be recovered by chromatography from the diisopropyl ether solution.

***N*-Phenyl-*N'*-[2-(3,4,6-trimethylbenzofuranyl)]hydrazine (5).** To a stirred solution of the azo compound **2f** (0.32 g) in acetone (50 mL) were added zinc dust (2.0 g) and a saturated aqueous solution of ammonium chloride (10 mL) portionwise at 0–5 °C; stirring was maintained until the color disappeared. The resulting suspension was filtered and the clear solution diluted with ice-cold water. The pH was adjusted to 8 with concentrated ammonium hydroxide solution, and the separated solid was extracted with chloroform. The organic layer was washed with water, dried (Na_2SO_4), and evaporated to dryness to give a residue, which was treated with diisopropyl ether. The undissolved solid was crystallized from toluene to give the title compound **5** (0.17 g); its analytical and spectral data were identical with those described above for the product obtained from the catalytic hydrogenation of **2f**.

Acknowledgment. We thank Prof. Raffaello Fusco for his helpful advice throughout this research.

Registry No. **1a**, 78241-05-1; **1b**, 112374-86-4; **1c**, 112374-87-5; **1d**, 112374-88-6; **1e**, 112374-89-7; **1f**, 112374-90-0; **1g**, 112374-91-1; **1h**, 112374-92-2; **2a**, 112374-93-3; **2b**, 112374-94-4; **2c**, 112374-95-5; **2d**, 112374-96-6; **2e**, 112374-97-7; **2f**, 112374-98-8; **2g**, 112374-99-9; **2h**, 112375-00-5; **3**, 112375-01-6; **4**, 112375-02-7; **5**, 112375-03-8; **6**, 16108-50-2; **7**, 112375-04-9; AcC(Cl)=NNHPh, 18440-58-9; $PhNH_2$, 62-53-3; 3,5-$(Me)_2C_6H_3NH_2$, 108-69-0; *p*-AcC(Cl)=$NNHC_6H_4Cl$, 18247-78-4; PhCOC(Cl)=NNHPh, 75482-50-7; PhOH, 108-95-2; 3,5-$(Me)_2C_6H_3OH$, 108-68-9; 3,5-$(Me)_2C_6H_3SH$, 38360-81-5; PhSH, 108-98-5.

Regioselective Ring Opening in Annelated Benzocyclopropenes

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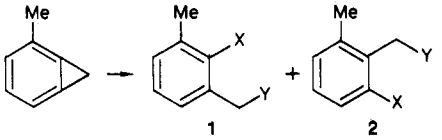
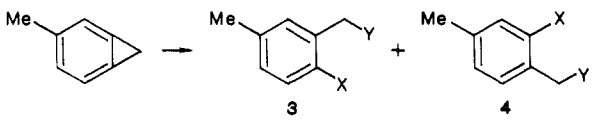
The facile cleavage of the three-membered ring of benzocyclopropenes by electrophiles is of interest with regard to both mechanism and synthesis.[1] Garratt and his coworkers[2] have prepared several asymmetrically substituted benzocyclopropenes and shown that the direction of ring cleavage can be controlled by the selection of electrophile. For example, 2-methylbenzocyclopropene reacts with bromine, iodine, and HCl to give the *m*-xylenes **1a–c** as the major products, whereas it reacts with silver nitrate



1 2

a, X = Y = Br; **b**, X = Y = I; **c**, X = H, Y = Cl; **d**, X = H, Y = OEt; **e**, X = H, Y = NHPh

in the presence of ethanol and aniline to give *o*-xylenes **2d,e** as the major products. Similarly, 3-methylbenzocyclopropene gives mainly *m*-xylenes **3a–c** with the halogens and HCl and gives *p*-xylenes **4d,e** with silver nitrate in ethanol or aniline.

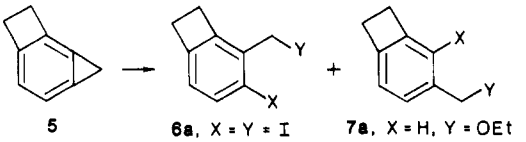


3 4

a, X = Y = Br; **b**, X = Y = I; **c**, X = H, Y = Cl; **d**, X = H, Y = OEt; **e**, X = H, Y = NHPh

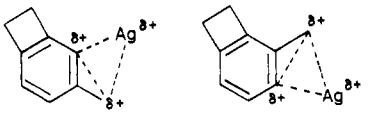
(1) See: Halton, B. *Ind. Eng. Chem. Prod. Res. Dev.* **1980**, *19*, 349. Billups, W. E. *Acc. Chem. Res.* **1978**, *11*, 245.
(2) Bee, L. K.; Garratt, P. J.; Mansuri, M. M. *J. Am. Chem. Soc.* **1980**, *102*, 7076.

Cyclopropa[3,4]benzocyclobutene (**5**) also gives different products with halogens (**6a,b**) and silver nitrate in ethanol (**7a**), but in this case HCl gives the same type of product (**7b**) as silver ion. These differences in electrophilic be-



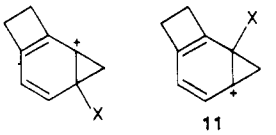
5 **6a**, X = Y = I; **b**, X = Y = Br **7a**, X = H, Y = OEt; **b**, X = H, Y = Cl

havior toward two types of reagents were suggested[2] to arise from attack of the silver ion (and the proton in the case of **5**) on the σ electrons of the cyclopropyl ring. If the reaction of **5** with silver ion proceeds via the σ route, then the observed regiochemistry would require that **8** be preferred to **9**.



8 9

The reaction with halogens presumably proceeds by attack on the π electrons to give the intermediate in which the positive charge is also located at the α position to the four-membered ring, i.e., **10**, in preference to **11**.



10 11

A tendency for benzocycloalkenes with strained rings to react with electrophiles mainly β to the ring junction was reported by Mills and Nixon[3] nearly 60 years ago. Subsequent studies on the electrophilic substitution reactions of benzocyclopropenes and biphenylene also show that the β position of these compounds is more reactive to electrophilic substitution.[4,5] Although a satisfying explanation[6] for these results has not been presented, rehybridization of the framework which occurs in these molecules because of the bond angle requirements of the small ring is most often presented.[7-9]

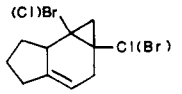
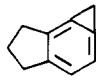
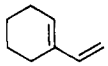
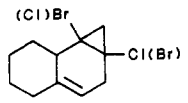
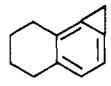
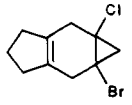
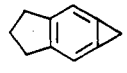
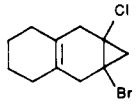
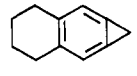
We report now the synthesis of two new asymmetrically fused benzocyclopropenes **12** and **13**, as well as their linearly fused isomers **14** and **15**, and their reactions with electrophiles. The syntheses were carried out by dehydrohalogenation of the Diels–Alder adducts of 1-bromo-2-chlorocyclopropene[10] and the appropriate diene. The starting materials and yields are presented in Table I.

Studies on the reactions of **12** and **13** with electrophiles showed that **12** follows a path similar to that observed by Garratt for **5**, whereas **13** yields both regioisomers with each electrophile. These results are presented in Table II. The linearly fused benzocyclopropenes **14** and **15** were

(3) Mills, W. H.; Nixon, I. G. *J. Chem. Soc.* **1930**, 2510.
(4) Loyd, J. B. F.; Ongley, P. A. *Tetrahedron* **1965**, *21*, 245.
(5) Blatchly, J. M.; Taylor, R. *J. Chem. Soc.* **1964**, 4641.
(6) For example, it is not readily apparent why a positive charge located at the α-position (as a **10**) should be preferred.
(7) Finnegan, R. A. *J. Org. Chem.* **1965**, *30*, 1333.
(8) Streitwieser, A.; Ziegler, G. R.; Mowery, P. C.; Lewis, A.; Lawler, R. G. *J. Am. Chem. Soc.* **1968**, *90*, 1357.
(9) Vaughan, J.; Wright, G. J. *J. Org. Chem.* **1968**, *33*, 2580.
(10) Billups, W. E.; Lin, L.-J.; Arney, B. E., Jr.; Rodin, W. A.; Casserly, E. W. *Tetrahedron Lett.* **1984**, *25*, 3935.

0022-3263/88/1953-1312$01.50/0

Table I. Synthesis of Benzocyclopropenes by Dehydrohalogenation of the Diels–Alder Adducts of 1-Bromo-2-chlorocyclopropene and Various Dienes

diene	Diels–Alder adduct	benzocyclopropene	yield, %
	 16	 12	44
	 17	 13	80
	 18	 14	83
	 19	 15	96

also used to synthesize indans and tetralins, respectively, with each electrophile.

The reactions of **12** can be rationalized in terms of the strain (and thus perhaps rehybridization) induced by the five-membered ring. In contrast to **12** (and **5**), the effect of strain would be insignificant with the six-membered ring in **13** and each electrophile yields both regioisomers.

Finally, these results confirm the earlier hypothesis[2] that fusion of a strained ring to the benzocyclopropene nucleus can lead to regioselective ring cleavage. These compounds may thus find use as reagents in syntheses.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Jeol FX-90Q spectrometer in $CDCl_3$ and are reported in δ units relative to TMS. Infrared spectra were recorded on a Beckman IR 3230 instrument as neat films. Mass spectra were recorded on a double-focusing CEC 21-110 spectrometer. Column chromatography was performed on Baker reagent-grade silica gel (60–200 mesh) or Florisil (100–200 mesh). Solvents were purified by standard methods.

1a-Bromo-6b-chloro-1,1a,2,4,5,6,6a,6b-octahydrocyclopropa[*e*]indene (16). 1-Vinylcyclopentene[11] (0.85 g, 9.0 mmol) and 1-bromo-2-chlorocyclopropene (5.0 mmol) were stored in THF at −20 °C for 3 days. The solvent was then removed in vacuo and the residue dissolved in dichloromethane, dried over magnesium sulfate, and concentrated in vacuo. Chromatography on silica gel (hexane) gave the desired **16** as a colorless oil (324 mg, 26%): NMR δ 5.25 (m, 1 H), 3.2–2.7 (m, 3 H), 2.6–1.4 (m, 6 H), and 1.25 (m, 2 H); IR 3090, 3020, 2960, 2870, 1670, 1630, 1410, 1105 cm^{-1}; mass spectrum, calcd *m/e* 245.9811, found *m/e* 245.9816.

1a-Bromo-7b-chloro-1a,2,4,5,6,7,7a,7b-octahydro-1*H*-cyclopropa[*b*]naphthalene (17). 1-Vinylcyclohexene[11] (0.50 g, 4.63 mmol) and 1-bromo-2-chlorocyclopropene (5.0 mmol) were stored in THF at −20 °C for 40 h. The product was isolated as a colorless oil (432 mg, 36%). NMR δ 5.1 (m, 1 H), 3.5–1.1 (m, 13 H); IR 3040, 2935, 2850, 1700, 1665, 1445, 1260, 730 cm^{-1}; mass spectrum calcd *m/e* 259.9967, found *m/e* 259.9970.

1a-Bromo-7a-chloro-1a,2,3,4,5,6,7,7a-octahydro-1*H*-cyclopropa[*b*]naphthalene (19). 1,2-Dimethylenecyclohexane[12] (0.70 g, 6.5 mmol) and 1-bromo-2-chlorocyclopropene (5.0 mmol) were stored in THF at −20 °C for 5 days. The product was isolated as a colorless oil (634 mg, 48%): NMR δ 3.1–2.4 (m, 4 H), 2.0–1.1 (m, 10 H); IR (neat) 2930, 2820, 1435, 1060, 1010 cm^{-1}; mass spectrum calcd *m/e* 259.9967, found *m/e* 259.9970.

1a-Bromo-6a-chloro-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]indene (18). A solution of 1-bromo-2-chlorocyclopropene (0.767 g, 5.0 mmol) and 1,2-dimethylenecyclopentane[12] (0.50 g, 5.3 mmol) in THF were stored at −20 °C for 2 days. The product was isolated as a colorless oil (472 mg, 38%): NMR δ 3.1–2.7 (d, 4 H), 2.5–2.0 (m, 4 H), 1.9–1.5 (m, 2 H), 1.44 (d, 2 H); IR (neat) 2960, 2900, 2850, 1440, 1072 cm^{-1}; mass spectrum calcd *m/e* 245.9811, found *m/e* 245.9816.

1,4,5,6-Tetrahydrocycloprop[*e*]indene (12). A solution of **16** (150 mg, 0.606 mmol) in dry THF (1.0 mL) was added rapidly under nitrogen at −50 °C to a suspension of potassium *tert*-butoxide (500 mg, 4.46 mmol) in dry THF (2.0 mL). The mixture was warmed to ca. −20 °C and stirred for 1 h. The solution was concentrated in vacuo and the residue washed with pentane. The washings were centrifuged to remove inorganic salts and the solvent removed in vacuo. The residue was chromatographed on Florisil (pentane) to give nearly pure **12** (34.9 mg, 44%): NMR δ 7.20–7.00 (qt, 2 H), 3.20 (s, 2 H), 3.05–2.80 (m, 4 H), 2.3–1.9 (m, 2 H); IR 3050, 2945, 2845, 1670, 1455, 1050, 795 cm^{-1}; mass spectrum, calcd *m/e* 130.0783, found *m/e* 130.0785.

4,5,6,7-Tetrahydro-1*H*-cyclopropa[*a*]naphthalene (13). Compound **13** was prepared by treating **17** (112 mg, 0.43 mmol) with potassium *tert*-butoxide (1.2 g, 10.7 mmol) as described above for **12**. Chromatography on Florisil (pentane) afforded **13** as a colorless oil (49.7 mg, 80%): NMR δ 7.13–6.90 (m, 2 H), 3.15 (s, 2 H), 2.80 (d, 4 H), 1.85 (m, 4 H); IR 3045, 2920, 2845, 1675, 1460, 1255, 1060, 800 cm^{-1}; mass spectrum calcd *m/e* 144.0939, found 144.0938.

1,3,4,5-Tetrahydrocycloprop[*f*]indene (14). Compound **14** was prepared by treating **18** (124 mg, 0.503 mmol) with potassium *tert*-butoxide (500 mg, 4.46 mmol) as described previously for **12**. Chromatography on Florisil (pentane) gave nearly pure **14** (54.4 mg, 83%) as a pale yellow oil: NMR δ 7.15 (s, 2 H), 3.35 (s, 2 H), 3.05–2.80 (t, 4 H), 2.28–1.92 (m, 2 H); IR 3045, 2940, 2840, 1655, 1450, 1345, 1055, 835 cm^{-1}; mass spectrum calcd *m/e* 130.0783, found *m/e* 130.0785.

3,4,5,6-Tetrahydro-1*H*-cycloprop[*b*]naphthalene (15). Compound **15** was prepared by treating **19** (153 mg, 0.589 mmol) with potassium *tert*-butoxide (500 mg, 4.46 mmol) as described above for **12**. Chromatography on Florisil (pentane) afforded **15** as a yellow oil (81.7 mg, 96%): NMR δ 6.97 (s, 2 H), 3.21 (s, 2 H), 2.90–2.65 (m, 4 H), 1.90–1.65 (m, 4 H); IR 3050, 3020, 2940, 2860, 1670, 1455, 1355, 1055, 840 cm^{-1}; mass spectrum calcd *m/e* 144.0939, found *m/e* 144.0938.

Reaction of 1,4,5,6-Tetrahydrocycloprop[*e*]indene (12) with Bromine. Compound **12** (9.2 mg, 0.071 mmol) in CCl_4 (5 mL) was cooled to ca. −20 °C under an atmosphere of nitrogen. A solution of bromine (50 mg) in CCl_4 was then added in one portion and the mixture stirred for 5 min and warmed to room temperature. Excess bromine was destroyed by washing with a sodium bisulfite solution, and the organics were dried over magnesium sulfate. Removal of the solvent in vacuo afforded 5-bromo-4-(bromomethyl)-2,3-dihydro-1*H*-indene (**20a**) as a yellow oil (16.1 mg, 78%): NMR δ 7.40–6.95 (m, 2 H), 4.64 (s, 2 H), 3.11–2.79 (m, 4 H), 2.30 (m, 2 H).

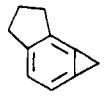
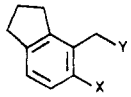
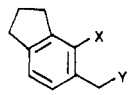
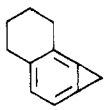
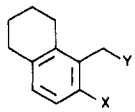
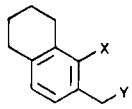
Reaction of 1,4,5,6-Tetrahydrocycloprop[*e*]indene (12) with Iodine. Compound **12** (8.8 mg, 0.068 mmol) was reacted with iodine as described above for bromine affording a mixture of the two isomeric ring-cleaved products, 2,3-dihydro-5-iodo-4-(iodomethyl)-1*H*-indene (**20b**) and 4-iodo-5-(iodomethyl)-1*H*-indene (**21a**) (ratio 68:32 by NMR). The combined yield was 19.2 mg (74%): NMR δ 7.6–6.7 (m, 2 H), 4.60, 4.51 (2 s, corresponding to **20b** and **21a**, 2 H), 3.1–2.7 (m, 4 H), 2.3–1.9 (m, 2 H).

Reaction of 1,4,5,6-Tetrahydrocycloprop[*e*]indene (12) with HCl. Compound **12** (10.0 mg, 0.077 mmol) in CCl_4 (5 mL) was treated with concentrated hydrochloric acid (100 μL) for 1 h with vigorous stirring. The organic phase was then washed with water and dried over magnesium sulfate. Removal of the solvent in vacuo afforded **21b** as a colorless oil (12.8 mg, 68%): NMR δ 7.25–7.05 (br t, 3 H), 4.58 (s, 2 H), 3.05–2.71 (br t, 4 H), 2.28–1.85 (m, 2 H).

Reaction of 1,4,5,6-Tetrahydrocycloprop[*e*]indene (12) with Silver Ion in Methanol. Compound **12** (11.2 mg, 0.086 mmol) and dry methanol in CCl_5 (5 mL) were treated with AgCN

(11) Thummel, R. P.; Nutakul, W. *J. Org. Chem.* **1977**, *42*, 300.
(12) Bartlett, P. D.; Wingrove, A. S.; Owyang, R. *J. Am. Chem. Soc.* **1968**, *90*, 6067.

Table II. Reactions of Benzocyclopropenes with Electrophiles

benzocyclopropene	electrophile	products (yield, %)	
			
12		20	21
	Br_2	a, X = Y = Br (100)	
	I_2	b, X = Y = I (68)	a, X = Y = I (32)
	HCl		b, X = H, Y = Cl (100)
	Ag^+/MeOH		c, X = H, Y = OMe (100)
			
13		22	23
	Br_2	a, X = Y = Br (80)	a, X = Y = Br (20)
	HCl	b, X = H, Y = Cl (45)	b, X = H, Y = Cl (55)
	Ag^+/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 δ 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-1*H*-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 δ 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-1*H*-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 δ 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-1*H*-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 δ 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).

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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-cyclocyclopropene, 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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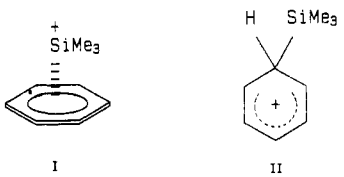
One of the major objectives of gas-phase ion chemistry is to provide highly simplified and generalized models of ionic reactions in condensed media. Consequently, a great deal of work has been devoted in recent years to extend to the gas phase the study of classical reactions, e.g., protonation, alkylation, nitration, nucleophilic displacement, etc. long familiar to organic chemists.[1] 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.[2]

Recently, formation of silylated adducts from the exothermic reaction in eq 1, $\Delta H° = -29.3$ kcal mol^{-1} in the case

$$SiMe_3^+ + ArH \rightarrow \underset{\mathbf{1}}{ArHSiMe_3^+} \qquad (1)$$

of PhH, was detected in a mass spectrometric study carried out at 3–5 Torr, at temperatures ranging from 300 to 600 K.[3] However, occurrence of a substitution reaction was excluded; the π-complex structure I was assigned to **1** rather than the σ-complex structure II, based on the inability of gaseous bases to undergo H^+, rather than $SiMe_3^+$ transfer from **1**.[3]



I II

Nevertheless, taking into account the tentative nature of structural assignments by purely mass spectrometric techniques, the role of σ-complexes demonstrated in closely related reactions such as aromatic alkylation by gaseous *t*-Bu^+,[4] 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.[1,5,6] 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).

$$1 + B \xrightarrow{k_2} ArH + BSiMe_3^+ \qquad (2)$$

$$1 + B \xrightarrow{k_3} ArSiMe_3 + BH^+ \qquad (3)$$

(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.

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