Gas-Phase Heteroaromatic Substitution. 9.[1] Silylation of Simple Five-Membered Heteroaromatic Rings by Trimethylsilyl Cations

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Abstract: Trimethylsilyl cation, obtained in the gas phase from the γ-radiolysis of $CH_4/(CH_3)_4Si$ mixtures, has been allowed to react with pyrrole, N-methylpyrrole, furan, and thiophene, both neat and in competition with toluene. Experiments have been carried out at pressures around 620–720 Torr and in the presence of variable concentrations of a gaseous base (NEt_3 0–10 Torr). The mechanism of the silylation process and of the subsequent isomerization of the relevant ionic intermediates is discussed and the intrinsic substrate and positional selectivity of the $(CH_3)_3Si^+$ ions evaluated. The poor substrate discrimination of $(CH_3)_3Si^+$ as well as its tendency to attack preferentially the substrate positions with the highest net negative charge, i.e. the C_β's of pyrrole (70%) and N-methylpyrrole (75%), the oxygen of furan, and the C_α's of thiophene (100%), characterize the reaction as dominated by extensive electrostatic interactions within the encounter pair. The pronounced site discrimination of $(CH_3)_3Si^+$ toward pyrroles ranks it as a "hard" electrophile, but less "hard" than expected on the grounds of its calculated LUMO energy. A plausible explanation is found in the much larger 3p LUMO of $(CH_3)_3Si^+$, if compared to the 2p LUMOs of alkylating carbocations.

Introduction

In the last decade, we have channelled part of our research effort toward kinetic investigation of electrophilic substitution on simple five-membered heteroaromatic compounds in the dilute gas state,[1,2] i.e. in a reaction environment entirely free from those complicating factors, such as solvation, ion pairing, etc., which normally prevent meaningful kinetic measurements of the same processes in solution. Under such conditions, the intrinsic reactivity and selectivity properties of simple heteroarenes, such as pyrrole (1), N-methylpyrrole (2), furan (3), and thiophene (4), toward charged electrophiles can be readily evaluated and compared with related quantities available from solution experiments or predicted by theoretical calculations.

The study, so far essentially focussed on electrophilic alkylation of 1–4 by t-$C_4H_9^+$,[2d] i-$C_3H_7^+$,[2f] $C_2H_5^+$,[1] CT_3^+,[2s] and $CH_3XCH_3^+$ (X = F, Cl),[2a–c] allowed us to establish a close correspondence between the electronic features of the ionic reagent and its selectivity toward the heteroaromatic ring positions.[3] In particular, a direct relationship was observed[1,2s] between the extent of β vs α substitution (the β/α ratio) within 1 and 2 and the "hardness" of the alkylating electrophile, taken as a function of its LUMO orbital energy.[4] Thus, "hard" electrophiles, such as t-$C_4H_9^+$, i-$C_3H_7^+$, $CH_3XCH_3^+$, and $C_2H_5^+$, are predominantly directed toward the ring positions of pyrroles with the highest net negative charge (the C_β and N centers), whereas the "soft" CT_3^+ cation formed from spontaneous nuclear decay in CT_4 attacks preferentially the ring sites of the selected heteroaromatics with the highest HOMO π-electron density (the C_α centers).[5] On these grounds, it was possible to draw a kinetic order of "hardness" for gaseous alkylating carbocations, i.e. $CH_3^+ < i$-$C_3H_7^+ = t$-$C_4H_9^+ < C_2H_5^+$,[1] which differs from Pearson's thermodynamic one, i.e. $CH_3^+ < C_2H_5^+ < i$-$C_3H_7^+ < t$-$C_4H_9^+$,[6] essentially for the exceedingly high "hard" character of $C_2H_5^+$ due to its most stable bridged geometry in the isolated state.[7]

At variance with the behavior of pyrroles 1 and 2, furan (3) undergoes predominant α substitution from all gaseous alkylating electrophiles investigated. The intimate mechanism is thought to involve either direct α attack by the "soft" CT_3^+ cation[2s] or preliminary electrostatic interaction between a "hard" electrophile and the lone pair n-electrons of 3, yielding an adduct which, if sufficiently long-lived, may evolve to the α-substituted intermediate by proximity effect.[1,2a–f] A similar electrostatic interaction may

contribute as well, although to a much lesser extent, to favor α-substitution in thiophene (4) by "hard" alkylating electrophiles.

With the aim of substantiating the direct correlation between the "hardness" of a gaseous electrophile, expressed by its LUMO orbital energy, and its site selectivity toward 1–4, expressed by its β/α ratio, the investigation is now extended to the determination of the substrate and positional selectivity of the trimethylsilyl cation, $(CH_3)_3Si^+$, toward 1–4. On the basis of Pearson's empirical "hardness" order,[6] in fact, trimethylsilyl cation is recognized to be among the "hardest" ionic electrophiles known and, thence, it is expected to exhibit the highest β/α substitution ratio in pyrroles 1 and 2. From a detailed analysis of this correspondence, it was hoped to ascertain whether the "hardness" of the ionic reagent is the only major factor determining its reactivity features toward heteroarenes or whether other factors, related to the intimate nature of the substitution transition state, may play a significant role.

Besides, information about the nature of the primary adduct involved in the attack of a charged alkylating electrophile on the n-electrons of 3 and 4 may, in principle, arise from a direct comparison of the relevant site selectivity displayed by ionic

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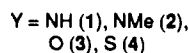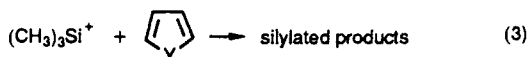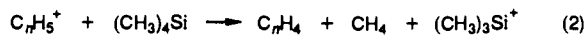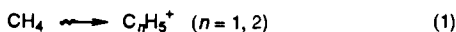
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reagents, such as $(CH_3)_3Si^+$ and $t\text{-}C_4H_9^+$, with similar "hardness", but largely different charge distribution.

The kinetic approach adopted in this study involves preparation of stationary concentrations of $(CH_3)_3Si^+$ ions from the γ-radiolysis of $CH_4/(CH_3)_4Si/O_2$ gaseous mixtures, under conditions, i.e. 620–720 Torr and the presence of a powerful proton acceptor (NEt_3, 0–10 Torr), ensuring efficient collisional thermalization and rapid neutralization of the silylating electrophile and its daughter heteroarenium intermediates, whose isomeric distribution can be therefore determined from the relative abundance of the corresponding silylated neutral derivatives.

$$CH_4 \longrightarrow C_nH_5^+ \quad (n = 1, 2) \tag{1}$$

$$C_nH_5^+ + (CH_3)_4Si \longrightarrow C_nH_4 + CH_4 + (CH_3)_3Si^+ \tag{2}$$

$$(CH_3)_3Si^+ + \left[\begin{array}{c} \text{\textbackslash\textbackslash} \\ Y \end{array}\right] \longrightarrow \text{silylated products} \tag{3}$$

$$Y = NH \text{ (1)}, NMe \text{ (2)},$$
$$O \text{ (3)}, S \text{ (4)}$$

Experimental Section

Materials. Methane and oxygen were research grade gases from Matheson Co., with a minimum purity of 99.99 mol %. Tetramethylsilane and triethylamine were obtained from Fluka AG, with a minimum purity of 99.5 mol %. Pyrrole, N-methylpyrrole, furan, and thiophene were research grade chemicals from Fluka AG. These compounds were analyzed by gas chromatography (GLC) to check for the absence of silylated impurities. Trimethylsilylated derivatives of 1–4 were obtained by conventional synthetic procedures,[8] purified by preparative GLC, and identified by conventional ^1H NMR spectroscopy.

Procedure. The gaseous samples used in the radiolytic trimethylsilylation were prepared according to standard procedures with use of a greaseless vacuum line and were introduced into carefully evacuated and outgassed 135-mL Pyrex vessels. The irradiations were carried out in a 220 Gammacell (Atomic Energy Canada Ltd.) to a total dose of 10^4 Gy at a rate of ca. 10^4 Gy h^{-1}. The irradiated samples were analyzed by GLC and GLC/MS with respectively Perkin-Elmer Sigma 1 and Sigma 3 gas chromatographs and a Hewlett-Packard Model 5970B mass selective detector on the following columns: i, a 3.5 m long, 2 mm i.d. stainless steel column, packed with SP 2100 20% deactivated with Carbowax 1500, 1% w/w on 100/120 mesh Supelcoport, operated at temperatures ranging from 130 to 150 °C, 4 °C min^{-1}; ii, a 12 m long, 0.2 mm i.d. fused-silica column, coated with a 0.33 μm thick film of cross-linked methylsilicone polymer (HP-Ultra 1), operated at temperatures ranging from 40 to 110 °C, 8 °C min^{-1}.

The identity of the products was established by comparison of their capacity factors with those of authentic samples, as well as from their mass spectra in the GLC/MS separations. The amounts of the products formed were determined from the areas of the corresponding elution peaks with use of the internal standard calibration method.

Computational Details. Standard quantum-mechanical calculations, with the Gaussian 80[9] set of programs, were performed in order to evaluate the STO 3G[10] SCF eigenvalues of the LUMO orbital for $(CH_3)_3Si^+$ and for several other alkylating electrophiles. The optimized geometry of this ion was obtained at the SCF STO-3G level of theory by gradient-based techniques, and C_1 point group symmetry framework was assumed. Optimized geometries, at the same level of computation, were taken for the alkylating electrophiles from literature data.[11] C_{2v} symmetry was assumed for $i\text{-}C_3H_7^+$ and bridged $C_2H_5^+$ and C_{3h} for $t\text{-}C_4H_9^+$ and CH_3^+. The following LUMO energies have been evaluated: CH_3^+ (-6.4 eV), bridged $C_2H_5^+$ (-1.9 eV); $i\text{-}C_3H_7^+$ (-3.9 eV); $t\text{-}C_4H_9^+$ (-3.1 eV); $(CH_3)_3Si^+$ (-1.8 eV).

Results

The absolute and relative yields of the silylated products from the gas-phase $(CH_3)_3Si^+$ ion attack on 1–4 are reported in Table I, together with the corresponding composition of the irradiated gaseous mixtures. The total absolute yields of the radiolytic
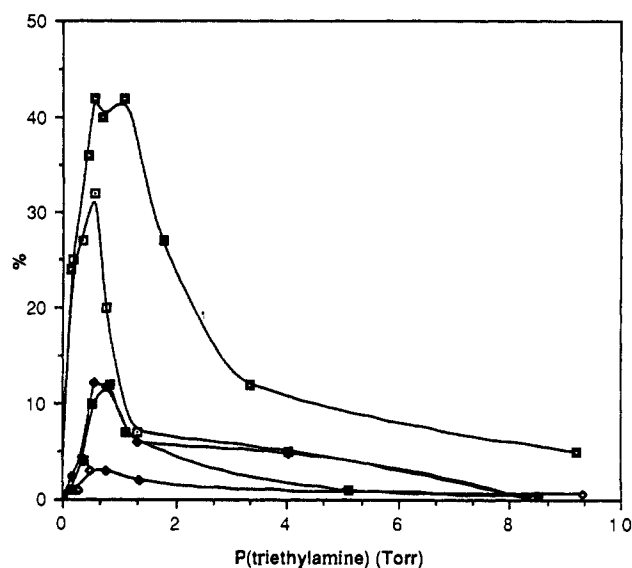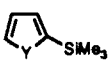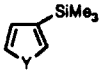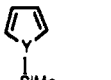
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Figure 1. Effect of the partial pressure of NEt_3 on the absolute yields of trimethylsilylated products 5–7 from 1 (⊞), 2 (□), 3 (◇), 4 (■), and 5–6 from 1 (◆).

products are given as the percent ratio of their $G(M)$ values, i.e. the number of molecules of product M formed per 100 eV of energy absorbed by the gaseous mixture, to the combined G value of ca. 3 for the formation of $C_nH_5^+$ ($n = 1, 2$) ions from the radiolysis of CH_4,[12] which are precursors of the silylating electrophile (eq 2).[13] The results of competition experiments with toluene as the reference substrate, carried out in the presence of an efficient proton acceptor, such as NEt_3, are given in Table II, together with the isomeric composition of the silylated derivatives of the heteroaromatic substrate(s). The reported apparent rate constant ratios k_S/k_R were obtained from the ratio of the yields of the products of the heteroarene and the reference substrate corrected by the inverse ratio of the substrate and reference concentrations. The data reported in Tables I and II represent the average of several determinations and are affected by an uncertainty level not exceeding 10%.

Inspection of the absolute yields of Table I reveals that no detectable amounts of the silylated products 5–7 are formed in the irradiation of $CH_4/(CH_3)_4Si/O_2$/heteroarene systems, unless NEt_3 is present. In general, increasing the NEt_3 concentration causes initial increase of the absolute yields, up to ca. 40% of their theoretical value (Figure 1). Further increase of the NEt_3 partial pressure causes a decline and the almost complete suppression of the trimethylsilylation yields. This peculiar NEt_3 effect on the absolute yields of 5–7 appears evident in the systems with pyrroles 1 and 2, whereas it is less pronounced in the systems with thiophene 4 and barely appreciable in those with furan (3), whose product yields are very low (<3%) under all conditions.

In analogy with the classical behavior of other gaseous electrophiles toward heteroarenes 1–4,[1,2] the trimethylsilyl cation efficiently adds to the heteroaromatic substrate yielding the corresponding isomeric trimethylsilylated derivatives 5–7 (Tables I and II). However, large deviations are observed as regards the isomeric composition of the silylated products from each individual substrate and its dependence upon the concentration of the NEt_3 base. In fact, while N-(trimethylsilyl)pyrrole (7, Y = N) is predominantly (90%) formed from 1 at the lowest NEt_3 partial pressure (0.19 Torr), its formation is inhibited in favor of its isomers 5 (Y = NH) (30%) and 6 (Y = NH) (70%) as the NEt_3 partial pressure is increased to 8.3 Torr. No silyldemethylation is observed in N-methylpyrrole (2), the α-(5, Y = NMe) (25%) and the β-(trimethylsilyl)-N-methylpyrrole (6, Y = NMe) (75%)

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Table I. Product Yields from the Gas-Phase Attack of $(CH_3)_3Si^+$ Ions on Simple Heteroarenes

system composition,[a] Torr			relative yields of products,[b] %				
			5	6	7	β/α substitution ratio	total absolute yield,[c] %
substrate	CH_4	NEt_3					
1, 1.7	700	none	n.d.[d]	n.d.	n.d.		
1, 2.3	670	0.19	5	5	90	1.00	25
1, 2.3	670	0.34	8	8	84	1.00	27
1, 2.6	690	0.57	17	21	62	1.23	32
1, 2.2	700	0.76	26	33	41	1.27	20
1, 2.4	700	1.31	41	54	6	1.32	7
1, 1.9	710	4.02	35	62	3	1.77	5
1, 1.5	660	8.30	30	70	n.d.	2.33	0.1
2, 1.4	700	none	n.d.	n.d.	n.d.		
2, 1.2	670	0.15	27	73	n.d.	2.70	24
2, 1.2	670	0.46	27	73	n.d.	2.70	36
2, 1.4	670	0.56	26	74	n.d.	2.85	42
2, 1.3	670	0.71	26	74	n.d.	2.85	40
2, 1.5	650	1.09	26	74	n.d.	2.85	42
2, 1.4	670	1.76	26	74	n.d.	2.85	27
2, 1.1	720	3.33	27	73	n.d.	2.70	12
2, 1.1	670	9.20	25	75	n.d.	3.00	5
3, 1.5	700	none	n.d.	n.d.			
3, 2.3	690	0.17	100	traces[e]		>200	1
3, 2.3	680	0.27	100	traces		>200	1
3, 2.3	680	0.50	100	traces		>200	3
3, 2.3	680	0.75	100	traces		>200	3
3, 2.3	680	1.36	100	traces		>200	2
3, 2.4	670	9.30	100	traces		>200	0.6
4, 1.6	700	none	n.d.	n.d.			
4, 1.1	690	0.16	100	traces		>200	1
4, 1.2	700	0.38	100	traces		>200	4
4, 1.2	680	0.52	100	traces		>200	10
4, 1.2	680	0.84	100	traces		>200	12
4, 1.3	675	1.10	100	traces		>200	7
4, 1.6	690	5.10	100	traces		>200	1
4, 1.3	670	8.50	100	traces		>200	0.3

[a] O_2, 10 Torr; $(CH_3)_4Si$, 20 Torr. Radiation dose, 1×10^4 Gy; dose rate, 1×10^4 Gy h⁻¹; irradiation temperature, 37 °C. [b] Ratio of the yield of each individual product to the combined yield of all products identified. Each value is the average of several determinations, with an uncertainty level of ca 5%. [c] Absolute yields estimated by using the $G_{(C_nH_5^+)}$ value available from the literature (ref 12, see text). [d] n.d. = below detection limit, ca 0.2%. [e] Traces = <0.5%.

Table II. Substrate Selectivity and Isomeric Composition of Products from Competitive Gas-Phase Trimethylsilylation of Aromatic Compounds

system composition,[a] Torr			isomeric composition of products,[b] %			apparent rate constant ratio,[c] k_S/k_R
competing substrates (S); (R)	CH_4	NEt_3	5	6	7	
1 (2.3); toluene (5.1)	665	4.00	22	74	4	1.09
2 (1.5); toluene (4.9)	675	4.75	24	76	n.d.[d]	5.66
3 (2.3); toluene (2.4)	660	4.67	100	traces[e]		0.19
4 (2.1); toluene (4.2)	670	3.95	100	traces		0.35
2 (1.3); 3 (3.3)	660	0.87	24 (Y = NMe); 100 (Y = O);	76 (Y = NMe); traces (Y = O)	n.d.	42.03
2 (1.0); 4 (0.9)	670	0.95	24 (Y = NMe); 100 (Y = S);	76 (Y = NMe); traces (Y = S)	n.d.	13.43
3 (2.7); 4 (1.6)	680	0.76	100	traces		0.48

[a] O_2, 10 Torr; $(CH_3)_4Si$, 20 Torr. Radiation dose, 1×10^4 Gy; dose rate, 1×10^4 Gy h⁻¹; irradiation temperature, 37 °C. [b] Ratio of the yield of each individual product from the same substrate to the combined yield of all substituted products from the same substrate. [c] k_S/k_T = {[substrate products]/[reference products]}{[reference]/[substrate]}. Each value is the average of several determinations, with an uncertainty level of ca. 10%. [d] n.d. = below detection limit, ca. 0.2%. [e] Traces = <0.5%.

being formed exclusively. Their relative concentration appears rather unaffected by the concentration of NEt_3 and is similar to that of the corresponding α-isomer 5 (Y = NH) (30%) and β-isomer 6 (Y = NH) (70%) from pyrrole (1), measured at high NEt_3 concentrations. Concerning furan (3) and thiophene (4), the attack of $(CH_3)_3Si^+$ apparently produces the corresponding α-substituted derivative 5 (Y = O or S) as the only isolable neutral product under all experimental conditions.

Discussion

Nature of the Ionic Reagent. The electrophile used in the present study is the gaseous $(CH_3)_3Si^+$ ion obtained from the

attack of radiolytically generated $C_nH_5^+$ (n = 1, 2) ions on tetramethylsilane (eqs 1 and 2). The exothermic reaction 2 ($\Delta H°$ = -38 (n = 1) kcal mol⁻¹ and $\Delta H°$ = -7 (n = 2) kcal mol⁻¹) is known to occur efficiently in ionized CH_4 containing traces of tetramethylsilane.[13,14] The combined $G(M)$ values of the $C_nH_5^+$ ions from the radiolysis of methane in the pressure range of interest is ca. 3,[12] which allows evaluation of the absolute yields of the silylated products 5–7 given in Table I, under the reasonable

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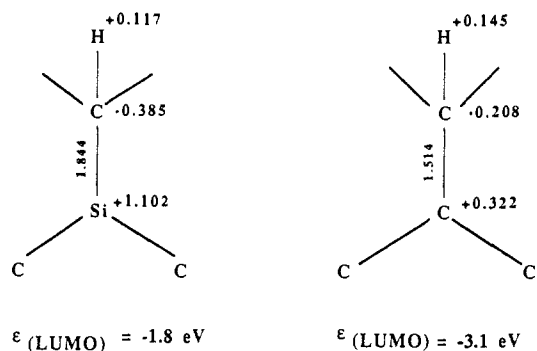
Figure 2. SCF STO-3G calculated charge distribution and LUMO orbital energy of trimethylsilyl and *tert*-butyl cations.

assumption that the $C_nH_5^+$ ions are consumed exclusively by tetramethylsilane (eq 2), present in large excess over the aromatic substrate(s) and other nucleophiles either deliberately introduced (NEt_3) or formed in the gaseous mixture during radiolysis. Use of a large excess (>250:1) of methane over the heteroaromatic substrate ensures complete thermalization of radiolytic $(CH_3)_3Si^+$ ions by multiple unreactive collisions with the methane molecules before a reactive encounter with the heteroarene.

In the gas phase, ground-state $(CH_3)_3Si^+$ is expected to be a planar ion with a C_{3h} symmetry due to trigonal sp^2 hybridization of silicon, whose relative stability with respect to the analogous planar carbocation, $t\text{-}C_4H_9^+$, has been recently assessed.[15] The two ionic electrophiles present substantial differences as regards their electronic distribution, as indicated by their largely different positive charge distribution and LUMO orbital energy, calculated at the STO 3G level (Figure 2).[10]

At variance with the combined Brønsted and Lewis acid character of $t\text{-}C_4H_9^+$ ion due to its extensive charge delocalization over both the central C and the H atoms, the pronounced positive charge located on the silicon atom of $(CH_3)_3Si^+$ makes this ion behave essentially as a typical Lewis-type acid. Thermochemical arguments also agree with this view. In fact, proton transfer from $(CH_3)_3Si^+$ to the selected heteroarenes 1–4, as well as to toluene, is calculated to be rather endothermic ($\Delta H° \text{ (kcal mol}^{-1}) = 19$ (1), 11 (2), 34 (3), 31 (4), 37 (toluene)),[16] whereas the same reaction by $t\text{-}C_4H_9^+$ on most selected substrates is exothermic.[2d] The exclusive Lewis acid character of $(CH_3)_3Si^+$ toward the selected substrates confers on the apparent rate constant ratios k_S/k_R of Table II the value of a direct estimate of the relative nucleophilic reactivity of 1–4 with respect to toluene toward the trimethylsilylating reagent.

The Trimethylsilylation Reaction. The general problem of mechanistically oriented radiolytic studies, i.e. the necessity of demonstrating the ionic origin of the products of interest, does not arise in the present case. In fact, no trimethylsilylated products 5–7 are formed from 1–4, unless an appropriate base (NEt_3) is present in the irradiated systems. This observation rules out any conceivable contribution from radicals or excited molecules to the silylated products 5–7, which therefore originate exclusively from $(CH_3)_3Si^+$. The ionic origin of the silylated products is independently ensured by the presence of an effective radical scavenger (O_2) in the mixtures and by the inhibition of the silylation process caused by large concentrations of the ion trap NEt_3.

The results of the radiolytic experiments are consistent with a trimethylsilylation pattern (eq 4), involving the primary attack of $(CH_3)_3Si^+$ on the heteroaromatic substrate, which leads to the intermediates I*, excited by the exothermicity of their formation process. No precise evaluation of the actual reaction enthalpy of eq 4 can be given at present, owing to the paucity of reliable thermochemical data concerning neutral and ionic Si-containing species. Nevertheless, a lower limit of the energy release involved in eq 4 can be roughly estimated as ranging around 30–40 kcal mol^{-1}, taking into account that the π-eccessive five-membered

(15) Eyler, J. R.; Silverman, G.; Battiste, M. A. *Organometallics* **1982**, *1*, 477.
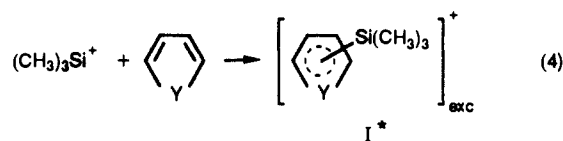
heteroarenes 1–4 are more activated than benzene, for which gas-phase trimethylsilylation is 23.9 kcal mol^{-1} exothermic.[13]

In analogy with previous conclusions from related studies on gas-phase aromatic silylations,[13] and in view of the nature of the products of Table I and the peculiar dependence of their yields on the presence and concentration of the added NEt_3, it is suggested that the excited intermediates I* undergo thermalization by unreactive collisions with the bath gas $M = CH_4$ before neutralization via the two competing processes 5a,b.
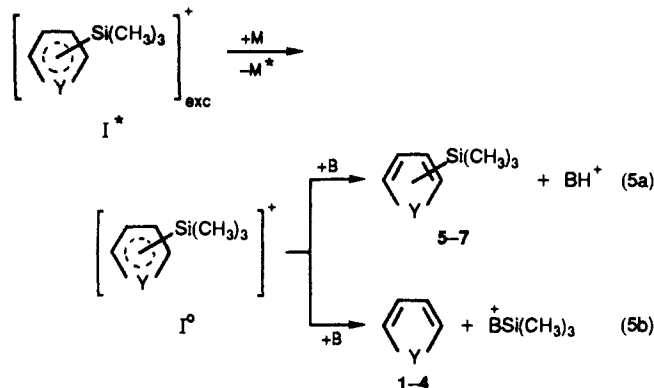
If no bases are deliberately added to the irradiated mixtures, the oxygenated nucleophiles unavoidably present, either as adventitious impurities (e.g. H_2O) or as radiolytic products (e.g. H_2O, CH_3OH, CH_2O, etc.), react with I° exclusively via reaction 5b, owing to the well-established high affinity of oxygenated bases for the silicon center of silylated arenium intermediates.[13] As a result, no heteroaromatic silylated products 5–7 are recovered from these mixtures. However, when a strong proton acceptor, such as NEt_3 (proton affinity PA = 232.3 kcal mol^{-1}),[16] is added to the gaseous mixtures, two opposing effects on the product yield can be envisaged. On the one hand, NEt_3 allows rapid deprotonation of I° favoring formation of the silylated products 5–7 via the exothermic process 5a. On the other hand, the amine effectively intercepts the $C_nH_5^+$ and $(CH_3)_3Si^+$ precursors, thus depressing the yields of their daughter intermediates I° and then of the ensuing neutral products 5–7. This dual behavior accounts for the characteristic bell-shaped dependence of the absolute yields of the silylated products 5–7 on the partial pressure of NEt_3 shown in Figure 1.

Their initial increase, as the amine gradually swamps the adventitious oxygenated nucleophiles, is followed by gradual decline as the higher concentrations allow the amine to intercept most of the charged precursors.

In order to account for the isomeric composition of silylated products 5–7 (Y = NH) from 1 and for its pronounced dependence on the concentration of NEt_3 (Table I), we suggest that the attack of $(CH_3)_3Si^+$ on pyrrole leads, in the kinetically controlled step of the reaction, to the predominant formation of the β-silylated intermediate I_β. Formation of I_β is accompanied by minor yields of the α-silylated isomer I_α, while no evidence for the occurrence of the N-silylated isomer I_N is obtained. Unless rapidly deprotonated by NEt_3 (eq 5a), intermediates I_α and I_β tend to isomerize to a thermodynamically more stable structure, which, according to the experimental evidence, is the N-silylated intermediate I_N (eq 6).

The fast isomerization process shown in eq 6 is favored by the significant fraction of positive charge located at the silicon atom of the heteroarenium intermediates and by the unfavorable en-

(16) Thermochemical values for ions and neutrals taken from: (a) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. (b) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Ibid.* **1988**, *17*, Suppl. 1.
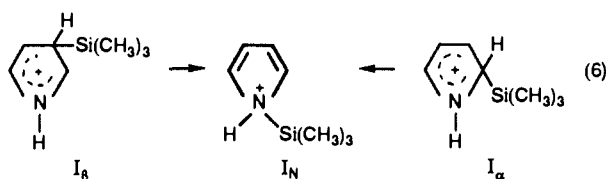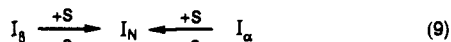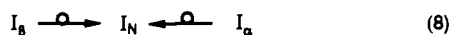
ergetics accompanying the competing intramolecular 1,2-shift of the ipso hydrogen, yielding II (eq 7).[17]
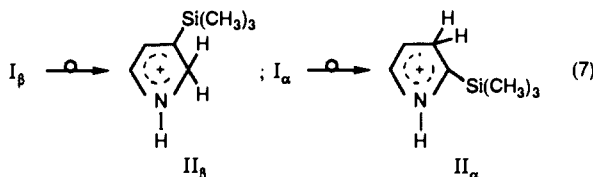
In fact, occurrence of fast isomerization 7 would involve immediate quenching of the trimethylsilyl-group position in the relevant intermediates, thus preventing observation of the distinct dependence of the isomeric composition of the silylated pyrroles **5**–**7** (Y = NH) upon the NEt_3 concentration (Figure 1). Besides, owing to the lowering of the stationary concentration of I_α and I_β due to eq 7, the extent of the blind channel 5b would be strongly depressed in favor of deprotonation of II_α and II_β by a suitable base, including the substrate itself. It follows, in contrast to experimental evidence, that formation of significant amounts of silylated products **5**–**7** (Y = NH) would be observed even in irradiated mixtures without any added NEt_3.

Isomerization 6 can involve either an intramolecular trimethylsilyl-group shift within the excited intermediates I* (eq 8) or an intermolecular trimethylsilyl-group transfer from I* to the N atom of another molecule of pyrrole (eq 9). The only available evidence allowing discrimination between the alternative isomerization mechanisms 8 and 9 is provided by the dependence of the isomeric distribution of the silylated products **5**–**7** (Y =

$$I_\beta \xrightarrow{\quad} I_N \xleftarrow{\quad} I_\alpha \qquad (8)$$

$$I_\beta \underset{-S}{\overset{+S}{\rightleftharpoons}} I_N \underset{-S}{\overset{+S}{\rightleftharpoons}} I_\alpha \qquad (9)$$

S = heteroaromatic substrate

NH) from **1** for a 10-fold variation of the partial pressure of the heteroaromatic substrate (Figure 3), keeping constant the total pressure of the gaseous mixture (710 Torr) and, especially, the concentration of the base NEt_3 (0.48 ± 0.05 Torr), which would efficiently compete with S for the intermediates I_α and I_β in the intermolecular isomerization paths 9. The limited decrease of the relative yield of **7** (Y = N) from **1** by increasing the pyrrole concentration is consistent with the intramolecular isomerization mechanism 8, ruling out the alternative intermolecular pathways 9, for which an opposite trend would be expected. In the framework of the isomerization pattern 8, the observation of a limited, but significant decrease of the relative yield of **7** (Y = N) in favor of the C-silylated isomers **5** and **6** (Y = NH) indicates that pyrrole may act as an additional base flanking NEt_3 in accepting a proton from the silylated ionic intermediates. Besides, the fact that decreasing the concentration of the bases, either NEt_3 (Table I) or pyrrole (Figure 3), in the gaseous mixtures with **1** leads to an increase of the relative yields of both the N- (**7**, Y = N) and the α-substituted product (**5**, Y = NH) to the expense of the β-silylated one (**6**, Y = NH) substantiates the hypothesis that the intramolecular isomerization process 8 proceeds via a sequence of 1,2-trimethylsilyl-group shifts (eq 10).

$$I_\beta \xrightarrow{\quad} I_\alpha \xrightarrow{\quad} I_N \qquad (10)$$
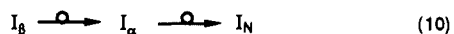
Similarly, attack of $(CH_3)_3Si^+$ on N-methylpyrrole (**2**) leads, in the kinetically controlled step of the reaction, to the predominant formation of the β-silylated intermediate III_β, together with minor

amounts of the α-silylated isomer III_α (eq 11). No evidence for the formation of N-(trimethylsilyl)pyrrole (**7**, Y = N), which would imply the intermediacy of III_N, was obtained from the analysis of the products from **2**, in spite of a specific search.

$$III_\beta \rightleftharpoons III_\alpha \xrightarrow{\quad X \quad} III_N \qquad (11)$$
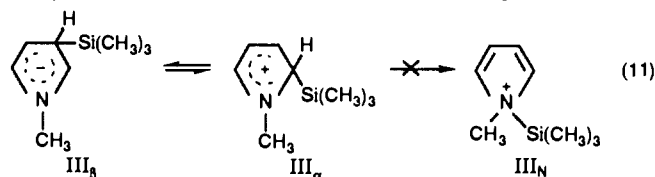
While this result is consistent with the low propensity of the N atom of pyrroles to undergo direct electrophilic attack in the gas phase,[1,2] failure to recover **7** (Y = N) from the irradiated mixtures with **2** does not allow one to exclude the actual occurrence of III_N, owing to the conceivable preference of III_N to release its trimethylsilyl rather than the methyl group to a suitable nucleophile, either an oxygenated base or the added NEt_3. However, close inspection of Tables I and II reveals that formation of III_N either by direct attack of $(CH_3)_3Si^+$ on **2** or via isomerization 11 does not take place appreciably under all conditions. In fact, the higher reactivity of **2** vs **1** toward $(CH_3)_3Si^+$, expressed by the corresponding k_S/k_R ratios of Table II (k_S/k_R = 5.66 (S = **2**); 1.09 (S = **1**)), cannot account by itself for the much higher absolute yields ratio of the C-silylated products from **2** vs **1**, measured under conditions allowing C-to-N trimethylsilyl-group shift within I* (10.8 at $P(NEt_3)$ = 0.15–0.19 Torr; 8.3 at $P(NEt_3)$ = 0.34–0.46 Torr), if not in terms of predominant formation of stable intermediates III_α and III_β from $(CH_3)_3Si^+$ attack on **2** with limited or no tendency to isomerize to III_N.

A rationale for the relative inefficiency of the second step of sequence 11, if compared to the same isomerization process shown in eq 10, can be found in the 2-fold inhibiting effect of the methyl group in allowing acceptance of the trimethylsilyl group by the N atom of **2**. First, such a transfer, as well as direct attack of the rather encumbered $(CH_3)_3Si^+$ ion on the N of **2**, is hampered by electrostatic and steric repulsion with the CH_3 moiety.[18] Second, hyperconjugative effect of the N-methyl group is expected to favor C-trimethylsilylation and to enhance the thermodynamic stability of III_α and III_β with respect to III_N. It follows that the relative distribution of the silylated products **5** and **6** (Y = NMe) from **2** (Table I) closely reproduces the actual abundance of their primary ionic precursors III_α and III_β, respectively.

The β/α substitution ratio, measured for the silylated products **5** and **6** (Y = NMe) from **2**, appears essentially constant (β/α
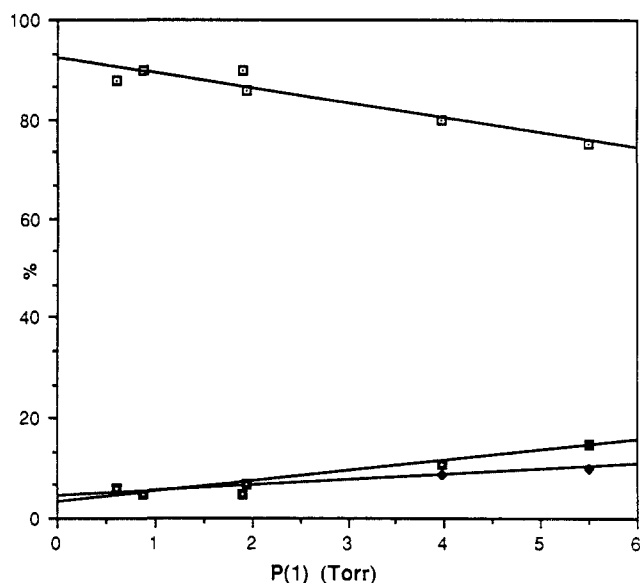

Figure 3. Effect of the partial pressure of pyrrole on the relative yields of isomeric trimethylsilylated pyrroles **5** (◆), **6** (■), and **7** (□).

(17) Cacace, F.; Crestoni, M. E.; DePetris, G.; Fornarini, S.; Grandinetti, F. *Can. J. Chem.* **1988**, *66*, 3099.

(18) Politzer, P.; Weinstein, H. *Tetrahedron* **1975**, *31*, 915.

= 2.85 ± 0.15) in spite of a 60-fold variation of the NEt_3 concentration (Table I). Since intervention of very high energy barriers in the first step of the isomerization sequence 11 can be reasonably excluded in view of the facile occurrence of the corresponding process in the systems with 1 (eq 10), the constancy of the β/α substitution ratio, measured for 2 under all conditions, can be interpreted as due to a kinetic distribution of III_α vs III_β coinciding with the thermodynamic one.

A reaction pattern, similar to sequence 4 → 5 is valid for $(CH_3)_3Si^+$ ion attack on thiophene (4). In fact, the typical bell-shaped dependence of the silylated product yields as a function of the NEt_3 concentration is observed (Figure 1). Quantitative analysis of the data of Figure 1 indicates a complete coincidence between the NEt_3 dependence of the absolute yields of the C-silylated products from 1 and 4. Such a coincidence suggests that direct attack of $(CH_3)_3Si^+$ ion takes place at the C sites of thiophene (4) to a substantial extent, much in the same way as in pyrroles 1 and 2. No direct information can be obtained as to what portion of the direct attack of $(CH_3)_3Si^+$ takes place at the sulfur of 4. Occurrence of the corresponding S-silylated intermediate may, in fact, account for the apparent lower reactivity of 4 ($k_S/k_R = 0.35$) if compared to that of 1 ($k_S/k_R = 1.09$) toward $(CH_3)_3Si^+$ (Table II). Close inspection of Table II, however, reveals some correspondence between the $k_2/k_4 = 16.2$ ratio, calculated from the relevant k_S/k_R values measured at $P(NEt_3) = $ ca. 4 Torr, where trimethylsilyl-group shift within silylated intermediates is minimized, and the direct $k_2/k_4 = 13.4$ value, obtained at $P(NEt_3) = 0.95$ Torr, namely under conditions where silyl-group migrations may take place. This correspondence would exclude isomerization of the C-silylated intermediates from 4 to the S-silylated one as a significant contribution to the population of the latter, in complete analogy with the behavior of the corresponding C-silylated intermediates from 2.

The very limited yields of C-silylated products from furan (3) can be explained by the predominant interaction between $(CH_3)_3Si^+$ and the oxygen of furan, which prevents formation of the C-silylated products 5 and 6 (Y = O) to any significant extent. This accounts for the exceedingly low apparent reactivity of 3 if compared to toluene ($k_S/k_R = 0.19$) and the other heteroaromatics ($k_2/k_3 = 42.03$; $k_3/k_4 = 0.48$). As with 4, the initial population of heteroatom-silylated ionic intermediate from 3, although significant, cannot be directly evaluated. It, however, represents a thermodynamic sink for the C-silylated intermediates from 3, as suggested by the significantly lower $k_3/k_4 = 0.48$ and, especially, $k_3/k_2 = 0.024$, measured at $P(NEt_3) = $ ca. 0.8 Torr, where C-to-O isomerization of the ionic intermediates from 3 is allowed, if compared to the $k_3/k_4 = 0.54$ and $k_3/k_2 = 0.034$, calculated from the data from competition experiments with toluene as the reference substrate carried out at $P(NEt_3) = $ ca. 4.5 Torr, where C-to-heteroatom silyl-group transfer within the ionic intermediates is minimized.

Substrate and Positional Selectivity. The values of the apparent k_S/k_R ratios for gas-phase trimethylsilylation of 1–4 in the presence of toluene, measured under kinetically controlled conditions ($P(NEt_3) = 4$–5 Torr; Table II), clearly indicate no distinct preference of the ionic electrophile toward toluene and the selected heteroarenes. This view is reinforced by the consideration that the significantly lower absolute yields of silylated products from 3 and 4 may be due to extensive direct attack of $(CH_3)_3Si^+$ on their heteroatom, an event that would increase substantially the actual k_S/k_R values for such substrates. On these grounds, it is found that simple five-membered heteroaromatic compounds 1–4, as well as toluene, react with gaseous $(CH_3)_3Si^+$ ion at rates falling within the same order of magnitude, in substantial agreement with the limited substrate discrimination shown by $(CH_3)_3Si^+$ in related gas-phase substitutions[13b,c] and by other gaseous alkylating reactants toward the same heteroaromatic substrates.[1,2]

The intrinsic directive properties of pyrroles 1 and 2 toward gaseous $(CH_3)_3Si^+$ demonstrate the tendency of the heteroaromatic molecule to drive the electrophile toward the ring carbons with the highest value of the net negative charge (C_β centers) (70% in 1; 75% in 2).[19] This tendency conforms to the positional

selectivity of other "hard" alkylating electrophiles toward simple pyrroles and may find a theoretical justification in the framework of Charge and Frontier Orbital Control Concept.[6] Within this model, the total perturbation energy in the orbital interaction between the pyrrole molecule and $(CH_3)_3Si^+$ is essentially determined by electrostatic interactions within the encounter pair, owing to the very large energy gap between the HOMO of the pyrrole ($\epsilon_H = -6.6$ eV for 1) and the LUMO of the electrophile ($\epsilon_L = -1.8$ eV) ($\epsilon_H - \epsilon_L = -4.8$ eV). Hence, since trimethylsilylation of simple pyrroles is a "charge-controlled" reaction, the "hard" $(CH_3)_3Si^+$ electrophile is primarily oriented toward the "hard" reaction sites of pyrroles, i.e. the ring carbons with the highest net negative charge (the C_β centers).

The same model may also account for the apparent exclusive formation of the α-silylated product 5 from both furan (3, Y = O) and thiophene (4, Y = S). Preferential interaction between the "hard" $(CH_3)_3Si^+$ electrophile and the most negatively charged site of furan (3), i.e. the oxygen atom, leads directly to its O-silylated intermediate. Its occurrence is favored not only for kinetic reasons but also by the high thermodynamic stability of the formed Si–O bond (average Si–O bond energy = 106 kcal mol⁻¹; heterolytic $(CH_3)_3Si-OR_2^+$ dissociation energy = 30–44 kcal mol⁻¹ (R = H or alkyl))[13a,20] relative to a Si–C bond (average Si–C bond energy = 73.2 kcal mol⁻¹; heterolytic $(CH_3)_3Si-ArH^+$ dissociation energy = 24–31 kcal mol⁻¹ (ArH = aromatic hydrocarbon)),[13a,20] which in addition makes unfeasible O-to-C intramolecular shifts of the trimethylsilyl group within the O-substituted intermediate. Predominant formation of a stable O-silylated intermediate accounts for the comparatively low absolute yields of C-substituted products from furan (<3%). In fact, no evidence for direct $(CH_3)_3Si^+$ ion attack on the C centers of 3 with the highest net negative charge, i.e. the β carbons, emerges from the experimental data under all conditions (Table I), thus confirming the absolute prevalence of the heteroatom over the C centers of 3 in directing the silylating electrophile. In this view and in analogy with the conclusions reached for other alkylating electrophiles,[1,2] exclusive formation, under kinetically controlled conditions, of the α-silylated furan 5 (Y = O), although in very limited yields, cannot be explained in terms of charge density on the C_α carbons of 3 that here reaches the minimum value.[19] Rather, preliminary electrostatic interactions between the hydrogen atoms of $(CH_3)_3Si^+$ and the heteroatom of 3 favor formation of a proton-bound adduct, whose evolution to the α-silylated intermediate I_α is favored by proximity of the Si atom to the C_α's of 3. Of course, the relative extent of such a process with respect to direct formation of the O-substituted intermediate is determined by competition of the H and the Si centers of $(CH_3)_3Si^+$ in establishing electrostatic interactions with the oxygen atom of 3. In this perspective, the relatively high fraction of positive charge located on the Si of $(CH_3)_3Si^+$, if compared to that on the central C of t-$C_4H_9^+$ (Figure 2), is expected to decrease the occurrence of proton-bound adducts with the heteroatom of 3 in favor of direct formation of the O-silylated intermediate. This provides an explanation of the comparatively poor yields of 5 (Y = O) (<3%) with respect to the α-substituted product from t-$C_4H_9^+$ ion attack on 3 (ca. 40% absolute yield).[2d]

Preliminary electrostatic interactions between the heteroatom of thiophene (4) and a "hard" electrophile, such as $(CH_3)_3Si^+$, are much less significant than those involved in furan (3).[21] A reason is that a large fraction of the net negative charge in 4 is

(19) (a) Hermann, R. B. *Int. J. Quantum Chem.* **1968**, *2*, 165. (b) Preston, H. J. T.; Kaufman, J. J. *Int. J. Quantum Chem. Symp.* **1973**, *7*, 207. (c) Kaufman, J. J.; Preston, H. J. T.; Kerman, E.; Cusachs, L. C. *Ibid.* **1973**, *7*, 249.

(20) Ebsworth, E. A. V. Physical Basis of the Chemistry of the Group IV Elements. In *Organometallic Compounds of the Group IV Elements*; Macdiarmid, A. G., Ed.; M. Dekker: New York, 1968.

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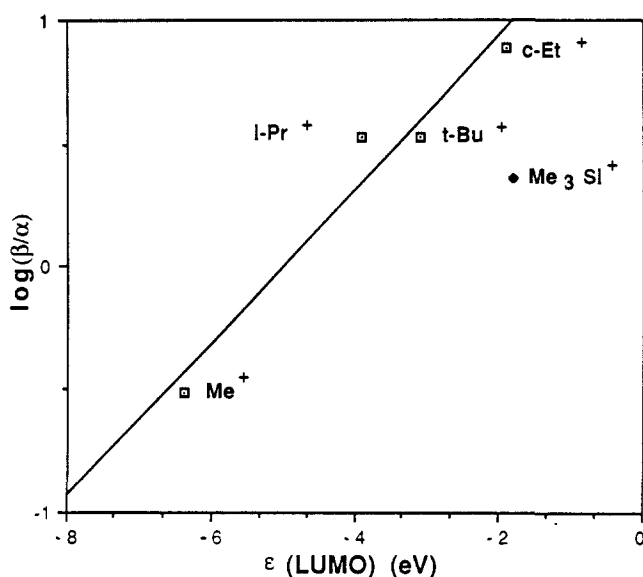
Figure 4. Plot of site selectivity of ionic electrophiles toward pyrrole, expressed as the log [6]/[5] (log (β/α)), as a function of SCF STO-3G calculated LUMO eigenvalues of the ionic electrophiles.

distributed over the C atoms and, especially, on the α carbons.[22] It follows, in agreement with the higher product yields from **4** if compared to those from **3**, that direct attack of $(CH_3)_3Si^+$ on the S atom of **4** to produce the S-silylated intermediate is rather limited, if compared to the same process in furan (**3**), owing to less favorable kinetic factors. Furthermore, the $\alpha > \beta > S$ charge density distribution is expected to favor direct attack of the silylating reactant on the C_α of **4**, as actually observed from the experimental results (Table I).

Comparison with Related Gas-Phase and Solution Data. The intrinsic substrate and positional selectivity of gaseous $(CH_3)_3Si^+$ ion toward simple five-membered heteroarenes **1–4** qualitatively corresponds to the expected behavior of a typical "hard" electrophile. However, if the intrinsic orienting properties of simple heteroarenes **1–4** can be used to rank order gaseous ionic electrophiles in terms of their "hardness", the results of the present study place the "hardness" of gaseous $(CH_3)_3Si^+$ ions higher than that of t-$C_4H_9^+$, as expected in view of the higher LUMO energy of the first ($\epsilon_L = -1.8$ eV) with respect to that of the latter ($\epsilon_L = -3.1$ eV), but well below that of bridged $C_2H_5^+$, in spite of their comparable LUMO energies ($\epsilon_L = -1.9$ eV for bridged $C_2H_5^+$). In other words, the measured site selectivity of $(CH_3)_3Si^+$ toward **1** ($\beta/\alpha = 2.3$) and **2** ($\beta/\alpha = 3.0$) hardly conforms to that expected

on the grounds of a linear correlation between the calculated LUMO energy of the ionic electrophile and its site selectivity toward pyrroles, proposed in the preceding paper of this series[1] and shown in Figure 4.

An explanation for the observed deviation of $(CH_3)_3Si^+$ ion from linearity can be found in the observation that the large $\epsilon_H - \epsilon_L$ gap between $(CH_3)_3Si^+$ and **1**, which would favor charge control in the attack of the ion on pyrrole, is offset by the comparatively large empty 3p orbital of the Si center of the electrophile, which instead would promote extensive electron mixing between the p-LUMO of the ion and the π-HOMO of pyrroles, whose maximum electron density is placed at the C_α carbons. It follows that the $(CH_3)_3Si^+$ ion is electrostatically oriented toward the ring carbons of pyrroles **1** and **2** with the highest net negative charge, i.e. the C_β centers, but this tendency is somewhat contrasted by a long-range orbital interaction that tends to drive the silylating electrophile toward the α carbons, namely the ring centers with the highest π-HOMO electron density.

Alternative explanations for the deviation from linearity of Figure 4 by $(CH_3)_3Si^+$ can be however advanced, including the observation that the Charge and Frontier Orbital Control concept[6] can provide only very qualitative estimates of reactivity, since it may fail in describing the actual nature of the transition state involved. This possibility is critically examined in further extensive investigations on the gas-phase reactivity of five-membered heteroaromatics, whose results will be presented in forthcoming papers.

Comparison of the present gas-phase results with those of related silylation reactions in solution is prevented by the lack of reliable kinetic data concerning electrophilic substitution on simple five-membered heteroaromatics in condensed phase. In fact, only very recently could a trimethylsilyl cation be generated and characterized in solution.[23] As a matter of fact, predominant β-silylation on **2** (83%) has been observed in mixtures of trimethylsilyl trifluoromethanesulfonate in triethylamine, wherein the occurrence of a free trimethylsilyl cation is however excluded.[8a] In this view, perhaps it is not unwarranted to claim that the results of the present study represent the only available kinetic data concerning the reactivity and selectivity features of a silylating electrophile toward fundamental heteroarenes.

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