-78 °C. ^{13}C NMR spectra of samples prepared in this manner were recorded at -80 °C. $[Cp^*(P(OMe)_3)CoCH_2CH(SiEt_3)$-$\mu$-$H]^+$ BAr'_4^- (**5a**) ^1H NMR (0 °C): 3.65 (d, 9 H, J_{HP} = 11.6 Hz, $P(OMe)_3$), 3.21 (m, 1 H, $CoCH_2$), 1.64 (d, 15 H, J_{HP} = 1.9 Hz, C_5M_5), 0.95 (m, 9 H, $SiCH_2CH_3$), 0.50 (m, 6 H, $SiCH_2CH_3$), -1.63 (m, 1 H, $CoCH_2CHSiEt_3$-μ-H), -10.40 ppm (m, μ-H). ^{13}C NMR (-80 °C) 97.0 (C_5Me_5), 52.8 (d, J_{CP} = 6.0 Hz, $P(OMe)_3$), 35.0 (dt, J_{CP} = 13.6 Hz, J_{CH} = 156 Hz, $CoCH_2$), 9.0 (C_5Me_5), -24.4 ppm (dd, J_{CH} = 128 Hz, $J_{C,\mu\text{-}H}$ = 74 Hz, $CoCH_2CHSiEt_3$-μ-H). $[Cp^*(P(OMe)_3)CoCH_2CH(SiMe_3)$-$\mu$-$H]^+$ BAr'_4^- (**5b**) ^1H NMR (0 °C): 3.65 (d, 9 H, J_{HP} = 11.0 Hz, $P(OMe)_3$), 3.23 (m, 1 H, $CoCH_2$), 1.65 (d, 15 H, J_{HP} = 1.9 Hz, C_5M_5), 0.10 (s, 9 H, $SiMe_3$), -1.63 (m, 1 H, $CoCH_2CHSiEt_3$-μ- H), -10.65 ppm (m, μ-H). ^{13}C NMR (-80 °C): 97.0 (C_5Me_5), 52.7 (d, J_{CP} = 6.0 Hz, $P(OMe)_3$), 35.0 (d, J_{CP} = 13.6 Hz, $CoCH_2$), 9.8 (C_5Me_5), -18.6 ppm ($CoCH_2CHSiMe_3$-μ-H).

Labeling Study. Et_3SiD was prepared by stirring Et_3SiCl (4.49 g, 29.8 mmol) and $LiAlD_4$ (1.50 g, 35.8 mmol, 99 atom % D) in ether (20 mL) for 12 h. Addition of water (10 mL) was followed by extraction with ether and then drying the organic fraction over $MgSO_4$. Evaporation of the solvent under reduced pressure gave Et_3SiD (1.64 g, 47%). A ^1H NMR spectrum of the labeled product showed Et_3SiH to be present in ca. 5% of total silane. To methylene chloride (3 mL) solutions of **1** (50 mg, 0.041 mmol) were added 1-hexene (1.0 mL, 8.2 mmol, 200 equiv) and Et_3SiD (solution A, 66 μL, 10 equiv; solution B, 0.66 mL, 100 equiv). A 1-mL aliquot of solution B was quenched after 20 min, and the remainder of solution B and solution A were stirred for 12 h. After workup, ^{13}C NMR spectra of the three samples were recorded. $Et_3Si(CH_2)_5CH_2D$ was identified as the sole product (<5% deuterium incorporation at any other position). The ^{13}C NMR spectrum of the labeled product was identical to that of its unlabeled analogue, except for the methyl resonance as indicated: $Et_3Si(CH_2)_5CH_2D$, 15.0 ppm (tt, J_{CH} = 124 Hz, J_{CD} = 18 Hz).

Kinetics Studies. Measurement of Initial Turnover Rates as a Function of Et_3SiH and 1-Hexene Concentrations. A typical run is given: A Schlenk tube was charged with **1** (50 mg, 0.41 mmol), 1-hexene (0.52 mL, 4.13 mmol, 100 equiv), dodecane (50 μL), and chlorobenzene (3.15 mL). To this well-stirred mixture was added quickly Et_3SiH, at which point timing of the reaction began. Aliquots taken at 2-min intervals were efficiently quenched by injecting them into vials containing a few milligrams of alumina and shaking vigorously. Twelve samples were taken in this manner, and each was analyzed by gas chromatography (oven temperature = 140 °C, head pressure = 22 psi). Rates were calculated by integration of the $Et_3Si(CH_2)_5CH_3$ (retention time = 3.3 min) signal versus the dodecane standard (retention time = 4.2 min). For each run, the volume of chlorobenzene was adjusted to maintain a constant concentration of **1**. A sample kinetics plot is shown in Figure 6; others are available in the supplementary material.

Acknowledgment is made to Dr. N. Pienta for assistance in preparing turnover rate plots and to the National Institutes of Health (Grant GM 28938) for support of this work.

Supplementary Material Available: Plots of initial turnover rates for reactions of various concentrations of silane and 1-hexene at catalyst concentration = 0.01 M (4 pages). Ordering information is given on any current masthead page.

Power-Variable Electrophilic Trifluoromethylating Agents. *S*-, *Se*-, and *Te*-(Trifluoromethyl)dibenzothio-, -seleno-, and -tellurophenium Salt System

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Contribution from the Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa, 229, Japan, and MEC Laboratory, Daikin Industries, Ltd., Miyukigaoka 3, Tsukuba, Ibaraki, 305, Japan. *Received September 21, 1992*

Abstract: *S*-, *Se*-, and *Te*-trifluoromethylated dibenzoheterocyclic onium salts, their derivatives, and related salts were synthesized by the direct fluorination of a mixture of 2-[(trifluoromethyl)thio- or seleno]biphenyls and triflic acid (TfOH) or HBF_4 etherate, by treatment of the corresponding sulfoxides and selenoxides with Tf_2O, by a new type of tellurium activation of 2-[(trifluoromethyl)telluro]biphenyl with Tf_2O and $(CH_3)_2SO$, or by derivation from the onium salts obtained. Examination of reactivity indicated the trifluoromethyl heterocyclic salts to be greatly reactive compared to nonheterocyclic salts and indicated that this heterocyclic salt system serves as a source of widely applicable trifluoromethylating agents. Their capacity to function as such varied remarkably and increased in the order of Te < Se < S and 2,8-dialkyl < 3,7-dialkyl < H < 3-NO_2 < 3,7-di-NO_2. For mixed heterocyclic salts, the orders differed, apparently being determined by the electron deficiency of the CF_3 group due to the electron-withdrawing or -donating effects of chalcogens and ring substituents, rather than the inherent nature of the chalcogens. Because of this variation, it was possible to trifluoromethylate a wide range of nucleophilic substrates differing in reactivity: carbanions, activated aromatics, heteroaromatics, enol silyl ethers, enamines, phosphines, thiolate anions, and iodide anions. The reaction mechanism is discussed, and a bimolecular ionic substitution mechanism competing with a free CF_3 radical chain mechanism is proposed. Thus, a new field, electrophilic trifluoromethylation, has been established by the present study.

Introduction

A trifluoromethyl group has unique features,[1] such as high electronegativity, stability, and lipophilicity. Thus, trifluoromethylated organic compounds are becoming increasingly important for developing new or more effective medicines[2] and agricultural chemicals[3] and new materials such as liquid crystals.[4] However, the methods for introducing a trifluoromethyl group into an organic compound are still unsatisfactory.[5] Free radicals[6] and nucleophilic trifluoromethylations[7] have been studied extensively and utilized for preparing trifluoromethylated compounds. Electrophilic trifluoromethylation, however, has yet to be developed.[5a,b] This is because a trifluoromethyl cation is quite

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(1) (a) *Organic Fluorine Chemistry*; Sheppard, W. A., Sharts, C. M., Eds.; Benjamin Inc.: New York, 1969. (b) Chambers, R. D. *Fluorine in Organic Chemistry*; A Wiley-Interscience Publication, John Wiley & Sons: New York, 1973. (c) Ishikawa, N.; Kobayashi, Y. *Fusso no Kagobutu*; Kodansha Ltd.: Tokyo, 1979.

(2) (a) *Biomedicinal Aspects of Fluorine Chemistry*, Filler, R., Kobayashi, Y., Eds.; Kodansha Ltd.: Tokyo, 1982. (b) Kumadaki, I. *J. Synth. Org. Chem., Jpn.* **1984**, *42*, 786. (c) Welch, J. T.; Eswarakrishnan, S. *Fluorine in Bioorganic Chemstry*; A Wiley-Interscience Publication, John Wiley & Sons, Inc.: New York, 1991.

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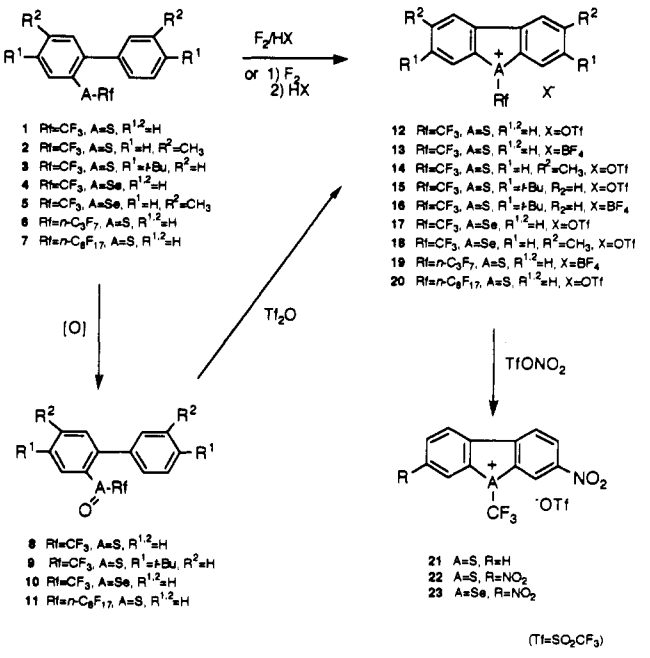
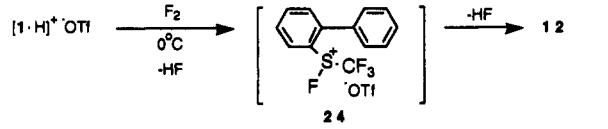
Scheme I

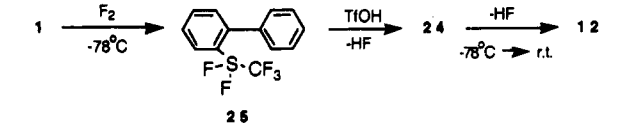


Scheme II

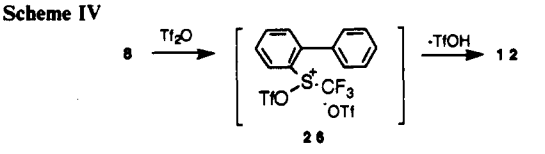


difficult to generate due to the three fluorine atoms, the element with the highest electronegativity, bonded to a cationic carbon center.[8] Widely applicable electrophilic perfluoroalkylations of two or more carbons are now available due to (perfluoroalkyl)-phenyliodonium triflates (FITS reagents) developed by the authors.[9] The synthesis of the corresponding trifluoromethyl analogue still has not been conducted, probably due to the abnormality of the trifluoromethyl group among perfluoroalkyl groups.[9a,10] According to Yagupol'skii et al.,[11] (trifluoromethyl)diarylsulfonium salts react with sodium *p*-nitrobenzenethiolate to give *p*-nitro[(trifluoromethyl)thio]benzene, but do not react with *N,N*-dimethylaniline, a strongly activated aromatic, even at elevated temperature. We have developed a new system of reactive electrophilic trifluoromethylating agents, a trifluoromethyl dibenzoheterocyclic salt series, whose reactivity is varied by sulfur, selenium, and tellurium atoms and electron-withdrawing and -donating substituents on the heterocyclic rings.[12] This article presents the synthesis and properties of *S*-, *Se*-, and *Te*-(trifluoromethyl)dibenzothio-, -seleno-, and -tellurophenium salts, their alkyl and nitro derivatives, and related salts and their applications.

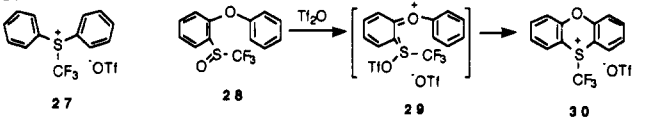
Scheme III



Scheme IV



Scheme V



Results and Discussion

Synthesis of *S*-, *Se*-, and *Te*-(Trifluoromethyl)dibenzothio-, -seleno-, and -tellurophenium Salts and Their Analogues. *S*-(Trifluoromethyl)dibenzothiophenium triflate (**12**) was successfully synthesized in high yield by the direct fluorination of an equimolar mixture of sulfide **1** and triflic acid (TfOH) with diluted molecular fluorine (10% F_2/90% N_2) in an inert solvent at relatively high temperature (0 °C) without significant side reactions such as fluorination of the benzene rings. The success of this one-step method may be due to the fluorination of sulfide **1** wholly protonated by a super acid, TfOH. The protonation of **1** should greatly decrease the reactivity of π-electron-rich benzene rings, which may cause side reactions with extremely reactive molecular fluorine, possibly resulting in the selective fluorination of the sulfur site to give **24** followed by its immediate cyclization to give **12** as a precipitate (Scheme II). The benzene rings of intermediate **24** should also be deactivated by its strongly electron-withdrawing substituent. This method is superior to the stepwise method of fluorinating **1** with 10% F_2/N_2 at very low temperature (−78 °C) and treating the resulting difluorosulfurane **25** with TfOH (57% overall yield of **12**) (Scheme III).

The one-step direct fluorination method was used to synthesize dimethylated thiophenium triflate **14** and *Se*-(trifluoromethyl)-dibenzoselenophenium triflates **17** and **18** and also thiophenium tetrafluoroborates **13** and **16** using HBF_4 etherate in place of TfOH. A lower reaction temperature for high yields was necessary possibly due to the relatively high reactivity of sulfides **2** and **3** and selenides or low acidity of HBF_4 etherate compared to TfOH. The necessity for high acidity is further supported by the fact that BF_3 etherate resulted in lower yields. Mono- and dinitrated thio- and selenophenium triflates **21–23** were obtained in good yields

(3) (a) Yoshioka, H.; Nakayama, C.; Matsuo, N. *J. Synth. Org. Chem., Jpn.* **1984**, *42*, 809. (b) *90 Nendai no Fussokei Seirikassei Bussitu. Kaihatu to Oyo*: Ishikawa, N., Ed.; CMC, Ltd.: Tokyo, 1990.

(4) Nohira, H. *J. Synth. Org. Chem., Jpn.* **1991**, *49*, 467.

(5) (a) Uneyama, K. *J. Synth. Org. Chem., Jpn.* **1991**, *49*, 612. (b) Umemoto, T. *Fusso Kagobutu no Gosei to Oyo*; Ishikawa, N. Ed.; CMC, Ltd.: Tokyo, 1987; pp 181–196. (c) Yamazaki, T.; Kitazume, T. *J. Synth. Org. Chem., Jpn.* **1991**, *49*, 721.

(6) Recent articles: (a) Tanabe, T.; Matsuo, N.; Ohno, N. *J. Org. Chem.* **1988**, *53*, 4582. (b) Akiyama, T.; Kato, K.; Kajitani, M.; Sakaguchi, Y.; Nakamura, J.; Hayashi, H.; Sugimori, A. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3531. (c) Kitazume, T.; Ikeya, T. *J. Org. Chem.* **1988**, *53*, 2350. (d) Yoshida, M.; Yoshida, T.; Kobayashi, M.; Kamigata, N. *J. Chem. Soc., Perkin Trans. 1* **1989**, 909. (e) Uneyama, K.; Watanabe, S. *J. Org. Chem.* **1990**, *55*, 3909. (f) Kamigata, N.; Fukushima, T.; Yoshida, M. *Chem. Lett.* **1990**, 649. (g) Tordeux, M.; Langlois, B.; Wakselman, C. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2293. (h) Uneyama, K.; Kitagawa, K. *Tetrahedron Lett.* **1991**, *32*, 375, 3385. (i) Uneyama, K.; Kanai, M. *Tetrahedron Lett.* **1991**, *32*, 7425. (j) Langlois, B. R.; Laurent, E.; Roidot, N. *Tetrahedron Lett.* **1991**, *32*, 7525; **1992**, *33*, 1291. Some of these reported trifluoromethylations were explained by a radical chain reaction mechanism induced by an one-electron transfer.

(7) Recent articles: (a) Kitazume, T.; Ikeya, T. *J. Org. Chem.* **1988**, *53*, 2349. (b) Sibille, S.; Perichon, J.; Chaussard, J. *Synth. Commun.* **1989**, *19*, 2449. (c) Prakash, G. S. K.; Krishnamurti, R.; Olah, G. *J. Am. Chem. Soc.* **1989**, *111*, 393. (d) Stahly, G. P.; Bell, D. R. *J. Org. Chem.* **1989**, *54*, 2873. (e) Chen, D.-B.; Wu, S.-W. *J. Chem. Soc., Chem. Commun.* **1989**, 709. (f) Burton, D. J.; Hartgraves, G. A.; Hsu, J. *Tetrahedron Lett.* **1990**, *31*, 3699. (g) Tordeux, M.; Francese, C.; Wakselman, C. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1951. (h) Su, D.-B.; Duan, J.-X.; Chen, Q.-Y. *Tetrahedron Lett.* **1991**, *32*, 7689. (i) Shono, T.; Ishifune, M.; Okada, T.; Kashimura, S. *J. Org. Chem.* **1991**, *56*, 2. (j) Urata, N.; Fuchikami, T. *Tetrahedron Lett.* **1991**, *32*, 91.

(8) (a) Olah, G. A.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020. (b) Reynolds, C. H. *J. Chem. Soc., Chem. Commun.* **1991**, 975.

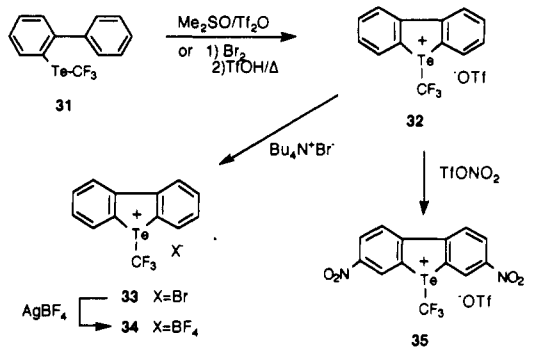
(9) (a) Umemoto, T.; Kuriu, Y.; Shuyama, H.; Miyano, O.; Nakayama, S. *J. Fluorine Chem.* **1986**, *31*, 37. (b) Umemoto, T.; Gotoh, Y. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 439. (c) Umemoto, T.; Miyano, O. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3361. (d) Umemoto, T. *J. Synth. Org. Chem., Jpn.* **1983**, *41*, 251 and references cited therein.

(10) Lyalin, V. V.; Orda, V. V.; Alekseeva, L. A.; Yagupol'skii, L. M. *J. Org. Chem. USSR* **1971**, *7*, 1524.

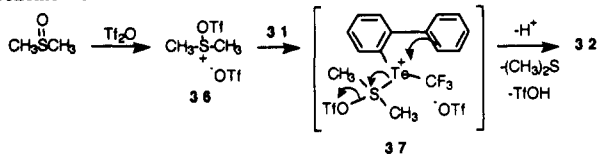
(11) Yagupol'skii, L. M.; Kondratenko, N. V.; Timofeeva, G. N. *J. Org. Chem. USSR* **1984**, *20*, 103.

(12) Preliminary note: Umemoto, T.; Ishihara, S. *Tetrahedron Lett.* **1990**, *31*, 3579.

Scheme VI



Scheme VII



by treatment with nitronium triflate.

Triflate **12** was prepared by the cyclization of sulfoxide **8** with triflic anhydride (Tf_2O), probably via intermediate **26** (Scheme IV). Selenoxide **10** and electron-donating-group-substituted sulfoxide **9** were cyclized more quickly than **8**.

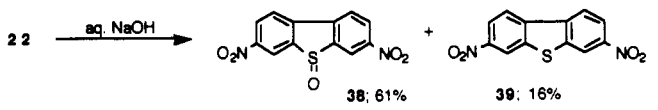
Higher perfluoroalkyl salts **19** and **20** were similarly synthesized from sulfide **6** and sulfoxide **11**. The starting materials **1**–**7** were prepared by allowing the sodium salts of the corresponding biphenylthiols to react with perfluoroalkyl bromides or iodides with or without irradiation, by treatment of the biphenylyl selenocyanates with sodium borohydride followed by trifluoromethyl iodide, or by treatment of the biphenylyl iodide with [(trifluoromethyl)thio]copper(I). Sulfoxides **8**, **9**, and **11** and selenoxide **10** were prepared by oxidation of the corresponding sulfides and selenide with *m*-chloroperbenzoic acid.

An intermolecular condensation reaction of phenyl trifluoromethyl sulfoxide with benzene by the action of Tf_2O, giving a noncyclic salt **27**, proceeded more slowly than the intramolecular condensation of biphenylyl trifluoromethyl sulfoxide **8** to a cyclic salt **12**. The yield was rather low and repeated chromatography was required to isolate and purify **27** due to its low crystalline nature. The intramolecular condensation of 1-phenoxy-2-[(trifluoromethyl)sulfinyl]benzene (**28**) with Tf_2O to give another heterocyclic salt **30** was very slow and its yield was low. This slow reaction may be explained by the great stabilization of the cationic sulfur atom of intermediate **29** by its ether oxygen atom at the ortho position through π-electron conjugation (Scheme V).

Te-(Trifluoromethyl)dibenzotellurophenium triflate (**32**) was synthesized in a different way, by treating telluride **31** with Tf_2O in the presence of dimethyl sulfoxide (Scheme VI). This reaction was fast and immediately resulted in the formation of the precipitate of **32** from the reaction solution. This ready cyclization of telluride **31** can be explained by the mechanism shown in Scheme VII. The generated sulfonium intermediate **36** thus activates a tellurium atom of **31**, and the resulting **37** immediately brings about cyclization to give tellurophenium salt **32**, dimethyl sulfide, and TfOH. Dimethyl sulfide was qualitatively detected by its characteristic smell. This mechanism is supported by the fact that, when a similar cyclization of 2-[(perfluoro-*n*-propyl)telluro]biphenyl to *Te*-(perfluoro-*n*-propyl)dibenzotellurophenium triflate was carried out using diphenyl sulfoxide in place of dimethyl sulfoxide, diphenyl sulfide was isolated in 58% yield.[13] This smooth reaction may have been due to the strong nucleophilicity or easy hypervalency of tellurium,[14] since this method could not be satisfactorily conducted to prepare selenophenium salts. This reaction is a new type of activation method of tellurium using a higher chalcogen. Salt **32** was also prepared by treating telluride **31** with bromine followed by heating with TfOH. Treatment of **32** with tetrabutylammonium bromide readily gave bromide **33**, which was converted with silver tetrafluoroborate to tellurophenium tetrafluoroborate **34**. The nitration of **32** with excess nitronium triflate gave dinito derivative **35**. The starting material **31** was prepared by the treatment of bis(2-biphenylyl) ditelluride with sodium borohydride–methanol followed by trifluoromethyl iodide or bromide.

(13) Umemoto, T.; Ishihara, S. Unpublished data.
(14) Petragnani, N.; Comasseto, J. V. *Synthesis* **1991**, 793, 897.

Scheme VIII



Scheme IX

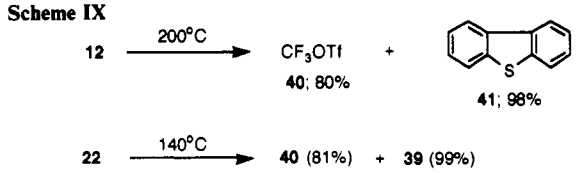


Table I. Controlled Trifluoromethylation of Aniline with a Series of Trifluoromethyl Onium Triflates[a]

run	CF_3^+	temp (°C)[e]	time (h)	yield of CF_3-aniline (%)[b] *o*-CF_3[c]	*p*-CF_3[d]	remaining CF_3^+ (%)[b]
1	**22**	rt	0.5	54	20	5
2	**23**	rt	0.5	39	16	30
3	**21**	rt	0.5	18	11	71
4	**12**	rt	0.5	0	0	100
			20	14	6	63
5	**12**	80	1	31	15	27
6	**35**	rt	20	12	6	82
7	**35**	80	1	20	10	60
			3	35	17	23
8	**17**	rt	20	7	4	83
9	**17**	80	2	38	19	17
			3	40	22	10
10	**15**	80	1	23	11	52
			2	27	13	39
11	**14**	80	1	20	9	63
			2	24	11	50
12	**27**	80	1	trace	trace	95
			3	5	2	86
13	**32**	80	4	0	0	99
			28	3	1	71

[a] See the Experimental Section. [b] The yields of $CF_3C_6H_4NH_2$ and the remainder of CF_3^+ were determined by an ^{19}F NMR technique using the triflate anion of the trifluoromethyl onium triflate as internal standard. [c] *o*-(Trifluoromethyl)aniline. [d] *p*-(Trifluoromethyl)aniline. [e] rt = room temperature.

Hydrolysis Experiments. Alkaline hydrolysis experiments of *S*- and *Se*-(trifluoromethyl)dibenzothio- and -selenophenium triflates and their nitro derivatives were carried out at 0 °C. The hydrolysis of thiophenium triflate **12** and its mononitro derivative **21** formed dibenzothiophene *S*-oxide and its mononitro *S*-oxide in 90 and 86% yields, respectively. Dinitro derivative **22** afforded a 16% yield of dinitrodibenzothiophene **39**, a reduction product, in addition to a 61% yield of the corresponding *S*-oxide **38** (Scheme VIII). Both selenophenium triflate **17** and its dinitro derivative **23** gave the corresponding *Se*-oxides in 86 and 82% yields, respectively. In neither case could the corresponding dibenzoselenophenes be detected.

Thermolysis Experiment. Crystals of triflate **12** were heated at 200 °C for 1.5 h to give trifluoromethyl triflate (**40**) and dibenzothiophene (**41**) in 80 and 98% yields, respectively. The thermolysis of dinitro triflate **22** at 140 °C for 1.25 h afforded **40** and **39** in 81 and 99% yields, respectively (Scheme IX).

Trifluoromethylation Power. As seen from Table I, the relative reactivity of a series of *S*-, *Se*-, and *Te*-(trifluoromethyl)dibenzothio-, -seleno-, and -tellurophenium triflates and nonheterocyclic salt **27** was determined by an ^{19}F NMR tracing ex-

periment on reactions with aniline in DMF at room temperature or 80 °C, giving *o*-(trifluoromethyl)aniline and *p*-(trifluoromethyl)aniline. Table II shows the results for the trifluoromethylation of various nucleophilic compounds with thio-, seleno-, and tellurophenium salts. The order of reactivity was determined as **32** < **27** < **14** < **15** < **17** ≤ **35** < **12** < **21** < **23** < **22**. The heterocyclic system (**12**) is thus much more reactive than the nonheterocylic system (**27**), and in the heterocyclic system, the relative reactivity of chalcogens increased in the order of Te (**32**) < Se (**17**) < S (**12**) and that of the ring substituents in the order of 2,8-dimethyl (**14**) < 3,7-di-*tert*-butyl (**15**) < H (**12**) < 3-nitro (**21**) < 3,7-dinitro (**22**).

The high reactivity of the heterocyclic system may be attributed to the additional driving force due to the restoration of lost aromaticity by transformation of the central 5-membered heterocyclic ring regarded as having 4π antiaromaticity to a 6π aromatic heterocycle, as discussed by Kevill et al.[15] and Horak et al.[16] In the nonheterocyclic onium salt system, there would be no such driving force.

The relative reactivity among a series of trifluoromethyl heterocyclic onium salts clearly indicated the capacity for reaction to vary greatly due to the electronegativity of trifluoromethyl-binding chalcogens and the electronic nature of ring substituents. Trifluoromethylation power increased with a decrease in the electron density of the trifluoromethyl group, as evident from the ^{19}F NMR chemical shifts of trifluoromethyl groups. Thus, downfield shifts occur with increasing power order of trifluoromethylation: for a sulfur series, 2,8-dimethyl **14** (53.8 ppm) < 3,7-di-*tert*-butyl **15** (53.1) < unsubstituted **12** (52.6) < 3-nitro **21** (50.5) < 3,7-dinitro **22** (48.4); for a selenium series, unsubstituted **17** (45.6) < 3,7-dinitro **23** (41.8); and for a tellurium series, unsubstituted **32** (41.0) < 3,7-dinitro **35** (39.3). A good linear correlation was indicated by plots of ^{19}F chemical shifts vs Hammett's constants[17] σ_p or σ_m for the sulfur series. A good linear correlation was also observed for the selenium series 2,8-dimethyl **18** (46.5 ppm), **17**, and **23**.

As expected from the electronegativities[18] of Te (2.1), Se (2.4), and S (2.5), the reactivity of tellurophenium salt **32** greatly differed from that of thiophenium salt **12** and that of selenophenium salt **17**. Thus, **32** never reacted with aniline at room temperature, while **12** and **17** did so as seen from Table I. With carbanion **42**, **32** could not produce any **43**, while both **12** and **17** gave **43** in high yields (Table II). However, 3,7-dinitro tellurophenium salt **35** was reactive toward aniline and **42** (Tables I and II), and its reaction power exceeds that of dialkylated thiophenium salts **14** and **15** and is equal to or greater than that of selenophenium salt **17**. Thus, the effects of chalcogens are sufficiently overcome by those of the ring substituents, as was also evident from the power order of **15** (S, 3,7-di-*tert*-butyl) < **17** (Se, H) or **21** (S, 3-nitro) < **23** (Se, 3,7-dinitro). The present study explains why there is no reactivity of the (4-chlorophenyl)(2,4-dimethylphenyl)(trifluoromethyl)sulfonium salt toward *N,N*-dimethylaniline, reported by Yagupol'skii et al.,[11] a nonheterocyclic salt having totally electron-donating substituents.

Trifluoromethylation by Power-Variable Reagents. As shown in Table II, trifluoromethylating agents made possible the trifluoromethylation of a wide range of nucleophilic substrates otherwise impossible or difficult by conventional nucleophilic or free radical methods. In general, less reactive substrates were trifluoromethylated smoothly by more powerful reagents, while reactive substrates required less powerful reagents. Intermediately reactive substrates were satisfactorily trifluoromethylated by moderately powerful reagents. This reaction concept was successfully used in fluorination by the *N*-fluoropyridinium salt system.[19]

Practical trifluoromethylation was shown to be possible by **22**, intermediately powerful **12**, and less powerful **17** according to the reaction concept. The most powerful dinitro thiophenium salt **22** thus smoothly trifluoromethylated aromatic and heteroaromatic compounds such as aniline, phenols, and pyrrole and triphenylphosphine. Naphthol and hydroquinone were readily trifluoromethylated with **22** in the presence of pyridine or 4-(dimethylamino)pyridine as a base. The use of the latter more basic pyridine made the reaction proceed faster than did pyridine itself. The reactive hydroquinone was trifluoromethylated even by unsubstituted thiophenium salt **12** using pyridine as a base, although slowly.[20] With less reactive phenol itself, the trifluoromethylation was not so satisfactory.[21] The reaction of triphenylphosphine with **22** resulted in a high yield of (trifluoromethyl)triphenylphosphonium triflate (**67**). Mononitro thio salt **21** and dinitro seleno salt **23** also trifluoromethylated triphenylphosphine, but at low rates. Unsubstituted thio and seleno salts **12** and **17** no longer trifluoromethylated triphenylphosphine, even at elevated temperature, and they decomposed.

Very reactive carbanion **50** and easily oxidizable alkanethiolate anion **63** were trifluoromethylated in the highest yields with the less powerful seleno salt **17**. That the reaction of **50** with the least powerful tellurophenium salt **32** gave the lowest yield (9%) of the product suggests the nature of the chalcogen to be another important factor. However, as discussed above, this is greatly controlled by the electronic nature of the ring substituents. The trifluoromethylation of *n*-butyllithium, *n*-octylmagnesium chloride, vinylmagnesium bromide, phenyllithium, and phenylmagnesium chloride using **12**, **15**, **17**, or **32** was not successful, and in most cases, trifluoromethane was detected. In the sulfur series, reaction of alkanethiolate **63** with **12** gave 30% yield of a disulfide, $(n\text{-}C_{12}H_{25})_2S_2$, as a byproduct (run 17 in Table II), while less powerful **14** and **15** decreased the amount of the disulfide and increased the yield of product **64** (runs 18 and 19).

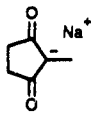
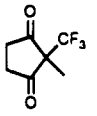
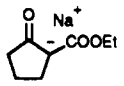
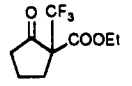
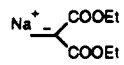
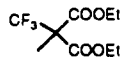
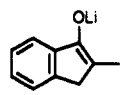
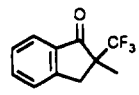
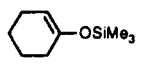
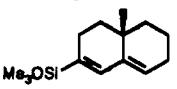
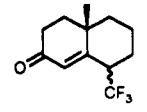
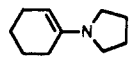
The sodium salts of active methylene compounds, lithium enolates, enol trimethylsilyl ethers, enamines, and sodium iodide were well-trifluoromethylated with moderately powerful **12**. In the reaction with lithium enolate **48**, a considerable amount (ca. 17%) of trifluoromethane was detected in addition to 51% of α-trifluoromethyl ketone **49**. The reaction with NaI was accelerated by light. Irradiation of the mixture with a high-pressure Hg lamp for 1 h gave CF_3I in 70% yield.

A comparison of heterocyclic onium salts with (perfluoroalkyl)phenyliodonium triflates (FITS)[9] was made. The reactivity of the heterocyclic onium salts appeared to be considerably less than that of FITS, since FITS readily reacted with anthracene at 0 °C (in methylene chloride),[22] while thiophenium salt **22** could not do so even at 80 °C (in DMF). A difference in reaction selectivity between them was also detected. The FITS-8 reagent reacted with sodium salt **42** of a diketone to give a mixture of *C*- and *O*-perfluorooctyl products.[9b] Perfluorooctyl thiophenium salt **20** afforded the C-perfluoroalkylation product, 2-methyl-2-(perfluorooctyl)-1,3-cyclopentanedione, only.

Reaction Mechanism. As seen from Tables I and II, trifluoromethyl heterocyclic onium salts are electrophilic in nature and act as sources of trifluoromethyl cations. These salts can generate trifluoromethyl cations, as is evident from the thermolysis experiments of **12** and **22** which provided trifluoromethyl triflate (**40**)[23] and dibenzothiophene **41** or **39** in high yields. The ionic mechanism for trifluoromethylation is supported by the finding that, at room temperature, the decomposition reaction of **22** giving

(15) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1991**, *56*, 1845.
(16) Hashmall, J. A.; Horak, V.; Khoo, L. E.; Quicksall, C. O.; Sun, M. K. *J. Am. Chem. Soc.* **1981**, *103*, 289.
(17) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970.
(18) Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(19) Umemoto, T.; Fukami, S.; Tomizawa, G.; Harasawa, K.; Kawada, K.; Tomita, K. *J. Am. Chem. Soc.* **1990**, *112*, 8563.
(20) After 2 days at room temperature in DMF, (trifluoromethyl)hydroquinone **60** was produced in 24% yield, and 76% of **12** remained.
(21) An equimolar mixture of phenol, dinitro salt **22**, and 4-(dimethylamino)pyridine in DMF was stirred at room temperature for 20 h, and ^{19}F NMR analysis of the reaction mixture indicated a 2:1 mixture of *o*- and *p*-(trifluoromethyl)phenols produced in ca. 35% yield.
(22) Umemoto, T.; Kuriu, Y.; Shuyama, H. *Chem. Lett.* **1981**, 1663.
(23) (a) Olah, G. A.; Ohyama, T. *Synthesis* **1976**, 319. (b) Kobayashi, Y.; Yoshida, T.; Kumadaki, I. *Tetrahedron Lett.* **1979**, *40*, 3865. (c) Noftle, R. E. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 195.

Table II. Trifluoromethylations of Various Compounds by Power-Variable Trifluoromethylating Agents

run	substrate	CF_3^+	molar ratio[a]	additive[b]	solv[c]	temp (°C)[w]	time	product	yield (%)[d]
1		**12**	1.3		DMF	−45 → rt	6 h		84
2		**17**	1.3		DMF	−45 → rt	1 day		84
3		**35**	1.3		DMF	0 → rt	1 h		55
4		**13**	1.0		DMF	−60 → rt	1 h		70
	42[f]							**43**	
5		**12**	1.0		DMF	−65 → rt	2.5 h		67
	44[g]							**45**	
6		**12**	1.0		DMF	−65 → rt	5 h		38
	46[h]							**47**[i]	
7		**12**	0.95		THF	−78	2 h		51
	48[j]							**49**	
8	PhC≡CLi (**50**)[k]	**12**	1.1		THF	−78 → rt	1.25 h	PhC≡C—CF_3 (**51**)[l]	58
9	**50**	**17**	1.1		THF	−78 → rt	1.25 h	**51**	89
10	**50**	**15**	1.1		THF	−78 → rt	3 h	**51**	67
11		**12**	1.0	py	DMF	80	overnight	2-$CF_3C_6H_9O$ (**53**)[m]	65
	52								
12		**12**	1.0	py	DMF	100	overnight		69
	54[n]							**55**[o]	
13		**12**	1.0	DMPy	DMF	0	2 h	**53** 2,6-di$(CF_3)_2C_6H_8O$ (**57**)[x]	57 26
	56								
14	2-naphthol	**22**	1.0	DMPy	DMF	−20 → rt	1.25 h	1-CF_3-2-naphthol (**58**)[p] 8-CF_3-2-naphthol (**59**)	52 6
15	*p*-hydroquinone	**22**	1.0	py	DMF	rt	2 h	2-CF_3-*p*-hydroquinone (**60**)[q] di$(CF_3)_2$-*p*-hydroquinone (**61**)[q,r]	61 11
16	pyrrole	**12**	2.5		DMF	80	1.5 h	2-CF_3-pyrrole (**62**)[s]	90
17	*n*-$C_{12}H_{25}SNa$ (**63**)[u]	**12**	1.0		THF	rt	0.5 h	*n*-$C_{12}H_{25}SCF_3$ (**64**)[t]	47[e,v]
18	**63**	**15**	1.0		THF	0 → rt	0.5 h	**64**	76[e,v]
19	**63**	**14**	1.0		THF	0 → rt	1 h	**64**	81[e,v]
20	**63**	**17**	1.0		THF	rt	0.5 h	**64**	87
21	2-Ph-C_6H_4SNa (**65**)[u]	**12**	1.0		DMF	−30 → rt	1 h	2-Ph-$C_6H_4SCF_3$ (**66**)	78
22	**65**	**17**	1.0		THF	0	0.5 h	**66**	89
23	NaI	**12**	1.0		DMF	rt	3 days	CF_3I	70
24	Ph_3P	**22**	1.2		CH_3CN	rt	5 h	$Ph_3P^+CF_3\ ^-OTf$ (**67**)	78

[a] Molar ratios of substrate/CF_3^+. [b] An equivalent amount of an additive was used; py = pyridine, DMPy = 4-(dimethylamino)pyridine. [c] DMF = *N*,*N*-dimethylformanide, THF = tetrahydrofuran. [d] The yields were determined by ^{19}F NMR, unless otherwise noted. [e] Isolated yields. [f-h] Each sodium salt of active methylene compounds was prepared in situ by treatment of the corresponding active methylene compound with equimolar sodium hydride (60% in oil) in DMF at 0 °C to room temperature for ca. 10–20 min. [i] Ishikawa, N.; Yokozawa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 724. [j] This lithium enolate was prepared in situ by treating the corresponding ketone with 0.95 equiv of lithium diisopropylamide in THF at −78 to 0 °C for 30–60 min. [k] Lithium phenylacetylide was prepared in situ treating phenylacetylene with equimolar *n*-butyllithium in THF at 0 °C for 30–60 min. [l] Kobayashi, Y.; Yamashita, T.; Takahashi, K.; Kuroda, H.; Kumadaki, I. *Chem. Pharm. Bull.* **1984**, *32*, 4402. [m] 2-(Trifluoromethyl)cyclohexanone: Cantacuzene, D.; Wakselman, C.; Dorme, R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1365. [n] This enol silyl ether was prepared from (*R*)-(−)-4,4a,5,6,7,8-hexahydro-4a-methyl-2(3*H*)-naphthalenone available from Aldrich. [o] α/β isomers = 3.6:1. [p] Fung, S.; Abraham, N. A.; Bellini, F.; Sestanj, K. *Can. J. Chem.* **1983**, *61*, 368. [q] Feiring, A. E.; Sheppard, W. A. *J. Org. Chem.* **1975**, *40*, 2543. Naumann, D.; Kischkewitz, J. *J. Fluorine Chem.* **1990**, *46*, 265. [r] **61**: ^1H NMR ($CDCl_3$) δ 5.98–6.16 (2 H, br s, OH), 7.12 (2 H, s, aromatic H); ^{19}F NMR ($CDCl_3$) (upfield from $CFCl_3$ as internal standard) 53.8 ppm (s, CF_3); GC–MS (*m*/*e*) 246 (M^+), 226 (M^+ − HF), 206 (M^+ − 2HF). [s] Tordeux, M.; Langlois, B.; Wakselman, C. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2293. [t] Umemoto, T.; Ando, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 447. [u] Sodium salt of a thiol was prepared in situ by treatment of a thiol with equimolar sodium hydride (60% in oil) in THF or DMF at 0 °C to room temperature for ca. 10–20 min. [v] Disulfide, $(n\text{-}C_{12}H_{25})_2S_2$, as a byproduct was isolated in 30, 13, and 13% yields in runs 17, 18, and 19, respectively. [w] rt = room temperature. [x] 2,6-Di(trifluoromethyl)cyclohexanone.

40 occurred in tetrahydrofuran (THF) and acetonitrile, but was faster in THF, which has a stronger solvating capacity, than in acetonitrile.

When treated with benzylamine at room temperature in DMF, **12** readily decomposed to form CF_3H while, with aniline, trifluoromethylation occurred. The reaction path thus changes greatly according to the nature of the nucleophile. Hence, different reaction mechanisms may complete with each other, depending on the nature or reaction power of nucleophiles and the trifluoromethyl heterocyclic onium salts and on the reaction conditions, as was also apparent from alkaline hydrolysis experiments. These features differ greatly from the methyl analogue, *S*-

methyldibenzothiophenium salt, which underwent nucleophilic attack (S_N2) on the CH_3 group only.[15]

As other possible reaction mechanisms giving trifluoromethylated products, a one-electron transfer leading to a CF_3 free radical chain reaction[6h,6i,24] and a sulfurane reaction (formation of σ-sulfurane followed by ligand coupling)[25] may be considered. However, the CF_3 free radical mechanism may be excluded, in that **12** and **22** were capable of trifluoromethylating *p*-hydroquinone to give 2-(trifluoromethyl)-*p*-hydroquinone, the hydroquinone being known to function as an effective free radical scavanger and to be converted to *p*-quinone by the action of a radical.[26] The trifluoromethylation of aniline with **12** was not affected by the presence of *p*-dinitrobenzene as a free radical scavenger. The latter sulfurane mechanism would appear to be unlikely since neither **12**, **15**, **17**, nor **32** could trifluoromethylate alkyl- or aryllithium and -magnesium halides, which would lead to the formation of sulfuranes as intermediates followed by ligand coupling.[25]

Thus, it would appear that the trifluoromethylation of nucleophiles with power-variable reagents may occur via a bimolecular ionic substitution mechanism competing with a free CF_3 radical chain mechanism. High yields are thus obtained when the power of the trifluoromethylating agent is best fit for bimolecular ionic substitution. Kinetic studies on trifluoromethylation, X-ray structural analysis,[27] and theoretical studies on a series of trifluoromethyl heterocyclic onium salts are now in progress.

Conclusions

Trifluoromethyl dibenzoheterocyclic salts constitute a new system of trifluoromethylating agents with high reactivity due to the recovery of aromaticity and varying degrees of trifluoromethylating power through variation in the electron density of trifluoromethyl carbons. The dibenzocyclic salt system thus makes possible for the first time the trifluoromethylation of a wide range of nucleophilic substrates differing in reactivity. These salts are easy to prepare and isolate owing to intramolecular cyclization and their high crystalline nature due to high symmetry. A new field, electrophilic trifluoromethylation, has thus been established, greatly broadening the scope of trifluoromethylation, mechanistic considerations, and chalcogen chemistry.

Experimental Section

General. Melting points are uncorrected. ^1H NMR spectra were recorded with a Varian XL-100, EM 390, or Gemini 200 NMR spectrometer with tetramethylsilane as an internal standard. ^{19}F NMR spectra were measured with a Hitachi R-20B and a Varian Gemini 200 NMR spectrometer. ^{19}F NMR chemical shifts are reported in ppm upfield from CCl_3F as an internal standard. $CDCl_3$ was used as a solvent for ^1H and ^{19}F NMR, unless otherwise noted. IR spectra were measured on a JASCO A-202 diffraction grating infrared spectrometer. Fluorination with molecular fluorine was carried out according to the procedure and the apparatus reported in the literature.[28] Photoreaction of CF_3Br was carried out by using an internal irradiation apparatus with a 400-W high-pressure Hg lamp.

Materials. 2-Mercaptobiphenyl[29] and 2-selenocyanatobiphenyl[30] were prepared from 2-aminobiphenyl according to the literature. For the former, a modified procedure was adopted because of a bad smell in the reduction step by $LiAlH_4$; the modified procedure consisted of $LiAlH_4$ or Zn reduction of bis(2-biphenylyl) disulfide. Similarly, 5,3′-dimethyl-2-mercaptobiphenyl and 5,3′-dimethyl-2-selenocyanatobiphenyl were prepared from 2-amino-5,3′-dimethylbiphenyl, which was prepared by coupling of 5-methyl-2-nitrobenzoic acid with *m*-iodotoluene in the presence of Cu_2O[31] and then reduction. 4,4′-Di-*tert*-butyl-2-iodobiphenyl was prepared according to the literature.[32] 2-Mercaptophenyl phenyl ether was prepared by reduction of phenoxathiin.[33] Bis(2-biphenylyl) ditelluride was prepared by the reaction of telluride with 2-biphenylylmagnesium bromide in THF according to the literature.[34] Phenyl trifluoromethyl sulfoxide was prepared by oxidation of phenyl trifluoromethyl sulfide[35] with *m*-chloroperbenzoic acid. [(Trifluoromethyl)thio]copper (I) was prepared by the known method.[36] Commercially available compounds were used without further purification, unless otherwise noted.

Preparation of Trifluoromethyl Sulfides 1 and 2 and 1-Phenoxy-2-[(trifluoromethyl)thio]benzene. Typical Procedure. Under an argon atmosphere, a solution of 5.59 g (30 mmol) of 2-mercaptobiphenyl in 50 mL of dry *N*,*N*-dimethylformamide (DMF) was placed in a reaction vessel for irradiation and cooled in an ice bath. To the solution was added 1.2 g (30 mmol) of NaH (60% in oil) in several portions with stirring. After evolution of hydrogen ceased, the solution was saturated with CF_3Br gas. The reaction mixture was irradiated with a high-pressure Hg lamp for 2 h while cooling in an ice bath, and during the irradiation, CF_3Br gas was bubbled into the stirred solution. The total amount of CF_3Br used was ca. 60 mmol. The reaction mixture was poured into water and extracted with pentane. The pentane layer was washed with water and saturated aqueous NaCl solution, dried with $MgSO_4$, and filtered. Evaporation of solvent gave 6.71 g (ca. 82%) of **1** as an oily product. For purification, distillation under reduced pressure or column chromatography on silica gel was carried out. Similarly, sulfide **2** and 1-phenoxy-2-[(trifluoromethyl)thio]benzene were prepared from 5,3′-dimethyl-2-mercaptobiphenyl and 2-mercaptophenyl phenyl ether in 71 and 85% yields, respectively.

2-[(Trifluoromethyl)thio]biphenyl (1): mp 37 °C; bp 96 °C/3 mmHg; ^1H NMR δ 7.20–7.60 (8 H, m), 7.78 (1 H, br d, J = 7.5 Hz, 3-H); ^{19}F NMR 42.5 (s); mass spectrum m/e 254 (M^+), 185 ($M^+ - CF_3$), 69 (CF_3^+). Anal. Calcd for $C_{13}H_9F_3S$: C, 61.41; H, 3.57. Found: C, 61.37; H, 3.65.

5,3′-Dimethyl-2-[(trifluoromethyl)thio]biphenyl (2): oil; ^1H NMR δ 2.41 (6 H, s, 5,3′-CH_3), 7.06–7.36 (6 H, m, 4,6,2′,4′,5′,6′-H), 7.68 (1 H, d, J = 8.3 Hz, 3-H); ^{19}F NMR 42.9 (s); mass spectrum m/e 282 (M^+), 213 ($M^+ - CF_3$), 198 (213 − Me). Anal. Calcd for $C_{15}H_{13}F_3S$: C, 63.82; H, 4.64. Found: C, 63.99; H, 4.88.

1-Phenoxy-2-[(trifluoromethyl)thio]benzene: oil; ^1H NMR δ 6.92 (1 H, dd, J = 8.3, 1.3 Hz, 3-H), 7.01 (2 H, dm, J = 8 Hz, 2′,6′-H), 7.13 (1 H, td, J = 7.6, 1.3 Hz, 5-H), 7.15 (1 H, tt, J = 8, 1.1 Hz, 4′-H), 7.36 (2 H, tm, J = 8 Hz, 3′,5′-H), 7.40 (1 H, ddd, J = 8.3, 7.6, 1.7 Hz, 4-H), 7.71 (1 H, dm, J = 7.6 Hz, 6-H); ^{19}F NMR 42.5 (s); mass spectrum m/e 270 (M^+), 201 ($M^+ - CF_3$). Anal. Calcd for $C_{13}H_9F_3OS$: C, 57.77; H, 3.36. Found: C, 57.62; H, 3.43.

Preparation of 4,4′-Di-*tert*-butyl-2-[(trifluoromethyl)thio]biphenyl (3). Under an argon atmosphere, 14.8 g (90 mmol) of [(trifluoromethyl)thio]copper(I) was added to a solution of 17.7 g (45 mmol) of 4,4′-di-*tert*-butyl-2-iodobiphenyl in 80 mL of dry *N*-methylpyrrolidinone, and the mixture was heated at 100 °C for 3 h. After cooling, 600 mL of Et_2O was added and the reaction mixture was filtered through celite. The filtrate was washed with water (4 times) and saturated aqueous NaCl solution, dried with $MgSO_4$, and filtered. After evaporation of solvent, the residue was column chromatographed on silica gel using hexane as eluent to give 14.5 g (88%) of **3**: mp 67–67.5 °C (hexane); ^1H NMR δ 1.38 (18 H, s, 4,4′-*t*-Bu), 7.25 (2 H, d, J = 8.4 Hz, 3′,5′-H), 7.35 (1 H, d, J = 8.1 Hz, 6-H), 7.43 (2 H, d, J = 8.4 Hz, 2′,6′-H), 7.52 (1 H, dd, J = 8.1, 2.1 Hz, 5-H), 7.80 (1 H, m, 3-H); ^{19}F NMR 42.4 (s); mass spectrum m/e 366 (M^+), 351 ($M^+ - CH_3$), 57 (*t*-Bu). Anal. Calcd for $C_{21}H_{25}F_3S$: C, 68.83; H, 6.88. Found: C, 68.90; H, 6.97.

Preparation of Trifluoromethyl Selenides 4 and 5. Typical Procedure. Under an argon atmosphere, 5.16 g (20 mmol) of 2-selenocyanatobiphenyl and 30 mL of dry DMF were placed in a flask and cooled in a bath of −30 °C. Then the atmosphere in the flask was replaced with CF_3I gas. $NaBH_4$ (915 mg, 24 mmol) was added to the cooled and stirred solution. After evolution of hydrogen ceased, the reaction mixture

(24) (a) Kornblum, N. *Aldrichimica Acta* **1990**, *23*, 71 and references cited therein. (b) Cantacuzene, D.; Wakselman, C.; Dorme, R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1365. (c) Boiko, V. N.; Dashevskaya, T. A.; Shchupak, G. M.; Yagupol'skii, L. M. *J. Org. Chem. USSR* **1979**, *14*, 347. (d) Wakselman, C.; Tordeux, M. *J. Org. Chem.* **1985**, *50*, 4047. (e) Feiring, A. E. *J. Org. Chem.* **1985**, *50*, 3269.

(25) (a) Oae, S.; Kawai, T.; Furukawa, N.; Iwasaki, F. *J. Chem. Soc., Perkin Trans. 2* **1987**, 405 and references cited therein. (b) Furukawa, N.; Ogawa, S.; Matsumura, K.; Fujihara, H. *J. Org. Chem.* **1991**, *56*, 6341. (c) Umemura, K.; Matsuyama, H.; Kamigata, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2593.

(26) (a) Pine, S. H.; Hendrickson, J. B.; Cram, D. J.; Hammond, G. S. *Organic Chemistry* 4th ed.; McGram-Hill, Inc.: New York, 1980. (b) Imoto, M.; Nakaya, T. *Yuki Hanno Ron*; Tokyo Kagaku Dojin: Tokyo, 1982.

(27) Abstract for 13th International Symposium on Fluorine Chemistry held at Bochum, Germany, in Sept., 1991; Ono, T.; Umemoto, T. *J. Fluorine Chem.* **1991**, *54*, 204.

(28) Umemoto, T.; Tomita, K.; Kawada, K. *Org. Synth.* **1990**, *69*, 129.

(29) Campaigne, E.; Osborn, S. W. *J. Org. Chem.* **1957**, *22*, 561.

(30) Chierici, L.; Passerini, R. *J. Chem. Soc.* **1954**, 3249.

(31) Nilsson, M. *Acta Chem. Scand.* **1966**, *20*, 423.

(32) Tashiro, M.; Yamato, T. *J. Org. Chem.* **1979**, *44*, 3037.

(33) Tomita, M.; Inubushi, Y.; Niwa, H. *J. Pharm. Soc. Jpn.* **1952**, *72*, 206.

(34) Petragnani, N.; Comasseto, J. V. *Synthesis* **1986**, 1.

(35) Boiko, V. N.; Shchupak, G. M.; Yagupol'skii, L. M. *J. Org. Chem. USSR* **1977**, *13*, 972.

(36) Clark, J. H.; Jones, C. W.; Kybett, A. P.; McClinton, M. A.; Miller, J. M.; Bishop, D.; Blade, R. J. *J. Fluorine Chem.* **1990**, *48*, 249.

was slowly warmed to room temperature over a period of ca. 3 h, and CF_3I gas was bubbled into the mixture during the period. The total amount of CF_3I used was 60 mmol. The reaction mixture was poured into water and extracted with hexane. The extract was washed with water and saturated aqueous NaCl solution, dried with Na_2SO_4, and filtered. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using a 1:20 mixture of ethyl acetate and hexane as eluent to give 4.05 g (67%) of **4** as white crystals. Similarly, **5** was obtained in 46% yield.

2-[(Trifluoromethyl)seleno]biphenyl (4): mp 44–45 °C; ^{1}H NMR δ 7.17–7.52 (8 H, m), 7.87 (1 H, br d, J = 6 Hz, 3-H); ^{19}F NMR 36.0 (s); mass spectrum m/e 301 (M^+), 232 ($M^+ - CF_3$), 69 (CF_3^+). Anal. Calcd for $C_{13}H_9F_3Se$: C, 51.85; H, 3.01. Found: C, 51.85; H, 3.09.

5,3′-Dimethyl-2-[(trifluoromethyl)seleno]biphenyl (5): oil; ^{1}H NMR δ 2.40 (6 H, s, 5,3′-Me), 7.02–7.35 (6 H, m, 4,6,2′,4′,5′,6′-H), 7.75 (1 H, d, J = 7.9 Hz, 3-H); ^{19}F NMR 36.3 (s); mass spectrum m/e 332, 330, 328, 327, 326 (M^+), 263, 261, 259, 258, 257 ($M^+ - CF_3$). Anal. Calcd for $C_{15}H_{13}F_3Se$: C, 54.72; H, 3.98. Found: C, 54.85; H, 4.01.

Preparation of Sulfoxides 8, 9, 11, and 28 and Selenoxide 10. Typical Procedure. Under an argon atmosphere, 7.77 g (31.5 mmol) of *m*-chloroperbenzoic acid was added in small portions to a stirred solution of 7.63 g (30 mmol) of 2-[(trifluoromethyl)thio]biphenyl (**1**) in 20 mL of dry CH_2Cl_2 cooled in an ice bath. The reaction mixture was stirred overnight at room temperature, filtered, and evaporated. The residue was column chromatographed on silica gel using a 1:10 mixture of ethyl acetate and hexane as eluent to give 7.93 g (98%) of **8**. Similarly, **9**, **10**, **11**, and **28** were obtained in 96, 85, 100, and 52% yields, respectively.

2-[(Trifluoromethyl)sulfinyl]biphenyl (8): mp 57–58 °C; ^{1}H NMR δ 7.21–7.48 (5 H, m, 4,5,3′,4′,5′-H), 7.51–7.65 (3 H, m, 6,2′,6′-H), 8.18–8.28 (1 H, m, 3-H); ^{19}F NMR 73.1 (s); mass spectrum m/e 270 (M^+), 201 ($M^+ - CF_3$). Anal. Calcd for $C_{13}H_9F_3OS$: C, 57.77; H, 3.36. Found: C, 57.52; H, 3.50.

4,4′-Di-*tert*-butyl-2-[(trifluoromethyl)sulfinyl]biphenyl (9): oil; ^{1}H, NMR δ 1.37 (9 H, s, 4′-*t*-Bu), 1.41 (9 H, s, 4-*t*-Bu), 7.22–7.29 (2 H, m, 3′,5′-H), 7.36 (1 H, d, J = 8.1 Hz, 6-H), 7.45 (2 H, d, J = 8.6 Hz, 2′,6′-H), 7.69 (1 H, dd, J = 8.1, 1.4 Hz, 5-H), 8.20 (1 H, s, 3-H); ^{19}F NMR 73.0 (s); mass spectrum m/e 383 ($M^+ + 1$), 57 (*t*-Bu). Anal. Calcd for $C_{21}H_{25}F_3OS$: C, 65.95; H, 6.59. Found: C, 66.08; H, 6.70.

2-[(Trifluoromethyl)seleninyl]biphenyl (10): mp 151–152 °C; ^{1}H NMR δ 7.25–7.75 (8 H, m), 8.23–8.34 (1 H, m, 3-H); ^{19}F NMR 63.0 (s); mass spectrum m/e 321, 319, 317, 316, 315 ($M^+ + 1$). Anal. Calcd for $C_{13}H_9F_3OSe$: C, 49.23; H, 2.86. Found: C, 49.12; H, 2.91.

2-[(Perfluorooctyl)sulfinyl]biphenyl (11): mp 62–63 °C; ^{1}H NMR δ 7.23–7.71 (8 H, m), 8.16–8.29 (1 H, m, 3-H); ^{19}F NMR 82.1 (3 F, m, CF_3), 122.6 (12 F, m), 126.9 (2 F, m, CF_2CF_3); mass spectrum m/e 621 ($M^+ + 1$), 601 ($M^+ - F$), 201 ($M^+ - C_8F_{17}$), 69 (CF_3^+). Anal. Calcd for $C_{20}H_9F_{17}OS$: C, 38.73; H, 1.46. Found: C, 38.54; H, 1.27.

1-Phenoxy-2-[(trifluoromethyl)sulfinyl]benzene (28): oil; ^{1}H NMR δ 6.85 (1 H, dd, J = 8, 1 Hz, 3-H), 7.04 (2 H, dm, J = 8 Hz, 2′,6′-H), 7.23 (1 H, tt, J = 8, 1 Hz, 4′-H), 7.33 (1 H, td, J = 8, 1 Hz, 4-H), 7.41 (2 H, dm, J = 8 Hz, 3′,5′-H), 7.51 (1 H, tm, J = 8 Hz, 5-H), 8.03 (1 H, dd, J = 8, 1 Hz, 6-H); ^{19}F NMR 74.0 (s); mass spectrum m/e 286 (M^+), 270 ($M^+ - O$), 217 ($M^+ - CF_3$). Anal. Calcd for $C_{13}H_9F_3O_2S$: C, 54.54; H, 3.17. Found: C, 54.29; H, 3.17.

Preparation of Higher Perfluoroalkyl Sulfides 6 and 7. Typical Procedure. Under an argon atmosphere, 481 mg (12 mmol) of NaH (60% in oil) was added in small portions to a stirred solution of 2.24 g (12 mmol) of 2-mercaptobiphenyl in 20 mL of dry DMF cooled in an ice bath. After evolution of hydrogen ceased, 1.73 mL (12 mmol) of perfluoropropyl iodide was added dropwise, and the reaction mixture was gradually warmed to room temperature. After stirring for 2 days, the reaction mixture was poured into water and extracted with hexane. The extract was washed with water, dried with $MgSO_4$, and filtered. After evaporation of the solvent, the residue was column chromatographed on silica gel using a 1:30 mixture of ethyl acetate and hexane as eluent to give 3.46 g (87%) of **6**. Sulfide **7** was prepared in 64% yield by the same method, except that the reaction time at room temperature was 2 h.

2-[(Perfluoro-*n*-propyl)thio]biphenyl (6): oil; ^{1}H NMR δ 7.18–7.87 (m); ^{19}F NMR 81.7 (3 F, t, J = 8.1 Hz, CF_3), 87.8 (2 F, m, SCF_2), 124.9 (2 F, t, J = 3.5 Hz, CF_2CF_3); mass spectrum m/e 354 (M^+), 185 ($M^+ - C_3F_7$), 69 (CF_3^+). Anal. Calcd for $C_{15}H_9F_7S$: C, 50.85; H, 2.56. Found: C, 50.96; H, 2.58.

2-[(Perfluoro-*n*-octyl)thio]biphenyl (7): oil; ^{1}H NMR δ 7.17–7.59 (8 H, m), 7.79 (1 H, br d, J = 6 Hz, 3-H); ^{19}F NMR 81.4 (3 F, t, J = 9.0 Hz, CF_3) 86.1 (2 F, m, SCF_2), 119.3 (2 F, m, SCF_2CF_2), 121.4 (8 F, m), 126.0 (2 F, m, CF_2CF_3); mass spectrum m/e 604 (M^+), 185 ($M^+ - C_8F_{17}$), 69 (CF_3^+). Anal. Calcd for $C_{20}H_9F_{17}S$: C, 39.75; H, 1.50. Found: C, 39.51; H, 1.49.

Preparation of (Trifluoromethyl)dibenzothio- and -selenophenium Salts 12–18 and Higher Perfluoroalkyl Homologues 19 and 20. Method A. Typical Procedure. A 1:9 mixture of F_2 and N_2 gas was introduced at a rate of 20 mL/min to a stirred solution of 509 mg (2 mmol) of **1** and 300 mg (2 mmol) of TfOH in 6 mL of CCl_3F cooled in a bath of 0 °C. The total amount of F_2 used was 6 mmol. After N_2 was flowed at a rate of 10 mL/min for 15 min, the reaction mixture was warmed to room temperature. Addition of Et_2O to the mixture resulted in a white precipitate of **12**, which was collected by filtration. The yield was 672 mg (83%). The direct fluorination of sulfide **2** and selenides **4** and **5** were carried out at −20, −35, and −60 °C to give salts **14**, **17**, and **18** in 76, 76, and 57% yields, respectively. Tetrafluoroborates **13** and **16** were synthesized in 74 and 74% yields by fluorination using HBF_4 etherate at 0 and −50 °C, respectively. In the former case, use of BF_3 etherate in place of HBF_4 etherate gave a 54% yield of **13**.

Method B. Typical Procedure. A 1:9 mixture of F_2 and N_2 gas was introduced at a rate of 40 mL/min in a stirred solution of 763 mg (3 mmol) of **1** in 10 mL of CCl_3F cooled in a bath of −78 °C. The total amount of F_2 used was 3.6 mmol. After that, 0.265 mL (3 mmol) of TfOH was added, and the reaction mixture was slowly warmed to room temperature over a period of ca. 1 h. Addition of Et_2O to the mixture resulted in a white precipitate of **12**, which was collected by filtration. The yield was 684 mg (57%). Tetrafluoroborates **13** and **19** were synthesized in 74 and 39% yields, respectively, by this method using BF_3 etherate in place of triflic acid.

Method C. Typical Procedure. Under an argon atmosphere, 2.52 mL (15 mmol) of Tf_2O was added to a solution of 4.05 g (15 mmol) of 2-[(trifluoromethyl)sulfinyl]biphenyl (**8**) in 30 mL of CCl_2FCClF_2, and the reaction mixture was stirred for 2 days at room temperature. The resulting white precipitate of **12** was collected by filtration. The yield was 4.51 g (75%). Dry CH_2Cl_2 was similarly used as a solvent in place of CCl_2FCClF_2. Salts **15**, **17**, and **20** were synthesized similarly in 83, 94, and 91% yields, except that the reaction conditions were 1 h and 2 h at 0 °C to room temperature and 5 days at room temperature, respectively.

***S*-(Trifluoromethyl)dibenzothiophenium triflate (12)**: mp 155 °C (CH_3CN–Et_2O); ^{1}H NMR (CD_3CN) δ 7.78–8.18 (4 H, m, 2,3,7,8-H), 8.38–8.55 (4 H, m, 1,4,6,9-H); ^{19}F NMR (CD_3CN) 52.6 (3 F, s, SCF_3), 78.1 (3 F, s, SO_2CF_3); IR (KBr) 1285, 1245, 1215, 1150, 1085, 1030, 770, 640 cm^{-1}; mass spectrum m/e 184 ($M^+ - OSO_2CF_3 - CF_3$), 69 (CF_3). Anal. Calcd for $C_{14}H_8F_6O_3S_2$: C, 41.80; H, 2.00. Found: C, 41.75; H, 1.84.

***S*-(Trifluoromethyl)dibenzothiophenium tetrafluoroborate (13)**: mp 171–172 °C (CH_3CN–Et_2O); ^{1}H NMR (CD_3CN) δ 7.79–8.22 (4 H, m, 2,3,7,8-H), 8.36–8.52 (4 H, m, 1,4,6,9-H); ^{19}F NMR (CD_3CN) 52.5 (3 F, s, CF_3), 150.1 (4 F, s, BF_4); IR (KBr) 1230, 1080, 770 cm^{-1}; mass spectrum (SIMS) m/e 253 ($M^+ - BF_4$), 184 (253 − CF_3). Anal. Calcd for $C_{13}H_8BF_7S$: S, 9.4. Found: S, 9.9.

2,8-Dimethyl-*S*-(trifluoromethyl)dibenzothiophenium triflate (14): dec 181 °C (CH_3CN–Et_2O); ^{1}H NMR (CD_3CN) δ 2.60 (6 H, s, 2,8-Me), 7.67 (2 H, d, J = 8.4 Hz, 3,7-H), 8.17 (2 H, s, 1,9-H), 8.25 (2 H, d, J = 8.4 Hz, 4,6-H); ^{19}F NMR (CD_3CN) 53.8 (3 F, s, SCF_3), 78.1 (3 F, s, SO_2CF_3); IR (KBr) 1264, 1076, 1031, 641 cm^{-1}; mass spectrum (FAB) m/e 281 ($M^+ - OSO_2CF_3$), 212 (281 − CF_3). Anal. Calcd for $C_{16}H_{12}F_6O_3S_2$: C, 44.65; H, 2.81. Found: C, 44.48; H, 2.58.

3,7-Di-*tert*-butyl-*S*-(trifluoromethyl)dibenzothiophenium triflate (15): dec 205 °C (CH_3CN–Et_2O); ^{1}H NMR δ 1.43 (18 H, s, 3,7-*t*-Bu), 7.95 (2 H, dd, J = 8.3, 1.6 Hz, 2,8-H), 8.00 (2 H, dd, J = 8.3, 0.7 Hz, 1,9-H), 8.38 (2 H, m, 4,6-H); ^{19}F NMR (CD_3CN) 53.1 (3 F, s, SCF_3), 78.1 (3 F, s, SO_2CF_3); IR (KBr) 2969, 1273, 1165, 1077, 1033, 637 cm^{-1}; mass spectrum (FAB) m/e 365 ($M^+ - OSO_2CF_3$), 296 (365 − CF_3). Anal. Calcd for $C_{22}H_{24}F_6O_3S_2$: C, 51.35; H, 4.70. Found: C, 51.31; H, 4.65.

3,7-Di-*tert*-butyl-*S*-(trifluoromethyl)dibenzothiophenium tetrafluoroborate (16): dec 202–203 °C (CH_2Cl_2); ^{1}H NMR (CD_3CN) δ 1.42 (18 H, s, 3,7-*t*-Bu), 8.12 (2 H, dd, J = 8.3, 1.8 Hz, 2,8-H), 8.24 (2 H, d, J = 8.3 Hz, 1,9-H), 8.40 (2 H, d, J = 1.8 Hz, 4,6-H); ^{19}F NMR (CD_3CN) 52.9 (3 F, s, SCF_3), 149.9 (4 F, s, BF_4); IR (KBr) 2968, 1480, 1224, 1064 cm^{-1}; mass spectrum (FAB) m/e 365 ($M^+ - OSO_2CF_3$), 296 (365 − CF_3). Anal. Calcd for $C_{21}H_{24}BF_7S$: S, 7.09. Found: S, 7.30.

***Se*-(Trifluoromethyl)dibenzoselenophenium triflate (17)**: mp 170–172 °C (CH_3CN–Et_2O); ^{1}H NMR (CD_3CN) δ 7.66–8.06 (4 H, m, 2,3,7,8-H), 8.23–8.43 (4 H, m, 1,4,6,9-H); ^{19}F NMR (CD_3CN) 45.6 (3 F, s, $SeCF_3$), 77.9 (3 F, s, SO_2CF_3); IR (KBr) 1285, 1225, 1155, 1080, 1020, 760, 630 cm^{-1}; mass spectrum (SIMS) m/e 301 ($M^+ - OSO_2CF_3 + 1$), 232 (301 − CF_3). Anal. Calcd for $C_{14}H_8F_6O_3SSe$: C, 37.43; H, 1.79. Found: C, 37.33; H, 1.76.

2,8-Dimethyl-*Se*-(trifluoromethyl)dibenzoselenophenium triflate (18): dec 217–218 °C (CH_3CN–Et_2O); ^{1}H NMR (CD_3CN) δ 2.56 (6 H, s, 2,8-Me), 7.59 (2 H, dm, J = 8.2 Hz, 3,7-H), 8.09 (2 H, m, 1,9-H), 8.14 (2 H, d, J = 8.2 Hz, 4,6-H); ^{19}F NMR (CD_3CN) 46.5 (3 F, s, $SeCF_3$), 77.9 (3 F, s, SO_2CF_3); IR (KBr) 1272, 1067, 1030, 636 cm^{-1}; mass spectrum (FAB) m/e 329, 327 ($M^+ - OSO_2CF_3$), 260 (329 − CF_3), 258

(327 - CF_3). Anal. Calcd for $C_{16}H_{12}F_6O_3SSe$: C, 40.26; H, 2.53. Found: C, 40.11; H, 2.30.

***S*-(Perfluoro-*n*-propyl)dibenzothiophenium tetrafluoroborate (19)**: mp 181 °C (AcOEt–hexane); ^1H NMR (CD_3CN) δ 7.79–8.27 (4 H, m, 2,3,7,8-H), 8.37–8.48 (4 H, m, 1,4,6,9-H); ^{19}F NMR (CD_3CN) 79.5 (3 F, t, J = 8.8 Hz, CF_3), 93.4 (2 F, q, J = 8.8 Hz, SCF_2), 118.7 (2 F, s, CF_2CF_3), 150.8 (4 F, s, BF_4); IR (KBr) 1245, 1140, 1080–1050, 1030, 820, 780, 735 cm^{-1}; mass spectrum (SIMS) m/e 353 ($M^+ - BF_4$), 184 (353 - C_3F_7). Anal. Calcd for $C_{15}H_8BF_{11}S$: C, 40.94; H, 1.83. Found: C, 40.67; H, 1.97.

***S*-(Perfluoro-*n*-octyl)dibenzothiophenium triflate (20)**: 191–192 °C (CH_3CN–Et_2O); ^1H NMR (CD_3CN) δ 7.75–8.18 (4 H, m, 2,3,7,8-H), 8.30–8.41 (4 H, m, 1,4,6,9-H); ^{19}F NMR (CD_3CN) 78.0 (3 F, s, SO_2CF_3), 79.8 (3 F, t, J = 9.2 Hz, CF_2CF_3), 91.4 (2 F, m, SCF_2), 113.6 (2 F, m, SCF_2CF_2), 119.3–121.1 (8 F, m), 124.5 (2 F, m, CF_2CF_3); IR (KBr) 1255, 1150, 1030, 770, 635 cm^{-1}; mass spectrum (SIMS) m/e 603 ($M^+ - OSO_2CF_3$), 184 (603 - C_8F_{17}). Anal. Calcd for $C_{21}H_8F_{20}O_3S_2$: C, 33.52; H, 1.07. Found: C, 33.40; H, 0.91.

(Trifluoromethyl)diphenylsulfonium Triflate (27). A solution of 3.03 g (15.6 mmol) of phenyl trifluoromethyl sulfoxide, 2.63 mL (15.6 mmol) of Tf_2O, and 2.09 mL (23.4 mmol) of dry benzene in 30 mL of CCl_2F-$CClF_2$ was stirred for 4 days at room temperature under an argon atmosphere. The resulting oil layer was separated from the solution by a decantation method and washed with CCl_2FCClF_2 several times. The oil was purified by column chromatography on silica gel using a 1:3 mixture of CH_3CN and CH_2Cl_2 as eluent and purified further by thin-layer chromatography on silica gel using a 1:2 mixture of them as eluent to give 5.64 g (59%) of **27** as crystals: mp 83.5–84.5 °C (AcOEt–hexane); ^1H NMR δ 7.40–8.07 (6 H, m, 3,4,5,3′,4′,5′-H), 8.27 (4 H, d, J = 9 Hz, 2,6,2′,6′-H); ^{19}F NMR 49.7 (3 F, s, SCF_3), 78.1 (3 F, s, SO_2CF_3): IR (KBr) 1270, 1250, 1150, 1090, 1025, 760, 630 cm^{-1}; mass spectrum (SIMS) m/e 255 ($M^+ - OSO_2CF_3$), 186 (255 - CF_3). Anal. Calcd for $C_{14}H_{10}F_6O_3S_2$: C, 41.59; H, 2.49. Found: C, 41.52; H, 2.41.

***S*-(Trifluoromethyl)phenoxathiinium Triflate (30).** According to method C above, a mixture of **28** and Tf_2O in CCl_2FCClF_2 was stirred for 6 days at room temperature. The resulting black oily residue was purified by thin-layer chromatography on silica gel using a 1:3 mixture of CH_3CN and CH_2Cl_2 as eluent to give 26% of **30** and ca. 20% of starting **28**. **30**: mp 154 °C (AcOEt–hexane); ^1H NMR δ 7.51–8.33 (m); ^{19}F NMR 58.5 (3 F, s, SCF_3), 78.4 (3 F, s, SO_2CF_3); IR (KBr) 1466, 1256, 1224, 1167, 1091, 1028, 634 cm^{-1}; mass spectrum m/e 269 ($M^+ - OSO_2CF_3$), 200 (269 - CF_3), 69 (CF_3). Anal. Calcd for $C_{14}H_8F_6O_4S_2$: C, 40.20; H, 1.93. Found: C, 40.18, H, 2.09.

Mononitration of 12. To 0.06 mL (1.3 mmol) of 94% concentrated nitric acid was added 0.27 mL (1.6 mmol) of Tf_2O at room temperature with stirring under an argon atmosphere. After the mixture was stirred for an additional 1.5 h, 2 mL of dry nitromethane and then 402 mg (1 mmol) of **12** were added to the solution. The reaction mixture was stirred overnight and concentrated by an evaporator. Addition of Et_2O to the residue resulted in pale yellow crystals of **21**, which were collected by filtration. The yield was 339 mg (76%).

3-Nitro-*S*-(trifluoromethyl)dibenzothiophenium triflate (21): mp 153 °C (CH_3CN–Et_2O); ^1H NMR (CD_3CN) δ 7.84–8.28 (2 H, m, 7,8-H), 8.44–8.64 (3 H, m, 1,6,9-H), 8.86 (1 H, dd, J = 9.0, 1.5 Hz, 2-H), 9.28 (1 H, d, J = 1.5 Hz, 4-H); ^{19}F NMR (CD_3CN) 50.5 (3 F, s, SCF_3), 78.1 (3 F, s, SO_2CF_3); IR (KBr) 1265, 1235, 1160, 1065, 1030 cm^{-1}; mass spectrum (SIMS) m/e 298 ($M^+ - OSO_2CF_3$), 229 (298 - CF_3). Anal. Calcd for $C_{14}H_7F_6NO_5S_2$: C, 37.59; H, 1.58; N, 3.13. Found: C, 37.49; H, 1.48; N, 3.42.

Dinitration of 12, 17, and 32. Typical Procedure. To 0.94 mL (22.4 mmol) of 94% concentrated nitric acid was added 4.57 mL (27.2 mmol) of Tf_2O at room temperature with stirring under an argon atmosphere. After stirring for an additional 1 h, 3.0 g (7.46 mmol) of powdered **12** was added and the reaction mixture was stirred for 2 days. Product **22** appeared as a precipitate from the solution. The liquid layer was removed by a decantation method. Et_2O was slowly added to the solid layer (**caution**! external cooling was needed because a vigorous exothermic reaction occurred on adding Et_2O). The resulting pale yellow crystals for **22** were collected by filtration. The yield was 2.57 g (70%). Stirring for 3 days gave an 85% yield of **22**. Salts **23** and **35** were synthesized in 83 and 76% yields by the same method except that the reaction times with nitronium triflate were 3 and 1 h, respectively.

3,7-Dinitro-*S*-(trifluoromethyl)dibenzothiophenium triflate (22):[37] dec 130–135 °C (CH_3CN–Et_2O); ^1H NMR (CD_3CN) δ 8.69 (2 H, d, J = 9 Hz, 1,9-H), 8.91 (2 H, dd, J = 9.0, 1.8 Hz, 2,8-H), 9.34 (2 H, d, J = 1.8 Hz, 4,6-H): ^{19}F NMR (CD_3CN) 48.4 (3 F, s, SCF_3), 78.1 (3 F, s, SO_2CF_3); IR (KBr) 1525, 1350, 1225, 1070, 1030 cm^{-1}; mass spectrum (SIMS) m/e 343 ($M^+ - OSO_2CF_3$), 274 (343 - CF_3).

3,7-Dinitro-*Se*-(trifluoromethyl)dibenzoselenophenium triflate (23): dec 198–200 °C (CH_3CN–Et_2O); ^1H NMR (CD_3CN) δ 8.62 (2 H, d, J = 9 Hz, 1,9-H), 8.83 (2 H, dd, J = 9.0, 2.1 Hz, 2,8-H), 9.27 (2 H, d, J = 2.1 Hz, 4,6-H); ^{19}F NMR (CD_3CN) 41.8 (3 F, s, $SeCF_3$), 77.9 (3 F, s, SO_2CF_3); IR (KBr) 1530, 1345, 1275, 1220, 1060, 1025 cm^{-1}; mass spectrum (SIMS) m/e 391 ($M^+ - OSO_2CF_3$), 322 (391 - CF_3). Anal. Calcd for $C_{14}H_6F_6N_2O_7SSe$: C, 31.19; H, 1.12; N, 5.20. Found: C, 31.26; H, 0.97; N, 5.17.

3,7-Dinitro-*Te*-(trifluoromethyl)dibenzotellurophenium triflate (35): dec 275–280 °C (CH_3CN–Et_2O); ^1H NMR (CD_3CN) δ 8.50 (2 H, d, J = 8.7 Hz, 1,9-H), 8.68 (2 H, dd, J = 8.7, 2.2 Hz, 2,8-H), 9.50 (2 H, d, J = 2.2 Hz, 4,6-H); ^{19}F NMR (CD_3CN) 39.3 (3 F, s, $TeCF_3$), 78.0 (3 F, s, SO_2CF_3); IR (KBr) 1527, 1344, 1256, 1170, 1067, 1023, 862, 738, 636 cm^{-1}; mass spectrum (FAB) m/e 441, 439, 437 ($M^+ - OSO_2CF_3$), 372 (441 - CF_3), 370 (439 - CF_3), 368 (437 - CF_3). Anal. Calcd for $C_{14}H_6F_6N_2O_7STe$: C, 28.60; H, 1.03; N, 4.77. Found: C, 28.65; H, 1.05; N, 4.54.

2-[(Trifluoromethyl)tellurolbiphenyl (31). Under an argon atmosphere, 476 mg (12.6 mmol) of $NaBH_4$ was added to a stirred solution of 3.36 g (6 mmol) of bis(2-biphenylyl) ditelluride in 45 mL of dry THF at room temperature. To the reaction mixture was added 1.02 mL of methanol dropwise at a rate so that hydrogen was evolved moderately. After stirring for an additional 30 min, the reaction mixture was cooled to −78 °C, and ca. 500 mL (ca. 20 mmol) of CF_3I gas was condensed. The reaction mixture was warmed to room temperature over a period of 3 h and stirred overnight. Then it was poured into water and extracted with Et_2O. The extract was washed with water and then saturated aqueous NaCl solution, dried with $MgSO_4$, and filtered. Evaporation of the solvent gave 4.59 g of oil, which was purified by column chromatography on silica gel using hexane and then a 1:5 mixture of ethyl acetate and hexane as eluent to give 3.52 g (84%) of **31** and 0.56 g (recovery 17%) of the starting ditelluride. When CF_3Br was used instead of CF_3I, the reaction took 2 days and the yield of **31** was 70%. **31**: bp 138.5 °C (6 mmHg); ^1H NMR δ 7.18–7.64 (8 H, m), 8.25 (1 H, d, J = 8 Hz, 3-H); ^{19}F NMR 26.2 (s); mass spectrum m/e 352, 350, 348, 347, 346 (M^+), 69 (CF_3^+). Anal. Calcd for $C_{13}H_9F_3Te$: C, 44.64; H, 2.59. Found: C, 44.56; H, 2.48.

***Te*-(Trifluoromethyl)dibenzotellurophenium Triflate (32). Method A.** Under an argon atmosphere, 5.5 mL (33 mmol) of Tf_2O was added dropwise to a stirred solution of 10.5 g (30 mmol) of **31** and 2.1 mL (30 mmol) of dry dimethyl sulfoxide in 30 mL of dry CH_2Cl_2 cooled in an ice bath. After the mixture was stirred for an additional 1 h at room temperature, addition of Et_2O resulted in complete precipitation of **32**, which was collected by filtration and recrystallized from CH_3CN–Et_2O to give 12.6 g (84%) of **32**.

Method B. Under an argon atmosphere, 0.103 mL (2 mmol) of Br_2 was added dropwise to a stirred solution of 700 mg (2 mmol) of **31** in 4 mL of dry 1,1,2-trichloroethane at room temperature, and the mixture was stirred for an additional 40 min. Then 0.177 mL (2 mmol) of TfOH was added and the reaction mixture was heated under reflux overnight. After the reaction was cooled to room temperature, addition of CH_3CN, filtration, and then evaporation of solvent from the filtrate resulted in a crystalline solid, which was washed thoroughly with Et_2O to give 630 mg (63%) of **32**. **32**: dec 212 °C (CH_3CN); ^1H NMR (CD_3CN) δ 7.75 (2 H, td, J = 7.6, 1.3 Hz, 2,8 or 3,7-H), 7.86 (2 H, td, J = 7.6, 1.3 Hz, 2,8 or 3,7-H), 8.23–8.10 (4 H, m, 1,4,6,9-H); ^{19}F NMR (CD_3CN) 41.0 (3 F, s, $TeCF_3$), 78.0 (3 F, s, SO_2CF_3); IR (KBr) 1252, 1123, 1080, 1034, 751, 650 cm^{-1}; mass spectrum (FAB) m/e 351, 349, 347, 346 ($M^+ - OSO_2CF_3$), 282 (351 - CF_3), 280 (349 - CF_3), 278 (347 - CF_3), 277 (346 - CF_3). Anal. Calcd for $C_{14}H_8F_6O_3STe$: C, 33.77; H, 1.62. Found: C, 33.72; H, 1.52.

***Te*-(Trifluoromethyl)dibenzotellurophenium Bromide (33).** Under an argon atmosphere, a solution of 332 mg (1 mmol) of tetrabutylammonium bromide in 1 mL of dry CH_3CN was added dropwise to a stirred solution of 498 mg (1 mmol) of **32** in 4 mL of dry CH_3CN at room temperature. After the mixture was stirred for an additional 3.5 h, the resulting white precipitate was collected by filtration and washed with CH_3CN and then Et_2O to give 350 mg (82%) of **33**. **33**: dec 245 °C (MeOH–hexane); ^1H NMR (CD_3CN–$(CD_3)_2SO$) δ 7.58 (2 H, td, J = 7.6, 1.3 Hz, 2,8 or 3,7-H), 7.73 (2 H, td, J = 7.6, 1.3 Hz, 2,8 or 3,7-H), 8.11 (2 H, dd, J = 7.6, 1.3 Hz, 1,9 or 4,6-H), 8.34 (2 H, dd, J = 7.6, 1.3 Hz, 1,9 or 4,6-H); ^{19}F NMR (CD_3CN–$(CD_3)_2SO$) 45.0 (s); IR (KBr) 1124, 1079, 750 cm^{-1}; mass spectrum (FAB) m/e 351, 349, 347 ($M^+ - OSO_2CF_3$). Anal. Calcd for $C_{13}H_8BrF_3Te$: C, 36.42; H, 1.88. Found: C, 36.68; H, 1.72.

(37) For further purification, **17** was recrystallized from CH_3CN–Et_2O. However, analytically pure crystals could not be obtained, since the surfce of the crystals deteriorated on standing. Its X-ray structural analysis[27] indicated the crystals to consist of a 1:1 complex of **17** and CH_3CN. The CH_3CN molecules gradually left the crystalline lattice on standing at room temperature.

Te-(Trifluoromethyl)dibenzotellurophenium Tetrafluoroborate (34). Under an argon atmosphere, a stirred mixture of 200 mg (0.467 mmol) of **33** and 91 mg (0.467 mmol) of $AgBF_4$ in 2 mL of dry CH_3CN was heated under reflux for 25.5 h. Filtration and then evaporation of the solvent gave a crystalline solid, which was thoroughly washed with CH_2Cl_2 to give 180 mg (89%) of **34**. **34**: dec 219–220 °C (CH_3CN–Et_2O); ^1H NMR (CD_3CN) δ 7.72 (2 H, t, d, J = 7.6, 1.4 Hz, 2,8 or 3,7-H), 7.89 (2 H, td, J = 7.6, 1.3 Hz, 2,8 or 3,7-H), 8.17–8.23 (4 H, m, 1,4,6,9-H); ^{19}F NMR (CD_3CN) 40.4 (3 F, s, $TeCF_3$), 149.4 (4 F, s, BF_4); IR (KBr) 1443, 1167, 1060, 1024, 754, 733 cm^{-1}; mass spectrum (FAB) m/e 351, 349, 347 ($M^+ - OSO_2CF_3$), 282 (351 – CF_3), 280 (349 – CF_3), 278 (347 – CF_3). Anal. Calcd for $C_{13}H_8BF_7Te$: C, 35.84; H, 1.85. Found: C, 35.75; H, 1.67.

Alkaline Hydrolysis Experiments of 12, 17, 21, 22, and 23. General Procedure. A triflate (1 mmol) was added to a stirred aqueous NaOH solution (1 mol/L, 5 mL) which was cooled in an ice bath, and the mixture was stirred for an additional 1 h. The resulting precipitate of the corresponding dibenzothiophene *S*-oxide or selenophene *Se*-oxide was collected by filtration and washed with water. For **22**, the collected precipitate was column chromatographed on silica gel using a 20:1 mixture of CH_2Cl_2 and CH_3CN as eluent to obtain dibenzothiophene **39** and its *S*-oxide **38**. The results are shown in Results and Discussion section.

Thermolysis Experiments of 12 and 22. General Procedure. The thermolysis apparatus consisted of two evacuated flasks connected with each other through a glass tube; one flask had been charged with 804 mg (2 mmol) of triflate **12** or 985 mg (calculated to contain 1.87 mmol of **22**) of crystals of **22** and the other flash was cooled in a dry ice–acetone bath. The former flask was heated to the desired temperature (200 °C for **12**, 140 °C for **22**) and maintained at that temperature for 1.25–1.5 h. Volatile **40** which condensed in the cooled flask was evaluated by ^{19}F NMR. For the case of **22**,[38] CH_3CN was detected as another volatile product, and its amount was determined to be 1.6 mmol by ^1H NMR. The solid product was purified by thin-layer chromatography on silica gel to obtain 361 mg (98%) of **41** from **12** and 510 mg (99% based on **22**) of **39** from **22**.

Controlled Trifluoromethylation of Aniline with Trifluoromethyl Onium Triflates. A trifluoromethyl onium triflate (0.25 mmol), dry DMF (0.6 mL), and then aniline (0.5 mmol) were charged in an NMR tube substituted with argon gas. Each reaction was run at room temperature and/or at 80 °C and monitored by ^{19}F NMR at intervals using a triflate anion of the trifluoromethyl onium triflate used in the experiment as internal standard. The reaction at 80 °C was conducted by using an oil bath set at the desired temperature. The results are shown in Table I.

Trifluoromethylation of Nucleophilic Substrates. General Procedure. Under an argon atmosphere, 1 mmol of a trifluoromethyl onium salt was added to a stirred solution of 0.95–2.5 mmol of substrate in 3–6 mL of dry solvent. The trifluoromethyl onium salts, substrates, their mole ratios, solvents, reaction times, temperatures, and presence or absence of an additive are shown in Table II. In the case of the reaction of **22** with triphenylphosphine (run 24 in Table II), triphenylphosphine was added in small portions to a solution of **22** in dry CH_3CN in order to avoid a side reaction of triphenylphosphine with the resulting 3,7-dinitrobenzothiophene (**39**), which gave triphenylphosphine oxide. After completion of the reaction, the reaction mixture was analyzed by an ^{19}F NMR technique using a triflate anion of the trifluoromethyl onium triflate used in the experiment as internal standard to determine the yields of products. The results are shown in Table II. When **22** was used, the resulting **39** was separated from the reaction solution as a yellow precipitate and thus **39** was easily removed by filtration. The structural assignments of the reaction products were carried out by spectral analyses of the products isolated by the usual methods and/or by comparison with authentic samples. Data for the new compounds are as follows.

2-Methyl-2-(trifluoromethyl)-1,3-cyclopentanedione (43): oil; ^1H NMR δ 1.38 (3 H, s, 2-Me), 2.68–3.15 (4 H, m, CH_2CH_2); ^{19}F NMR 69.8 (s); IR (neat) 1740 cm^{-1} (C=O); mass spectrum m/e 180 (M^+), 111 ($M^+ - CF_3$), 69 (CF_3). Anal. Calcd for $C_7H_7F_3O_2$: C, 46.68; H, 3.92. Found: C, 46.86; H, 3.89.

Ethyl 2-oxo-1-(trifluoromethyl)cyclopentanecarboxylate (45): oil; ^1H NMR δ 1.28 (3 H, t, J = 6.5 Hz, CH_2CH_3), 1.85–2.68 (6 H, m, $CH_2CH_2CH_2$), 4.23 (2 H, q, J = 6.5 Hz, CH_2CH_3); ^{19}F NMR 69.0 (s); IR (neat) 1770, 1745 cm^{-1} (C=O); mass spectrum m/e 224 (M^+), 151 ($M^+ - CO_2Et$), 69 (CF_3). Anal. Calcd for $C_9H_{11}F_3O_3$; C, 48.22; H, 4.95. Found: C, 48.39; H, 4.84.

2-Methyl-2-(trifluoromethyl)-1-indanone (49): oil, ^1H NMR δ 1.50 (3 H, s, 2-Me), 3.03 (1 H, d, J = 17.6 Hz), 3.57 (1 H, d, J = 17.6 Hz), 7.44 (1 H, t, J = 7.7 Hz), 7.49 (1 H, dd, J = 1.0, 7.7 Hz), 7.67 (1 H, dt, J = 1.0, 7.7 Hz), 7.82 (1 H, d, J = 7.7 Hz); ^{19}F NMR 74.1 (s); IR (neat) 1732 cm^{-1} (C=O); mass spectrum m/e 214 (M^+), 199 (M^+ – Me), 145 ($M^+ - CF_3$). Anal. Calcd for $C_{11}H_9F_3O$: C, 61.69; H, 4.24. Found: C, 61.55; H, 4.40.

4,4a,5,6,7,8-Hexahydro-4a-methyl-8-(trifluoromethyl)-2(3*H*)-naphthalenone (55α, 55β): oil; ^1H NMR δ α-isomer 1.26 (3 H, s, 4a-Me), 2.25–2.20 (1 H, m), 2.50 (1 H, ddd, J = 16.8, 12.6, 6.3 Hz, 3-H), 3.05 (1 H, m, 8-H), 6.01 (1 H, m, 1-H), β-isomer 1.29 (3 H, s, 4a-Me), 2.20–2.15 (1 H, m), 2.65 (1 H, ddd, J = 17.8, 15.0, 5.1 Hz, 3-H), 3.05 (1 H, m, 8-H), 5.89 (1 H, s, 1-H); ^{19}F NMR 66.44 (d, J = 11.5 Hz, β-isomer), 68.38 (dd, J = 8.2, 2.2 Hz, α-isomer); IR (neat) 1681 cm^{-1} (C=O); mass spectrum m/e 232 (M^+). Anal. Calcd for $C_{12}H_{15}F_3O$: C, 62.06; H, 6.51. Found: C, 62.04; H, 6.59.

2,6-Bis(trifluoromethyl)cyclohexanone (57): mp 75.5 °C; ^1H NMR δ 1.77–1.92 (3 H, m), 2.12–2.18 (1 H, m), 2.41–2.49 (2 H, m), 3.03–3.13 (2 H, m, 2,6-H); ^{19}F NMR 69.8 (d, J = 8 Hz); IR (neat) 1730 cm^{-1} (C=O); mass spectrum m/e 234 (M^+). Anal. Calcd for $C_8H_8F_6O$: C, 41.04; H, 3.44. Found: C, 41.12; H, 3.40.

8-(Trifluoromethyl)-2-naphthol (59): mp 77 °C; ^1H NMR δ 5.30 (1 H, s, O*H*), 7.20 (1 H, dd, J = 9.0, 2.3 Hz, 3-H), 7.36 (1 H, ddm, J = 8.0, 8.0 Hz, 6-H), 7.47 (1 H, m, 1-H), 7.65–7.80 (2 H, m, 4,5-H), 7.94 (1 H, dm, J = 8.0 Hz, 7-H); ^{19}F NMR 60.9 (s); IR (KBr) 3320 cm^{-1} (OH); mass spectrum m/e 212 (M^+); high-resolution mass calcd for $C_{11}H_7F_3O$ 212.04490, found 212.04496.

(Trifluoromethyl)triphenylphosphonium triflate (67): mp 139 °C; ^1H NMR δ 7.65–8.20 (m); ^{19}F NMR 58.3 (3 F, d, J = 93 Hz, PCF_3), 78.6 (3 F, s, CF_3); IR (KBr) 1265, 1165, 1140, 1030, 730, 615 cm^{-1}; mass spectrum (SIMS) m/e 331 ($M^+ - OSO_2CF_3$), 262 (331 – CF_3). Anal. Calcd for $C_{20}H_{15}F_6O_3PS$: C, 50.01; H, 3.15. Found: C, 50.19; H, 3.08.

Reaction of *S*-(Perfluoro-*n*-octyl)dibenzothiophenium Triflate (20) with Sodium Salt 42 of 2-Methyl-1,3-cyclopentanedione. Under an argon atmosphere, 40 mg (1 mmol) of NaH (60% in oil) was added to a stirred solution of 114 mg (1 mmol) of 2-methyl-1,3-cyclopentanedione in 3 mL of dry DMF cooled in an ice bath. Then the mixture was stirred at room temperature for 20 min. After the mixture was cooled to −65 °C, 752 mg (1 mmol) of **20** was added and the reaction mixture was stirred for 1 h and then warmed to room temperature over a period of ca. 1 h. After stirring for an additional 1 h, the mixture was poured into water and extracted with Et_2O. The organic layer was washed with water and then saturated aqueous NaCl solution, dried with $MgSO_4$, and filtered. After evaporation of the solvent, the residue was column chromatographed on silica gel (CH_2Cl_2:hexane = 1:1) to give 204 mg (38%) of 2-methyl-2-(perfluoro-*n*-octyl)-1,3-cyclopentanedione. The spectral data were in agreement with those of an authentic sample.[9b]

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(38) The crystals of **17** contain CH_3CN molecules; see ref 37.