0.02% HOAc (90:10) at 1 mL/min. Retention times for D,L-5BH, *N*-carbamoyl-D,L-phenylalanine, and D,L-phenylalanine are 15.8, 13.9, and 5.3 min, respectively. All UV measurements were taken on a Hewlett-Packard 8451 diode array spectrophotometer. pH measurements were made at 25 °C using a Corning 125 pH meter with a Corning 476223 combination electrode.

Synthesis. Optically pure L- or D-5-benzylhydantoin were synthesized in 70% yields from the corresponding amino acid and potassium cyanate according to the method of Finkbeiner.[11] L-5BH: mp 173 °C (lit.[12] mp 181–183 °C); MS *m/e* 190 (M^+), 160, 146, 128, 117, 103, 91; $[\alpha]^{24}_D$ = −93.7° (*c* = 1, acetone), ϵ_{240} = 0.45 mM^{-1} (H_2O). Identical parameters were observed for D-5BH except that $[\alpha]^{24}_D$ = +94.0° (*c* = 1, acetone).

Optically pure *N*-carbamoyl-L- and -D-phenylalanine were prepared in 60% yields from the corresponding amino acid as previously described.[13] *N*-Carbamoyl-L-phenylalanine: mp 181 °C (recrystallized from MeOH–H_2O) (lit.[13] mp 192–193 °C); $[\alpha]^{24}_D$ = +40° (*c* = 0.2, MeOH), ϵ_{240} = 0.085 mM^{-1} (H_2O). *N*-Carbamoyl-D-phenylalanine: mp 179 °C (recrystallized from MeOH–H_2O); $[\alpha]^{24}_D$ = −40° (*c* = 0.2, MeOH).

L-5-Benzyl-3-methylhydantoin was synthesized from L-phenylalanine and methylisocyanate according to the method of Dudley and Bius[14] in an overall yield of 50%. The intermediate L-2-benzyl-5-methylhydantoin acid that precipitated at pH 2 was isolated and cyclized to optically active L-5-benzyl-3-methylhydantoin by refluxing in 0.5 N HCl for 30 min. The white crystals were washed with cold water and dried in vacuo: mp 166–167 °C; MS *m/e* 204 (M^+), 160, 146, 117, 91; $[\alpha]^{24}_D$ = −113° (*c* = 1.0, acetone).

Kinetics. The racemization of L(or D-)-BH_2 was measured by following the change in circular dichroism, θ, at 230 nm with respect to time as measured on a JASCO J-500A spectropolarimeter. The cuvette was housed in a thermostable cell maintained at 37 °C by a Lauda circulatory water bath. Stock solutions of optically active L- or D-5BH in H_2O at 4 °C were added to preequilibrated buffer to give 0.1 mg/mL solutions. Aliquots were taken from stoppered glass vials at 37 °C for slower reactions. Reactions were followed for at least 3 half-lives; no optical activity is observed after complete racemization. The observed pseudo-first-order rate constants for racemization k_{obs} were calculated from the slopes of linear plots of ln $(\theta_t - \theta_\infty)$ against time. Plots were generally linear to 3 half-lives. Buffers employed (0.25–1 M) were phosphate, Tris, carbonate, and hydroxide. General acid–base catalysis was observed for these species. The pH–rate profile for lyate species was determined by extrapolation of the racemization rate to zero buffer concentration.

pK_a Determination. The pK_a for 5-BH (8.65 ± 0.10) was determined by spectrophotometric titration at 230 mm where ϵ_{230} = 1.45 mM^{-1} for the neutral free acid form and ϵ_{230} = 3.04 mM^{-1} for the anionic free base form.

Product Determination. There was no detectable hydrolysis of 5-BH during the course of the racemization studies as evidenced by (a) no observable change in UV absorbance at 240 nm and (b) only one peak corresponding to 5-BH detected by HPLC.

Acknowledgment. I would like to thank Brad Snedecor, Chung Hsu, and Bill Rastetter for their helpful discussions and John Chakel for the mass spectrometer data.

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Notes

Antimony(III) Chloride Exerts Potent Catalysis of the Conversion of Sulfoxides to α-Fluoro Thioethers with (Diethylamino)sulfur Trifluoride

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Received January 23, 1990

Intensive efforts on the synthesis and biological evaluation of various types of organofluorine compounds have been reviewed.[1-3] The size and electronegativity of the fluorine atom make isosteres of important biological molecules in which hydrogen has been replaced by fluorine of significant interest. We now report details of the dramatic catalysis by antimony(III) chloride for the conversion of sulfoxides to α-fluoro thioethers with (diethylamino)-sulfur trifluoride (DAST).

Zupan[4] and Janzen and co-workers[5] reported syntheses of α-fluoro thioethers by treatment of thioethers with xenon difluoride. Rigorously dried potassium fluoride in the presence of 18-crown-6 ethers has been employed to convert α-chloro to α-fluoro thioethers.[6] McCarthy et al. discovered that DAST converted sulfoxides to α-fluoro thioethers.[7] They noted that *p*-methoxyphenyl thioethers were much more reactive than phenyl thioethers, and the reaction was catalyzed by zinc(II) iodide. Thioethers have since been α-fluorinated with *N*-fluoropyridinium triflate,[8] and dithioacetals have been converted to α-fluoro thioethers with mercury(II) fluoride.[9]

Zupan[4] and McCarthy and co-workers[7] reported syntheses of α,α-difluoro thioethers from α-fluoro thioethers and α-fluoro sulfoxides, respectively. Some α-(fluoromethyl) thioethers have been converted[7,9] to α-fluoro sulfoxides,[10] α-fluoro sulfones,[11] and α-fluoro sulfoximines,[12] precursors for "fluoromethylene-Wittig" reag-

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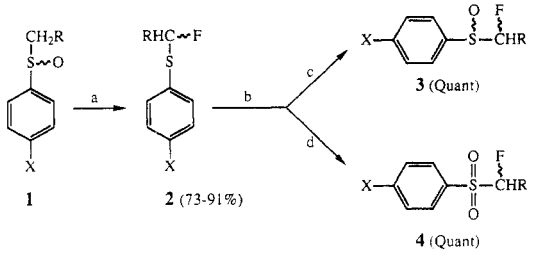
Scheme I[a]



1-4	X	R
a	H	H
b	H	$(CH_2)_3CH_3$
c	H	$(CH_2)_{10}CH_3$
d	H	$CH_2C_6H_5$
e	H	C_6H_5
f	OCH_3	C_6H_5
g	H	$(CH_2)_2CO_2Et$
h	OCH_3	$(CH_2)_2CO_2Et$
i	H	F
j	OCH_3	F

[a] (a) DAST/$SbCl_3$/CH_2Cl_2/0 °C to ambient/1.5–5 h; (b) MCPBA/$CHCl_3$; (c) −30 °C/5 min; (d) −10 °C to ambient/4 h.

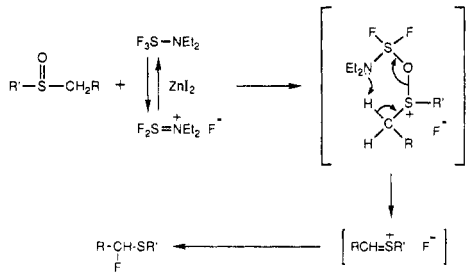
ents,[13] which have been used for the preparation of terminal vinyl fluorides.

Our initial attempts[14] to apply the McCarthy et al. DAST procedure[7] to the diastereomeric sulfoxides derived by oxidation of 2′,3′-di-*O*-acetyl-5′-*S*-phenylthioadenosine were disappointing. Addition of zinc(II) iodide resulted in highly predominant deoxygenation at sulfur. An analogously efficient reduction of sulfoxides to thioethers with sodium iodide/boron trifluoride etherate had been described.[15] Boys and co-workers[12] have recently reported similar problems with the reproducibility of fluorination yields with DAST/ZnI_2. They noted variations in ratios of (methylthio)benzene to [(fluoromethyl)thio]benzene ranging from 100:0 to 0:100 upon treatment of methyl phenyl sulfoxide with DAST/ZnI_2, and obtained reliable results only when DAST was used without zinc(II) iodide. Sufrin et al.[16] also noted partial reduction of a protected 5′-methylthioadenosine sulfoxide upon its treatment with (dimethylamino)sulfur trifluoride.

Our previously reported antimony(III) halide catalysis[17] of nonaqueous diazotization/halodediazoniation reactions with 2-amino-6-substituted-purine nucleosides suggested a possible alternative. Of a variety of Lewis acids presently examined, antimony(III) chloride and antimony(V) fluoride provided the most clean and rapid reactions at ambient temperature. Owing to relative costs and ease of handling, the trivalent antimony catalyst was adopted. A standard procedure was developed with 1 equiv of thioether/2 equiv of DAST/0.1 equiv of $SbCl_3$ in dichloromethane solution at ambient temperature for 1.5–18 h. Reaction progress is readily monitored by TLC (on silica the polar sulfoxides migrate slowly relative to the α-fluoro thioether products). We recently found that under $SbCl_3$ catalysis the ratio of thioether/DAST can be reduced to 1:1.3 with newly purchased reagent and likely could be reduced further in a rigorously anhydrous/inert atmosphere with purified DAST. Reactions usually are complete within 5 h (see Scheme I).

Since [(fluoromethyl)thio]benzene (**2a**) has been employed as a precursor for "fluoromethylene-Wittig" reag-

Scheme II



ents,[11] we have examined its formation from methyl phenyl sulfoxide (**1a**) in a "side-by-side" comparison with the earlier procedure.[7] Treatment of **1a** (1 mmol) with DAST (1.3 mmol) and $SbCl_3$ (0.1 mmol) in 2 mL of dry CH_2Cl_2 under anhydrous conditions in a nitrogen atmosphere resulted in complete conversion (TLC) of **1a** to **2a** within 4 h. [Initial cooling in an ice bath before addition of DAST was required when the reaction was performed on a larger (10 mmol) scale in order to avoid exothermic heating of the solution.] The ^1H NMR spectrum of the crude reaction product (**2a**) after 4 h was very clean with a peak at δ 5.70 (d, $^2J_{H,F}$ = 52.8 Hz, 2, SCH_2F) and no observed signals remained at δ 2.50 (s, 3, SCH_3) (deoxygenated-**1a**) or δ 2.71 (s, 3, $SOCH_3$) (**1a**). Kugelrohr distillation provided **2a** (88%) with appropriate physical and spectral data (see Table I). The comparative uncatalyzed reaction had proceeded <20% in 4 h and required 3–4 days at ambient temperature (or 24 h plus heating at 50 °C) for completion.[18]

This $SbCl_3$ catalysis provides dramatic rate enhancements and also permits the routine use of the much less reactive phenyl sulfoxides in addition to their *p*-methoxyphenyl[7] counterparts. Although the transformations of *p*-methoxyphenyl sulfoxides to α-fluoro thioethers are cleaner, this results from the instability[9] of the product α-fluoro thioethers[19] **2** rather than the absence of conversion of the phenyl sulfoxides **1** in the catalyzed reactions. For example, treatment of benzyl phenyl sulfoxide (**1e**) with DAST/$SbCl_3$ resulted in the disappearance of **1e** with accompanying formation of 30–50% of benzaldehyde after the usual aqueous workup. Likewise **1g** reacted readily with DAST/$SbCl_3$ to give **2g** in moderate isolated yields plus byproducts that contained no fluorine, but **3g** was obtained in 79% yield by rapid in situ oxidation of the crude **1g** → **2g** reaction mixture. Purification of **2a** and **2h** (the more stable *p*-methoxyphenyl analogue of **2g**) in high yields by flash chromatography[20] or Kugelrohr distillation proceeded readily, but in most cases it was more convenient to oxidize the sensitive[8,9,19] α-fluoro thioethers **2** into the more stable sulfoxides **3** or sulfones **4** in situ. $SbCl_3$ also catalyzed the smooth conversion of dimethyl sulfoxide to [(fluoromethyl)thio]methane (oxidized in situ and isolated as [(fluoromethyl)sulfonyl]methane).

Unfortunately, the DAST/$SbCl_3$ system failed to give satisfactory conversion of fluoromethyl phenyl sulfoxide (**1i**) to [(difluoromethyl)thio]benzene (**2i**). Treatment of **1i** under our standard conditions for 72 h resulted in a mixture of **2a**/**2i** (62:38) in 56% combined yield plus 32% of unreacted **1i**. In a side-by-side comparison without $SbCl_3$, 26% of combined **2a**/**2i** and 63% of unreacted **1i** were observed by chromatography and ^1H NMR analysis

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Table I. Data for α-Fluoro Thioethers 2, Sulfoxides 3, and Sulfones 4

compd	reactn time (h)[a]	yield (%)[b]	mp (°C) (solvent)	formula or lit. ref	^{1}H NMR δ (J in Hz)	MS m/z (rel int)
2a	4	88	60/0.3[c]	60/0.2[7]	5.70 (d, J = 52.8, 2, CH_2F), 7.28–7.56 (m, 5, Ph)	142 (M^+, 100), 110 (20)
2h	2	91	oil	oil[7]	1.25 (t, J = 7, 3, CH_3), 1.95–2.99 (m, 4, CH_2's), 3.79 (s, 3, OCH_3), 4.15 (q, J = 7, 2, OCH_2), 5.69 (dt, $^2J_{H,F}$ = 54.4, $^3J_{H,F}$ = 6, 1, CHF), 6.95 (d, J = 9, 2, Ar), 7.45 (d, J = 9, 2, Ar)	272 (M^+, 29), 227 (15), 179 (8), 139 (38), 105 (100)
3a	4	89	75/0.3[c]	80/0.5[7]	5.11 (d, J = 47.4, 2, CH_2F), 7.45–7.74 (m, 5, Ph)	158 (M^+, 84), 125 (100)
3b	2	81	oil	$C_{11}H_{15}FOS$[d]	0.85–1.99 (m, 9, C_4H_9), 5.08 (dm, J = 49, 1, CHF), 7.32–7.74 (m, 5, Ph)	214 (M^+, 3), 126 (100), 78 (48)
3c	1.5	84	viscous oil	$C_{18}H_{29}FOS$[d]	0.80–2.06 (m, 23, $C_{11}H_{23}$), 4.99 (dm, J = 49, 1, CHF), 7.30–7.86 (m, 5, Ph)	312 (M^+, 2), 155 (41), 109 (100), 77 (32)
3d	3	88	oil	$C_{14}H_{13}FOS$[d]	2.96–3.51 (m, 2, CH_2), 5.02 (dm, J = 49, 1, CHF), 7.25–7.62 (m, 10, Ph's)	248 (M^+, 17), 126 (52), 123 (100), 103 (81), 77 (65)
3e	1.5	73	87–89 (EtOAc/hexane)	$C_{13}H_{11}FOS$[d,e]	5.92 (d, J = 47, 1, CHF), 6.99–7.68 (m, 10, Ph's)	234 (M^+, 1), 125 (3), 109 (100)
3f	1.5	88	55–58 (hexane)	$C_{14}H_{13}FO_2S$[d]	3.82 (s, 3, OCH_3), 5.84 (d, J = 47.5, 1, CHF), 6.89–7.58 (m, 9, Ar)	264 (M^+, 2), 155 (41), 109 (100)
3g	2	79	viscous oil	$C_{12}H_{16}FO_3S$[d]	1.22 (t, J = 7, 3, CH_3), 1.91–2.58 (m, 4, CH_2's), 4.16 (q, J = 7, 2, OCH_2), 5.11 (dm, J = 48, 1, CHF), 7.32–8.05 (m, 5 Ph)	213 (M^+ – OEt, 26), 156 (42), 133 (55), 126 (34), 105 (100), 85 (62)
3h	2	90	oil	oil[7]	1.23 (t, J = 7, 3, CH_3), 1.82–2.56 (m, 4, CH_2's), 3.85 (s, 3, OCH_3), 4.11 (q, J = 7, 2, OCH_2), 5.06 (dm, J = 49, 1, CHF), 6.99 (d, J = 8.5, 2, Ar), 7.60 (d, J = 8.5, 2, Ar)	243 (M^+ – OEt, 16), 156 (37), 155 (57), 133 (70), 105 (100), 85 (48)
4a	4	90	50–51 (MeOH)	$C_7H_7FO_2S$[d,f] 47–48[21]	5.15 (d, J = 47.2, 2, CH_2F), 7.58–8.01 (m, 5, Ph)	174 (M^+, 32), 141 (56), 77 (100)

[a] Times are given for the reaction of sulfoxides 1 with DAST/$SbCl_3$ to give the corresponding α-fluoro thioethers 2. [b] Yields of isolated products based on starting sulfoxide 1 (one or two-step sequence). [c] Oven temperatures (°C) and pressures (mbar) from Kugelrohr distillations. [d] Microanalyses agreed within ±0.33 of theory. [e] 3e is described in ref 7 as an oil. [f] 4a is reported with no mp or spectroscopic data in ref 11.

[δ 5.70 (d, $^2J_{H,F}$ = 52.8 Hz, 2, SCH_2F; **2a**) and δ 6.82 (t, $^2J_{H,F}$ = 56.5 Hz, 1, $SCHF_2$; **2i**)]. In contrast, the uncatalyzed treatment of the more reactive *p*-anisyl analogue [fluoromethyl 4-methoxyphenyl sulfoxide (**1j**)], with DAST afforded 1-[(difluoromethyl)thio]-4-methoxybenzene (**2j**) in 68% yield.[7]

McCarthy et al.[7] proposed a mechanism (Scheme II) involving catalysis of fluoride removal from DAST by zinc(II) iodide. The resulting sulfeniminium fluoride was suggested to react with the starting sulfoxide to give a sulfonium fluoride intermediate. Intramolecular abstraction of an α-proton by the diethylamino electron pair of this intermediate was proposed to give a sulfenium fluoride that collapsed to the product α-fluoro thioether.

Marat and Janzen[5a] noted that treatment of diphenyl thioether with xenon difluoride resulted in rapid oxidative fluorination at sulfur to give the "stable" tetravalent diphenylsulfur difluoride. They proposed analogous rapid formation of tetravalent sulfur difluorides from thioethers bearing α-hydrogen atoms, followed by loss of hydrogen fluoride and rearrangement to give the α-fluoro thioethers. Formation of tetravalent sulfur intermediates with a Lewis acid complexed at the electronegative oxygen was proposed by Vankar and Rao[15] to rationalize reduction of sulfoxides to thioethers by sodium iodide/boron trifluoride etherate.

Lewis acid–base reaction of $SbCl_3$ and DAST could catalyze formation of the same sulfeniminium species of Scheme II plus a complex antimony fluoride anion. Formation and collapse of the indicated intermediates of Scheme II, or further involvement of fluorine-linked tetravalent sulfur intermediates analogous to the Marat and Janzen[5a] and Vankar and Rao[15] processes, might occur.

Experimental Section

All reagents and solvents were of commercial reagent quality. DAST was purchased from Aldrich Chemical Co. and used without purification. TLC plates and silica gel (kieselgel 60, 230–400 mesh) were purchased from Merck. Anhydrous CH_2Cl_2 and $CHCl_3$ were refluxed with and distilled from CaH_2 and P_4O_{10}, respectively. Rotary flash evaporations were performed at reduced pressure at <25 °C. Melting points and oven temperatures from Kugelrohr distillations are uncorrected. Mass spectra were measured at 75 eV. ^{1}H NMR spectra were determined on solutions in $CDCl_3$ at 90 or 200 MHz. Commercially unavailable thioethers (and sulfoxides) were prepared in high yields by S_N2 displacement reactions of alkyl bromides with the potassium salts of benzenethiol or 4-methoxybenzenethiol in ethanol (followed by oxidation at −20 °C with *m*-chloroperoxybenzoic acid (MCPBA) in $CHCl_3$). The sulfoxides were purified by column chromatography to give samples with spectral data consistent with the proposed structures (and compared with literature values if reported).

Ethyl 4-[(4-Methoxyphenyl)thio]butanoate. General Procedure for the Synthesis of Thioethers. Ethyl 4-bromobutanoate (2.09 mL, 2.93 g, 15 mmol) was added dropwise to a stirred solution of 4-methoxybenzenethiol (1.84 mL, 2.10 g, 15 mmol) and potassium hydroxide (0.84 g, 15 mmol) in absolute EtOH (120 mL) at ambient temperature. After 5 h the precipitate (KBr) was filtered and the filtrate evaporated. The crude residue (TLC homogeneous) was used directly in the following reaction.

Ethyl 4-[(4-Methoxyphenyl)sulfinyl]butanoate[7] (1h). General Procedure for the Sulfoxidation of Thioethers. A solution of *m*-chloroperoxybenzoic acid (MCPBA) (3.04 g of 85% reagent, 15 mmol) in $CHCl_3$ (70 mL) was added dropwise to a cooled (−20 °C) stirred solution of the above crude thioether (15 mmol) in $CHCl_3$ (100 mL) and stirring was continued at −20 °C for 5 min after the addition was completed. The reaction mixture was poured into saturated $NaHCO_3/H_2O$ (50 mL) with vigorous stirring and the layers were separated. The aqueous layer was extracted twice with $CHCl_3$, and the combined organic phase was washed with $NaHCO_3/H_2O$, H_2O, and $NaCl/H_2O$, dried ($MgSO_4$), and evaporated to give an oil. Purification by flash chromatography (EtOAc/hexane, 1:5) gave 3.76 g (93%) of **1h** as a colorless

oil with clean ^1H NMR and mass spectra.

General Procedure for the Conversion of Sulfoxides 1 to α-Fluoro Thioethers 2. A flame-dried, round-bottomed flask fitted with rubber septa was purged with N_2 and charged with anhydrous CH_2Cl_2 or $CHCl_3$ (20 mL), 1 (10 mmol), and $SbCl_3$ (68 mg, 0.3 mmol). The resulting solution was cooled to ~4 °C (ice-bath cooling is unnecessary on a 1-mmol scale) and DAST (2.31 mL, 2.82 g, 17.5 mmol) was injected. After 15 min the ice bath was removed and stirring at ambient temperature was continued until TLC (EtOAc/hexane, 1:4) indicated complete consumption of starting 1 (normally 1.5–5 h). The reaction mixture was poured into vigorously stirred ice-cold saturated $NaHCO_3$ (20 mL) and stirring was continued for 30 min. The mixture was extracted with $CHCl_3$ (2 × 30 mL) and the combined organic phase was washed with $NaHCO_3/H_2O$ (10 mL), H_2O (20 mL), and $NaCl/H_2O$ (20 mL), dried ($MgSO_4$), and evaporated to give a brown oil. This crude product was usually oxidized directly to the sulfoxides 3 or sulfones 4. Purification by flash chromatography (EtOAc/hexane, 1:15) or Kugelrohr distillation afforded pure **2a** and **2h** (see Table I).

General Procedure for the Oxidation of α-Fluoro Thioethers 2 to α-Fluoro Sulfoxides 3. A solution of MCPBA (1.02 g of 85% reagent, 5 mmol) in $CHCl_3$ (30 mL) was added dropwise to a cooled (−30 °C) stirred solution of crude **2** (5 mmol) in $CHCl_3$ (30 mL). TLC (EtOAc/hexane, 1:4) indicated complete oxidation after ~5 min. The reaction mixture was worked up as in the above procedure for **1h**. The oily residue was purified by flash chromatography (EtOAc/hexane, 1:10 to 1:3) or Kugelrohr distillation (**3a**) to give the α-fluoro sulfoxides **3** as slightly yellow oils. Careful chromatography separated the diastereomeric pairs of enantiomers of **3b**, **3c**, **3d**, and **3h** (yields and ^1H NMR and mass spectral data are given for the stereoisomeric mixtures in Table I).

[(Fluoromethyl)sulfonyl]benzene[21] (4a). A solution of MCPBA (4.46 g of 85% reagent, 22 mmol) in $CHCl_3$ (70 mL) was added dropwise to a cooled (−10 °C), stirred solution of **2a** (1.42 g, 10 mmol, based on starting **1a**) in $CHCl_3$ (30 mL). The reaction mixture was allowed to warm to ambient temperature and was stirred for an additional 4 h. Workup as described for **1h** afforded **4a** (1.57 g, 90%) as colorless crystals (see Table I).

[(Fluoromethyl)sulfonyl]methane.[7] Dimethyl sulfoxide (0.71 mL, 0.78 g, 10 mmol) was converted to [(fluoromethyl)thio]methane according to the general procedure for **1 → 2** (except the combined solution in $CHCl_3$ (~100 mL) after drying ($MgSO_4$) was not evaporated owing to product volatility). This solution was cooled to −10 °C and oxidized as in the above procedure for **4a**. The reaction mixture was concentrated to ~15 mL, cooled at 0 °C, and filtered. The filtrate was dried ($KHCO_3/MgSO_4$, 3:1) and evaporated to give a solidified yellow oil. Kugelrohr distillation at 55 °C/0.4 mmHg gave 0.85 g (76% based on starting dimethyl sulfoxide) of [(fluoromethyl)sulfonyl]methane as a slightly yellow solidified oil, mp 40–42 °C (lit.[7] mp 40–43 °C): ^1H NMR δ 3.01 (s, 3, CH_3), 5.12 (d, J = 46.8 Hz, 2, CH_2F); MS m/z 112 (M^+, 18), 97 (M − CH_3, 89), 79 (M − CH_2F, 100), 63 (81).

Acknowledgment. We thank the American Cancer Society (Grant No. CH-405) and the Polish Academy of Sciences (Grant No. CPBP 01.13.1) for generous financial support.

Registry No. **1a**, 20696-08-6; **1b**, 127594-85-8; **1c**, 127594-86-9; **1d**, 114045-23-7; **1e**, 73610-10-3; **1f**, 127594-87-0; **1g**, 127594-88-1; **1h**, 127594-89-2; **1i**, 127594-90-5; **1j**, 127594-91-6; **2a**, 60839-94-3; **2b**, 127594-92-7; **2c**, 127594-93-8; **2d**, 127594-94-9; **2e**, 127594-95-0; **2f**, 127594-96-1; **2g**, 127594-97-2; **2h**, 127594-98-3; **2i**, 1535-67-7; **2j**, 81931-98-8; **3b** (isomer 1), 127594-99-4; **3b** (isomer 2), 127595-00-0; **3c** (isomer 1), 127595-01-1; **3c** (isomer 2), 127595-02-2; **3d** (isomer 1), 127595-03-3; **3d** (isomer 2), 127595-04-4; **3e**, 94404-43-0; **3f**, 127595-05-5; **3g**, 127595-06-6; **3h** (isomer 1), 127595-07-7; **3h** (isomer 2), 127595-08-8; **4a**, 20808-12-2; DAST, 38078-09-0; p-$MeOC_6H_4S(CH_2)_3CO_2Et$, 127594-84-7; $Br(CH_2)_3CO_2Et$, 2969-81-5; p-$MeOC_6H_4SH$, 696-63-9; $SbCl_3$, 10025-91-9; MeS(O)Me, 67-68-5; FCH_2SMe, 65038-44-0; FCH_2SO_2Me, 94404-44-1.

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A 1:1 Complex of Silver with a Cofacial Stilbene: ((*Z*)-2,2,5,5-Tetramethyl-3,4-diphenylhex-3-ene)silver(I) Triflate

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Received January 3, 1990

Sterically congested stilbene, (*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene (1) was recently shown to possess face-to-face or cofacial benzene rings.[1,2] The π-electron-rich cleft in this simple molecule, Scheme I, offers an interesting site for complexation. The exterior faces of the rings in 1, in contrast to related cofacial hydrocarbons,[3] were thought to be unlikely complexation sites due to the proximity of the large *tert*-butyl groups. Similarly, stereoisomer 2 would not be expected to form complexes. Finally, steric hindrance should prevent complexation of 1 and 2 at the normally preferred site of interaction, the central double bond. As a validation of these concepts, the preparation and characterization of the first metal complex of this system, the silver trifluoromethanesulfonate (silver triflate, AgOTf) complex, is described below.

Results

Attempts to detect a silver ion complex of 1[1] by ^1H NMR with silver nitrate in ethanol or silver triflate in either tetrahydrofuran (THF) or methanol gave no indication of appreciable complexation. A stoichiometric solution of 1 and silver triflate was prepared in dry tetrahydrofuran. Evaporation of the solvent produced colorless crystals of a new material, 3, which melted at 195–196 °C, in contrast to 1, mp = 89–90 °C, and which readily dissolved in chloroform, in contrast to silver triflate. The ^1H NMR and ^{13}C NMR spectra of 3 (Table I) were similar to 1 but all resonances were shifted downfield. Silver triflate in excess of the 1:1 stoichiometry did not effect the observed ^1H NMR chemical shifts of 3. In contrast, a 100% excess (2:1 for 1:silver triflate) of 1 shifted the observed resonances to points equidistant between those of 1 and 3. Although the ^1H NMR spectrum of 3 showed no changes when a normal $CDCl_3$ solution was cooled, similar treatment of a very dilute, 0.00038 M, solution showed some peak broadening and coalescence at the lowest temperature, −50 °C. Stereoisomer 2 showed no ^1H NMR evidence for complex formation in the presence of silver triflate. Crystals of the new complex were stable to moisture and oxygen. Slight darkening occurred upon exposure to room

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