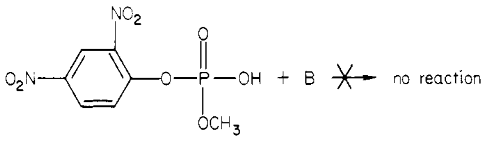
methyl 2,4-dinitrophenyl phosphate (**4**) is stable under comparable conditions.



4

Experimental Section

2,4-Dinitrophenyl dihydrogen phosphate (**1**) was prepared as described.[12]

Methyl 2,4-dinitrophenyl phosphate[13] (**4**) was isolated as its diisopropylethylammonium salt as follows. 2,4-Dinitrophenol was converted into dimethyl 2,4-dinitrophenyl phosphate (∂ ^{31}P −6.4 ppm in $CDCl_3$) by reaction with dimethylphosphorochloridate in dichloromethane, in the presence of 1 mol equiv of imidazole. The phosphotriester was converted into methyl sodium 2,4-dinitrophenyl phosphate by reaction with sodium iodide in acetone. The sodium salt of **4** was dissolved in warm methanol, and the solution was passed through a column of Bio-Rad AG 50W-X-8 resin in the diisopropylethylammonium form. The column was eluted with methanol and the solution was evaporated at 20 °C (30 mm). The desired trialkylammonium salt (∂ ^{31P} −7.6 ppm in CD_3CN) was freed from methanol by repeated evaporations with acetonitrile. Solutions of this salt in acetonitrile (0.4 M) were stable after 2 days at 25 °C and after 1 day at 70 °C.

***erythro*-1-Phenyl-1,2-dibromopropylphosphonic acid** (**2**) was prepared as shown in Scheme I, following the procedure of Kenyon and Westheimer.[7b] The acid **2** had mp 186–187 °C (after three recrystallizations from acetonitrile). **Dimethyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate**[7c] (**19**) was obtained as an oil when a methanol solution of the acid **2** was treated with ethereal diazomethane. **Methyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate**[7c] (**3**), mp 158–159 °C (from acetonitrile) was obtained when an acetone solution of the triester **19** and LiBr was kept at 25 °C for 2 days, followed by acidification of an aqueous solution of the salt.

Decomposition of 2,4-Dinitrophenyl Dihydrogen Phosphate (1), *erythro*-1-Phenyl-1,2-dibromopropylphosphonic Acid (2), and Methyl Hydrogen *erythro*-1-Phenyl-1,2-dibromopropylphosphonate (3) in the Presence of a Tertiary Amine. Solutions of the phosphate and phosphonates in the solvents indicated in Table I were allowed to decompose in the presence of diisopropylethylamine, under the conditions indicated in the table. The course of the reactions was followed by ^{31}P and ^{1}H NMR spectrometry. The ^{31}P NMR spectra were obtained on a Brucker WH-360 spectrometer at 145.7 MHz. The ^{31}P chemical shifts of the pertinent compounds are summarized in Table II.

Methyl 3-Oxo-1-cyclohexenyl Phosphate (15). 1,3-Cyclohexanedione (0.024 g, 0.2 mmol; from Aldrich Chemical Co., stabilized with 3% NaCl) was mixed with CD_3CN (0.5 mL) and diisopropylethylamine (0.052 mL, 0.3 mmol). The clear solution was decanted into an NMR tube containing methyl *erythro*-1-phenyl-1,2-dibromopropylphosphonate (**3**; 0.037 g, 0.1 mmol). The ^{1}H NMR of the clear solution was observed at various times, at 25 and at 70 °C. After 17 h at 70 °C, the reaction was complete. The solution was evaporated at 35 °C (20 mm) and the residue was treated with diethyl ether (3 × 5 mL). The ether-soluble fraction contained 1-phenyl-1-bromopropene. The ether-insoluble fraction was the diisopropylethylammonium salt of methyl 3-oxo-1-cyclohexenyl phosphate; it was dissolved in water (5 mL) and was converted into the sodium salt by means of a Bio-Rad AG50W-X8 cation-exchange resin in its Na^+ form. Elution of the column with water (10 mL), and evaporation of the solution at 30 °C (20 mm) afforded **sodium methyl 3-oxo-1-cyclohexenyl phosphate** (0.028 g), δ ^{31}P −7.8 ppm; τ 4.10 ppm (vinyl proton) and 5.70 (methoxy protons); λ_{max} 254 nm (all measurements in D_2O).

The crude diisopropylethylammonium salt of methyl 3-oxo-1-cyclohexenylphosphate obtained by the above procedure was also purified by means of a column of DEAE-cellulose (Cellex-D), using a linear gradient of triethylammonium bicarbonate buffer. The triethylammonium salt of the enol phosphate methyl ester was converted into its sodium salt by NaI in methanol/acetone.

Monoanilinium 1-phenylethenyl hydrogen phosphate (**12**) was prepared from phenacyl chloride and trimethyl phosphite as described.[11] The anilinium salt (0.50 g) was dissolved in warm methanol (10 mL). The solution was passed rapidly through a column containing BioRad-AG 50W-X8 resin in its protonated form. The effluent was collected in a flask containing 1 mol equiv of diisopropylethylamine cooled to 0°, and the resulting solution was evaporated at 0 °C (0.5 mm). The residue was washed with ether and dried to yield **monodiisopropylethylammonium 1-phenylethenyl hydrogen phosphate**; δ ^{31}P −5.6 ppm (in CD_3CN). A 1 M CD_3CN solution of this salt containing 1 or 2 mol equiv of diisopropylethylamine exhibited no changes after 24 h at 25 °C.

Acknowledgment. The ^{31}P NMR measurements were carried out at Brookhaven National Laboratories under auspices of the U.S.A. Department of Energy. We are grateful to Dr. Alan McLaughlin and Mr. Donald Lawler for their assistance in obtaining NMR spectra.

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A ^{13}C and ^{29}Si NMR Spectroscopic Study of α- and β-Trimethylsilyl-Substituted Carbocations[1]

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Contribution from the Hydrocarbon Research Institute and the Department of Chemistry, University of Southern California, Los Angeles, California 90007. *Received June 17, 1981*

Abstract: A series of trimethylsilyl-substituted carbocations was prepared under long-lived stable ion conditions at low temperatures and characterized by ^{13}C and ^{29}Si NMR spectroscopy. The α-trimethylsilyl group in the diphenyl(trimethylsilyl)methyl cation significantly deshields the cationic center in the ^{13}C NMR spectrum. At higher temperatures (≥0 °C) the diphenyl(trimethylsilyl)methyl cation undergoes rearrangement through methyl migration to the cationic center from the silicon atom followed by nucleophilic quenching of the developing silicon cation. No long-lived silicenium ion was, however, observed. Attempted generation of α-phenyl-α-(trimethylsilyl)ethyl and α-methyl-α-(trimethylsilyl)ethyl cations gave instead cumyl and *tert*-butyl cations through methyl migration, nucleophilic attack, oxidative β-desilylation, and subsequent protonation. (Trimethylsilyl)ethynyl-substituted carbocations besides showing the usual mesomeric vinyl cation character, also show significant β-carbon deshielding possibly due to C–Si $p\pi$–$d\pi$ bonding. Protonated acyl silanes and their progenitors also show significant carbonyl carbon deshielding as compared to their carbon analogues.

The effect of silicon substituents on the reactivity and stability of organic compounds has been extensively studied in recent years.[2] Of particular interest is the effect of α- or β-silicon groups on an unsaturated organic moiety. The traditional view that a silyl

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Table I. ^{13}C NMR Chemical Shifts of Diphenyl-Substituted Cations[a]

compound	C$^+$(OH)	C$_{ipso}$	C$_o$	C$_m$	C$_p$	other
1	75.5	146.6	127.9	126.6	126.0	Me −2.3
2	259.0	148.5	141.8	131.5	147.4	Me 1.9
Ph$_2$C$^+$-CH$_3$ [b]	229.2	141.5	141.2	131.5	148.1	CH$_3$ 30.5
Ph$_2$C$^+$-H [b]	200.6	138.3	143.4 149.1	133.7	150.9	

[a] Referenced to external Me$_4$Si. [b] Reference 14.

substituent, because of its greater electron-donating inductive effect, is better able to stabilize an electron-deficient center than the related carbon substituent[3] has, in recent years, been disputed by numerous experimental and theoretical studies.[4]

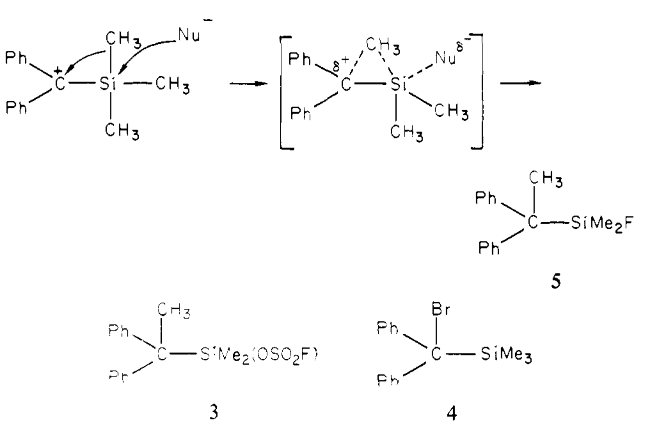
Indeed, the extremely low reactivity of substituted α-silylmethyl halides under S$_N$1 conditions[5] implies that the α-silyl substituent destabilizes the electron-deficient carbon in solvolytic reactions. Much smaller destabilizing effects have been found in other silicon systems.[6] For instance, a trimethylsilyl substituent has a similar effect on the rate of electrophilic aromatic substitution reactions as hydrogen, but is slightly deactivating relative to a methyl group.[6] Recent theoretical studies[7,8] have indicated that a silyl group is slightly more effective in stabilizing a carbocationic center than methyl, if optimized geometries and d-orbital functions are included in the calculations. Moreover, the study[8] suggested that the silyl group is a stronger inductive and weaker hyperconjugative electron donor than the methyl substituent.

The basis for this kind of silicon interaction with π systems has been previously established by experimental studies.[9] The silyl substituent acts as a weak electron acceptor apparently by a conjugative mechanism and as an electron donor by an inductive effect.[9] The hyperconjugative effect has been attributed to pπ–dπ interactions between empty d orbitals on silicon and the p orbital of carbon. In many cases the electron-donating inductive effect and the electron-withdrawing conjugative effect occur to the same extent and this causes the silicon substituent to appear as a very weak acceptor or donor.[9] In view of the foregoing discussion the preparation and study of silyl-substituted carbocations was considered to be of substantial interest particularly with regard to the charge-delocalizing ability of silyl substituents.

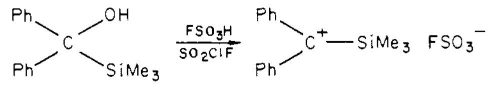
Results and Discussion

While probably the most important handle in the study of carbocations generated under long lived stable ion conditions, the ^{13}C NMR chemical shifts cannot directly reveal the charge density of carbocations. Indeed, many factors besides charge affect carbon chemical shifts. However, in closely related systems the shielding or deshielding effects reflect the trend of charge distribution. The validity of this was shown in several studies[10] involving the relative charge-delocalizing abilities of alkyl and aryl substituents. The charge-delocalizing ability of silyl substituents, however, has been little studied until now. Besides a few solvolytic studies,[11] only two attempts to observe α-silyl-substituted carbocations by ^{1}H NMR have been reported.[12,13] In the present study we describe the preparation of several silyl-substituted carbocations under stable ion conditions and report their ^{13}C and ^{29}Si NMR spectroscopic data. In order to establish the charge-delocalizing ability of the trimethylsilyl group, we compare shifts determined in this study with the previously reported[14–16] data on related carbocations. We have also prepared the analogous *tert*-butyl-substituted carbocations in several instances for further comparison.

Scheme I



α-Silyl Carbocations. The careful addition of diphenyl(trimethylsilyl)methyl alcohol (**1**) to a solution of FSO$_3$H/SO$_2$ClF at −78 °C led to the formation of a dark red solution of the diphenyl(trimethylsilyl)methyl cation **2**. The ^{13}C NMR chemical shifts for **1** and **2** are listed in Table I. The diphenyl(trimethylsilyl)methyl cation **2** is quite stable as no apparent rearrangement or decomposition occurred for 2 days at −78 °C.



The carbocationic center is considerably deshielded when compared to other diphenyl-substituted carbocations. The ^{13}C NMR chemical shift of the cationic carbon in ion **2** is δ ^{13}C 259.0, nearly 30 and 60 ppm deshielded from those in the α,α-diphenylethyl and benzhydryl cations,[14] respectively. However, the chemical shifts of the ortho, meta, and para carbons of the phenyl groups are similar in all three cations. The para carbon chemical shifts for the trimethylsilyl-, methyl-,[14] and hydrogen[14]-substituted cations are observed at δ ^{13}C 147.4, 148.1, and 150.9, respectively. With use of the para carbon chemical shifts as an indicator of positive charge delocalization, the slight shielding observed for the trimethylsilyl-substituted analogue **2** seems to show that the

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(1) Stable Carbocations. Part 236. For part 235 see: G. A. Olah, G. K. S. Prakash, G. Liang, P. v. R. Schleyer, and D. W. Graham, *J. Org. Chem.*, in press.

(2) (a) For a review see: C. J. Attridge, *Organomet. Chem. Rev., Sect A*, **5**, 323–353 (1970); (b) C. Eaborn, "Organosilicon *Compounds*", Butterworths, London, 1960.

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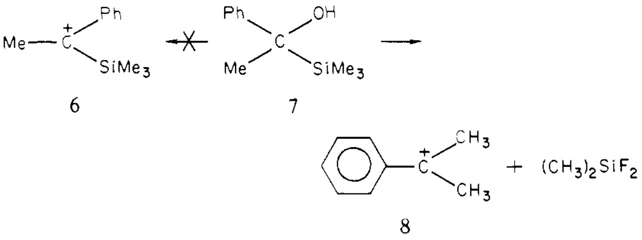
trimethylsilyl group stabilizes charge better than a methyl or hydrogen substituent. However, the larger steric requirement of the bulky trimethylsilyl group could force the phenyl ring out of the plane of the carbocationic carbon and thus decrease the necessary overlap for charge delocalization. Attempts to prepare the *tert*-butyl-substituted analogue from diphenyl(*tert*-butyl)methyl alcohol failed and therefore no direct comparison between the stabilizing effects of the trimethylsilyl and *tert*-butyl groups is possible.

A substantial deshielding (7–10 ppm) of the ipso carbon of the phenyl group in cation **2** relative to the ipso carbons of the α,α-diphenylethyl and benzhydryl cations is also observed. Similar deshielding of β carbons is observed in numerous other cations prepared in this study and will be discussed later.

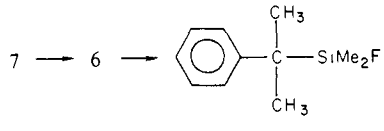
Although stable at −78 °C, ion **2** rearranged upon warming in FSO_3H to 0 °C for several minutes. From the ^{13}C and ^1H NMR spectra,[17a] it was deduced that the rearranged product had structure **3** resulting from methyl migration from silicon to carbon and subsequent formation of the related fluorosulfate. Similarly it was found that addition of silver tetrafluoroborate to a solution of **2** or the treatment of the bromo compound **4** with silver hexafluoroantimonate in SO_2 and subsequent warming led to the rearranged product **5** (quenched by fluoride).[17b] This migration of an alkyl group from silicon to an electron-deficient α carbon has been noted in the past[12,13,18] and may be considered to be analogous to the Wagner–Meerwein rearrangement[13,19] common in carbocations. Migration of the alkyl group from silicon to carbon occurs with immediate nucleophilic attack on silicon by the counterion. This shows substantial nucleophilicity even in the case of FSO_3^-, BF_4^-, and SbF_6^- gegenions toward the electron-deficient silicenium center.

The existence of any long-lived free silicenium ion intermediate is doubtful.[19] A more concerted mechanism proposed for the rearrangement of cation **2** is shown in Scheme I.

All attempts to prepare the α-phenyl-α-(trimethylsilyl)ethyl cation **6** from the corresponding alcohol **7** failed. The treatment of **7** with FSO_3H/SbF_5 in SO_2ClF at −78 °C gave only the cumyl cation **8**,[20] with formation of difluorodimethylsilane.[21]



The instability of cation **6** and the relative ease at which the cumyl cation **8** is formed is of interest. Analogous carbon-substituted methylphenyl cations have been prepared previously[22] and were found stable. The presence of the trimethylsilyl group should not per se destabilize the ion **6** as evident from the behavior of ion **2**. Therefore it appears that the facile rearrangement and the inability to observe **6** may be attributed to the replacement of a phenyl group in cation **2** with a methyl group. This causes a substantial increase in the amount of positive charge localized at the cationic center and thus results in a more electrophilic silicon. The electrophilic silicon promotes methyl migration and formation of fluorosilane **9**, which upon oxidative desilylation gives α-methylstyrene.

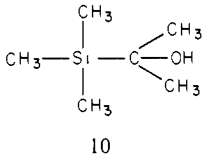


9

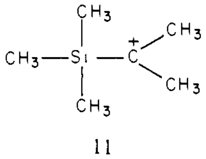
Subsequent protonation gives the cumyl cation. The oxidative desilylation of alkylsilanes resulting in alkenes is well known[23] and proceeds through hydride abstraction β to the silicon atom. The superacidic $FSO_3H{:}SbF_5$ mixture is indeed a very good hydride abstractor.[24]

An alternative pathway involving protolysis of the carbon–silicon bond in **9** was also considered. The protolysis would yield dimethyldifluorosilane and cumene. Hydride abstraction from cumene would yield the cumyl cation. However, this pathway was discounted when control experiments failed to produce cumyl cation from cumene under the same acid conditions and showed only ring protonation.

Another example of the rearrangement process found for **7** was observed in the attempted ionization of dimethyl(trimethylsilyl)methyl alcohol (**10**). The expected α-methyl-α-(trimethylsilyl)ethyl cation **11** could not be generated under a variety of superacid conditions. Instead *tert*-butyl cation[25] and difluorodimethylsilane were observed. A rearrangement cleavage process analogous to the previous one explains the observed products.



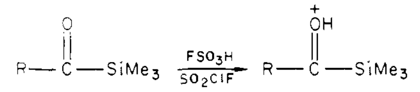
10



11

The inability to observe either **6** or **11** under stable ion conditions with low nucleophilicity solvent systems is in sharp contrast to the claimed formation of **11** in nitromethane solution based on a ^1H NMR study.[12] We feel that in this study no free carbocations were observed in the nitromethane media and the reported ^1H NMR data are inconclusive.

Protonation of Acyl Silanes. The addition of the acyl silanes **12** and **13** to FSO_3H/SO_2ClF at −78 °C resulted in the protonated ketones **14** and **15**. The ^{13}C NMR chemical shifts for **12–15** are listed in Table II. The protonation of **12** leads to a substantial deshielding of the carbonyl carbon (244.3 to 291.7 ppm). A similar magnitude of deshielding (45.2 and 42.4 ppm) is observed upon protonation of acetone[15] and pinacolone. This similarity indicates that the trimethylsilyl substituent is not substantially different than a methyl or *tert*-butyl group in its ability to stabilize (delocalize charge) an electron-deficient center.



12, R = Me 14, R = Me
13, R = Ph 15, R = Ph

The protonation of phenyl trimethylsilyl ketone (**13**) also deshields the carbonyl carbon but to a lesser extent (15.3 ppm) than the methyl-substituted ketone due to increased charge delocalization into the aromatic ring. Again, the carbon analogues acetophenone[15] and phenyl *tert*-butyl ketone show a deshielding of the carbonyl carbon upon protonation (24.2 and 23.3 ppm, respectively). However, the deshielding observed for these two

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(17) (a) δ ^{13}C Si–CH_3, −3.3, Si–C– 41.2, C–CH_3 24.4, C_o, C_m 130.0, 129.9, C_{ipso} 127.8, C_p 145.9; (b) δ ^{13}C Si–CH_3 −2.9 (J_{C-F} = 13.8 Hz), Si–C– 42.2 (J_{C-F} = 10.3 Hz), C–*CH* 23.4, C_{ipso} 118.8, C_o 130.0, C_m 126.5, C_p 151.1. δ ^1H 7.28–7.35 (m, 10 H), 1.82 (J_{H-F} = 1.08 Hz, 3 H), 0.24 (J_{H-F} = 7.5 Hz, 6 H).

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(20) ^{13}C NMR data identical with that previously reported.[14]

(21) δ ^{13}C −7.3 (J_{C-F} = 16.3 Hz), identical with authentic sample.

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(25) ^{13}C NMR data identical with that previously reported.[15]

Table II. ^{13}C NMR Chemical Shifts of Methyl-, *tert*-Butyl-, and Trimethylsilyl-Substituted Ketones[a]

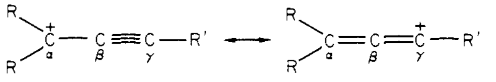
	δ				
	C=O	CH_3	Me	other	ref
$CH_3C(=O)SiMe_3$ (12)	244.3	36.5	−2.0		
$CH_3C(=^+OH)SiMe_3$ (14)	291.7	38.0	−3.6		
$CH_3C(=O)CH_3$	205.1	28.1			*b*
$CH_3C(=^+OH)CH_3$	250.3	32.6, 31.3			*b*
$CH_3C(=O)CMe_3$	210.5	23.3	25.4	$-C(Me)_3$ 43.1	
$CH_3C(=^+OH)CMe_3$	252.9	25.7	24.5	$-C(Me)_3$ 46.4	
$PhC(=O)SiMe_3$ (13)	237.5		−0.3	C_{ipso} 141.2, C_o 129.8, C_m 128.7, C_p 134.2	
$PhC(=^+OH)SiMe_3$ (15)	252.8		−2.2	C_{ipso} 135.5, C_o 131.3, C_m 131.3, C_p 146.4	
$PhC(=O)CH_3$	196.0	24.9		C_{ipso} 136.6, C_o 128.4, C_m 128.4, C_p 131.6	*b*
$PhC(=^+OH)CH_3$	220.2			C_{ipso} 129.0, C_o 138.5, 133.0, C_m 130.9, C_p 145.3	*c*
$PhC(=O)CMe_3$	207.8		27.7	$-C(Me)_3$ 43.7, C_{ipso} 138.3, C_o, C_m 127.8, 127.7, C_p 130.6	
$PhC(=^+OH)CMe_3$	231.1		26.5	$-C(Me)_3$ 44.3, C_{ipso} 127.3, C_o 131.9, C_m 128.6, C_p 141.8	

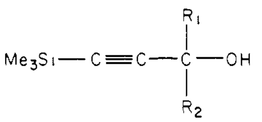
[a] Referenced to external Me_4Si. [b] J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972. [c] D. Forsyth, R. J. Spear, and G. A. Olah, *J. Am. Chem. Soc.*, 98, 2512–2518 (1976).

ions is greater than that of the silyl-substituted cation.

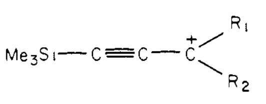
Using the para-carbon chemical shifts as an indicator of the amount of charge delocalized into the aromatic ring, we observe deshielding to a similar degree for the three cations. The chemical shift of the para carbon for cation **15** is δ ^{13}C 146.4, while that of protonated acetophenone[15] is δ ^{13}C 145.3, a difference of just 1.1 ppm. However, a larger difference of 4.6 ppm is observed between ion **15** and protonated phenyl *tert*-butyl ketone (δ ^{13}C 141.8). While substantial, this large difference may be due to the steric bulk of the *tert*-butyl group forcing the phenyl ring out of the plane of the carbonyl π bond rather than the *tert*-butyl group being better able to delocalize positive charge. Also noteworthy is the deshielding of the carbonyl carbon of both the acylsilanes and protonated acylsilanes relative to the carbon analogues, the deshielding effect being approximately 30–40 ppm.

(Trimethylsilyl)ethynyl-Substituted Carbocations. While vinyl cations have not been experimentally observed under stable ion conditions, the mesomeric vinylic cation forms of alkynyl carbenium ions have been shown to contribute extensively to the total ion structure.[16] A systematic study[16] of the relative charge delocalizing abilities of methyl, cyclopropyl, and phenyl substituents in these ions has shown that the cyclopropyl group delocalizes charge to a greater extent than the phenyl substituent which in turn is better than a methyl group. Interested in the ability of the trimethylsilyl group to delocalize charge in assorted cationic systems, we prepared a series of (trimethylsilyl)alkynyl methanols **16** and observed their behavior under superacidic conditions.





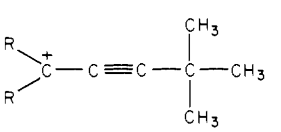
16a, $R_1 = R_2$ = Ph
b, $R_1 = R_2$ = —◁
c, $R_1 = R_2 = -CH_3$
d, R_1 = Ph; R_2 = —◁
e, R_1 = Ph; $R_2 = CH_3$
f, R_1 = —◁, $R_2 = CH_3$



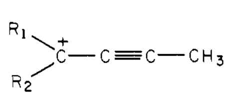
17a, $R_1 = R_2$ = Ph
b, $R_1 = R_2$ = —◁
c, $R_1 = R_2 = -CH_3$
d, R_1 = Ph; R_2 = —◁
e, R_1 = Ph; $R_2 = CH_3$
f, R_1 = —◁; $R_2 = CH_3$

The addition of alcohols **16a–d** to solutions of FSO_3H or SbF_5 in SO_2ClF at −78 °C led to the formation of the corresponding cations **17a–d**. Cations **17e,f** could not be obtained from **16e,f** under a variety of conditions. The carbon chemical shifts of both C_α and C_γ in **17a–d** are markedly deshielded with respect to **16a–d** (Table III) indicating substantial positive charge at these two carbons. The extent of charge localization of C_α and C_γ is strongly dependent on the nature of the substituents at C_α. The shielding of C_γ in **17a–d** indicates that the relative importance of the mesomeric vinyl cation forms is decreased by the presence of strongly delocalizing substituents (phenyl, cyclopropyl) at C_α and is in accord with previous studies on related systems.[16]

The comparison of cations **17a–d** with the *tert*-butyl-substituted cations **18a–c** and the previously studied methyl-substituted cations[16] **19a–d** provides additional insight into the charge-delocalizing ability of the trimethylsilyl substituent.



18a, R = Ph
b, R = —◁
c, R = CH_3



19a, $R_1 = R_2$ = Ph
b, $R_1 = R_2$ = —◁
c, $R_1 = R_2 = CH_3$
d, R_1 = Ph; R_2 = —◁

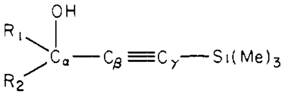
In cation **17a**, the carbocationic chemical shift is δ ^{13}C 192.9 while those for the related ions **18a** and **19a**[16] are 194.5 and 195.7 ppm, respectively. The similarity of these chemical shifts indicates that the amount of charge localized on C_α is of the same magnitude in these three diphenyl-substituted cations. In accord with this observation is the fact that the para (and ortho and meta) carbons of the phenyl rings also show similar chemical shifts. However, the para carbons of **17a** are slightly deshielded with respect to **18a** and **19a**[16] (2.0 and 1.6 ppm, respectively). The amount of charge delocalized into the aromatic ring, therefore, is slightly greater in the trimethylsilyl-substituted cation **17a** implying that the silyl substituent is less effective in delocalizing charge than methyl or *tert*-butyl groups in these cationic systems.

In the series of cyclopropyl-substituted cations **17b,18b**, and **19b**,[16] the cationic carbons again show similar chemical shifts. However, the amount of charge delocalized into the cyclopropyl ring is evident by the deshielding of the methine and methylene carbons. These carbons are more deshielded in cation **17b** relative to **18b** and **19b** indicating increased charge delocalization. Again, the trimethylsilyl group appears to be less effective in delocalizing positive charge.

In the methyl-substituted cations **17c**, **18c**, and **19c**, there is not a good charge-delocalizing group present at C_α. The ability of the C_γ substituents (methyl, *tert*-butyl and trimethylsilyl) to delocalize positive charge is therefore more important in these ions than in the previously discussed ones. The carbocationic carbon of the trimethylsilyl-substituted ion **17c** is the most deshielded, indicating that the silyl group is again the least effective in delocalizing charge. The chemical shifts of the α-methyl carbons reinforce this conclusion, the methyl carbon of **17c** being the most deshielded. The *tert*-butyl group appears to be better able to delocalize charge than the methyl group as indicated by the α-methyl and cationic carbon chemical shifts, those for cation **18c** being shielded with respect to **19c**.

A noteworthy observation of the ^{13}C NMR data of the trimethylsilyl-substituted cations **17a–d** is the substantial deshielding of the C_β and C_γ carbons with respect to the carbon analogues. For example, C_β of cation **17a** is approximately 18 ppm deshielded

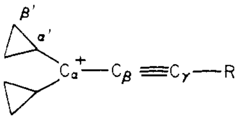
Table III. ^{13}C NMR Shifts of Methyl, *tert*-Butyl-, and (Trimethylsilyl)ethynyl-Substituted Alcohols and Carbocations[a]



	R_1	R_2	C_α	C_β	C_γ	Me	other
16a	Ph	Ph	75.3	108.9	92.4	0.6	C_{ipso} 146.5, C_o 128.8, C_m 126.7, C_p 128.3
16b	>—	>—	72.0	105.3	91.3	−1.8	$C_\alpha{}'$ 22.6, $C_\beta{}'$ 4.2, 2.8
16c	CH_3	CH_3	63.6	109.2	84.1	−1.7	CH_3 29.8
16d	Ph	>—	74.2	104.7	89.9	−0.7	$C_\alpha{}'$ 22.8, $C_\beta{}'$ 2.5, 1.8, C_{ipso} 144.0, C_o 127.4, C_m 124.8, C_p 126.9

$\mathrm{Ph_2C_\alpha{}^+{-}C_\beta{\equiv}C_\gamma{-}R}$

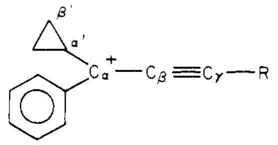
	R	C_α	C_β	C_γ	C_{ipso}	C_o	C_m	C_p	other
17a	$SiMe_3$	192.9	111.3	171.5	141.3	142.3	132.4	147.0	Me −2.0
18a	CMe_3	194.5	92.9	173.0	140.2	141.0	131.0	145.0	>:< 33.2, Me 28.2
19a	CH_3[b]	195.7	93.2	165.1	144.8	141.5	131.4	145.4	CH_3 9.1



	R	C_α	C_β	C_γ	$C_\alpha{}'$	$C_\beta{}'$	other
17b	$SiMe_3$	242.7	98.3	149.0	47.6	42.1	Me −1.5
18b	CMe_3	242.4	77.4	149.9	44.9	39.2	>:< 28.8, Me 28.1
19b	CH_3[b]	243.3	77.9	141.2	45.5	39.1	CH_3 7.6

$\mathrm{(CH_3)_2C_\alpha{}^+{-}C_\beta{\equiv}C_\gamma{-}R}$

	R	C_α	C_β	C_γ	$CH_3(C\alpha)$	other
17c	$SiMe_3$	270.2	126.3	230.6	45.0	Me −3.2
18c	CMe_3	266.6	110.5	223.6	43.2	>:< 36.9, Me 27.4
19c	CH_3[b]	269.0	110.6	219.1	43.7	CH_3 14.0



	R	$C\alpha$	C_β	C_γ	$C_\alpha{}'$	$C_\beta{}'$	C_{ipso}	C_o	C_m	C_p	other
17d	$SiMe_3$	208.5	98.1	149.5	41.7	39.8	136.1	138.8	131.3	145.5	Me −5.0
19d	CH_3[b]	214.9	83.3	147.7	43.3	44.5	139.5	138.1	130.9	145.3	CH_3 7.6

[a] Referenced to external Me_4Si. [b] Reference 16.

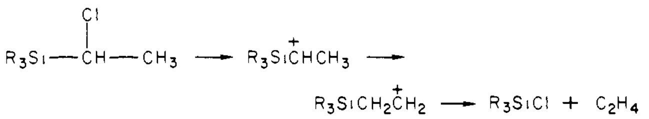
when compared to ions **18a** and **19a**. A similar effect has been attributed to the presence of C–Si pπ–dπ bonding[26] in which the deshielding was explained by a significant contribution of resonance structure B. This effect was limited to C_α and did not significantly perturb the chemical shifts of either α-phenyl or α-alkenyl substituents.[27,28]

$$\mathrm{R{-}C_\alpha{\equiv}C_\beta{-}SiMe_3 \longleftrightarrow R{-}\overset{+}{C}_\alpha{=}C_\beta{=}\overset{-}{Si}Me_3}$$

A B

The deshielding in the C_γ shifts for cations **17a–c** does not appear to be a result of the silicon substitution as a similar deshielding is observed in the case of the *tert*-butyl cations **18a–c**.

Attempted Generation of β-Silyl Carbocations. The reactions of chloroalkylsilanes with Lewis acids have been extensively investigated.[18,29] Whitmore, Sommer, and Gold[18] found that trimethyl(chloromethyl)silane rearranges to ethyldimethylchlorosilane. Sommer et al.[29] have subsequently reported the treatment of a variety of chloroalkylsilanes with aluminum chloride. Similarly, (α-chloroethyl)trimethylsilane and (α-chloroethyl)triethylsilane[29a] undergo analogous rearrangements. However, in the latter two cases, an additional rearrangement pathway is observed. A hydride shift from the methyl group adjacent to the α carbon occurs giving a β-silyl carbocation which subsequently eliminates ethylene.



$$\mathrm{R_3Si{-}\overset{\displaystyle Cl}{\overset{|}{C}}H{-}CH_3 \longrightarrow R_3Si\overset{+}{C}HCH_3 \longrightarrow R_3SiCH_2\overset{+}{C}H_2 \longrightarrow R_3SiCl + C_2H_4}$$

The rearrangement of a secondary carbocation to a primary one is generally energetically unfavorable but takes readily in these systems. The above example and other related observations such as the anti-Markovnikov addition of hydrogen halides[30] under ionic

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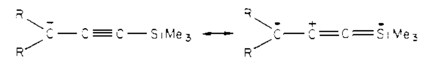
(26) G. C. Levy, D. M. White, and J. D. Cargioli, *J. Magn. Reson.*, **8**, 280–283 (1971).

(27) M. T. W. Hearn, *J. Magn. Reson.*, **22**, 521–526 (1976).

(28) A similar pπ–dπ interaction in cations **17a–c** would involve resonance forms of the type A′ and B′. As this type of interaction would tend to localize



$$\mathrm{R_2\overset{-}{C}{-}C{\equiv}C{-}SiMe_3 \longleftrightarrow R_2\overset{-}{C}{-}\overset{+}{C}{=}C{=}\overset{-}{Si}Me_3}$$

A′ B′

charge of C_β, it would be expected that the polarization would be greatest in cation **17b** in which the two cyclopropyl groups delocalize the positive charge the most. Conversely, the contribution of structure B′ would be the least in cation **17c** in which two relatively poor charge delocalizing methyl groups are present. This appears to be the case for cations **17a–c** in which the largest deshielding of C_β is observed for **17b** and the least deshielding observed in cation **17c**.

(29) (a) L. H. Sommer, R. E. van Strien, and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 3056–3060 (1949); (b) L. H. Sommer, D. L. Bailey, and F. C. Whitmore, *ibid.*, **70**, 2869–2872 (1948).

(30) C. Eaborn and S. Parker, *J. Chem. Soc.*, 939 (1954).

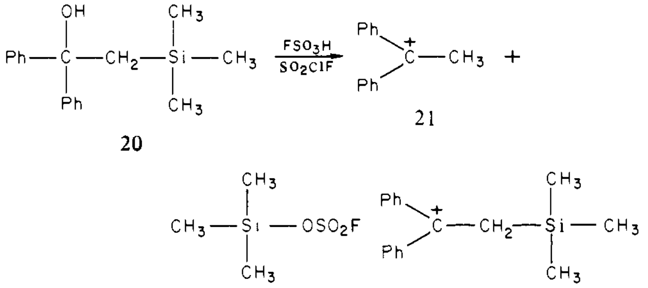
Table IV. ^{29}Si NMR Chemical Shifts[a]

compd	δ ^{29}Si	compd	δ ^{29}Si
1	4.7	16b	−18.6
2	5.4	16c	−18.4
4	2.8	16d	−18.0
12	−10.1	17a	−10.5
13	−15.1	17b	−11.1
14	11.0	17c	−6.2
15	2.9	17d	−10.5
16a	−19.8		

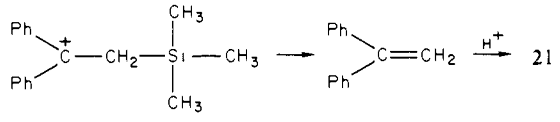
[a] Referenced to external Me_4Si.

conditions to vinylsilanes depicts the high reactivity of β-chloroalkylsilanes. This high reactivity has been attributed to the stabilizing interaction of the β-silyl group.[7,31]

In order to study the nature of this stabilizing effect we attempted to prepare β-silyl-substituted carbocations in superacid solution. However, ionization of **20** in FSO_3H/SO_2ClF at both −78 °C and −140 °C led only to the formation of the diphenylmethyl cation[14] **21** along with trimethylsilyl fluorosulfate. No evidence was obtained for the intermediacy of a long-lived β-silyl-substituted cation **22**. The failure to observe **22** can be attributed to the facile elimination reaction observed previously[18,29] in the solvolytic and aluminum chloride catalyzed rearrangement studies on β-chlorosilylalkanes. The most probable mechanism involves nucleophilic attack on silicon by fluorosulfate and is analogous to the oxidative desilylation reactions discussed previously.



20 21 22



22

An alternate but less probable possibility is the initial protolysis of the carbon–silicon bond giving α,α-diphenylethanol which undergoes subsequent ionization.

^{29}Si NMR Spectroscopic Study. Although ^{29}Si NMR spectroscopy has become increasingly important in recent years in the structural study of organosilanes, the factors influencing ^{29}Si chemical shifts are not yet well understood.[32] While electron density and ^{1}H chemical shifts are closely related, for heavier nuclei such as ^{13}C and ^{29}Si the situation is more complicated. The ^{13}C chemical shift and electron density relationship has been described previously. Ernst et al.[33] have demonstrated a linear relationship between ^{29}Si chemical shifts and Hammett substituent constants within a series of trialkylsilyl-substituted aromatic compounds $X–C_6H_4–SiR_3$. This suggests that between closely related systems, as in the case of ^{13}C shifts, a relationship between charge density and ^{29}Si chemical shifts may exist.

Our preceding studies[34] suggest that factors which influence ^{13}C chemical shifts also affect ^{29}Si chemical shifts. We have therefore determined the ^{29}Si chemical shifts of the studied cations to ascertain the extent of neighboring group deshielding of a trimethylsilyl substituent adjacent to an electron-deficient center. The ^{29}Si chemical shifts are listed in Table IV. All the ^{29}Si chemical shifts were referenced to external tetramethylsilane.

The ^{29}Si chemical shift of diphenyl(trimethylsilyl)methyl cation **2** was observed at δ ^{29}Si 5.4, about 0.7 ppm deshielded compared to its progenitor alcohol. The observation of a rather small neighboring group deshielding is due to charge delocalization into the aryl ring. However in cations **17a–d** the silicon atoms are significantly deshielded relative to the precursor alcohols **16a–d**. The deshieldings of the ^{29}Si shifts range from 7.5 to 12.2 ppm. The magnitude of ^{29}Si deshielding is apparently dependent upon the charge-delocalizing ability of the C_α substituent. Effective charge-delocalizing groups such as a cyclopropyl or a phenyl group significantly diminish the ^{29}Si deshielding.

The ^{29}Si chemical shifts of methyl trimethylsilyl ketone and phenyl trimethylsilyl ketone are observed at δ ^{29}Si −10.1 and −15.1, respectively. However, upon protonation they get unexpectedly deshielded by 21.1 and 18.0 ppm. This deshielding cannot be indicative of a substantial neighboring group deshielding effect alone, which would be rather difficult to accommodate in view of the much smaller neighboring group deshielding observed for the corresponding carbon analogues.

Experimental Section

Diphenyl(trimethylsilyl)methanol (**1**),[35] diphenyl(trimethylsilyl)methyl bromide (**4**),[35] and methyl trimethylsilyl ketone (**11**)[36] were prepared as described in the literature.

Phenyl Trimethylsilyl Ketone (13). A solution of benzyltrimethylsilane (10 g, 0.06 mol), *N*-bromosuccimide (22 g, 0.12 mol), and benzoyl peroxide (0.4 g) in CCl_4 (250 mL) was refluxed overnight. The cooled solution was filtered and the solid washed with CCl_4. The organic phases were combined and the CCl_4 removed on a rotary evaporator to yield 23 g of crude (α,α-dibromotolyl)-α-trimethylsilane. A mixture of crude (α,α-dibromotolyl)-α-trimethylsilane (16 g, 0.05 mol), silver acetate (16.8 g, 0.1 mol), ethanol (200 mL), acetone (150 mL), and water (70 mL) was stirred at room temperature overnight. The silver salts were removed by filtration and most of the acetone and ethanol removed by evaporation. The remaining mixture was dissolved in petroleum ether and washed several times with water and finally with brine. After drying (Na_2SO_4), the solvent was removed to give 7.5 g of a yellow oil. Distillation (64–66 °C (1 mmHg)) yielded pure **13** (6.0 g, 68% yield).

Methylphenyl(trimethylsilyl)methanol (7). To a solution of phenyl trimethylsilyl ketone (**13**) (1 g, 5.6 mmol) in ether at −78 °C was added methyllithium (5.8 mmol). The mixture was stirred at −78 °C for 2 h, allowed to warm to room temperature, and stirred overnight. The mixture was cooled (0 °C), quenched with water (3 mL), decanted, and dried over Na_2SO_4. Removal of the ether in vacuo at room temperature yielded a colorless oil which ^{1}H NMR, ^{13}C NMR, and IR analysis indicated to be pure **7**.

Dimethyl(trimethylsilyl)methanol (10) was prepared from **11** by the same procedure used for the synthesis of **7**.

((Trimethylsilyl)ethynyl)methanols 16a–f. Methyllithium (12 mmol) was added to an etheral solution of (trimethylsilyl)acetylene (1.47 g, 15 mmol) at 0 °C. After being stirred for 2 h at room temperature, 10 mmol of the corresponding ketone was added dropwise. The mixture was stirred overnight after which water (3 mL) was added. After being decanted and dried, the ether solution was concentrated under reduced pressure. The product was pure alcohol as shown by IR and NMR analysis. Alcohols **18a–c** were prepared similar to **16a–c** with *tert*-butylacetylene.

Preparation of Carbocations. A solution or slurry of the appropriate precursor in SO_2ClF or SO_2 was added to a twofold excess of FSO_3H or SbF_5 in SO_2ClF or SO_2 at −78 °C or −140 °C to give approximately a 10 to 15% solution of the ion.

The **^{13}C and ^{29}Si NMR spectra** were determined with a Varian Associates Model FT-80 NMR Spectrometer equipped with a broadband

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(31) (a) C. Eaborn and R. W. Bott in "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, A. G. MacDiarmid, Ed., Marcel Dekker, New York, 1968, p 464; (b) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715–5725 (1971).

(32) R. K. Harris, J. D. Kennedy, and W. McFarlane, "NMR and the Periodic Table", R. K. Harris and B. E. Mann, Eds., Academic Press, New York, 1978.

(33) C. R. Ernst, L. Spialter, G. R. Buell, and D. L. White, *J. Am. Chem. Soc.*, 96, 5375–5381 (1974).

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(36) A. G. Brook, J. M. Duff, P. F. Jones, and N. R. Davis, *J. Am. Chem. Soc.*, **89**, 431–434 (1967); E. J. Corey, D. Seebach, and R. Freedman, *ibid.*, **89**, 434–436 (1967).

variable temperature probe. The chemical shifts were referenced to external tetramethylsilane.

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Registry No. 1, 17964-42-0; **2**, 80515-45-3; **3**, 80515-46-4; **4**, 17922-21-3; **5**, 30274-47-6; **7**, 53173-00-5; **10**, 40965-54-6; **12**, 13411-48-8; **13**, 5908-41-8; **14**, 80515-47-5; **15**, 80515-48-6; **16a**, 73502-43-9; **16b**, 80515-49-7; **16c**, 5272-33-3; **16d**, 80515-50-0; **17a**, 80515-51-1; **17b**, 80515-52-2; **17c**, 80515-53-3; **17d**, 80532-00-9; **18a**, 80515-54-4; **18b**, 80515-55-5; **18c**, 80515-56-6; **19a**, 38252-96-9; **19b**, 80515-57-7; 19c, 53474-96-7; **19d**, 80515-58-8; benzyltrimethylsilane, 770-09-2; (α,α-dibromotolyl)-α-trimethylsilane, 17921-71-0; (trimethylsilyl)acetylene, 1066-54-2; *tert*-butylacetylene, 917-92-0; $CH_3C(O)CMe_3$, 75-97-8; $CH_3C(OH^+)CMe_3$, 68706-39-8; $PhC(O)CMe_3$, 938-16-9; $PhC(OH^+)CMe_3$, 80515-59-9.

Structures of the 1:1 Complexes of 18-Crown-6 with Hydrazinium Perchlorate, Hydroxylammonium Perchlorate, and Methylammonium Perchlorate

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Abstract: The structures of the crystalline 1:1 complexes of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) with hydrazinium perchlorate, hydroxylammonium perchlorate, and methylammonium perchlorate have been determined by X-ray diffractometry. The first two structures were determined at 115 K, the last at 296 K. The hydrazinium complex (**1**) has space group $Pn2_1a$, with a = 14.567 (3) Å, b = 13.652 (2) Å, c = 9.244 (2) Å, and Z = 4. The hydroxylammonium complex (**2**), which crystallizes as a hemihydrate, has space group $C2/c$, with a = 19.410 (5) Å, b = 10.231 (3) Å, c = 21.321 (5) Å, β = 116.71°, and Z = 8. The methylammonium complex (**3**) has space group $C2/c$, with a = 24.518 (4) Å, b = 8.594 (2) Å, c = 21.447 (4), β = 117.04 (1)°, and Z = 8. Each structure was solved by direct methods and refined by full-matrix least squares. The radiation used, number of unique reflections, and final value of R are: for **1**, Mo Kα, 4198, 0.057; for **2**, Mo Kα, 6898, 0.066; for **3**, Cu Kα, 3590, 0.086. The perchlorate ion in room-temperature structure **3** exhibits apparent high-amplitude librational motion. The macrocycle in each of these structures is in the ideal crown conformation, with all C–C bonds gauche and all C–O bonds trans. The hydrazinium complex, **1**, is unique among complexes of crowns with ammonium and substituted ammonium ions in that the $-NH_3^+$ nitrogen atom lies close to the median plane of the six oxygen atoms of the crown ring, in a nesting position just 0.11 Å from this plane. It is hydrogen bonded to the *lower* triangle of oxygen atoms; the $-NH_2$ group is hydrogen bonded in turn to two oxygen atoms of the *upper* triangle in the host, one of these bonds being weakly bifurcated, involving a perchlorate oxygen atom as well. The assertion that the diameter of NH_4^+ is too large to permit this ion to be in a nesting position in a complex is clearly incorrect; the depth of penetration of an ammonium or substituted ammonium ion appears to depend on the relative strengths of the ion's interactions within and external to the complex. In the hydroxylammonium complex, **2**, the nitrogen of the $-NH_3^+$ group lies 0.68 Å from the plane of the oxygens of the crown ring; the hydrogen atoms of this $-NH_3^+$ group are involved in bifurcated hydrogen bonds, each to two adjacent oxygen atoms of the crown ring. The hydroxyl group of the hydroxylammonium ion is hydrogen bonded to a water molecule that lies on a twofold axis; the water molecule is in turn hydrogen bonded to two perchlorate ions. The nitrogen atom of the $-NH_3^+$ group in **3** lies 0.83 Å above the plane of the six oxygens of the crown ring, with the $-NH_3^+$ group perching on the upper triangle of oxygen atoms. In structures **1** and **2**, for which atomic vibrational parameters could be measured with fair precision, the 18-crown-6 ring is rigid and holds the $-NH_3^+$ group quite firmly. The atoms attached to the $-NH_3^+$ group undergo considerably greater motion, in directions predictable from their patterns of hydrogen bonding. It appears that in structures of this kind the orientation of the $N^+ \cdots O$ line relative to the tetrahedral and trigonal directions at each C–O–C group of a crown ring is governed primarily by the depth of penetration of the $-NH_3^+$ into the ring, irrespective of the disposition of hydrogen bonds to the ring oxygen atoms.

The structures of many complexes of crown ethers with ammonium ion and substituted ammonium ions have been reported.[1] All so far described have the $-NH_3^+$ group in the *perching*[2] position, about 1 Å out of the best plane of the oxygen atoms of the crown ring, rather than in the *nesting*[2] position, essentially in the plane and encircled by the crown ring. For example, in the crystalline complex of ammonium bromide with 18-crown-6 (which has also two molecules of water per formula unit),[1a] the ammonium ion is 1.0 Å above the best plane of the six oxygens of the crown ring. In contrast, in the crystalline complex[3] of potassium thiocyanate with 18-crown-6, the potassium ion lies at the center of the crown ring, in the ideal nesting position. These findings have been widely interpreted as a consequence of the relative diameters of potassium ion (about 1.33 Å) and ammonium ion (1.48 Å), the latter almost the same as that of rubidium ion, which perches[4] about 1.19 Å out of the plane of 18-crown-6.

Studies of complexes of diammonium ions with crown ethers have been reported by several groups,[5,6] but attempts to prepare

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