $\text{PhMe}_2\text{SiClO}_4$ , and  $\text{Ph}_3\text{SiClO}_4$  (Table II). We chose dichloromethane as solvent because it is the weakest nucleophile of those studied. Any added nucleophile therefore should be able to replace it if the silyl cation is present as  $\text{Me}_3\text{Si-Y}^+$ . When acetonitrile or sulfolane is present as Y, there is little increase in the conductance and no observed break at 0.5 equiv. These results require that these two materials are not able to form a complex with silyl perchlorate. Because the solvent dichloromethane is a weaker nucleophile than either additive, it is necessary that it too is not strongly complexed with the silyl perchlorate. We showed in the section on ionicity that perchlorate was not coordinated in dilute sulfolane solution. The necessary conclusion therefore is that complexation by solvent is not contributing to the structure in dichloromethane, sulfolane, or acetonitrile.

A more nucleophilic additive, *N*-methylpyrrole, brought about a change in behavior. As trityl perchlorate was titrated into the solution of phenyldimethylsilane containing 0.5 equiv of this additive, the specific conductance increased rapidly and leveled out at about 0.4 equiv. Above this level, addition of more trityl perchlorate increased the conductance very modestly, until the equivalent point was reached (0.01 or 0.05 M). Similar behavior occurred for triphenylsilyl perchlorate. When 0.5 equiv of pyridine was present in the solution of phenyldimethylsilane, addition of trityl perchlorate brought about a very rapid increase in the specific conductance. Unfortunately, starting at about 0.5 equiv, the conducting material (presumably  $\text{Me}_3\text{Si-pyr}^+$ ) started to come out of solution, causing a large decrease in the specific conductance (similar observations<sup>4</sup> were made with triphenylsilane). These results are consistent with weak and strong coordination between silyl perchlorate and *N*-methylpyrrole and pyridine, respectively, confirming that the test is indeed sensitive to coordination when present.

### Summary and Conclusions

Solutions of trimethylsilyl, phenyldimethylsilyl, and methyl-diphenylsilyl perchlorates may be prepared in their ionic forms in dilute solutions of nonnucleophilic solvents, and the ionic phenyldimethylsilyl tetraphenylborate was prepared in acetonitrile. We are able to prepare 0.05 M sulfolane solutions and 0.01 M dichloromethane solutions for NMR measurements with about 9% hydrolysis (Table I).

The molar conductances in dichloromethane at 0.01 M indicate a nonconducting species for trimethylsilyl azide, poorly conducting species for triphenylsilyl, trimethylsilyl, phenyldimethylsilyl, and methyl-diphenylsilyl perchlorates (and trimethylsilyl triflate), and highly conducting species for trityl perchlorate and tris(2-propylthio)silyl perchlorate. This structurally reasonable gradation in conductance is inconsistent with an entirely covalent model (and with full hydrolysis). The plot of molar conductance vs concentration for trimethylsilyl perchlorate has a negative slope (Figure 2), indicating the presence of ion pairs. The addition of acetonitrile or sulfolane to a solution of trimethylsilyl or phenyldimethylsilyl perchlorate in dichloromethane has no palpable effect on the conductance, indicating that none of these materials can form complexes ( $\text{R}_3\text{Si-Y}^+$ ). On the other hand the addition of *N*-methylpyrrole or pyridine results in much increased conductance, indicative of complex formation. Conductance titrations on dichloromethane solutions of trimethylsilyl

perchlorate containing 0.5 M added acetonitrile or sulfolane show no evidence for complexation, whereas similar experiments with *N*-methylpyrrole or pyridine show characteristic breaks expected for complexed forms.

Conductance in sulfolane at 0.01 or 0.05 M is very high for all the perchlorates, intermediate for trimethylsilyl triflate, and extremely low for the covalent trimethylsilyl azide. The situation is similar in acetonitrile. The tetraphenylborate of phenyldimethylsilyl is highly conducting in acetonitrile. These conductance experiments indicate that only trimethylsilyl azide and possibly trimethylsilyl triflate are in agreement with Olah's covalent model.<sup>9,10</sup> All the other species are ionic to varying degrees. These conclusions have taken hydrolysis into full consideration.

The cryoscopic molecular weights are exceedingly clear. In 0.02–0.05 M sulfolane, trimethylsilyl and phenyldimethylsilyl perchlorates (as well as triphenylsilyl and tris(2-propylthio)silyl perchlorates) are present as two particles (Table III), with errors from the actual molecular weight of around 2–3%. The azides and the triflates by the same technique exist as single particles, with errors of only 1%. This consistency over eight systems corroborates very low levels of hydrolysis.

These experiments demonstrate that these methyl-substituted silyl perchlorates are ionic to varying degrees in the nonnucleophilic solvents used. In addition, phenyldimethylsilyl tetraphenylborate is entirely ionic in acetonitrile. The methyl substituents provide the worst case scenario (after hydrogen) so far as stabilization of the silyl cation goes, and yet strong evidence is amassed for ionic character. The fact that even these poorly stabilized silyl cations can exist as ions in dilute solution corroborates the previous conclusions about triphenylsilyl and tris(2-propylthio)silyl perchlorates.<sup>4</sup> Nonetheless, it should be appreciated that the ionicity of trimethylsilyl or triphenylsilyl perchlorate is much lower than that of tris(2-propylthio)silyl or trityl perchlorate and is exhibited clearly only in dilute solution.

We have shown that hydrolysis is not important in our conductance and cryoscopic experiments. We have shown that these silyl perchlorates unequivocally are ionic under proper conditions and that there is no evidence for the covalent model except for the azide and possibly the triflate. We have shown that solvent does not complex strongly with silicon. With these points firmly established, work should turn to clarifying the structure of these ions in terms of details of interaction with solvent, whether the geometry about silicon is planar, and what the nature of association at higher concentrations is. It is possible, for example, that solvent is close to but not bonded to both faces of the cation. Such solvation may not be detected by the conductance or cryoscopic tests (which indicate ionicity) but could influence the chemical shifts (which do not correspond to free ionic form).

### Experimental Section

**Solvents.** Commercial sulfolane (Aldrich) was distilled from NaOH pellets, and the fraction boiling at 101–106 °C (0.6 mmHg) was collected. The distillate was stirred overnight under  $\text{N}_2$  over a fresh portion of NaOH. Sulfolane was distilled again under vacuum and stirred overnight over powdered  $\text{CaH}_2$ . The process of distillation from  $\text{CaH}_2$  and stirring overnight over fresh  $\text{CaH}_2$  was repeated twice more. The last distillation from  $\text{CaH}_2$  gave a colorless product with bp 106–111 °C (0.6–0.8 mmHg). Sulfolane was always stored under  $\text{N}_2$  and distilled once again before use. Dichloromethane was shaken with concentrated  $\text{H}_2\text{SO}_4$ , rinsed twice with  $\text{H}_2\text{O}$ , rinsed with 5% aqueous  $\text{NaHCO}_3$ , rinsed with  $\text{H}_2\text{O}$ , and dried overnight over  $\text{CaCl}_2$ . The solvent was decanted and stirred at reflux under  $\text{N}_2$  and over  $\text{CaH}_2$  overnight and distilled. The process was repeated, and the resulting  $\text{CH}_2\text{Cl}_2$



was stored under  $N_2$  over dried molecular sieves. Acetonitrile was shaken twice with fresh portions of 4A molecular sieves and then was stirred over  $CaH_2$  powder for 2 days under  $N_2$  at gentle reflux. The solvent was fractionally distilled under  $N_2$  from  $CaH_2$  and collected in a flask containing a new portion of fresh 4A molecular sieves. The distillate was passed slowly through a column of fresh molecular sieves and was collected in a flask containing fresh molecular sieves.

**Manipulations.** All glassware was dried before use overnight at 135 °C. All manipulations, including those with syringes, were carried out under nitrogen.

Conductance measurements were carried out with an apparatus attached to a vacuum line under  $N_2$ . A 100-mL, three-necked, round-bottomed flask was fitted on one neck with a conductance cell with its tip extending to the bottom of the flask. The other two necks respectively had a rubber septum and a  $N_2$  inlet. The dried solvent (50 mL) and silane solute (approximately 0.015 M) were introduced under  $N_2$  via syringe. In the case of  $Me_3SiH$ , the solute gas was introduced by a bubbler, and the flask (without the conductance cell) was sealed and weighed periodically until the correct amount of solute was achieved. In later runs, the time of bubbling was calibrated, and the amount of  $Me_3SiH$  later was confirmed from the end point (color change and large conductance increase). After introduction of the silane, the septum on the center neck was replaced with a 25-mL buret carrying a septum at the top. Trityl perchlorate was weighed out in a volumetric flask (approximately twice the molar amount of silane) under  $N_2$ , a septum was placed on the mouth of the flask, and solvent was introduced to the mark via syringe, to achieve a precisely known concentration. This solution was transferred via syringe to the buret. The entire setup had been arranged so that  $N_2$  entered through all three necks: from the top of the conductance cell, from the top of the buret, and through the normal inlet. All three inlets came from a common source via the vacuum line with a common bubbler. Thus the entire system was under  $N_2$  continuously during measurements. A single aliquot of trityl perchlorate, corresponding to about  $1/20$ th of the total, was dripped with stirring into the flask containing solute. Stirring was stopped, and the  $N_2$  sources leading to the cell and the buret were cut off at the vacuum line, causing a slight pressure to build up in the flask so that the solution was forced up into the conductance cell. When the solution reached the conductance leads, a measurement was made, and the  $N_2$  flow was resumed to the cell and the burette with the result that the solution drained from the cell back into the reaction flask. A second aliquot of trityl perchlorate was added and the process was repeated. In this fashion some 20 points were obtained, including the equivalence point (equal amounts of solute and trityl perchlorate) and several points with excess trityl perchlorate (since we purposely had twice the molar amount of trityl perchlorate to solute). This procedure was used for dichloromethane and acetonitrile. Because of its viscosity and high

melting point, sulfolane required a slight variation. The third neck of the flask was fitted with a septum rather than with the conductance cell. About 15 mL of solution was removed via syringe and injected into the cell through a septum (this cell was attached to the same  $N_2$  source via a second needle). After the measurement was made, the solution was returned to the reaction flask and the process was repeated.

For the cryoscopic measurements, a 25-mL, three-necked, round-bottomed flask was fitted with an Anschutz thermometer (NBS certified), a septum, and a  $N_2$  inlet. The  $N_2$  source was cut off by a stopcock, the  $N_2$  tubing to the inlet was removed, and the flask was tared. Flow of  $N_2$  was resumed, and approximately 25 mL of sulfolane was introduced via syringe. The weighing procedure then was repeated. Except during actual weighings, the flask was attached to the  $N_2$  source. The flask was heated to about 36 °C with warm water to melt the sulfolane, and the flask was immersed in a cold water bath. Temperature measurements were taken every 15–30 s until the value remained unchanged, indicating that the contents had solidified. The cycle of heating, cooling, and making measurements was repeated three times to provide a mean freezing point of pure sulfolane. An exactly weighed amount of solid trityl perchlorate was added to give a known molality of about 0.05. The freezing point of this solution was measured 3–4 times as for the pure sulfolane. Finally, an equivalent amount of silane was introduced via syringe, and the freezing point of the silyl perchlorate in the presence of triphenylmethane was measured by the same procedure. The molecular weight of the silyl perchlorate was calculated by the formulas published previously.<sup>4</sup>

For NMR measurements, a stock solution approximately 0.2–0.5 M in silyl perchlorate was prepared. Trityl perchlorate was weighed into a 10–25 mL pear-shaped flask, which was fitted with a septum and placed under  $N_2$ . The appropriate amount of solvent was introduced via syringe. Sulfolane solutions contained 10%  $CD_2Cl_2$  to reduce the melting point and to provide a lock signal. To this solution was introduced via syringe an equivalent of the silane. In the case of the gas  $Me_3SiH$ , bubbling was continued until the deep yellow color of trityl perchlorate disappeared. Excess silane was allowed to evaporate (under  $N_2$ ), but a small amount usually persisted (Figure 1). A NMR tube was fitted with a septum, through which a needle brought  $N_2$  from the usual vacuum line apparatus. Solvent and stock solution were introduced via syringe to achieve the desired concentration. The final volume was adjusted to about 1 mL. For particularly dilute solutions, multiple dilution stages were required. The syringe needles were removed from the septum, which was wrapped with Parafilm prior to spectroscopic measurements. Measurements were made immediately upon preparation, after 12 h (wrapped in Al foil and stored at room temperature), and after 24 h. There was no increase in hydrolysis during this period, so that the samples picked up no additional moisture from the atmosphere.