

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

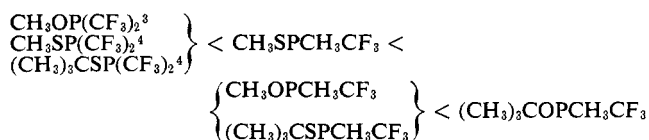
## Oxygen and Sulfur Chemistry of Methyltrifluoromethylphosphines<sup>1</sup>

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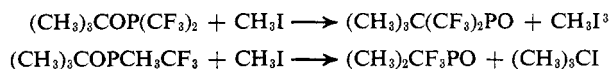
**Abstract:** The new alkoxyphosphines  $\text{CH}_3\text{OPCH}_2\text{CF}_3$  (bp  $61^\circ$ ) and  $(\text{CH}_3)_3\text{COPCH}_2\text{CF}_3$  (bp  $113^\circ$ ) undergo normal Arbuzov reactions with  $\text{CH}_3\text{I}$  to form  $(\text{CH}_3)_3\text{CF}_3\text{PO}$  (mp  $72^\circ$ , bp  $193^\circ$ ) but react differently with  $\text{HCl}$ : 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  $-9.3^\circ$ , bp  $169^\circ$ ). Both  $\text{CH}_3\text{SPCH}_2\text{CF}_3$  (bp  $107^\circ$ ) and  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$  (mp  $-30^\circ$ , bp  $152^\circ$ ) undergo Arbuzov reactions with  $\text{CH}_3\text{I}$  to form the new phosphine sulfide  $(\text{CH}_3)_3\text{CF}_3\text{PS}$  (mp  $49^\circ$ , bp  $163^\circ$ ), and both are cleaved by  $\text{HCl}$  to  $\text{CH}_3\text{CF}_3\text{PSH}$  and mercaptan. The new thiobisphosphine  $(\text{CH}_3)_2(\text{CF}_3)_2\text{P}_2\text{S}$  (bp  $154^\circ$ ) 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  $(\text{CH}_3\text{CF}_3)_2\text{S}$ , 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.

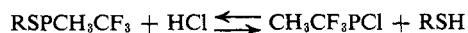
(2) A. B. Burg, K. K. Joshi, and J. F. Nixon, *J. Amer. Chem. Soc.*, **88**, 31 (1966).

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

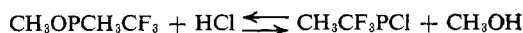
(4) A. B. Burg and K. Gosling, *ibid.*, **87**, 2113 (1965).

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  $\text{HCl}$ . 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).

In contrast, the phosphine sulfide  $\text{CH}_3\text{CF}_3\text{HPS}$  seems to be unstable in more than one way and could be recognized only in mixtures.

The new thiobisphosphine  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$  decomposes very slowly at  $25^\circ$  to  $(\text{CH}_3\text{CF}_3\text{P})_2$  and a nonvolatile solid. It may well convert first to  $\text{CH}_3\text{CF}_3(\text{S})\text{P}-\text{PCH}_3\text{CF}_3$ , from which group exchange would form  $(\text{CH}_3\text{CF}_3\text{P})_2$  and  $(\text{CH}_3\text{CF}_3\text{PS})_2$ . A similar decomposition could account for our failures to make  $(\text{CH}_3\text{CF}_3\text{P})_2\text{O}$ ; all attempts led only to  $(\text{CH}_3\text{CF}_3\text{P})_2$  and non-volatile products.

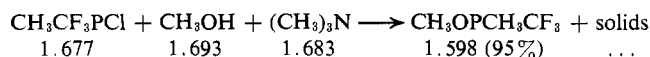
This thiobisphosphine provided an opportunity for an interesting study of isomers: with two phosphorus atoms capable of slow ammonia-type inversion, there are optically active and *meso* isomers clearly showing different  $^{19}\text{F}$  nmr spectra. A separate paper will describe their interpretation, the rates of interconversion, and the shift of equilibrium with temperature.

### Experimental Methods

Modified Stock quantitative high-vacuum methods were used for all work with volatile compounds. The usual reaction vessel was a closed chamber (tube or bulb) with a stopcock leading through a ground joint to the high-vacuum system. For reactions above  $25^\circ$ , sealed containers with vacuum tube-opener tips were preferred. Separations were done either by high-vacuum fractional condensation through a series of U-tubes separated by mercury float-valves, or by small reflux columns. The instruments included the Varian M-66 mass spectrometer, the Varian A-60 and HA-100 nmr instruments, the Perkin-Elmer 337 infrared spectrophotometer, and, for ultimate infrared data, the Beckman IR7 with NaCl or CsI optics and a heater-blower cell chamber for vapor-phase work at elevated temperatures.

### The Methoxyphosphine

**Synthesis.** An exploratory methanolysis of  $\text{CH}_3\text{CF}_3\text{PCl}$  was begun in our laboratories by Dr. John F. Nixon, but the reaction was far from complete and the desired new compound  $\text{CH}_3\text{OPCH}_3\text{CF}_3$  could not be isolated. The successful method used trimethylamine to avoid reversal by HCl. In the larger of two experiments, the reactants were condensed into a 250-ml stopcocked tube and warmed rapidly from  $-196^\circ$ . The millimole stoichiometry of the reaction is shown as follows.



The volatile product was treated with dry calcium chloride to remove any residual methanol and purified further by means of a small high-vacuum reflux column. Its molecular weight (vapor phase) was determined as 145.5 (calculated for  $\text{CH}_3\text{OPCH}_3\text{CF}_3$ , 146.1). The volatility data in Table I are consistent with purity.

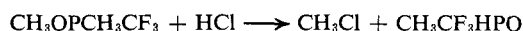
**Table I.** Volatility of  $\text{CH}_3\text{OPCH}_3\text{CF}_3$   
( $\log P = 5.8501 + 1.75 \log T - 0.0057 - 1908/T$ )  
( $t_{760} = 60.6^\circ$ ; Trouton constant = 20.7 eu)

$t, ^\circ\text{C}$	-40.65	-33.77	-25.75	0.00	10.15	11.85
$P_{\text{obsd}}, \text{mm}$	4.18	7.01	12.36	58.2	97.8	105.8
$P_{\text{calcd}}, \text{mm}$	4.19	7.01	12.29	57.9	97.8	106.2

The formula  $\text{CH}_3\text{OPCH}_3\text{CF}_3$  agreed with the infrared spectrum (see later) and was more surely confirmed by the nmr spectra. The two different methyl groups were proved by two equally intense proton doublets with

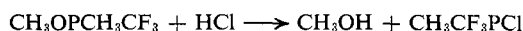
chemical shifts 0.94 ( $J = 6.9$  cps) and 2.84 ( $J = 13.1$  cps) ppm downfield from tetramethylsilane. It is assumed that the larger  $J$  value corresponds to the  $\text{CH}_3\text{O}$  group, since  $J_{\text{H-P}}$  for a  $\text{POCH}_3$  bond often is larger than for a  $\text{P-CH}_3$  pattern.<sup>7</sup> The  $^{19}\text{F}$  spectrum was a doublet at 94.4 ppm ( $J = 68.9$  cps) downfield of  $\text{C}_6\text{F}_6$ , without observable fine structure. The  $^{31}\text{P}$  spectrum showed a quartet with  $J$  measured as 69.2 cps (assignable to  $\text{P-CF}_3$  coupling) at 21.2 ppm upfield of  $(\text{CH}_3\text{O})_3\text{P}$ ; a complex fine structure was attributable to the two different methyl groups.

**Cleavage by Hydrogen Chloride.** A mixture of 0.529 mmol of  $\text{CH}_3\text{OPCH}_3\text{CF}_3$  and 0.560 mmol of HCl was left for 11 hr at  $25^\circ$ , consuming 0.387 mmol of the HCl. After 3 hr at  $110^\circ$  the consumption of HCl had risen to 0.504 mmol and remained the same during a further 11 hr at  $110^\circ$ . At this point it was possible to isolate a 4.3% yield of the compound  $\text{CH}_3\text{CF}_3\text{HPO}$  (identified by comparison with the authentic product described later), and the accompanying trace of  $\text{CH}_3\text{Cl}$  also was recognized (by its infrared spectrum), showing that the process



did occur slightly.

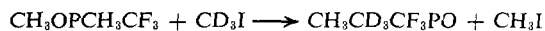
The main mixture of  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{CF}_3\text{PCl}$ , and residual  $\text{CH}_3\text{OPCH}_3\text{CF}_3$  could not be resolved by high-vacuum fractional condensation, but the methanol was identified by its infrared bands with Q branches at 1030 and  $3620 \text{ cm}^{-1}$ , and the characteristic peak for  $\text{CH}_3\text{CF}_3\text{PCl}$  at  $1160 \text{ cm}^{-1}$  could be seen, between the 1125–1140- and 1180–1190- $\text{cm}^{-1}$  regions where peaks belonging to  $\text{CH}_3\text{OPCH}_3\text{CF}_3$  would interfere. Thus it appeared that the major reaction



was not quite complete at equilibrium.

The reversibility of this process was demonstrated by allowing the remixed components to stand at  $25^\circ$ , with stepwise removal of the HCl by fractional condensation through a U-trap at  $-130^\circ$ . After nine such steps the total recovered HCl was 0.348 mmol, representing roughly 60% reversal of the cleavage.

**The Arbuzov Rearrangement.** Closely related to the slight conversion of  $\text{CH}_3\text{OPCH}_3\text{CF}_3$  to  $\text{CH}_3\text{CF}_3\text{HPO}$  by HCl would be its reaction with  $\text{CH}_3\text{I}$  to make  $(\text{CH}_3)_2\text{CF}_3\text{PO}$ —a normal Arbuzov rearrangement which would be expected to occur far more easily than for  $\text{CH}_3\text{OP}(\text{CF}_3)_2$ .<sup>3</sup> In fact, equimolar mixtures of  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{OPCH}_3\text{CF}_3$ , heated in sealed tubes for 21–24 hr at  $100$ – $110^\circ$ , showed 87–92% conversion, with only slight side reactions. The classical mechanism of this process was proved by using  $\text{CD}_3\text{I}$ .



This experiment began with a mixture of 1.109 mmol of  $\text{CH}_3\text{OPCH}_3\text{CF}_3$  and 1.125 mmol of  $\text{CD}_3\text{I}$ , in an nmr tube so that the course of the reaction could be observed by means of the proton nmr spectrum. Measuring the chemical shift  $\delta$  in ppm downfield from TMS, the initial mixture was found to have  $\delta_1$  3.48 ( $J = 13.3$  cps) and  $\delta_2$  1.28 ( $J = 6.7$  cps), both downfield of the original "neat" values. After 16 hr at  $25^\circ$ , a singlet at  $\delta$  1.97 indicated a small formation of  $\text{CH}_3\text{I}$ , and a peak at  $\delta$

(7) A. B. Burg and I. B. Mishra, *Inorg. Chem.*, **8**, 1199 (1969).

1.62 could be recognized as the lower field member of the doublet for  $\text{CH}_3\text{CD}_2\text{CF}_3\text{PO}$ ; the higher field member would superpose upon the  $\text{CH}_3\text{OPCH}_2\text{CF}_3$  peak at  $\delta$  1.28. During 5 hr at  $63^\circ$  the  $\delta$  1.97 and 1.62 peaks grew quite noticeably, maintaining the 2:1 area ratio expected for equal increase of the  $\text{CH}_3\text{I}$  singlet and the  $\text{CH}_3\text{CD}_2\text{CF}_3\text{PO}$  doublet. However, as the concentration of the  $\text{CH}_3\text{I}$  increased, it could be expected to participate more and more in the Arbuzov process; indeed, we could calculate statistically that the final ratio of  $\text{CH}_3\text{CD}_2\text{CF}_3\text{PO}$  to  $(\text{CH}_3)_2\text{CF}_3\text{PO}$  would be 1.75, from the initial mixture of  $\text{CH}_3\text{OPCH}_2\text{CF}_3$  and  $\text{CD}_3\text{I}$  here used. In fact, after 23 hr at  $63^\circ$ , the process was complete (disappearance of the two doublets for  $\text{CH}_3\text{OPCH}_2\text{CF}_3$ ), and this 1.75 ratio was confirmed by a quantitative infrared analysis of the mixture of  $\text{CH}_3\text{I}$  and  $\text{CD}_3\text{I}$ . The proton nmr spectrum of the phosphine oxide was the expected doublet ( $\delta$  1.70 ppm;  $J$  = 14.4 cps), well separated from the methyl iodide singlet ( $\delta$  2.13 ppm).

The isotopic mixing involved only whole methyl groups and occurred only during the Arbuzov reaction, for the infrared spectra showed no C-H peaks assignable to  $\text{CH}_2\text{D}$  or  $\text{CHD}_2$  groups, and there was no nmr-detectable formation of  $\text{CH}_3\text{I}$  when a 10:1 mixture of  $\text{CD}_3\text{I}$  and  $(\text{CH}_3)_2\text{CF}_3\text{PO}$  was heated for 4 days at  $63^\circ$ .

In sum, then, the Arbuzov rearrangement in this case occurred cleanly in accord with the classical mechanism. However, at no point in the nmr-monitored process was there any indication of the expected intermediates, such as  $(\text{CH}_3)_2\text{CF}_3\text{POCH}_2^+\text{I}^-$  or  $\text{CH}_3\text{CD}_2\text{CF}_3\text{POCH}_2^+\text{I}^-$ , which apparently would be very short-lived.

**Characterization of the Phosphine Oxide.** A highly purified sample of the phosphine oxide  $(\text{CH}_3)_2\text{CF}_3\text{PO}$  was subjected to vapor-pressure equilibrium measurements. For the solid, the values were 1.17 mm at  $46.9^\circ$ , 2.33 mm at  $54.8^\circ$ , 3.94 mm at  $61.1^\circ$ , and 6.88 mm at  $68.1^\circ$ , all reproduced within 0.01 mm by the equation  $\log P = 12.3839 - 3940/T$ . For the liquid, the results were 10.20 mm at  $73.66^\circ$ , 12.61 mm at  $77.73^\circ$ , 15.51 mm at  $81.7^\circ$ , and 19.74 mm at  $86.6^\circ$ , all very closely reproduced by the equation  $\log P = 8.706 + 1.75 \log T - 0.007T - 3369/T$ . This would give the normal boiling point as  $193^\circ$  and the Trouton constant as 21.6 eu. Taken with the solid, it implies that the melting point should be  $71.7^\circ$  (observed, sharp at  $71.7^\circ$ ).

The vapor-phase molecular-weight determination gave the value 146.3 [calculated for  $(\text{CH}_3)_2\text{CF}_3\text{PO}$ , 146.1]. In the basic hydrolysis (48.5-mg sample; 10% NaOH; sealed tube), bubbles appeared at  $25^\circ$ , but completion was assured by a 17-hr heating at  $95^\circ$ . The resulting  $\text{HCF}_3$  was measured as 0.331 mmol (calculated, 0.332 mmol). Since the phosphine oxide was the virtually quantitative rearrangement product of  $\text{CH}_3\text{OPCH}_2\text{CF}_3$ , these results serve as further confirmation of its molecular formula.

The proton nmr spectrum of  $(\text{CH}_3)_2\text{CF}_3\text{PO}$  (0.679 mmol of sample in 4.94 mmol of  $\text{CH}_3\text{I}$ ) showed  $\delta$  0.39 ppm upfield of  $\text{CH}_3\text{I}$ , with  $J$  = 14.1 cps, as before. The quartet fine structure gave  $J_{\text{HCPCH}} = 0.83$  cps. The  $^{19}\text{F}$  spectrum showed  $\delta$  76.3 ppm upfield of  $\text{Cl}_3\text{CF}$ , with  $J_{\text{FCP}} = 84.3$  cps and the septet fine structure showing  $J_{\text{FCPCH}} = 0.78$  cps, close to the proton-spectrum value.

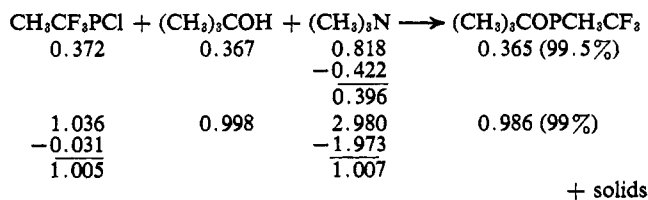
**Boron Fluoride Adducts.** The compound  $\text{CH}_3\text{OPCH}_2\text{CF}_3$  might be expected to attach boron trifluoride to either oxygen or phosphorus (or both), and it would be difficult to argue which atom would provide the better bond to boron. Actually, it was not easy to establish accurately a simple combining ratio. For example, a mixture of 0.283 mmol of  $\text{CH}_3\text{OPCH}_2\text{CF}_3$  and 0.787 mmol of  $\text{BF}_3$ , left for 10 hr at  $-78^\circ$ , delivered only 0.472 mmol of  $\text{BF}_3$  on pumping at  $-78^\circ$ ; thus the glassy residue contained 1.11  $\text{BF}_3$  per  $\text{CH}_3\text{OPCH}_2\text{CF}_3$ . However, after remixing and removal of excess  $\text{BF}_3$  at  $-120^\circ$ , the residue showed 1.96  $\text{BF}_3$  per  $\text{CH}_3\text{OPCH}_2\text{CF}_3$ . This residue was subjected to high-vacuum fractional condensation through a trap at  $-120^\circ$ , wherein the condensate contained 1.19  $\text{BF}_3$  per  $\text{CH}_3\text{OPCH}_2\text{CF}_3$ . By further fractional condensation at higher temperatures, the combining ratio could be reduced to 0.995, in a glassy, slightly volatile product which proved to be stable at  $25^\circ$ . Thus it appeared that a 1:1 adduct is stable, and that a very unstable 2:1 adduct may exist, but it would be difficult to devise an experiment for proving whether it is oxygen or phosphorus which makes the stronger bond to  $\text{BF}_3$ .

**The Fluorophosphine.** The  $\text{BF}_3$ -adduct experiments gave slight yields (as high as 2%) of the new compound  $\text{CH}_3\text{CF}_3\text{PF}$ . It would be tempting to suppose that it came from a fluoride shift like that by which  $\text{CH}_3\text{OAs}(\text{CF}_3)_2 \cdot \text{BF}_3$  forms  $(\text{CF}_3)_2\text{AsF}$ ,<sup>8</sup> but the very small yields would suggest that the real source was an impurity. Such an impurity would not be  $\text{CH}_3\text{CF}_3\text{PCL}$ , which failed to react with  $\text{BF}_3$  under a wide range of conditions.

The fluorophosphine was identified by comparison with a larger sample, made from 1.9 mmol of  $\text{CH}_3\text{CF}_3\text{PCL}$  with 1.2 g of  $\text{ZnF}_2$  in a sealed tube (5 days,  $25^\circ$ ). The yield was 0.56 mmol, or 30%. The volatility of the product was close to 1 mm at  $-78^\circ$ . Its proton nmr spectrum left no doubt of its identity: the observed doublet of doublets ( $\delta$  0.88 ppm downfield of TMS, with  $J$  values 7.7 and 19.3 cps) would be expected from the splitting effect of P and P-connected F. Fine structure due to  $\text{CF}_3$  was not seen.

### The *t*-Butoxyphosphine

**Synthesis.** The trimethylamine method was applied also to the reaction of *t*-butyl alcohol with  $\text{CH}_3\text{CF}_3\text{PCL}$ . The three components were condensed from the high-vacuum line into a stopcocked tube at  $-196^\circ$  and allowed to warm slowly from  $-30^\circ$ . The desired product was purified by high-vacuum fractional condensation, leading to the following millimole stoichiometry of two experiments.



**Characterization.** The molecular formula of the product, indicated by the nearly quantitative reaction balance, was confirmed by the molecular weight (vapor

(8) A. B. Burg and J. Singh, *J. Amer. Chem. Soc.*, **87**, 1213 (1965).

phase; found 186 *vs.* calcd 188) and a strong mass-spectrum peak at  $m/e$  188.

The proton nmr spectrum showed the P-CH<sub>3</sub> doublet at  $\delta$  1.11 ppm downfield of TMS, with  $J = 6.86$  cps; and each member of this doublet showed secondary splitting into a quartet due to the CF<sub>3</sub> group;  $J_{\text{HPCF}} = 0.64$  cps. Then within the P-CH<sub>3</sub> doublet was another doublet centered at  $\delta$  1.10 ppm downfield of TMS, obviously due to the *t*-butyl group;  $J_{\text{HCCOP}} = 0.59$  cps. The <sup>19</sup>F spectrum showed  $\delta$  92.8 ppm upfield of Cl<sub>3</sub>CF, with  $J_{\text{FCP}} = 74.0$  cps. In sum, then, the nmr spectra fully confirmed the expected molecular structure.

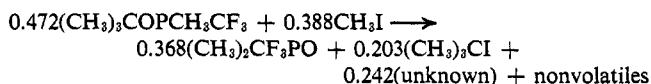
The equilibrium vapor-pressure values for (CH<sub>3</sub>)<sub>3</sub>COPCH<sub>2</sub>CF<sub>3</sub>, shown in Table II, indicated a pure sample.

Table II. Volatility of (CH<sub>3</sub>)<sub>3</sub>COPCH<sub>2</sub>CF<sub>3</sub>

(Log  $P = 7.1119 + 1.75 \log T - 0.0065T - 2414/T$ )  
( $t_{760} = 113.2^\circ$ ; Trouton constant = 20.6 eu)

$t, ^\circ\text{C}$	0.00	23.02	29.50	34.78	39.85	46.40
$P_{\text{obsd}}, \text{mm}$	5.79	22.91	32.47	42.19	53.95	73.03
$P_{\text{calcd}}, \text{mm}$	5.79	22.98	32.38	42.23	53.95	73.03

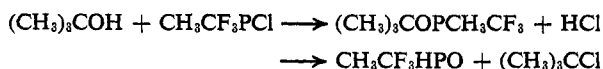
**The Arbuzov Reaction.** In the main experiment on the reaction of (CH<sub>3</sub>)<sub>3</sub>COPCH<sub>2</sub>CF<sub>3</sub> with CH<sub>3</sub>I, the latter was employed in deficient proportion, on the assumption that it would be catalytic as in the case of (CH<sub>3</sub>)<sub>3</sub>COP(CF<sub>3</sub>)<sub>2</sub>.<sup>3</sup> Actually, the proton nmr spectra of (CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>PO and (CH<sub>3</sub>)<sub>3</sub>CI appeared early and then grew large during 3 days at 62°. The main process now could be described (with millimole coefficients) as follows.



The product (CH<sub>3</sub>)<sub>2</sub>CF<sub>3</sub>PO was identified by its infrared, proton nmr, and mass spectra, but contained a trace of an unidentified impurity which could not be removed. However, it must have represented more than 90% of the CH<sub>3</sub>I. The unused CH<sub>3</sub>I could not be isolated from the 0.242-mmole "unknown" fraction, the infrared spectrum of which showed CF<sub>3</sub> groups and hydrocarbon features accounting for most of the missing *t*-butyl groups. It is apparent that CH<sub>3</sub>I attacked (CH<sub>3</sub>)<sub>3</sub>COPCH<sub>2</sub>CF<sub>3</sub> in the classical Arbuzov manner, whereas (CH<sub>3</sub>)<sub>3</sub>CI was not at all effective; in fact, we could not find any fraction corresponding to the expected product (CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>CF<sub>3</sub>PO, even with the aid of the mass spectrograph.

### Methyltrifluoromethylphosphine Oxide

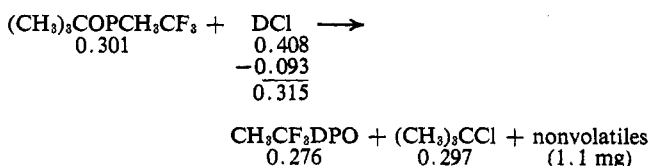
**Synthesis.** The initial attempts to make (CH<sub>3</sub>)<sub>3</sub>COPCH<sub>2</sub>CF<sub>3</sub> from (CH<sub>3</sub>)<sub>3</sub>COH and CH<sub>3</sub>CF<sub>3</sub>PCl (without the amine) produced instead the interesting new compound CH<sub>3</sub>CF<sub>3</sub>HPO. The process could not easily be monitored by the very complex proton nmr spectrum, but probably occurred in two main steps



The second step obviously is a classical Arbuzov-type reaction with the proton playing the role of a hydrocar-

bon group. In two of the three experiments, using CH<sub>3</sub>CF<sub>3</sub>PCl in slight excess over the *t*-butyl alcohol (0.5 or 4 days, at 25°), the yield of pure CH<sub>3</sub>CF<sub>3</sub>HPO corresponded to at least 95% of the *t*-butyl alcohol; then the slight excess of CH<sub>3</sub>CF<sub>3</sub>PCl was an impurity in the (CH<sub>3</sub>)<sub>3</sub>CCl. Even though slightly impure, this product could be identified by its molecular weight, volatility, and infrared and proton nmr spectra; the yield was nearly quantitative, and only very small traces of HCl could be found.

The reality of the second step of the synthesis was shown by the reaction of DCl with the *t*-butoxyphosphine (10 hr, 25°), described with millimole quantities as follows.



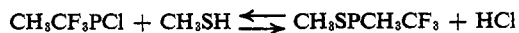
This nearly quantitative experiment not only confirmed the molecular formula of the phosphine oxide but also provided an infrared comparison proving the structure: the Q branches for P-H and P-D stretching were observed at 2359 and 1716 cm<sup>-1</sup>, respectively, with nearly equal intensities. No O-H or O-D stretching mode could be found.

**Characterization.** The two phosphine oxide species were trapped at -40° in high-vacuum fractional condensation (or could be purified by a high-vacuum column with -25° reflux). The melting range of CH<sub>3</sub>CF<sub>3</sub>HPO was -9.3 to -9.0°; of CH<sub>3</sub>CF<sub>3</sub>DPO, -10.0 to -9.7°. The molecular weight of CH<sub>3</sub>CF<sub>3</sub>HPO (45.7-mg sample, 638-ml volume, 70°) was determined as 133 (calculated, 132). Its vapor-tension values (2.29 mm at 31.98°, 4.45 mm at 42.38°, 5.48 mm at 45.75°, and 6.53 mm at 48.70°) conformed within 0.01 mm to the equation log  $P = 7.7278 + 1.75 \log T - 0.006T - 3016/T$ ; normal bp 169°; Trouton constant 22.6 eu. A liquid sample was only very slightly decomposed during 40 min at 110°, yielding a trace of CH<sub>3</sub>CF<sub>3</sub>PH, identified by its infrared spectrum.

The proton nmr spectrum of CH<sub>3</sub>CF<sub>3</sub>HPO showed  $\delta$  1.43 ppm downfield of TMS ( $J = 15.7$  cps; no fine structure seen) for the CH<sub>3</sub> group. The H-P proton showed as a doublet centered at  $\delta$  6.87 ppm downfield of TMS ( $J = 516$  cps), with each member interpretable as an overlapped quartet of quartets ( $J_{\text{HPCF}} = 5.4$  and  $J_{\text{HPCH}} = 3.4$  cps). For <sup>19</sup>F,  $\delta = 97$  ppm upfield of Cl<sub>3</sub>CF ( $J = 91$  cps); no fine structure could be seen.

### Alkanethiophosphines

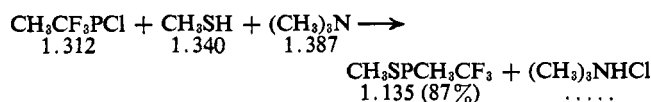
**Synthesis.** Unlike the thiolysis of (CF<sub>3</sub>)<sub>2</sub>PCl,<sup>4,9</sup> or the just-described alcoholyses of CH<sub>3</sub>CF<sub>3</sub>PCl, the reaction



equilibrates in favor of the products;  $K$  was measured roughly as 5. Accordingly, a mixture of 0.812 mmol of CH<sub>3</sub>CF<sub>3</sub>PCl and 0.958 mmol of CH<sub>3</sub>SH, in a 60-ml tube on the vacuum line at 25°, gave 0.780 mmol (96% yield) of CH<sub>3</sub>SPCH<sub>2</sub>CF<sub>3</sub> as a result of removing both products at three stages. The alternative amine method

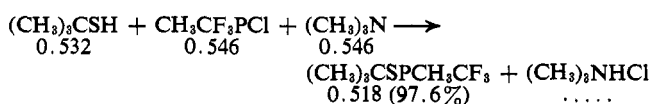
(9) R. G. Cavell and H. J. Emeléus, *J. Chem. Soc.*, 5825 (1964).

(fast at 25°) is described with millimole quantities as follows.



In this case the excess mercaptan was not recovered but might have been consumed to form a slight impurity which was trapped out at  $-10^\circ$  during the purification of the main product by high-vacuum fractional condensation. For final purification, a high-vacuum micro column was used, with reflux at  $-35^\circ$ .

The initial synthesis of  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$  employed 0.805 mmol of  $(\text{CH}_3)_3\text{CSH}$ , 0.965 mmol of  $\text{CH}_3\text{CF}_3\text{-PCl}$ , and 3.742 mmol of  $(\text{CH}_3)_3\text{N}$  (slowly warmed from  $-78$  to  $25^\circ$ , and held there for 2 hr), giving only 0.485 mmol of  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$  and nonvolatile solids. The side reaction was almost wholly avoided by using equimolar proportions of the reactants in another experiment (10 hr, warming from  $-78$  to  $25^\circ$ ) for which the reaction balance (millimoles) was



The only volatile by-product was 0.029 mmol of an unidentified gas, passing a trap *in vacuo* at  $-78^\circ$ . The purification of the desired mercaptophosphine was easily accomplished by high-vacuum fractional condensation.

**Formulas and Physical Properties.** The formula  $\text{CH}_3\text{SPCH}_2\text{CF}_3$  was confirmed by the vapor-phase molecular weight (163.1 *vs.* calcd 162.1) and basic hydrolysis to give the expected amount of  $\text{HCF}_3$ . The substance formed a glass at low temperatures, so that its melting point could not be observed. For  $(\text{CH}_3)_3\text{-CSPCH}_2\text{CF}_3$ , the molecular weight was determined as 205.3 (calculated, 204.1); the compound melted sharply near  $-30^\circ$ . The equilibrium vapor pressure values for the mercaptophosphines are shown in Tables III and IV.

**Table III.** Volatility of  $\text{CH}_3\text{SPCH}_2\text{CF}_3$   
( $\log P = 6.0865 + 1.75 \log T - 0.0057T - 2214/T$ )  
( $t_{760} = 107.3^\circ$ ; Trouton constant = 21.4 eu)

$t, ^\circ\text{C}$	0.00	14.30	22.03	29.70	36.66	40.30
$P_{\text{obsd}}, \text{mm}$	7.63	17.71	27.12	40.13	56.46	66.82
$P_{\text{calcd}}, \text{mm}$	7.57	17.77	27.10	40.17	56.30	66.73

**Table IV.** Volatility of  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$   
( $\log P = 5.6743 + 1.75 \log T - 0.0047T - 2420/T$ )  
( $t_{760} = 152^\circ$ ; Trouton constant = 21.8 eu)

$t, ^\circ\text{C}$	23.20	31.73	38.50	43.80	49.75	56.50	64.05
$P_{\text{obsd}}, \text{mm}$	4.47	7.34	10.56	13.96	18.96	26.29	37.36
$P_{\text{calcd}}, \text{mm}$	4.45	7.32	10.63	14.07	19.01	26.39	37.37

**Nmr Spectra.** The proton nmr spectrum of  $(\text{CH}_3)_3\text{-CSPCH}_2\text{CF}_3$  was recorded by the A-60 instrument at maximum scale-expansion showing  $\delta$  1.19 ppm downfield of TMS (by substitution) for the *t*-butyl group ( $J_{\text{HCCP}} = 0.92$  cps). The  $\text{PCH}_3$  protons appeared as a doublet of quartets with total area one-third that of *t*-butyl;  $\delta$  1.21;  $J_{\text{HCP}} = 7.67$  cps;  $J_{\text{HPCF}} = 0.38$  cps. By anal-

ogy, the  $\text{PCH}_3$  protons of  $\text{CH}_3\text{SPCH}_2\text{CF}_3$  belong to the doublet at  $\delta$  1.32 ( $J_{\text{HCP}} = 7.1$  cps), leaving to the mercapto group the doublet at  $\delta$  2.11 ppm, with  $J_{\text{HCSF}} = 12.6$  cps. By this fairly reasonable assignment, it seems that the sulfur linkage increases the coupling, just as oxygen often does.<sup>7</sup>

The  $^{19}\text{F}$  spectra (measured upfield from  $\text{Cl}_3\text{CF}$ , by substitution) showed for  $\text{CH}_3\text{SPCH}_2\text{CF}_3$   $\delta$  62.0 ppm and  $J_{\text{FCP}} = 64$  cps, and for  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$   $\delta$  21.1 ppm and  $J_{\text{FCP}} = 65$  cps. The  $^{31}\text{P}$  spectrum of  $\text{CH}_3\text{-SPCH}_2\text{CF}_3$  showed  $\delta$  113 ppm upfield of  $\text{P}(\text{OCH}_3)_3$ . It was too complex and poorly resolved for a recheck of  $J_{\text{PCF}}$ .

**The Arbuzov Reactions.** The conversion of  $\text{CH}_3\text{-SPCH}_2\text{CF}_3$  to  $(\text{CH}_3)_2\text{CF}_3\text{PS}$  by methyl iodide was insignificant during 35 hr at  $63^\circ$ , 8 hr at  $105^\circ$ , or 18 hr under ultraviolet irradiation at  $25^\circ$ ; but nearly 35% conversion occurred during 6 months at  $25^\circ$ . An unknown side reaction consumed an equal amount of the original  $\text{CH}_3\text{SPCH}_2\text{CF}_3$ .

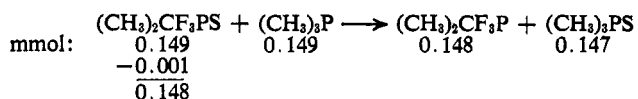
For the identification of the product  $(\text{CH}_3)_2\text{CF}_3\text{PS}$ , this compound was made also by direct addition of sulfur (70.8 mg) to  $(\text{CH}_3)_2\text{CF}_3\text{P}$  (0.193 mmol), first only during 2.5 hr at  $100^\circ$  (for a 22% yield), and then during 7 hr at  $150^\circ$  to bring the yield to 0.190 mmol, or 98.5%. The second experiment (4 hr at  $150^\circ$ ) employed 86.3 mg of sulfur and 1.150 mmol of  $(\text{CH}_3)_2\text{CF}_3\text{P}$ , giving a 94.7% yield of  $(\text{CH}_3)_2\text{CF}_3\text{PS}$ . The product melted in the range  $49.9$ – $50.0^\circ$  after purification by high-vacuum fractional condensation at  $-50^\circ$ .

The molecular weight of  $(\text{CH}_3)_2\text{CF}_3\text{PS}$  was determined at  $81^\circ$  (30.5 mm) as 162.1 (calculated, 162.1). Its equilibrium vapor pressures are given in Table V.

**Table V.** Volatility of Solid and Liquid  $(\text{CH}_3)_2\text{CF}_3\text{PS}$

Solid: $\log P = 11.9842 - 3551/T$						
$t, ^\circ\text{C}$	27.05	32.30	37.28	42.60	47.23	
$P_{\text{obsd}}, \text{mm}$	1.43	2.23	3.51	5.47	7.95	
$P_{\text{calcd}}, \text{mm}$	1.43	2.28	3.51	5.47	7.95	
Liquid: $\log P = 6.8204 + 1.75 \log T - 0.0057T - 2783/T$						
( $t_{760} = 163^\circ$ ; Trouton constant = 22.7 eu; mp $49.2^\circ$ )						
$t, ^\circ\text{C}$	49.90	55.00	60.15	65.45	71.05	83.50
$P_{\text{obsd}}, \text{mm}$	9.63	12.67	16.52	21.74	28.53	50.20
$P_{\text{calcd}}, \text{mm}$	9.59	12.65	16.56	21.64	28.42	50.18

The formula  $(\text{CH}_3)_2\text{CF}_3\text{PS}$  was confirmed by basic hydrolysis (10% NaOH, 5 hr,  $100^\circ$ ) giving a 99.1% yield of  $\text{HCF}_3$ , and by a quantitative abstraction of sulfur (30 days,  $135^\circ$ ).



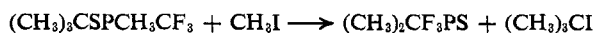
The product  $(\text{CH}_3)_2\text{CF}_3\text{P}$  was identified by its molecular weight (129.6 *vs.* calcd 130.1), volatility, and infrared spectrum. The product  $(\text{CH}_3)_3\text{PS}$  was identified by its melting point ( $155.5$ – $155.7^\circ$ ), proton nmr spectrum, and infrared spectrum.<sup>10</sup>

The compound  $(\text{CH}_3)_2\text{CF}_3\text{PS}$ , unlike  $(\text{CH}_3)_3\text{PS}$ , failed to form any adduct with  $\text{CH}_3\text{I}$  (6 hr,  $25^\circ$ ). Also, like its precursor  $\text{CH}_3\text{SPCH}_2\text{CF}_3$ , it failed to form a  $\text{BF}_3$  adduct. Its nmr spectra in  $\text{CS}_2$  solution showed protons at  $\delta$  1.86 ppm downfield of TMS ( $J = 14.3$  cps)

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

and  $^{19}\text{F}$  at 104.7 ppm upfield of  $\text{Cl}_3\text{CF}$  ( $J = 85.5$  cps). The fine structure of these doublets was not observed.

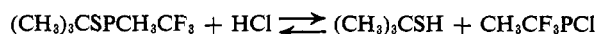
The classical Arbuzov reaction



was observed by means of the proton nmr spectrum, showing less intensity for  $\text{CH}_3\text{I}$  as the  $(\text{CH}_3)_3\text{CI}$  singlet and the  $(\text{CH}_3)_2\text{CF}_3\text{PS}$  doublet of quartets appeared and increased. The extent of reaction was about 6% after 31 hr at  $63^\circ$ , 30% after a further 6 hr at  $100^\circ$ , and not more than 60% after 23 hr at  $103^\circ$ . Significant amounts of nonvolatile by-products now had appeared.

**Hydrogen Chloride Cleavages.** The cleavage of  $\text{CH}_3\text{SPCH}_2\text{CF}_3$  by  $\text{HCl}$  (3.3 volumes) to form  $\text{CH}_3\text{SH}$  and  $\text{CH}_3\text{CF}_3\text{PCI}$  (reversing the original synthesis) was about 70% complete after 10 hr at  $25^\circ$ .

The compound  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$  with a small excess of  $\text{HCl}$  reacted during 19 hr at  $25^\circ$  to a limited extent which did not increase appreciably during 13 hr at  $100^\circ$ . The products  $(\text{CH}_3)_3\text{CSH}$  and  $\text{CH}_3\text{CF}_3\text{PCI}$  passed a U-trap at  $-65^\circ$  and condensed at  $-130^\circ$  (under high vacuum); since further separation would have been difficult, they were determined by their infrared spectra, showing equilibration at 9% progress of the reaction

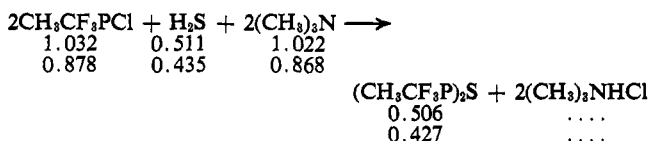


and no appreciable side reactions. Apparently the reverse process could be used efficiently for making  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$ , without the use of an amine to remove  $\text{HCl}$ .

Of special interest here was the absence of any trace of  $\text{CH}_3\text{CF}_3\text{HPS}$  from either cleavage; there was no analogy to the formation of  $\text{CH}_3\text{CF}_3\text{HPO}$  from  $\text{HCl}$  and  $(\text{CH}_3)_3\text{COPCH}_2\text{CF}_3$ . However, it was possible to obtain evidence for the existence of  $\text{CH}_3\text{CF}_3\text{HPS}$  in relation to the study of  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$ , next described.

### Thiobis(methyltrifluoromethylphosphine)

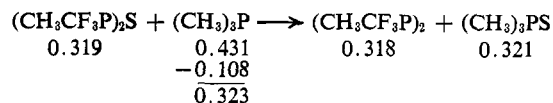
**Synthesis and Characterization.** The formation of the thiobisphosphine  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$  in two experiments is described (with respective millimole quantities) as follows.



In both experiments, the components were warmed very slowly from  $-78$  to  $25^\circ$ . In another experiment, with twice as much of each component and faster warming, some of the product decomposed, giving a 14% yield of the diphosphine  $(\text{CH}_3\text{CF}_3\text{P})_2$ . This thermal decomposition could be observed during months of storage at  $25^\circ$ . A pure sample, heated at  $100^\circ$  for 34 hr, was 5% decomposed to form a nonvolatile solid presumed to be the diphosphine disulfide  $(\text{CH}_3\text{CF}_3\text{PS})_2$ , and the corresponding formation of  $(\text{CH}_3\text{CF}_3\text{P})_2$  was proved by its infrared spectrum. This decomposition product is so difficult to remove from the thiobisphosphine that the synthesis of this in pure form must depend upon prevention of the decomposition.

The quantitative syntheses left no doubt of the molecular formula  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$ , which was further confirmed by the molecular weight (263.2 *vs.* calcd 262.1)

and hydrolysis by 10%  $\text{NaOH}$  to give a 98% yield of  $\text{HCF}_3$  (after 22.5 hr at  $120^\circ$ ). Yet further proof of the formula came from the process (with millimole quantities)



which was completed during 19.5 hr at  $82^\circ$ . The resulting  $(\text{CH}_3\text{CF}_3\text{P})_2$  was identified by its infrared spectrum, volatility (4.0 mm at  $0^\circ$ ),<sup>2</sup> and molecular weight (231 *vs.* calcd 230), and the  $(\text{CH}_3)_3\text{PS}$  by its melting point, infrared spectrum, and proton nmr spectrum, as before.

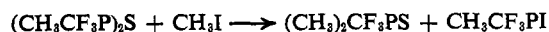
Although such experiments established the purity of the product  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$  beyond doubt, its melting point was not sharp, on account of two possible kinds of isomerism: with two asymmetric phosphorus atoms, there could be a *meso* form along with the expected optical isomers; and for each of these three isomers there should be P-S-bond rotational isomers stabilized in the solid phase. The latter type of isomerism was suggested by a change of melting range with time: a sample which had been condensed from the vapor phase at  $-78^\circ$  began to melt between  $-45.7$  and  $-42.7^\circ$  and was all melted at  $-33^\circ$ , but the same sample, after 1 hr at  $-45^\circ$ , melted in the range  $-33.6$  to  $-27.5^\circ$ . The digestion at  $-45^\circ$  could have allowed extensive conversion to the more stable conformations, which would be expected to melt at higher temperatures. Less probably, the effect might be due to a crystal-structure change, with unchanged conformations.

Despite such isomerism, the volatility behavior of pure  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$  was normal, as indicated by the data of Table VI.

**Table VI.** Volatility of  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$   
( $\log P = 7.8113 + 1.75 \log T - 0.0065T - 2888/T$ )  
( $t_{760} = 154.3^\circ$ ; Trouton constant = 21.7 eu)

$t, ^\circ\text{C}$	43.17	48.30	55.47	62.30	68.65
$P_{\text{obsd}}, \text{mm}$	10.01	13.32	19.58	27.63	37.52
$P_{\text{calcd}}, \text{mm}$	10.01	13.34	19.55	27.63	37.52

**Cleavage by Methyl Iodide.** The Arbuzov-like reaction



was investigated by heating the reactants (0.213 mmol of each) in a sealed tube. There was no change during 4 hr at  $50^\circ$ , but after 30 hr at  $100^\circ$ , 0.103 mmol of  $\text{CH}_3\text{I}$  could be recovered (consumed, 0.110 mmol) and it was possible to isolate a 30.8-mg fraction having the volatility, mercury-reactivity, and infrared spectrum (with some impurity bands) of  $\text{CH}_3\text{CF}_3\text{PI}$ . Allowing for the impurities, this would represent all of the consumed  $\text{CH}_3\text{I}$ . The other product,  $(\text{CH}_3)_2\text{CF}_3\text{PS}$ , could not be isolated from the unused  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$ , but the latter could be destroyed by heating with  $\text{CH}_3\text{I}$  in large excess (3 hr,  $153^\circ$ ), forming mostly a black tar, but permitting the isolation of 5.3 mg (0.033 mmol) of  $(\text{CH}_3)_2\text{CF}_3\text{PS}$ . This was clearly identified by its infrared spectrum.

**The Quest for Methyltrifluoromethylphosphine Sulfide.** Our attempts to isolate the phosphine sulfide  $\text{CH}_3\text{CF}_3\text{-}$

Table VII. Comparison of Infrared Spectra

Suggested Assignment	CH <sub>3</sub> CF <sub>3</sub> PF	CH <sub>3</sub> OP <sup>CH<sub>3</sub></sup> <sub>CF<sub>3</sub></sub>	(CH <sub>3</sub> ) <sub>3</sub> COP <sup>CH<sub>3</sub></sup> <sub>CF<sub>3</sub></sub>	CH <sub>3</sub> SP <sup>CH<sub>3</sub></sup> <sub>CF<sub>3</sub></sub>	(CH <sub>3</sub> ) <sub>3</sub> CSP <sup>CH<sub>3</sub></sup> <sub>CF<sub>3</sub></sub>	(CH <sub>3</sub> CF <sub>3</sub> P) <sub>2</sub> S	H <sub>2</sub> C=CH <sub>2</sub> O=C=O	D <sub>2</sub> C=CH <sub>2</sub> O=C=O	(CH <sub>3</sub> ) <sub>2</sub> C=O	(CH <sub>3</sub> ) <sub>2</sub> C=S
C-H stretching	3000 (0.15) (wide) 2930 (0.10)	sh 3009 (1.4) 3004 (1.9) 2994 (1.4) 2952 (2.4) 2851 (1.6)	2989 (13) 2947 (1.8) 2923 (1.7) 2883 (0.8) 2826 (0.24)	3009 (0.6) 3001 (0.6) 2947 (2.0) Q 2943 (2.5) P 2940 (2.2) 2853 (0.4)	2980 (7.0) 2956 (3.6) 2934 (2.7) 2911 (2.8) 2876 (1.6) 2831 (0.2)	2928 (0.7)	? 3030 (0.10) 2936 (0.11)	not seen	3012 (0.27) 3006 (0.29) 2935 (0.22)	3007 (0.3) 3000 (0.3) 2930 (0.2)
P-H or P-D stretching	.....	.....	.....	.....	.....	.....	2359 (4)	R 1725 (1.2) Q 1716 (4.6) P 1710 (1.2)	.....	.....
CH <sub>3</sub> asym. deformation	R 1424 (1.0) Q 1418 (1.3) P 1412 (1.0)	sh 1450 (0.6) sh 1430 (1.1) 1422 (1.3) 1418 (1.2) 1371 (0.16)	1476 (1.0) 1425 (1.7) 1398 (2.2) 1375 (6.5)	1436 (1.8) 1429 (1.8) R 1331 (0.7) Q 1326 (0.8) P 1322 (0.7) R 1302 (0.4) Q 1299 (0.5) P 1294 (0.4)	1478 (1.4) 1463 (2.0) 1429 (1.5) 1397 (0.6) 1371 (3.8) 1300 (0.6)	1426 (3.2)	1420 (0.69)	1411 (1.2)	1432 (1.6) 1378 (0.44) R 1322 (3.6) Q 1316 (7.6) P 1309 (4.5)	sh 1434 (0.9) sh 1429 (1.6) sh 1424 (1.5) 1420 (1.7) sh 1410 (1.0)
CH <sub>3</sub> symm. deformation (or P=O stretching)	1298 (0.9)	1299 (0.7) sh 1277 (0.3) sh 1268 (0.3)	1292 (1.0)	Q 1326 (0.8) P 1322 (0.7) R 1302 (0.4) Q 1299 (0.5) P 1294 (0.4)	1298 (1.1) 1275 (0.4)	1298 (1.1) 1275 (0.4)	1381 (0.35) 1313 (1.3) 1308 (9.4) 1284 (9.2) 1279 (9.7)	1312 (6.1) 1308 (6.1)	R 1280 (4.7) Q 1273 (8.1) P 1266 (4.7)	sh 1365 (0.2) 1306 (2.1) 1295 (2.1) 1276 (0.5)
C-F stretching	R 1206 (8.5) Q 1200 (14.0) P 1194 (13.4) R 1154 (23) Q 1144 (34) P 1137 (29)	1191 (10)	1187 (26)	1175 (18) 1143 (20) 1125 (25) 1120 (25)	1176 (25) 1141 (26) 1119 (38) 1116 (37)	1174 (38) 1144 (41) 1125 (67)	sh 1217 (14) 1211 (22) 1205 (22) 1172 (25) 1144 (41) 1153 (28) 1147 (28)	sh 1215 (11) 1209 (17) 1204 (17) 1172 (18)	R 1218 (7.1) Q 1213 (11.1) P 1208 (9.3)	1207 (20) 1168 (17) 1131 (16)
C-O stretching	.....	1057 (9.1) 1051 (8.1)	954 (27)	.....	.....	.....	.....	.....	.....	.....
CH <sub>3</sub> rocking	898 (3.4) sh 892 (2.1) R 874 (3.0) Q 867 (4.2) P 862 (2.6)	896 (2.4) R 882 (4.2) Q 876 (4.7) P 871 (3.5)	920 (2.1) 896 (2.7)	965 (0.4) 901 (2.2)	901 (2.8)	900 (5.0) 876 (7.1)	1013 (2.5) R 968 (11) Q 961 (14) P 957 (9)	1016 (0.9) R 966 (4.3) Q 960 (5.8) P 953 (3.2)	R 935 (2.8) Q 928 (3.7) P 923 (2.9) 906 (2.1) R 891 (2.4) Q 883 (3.3)	954 (9.4) sh 924 (8.8) 921 (9.8)
P-F stretching	808 (8)	.....	.....	.....	.....	.....	.....	.....	sh 901 (2.3)	860 (2.3)
CH <sub>3</sub> wagging ?	.....	.....	811 (1.5)	.....	.....	.....	856 (1.6) 819 (6.6) 798 (1.9)	P 880 (1.8) 819 (2.3) 778 (2.9)	875 (4.9) 869 (7.2) 836 (0.7) 749 (1.5)	852 (2.7)
CF <sub>3</sub> symm. deformation	not seen	753 (4.7)	not seen	R 743 (0.5) Q 738 (0.6) P 733 (0.5)	737 (0.5)	737 (2.0)	R 730 (1.6) Q 723 (2.0) P 716 (1.3)	R 705 (0.9) Q 698 (2.1) P 693 (0.9)	R 697 (1.7) Q 693 (2.4) P 685 (1.5)	761 (8.1) Q 616 (5.8) P 610 (3.7)
P-CH <sub>3</sub> stretching (P-O stretching?)	R 711 (1.0) Q 705 (1.6) P 700 (0.8)	707 (1.7)	715 (2.2) 686 (1.4)	700 (1.6)	699 (1.5)	695 (3.5)	.....	.....	.....	.....
CF <sub>3</sub> asym. deformation	not sought	545 (0.47) 537 (0.40)	545 (0.4)	541 (0.6)	544 (1.1)	540 (1.0)	not seen	not seen	not seen	not seen
P-S stretching	.....	.....	.....	508 (2.9)	523 (1.8)	497 (13)	.....	.....	R 447 (5.1) Q 441 (8.0) P 435 (5.0)	R 415 (2.0) Q 409 (2.8) P 402 (1.6)
P-CF <sub>3</sub> stretching	.....	442 (2.0)	sh 460 (0.4) 438 (2.0) sh 434 (1.7)	425 (2.1)	430 (2.2)	422 (5.9)	438 (1.3)	not sought	.....	.....
CF <sub>3</sub> rocking or CH <sub>3</sub> torsion	.....	380 (0.55)	413 (0.6)	338 (0.3)	410 (0.3)	.....	377 (0.9)	.....	378 (3.6) 295 (3.4)	.....

HPS included experiments on the H<sub>2</sub>S reaction of CH<sub>3</sub>-CF<sub>3</sub>PCl, with or without trimethylamine, and the cleavage of (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S by H<sub>2</sub>S. In no case could we separate the desired compound from the similarly volatile (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S, but the proton and <sup>19</sup>F nmr spectra of the mixtures left no doubt of the presence of the desired compound.

Relatively successful was an experiment employing 0.606 mmol of CH<sub>3</sub>CF<sub>3</sub>PCl and 1.807 mmol of H<sub>2</sub>S, which were allowed to react for 12 hr in a 200-ml stopcocked tube at 25°. Only one-third of the chlorophosphine was consumed (using 0.105 mmol of the H<sub>2</sub>S); now (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S was clearly recognized as a major product, both by its characteristic infrared peaks and by its complex proton and <sup>19</sup>F nmr spectra. Another product, having nearly the same total intensity of proton nmr absorption, and not separable by distillation methods, showed proton and <sup>19</sup>F nmr spectra strictly consistent with CH<sub>3</sub>CF<sub>3</sub>HPS. For CH<sub>3</sub>, there was a doublet of doublets centered at δ 2.08 ppm downfield of TMS, with J<sub>HCP</sub> = 15.5 and J<sub>HCPH</sub> = 4.9 cps; and for H-P there was a complex doublet centered at δ 7.39 ppm, with J<sub>HP</sub> = 487 cps and total intensity one-third that for CH<sub>3</sub>. The <sup>19</sup>F spectrum was a doublet of doublets centered at 72.3 ppm upfield of Cl<sub>3</sub>CF, with J<sub>FCP</sub> = 93.9 and J<sub>FCPH</sub> = 4.7 cps.

A second approach employed CH<sub>3</sub>CF<sub>3</sub>PCl and H<sub>2</sub>S, with (CH<sub>3</sub>)<sub>3</sub>N to remove HCl. Three experiments, using different procedures for mixing (even including vapor-phase mixing at -8°), all gave essentially the same result: the main product again was the moderately volatile mixture of CH<sub>3</sub>CF<sub>3</sub>HPS and (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S. However, a trace of CH<sub>3</sub>CF<sub>3</sub>PH (identified by its strong infrared bands) always appeared and increased slightly as the mixture stood at 25°; small amounts of a white nonvolatile solid also were seen. A reasonable explanation would be a disproportionation.



One mixture was subjected to high-vacuum fractionation in a micro column with the reflux head at -78°. Neither main component could possibly have come through at that temperature, even during the 12-hr period of operation, but the actual effluent did show the infrared spectrum assigned to CH<sub>3</sub>CF<sub>3</sub>HPS, with a much smaller proportion of (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S; then after 24 hr at 25°, the infrared spectrum showed the normal mixture of these components. The most plausible explanation would be that a very small trace of CH<sub>3</sub>-CF<sub>3</sub>PSH exists in a rapidly established equilibrium with CH<sub>3</sub>CF<sub>3</sub>HPS, and would be volatile enough for slow delivery through the -78° column under high vacuum. Then upon warming to 25°, reversal would occur.



In a third approach, the cleavage of (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S by H<sub>2</sub>S was attempted in a sealed tube at 100° (20 hr). The 0.203-mmol sample of the thiobisphosphine consumed 0.204 mmol of H<sub>2</sub>S (from the 2.249-mmol sample), but the chief volatile product was 0.167 mmol of CH<sub>3</sub>CF<sub>3</sub>PH (mol wt 117.8 vs. calcd 116; confirmed by the infrared spectrum). It would have formed by the disproportionation of CH<sub>3</sub>CF<sub>3</sub>HPS, yielding an equal amount of CH<sub>3</sub>CF<sub>3</sub>PS<sub>2</sub>H, but this hypothetical compound could not be isolated from a fraction containing (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S (infrared-identified). On standing at 25°, this fraction slowly formed a nonvolatile solid, while evolving traces of H<sub>2</sub>S and CH<sub>3</sub>CF<sub>3</sub>PH (0.009 and 0.012 mmol, respectively).

In sum, then, it is clear that the phosphine sulfide CH<sub>3</sub>CF<sub>3</sub>HPS exists well enough but equilibrates fairly soon with H<sub>2</sub>S and (CH<sub>3</sub>CF<sub>3</sub>P)<sub>2</sub>S, and a very small component may be CH<sub>3</sub>CF<sub>3</sub>PSH. More slowly, its dispropo-



portionation yields  $\text{CH}_3\text{CF}_3\text{PH}$  and probably more than one other product.

### Infrared Spectra

The vapor-phase infrared spectra of ten new  $\text{CH}_3\text{-CF}_3\text{P}$  compounds were recorded by means of the Beckman IR7 instrument, calibrated to  $1\text{ cm}^{-1}$  although some wide peaks could not be read that accurately. The apparent intensity of each peak or shoulder was calculated as  $k = (100/PL) \log I_0/I$  for pressure  $P$  and path  $L$  both in cm, with  $I$  taken literally as per cent transmission; these  $k$  values were recorded in parentheses after the respective frequencies ( $\text{cm}^{-1}$ ). Table VII shows the main results, with group-frequency assignments according to experience with many related compounds. However, some assignments remain uncertain: for example,  $\text{P=O}$  stretching and  $\text{CH}_3$  symmetric deformation occur at similar frequencies, and some of the strong peaks in the  $\text{C-F}$  stretching region may be  $\text{CF}_3$  symmetric deformation overtones, greatly enhanced by Fermi resonance. Also, some fundamental modes are missing or unrecognizable. The following notes supplement the tabulated information.

For  $\text{CH}_3\text{CF}_3\text{PF}$ , the  $808\text{-cm}^{-1}$  band ( $5\text{ cm}^{-1}$  wide at the peak) could represent coupling of  $\text{P-F}$  stretching with  $\text{CH}_3$  rocking, leaving exact assignments uncertain in this region. Very weak peaks at 2355, 2295, 2255, 1996, 1880, and  $1605\text{ cm}^{-1}$  represent overtones and combinations.

For  $\text{CH}_3\text{OPCH}_2\text{CF}_3$ , combinations and overtones were seen at 2322 (0.2), 2247 (0.2), 2095 (0.1), 1800 (0.2), and probably 577 (0.09)  $\text{cm}^{-1}$ . For  $(\text{CH}_3)_3\text{COP-CH}_2\text{CF}_3$ , combinations appeared at 1765 (0.2) and 1637 (0.4)  $\text{cm}^{-1}$ , and a peak at 489 (0.2)  $\text{cm}^{-1}$  was not assigned. Similarly,  $(\text{CH}_3)_3\text{CSPCH}_2\text{CF}_3$  showed peaks

at 575 (0.8) and  $460 (0.14)\text{ cm}^{-1}$ , omitted from Table VII for lack of assignment.

The recorded spectrum for  $(\text{CH}_3\text{CF}_3\text{P})_2\text{S}$  was relatively simple, not only because band structure was unresolvable, but also because the vapor pressures attainable without decomposition were too low for observation of many weak bands. The simpler phosphine oxides and sulfide could be vaporized at higher temperatures, and showed typical PQR features (central spike and two shoulders). For  $(\text{CH}_3)_2\text{CF}_3\text{PO}$ , an overtone at 2352 (0.05) and a combination at 1995 (0.15)  $\text{cm}^{-1}$  were observed.

### Mass Spectra

The mass spectra of  $(\text{CH}_3)_2\text{CF}_3\text{PO}$ ,  $(\text{CH}_3)_3\text{COP-CH}_2\text{CF}_3$ , and  $\text{CH}_3\text{CF}_3\text{HPO}$  were recorded in detail, with fluorocarbon calibration of the M-66 instrument. The full record is to be found in the original dissertation.<sup>1</sup>

### Miscellaneous Nmr Spectra

Beyond the nmr spectra already listed for seven compounds, the results shown in Table VIII also were recorded. The  $\delta$  values were measured in ppm, for protons downfield from TMS, for F, upfield from  $\text{Cl}_3\text{CF}$ , and for P, upfield from  $\text{P(OCH}_3)_3$ .

Table VIII. Nmr Comparison of Chloro and Iodo Phosphines

	$\text{CH}_3\text{CF}_3\text{P-Cl}$		$\text{CH}_3\text{CF}_3\text{P-I}$	
	$\delta$	$J$	$\delta$	$J$
$^1\text{H}$	1.44	10.4 HCP 0.51 HCPCF	2.28	11.2 HCP 0.36 HCPCF
$^{19}\text{F}$	112	...	144	60.4 FCP
$^{31}\text{P}$	63.4	73.6 PCF	118	60.9 PCF

## Signs of Phosphorus-Phosphorus Coupling Constants in Coordination Compounds

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**Abstract:** Using double resonance nmr methods, the signs and magnitudes of the  $^{31}\text{P}$ - $^{31}\text{P}$  coupling constant were obtained in 13 complexes of the type *cis*- and *trans*-( $\text{OC}$ ) $_4\text{ML}_2$  (where  $\text{M} = \text{Cr}, \text{Mo},$  or  $\text{W}$ ), *trans*-( $\text{OC}$ ) $_3\text{FeL}_2$ , and *cis*- and *trans*- $\text{PdL}_2\text{X}_2$  (where  $\text{X} = \text{Cl}$  or  $\text{I}$ ) in which  $\text{L} = \text{P}(\text{CH}_3)_3$ ,  $\text{P}[\text{N}(\text{CH}_3)_2]_3$ , or  $\text{P}(\text{OCH}_3)_3$ . The signs and magnitudes of  $\delta(^{31}\text{P})$ ,  $\delta(^{13}\text{C})$ ,  $^3J_{\text{PH}}$ ,  $^5J_{\text{PH}}$ ,  $^3J_{\text{PC}}$ ,  $^4J_{\text{PC}}$ , and  $^1J_{\text{CH}}$  and their relationship to the  $^{31}\text{P}$ - $^{31}\text{P}$  couplings ( $^2J_{\text{PP}}$ ) are presented and discussed. The *cis* zerovalent group VI complexes have negative  $^2J_{\text{PP}}$  values in all cases. The rest of the complexes possess positive  $^2J_{\text{PP}}$  values except for chromium. The sign results for the *cis* and *trans* group VI carbonyl complexes are discussed from a Pople-Santry MO point of view.  $\text{D}_{4h}$  and  $\text{C}_{2v}$  MO energy level diagrams are presented which appear to be consistent with the signs and trends.

The transfer of nuclear spin information between two phosphorus nuclei bound to a metal atom in a complex such as *trans*-( $\text{OC}$ ) $_4\text{Mo[P(CH}_3)_3]_2$  is a function of the electron distribution among these atoms and there-

fore such couplings ( $^2J_{\text{PP}}$ ) should reflect some aspects of the nature of phosphorus-metal bonding. Since our original reports<sup>2</sup> on estimating values of  $^2J_{\text{PP}}$  from

(1) American Chemical Society Petroleum Research Foundation Fellow.

(2) (a) J. G. Verkade, R. E. McCarley, D. G. Hendrick, and R. W. King, *Inorg. Chem.*, **4**, 228 (1965); (b) D. G. Hendrick, R. E. McCarley, R. W. King, and J. G. Verkade, *ibid.*, **5**, 639 (1966).