mated for the iron(III) hydrogen carbonate complex²⁸ and use of this value allows estimation of the value $k \simeq 9 \times 10^{-2} \, \mathrm{s}^{-1}$ for the reaction of (hydrogen carbonate)chromium(III) ion with dimethyl sulfoxide at Z = 0.01. Thus, the magnitude of the labilization by coordinated hydrogen carbonate ion is similar to that of coordinated nitrate ion.

The labilization of chromium(III) ion by carbon dioxide through the formation of carbonate or hydrogen carbonate containing transition states for substitution reactions suggests that carbon dioxide may be a useful catalyst in procedures for forming complexes of chromium(III).²⁹

Registry No. Cr(ONO₂)(H₂O)₅²⁺, 17500-09-3; (CH₃)₂SO, 67-68-5; $Cr(OH_2)_6^{3+}$, 14873-01-9; hydrogen sulfite, 15181-46-1; hydrogen carbonate, 71-52-3; $Cr(H_2O)(OS(CH_3)_2)_5^{3+}$, 24269-28-1; Cr- $(H_2O)_5(OS(CH_3)_2)^{3+}$, 24283-89-4.

(29) G. Rábai, G. Bazsa, and M. Beck, Magy. Kem. Foly., 82 60 (1976), have studied the labilizing effect of nitrite ion and hydrogen carbonate ion upon the reaction of chromium(III) ion with dimethyl sulfoxide.

> Contribution from the Department of Chemistry, University of Idaho, Moscow, Idaho 83843

Reactions of Hexafluoroacetone with Sulfur-Containing Compounds

QUI-CHEE MIR and JEAN'NE M. SHREEVE*

Received December 7, 1979

Reactions of hexafluoroacetone with simple alkyl sulfides were studied. With trimethylene sulfide, a concerted addition reaction resulted in the formation of a six-membered ring, $(CF_3)_2COSCH_2CH_2CH_2$; with tetramethylene sulfide, dimethyl sulfide, or dimethyldisulfane, insertion into the α position occurred to give SCH[C(OH)(CF₃)₂)CH₂CH₂CHC(OH)(CF₃)₂) $HO(CF_3)_2CCH_2SCH_2C(CF_3)_2OH$, and $HO(CF_3)_2CCH_2SSCH_2C(\tilde{C}F_3)_2OH$, respectively. With thiophosphoryl chloride, where no α -hydrogen is present, oxidative addition at sulfur (II) gave OC(CF₃)₂C(CF₃)₂OS=PCl₃. No reaction was observed with F-alkyl sulfides under the conditions used, with the exception that those with active functional groups such as NH_2 behave as primary aliphatic amines in their reactions with hexafluoroacetone; e.g., with H₂N(CF₃)COCH₂CH₂O and H₂N(CF₃)CSCH₂CH₂S, (CF₃)₂C=N(CF₃)COCH₂CH₂O, (CF₃)₂C=N(CF₃)CSCH₂CH₂S, and HO(CF₃)₂CNH(C-F3)CSCH2CH2S were obtained. No reaction was observed when a sulfur-phosphorus mixed ligand such as SCH2C- H_2 SPSCH₂CH₂SPSCH₂CH₂S or ethylene sulfide was reacted with hexafluoroacetone. When (CF₃)₂C(OH)SH was mixed with SCl₂ and Cl₂, compounds such as HO(CF₃)₂CSSSC(CF₃)₂OH and HO(CF₃)₂CSSC(CF₃)₂OH were formed, respectively. The latter two compounds as well as $(CF_3)_2C(OH)SH$, when reacted with SF_4 , gave hexafluorothioacetone. $(CF_3)_2C(OH)SH$ also was reacted with ClF in Pyrex glass to give $(CF_3)_2C(OH)_2$.

The reactions of hexafluoroacetone (HFA) with various phosphites and phosphines have been examined extensively as a synthetic route to cyclic phosphoranes.¹⁻⁴ Sulfur analogues such as the spirosulfurane A and the monocyclic thionyl compound B were obtained from reactions of an F-pinacol salt with SCl_2^5 and $SOCl_2^6$ respectively (Scheme I).

Although a modified synthesis of sulfurane A has appeared in the literature recently, 7 use of the extremely toxic F-pinacol was still required. We have investigated reactions between HFA and simple sulfur compounds as a route to make cyclic sulfuranes. A dipolar 1:1 adduct has been postulated as the intermediate in the synthesis of cyclic phosphoranes,8ª and it

- (a) Oram, R. K.; Trippett, S. J. Chem. Soc., Chem. Commun. 1972, 554. (b) Oram, R. K.; Trippett, S. J. Chem. Soc., Perkin Trans. 1 1973, 1300. (c) Trippett, S.; Whittle, J. Ibid. 1973, 2302. (d) Trippett, S.; Whittle, J. Ibid. 1974, 2125. (c) Provide The Science Field Content of the Content (1)
- (a) Ramirez, F.; Smith, C. P.; Pilot, J. F. J. Am. Chem. Soc. 1968, 90, 6726.
 (b) Ramirez, F.; Smith, C. P.; Pilot, J. F.; Gulatie, A. S. J. Org. Chem. 1968, 33, 3787 and references therein.
 (a) Ramirez, F.; Magabhushanam, M.; Smith, C. P. Tetrahedron 1968, (2)
- (3)
- (a) Ramirez, F.; Magabhushanam, M.; Smith, C. P. Tetrahedron 1968, 24, 1975. (b) Ramirez, F.; Bhatia, S. B.; Smith, C. P. Ibid. 1967, 23, 2067. (c) Stokel, R. F. Tetrahedron Lett. 1966, 25, 2833.
 (a) Gibson, J. A.; Röschenthaler, G. V.; Schmutzler, R. Z. Naturforsch., B 1977, 32, 599. (b) Storzer, W.; Röschenthaler, G. V. Ibid. 1978, 33, 305. (c) Röschenthaler, G. V.; Schmutzler, R. Z. Naturforsch., Schmutzler, R. Chem. Ber. 1979, 112, 2380 and references therein.
 (a) Allan, M; Janzen, A. F.; Willis, C. J. Can. J. Chem. 1968, 46, 3671.
 (c) Conroy, A. P.; Dresdner, R. D. Inorg. Chem. 1970, 9, 2739.
 (a) Stokel, R. F. Tetrahedron Lett. 1966, 25, 2833. (b) Hall, D.; Emsley, J. "The Chemistry of Phosphorus"; Wiley: New York, 1976; Chapter 3.

- Chapter 3.



is likely that the same mechanism also applies in reactions with sulfur-containing compounds. In order to stabilize such an intermediate, the sulfur atom must be rich in electron density. Indeed, we found that no reaction occurred with F-alkyl sulfides, such as CF₃SSCF₃, CF₂SCF₂S, etc., under the conditions used. In the case of nonfluorinated sulfides, with two exceptions, substitution into the α position by HFA was the reaction mode. However, when hexafluoroacetone was reacted with thiophosphoryl trichloride, where no α -hydrogen was

⁽²⁸⁾ R. Patel and G. Atkinson, paper 161 presented before the Division of Physical Chemistry, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 14-18, 1970.

Hexafluoroacetone and Sulfur-Containing Compounds



available, oxidative addition of 2 mol of HFA to sulfur resulted in the formation of a cyclic phosphasulfinyl compound. The initial attack is by the sulfur of $S=PCl_3$ on the carbonyl oxygen of HFA, and the negative charge so generated is stabilized by the electron-withdrawing CF₃ groups on carbon (Scheme II). The second step then involves nucleophilic addition of the carbanion to the carbonyl carbon of a second HFA molecule and ring closure to the products. It was not possible, however, to cause a similar oxidative addition at sulfur in CS_2 under the same conditions. The structure of I is supported by spectral data. The ¹⁹F NMR spectrum has a singlet at ϕ -78.0. This is in contrast to its isostructural thionyl analogue (B),⁶ which has two heptets which arise because of the existence of the lone electron pair on the sulfur atom. The equivalence of the CF₃ groups on the NMR time scale in I may be due to a lower energy barrier arising from $p\pi$ -d π bonding in the sulfur-phosphorus bond and, thus, a more rapid rate of inversion at the sulfur atom. The ³¹P NMR spectrum is a singlet at 34.94 ppm (downfield from H_3PO_4). This further strengthens the argument for the proposed structure for I and excludes all other possible alternate structures, such as a thiophosphite, $S=P[OCCl(CF_3)_2]_3$, or a phosphorane, e.g., SOC(CF₃)₂C(CF₃)₂OPCl₃, whose ³¹P NMR shifts

would be found at much lower or markedly higher fields, respectively.^{8b} Compound I is stable at 25 °C. There is no apparent decomposition or hydrolysis in a capped tube after 1 month at ambient temperature.

The other exception is the reaction of trimethylene sulfide, SCH₂CH₂CH₂, with HFA to form six-membered-ring compound II, rather than a product formed from insertion into $(CF_{2})_{2}C = 0 +$

$$SCH_2CH_2CH_2 \rightarrow (CF_3)_2COSCH_2CH_2CH_2$$

$$II$$

$$\# (CF_3)_2C(OH)CHCH_2CH_2S$$

the α -hydrogen bond. This can be explained on the basis of conclusions from an ultraviolet spectral study of ethylene sulfide.⁹ An excited state, such as $^+CH_2CH_2CH_2S^-$, is suggested, which can then induce a favored geometry for concerted reaction as in eq 1.



(9) Davis, R. E. J. Org. Chem. 1958, 23, 1380.

Compound II is an amorphous white solid which melts as 52 °C. The proposed structure is supported by spectral data. The ¹⁹F NMR spectrum has a band at ϕ -83.24 (⁴J_{HF} = 3.7 Hz). This shift tends to rule out the alternate structure



when one compares this value with the ¹⁹F chemical shifts for the compounds¹⁰



The mass spectrum, in addition to a parent peak at m/e 240 (M⁺), has fragments such as $m/e \ 115 \ [(CF)_2 CCH_2 CH_2 CH]$ and m/e 95 [(CF₃CCH₂)⁺] which further support II as a reasonable structure.

It is interesting to note that there is no reaction between ethylene sulfide, SCH₂CH₂, and HFA. The former fails to undergo a concerted reaction (eq 2), as is the case in the



formation of II, because of an unfavorable excited state,⁹ which is suggested by a shift to higher energy of the weak band (σ^2 $\rightarrow \sigma \sigma^*$) in its UV spectrum. This would eventually lead at best to the formation of an unstable sulfur vlide. Its failure to undergo substitution into α -hydrogen may be due to its inability to polarize the S-CH₂ p-sp³ bond, and thus saturation of the sp² state in $(CF_3)_2C=O$ to sp³ is not possible.

When hexafluoroacetone was reacted with tetramethylene sulfide, CH₂CH₂CH₂CH₂S, dimethyl sulfide, CH₃SCH₃, or dimethyldisulfane, CH₃SSCH₃, direct insertion into an α position to form alcohols took place and resulted in the formation of compounds III, IV, and V (eq 3-5). Polarization

$$2(CF_3)_2C = 0 + \sqrt{S} \xrightarrow{UV}_{O \circ C} (CF_3)_2C \xrightarrow{C(CF_3)_2}_{HO} (3)$$
III

 $2(CF_3)_2C \longrightarrow 0 + CH_3SCH_3 \xrightarrow{UV} HOC(CF_3)_2CH_2SCH_2C(CF_3)_2OH$ (4) IV

$$2(CF_3)_2C = O + CH_3SSCH_3 \frac{UV}{O * C} HOC(CF_3)_2CH_2SSCH_2C(CF_3)_2OH$$
(5)

of the p-sp³ bond between the sulfur and carbon atoms contributes significantly to the excited states in these sulfides.¹¹ This enhances the negative trifluoromethyl group to further destabilize the carbonyl group in hexafluoroacetone by increasing the electrophilicity of the carbonyl carbon and reducing the ionic contribution to resonance in the carbonyl group. The sp³ state at the carbonyl carbon is therefore favored.

⁽¹⁰⁾ Glemser, O.; Shreeve, J. M. Inorg. Chem. 1979, 18, 2319.
(11) (a) Ley, J.; Arends, B. Z. Phys. Chem. 1932, 15, 311. (b) Koch, H. P. J. Chem. Soc. 1949, 387.

Compound III was obtained by photolyzing hexafluoroacetone with tetramethylene sulfide at 0 °C for several days. After removal of the volatile materials via trap-to-trap distillation, a light yellow oil remained which was recrystallized to a white solid from CCl₄. The ¹⁹F NMR spectrum consists of four quartets at ϕ -72.4, -72.7, -75.0, and -75.3 with J_{F-F} = 12 Hz. The ¹³C NMR spectrum is a quartet (J_{C-F} = 287 Hz) for the trifluoromethyl carbon atoms at δ 120 (Me₄Si). The fact that the carbon atoms of the CF₃ groups have the same chemical shift indicates very subtle differences in the magnetic environments which are not observed in the less well resolved ¹³C case. The chemical nonequivalence of the CF_3 groups in the ¹⁹F NMR spectrum is rationalized as follows. Compound III exists as a trans isomer in which $CF_3(a,b) \neq a$



 $CF_3(c,d)$. The nonequivalence of $CF_3(a)$ and $CF_3(b)$ and of $CF_3(c)$ and $CF_3(d)$ is easily seen from Newman projections C and D. For example, in rotamer C, CF_3' is trans to S, and



 CF_3 is cis to S. In rotamer D, both CF_3' and CF_3 are cis to S. Therefore, CF_3' does not perceive CF_3 in D in the same way as CF_3' perceives CF_3 in C, and thus the trifluoromethyl groups are chemically nonequivalent.

It is interesting to note that hexafluoroacetone undergoes substitution into only one of the α positions of thiophene.¹² This is also the case when hexafluoroacetone is reacted with an activated aromatic such as thiophenol¹³ (eq 6).

$$(CF_3)_2C = 0 + \bigcup_S \xrightarrow{\Delta} \bigcup_S C(CF_3)_2OH$$
 (6)

Compound IV was obtained as a white solid in good yield when CH₃SCH₃ was photolyzed with hexafluoroacetone at 0 °C. There was no reaction when the mixture was heated. It is worthwhile to contrast this reaction with that of HFA with the isoelectronic compound $(CH_3)_2PH$. When hexafluoroacetone was reacted with $(CH_3)_2 PH$ at 25 °C,¹⁴ no $(CH_3)_2$ - $PC(CF_3)_2OH$ was isolated. However, compounds such as $[(CH_3)_2P]_2$ and $(CH_3)_2P(O)OCH(CF_3)_2$ were found, among others. Also, when hexafluoroacetone was reacted with (CH₃)₂PF,^{4a} a phosphorus ylide was suggested as an intermediate which then led to the formation of the phosphorane product (eq 7). A sulfur ylide, which would result in the



- (12) England, D. C. U.S. Patent 3 197 480, 1965.
 (13) Astrologes, G. W.; Martin, J. C. J. Am. Chem. Soc. 1975, 97, 6907.
 (14) Röschenthaler, G. V. Z. Naturforsch., B 1971, 33, 5595.

formation of a highly strained sulfurane, does not form in the CH₃SCH₃-HFA reaction (eq 8). Isolation of such a sulfurane is not likely.¹⁵ Compound IV behaves as a typical diol in its reaction with SF_4 to give compound VI (eq 9).



Compounds IV and V were formed under similar reaction conditions except that V required a longer reaction time and the yield was much lower. This is probably associated with polarization of the S-S bond,¹⁶ which results in conjugation between the unshared electrons of the two sulfur atoms¹⁷ and raises the energy for polarization of the p-sp³ bond between the sulfur and carbon atoms.

As mentioned above, no reaction was observed between hexafluoroacetone and fluorinated sulfides. When H₂NC- $(CF_3)SCH_2CH_2S$ was reacted with hexafluoroacetone at 25 °C, a mixture of compounds VII and VIII was obtained (eq



of a primary aliphatic amine, and VIII is rarely observed since dehydration to the imine is generally not observed in these reactions. It has been demonstrated that the conditions for preferential elmination of water from other types of NH₂ adducts of HFA have not been found. In some instances, the imine of HFA was prepared from HFA by special dehydration techniques.¹⁸ Compound VII converts slowly to compound VIII on standing at 25 °C for several days, as determined by ¹⁹F NMR spectra. Complete conversion, however, was not

observed. In contrast, when H₂N(CF₃)COCH₂CH₂O was reacted with HFA at 25 °C for the same period of time, only compound IX was obtained (eq 11). Both compounds VIII



and IX have characteristic C=N stretching frequencies at about 1680 cm⁻¹ in their infrared spectra.

- (16) Koch, H. P. J. Chem. Soc. 1949, 394.
 (17) Bauer, J. E.; Carmack, M. J. Am. Chem. Soc. 1949, 71, 1215.
 (18) Krespan, C. G.; Middleton, W. J. Fluorine Chem. Rev. 1967, 1, 155.

⁽a) Sheppard, W. A. J. Am. Chem. Soc. 1971, 93, 5595. (b) Sheppard, W. A.; Foster, S. S. J. Fluorine Chem. 1972, 2, 53. (c) Sheppard, W. (15)A. J. Am. Chem. Soc. 1962, 84, 3058.

Compound X was obtained when PCl_3 was reacted with $HSCH_2CH_2SH$ in a 2:3 ratio. When hexafluoroacetone was reacted with X, there was neither oxidative addition at phosphorus(III) nor substitution into α -hydrogen under any conditions used (eq 12).

$$(CF_3)_2 C = 0 + S S S S S S S (12)$$

Hydrogen sulfide adds spontaneously at moderate temperature to HFA to form $(CF_3)_2C(OH)SH$.¹⁹ Because of the negative trifluoromethyl group, the hydrogen of the hydroxyl group is not acidic enough to participate in reactions, and the chemistry of the 1-hydroxy-1-thiol is mainly the chemistry of its SH group.¹⁹ When $(CF_3)_2C(OH)SH$ was reacted with a strong oxidizing agent such as CIF, cleavage of the C–S bond occurred to give compounds such as SCl₂, HFA, and HF (SiF₄ and H₂O) (eq 13). The HFA is hydrated by the water formed

$$(CF_3)_2C(OH)SH + SF_4 \xrightarrow{Pyrex} (CF_3)_2C = S + SOF_2 + SiF_4 (13)$$

to give white crystalline $(CF_3)_2C(OH)_2$.

With SF₄, dehydration does occur, resulting in the formation of the blue thicketone. When $(CF_3)_2C(OH)SH$ was reacted with SCl₂, compound XI was obtained with concomitant formation of HCl (eq 14). Compound XI is a colorless,

$$(CF_3)_2C$$
 H + SCl_2 $Pyrex$ $(CF_3)_2C$ S S S S $C(CF_3)_2$ (14)
IX

high-boiling liquid which exists as hexagonal crystals at 0 °C. Compound XII was obtained by simply mixing Cl_2 with $(CF_3)_2C(OH)SH$ at 25 °C (eq 15). Both compound XI and

$$(CF_3)_2C \xrightarrow{OH} + CI_2 \xrightarrow{OF} (CF_3)_2C \xrightarrow{OH} OH \xrightarrow{OH} C(CF_3)_2 + HCI (15)$$

SH

compound XII behave identically with their precursor (C- F_3)₂C(OH)SH when reacted with SF₄, giving the thioketone and elemental sulfur (eq 16). An analogue of compound XII,

XI (or XII) + SF₄
$$\xrightarrow{\text{Pyrex}}$$
 (CF₃)₂C=S + SiF₄ + S + SOF₂ (16)

 $H(CF_3)_2CSSC(CF_3)_2OH$, was obtained²⁰ when $(CF_3)_2C=S$ was hydrated in the presence of trifluoroacetic acid

$$(CF_3)_2C = S + H_2O \xrightarrow{CF_3COOH} HC - S - S - COH (17)$$

 $| CF_3 - CH (17)$
 $| CF_3 - CH (17)$

Experimental Section

Materials. The following compounds were obtained from the sources indicated: CH_2CH_2S , $CH_2CH_2CH_2S$, and $CH_2CH_2CH_2-CH_2S$ (Eastman), SF₄ (Matheson, Inc.), CIF (Ozark-Mahoning, Inc.), S=PCl₃ (Columbia Organic), CH₃SCH₃ (Aldrich Chemical Inc.), CH₃SSCH₃ (Crown Zellerbach), SCl₂, (CF₃)₂CO (PCR), Cl₂ (Baker). (CF₃)₂C(OH)SH,¹⁹ CF₃C(NH₂)SCH₂CH₂S,¹⁰ and CF₃C(NH₂)O-CH₂CH₂O,¹⁰ were prepared according to literature methods.

General Procedures. Gases and volatile liquids were handled in a conventional Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge. Infrared spectra were taken by using a Perkin-Elmer 457 or 599B spectrometer. Mass spectra were recorded with a Hitachi Perkin-Elmer RMU-6E spectrometer at 17 or 70 eV. The ¹⁹F NMR spectra were obtained by using a Varian HA-100 spectrometer with CCl₃F as internal reference. ³¹P and ¹³C NMR spectra were taken on a Bruker WH-90 spectrometer with 85% H₃PO₄ as external reference or with CDCl₃ as internal lock (Me₄Si as reference). ¹H NMR spectra were obtained by using a Varian EM-360 spectrometer with Me₄Si as reference.

Preparation of OC(CF₃)₂C(CF₃)₂OS=PCl₃ (I). A 3-mmol sample of $(CF_3)_2C=O$ was condensed onto 1.5 mmol of SPCl₃ in a Pyrex vessel. The mixture was photolyzed at 0 °C for 5 days. A yellow involatile liquid remained after removing the unreacted volatile materials. The ¹⁹F NMR spectrum has a singlet at $\phi = -78.0$. The ³¹P NMR spectrum is a singlet at 34.97 ppm (H₃PO₄ reference), and the ¹³C NMR spectrum of the trifluoromethyl carbons is a quartet at 122 ppm (relative to Me₄Si). The latter has some fine structure (J < 5 Hz) probably arising from long range ³¹P-¹³C coupling. A molecular ion with appropriate isotope peaks was observed at m/e 500-506 together with fragments such as m/e 465-469 [(M - Cl)⁺], m/e 334-340 [[M - (CF₃)₂CO]⁺], and m/e 299-303 [[(CF₃)₂COSPCl₃]⁺]. The infrared spectrum has bands at 1294 (s), 1238 (vs), 1182 (m), 1122 (m), 1076 (s), 960 (s), 886 (m), 863 (m), 812 (w), 762 (w), 730 (m), 718 (s), and 701 (w) cm⁻¹. Anal. Calcd for C₆O₂SPCl₃F₁₂: C, 14.36; F, 45.55; P, 6.19. Found: C, 14.50; F, 46.0; P, 6.06.

Preparation of (CF₃)₂COSCH₂CH₂CH₂ (II). (CF₃)₂C=O (2 mmol) was condensed into a vessel containing approximately 1 mmol of CH₂CH₂CH₂S, and the mixture was allowed to warm from -196 °C to 25 °C immediately and was agitated at 25 °C for 24 h. A white amorphous solid was then obtained. The unreacted starting materials were removed under dynamic vacuum at 25 °C. On the basis of volatile materials recovered, the yield is approximately 30%. The ¹⁹F NMR spectrum (tetrahydrofuran as solvent) contains a band at ϕ -83.2 (⁴J_{HF} = 3.7 Hz). The ¹H NMR spectrum has a multiplet at δ 2.7. A molecular ion at m/e 240 (M⁺) was obtained in the mass spectrum with other appropriate peaks such as m/e 221 [(M - F)⁺], m/e 171 [(M - CF₃)⁺], m/e 95 [(CF₃CCH₂)⁺], and m/e 90 [(OSCH₂CH₂CH₂)⁺]. The infrared spectrum (tetrahydrofuran as solvent for making capillary film) has bands at 1273 (s), 1251 (s), 1212 (vs), 1186 (s), and 1151 (s) cm⁻¹.

Preparation of C(CF₃)₂(OH)CHCH₂CH₂CH(C(CF₃)₂OH]S (III). Tetramethylene sulfide (1 mmol) and hexafluoroacetone (2 mmol) were condensed together in a Pyrex vessel, were allowed to warm to 0 °C, and were then photolyzed at this temperature for 3-4 days. After removal of unreacted starting materials, a light yellow involatile oil was obtained which can be recrystallized as a white solid in CCl₄. The ¹⁹F NMR spectrum consists of four quartets at ϕ -72.4, -72.66, -75.03, and -75.29 with $J_{FF} = 12$ Hz. The ¹H NMR spectrum has two multiplets at δ 1.65 and 3.55. The ¹³C spectrum for carbon of CF_3 consists of a quartet at 120 ppm (relative to Me₄Si) with J_{CF} = 287 Hz. A molecular ion at m/e 240 (M⁺) was observed in the mass spectrum with other fragments such as $m/e 351 [(M - CF_3)^+]$, 254 $[(M - (CF_3)_2CO)^+]$, and m/e 185 m/e [$(SCH_2CH_2CH_2CH_2OCCF_3)^+$]. The infrared spectrum has bands at 2960 (w), 1452 (w), 1278 (s), 1233 (vs, br), and 1148 (m). Anal. Calcd for C₁₀F₁₂O₂SH₈: C, 28.57; H, 1.90. Found: C, 29.58; H, 1.92.

Preparation of HOC(CF₃)₂CH₂SCH₂C(CF₃)₂OH (IV). Dimethyl sulfide (1.5 mmol) was condensed with 3 mmol of $(CF_3)_2C=0$ at -196 °C into a Pyrex vessel. After photolysis at 0 °C for 3 days, the volatile materials were separated via trap-to-trap distillation. The white solid residue which was purified by pumping at 25 °C for 30 min has a melting point of 52 °C. The ¹⁹F NMR spectrum has a singlet at ϕ -77.6. The ¹H NMR spectrum consists of a singlet at δ 3.05 and a broad band at δ 4.15 with an area ratio of 2:1. Freon 11 was used as solvent. The mass spectrum has a molecular ion at m/e 394 (M⁺) in addition to peaks at m/e 375 [(M - F)⁺], m/e 325 (M - CF₃⁺), and m/e 227 [[CH₂SCH₂C(CF₃)₂OH]⁺]. The infrared spectrum has bands at 3380 (s, br), 1428 (m), 1330 (w), 1210 (vs, br), 1148 (s), 1018 (s), 978 (s), and 708 (m). Anal. Calcd for C₈F₁₂SO₂H₆: C, 24.37; H, 1.52. Found: C, 24.06; H, 1.3.

Preparation of HOC(CF_3)₂ $CH_2SSCH_2C(CF_3)_2OH$ (V). Dimethyldisulfane (1 mmol) and (CF_3)₂C=O (2 mmol) were condensed

together in a Pyrex vessel. After photolysis at 0 °C for several days, a yellow oil was obtained in poor yield. The ¹⁹F NMR spectrum has a band at ϕ -77.5. The ¹H NMR spectrum has a singlet at δ 3.15 and a broad band at δ 3.6 with an area ratio of 2:1. A molecular ion at m/e 426 (M⁺) was obtained in the mass spectrum along with other appropriate fragments such as m/e 407 [(M - F)⁺] and m/e 357 [(M - CF₃)⁺]. The infrared spectrum has bands at 3420 (s, br), 2928 (w), 1422 (m), 1370 (m), 1320 (s), 1225 (vs, br), 1147 (s), 1010 (s), 960 (s), 740 (w), and 700 (m) cm⁻¹. Anal. Calcd for C₈F₁₂S₂O₂H₆: C, 22.54.

Preparation of $F(CF_3)_2CCH_2SCH_2C(CF_3)_2F$ (VI). Approximately 0.4 g of HO(CF₃)₂CCH₂SCH₂C(CF₃)₂OH (1 mmol) was reacted with excess SF₄ at 25 °C overnight. After removal of the volatile SOF₂, the light pink solid, which was recrystallized from anhydrous ether, had a melting point of 63 °C. The ¹⁹F NMR spectrum has bands at ϕ -151.4 (CF) and ϕ -76 (CF₃) with an area ratio 1:6. Tetrahydrofuran was used as solvent. A molecular ion was not observed in the mass spectrum; however, fragments such as m/e 329 [(M - CF₃)⁺] and m/e 215 [(CF₃)₂CFCH₂S]⁺ were obtained.

Preparation of HO(CF₃)₂CNH(CF₃)CSCH₂CH₂S (VII) and (CF₃)₂C=N(CF₃)CSCH₂CH₂S (VIII). Approximately 1 mmol of H₂N(CF₃)CSCH₂CH₂S was reacted with a slight excess of (C-F₃)₂C=O at 25 °C for 3 days. The colorless, involatile material thus obtained is a mixture of VII and VIII. If the mixture was agitated at 25 °C for a longer time, only a slight increase in the amount of VIII occurred. Complete automatic dehydration was not possible under the conditions used. The ¹⁹F NMR spectrum for VII has bands at ϕ -77.59 (CF₃CS) and ϕ -79.23 [(CF₃)₂CO]. Compound VIII has bands at ϕ -77.85 (CF₃C-N) and ϕ -75.62 [(CF₃)₂C=N]. The infrared spectrum of a mixture of VII and VIII has bands at 3440 (w), 3419 (w), 1668 (m), 1231 (vs), 1191 (vs), 1160 (vs), 1075 (vw), 970 (s), 960 (s), and 718 (m) cm⁻¹. The mass spectrum contained a molecular ion for VII together with other fragments such as m/e 318 [[(CF₃)₂CN(CF₂)CSCH₂CH₂S]⁺], m/e 268 [(CF₃CNCF₃-

 $CSCH_2CH_2S)^+$, and m/e 221 [($CF_2CSSNCCF_3$)⁺].

Preparation of (CF₃)₂C=N(CF₃)COCH₂CH₂O (IX). Excess (CF₃)₂C=O was condensed into a vessel containing 1 mmol of H₂N(CF₃)COCH₂CH₂O. After warming from -196 to 25 °C, the mixture was allowed to stand at 25 °C for 3 days. The ¹⁹F NMR spectrum of the colorless, high-boiling liquid has bands at ϕ -85.3 (CF₃-C-N) and ϕ -80.8 and -81 [(CF₃)₂C=N] with an area ratio of 1.2. The mass spectrum had no parent peak but contained fragments at *m/e* 286 [(M - F)⁺], *m/e* 218 [(CF₃OCOCH₂NCCFCF₂)⁺], *m/e* 141 [(CF₃COCH₂CH₂O)⁺¹, and *m/e* 127 [(CF₃OCOCH₂)⁺]. The infrared spectrum had absorption bands at 2958 (ww), 1695 (m), 1381 (w), 1218 (vs, br), 1171 (s), 1020 (w), 965 (m), 952 (m), and 725 (w) cm⁻¹.

Preparation of SCH₂**CH**₂**SPSCH**₂**CH**₂**SPSCH**₂**CH**₂**SPSCH**₂**CH**₂**S**(X). PCl₃ (2 mmol) was reacted with 3 mmol of $HSCH_2CH_2SH$ at 25 °C for 2 days with occasional agitation. After removal of unreacted starting materials, the involatile compound was recrystallized from anhydrous

ether. The ¹H NMR spectrum of the white solid obtained has multiplets at δ 2.35. A molecular ion at m/e 338 (M⁺) was obtained in the mass spectrum with other peaks such as m/e 278 [(M - CH₂CH₂S)⁺], m/e 215 [(M - PSCH₂CH₂SPS)⁺], and m/e 123 [(SCH₂CH₂SP)⁺].

Preparation of HO(CF₃)₂CSSSC(CF₃)₂OH (XI). (CF₃)₂C(OH)SH (2 mmol) and SCl₂ (1 mmol) were condensed at -196 °C and allowed to warm to and remain at 0 °C for 30 h. The volatile compounds, including HCl, were removed via trap-to-trap distillation. The ¹⁹F NMR spectrum of the colorless, high-boiling liquid obtained has a band at ϕ -75.7. The ¹H NMR spectrum has a singlet at δ 4.4. A molecular ion was not obtained in the mass spectrum, but fragments such as *m/e* 182 [[(CF₃)₂C-S]⁺] and *m/e* 166 [[(CF₃)₂CO]⁺] appeared. The infrared spectrum has bands at 3580–3460 (m, br), 1372 (m), 1280 (vs), 1221 (vs), 1165 (s), 1135 (s), 940 (s), 895 (s), 752 (s), and 712 (s) cm⁻¹. Anal. Calcd for C₆F₁₂S₃O₂H₂: C, 16.74; F, 53.02; S, 22.33. Found: C, 16.86; F, 52.9; S, 22.57.

Preparation of HO(CF₃)₂CSSC(CF₃)₂OH (XII). (CF₃)₂C(OH)SH (2 mmol) was condensed with excess Cl₂ at -196 °C. After the mixture was allowed to warm to 25 °C and stand at 25 °C overnight, a colorless involatile liquid was obtained. The ¹⁹F NMR spectrum has a band at ϕ -76.2. The ¹H NMR spectrum contains a singlet at δ 4.2. Only appropriate fragments such as m/e 182 [[(CF₃)₂C-S]⁺] and m/e 166 [[(CF₃)₂CO]⁺] were observed in the mass spectrum. The infrared spectrum has bands at 3685–3160 (s, br), 1368 (m), 1280–1210 (vs, br), 1170 (s), 1133 (s), 940 (s), 880 (s), 750, and 710 (s) cm⁻¹. Anal. Calcd for C₆F₁₂S₂O₂H₂: C, 18.09; F, 57.29; S, 16.08. Found: C, 18.13; F, 56.98; S, 15.90.

Reactions of SF₄ with (CF₃)₂C(OH)SH, XI, and XII. In all cases, approximately 1 mmol of reactant was reacted with a slight excess of SF₄ at -78 °C. An intense blue color due to (CF₃)₂C=S was observed after a few hours. For compounds XI and XII, a yellow solid identified as sulfur was also observed. The thioketone was identified by its authentic spectral data.²⁰

Reaction of (CF_3)_2C(OH)SH with CIF. A 1-mmol sample of $(CF_3)_2C(OH)SH$ was reacted with 1 mmol of CIF at -78 °C in a Hoke metal vessel for several hours. After trap-to-trap distillation, SCl_2 and $(CF_3)_2CO\cdotH_2O$ were found in the volatile materials.

Acknowledgment is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grant CHE-7727395) for support of this research.

Registry No. I, 73116-99-1; II, 73117-00-7; III, 73117-01-8; IV, 73117-02-9; V, 73117-03-0; VI, 73117-04-1; VII, 73117-05-2; VIII, 73117-06-3; IX, 73117-07-4; X, 4824-97-9; XI, 73117-08-5; XII, 73117-09-6; $(CF_3)_2C=O$, 684-16-2; $CH_2CH_2CH_2S$, 287-27-4; CH_3SCH_3 , 75-18-3; CH_3SSCH_3 , 624-92-0; $H_2N(CF_3)CSCH_2CH_2S$, 70247-65-3; $H_2N(CF_3)COCH_2CH_2O$, 70247-62-0; $HSCH_2CH_2SH$, 540-63-6; $(CF_3)_2C(OH)SH$, 2056-81-7; $SPCl_3$, 3982-91-0; SF_4 , 7783-60-0; PCl_3 , 7719-12-2; SCl_2 , 10545-99-0; CIF, 7790-89-8; $(CF_3)_2C(OH)_2$, 677-71-4; $CH_2CH_2CH_2CH_2S$, 110-01-0.