considered. Other reaction pathways are of minimal importance and are neglected in this zero-order treatment of the experimental data.

The amount of propene-t was small in both moderated and unmoderated samples.[12] It was possible for fragmentation to yield a C_3 unit in a manner akin to that observed in certain pyrolysis studies.[37] The small yield of this product did not allow the discerning of yield differences in the various systems.

Polymeric materials were arbitrarily defined as those tritiated species C_8-t or greater which were not eluted through the column during the forward-flow sequence. The higher yields in helium-moderated samples were interpreted as resulting from ion-molecule contributions in this environment. Possible reaction pathways have been mentioned previously.[11] It is interesting to note that in unmoderated samples there is a trend for light polymer-t to exceed heavy polymer-t several-fold. The opposite is true in moderated samples.

The yield of methylcyclohexane appears to be higher in moderated samples. There is an obvious increase in the yield of this product with increasing mole fraction in helium-moderated samples, and this may be interpreted as being due to IM contributions. One possible reaction pathway for this product would be tritium attack on a given carbon atom, with the subsequent cleavage of contiguous C–C bonds to form a CH_2T radical or ion. Radical formation by addition of this species to the cyclohexene double bond where followed by hydrogen abstraction would give methylcyclohexane.

Conclusions

As expected for recoil chemistry, a wide variety of products has been observed in this work. A median excitation energy for the unimolecular decompositions of cyclohexene-t has been determined to be 5 eV for the gas-phase studies. The liquid-phase studies gave a median excitation energy of 8 eV. These calculations are based on the premise that the formation of ethene-t and 1,3-butadiene-t results primarily from the unimolecular decomposition of an initially excited cyclohexene-t molecule. It is possible that other minor pathways also contribute to these products.

The S/D ratio of decomposition of the cyclohexyl-t radical was shown to be a function of the mole ratio of moderator in moderated samples. In unmoderated samples a pressure dependence of the ratio was observed. The fact that $(S/D)^{-1}$ was not a linear function of P^{-1} in either moderated or unmoderated samples showed that the postulated cyclohexyl-t precursor had a wide variety of excitation energies. The rate constant for the decomposition of the cyclohexyl-t radical was determined to be 1.0×10^8 sec^{-1}.

Acknowledgments. Fellowship support from the Gulf Oil Corp., Monsanto Co., and the donors of the Petroleum Research Fund is gratefully acknowledged by R. W. W., Jr. The calculations by Dr. A. P. Yu are appreciated.

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[37] D. L. Fanter, J. Q. Walker, and C. J. Wolf, *Anal. Chem.*, **40**, 2168 (1968).

Synthesis and Characterization of Bis(trifluoromethyl)-thiophosphoryl-μ-thio-bis(trifluoromethyl)phosphine and Di(bis(trifluoromethyl)thiophosphoryl) Disulfide

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Abstract: Bis(trifluoromethyl)iodophosphine sulfide reacts with limited quantities of mercury to give the diphosphorus compound $(CF_3)_2P(S)$–S–$P(CF_3)_2$ in which the phosphorus atoms are bridged by a sulfur atom. This same compound is better synthesized from the reaction of bis(trifluoromethyl)dithiophosphinic acid with either dimethylaminobis(trifluoromethyl)phosphine or with chlorobis(trifluoromethyl)phosphine. The mixed-valence compound is stable to air or sulfur oxidation but reacts with hydrogen halides, halogens, and mercury. Hydrolysis by water and alkaline solutions gave 1 and 3 mol of CF_3H, respectively, per mole of compound. The diphosphine tetrasulfide, $(CF_3)_2P(S)SSP(S)(CF_3)_2$, was best prepared by bromination of salts of bis(trifluoromethyl)dithiophosphinic acid. The tetrasulfide also reacted with mercury, halogens, hydrogen halides, and hydrogen sulfide, but not with oxygen or sulfur. Alkaline hydrolysis gave 2 mol of CF_3H per mole of compound, while neutral water yielded no CF_3H. A simpler synthesis of $(CF_3)_2P(S)SH$ is also described.

The recent syntheses of bis(trifluoromethyl)dithiophosphinic acid[1,2] and related trifluoromethylphosphine sulfides has led to an extensive study of the chemistry of this system. We wish to report herein details of the synthesis and properties of the mixed-valence compound[3] $(CF_3)_2P(S)$–S–$P(CF_3)_2$ and the related tetrasulfur–diphosphorus compound $[(CF_3)_2P(S)]_2S_2$. The possible existence of the mixed-valence compound

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[1] R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Amer. Chem. Soc.*, **90**, 2015 (1968).

[2] K. Gosling and A. B. Burg, *ibid.*, **90**, 2011 (1968).

[3] For a preliminary communication on the mixed-valence compound, see R. G. Cavell, T. L. Charlton, and A. A. Pinkerton, *Chem. Commun.*, 424 (1969).

as an unstable intermediate was suggested by Burg and Gosling;[2] however, we find the compound to be quite stable and easily handled *in vacuo*.

Results

Synthesis and Structure of the Mixed-Valence Compound. The reaction of $(CF_3)_2P(S)I$ with a stoichiometric quantity of mercury leads to the coupling of two $(CF_3)_2P(S)$ units to form a dimer

$$2(CF_3)_2P(S)I + Hg \longrightarrow (CF_3)_4P_2S_2 + HgI_2 \qquad (1)$$

in a manner reminiscent of the synthesis of $(CF_3)_4P_2$.[4] The product, however, does not possess a P–P bond but rather has the isomeric structure with pentavalent and trivalent phosphorus atoms in the same molecule: $(CF_3)_2P(S)\text{–}S\text{–}P(CF_3)_2$. Reaction of this mixed-valence diphosphorus compound with excess mercury gave the known sulfur-bridged diphosphine[5,6] $(CF_3)_2P\text{–}S\text{–}P(CF_3)_2$, in agreement with our earlier report[1] that reaction of $(CF_3)_2P(S)I$ with excess mercury gave only $(CF_3)_2P\text{–}S\text{–}P(CF_3)_2$ in nearly quantitative yield; thus this product arises from a simple reduction of the mixed-valence compound and not a complicated series of exchanges.[2] Reaction 1 is not a suitable preparative method for the mixed-valence compounds because complete consumption of the iodo compound requires an excess of mercury, which results in the formation of only $(CF_3)_2P\text{–}S\text{–}P(CF_3)_2$, since it appears that the second reduction step proceeds readily under conditions required for eq 1. The reactants and products are also difficult to separate.

A more suitable synthesis was devised from the knowledge that the structure contained pentavalent and trivalent phosphorus atoms. The reaction

$$2(CF_3)_2P(S)SH + (CF_3)_2P\text{–}N(CH_3)_2 \longrightarrow (CF_3)_2P(S)\text{–}S\text{–}P(CF_3)_2 + (CH_3)_2NH_2^+S_2P(CF_3)_2^- \qquad (2)$$

gave a good yield of the mixed-valence diphosphorus compound and the product was easily separable from the reactants and other impurities. The desired compound can also be obtained from the reaction

$$(CF_3)_2P(S)SH + (CF_3)_2PCl \rightleftharpoons (CF_3)_2P(S)\text{–}S\text{–}P(CF_3)_2 + HCl \qquad (3)$$

which is written as an equilibrium since the reverse reaction is known to proceed when the mixed-valence compound is treated with excess HCl (*vide infra*). A good yield of $(CF_3)_2P(S)SP(CF_3)_2$ can be obtained from the reaction if a large excess of $(CF_3)_2PCl$ is used. Since the components involved in reaction 3 can be readily separated from each other, the reaction is also convenient for synthetic purposes.

Other reactions also give this mixed-valence compound in reasonable yield. A preliminary experiment conducted in these laboratories in 1967 by Dr. R. C. Dobbie involved heating excess elemental sulfur with tetrakis(trifluoromethyl)diphosphine for 4 days at 160°. We can now identify the mixed-valence compound $(CF_3)_2P(S)\text{–}S\text{–}P(CF_3)_2$ as the major constituent of the volatile portion of the products by means of its characteristic nmr spectrum. Two other as yet unidentified volatile products were obtained in the same fraction as the mixed-valence compound and an involatile product was also found in the original reaction tube. Similarly, heating sulfur with $(CF_3)_2P\text{–}S\text{–}P(CF_3)_2$ yields the mixed-valence compound plus unidentified volatile products. Not surprisingly, the tetrasulfide $(CF_3)_4P_2S_4$ was not found among the volatile products, probably because of its thermal instability (*vide infra*). In neither of these systems can the mixed-valence compound be easily separated; hence these reactions are not particularly useful for synthetic purposes. The presence of the mixed-valence compound, however, suggests that our simple two-step synthesis of $(CF_3)_2P(S)SH$ from tetrakis(trifluoromethyl)diphosphine, sulfur, and hydrogen sulfide described in the Experimental Section probably proceeds through the initial formation of $(CF_3)_2P(S)\text{–}S\text{–}P(CF_3)_2$, which appears to be the most stable member of this phosphorus–sulfur system. The mixed-valence compound is then easily converted to the acid by hydrogen sulfide in the presence of excess sulfur. Higher related polysulfide intermediates may also be involved and cannot be excluded from consideration, although their presence is not necessary.

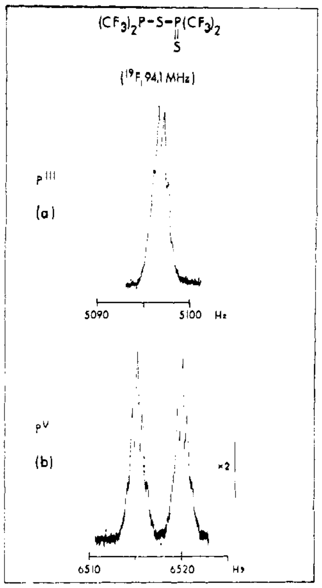

Figure 1. Part of the ^{19}F nmr spectrum of $(CF_3)_2P(S)\text{–}S\text{–}P(CF_3)_2$ measured at 94.1 MHz on a 15% solution of the compound in CCl_3F. Temperature of measurement was 40°. Frequencies are measured relative to CCl_3F: (a) the high-field component of the doublet arising from CF_3 attached to P(III) which shows the overlapping pattern resulting from near equality of $^4J_{FP^V}$ and $^6J_{FF}$ (an identical peak is found about 80 Hz to low field), (b) the high-field component of the major doublet arising from CF_3 attached to P^V showing the clearly resolved $^4J_{FP^{III}}$ doubling and the partially resolved "septet" due to $^6J_{FF}$. The vertical scale of arbitrary absorption units has been multiplied by two for this region; therefore, the total intensity in each of the two regions is identical. Another identical doublet is found about 110 Hz to low field.

The nmr spectra provide the best evidence for the mixed-valence structure of $(CF_3)_4P_2S_2$. The ^{19}F nmr spectrum shows two major doublets, one of which has a chemical shift (ϕ 68.7 ppm *vs.* $CFCl_3$)[7a] and coupling constant ($^2J_{FP^V}$ = 111.7 Hz)[7b,c] which are characteristic of a pentavalent trifluoromethylthiophosphoryl group.[1] Each component of this doublet is clearly split into a doublet of septets, as illustrated in Figure 1, which

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[4] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

[5] R. G. Cavell and H. J. Emeléus, *ibid.*, 5825 (1964).

[6] A. B. Burg and K. Gosling, *J. Amer. Chem. Soc.*, 87, 2113 (1965).

[7] (a) Positive values indicate resonances to high field of the reference; (b) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962); (c) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

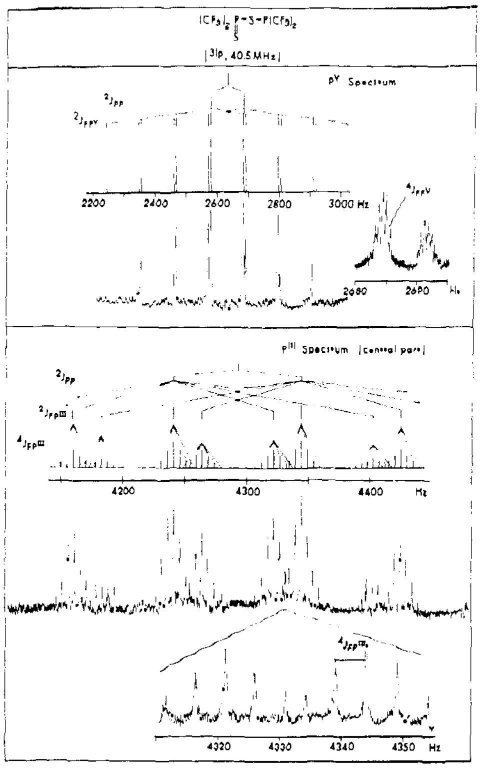


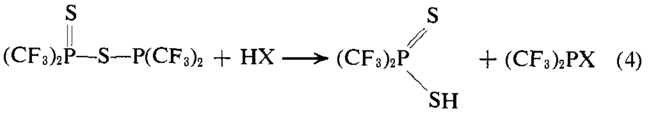
Figure 2. Portions of the 40.5-MHz ^{31}P spectrum of $(CF_3)_2P(S)SP(CF_3)_2$. In the upper compartment most of the P^V spectrum is shown illustrating the overlapping pattern due to $^2J_{PP}$ and $^2J_{FP^V}$. The higher resolution display of one of the central members in the inset illustrates the pattern which arises from $^4J_{PP^V}$ coupling. The lower compartment shows the central portion of the P(III) spectrum arising from $^2J_{PP}$, $^2J_{FP^{III}}$, and $^6J_{FP^{III}}$ coupling interactions on the P(III). The high-resolution inset shows clearly the five central members of the septets which are in correct intensity ratio for septet components. The frequency scale is measured relative to P_4O_6 with positive sign denoting high field.

can be assigned to long-range CF_3-P-P^{III} coupling ($^4J_{FP^{III}}$ = 4.9 Hz) and long-range F-F coupling ($^6J_{FF}$ = 0.5 Hz). The second major doublet with total intensity equal to the first has a chemical shift (ϕ 53.8 ppm *vs.* $CFCl_3$) and coupling constant ($^2J_{FP^{III}}$ = 81.3 Hz) which are characteristic of a trivalent CF_3P group.[8] Each component of the doublet arising from the CF_3 groups attached to P^{III} is complex, as shown in Figure 1a and is best understood on the basis of a first-order analysis with the long-range P-F coupling constant ($^4J_{FP^V}$ = 0.6 Hz) nearly equal to the long-range F-F coupling constant ($^6J_{FF}$). The ^{31}P spectrum of the mixed-valence compound illustrated in part in Figure 2 clearly demonstrates the existence of two chemically shifted phosphorus atoms. The P^V region (δ +65.2 ppm *vs.* P_4O_6)[7a] shows a complex pattern of an overlapping doublet of septets owing to very similar values of $^2J_{FP^V}$ and the phosphorus-to-phosphorus coupling constant ($^2J_{PP}$ = 103.0 Hz). Closer examination of one component shows the "septet" structure due to coupling of the phosphorus with the fluorines of the $(CF_3)_2P^{III}$ group ($^4J_{FP^V}$ = 0.6 Hz). The P^{III} spectrum (δ +106.0 ppm *vs.* P_4O_6)[7a] is fully assigned on the basis of first-order spin-coupling interactions. A notable feature of the spectra is the dramatic difference between $^4J_{FP^V}$ and $^4J_{FP^{III}}$ coupling constants, which contributes to the more clearly resolved P^{III} spectrum. A similar phenomenon was observed[7c] in the spectra of $(CH_3)_2P\cdot P(S)(CH_3)_2$, except that in this case $^3J_{HP^{III}}$ (5.8 Hz) is smaller than $^3J_{HP^V}$ (17.6 Hz), whereas the reverse is observed here.

Infrared spectral studies gave less conclusive structural information, but did show a complex overlapping series of bands in the CF_3 region and a reasonably strong band at 783 cm^{-1} which could be assigned to a P=S absorption.[9]

Properties of the Mixed-Valence Compound. The mixed valence diphosphorus compound was thermally stable to 165° and it was not oxidized by sulfur at this temperature or oxygen at room temperature. Alkaline hydrolysis yielded 3 mol of CF_3H per mol of compound, presumably because the pentavalent end of the molecule ultimately hydrolyzes to the hydrolytically stable[10,11] trifluoromethylphosphorus(V) acid salt, whereas the trivalent end hydrolyzes with complete removal of CF_3 groups. Neutral hydrolysis of the mixed-valence compound yields only 1 mol of CF_3H per mol of compound, a result which can perhaps be explained by a consideration of the attack of a series of protonic acids and bases on this compound.

In general, hydrogen sulfide and the hydrogen halides split the P-S-P bridge at the P^{III}-S bond according to the equation



$$(CF_3)_2\overset{S}{\overset{\|}{P}}-S-P(CF_3)_2 + HX \longrightarrow (CF_3)_2P(=S)SH + (CF_3)_2PX \quad (4)$$

where X = SH, Cl, or Br.

The observed complex mixture of products obtained from the reaction of hydrogen iodide with the mixed-valence compound can be satisfactorily explained if the reaction is considered to proceed initially according to eq 4 and the products are then permitted to react further with HI: thus the acid is reduced to $(CF_3)_2PSH$ (as we have verified by a separate experiment)

$$(CF_3)_2P(S)SH + 2HI \longrightarrow (CF_3)_2PSH + H_2S + I_2 \quad (5)$$

and the iodo phosphine is reduced by HI.[12]

$$(CF_3)_2PI + HI \longrightarrow (CF_3)_2PH + I_2 \quad (6)$$

Since reactions 5 and 6 proceed readily under conditions required for the initial cleavage, the use of a limited quantity of HI leads to a mixture of the above products.

The neutral hydrolysis result can then be explained by assuming that water reacts initially according to eq 4 to yield $(CF_3)_2P(S)SH$ and $(CF_3)_2POH$, similar to the products from the reaction of H_2S. The former is stable in water,[11] whereas the latter hydrolyzes[10b,11] to $CF_3P(H)O_2^-$, yielding 1 mol of fluoroform.

Chlorine and bromine reacted with the mixed-valence diphosphorus compound to yield the monophosphorus compounds $(CF_3)_2P(S)X$ and $(CF_3)_2PX$ (X = Cl or Br) expected from cleavage of the P^{III}-S bridge bond, possibly with the formation of $(CF_3)_2PS_2\cdot$ radicals. Excess halogen oxidizes the trivalent halogenophosphines

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(8) K. J. Packer, *J. Chem. Soc.*, 960 (1963).

(9) R. G. Cavell and H. J. Emeléus, *ibid.*, 5896 (1964).

(10) (a) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *ibid.*, 3896 (1954); (b) *ibid.*, 3598 (1954).

(11) R. G. Cavell, A. A. Pinkerton, and R. D. Leary, unpublished observations.

(12) R. G. Cavell and R. C. Dobbie, *J. Chem. Soc. A*, 1308 (1967).

to the pentavalent compounds $(CF_3)_2PX_3$, and chlorine but not bromine converts $(CF_3)_2P(S)X$ to $(CF_3)_2PX_3$. A small amount of CF_3Br detected in the reaction products may arise from the decomposition of $(CF_3)_2PBr_3$.[13] The sulfur halides, which could not be properly characterized, may arise from decomposition of compounds such as $(CF_3)_2P(S)SCl$ which, however, were not isolated.

Reaction of approximately equimolar ratios of halogen and $(CF_3)_2P(S)–S–P(CF_3)_2$ under similar conditions have essentially the same results except that complete consumption of the original diphosphorus compound was not achieved and only limited oxidation of phosphines to halogenophosphoranes was observed. The new diphosphine tetrasulfide was obtained in small yield from both of these reactions, suggesting the presence of $(CF_3)_2PS_2\cdot$ radicals in the system.

Synthesis and Properties of the Tetrasulfide. The new tetrasulfide, $(CF_3)_2P(S)–S–S–P(S)(CF_3)_2$, was best obtained from the reaction of salts of the dithiophosphinic acid with bromine.[14]

$$2(CF_3)_2PS_2^-Na^+ + Br_2 \longrightarrow (CF_3)_4P_2S_4 + 2NaBr \qquad (7)$$

The nmr and infrared spectra of the tetrasulfide are compatible with the disulfide bridge structure. The ^{19}F nmr spectrum is second order, showing a sharp doublet due to $|^2J_{PF} + {}^5J_{PF}|$ with a separation of 105.5 Hz with smaller peaks on either side of the major doublet characteristic of the second-order ^{19}F spectra of molecules of the type $(CF_3)_2P\cdot S\cdot P(CF_3)_2$, $(CF_3)_2P\cdot O\cdot P(CF_3)_2$, and $(CF_3)_4P_2$.[11] Complete analysis is not possible at this time but it is clear that the ^{19}F and ^{31}P chemical shift parameters (ϕ +66.5 ppm *vs.* $CFCl_3$ and δ +55.4 ppm *vs.* P_4O_6) are compatible with the existence of equivalent pentavalent phosphorus atoms. Infrared spectra are relatively simple showing strong $P^V(C–F)$ bands in the 1100–1200-cm^{-1} region and a P=S band at 781 cm^{-1}.

Heating the tetrasulfide to 165° for 2 days resulted in thermal decomposition of the compound to the mixed-valence compound and sulfur. No $(CF_3)_2P(S)–S–P(S)(CF_3)_2$ was observed. Alkaline hydrolysis gave 2 mol of CF_3H per mol of compound, which suggests that the tetrasulfide is initially cleaved at the S–S bond to yield 2 mol of pentavalent trifluoromethylthiophosphorus anions, which are subsequently hydrolyzed by base to yield 1 mol of CF_3H and 1 mol of the hydrolytically stable CF_3P^V anion. Water yielded elemental sulfur but no CF_3H, in agreement with observations that the bis(trifluoromethyl)thio- and -oxyphosphinic acids and their salts are stable in water.[11]

Treatment of the tetrasulfide with H_2S gave good yields of $(CF_3)_2PS_2H$, whereas HCl and HBr gave a 1 molar equiv of the same acid plus the halogenophosphine sulfide. Both results can be summarized by the overall equation

$$(CF_3)_2P(S)–S–S–P(S)(CF_3)_2 + HX \longrightarrow (CH_3)_2P(S)SH + (CF_3)_2P(S)X + S \qquad (8)$$

where X = HS, Cl, or Br. Sulfur is also obtained from the reaction.

Hydrogen iodide reactions are much more complicated. Excess hydrogen iodide converts all of the tetrasulfide to $(CF_3)_2PSH$, leaving iodine and hydrogen sulfide as the only other volatile products. A twofold molar ratio of hydrogen iodide gave nearly 2 mol of the acid $(CF_3)_2P(S)SH$ from 1 mol of the tetrasulfide plus small amounts of $(CF_3)_2PSH$, H_2S, HI, and a large amount of iodine. Sulfur was not obtained in either reaction. The stoichiometry is best represented by

$$(CF_3)_4P_2S_4 + 2HI \longrightarrow (CF_3)_2P(S)SH + I_2 \qquad (9)$$

noting, however, that in the presence of excess hydrogen iodide the acid is further reduced to the thiophosphine $(CF_3)_2PSH$ (eq 5). Also, excess hydrogen iodide will react readily with sulfur to give hydrogen sulfide and iodine.[15] The reaction probably involves the splitting of the tetrasulfide molecule at the S–S bond with the initial formation of unstable compounds of the type $(CF_3)_2P(S)SX$ rather than $(CF_3)_2P(S)X$ compounds. The unstable sulfenyl compounds either decompose to sulfur and the observed $(CF_3)_2P(S)X$ products

$$(CF_3)_2P(S)SX \longrightarrow (CF_3)_2P(S)X + S \qquad (10)$$

where X = Cl, Br, or SH, or, where X = I, are reduced to the acid by hydrogen iodide.

$$(CF_3)_2P(S)SI + HI \longrightarrow (CF_3)_2P(S)SH + I_2 \qquad (11)$$

Support for this interpretation comes mainly from the formation of only the acid and not $(CF_3)_2P(S)I$ from the stoichiometric hydrogen iodide reaction, since separate experiments have demonstrated that H_2S (which may be present in the system from the reaction of sulfur and HI[15]) only slowly reduced $(CF_3)_2P(S)I$ to a mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2PI$, whereas the process represented by eq 9 is fast Also, $(CF_3)_2P(S)I$ is rather quickly reduced to $(CF_3)_2PSH$ by HI.

Chlorine splits the tetrasulfide and removes sulfur to yield $(CF_3)_2PCl_3$, whereas bromine gives only $(CF_3)_2P(S)Br$. Sulfur or air did not react with the tetrasulfide.

Mercury reacted with the tetrasulfide to form the Hg^{II} complex $[(CF_3)_2PS_2]_2Hg$, which, upon heating, gave a small amount of HgS and $(CF_3)_2P–S–P(CF_3)_2$. Further studies on this and other dithiophosphinate complexes will be reported elsewhere.

Mass Spectra. Both compounds show the expected[16] fragmentation and rearrangement patterns in the mass spectrometer. The mixed-valence compound does not show a parent ion, but the ions at *m/e* 333 and 233 have been shown to contain the P_2S_2 group by mass measurement, thus supporting the structural formula. The latter ion (which is $(CF_3)_2PS_2^+$) is the smallest fluorocarbon fragment containing two sulfur atoms. The fragmentation pattern of the mixed-valence compound follows two pathways. (a) Initial loss of sulfur from the parent molecule is followed by loss of a CF_3 group

$$C_4F_{12}P_2S^+ \longrightarrow C_3F_9P_2S^+ + CF_3$$

as demonstrated by the metastable peak at *m/e* 245.0 (calcd *m/e* 244.9) followed by successive loss of two CF_2 groups from the $C_3F_9P_2S^+$ ion as demonstrated by the metastable peaks at *m/e* 209.0 and 161.0 (calcd *m/e* 209.3 and 161.0, respectively) to give an overall pattern similar to that of $(CF_3)_4P_2S$.[16b] (b) The second path involves the initial loss of CF_3 from the parent molecule, followed by loss of CF_2 from the ion containing a P_2S_2

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[13] A. B. Burg and J. E. Griffiths, *J. Amer. Chem. Soc.*, **82**, 3514, (1960).

[14] L. Maier, *Top. Phosphorus Chem.*, **2**, 43 (1965).

[15] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, **7**, 2195 (1968).

[16] (a) R. G. Cavell and R. C. Dobbie, *ibid.*, **7**, 101 (1968); (b) *ibid.*, **7**, 690 (1968).

group

$$C_3F_9P_2S_2^+ \longrightarrow C_2F_7P_2S_2^+ + CF_2$$

as indicated by the metastable peak at *m/e* 240.5 (calcd *m/e* 240.5).

The mass spectrum of $(CF_3)_2P(S)SSP(S)(CF_3)_2$ shows a strong parent ion, the identity of which has been demonstrated by mass measurement. The initial step in the fragmentation pattern involves loss of a CF_3 group from the parent ion

$$C_4F_{12}P_2S_4^+ \longrightarrow C_3F_9P_2S_4^+ + CF_3$$

as confirmed by the observed metastable ion at *m/e* 338.1 (calcd *m/e* 338.2) and then the path splits, the next step involving either loss of S or CF_3.

Discussion

In contrast to the P-P-bonded structure observed in organodiphosphine disulfides and in diphosphine monoxide and monosulfides,[17] both the trifluoromethyldiphosphine disulfide discussed herein and the analogous fluorodiphosphine disulfide[18] and diphosphine dioxide[18,19] possess a P–X–P structure which is confirmed by nmr and infrared structural evidence as well as by the chemical syntheses and properties of the compounds.

This marked difference in the structures of diphosphine disulfides may be due to a stabilization of the trivalent state of phosphorus by the CF_3 or F group, in keeping with earlier observations on related compounds.[5,6,20,21] The observed structure is probably a compromise between full stabilization of the trivalent state of both phosphorus atoms, which would lead to the disulfide structure P–S–S–P with probably a readily cleaved S–S bond, and the minimal stability provided by the phosphorus–phosphorus-bonded pentavalent state.

It is surprising that the mixed-valence compound appears to be the most stable compound in the system. Attempts to make the diphosphine trisulfide $(CF_3)_4P_2S_3$, which would undoubtedly have the P(S)–S–P(S) structure, have so far been unsuccessful, although there appears to be no inherent reason why this intermediate member of the diphosphorus sulfide series of compounds should be unstable. For example, it has not proved possible to oxidize the mixed-valence compound with sulfur, and thermal decomposition of the tetrasulfide leads only to the mixed-valence disulfide. Other attempted syntheses have also been unsuccessful, but work is now in progress which will hopefully lead to the successful preparation of the desired diphosphine trisulfide and further information about the behavior of this system.

Experimental Section

Standard vacuum techniques were used throughout. The system was constructed of Pyrex glass and stopcocks were lubricated with Apiezon grease. Infrared spectra were routinely recorded for identification on a Perkin-Elmer 337. Spectra of new compounds were recorded on a Perkin-Elmer 421 dual-interchange (4000–300 cm^{-1}) or Beckman IR 11 and 12 instruments. Fluorine nmr spectra were obtained on a Varian A56/60A or a Varian HA100 spectrometer operating at 56.4 and 94.1 MHz, respectively, using approximately 15% solutions in CCl_3F. Phosphorus spectra were recorded on neat liquid samples at 40.3 MHz with the Varian HA-100 instrument. Fluorine chemical shifts were measured relative to CCl_3F and phosphorus chemical shifts were measured relative to a capillary of P_4O_6.[22] Mass spectra were recorded on an AEI MS9 operating at 70 eV with samples introduced as gases or as liquids in a heated capillary where appropriate. Trifluoromethyliodophosphines were prepared from CF_3I and phosphorus,[4] other compounds by literature methods. Reagent grade chemicals, including gaseous dimethylamine and hydrogen sulfide (Matheson), were checked for purity before use, but in general were used as supplied. Hydrogen iodide (Matheson) was vacuum distilled before use. All reactions were carried out in sealed glass tubes.

Preparation of Bis(trifluoromethyl)dithiophosphinic Acid. The diphosphine,[4] $(CF_3)_2P–P(CF_3)_2$ (0.420 g, 1.24 mmol) and excess sulfur (~1 g) were allowed to react for 2 days at 170°. The unidentified products of the reaction were heated at 100° for a further 24 hr with excess H_2S (~2.4 mmol). Vacuum fractionation gave $(CF_3)_2PS_2H$ (0.481 g, 2.06 mmol) in 83% yield (collected at −63°) which was identified by comparison with products prepared by literature methods.[1,2]

The Reaction of Bis(trifluoromethyl)dithiophosphinic Acid with Hydrogen Iodide. $(CF_3)_2PS_2H$ (0.117 g, 0.50 mmol) and HI (0.160 g, 1.23 mmol) reacted immediately on contact at room temperature. After 24 hr vacuum fractionation gave $(CF_3)_2PSH$ (0.096 g, 0.475 mmol) in 95% yield collected at −95°. The more volatile fraction contained H_2S and excess HI identified by their reactions with lead acetate solution. Iodine crystals remained in the reaction tube.

The Reaction of $(CF_3)_2P(S)I$ with Hydrogen Sulfide. $(CF_3)_2P(S)I$ (0.0484 g, 0.147 mmol)[1,2] was combined with excess H_2S (~1.5 mmol) at room temperature for 40 hr. Analysis of the mixture trapped at −116° by nmr revealed $(CF_3)_2P(S)I$, $(CF_3)_2PI$, $(CF_3)_2PSH$,[5,6] and $(CF_3)_2PS_2H$ in the ratio 1:1.2:8.0:11.2.

The reaction of $(CF_3)_2P(S)I$ (0.111 g, 0.337 mmol) with H_2S (0.006 g, 0.18 mmol) for 12 hr while warming from −78° to room temperature followed by 3 days at room temperature gave an unseparated mixture trapped at −116° of $(CF_3)_2PI$, $(CF_3)_2PSH$, $(CF_3)_2PS_2H$, and $(CF_3)_2P(S)I$ in the ratio 1:3.7:5.7:6.8 (by nmr).

The Reaction of $(CF_3)_2P(S)I$ with Hydrogen Iodide. $(CF_3)_2P(S)I$ (0.074 g, 0.23 mmol) and excess hydrogen iodide (~0.9 mmol) were allowed to react in a sealed tube at room temperature. Visible production of iodine began following mixing of the reagents. Fractionation of the volatile products after 24 hr at room temperature gave $(CF_3)_2PSH$ (0.047 g, 0.23 mmol), excess HI, and a barely detectable trace of $(CF_3)_2PH$ as the only observed products.

Preparation of $(CF_3)_2P(S)–S–P(CF_3)_2$. 1. From $(CF_3)_2PS_2H$ and $(CF_3)_2P–N(CH_3)_2$. Bis(trifluoromethyl)dithiophosphinic acid (0.481 g, 2.06 mmol) and dimethylaminobis(trifluoromethyl)phosphine[23] (0.220 g, 1.043 mmol; prepared from $(CF_3)_3P$ and $(CH_3)_2NH$[11]) were allowed to react at room temperature for 24 hr. Vacuum fractionation gave $(CF_3)_2P(S)–S–P(CF_3)_2$ (0.345 g, 0.86 mmol) in 83% yield, collected at −45°. Purification of the crude product from unreacted $(CF_3)_2PS_2H$ and $(CF_3)_2PN(CH_3)_2$ was best achieved by refluxing[24] the crude fraction at −45°. The salt $(CH_3)_2NH_2^+$-$S_2P(CF_3)_2^-$ remained as an involatile residue in the reaction tube.

2. From $(CF_3)_2PS_2H$ and $(CF_3)_2PCl$. Bis(trifluoromethyl)dithiophosphinic acid (0.460 g, 1.97 mmol) and bis(trifluoromethyl)chlorophosphine[25] (1.712 g, 8.37 mmol) were allowed to react for 4 days at 70°. Vacuum fractionation gave $(CF_3)_2P(S)–S–P(CF_3)_2$ (0.670 g, 1.67 mmol) in 85% yield, and excess $(CF_3)_2PCl$ collected at −116°. Final purification was achieved by refluxing at −45°.

3. From $(CF_3)_2P(S)I$ and Hg. Iodobis(trifluoromethyl)phosphine sulfide[1,2] (0.182 g, 0.55 mmol) and mercury (0.058 g, 0.29 mmol) were shaken together for 4 days at room temperature. Vacuum fractionation gave a mixture of $(CF_3)_2P(S)–S–P(CF_3)_2$ and $(CF_3)_2P–S–P(CF_3)_2$ trapping at −45°, and excess $(CF_3)_2P(S)I$ passing −45°. A total of 0.083 g of volatile material was obtained, from which pure $(CF_3)_2P(S)–S–P(CF_3)_2$ was obtained with difficulty by refluxing in the microreflux column.

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Table I. Mass Spectrum of $(CF_3)_4P_2S_2$

Mass no.	Species	Rel abundance[a]	Mass no.	Species	Rel abundance[a]	Mass no.	Species	Rel abundance[a]
370	$C_4F_{12}P_2S^+$	0.7	351	$C_4F_{11}P_2S^+$ [b]	0.3	333	$C_3F_9P_2S_2^+$ [c]	3.2
301	$C_3F_9P_2S^+$ [d]	6.1	283	$C_2F_7P_2S_2^+$	1.2	251	$C_2F_7P_2S^+$	2.4
250	$C_3F_8P_2^+$	0.4	233	$C_2F_6PS_2^+$ [e]	0.3	227	CF_8PS^+	0.2
201	$C_2F_6PS^+$	0.2	169	$C_2F_6P^+$	0.3	163	$C_2F_4PS^+$	1.4
162	$C_3F_5P^+$	0.4	151	CF_4PS^+	1.1	150	$C_2F_5P^+$	1.4
131	$C_2F_4P^+$, $CF_3P_2^+$	1.1	119	CF_4P^+, $C_2F_5^+$	3.3	113	CF_2PS^+	3.7
101	SPF_2^+	0.2	100	CF_3P^+, $C_2F_4^+$	3.6	95	PS_2^+	0.3
94	$CFPS^+$	0.4	81	CF_2P^+	1.9	75	CPS^+	0.5
69	CF_3^+, PF_2^+	31.2	63	PS^+	22.7	62	P_2^+, $C_2F_2^+$, PCF^+	0.7
50	CF_2^+, PF^+	2.2	32	S^+	0.3	31	P^+, CF^+	4.5

[a] Intensities are expressed relative to the total ionization defined as Σ_n (intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. All masses are calculated for the ^{32}S isotope unless otherwise noted. [b] Identity confirmed by mass measurement. Calcd for $C_4F_{11}P_2{}^{32}S$: *m/e*, 350.9020. Found: *m/e*, 350.9024. [c] Identity confirmed by mass measurement. Calcd for $C_3F_9P_2{}^{32}S_2$: *m/e*, 332.8773. Found: *m/e*, 332.8779. [d] Identity confirmed by mass measurement. Calcd for $C_3F_9P_2{}^{32}S$: *m/e*, 300.9052. Found: *m/e*, 300.9053. [e] Identity confirmed by mass measurement. Calcd for $C_2F_6P^{32}S_2$: *m/e*, 232.9084. Found: *m/e*, 232.9084.

Table II. Mass Spectrum of $(CF_3)_4P_2S_4$

Mass no.	Species	Rel abundance[a]	Mass no.	Species	Rel abundance[a]	Mass no.	Species	Rel abundance[a]
466	$C_4F_{12}P_2S_4^+$ [b]	37.5	397	$C_3F_9P_2S_4^+$	5.3	365	$C_3F_9P_2S_3^+$	1.7
333	$C_3F_9P_2S_2^+$	2.3	297	$C_2F_6PS_4^+$	3.4	283	$C_2F_7P_2S_2^+$	1.0
265	$C_2F_6PS_3^+$	2.3	234	$CF_5PS_3^+$	8.8	233	$C_2F_6PS_2^+$	6.9
201	$C_2F_6PS^+$	2.9	165	$F_2PS_3^+$	4.2	133	$F_2PS_2^+$	1.2
119	$C_2F_5^+$, CF_4P^+	3.2	114	FPS_2^+	0.5	113	CF_2PS^+	0.7
101	SPF_2^+	0.7	100	CF_3P^+, $C_2F_4^+$	0.5	95	PS_2^+	1.8
82	PSF^+	0.8	69	CF_3^+ [c]	3.6	64	S_2^+	2.1
63	PS^+	5.2	58	(?)	1.4	32	S^+	1.5
31	CF^+, P^+	0.5						

[a] See footnote *a* of Table I. [b] Identify confirmed by mass measurement. Calcd for $C_4F_{12}P_2{}^{32}S_4$: *m/e*, 465.8168. Found: *m/e*, 465.8167. [c] Identity confirmed by mass measurement. Calcd for CF_3: *m/e*, 68.9952. Found *m/e*, 68.9952.

The reaction tube contained HgI_2 and white crystals of a compound which appeared to be identical with $(CF_3)_4P_2S_4Hg$ obtained below.

Mass Spectrum of $(CF_3)_4P_2S_2$. The mass spectrum is shown in Table I.

Infrared Spectrum of $(CF_3)_4P_2S_2$. The infrared spectrum in the gas phase showed the following peaks:[26] 1202 (vs), 1192 (vs), 1173 (vs), 1160 (vs) (ν_{CF_3}), 1138 (s), and 1125 (s) (all six bands assigned to ν_{CF_3}); 783 (m) ($\nu_{P=S}$); 749 (w) and 734 (m) (δ sym CF_3); 561 (w) and 558 (w) (δ asym CF_3); 548 (w); 500 (s) (ν_{P-S}); 480 (w); 447 (w) cm^{-1}.

Preparation of Tetrakis(trifluoromethyl)diphosphine Tetrasulfide. The anhydrous sodium salt of bis(trifluoromethyl)dithiophosphinic acid[1,2] was obtained by combining the acid (1.615 g, 6.90 mmol) with sodium bicarbonate (0.574 g, 6.84 mmol) in aqueous solution followed by removal of water under vacuum at room temperature. The total yield of salt was combined with bromine (0.55 g, 3.4 mmol) at room temperature for 3 hr, whereupon the bromine color disappeared. Vacuum fractionation gave $(CF_3)_2P(S)$–S–S–$P(S)(CF_3)_2$ (1.490 g, 3.20 mmol) in 94% yield collected at −23°.

Similar results were obtained when the dimethylammonium salt of bis(trifluoromethyl)dithiophosphinic acid was treated with bromine under similar conditions.

The Mass Spectrum of $(CF_3)_4P_2S_4$. The mass spectrum is shown in Table II.

The Infrared Spectrum of $(CF_3)_4P_2S_4$. The gas-phase infrared spectrum showed the following absorptions:[26] 1198 (vs), 1183 (vs), and 1166 (vs) (all due to ν_{CF_3}); 1131 (m); 781 (s) ($\nu_{P=S}$); 731 (s) (δ sym CF_3); 554 (m) (δ asym CF_3); 540 (w); 447 (s) (ν_{P-S}); 458 (w, sh) (ν_{PCF_3}); 370 (w) (P=S bend) cm^{-1}.

Reactions of $(CF_3)_2P(S)$–S–$P(CF_3)_2$. 1. With Heat. Heating a sample of $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.0354 g, 0.088 mmol) for 2 days at 165° resulted in almost quantitative recovery (0.0322 g, 0.080 mmol) of unchanged material.

2. Hydrolysis. (a) Alkaline Solution. Hydrolysis of $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.0533 g, 0.132 mmol) with 5 ml of 10% NaOH solution for 24 hr at room temperature gave CF_3H (0.0279 g, 0.398 mmol) as the only volatile material. Nmr spectra of the remaining aqueous solution indicated the presence of the $CF_3PS_2O^{2-}$ ion.[11]

(b) Water. Hydrolysis of $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.0565 g, 0.140 mmol) with approximately 0.1 ml of H_2O at room temperature for 16 hr gave CF_3H (0.0096 g, 0.137 mmol) as the only volatile material. Nmr spectra of the remaining aqueous solution indicated the presence of $(CF_3)_2PS_2^-$ and $CF_3P(H)O_2^-$ ions.[11]

3. With H_2S. Heating hydrogen sulfide (0.0472 g, 1.39 mmol) with $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.0553 g, 0.137 mmol) at 150° for 9 days gave 0.057 g of a 1:1 mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2PSH$ (analyzed by nmr), corresponding to a 95% yield.

4. With HCl and HBr. (a) Reaction of excess hydrogen chloride (~1.0 mmol) with $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.0402 g, 0.100 mmol) for 10 days at room temperature gave 0.0427 g of a 1:1 mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2PCl$ (analyzed by nmr).

(b) A similar reaction between HBr (~0.4 mmol) and $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.062 g, 0.155 mmol) gave 0.0732 g of a 1:1 mixture of the acid and $(CF_3)_2PBr$. In both cases some difficulty was experienced in separating excess HX from $(CF_3)_2PS_2H$.

5. With HI. Room-temperature reaction of hydrogen iodide (~0.3 mmol) and $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.0547 g, 0.136 mmol) for 30 hr gave $(CF_3)_2PS_2H$ and $(CF_3)_2PI$ as the major products. The volatile materials were returned to the reaction tube along with a further quantity of HI (~0.4 mmol), and reaction was continued for 3 more days. The volatile products obtained were a mixture of $(CF_3)_2PSH$, $(CF_3)_2PI$, and $(CF_3)_2PH$ in the ratio 4.9:4.5:1.0 (total weight, 0.560 g) according to nmr spectra. The volatile materials passing −131° were H_2S and excess HI (identified by their reactions with lead acetate) and a trace of SiF_4.

6. With Cl_2. (a) Reaction of chlorine (0.0328 g, 0.462 mmol) and $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.0480 g, 0.120 mmol) while warming slowly from −45° to room temperature over 24 hr gave $(CF_3)_2PCl_3$ (0.0468 g, 0.170 mmol) trapping at −84° and a little $(CF_3)_2P(S)Cl$ in the more volatile fraction. A yellow low volatile oil having properties expected for S_2Cl_2 was also obtained.

(b) In a second reaction, chlorine (0.018 g, 0.254 mmol) and $(CF_3)_2P(S)$–S–$P(CF_3)_2$ (0.1066 g, 0.265 mmol) were allowed to react at −78° for 24 hr. Analysis of the volatile products by nmr and

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(26) Abbreviations: ν, stretching; δ, deformation; s, strong; m, medium; w, weak; v, very.

ir showed 11% unreacted $(CF_3)_2P(S)–S–P(CF_3)_2$, 25% $(CF_3)_2PCl$, 40% $(CF_3)_2PCl_3$, 8% $(CF_3)_2P(S)Cl$, and 16% $(CF_3)_2P(S)–S–S–P(S)(CF_3)_2$.

7. With Br_2. Reaction of bromine (0.019 g, 0.120 mmol) with $(CF_3)_2P(S)–S–P(CF_3)_2$ (0.0580 g, 0.144 mmol) at 0° for 1 hr, followed by reaction at room temperature for 24 hr, gave a mixture (0.0552 g) of $(CF_3)_2PBr$ (29%) and $(CF_3)_2P(S)Br$ (71%) according to nmr. A small amount of $(CF_3)_2P(S)–S–S–P(S)(CF_3)_2$ was obtained in a less volatile fraction and in addition a small amount of involatile oil (S_2Br_2) was obtained.

A second reaction with excess bromine and $(CF_3)_2P(S)SP(CF_3)_2$ for 11 days at room temperature gave $(CF_3)_2P(S)Br$ and $(CF_3)_2PBr_3$. A trace of CF_3Br was also detected in the volatile products.

8. With Hg. Heating mercury (0.025 g, 0.125 mmol) and $(CF_3)_2P(S)–S–P(CF_3)_2$ (0.129 g, 0.32 mmol) at 70° for 6 days gave $(CF_3)_2P–S–P(CF_3)_2$ (0.0808 g, 0.218 mmol). A yellow solid remained which was shown by mass spectrometry to be $(CF_3)_4P_2S_4Hg$. A similar experiment carried out at 100° gave only $(CF_3)_2P–S–P(CF_3)_2$ and a solid residue of HgS.

9. With Sulfur and Oxygen. Heating equimolar portions of freshly sublimed sulfur and $(CF_3)_2P(S)SP(CF_3)_2$ for 2 days at 165° followed by 4 days at 180° led to 90% recovery of unchanged $(CF_3)_2P(S)SP(CF_3)_2$ which was, however, contaminated with small amounts of unidentified species.

Dry air and $(CF_3)_2P(S)SP(CF_3)_2$ did not react after 9 days at room temperature and the mixed-valence compound was quantitatively recovered.

Reactions of Tetrakis(trifluoromethyl)diphosphine Tetrasulfide. $(CF_3)_2P(S)–S–S–P(S)(CF_3)_2$. 1. Thermal Stability. Heating a sample of $(CF_3)_4P_2S_4$ (0.0370 g, 0.0795 mmol) for 2 days at 165° gave $(CF_3)_2P(S)–S–P(CF_3)_2$ (0.0270 g, 0.067 mmol), a little starting material, and a trace of unidentified volatile material. Elemental sulfur remained in the reaction tube.

2. Hydrolysis. (a) Alkaline Solution. Alkaline hydrolysis of $(CF_3)_4P_2S_4$ (0.0240 g, 0.0515 mmol) with 5 ml of 10% NaOH solution for 4 days at room temperature gave only CF_3H (0.0070 g, 0.100 mmol). Some elemental sulfur remained in the aqueous product.

(b) Water. Degassed water (0.1 ml) was shaken with $(CF_3)_4P_2S_4$ (0.0473 g, 0.101 mmol) for 24 hr at room temperature. Elemental sulfur was produced, but no fluorocarbon-containing volatiles were obtained.

3. With H_2S. Heating hydrogen sulfide (1.2 mmol) and $(CF_3)_4P_2S_4$ (0.0566 g, 0.122 mmol) to 100° for 12 hr gave $(CF_3)_2PS_2H$ (0.0484 g, 0.206 mmol).

4. With HCl and HBr. Heating hydrogen chloride (1.2 mmol) and $(CF_3)_4P_2S_4$ (0.0566 g, (0.121 mmol) to 100° for 10 days gave a mixture (0.0400 g) of $(CF_3)_4PS_2H$ and $(CF_3)_2P(S)Cl$ in the ratio of 1:1.14 (by nmr). A small amount of unchanged $(CF_3)_4P_2S_4$ was recovered and sulfur remained in the reaction tube.

Heating $(CF_3)_4P_2S_4$ (0.0301 g, 0.065 mmol) with excess HBr (~0.65 mmol) at 70° for 9 days gave 0.0315 g of a mixture of $(CF_3)_2PS_2H$ and $(CF_3)_2P(S)Br$ in the ratio 1.0:1.3. Sulfur and a small amount of an involatile oil remained in the reaction tube.

In both cases some difficulty was experienced in separating excess HX from $(CF_3)_2PS_2H$.

5. With HI. (a) Excess hydrogen iodide (0.9 mmol) was allowed to react with $(CF_3)_4P_2S_4$ (0.0323 g, 0.069 mmol) at room temperature for 3 days. Formation of I_2 was noted immediately on warming the condensed reactants to room temperature. Vacuum fractionation gave $(CF_3)_2PSH$ (0.0265 g, 0.131 mmol) and a more volatile fraction which contained a mixture of H_2S and HI identified by their reactions with lead acetate. I_2 crystals remained in the reaction tube.

(b) In a second reaction a tube containing hydrogen iodide (0.0568 g, 0.445 mmol) in twofold molar ratio relative to $(CF_3)_4P_2S_4$ (0.0882 g, 0.189 mmol) was allowed to warm from −78° to room temperature over 10 hr. Vacuum fractionation gave $(CF_3)_2PS_2H$ (0.0781 g, 0.334 mmol) trapped at −84° and a trace of $(CF_3)_2PSH$, along with H_2S, and HI. I_2 remained in the reaction tube.

6. With Cl_2 and Br_2. (a) Chlorine (~0.6 mmol) and $(CF_3)_4P_2S_4$ (0.0253 g, 0.054 mmol) were slowly warmed from −78° to room temperature and allowed to stand for 3 days. Vacuum fractionation gave 0.0501 g of a mixture of $(CF_3)_2PCl$ and a yellow liquid, which appeared to be SCl_2 and was difficult to separate. The SCl_2 was identified by its reaction with H_2O to give chloride ion, elemental sulfur, and a reducing solution from which $BaSO_4$ could be precipitated after oxidation.

(b) The reaction of Br_2 (0.0392 g, 0.245 mmol) with $(CF_3)_4P_2S_4$ (0.620 g, 0.133 mmol) at 100° for 16 hr gave $(CF_3)_2P(S)Br$ (0.0675 g, 0.241 mmol) on vacuum fractionation. An involatile brown oil was also produced (S_2Br_2 from the stoichiometry and observed physical properties).

7. With Mercury. A nearly equimolar ratio of mercury (0.0244 g, 0.122 mmol) was vigorously shaken with $(CF_3)_4P_2S_4$ (0.0550 g, 0.118 mmol) at room temperature for 4 days. At this point a white crystalline solid plus significant quantities of metallic mercury remained in the reaction tube. Heating the tube to 70° for 3 days led to disappearance of mercury. Further heating to 100° for 24 hr converted the white crystals to yellow plates. Heating to 170° for 24 hr gave a clear liquid which gave white crystals on cooling and a trace of black HgS. A trace of $(CF_3)_2P–S–P(CF_3)_2$ was the only volatile product which could be distilled into the vacuum system. The white crystalline solid remaining in the reaction tube was identified as $(CF_3)_4P_2S_4Hg$ by mass spectroscopy including mass measurement of the molecular ion. *Anal.* Calcd for $C_4F_{12}P_2{}^{32}S_4{}^{202}Hg$: *m/e*, 667.7874. Found: *m/e*, 667.7864.

8. With Sulfur and Oxygen. Heating sulfur (0.0460 g, 1.44 mmol) with $(CF_3)_4P_2S_4$ (0.0383 g, 0.082 mmol) for 2 days at 160° gave $(CF_3)_4P_2S_2$ (0.0256 g, 0.064 mmol) and a trace of unidentified volatile material.

Dry air did not react with $(CF_3)_4P_2S_4$ after 2 days at room temperature; the starting material was recovered unchanged.

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