in the tetramer, and that of N(3) in the monomer (−0.74) was reduced to −0.29 in the tetramer. All other ring charges and overlap populations are consistent with those of crystallographic **1a**.

Two other conformation of $[H_2B(ut)]_4$ were examined: (a) one in which the ring systems were rotated such that all atoms except the H atoms on B were coplanar (8.3 eV above the crystallographic geometry), and (b) one in which ring systems were rotated to a position perpendicular to the *xy* plane (13.62 eV above the observed conformation). These high-energy barriers indicate that there is little likelihood of rotation of the triazole rings in the free molecule from the staggered up–down tilted positions of the crystallographic geometry. In addition, coordination of the four apical N atoms with a metal atom would be unlikely in a square-planar geometry. Instead, the metal would have to be located in the three-dimensional dispheroidal cavity formed by the apical N atoms.

Conclusion. The results of the ASED MO calculations are clearly in consonance with the experimental observations concerning the oligomerization of *N*-triazolylboranes. Furthermore, the calculations illustrate that the approximate D_{2d} conformation of **1a** is indeed near the minimum of the energy surface. Surprisingly, despite the variety of structures observed in the related macrocycles of types **1** and **2**, respectively, which supports the concept of highly flexible systems, MO calculations suggest that the structures in which the five-membered rings are linked by BR_2 groups are more rigid.

Acknowledgment. This work was supported by the Office of Naval Research (K.N.). We also acknowledge support of the University of Kentucky Major Research Instrumentation Bond Program for the purchase of equipment used in this study (Bond ID No. 7E-8E48-25) and a generous grant of free computing time from the University of Kentucky Computer Center. The ASED MO program was formulated for the IBM 3090 by the late David P. Onwood. ASEDGE was written by Vernon C. Hicks.

Supplementary Material Available: Tables of crystallographic data and experimental details of the structure determinations, anisotropic displacement parameters (*U* values), bond lengths and angles involving hydrogen atoms, search questions (Cambridge Structural Database), and bibliographic citations for structures retrieved from the Cambridge Structural Database (11 pages); tables of structure factors (25 pages). Ordering information is given on any current masthead page.

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Novel Synthesis of Unusual Classes of Fluorocarbon Organosulfur Compounds Using Elemental Fluorine as a Reagent

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Received February 20, 1990

The reactions of elemental fluorine with branched alkyl mercaptans, alkanesulfonyl fluorides, alkyl thioethers, cyclic alkyl thioethers, alkyl sulfones, and an alkanesultone have been studied. The synthesis and characterizations of perfluoroisobutylsulfur pentafluoride, perfluoroneopentylsulfur pentafluoride, perfluoropropylsulfur pentafluoride, perfluorotetramethylenesulfur tetrafluoride, perfluoro-1,4-thioxane tetrafluoride, perfluoro-2-propanesulfonyl fluoride, 1,1,1,3,3,3-hexafluoro-2-propanesulfonyl fluoride, perfluorotetramethylene sulfone, perfluorobutanesulfonyl fluoride, perfluoro-1,4-butanesultone, and perfluoropropanesulfonyl fluoride are discussed. The ^{19}F and $^{13}C\{^{19}F\}$ NMR assignments of the fluorinated products are also reported.

Introduction

In 1977, this laboratory published the first report on temperature and kinetic control of elemental fluorine with sulfur-containing organic molecules such that conditions could be differentiated for obtaining four-coordinate compounds (sulfur tetrafluoride analogues) and six-coordinate compounds (sulfur hexafluoride analogues).[1] Subsequently, Ruppert and others have shown that such oxidative control during fluorination is also possible for organic heteroatom systems containing phosphorus, arsenic, antimony, and bismuth.[2] In this manuscript we present a series of novel sulfur-containing molecules (see Figure 1) that have been preserved by careful fluorination, which are in many ways a study of the current state-of-the-art for such synthetic techniques in organosulfur chemistry. A number of the compounds produced in the study are also potential precursors for use in several areas of materials-related chemistry.

Because they have unusually great acid strength,[3] perfluoroalkanesulfonic acids have been widely used as catalysts in organic reactions and polymerizations.[4] In contrast, derivatives of these acids are attractive for numerous material applications such as electrolytes, surfactants, and coatings due to their high thermal stability, unusual chemical resistance, and surface properties.[5] Syntheses of structurally different perfluorinated precursors such as perfluoroneopentanesulfonyl fluoride, perfluoro-2-propanesulfonyl fluoride, and perfluoro-2-butanesulfonyl fluoride would certainly be important for the purpose of determining how branching affects the overall physical and chemical properties of several classes of sulfuric acid compounds. Electrochemical fluorination has been the major method used for preparation of fluorinated alkanesulfonyl fluorides and is limited to compounds with straight-chain structure unless one is satisfied with very low yields. Additionally, preparation of perfluoroalkylsulfur pentafluorides by this electrolytic cell often results, in low yields,[7] and many of the compounds we report here are inaccessible. Due to their high chemical and thermal stability and usefulness as intermediates, syntheses of perfluoroalkyl derivatives of sulfur hexafluoride have received considerable attention.[8]

Recently, successful direct fluorination of highly branched or even structurally crowded alkyl ethers[9] has led us to continue investigating the synthesis of sulfur-containing perfluorinated organic compounds. Cleavage of the relatively weak C–S bond,[10] a problem giving fragments such as sulfur hexafluoride and

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(1) Shimp, L. A.; Lagow, R. J. *Inorg. Chem.* **1977**, *16*, 2974.

(2) (a) Ruppert, I.; Bastian, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *16*, 718. (b) Ruppert, I.; Bastian, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 214.

(3) In terms of acid strength, trifluoromethanesulfonic acid is 400 times as strong as nitric acid (3M product information).

(4) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.

(5) Guenther, R. A.; Vietor, M. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1962**, *1*, 165.

(6) (a) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 2640. (b) Burdon, J.; Farazmand, I.; Stacey, M.; Tatlow, J. C. *J. Chem. Soc.* **1957**, 2574.

(7) Burdon, J.; Tatlow, J. C. *Adv. Fluorine Chem.* **1960**, *1*, 129.

(8) (a) Baba, H.; Kodaira, K.; Nagase, S.; Abe, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1891. (b) Abe, T.; Nagase, S.; Baba, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3845.

(9) Persico, D. F.; Huang, H. N.; Lagow, R. J. *J. Org. Chem.* **1985**, *50*, 5156.

(10) The average bond energy for C–S is 65 kcal/mol and for C–H is 98.7 kcal/mol: Cottrell, T. L. *The Strengths of Chemical Bonds*, 2nd ed.; Butterworths Scientific Publications: London, 1958.

0020-1669/91/1330-0789$02.50/0 © 1991 American Chemical Society

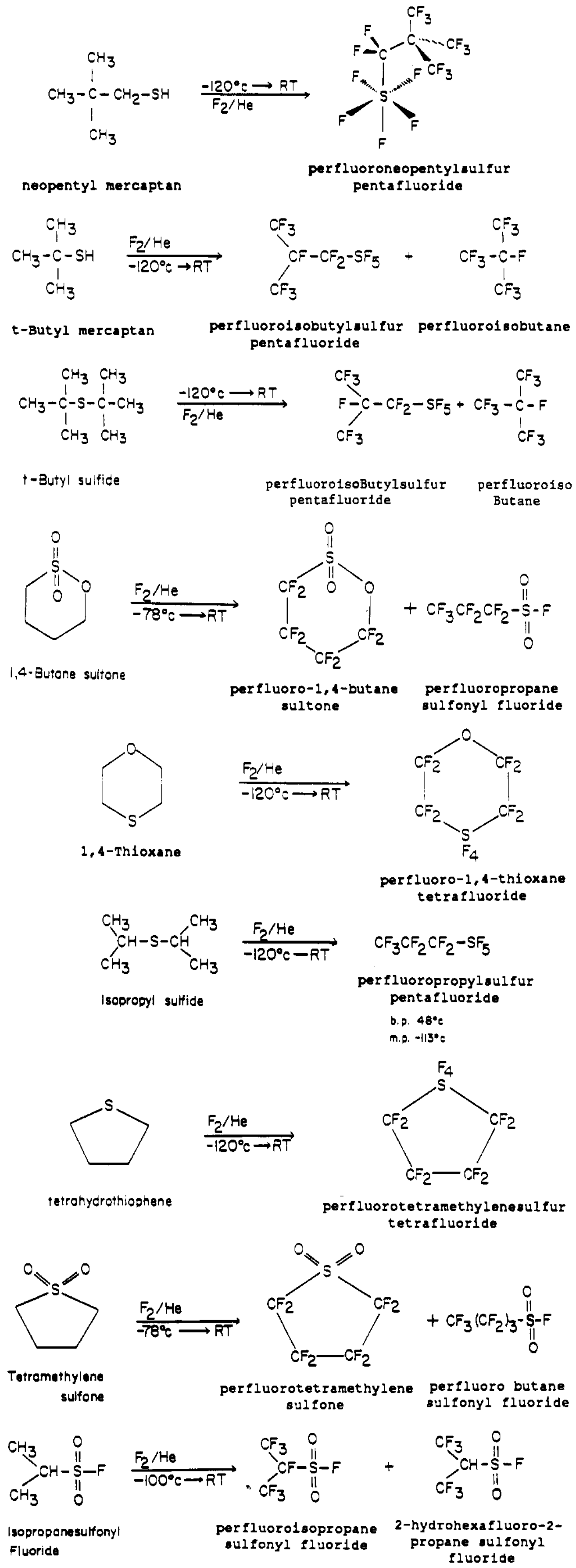

Figure 1. Direct fluorination of sulfur-containing compounds.

fluorinated alkanes, was minimized by carefully controlling the conditions. Perfluorinated alkanesultones, key intermediates in the preparation of chlor-alkali membranes,[11] are usually obtained from tetrafluoroethylene, which is difficult to handle in the laboratory due to the very exothermic nature of its polymerization. The direct fluorination technique we have developed is so generally applicable that it has also become a new technique for synthesis of an unlimited number of perfluorinated cyclic alkanesulfonyl esters.

Table I. Fluorination Conditions for Neopentyl Mercaptan

time, days	He, cm^3/min	F$_2$, cm^3/min	zone temp, °C 1	2	3	4
1	60	1	-120	-120	-120	-120
1	30	1	-120	-120	-120	-120
1	30	2	-120	-120	-120	-120
1	10	1	-120	-120	-120	-120
1	10	2	-110	-110	-110	-110
1	0	1	-110	-110	-110	-110
1	0	1	-95	-95	-95	-95
1	0	1	-85	-85	-85	-85
1	0	1	-78	-78	-78	-78
1	0	1	amb[a]	-78	-78	-78
1	0	1	amb	amb	-78	-78
1	0	1	amb	amb	amb	-78
1	0	1	amb	amb	amb	amb
1	60	0	amb	amb	amb	amb

[a] Ambient temperature.

Experimental Section

Materials, Analyses, and Physical Measurements. *tert*-Butyl mercaptan, isopropyl sulfide, *tert*-butyl sulfide, 1,4-butanesultone, 1,4-thioxane, tetrahydrothiophene, 2-propanesulfonyl chloride, tetramethylene sulfone, and anhydrous potassium fluoride powder were obtained from Aldrich Chemical Co., Inc. Neopentyl mercaptan was obtained from API Standard Reference Materials. All of the starting materials were used as received. 2-Propanesulfonyl fluoride was prepared by the methods reported in the literature.[12] Fluorine gas was technical grade and obtained from Air Products and Chemicals, Inc. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, NY, or E + R Microanalytical Laboratory, Inc., Corona, NY. ^{19}F and ^{1}H NMR spectra were obtained on a Varian EM 390 spectrometer operating at 84.67 and 89.66 MHz, respectively. The ^{13}C{^{19}F} NMR spectra were run on a Bruker WH-100 instrument with a specially built probe. All of the NMR spectra were run as neat samples for liquid products, and Freon 11 was used as a solvent for solid products. Mass spectra were obtained with a Bell and Howell Model 21-490 mass spectrometer at 70 eV. Gas chromatography was done on a Bendix 2300 programmable gas chromatograph equipped with a cryogenic controller and thermal conductivity detector. The column used for separation was either $^1/_4$ in. × 24 ft packed with 10% Fluorosilicone (QF-1-0065) on Chromosorb P (60/80 mesh) or 3/8 in. × 24 ft packed with 20% Fomblin (Y-45) on Chromosorb P (60/80 mesh). The helium flow rate was 60 cm^3/min. The melting and boiling points were measured in a 6-mm sealed glass tube, as described previously.[13]

Fluorination Apparatus. The apparatus used for cryogenic fluorinations has been previously described.[14] There were tightly packed fluorinated copper turnings inside the four-zone cryogenic reactor for all of the reactions. The sodium fluoride trap had been changed into a 1.5 in. (i.d.) × 6.5 in. brass tube with $^1/_4$ in. pipe fittings on the ends.

Fluorination of Neopentyl Mercaptan To Produce Perfluoroneopentylsulfur Pentafluoride. A 2-mL (1.60 × 10^{-2} mol) sample of neopentyl mercaptan was evaporated into a four-zone cryogenic reactor with zones 3 and 4 cooled to -120 °C by a liquid-nitrogen cryogenic system. The evaporation coil was held at 90 °C by an oil bath, and the helium flow rate was 100 cm^3/min. Four hours after injection, the first two zones were also cooled to -120 °C. The fluorination system was flushed with helium for another 8 h. The helium flow rate was 60 cm^3/min. Fluorinations were conducted by following the reaction conditions listed in Table I. The raw products collected in the glass trap maintained at -78 °C with dry ice/2-propanol slush were vacuum distilled through -45,

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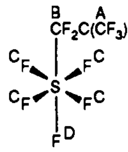
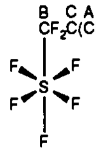
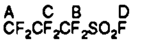
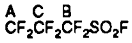
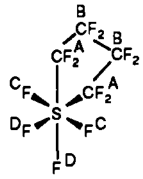
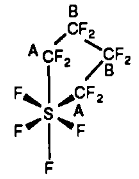
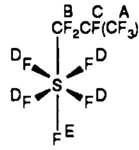
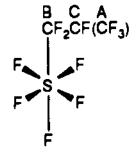
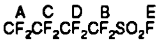
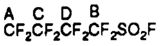
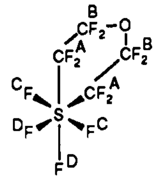
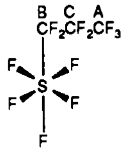
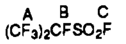
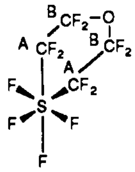
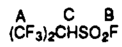
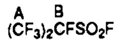
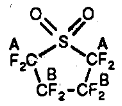
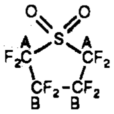
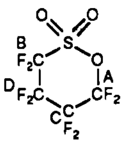
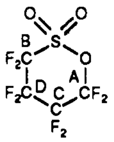
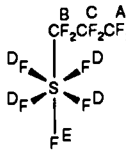
(11) *Perfluorinated Ionomer Membranes*; Eisenberg, A., Yeager, H. L., Eds.; ACS Symposium Series 180; American Chemical Society: Washington, DC, 1982.

(12) (a) Reigh, B. A.; Strating, J.; van Leusen, A. M. *J. Org. Chem.* **1974**, *39*, 2728. (b) Ziegler, C.; Sprague, J. M. *J. Org. Chem.* **1951**, *16*, 621.

(13) Gerhardt, G. E.; Lagow, R. J. *J. Org. Chem.* **1978**, *43*, 4505.

(14) (a) Maraschin, N. J.; Lagow, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 860. (b) Adcock, J. L.; Beh, R. A.; Lagow, R. J. *J. Org. Chem.* **1975**, *40*, 3271.

Table II. ^{19}F and $^{13}C\{^{19}F\}$ NMR Assignments of Fluorinated Products

compd	^{19}F chem shift,[a] ppm	*J*,[b] Hz	compd	$^{13}C\{^{19}F\}$ chem shift,[c] ppm
	(A) 64.0 (he-m)[d] (B) 78.8 (de-d) (C) 41.2 (d-de) (D) 59.2 (p-t)	*J*(C–A) = *J*(A–C) = 10.4 *J*(B–A) = *J*(A–B) = 10.2 *J*(B–D) = *J*(D–B) = 6.2 *J*(C–D) = *J*(D–C) = 141.1		(A) 125.2 (B) 119.7 (C) 69.2
 $\overset{A}{C}F_2\overset{C}{C}F_2\overset{B}{C}F_2SO_2\overset{D}{F}$	(A) 83.2 (t) (B) 110.6 (C) 126.6 (d) (D) 44.4	*J*(B–A) = 10.2 *J*(D–C) = 7.9	 $\overset{A}{C}F_2\overset{C}{C}F_2\overset{B}{C}F_2SO_2F$	(A) 117.1 (B) 114.6 (C) 107.9
	(A) 109.8 (B) 135.4 (C) 12.2 (t) (D) 39.6 (t)	*J*(C–D) = *J*(D–C) = 101.6		(A) 117.0 (B) 106.8
	(A) 73.6 (p-d) (B) 88.9 (C) 184.0 (D) 42.0 (d-m) (E) 60.2 (p-t)	*J*(E–D) = *J*(D–E) = 143.9 *J*(D–A) = 11.6 *J*(C–A) = 5.1 *J*(B–E) = 5.4 *J*(C–E) = 1.7		(A) 122.4 (B) 118.9 (C) 91.8
 $\overset{A}{C}F_2\overset{C}{C}F_2\overset{D}{C}F_2\overset{B}{C}F_2SO_2\overset{E}{F}$	(A) 85.5 (t-t) (B) 110.8 (t-m) (C) 123.3 (D) 128.2 (t-m) (E) 43.2	*J*(D–A) = 11.0 *J*(C–A) = 2.5 *J*(B–C) = 14.3	 $\overset{A}{C}F_2\overset{C}{C}F_2\overset{D}{C}F_2\overset{B}{C}F_2SO_2F$	(A) 117.2 (B) 114.8 (C) 109.7 (D) 108.6
	(A) 81.5 (B) 101.6 (p) (C) 15.1 (t) (D) 43.2 (t-p)	*J*(C–D) = *J*(D–C) = 101.6 *J*(A–D) = 14.1 *J*(A–B) = 1.7		(A) 120.6 (B) 117.6 (C) 108.2
 $(\overset{A}{C}F_3)_2\overset{B}{C}FSO_2\overset{C}{F}$	(A) 74.3 (d-d) (B) 169.3 (he-d) (C) 53.0 (he-d)	*J*(B–A) = *J*(A–B) = 6.5 *J*(C–A) = *J*(A–C) = 10.2 *J*(B–C) = *J*(C–B) = 4.0		(A) 118.3 (B) 114.4
 $(\overset{A}{C}F_3)_2\overset{C}{C}HSO_2\overset{B}{F}$	(A) 64.2 (d-d) (B) 64.5 (he-d) (^1H)[e] 4.6 (he-d)	*J*(B–A) = *J*(A–B) = 12.1 *J*(C–A) = *J*(A–C) = 7.1 *J*(C–B) = *J*(B–C) = 1.7	 $(\overset{A}{C}F_3)_2\overset{B}{C}FSO_2F$	(A) 117.9 (B) 97.5
	(A) 119.2 (B) 135.0			(A) 112.9 (B) 107.5
	(A) 88.0 (p) (B) 119.0 (p) (C) 130.8 (D) 132.8			(A) 114.6 (B) 112.6 (C) 107.7 (D) 107.3
	(A) 84.3 (t) (B) 97.6 (C) 129.5 (m) (D) 41.0 (d-m) (E) 59.2 (p-t)	*J*(E–D) = *J*(D–E) = 155.2 *J*(A–B) = *J*(B–A) = 12.7 *J*(B–E) = 5.4		

[a] ^{19}F NMR chemical shifts are relative to external $CFCl_3$. [b] Only obvious coupling constants are given. [c] ^{13}C and ^1H NMR chemical shifts are relative to external $(CH_3)_4Si$. [d] he = heptet; m = multiplet; de = dectet; d = doublet; p = pentet; t = triplet.

−78, −131, and −196 °C traps and then purified by gas chromatography (Fomblin column) at 110 °C. A 1.55-g amount of perfluoroneopentylsulfur pentafluoride was obtained, corresponding to a 24.5% yield.

Perfluoroneopentylsulfur pentafluoride is a colorless liquid with a melting point of −87 °C and boiling point of 108 °C. The ^{19}F and $^{13}C\{^{19}F\}$ NMR assignments are shown in Table II. The highest *m*/*e* in the mass spectrum was at 269 and corresponded to the parent minus SF_5 fragment. Other fragments (*m*/*e*) in the mass spectrum were as follows: 200, $(C_4F_8)^+$; 131, $(C_3F_5)^+$; 127, $(SF_5)^+$; 93, $(C_3F_3)^+$; 89, $(SF_3)^+$; 69, $(CF_3)^+$ (base peak). Elemental analyses are as follows for $C_5F_{16}S$. Anal. Calcd: C, 15.15; F, 76.77; S, 8.08. Found: C, 15.20; F, 76.74; S, 8.05.

Fluorination of *tert*-Butyl Mercaptan To Produce Perfluoroisobutylsulfur Pentafluoride. A 2-mL (1.78 × 10^{-2} mol) sample of *tert*-butyl mercaptan (bp 62 °C, mp 1 °C) was evaporated into a four-zone cryo-

Table III. Fluorination Conditions for Tetrahydrothiophene

time, days	He, cm³/min	F_2, cm³/min	zone temp, °C 1	2	3	4
1	60	1	−120	−120	−120	−120
1	30	1	−120	−120	−120	−120
1	30	2	−120	−120	−120	−120
1	10	1	−120	−120	−120	−120
1	20	2	−110	−110	−110	−110
1	0	1	−110	−110	−110	−110
1	0	1	−95	−95	−95	−95
1	0	1	−85	−85	−85	−85
1	0	1	−78	−78	−78	−78
1	0	1	amb[a]	−78	−78	−78
1	0	1	amb	amb	amb	−78
0.5	60	0	amb	amb	amb	−78 to amb
1	60	0	amb	amb	amb	amb

[a] Ambient temperature.

genic reactor with zones 3 and 4 cooled to −40 °C. The evaporation coil was held at 60 °C by an oil bath, and the helium flow rate was at 100 cm³/min. Four hours after injection, all the zones were cooled to −120 °C and the helium flow rate was kept the same. After another 8 h, fluorination was started by following the conditions listed in Table I. The products collected in a glass trap maintained at −78 °C were purified by gas chromatograph (Fomblin column) at 65 °C and then further separated by a Fluorosilicone column at 60 °C. The major product was perfluoro-2-butane, which was characterized by gas chromatograph and ^{19}F NMR spectroscopy. Due to very difficult purification, the only fully characterized sulfur pentafluoride containing product was 0.49 g of perfluoroisobutylsulfur pentafluoride (bp 75 °C, mp <−120 °C), corresponding to an 8.0% yield. The ^{19}F and $^{13}C\{^{19}F\}$ NMR assignments of perfluoroisobutylsulfur pentafluoride are given in Table II. The highest *m/e* in the mass spectrum was at 219 and corresponded to the parent minus SF_5 fragment. Other intense fragments (*m/e*) were as follows: 150, $(C_3F_6)^+$; 131, $(C_3F_5)^+$; 127, $(SF_5)^+$; 100, $(C_2F_4)^+$; 89, $(SF_3)^+$; 69, $(CF_3)^+$ (base peak). Elemental analyses for $C_4F_{14}S$ are as follows. Anal. Calcd: F, 76.88. Found: F, 76.81.

Fluorination of *tert*-Butyl Sulfide to Produce Perfluoroisobutylsulfur Pentafluoride. A 2-mL (1.11×10^{-2} mol) amount of *tert*-butyl sulfide (bp 140 °C) was evaporated into a four-zone cryogenic reactor with zones 3 and 4 cooled to −40 °C. The evaporation coil was held at 150 °C, and the helium flow rate was 150 cm³/min. There was 5 g of anhydrous sodium fluoride powder suspended inside the four-zone cryogenic reactor. The four zones were cooled to −120 °C 4 h after injections. The fluorination system was flushed with helium gas at the same flow rate for another 6 h. Fluorinations were conducted by following the reaction conditions listed in Table I. The raw products collected in the glass trap maintained at −78 °C were worked up by the same procedures as used for purification of perfluoroisobutylsulfur pentafluoride. The only fully characterized product was 0.21 g of perfluoroisobutylsulfur pentafluoride, corresponding to a 5.1% yield. Neither bis(perfluoro-*tert*-butyl)sulfur tetrafluoride nor bis(perfluoro-*tert*-butyl)sulfur difluoride could be found.

Fluorination of Isopropyl Sulfide To Produce Perfluoropropylsulfur Pentafluoride. A 2-mL (1.38×10^{-2} mol) sample of isopropyl sulfide (bp 120 °C, mp −78 °C) was evaporated into a four-zone cryogenic reactor with zones 3 and 4 cooled to −120 °C. The evaporation coil was held at 140 °C with an oil bath, and the helium flow rate was 100 cm³/min. Fluorination conditions and workup procedures were the same as used for fluorination of the *tert*-butyl mercaptan. The gas chromatography separations were done by Fomblin column at 45 °C. A 1.2-g amount of perfluoropropylsulfur pentafluoride was obtained, corresponding to a 29.1% yield. Because of the difficulty in separation, the numerous byproducts were not fully characterized. The ^{19}F and $^{13}C\{^{19}F\}$ NMR assignments of perfluoropropylsulfur pentafluoride are shown in Table II, and its mass spectrum (*m/e*) contained the following strong peaks: 169, $(C_3F_7)^+$; 127, $(SF_5)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$; 89, $(SF_3)^+$; 69, $(CF_3)^+$ (base peak). Elemental analyses are as follows. Anal. Calcd: C, 12.16; F, 77.03. Found: C, 12.20; F, 76.96.

Table IV. Fluorination Conditions for Tetramethylene Sulfone

time, days	He, cm³/min	F_2, cm³/min	zone temp, °C 1	2	3	4
1	30	1	−78	−78	−78	−78
1	30	2	−78	−78	−78	−78
1	15	2	−78	−78	−78	−78
1	0	2	amb[a]	−78		
1	0	2	amb	amb	−78	−78
1	0	2	amb	amb	amb	−78
0.5	0	2	amb	amb	amb	−78 to amb
0.5	30	0	amb	amb	amb	amb
1	60	0	amb	amb	amb	amb

[a] Ambient temperature.

Table V. Fluorination Conditions for 1,4-Butanesulfone

time, days	He, cm³/min	F_2, cm³/min	zone temp, °C 1	2	3	4
1	30	1	−78	−78	−78	−78
1	30	2	−78	−78	−78	−78
1	15	2	−78	−78	−78	−78
1	0	2	−78	−78	−78	−78
1	0	2	amb[a]	−78	−78	−78
1	0	2	amb	amb	−78	−78
0.5	0	2	amb	amb	amb	−78
0.5	40	0	amb	amb	amb	−78
1	60	0	amb	amb	amb	amb

[a] Ambient temperature.

Fluorination of Tetrahydrothiophene to Produce Perfluorotetramethylenesulfur Tetrafluoride. A 3-mL (3.40×10^{-2} mol) sample of tetrahydrothiophene (bp 119 °C, mp −96 °C) was evaporated into a four-zone cryogenic reactor with zones 3 and 4 cooled to −120 °C. The evaporation coil was held at 110 °C by an oil bath, and the helium flow rate was set at 100 cm³/min. There was 7 g of anhydrous sodium fluoride powder suspended inside the first two zones. The helium flow rate and temperature of the last two zones were kept at the same conditions for another 4 h after injections. All of the four zones were then cooled to −120 °C and purged with a 60 cm³/min of helium flow rate for another 8 h. Fluorinations were done by the reaction conditions listed in Table III. The products evolving from the reactor were stopped in a glass trap maintained at −78 °C. After vacuum distillation through −45, −78, −131, and −196 °C traps, the mixtures left in the −45 and −78 °C traps were further purified by gas chromatography (Fomblin column) at 85 °C. A 5.4-g sample of perfluorotetramethylenesulfur tetrafluoride was obtained, corresponding to an overall yield of 51.6%.

Perfluorotetramethylenesulfur tetrafluoride sublimes at room temperature. The physical properties and ^{19}F NMR spectrum agree with the data reported by Shreeve.[15] On the basis of the ^{19}F NMR spectrum, the perfluorotetramethylene group is bonded to sulfur at axial and equatorial positions of a bipyramidal structure. The ^{19}F and $^{13}C\{^{19}F\}$ NMR assignments are shown in Table II. The mass spectrum (*m/e*) contained the following strong peaks: 219, $(C_4F_9)^+$; 181, $(C_4F_7)^+$; 169, $(C_3F_7)^+$; 131, $(C_3F_5)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$ (base peak); 89, $(SF_3)^+$; 69, $(CF_3)^+$.

Fluorination of Tetramethylene Sulfone To Produce Perfluorotetramethylene Sulfone and Perfluorobutanesulfonyl Fluoride. Due to the relatively low vapor pressure of the starting material, 3 mL (3.15×10^{-2} mol) of tetramethylene sulfone (bp 285 °C, mp 27 °C) was well mixed with 7 g of anhydrous sodium fluoride powder. The "wet" powder was then suspended inside the first two zones. The fluorination system was flushed with helium gas with all zones cooled to −78 °C for 8 h, and the helium flow rate was set at 60 cm³/min. Fluorination conditions are listed in Table IV. The crude reaction products collected in −78 °C traps were fractionated through −45, −78, −131, and −196 °C traps. The products left in the −45 and −78 °C traps were further purified by gas chromatography (Fomblin column) at 70 °C. The reaction gave a 28.1% yield of perfluorotetramethylene sulfone (mp 42 °C) and 9.7% yield of perfluorobutanesulfonyl fluoride (bp 72 °C, mp <−120 °C). The physical properties and ^{19}F NMR spectrum of perfluorotetramethylene sulfone matched with the reported data.[15] The ^{19}F and $^{13}C\{^{19}F\}$ NMR assignments of these products are shown in Table II. Their mass spectra (*m/e*) contained strong peaks at as follows. Perfluorotetramethylene sulfone: 245, $(M - F)^+$; 232, $(P - O_2)^+$; 201, $(C_3F_7S)^+$; 181, $(C_4F_7)^+$; 169, $(C_3F_7)^+$; 131, $(C_3F_5)^+$; 100, $(C_2F_4)^+$ (base peak); 93, $(C_3F_3)^+$; 81, $(C_2F_3)^+$; 69, $(CF_3)^+$; 64, $(SO_2)^+$. Perfluorobutanesulfonyl fluoride: 283, $(M - F)^+$; 219, $(C_4F_9)^+$; 131, $(C_3F_5)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$ (base peak); 67, $(SOF)^+$; 64, $(SO_2)^+$. Elemental analyses for $C_4F_{10}SO_2$ are as follows. Anal. Calcd: C, 15.89; F, 62.91. Found: C, 15.63; F, 62.68.

Fluorination of 1,4-Butanesultone To Produce Perfluoro-1,4-butanesultone and Perfluoropropanesulfonyl Fluoride. A 3-mL (2.93×10^{-2} mol) amount of 1,4-butanesultone (mp −6 °C) was loaded into a four-zone cryogenic reactor by the same procedures as used for tetramethylene

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Table VI. Fluorination Conditions for 1,4-Thioxane

time, days	He, cm^3/min	F$_2$, cm^3/min	zone temp, °C 1	2	3	4
1	60	1	-120	-120	-120	-120
1	30	1	-120	-120	-120	-120
1	30	2	-120	-120	-120	-120
1	10	1	-110	-110	-110	-110
1	10	2	-95	-95	-95	-95
1	0	1	-85	-85	-85	-85
1	0	1	-78	-78	-78	-78
3	0	1	amb[a]	amb	-78	-78
0.5	60	0	amb	amb	amb	-78 to amb
1	60	0	amb	amb	amb	amb

[a] Ambient temperature.

sulfone. Fluorinations followed the reaction conditions listed in Table V. The products collected in the glass trap maintained at -78 °C were vacuum distilled through -45, -78, -131, and -196 °C traps. Further purifications were done by gas chromatography (Fomblin column) at 75 °C. The major product was 2.3 g of perfluoro-1,4-butanesultone (bp 83 °C, mp -106 °C), corresponding to a 28.2% yield. One of the cleavaged products was 1.0 g of perfluoropropanesulfonyl fluoride (bp 42 °C, mp <-120 °C). The ^{19}F and ^{13}C{^{19}F} NMR assignments of these two perfluorinated products are shown in Table II. The mass spectra (*m/e*) for perfluoro-1,4-butanesultone contained strong peaks as follows: 200, $(C_4F_8)^+$; 181, $(C_4F_7)^+$; 169, $(C_3F_7)^+$; 150, $(C_3F_6)^+$; 131, $(C_3F_5)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$ (base peak); 69, $(CF_3)^+$; 64, $(SO_2)^+$. Elemental analyses are as follows for $C_5F_8SO_3$. Anal. Calcd: C, 17.14; F, 54.28; S, 11.43. Found: C, 17.07; F, 53.81; S, 11.16. The mass spectra (*m/e*) for perfluoropropanesulfonyl fluoride are as follows: 169, $(C_3F_7)^+$; 100, $(C_2F_4)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$ (base peak); 67, $(SOF)^+$; 64, $(SO_2)^+$. Elemental analyses are as follows for $C_3F_8SO_2$. Anal. Calcd: C, 14.25; F, 60.32. Found: C, 14.52; F, 60.26.

Fluorination of 1,4-Thioxane To Produce Perfluoro-1,4-thioxane Tetrafluoride. A 3-mL (3.21×10^{-2} mol) volume of 1,4-thioxane (bp 149 °C) was loaded into a four-zone cryogenic reactor by the same procedures used for tetramethylene sulfone. The fluorination system was flushed with helium with four zones cooled to -120 °C for 8 h, and the helium flow rate was set at 60 cm^3/min. Fluorinations were done by the reaction conditions listed in Table VI. After vacuum distillation through -45, -78, -131, and -196 °C traps, the products left in the -45 and -78 °C traps were purified by gas chromatography (Fomblin column) at 90 °C. The amount of perfluoro-1,4-thioxane tetrafluoride isolated was 1.67 g, corresponding to a 16.1% yield.

Perfluoro-1,4-thioxane tetrafluoride is a colorless liquid with a melting point of 18 °C and a boiling point of 82 °C, which matched with the physical properties reported in literature.[16] The ^{19}F and ^{13}C{^{19}F} NMR assignments are shown in Table II. The mass spectrum (*m/e*) showed the following intense peaks: 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$ (base peak); 89, $(SF_3)^+$; 69, $(CF_3)^+$.

Fluorination of 2-Propanesulfonyl Fluoride to Produce Perfluoro-2-propanesulfonyl Fluoride and 1,1,1,3,3,3-Hexafluoro-2-propanesulfonyl Fluoride. A 1.5-mL (1.31×10^{-2} mol) volume of 2-propanesulfonyl fluoride and 4 g of anhydrous sodium fluoride powder were well mixed and then loaded into a four-zone cryogenic reactor by the same procedures as used for fluorination of tetramethylene sulfone except the four zones were cooled to -100 °C while being purged with helium. Fluorination conditions are listed in Table VII. After vacuum distillation through -45, -78, -131, and -196 °C traps, the products left in the -45 and -78 °C traps were further purified by gas chromatography (Fomblin column) at 60 °C. The reaction gave a 29.0% yield of perfluoro-2-propanesulfonyl fluoride (bp 38 °C, mp -59 °C) and a 15.0% yield of 1,1,1,3,3,3-hexafluoropropanesulfonyl fluoride (bp 79 °C, mp -55 °C). The ^{19}F and ^{13}C{^{19}F} NMR assignments are shown in Table II. The physical properties and ^{19}F NMR spectra of the perfluorinated products agreed with the reported data.[17] The mass spectra (*m/e*) for perfluoro-2-propanesulfonyl fluoride showed the following intense peaks: 233, $(M - F)^+$; 169, $(C_3F_7)^+$; 150, $(C_3F_6)^+$; 119, $(C_2F_5)^+$; 100, $(C_2F_4)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$ (base peak); 67, $(SOF)^+$; 64, $(SO_2)^+$. Elemental analyses are as follows for $C_3F_8SO_2$. Anal. Calcd: F, 60.32. Found: F, 60.29. The mass spectra (*m/e*) for 1,1,1,3,3,3-hexafluoropropanesulfonyl fluoride are as follows: 215, $(M - F)^+$; 195, $(P - F_2H)^+$; 151, $(C_3F_6H)^+$; 146, $(P - CF_4)^+$; 132, $(C_3F_5H)^+$; 113, $(C_3F_4H)^+$; 93, $(C_3F_3)^+$; 83, $(SO_2F)^+$; 69, $(CF_3)^+$ (base peak); 64, $(SO_2)^+$; 51, $(CF_2H)^+$. Elemental analyses are as follows for $C_3F_7HSO_2$. Anal. Calcd: C, 15.39; F, 56.84; S, 13.68; H, 0.42. Found: C, 15.57; F, 56.43; S, 13.76; H, 0.37.

Table VII. Fluorination Conditions for 2-Propanesulfonyl Fluoride

time, days	He, cm^3/min	F$_2$, cm^3/min	zone temp, °C 1	2	3	4
0.5	30	1	-100	-100	-100	-100
0.5	30	2	-100	-100	-100	-100
0.5	15	2	-100	-100	-100	-100
1	0	2	-100	-100	-100	-100
1	0	2	-85	-85	-85	-85
1	0	2	-78	-78	-78	-78
1	0	2	amb[a]	-78	-78	-78
1	0	2	amb	amb	-78	-78
1	0	2	amb	amb	amb	-78
0.5	30	2	amb	amb	amb	-78 to amb
1	30	0	amb	amb	amb	amb

[a] Ambient temperature.

Results and Discussion

As compared with the cobalt trifluoride or electrochemical fluorination process, structural rearrangements occurring in preparation of highly branched perfluorinated *alkanes* have been almost eliminated by direct fluorination techniques,[18] using low temperatures and helium dilution. In spite of this advantage, unexpected isomerizations occurred in the cases of direct fluorination of heteroatom-containing compounds.[19] For instance, perfluoroisobutylsulfur pentafluoride was obtained from *tert*-butyl mercaptan. Likewise, perfluoroisobutyl methyl ether was obtained with perfluoro-*tert*-butyl methyl ether and perfluoroisopropyl *n*-propyl ether resulted from the fluorination of isopropyl ether.[19] However, the overall yield of the individual product obtained by our approach is higher than that of any other method involving fluorination of the respective starting materials. In fact, the LaMar direct fluorination process is the only known method for preparing many types of interesting perfluorinated chemicals.[18] A possible and perhaps the most obvious explanation for the skeletal rearrangements with some systems are that the presence of lone-pair electrons on the heteroatoms and steric effects. In other words, replacement of hydrogen by fluorine would start before the complete conversion of the divalent state of sulfur atom into its six-coordinate state. By contrast, structural rearrangement was not observed in the cases of fluorination of fully oxidized sulfur-containing materials such as 2-propanesulfonyl fluoride.

The rupture of the sulfur–carbon bond was minimized in fluorination of tetramethylene sulfide. A 51.6% yield of perfluorotetramethylenesulfur tetrafluoride was obtained from tetrahydrothiophene, and the purity based on the crude products was over 95% by gas chromatograph analysis. By contrast, the electrochemical fluorination of tetramethylene sulfide produced perfluorotetramethylenesulfur tetrafluoride with 11.4% yield.[8b] A "polyfunction" chemical, perfluoro-1,4-thioxane tetrafluoride was prepared by direct fluorination. In addition, preparation of perfluoroneopentylsulfur pentafluoride, a very intriguing new compound, demonstrated most effectively the unique applications of the fluorination technique.

Although the straight-chain perfluoroalkanesulfonyl fluorides have been prepared by the electrochemical fluorination of their hydrocarbon sulfonyl chlorides or fluorides,[6] to the best of our knowledge the syntheses of perfluorinated branched structural homologues by the electrolytic cell have never been reported. The preparation of perfluoro-2-propanesulfonyl fluoride, by reaction of perfluoroolefin with sulfuryl fluoride[17] or diaminotrifluorosulfuranes[20] in the presence of cesium fluoride, resulted in either low yield or multistep procedures. Our successful one-step synthesis of perfluoro-2-propanesulfonyl fluoride opens the possibility of preparation of many novel precursors of highly branched

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perfluoroalkanesulfonic acids and derivatives that would be difficult to obtain by other methods. For instance, it should be straightforward to prepare perfluoroneopentanesulfonyl fluoride and perfluoro-2-butanesulfonyl fluoride from the hydrocarbon starting materials with elemental fluorine. In addition, perfluorotetramethylene sulfone was obtained along with one useful byproduct, perfluorobutanesulfonyl fluoride. The previously reported preparation of this perfluorinated cyclic sulfone involves at least six steps starting from tetrafluoroethylene, iodine, and elemental sulfur.[15]

Although the first successful fluorination of ethyl acetate has been accomplished in our research program,[14b] the instability of the ester linkage toward hydrogen fluoride produced by the fluorination makes fluorination of hydrocarbon esters still challenging. In fact, fluorination of esters by other methods produces only the corresponding perfluoroalkanoyl fluoride.[21] By contrast, fluorination of cyclic alkanesulfonic ester would be more challenging. In addition to the relatively weak carbon–sulfur bond, the sulfur–oxygen, oxygen–carbon, and even carbon–carbon bonds could be ruptured either by elemental fluorine or hydrogen fluoride. Our successful production of perfluoro-1,4-butanesultone is significant. The conventional preparation of a perfluorinated sultone, by reaction of tetrafluoroethylene with sulfur trioxide, allows only an even number of carbons in the cyclic system. Furthermore, no branched structural sultone can be obtained by this conventional method. The direct fluorination of corresponding hydrocarbon analogues opens the possibility of preparation of structurally different pendant groups on the perfluorinated polymers, which should be useful in the areas of electrochemical membranes, battery separators, and chromatographic separations.[11,22]

Acknowledgment. We are grateful for the support of this work by the Air Force Office of Scientific Research (Grant AF0SR-88-0084) and by a NATO grant to R.J.L. and H.R.

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Hydrothermal Crystallization of Porphyrin-Containing Layer Silicates

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Received June 22, 1990

Porphyrins and metalloporphyrins have been demonstrated as organic templates in the hydrothermal crystallization of layered silicate smectite clays. Two water-soluble free-base porphyrins, tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin (TMPyP) and tetrakis(*N*,*N*,*N*-trimethyl-4-aniliniumyl)porphyrin (TAP), along with metallo derivatives like Fe^{III}TAP, were utilized as their chloride salts. Aqueous gels consisting of a 0.0166:0.20:1.00:1.52 porphyrin:LiF:$Mg(OH)_2$:SiO_2 molar ratio heated at reflux temperature crystallized synthetic porphyrin-containing hectorite clays in just 2 days. X-ray powder diffraction (XRD) gave (001) reflections of 15.0, 16.7, and 16.4 Å for TMPyP–, TAP–, and FeTAP–hectorite, respectively, indicating that the organic macrocycles are intercalated parallel between the clay layers. Microanalysis data and UV-visible diffuse reflectance (DR) absorption spectra reveal that the porphyrin is incorporated intact. XRD and DR spectra also reveal that the free-base forms of the porphyrins dominate in hydrothermal crystallization products, while in ion-exchanged products the dication forms predominate. Small-angle neutron scattering (SANS) was used to follow the crystallization of these systems and to analyze interactions that exist when porphyrin is reacted with silica sol and magnesium hydroxide alone. Guinier analysis of the scattering curves yields structural information about the growth process of the clay system. Random network structures are observed for the porphyrin–silica system.

Introduction

Smectite clay minerals constitute a naturally occurring class of inorganic catalysts and supports. These minerals have layered lattice structures in which clay sheets are separated by layers of hydrated cations. Two tetrahedral silica sheets sandwiching a central sheet of octahedral sites form a 2:1 smectite clay layer.[1] The octahedral sites are occupied by aluminum in montmorillonite and by magnesium in hectorite. Substitution of Li^+ ions for Mg^{2+} ions in the octahedral sheet of hectorite causes a net negative layer charge, distributed over all oxygens in the framework, which is compensated by the interlayer cations. Ion exchange of these cations allows the introduction of organic and metal complex cations for a variety of applications.[2,3] The (001) reflection along the *c* axis is a measure of the distance between clay layers; this *d* spacing is a function of both the type of cation and the amount of water present.

Organic molecules are commonly used as templates in zeolite syntheses. Although their role as structure directors is under some debate,[4] small organic cations do exist in the pores and channels of the resulting zeolite crystallites. The influence of templates is both steric and electronic in these systems, and they typically exhibit the stoichiometry and space-filling characteristics illustrated for molecular sieves such as $AlPO_4$-5.[5] Assuming that silicate structures can be determined, at least in part, by the geometry of an encapsulated molecule, then the use of a large, flat macrocycle like a porphyrin should help to induce silicate layer formation. Among the few reports of synthetic clays made with organic molecules in the synthesis gel is one by Barrer and Dicks,[6] who prepared synthetic alkylammonium hectorites and montmorillonites. Porphyrin-containing hectorite clays have now been prepared from synthesis gels by using similar techniques, with a resulting reduction in reaction time from 5 to 2 days. The specific porphyrins used are the water-soluble chloride salts of tetrakis(*N*-methyl-4-pyridiniumyl)porphyrin (TMPyP) and tetrakis(*N*,*N*,*N*-trimethyl-4-aniliniumyl)porphyrin (TAP) and their metallo derivatives.

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