Continued Search for Elusive Persistent Trivalent Organosilyl Cations: The Claimed Trimethylsilyl Cation Revisited. Attempted Preparation of Cyclic and Halogen-Bridged Organosilicenium Ions[1]

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Abstract: Comparison of ab initio/IGLO calculated ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts with the experimental data on trimethylsilyl perchlorate and related derivatives supports the conclusion that no long-lived persistent trimethylsilicenium ion has been observed in solution. Attempts were made to prepare 5-methyl-5*H*-dibenzo[*b,f*]silepinium ion to probe whether cyclic aromatically stabilized silicenium could be prepared under stable ion conditions. The attempts were unsuccessful, and the related perchlorate was found to be a covalent compound. Similarly the products of hydride abstraction of 1-methyl- and 1-phenyl-substituted tetraphenylsilole were also found to be covalent perchlorates in contrast to a reported study wherein ionization was claimed. Both silepinium and silole perchlorates are covalent in nature with no manifestation of aromatic and antiaromatic character, respectively, indicating very little Si–O bond polarization. Attempted preparation of sila-substituted cyclic halonium ions resulted only in donor–acceptor complex formation and decomposition. In the case of the (bromomethylsilyl)diphenylcarbenium ion, there is little indication of bromine bridging.

Introduction

A recent paper[2] reiterated claims of having observed persistent trimethylsilyl and related cations by generating related perchlorates in solvents such as sulfolane and dichloromethane under high dilution, despite our previous report in which we were unable to substantiate these claims. They are also in contrast to the recent observation by Eaborn that sterically hindered $(Me_3Si)_3CSiMe_2OClO_3$ undergoes solvolysis fairly slowly in CH_3OH and much more so in highly ionizing CF_3CH_2OH solvent. If, as claimed,[2] organosilyl perchlorates were, indeed, ionized to any detectable extent in solvents such as dichloromethane or sulfolane, it seems highly improbable that $(Me_3Si)_3CSiMe_2OClO_3$ would not be significantly ionized in highly ionizing solvents such as CH_3OH and CF_3CH_2OH.[4a] Eaborn strongly cautioned[4a] against accepting ionic nature of organosilyl perchlorates.

Kira and Sakurai have recently[4b] attempted to obtain free silicenium ions by hydride abstraction of trialkylsilanes using trityl tetrakis[bis-3,5-(trifluoromethyl)phenyl)]borate in dichloromethane solution. In the presence of bases such as ethers, acetonitrile, and ketones, the corresponding silylated onium ions were observed. However, in the absence of any base, no long-lived free silicenium ions were obtained. The corresponding silyl perchlorates did not show any significant interaction with these weak bases under similar conditions in accordance with their covalent nature. Similarly, silylated nitrilium ions were also observed by Bahr and Boudjouk[4c] using the same hydride abstracting conditions, but no free silicenium ions were obtained.

In our further searching for elusive persistent trivalent organosilyl cations, we have investigated the claimed trimethylsilyl cation by ab initio/IGLO methods and report our attempts to prepare cyclic and halogen-bridged silicenium cations.

Results and Discussion

Ab Initio/IGLO Investigations. In order to settle the question whether trialkyl(aryl)silyl perchlorates, $R_3SiOClO_3$, ionize in solvents such as dichloromethane and sulfolane to give persistent silyl cations, we report the results of comparing experimental values with calculated ab initio/IGLO ^{1}H, ^{13}C, and ^{29}Si NMR chemical shifts (using the methods[5] developed by Kutzelnigg and Schindler) of the trimethylsilyl cation, $(CH_3)_3Si^+$ (**9**), as well as its related covalent derivatives **1**–**8**. Kutzelnigg and Schindler were the first to apply IGLO calculations on silicon compounds to obtain ^{29}Si NMR shifts.[6] They have investigated compounds such as $(CH_3)_4Si$, $(CH_3)_3SiH$, Si_2H_6, etc. Although the obtained ^{29}Si NMR shifts compare very well with the experimental results, the source of structural parameters used was not described. Kutzelnigg and Schindler have also reported preliminary results on H_3Si^+ as well as $(CH_3)_3Si^+$. For the trimethylsilyl cation they obtained a chemical shift of $\delta(^{29}Si)$ 351. The level of theory used to calculate the structural parameters was not discussed. As IGLO-calculated NMR chemical shifts are influenced by structural parameters (demonstrated many times by Kutzelnigg and Schindler), the level of ab initio theory used is critical. We now report IGLO-calculated ^{29}Si, ^{13}C, and ^{1}H NMR chemical shifts determined using high level ab initio geometries for a series of organosilicon compounds as well as the controversial trimethylsilyl cation and their comparison to the available experimental results.

All the geometries were optimized at the HF/6-31G* level except for trimethylsilyl perchlorate (**8**) which was minimized at the HF/3-21G* level of theory. IGLO basis set II was used for HF/6-31G* geometries and II′ for the 3-21G* structure. The basis set II differs from II′ in that II′ does not have a p-orbital with an exponent of 0.7 on the hydrogen atoms. Therefore, we could not calculate ^{1}H NMR chemical shifts of **8** at the IGLO II basis level due to the large number of basis sets involved in the calculation. The theoretically calculated and experimentally observed ^{1}H, ^{13}C and ^{29}Si NMR shifts of a series of silyl derivatives (**1**–**9**) are listed in Table I. The Cartesian coordinates of the silyl

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[1] Organometallic Chemistry. 24. For 23, see ref 3b. Presented in part at the 25th Silicon Symposium, Los Angeles. April, 1992.

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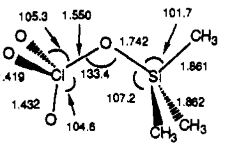
Table I. ^{29}Si, ^{13}C, and ^{1}H NMR Chemical Shifts (ppm from TMS)

compound	sym	atom	II//HF/ 6-31G*	exptl
1 $(CH_4)_4Si^a$	T_d	Si	0.0	0.0
		C	0.0	0.0
		H	0.0	0.0
2 SiH_3SiH_3	D_{3d}	Si	−106.5	-104.8^b
		H	3.45	
3 H_3Si^-	C_{3v}	Si	−165.9	-165.0^c
		H	1.29	1.17^c
4 SiH_3CH_3	C_{3v}	Si	−66.7	-65.2^b
		C	−9.2	
		H(Si)	0.12	0.06^d
		H(C)	3.84	3.49^d
5 $(CH_3)_3SiH$	C_{3v}	Si	−16.6	$-16.3,^e -17.5^f$
		C	−2.2	$-2.6,^f -2.65^e$
		H(Si)	4.27	3.91^g
		H(C)	0.05	0.09^g
6 $(CH_3)_3SiOCH_3$	C_s	Si	12.2	17.0^h
		$C(CH_3Si)$	−0.7	-1.7^h
		$C(OCH_3)$	48.3	49.0^h
		$H(CH_3Si)$	0.05	0.07^i
		$H(OCH_3)$	3.18	3.35^i
7 $(CH_3)_3SiF$	C_{3v}	Si	27.1	30.5^e
		C	−0.1	-0.3^e
		H	0.18	0.20^i
8 $(CH_3)_3SiOClO_4{}^j$	C_s	Si	40.2	$43.4,^k 47.0^l$
		C	−0.2	$-0.55-0.3^g$
9 $(CH_3)_3Si^+$	C_{3h}	Si	355.7	
		C	9.0	
		H	1.79	

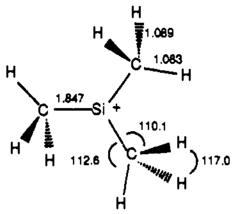
[a] Calculated IGLO chemical shifts of TMS at II//6-31G* level are $^{29}Si = 4.83$, $^{13}C = 6.01$, and $^{1}H = 0.90$ from internal IGLO TMS reference. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 14. [f] Reference 15. [g] Reference 2. [h] Reference 16. [i] Reference 17. [j] At II′//3-21G* level. [k] Reference 18. [l] Reference 3b.

derivatives **1–9** are in the supplementary material.

Disilane (**2**), with its D_{3d} symmetry, shows excellent correlation between IGLO-calculated and experimental ^{29}Si NMR chemical shifts. The obtained result is better than that earlier reported.[6] Similarly, trimethylsilane (**5**) shows good correlation of ^{29}Si, ^{1}H, and ^{13}C NMR chemical shifts. Trimethylsilyl perchlorate (**8**) with C_s symmetry, at the II′//HF/3-21G* level also shows excellent agreement with the experimental ^{29}Si and ^{13}C NMR chemical shifts[3a] as do silyl anion (**3**), methylsilane (**4**), trimethylsilane (**5**), methoxytrimethylsilane (**6**), and fluorotrimethylsilane (**7**). Such excellent correlations give confidence in calculating the chemical shifts of the trimethylsilyl cation (**9**). At HF/6-31G* the minimum structure was found to be of C_{3h} symmetry. The calculated ^{29}Si NMR chemical shift is $\delta(^{29}Si)$ 355.7 (from TMS), a highly deshielded absorption. The calculated ^{13}C and ^{1}H NMR shifts are $\delta(^{13}C)$ 9.0 and $\delta(^{1}H)$ 1.79, respectively.



8 (C_s)



9 (C_{3h})

The reported[2] ^{1}H NMR chemical shifts of trimethylsilyl perchlorate in methylene chloride or sulfolane at various dilutions where ionization was claimed range from $\delta(^{1}H)$ 0.494 to 0.503. The ^{13}C NMR chemical shifts range upon 27-fold dilution from $\delta(^{13}C)$ −0.55 to −0.3. These changes are insignificant and do not substantiate the formation of the claimed persistent trimethylsilicenium ion. In fact, the observed ^{13}C NMR shifts at various concentrations in sulfolane–CD_2Cl_2 (0.27–0.01 M) correspond closely to the calculated IGLO ^{13}C NMR chemical shift of $\delta(^{13}C)$ −0.2 of the covalent trimethylsilyl perchlorate. To further probe the reliability of the theoretical calculations, we plotted experimental ^{29}Si NMR chemical shifts with the IGLO-calculated ones, and the obtained correlation is excellent with a correlation coefficient of 1.

$^{35/37}Cl$ NMR experiments have also been used to support the ionic character of trimethylsilyl perchlorate.[7] It was claimed[7] that at 0.584, 0.29, and 0.15 M concentrations of trimethylsilyl perchlorate in sulfolane, 20%, 29%, and 35% free ion was found to be present, respectively. Earlier[3a] we were able to obtain ^{29}Si NMR spectra at these same concentration ranges but found only the unchanged identical signal of the covalent perchlorate at $\delta(^{29}Si)$ 47.0. Considering the IGLO-calculated chemical shift of $\delta(^{29}Si)$ 355.7 for the trimethylsilyl cation, we can compute the following averaged ^{29}Si NMR chemical shifts for the equilibria: the 20% ionic system should have an average chemical shift of $\delta(^{29}Si)$ 108.7, the 29% ionic system $\delta(^{29}Si)$ 136.5, and the 35% system $\delta(^{29}Si)$ 155.0. These are fundamentally different from the experimentally obtained ^{29}Si NMR shift of $\delta(^{29}Si)$ 47.0 (corresponding to covalent trimethylsilyl perchlorate). The IGLO-calculated NMR shifts and their comparison to experimental results fully support the conclusion that no persistent trimethylsilicenium ions were observed in solution, contrary to repeated claims.[2]

Support for the claimed ionic nature of trialkyl(aryl)silicenium ions by conductivity and cryoscopic measurements[2] must be considered with caution. Rochow and Thomas pointed out 35 years ago[8] that in their conductometric studies of various triarylsilyl chlorides in stringently dried acetonitrile, inevitably present traces of water always accounted for the observed conductivities. The work[7] covered a concentration range from 1×10^{-4} to 2×10^{-3} M, similar to the range used in the disputed studies.[2,7,9,10] Whereas these earlier studies initially[7,9,10] claimed strictly anhydrous nonhydrolyzing conditions, the most recent paper[2] reported limited, but NMR detectable, hydrolysis (in accord with our preceding report to this effect[3b]). Rochow's caution[8] thus remains valid.

Present ab initio/IGLO ^{13}C, ^{1}H, and ^{29}Si NMR chemical shifts calculations and their comparison with the experimental data clearly show that no persistent trimethylsilyl cations were observed as the perchlorate salt in solution. In extremely dilute solutions a very limited ionization equilibrium may be possible but is difficult to prove (or disprove). Care is necessary in interpreting conductivity and cryoscopic data obtained under conditions where some hydrolysis was shown to be inevitable. It is improbable that highly electron deficient and thus reactive simple alkyl(aryl)-silicenium ion could persist in appreciable concentration in any of the so far reported systems as long-lived stable ions.

Attempted Preparation of Cyclic Organosilicenium Ions. In 1975, Corey reported the generation of 1-((dimethylamino)-phenyl)-1-siladibenzodihydrotropylium ion by the hydride transfer reaction of the corresponding silane with ionic trityl perchlorate. Subsequently such compounds were shown to be covalent in nature.[22b] An alternative possibility for the preparation of persistent silicenium ions is charge delocalization from the developing sil-

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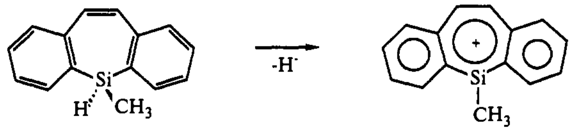
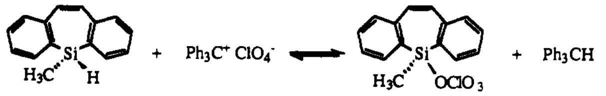
icenium center into an aromatic ring system. Recently Beauchamp et al.[22c] indicated formation of silacycloheptatrienyl and phenylsilyl cations by electron impact ionization of phenylsilane. Their studies also concluded that the silacycloheptatrienyl cation was relatively more stable than the phenylsilyl cation in the gas phase.



10 **11**

Consequently, 5-methyl-5*H*-dibenzo[*b*,*f*]silepinium ion (**11**) was considered conceivably capable of such charge delocalization in solution, analogous to the dibenzotropylium ion.

When 5-methyl-5*H*-dibenzo[*b*,*f*]silepin, (**10**) was reacted with trityl chloride/SbF_5 in SO_2ClF at −78 °C, the ^1H, ^{13}C, and ^{29}Si NMR spectra obtained did not indicate ionization to **11**. The ^1H and the ^{13}C NMR spectra were not consistent with **11** and showed multiple absorptions indicative of decomposition and silyl fluoride formation. No deshielded ^{29}Si NMR signal could be observed, indicating the absence of any resonance-stabilized silicenium ions. When an equimolar amount of **10** was reacted with trityl perchlorate as hydride abstractor in acetonitrile solution, no decomposition occurred, but the reaction resulted only in incomplete transformation to the corresponding perchlorate. This could either mean that the hydride abstraction is slow with **10** or that the corresponding silyl perchlorate **12** is in equilibrium.



10 **12**

The initial appearance of brown coloration upon addition of **10** to a solution of trityl perchlorate in CH_3CN which fades to the original yellow-orange color while vortexing the mixture suggests an initial hydride abstraction reaction which then reverses due to an equilibrium. After an equimolar amount of silepin **10** is added to the solution of trityl perchlorate, the ^{13}C and ^{29}Si NMR spectra show resonances only for the starting materials along with a very small amount of Ph_3CH formed as evidenced by ^1H NMR signal at δ 5.2. For this reversibility to occur, ion **11** or, more likely, the CH_3CN-complexed **11** must not be quenched immediately by perchlorate anion upon its formation but should have some lifetime under the reaction conditions. After addition of another 2 equiv of trityl perchlorate, the methyl doublet of **10** in the ^1H NMR spectrum completely disappears and is replaced by a singlet resonance at +0.4 ppm. The ^{29}Si and ^{13}C NMR data confirm the formation of a covalent silyl perchlorate (**12**) with peaks at $\delta(^{13}C)$ −4.5 for the Si–CH_3 (q, $^1J_{CH}$ = 124 Hz) and $\delta(^{29}Si)$ 23 ($\Delta\delta$ ^{29}Si) 40, compared to its progenitor), respectively. The ^{13}C NMR shifts of the aromatic region, however, could not be assigned unequivocally due to considerable overlap of the aromatic absorptions.

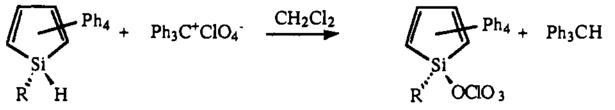
In an attempt to trap the intermediate responsible for the initial brown coloration, which could potentially be silicenium ion **11**, we restudied the reaction in a 1:3 SO_2/SO_2ClF solvent mixture which is less nucleophilic than CH_3CN and allows for low temperature recording of the NMR spectra where otherwise unstable intermediates frequently can be detected.[19] Indeed, when a 2-fold excess of trityl perchlorate and **10** was mixed in SO_2/SO_2ClF at −78 °C, the brown coloration persisted and the ^1H NMR spectrum proved formation of triphenylmethane and absence of unreacted **10**. The ^{13}C NMR data and the lack of a deshielded ^{29}Si signal, however, clearly demonstrated that decomposition had occurred, analogous to the reaction of **10** under stable ion conditions, proving again that persistent silicenium ions cannot be observed in solution.

Table II. ^1H, ^{13}C, and ^{29}Si NMR Data on Potentially Aromatic, Antiaromatic, and Nonaromatic Organosilyl Perchlorates

substrate	$\delta(^1H)$ (CH_3)	$\delta(^{13}C)$ (CH_3)	$\delta(^{29}Si)$
12	0.4	−4.5	23
15	−0.2	−5.2	22.8
16			3.8
$Ph_3SiOClO_3$			3

From these results, it is difficult to discern whether a potentially stabilized aromatic system is formed upon ionization of **10** to **11**, i.e., whether 2p–3p delocalization in **11** could be detected by a change of charge density around the silicon atom relative to a similar system without aromatic stabilization. There are no silicenium ions known for comparison, but certain trends should be observed even without full ionization to a silicenium ion. It is well recognized that tropone (cycloheptatrienone), a naturally abundant compound, can be considered as having some aromatic character as an uncharged model of the tropylium ion by virtue of its polarized carbonyl carbon. In contrast, cyclopentadienone, a neutral model of the antiaromatic cyclopentadienyl cation, is sufficiently destabilized that it has not yet been prepared.[20] By analogy, the more polar the Si–X bond in an organosilyl derivative whose projected sp^2-hybridized silicon atom would be part of an aromatic (or antiaromatic) ring system, the more pronounced the aromatic (or antiaromatic) character should become.[20] Therefore, potentially aromatic silyl perchlorates could serve as analogues for the elusive silicenium ions in solution, since they represent well-characterized, stable compounds with high Si–X bond polarity. If there were indeed a noticeable aromatic contribution, then the positively polarized ^{29}Si nucleus in the corresponding perchlorate **12**, as a model for the "aromatic" silicenium ion **11**, should be more shielded than a silicon nucleus in an analogous system with nonaromatic or even antiaromatic character, provided these compounds are of comparable stability.

We also reinvestigated the possible ionization of 1-methyl- and 1-phenyl-substituted 2,3,4,5-tetraphenylsilole,[21] (**13** and **14**) by subjecting them to hydride abstraction with trityl perchlorate in CH_2Cl_2 and recorded the ^1H, ^{13}C, and ^{29}Si NMR spectra of the obtained perchlorates, **15** and **16**. These were found to be covalent perchlorates in contrast to claims[9e] that these perchlorates are persistent silicenium ions. Table II summarizes the relevant NMR data of the four perchlorates.



13 R=CH3 **15** R=CH3

14 R=Ph **16** R=Ph

The ^{29}Si chemical shifts of **12** and **15** are almost identical, even though the former should be noticeably shielded from the latter if some aromatic delocalization were to contribute. The near conformity of the ^{13}C chemical shift of the methyl group adjacent to the positively polarized silicon confirms the conclusion that both perchlorates have very similar electronic environments about the silicon center, i.e., the degree of covalency and Si–$OClO_3$ bond polarization is nearly identical, negating any aromatic–antiaromatic contribution. Similarly, the ^{29}Si resonance of **16** closely resembles the ^{29}Si chemical shift of $Ph_3SiOClO_3$,[3b] the latter having neither aromatic nor antiaromatic character. Similar trends have been observed in the gas phase as well.[22d] When we com-

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(19) For a comprehensive review, see: Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 19. Also see: Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley Interscience: New York, 1985.

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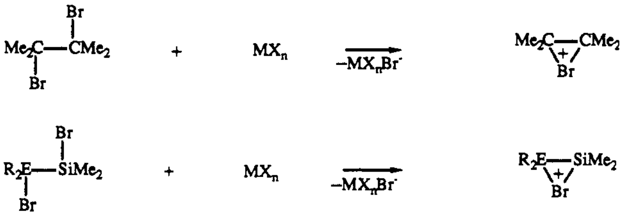
pared the fragmentation pattern in the mass spectra of 5,5-dimethyl-5*H*-dibenzo[*b,f*]silepin and its 10,11-dihydro analogue via their respective P-15 peak, i.e. "aromatic" versus "nonaromatic" silicenium ion peak, no augmented stability for the potentially aromatic system was observed as both the appearance potential and relative abundance of the P-15 peak were nearly identical.[22d] Also, theoretical calculations on silacyclopropenium ion indicate no aromatic stabilization.[22e] However, these results contrast recent gas-phase studies on silacycloheptatrienyl cation.[22c]

From our studies, it can be concluded that silicenium ions are not stabilized in solution by incorporation of the silicon atom into a potentially aromatic ring system in contrast to their carbon analogues. In solution the weak 2p–3p interaction is not sufficiently stabilizing (if present at all) to preclude quenching of the potential cation by its gegenion or its decomposition whenever quenching is circumvented. In the gas phase, where silicenium ions are stable, they appear to have no tendency to prefer incorporation into aromatic over nonaromatic ring structures with the exception of recent results found by Beauchamp.[22c] On similar grounds, silicenium ions are not further destabilized by incorporation of the silicon into an antiaromatic system. Covalent polar organosilyl perchlorates, chosen to model the elusive silicenium ions in solution, display no change in their electronic environment about silicon whether in potentially aromatic or potentially antiaromatic ring structures but show electronic characteristics nearly identical to those of their cyclic analogues.

Attempted Preparation of Sila-Substituted Cyclic Organohalonium Ions. Based on the well-recognized ability of halogens (Cl, Br, and I) with the exception of fluorine to engage in charge delocalization through bridging to neighboring carbocation centers to form cyclic halonium ions,[23] we also investigated ionizations of various model α,β-bromoalkylsilanes for possible formation of α-silabromonium ions.



E = C, Si R = Me, Ph M = Al, Sb, X = Br, Cl, F

17: R=Me, E=C **19**: R=Ph, E=C

18: R=Me, E=Si **21**: R=Ph, E=Si

Table III summarizes the results of the systems studied. The data reveal some interesting trends. $AlBr_3$ in saturated CH_2Br_2 solutions has virtually no effect on the ^{13}C and ^{29}Si chemical shifts of the precursors relative to solutions examined in the absence of $AlBr_3$. The dimethylsilyl bromide group must therefore exercise a destabilizing effect on a potential carbocationic center, since the *tert*-butyl cation (with a methyl substituent in place of the silyl group) is well-characterized under these conditions.[24a] A similar destabilizing effect of a trimethylsilyl group has been earlier demonstrated by Apeloig and Stanger in solvolysis reactions.[24b] Using less nucleophilic solvents (SO_2 or SO_2ClF) to enhance the acidity of the Lewis acid resulted in halogen exchange and/or decomposition as exemplified by the reaction of **18** with $SbCl_5$ in SO_2, giving trimethylsilyl chloride ($\delta(^{29}Si)$ 34). The only substrate which ionized cleanly and to an identifiable silylated carbocation was **19** in $AlBr_3/SO_2ClF$.

$$\mathrm{BrPh_2C\text{-}SiMe_2Br} + \mathrm{AlBr_3} \xrightarrow[-78^\circ C]{SO_2ClF} \mathrm{Ph_2\overset{+}{C}\text{-}SiMe_2Br} + \mathrm{AlBr_4^-}$$

19 **20**

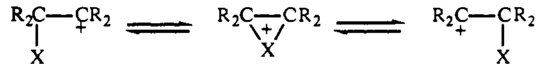
Table III. ^{13}C and ^{29}Si NMR Data of Silahalonium Ion Precursors and Their Ionization Procedures with Different Lewis Acids

substrate	Lewis acid	solvent	*T* (°C)	$\delta(^{13}C)$	$\delta(^{29}Si)$
17		SO_2ClF	−20	−1 (Si–CH_3); 28(C–CH_3); 53(–Br)	25
	$AlBr_3$	SO_2ClF	−78	dec	
	SbF_5	SO_2ClF	−78	dec	
	$AlBr_3$	CH_2Br_2	−30	not recorded	22
18		CH_2Br_2	rt[a]	0.8	12
	$AlBr_3$	CH_2Br_2	−30	0.8	16
	$SbCl_5$	SO_2	−50	6	34
	SbF_5	SO_2ClF	−79	dec	
19		CCl_4	rt	3.5 (CH_3); 66.1 (C–Br); 142.4 (i); 130 (m); 127.5 (o); 127.3 (p)	14
	SbF_5	SO_2ClF	−78	dec	
20	$AlBr_3$	SO_2ClF	−78	4.2 (CH_3); 238 (C^+); 145.7 (i); 131.1 (m); 142.4 (o); 147.5 (p)	13.5
21		CCl_4	rt	132.2 (i); 127.9 (m); 134.8 (o); 130.4 (p)	
		SO_2ClF	−78	insoluble/dec	
	SbF_5	SO_2ClF	−78	dec	
22	HSO_3F	SO_2ClF	−78	1.9 (CH_3); 259 (C^+); 148.5 (i); 131.5 (m); 141.8 (o); 147.4 (p)	5.4

[a] Room temperature.

By comparing **20** with previously studied[25] diphenyltrimethylsilylmethyl cation **22** as an analogue without possible halogen participation, we found that bromine bound to silicon accounts for a 21 ppm shielding of the ^{13}C NMR signal of the cationic center. The effect on the α-silicon should be best ascertained by the ^{29}Si chemical shift changes occurring upon the ionization of the respective progenitor alcohol and bromide. Surprisingly though, in neither case does the cationic center in a position α to the silicon affect any apparent change of the ^{29}Si resonance (0.7 versus −0.5 ppm). Taking the para carbon chemical shift as an indicator of positive charge delocalization into the phenyl ring system, nearly identical shifts for both ions seem to suggest equal resonance stabilization provided by the phenyl rings. The methyl substituents on silicon, however, experience a 4.2 ppm deshielding effect upon ionization of the alcohol, whereas the methyl groups of the bromide precursor are deshielded by only 0.7 ppm upon ionization. These observations can be best explained by assuming that whatever inductive electron withdrawal silicon experiences by the generation of positive charge at the α position, the methyl groups compensate by inductive electron release to the silicon. Replacement of one methyl by a bromine substituent β to the charged center yields a charge stabilizing effect for the cationic carbon as well as for the silicon in the α position, manifested in the conformity of the methyl and the silicon resonances upon ionization in addition to the net shielding effect on the cationic center compared to ion **22**. The magnitude of this stabilization is small compared to that of carbon analogues which form symmetrically bridged bromonium ions where the positive charge is truly delocalized between two carbons and the bridging bromine.

The overall ^{13}C chemical shift shielding effect of symmetrically σ delocalized ions, however, is critically dependent on the substitution on the three-membered ring structure.[23] Increasing methyl substitution decreases the halogen involvement in stabilizing the charge, and consequently the carbenium ion character becomes more pronounced, eventually leading to an averaged signal for the rapidly equilibrating open ions.



R = alkyl

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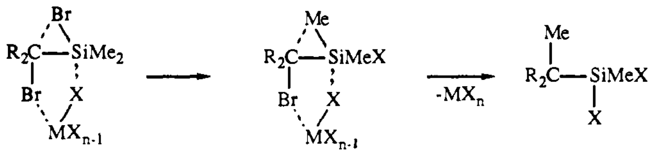
The net chemical shift shielding effect on these rapidly interconverting ions arises from the change in hybridization at the carbons (sp^2 to sp^3) during the transition from the open form to the σ-bridged one. In the limiting cast of a static ion versus a symmetrically bridged structure, this difference amounts to as much as 80 ppm as exemplified by the ^{13}C NMR chemical shift data of the tetramethylethylene chloronium ion which show a total ^{13}C shielding effect of roughly 80 ppm compared to the projected open static ion.

For cation **20**, any equilibration is excluded by virtue of the high field ^{29}Si chemical shift and the conformity of the para carbon ^{13}C signal for both ions **20** and **22**, the latter necessarily being static. Rather, cation **20** experiences an additional charge delocalization by $4p\pi \rightarrow 2p\pi$ donation from the bromine to the cationic center made possible by the proximity and polarizability of the large bromine substituent in the β position. Since no other α-(halodimethylsilyl)carbenium ions could be observed under any circumstances, the stability of **20** is solely attributed to the intrinsic ability of aryl substituents to delocalize charge into the ring structure commonly depicted by quinoidal resonance structures.

Where such or similar stabilization is lacking, the developing carbocationic center induces methyl or halide migration from silicon to carbon while the silicon is nucleophilically attacked by the counterion of the Lewis acid system as indicated below.



These migrations have been noted in the past, known as the Whitmore rearrangement, under Friedel–Crafts conditions[26] and may be considered analogous to the Wagner–Meerwein rearrangement.[27] Indeed, they seem to be predominant whenever fluorine-containing Lewis acids are employed. Usually, the reactions do not cease after incorporation of one fluorine atom but proceed by further fluorine–methyl exchange at the silicon center and/or protolytic cleavage of a Si–C bond by protic traces in the Lewis acid.

In conclusion, bromine substitution neighboring silicon does not allow for stabilization of a cationic center by means of bridged bromonium ion formation, such as is commonly observed for the analogous carbon compounds. Any significant electron deficiency built up at silicon results in abstracting a fluoride (or chloride) ion from the Lewis acid employed to polarize the leaving group at the α-carbon rather than forming a bridged halonium ion.

Conclusions

Comparison of ab initio/IGLO ^{29}Si, ^{13}C, and ^{1}H NMR chemical shift calculations with experimentally reported data on the purported trimethylsilyl cation shows that no such long-lived ion has been obtained in solution. Attempts to prepare cyclic aromatic and antiaromatic organosilicenium ions as well as halogen-bridged organosilyl cations also were unsuccessful. All attempts to observe long-lived trivalent trialkyl(aryl)organosilyl cations in solution by NMR spectroscopy have failed. Extreme care is needed in interpreting conductivity and cryoscopy data under conditions where some hydrolysis was shown inevitable. The observation of persistent trivalent silyl cations in solution would necessitate finding new extremely low nucleophilicity systems which would not interact with free silicenium ions. As stated previously, stable ion conditions used for carbocations are not suitable for preparing persistent organosilyl cations in solution because of the very high affinity of Si^+ toward oxygen and fluorine, which are generally present in these systems.

Experimental Part

Method, Basis Set, and Geometry. Geometries of the compounds were optimized at the HF/6-31G* level (except trimethylsilyl perchlorate (**8**), which was minimized at the HF/3-21G* level) by using the GAUSSIAN-86[28] series of programs on an Alliant FX/40 computer. IGLO calculations were performed according to the reported method.[5b] Huzinaga[29] Gaussian lobes were used as follows: basis II for C, O, or F, 9s 5p 1d contracted to [51111, 2111, 1], *d* exponent = 1.0; for Si or Cl, 11s 7p 2d contracted to [5111111, 211111, 11], *d* exponent = 1.4 and 0.35; and for H, 5s 1p contracted to [311, 1], *p* exponent = 0.70; basis II′ for C or O, same as basis II; for Si or Cl, same as basis II; and for H, 3s contracted to [21].

Reagents, Solvents, and NMR Spectroscopy. $AlBr_3$ (Alfa), $SbCl_5$, and *n*-BuLi, (1.6 M in hexanes, Aldrich) were used as received. NBS was recrystallized from water and dried in vacuo to yield shiny white scales. Bromine was dried with H_2SO_4. TMEDA was refluxed, distilled, and stored over CaH_2. Me_2SiHCl and $MeSiHCl_2$ were distilled from Mg powder prior to use. SbF_5 (Allied) was triply distilled before use. All manipulations involving air- and moisture-sensitive materials (anhydrous Lewis acid halides, organometallic compounds, silicon halides, etc.) were carried out in an argon gas atmosphere using flame-dried glassware or NMR tubes purged with Ar and having rubber or fluorinated polymer septums. Liquids or solutions of solids in the appropriate solvents were added by syringe. $Ph_2BrSi–SiBrPh_2$ was prepared by the procedure of Winkler and Gilman.[30] 1-Methyl- and 1-phenyl-substituted 2,3,4,5-tetraphenylsiloles were provided by Prof. Boudjouk.[21]

Benzene, diethyl ether, and THF were distilled from sodium benzophenone ketyl and stored over sodium. Tetrachloro- and dichloromethane were refluxed over P_2O_5, distilled, and stored over 4-Å molecular sieves. SO_2 (anhydrous, Matheson), pentane (Aldrich, Gold Label), and hexanes for elution were used as purchased. SO_2ClF, which was available in our laboratory, was doubly distilled before use.

^{13}C spectra were recorded on a Varian Associates Model VXR 200 (data system VXR 4000) NMR spectrometer equipped with a 5-mm broadband variable temperature probe. All ^{1}H, ^{29}Si, and ^{19}F spectra were obtained with an internal lock provided by an acetone-d_6 capillary. ^{1}H, ^{13}C, and ^{29}Si resonances were referenced to external (capillary) tetramethylsilane and ^{19}F signals to external $CFCl_3$ at $\delta = 0.00$.

Preparation of 5-Methyl-5*H*-dibenzo[*b*,*f*]silepin (10). *cis*-Stilbene (2 g) was added to 15 mL of *n*-BuLi (1.6 M in hexanes) containing 3.4 mL of TMEDA at room temperature, whereupon the originally slightly yellow solution almost instantaneously turned dark red. Immediate quenching with D_2O showed incorporation of two deuterium atoms, i.e., conversion to the *o*,*o*′-dilithiostilbene to be complete after 1 min (without TMEDA present no reaction occurs). The mixture was cooled to 0 °C, and 100 mL of dry benzene was added into the reaction flask to decrease the viscosity of the solution. Subsequently, 1.2 mL of freshly distilled $MeSiHCl_2$ was added dropwise via a disposable plastic syringe. It was not until the last few drops of $MeSiHCl_2$ were added that the color faded from dark red to yellow to colorless. The mixture was thereupon quenched with aqueous ammonium chloride solution and extracted three times with CH_2Cl_2. The combined extracts were washed with water and dried over $MgSO_4$. The GC/MS analysis of the crude mixture showed two products, of which the major one was the silepin (70%). Attempted purification by distillation under reduced pressure proved unsuccessful due to decomposition. Flash-column chromatography over silica gel (grade 60, 230–400 mesh, 60 Å) with hexane as eluent improved the purity to 90% (GC/MS) but reduced the overall yield to approximately 50%. Similar decomposition was reported by Corey et al. in attempted purification of unsymmetrically substituted silepins.[31] The 90% pure material was a colorless viscous oil, slowly decomposing upon standing at room temperature. NMR: $\delta(^{1}H)$ 0.48 (d, 3 H), 3.95 (q, 1 H), 6–6.6 (m, 14 H); $\delta(^{13}C)$ –6.3 (CH_3), 124.4, 126.75, 127.1, 128.59, 130.21 (vinylic and aromatic Cs), 132.48 (Si–C), 142.39; $\delta(^{29}Si)$ –17.7. Mass spectroscopy *m/z*: 222 ($M^{\cdot +}$, 49), 207 ($M^{\cdot +}$ – Me, 100), 178 ($M^{\cdot +}$ – SiHMe, 17), 105 ($M^{\cdot +}$ – 117, 14).

Triphenylsilyl Perchlorate. Silver perchlorate hydrate (Alfa) (2.5 g, 11.1 mmol) was dissolved in 50 mL of benzene in a three-necked 100-mL

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round-bottom flash equipped with a Dean–Stark condenser, and the solution was refluxed under a blanket of dry argon over a period of 16 h to remove the water of hydration from silver perchlorate. After the dehydration the benzene solution was cooled to room temperature followed by dropwise addition of a solution of triphenylsilyl chloride (3.13 g, 10.6 mmol) in 20 mL of dry benzene over a period of 5 min. The resulting mixture was stirred for 16 h at room temperature. After the reaction the benzene was evaporated under vacuum, the residue was extracted with 50 mL of dry dichloromethane, and the insoluble silver chloride was discarded. The dichloromethane extract on evaporation provided triphenylsilyl perchlorate as a gray powder, 2.5 g (66% yield). The material was further purified by recrystallization from a CH_2Cl_2/*n*-hexane solvent system and stored at 0 °C under dry argon.

Hydride-Transfer Experiments. To a suspension of 86 mg (0.25 mmol) of trityl perchlorate in 1.5 mL of dry dichloromethane in a flame-dried 10-mm NMR tube under a blanket of dry argon was added a solution of silane (0.25 mmol) in 1 mL of dry dichloromethane with vigorous stirring. A similar procedure was employed with other solvents. With the SO_2/SO_2ClF mixture the reaction was carried out at −78 °C. A similar mixing procedure was employed with SbF_5/SO_2ClF/trityl chloride as the hydride abstracting agent (−78 °C).

Preparation of $Me_2BrCSiBrMe_2$ (17). ^{i}PrMgBr in Et_2O, prepared by Grignard reaction of ^{i}PrBr (9 mL) and Mg turnings (2.7 g) was added dropwise to an ethereal solution of Me_2SiHCl (10.9 mL) at 0 °C, allowed to warm up to room temperature, and stirred for 1 h. The white finely powdered precipitate (MgBrCl) was filtered off, and the filtrate was distilled through a Vigreux column (<50 °C bath temperature) to remove the ether. The remaining solution was diluted with 10 mL of pentane and cooled to 0 °C. Bromine (2.5 g) in 5 mL of pentane was added dropwise whereby the bromine was immediately discolored. After the addition the pentane was distilled off, and the solution was kept at 60 °C while another 2.5 mL of bromine (neat) was introduced at such a rate as to maintain a slightly red solution. Toward the end of the addition the crude product started to precipitate and stick to the walls of the reaction flask. The crude solid was transferred into a sublimer, and after the sublimation pure product was obtained as a white waxlike material that fumed and turned brown when exposed to moist air. The overall yield was 55%. NMR: $\delta(^1H)$ 0.4 (Si–CH_3, 6 H), 1.5 (C–CH_3, 6 H); $\delta(^{13}C)$ −1 (Si–CH_3); 28 (C–CH_3); 53 (C–Br), $\delta(^{29}Si)$ 25.

Preparation of $Me_2BrSiSiBrMe_2$ (18). A suspension of 5 g of poly(dimethylsilane) in CCl_4 was cooled to −10 °C, and 3.6 g of bromine in 20 mL of CCL_4 was added dropwise over 2 h. The mixture was allowed to stand at room temperature for 1 h, and subsequently the solvent was evaporated under aspirator vacuum to yield 60% of the pure product (bp = 120 °C at 20 mmHg; mp = 40 °C). NMR: $\delta(^1H)$ 0.2; $\delta(^{13}C)$ 0.8; $\delta(^{29}Si)$ 12.

Note: The distillation jacket must be heated with steam or hot air to prevent clogging of the apparatus by the solid product.

Preparation of $Ph_2CBrSiBrMe_2$ (19). To 1.7 g of Ph_2CH_2 in 20 mL of dry THF was added dropwise 6.5 mL of *n*-BuLi (1.6 M in hexanes) at −78 °C, and the mixture was allowed to warm up to room temperature, whereupon the originally orange solution turned cherry red. Me_2SiHCl (1.1 mL) was then introduced at 0 °C, and the mixture was warmed up to room temperature and stirred overnight. After quenching with water, extraction with Et_2O (three times), and evaporation of the solvents, the remaining oil was slowly fractionated (Vigreux column) under reduced pressure, and the $Ph_2CHSiHMe_2$ fraction boiling at 80 °C (0.05 torr) was collected.

One gram of the pure $Ph_2CH–SiHMe_2$ was placed in a two-necked round-bottom flask equipped with a side arm containing a filter frit and was dissolved in 25 mL of dry CCl_4. Freshly recrystallized NBS (1.6 g) was introduced, and the mixture was stirred for 30 min. The bromination occurred rapidly, with no radical initiator added. The reaction was complete after gentle reflux for 1 h. The succinimide was filtered off through the side arm of the reaction flask. After evaporation of the CCl_4, the viscous yellow residue isolated in 50% overall yield was shown to be pure by ^1H NMR. NMR: $\delta(^1H)$ 0.2 (6 H), 6.13 (6 H); 6.43 (d, 4 H); $\delta(^{13}C)$ 3.47 (CH_3), 66.1 (C–Br); 142.4 (i), 127.6 (o), 130.0 (m), 127.31 (p); $\delta(^{29}Si)$ 13.5.

$Ph_2BrSiSiBrPh_2$ (21).[30] NMR: $\delta(^{13}C)$ 134.8 (o), 127.9 (m), 130.4 (p), 132.2 (i); $\delta(^{29}Si)$ −4.4.

Attempted Preparation of Bridged Halonium Ions. Freshly sublimed $AlBr_3$ or triply distilled SbF_5 was used. A preweighed amount of SbF_5 or $AlBr_3$ dissolved (slurried in the case of $AlBr_3$) in 1 mL of dry SO_2ClF was treated with the appropriate amount of halide at −78 °C (using dry ice/acetone bath) in a dry 5-mm NMR tube under argon with vigorous stirring.

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Supplementary Material Available: Cartesian coordinates of the optimized structures of **1–9** (4 pages). Ordering information is given on any current masthead page.

Formation, Isomerization, and Cyclization Reactions of Hydroperoxyalkyl Radicals in Hexadecane Autoxidation at 160–190 °C

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Contribution from Ford Motor Company, SRL-3083, P.O. Box 2053, Dearborn, Michigan 48121-2053. *Received January 21, 1992*

Abstract: Kinetic and mechanistic investigations of the effects of oxygen pressure on liquid-phase autoxidation reactions in hydrocarbons at elevated temperatures were carried out with hexadecane at 160–190 °C and at oxygen pressures from 4 to 120 kPa using a stirred-flow reactor. Results of studies of formation of primary oxidation products showed that the intramolecular α,γ and α,δ hydrogen abstraction reactions of peroxy radicals (reactions 4) are highly reversible and that the intermediate hydroperoxyalkyl radicals formed from these abstractions, besides addition of oxygen and reverse intramolecular hydrogen abstraction (isomerization) reactions (reactions −4) undergo cyclization reactions leading to formation of cyclic ether products (reaction 10). Kinetic analyses based on the proposed reaction scheme allowed derivation of the absolute rate constants for reactions 4, −4, and 10 of the intermediate α,γ- and α,δ-hydroperoxyhexadecyl radicals, HOOR$^\bullet$. The derived rate constants are in good agreement with published values from gas-phase oxidations.

Introduction

Investigations of the liquid-phase autoxidation of hexadecane with pure oxygen carried out in the stirred-flow microreactor at 100–110 kPa of O_2 and 120–180 °C led to the discoveries of α,γ and α,δ intramolecular hydrogen abstraction reactions of alkylperoxy radicals[1] and the cleavage reaction of α,γ-hydroperoxy-substituted ketones.[2] The occurrence of intramolecular hydrogen

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