scission and formation of (3-chloropropoxy)trimethylsilanes. In the presence of sodium metal these undergo further reaction.

An alternative possibility, S_N1 cleavage (Scheme I) of the silyl-substituted oxonium ion/chloride ion pair to a carbocation/chloride ion pair, can be eliminated since no products resulting from a neopentyl rearrangement are observed with 3,3-dimethyloxetane.[10] Neopentyl rearrangement would rapidly convert a primary carbocation to a more stable tertiary carbocation via a 1,2 Wagner–Meerwein rearrangement. In addition, 2-methyloxetane would be expected to open to a more stable secondary carbocation rather than a primary one if the silyl-substituted oxonium ion underwent S_N1-type cleavage. No products predicted from such an S_N1 cleavage are observed.

We believe these results provide additional evidence that great caution should be used in proposing the existence of dimethylsilylene in the solution-phase reaction of dimethyldichlorosilane and sodium metal.[11] In addition, our results provide evidence for the mechanism of C–O cleavage of oxetanes by chlorosilanes.

Experimental Section

IR spectra were recorded as 2% CCl_4 solutions on a Perkin-Elmer 281 spectrometer. ^1H NMR spectra were recorded on a Varian XL-100 spectrometer operating in the FT mode by using 1% solutions in $CDCl_3$ with an internal standard of chloroform. Elemental analysis were performed by Galbraith Laboratories, Inc. Samples of all compounds for spectra and elemental analyses were purified by preparative vapor-phase chromatography on a Hewlett-Packard F&M 700 using a 26 ft × 0.25 in. 20% SE-30 on Chromosorb W (60–80 mesh) column.

Oxetane, 3,3-dimethyloxetane, and 2-methyloxetane were purchased from Aldrich Chemical Co. Trimethylchlorosilane and dimethyldichlorosilane were purchased from Silar Chemical Co.

Reaction of Oxetanes with Dimethyldichlorosilane and Sodium. A typical run of dimethyldichlorosilane, oxetane, and sodium is described below. Oxetane (0.05 mol), sodium (2.3 g, 0.1 mol), and 20 mL of toluene were placed in a 100-mL, three-necked, round-bottomed flask equipped with a pressure-equalizing addition funnel, a reflux condenser, and a Teflon-covered magnetic stirring bar. Freshly distilled dimethyldichlorosilane (0.055 mol) in 20 mL of toluene was added dropwise to the refluxing, stirred solution. After the addition was complete, the solution was refluxed for 8 h. The reaction mixture was cooled to room temperature. Ethanol was added to the solution to destroy residual sodium. The reaction mixture was washed with water, dried over Na_2SO_4, and filtered. The filtrate was subjected to GLPC analysis.

2,2-Dimethyl-1-oxa-2-silacyclopentane[3] was obtained from the reaction of dimethyldichlorosilane, oxetane, and sodium in toluene as above: 42% yield; NMR δ 3.85 (t, 2 H, $J = 6$ Hz), 2.02–1.70 (m, 2 H), 0.70 (t, 2 H, $J = 8$ Hz), 0.18 (s, 6 H).

2,2,4,4-Tetramethyl-1-oxa-2-silacyclopentane[1,14] was obtained from the reaction of dimethyldichlorosilane, 3,3-dimethyloxetane, and sodium in toluene: 47% yield; NMR δ 3.35 (s, 2 H) 1.04 (s, 6 H), 0.67 (s, 2 H), 0.21 (s, 6 H).

Reaction of Oxetane and Dimethyldichlorosilane. Oxetane (2.9 g, 50 mmol) and freshly distilled dimethyldichlorosilane (7.1 g, 55 mmol) were placed in a 25-mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar. The mixture was stirred at reflux for 2.5 h. The reaction mixture was cooled and subjected to fractional distillation through a 15-cm Vigreux distillation column. There was obtained (3-chloroproxy)dimethylchlorosilane: 8.9 g (47.6 mmol, 95.2%); bp 190–194 °C [lit.[3] bp 72 °C (16 mm)]; NMR δ 3.90 (2 H, t, $J = 5.5$ Hz), 3.61 (2 H, t, $J = 6$ Hz), 2.01 (2 H, q, $J = 6$ Hz), 0.48 (6 H, s).

Reaction of (3-Chloropropoxy)dimethylchlorosilane and Sodium Metal. (3-Chloropropoxy)dimethylchlorosilane (8.9 g, 47.6 mmol), 50 mL of *n*-decane, and sodium metal (1.2 g, 52 mmol) were placed into a 100-mL round-bottomed flask equipped with a reflux condenser and a Teflon-covered magnetic stirring bar. The mixture was stirred at reflux for 10 h. The reaction mixture was cooled. Ethanol (10 mL) was added into the mixture slowly to destroy excess sodium metal. The mixture was washed with two portions of 10 mL of water. The organic layer was dried and subjected to fractional distillation through a 15-cm Vigreux distillation column to give 2,2-dimethyl-1-oxa-2-silacyclopentane: 2.58 g (22.2 mmol, 47%); bp 93–95 °C (lit.[3] bp 95 °C).

Reaction of Oxetanes with Trimethylchlorosilane and Sodium. A typical reaction of trimethylchlorosilane, oxetane, and sodium is described below. Oxetane (0.05 mol), sodium (2.3 g, 0.1 mol), and 20 mL of toluene or *n*-decane were placed in a 100-mL, three-necked round-bottomed flask equipped with a pressure-equalizing funnel, reflux condenser, and a Teflon-covered magnetic stirrer. Freshly distilled trimethylchlorosilane (0.11 mol) in 20 mL of toluene or *n*-decane was added dropwise to the refluxing, stirred solution. After the addition was complete, the solution was refluxed for 3 h. The reaction mixture was cooled to room temperature. Ethanol was added to destroy residual sodium metal. The reaction mixture was washed with water, dried over Na_2SO_4, and filtered. The filtrate was subjected to GLPC analysis.

[3-(Trimethylsiloxy)propyl]trimethylsilane[12] was isolated from the reaction trimethylchlorosilane, oxetane, and sodium in *n*-decane as above: 55% yield; NMR δ 3.50 (t, 2 H, $J = 7$ Hz), 1.72–1.36 (m, 2 H), 0.55–0.34 (m, 2 H), 0.10 (s, 9 H), –0.03 (s, 9 H); IR $\bar{\nu}$ 1094 (Si–O–C), 1248 and 840 cm^{-1} ($Si(CH_3)_2$).

(3-Chloropropoxy)trimethylsilane[13] was found in 8% yield: NMR δ 3.76 (t, 2 H, $J = 6$ Hz), 3.68 (t, 2 H, $J = 6$ Hz), 1.96 (q, 2 H, $J = 6$ Hz), 0.12 (s, 9 H); IR $\bar{\nu}$ 1250 (Si–O–C), 1100 and 848 cm^{-1} ($Si(CH_3)_2$).

[2,2-Dimethyl-3-(trimethylsiloxy)propyl]trimethylsilane was obtained from the reaction of trimethylchlorosilane, 3,3-dimethyloxetane, and sodium in toluene as above: 48% yield; NMR δ 3.15 (s, 2 H), 0.88 (s, 6 H), 0.59 (s, 2 H), 0.07 (s, 9 H), 0.02 (s, 9 H); IR $\bar{\nu}$ 1078 (Si–O–C), 1250 and 840 cm^{-1} ($Si(CH_3)_2$). Anal. Calcd for $C_{11}H_{28}OSi$: C, 56.82, H, 12.14. Found: C, 56.75, H, 12.11.

[3-Methyl-3-(trimethylsiloxy)propyl]trimethylsilane was obtained from the reaction of trimethylchlorosilane, 2-methyloxetane, and sodium in toluene: 52% yield; NMR δ 3.70–3.42 (m, 1 H), 1.54–1.22 (m, 2 H), 1.13 (d, 3 H, $J = 6$ Hz), 0.54–0.33 (m, 2 H), 0.11 (s, 9 H), –0.03 (s, 9 H). Anal. Calcd for $C_{10}H_{26}OSi_2$: C, 54.97, H, 11.99. Found: C, 54.74, H 12.37.

Acknowledgment. This work was supported in part by the Air Force Office of Scientific Research (Grant No. 80-0006).

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[10] J. March, "Advanced Organic Chemistry Reaction Mechanisms and Structure", 2nd Ed., McGraw-Hill, New York, 1977, pp 964, 967.

[11] D. Tzeng and W. P. Weber, *J. Org. Chem.* **46**, 693 (1981), and references cited therein.

[12] G. S. Smirnova, D. N. Andreev, and E. A. Belinkina, *Zh. Obshch. Khim.*, 41, 2684 (1971).

[13] J. Pola and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **38**, 1674 (1973).

[14] E. J. P. Fear, J. Thorwer, and I. M. White, *Chem. Ind.* (*London*), 1877 (1961).

Reactions of 2,6-Di-*tert*-butylpyridine Derivatives with Methyl Fluorosulfate under High Pressure

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Introduction of alkyl groups into the 2- and 6-positions of pyridine results in a decrease in the rate of reaction with alkyl halides which becomes more and more pronounced as the size of the alkyl group increases.[1] The most highly

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[1] W. J. Le Noble and Y. Ogo, *Tetrahedron*, **26**, 4119 (1970).

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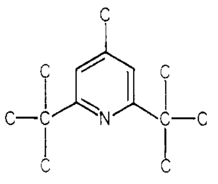
hindered compound of this series is Brown's base, 2,6-di-*tert*-butylpyridine, which possesses interesting and unusual properties.[2] It did react with a protoic acid but did not react with Lewis acids such as boron trifluoride or methyl iodide, because of steric hindrance between the bulky *tert*-butyl groups and the reactants.

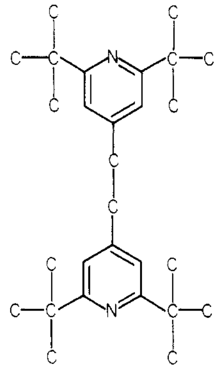
In 1966, we showed that 2,6-di-*tert*-butylpyridine (1) reacted with methyl iodide under high pressure to yield 2,6-di-*tert*-butyl-*N*-methylpyridinium iodide.[3] Later, we also studied the reaction of highly hindered bases, including 2,4,6-tri-*tert*-butylpyridine and 4,5-dimethylacridine, with methyl fluorosulfate (FSO_3CH_3) under high pressure.[4] Thus, the reaction of 1 with FSO_3CH_3 under 5500 atm at 60 °C for 15 h produced 2,6-di-*tert*-butyl-*N*-methylpyridinium fluorosulfate and 2,6-di-*tert*-butylpyridinium fluorosulfate in good yield. The ratio of the *N*-methyl and N-protonated compounds was found to be 4:1, respectively. The formation of the N-protonated product was believed to occur by reaction of 1 with fluorosulfuric acid produced by hydrolysis of FSO_3CH_3 fortuitously contaminated with water or by α elimination of the hydrogen of the methyl group in FSO_3CH_3.[5]

Recently, Weber and co-workers reported that the reactions of 1 and 2,6-di-*tert*-butyl-4-methylpyridine (2) with FSO_3CH_3 gave only the N-protonated compound (>99%) even under 10000-atm pressures.[6]

Thus, in order to clarify this discrepancy, we investigated further the reactions of 2 and 1,2-bis(2,6-di-*tert*-butyl-4-pyridyl)ethane (3) with FSO_3CH_3 under high pressure.



2



3

Results and Discussion

Compounds 2 and 3 were allowed to react with FSO_3CH_3 in methylene chloride under 4500 atm at 80 °C for several hours. The solid products obtained were found to be mixtures of the *N*-methyl and N-protonated compounds as in the case reported earlier.[4] However, under extremely dry conditions, the *N*-methyl products were found to be predominant (>90%) over the protonated compounds. Even under the same conditions, the ratio of the *N*-methyl and N-protonated products varied and depended on the dryness of the system. When the solvent was wetted with water, the *N*-protonated compound was obtained quantitatively. Thus, the formation of N-protonated compounds was due to the reactions of the pyridine compounds with fluorosulfonic acid produced by the hydrolysis of FSO_3CH_3.

The solution of compounds 2 or 3 with FSO_3CH_3 in methylene chloride was heated in a sealed tube at 100 °C for 72 h. The reaction was also carried out in chlorobenzene solution at 120–130 °C for 48 h. Neither reaction yielded *N*-methyl compounds.

Table I. ^1H NMR Spectral Data of 2 and 3 and Their *N*-Methyl Compounds

	shift,[a] δ			
compd	CH_3	*t*-Bu	ethylene	*N*-methyl
2	2.27[b]	1.35[b]		
3		1.35[b]	2.93[b]	
N-methyl of 2	2.66,[c] 2.78,[d] (2.60[f])	1.70,[c] 1.78,[d] (1.60[f])		4.51,[c] 4.63,[d] (4.57[d])
N-methyl of 3		1.79[e]	3.40[e]	4.70[e]

[a] All relative to internal tetramethylsilane. [b] In $CDCl_3$. [c] FSO_3^- salt in $CDCl_3$. [d] I^- salt in $CDCl_3$. [e] FSO_3^- salt in CF_3COOH. [f] ClO_4^- salt in Me_2SO-d_6. Figures in parentheses reported in ref 6.

The FSO_3^- ions of the *N*-methyl compounds of 2 and 3 were exchanged with I^- by means of an exchange resin. ^1H NMR spectral data for these compounds are shown in Table I.

Weber and co-workers successfully synthesized 2,6-di-*tert*-butyl-*N*-methylpyridinium fluorosulfate (yield ~10%) by refluxing 1 with FSO_3CH_3 at 180 °C for 48 h in *p*-chlorotoluene. They have investigated the crystal structure of the iodide and perchlorate of 1 by X-ray diffraction and shown that the pyridinium ring is slightly deformed. However, the compounds do not show unusual properties; e.g., there is no special thermal stability, in contrast with our early report.[4] We investigated carefully the thermal properties of 2,6-di-*tert*-butyl-4,*N*-dimethylpyridinium iodide by means of thermal gravimetry and found that the compound started to decompose at 125 °C. Thus, the methyl group was not sterically protected, in agreement with Weber's observations. However, this work again showed that sterically hindered bases such as 2,6-di-*tert*-butylpyridine derivatives can be methylated readily under high pressure.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer Model 457 grading spectrophotometer. Melting points were measured with an electrothermal melting point apparatus and are uncorrected. ^1H NMR spectra were obtained on a Varian A-60 instrument. Reactions at high pressure (4000–6000 atm) were run in Teflon capsules (3 mL) placed in a steel die equipped with a heating band on a hydraulic press (Clifton 200-ton press). The reactants were mixed in a dry nitrogen atmosphere. The thermal property of the product was measured by using a Du Pont 990 thermal gravimetric analyzer.

2,6-Di-*tert*-butyl-4-methylpyridine (2). This pyridine compound was synthesized by the method described in the literature.[7]

1,2-Bis(2,6-di-*tert*-butyl-4-pyridyl)ethane (3). (2,6-Di-*tert*-butyl-4-pyridyl)methylene bromide was synthesized by the bromination of 2,6-*tert*-butyl-4-methylpyridine with NBS in CCl_4. The crude bromide was purified by distillation at 94 °C (2 mmHg): NMR (CCl_4) δ 1.35 (s, 18 H, *t*-Bu) 4.30 (s, 2 H, CH_2Br), 7.10 s, 2 H, aromatic H).

To an ether solution containing 1.7 g (0.24 mol) of lithium wire was added the ether solution of the bromide (28.4 g, 0.1 mol) at such a rate that the solvent refluxed continuously. The mixture was stirred and refluxed for 3 h. The mixture was cooled by use of an ice bath and decomposed by addition of cold water. After the ether solution was dried over magnesium sulfate and the solvent removed, the crude solid product was repeatedly recrystallized from *n*-heptane (yield 65%). Compound 3 was ob-

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(2) H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, 88, 986 (1966).
(3) Y. Okamoto and Y. Shimakawa, *Tetrahedron Lett.*, 317 (1966).
(4) Y. Okamoto and K. I. Lee, *J. Am. Chem. Soc.*, 97, 4015 (1975).
(5) Y. Okamoto, *J. Am. Chem. Soc.*, 90, 5639 (1968).
(6) H. Weber, J. Pant, M. Liedigk, and H. Wunderlich, *Chem. Ber.*, 114, 1455 (1981).
(7) A. G. Anderson and P. J. Stang, *J. Org. Chem.*, 41, 3034 (1976).

tained: mp 116–117 °C; NMR ($CDCl_3$) δ 1.35 (s, 36 H, butyl) 2.94 (s, 4 H, CH_2CH_2), 6.97 (s, 4 H aromatic H); mass spectrum, m/e 408 (M^+). Anal. Calcd for $C_{28}H_{44}N_2$: C, 82.35; H, 10.78; N, 6.88. Found: C, 82.10; H, 10.99; N, 6.95.

Methyl fluorosulfate was prepared by the method described in the literature.[8] The compound was distilled under a nitrogen atmosphere at 92–94 °C (760 mmHg).

Reactions of 2 and 3 with FSO_3CH_3 under High Pressure. Various conditions were used for the reactions. A typical reaction procedure was as follows. A mixture of **2** (0.58 g, 3 mmol) and 0.38 g (3.3 mmol) of FSO_3CH_3 in 3.3 mL of dried methylene chloride was prepared in a drybox, placed in a Teflon capsule, and pressurized to 4000–4500 atm at 60 °C for several hours. After unreacted FSO_3CH_3 and methylene chloride were removed under reduced pressure, a mixture of 2,6-di-*tert*-butyl-4-methyl-*N*-methylpyridinium and 2,6-di-*tert*-butyl-4-methylpyridinium fluorosulfate was obtained. The NMR spectrum clearly showed two different proton peaks for *tert*-butyl in these two salts, δ 1.72 and 1.47, respectively. Treatment of the mixture with aqueous sodium bicarbonate and chloroform afforded 0.62 g of the *N*-methyl salt. Anal. Calcd for $C_{15}H_{26}NO_3SF$: C, 56.78; H, 8.20; N, 4.42. Found: C, 56.42; H, 8.31; N, 4.63.

Preparation and Properties of 2,6-Di-*tert*-butyl-4-methyl-*N*-methylpyridinium Iodide. 2,6-Di-*tert*-butyl-4-methyl-*N*-methylpyridinium fluorosulfate was allowed to exchange with I^- on Amberlite I ion-exchange resin: NMR ($CDCl_3$) δ 1.78 (s, 18 H, *t*-Bu) 4.63 (s, 3 H, *N*-methyl). The thermal properties of the iodide were investigated with a Du Pont thermal gravimetric analyzer under a nitrogen atmosphere. It was found that it started to decompose at around 125 °C.

Registry No. 2, 38222-83-2; **3**, 81142-31-6; (2,6-di-*tert*-butyl-4-pyridyl)methylene bromide, 81142-32-7; methyl fluorosulfate, 421-20-5; 2,6-di-*tert*-butyl-4,*N*-dimethylpyridinium fluorosulfate, 78008-53-4; 2,6-di-*tert*-butyl-4,*N*-dimethylpyridinium iodide, 78020-53-8; 2,6-di-*tert*-butyl-4,*N*-dimethylpyridinium perchlorate, 78008-52-3; 1,2-bis(2,6-di-*tert*-butyl-*N*-methylpyridinium)ethane fluorosulfate, 81142-34-9.

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(8) M. Fieser and L. F. Fieser, "Reagents for Organic Synthesis", Vol. III, Wiley-Interscience, New York, 1972, pp 202.

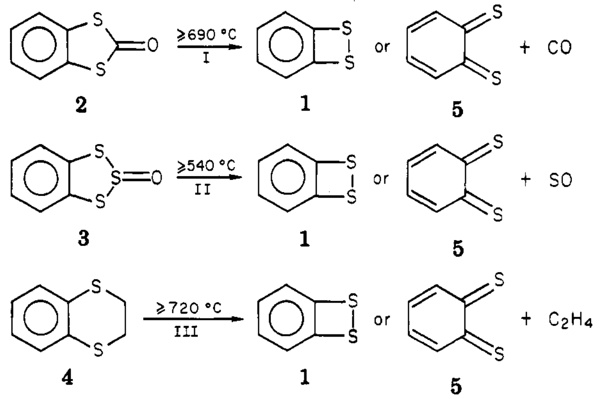
Communications

Photoelectron Spectrum and Infrared Spectrum of Thermally Generated Transient Benzodithiete[1]

Summary: Thermal routes to transient benzodithiete and 4-methylbenzodithiete are described, and the structure is proved from the gas-phase UV photoelectron spectrum and the infrared spectrum in an argon matrix.

Sir: 1,3-Benzodithiol-2-one loses carbon monoxide photochemically to give transient benzodithiete (**1**).[2] The sole property that has been known so far from this species is that it exhibits a weak UV absorption at 370 nm.[2] Below we describe new thermal pathways to **1** and contribute the full UV photoelectron and infrared spectra of the hitherto rather unexplored transient system.

We found that 1,3-benzodithiol-2-one (**2**),[3] 1,2,3-benzotrithiole 2-oxide (**3**),[4] and benzodithiene (**4**)[5] undergo the following smooth gas-phase reactions I to III in a variable-temperature photoelectron spectrometer (VTPES method[6]). The reactor of the spectrometer consisted of a stainless steel tube ca. 20 × 0.5 cm. Pressures and contact times were ca. 0.05 mbar and ca. 100 ms in all cases.



The recorded photoelectron spectra testify that the only byproducts are CO, SO, and C_2H_4 in reactions I, II, and III, respectively. Therefore **1** or dithiobenzoquinone (**5**) must have formed as the main product (assuming secondary reactions to be slow) in these reactions. As an example, Figure 1 shows the UV photoelectron spectrum of the products of reaction I.

Ab initio[7] (using the 4-31G basis set[8]) and semiempirical CNDO/S[9]–PERTCI[10] calculations[11] predict two ionizations

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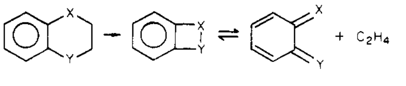
(1) Part 96 of "Theory and Application of Photoelectron Spectroscopy". Part 95: Märkl, G.; Rudnick, D.; Schulz, R.; Schweig, A. *Angew. Chem.*, **1982**, *94*, 211; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 221; *Angew. Chem. Suppl.* **1982**, 523.

(2) DeMayo, P.; Weedon, A. C.; Wong, G. S. K. *J. Org. Chem.* **1979**, *44*, 1977.

(3) For the synthesis of **2**, see ref 2. The photoelectron spectral data (vertical ionization potentials and assignments in parentheses) of **2** gathered in the present work are as follows: 8.68 (π), 9.21 (π), 10.00 (n_0), 10.92 eV.

(4) For the synthesis of **3**, see Steinle, K.; Schmidt, M. *Z. Naturforsch. B* **1972**, *27*, 83. The photoelectron spectral data (vertical ionization potentials and assignments in parentheses) of **3** obtained in the present work are as follows: 8.73 (π), 9.07 (π), 9.90 (π, S=O) eV.

(5) For the synthesis of **4**, see Parham, W. E.; Roder, T. M.; Hasek, W. R. *J. Am. Chem. Soc.* **1953**, *75*, 1647. The photoelectron spectral data are as follows (vertical ionization potentials and assignments in parentheses): 7.91 (π), 8.45 (π), 10.11 eV. The general applicability of thermal reactions of the type:



has been recognized by Wiersum, U. E., Akzo Research, Arnhem, Holland, 1980, personal communication.

(6) Schweig, A.; Vermeer, H.; Weidner, U. *Chem. Phys. Lett.* **1974**, *26*, 299. Schäfer, W.; Schweig, A. *Z. Naturforsch. A* **1975**, *30*, 1785. Schulz, R.; Schweig, A. *Angew. Chem.* **1981**, *93*, 603; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 570.

(7) The calculations were carried out by use of GAUSSIAN 76 with parts integrated from GAUSSIAN 80. GAUSSIAN 76: Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *No. 368*. GAUSSIAN 80: Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *No. 406*.

(8) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. Hehre, W. J.; Lathan, W. A. *J. Chem. Phys.* **1972**, *56*, 5255.

(9) Schulte, K.-W.; Schweig, A. *Theor. Chim. Acta* **1974**, *33*, 19.

(10) Hase, H.-L.; Lauer, G.; Schulte, K.-W.; Schweig, A. *Theor. Chim. Acta* **1978**, *48*, 47.

0022-3263/82/1947-1979$01.25/0