

# Further Knowledge of the Thiotetraphosphine $(CF_3P)_4S$ . The New Heterocycle $(CF_3PS)_3S_2$ <sup>1</sup>

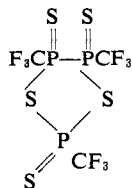
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**Abstract:** The heterocyclic thiotetraphosphine  $(CF_3P)_4S$  now has been made by several methods, none of which yield isolable quantities of other  $(CF_3P)_mS_n$  heterocyclics, although  $(CF_3P)_3S$  and  $(CF_3P)_3S_2$  seem to be indicated by mass spectrography. With excess sulfur at 180–200°,  $(CF_3P)_4S$  is converted to the very stable dithiotriphosphorane heterocycle  $(CF_3PS)_3S_2$  (mp 133°; volatility 6.1 mm at 99.4°; *d* 2.45) with no clearly observable intermediates. Desulfuration of this by mercury restores  $(CF_3P)_4S$  with polymeric by-products but again no discernible intermediates. Attempts to insert S into the P–P bond of the  $P_3S_2$  ring in  $(CF_3PS)_3S_2$  led only to resinous products. It is clear that both  $(CF_3P)_4S$  and  $(CF_3PS)_3S_2$  are especially stable heterocyclic compounds, homologs of which are far less stable.

The discovery of the heterocyclic compound  $(CF_3P)_4S$ , which was made by direct addition of sulfur to the homocyclic  $(CF_3P)_4$ ,<sup>2</sup> left open the question whether other sulfur–phosphorus(III) heterocycles also might be stable. After extensive efforts toward isolating them, we believe that such other heterocycles do exist but are far less stable than  $(CF_3P)_4S$ . This conclusion is related to the known lability of the  $(CF_3P)_n$  ring compounds; for example,  $(CF_3P)_5$  at 255° was extensively converted to  $(CF_3P)_4$ ,<sup>3</sup> and in general such interconversions occur more easily in the presence of adventitious catalysts such as very weak bases or even mercury condensed from a Stock-type high-vacuum manifold. Accordingly, it is most improbable that  $(CF_3P)_4S$  is formed by any highly selective mechanism, tending to exclude the formation of other  $(CF_3P)_mS_n$  heterocycles. Indeed, when  $(CF_3P)_5$  is heated with sulfur at 180°, the only clearly identified product is  $(CF_3P)_4S$ . Certainly the conversion of  $(CF_3P)_5$  to  $(CF_3P)_4S$  leaves at least one odd  $CF_3P$  unit to be accounted for in the mechanism, providing ample opportunity for the formation of any other stable  $(CF_3P)_mS_n$  heterocycles. Actually, the crude reaction mixture does show mass-spectral peaks at *m/e* 332 and 364 (with mutually unrelated intensities independent of the main pattern), strongly suggesting  $(CF_3P)_3S$  and  $(CF_3P)_3S_2$ . However, any such products seem to be destroyed during attempts to isolate them in a glass–mercury high-vacuum manifold.

More successful was the addition of sulfur to  $(CF_3P)_4S$ , to form the new heterocyclic compound  $(CF_3PS)_3S_2$ , for which the <sup>19</sup>F nmr spectrum indicates the molecular structure



This must be the thermochemically preferred  $S-(CF_3P=S)$  heterocycle, for it was the exclusive prod-

(1) Supported through Grant GP 6751X from the National Science Foundation, to which we are grateful also for helping to provide the necessary instruments.

(2) A. B. Burg, *J. Amer. Chem. Soc.*, **88**, 4298 (1966).

(3) W. Mahler and A. B. Burg, *ibid.*, **80**, 6164 (1958).

uct of a  $CF_3P$  scramble reaction, and other approaches led to no other  $S-(CF_3P=S)$  heterocycle.

For example, attempts to insert sulfur directly into the P–P bond of  $(CF_3PS)_3S_2$  led only to nonvolatiles for which no <sup>19</sup>F spectrum could be recorded. Equally fruitless were attempts to dissociate it into something new and significant: it proved to be permanently stable at 185°, and at 235° its destruction occurred by reaction with the Pyrex-glass bomb-tube walls. No sulfur was removed by either iodine or diborane, and sulfur abstraction by  $(CH_3)_3P$  gave only unintelligible nonvolatiles. Hot mercury removed sulfur from  $(CF_3PS)_3S_2$ , but the only recognizable product was  $(CF_3P)_4S$ ; again this was the strongly favored heterocycle.

Even a qualitative theory of the special stability of  $(CF_3P)_4S$  and  $(CF_3PS)_3S_2$  is very difficult to develop. Assuming that each is stabilized by full electronic occupation of low-level ring- $\pi$  molecular orbitals (by “lone-pair” electrons), whereas other conceivable heterocycles might have less useful  $\pi$  patterns, one might seek to construct the best ring- $\pi$  system for each case. However, the task would be complicated by the need to consider not only the phosphorus 3d, 4s, and 4p atomic orbitals, but also the P– $CF_3$   $\sigma$  antibonding orbitals, which would be significant because of strong  $\sigma$ -electron withdrawal by the  $CF_3$  groups. Even so, the errors of calculation could exceed the energy differences among the various heterocycles.

## Experiments Concerning the Tetramer Sulfide

**Further Study of the Original Synthesis.** The original addition reaction was repeated with 3.89 g of  $(CF_3P)_4$  and 0.312 g of sulfur, in a sealed tube at 180° (20 hr). The product was subjected to thorough high-vacuum fractionation in a micro column, yielding only  $(CF_3P)_4S$  and impurities which could not be isolated but appeared in the <sup>19</sup>F nmr spectrum. The mass spectrum showed a fairly strong *m/e* 364 peak, suggesting  $(CF_3P)_3S_2$ , while a 332 peak (see next section) was minimal.

**The Pentamer–Sulfur Reaction.** In a preliminary experiment, 2.6 g of  $(CF_3P)_5$  (26 mmol of  $CF_3P$  units) and 170 mg of sulfur (5.3 mg-atoms), heated for 6 days at 185°, gave a liquid mixture which was fractionated in a high-vacuum micro column. The less volatile part, passing the reflux at 0°, had the mass spectrum of pure

(CF<sub>3</sub>P)<sub>4</sub>S. The more volatile part, passing the reflux at  $-5^{\circ}$ , showed the (CF<sub>3</sub>P)<sub>4</sub> mass spectrum, and also peaks at  $m/e$  332 and 364. In various mixtures, these showed intensities independent of each other and of the mass spectra of (CF<sub>3</sub>P)<sub>4</sub> or (CF<sub>3</sub>P)<sub>4</sub>S, and so may be assigned with some confidence to (CF<sub>3</sub>P)<sub>3</sub>S and (CF<sub>3</sub>P)<sub>3</sub>S<sub>2</sub>, respectively. However, in no fraction could we find anything corresponding to (CF<sub>3</sub>P)<sub>5</sub>S; any of this which may have formed must have decomposed very rapidly.

A more systematic experiment employed just 1 g-atom of sulfur per (CF<sub>3</sub>P)<sub>5</sub>, in a sealed nmr tube. The <sup>19</sup>F nmr spectrum was recorded at 0.5-hr intervals during a 5-hr heating from 100 to 180°, showing initial reaction at 150°. After 0.5 hr at 180°, the mass spectrum showed unused (CF<sub>3</sub>P)<sub>5</sub>, good peaks for (CF<sub>3</sub>P)<sub>4</sub>S and (CF<sub>3</sub>P)<sub>3</sub>S ( $m/e$  332), and a very small  $m/e$  364 peak for (CF<sub>3</sub>P)<sub>3</sub>S<sub>2</sub>. However, after 6 days at 180°, the (CF<sub>3</sub>P)<sub>5</sub> had disappeared and the  $m/e$  332 peak was far weaker than the 364 peak.

Our purest samples of (CF<sub>3</sub>P)<sub>4</sub>S from this source gave <sup>19</sup>F nmr spectra with foreign peaks possibly assignable to (CF<sub>3</sub>P)<sub>3</sub>S or (CF<sub>3</sub>P)<sub>3</sub>S<sub>2</sub>. A typical pattern is shown in Figure 1. Here the multiplets at 44.2 and 52.3 ppm belong to (CF<sub>3</sub>P)<sub>4</sub>S and the others to impurities, often showing far more strongly in other samples. However, in all attempts to isolate the secondary material, its intensity merely became less and less; none of it could be isolated as a clean fraction. It is useful to mention that all features in Figure 1 become more complex at higher resolution; for example, the apparent doublet of quartets centered at 60.6 ppm develops a different and more complex pattern, and the doublet of doublets at 55.1 ppm also is not so simple as it seems. These are higher order spectra, very difficult to analyze. However, a generic relationship between the spectra of the impurities and the main (CF<sub>3</sub>P)<sub>4</sub>S spectrum would suggest the kind of structural relationship which we might expect for the (CF<sub>3</sub>P)<sub>3</sub>S and (CF<sub>3</sub>P)<sub>3</sub>S<sub>2</sub> heterocycles.

**The Polysulfide-Chain Approach.** Assuming that the slow aspect of the addition of sulfur to (CF<sub>3</sub>P)<sub>4</sub> was the opening of the S<sub>8</sub> ring, we hoped to get a lower temperature reaction by using the open-chain compound CF<sub>3</sub>S<sub>4</sub>CF<sub>3</sub> as the source of sulfur. However, the reaction still required heating to 185°, with extensive progress only after 6.5 hr. From 0.56 mmol of CF<sub>3</sub>S<sub>4</sub>CF<sub>3</sub> and 1.12 mmol of (CF<sub>3</sub>P)<sub>4</sub>, the only products actually isolated (from the unused tetramer) were (CF<sub>3</sub>P)<sub>4</sub>S and CF<sub>3</sub>S<sub>3</sub>CF<sub>3</sub>. However, the mass spectrum did show (CF<sub>3</sub>P)<sub>3</sub>S ( $m/e$  332), while the  $m/e$  364 peak for (CF<sub>3</sub>P)<sub>3</sub>S<sub>2</sub> was very weak in the whole mixture but strong in the less volatile fraction (column at 0°).

**Base-Assisted Acid Eliminations.** A report that the base-assisted reaction of CF<sub>3</sub>PCl<sub>2</sub> with H<sub>2</sub>S led to mass-spectrographic evidence for the formation of (CF<sub>3</sub>P)<sub>4</sub>S<sup>5</sup> offered hope that some intermediate heterocycle might be isolated. For this purpose we employed the delicate procedure which had succeeded for the synthesis of P<sub>3</sub>(CF<sub>3</sub>)<sub>3</sub>:<sup>6</sup> just the right amount of (CH<sub>3</sub>)<sub>3</sub>N was introduced from below, into a gaseous equimolar mixture of CF<sub>3</sub>PCl<sub>2</sub> and H<sub>2</sub>S at  $-40^{\circ}$ . However, the immediate

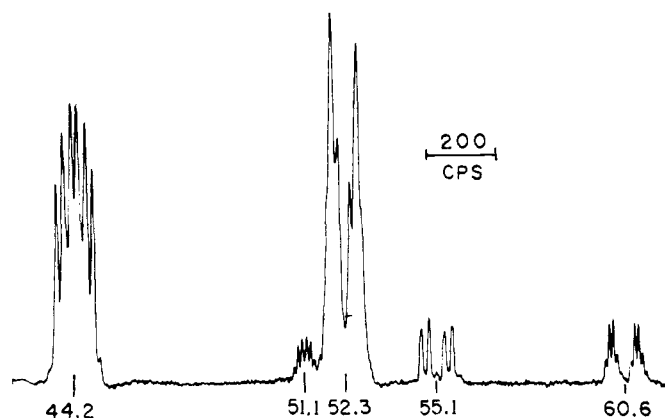


Figure 1. The <sup>19</sup>F nmr spectrum (at 94.1 Mc) of (CF<sub>3</sub>P)<sub>4</sub>S and impurities. The chemical shifts are measured in ppm upfield from Cl<sub>3</sub>CF by the substitution method. The pseudo-sextet at 44.2 ppm has peak separations (in upfield order) 18.9, 23.5, 16.1, 23.7, and 18.5 cps, and the small outside shoulders are real, both for this and for the pattern at 52.3 ppm.

reaction produced only white nonvolatile solids; nothing volatile could be obtained.

The results were similar when an equimolar gaseous mixture of CF<sub>3</sub>PH<sub>2</sub> and SCl<sub>2</sub> at  $-60^{\circ}$  was treated in a like manner with (CH<sub>3</sub>)<sub>3</sub>N.

#### The Action of Sulfur on Trifluoromethylphosphine.

In an attempt to find another route to (CF<sub>3</sub>P)<sub>4</sub>S and its congeners, 1.44 mg-atoms of sulfur and 1.45 mmol of CF<sub>3</sub>PH<sub>2</sub> were heated in a sealed tube, first for 2 hr at 90° without reaction, and then for 17 hr at 120°, consuming all of the sulfur. The volatile part now was exclusively CF<sub>3</sub>PH<sub>2</sub> and H<sub>2</sub>S (equimolar); no (CF<sub>3</sub>P)<sub>4</sub>S was found. The nonvolatile part yielded to the mass spectrograph enough vapor to show the (CF<sub>3</sub>P)<sub>3</sub>S<sub>2</sub> peak at  $m/e$  364 quite strongly. In the absence of other volatile species, there was no peak for any P-P-P bonded fragment, meaning that the P<sub>3</sub>S<sub>2</sub> ring probably

has the  $\overline{\text{P-S-P-S-P}}$  form as in (CF<sub>3</sub>PS)<sub>3</sub>S<sub>2</sub>. Again, however, no (CF<sub>3</sub>P)<sub>3</sub>S<sub>2</sub> could be isolated, even by trying a gas-flow synthesis.

**Alcoholic Cleavage.** The original publication on the tetramer sulfide (CF<sub>3</sub>P)<sub>4</sub>S<sup>2</sup> included the suggestion that P<sub>n</sub>S open-chain compounds might be obtained by alcoholic ring cleavage in a somewhat random manner, just as open P<sub>n</sub> chains were obtained from (CF<sub>3</sub>P)<sub>4</sub> and (CF<sub>3</sub>P)<sub>5</sub>.<sup>7</sup> For a test of this possibility, a 507-mg sample of (CF<sub>3</sub>P)<sub>4</sub>S was treated with 10 ml of 2-octanol in the boiler of a high-vacuum micro fractionating column. The mixture was heated at 40° while the reflux head was warmed from  $-20$  to 25° for delivery of possible volatile products in their order of volatility. However, the alcoholysis seemed to be thorough and quite directive, for the only volatile products were H<sub>2</sub>S and CF<sub>3</sub>PH<sub>2</sub>. Any C<sub>8</sub>H<sub>17</sub>OP compounds, of course, would have remained in the boiler.

#### The Dithiotriphosphorane Heterocycle

**Synthesis from the Tetramer Sulfide.** The new compound (CF<sub>3</sub>PS)<sub>3</sub>S<sub>2</sub> was discovered by heating a small sample of (CF<sub>3</sub>P)<sub>4</sub>S with a large excess of sulfur, in a sealed tube for 72 hr at 200°. The (CF<sub>3</sub>P)<sub>4</sub>S was wholly

(4) G. R. A. Brandt, H. J. Emelús, and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).

(5) R. G. Cavell and R. C. Dobbie, *Inorg. Chem.*, **7**, 690 (1968).

(6) A. B. Burg and J. F. Nixon, *J. Amer. Chem. Soc.*, **86**, 356 (1964).

(7) L. K. Peterson and A. B. Burg, *Inorg. Chem.*, **5**, 943 (1966).

consumed, leaving traces of volatile products (possibly due to a trace of desorbed water) and solids not appreciably volatile at 25°. These solids were transferred under dry nitrogen to a high-vacuum sublimation apparatus, in which the main product, later shown to be  $(\text{CF}_3\text{PS})_3\text{S}_2$ , was isolated as a white crystalline sublimate.

**Synthesis from the Tetramer.** For a more direct method, 1.6 g of  $(\text{CF}_3\text{P})_4$  and a large excess of sulfur were heated in a sealed tube for 5 hr at 185°. This time there were no products volatile at 25°. The yield of the white sublimate was 1.8 g, representing 98% conversion of  $(\text{CF}_3\text{P})_4$  to  $(\text{CF}_3\text{PS})_3\text{S}_2$ .

**Formula and Characterization.** A 37.7-mg sample of the sublimate was evaporated in an immersible tensimeter, giving the molecular weight as 461 (calculated for  $(\text{CF}_3\text{PS})_3\text{S}_2$ , 460). A 53.2-mg sample was heated with 6 *M* hydrochloric acid in a sealed tube (36 hr, 130°); then the liberated  $\text{H}_2\text{S}$  was absorbed by lead acetate solution and reliberated as 0.576 mmol. This represents 4.98 S per molecule of the compound.

The  $^{19}\text{F}$  nmr spectrum of  $(\text{CF}_3\text{PS})_3\text{S}_2$  (in  $\text{CCl}_4$ ) consists of doublets centered at 70.3 and 74.5 ppm upfield of  $\text{Cl}_3\text{CF}$ , with  $J_{\text{FCP}} = 131$  cps for both. Both doublets seem simple, with no second-order effects, meaning that P-P coupling is minimal. However, there must be a P-P bond in the ring, for the only alternatives to the  $\text{P}_3\text{S}_2$  ring with three *exo* P=S bonds would be structures containing trivalent phosphorus, for which  $J_{\text{FCP}}$  should be far smaller than 131 cps.

Pure  $(\text{CF}_3\text{PS})_3\text{S}_2$ , in a sealed capillary tube with dry  $\text{N}_2$ , melted sharply at 133°. A preliminary X-ray study by Dr. Paul Simpson (Stanford University) gave the density of the solid as 2.45, on the basis of four molecules (mol wt 460) per unit cell.

Three equilibrium vapor pressures were obtained: 2.81 mm at 90.4°, 4.05 mm at 94.4°, and 6.08 mm at 99.4°. The equation  $\log P = 14.327 - 5044/T$  would give these pressures as 2.83, 4.01, and 6.13 mm.

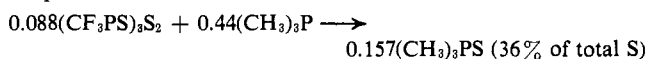
**Formation from Trifluoromethylphosphine with Excess Sulfur.** Although  $(\text{CF}_3\text{P})_4\text{S}$  was not obtained by heating  $\text{CF}_3\text{PH}_2$  with an equimolar proportion of sulfur, one might still hope that more sulfur would attack the actual products to make interesting intermediates and finally some  $(\text{CF}_3\text{PS})_3\text{S}_2$ . Actually, when 1.71 mmol of  $\text{CF}_3\text{PH}_2$  and 15 mg-atoms of sulfur were heated together in a sealed tube (3 days, 100°), 0.684 mmol of  $\text{H}_2\text{S}$  was obtained, and the solid residue yielded a small white sublimate. In  $\text{CCl}_4$  solution, this showed the  $^{19}\text{F}$  nmr spectrum of  $(\text{CF}_3\text{PS})_3\text{S}_2$  with unknown impurities observed as smaller peaks at 77.9 and 79.4 ppm upfield of  $\text{Cl}_3\text{CF}$ .

**Formation from the Diiodophosphine.** In an attempt to make  $\text{CF}_3\text{P}(\text{S})\text{I}_2$  as a precursor for new heterocycles, a small sample of  $\text{CF}_3\text{PI}_2$  was heated with an equivalent quantity of sulfur, in a sealed tube at 100°, until the color of iodine appeared. The open tube yielded no volatiles, but the  $^{19}\text{F}$  nmr spectrum of the  $\text{CCl}_4$  extract clearly showed  $(\text{CF}_3\text{PS})_3\text{S}_2$ , along with numerous unidentified components.

**Thermal Stability.** The compound  $(\text{CF}_3\text{PS})_3\text{S}_2$  seemed to be permanently stable at 200°, but at 235° (42 hr) it reacted with the Pyrex container, forming  $\text{SiF}_4$ ,  $\text{PF}_3$ , and a number of less identifiable components probably representing ring fragments. How stable it might be in an inert container cannot be judged.

**Further Treatment with Sulfur.** In order to determine whether the P-P bond in  $(\text{CF}_3\text{PS})_3\text{S}_2$  could receive sulfur, hypothetically to form the six-atom heterocyclic  $(\text{CF}_3\text{PS}_2)_3$ , a 138-mg sample was heated with a large excess of  $\text{S}_8$ , first for 19 hr at 190°. Now a sublimate (dissolved in  $\text{CCl}_4$ ) showed the  $^{19}\text{F}$  nmr spectrum of pure  $(\text{CF}_3\text{PS})_3\text{S}_2$ , but the  $\text{CS}_2$  extract of the residue showed additional features suggestive of an incipient reaction. Accordingly, the main mixture was heated further (7 hr at 210–225°), but the product now was a darkened nonvolatile material, apparently of resinous character, for which the  $\text{CS}_2$  extract showed no  $^{19}\text{F}$  nmr signal. There were traces of volatile products having the same infrared spectra as those accompanying the original formation of  $(\text{CF}_3\text{PS})_3\text{S}_2$  from  $(\text{CF}_3\text{P})_4\text{S}$  and sulfur during 72 hr at 200°. It seems reasonable to assume that  $(\text{CF}_3\text{PS}_2)_3$  is unstable relative to resinous condensation products, or at least cannot be formed under the conditions of the present experiment. However, we cannot exclude a possible effect of reaction with the Pyrex container.

**Reaction with Trimethylphosphine.** The initial experiment on the reaction of  $(\text{CF}_3\text{PS})_3\text{S}_2$  with  $(\text{CH}_3)_3\text{P}$  was for the purpose of determining sulfur as  $(\text{CH}_3)_3\text{PS}$ . However, the yield of the phosphine sulfide always was deficient, and resin formation seemed to intervene, however much the reaction conditions were varied. The resin formation was especially visible when toluene was used as a solvent, for the 110-mg sample, treated batchwise with 0.72 mmol of  $(\text{CH}_3)_3\text{P}$  at -64°, formed more and more of a fine suspension. The toluene now was distilled off, and all  $(\text{CH}_3)_3\text{P}$  had been consumed. The nonvolatile residue could not be dissolved in the usual organic solvents, but an acetone extract did show a very broad  $^{19}\text{F}$  nmr signal, suggestive of high-polymeric character. The low-temperature reaction in toluene might have been expected to remove the nonring sulfur, leaving the  $(\text{CF}_3\text{P})_3\text{S}_2$  heterocycle, but it seems that resin formation intervened. In all experiments, the yields of  $(\text{CH}_3)_3\text{PS}$  were deficient; for example



**Desulfuration by Mercury.** A 90-mg sample of  $(\text{CF}_3\text{PS})_3\text{S}_2$  with excess mercury was heated for 18.5 hr in a sealed tube at 115°. Much of the sample was lost as nonvolatile material, but there was a small yield of  $(\text{CF}_3\text{P})_4\text{S}$ , easily identified by its  $^{19}\text{F}$  nmr and mass spectra. In a second experiment,  $(\text{CF}_3\text{PS})_3\text{S}_2$  and mercury were heated together for 1 hr at 155°, forming only a nonvolatile, nonworkable product.

**Diborane Treatment.** An attempt to use diborane to reduce the phosphorus in  $(\text{CF}_3\text{PS})_3\text{S}_2$  did not succeed: after 12 hr at 50°, the only result was partial decomposition of the diborane. In relation to this experiment, it had been determined beforehand that diborane also would not react with  $(\text{CF}_3\text{P})_4\text{S}$ .

**Iodine Treatment.** The heterocyclic  $(\text{CF}_3\text{PS})_3\text{S}_2$  was not disrupted by iodine. The  $^{19}\text{F}$  nmr spectrum of the  $\text{CCl}_4$  solution of the mixture failed to change during 2 weeks at 25°, and then a 21-hr heating at 150°, of the "neat"  $(\text{CF}_3\text{PS})_3\text{S}_2\text{-I}_2$  mixture, also showed no change.

**Infrared Spectrum.** The infrared spectrum of the vapor of  $(\text{CF}_3\text{PS})_3\text{S}_2$  was recorded by the Beckman IR7 instrument, using NaCl and CsI optics and a special

heater-blower box within the cell chamber. The relative intensities, calculated by the definition  $k = (100/PL) \log I_0/I$  (for pressure  $P$  and path length  $L$  both in cm) are shown in parentheses after the frequencies ( $\text{cm}^{-1}$ ) of the peaks in the following listing: C—F stretching, 1175 (203) and 1163 (145);  $\text{CF}_3$  symmetric deformation,

767 (40); P=S stretching, 738 (65);  $\text{CF}_3$  asymmetric deformation, 590 (5.3); P—S—P asymmetric stretching, 536 (3.7); P— $\text{CF}_3$  stretching, 490 (35).

The infrared spectrum of  $(\text{CF}_3\text{PS})_2\text{S}_2$  in a Nujol mull was very similar to the vapor-phase spectrum, except that the frequencies were lower by 1–7  $\text{cm}^{-1}$ .

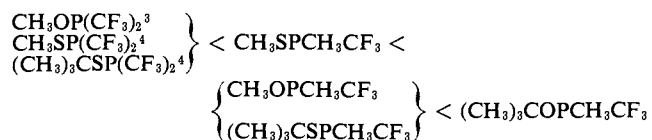
## Oxygen and Sulfur Chemistry of Methyltrifluoromethylphosphines<sup>1</sup>

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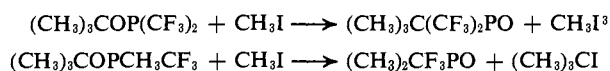
**Abstract:** The new alkoxyphosphines  $\text{CH}_3\text{OPCH}_2\text{CF}_3$  (bp 61°) and  $(\text{CH}_3)_3\text{COPCH}_2\text{CF}_3$  (bp 113°) undergo normal Arbuzov reactions with  $\text{CH}_3\text{I}$  to form  $(\text{CH}_3)_2\text{CF}_3\text{PO}$  (mp 72°, bp 193°) but react differently with HCl: the methoxyphosphine reverts to  $\text{CH}_3\text{OH}$  and  $\text{CH}_3\text{CF}_3\text{PCl}$  whereas the *t*-butoxyphosphine yields the new and unexpectedly stable phosphine oxide  $\text{CH}_3\text{CF}_3\text{HPO}$  (mp -9.3°, bp 169°). Both  $\text{CH}_3\text{SPCH}_2\text{CF}_3$  (bp 107°) and  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$  (mp -30°, bp 152°) undergo Arbuzov reactions with  $\text{CH}_3\text{I}$  to form the new phosphine sulfide  $(\text{CH}_3)_2\text{CF}_3\text{PS}$  (mp 49°, bp 163°), and both are cleaved by HCl to  $\text{CH}_3\text{CF}_3\text{PCl}$  and mercaptan. The new thiobisphosphine  $(\text{CH}_3)_2\text{CF}_3\text{P}_2\text{S}$  (bp 154°) shows a variable melting range, ascribed to conformational isomerism. Its Arbuzov-like cleavage by  $\text{CH}_3\text{I}$  to form  $\text{CH}_3\text{CF}_3\text{PI}$  and  $(\text{CH}_3)_2\text{CF}_3\text{PS}$  is observable. The phosphine sulfide  $\text{CH}_3\text{CF}_3\text{HPS}$  probably exists in equilibrium with  $\text{H}_2\text{S}$  and  $(\text{CH}_3)_2\text{CF}_3\text{P}_2\text{S}$ , with possible traces of  $\text{CH}_3\text{CF}_3\text{PSH}$ ; eventually  $\text{CH}_3\text{CF}_3\text{PH}$  also is found. Extensive nmr and infrared spectra are reported.

Earlier studies of the  $\text{CH}_3\text{CF}_3\text{PX}$  chemistry<sup>2</sup> now have been extended to include X groups containing oxygen or sulfur, again with some results not predictable from the corresponding  $(\text{CH}_3)_2\text{PX}$  and  $(\text{CF}_3)_2\text{PX}$  chemistry. Especially interesting are the Arbuzov-related reactions. For the classical type in which alkyl goes from I to P while another alkyl goes from O or S to I, we now can recognize the following order of increasing ease or rate of reaction.



Thus it appears that the C—S bond is harder to break than C—O, but *t*-butyl detaches more easily than methyl, from either S or O.

An interesting contrast appears in the high-yield processes



In the first of these, it seems that a very weakly basic oxygen allowed an easy exchange of *t*-butyl for methyl, and then *t*-butyl could attach to the very weakly basic P atom far faster than methyl could. This process is

(1) The major part of this research is described in more detail in the Ph.D. dissertation by Dae-Ki Kang (University of Southern California Libraries, June 1969). We gratefully acknowledge support by the National Science Foundation, which assisted us also toward acquisition of the required instruments.

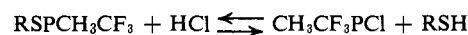
(2) A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Amer. Chem. Soc.*, **88**, 31 (1966).

(3) J. E. Griffiths and A. B. Burg, *ibid.*, **84**, 3442 (1962).

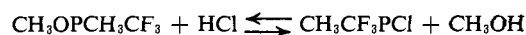
(4) A. B. Burg and K. Gosling, *ibid.*, **87**, 2113 (1965).

actually faster than the second, wherein the more basic oxygen does not exchange groups so easily, and the more basic phosphorus receives  $\text{CH}_3$  slowly from  $\text{CH}_3\text{I}$ , in the classical Arbuzov manner.

Another contrast was found in the reactions of the new alkoxy and alkanethio compounds with HCl. The equilibria



(R = methyl or *t*-butyl) strongly favor the reactants, and there is no tendency to attach H to P and cleave the C—S bonds. In contrast, the cleavage equilibrium



strongly favors the product, and a small side reaction forming  $\text{CH}_3\text{Cl}$  and the new compound  $\text{CH}_3\text{CF}_3\text{HPO}$  means that it is not much harder to cleave the C—O than the P—O bond. In the case of  $(\text{CH}_3)_3\text{COPCH}_2\text{CF}_3$ , however, the C—O bond cleavage is the main effect: high yields of  $\text{CH}_3\text{CF}_3\text{HPO}$  and  $(\text{CH}_3)_3\text{CCl}$  are obtained. Here again the lability of the *t*-butyl group is governing.

The new phosphine oxide  $\text{CH}_3\text{CF}_3\text{HPO}$  proved to be far more stable than expected: it seems to lack the mechanism for a disproportionation in the manner of  $2(\text{CH}_3)_2\text{HPO}$  going to  $(\text{CH}_3)_2\text{PH}$  and  $(\text{CH}_3)_2\text{POOH}$ ,<sup>5</sup> while a process like the rapid conversion of  $(\text{CF}_3)_2\text{HPO}$  to  $(\text{CF}_3)_2\text{POH}$  is energetically unfavorable in this case. Presumably the fair stability of  $(\text{C}_6\text{H}_5)_2\text{HPO}$ <sup>6</sup> has a similar cause.

(5) J. E. Griffiths and A. B. Burg, *Proc. Chem. Soc.*, 12 (1961).

(6) B. B. Hunt and B. C. Saunders, *J. Chem. Soc.*, 2413 (1957).