

Synthesis and Reactions of Phenyliodonium Bis(perfluoroalkanesulfonyl) Methides

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ABSTRACT

Phenyliodonium bis(perfluoroalkanesulfonyl) methides $\text{PhI}^+ - \text{C}(\text{SO}_2\text{R}_F)_2$ (**3**) were prepared by the reaction of bis(perfluoroalkanesulfonyl)methanes with diacetoxyiodobenzene. The photochemical reactions of **3** with alkenes, methanol, bromine, and benzene gave the corresponding addition or insertion products. When **3** was irradiated in the presence of methyl sulfide, pyridine, and triphenylphosphine, it afforded the ylides containing the bis(perfluoroalkanesulfonyl)methylene functionality, $\text{Y}^+ - \text{C}(\text{SO}_2\text{R}_F)_2$. In these reactions the bis(perfluoroalkanesulfonyl)carbene intermediate $(\text{R}_F\text{SO}_2)_2\text{C}:$ may be involved. Irradiation or heating of **3** in DMSO gave a 1:1 complex, the structure of which was confirmed by X-ray diffraction analysis. Bis(perfluoroalkanesulfonyl)-methylene dimethylxosulfonium ylides $\text{Me}_2(\text{O})\text{S}^+ - \text{C}(\text{SO}_2\text{R}_F)_2$ were obtained by air oxidation of bis(perfluoroalkanesulfonyl)methylene dimethylsulfonium ylides.

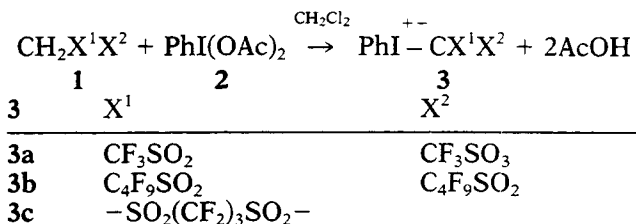
INTRODUCTION

During studies on the synthesis and reactions of per- and polyfluoroalkanesulfonyl acids and their derivatives, we have discovered a new series of difluorocarbene precursors, such as $\text{HCF}_2\text{SO}_2\text{Z}$ [1] (Z: F, OH, OR) and $\text{FO}_2\text{SCF}_2\text{CO}_2\text{R}$ [2] (R: H, CH_3). Both types of compound are convenient difluorocarbene precursors under different reaction conditions. As a part of this work, we report the synthesis and reactions of phenyliodonium bis(perfluoroalkanesulfonyl) methides. They are efficient

bis(perfluoroalkanesulfonyl)carbene precursors and react readily with many reagents, such as alkenes, halogens, alcohols, benzene, methyl sulfide, pyridine, triphenylphosphine, etc. This type of reaction offers a good way to introduce the bis(perfluoroalkanesulfonyl) functionality into various organic molecules.

RESULTS AND DISCUSSION

Compounds such as phenyliodonium bis(perfluoromethanesulfonyl) methide $\text{PhI}^+ - \text{C}(\text{SO}_2\text{CF}_3)_2$ (**3**) have been prepared in good yields by the reaction of bis(perfluoroalkanesulfonyl)methanes with diacetoxyiodobenzene [3,4].



This reaction was conveniently carried out in dichloromethane at room temperature. For the preparation of **3c**, a somewhat higher reaction temperature was favored (Table 1)

Two similar compounds, $\text{PhI}^+ - \text{C}(\text{RCO})_2$ and $\text{PhI}^+ - \text{C}(\text{PhSO}_2)_2$, were prepared by the reaction of $(\text{RCO}_2)_2\text{CH}_2$ or $(\text{PhSO}_2)_2\text{CH}_2$ with $\text{PhI}(\text{OAc})_2$ under basic conditions [5-7]:

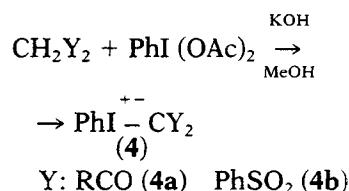
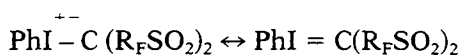


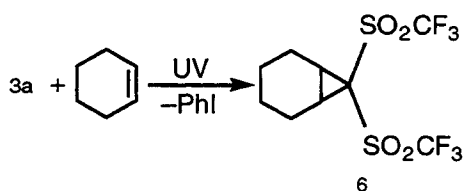
TABLE 1 Preparation of Compounds 3

Entry	Temperature T (°C)	Time t (h)	Product	Mp (°C)	Yield (%)
1	20	24	3a	140	71
2	20	24	3b	165 (dec)	59
3	20	24	3c	193	40
4	40	12	3c	193	75

In the preparation of **3**, however, no KOH was needed. Owing to the stronger acidity of **1** [8], the carbonyl oxygen atom of **2** was easily protonated during the reaction process. Acetic acid was the leaving group. It was also noticed that both **4a** and **4b** are unstable. For example, the decomposition of $\text{PhI}^+ - \text{C}(\text{PhSO}_2)^-$ occurred during recrystallization, and the compound had to be stored at -10°C [6,7]. Compound **3**, however, is more stable. It could be stored at room temperature for several months without alteration. Recrystallization of **3** from a mixture of acetone and acetonitrile (1:1) gave fine colorless crystals. The X-ray crystal structures of both **3a** and **3c** show that the four atoms, I, C, S, S, are coplanar, and the C–I bond distance (1.89 Å in **3a** and 2.03 Å in **3c**) is shorter than that of a normal C–I single bond ($\text{SP}^3\text{C-I}$, 2.14 Å; $\text{SP}^2\text{C-I}$, 2.03 Å [9]; see Figures 1 and 2). All these data indicate some double-bond character for the C–I bond in compounds **3**.



The expected cycloaddition product 7,7-bis(trifluoromethanesulfonyl)bicyclo[4, 1, 0]heptane was obtained in moderate yield when **3a** was irradiated with UV light in excess cyclohexene:



Koshar mentioned that $(\text{EtO}_2\text{C})_2\text{C}=\text{C}(\text{CO}_2\text{Et})_2$ could be obtained by heating $(\text{EtO}_2\text{C})_2\text{CBrNa}$. This product was presumably obtained by dimerization of $(\text{EtO}_2\text{C})_2\text{C}^{\cdot-}$, formed as an intermediate [8]. Another similar compound, $(\text{MeO}_2\text{C})_2\text{C}=\text{C}(\text{CO}_2\text{Me})_2$, was also reported as a by-product of the reaction of $\text{PhI}^+ - \text{C}(\text{CO}_2\text{Me})_2^-$ with cyclohexene [10].

Unfortunately, an attempt to synthesize tetra(trifluoromethanesulfonyl)ethylene failed. Photolysis or heating of **3a** without solvent or other substrate led to the recovery of starting material in addition to a small amount of iodobenzene and bis(trifluoromethanesulfonyl)methane. No $(\text{CF}_3\text{SO}_2)_2\text{C}=\text{C}(\text{CF}_3\text{SO}_2)_2$ could be detected. Difluoromethyl ether, ROCF_2H , and the difluoromethyl

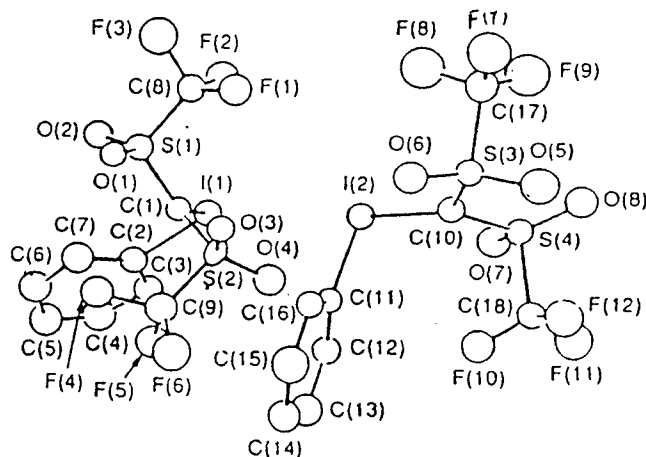
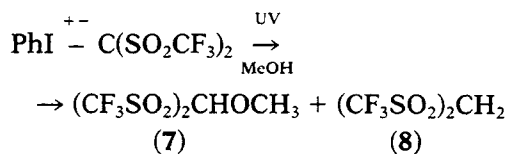


FIGURE 1 The structure of **3a** (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (°): I(2)–C(10), 1.890(1); I(1)–C(1), 2.012(2); I(2)–C(11), 2.075(9); I(1)–C(2), 2.110(2); S(1)–O(1), 1.432(7); S(1)–O(2), 1.390(7); S(4)–O(7), 1.417(8); S(4)–O(8), 1.414(8); C(1)–I(1)–C(2), 98.2(4); S(1)–C(1)–I(1), 118.2(5); S(2)–C(1)–S(1), 122.2(5); S(2)–C(1)–I(1); 117.3(4).

Crystal data: $\text{C}_{18}\text{H}_{10}\text{O}_8\text{F}_{12}\text{S}_4\text{I}_2$, $M = 964.32$, monoclinic, space group P21/n , $a = 10.132(5)$, $b = 13.486(1)$, $c = 21.600(2)$ Å, $\beta = 94.50(4)^\circ$, $V = 2942.3 \text{ \AA}^3$, $Z = 4$, $D_c = 2.177 \text{ g/cm}^3$, $F(000) = 1840$, $(\text{Mo K}\alpha) = 25.014 \text{ cm}^{-1}$, crystal dimensions $0.2 \times 0.2 \times 0.1 \text{ mm}$. Intensity data were collected at 20°C with a Enraf-Nonius CAD4 diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation. 2519 unique reflections were measured in the range $2^\circ < 2\theta < 50^\circ$ with $0 < h < 12$, $0 < k < 16$, $-25 < l < 25$. The correction of LP and absorption was applied for the reflection data. The structure was solved by direct method MULTAN11/82. All position parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least-squares technique. Final R , R_w , and S values were 0.10, 8.87, respectively, for 2414 observed reflections ($F > 3\sigma(F)$). All calculations were performed on a MICROVAX II computer with SDP, MULTAN11/82 and ORTEP programs. Scattering factors were taken from the International Table for X-ray Crystallography (1974).

ester, $\text{RCO}_2\text{CF}_2\text{H}$ or $\text{RSO}_3\text{CF}_2\text{H}$, were synthesized in our laboratory [11] by the O–H bond insertion reaction of difluorocarbene with the alcohol or the carboxylic acid or sulfonic acid. Like the difluorocarbene, the O–H bond insertion product of bis(trifluoromethanesulfonyl)carbene could be obtained from the photoreaction of **3a** in methanol:



When this reaction was carried out in a fluoroalkancarboxylic acid, however, no O–H bond insertion product was formed. The main product was $(\text{CF}_3\text{SO}_2)_2\text{CH}_2$. It seems reasonable to assume that the protonation of **3a** was faster than its de-

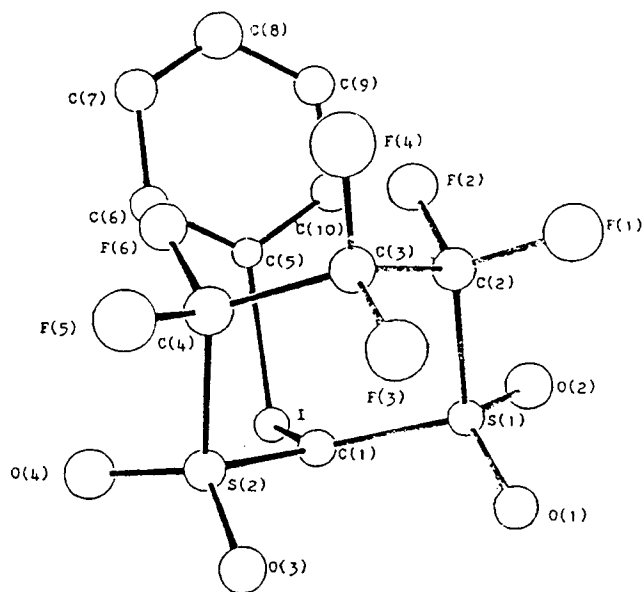
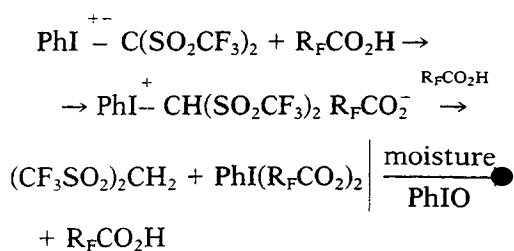


FIGURE 2 The structure of **3c** (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (°): C(1)–I, 2.028(8); C(5)–I, 2.078(7); S(1)–C(1), 1.696(8); S(2)–C(1), 1.701(7); S(2)–O(4), 1.415(7); S(2)–O(3), 1.440(6). S(1)–C(1)–S(2), 117.5(5); I–C(1)–S(1), 119.7(4); I–C(1)–S(2), 121.7(4). Crystal data: $C_{10}H_5O_4F_6S_2I$, $M = 494.17$ monoclinic, space group $P21/n$, $a = 7.387(3)$, $b = 20.403(8)$, $c = 10.206(3)$ Å, $\beta = 99.28(3)^\circ$, $V = 1518.0$ Å³, $Z = 4$, $D_c = 2.162$ g/cm³, $F(000) = 944$, $(Mo K\alpha) = 24.269$ cm⁻¹, crystal dimensions $0.2 \times 0.1 \times 0.2$ mm. Intensity data were collected at 20°C with a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation. 2315 unique reflections were measured in the range $2 < 2\theta < 50$ with $0 < h < 8$, $0 < k < 24$, $-12 < l < 12$. The correction of LP and absorption was applied for the reflection data. The structure was solved by direct method MULTAN11/82. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least squares technique. Final R, R_w and S values were 0.073 0.080, 3.95, respectively, for 1757 observed reflections ($F > 3\sigma(F)$). All calculations were performed on a MICROVAX II computer with SDP, MULTAN11/82 and ORTEP programs. Scattering factors were taken from International Tables for X-ray Crystallography (1974).

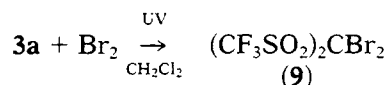
composition and that the protonated **3a** reacted with another mole of the acid to give $(CF_3SO_2)_2CH_2$. In other words, no $(CF_3SO_2)_2C$: intermediate was formed during this reaction.



SCHEME 2

Recently, Varvoglis reported a new route for the synthesis of a dihalobis(phenylsulfonyl)-methane by the reaction of **4b** with an N-halosuccinimide [6,12]

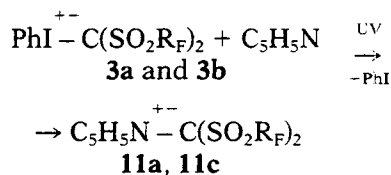
The dibromides, $(CF_3SO_2)_2CBr_2$ and $O_2S(CF_2)_3SO_2CBr_2$, could be prepared by the reaction of **3a** or **3c** with bromine in high yield (89%, for example):



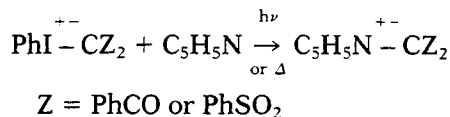
When **3a** was irradiated in benzene, a C–H bond insertion reaction occurred, yielding phenyl-bis(trifluoromethanesulfonyl)methane. If this reaction was carried out in toluene, which has two different types of C–H bonds, however, the insertion occurred only at the sp^2 C–H bond, giving the appropriate arylated disulfone **10b**.

As mentioned previously, when the photolysis of **3a** was carried out without an added substrate, no $(CF_3SO_2)_2C=C(CF_3SO_2)_2$ or $(CF_3SO_2)_2CHC_6H_4I$ -p was detected. A plausible explanation is that the recombination of the electrophilic carbene $(CF_3SO_2)_2C$: with iodobenzene, in which the polarizable iodine atom acts as an electron donor, is faster than a dimerization or insertion reaction. The results of the reaction of **3** with pyridine supported this hypothesis.

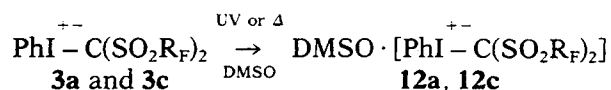
Photolysis of **3a** in an excess of pyridine gave only the pyridinium ylide:



Similar results have been reported recently [5,13].



In the same manner, Varvoglis also obtained the dimethylsulfonium ylide [13], $\text{Me}_2(\text{O})\text{S}^+ - \overset{-}{\text{C}}(\text{PhSO}_2)_2$. However, irradiation of **3** in DMSO gave no corresponding free $\text{Me}_2(\text{O})\text{S}^+ - \overset{-}{\text{C}}(\text{R}_F\text{SO}_2)_2$, the sole product being a 1:1 adduct:



The complexes **12a** and **12c** are obtained as fine colorless crystals. Both of them are stable at room temperature and in the air. Their X-ray structures are shown in Figures 3 and 4. On the basis of the X-ray structures of **3a** and **3c**, we have proposed that the C–I bond has some double-bond character. In complex **12a**, the C–I bond is longer (2.08

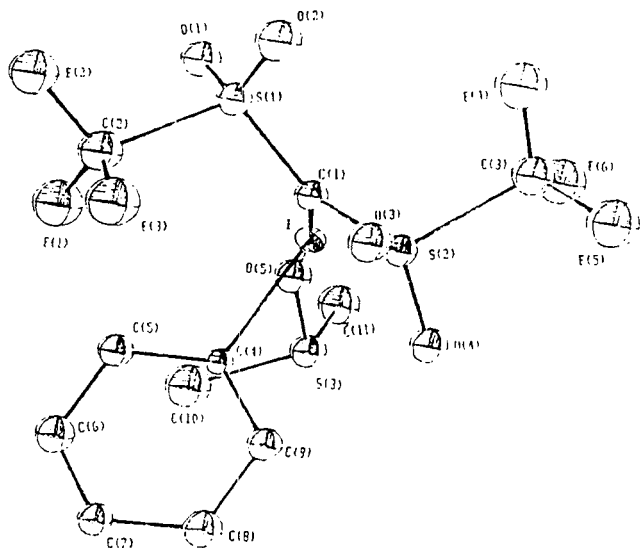


FIGURE 3 The structure of **12a** (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (°). I–O(5), 2.59(2); I–C(1), 2.08(1); I–C(4), 2.11(1); C(1)–S(1), 1.67(1); C(1)–S(2), 1.68(1); C(2)–S(1), 1.86(2); C(3)–S(2), 1.84(2); C(1)–I–C(4), 98.9(4); O(5)–I–C(1), 173.5(4); O(5)–I–C(4), 81.8(4); S(1)–C(1)–S(2), 124.2(7). Crystal data: **2a**, $C_{11}H_{11}O_5F_6S_3I$, $M = 560.29$, orthorhombic, space group $P2_12_12_1$. $a = 10.180(3)$, $b = 11.768(3)$, $c = 15.808(2)$ Å. $v = 1893.8$ Å³, $z = 4$, $D_c = 1.965$ g/cm³, $F(000) = 1088$, $(Mo\ K_\alpha) = 20.63$ cm⁻¹, crystal dimensions $0.2 \times 0.2 \times 0.2$ mm. Intensity data were collected at 20°C with a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo K_α radiation. 1944 unique reflections were measured in the range $2^\circ < 2\theta < 50^\circ$ with $0 < h < 12$, $0 < k < 14$, $0 < l < 18$. The correction of LP and absorption was applied for the reflection data. The structure was solved by direct method MULTAN11/82. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least-squares technique. Final R , R_w , and S values were 0.053, 0.096, 5.14, respectively, for 1544 observed reflections ($F > 3\sigma(F)$). All calculations were performed on a MICROVAX II computer with SOP, MULTAN11/82, and ORTEP programs. Scattering factors were taken from International Tables for X-ray Crystallography (1974).

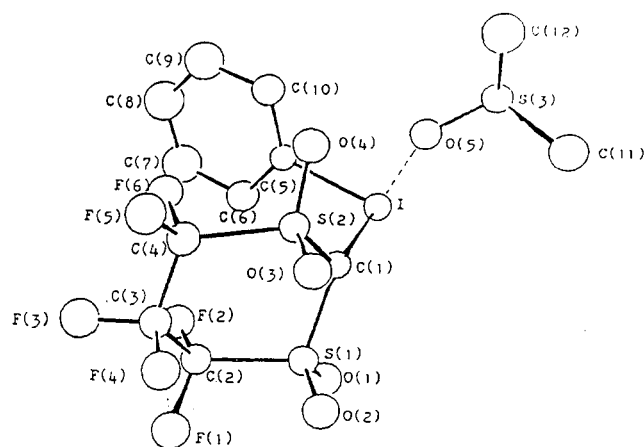
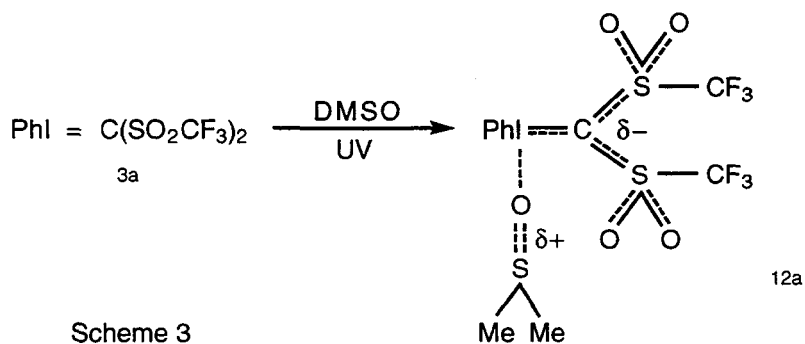


FIGURE 4 The structure of **2c** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and bond angles (°). I–O(5) 2.564(4); I–C(1) 2.058(5); I–C(5) 2.110(6); S(1)–C(1) 1.686(5); S(2)–C(1) 1.678(6); O(5)–I–C(1) 176.1(2); O(5)–I–C(5) 77.1(2); C(1)–I–C(5) 99.0(2); S(1)–C(1)–S(2) 117.6(3); S(1)–C(1)–S(2) 117.6(3). Crystal data: $C_{12}H_{11}OFS_3I$ $M = 572.30$, monoclinic, space group $P2_1/n$. $a = 9.733(1)$, $b = 10.239(2)$, $c = 21.101(1)$, $\beta = 94.47(4)^\circ$, $V = 1091.0$ Å³, $Z = 4$, $D_c = 2.021$ g/cm³, $F(000) = 1112$, $(Mo\ K_\alpha) = 20.794$ cm, crystal dimensions $0.2 \times 0.2 \times 0.1$ mm. Intensity data were collected at 20°C with a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo- K_α radiation. unique reflections were measured in the range $2^\circ < 2\theta < 50^\circ$ with $0 < h < 0$, $0 < k < 12$, $-25 < l < 25$. The correction of LP and absorption was applied for the reflection data. The structure was solved by direct method MULTAN11/82. All positional parameters and anisotropic thermal parameters for non-H atoms were refined by full-matrix least-squares technique. Final R , R_w , and S values were 0.04 0.048, 2.79, respectively, for 2158 observed reflections ($F > 3\sigma(F)$). All calculations were performed on a MICROVAX II computer with SOP, MULTAN11/82, and ORTEP programs. Scattering factors were taken from International Tables for X-ray Crystallography (1974).



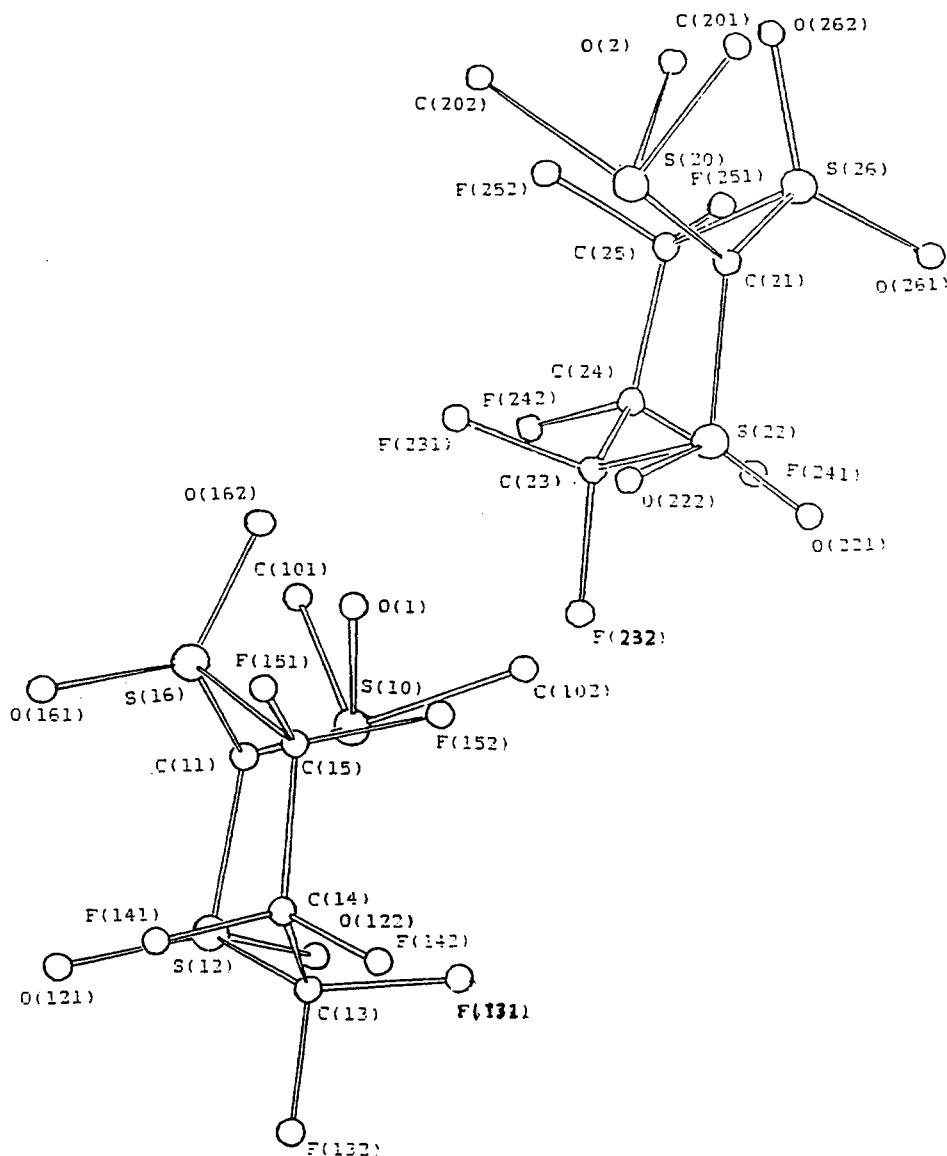
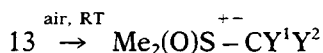


FIGURE 5 A view of **15c** with atom-numbering scheme.

was noteworthy that, after storage for 2 months in a flask at RT, the ylides **13** were oxidized to the sulfoxonium ylides completely.



$\text{Y}^1=\text{Y}^2=\text{CF}_3\text{SO}_2$ (**15a**); $\text{Y}^1=\text{Y}^2=\text{C}_4\text{F}_9\text{SO}_2$ (**15b**);

$\text{Y}^1, \text{Y}^2: -\text{SO}_2(\text{CF}_2)_3\text{SO}_2-$ (**15c**)

Their structures were characterized by spectral data and microanalyses. The X-ray diffraction analysis of **15c** showed that the crystal contains two independent molecules in one asymmetric unit (Figure 5). The bond distance between the C(11) and S(10) atoms is 1.75 Å, which is longer than that of the average bond length of two C–S bonds (1.68 Å)

[C(11)–S(16), 1.69 Å, C(11)–S(12), 1.67 Å]. Both are shorter than the normal C–S single bond (1.86 Å), but the latter has more double bond character. This shows that, even if the S atom of the DMSO is partially positively charged, however, the electron delocalization of the carbon anion C(11) inclines extensively toward the perfluoroalkanesulfonyl moiety due to its stronger electron-withdrawing ability [15,16].

CONCLUSIONS

Phenyliodonium bis (perfluoroalkanesulfonyl) methides were synthesized in moderate to good yields. They are reactive compounds and able to

react with alkenes, alcohols, halogens, and arenes to give the appropriate addition or insertion products. When they are treated by some noncharged and polarizable nucleophiles, a series of new ylides containing the bis(perfluoroalkanesulfonyl)methylene group are obtained. In all these reactions, bis(perfluoroalkanesulfonyl)carbene intermediates may be involved. The convenience in preparation of compounds **3**, together with their chemical reactivity, makes them attractive and useful reagents to introduce the bis(perfluoroalkanesulfonyl)methylene moiety into many different organic molecules.

EXPERIMENTAL

Mps and bps were measured on a Thiele apparatus and are uncorrected. ^1H NMR and ^{19}F NMR spectra were recorded on a Varian-360L instrument with Me_4Si and $\text{CF}_3\text{CO}_2\text{H}$ as internal and external standards, respectively. IR spectra were obtained on a IR-440 Shimadzu spectrophotometer. Low resolution mass spectra were taken on a Finnigan GC-MS 4021 instrument. Elemental analyses were performed by the analysis department of this institute. All of the photoreactions were carried out in a quartz flask with use of a 400 W low pressure mercury lamp. Compounds **1** were prepared according to the literature methods [8,14].

Preparation of Phenyliodonium Bis(perfluoroalkanesulfonyl) Methides (**3**)

General Procedure. Bis(perfluoromethanesulfonyl)methane (1.4 g, 5 mmol), diacetoxyiodobenzene (1.6 g, 5 mmol), and CH_2Cl_2 (30 mL) were placed in a 50 mL three-necked round-bottomed flask equipped with a magnetic stirring bar. The reaction mixture was stirred for 24 hours at RT. The solvent and the formed AcOH were evaporated under vacuum. The remaining solid was crystallized from CH_3CN . Recrystallization from $\text{CH}_3\text{CN} + \text{CH}_2\text{Cl}_2$ gave pure **3a**. Similarly, **3b** and **3c** were prepared. For yields and mps, see Table 1.

Phenyliodonium Bis(trifluoroalkanesulfonyl) Methide **3a**

Anal. calcd for $\text{C}_9\text{H}_5\text{F}_6\text{IO}_4\text{S}_2$: C, 22.41; H, 1.03; F, 23.65. Found: C, 22.42; H, 0.86; F, 23.47.

IR ν_{max} (KCl): 3020 (w), 1550 (w), 1460 (m), 1440 (m), 1360 (vs), 1338 (s), 1330 (m), 1180 (vs), 1110 (vs), 990 (vs), 890 (m), 738 (s), 720 (m), 630 (m), 650 (m), 600 (m), 500 (m) cm^{-1} . MS m/e (fragment, rel intensity): 483 (M^+H , 1.67), 482 (M^+ , 0.56), 413 ($\text{M}^+ - \text{CF}_3$, 13.62), 204 ($\text{C}_6\text{H}_5\text{I}^+$, 43.28), 133 (CF_3SO_2^+ , 1.04), 117 (CF_3SO^+ , 1.07), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 27.10), 77 (C_6H_5^+ , 100), 69 (CF_3^+ , 43.8), 65 (C_5H_5^+ , 23.95). ^1H NMR: ($\text{CD}_3)_2\text{CO}$ (δ), 8.3–8.1 (m, 2ArH) 7.7–7.5 (m, 3ArH). ^{19}F NMR: 2.0 (s, 2XCF₃).

Phenyliodonium Bis(perfluorobutanesulfonyl) Methide **3b**

Anal. calcd for $\text{C}_{15}\text{H}_5\text{F}_{18}\text{IO}_4\text{S}_2$: C, 23.02; H, 0.64; F, 43.73. Found: C, 22.63; H, 0.79; F, 43.91.

IR ν_{max} (KCl): 3060 (w), 1610 (w), 1450 (w), 1370 (vs), 1342 (m), 1230 (s), 1200 (s), 1160 (m), 1140 (s), 1120 (s), 990 (m), 900 (w), 800 (w), 740 (s), 680 (w), 582 (m), 510 (m) cm^{-1} . MS m/e : 783 (M^+H , 0.47), 782 (M^+ , 3.01), 562 ($\text{M}^+ - \text{C}_4\text{F}_9\text{H}$, 65.04), 546 ($\text{M}^+ - \text{C}_4\text{HF}_9 - \text{O}$, 16.19), 283 ($\text{C}_4\text{F}_9\text{SO}_2^+$, 1.20), 267 ($\text{C}_4\text{F}_9\text{SO}^+$, 1.85), 219 (C_4F_9^+ , 16.52), 204 ($\text{C}_6\text{H}_5\text{I}^+$, 97.02), 105 ($\text{C}_6\text{H}_5\text{CO}^+$, 8.02), 100 (C_2F_4^+ , 4.61), 77 (C_6H_5^+ , 100), 69 (CF_3^+ , 35.35), 65 (C_5H_5^+ , 10.76). ^1H NMR: 8.35–8.2 (m, 2ArH) 7.75–7.60 (m, 3ArH). ^{19}F NMR: 6.0 (s, 2XCF₃); 34.7 (m, 2XCF₂); 45.3 (m, 2XCF₂); 50.5 (s, 2XCF₂S)

Phenyliodonium 1,1,3,3-Tetraoxythiohexafluorocyclohexylidene **3c**

Anal. calcd for $\text{C}_{10}\text{H}_5\text{F}_6\text{IO}_4\text{S}_2$: C, 24.29; H, 1.01; F, 23.07. Found: C, 24.01; H, 0.71; F, 23.01.

IR ν_{max} : 3080 (w), 1560 (m), 1470 (w), 1443 (m), 1360 (vs), 1343 (s), 1275 (s), 1242 (m), 1200 (vs), 1164 (s), 1152 (s), 1138 (vs), 972 (vs), 930 (s), 897 (s), 744 (s), 680 (m), 642 (m), 602 (m), 540 (m), 530 (m) cm^{-1} . MS m/e : 495 (M^+H , 24.01), 367 ($\text{M}^+ - \text{I}$, 7.63), 330 ($\text{M}^+ - \text{C}_2\text{F}_4\text{SO}_2$, 8.08), 291 ($\text{M}^+\text{H} - \text{C}_6\text{H}_5\text{I}$, 49.12), 205 ($\text{C}_6\text{H}_5\text{I}^+\text{H}$, 14.13), 154 ($\text{C}_6\text{H}_5\text{CH}^+\text{SO}_2$, 49.12), 106 ($\text{C}_6\text{H}_5\text{CHO}^+$, 100), 77 (C_6H_5^+ , 31.13). ^1H NMR: 8.30–8.15 (m, 2ArH), 7.90–7.66 (m, 3ArH). ^{19}F NMR: 41.3 (broad, 2XCF₂S); 46.0 (broad CF₂).

Reaction of **3a** with Cyclohexene

A mixture of **3a** (0.48 g, 1 mmol) cyclohexene (10 mL) and CH_2Cl_2 (10 mL) in a quartz flask was irradiated for 4 hours under a nitrogen atmosphere. After the solvent and excess cyclohexene had been evaporated under vacuum, the residue was column chromatographed using petroleum ether and CH_2Cl_2 as eluents and gave **6** (0.15 g, yield 40%), mp 121–123°C. Anal. calcd for $\text{C}_9\text{H}_{10}\text{F}_6\text{O}_4\text{S}_2$: C, 30.00; H, 2.78; F, 31.67. Found: C, 30.05; H, 2.46; F, 31.97.

IR ν_{max} : 2950 (w), 2850 (m), 2800 (w), 1500 (m), 1440 (m), 1360 (m), 1320 (s), 1220 (s), 1160 (s), 1105 (s), 1080 (s), 1005 (m), 960 (s), 820 (m), 740 (w), 705 (w), 680 (w), 630 (s), 590 (s), 560 (s) cm^{-1} . MS m/e : 361 (M^+H , 0.45), 348 ($\text{M}^+ - \text{C}$, 4.50), 306 ($\text{M}^+ - \text{C}_4\text{H}_6$, 2.37), 227 [$(\text{CF}_3\text{S})_2\text{C}=\text{C}^+\text{H}$, 7.35], 193 ($\text{CF}_3\text{SC}_7\text{H}_8^+$, 14.68), 179 ($\text{CF}_3\text{SC}_6\text{H}_6^+$, 6.20), 165 ($\text{CF}_3\text{SC}_5\text{H}_4^+$, 8.28), 151 ($\text{CF}_3\text{SC}_4\text{H}_3^+$, 8.46), 133 (CF_3SO_2^+ , 3.86), 131 ($\text{CF}_3\text{SOCH}_2^+$, 7.31), 101 (CF_3S^+ , 8.57), 81 (C_6H_9^+ , 38.57), 69 (CF_3^+ , 100), 43 (C_3H_7^+ , 99.62). ^1H NMR: 2.7–1.6 (m, 10H). ^{19}F NMR: 5.5 (s, 2XCF₃).

Reaction of **3a** with Methanol

A mixture of **3a** (0.48 g mmol) and methanol (5 ml) was irradiated under a N_2 atmosphere for 7 hours.

Chromatographic purification gave **7** (0.15 g, yield 49%) and **8** (0.1 g, 46%) which were identified by spectral comparisons with authentic samples. Bis(trifluoromethanesulfonyl)methoxy methane **7**, mp 31–2°C.

Anal. calcd for $C_4H_4F_6O_5S_2$: C 15.47; H 1.28; F 36.77. Found: C, 15.48; H, 1.43; F, 36.63.

IR ν_{\max} (film): 2990 (m), 2900 (m), 1400 (s), 1358 (m), 1210 (vs), 1110 (vs), 1000 (w), 830 (w), 780 (m), 730 (m), 650 (w), 630 (w), 615 (w), 580 (m), 565 (m) cm^{-1} . MS m/e : 295 ($M^+ - CH_3$, 0.82), 280 ($M^+ - OCH_3$, 5.29), 227 ($M^+ - H - SO_2 - O$, 1.10), 211 ($M^+ - H - SO_2 - 2O$, 6.73), 133 ($CF_3SO_2^+$, 10.29), 117 (CF_3SO^+ , 13.10), 101 (CF_3S^+ , 98.30), 59 (CH_3OCO^+ or CH_3CS^+ , 100), 43 (CH_3OC^+ , 71.65). 1H NMR 3.40 (s, CH_3), 4.92 (s, 1H). ^{19}F NMR: 2.5 (s, $2XCF_3$).

Reaction of **3a** with $FO_2SCF_2CO_2H$

A mixture of **3a** (0.48 g, 1 mmol), $FO_2SCF_2CO_2H$ (0.5 g, 3 mmol), and 15 mL of CH_2Cl_2 was irradiated for 8 hours. The solvent was evaporated. Vacuum distillation gave $FO_2SCF_2CO_2H$, 0.45 g, bp 60°C/12 mm Hg. The residue was chromatographed, affording **8** (0.2 g, yield 70%) and PhIO (0.1 g, yield 50%) which were identified by spectral comparison with authentic samples.

Reaction of **3a** with Bromine

A mixture of **3a** (0.5 g, 1.03 mmol), bromine (0.5 mL), and dichloromethylene (10 mL) was irradiated for 2 hours. Fractional distillation gave **9** (0.4 g, yield 89%), bp 98–100°C/10 mm Hg. (Ref. [8] 107–8°C/17 mm Hg.)

Reaction of **3a** with Benzene or Toluene

3a (0.5 g, 1.03 mmol) in benzene (5 mL) was irradiated for 8 hours. The excess of benzene was evaporated. The residue was crystallized from acetone, giving **10a** (0.22 g, yield 61%). Recrystallization of the crude product from a mixture of CH_3CN and CH_2Cl_2 (1:1) gave the pure compound. Similarly, treatment of **3a** (0.5 g, 1.03 mmol) with toluene (5 mL) gave **10b** (0.26 g, yield 72%).

Phenylbis(trifluoromethanesulfonyl)methane **10a**, Mp 104°C

Anal. calcd for $C_9H_6F_6O_4S_2$: C, 30.30; H, 1.68; F, 32.02. Found: C, 30.07; H, 1.42; F, 32.06.

IR ν_{\max} (KCl): 3030 (w), 2950 (w), 1500 (w), 1450 (w), 1380 (vs), 1370 (s), 1240 (s), 1220 (vs), 1185 (s), 1160 (m), 1100 (vs), 805 (m), 700 (m), 660 (m), 605 (m), 580 (m), 510 (s) cm^{-1} . MS m/e : 356 (M^+ , 0.15), 287 ($M^+ - CF_3$, 1.20), 223 ($M^+ - CF_3SO_2$, 49.37), 154 ($M^+ - CF_3SO_2 - CF_3$, 4.36), 106 ($C_6H_5CHO^+$, 100), 90 ($C_7H_6^+$, 52.81), 77 ($C_6H_5^+$, 43.65), 69 (CF_3^+ , 19.91), 51 ($C_4H_3^+$, 11.77). 1H NMR 7.80–8.20 (m, 5H), 4.70 (s, 1H) ^{19}F NMR –2.0 (s, $2XCF_3$).

p-Tolylbis(trifluoromethanesulfonyl)methane **10b**, Mp 94°C

Anal. calcd for $C_{10}H_8F_6O_4S_2$: C, 32.11; H, 2.16; F, 30.69. Found: C, 31.85; H, 1.75; F, 30.69.

IR ν_{\max} (KCl): 3030 (m), 2950 (w), 1600 (w), 1498 (m), 1378 (vs), 1350 (s), 1250 (s), 1205 (vs), 1190 (s), 1150 (s), 1120 (s), 1020 (m), 980 (s), 880 (s), 808 (s), 708 (m), 610 (s), 580 (m) cm^{-1} . MS m/e : 301 ($M^+ - CF_3$, 4.59), 253 ($M^+ - CF_3SO$, 3.63), 237 ($M^+ - CF_3SO_2$, 4.72), 167 ($CH_3C_6H_4C^+SO_2$, 5.25), 155 ($CH_3C_6H_4SO_2^+$, 1.29), 136 ($CH_3C_6H_4C^+HS$, 2.85), 133 ($CF_3SO_2^+$, 1.60), 117 (CF_3SO^+ , 2.19), 107 ($CH_3C_6H_4O^+$, 100), 91 ($CH_3C_6H_4^+$, 7.82), 77 ($C_6H_5^+$, 35.67), 69 (CF_3^+ , 77.86) 1H NMR 7.63–8.10 (m, 4H), 2.35 (s, CH_3), ^{19}F NMR 5.0 (s, $2XCF_3$).

Reaction of **3** with Pyridine

A mixture of **3a** (1.2 g, 2.5 mmol) and pyridine (5 mL) in a 25 mL quartz flask equipped with a reflux condenser, dry tube, and magnetic stirring bar was irradiated at RT for 8 hours. After removal of the excess pyridine, the residue was allowed to stand overnight. The precipitated solid was filtered off and crystallized from CH_3CN and $(CH_3)_2CO$ (1:1), giving pure **11a** (0.7 g, 78%). By the same procedures, **11c** was obtained.

Pyridinium Bis(trifluoromethanesulfonyl) Methide **11a**

Anal. calcd for $C_8H_5F_6NO_4S_2$: C, 26.89; H, 1.40; N, 3.92; F 31.93. Found: C, 27.20; H, 1.54; N, 4.14; F, 31.50.

IR ν_{\max} (KBr): 3010 (vw), 1591 (w), 1440 (m), 1360 (s), 1328 (m), 1250 (m), 1200 (m), 1138 (vs), 987 (s), 918 (s), 879 (m), 738 (m), 698 (s), 600 (s), 550 (s) cm^{-1} . 1H NMR 7.66–7.9 (m, 3ArH), 8.13–8.40 (m, 2ArH). ^{19}F NMR 3.8 (s, $2XCF_3$).

Pyridinium 1,1,3,3-Tetraoxythiohexafluorocyclohexylidene **11c**

Anal. calcd for $C_9H_5F_6NO_4S_2$: C, 29.27; H, 1.36; N, 3.79; F, 30.90. Found: C, 29.70; H, 1.32; N, 3.79; F, 30.50.

IR ν_{\max} (KBr): 3002 (vw), 1592 (w), 1442 (m), 1358 (s), 1330 (m), 1271 (m), 1242 (m), 1199 (m), 1140 (vs), 980 (s), 920 (s), 898 (m), 740 (m), 700 (m), 679 (s), 642 (m), 600 (s), 560 (s), 538 (s) cm^{-1} . MS m/e : 370 (M^+H , 1.71), 3.69 (M^+ , 3.94), 3.53 ($M^+ - O$, 0.38), 337 ($M^+ - 2O$, 0.51), 253 ($M^+ - O - C_2F_4$, 4.75), 240 ($M^+ - CF_2 - C_5H_5N$, 1.08), 205 ($M^+ - C_2F_4 - SO_2$, 45.76), 100 ($C_2F_4^+$, 18.09), 80 (SO_3 or $C_5H_5NH^+$, 78.96), 79 ($C_5H_5N^+$, 57.13), 64 (SO_2^+ , 15.41), 52 ($C_3H_2N^+$, 100) 1H NMR: 7.63–7.90 (m, 3H), 8.10–8.33 (m, 2H), ^{19}F NMR: 42.3 (m $2XCF_2S$), 49.8 (m CF_2).

Reaction of 3 with DMSO

A solution of **3a** (1.21 g 2.5 mmol) and DMSO (5 mL) was irradiated at RT for 8 hours. After removal of the DMSO, the residue was allowed to stand overnight. The precipitated colorless crystals were filtered off, giving **12a** (1.1 g, 80%), mp 116–8°C. Anal. calcd for $C_{11}H_{11}F_6IO_5S_3$: C, 23.56; H, 1.96; F, 20.36. Found: C, 23.19; H, 1.91; F, 20.43.

IR ν_{\max} (KBr): 3080 (w), 2990 (vw), 1471 (m), 1442 (m), 1352 (vs), 1339 (m), 1310 (m), 1216 (s), 1190 (vs), 1175 (vs), 1120 (s), 1000 (s), 990 (s), 949 (m), 898 (s), 742 (s), 640 (s), 600 (s), 562 (m), 501 (s) cm^{-1} . MS (*m/e*): 560 (M^+ , 0.82), 482 (M^+ -DMSO, 4.32), 205 (Me_2SOI^+ , 3.31), 204 (PhI^+ , 6.85), 133 ($CF_3SO_2^+$, 3.20), 127 (I^- , 1.88), 78 (Me_2SO^+ , 89.57), 77 ($C_6H_5^+$, 11.28), 69 (CF_3^+ , 4.44), 63 ($MeSO^+$, 100), 47 (MeS^+ , 10.14). 1H NMR: 3.45 (s, 2XCH₃), ^{19}F NMR: 1.8 (s, 2XCF₃)

12c, *Mp*, 180–182°C

Anal. calcd for $C_{12}H_{11}F_6IO_5S_3$: C, 25.17; H, 1.92, F, 19.93. Found: C, 25.20; H, 1.72; F, 19.85.

IR ν_{\max} (KBr): 3070 (vw), 2995 (w), 2990 (w), 1475 (m), 1442 (m), 1352 (s), 1330 (m), 1275 (s), 1195 (s), 1178 (s), 1148 (s), 1020 (s), 982 (s), 921 (s), 740 (m), 680 (m), 640 (m), 600 (s), 562 (m), 540 (m) cm^{-1} . MS (*m/e*): 555 (M^+ -H-O, 2.04), 494 (M^+ -DMSO, 10.79), 445 (M^+ -I, 1.37), 353 (M^+ -CH₃-PhI, 8.75), 352 (M^+ -O-PhI, 5.79), 205 (Me_2SOI^+ , 88.79), 204 (PhI^+ , 76.93), 155 ($Me_2SOC_6H_5^+$, 31.28), 100 ($C_2F_4^+$, 19.78), 127 (I^- , 11.07), 78 (Me_2SO^+ , 100), 77 ($C_6H_5^+$, 41.62), 63 ($MeSO^+$, 44.29), 62 (Me_2S^+ , 30.90), 47 (MeS^+ , 10.21). 1H NMR: 3.48 (s, 2XCH₃), 7.52–7.80 (m, 3ArH), 8.02–8.08 (m, 2ArH), ^{19}F NMR: 41.0 (broad, 2XCF₂S), 45.7 (broad, CF₂).

Reaction of 3 with Methyl Sulfide

A mixture of **3a** (1.2 g, 2.5 mmol) and methyl sulfide (3.1 g, 50 mmol) was irradiated for 8 hours. After removal of the excess of Me₂S, a colorless solid was obtained. Crystallization from CH₃CN and CH₂Cl₂ (1:1) afforded pure **13a** (0.75 g, 88%) Dimethylsulfonium-bis(trifluoromethanesulfonyl) methide **13a**.

Anal. calcd for $C_5H_6F_6O_4S_3$: C, 17.64; H, 1.76; F, 33.53. Found: C, 17.64; H, 1.54; F, 34.03.

IR ν_{\max} (KBr): 3000 (m), 2900 (w), 1422 (w), 1362 (vs), 1343 (s), 1320 (m), 1220 (vs), 1180 (vs), 1124 (s), 1105 (m), 1060 (m), 1020 (s), 983 (s), 950 (s), 680 (m), 648 (s), 602 (vs), 562 (m), 501 (m) cm^{-1} . MS (*m/e*): 341 (M^+ H, 31.72), 340 (M^+ , 5.64), 331 (M^+ -CF₃S, 7.27), 272 (M^+ H-CF₃, 100), 255 (M^+ -CF₃-O, 13.61), 239 (M^+ -CF₃S, 7.27), 191 (M^+ -CF₃SO₂-O, 9.50), 163 (Me_2S^+ CF₃, 11.03), 145 (CF_3SCS^+ , 15.54), 117 (CF_3SO^+ , 7.65), 69 (CF_3^+ , 5.15), 62 (Me_2S^+ , 29.19), 59 ($MeSC^+$, 45.23), 47 (MeS^+ , 17.39). 1H NMR, 3.36 (s, 2XCH₃), ^{19}F NMR: 3.7 (s, 2XCF₃).

*Dimethylsulfonium**Bis(perfluorobutanesulfonyl) Methide 13b*

Anal. calcd for $C_{11}H_6F_{18}O_4S_2$: C, 20.62; H, 0.93; F, 53.43. Found: C, 20.61; H, 0.76; F, 53.21.

IR ν_{\max} (KBr): 3000 (w), 2980 (w), 1422 (w), 1380 (vs), 1350 (m), 1282 (m), 1261 (m), 1230 (s), 1200 (vs), 1150 (s), 1130 (s), 1110 (m), 1038 (s), 982 (m), 951 (m), 800 (m), 738 (m), 640 (m), 582 (s), 530 (m), 502 (m) cm^{-1} . MS (*m/e*): 641 (M^+ H, 1.45), 640 (M^+ , 1.85), 557 (M^+ -F-SO₂, 1.55), 421 (M^+ -C₄F₉, 100), 405 (M^+ -C₄F₉-O, 18.72), 341 (M^+ -C₄F₉SO₂-O, 1.07), 219 ($C_4F_9^+$, 10.36), 122 (Me_2SCSO^+ , 3.44), 69 (CF_3^+ , 15.53), 62 (Me_2S^+ , 99.90), 47 (MeS^+ , 5.87). 1H NMR: 3.30 (s, 2XCH₃), ^{19}F NMR: 6.0 (s, 2XCF₃), 34.8 (m, 2XCF₂), 45.5 (m, 2XCF₂), 50.6 (s, 2XCF₂S).

*Dimethylsulfonium 1,1,3,3,-**Tetraoxythiohexafluorocyclohexylidene 13c*

Anal. calcd for $C_6H_6F_6O_4S_3$: C, 20.46; H, 1.70; F, 32.38. Found: C, 20.70; H, 1.27; F, 32.45.

IR ν_{\max} (KBr): 3000 (w), 2982 (w), 1428 (m), 1378 (vs), 1358 (m), 1340 (m), 1280 (m), 1260 (m), 1218 (s), 1160 (vs), 1060 (m), 1023 (s), 978 (s), 957 (s), 900 (m), 705 (s), 653 (m), 620 (m), 565 (m), 550 (s) cm^{-1} . 1H NMR 3.35 (s, 2XCH₃), ^{19}F NMR 42.5 (m, 2XCF₂S), 50.0 (m, CF₂).

Reaction of 3a with Ph₃P

A solution of **3a** (1.2 g, 2.5 mmol), CH₂Cl₂ (10 mL) and Ph₃P (0.65 g, 2.5 mmol) was irradiated at RT for 4 hours. After evaporation of the solvent, the residue was crystallized from CH₃CN and (CH₃)₂CO (1:1), giving **14a** (0.9 g, 67%), mp 247–9°C. Anal. calcd for $C_{21}H_{15}F_6O_4PS_2$: C, 46.67; H, 2.78. Found: C, 46.81; H, 2.93.

IR ν_{\max} (KBr): 3040 (m), 1590 (m), 1481 (m), 1440 (m), 1340 (s), 1220 (m), 1180 (m), 1162 (s), 1118 (s), 1098 (s), 1000 (m), 962 (s), 742 (m), 721 (s), 698 (s), 600 (s), 540 (s), 500 (m) cm^{-1} . MS (*m/e*): 541 (M^+ H, 1.95), 477 (MH^+ -SO₂, 2.96), 463 (M^+ -C₆H₅, 3.33), 355 (M^+ -PPh₂, 36.34), 279 (M^+ -PPh₃, 100), 262 (Ph_3P^+ , 14.10), 199 ($CF_3SO_2P^+$ OF, 21.16), 185 (Ph_2P^+ , 14.10), 183 ($CF_3SO_2P^+$ F, 33.11), 133 ($CF_3SO_2^+$, 7.01), 108 (PhP^+ , 7.99), 77 ($C_6H_5^+$, 35.15). 1H NMR 7.63–8.10 (m, 15H). ^{19}F NMR 5.0 (s, 2XCF₃).

Oxidation of Compounds 13

13a (1.8 g, 5.3 mmol) was stored in a 5 mL bottle. After 2 months, it was found that **13a** had been oxidized completely to **4a**. Similarly, **13b** and **13c** were transformed into **15b** and **15c**.

15a: mp 146°C. IR(KBr): ν_{\max} (cm^{-1}), 3010 (m), 2900 (m), 2810 (w), 1401 (m), 1360 (s), 1350 (s), 1230–1170 (vs), 1120 (s), 1020 (s), 992 (s), 955 (s),

690 (m), 650 (s), 610 (s), 570 (m), 507 (m). ^1H (acetone- d_6): 3.33 (s, 2XCH_3) ppm. ^{19}F : δ 3.5 (s, 2XCF_3) ppm. MS (m/e , %): 356 (M^+ , 0.51), 355 ($\text{M}^+ - 1$, 4.91), 341 ($\text{M}^+ - \text{CH}_3$, 47.61), 308 ($\text{M}^+ - \text{SO}$, 6.64), 287 ($\text{M}^+ - \text{CF}_3$, 0.38), 272 ($\text{M}^+ - \text{CF}_3 - \text{CH}_3$, 100), 255 ($\text{M}^+ - \text{CF}_3\text{S}$, 13.61), 239 ($\text{M}^+ - \text{CF}_3\text{SO}$, 1.82), 75 ($^{\circ}\text{C}=\text{S}(\text{O})\text{CH}_3$ and $\text{M}^+ - 2\text{CF}_3\text{SO}_2 - \text{CH}_3$, 1.99), 69 (CF_3^+ , 5.15), 62 (Me_2S^+ , 29.69), 47 (CH_3S^+ , 1.59). Anal. calcd for $\text{C}_5\text{H}_6\text{F}_6\text{O}_5\text{S}_3$: C, 16.85; H, 1.68; F, 32.02. Found: C, 17.28; H, 1.51; F, 32.78.

15b: mp 162°C . IR (KBr): ν_{max} (cm^{-1}), 3008 (m), 2910 (m), 2814 (m), 1408 (m), 1365 (s), 1350 (s), 1330 (m), 1205–1110 (vs), 1018 (s), 990 (m), 952 (m), 648 (s), 610 (s), 560 (m). ^1H δ : 3.33 (s, 2XCH_3) ppm. ^{19}F δ : 6.0 (s, 2XCF_3), 34.0 (m, $2\text{XCF}_2\text{S}$), 45.3 (m, 2XCF_3), 50.6 (m, 2XCF_2) ppm. MS (m/e , %): 657 (M^+H , 1.33), 656 (M^+ , 1.96), 421 ($\text{M}^+ - \text{O} - \text{C}_4\text{F}_9$, 100), 341 ($\text{M}^+ - 20 - \text{C}_4\text{F}_9\text{SO}_2$, 1.88), 219 (C_4F_9^- , 15.86), 122 (Me_2SCSO^+ , 8.221), 69 (CF_3^+ , 18.84), 63 (MeSO^+ , 7.28), 62 (Me_2S^+ , 83.20), 47 (MeS^+ , 5.66).

15c: mp 188°C . IR (KBr): ν_{max} (cm^{-1}), 3008 (m), 2892 (m), 2820 (w), 1420 (m), 1368 (s), 1350 (m), 1330 (m), 1205 (m), 1180 (s), 1150 (s), 1012 (m), 970 (m), 950 (s), 700 (m), 642 (m), 612 (m), 540 (m). ^1H : 3.30 (s, 2XCH_3) ppm. ^{19}F δ : 43.0 (m, $2\text{XCF}_2\text{S}$), 50.0 (m, CF_2) ppm. MS (m/e , %): 369 ($\text{M}^+ + 1$, 1.43), 367 ($\text{M}^+ - 1$, 2.49), 353 ($\text{M}^+ - \text{CH}_3$, 36.63), 352 ($\text{M}^+ - \text{O}$, 28.75), 288 ($\text{M}^+ - \text{O} - \text{SO}_2$, 7.48), 273 ($\text{M}^+ - \text{O} - \text{SO}_2 - \text{CH}_3$, 22.60), 260 ($\text{M}^+ - \text{C}_2\text{F}_4$, 10.97), 209 ($\text{M}^+ - \text{O} - \text{SO}_2 - \text{CH}_3$, 25.05), 159 ($\text{M}^+ - \text{O} - 2\text{SO}_2 - \text{CH}_3 - \text{CF}_2$, 6.23), 124 ($\text{M}^+ - \text{O} - 2\text{SO}_2 - \text{C}_2\text{F}_4$, 32.76), 109 ($\text{M}^+ - \text{O} - 2\text{SO}_2 - \text{CH}_3 - \text{C}_2\text{F}_4$, 18.76), 79 (CH_3SO_2^+ , 10.74), 78 (Me_2SO^+ , 1.77), 63 (CH_3SO^+ , 20.42), 62 (Me_2S^+ , 100). Anal. calcd for $\text{C}_6\text{H}_6\text{F}_6\text{O}_5\text{S}_3$: C, 19.57; H, 1.63; F, 30.98. Found: C, 19.69; H, 1.51; F, 30.63.

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