

Cis and Trans Derivatives of Sulfur Hexafluoride Resulting from Oxidative-Addition-Displacement Reactions of (Trifluoromethyl)imidodisulfites with Chlorine Fluoride

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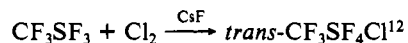
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Oxidative-addition reactions between chlorine fluoride and (trifluoromethyl)imidodisulfites, $\text{CF}_3\text{N}=\text{S}(\text{OR}_f)_2$ ($\text{R}_f = \text{CF}_3\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2$, and $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2$), result in the formation of both the *cis*- and *trans*-tetrafluorobis(polyfluoroalkoxy)sulfur isomers, $\text{F}_4\text{S}(\text{OR}_f)_2$. The isomers are easily separated, with the *trans* form predominating. The (trifluoromethyl)imidodisulfites $\text{CF}_3\text{N}=\text{S}(\text{OR}_f)_2$ ($\text{R}_f = \text{CF}_3\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CH}_2$, $\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2$, $(\text{CF}_3)_2\text{C}(\text{CH}_3)$, $(\text{CF}_3)\text{C}(\text{CH}_3)_2$, and $(\text{CF}_3)_2\text{C}(\text{H})$) and $\text{CF}_3\text{N}=\text{SOC}-\text{H}_2(\text{CF}_2)_2\text{CH}_2\text{O}$ were prepared from the reaction of the lithium salts of the polyfluoroalkyl alcohols and (trifluoromethyl)imidodisulfurous difluoride. Reaction of ClF with $(\text{CF}_3\text{CH}_2\text{O})_2\text{S}=\text{NC}(\text{O})\text{OCH}_2\text{CF}_3$ also resulted in *cis*- and *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$. The reaction of ethylene glycol with (trifluoromethyl)imidodisulfurous difluoride resulted in the imidosulfite $\text{CF}_3\text{N}=\text{SOCH}_2\text{CH}_2\text{O}$, when NaF was used as a base.

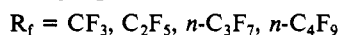
Introduction

The high kinetic stability of sulfur hexafluoride has caused it to be employed only rarely as a precursor to sulfur(VI)-containing compounds. Because of the inertness of the formal parent molecule, the search for alternate routes to monosubstituted, disubstituted and more highly substituted sulfur hexafluoride derivatives has continued to attract the attention of chemists with goals of synthesizing compounds of equivalent thermal and hydrolytic stability but e.g. with higher boiling points or improved dielectric properties.

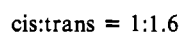
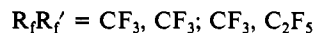
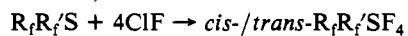
The starting material of choice has been sulfur tetrafluoride, which when reacted with peroxides,¹⁻³ trioxides,⁴ fluoroxy compounds,³ hypochlorites,⁵⁻⁷ or mixtures of other compounds⁸ that are good sources of free radicals, formed the *cis* addition product only, *cis*-(R_fO)₂ SF_4 . However, when bis(alkyl) sulfides were subjected to electrochemical fluorination, only the *trans*-tetrafluorobis(perfluoroalkyl)sulfur isomers, *trans*-(R_f)₂ SF_4 , were obtained.⁹⁻¹¹ Similarly, when reactions were carried out under ionic conditions, only the *trans* isomers were formed



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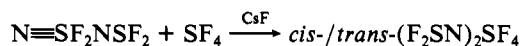


There are few reactions known that result in the formation of both *cis* and *trans* isomers of the sulfur(VI) derivative. Oxidative-addition reactions of chlorine fluoride with bis(perfluoroalkyl)sulfides resulted in formation of mixtures of *cis*- and *trans*-tetrafluorobis(perfluoroalkyl)sulfur isomer with the *trans* isomer predominant,¹⁴ viz.

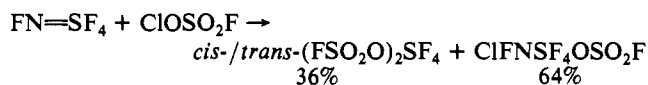


In contrast, alkyl perfluoroalkyl sulfides and $\text{CF}_3\text{SCH}_2\text{SCF}_3$ form only *trans* isomers under the same conditions. These results are identical with those for the unsymmetrically substituted R_fSCI moieties where one substituent, in this case chlorine, does not contain fluorine but is highly electron withdrawing.

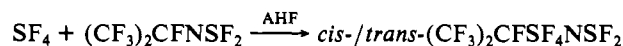
A *cis*/*trans* isomeric mixture formed in a ratio of 1:3 when sulfur tetrafluoride was reacted with (difluoronitridothio)imidodisulfurous difluoride in the presence of CsF .¹⁶



The addition of chlorine fluorosulfate to (fluoroimido)tetrafluorosulfur led to a mixture that contained *cis*-/*trans*-(FSO_2O)₂ SF_4 (1:1.4 ratio) and only *cis*- $\text{ClFNSF}_4\text{OSO}_2\text{F}$.¹⁷



However, there is only a limited number of examples in the literature where the *cis* and *trans* isomers have been separated, e.g., in the case of $(\text{CF}_3)_2\text{CFSF}_4\text{NSF}_2$.¹⁸ In anhydrous hydrogen fluoride (AHF), sulfur tetrafluoride was reacted with (pentafluoroisopropyl)imidodisulfurous difluoride to give an isomeric mixture



which was separated by gas chromatography. The presence and relative quantities of the *cis* and *trans* isomers have been often determined by nuclear magnetic resonance measurements on mixtures. However, in a particularly nice piece of work, Martin and Michalak¹⁹ were able to oxidatively fluorinate a stable sulfuran with two bidentate ligands to the *trans*- and *cis*-difluoro-dialkoxydiarylsulfur(VI) isomers with bromine trifluoride in varying amounts. If the BrF_3 :sulfurane ratio was equal to 0.67, the *trans* isomer was obtained, and if the ratio was greater than 0.67, the *cis* isomer resulted. The structures of these crystalline compounds were determined by X-ray analysis. In addition, thermodynamic studies indicate that the *cis* form is energetically slightly more favored at 25 °C, with acid-catalyzed isomerization of *trans* to *cis* occurring via a dissociative mechanism.

We now wish to report the preparation and characterization of the *cis* and *trans* isomers of tetrafluorobis(polyfluoroalkoxy)-

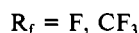
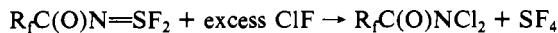
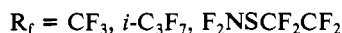
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sulfur as well as the preparation and characterization of their acyclic and cyclic bis(polyfluoroalkyl) (trifluoromethyl)imidosulfite precursors.

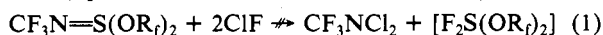
Results and Discussion

Earlier in these laboratories, a powerful route to the synthesis of dichloro(perfluoroalkyl)amines and dichloro(perfluoroalkyl)amides, R_fNCl_2 and $R_fC(O)NCl_2$, was discovered when the appropriate imidosulfurous difluorides were reacted with chlorine fluoride:²⁰

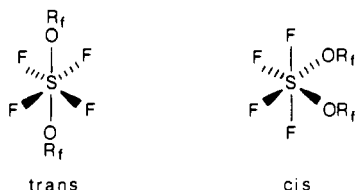
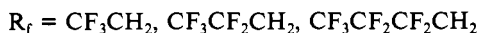
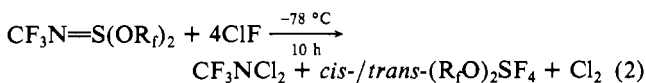


The reaction chemistry of imidosulfurous difluorides has been widely investigated particularly with respect to metathetical reactions where nucleophiles displace the sulfur-fluorine bond to form S-substituted sulfur(IV) imides.²¹

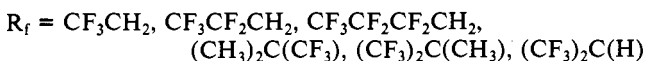
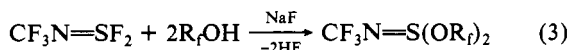
In an attempt to determine the effect that less electronegative substituents on sulfur (other than fluorine) would have on the products formed when $R_fN=SX_2$ ($X \neq F$) was reacted with chlorine fluoride, we synthesized a variety of bis(polyfluoroalkyl) (trifluoromethyl)imidosulfites. Regardless of what stoichiometry was used and although dichloro(trifluoromethyl)amine, CF_3NCl_2 , was always generated, it was not possible to isolate a sulfur(IV) derivative (eq 1). Rather, chlorine fluoride oxidatively fluorinated



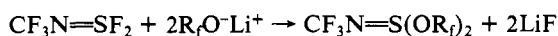
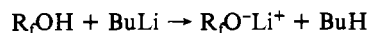
sulfur(IV) to a new family of *cis*-/*trans*-sulfur hexafluoride derivatives in essentially the same ratio of *cis*:*trans* isomers (eq 2).



Bis(polyfluoroalkyl) (trifluoromethyl)imidosulfites were prepared from the reaction of (trifluoromethyl)imidosulfurous difluoride and polyfluorinated alcohols in the presence of sodium fluoride as the base (eq 3). However, these reactions were very



slow (~ 7 days) and the resulting yields were rather low for *tert*-butyl and isopropyl alcohols. A superior method was to use butyllithium to preform the lithium salt of the fluorinated alcohol, which was then reacted with (trifluoromethyl)imidosulfurous difluoride:



The (trifluoromethyl)imidosulfites formed were thermally and hydrolytically stable colorless liquids of low volatility (vapor pressure at room temperature was less than 60 torr).

While the ^{19}F NMR spectrum of $CF_3N=SF_2$ does show coupling between the fluorine atoms bonded to sulfur and the tri-

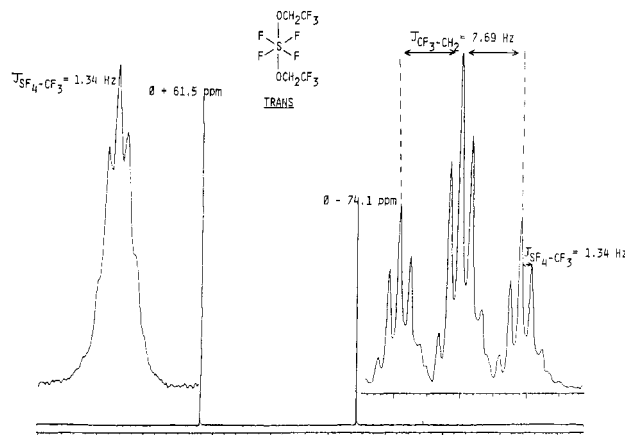
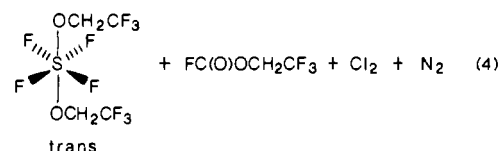
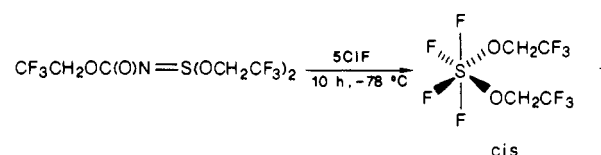


Figure 1. ^{19}F NMR spectrum of *trans*- $F_4S(OCH_2CF_3)_2$.

fluoromethyl group ($J_{CF_3-SF_2} \approx 11$ Hz), coupling is not observed between the trifluoromethyl group bonded to the nitrogen and the OR_f group in the imidosulfite. A resonance band that is a singlet falling between $\phi -42$ and -48 in the ^{19}F NMR spectrum is characteristic of these compounds. The infrared spectra of organoimidosulfurous difluorides show a strong absorption band due to the $N=S$ stretching vibration between 1400 and 1350 cm^{-1} .²² While there are no molecular ion peaks in the mass spectra of the imidosulfites, fragments due to the loss of fluorine, trifluoromethyl, and polyfluoroalkoxy fragments are observed, i.e., $M^+ - F$, $M^+ - R_f$, $M^+ - OR_f$.

The addition of chlorine fluoride to the (trifluoromethyl)imidosulfites, where the R_fO group is a primary polyfluoroalkyl chain, gave *cis* and *trans* isomeric mixtures (eq 2). Similarly, (fluorocarbonyl)imidosulfurous difluoride, when reacted with 2,2,2-trifluoroethanol in the presence of NaF as the base, gave bis(2,2,2-trifluoroethyl) [(2,2,2-trifluoroethoxy)carbonyl]imidosulfite in high yield as a stable colorless involatile liquid (eq 4). On



treatment with ClF, the *cis* and *trans* sulfur(VI) compounds were obtained, with concomitant loss of nitrogen, chlorine, and 1,1,1-trifluoroethyl carbonfluoride. In both cases the yield ($\sim 70\%$) as well as the ratio of the *cis*:*trans* isomers was approximately the same. When the number of equivalents of chlorine fluoride was reduced, the same products, in the same ratios, were obtained in addition to unreacted imidosulfite.

After an initial trap-to-trap distillation, the *cis* and *trans* isomers were easily separated by gas chromatography. Each isomer was then characterized independently; e.g., for the case of $F_4S(OC_2H_4CF_3)_2$, in the ^{19}F NMR spectrum of the *trans* isomer (Figure 1) the expected triplet of pentets at $\phi -74$ due to coupling of the CF_3 groups with the CH_2 groups and with the four equivalent equatorial fluorine atoms bonded to sulfur was observed. The sulfur-fluorine resonance at $\phi 61.5$ is an incompletely resolved septet arising from coupling with the CF_3 groups. No $SF-CH_2$ coupling was observed. In contrast, the ^{19}F NMR spectrum of

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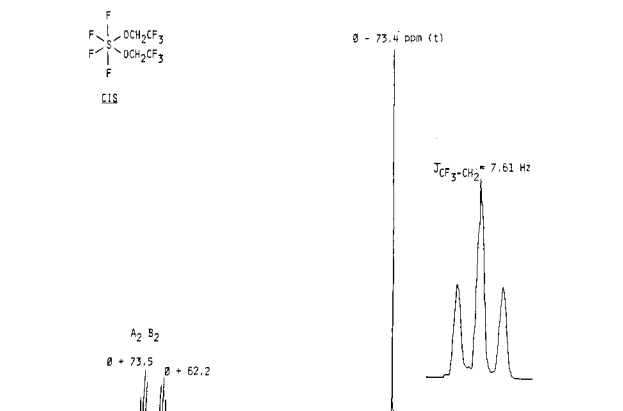


Figure 2. ^{19}F NMR spectrum of *cis*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$.

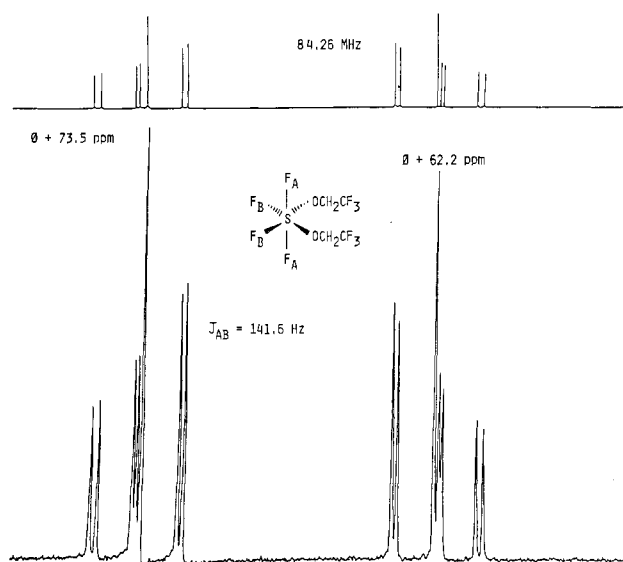


Figure 3. Experimental (bottom) and computer-simulated (top) A_2B_2 patterns for *cis*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$ at 84.26 MHz.

the *cis* isomer (Figure 2) has a triplet for $\text{CF}_3\text{-CH}_2$ coupling at $\phi - 73.4$ only. No $\text{CF}_3\text{-SF}$ coupling was observed. The equatorial and axial fluorine resonances comprise an A_2B_2 pattern centered at $\phi 73.5$ and 62.2 .²³ The $J_{\text{FA}-\text{FB}}$ value was calculated to be 141.6 Hz. To confirm this, an computer-simulated NMR spectrum was obtained (Figure 3) and was found to agree. Some subtle changes were observed in the A_2B_2 pattern (Figure 4) when a higher field (188 MHz) instrument was used to measure the spectrum. As expected, some of the lines are now closer together. In addition, some very small couplings are seen. This may be due to a SF-CH_2 interaction.

None of the Cl^+ mass spectra of the *cis* and *trans* isomers of the $\text{F}_4\text{S}(\text{OR})_2$ compounds contained a molecular ion, but all had intense fragments due to the loss of HF or of a polyfluoroalkoxy group. Interestingly the Cl^- mass spectra show SF_4^- , SF_3^- , SF_2^- , and R_fO^- fragments, presumably due to the ability of sulfur and oxygen in their electron-deficient environments to hold the negative charge.

Despite the difference in symmetry of the *cis* and *trans* isomers, the infrared spectra did not show any marked differences. This was also the case for *cis*- and *trans*- $(\text{CF}_3)_2\text{CFSF}_4\text{N}=\text{SF}_2$.¹⁸

All of these sulfur(VI) compounds are colorless liquids of low volatility. They are thermally and hydrolytically stable. A preliminary investigation into the reactions of a *cis*:*trans* mixture of $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$ showed that they are unreactive with a variety of nucleophiles. On the basis of NMR analyses, there was no

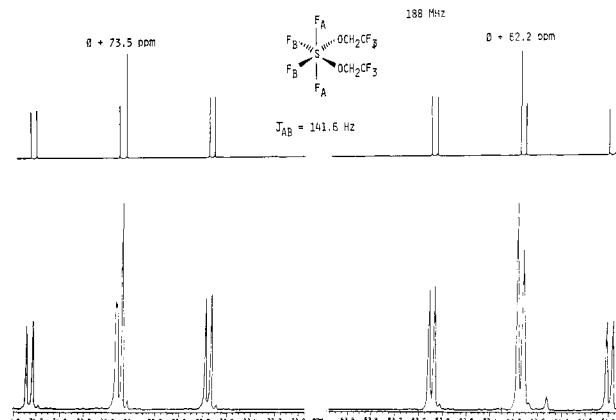
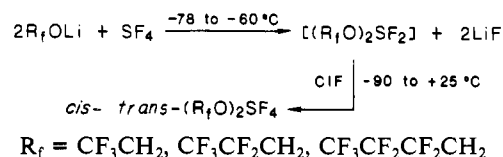


Figure 4. Experimental (bottom) and computer-simulated (top) A_2B_2 patterns for *cis*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$ at 188 MHz.

evidence that the *cis* and *trans* isomers were interconvertible after being allowed to remain at room temperature in Pyrex glass for a number of months. This agrees with the observation for the isomers of $(\text{CF}_3)_2\text{CFSF}_4\text{N}=\text{SF}_2$. However, in the case of the *cis*/*trans* mixture of $(\text{CF}_3)_2\text{SF}_4$ in Freon 11, there was a slow (over a period of 2 years) conversion from an initial *cis*:*trans* ratio of 1:1.6 to 1:1.

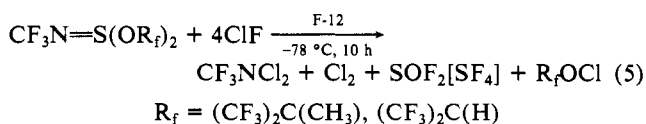
The mechanism of the reaction is uncertain. However, recent work in these laboratories has been able to demonstrate that an intermediate such as $(\text{R}_f\text{O})_2\text{SF}_2$ was likely since



With only one exception in these sulfur(VI) tetrafluorosulfanes, $(\text{CF}_3)_2\text{CFSF}_4\text{NSF}_2$,¹⁸ when isomeric product mixtures were formed, the *trans* isomer was predominant, i.e., $(\text{CF}_3)_2\text{SF}_4$,¹⁴ $(\text{NSF}_2)_2\text{SF}_4$,¹⁶ and $(\text{FSO}_2\text{O})_2\text{SF}_4$.¹⁷ In an earlier study in an effort to understand the formation of both *cis*- and *trans*- $(\text{CF}_3)_2\text{SF}_4$ when chlorine fluoride was reacted with $(\text{CF}_3)_2\text{S}$, we also reacted chlorine fluoride with the supposed intermediate, $(\text{CF}_3)_2\text{SF}_2$.¹⁵ Although the yield of products was reduced, the ratio of the *cis* and *trans* isomers of $(\text{CF}_3)_2\text{SF}_4$ was essentially identical with that obtained from the bis(trifluoromethyl) sulfide regardless of the reaction temperature (-78 vs. $+25^\circ\text{C}$) or the stoichiometry used. However, when our efforts were extended to the system R_fSR ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{Cl}$) where a *trans*-only product was always obtained from $\text{R}_f\text{SR} + \text{ClF}$, we were unable to stabilize the proposed intermediate $\text{R}_f\text{SF}_2\text{R}$ in order to study its reaction with chlorine fluoride.

In the case of bis(2,2,2-trifluoroethyl)[(2,2,2-trifluoroethoxy)-carbonyl]sulfite the mechanism would be analogous, but the $\text{CF}_3\text{CH}_2\text{OC}(\text{O})\text{NCl}_2$ that formed would react further with ClF to give $\text{FC}(\text{O})\text{OCH}_2\text{CF}_3$ and NCl_3 . The latter decomposed to nitrogen and chlorine (eq 4). When CsF was used in the reaction, no sulfur(VI) isomers and only decomposition products, SF_5Cl , $(\text{CF}_3\text{CH}_2\text{O})_2\text{CO}$, $\text{FC}(\text{O})\text{OCH}_2\text{CF}_3$, N_2 , Cl_2 , and others, were found.

The action of ClF on 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol and 1,1,1,3,3,3-hexafluoro-2-propanol imidosulfite derivatives resulted in cleavage of the sulfur-oxygen bonds in addition to the nitrogen-sulfur bond, even when the reaction was carried out at low temperature in the presence of Freon 12 (F-12) as a solvent and heat sink (eq 5). The resulting hypochlorites are known



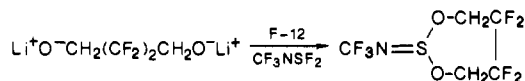
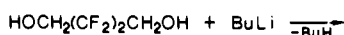
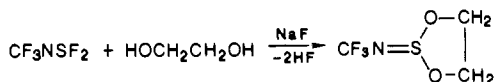
compounds.²⁴ In the case of the 1,1,1-trifluoro-2-propanol im-

(23) Emsley, J. W.; Feeney, J.; Sutcliffe, L. H. *High Resolution Nuclear Magnetic Resonance Spectroscopy*; Pergamon: Oxford, England, 1965; Vol. 1, p 347.

idosulfite derivative, $\text{CF}_3\text{N}=\text{S}[\text{OC}(\text{CH}_3)_2\text{CF}_3]_2$, decomposition products (CF_3NCl_2 , Cl_2 , SOF_2) were seen in addition to an unidentified material whose ^{19}F NMR spectrum indicated that ClF attack had occurred on the methyl group. Again, in this case, when the lithiated branched alcohol is reacted first with SF_4 at low temperature and then with ClF , identical products are formed (eq 5).

Considering the range of electronic effects of the secondary and tertiary alcohol imidosulfite derivatives used, the marked change in behavior when they were reacted with chlorine fluoride can not be explained on the basis of the electronegativity of the R_fO group. There is no reason to expect a different mode of attack by ClF . Thus, the sulfur-oxygen bond must be weakened because of steric requirements of the bulky tertiary and secondary substituents, requirements which facilitate formation of sulfur-fluorine bonds and the polyfluoroalkyl hypochlorites.

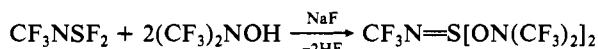
Since we also wished to study the action of chlorine fluoride on cyclic imidosulfite systems, ethylene glycol and 2,2,3,3-tetrafluoro-1,4-butanediol were reacted with (trifluoromethyl)imidosulfurous difluoride according to the equations



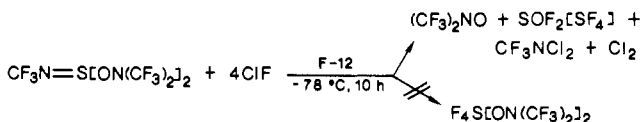
Since the latter reaction was very vigorous, Freon 12 was used as a diluent.

Chlorine fluoride addition to $\text{CF}_3\text{N}=\text{SOCH}_2\text{CH}_2\text{O}$ and $\text{CF}_3\text{N}=\text{SOCH}_2(\text{CF}_2)_2\text{CH}_2\text{O}$ did not give the sulfur(VI) derivatives, $\text{F}_4\text{SOCH}_2\text{CH}_2\text{O}$ and $\text{F}_4\text{SOCH}_2(\text{CF}_2)_2\text{CH}_2\text{O}$. Even at low temperatures, in the presence of a solvent, the ^{19}F NMR spectra indicated that the compounds that may have been formed initially were decomposed by ring opening to give an SF_5X type of compound. It was not possible to purify and characterize the products.

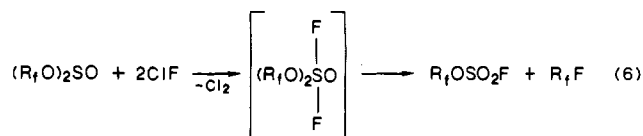
An attempt was made to react bis(trifluoromethyl)hydroxylamine²⁵ with $\text{CF}_3\text{N}=\text{SF}_2$ to give the (trifluoromethyl)imidosulfite derivative as a colorless liquid:



It was not possible to obtain this compound pure, and at room temperature it decomposed to give the characteristic purple bis(trifluoromethyl)nitroxide radical, $(\text{CF}_3)_2\text{NO}^\bullet$.²⁶ Thus, it was not surprising when, upon ClF addition even at -78°C in the presence of Freon 12, decomposition products were observed rather than a sulfur(VI) derivative:



It is particularly interesting to compare the relative reaction behavior of bis(polyfluoroalkyl) sulfites and that of the isoelectronic (trifluoromethyl)imidosulfites with chlorine fluoride. With $\text{R}_f\text{O} = \text{CF}_3\text{CH}_2\text{O}$, compare for instance the reaction of the imidosulfite (eq 2) with that of the analogous normal sulfite (eq 6). Whereas, in the case of the sulfite, the unstable sulfur(VI) intermediate undergoes a Michaelis-Arbusov rearrangement to give the corresponding fluorosulfate and polyfluoroalkyl fluoride,²⁷ for the



imidosulfite we find severing of the weaker $\text{N}=\text{S}$ bond to form CF_3NCl_2 (relative to $\text{O}=\text{S}$) and subsequent oxidation of sulfur(IV) to sulfur(VI). Although addition of ClF across a sulfur-oxygen bond does occur in sulfur(VI) compounds in the presence of fluoride ion, e.g., $\text{SOF}_4 + \text{ClF} \rightleftharpoons \text{F}_3\text{SOCl}$,²⁸ there are no known examples where a similar reaction occurs to give a sulfur(IV) hypochlorite, e.g., $\text{OSF}_2 + \text{ClF} \rightleftharpoons \text{F}_3\text{SOCl}$. While this is ruled out for $>\text{S}=\text{O}$, addition across the highly polarized $-\text{N}=\text{S}$ bond has been demonstrated often and here is accompanied by subsequent bond breaking to form the quite stable dichloro-(trifluoromethyl)amine and an isolable intermediate, bis(polyfluoroalkoxy)sulfur difluoride, whose existence is supported by the formation of the stable tetrafluorobis(polyfluoroalkoxy)sulfur as an isolable final product.

Experimental Section

Materials. The alcohols were used as received from commercial suppliers. Sources were as follows: $\text{CF}_3\text{CH}_2\text{OH}$ and $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ from Aldrich; $(\text{CF}_3)_2\text{CHOH}$, $(\text{CF}_3)_2\text{CH}_2\text{COH}$, and $\text{CF}_3(\text{CH}_2)\text{CHOH}$ from PCR; $\text{CF}_3\text{CF}_2\text{CH}_2\text{OH}$ from Fairfield; $\text{HOCH}_2\text{CH}_2\text{OH}$ from Baker; $\text{HOCH}_2\text{CF}_2\text{CF}_2\text{CH}_2\text{OH}$ from 3M. (Trifluoromethyl)imidosulfurous difluoride was prepared from cyanuric fluoride and sulfur tetrafluoride in the presence of CsF .²⁹ The literature method was used to prepare $\text{FC}(\text{O})\text{NSF}_2$.³⁰ Other materials were as follows: cyanuric fluoride from Pflatz and Bauer; chlorine fluoride from Ozark Mahoning; butyllithium from Aldrich. All were used as received. Cesium fluoride (Aldrich) and sodium fluoride (Baker) were dried at 160°C for 2 days and finely powdered prior to use.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex glass vacuum system equipped with a Heise Bourdon tube gauge and a Televac thermocouple gauge. Most of the starting materials and products were measured quantitatively by using PVT techniques. Products were separated by fractional condensation (trap-to-trap distillation).

Final purification of the imidosulfites and of the sulfur(VI) isomers was achieved on a Hewlett-Packard 5710A gas chromatograph. Chromosorb P was used as the packing material, and all columns were constructed from $1/4$ in. o.d. copper tubing.

Infrared spectra were recorded with a Perkin-Elmer 599 or a 1710 infrared Fourier transform spectrometer by using a 10-cm cell equipped with KBr windows or a KBr liquid-film cell. UV data were obtained on a Varian Cary 2200 spectrometer equipped with cells of 1 cm path length. ^{19}F and ^1H NMR spectra were measured on either a JEOL FX-90Q Fourier transform spectrometer operating at 84.26 MHz or a Varian EM-360L spectrometer operating at 54.6 MHz by using CDCl_3 and/or CFCl_3 as a solvent and CFCl_3 as an internal or external reference. Chemical shifts upfield of the reference are assigned negative values. Mass spectra were recorded with a VG 7070HS mass spectrometer. Methane was the ionizing gas used for chemical ionization. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany.

Slush baths were made as follows: -98°C , methanol/liquid N_2 ; -78°C , ethanol/dry ice; -40°C , 4:3 ratio of ethanol to water (by volume)/liquid N_2 .

General Method for the Preparation of (Trifluoromethyl)imidosulfites. To a dry 500 mL Pyrex round-bottomed flask, equipped with a Kontes Teflon stopcock, 19 mL (~ 30.4 mmol) of 1.6 M BuLi in hexane was added under an inert atmosphere. The vessel was evacuated at -196°C , and a slight excess (~ 33 mmol) of the alcohol was condensed into the flask. It was allowed to warm to room temperature and left for several hours. All the volatile materials (hexane, butane, unreacted alcohol) were removed under vacuum to leave behind the white $\text{R}_f\text{O}^- \text{Li}^+$. Into the flask at -196°C was then condensed 15 mmol of CF_3NSF_2 . It was allowed to warm slowly to room temperature over a 2-h period. After 1 day the mixture was separated by trap-to-trap distillation. The imidosulfite was

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left in the trap at -40°C . Final purification of the liquid was accomplished by gas chromatography, but this was not necessary for further reactions. Yields are based upon the amount of CF_3NSF_2 consumed. Generally a small amount of this compound was found in the trap at -98°C .

Properties of $\text{CF}_3\text{N}=\text{S}(\text{OCH}_2\text{CF}_3)_2$. The colorless liquid was obtained in $>97\%$ yield. Further purification could be achieved on a 2-m QF-1 gas chromatographic column at 120°C . The gas-phase infrared spectrum showed bands at 2976 (m), 1757 (m), 1452 (s), 1410 (vs), 1275 (br, vs), 1171 (br, vs), 1011 (vs), 962 (vs), 854 (s), 741 (br, s), 688 (s), 651 (s), 552 (m), 505 (w), and 470 (w) cm^{-1} . ^{19}F NMR spectrum: $\phi -42.3$ (s) (CF_3N), -72.3 (t) (CF_3). ^1H NMR: δ 4.43 (q), 4.39 (q) ($J_{\text{CF}_3-\text{CH}_2} = 7.8$ Hz). The EI⁺ mass spectrum at 70 eV did not have a molecular ion, but an appropriate fragmentation pattern was observed: m/e 294 ($\text{M}^+ - \text{F}$) 5.1%, 214 ($\text{M}^+ - \text{OCH}_2\text{CF}_3$) 64.5%, 147 ($\text{CF}_3\text{NSO}_2^+$) 21.2%, 115 (CF_3NS^+) 10.2%, 83 (CF_3CH_2^+) 100%, 69 (CF_3^+) 33.9%, 46 (NS^+) 18.1%. Anal. Calcd for $\text{C}_5\text{F}_9\text{H}_4\text{NO}_2\text{S}$: C, 19.24; F, 54.8; H, 1.29. Found: C, 19.28; F, 54.1; H, 1.76.

Properties of $\text{CF}_3\text{N}=\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$. The compound was obtained in $>90\%$ yield as a colorless liquid. Final purification was obtained by gas chromatography on a 2-m QF-1 column at 100°C . The infrared spectrum (liquid film) had bands at 2970 (m), 1460 (m), 1360 (s), 1310 (vs), 1210 (br, vs), 1165 (s), 1110 (s), 1000 (br, ms), 963 (m), 940 (m), 810 (m), 740 (m), 627 (m), and 535 (w) cm^{-1} . ^{19}F NMR spectrum: $\phi -42.7$ (s) (CF_3N), -82.4 (s) (CF_3), -122 (t) (CF_2). The ^1H NMR spectrum showed two overlapping triplets at δ 4.51 and 4.43 due to overlapping of the two triplets arising from the inequivalent protons ($J_{\text{CF}_2-\text{CH}_2} = 12.5$ Hz). The EI mass spectrum at 70 eV did not show a molecular ion, but appropriate fragments seen were as follows: m/e 394 ($\text{M}^+ - \text{F}$) 8.7%, 264 ($\text{M}^+ - \text{OCH}_2\text{CF}_2\text{CF}_3$) 100%, 133 ($\text{C}_3\text{F}_5\text{H}_2^+$) 54%, 132 ($\text{C}_3\text{F}_5\text{H}^+$) 9%, 119 (C_2F_3^+) 3.9%, 115 (CF_3NS^+) 9.5%, 112 (C_3F_4^+) 23%, 100 (C_2F_4^+) 2.6%, 69 (CF_3^+) 68.1%, 64 (SO_2^+) 6.8%, and 46 (NS^+) 14.4%. Anal. Calcd for $\text{C}_7\text{F}_{13}\text{H}_4\text{NO}_2\text{S}$: C, 20.35; F, 59.77; H, 0.97; S, 7.76. Found: C, 20.65; F, 60.1; H, 0.99; S, 7.85.

Properties of $\text{CF}_3\text{N}=\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3)_2$. The compound was obtained in $>90\%$ yield as a colorless liquid. Final purification could be achieved by gas chromatography on a heated 12-ft QF-1 column. The infrared spectrum (liquid film) had bands at 2975 (w), 1460 (m), 1400 (m), 1365 (s), 1310 (vs), 1240 (br, vs), 1140 (br, vs), 1015 (s), 970 (s), 920 (s), 800 (s), 755 (s), 680 (ms), and 545 (m) cm^{-1} . ^{19}F NMR spectrum: $\phi -45.7$ (s) (CF_3N), -82.6 (t) (CF_2), ($J_{\text{CF}_3-\text{CF}_2} = 9$ Hz as shown by resonance decoupling), -121.7 (mult) (CF_2), -129.0 (br, s) (CF_2). The ^1H NMR spectrum had a multiplet of ~ 8 lines at δ 4.5, due to coupling with CF_2 and the inequivalent methylene protons. The EI mass spectrum at 70 eV did not show a molecular ion, but an appropriate fragmentation pattern was observed: m/e 494 ($\text{M}^+ - \text{F}$) 8.6%, 314 ($\text{M}^+ - \text{OCH}_2\text{CF}_2\text{CF}_2\text{CF}_3$) 100%, 183 ($\text{CH}_2\text{CF}_2\text{CF}_2\text{CF}_3^+$) 10.7%, 169 (C_3F_7^+) 1.7%, 119 (C_2F_3^+) 13.0%, 115 (CF_3NS^+) 11.0%, 113 ($\text{C}_3\text{F}_4\text{H}^+$) 71.3%, 112 (C_3F_4) 20.0%, 83 (CF_3N^+) 3.3%, 69 (CF_3^+) 65.1%, 64 (SO_2^+) 7.2%. Anal. Calcd for $\text{C}_9\text{F}_{17}\text{H}_4\text{NO}_2\text{S}$: C, 21.07; F, 62.9; H, 0.78; S, 6.24. Found: C, 20.83; F, 63.8; H, 0.95; S, 6.57.

Properties of $\text{CF}_3\text{N}=\text{S}[\text{OC}(\text{CF}_3)_2\text{CH}_3]_2$. The colorless liquid was obtained in $\sim 48\%$ yield. Final purification could be done by gas chromatography on a 2-m QF-1 column at 90°C . The infrared spectrum (liquid film) showed bands at 2980 (w), 1465 (m), 1350 (vs), 1310 (vs), 1230 (vs), 1160 (vs), 1120 (vs), 1090 (vs), 940 (m), 885 (vw), 915 (m), 790 (m), 750 (m), 715 (m), 680 (m), 640 (w), 550 (vw), and 500 (vw) cm^{-1} . The ^{19}F NMR spectrum had a singlet at $\phi -48.3$ for the CF_3N group and a quartet at $\phi -79.1$ for the isopropyl CF_3 group. The ^1H NMR spectrum had a septet at δ 1.96 ($J_{\text{CF}_3-\text{CH}_3} = 0.98$ Hz). The EI mass spectrum at 70 eV did not show a molecular ion, but an appropriate fragmentation pattern was seen: m/e 296 ($\text{M}^+ - \text{OC}(\text{CF}_3)_2\text{CH}_3$) 1.2%, 134 ($\text{C}_4\text{F}_2\text{SO}^+$) 100%, 115 (CF_3NS^+) 4.1%, 69 (CF_3^+) 44.8%, 46 (NS^+) 42.6%. Anal. Calcd for $\text{C}_9\text{F}_{15}\text{H}_6\text{NO}_2\text{S}$: C, 22.65; F, 59.7; H, 1.26. Found: C, 20.91; F, 60.8; H, 1.27.

Properties of $\text{CF}_3\text{N}=\text{S}[\text{OC}(\text{CF}_3)(\text{CH}_3)]_2$. The colorless liquid was found in the trap at -40°C in $\sim 60\%$ yield. Absolute purification could be achieved by gas chromatography on a 2-m QF-1 column at 90°C . The infrared spectrum (liquid film) showed bands at 3000 (m), 2980 (w), 1480 (s), 1455 (m, sh), 1410 (s), 1330 (br, vs), 1150 (br, vs), 1010 (m), 954 (s), 877 (vs), 806 (s), 784 (s), 745 (s), 686 (s), 665 (s), 632 (s), 597 (w), 577 (w), 549 (m), 506 (m), and 476 (w) cm^{-1} . The ^{19}F NMR spectrum had a singlet at $\phi -44.3$ for the CF_3N group and a septet at $\phi -81.4$ for the other CF_3 group. The ^1H NMR spectrum had a quartet at δ 1.7 ($J_{\text{CF}_3-\text{CH}_3} = 1.02$ Hz). The EI⁺ mass spectrum showed a $\text{M}^+ + 1$ peak at m/e 370 (1.3%). Other fragments observed were as follows: m/e 350 ($\text{M}^+ - \text{F}$) 3.6%, 258 ($\text{M}^+ - (\text{CF}_3)(\text{CH}_3)_2$) 12%, 242 ($\text{M}^+ - \text{OC}(\text{CF}_3)(\text{CH}_3)_2$) 1.9%, 131 (CF_3NSO^+) 1.2%, 115 (CF_3NS^+) 3.1%, 111 ($\text{C}_4\text{F}_3\text{H}_6^+$) 21%, 92 ($\text{C}_4\text{F}_2\text{H}_6^+$) 5.8%, 91 ($\text{C}_4\text{F}_2\text{H}_5^+$) 100%, 69 (CF_3^+) 9.6%.

Properties of $\text{CF}_3\text{N}=\text{S}[\text{OC}(\text{CF}_3)_2\text{H}]_2$. The colorless liquid was obtained in approximately 60% yield. Final purification was achieved by gas chromatography on a 2-m QF-1 column at 70°C . The infrared spectrum (liquid film) showed bands at 2956 (w), 1371 (s), 1291 (vs), 1237 (vs), 1206 (vs), 1153 (s), 1113 (vs), 1071 (s), 1053 (ms), 1033 (s), 907 (m), 880 (s), 806 (m), 768 (m), 689 (s), 631 (w), 588 (w), 537 (w), and 474 (w) cm^{-1} . The ^{19}F NMR spectrum had a singlet at $\phi -46.8$ for the CF_3N group and a doublet at $\phi -74$ for the other CF_3 . The ^1H NMR spectrum had a septet at δ 5.0 ($J_{\text{CF}_3-\text{H}} = 5.3$ Hz). The EI⁺ mass spectrum showed a molecular ion at m/e 449 (5.5%). Intense fragments were seen at m/e 429 ($\text{M}^+ - \text{HF}$) 24.8%, 282 ($\text{M}^+ - \text{OC}(\text{CF}_3)_2\text{H}$) 12.8%, 281 ($\text{M}^+ - \text{OC}(\text{CF}_3)_2$) 63%, 263 ($\text{C}_4\text{F}_8\text{HNSO}^+$) 9.5%, 262 ($\text{C}_4\text{F}_8\text{NSO}^+$) 5.7%, 214 ($\text{C}_2\text{F}_6\text{SO}_2^+$) 8.9%, 150 (C_3F_6) 13.4%, 147 ($\text{CF}_3\text{NSO}_2^+$) 18.8%, 131 (CF_3NSO^+) 19.8%, 115 (CF_3NS^+) 33%, 97 ($\text{C}_2\text{F}_5\text{O}^+$) 23.3%, and 69 (CF_3^+) 100%. Anal. Calcd for $\text{C}_7\text{F}_{15}\text{H}_2\text{NO}_2\text{S}$: C, 18.72; F, 63.5; H, 0.45; S, 7.12. Found: C, 18.84; F, 63.4; H, 0.54; S, 7.23.

Preparation of $\text{CF}_3\text{N}=\text{SOCH}_2\text{CH}_2\text{O}$. To a hot, dry 250-mL Pyrex round-bottomed flask equipped with a Kontes Teflon stopcock and a Teflon-coated stirring bar was added approximately 3 g of anhydrous NaF, ~ 25 mL of chloroform, and 20 mmol of ethylene glycol. The vessel was evacuated at -196°C , and 20 mmol of $\text{CF}_3\text{N}=\text{SF}_2$ was condensed into the flask. The flask was allowed to warm to room temperature, and the reaction mixture was stirred on a magnetic plate for 7–10 days. As the reaction proceeded, a yellow, then deep orange, color was observed. Trap-to-trap distillation removed all the volatile materials, leaving the orange involatile compound on the surface of the sodium fluoride. Extraction of chloroform produced the compound in $\sim 70\%$ yield.

The infrared spectrum (liquid film) had bands at 2990 (w), 2920 (vw), 1365 (vw), 1300 (s), 1125 (br, s), 1025 (ms), 920 (ms), 810 (m), 725 (m), 675 (m), 615 (w), 540 (w), and 490 (w) cm^{-1} . The ^{19}F NMR spectrum had a singlet at $\phi -43$. The ^1H NMR spectrum had two complex multiplets centered at δ 4.69 and 4.3. The UV/vis spectrum taken in CHCl_3 had a large broad band between 600 and 300 nm. The EI mass spectrum at 70 eV showed a molecular ion at m/e 175 (1.1%). Other peaks were observed at m/e 156 ($\text{M}^+ - \text{F}$) 4%, 131 (CF_3NSO^+) 1.4%, 118 ($\text{C}_3\text{H}_4\text{NSO}_2^+$) 6.9%, 115 (CF_3NS^+) 100%, 112 (CF_2NSO^+) 60%, 92 ($\text{C}_2\text{H}_4\text{SO}_2^+$) 2.7%, 69 (CF_3^+) 64%, 64 (SO_2^+) 5.5%, 48 (SO^+) 12.3%, 46 (NS^+) 48.3%, 44 ($\text{C}_2\text{H}_4\text{O}^+$) 33.6%, and 43 ($\text{C}_2\text{H}_3\text{O}^+$) 47.5%. Anal. Calcd for $\text{C}_3\text{F}_7\text{H}_4\text{NO}_2\text{S}$: C, 20.57; F, 32.5; S, 18.31; H, 2.3. Found: C, 21.5; F, 31.5; S, 17.66; H, 2.5.

Preparation of $\text{CF}_3\text{N}=\text{SOCH}_2(\text{CF}_2)_2\text{CH}_2\text{O}$. To a dry 500-mL Pyrex round-bottomed flask equipped with a Kontes Teflon stopcock and a Teflon-coated stirring bar was added 9 mL (~ 14.4 mmol) of 1.6 M BuLi in hexane under an inert atmosphere. The flask was held at 0°C while a solution of 2.13 g (13.1 mmol) of $\text{HOCH}_2(\text{CF}_2)_2\text{CH}_2\text{OH}$ dissolved in ~ 30 mL of ether was added slowly while being stirred continuously on a magnetic plate. The reaction mixture was allowed to come to room temperature and was stirred for ~ 4 h. All the volatile materials were then removed under vacuum to leave the $\text{Li}^+\text{O}^-\text{CH}_2(\text{CF}_2)_2\text{CH}_2\text{O}^-\text{Li}^+$ salt. The flask was held at -196°C while 20 mmol of Freon-12 (CCl_2F_2) was condensed into the flask to serve as a heat sink and diluent followed by 13.3 mmol of $\text{CF}_3\text{N}=\text{SF}_2$. The reaction mixture was allowed to warm slowly to room temperature over a 2-h period. After 1 day the mixture

was separated by trap-to-trap distillation. $\text{CF}_3\text{N}=\text{SOCH}_2(\text{CF}_2)_2\text{CH}_2\text{O}$ was found as a colorless liquid in $\sim 33\%$ yield in the trap at -40°C .

The infrared spectrum (liquid film) had bands at 3030 (vs), 2975 (m), 2898 (vw), 1455 (s), 1390 (s), 1310 (br, s), 1245 (s), 1220 (s), 1150 (vbr, vs), 1032 (vs), 937 (vs), 845 (s), 810 (s), 772 (s), 730 (s), 687 (s), 670 (s), 583 (m), 555 (m), and 542 (m) cm^{-1} . The ^{19}F NMR spectrum had a singlet at $\phi -44.4$ and two complex multiplets centered at $\phi -128.6$ and -129.0 . The area ratios are 3:2:2. The ^1H NMR spectrum had two complex multiplets centered at δ 4.71 and 4.23. The UV/vis spectrum taken in CH_3CN had a large broad band between 350 and 200 nm. The EI mass spectrum at 70 eV had a molecular ion at m/e 275 (1.1%). Other fragments observed were m/e 256 ($\text{M}^+ - \text{F}$) 11.8%, 245 ($\text{M}^+ - \text{OCH}_2$) 22%, 143 ($\text{C}_4\text{F}_8\text{H}_3\text{O}^+$) 28%, 115 (CF_3NS^+) 78.1, 114 ($\text{C}_3\text{F}_4\text{H}_2^+$) 33%, 113 ($\text{C}_3\text{F}_4\text{H}^+$) 66.8%, 83 (CF_3N^+) 8.9%, 69 (CF_3^+) 31%, 64 (SO_2^+) 100%, 48 (SO^+) 10.8%, and 46 (NS^+) 31.3%. Anal. Calcd for $\text{C}_7\text{F}_9\text{H}_4\text{NO}_2\text{S}$: C, 21.82; F, 48.4; S, 11.63; H, 1.45. Found: C, 23.8; F, 48.8; S, 10.99; H, 1.61.

Preparation of $(\text{CF}_3\text{CH}_2\text{O})_2\text{S}=\text{NC}(\text{O})\text{OCH}_2\text{CF}_3$. To a hot, dry 500-mL round-bottomed Pyrex glass flask equipped with a Kontes Teflon stopcock and a Teflon-coated stirring bar was added about 6 g of powdered anhydrous NaF. When the flask was evacuated, 64.5 mmol of 2,2,2-trifluoroethanol and 20 mmol of (fluorocarbonyl)imidodisulfur difluoride were condensed into it at -196°C . The flask was allowed to warm to room temperature, and the reaction mixture was stirred on a magnetic plate for about 5 days. All volatile materials were removed

under vacuum. Dry chloroform was added to the flask containing the NaF and $(\text{CF}_3\text{CH}_2\text{O})_2\text{S}=\text{NC}(\text{O})\text{OCH}_2\text{CF}_3$, and the mixture was filtered several times to remove the NaF. The chloroform was removed on a rotary evaporator, leaving a 77% yield of the colorless, involatile, liquid compound. The infrared spectrum (liquid film) had bands at 2998 (m), 1740 (s), 1695 (s), 1458 (m), 1414 (s), 1290 (vs), 1260 (vs), 1120 (m), 1015 (vs), 974 (m), 860 (m), 795 (s), and 665 (m) cm^{-1} . The ^{19}F NMR spectrum had two triplets at δ -73.4 ($J_{\text{CF}_3-\text{CH}_2} = 7.81$ Hz) and -73.9 ($J_{\text{CF}_3-\text{CH}_2} = 8.3$ Hz) in a 2:1 ratio. The ^1H NMR spectrum had three overlapping quartets centered at δ 4.529, 4.527, and 4.500. The EI mass spectrum at 70 eV did not have a molecular ion but did have the following peaks: m/e 352 ($\text{M}^+ - \text{F}$) 1.1%, 272 ($\text{M}^+ - \text{OCH}_2\text{CF}_3$) 48%, 173 ($\text{C}_3\text{F}_6\text{H}_4\text{NSO}_3^+$) 5.3%, 127 ($\text{C}_3\text{F}_3\text{H}_2\text{O}_2^+$) 19%, 83 (CF_3CH_2^+) 100%, 69 (CF_3^+) 5.3%, and 46 (NS^+) 16.8%. Anal. Calcd for $\text{C}_3\text{F}_9\text{H}_4\text{NO}_4\text{S}$: C, 22.64; F, 46.09; H, 1.61; S, 8.62. Found: C, 22.72; F, 46.20; H, 1.69; S, 8.54.

Reaction of $(\text{CF}_3\text{CH}_2\text{O})_2\text{S}=\text{NC}(\text{O})\text{OCH}_2\text{CF}_3$ with ClF. To a 75-mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve was added 14 mmol of $(\text{CF}_3\text{CH}_2\text{O})_2\text{S}=\text{NC}(\text{O})\text{OCH}_2\text{CF}_3$. Into the cylinder, which was cooled to -196 °C and evacuated, was condensed 60 mmol of ClF. The cylinder was placed in a slush bath at -78 °C and allowed to warm to -10 °C over 12–15 h. The cylinder was then cooled to -78 °C, and all the volatile materials were removed. These were distilled (trap to trap), as were the remaining contents of the cylinder, as it was allowed to warm to room temperature under dynamic vacuum. The trap at -40 °C contained a colorless liquid. Separation by gas chromatography on a heated (temperature programmed between 70 and 100 °C) 2-m QF-1 column gave *cis*- and *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$ in approximately 18% and 47% yields, respectively.

Reaction of $\text{CF}_3\text{N}=\text{S}(\text{OCH}_2\text{CF}_3)_2$ with ClF. Into an evacuated 75-mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve were condensed 14 mmol of $\text{CF}_3\text{N}=\text{S}(\text{OCH}_2\text{CF}_3)_2$ and 60 mmol of ClF at -196 °C. The cylinder was placed in a slush bath at -78 °C and allowed to warm to approximately -10 °C over 12 h. The cylinder was then cooled to -78 °C and all the volatile materials were removed. These were distilled under dynamic vacuum, as were the remaining contents of the cylinder, as it was allowed to warm slowly to room temperature. The trap at -40 °C contained a colorless liquid, which upon gas chromatographic separation gave an $\sim 20\%$ yield of *cis*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$ and an $\sim 50\%$ yield of *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$.

Properties of *cis*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$. The compound is a colorless liquid with a vapor pressure of ~ 30 torr at room temperature. The infrared spectrum (liquid film) had bands at 3000 (m), 1465 (w), 1420 (m), 1300 (vs), 1185 (vs), 1110 (m, sh), 1090 (s), 1070 (m, sh), 975 (s), 880 (br, vs), 615 (m), and 590 (m) cm^{-1} . The ^{19}F NMR spectrum is an A_2B_2 pattern for the fluorine atoms bonded to sulfur centered at ϕ 73.5 and 62.2 (Figure 1). The CF_3 resonance appears as a triplet at ϕ -73.4. The ^1H NMR spectrum had a quartet at δ 4.55. Coupling constants were $J_{\text{CF}_3-\text{CH}_2} = 7.6$ Hz and $J_{\text{FA}-\text{FB}} = 141.6$ Hz. The CI^+ mass spectrum did not show a molecular ion, but appropriate fragments observed were m/e 287 ($\text{M}^+ - \text{F}$) 22.9%, 207 ($\text{M}^+ - \text{OCH}_2\text{CF}_3$) 35.6%, 105 (SOF_3^+) 18.7%, 89 (SF_3^+) 6.9%, 83 (CF_3CH_2^+) 100%, 70 (SF_2^+) 1.0%, 69 (CF_3^+) 5.3%, and 64 (SO_2^+) 1.4%.

Properties of *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$. The compound is a colorless liquid with a vapor pressure of ~ 30 torr at room temperature. The infrared spectrum (liquid film) had bands at 3000 (m), 1465 (w), 1420 (m), 1300 (vs), 1185 (vs), 1100 (vs), 975 (s), 885 (vs), 850 (s, sh), 830 (vs), 690 (w), 605 (s), and 585 (vs) cm^{-1} . The ^{19}F NMR spectrum had a septet at ϕ 61.5 and a triplet of quintets at ϕ -74.1. The ^1H NMR spectrum showed a quartet at δ 4.52. Coupling constants are $J_{\text{CF}_3-\text{CH}_2} = 7.69$ Hz and $J_{\text{CF}_3-\text{SF}_4} = 1.34$ Hz. The CI^+ mass spectrum did not show a molecular ion, but appropriate fragments observed were: m/e 287 ($\text{M}^+ - \text{F}$) 63.2%, 207 ($\text{M}^+ - \text{OCH}_2\text{CF}_3$) 78.9%, 185 ($\text{C}_2\text{F}_4\text{H}_2\text{SO}_3$) 7.5%, 147 ($\text{C}_2\text{F}_3\text{H}_2\text{SO}_2^+$) 1.7%, 105 (SOF_3^+) 18.1%, 99 ($\text{CF}_3\text{CH}_2\text{O}^+$) 1.6%, 89 (SF_3^+) 4.7%, 83 (CF_3CH_2^+) 100%, 70 (SF_2^+) 1.4%, 69 (CF_3^+) 4.8%, 67 (SOF^+) 1.7%, 64 (SO_2^+) 1.5%, and 51 (SF^+) 3.4%. The CI^- mass spectrum also did not show a molecular ion, but the following fragments were observed: m/e 207 ($\text{M}^- - \text{OCH}_2\text{CF}_3$) 7.6%, 119 ($\text{SF}_3\text{OCH}_2^-$) 2%, 118 (F_3SOCH^-) 36.8%, 108 (SF_4^-) 1.7%, 105 (OSF_3^-) 8.9%, 99 ($\text{CF}_3\text{C}-\text{H}_2\text{O}^-$) 1.4%, 98 (CF_3CHO^-) 43%, 89 (SF_3^-) 86.1%, and 70 (SF_2^-) 100%.

Preparation of *cis*- and *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_3)_2$. Into a 75-mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve was placed 11 mmol of $\text{CF}_3\text{N}=\text{S}(\text{OCH}_2\text{CF}_3)_2$. When the cylinder was cooled to -196 °C and evacuated, 48 mmol of ClF was added. The cylinder was placed in a slush bath at -78 °C and held at that temperature for ~ 10 h. All the volatile materials were then removed under dynamic vacuum. These were distilled (trap to trap), as were the remaining contents of the cylinder, as it was allowed to warm to room temperature. The liquid obtained in the trap at -40 °C was shown by gas chromatography and spectroscopy to contain mainly *cis*- and *trans*-

$\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$, total yield 60% (*cis*:*trans* \approx 1:3).

Properties of the *Cis-Trans* Mixture of $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$. The *cis-trans* mixture is a colorless liquid with a vapor pressure of ~ 10 torr at 25 °C. The infrared spectrum (liquid film) of the *cis-trans* mixture had bands at 2990 (m), 1790 (w), 1470 (m), 1415 (s), 1380 (m), 1355 (s), 1310 (s), 1280 (vs), 1210 (br, vs), 1170 (vs), 1115 (vs), 1090 (s), 1040 (s), 960 (s), 880 (vs), 840 (vs), 670 (w), 650 (s), and 620 (m) cm^{-1} . The ^{19}F NMR spectrum had the A_2B_2 pattern for the fluorine atoms bonded to sulfur of the *cis* isomer centered at ϕ 73.7 and 62.5 ($J_{\text{FA}-\text{FB}} = 140.8$ Hz). The fluorine atoms bonded to sulfur of the *trans* isomer are at ϕ 62.2 as a broad singlet. The CF_3 and CF_2 resonances occur at the same chemical shift for both isomers, ϕ -82.1 (s) and -122.3 (t), respectively ($J_{\text{CF}_3-\text{CF}_2} \approx 0$, $J_{\text{CF}_3-\text{CH}_2} = 8$ Hz). The ^1H NMR spectrum of the *cis-trans* mixture showed one triplet at δ 4.6 ($J = 11.7$ Hz) due to overlapping of the two triplets arising from the inequivalent protons. The CI^+ mass spectrum does not show a molecular ion, but appropriate fragments observed were m/e 386 ($\text{M}^+ - \text{HF}$) 39%, 257 ($\text{M}^+ - \text{OCH}_2\text{CF}_2\text{CF}_3$) 4.1%, 256 ($\text{M}^+ - \text{OCHCF}_2\text{CF}_3$) 100%, 232 ($\text{C}_3\text{F}_6\text{H}_2\text{SO}_3^+$) 13.8%, 132 ($\text{C}_3\text{F}_3\text{H}^+$) 44%, 105 (OSF_3^+) 27%, 89 (SF_3^+) 11.3%, 69 (CF_3^+) 38.5%, 64 (SO_2^+) 6.5%, and 51 (SF^+) 34%. Anal. Calcd for $\text{C}_6\text{F}_{14}\text{H}_4\text{SO}_2$: C, 17.74; F 65.4; S, 7.89; H, 0.99. Found: C, 18.04; F, 64.1; S, 6.89; H, 1.12.

Preparation of *cis*- and *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$. This was accomplished by using the same method as was adopted for $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$ above. Separation of the *cis* and *trans* isomers was easily achieved on a heated 2-m QF-1 column. Yields obtained were approximately 24% *cis*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$ and 44% *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$.

Properties of *cis*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$. The compound is a colorless liquid with a vapor pressure of < 5 torr at room temperature. The infrared spectrum (liquid phase) had bands at 2985 (m), 1785 (w), 1435 (s), 1406 (s), 1353 (vs), 1299 (vs), 1230 (br, vs), 1191 (vs), 1132 (vs), 1098 (vs), 1073 (vs), 1022 (vs), 966 (vs), 926 (vs), 851 (br, vs), 764 (s), 750 (s), 660 (s), 640 (s), 611 (s), 589 (s), and 549 (s) cm^{-1} . The ^{19}F NMR spectrum was a 14-line A_2B_2 pattern for the axial and equatorial fluorine atoms bonded to sulfur, centered at ϕ 73.7 and 63.0 with $J_{\text{FA}-\text{FB}} = 150.4$ Hz. Other assignments were as follows: ϕ -79.1 (t), CF_3^a ; ϕ -118.9 (mult), CF_2^b ; ϕ -125.6 (br, s), CF_2^b ; $J_{\text{CF}_3-\text{CF}_2} = 9.2$ Hz as shown by resonance decoupling. The ^1H NMR spectrum had a triplet at δ 4.67 with $J = 12.3$ Hz due to overlapping of the two triplets arising from the nonequivalent protons and to $J_{\text{CF}_3-\text{CH}_2}$ coupling. The CI^+ mass spectrum shows the following major fragment ions: m/e 487 ($\text{M}^+ - \text{F}$) 1.6%, 307 ($\text{M}^+ - \text{OCH}_2\text{CF}_2\text{CF}_3$) 77.3%, 263 ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2\text{OSO}_2^+$) 1.3%, 183 ($\text{CF}_3\text{CF}_2\text{CF}_2\text{CH}_2^+$) 29.3%, 169 ($\text{CF}_3\text{CF}_2\text{CF}_2^+$) 2.4%, 119 (C_2F_3^+) 15%, 113 ($\text{C}_3\text{F}_3\text{H}^+$) 100%, 89 (SF_3^+) 17.5%, 69 (CF_3^+) 61.8%, and 64 (SO_2^+) 8.9%. The CI^- mass spectrum shows m/e 323 ($\text{F}_4\text{SOCH}_2\text{CF}_2\text{CF}_3^-$) 1.3%, 307 ($\text{F}_4\text{SOCH}_2\text{CF}_2\text{CF}_3^-$) 23.6%, 199 ($\text{CF}_3\text{CF}_2\text{CF}_2\text{C}-\text{H}_2\text{O}^-$) 1.6%, 178 ($\text{C}_2\text{F}_4\text{CH}_2\text{OSO}^-$) 100%, 108 (SF_4^-) 5%, 89 (SF_3^-) 17.6%, and 70 (SF_2^-) 27%.

Properties of *trans*- $\text{F}_4\text{S}(\text{OCH}_2\text{CF}_2\text{CF}_3)_2$. The compound is a colorless liquid with a vapor pressure of < 5 torr at room temperature. The infrared spectrum (liquid film) had bands at 2984 (m), 1785 (w), 1719 (w), 1463 (s), 1408 (s), 1348 (vs), 1300 (vs), 1231 (br, vs), 1191 (br, vs), 1132 (br, vs), 1092 (vs), 1022 (vs), 967 (s), 926 (vs), 867 (vs), 833 (vs), 763 (s), 750 (s), 689 (m), 677 (m), 658 (m), 636 (vs), 612 (m), 575 (s), 551 (s), and 534 (m) cm^{-1} . The ^{19}F NMR spectrum had a broad singlet at ϕ 61.7 for the equivalent equatorial fluorine atoms bonded to sulfur. Other chemical shifts were as follows: ϕ -79.9 (t) ($J_{\text{CF}_3-\text{CF}_2} = 9.27$ Hz as shown by resonance decoupling), CF_3^a ; ϕ -80.1 (mult), CF_2^b ; ϕ -126.5 (s), CF_2^b . The ^1H NMR spectrum showed a triplet at δ 4.6 with $J = 12.2$ Hz due to the overlapping of the two triplets arising from the inequivalent protons and to $J_{\text{CF}_3-\text{CH}_2}$ coupling. The CI^+ mass spectrum had bands at m/e 487 ($\text{M}^+ - \text{F}$) 25%, 307 ($\text{M}^+ - \text{OCH}_2\text{CF}_2\text{CF}_3$) 98%, 183 ($\text{CH}_2\text{CF}_2\text{CF}_3^+$) 32.5%, 119 (C_2F_3^+) 14.0%, 113 ($\text{C}_3\text{F}_3\text{H}^+$) 100%, 105 (SOF_3^+) 54%, 89 (SF_3^+) 12.5%, 69 (CF_3^+) 53.3%, and 64 (SO_2^+) 8.7%. The CI^- mass spectrum showed m/e 307 ($\text{F}_4\text{SOCH}_2\text{CF}_2\text{CF}_3^-$) 7.2%, 178 ($\text{C}_2\text{F}_4\text{CH}_2\text{OSO}^-$) 100%, 108 (SF_4^-) 44.3%, 89 (SF_3^-) 32.5%, and 70 (SF_2^-) 17.2%.

Reaction of ClF with $\text{CF}_3\text{N}=\text{S}(\text{OR})_2$ [$\text{R} = \text{OC}(\text{CF}_3)_2\text{H}$, $\text{OC}(\text{CF}_3)_2\text{CH}_3$, $\text{OC}(\text{CF}_3)(\text{CH}_3)_2$]. For example, into an evacuated 75-mL stainless steel Hoke cylinder fitted with a stainless steel Hoke valve were condensed ~ 10 mmol of $\text{CF}_3\text{N}=\text{S}(\text{OR})_2$, 10 mmol of Freon-12, and 45 mmol of ClF at -196 °C. The bis(polyfluoroalkyl) (trifluoromethyl)imidosulfites used were contaminated with a small amount of CF_3NSF_2 and some of the parent alcohol ($\sim 20\%$). The cylinder was placed in a slush bath at -78 °C and held at that temperature for ~ 9 h. The volatile material was removed and distilled under dynamic vacuum. When $\text{R}_f = \text{OC}(\text{CF}_3)_2\text{H}$ or $\text{OC}(\text{CF}_3)_2\text{CH}_3$, Cl_2 , $\text{SOF}_2[\text{SF}_4]$, CF_3NCl_2 , and the appropriate amount of hypochlorite²⁸ were found. When $\text{R}_f = \text{OC}(\text{C}-\text{F}_3)(\text{CH}_3)_2$, Cl_2 , $\text{SOF}_2[\text{SF}_4]$, CF_3NCl_2 , and an unknown compound

(which arose from the attack of ClF on the methyl groups) were found. Chlorine, SOF₂ (resulting from hydrolysis of SF₆), and CF₃NCl₂ were identified by molecular weight and infrared spectra, respectively.

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Menschutkin Type Amine Alkylations Involving Ethyl Transfer from Platinum(II) Chelate Complexes of *o*-(Diphenylphosphino)thiophenole

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The compound *o*-Ph₂PC₆H₄SEt has been used as a chelate ligand to synthesize the platinum(II) complexes *cis*-[Pt(*o*-Ph₂PC₆H₄SEt)₂](BF₄)₂ and *cis*-[Pt(*o*-Ph₂PC₆H₄S)(*o*-Ph₂PC₆H₄SEt)]BF₄. The complex *cis*-Pt(*o*-Ph₂PC₆H₄SEt)₂²⁺ reacts with amines to give *cis*-Pt(*o*-Ph₂PC₆H₄S)(*o*-Ph₂PC₆H₄SEt)⁺ and then Pt(*o*-Ph₂PC₆H₄S)₂. The rate laws are first order in both platinum complex and amine. In acetonitrile solvent the rate constants and thermodynamic parameters (ΔH^\ddagger and ΔS^\ddagger) have been obtained for the first reaction step with dibenzylamine, butylamine, dibutylamine, tributylamine, diethylamine, and triethylamine. In DMF solvent the analogous data have been measured for the second step by using butylamine, dibutylamine, and tributylamine. The ΔH^\ddagger (13–18 kcal mol⁻¹) and ΔS^\ddagger (-12 to -31 cal K⁻¹ mol⁻¹) values are in the range expected for a Menschutkin type S_N2 alkylation reaction. The reaction rates decrease in the amine sequence primary > secondary > tertiary, but for benzylamines the rate only differs by a factor of 5 from benzylamine to tribenzylamine.

Introduction

Methyl transfer is a topic of considerable significance in biological chemistry. One of the most important compounds that has been implicated in such reactions is *S*-adenosylmethionine.¹ This compound is widely involved as an in vivo carbonium ion type methylating agent. Carbonium ion alkylation by *S*-adenosylmethionine is an important route for the methylation of ethanolanolamine and noradrenaline, and the methylation of DNA may eventually be proven to be of significance to cancer mechanisms.²

Methyl transfer from methylthioether groups complexed to transition-metal ions is a well-documented reaction,³ and we have recently shown that such a transfer to thiocyanate or iodide ion or to benzylamine can be explained on the basis of a S_N2 type nucleophilic displacement at the electrophilic methyl carbon.⁴ These previous rate data were collected with a complex having a methylthioether moiety coordinated to palladium(II), and the reaction was complicated by the presence of a side reaction which resulted in substitution of the complexed methylthioether ligand

by the incoming nucleophile. Since the electrophilicity orders for carbon and palladium(II) appear to be closely similar,⁵ it is difficult to achieve selectivity to attack at carbon rather than at palladium(II) by judicious choice of nucleophile. In this paper we report that we can achieve this regioselectivity by complexation of the thioether group to the kinetically inert platinum(II) center, rather than with the labile palladium(II) ion. Finally, we use our data to compare the reactivity of coordinated thiomethyl and thioethyl ligands.

Experimental Section

The compound *o*-(diphenylphosphino)thioanisole (*o*-Ph₂PC₆H₄SMe) and the complexes [Pd(*o*-Ph₂PC₆H₄SMe)₂](BF₄)₂ and Pd(*o*-Ph₂PC₆H₄S)₂ were prepared by published procedures.³ Sodium tetrachloropalladate(II) and potassium tetrachloroplatinate(II) were purchased from Johnson Matthey, Inc. The solvents DMF and CH₃CN used in the kinetic measurements were spectral grade purity from Aldrich Chemical Co. These solvents were dried over phosphorus pentoxide in the manner proposed by Burfield.⁶ Triethylamine and tributylamine were purchased from Matheson Coleman and Bell; benzylamine, butylamine, and dibutylamine were purchased from Aldrich. All amines were dried over 4 Å molecular sieves prior to distillation. Tetraethylammonium bromide was purified by recrystallization from a mixture of dichloromethane and diethyl ether. Infrared spectra were obtained as KBr pellets on a Perkin-Elmer Model 683 spectrophotometer. ³¹P NMR data were collected on a JEOL FX 60 FTNMR spectrometer operating at 24.15 MHz and referenced to external trimethyl phosphite (δ 140). ¹H NMR data were collected on a Varian EM 390 spectrometer operating at 90 MHz and referenced to internal Me₄Si. CDCl₃ was purchased from Aldrich, and CD₃CN from Stohler Isotope Co. Photochemical experiments were carried out by using a 200-W mercury lamp purchased from Illumination Industries enclosed in a fan-cooled Ealing Corp. housing. A Pyrex glass cutoff filter ($\lambda > 320$ nm) was used. Electronic absorption spectra were measured on a Hewlett-Packard Model 8451A diode-array spectrometer. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN. Conductivity measurements were made with an Industrial Instruments conductivity unit incorporating a cell with a platinized electrode.

***o*-(Diphenylphosphino)thiophenole (*o*-Ph₂PC₆H₄SEt).** To a solution of *o*-aminobenzenethiol (100 g, 0.8 mol) in absolute alcohol (300 mL) was added sodium metal (18.4 g) in chunks while the temperature of the mixture was maintained at 0 °C with an ice bath. After completion of the reaction, ethyl iodide (125 g, 0.8 mol) was added from a dropping

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