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Stable Fluorinated Sulfuranes and Sulfurane Oxides. Synthesis and Reactions[1]

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Received September 8, 1977

Bis(trifluoromethyl) sulfide, tetrafluoro-1,3-dithietane, and bis(trifluoromethyl) sulfoxide undergo oxidative addition when photolyzed with trifluoromethyl hypochlorite to form a new family of sulfuranes, bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane (**1**) and tetrafluoro-1,3-tetrakis(trifluoromethoxy)dithietane (**3**), and of sulfurane oxides, bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane oxide (**2**). Compounds **1** and **2** are hydrolyzed to bis(trifluoromethyl) sulfoxide and bis(trifluoromethyl) sulfone, respectively. Pyrolysis of **1**, **2**, or **3** gives bis(trifluoromethyl) sulfide, bis(trifluoromethyl) sulfoxide, and tetrafluoro-1,3-dithietane, respectively, plus bis(trifluoromethyl) peroxide. With primary amines, **1** and **2** yield *N*-alkylbis(trifluoromethyl)sulfimides and sulfoxyimides, and with *N,N'*-diethylaminotrimethylsilane, imine formation occurs. Sulfurane oxide **2** forms a new type of stable sulfurane oxide (**4**), bis(trifluoromethyl)bis(hexafluoroisopropylidenimido)sulfurane oxide, with lithium hexafluoroisopropylidenimine. Sulfurane **1** acts in a similar manner with the nucleophile but the sulfurane **5** is not isolated. Compounds **1** and **2** form α,α,α-(trifluoromethyl)anisole derivatives with substituted phenols. Secondary and tertiary alcohols are dehydrated by **1** or **2** to olefins but symmetrical alkyl ethers result when primary alcohols are reacted.

Introduction

In the past several years, preparative chemists have found the synthesis[2-16] of aryl- or tetraoxysulfuranes to be a lucrative area for designing new compounds from which studies concerning geometry at sulfur[17,18] and synthetic utility[19-24] could result. Although there is considerable indirect evidence for alkylsulfuranes as intermediates in nucleophilic displacement reactions of sulfonium salts,[25,26] none has been isolated.

Since it has been demonstrated that reactions of aryloxytrimethylsilane[3,6,27] or pentafluorophenyllithium[5] with fluorosulfuranes, SF_4 or R_fSR_3, or fluorosulfurane oxides, OSF_4, yield tetraoxy- or arylsulfuranes or sulfurane oxides, other substituted fluorosulfuranes should be useful precursors to similar compounds. However, fluorosulfuranes, such as $(R_f)_2SF_2$, tend to form unstable products when reacted with lithium salts or not to undergo oxidative addition reactions readily with perfluoroalkoxy groups.[28]

The first stable members of new perfluoroalkylsulfurane and perfluoroalkylsulfurane oxide families, sulfuranes **1** and **3**, and sulfurane oxides **2** and **4**, respectively, have been isolated and characterized. The work described here suggests that perfluoroalkylsulfurane oxides have useful properties and applications in contrast to the relative inertness of arylsulfurane oxides.

Results and Discussion

The new sulfurane **1**[1] and sulfurane oxide **2** result when a

$$\left.\begin{matrix}CF_3SCF_3\\ CF_3S(O)CF_3\end{matrix}\right\} \xrightarrow[h\nu]{CF_3OCl} \begin{matrix}(CF_3)_2S(OCF_3)_2 + Cl_2\\ \mathbf{1}\end{matrix}$$
$$\xrightarrow[h\nu]{CF_3OCl} \begin{matrix}(CF_3)_2S(O)(OCF_3)_2 + Cl_2\\ \mathbf{2}\end{matrix}$$

mixture of bis(trifluoromethyl) sulfide or bis(trifluoromethyl) sulfoxide and trifluoromethyl hypochlorite is photolyzed. These are stable in Pyrex glass at 25 °C for a few days. However, hydrolysis of **1** occurs rapidly to form bis(trifluoromethyl) sulfoxide and carbonyl fluoride.

While the dialkoxydiarylsulfurane oxide reported by Martin et al.[12] does not undergo hydrolysis, sulfurane oxide **2** does hydrolyze in water forming bis(trifluoromethyl) sulfone and carbonyl fluoride. This behavior of the acyclic sulfurane and sulfurane oxide is in keeping with their higher reactivity toward nucleophiles and contrasts with the inertness of the arylsulfurane oxide[12,14] under similar attack.

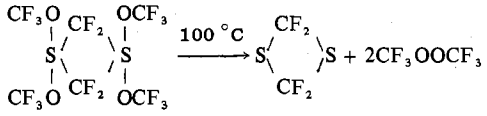
The pyrolysis of compound **1** or **2** in a stainless steel Hoke vessel generates the corresponding bis(trifluoromethyl) sulfide or sulfoxide and bis(trifluoromethyl) peroxide quantitatively, viz.

$$(CF_3)_2S(OCF_3)_2 \xrightarrow[70\ ^\circ C]{H_2O} \begin{matrix}CF_3S(O)CF_3 + 2CF_2O + 2HF\\ CF_3SCF_3 + CF_3OOCF_3\end{matrix}$$

$$(CF_3)_2S(O)(OCF_3)_2 \xrightarrow[100\ ^\circ C]{H_2O} \begin{matrix}CF_3SO_2CF_3 + 2CF_2O + 2HF\\ CF_3S(O)CF_3 + CF_3OOCF_3\end{matrix}$$

Spectroscopic data support the identity of these new compounds. The ^{19}F NMR spectrum of sulfurane **1** shows two septets (J_{FF} = 7.4 Hz) at ϕ 56.2 and 73.6, respectively, with an area ratio of 1:1. The former is assigned to the trifluoromethyl groups split by the trifluoromethoxy groups. For the sulfurane oxide **2**, two signals appear at ϕ 67.4 and 74.1, respectively, with an area ratio of 1:1 and each is a septet (J_{FF} = 9.6 Hz). Both compounds **1** and **2** exhibit trigonal-bipyramidal geometry with the CF_3O groups being assigned the axial positions[29,30] based on electronegativity and apicophilicity considerations.

When the cyclic sulfide, tetrafluoro-1,3-dithietane, is reacted with trifluoromethyl hypochlorite, a cyclic sulfurane **3**, which is a stable liquid, results. It is thermally decomposed at 100 °C.



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Sulfurane **1** undergoes reactions with primary amines and is, thus, a useful precursor to a series of *N*-alkylbis(trifluoromethyl)sulfimides.[31] Because of reports on the low thermal stabilities of fluorosulfuranes,[31,32] the reactions were carried out at −78 °C.

$$(CF_3)_2S(OCF_3)_2 \xrightarrow[-78\ ^\circ C]{3RNH_2} (CF_3)_2S{=}NR + 2CF_2O + 2RNH_2{\cdot}HF$$
$$R = H, CH_3, C_2H_5$$

A direct route to a series of *N*-alkylbis(trifluoromethyl)-sulfoxyimides[33] was found when sulfurane oxide **2** showed high reactivity toward primary amines at 0 °C, viz.

$$(CF_3)_2\overset{O}{\overset{\|}{S}}(OCF_3)_2 \xrightarrow{3RNH_2} (CF_3)_2\overset{O}{\overset{\|}{S}}{=}NR + 2CF_2O + 2RNH_2{\cdot}HF$$

The formation of the carbonyl fluoride acts as a strong driving force in this reaction.

Treatment of sulfurane **1** or sulfurane oxide **2** with *N,N'*-diethylaminotrimethylsilane in the presence of sodium

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$$\left.\begin{matrix}1\\2\end{matrix}\right\} + (C_2H_5)_2NSi(CH_3)_3 \xrightarrow{NaF} \begin{cases} \rightarrow CF_3SCF_3 + CH_3CH{=}NCH_2CH_3 \\ \rightarrow CF_3S(O)CF_3 + CH_3CH{=}NCH_2CH_3 \end{cases} \quad (A)$$

fluoride leads to imine formation (see eq A).

Sulfurane oxide **2** may be used also to form a new type of sulfurane oxide, **4**, by undergoing a ligand exchange reaction with hexafluoroisopropylidenimine.

$$(CF_3)_2S(OCF_3)_2 \xrightarrow{LiN=C(CF_3)_2} \underset{\mathbf{4}}{(CF_3)_2S[N=C(CF_3)_2]_2} + 2CF_2O + 2LiF$$

Hydrolysis of **4** proceeds slowly to yield $CF_3SO_2CF_3$ and $HN{=}C(CF_3)_2$. When **4** is pyrolyzed at 50 °C for 1 h, $CF_3S(O)CF_3$ and $[(CF_3)_2C{=}N]_2$ form quantitatively

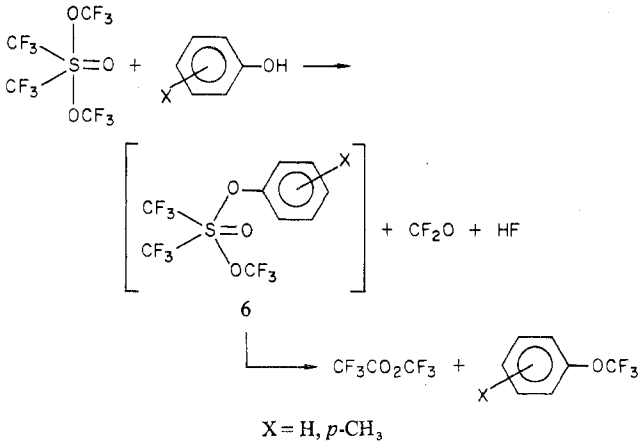
$$(CF_3)_2S[N=C(CF_3)_2]_2 \xrightarrow[50\ ^\circ C]{H_2O} \begin{cases} (CF_3)_2C{=}NH + CF_3SO_2CF_3 \\ CF_3S(O)CF_3 + [(CF_3)_2C{=}N]_2 \end{cases}$$

Sulfurane **1** undergoes a similar ligand exchange with $LiN{=}C(CF_3)_2$ to form a new type of sulfurane, **5**. However, the latter is unstable decomposing to CF_3SCF_3 and $[(CF_3)_2C{=}N]_2$.

$$(CF_3)_2S(OCF_3)_2 \xrightarrow{LiN=C(CF_3)_2} \underset{\mathbf{5}}{[(CF_3)_2S(N=C(CF_3)_2)_2]} + 2CF_2O + 2LiF$$

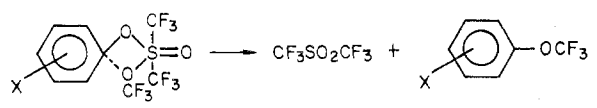
$$\rightarrow [(CF_3)_2C{=}N]_2 + CF_3SCF_3$$

The great versatility of sulfurane **1** or sulfurane oxide **2** is demonstrated by reactions which result in α,α,α-(trifluoromethyl)anisole derivatives

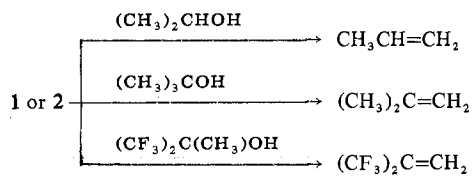


X = H, *p*-CH_3

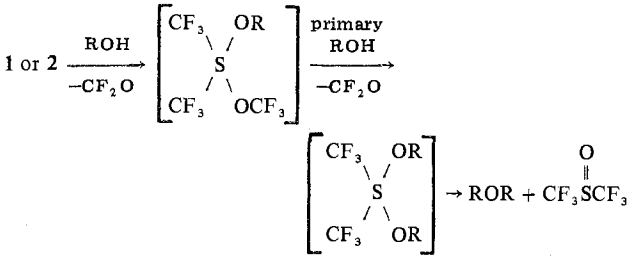
The formation of α,α,α-(trifluoromethyl)anisole by **1** or **2** in ethyl ether at 25 °C is complete within 30 min. This product could result from an intramolecular decomposition of sulfurane oxide, **6**, and in particular, the formation of *p*-(trifluoromethoxy)toluene supports the contribution of an electrocyclic mechanism.[16]



While secondary and tertiary alcohols are dehydrated by sulfurane **1** and sulfurane oxide **2** to give olefins, viz.



with primary alcohols, symmetrical alkyl ethers are obtained. The following scheme accounts for this behavior.



Experimental Section

Materials. Literature methods were used to prepare CF_3SCF_3,[34] $CF_3S(O)CF_3$,[34] CF_3OCl,[35] and $LiN{=}C(CF_3)_2$.[36] Tetrafluoro-1,3-dithietane (PCR, Inc.), amines, alcohols, and phenols were used without further purification.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge. Volatile starting materials and purified products were measured quantitatively by *PVT* techniques. Vapor pressure studies were carried out by using an isoteniscopic method. Known products were identified from the spectral data of authentic samples.

Infrared spectra were taken by using a Perkin-Elmer 457 spectrometer with a 5-cm gas cell fitted with KBr windows. The ^{19}F and ^1H NMR spectra were obtained using a Varian HA-100 spectrometer with CCl_3F or $(CH_3)_4Si$ as an internal standard. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 eV.

Preparation of Sulfurane 1. CF_3SCF_3 (2 mmol) and CF_3OCl (4 mmol) were condensed at −196 °C into a 100-mL quartz vessel equipped with a Teflon stopcock. The reaction mixture was warmed slowly to 25 °C and photolyzed for 20 h with a Hanovia utility ultraviolet lamp. Bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane (**1**) (1.31 mmol) is retained in a trap at −78 °C by using trap-to-trap separation techniques. This sulfurane is a pale yellow liquid with an extrapolated boiling point at 72 °C from the equation $\log P_{Torr} = 7.32 - 1532/T$ (valid between 0 and 52 °C). The molar heat of vaporization is 7.0 kcal and the Trouton constant is 20.3 eu. NMR: ^{19}F, ϕ 56.2 (CF_3, sept), 73.6 (OCF_3, sept, J = 7.2 Hz). The infrared spectrum is as follows: 1320 (m), 1263 (vs), 1220 (s), 1198 (m), 1104 (vs), 841 (m), 755 (w), 581 cm^{-1} (w). When the mass spectral data are obtained at 100 °C, the molecular ion is absent; however, other fragment peaks, such as m/e 255 ($C_3OSF_9^+$, M − OCF_3), 170 ($C_2SF_6^+$, $C_2O_2F_6^+$), 138 ($C_2F_6^+$), 117 ($COSF_3^+$), 101 (CSF_3^+), 85 (OCF_3^+), and 69 (CF_3^+) appeared.

Anal. Calcd for $C_4O_2SF_{12}$: C, 14.13. Found: C, 14.06.

Hydrolysis of Sulfurane 1. $(CF_3)_2S(OCF_3)_2$ (1 mmol) was condensed onto excess H_2O at −196 °C and warmed to 25 °C. After 1 h, the products were separated by trap-to-trap distillation and identified as $CF_3S(O)CF_3$ (0.86 mmol) and CF_2O (1.76 mmol) based on their infrared spectra.

Pyrolysis of Sulfurane 1. $(CF_3)_2S(OCF_3)_2$ (1 mmol) was condensed in a stainless steel Hoke vessel and heated at 70 °C for 1 h. After trap-to-trap distillation, CF_3SCF_3 and CF_3OOCF_3[37] were obtained quantitatively.

Preparation of Sulfurane Oxide 2. $CF_3S(O)CF_3$ (2 mmol) and CF_3OCl (4 mmol) were condensed together at −196 °C into a 100-mL quartz vessel and warmed to 25 °C. The reaction mixture was photolyzed for 20 h with a Hanovia utility ultraviolet quartz lamp. Bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane oxide (**2**) (1.72 mmol) was obtained by trap-to-trap distillation. It is a liquid with a boiling point of 97 °C obtained from the equation $\log P_{Torr} = 7.60 - 1746/T$ (valid between 0 and 62 °C). The molar heat of vaporization is 8.0 kcal and the Trouton constant is 21.6 eu. NMR: ^{19}F, ϕ 67.4 (CF_3, sept), 74.1 (OCF_3, sept, J = 9.6 Hz). The infrared spectrum is as follows: 1323 (m), 1265 (vs), 1234 (s), 1218 (ms), 1195 (m), 1186 (m), 1106 (vs), 989 (w), 845 (m), 752 (w), 586 cm^{-1} (w). In the mass spectrum at 100 °C, the molecular ion is absent; however, other fragment peaks, such as m/e 271 ($C_3O_2SF_9^+$, M − OCF_3), 255

($C_3OSF_9^+$), 186 ($C_2OSF_6^+$), 170 ($C_2SF_6^+$), 119 ($C_2F_5^+$), 117 ($COSF_3^+$), 101 (CSF_3^+), 98 ($COSF_2^+$), 85 (OCF_3^+), 82 (CSF_2^+), 69 (CF_3^+), and 48 (OS^+) appeared.

Anal. Calcd for $C_4O_3SF_{12}$: C, 13.49. Found: C, 13.51.

Hydrolysis of Sulfurane Oxide 2. $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) was condensed onto water (excess) at −196 °C and warmed to 25 °C. After 1 h, volatile products were separated by fractional distillation, and $CF_3SO_2CF_3$ and CF_2O were recovered quantitatively.

Pyrolysis of Sulfurane Oxide 2. $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) in a stainless steel Hoke vessel was heated at 100 °C for 1 h. The yields of $CF_3S(O)CF_3$ and CF_3OOCF_3 were quantitative.

Preparation of Sulfurane 3. Tetrafluoro-1,3-dithietane (2 mmol) and trifluoromethyl hypochlorite (8 mmol) were condensed into a 100-mL quartz vessel and photolyzed. After 20 h, sulfurane **3** (0.98 mmol) was retained in a trap at −30 °C by trap-to-trap distillation. It is a liquid with an extrapolated boiling point of 131 °C obtained from the equation $\log P_{Torr} = 7.67 - 1935/T$. The molar heat of vaporization is 8.6 kcal and the Trouton constant is 21.9 eu. The ^{19}F NMR spectrum contains resonances at ϕ 72.1 and 96.2 in the ratio 12:4. The resonance at ϕ 96.2, assigned to the CF_2 groups, is split by OCF_3 groups on sulfur (J = 12.1 Hz). The resonance at ϕ 72.1 is assigned to the OCF_3 groups on sulfur. The infrared spectrum has absorption bands at 1290 (m), 1233 (ms), 1184 (s), 1120 (s), 1071 (s), 1025 (m), 992 (ms), 955 (m), 733 (m), 528 cm^{-1} (w). In the mass spectrum, the fragment peaks, m/e 419 ($C_5O_3S_2F_{13}^+$, M − OCF_3), 334 ($C_4O_2S_2F_{10}^+$), 249 ($C_3OS_2F_7^+$), 170 ($C_2O_2F_6^+$), 164 ($C_2S_2F_4^+$), 85 (COF_3^+), 82 (CSF_2^+), and 69 (CF_3^+) appeared.

Anal. Calcd for $C_6O_4S_2F_{16}$: C, 14.29. Found: C, 14.31.

Pyrolysis of Sulfurane 3. Heating sulfurane **3** (1.0 mmol) at 100 °C for 2 h in a stainless steel Hoke vessel, tetrafluoro-1,3-dithietane and bis(trifluoromethyl) peroxide were collected quantitatively.

Preparation of $(CF_3)_2S{=}NH$.[31] $(CF_3)_2S(OCF_3)_2$ (1 mmol) was condensed onto ammonia (3.0 mmol) at −196 °C in a Pyrex glass vessel equipped with a Teflon stopcock. The reaction mixture was allowed to warm slowly to and remain at −78 °C for 1 h. $(CF_3)_2{=}NH$ (0.75 mmol) was recovered and the other product isolated was CF_2O (1.88 mmol) by fractional distillation.

Preparation of $(CF_3)_2S{=}NCH_3$.[31] In the usual procedure, 1.0 mmol of $(CF_3)_2S(OCF_3)_2$ was condensed onto 3.0 mmol of CH_3NH_2 at −196 °C and reacted as with NH_3. Bis(trifluoromethyl)-*N*-methylsulfimide (0.82 mmol) and carbonyl fluoride (1.90 mmol) were recovered by trap-to-trap distillation.

Preparation of $(CF_3)_2S{=}NCH_2CH_3$.[31] When monoethylamine (3 mmol) was used as in the previous reaction, $(CF_3)_2S{=}NCH_2CH_3$ (0.85 mmol) and CF_2O (1.82 mmol) were obtained.

Preparation of $(CF_3)_2S(O){=}NH$.[33] $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) and NH_3 (3 mmol) were condensed into a Pyrex glass vessel equipped with a Teflon stopcock and retained at −78 °C for 1 h. Bis(trifluoromethyl)sulfur oxyimine (0.93 mmol) and carbonyl fluoride (1.92 mmol) were recovered by fractional condensation.

Preparation of $(CF_3)_2S(O){=}NCH_3$.[33] A total of 1.0 mmol of bis(trifluoromethyl)bis(trifluoromethoxy)sulfurane oxide was condensed onto 3.0 mmol of monomethylamine and reacted as above. *N*-Methylbis(trifluoromethyl)sulfur oxyimine (0.88 mmol) and carbonyl fluoride (1.86 mmol) were obtained by trap-to-trap distillation.

Preparation of $(CF_3)_2S(O){=}NCH_2CH_3$.[33] Monoethylamine (3.0 mmol) was used as in the previous reaction. The products isolated were $(CF_3)_2S(O){=}NCH_2CH_3$ (0.92 mmol) and CF_2O (1.86 mmol).

Reaction of Sulfurane 1 and $(CH_3CH_2)_2NSiMe_3$. $(CF_3)_2S(OCF_3)_2$ (1 mmol) and $(CH_3CH_2)_2NSiMe_3$ (1 mmol) were condensed at −196 °C into a Pyrex glass vessel, which contained excess NaF. The reaction mixture was allowed to warm from −196 to −78 °C and to remain for 1 h. After fractional distillation, products identified were CF_3SCF_3 (0.92 mmol), Me_3SiF (0.95 mmol), CF_2O (1.68 mmol), and $CH_3CH{=}NCH_2CH_3$ (0.73 mmol).

Reaction of Sulfurane Oxide 2 with $(CH_3CH_2)_2NSiMe_3$. Sulfurane oxide **2** (1.0 mmol) was used as in the previous reaction, and the same reaction conditions were used. After trap-to-trap distillation, products isolated were $CF_3S(O)CF_3$ (0.87 mmol), Me_3SiF (0.96 mmol), CF_2O (1.77 mmol), and $CH_3CH{=}NCH_2CH_3$ (0.85 mmol).

Preparation of Sulfurane 4. The literature method was used to prepare $LiN{=}C(CF_3)_2$ (2 mmol) in a rigorously flame-dried 50-mL Pyrex vessel. The solvent was removed under dynamic vacuum leaving a brown amorphous solid. Onto the solid was condensed $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) at −196 °C and the vessel was warmed slowly to −78 °C. After 1 h, volatile products were separated by low-temperature fractional distillation and $(CF_3)_2S(O)[N{=}C(CF_3)_2]_2$ (0.86 mmol) was obtained. The other product isolated was CF_2O (1.84 mmol). $(CF_3)_2S(O)[N{=}C(CF_3)_2]_2$ is a stable liquid which obeys the vapor pressure equation $\log P_{Torr} = 7.52 - 2069/T$ between 0 and 60 °C. The molar heat of vaporization is 9.5 kcal and the Trouton constant is 21.2 eu. The ^{19}F NMR spectrum shows resonances at ϕ 63.2, 70.1, and 71.6 in the ratio 2:6:6. At ϕ 70.1 and 71.6, CF_3 groups bonded to carbon (>C=N−) are magnetically nonequivalent, which has been previously reported.[38-40] The resonance bands were broad. That at ϕ 63.2 is assigned to the trifluoromethyl groups bonded to sulfur. The infrared spectrum is as follows: 1721 (w), 1416 (m), 1386 (m), 1321 (ms), 1281 (s), 1260 (ms), 1212 (vs), 1189 (m), 1176 (m), 1105 (ms), 997 (ms), 845 (m), 753 (w), 583 cm^{-1} (w). The mass spectrum does not contain a molecular ion; however, other fragment peaks appear.

Anal. Calcd for $C_8N_2OSF_{18}$: C, 18.69; N, 5.45. Found: C, 18.56; N, 5.47.

Pyrolysis of Sulfurane Oxide 4. One millimole of sulfurane oxide **4** was heated at 100 °C for 1 h in a stainless steel Hoke vessel. After fractional distillation, the isolated products were $CF_3S(O)CF_3$ and $[(CF_3)_2C{=}N]_2$[41] quantitatively.

Reaction of Sulfurane 1 with $LiN{=}C(CF_3)_2$. Sulfurane **1** (1.0 mmol) was condensed onto $LiN{=}C(CF_3)_2$ (2 mmol) at −196 °C and warmed to −78 °C. After 1 h, the volatile products were separated by distillation and isolated as CF_3SCF_3 (0.85 mmol), $[(CF_3)_2C{=}N]_2$ (0.93 mmol), and CF_2O (1.84 mmol).

Preparation of α,α,α-(Trifluoromethyl)anisole.[42-44] (a) $(CF_3)_2S(O)(OCF_3)_2$ (1.5 mmol) was condensed into a Pyrex reaction vessel which contained phenol (1.5 mmol) in dry ethyl ether (2 mL). The reaction mixture was allowed to warm to 25 °C and was stirred for 30 min. The products were purified by fractional condensation and gas chromatography. $CF_3SO_2CF_3$ (1.15 mmol) and $C_6H_5OCF_3$ (1.13 mmol) were obtained.

(b) As in the previous procedure, 1.5 mmol of $(CF_3)_2S(OCF_3)_2$ was used and worked up as usual. $CF_3S(O)CF_3$ (1.02 mmol) and $C_6H_5OCF_3$ (0.80 mmol) were recovered.

Preparation of *p*-(Trifluoromethoxy)toluene.[42-44] (a) $(CF_3)_2S(O)(OCF_3)_2$ (1.5 mmol) and *p*-cresol (1.5 mmol) in dry Et_2O (2 mL) were reacted at 25 °C and distilled. The isolated products were $(CF_3)_2SO_2$ (1.32 mmol) and *p*-$CH_3C_6H_4OCF_3$ (1.21 mmol).

(b) When $(CF_3)_2S(OCF_3)_2$ (1.5 mmol) was used as in the above procedure, $CF_3S(O)CF_3$ (1.18 mmol) and *p*-$CH_3C_6H_4OCF_3$ (1.01 mmol) were recovered.

Preparation of $CH_3CH{=}CH_2$. (a) $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) was condensed onto a mixture of isopropyl alcohol (1 mmol) and sodium fluoride (excess). The reaction mixture was allowed to warm to 25 °C and retained for 1 h. After fractional condensation, $CF_3SO_2CF_3$ (0.92 mmol), CF_2O (1.87 mmol), and $CH_3CH{=}CH_2$ (0.91 mmol) were recovered.

(b) A total of 1.0 mmol of $(CF_3)_2S(OCF_3)_2$ was used as in the above reaction, and the products isolated were $CF_3S(O)CF_3$ (0.89 mmol), CF_2O (1.83 mmol), and $CH_3CH{=}CH_2$ (0.81 mmol).

Preparation of $(CH_3)_2C{=}CH_2$. (a) $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) was condensed onto a mixture of *tert*-butyl alcohol (1 mmol) and sodium fluoride (excess) and warmed to 25 °C. After 1 h, $CF_3SO_2CF_3$ (0.95 mmol), CF_2O (1.86 mmol), and $(CH_3)_2C{=}CH_2$ (0.92 mmol) were recovered by trap-to-trap distillation.

(b) When $(CF_3)_2S(OCF_3)_2$ (1.0 mmol) was used as in the previous procedure, $CF_3S(O)CF_3$ (0.96 mmol), CF_2O (1.78 mmol), and $(CH_3)_2C{=}CH_2$ (0.83 mmol) were isolated.

Preparation of $(CF_3)_2C{=}CH_2$. (a) In the usual procedure, $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) reacted with $(CF_3)_2C(CH_3)OH$ (1 mmol) in the presence of NaF (excess) to yield $CF_3SO_2CF_3$ (0.93 mmol), CF_2O (1.92 mmol), and $(CF_3)_2C{=}CH_2$ (0.84 mmol).

(b) $(CF_3)_2S(OCF_3)_2$ (1 mmol) was used as in the above reaction. The products isolated were $CF_3S(O)CF_3$ (0.93 mmol), CF_2O (1.81 mmol), and $(CF_3)_2C{=}CH_2$ (0.67 mmol).

Preparation of CH_3OCH_3. (a) $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) and CH_3OH (2 mmol) were condensed at −196 °C onto excess sodium fluoride. The reaction mixture was allowed to warm to 25 °C and retained for 3 h. After fractional condensation, the products isolated were $CF_3SO_2CF_3$ (0.87 mmol), CF_2O (1.83 mmol), and CH_3OCH_3 (0.81 mmol).

(b) When $(CF_3)_2S(OCF_3)_2$ (1 mmol) was used as in the above reaction, $CF_3S(O)CF_3$ (0.86 mmol), CF_2O (1.79 mmol), and

CH_3OCH_3 (0.78 mmol) were recovered.

Preparation of $CH_3CH_2OCH_2CH_3$. (a) $(CF_3)_2S(O)(OCF_3)_2$ (1 mmol) and CH_3CH_2OH (2 mmol) were condensed into a Pyrex glass vessel which contained excess NaF and reacted as above. The products isolated were $CF_3SO_2CF_3$ (0.92 mmol), CF_2O (1.91 mmol), and $CH_3CH_2OCH_2CH_3$ (0.91 mmol).

(b) As in the previous procedure, $(CF_3)_2S(OCF_3)_2$ (1 mmol) was used and $CF_3S(O)CF_3$ (0.89 mmol), CF_2O (1.82 mmol), and $CH_3CH_2OCH_2CH_3$ (0.80 mmol) were recovered.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for support of this research.

Registry No. **1**, 63465-11-2; **2**, 66632-46-0; **3**, 63441-15-6; **4**, 66632-47-1; CF_3SCF_3, 371-78-8; CF_3OCl, 22082-78-6; $CF_3S(O)CF_3$, 30341-37-8; tetrafluro-1,3-dithietane, 1717-50-6; $(CF_3)_2S{=}NH$, 60646-40-4; $(CF_3)_2S{=}NCH_3$, 60646-41-5; $(CF_3)_2S{=}NCH_2CH_3$, 60646-42-6; $(CF_3)_2S(O){=}NH$, 34556-22-4; $(CF_3)_2S(O){=}NCH_3$, 34556-25-7; $(CF_3)_2S(O){=}NCH_2CH_3$, 60646-44-8; $(CH_3CH_2)_2NSiMe_3$, 996-50-9; $C_6H_5OCF_3$, 456-55-3; *p*-$CH_3C_6H_4OCF_3$, 706-27-4; $CH_3CH{=}CH_2$, 115-07-1; $(CH_3)_2C{=}CH_2$, 115-11-7; $(CF_3)_2C{=}CH_2$, 382-10-5; CH_3OCH_3, 115-10-6; $CH_3CH_2OCH_2CH_3$, 60-29-7; $LiN{=}C(CF_3)_2$, 31340-36-0; phenol, 108-95-2; *p*-cresol, 106-44-5; isopropyl alcohol, 67-63-0; *tert*-butyl alcohol, 75-65-0; $(CF_3)_2C(CH_3)OH$, 1515-14-6; CH_3OH, 67-56-1; CH_3CH_2OH, 64-17-5; NH_3, 7664-41-7; CH_3NH_2, 74-89-5; monoethylamine, 75-04-7.

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Newly Synthesized Sulfhydryl- and Imidazole-Containing Tripeptides with a Specific Copper-Binding Site

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Received December 15, 1977

New tripeptides, *N*-mercaptoacetylglycyl-L-histidine (MAGH) and *N*-mercaptoacetyl-DL-histidyl-DL-histidine (MAHH), were synthesized as an artificial sulfhydryl-containing peptide with a histidine component in the third position of the molecular sequence. Their remarkably stable Cu(II) complexes were characterized by electronic, circular dichroism, electron spin resonance (ESR), and X-ray photoelectron spectra. The ESR spectra for the 1:1 Cu(II) complexes of MAGH and MAHH showed the seven and nine lines of nitrogen superhyperfine splitting, indicating clearly the coordination of three and four nitrogen atoms toward Cu(II), respectively. The ESR and bonding parameters estimated were as follows: $A_{\parallel} = 195 \times 10^{-4}$ cm^{-1}, $g_{\parallel} = 2.206$, $g_{\perp} = 2.099$, $A_N = 12.61 \times 10^{-4}$ cm^{-1}, $\alpha^2 = 0.81$, $\beta_1^2 = 0.67$, and $\beta^2 = 1.19$ for the MAGH–Cu(II) complex and $A_{\parallel} = 180 \times 10^{-4}$ cm^{-1}, $g_{\parallel} = 2.183$, $g_{\perp} = 2.060$, $A_N = 12.70 \times 10^{-4}$ cm^{-1}, $\alpha^2 = 0.75$, $\beta_1^2 = 0.65$, and $\beta^2 = 0.96$ for the MAHH–Cu(II) complex. These results support square-planar and square-pyramidal configurations for the Cu(II) complexes of MAGH and MAHH, respectively. In addition, proton nuclear magnetic resonance measurements for the 1:1 Cu(I) complexes of these peptides revealed that the sulfhydryl and imidazole groups participate in the coordination of Cu(I).

Introduction

The N-terminal portion Asp–Ala–His of human (or bovine) serum albumin coordinates Cu(II) ion strongly in a square-planar complex involving the amino group of the aspartic acid residue, an imidazole nitrogen of the histidine, and two intermediate peptide nitrogens.[1] Recent work by Sarkar and co-workers[1] has demonstrated that the tripeptide molecule glycylglycyl-L-histidine (GGH) contains the same potential metal-binding sites, is an adequate model for the specific Cu(II) transport site of human serum albumin, and may be

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