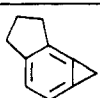
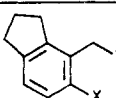
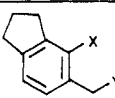
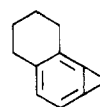
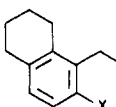
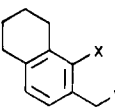


Table II. Reactions of Benzocyclopropenes with Electrophiles

benzo-cyclopropene	electrophile	products (yield, %)	
			
12	Br <sub>2</sub>	a, X = Y = Br (100)	a, X = Y = I (32)
	I <sub>2</sub>	b, X = Y = I (68)	b, X = H, Y = Cl (100)
	HCl		c, X = H, Y = OMe (100)
	Ag <sup>+</sup> /MeOH		
			
13	Br <sub>2</sub>	a, X = Y = Br (80)	a, X = Y = Br (20)
	HCl	b, X = H, Y = Cl (45)	b, X = H, Y = Cl (55)
	Ag <sup>+</sup> /MeOH	c, X = H, Y = OMe (44)	c, X = H, Y = OMe (56)

(3.2 mg) for 1 h. The solution was diluted with dichloromethane, washed with water, and dried over magnesium sulfate. Removal of the solvent in vacuo afforded the ether 21c as a colorless oil (10.5 mg, 75%): NMR  $\delta$  7.30-6.95 (m, 3 H), 4.43 (s, 2 H), 3.29 (s, 3 H), 3.03-2.76 (t, 4 H), 2.24-1.90 (m, 2 H).

**Reaction of 4,5,6,7-Tetrahydro-1H-cyclopropa[a]-naphthalene (13) with Bromine.** Compound 13 (10.2 mg, 0.071 mmol) was reacted with bromine by using the procedure described above for 12 to give a mixture of the two ring-cleaved products 22a and 23a (product ratio 80:20 by NMR). The combined yield was 17.2 mg (80%): NMR  $\delta$  7.40-6.84 (m, 2 H), 4.68, 4.65 (2 s, corresponding to 22a and 23a, 2 H), 3.00-2.60 (m, 4 H), 2.04-1.60 (m, 4 H).

**Reaction of 4,5,6,7-Tetrahydro-1H-cyclopropa[a]-naphthalene (13) with HCl.** Compound 13 (13.0 mg, 0.090 mmol) was reacted with HCl by using the procedure described above to afford a mixture of the two ring-cleaved products 22b and 23b (product ratio 45:55 by NMR). The combined yield was 11.7 mg (72%): NMR  $\delta$  7.20-6.94 (m, 3 H), 4.59, 4.52 (2 s, corresponding to 22b and 23b, 2 H), 3.00-2.60 (m, 4 H), 2.00-1.68 (m, 4 H).

**Reaction of 4,5,6,7-Tetrahydro-1H-cyclopropa[a]-naphthalene (13) with Silver Ion in Methanol.** Compound 13 (10.0 mg, 0.069 mmol) was treated with silver ion in methanol using the procedure of 12 to afford a mixture of 22c and 23c (product ratio 44:56 by NMR). The combined yield was 8.8 mg (72%): NMR  $\delta$  7.20-6.96 (m, 3 H), 4.43, 4.40 (2 s, corresponding to 29 and 30, 2 H), 3.41, 3.39 (2 s, 3 H), 2.94-2.60 (m, 4 H), 2.00-1.62 (m, 4 H).

**Acknowledgment.** We gratefully acknowledge The Robert A. Welch Foundation for support of this work. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

**Registry No.** 12, 5266-64-8; 13, 112504-80-0; 14, 112504-81-1; 15, 112504-82-2; 16, 112504-83-3; 17, 112504-84-4; 18, 112504-85-5; 19, 112504-86-6; 20a, 112504-87-7; 20b, 112504-88-8; 21a, 112504-89-9; 21b, 18775-42-3; 21c, 112504-90-2; 22a, 112504-91-3; 22b, 17450-62-3; 22c, 112504-92-4; 23a, 112504-93-5; 23b, 17450-63-4; 23c, 112504-94-6; 1-bromo-2-cyclopropene, 88180-95-4; 1-vinylcyclopentene, 28638-58-6; 1-vinylcyclohexene, 2622-21-1; 1,2-dimethylenecyclohexane, 2819-48-9; 1,2-dimethylenecyclopentane, 20968-70-1.

## Direct Aromatic Substitution by Trimethylsilyl Cations

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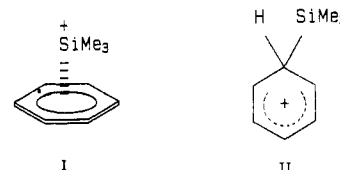
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One of the major objectives of gas-phase ion chemistry is to provide highly simplified and generalized models of ionic reactions in condensed media. Consequently, a great deal of work has been devoted in recent years to extend to the gas phase the study of classical reactions, e.g., protonation, alkylation, nitration, nucleophilic displacement, etc. long familiar to organic chemists.<sup>1</sup> The opposite case of ionic reactions which are not known in solution and have first been demonstrated in the gas phase is by far less common. This note is aimed at reporting one such rare example, concerning normal electrophilic aromatic silylation, not yet achieved in solution.<sup>2</sup>

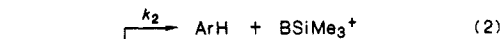
Recently, formation of silylated adducts from the exothermic reaction in eq 1,  $\Delta H^\circ = -29.3$  kcal mol<sup>-1</sup> in the case



of PhH, was detected in a mass spectrometric study carried out at 3-5 Torr, at temperatures ranging from 300 to 600 K.<sup>3</sup> However, occurrence of a substitution reaction was excluded; the  $\pi$ -complex structure I was assigned to 1 rather than the  $\sigma$ -complex structure II, based on the inability of gaseous bases to undergo H<sup>+</sup>, rather than SiMe<sub>3</sub><sup>+</sup> transfer from 1.<sup>3</sup>



Nevertheless, taking into account the tentative nature of structural assignments by purely mass spectrometric techniques, the role of  $\sigma$ -complexes demonstrated in closely related reactions such as aromatic alkylation by gaseous *t*-Bu<sup>+</sup>,<sup>4</sup> and the high binding energy of 1, the actual occurrence of an electrophilic trimethylsilylation could not be excluded. Accordingly, the reaction was investigated with an integrated approach, based on the combination of mass spectrometry with radiolytic techniques, over a wide pressure range (up to 760 Torr) and by the actual isolation of the neutral end products, which allows their positive structural characterization.<sup>1,5,6</sup> It was reasoned that the failure to detect deprotonation of 1 could arise from the overwhelming competition of detrimethylsilylation, rather than from structural factors (eq 2 and 3).



(1) For a recent review, cf.: Cacace, F. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; D. Reidel: Dordrecht, 1987; and references therein.

(2) Even highly activated aromatics do not undergo electrophilic C-silylation, cf.: Häbich, D.; Effenberger, F. *Synthesis* 1979, 844. Only a few examples of heteroaromatic silylation by the trimethylsilyltriflate/triethylamine complex have been reported, cf.: Frick, U.; Simchen, G. *Synthesis* 1984, 929.

(3) Wojtyniak, A. C. M.; Stone, J. A. *Int. J. Mass Spectrom. Ion Processes* 1986, 74, 59.

(4) Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* 1973, 95, 5851.

(5) Cacace, F. *Radiat. Phys. Chem.* 1982, 20, 99.

(6) Speranza, M. *Gazz. Chim. Ital.* 1983, 113, 37.

Table I. Aromatic Trimethylsilylation in CH<sub>4</sub>/SiMe<sub>4</sub> at 700 Torr, 37 °C

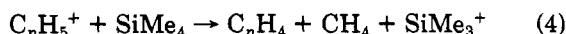
system composition, torr <sup>a</sup>			product yields <sup>b</sup> (G <sub>+M</sub> )		orientation in TolySiMe <sub>3</sub> , %	
arenes					meta	para
additives						
PhH: 3.00	PhMe: 1.60	none	c			
	1.64	NEt <sub>3</sub> : 0.45	TolySiMe <sub>3</sub> : 0.27 (9%)		15	85
	1.94	1.10	0.58 (19%)		15	85
	1.94	2.31	0.37 (12%)		15	85
PhH: 1.32	PhMe: 7.41	0.54	PhSiMe <sub>3</sub> : 0.02 (0.6%)	TolySiMe <sub>3</sub> : 0.54 (18%)	15	85
2.15	1.50	0.56	0.51 (17%)	1.21 (41%)	17	83
7.14	1.50	0.68	0.19 (6.3%)	0.13 (4.4%)	17	83
1.67	1.46	1.25	0.09 (3.1%)	0.33 (11%)	14	86
2.10	2.10	Me <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH: 1.0	0.01 (0.3%)	0.02 (0.6%)		
	1.28	c-C <sub>6</sub> H <sub>10</sub> O: 0.56	c			
	1.49	Et <sub>2</sub> O: 1.1	c			
	1.80	c-C <sub>6</sub> H <sub>10</sub> O: 1.12	TolySiMe <sub>3</sub> : 0.07 (2.2%)			
		NEt <sub>3</sub> : 1.23	c			
PhMe: 2.40	mesitylene: 2.10	none	c			
3.60	2.30	NEt <sub>3</sub> : 0.95	TolySiMe <sub>3</sub> : 0.37 (12%)		14	86
1.30	<i>o</i> -xylene: 1.60	NEt <sub>3</sub> : 0.63	TolySiMe <sub>3</sub> : 0.49 (16%)	XylylSiMe <sub>3</sub> : 1.76 (59%)	16	84
1.48	<i>m</i> -xylene: 1.48	NEt <sub>3</sub> : 0.78	TolySiMe <sub>3</sub> : 0.30 (10%)	2,4-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SiMe <sub>3</sub> : 0.31 (10%)	12	88
				3,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SiMe <sub>3</sub> : 0.13 (4.3%)		
1.37	<i>p</i> -xylene: 1.78	NEt <sub>3</sub> : 0.52	TolySiMe <sub>3</sub> : 0.20 (7%)	2,5-Me <sub>2</sub> C <sub>6</sub> H <sub>3</sub> SiMe <sub>3</sub> : 0.17 (6%)	11	89

<sup>a</sup> All systems contained O<sub>2</sub> (10 Torr) as a radical scavenger. <sup>b</sup> The absolute *G* values are affected by a large uncertainty ( $\pm 30\%$ ) related to absolute dosimetry, while their internal consistency, and therefore the relative yields given in parentheses have a much lower ( $\pm 5\%$ ) standard deviation. <sup>c</sup> Below detection limit, corresponding to a yield of ca. 0.2%.

Consequently, it appeared that successful demonstration of electrophilic trimethylsilylation could depend on the judicious choice of the gaseous base.

### Results and Discussion

Preliminary ICR experiments on the reactions of SiMe<sub>3</sub><sup>+</sup> and PhHSiMe<sub>3</sub><sup>+</sup> ions with various bases, showed that oxygenated nucleophiles undergo exclusively trimethylsilylation and suggested nitrogen bases, in particular NEt<sub>3</sub>, as more promising candidates.<sup>7</sup> Accordingly, NEt<sub>3</sub> was used in the radiolytic silylation, illustrated in Table I, where the absolute yields are expressed by the *G*<sub>(+M)</sub> values of the products, i.e., by the number of molecules formed per 100 eV. The silylating agent is obtained from the reaction of tetramethylsilane with the C<sub>*n*</sub>H<sub>5</sub><sup>+</sup> (*n* = 1, 2) ions formed from the radiolysis of CH<sub>4</sub> with a combined *G* value of ca. 3<sup>8</sup> (eq 4).



This exothermic process ( $\Delta H^\circ = -38$  (*n* = 1) and  $-7$  (*n* = 2) kcal mol<sup>-1</sup>) (eq 4) is known to occur efficiently in ionized CH<sub>4</sub> containing traces of SiMe<sub>4</sub>.<sup>3,9-11</sup>

The radiochemical yield of SiMe<sub>3</sub><sup>+</sup> is thus defined by the *G* value of C<sub>*n*</sub>H<sub>5</sub><sup>+</sup> as long as SiMe<sub>4</sub> is in large excess over competing nucleophiles such as the aromatic substrate itself, oxygenated nucleophiles formed in traces by the radiolysis or deliberately added bases. Assuming this condition to be verified, relative trimethylsilylation yields have been evaluated.

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, since no trimethylsilylated products are

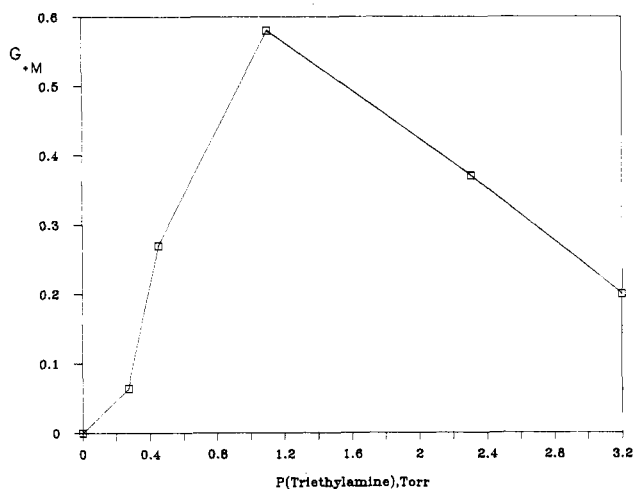


Figure 1. Absolute yield of (trimethylsilyl)toluenes as a function of NEt<sub>3</sub> partial pressure.

formed at all unless an appropriate base is present, which rules out contributions from radical, or excited molecule, radiolytic processes.<sup>12</sup>

In the absence of additives the oxygenated compounds invariably present in the gas as impurities (H<sub>2</sub>O) or formed from the radiolysis (H<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>2</sub>O, etc.) react exclusively according to eq 2, which prevents formation of silylated aromatics, as, for that matter, do deliberately added oxygenated bases, e.g., Et<sub>2</sub>O and c-C<sub>6</sub>H<sub>10</sub>O (Table I), despite their high proton affinity (PA).<sup>13</sup> Addition of NEt<sub>3</sub> has two opposing effects. On the one hand, it allows deprotonation of sterically unhindered adducts 1 (eq 3) and therefore formation of neutral silylated products via a highly exothermic process.<sup>14</sup> On the other hand, the

(7) Fornarini, S.; et al., to be published.

(8) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* 1963, 39, 3341.

(9) Klevan, L.; Munson, B. *Int. J. Mass Spectrom. Ion Phys.* 1974, 13, 261.

(10) Krause, J. R.; Potzinger, P. *Int. J. Mass Spectrom. Ion Phys.* 1975, 13, 303.

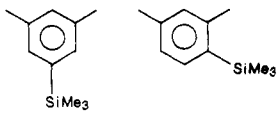
(11) Clemens, D.; Munson, B. *Org. Mass Spectrom.* 1985, 20, 368.

(12) In any case, the ionic origin of the products is confirmed by the presence of an effective radical scavenger (O<sub>2</sub>) and by the gradual suppression of the silylation process in the presence of increasing amounts of NEt<sub>3</sub> and other bases.

(13) PA's of Et<sub>2</sub>O and c-C<sub>6</sub>H<sub>10</sub>O are respectively 200.2 and 201.4 kcal mol<sup>-1</sup>. All PA values were taken from: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* 1984, 13, 695.

(14) The PA of NEt<sub>3</sub> is as high as 232.3 kcal mol<sup>-1</sup>, see ref 13.

**Table II. Selectivity of the Gas-Phase Trimethylsilylation and *tert*-Butylation of Methylbenzenes<sup>a</sup>**

substrate	$k_S/k_B^b$	$k_S/k_T^b$	orientation <sup>c</sup> (%)
toluene <sup>d</sup>	3.8 (55)	1.00	meta: 14 (6) para: 86 (94)
<i>o</i> -xylene <sup>e</sup>		3.3 (2.0)	
<i>m</i> -xylene <sup>e</sup>		1.5 (1.6)	
			
			30 (13)      70 (87)
<i>p</i> -xylene <sup>e</sup>	0.6	(unreactive)	
mesitylene <sup>f</sup>	unreactive	(unreactive)	

<sup>a</sup> Values in parentheses refer to *tert*-butylation. <sup>b</sup> Standard deviation ca. 10%.  $k_S/k_B$  and  $k_S/k_T$  denote the reactivity of the substrate toward the electrophiles,  $\text{SiMe}_3^+$  and  $\text{CMe}_3^+$ , relative respectively to that of benzene and of toluene. Such ratios have been calculated from the relative yields of products measured in competition experiments, taking into account the concentrations of the competing substrates. <sup>c</sup> Standard deviation ca. 3%. <sup>d</sup> Data for *tert*-butylation from ref 4. <sup>e</sup> Data for *tert*-butylation from ref 16. <sup>f</sup> Data for *tert*-butylation from ref 17.

amine effectively intercepts the  $\text{C}_7\text{H}_5^+$  and  $\text{SiMe}_3^+$  ionic precursors, thus depressing the yields. This accounts for the peculiar dependence of the yields on the partial pressure of  $\text{NEt}_3$  illustrated in Figure 1. The 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. The kinetic, rather than thermodynamic character of the factors controlling the  $k_2/k_3$  branching ratio emerges from the effect of the simultaneous addition of  $\text{NEt}_3$  and  $\text{c-C}_6\text{H}_{10}\text{O}$ , and especially of  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$ , whose PA is as high as of  $\text{NEt}_3$ ,<sup>15</sup> but containing an oxygenated nucleophilic center. The high reactivity of the latter toward  $\text{SiMe}_3^+$  favors process (eq 2) over deprotonation (eq 3) and hence prevents formation of neutral silylated products.

In conclusion, formation of trimethylphenylsilanes is traced to a reaction sequence initiated by the electrophilic attack (eq 1), followed by deprotonation (eq 3), whose competition with desilylation (eq 2) is affected by the nature of the base.

Table II compares the selectivity of gaseous  $\text{SiMe}_3^+$ <sup>18</sup> and  $t\text{-Bu}^+$  ions. Despite the extremely high  $k_T/k_B$  ratio in *tert*-butylation,<sup>19</sup> the substrate and positional selectivity of the cations are similar. This reflects the operation of steric factors which determines, in both cases, the reactivity order of the xylenes. The lack of reactivity of mesitylene has been traced, in the case of *tert*-butylation, to steric hindrance to deprotonation.<sup>17</sup> As a whole,  $\text{SiMe}_3^+$  appears noticeably less selective, as shown, inter alia, by the para:meta ratio in toluene, ca. 12, considerably lower than observed in *tert*-butylation, ca. 32.

(15) The PA of  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$  was estimated to be ca. 232 kcal  $\text{mol}^{-1}$  by applying a group-additivity method to the data from ref 13.

(16) Giacomello, P.; Cacace, F. *J. Am. Chem. Soc.* 1976, 98, 1823.

(17) Aliprandi, B.; Cacace, F.; Cipollini, R. *Radiochimica Acta* 1982, 31, 107.

(18) The evidence from chemical ionization mass spectrometry, cf. ref 3, 9-11, suggests that at the relatively high  $\text{SiMe}_4$  pressures and low temperatures prevailing in the radiolytic experiments,  $\text{SiMe}_3^+$  is reversibly associated with one or more  $\text{SiMe}_4$  molecules. The effects on the energetics of eq 1 are probably limited, since there are reasons to believe that the  $\text{SiMe}_3^+\text{-SiMe}_4$  binding energy is low.

(19) Sen Sharma, D. K.; Ikuta, S.; Kebarle, P. *Can. J. Chem.* 1982, 60, 2325.

## Experimental Section

The gases, with a stated purity in excess of 99.99 mol %, were purchased from Matheson Gas Products Inc.; tetramethylsilane, obtained from Fluka A. G., had a purity of 99.5 mol %. The chemicals used as substrates or reference standards in the analyses were obtained from commercial sources, or prepared according to unexceptional procedures, except (trimethylsilyl)arenes which were prepared from the reaction of the corresponding aryl Grignard derivative with trimethylsilyl triflate. The gaseous samples, prepared in a greaseless line by standard vacuum procedures and introduced into 135-mL Pyrex ampules, were irradiated in a 220 Gammacell (Nuclear Canada Ltd.) to a total dose of ca.  $10^4$  Gy, at a dose rate of ca.  $10^4$  Gy  $\text{h}^{-1}$ . The analysis of the irradiated mixture was carried out by GLC and GLC/MS, with the following columns: (i) a 50 m long, 0.2 mm i.d. silica column, coated with methylsilicone SP 2100 fluid, deactivated with Carbowax 20M; (ii) a 3.5 m long, 3 mm i.d. stainless steel column, packed with SP-2100, 20% w/w on 100-200 mesh Supelcoport, deactivated with 1% Carbowax 1500; (iii) a 12-m long, 0.2-mm i.d. silica column, coated with a 0.33- $\mu\text{m}$  film of cross-linked methylsilicone polymer.

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 recorded with a Hewlett-Packard 5970B mass selective detector. The amounts of products formed were determined from the areas of the corresponding elution peaks, by using the internal standard calibration method.

The ICR measurements were carried out at typical pressures of  $5 \times 10^{-7}$  Torr with a Nicolet FT-MS 1000 spectrometer.

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**Registry No.** PhH, 71-43-2; PhMe, 108-88-3;  $\text{SiMe}_3^+$ , 28927-31-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3.

## Achiral Hexaisopropylbenzene Isotopomers: Analogues of the Achiral Trihydroxyglutaric Acid Diastereomers

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Certain derivatives of hexaisopropylbenzene (hib) may exist as achiral diastereomers which are distinguished by the sense of directionality of the isopropyl C-H methine vectors and which, though devoid of conventional stereocenters, are conceptually related to the achiral 2,3,4-trihydroxyglutaric acid diastereomers.<sup>1</sup> We now report the first synthesis of such stereoisomers.

**Synthesis and <sup>1</sup>H NMR Spectra of Hexaisopropylbenzene-*d*<sub>18</sub>.** Addition of (3-methyl-1-butyn-1-yl)magnesium bromide to acetone-*d*<sub>6</sub> afforded 2,5-dimethylhex-3-yn-2-ol-*d*<sub>6</sub>. Reduction of the alcohol functionality yielded diisopropylacetylene-*d*<sub>6</sub> in which one isopropyl group was perdeuteriated at the methyl positions. Cyclotrimerization of the labeled acetylene yielded hib-*d*<sub>18</sub>. In the absence of significant isotope effects, three isomers of hib-*d*<sub>18</sub> should be formed in a statistical ratio 1:2:3 = 2:3:3 (Figure 1), where 2 and 3 are conformational dia-

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