mated for the iron(III) hydrogen carbonate complex[28] and use of this value allows estimation of the value $k \simeq 9 \times 10^{-2}$ 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. $Cr(ONO_2)(H_2O)_5^{2+}$, 17500-09-3; $(CH_3)_2SO$, 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.

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[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.

[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.

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Reactions of Hexafluoroacetone with Sulfur-Containing Compounds

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

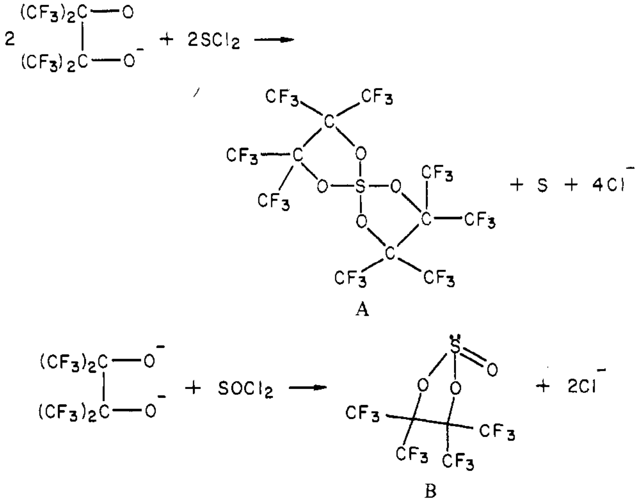
Received December 7, 1979

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, $(CF_3)_2\overline{COSCH_2CH_2CH_2}$; with tetramethylene sulfide, dimethyl sulfide, or dimethyldisulfane, insertion into the α position occurred to give $\overline{SCH[C(OH)(CF_3)_2]CH_2CH_2CH}C(OH)(CF_3)_2$, $HO(CF_3)_2CCH_2SCH_2C(CF_3)_2OH$, and $HO(CF_3)_2CCH_2SSCH_2C(CF_3)_2OH$, respectively. With thiophosphoryl chloride, where no α-hydrogen is present, oxidative addition at sulfur (II) gave $\overline{OC(CF_3)_2C(CF_3)_2OS}{=}PCl_3$. 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 $H_2N(CF_3)\overline{COCH_2CH_2O}$ and $H_2N(CF_3)\overline{CSCH_2CH_2S}$, $(CF_3)_2C{=}N(CF_3)\overline{COCH_2CH_2O}$, $(CF_3)_2C{=}N(CF_3)\overline{CSCH_2CH_2S}$, and $HO(CF_3)_2CNH(CF_3)\overline{CSCH_2CH_2S}$ were obtained. No reaction was observed when a sulfur–phosphorus mixed ligand such as $\overline{SCH_2CH_2SP}SCH_2CH_2S\overline{PSCH_2CH_2S}$ or ethylene sulfide was reacted with hexafluoroacetone. When $(CF_3)_2C(OH)SH$ was mixed with SCl_2 and Cl_2, compounds such as $HO(CF_3)_2CSSSC(CF_3)_2OH$ and $HO(CF_3)_2CSSC(CF_3)_2OH$ 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 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 CF_3SCF_3, $\overline{CF_2SCF_2S}$, 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

Scheme I



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[1] (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.

[2] (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.

[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.

[4] (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.; Sauerbrey, K.; Schmutzler, R. *Ibid.* **1979**, *34*, 107. (d) Gibson, J. A.; Sauerbrey, K.; Röschenthaler, G. V.; Schmutzler, R. *Chem. Ber.* **1979**, *112*, 2380 and references therein.

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[8] (a) Stokel, R. F. *Tetrahedron Lett.* **1966**, *25*, 2833. (b) Hall, D.; Emsley, J. "The Chemistry of Phosphorus"; Wiley: New York, 1976; Chapter 3.

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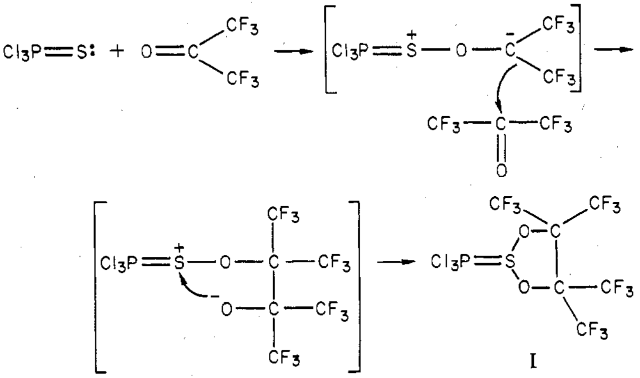
Scheme II

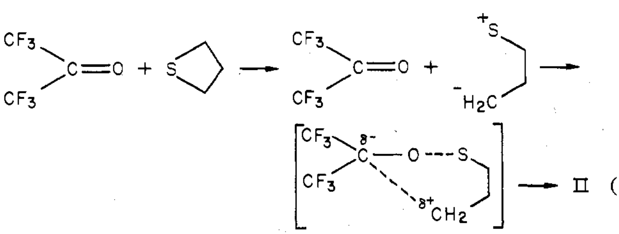


available, oxidative addition of 2 mol of HFA to sulfur resulted in the formation of a cyclic phosphasulfinyl compound. The initial attack is by the sulfur of S=PCl$_3$ on the carbonyl oxygen of HFA, and the negative charge so generated is stabilized by the electron-withdrawing CF$_3$ groups on carbon (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 ^{19}F 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 CF$_3$ groups on the NMR time scale in I may be due to a lower energy barrier arising from pπ–dπ bonding in the sulfur–phosphorus bond and, thus, a more rapid rate of inversion at the sulfur atom. The ^{31}P NMR spectrum is a singlet at 34.94 ppm (downfield from H$_3$PO$_4$). 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., $\overline{SOC(CF_3)_2C(CF_3)_2OPCl_3}$, whose ^{31}P 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.

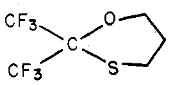
The other exception is the reaction of trimethylene sulfide, $\overline{SCH_2CH_2CH_2}$, with HFA to form six-membered-ring compound II, rather than a product formed from insertion into

$$(CF_3)_2C{=}O + \overline{SCH_2CH_2CH_2} \rightarrow \underset{\text{II}}{(CF_3)_2\overline{COSCH_2CH_2CH_2}}$$
$$\not\rightarrow (CF_3)_2C(OH)\overline{CHCH_2CH_2S}$$

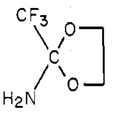
the α-hydrogen bond. This can be explained on the basis of conclusions from an ultraviolet spectral study of ethylene sulfide.[9] An excited state, such as $^+CH_2CH_2CH_2S^-$, is suggested, which can then induce a favored geometry for concerted reaction as in eq 1.

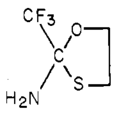


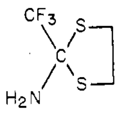
Compound II is an amorphous white solid which melts as 52 °C. The proposed structure is supported by spectral data. The ^{19}F NMR spectrum has a band at ϕ −83.24 ($^4J_{HF}$ = 3.7 Hz). This shift tends to rule out the alternate structure



when one compares this value with the ^{19}F chemical shifts for the compounds[10]

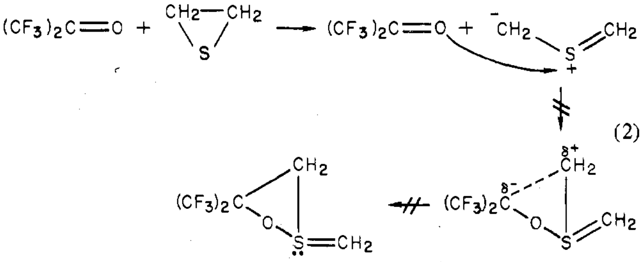

ϕ −84.8


ϕ −81.8


ϕ −77.4

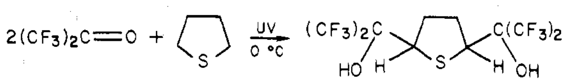
The mass spectrum, in addition to a parent peak at m/e 240 (M$^+$), has fragments such as m/e 115 [(CF)$_2$CCH$_2$CH$_2$CH] and m/e 95 [(CF$_3$CCH$_2$)$^+$] which further support II as a reasonable structure.

It is interesting to note that there is no reaction between ethylene sulfide, $\overline{SCH_2CH_2}$, 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 ($\sigma^2 \rightarrow \sigma\sigma^*$) in its UV spectrum. This would eventually lead at best to the formation of an unstable sulfur ylide. Its failure to undergo substitution into α-hydrogen may be due to its inability to polarize the S–CH$_2$ p–sp^3 bond, and thus saturation of the sp^2 state in (CF$_3$)$_2$C=O to sp^3 is not possible.

When hexafluoroacetone was reacted with tetramethylene sulfide, $\overline{CH_2CH_2CH_2CH_2S}$, dimethyl sulfide, CH$_3SCH_3$, or dimethyldisulfane, CH$_3$SSCH$_3$, 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



III

$$2(CF_3)_2C{=}O + CH_3SCH_3 \xrightarrow[0\ °C]{UV} HOC(CF_3)_2CH_2SCH_2C(CF_3)_2OH \quad (4)$$

IV

$$2(CF_3)_2C{=}O + CH_3SSCH_3 \xrightarrow[0\ °C]{UV} HOC(CF_3)_2CH_2SSCH_2C(CF_3)_2OH \quad (5)$$

V

of the p–sp^3 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 sp^3 state at the carbonyl carbon is therefore favored.

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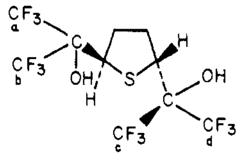
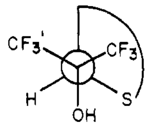
(11) (a) Ley, J.; Arends, B. *Z. Phys. Chem.* **1932**, *15*, 311. (b) Koch, H. P. *J. Chem. Soc.* **1949**, 387.

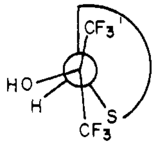
Compound III was obtained by photolyzing hexafluoroacetone with tetramethylene sulfide at 0 °C for several days. After removal of the volatile materials via trap-to-trap distillation, a light yellow oil remained which was recrystallized to a white solid from CCl$_4$. The ^{19}F NMR spectrum consists of four quartets at ϕ −72.4, −72.7, −75.0, and −75.3 with J_{F-F} = 12 Hz. The ^{13}C NMR spectrum is a quartet (J_{C-F} = 287 Hz) for the trifluoromethyl carbon atoms at δ 120 (Me$_4$Si). The fact that the carbon atoms of the CF$_3$ groups have the same chemical shift indicates very subtle differences in the magnetic environments which are not observed in the less well resolved ^{13}C case. The chemical nonequivalence of the CF$_3$ groups in the ^{19}F NMR spectrum is rationalized as follows. Compound III exists as a trans isomer in which CF$_3$(a,b) $\neq$ 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.



III

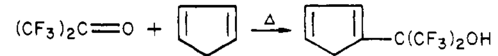


C



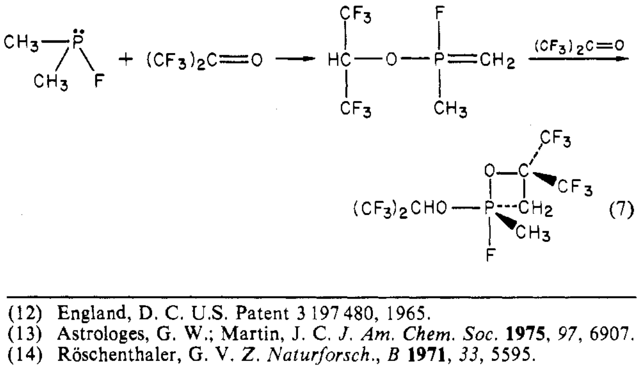
D

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 thiophenol[13] (eq 6).

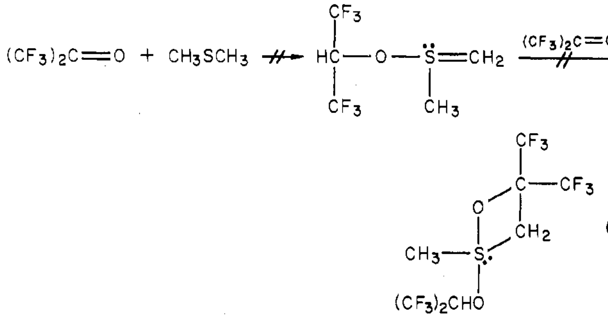


(6)

Compound IV was obtained as a white solid in good yield when CH$_3$SCH$_3$ 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$_3$)$_2$PH. When hexafluoroacetone was reacted with (CH$_3$)$_2$PH at 25 °C,[14] no (CH$_3$)$_2$PC(CF$_3$)$_2$OH was isolated. However, compounds such as [(CH$_3$)$_2$P]$_2$ and (CH$_3$)$_2$P(O)OCH(CF$_3$)$_2$ were found, among others. Also, when hexafluoroacetone was reacted with (CH$_3$)$_2$PF,[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 formation of a highly strained sulfurane, does not form in the CH$_3$SCH$_3$–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).



(7)



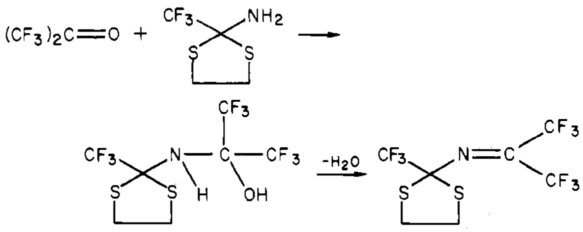
(8)

$$\text{IV} + SF_4 \longrightarrow (i\text{-}C_3F_7CH_2)_2S \qquad (9)$$

VI

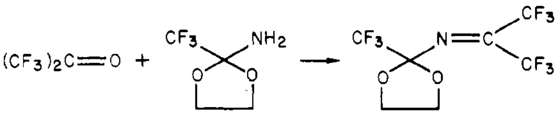
Compounds IV and V were formed under similar reaction conditions except that V required a longer reaction time and the yield was much lower. This is probably associated with polarization of the S–S bond,[16] which results in conjugation between the unshared electrons of the two sulfur atoms[17] and raises the energy for polarization of the p–sp^3 bond between the sulfur and carbon atoms.

As mentioned above, no reaction was observed between hexafluoroacetone and fluorinated sulfides. When H$_2$NC(CF$_3$)SCH$_2$CH$_2$S was reacted with hexafluoroacetone at 25 °C, a mixture of compounds VII and VIII was obtained (eq 10). Compound VII is the product expected from the reaction 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 NH$_2$ 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 ^{19}F NMR spectra. Complete conversion, however, was not observed. In contrast, when H$_2$N(CF$_3$)COCH$_2$CH$_2$O 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.



(10)

VII VIII



(11)

IX

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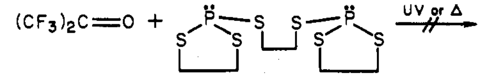
[16] Koch, H. P. *J. Chem. Soc.* **1949**, 394.

[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.

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).



(12)

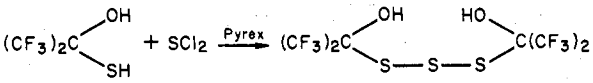
X

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 ClF, cleavage of the C–S bond occurred to give compounds such as SCl_2, HFA, and HF (SiF_4 and H_2O) (eq 13). The HFA is hydrated by the water formed

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

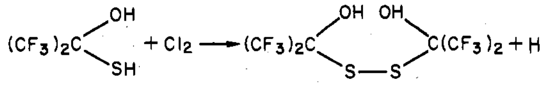
to give white crystalline $(CF_3)_2C(OH)_2$.

With SF_4, dehydration does occur, resulting in the formation of the blue thioketone. When $(CF_3)_2C(OH)SH$ was reacted with SCl_2, compound XI was obtained with concomitant formation of HCl (eq 14). Compound XI is a colorless, 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 compound XII behave identically with their precursor $(CF_3)_2C(OH)SH$ when reacted with SF_4, giving the thioketone and elemental sulfur (eq 16). An analogue of compound XII,



(14)

IX

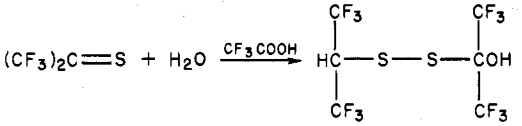


(15)

XII

$$\text{XI (or XII)} + SF_4 \xrightarrow{\text{Pyrex}} (CF_3)_2C{=}S + SiF_4 + S + SOF_2 \quad (16)$$

$H(CF_3)_2CSSC(CF_3)_2OH$, was obtained[20] when $(CF_3)_2C{=}S$ was hydrated in the presence of trifluoroacetic acid



(17)

Experimental Section

Materials. The following compounds were obtained from the sources indicated: $\overline{\mathrm{CH_2CH_2S}}$, $\overline{\mathrm{CH_2CH_2CH_2S}}$, and $\overline{\mathrm{CH_2CH_2CH_2CH_2S}}$ (Eastman), SF_4 (Matheson, Inc.), ClF (Ozark-Mahoning, Inc.), $S{=}PCl_3$ (Columbia Organic), CH_3SCH_3 (Aldrich Chemical Inc.), CH_3SSCH_3 (Crown Zellerbach), SCl_2, $(CF_3)_2CO$ (PCR), Cl_2 (Baker). $(CF_3)_2C(OH)SH$,[19] $CF_3\overline{\mathrm{C(NH_2)SCH_2CH_2S}}$,[10] and $CF_3\overline{\mathrm{C(NH_2)OCH_2CH_2O}}$,[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 ^{19}F NMR spectra were obtained by using a Varian HA-100 spectrometer with CCl_3F as internal reference. ^{31}P and ^{13}C NMR spectra were taken on a Bruker WH-90 spectrometer with 85% H_3PO_4 as external reference or with $CDCl_3$ as internal lock (Me_4Si as reference). ^{1}H NMR spectra were obtained by using a Varian EM-360 spectrometer with Me_4Si as reference.

Preparation of $\overline{\mathrm{OC(CF_3)_2C(CF_3)_2OS}}{=}PCl_3$ (I). A 3-mmol sample of $(CF_3)_2C{=}O$ was condensed onto 1.5 mmol of $SPCl_3$ 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 ^{19}F NMR spectrum has a singlet at $\phi = -78.0$. The ^{31}P NMR spectrum is a singlet at 34.97 ppm (H_3PO_4 reference), and the ^{13}C NMR spectrum of the trifluoromethyl carbons is a quartet at 122 ppm (relative to Me_4Si). The latter has some fine structure ($J < 5$ Hz) probably arising from long range ^{31}P–^{13}C 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 [$[M - (CF_3)_2CO]^+$], and m/e 299–303 [$[(CF_3)_2COSPCl_3]^+$]. 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 $C_6O_2SPCl_3F_{12}$: C, 14.36; F, 45.55; P, 6.19. Found: C, 14.50; F, 46.0; P, 6.06.

Preparation of $(CF_3)_2\overline{\mathrm{COSCH_2CH_2CH_2}}$ (II). $(CF_3)_2C{=}O$ (2 mmol) was condensed into a vessel containing approximately 1 mmol of $\overline{\mathrm{CH_2CH_2CH_2S}}$, 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 ^{19}F NMR spectrum (tetrahydrofuran as solvent) contains a band at ϕ −83.2 ($^{4}J_{HF} = 3.7$ Hz). The ^{1}H 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 [$(M - CF_3)^+$], m/e 95 [$(CF_3CCH_2)^+$], and m/e 90 [$(OSCH_2CH_2CH_2)^+$]. 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 $C(CF_3)_2(OH)\overline{\mathrm{CHCH_2CH_2CH(C(CF_3)_2OH]S}}$ (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 CCl_4. The ^{19}F NMR spectrum consists of four quartets at ϕ −72.4, −72.66, −75.03, and −75.29 with $J_{FF} = 12$ Hz. The ^{1}H NMR spectrum has two multiplets at δ 1.65 and 3.55. The ^{13}C spectrum for carbon of CF_3 consists of a quartet at 120 ppm (relative to Me_4Si) 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 [$(M - CF_3)^+$], m/e 254 [$(M - (CF_3)_2CO)^+$], and m/e 185 [$(SCH_2CH_2CH_2CH_2OCCF_3)^+$]. The infrared spectrum has bands at 2960 (w), 1452 (w), 1278 (s), 1233 (vs, br), and 1148 (m). Anal. Calcd for $C_{10}F_{12}O_2SH_8$: C, 28.57; H, 1.90. Found: C, 29.58; H, 1.92.

Preparation of $HOC(CF_3)_2CH_2SCH_2C(CF_3)_2OH$ (IV). Dimethyl sulfide (1.5 mmol) was condensed with 3 mmol of $(CF_3)_2C{=}O$ 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 ^{19}F NMR spectrum has a singlet at ϕ −77.6. The ^{1}H 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 ($M - CF_3^+$), and m/e 227 [$[CH_2SCH_2C(CF_3)_2OH]^+$]. 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 $C_8F_{12}SO_2H_6$: C, 24.37; H, 1.52. Found: C, 24.06; H, 1.3.

Preparation of $HOC(CF_3)_2CH_2SSCH_2C(CF_3)_2OH$ (V). Dimethyldisulfane (1 mmol) and $(CF_3)_2C{=}O$ (2 mmol) were condensed

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together in a Pyrex vessel. After photolysis at 0 °C for several days, a yellow oil was obtained in poor yield. The ^{19}F NMR spectrum has a band at ϕ −77.5. The ^{1}H 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 [$(M - CF_3)^+$]. 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 $C_8F_{12}S_2O_2H_6$: C, 22.54. Found: C, 22.20.

Preparation of $F(CF_3)_2CCH_2SCH_2C(CF_3)_2F$ (VI). Approximately 0.4 g of $HO(CF_3)_2CCH_2SCH_2C(CF_3)_2OH$ (1 mmol) was reacted with excess SF_4 at 25 °C overnight. After removal of the volatile SOF_2, the light pink solid, which was recrystallized from anhydrous ether, had a melting point of 63 °C. The ^{19}F NMR spectrum has bands at ϕ −151.4 (CF) and ϕ −76 (CF_3) 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 [$(M - CF_3)^+$] and *m/e* 215 [$(CF_3)_2CFCH_2S]^+$ were obtained.

Preparation of $HO(CF_3)_2CNH(CF_3)\overline{CSCH_2CH_2S}$ (VII) and $(CF_3)_2C{=}N(CF_3)\overline{CSCH_2CH_2S}$ (VIII). Approximately 1 mmol of $H_2N(CF_3)\overline{CSCH_2CH_2S}$ was reacted with a slight excess of $(CF_3)_2C{=}O$ 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 ^{19}F NMR spectrum for VII has bands at ϕ −77.59 (CF_3CS) and ϕ −79.23 [$(CF_3)_2CO$]. Compound VIII has bands at ϕ −77.85 ($CF_3C{-}N$) and ϕ −75.62 [$(CF_3)_2C{=}N$]. 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 [$[(CF_3)_2CN(CF_2)\overline{CSCH_2CH_2S}]^+$], *m/e* 268 [$(CF_3CNCF_3\text{-}\overline{CSCH_2CH_2S})^+$], and *m/e* 221 [$(CF_2CSSNCCF_3)^+$].

Preparation of $(CF_3)_2C{=}N(CF_3)\overline{COCH_2CH_2O}$ (IX). Excess $(CF_3)_2C{=}O$ was condensed into a vessel containing 1 mmol of $H_2N(CF_3)\overline{COCH_2CH_2O}$. After warming from −196 to 25 °C, the mixture was allowed to stand at 25 °C for 3 days. The ^{19}F NMR spectrum of the colorless, high-boiling liquid has bands at ϕ −85.3 ($CF_3{-}C{-}N$) and ϕ −80.8 and −81 [$(CF_3)_2C{=}N$] 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 [$(CF_3COCH_2NCCFCF_2)^+$], *m/e* 141 [$(CF_3\overline{COCH_2CH_2O})^+$], and *m/e* 127 [$(CF_3OCOCH_2)^+$]. The infrared spectrum had absorption bands at 2958 (vw), 1695 (m), 1381 (w), 1218 (vs, br), 1171 (s), 1020 (w), 965 (m), 952 (m), and 725 (w) cm^{-1}.

Preparation of $\overline{SCH_2CH_2S}P\overline{SCH_2CH_2S}P\overline{SCH_2CH_2S}$ (X). PCl_3 (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 ^{1}H 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 [$(M - CH_2CH_2S)^+$], *m/e* 215 [$(M - PSCH_2CH_2SPS)^+$], and *m/e* 123 [$(SCH_2CH_2SP)^+$].

Preparation of $HO(CF_3)_2CSSSC(CF_3)_2OH$ (XI). $(CF_3)_2C(OH)SH$ (2 mmol) and SCl_2 (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 ^{19}F NMR spectrum of the colorless, high-boiling liquid obtained has a band at ϕ −75.7. The ^{1}H 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 [$[(CF_3)_2C{-}S]^+$] and *m/e* 166 [$[(CF_3)_2CO]^+$] 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 $C_6F_{12}S_3O_2H_2$: C, 16.74; F, 53.02; S, 22.33. Found: C, 16.86; F, 52.9; S, 22.57.

Preparation of $HO(CF_3)_2CSSC(CF_3)_2OH$ (XII). $(CF_3)_2C(OH)SH$ (2 mmol) was condensed with excess Cl_2 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 ^{19}F NMR spectrum has a band at ϕ −76.2. The ^{1}H NMR spectrum contains a singlet at δ 4.2. Only appropriate fragments such as *m/e* 182 [$[(CF_3)_2C{-}S]^+$] and *m/e* 166 [$[(CF_3)_2CO]^+$] 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 $C_6F_{12}S_2O_2H_2$: C, 18.09; F, 57.29; S, 16.08. Found: C, 18.13; F, 56.98; S, 15.90.

Reactions of SF_4 with $(CF_3)_2C(OH)SH$, XI, and XII. In all cases, approximately 1 mmol of reactant was reacted with a slight excess of SF_4 at −78 °C. An intense blue color due to $(CF_3)_2C{=}S$ 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 ClF. A 1-mmol sample of $(CF_3)_2C(OH)SH$ was reacted with 1 mmol of ClF at −78 °C in a Hoke metal vessel for several hours. After trap-to-trap distillation, SCl_2 and $(CF_3)_2CO{\cdot}H_2O$ were found in the volatile materials.

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