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 (cm^{-1}) of the peaks in the following listing: C—F stretching, 1175 (203) and 1163 (145); CF_3 symmetric deformation, 767 (40); P=S stretching, 738 (65); CF_3 asymmetric deformation, 590 (5.3); P—S—P asymmetric stretching, 536 (3.7); P—CF_3 stretching, 490 (35).

The infrared spectrum of $(CF_3PS)_3S_2$ in a Nujol mull was very similar to the vapor-phase spectrum, except that the frequencies were lower by 1–7 cm^{-1}.

Oxygen and Sulfur Chemistry of Methyltrifluoromethylphosphines[1]

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Abstract: The new alkoxyphosphines $CH_3OPCH_3CF_3$ (bp 61°) and $(CH_3)_3COPCH_3CF_3$ (bp 113°) undergo normal Arbuzov reactions with CH_3I to form $(CH_3)_2CF_3PO$ (mp 72°, bp 193°) but react differently with HCl: the methoxyphosphine reverts to CH_3OH and CH_3CF_3PCl whereas the *t*-butoxyphosphine yields the new and unexpectedly stable phosphine oxide CH_3CF_3HPO (mp −9.3°, bp 169°). Both $CH_3SPCH_3CF_3$ (bp 107°) and $(CH_3)_3CSPCH_3CF_3$ (mp −30°, bp 152°) undergo Arbuzov reactions with CH_3I to form the new phosphine sulfide $(CH_3)_2CF_3PS$ (mp 49°, bp 163°), and both are cleaved by HCl to CH_3CF_3PCl and mercaptan. The new thiobisphosphine $(CH_3CF_3P)_2S$ (bp 154°) shows a variable melting range, ascribed to conformational isomerism. Its Arbuzov-like cleavage by CH_3I to form CH_3CF_3PI and $(CH_3)_2CF_3PS$ is observable. The phosphine sulfide CH_3CF_3HPS probably exists in equilibrium with H_2S and $(CH_3CF_3P)_2S$, with possible traces of CH_3CF_3PSH; eventually CH_3CF_3PH also is found. Extensive nmr and infrared spectra are reported.

Earlier studies of the CH_3CF_3PX chemistry[2] now have been extended to include X groups containing oxygen or sulfur, again with some results not predictable from the corresponding $(CH_3)_2PX$ and $(CF_3)_2PX$ 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.

$$\left.\begin{array}{l} CH_3OP(CF_3)_2{}^{3} \\ CH_3SP(CF_3)_2{}^{4} \\ (CH_3)_3CSP(CF_3)_2{}^{4} \end{array}\right\} < CH_3SPCH_3CF_3 < \left\{\begin{array}{l} CH_3OPCH_3CF_3 \\ (CH_3)_3CSPCH_3CF_3 \end{array}\right\} < (CH_3)_3COPCH_3CF_3$$

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

$$(CH_3)_3COP(CF_3)_2 + CH_3I \longrightarrow (CH_3)_3C(CF_3)_2PO + CH_3I^{3}$$

$$(CH_3)_3COPCH_3CF_3 + CH_3I \longrightarrow (CH_3)_2CF_3PO + (CH_3)_3CI$$

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 actually faster than the second, wherein the more basic oxygen does not exchange groups so easily, and the more basic phosphorus receives CH_3 slowly from CH_3I, in the classical Arbuzov manner.

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

$$RSPCH_3CF_3 + HCl \rightleftarrows CH_3CF_3PCl + RSH$$

(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

$$CH_3OPCH_3CF_3 + HCl \rightleftarrows CH_3CF_3PCl + CH_3OH$$

strongly favors the product, and a small side reaction forming CH_3Cl and the new compound CH_3CF_3HPO means that it is not much harder to cleave the C–O than the P–O bond. In the case of $(CH_3)_3COPCH_3CF_3$, however, the C–O bond cleavage is the main effect: high yields of CH_3CF_3HPO and $(CH_3)_3CCl$ are obtained. Here again the lability of the *t*-butyl group is governing.

The new phosphine oxide CH_3CF_3HPO proved to be far more stable than expected: it seems to lack the mechanism for a disproportionation in the manner of $2(CH_3)_2HPO$ going to $(CH_3)_2PH$ and $(CH_3)_2POOH$,[5] while a process like the rapid conversion of $(CF_3)_2HPO$ to $(CF_3)_2POH$ is energetically unfavorable in this case. Presumably the fair stability of $(C_6H_5)_2HPO$[6] has a similar cause.

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(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).

(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 CH_3CF_3HPS seems to be unstable in more than one way and could be recognized only in mixtures.

The new thiobisphosphine $(CH_3CF_3P)_2S$ decomposes very slowly at 25° to $(CH_3CF_3P)_2$ and a nonvolatile solid. It may well convert first to $CH_3CF_3(S)P$-PCH_3CF_3, from which group exchange would form $(CH_3CF_3P)_2$ and $(CH_3CF_3PS)_2$. A similar decomposition could account for our failures to make $(CH_3CF_3P)_2O$; all attempts led only to $(CH_3CF_3P)_2$ and nonvolatile 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}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°, 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 CH_3CF_3PCl was begun in our laboratories by Dr. John F. Nixon, but the reaction was far from complete and the desired new compound $CH_3OPCH_3CF_3$ 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°. The millimole stoichiometry of the reaction is shown as follows.

$$\begin{array}{lllll} CH_3CF_3PCl & + \; CH_3OH & + \; (CH_3)_3N & \longrightarrow CH_3OPCH_3CF_3 & + \text{ solids} \\ 1.677 & 1.693 & 1.683 & 1.598\ (95\%) & \ldots \end{array}$$

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 $CH_3OPCH_3CF_3$, 146.1). The volatility data in Table I are consistent with purity.

Table I. Volatility of $CH_3OPCH_3CF_3$
($\log P = 5.8501 + 1.75 \log T - 0.005T - 1908/T$)
($t_{760} = 60.6°$; Trouton constant = 20.7 eu)

t, °C	−40.65	−33.77	−25.75	0.00	10.15	11.85
P_{obsd}, mm	4.18	7.01	12.36	58.2	97.8	105.8
P_{calcd}, mm	4.19	7.01	12.29	57.9	97.8	106.2

The formula $CH_3OPCH_3CF_3$ 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 CH_3O group, since J_{H-P} for a $POCH_3$ bond often is larger than for a P–CH_3 pattern.[7] The ^{19}F spectrum was a doublet at 94.4 ppm (J = 68.9 cps) downfield of C_6F_6, without observable fine structure. The ^{31}P spectrum showed a quartet with J measured as 69.2 cps (assignable to P–CF_3 coupling) at 21.2 ppm upfield of $(CH_3O)_3P$; a complex fine structure was attributable to the two different methyl groups.

Cleavage by Hydrogen Chloride. A mixture of 0.529 mmol of $CH_3OPCH_3CF_3$ and 0.560 mmol of HCl was left for 11 hr at 25°, consuming 0.387 mmol of the HCl. After 3 hr at 110° the consumption of HCl had risen to 0.504 mmol and remained the same during a further 11 hr at 110°. At this point it was possible to isolate a 4.3% yield of the compound CH_3CF_3HPO (identified by comparison with the authentic product described later), and the accompanying trace of CH_3Cl also was recognized (by its infrared spectrum), showing that the process

$$CH_3OPCH_3CF_3 + HCl \longrightarrow CH_3Cl + CH_3CF_3HPO$$

did occur slightly.

The main mixture of CH_3OH, CH_3CF_3PCl, and residual $CH_3OPCH_3CF_3$ 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 cm^{-1}, and the characteristic peak for CH_3CF_3PCl at 1160 cm^{-1} could be seen, between the 1125–1140- and 1180–1190-cm^{-1} regions where peaks belonging to $CH_3OPCH_3CF_3$ would interfere. Thus it appeared that the major reaction

$$CH_3OPCH_3CF_3 + HCl \longrightarrow CH_3OH + CH_3CF_3PCl$$

was not quite complete at equilibrium.

The reversibility of this process was demonstrated by allowing the remixed components to stand at 25°, with stepwise removal of the HCl by fractional condensation through a U-trap at −130°. 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 $CH_3OPCH_3CF_3$ to CH_3CF_3HPO by HCl would be its reaction with CH_3I to make $(CH_3)_2CF_3PO$—a normal Arbuzov rearrangement which would be expected to occur far more easily than for $CH_3OP(CF_3)_2$.[3] In fact, equimolar mixtures of CH_3I and $CH_3OPCH_3CF_3$, heated in sealed tubes for 21–24 hr at 100–110°, showed 87–92% conversion, with only slight side reactions. The classical mechanism of this process was proved by using CD_3I.

$$CH_3OPCH_3CF_3 + CD_3I \longrightarrow CH_3CD_3CF_3PO + CH_3I$$

This experiment began with a mixture of 1.109 mmol of $CH_3OPCH_3CF_3$ and 1.125 mmol of CD_3I, 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 δ in ppm downfield from TMS, the initial mixture was found to have δ_1 3.48 (J = 13.3 cps) and δ_2 1.28 (J = 6.7 cps), both downfield of the original "neat" values. After 16 hr at 25°, a singlet at δ 1.97 indicated a small formation of CH_3I, and a peak at δ

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[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 $CH_3CD_3CF_3PO$; the higher field member would superpose upon the $CH_3OPCH_3CF_3$ peak at δ 1.28. During 5 hr at 63° the δ 1.97 and 1.62 peaks grew quite noticeably, maintaining the 2:1 area ratio expected for equal increase of the CH_3I singlet and the $CH_3CD_3CF_3PO$ doublet. However, as the concentration of the CH_3I increased, it could be expected to participate more and more in the Arbuzov process; indeed, we could calculate statistically that the final ratio of $CH_3CD_3CF_3PO$ to $(CH_3)_2CF_3PO$ would be 1.75, from the initial mixture of $CH_3OPCH_3CF_3$ and CD_3I here used. In fact, after 23 hr at 63°, the process was complete (disappearance of the two doublets for $CH_3OPCH_3CF_3$), and this 1.75 ratio was confirmed by a quantitative infrared analysis of the mixture of CH_3I and CD_3I. The proton nmr spectrum of the phosphine oxide was the expected doublet (δ 1.70 ppm; $J = 14.4$ cps), well separated from the methyl iodide singlet (δ 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 CH_2D or CHD_2 groups, and there was no nmr-detectable formation of CH_3I when a 10:1 mixture of CD_3I and $(CH_3)_2CF_3PO$ was heated for 4 days at 63°.

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 $(CH_3)_2CF_3POCH_3{}^+I^-$ or $CH_3CD_3CF_3POCH_3{}^+I^-$, which apparently would be very short-lived.

Characterization of the Phosphine Oxide. A highly purified sample of the phosphine oxide $(CH_3)_2CF_3PO$ was subjected to vapor-pressure equilibrium measurements. For the solid, the values were 1.17 mm at 46.9°, 2.33 mm at 54.8°, 3.94 mm at 61.1°, and 6.88 mm at 68.1°, 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°, 12.61 mm at 77.73°, 15.51 mm at 81.7°, and 19.74 mm at 86.6°, 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° and the Trouton constant as 21.6 eu. Taken with the solid, it implies that the melting point should be 71.7° (observed, sharp at 71.7°).

The vapor-phase molecular-weight determination gave the value 146.3 [calculated for $(CH_3)_2CF_3PO$, 146.1]. In the basic hydrolysis (48.5-mg sample; 10% NaOH; sealed tube), bubbles appeared at 25°, but completion was assured by a 17-hr heating at 95°. The resulting HCF_3 was measured as 0.331 mmol (calculated, 0.332 mmol). Since the phosphine oxide was the virtually quantitative rearrangement product of $CH_3OPCH_3CF_3$, these results serve as further confirmation of its molecular formula.

The proton nmr spectrum of $(CH_3)_2CF_3PO$ (0.679 mmol of sample in 4.94 mmol of CH_3I) showed δ 0.39 ppm upfield of CH_3I, with $J = 14.1$ cps, as before. The quartet fine structure gave $J_{HCPCF} = 0.83$ cps. The ^{19}F spectrum showed δ 76.3 ppm upfield of Cl_3CF, with $J_{FCP} = 84.3$ cps and the septet fine structure showing $J_{FCPCH} = 0.78$ cps, close to the proton-spectrum value.

Boron Fluoride Adducts. The compound $CH_3OPCH_3CF_3$ 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 $CH_3OPCH_3CF_3$ and 0.787 mmol of BF_3, left for 10 hr at −78°, delivered only 0.472 mmol of BF_3 on pumping at −78°; thus the glassy residue contained 1.11 BF_3 per $CH_3OPCH_3CF_3$. However, after remixing and removal of excess BF_3 at −120°, the residue showed 1.96 BF_3 per $CH_3OPCH_3CF_3$. This residue was subjected to high-vacuum fractional condensation through a trap at −120°, wherein the condensate contained 1.19 BF_3 per $CH_3OPCH_3CF_3$. 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°. 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 BF_3.

The Fluorophosphine. The BF_3-adduct experiments gave slight yields (as high as 2%) of the new compound CH_3CF_3PF. It would be tempting to suppose that it came from a fluoride shift like that by which $CH_3OAs(CF_3)_2 \cdot BF_3$ forms $(CF_3)_2AsF$,[8] but the very small yields would suggest that the real source was an impurity. Such an impurity would not be CH_3CF_3PCl, which failed to react with BF_3 under a wide range of conditions.

The fluorophosphine was identified by comparison with a larger sample, made from 1.9 mmol of CH_3CF_3PCl with 1.2 g of ZnF_2 in a sealed tube (5 days, 25°). The yield was 0.56 mmol, or 30%. The volatility of the product was close to 1 mm at −78°. Its proton nmr spectrum left no doubt of its identity: the observed doublet of doublets (δ 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 CF_3 was not seen.

The *t*-Butoxyphosphine

Synthesis. The trimethylamine method was applied also to the reaction of *t*-butyl alcohol with CH_3CF_3PCl. The three components were condensed from the high-vacuum line into a stopcocked tube at −196° and allowed to warm slowly from −30°. The desired product was purified by high-vacuum fractional condensation, leading to the following millimole stoichiometry of two experiments.

$$\begin{array}{ccccccc} CH_3CF_3PCl & + & (CH_3)_3COH & + & (CH_3)_3N & \longrightarrow & (CH_3)_3COPCH_3CF_3 \\ 0.372 & & 0.367 & & 0.818 & & 0.365\ (99.5\%) \\ & & & & \underline{-0.422} & & \\ & & & & 0.396 & & \\ 1.036 & & 0.998 & & 2.980 & & 0.986\ (99\%) \\ \underline{-0.031} & & & & \underline{-1.973} & & \\ 1.005 & & & & 1.007 & & \\ & & & & & & +\ \text{solids} \end{array}$$

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

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[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$_3$ doublet at δ 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$_3$ group; $J_{HCPCF} = 0.64$ cps. Then within the P–CH$_3$ doublet was another doublet centered at δ 1.10 ppm downfield of TMS, obviously due to the *t*-butyl group; $J_{HCCOP} = 0.59$ cps. The ^{19}F spectrum showed δ 92.8 ppm upfield of Cl$_3$CF, with $J_{FCP} = 74.0$ cps. In sum, then, the nmr spectra fully confirmed the expected molecular structure.

The equilibrium vapor-pressure values for $(CH_3)_3COPCH_3CF_3$, shown in Table II, indicated a pure sample.

Table II. Volatility of $(CH_3)_3COPCH_3CF_3$
(Log $P = 7.1119 + 1.75 \log T - 0.0065T - 2414/T$)
($t_{760} = 113.2°$; Trouton constant = 20.6 eu)

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

The Arbuzov Reaction. In the main experiment on the reaction of $(CH_3)_3COPCH_3CF_3$ with CH$_3$I, the latter was employed in deficient proportion, on the assumption that it would be catalytic as in the case of $(CH_3)_3COP(CF_3)_2$.[3] Actually, the proton nmr spectra of $(CH_3)_2CF_3PO$ and $(CH_3)_3CI$ appeared early and then grew large during 3 days at 62°. The main process now could be described (with millimole coefficients) as follows.

$$0.472(CH_3)_3COPCH_3CF_3 + 0.388CH_3I \longrightarrow 0.368(CH_3)_2CF_3PO + 0.203(CH_3)_3CI + 0.242(\text{unknown}) + \text{nonvolatiles}$$

The product $(CH_3)_2CF_3PO$ 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$_3$I. The unused CH$_3$I could not be isolated from the 0.242-mmol "unknown" fraction, the infrared spectrum of which showed CF$_3$ groups and hydrocarbon features accounting for most of the missing *t*-butyl groups. It is apparent that CH$_3$I attacked $(CH_3)_3COPCH_3CF_3$ in the classical Arbuzov manner, whereas $(CH_3)_3CI$ was not at all effective; in fact, we could not find any fraction corresponding to the expected product $(CH_3)_3CCH_3CF_3PO$, even with the aid of the mass spectrograph.

Methyltrifluoromethylphosphine Oxide

Synthesis. The initial attempts to make $(CH_3)_3COPCH_3CF_3$ from $(CH_3)_3COH$ and CH$_3$CF$_3$PCl (without the amine) produced instead the interesting new compound CH$_3$CF$_3$HPO. The process could not easily be monitored by the very complex proton nmr spectrum, but probably occurred in two main steps

$$(CH_3)_3COH + CH_3CF_3PCl \longrightarrow (CH_3)_3COPCH_3CF_3 + HCl \longrightarrow CH_3CF_3HPO + (CH_3)_3CCl$$

The second step obviously is a classical Arbuzov-type reaction with the proton playing the role of a hydrocarbon group. In two of the three experiments, using CH$_3$CF$_3$PCl in slight excess over the *t*-butyl alcohol (0.5 or 4 days, at 25°), the yield of pure CH$_3$CF$_3$HPO corresponded to at least 95% of the *t*-butyl alcohol; then the slight excess of CH$_3$CF$_3$PCl was an impurity in the $(CH_3)_3CCl$. 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.

$$\underset{0.301}{(CH_3)_3COPCH_3CF_3} + \underset{\begin{array}{r}0.408\\ -0.093\\ \hline 0.315\end{array}}{DCl} \longrightarrow$$

$$\underset{0.276}{CH_3CF_3DPO} + \underset{0.297}{(CH_3)_3CCl} + \underset{(1.1\text{ mg})}{\text{nonvolatiles}}$$

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^{-1}, 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$_3$CF$_3$HPO was −9.3 to −9.0°; of CH$_3$CF$_3$DPO, −10.0 to −9.7°. The molecular weight of CH$_3$CF$_3$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$_3$CF$_3$PH, identified by its infrared spectrum.

The proton nmr spectrum of CH$_3$CF$_3$HPO showed δ 1.43 ppm downfield of TMS ($J = 15.7$ cps; no fine structure seen) for the CH$_3$ group. The H–P proton showed as a doublet centered at δ 6.87 ppm downfield of TMS ($J = 516$ cps), with each member interpretable as an overlapped quartet of quartets ($J_{HPCF} = 5.4$ and $J_{HPCH} = 3.4$ cps). For ^{19}F, $\delta = 97$ ppm upfield of Cl$_3$CF ($J = 91$ cps); no fine structure could be seen.

Alkanethiophosphines

Synthesis. Unlike the thiolysis of $(CF_3)_2PCl$,[4,9] or the just-described alcoholyses of CH$_3$CF$_3$PCl, the reaction

$$CH_3CF_3PCl + CH_3SH \rightleftarrows CH_3SPCH_3CF_3 + HCl$$

equilibrates in favor of the products; K was measured roughly as 5. Accordingly, a mixture of 0.812 mmol of CH$_3$CF$_3$PCl and 0.958 mmol of CH$_3$SH, in a 60-ml tube on the vacuum line at 25°, gave 0.780 mmol (96% yield) of CH$_3$SPCH$_3$CF$_3$ as a result of removing both products at three stages. The alternative amine method

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

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

$$\underset{1.312}{\mathrm{CH_3CF_3PCl}} + \underset{1.340}{\mathrm{CH_3SH}} + \underset{1.387}{\mathrm{(CH_3)_3N}} \longrightarrow \underset{1.135\ (87\%)}{\mathrm{CH_3SPCH_3CF_3}} + \underset{.....}{\mathrm{(CH_3)_3NHCl}}$$

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° 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°.

The initial synthesis of $(CH_3)_3CSPCH_3CF_3$ employed 0.805 mmol of $(CH_3)_3CSH$, 0.965 mmol of CH_3CF_3PCl, and 3.742 mmol of $(CH_3)_3N$ (slowly warmed from −78 to 25°, and held there for 2 hr), giving only 0.485 mmol of $(CH_3)_3CSPCH_3CF_3$ 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°) for which the reaction balance (millimoles) was

$$\underset{0.532}{\mathrm{(CH_3)_3CSH}} + \underset{0.546}{\mathrm{CH_3CF_3PCl}} + \underset{0.546}{\mathrm{(CH_3)_3N}} \longrightarrow \underset{0.518\ (97.6\%)}{\mathrm{(CH_3)_3CSPCH_3CF_3}} + \underset{.....}{\mathrm{(CH_3)_3NHCl}}$$

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

Formulas and Physical Properties. The formula $CH_3SPCH_3CF_3$ was confirmed by the vapor-phase molecular weight (163.1 *vs.* calcd 162.1) and basic hydrolysis to give the expected amount of HCF_3. The substance formed a glass at low temperatures, so that its melting point could not be observed. For $(CH_3)_3CSPCH_3CF_3$, the molecular weight was determined as 205.3 (calculated, 204.1); the compound melted sharply near −30°. The equilibrium vapor pressure values for the mercaptophosphines are shown in Tables III and IV.

Table III. Volatility of $CH_3SPCH_3CF_3$
(Log $P = 6.0865 + 1.75 \log T - 0.005T - 2214/T$)
($t_{760} = 107.3°$; Trouton constant = 21.4 eu)

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

Table IV. Volatility of $(CH_3)_3CSPCH_3CF_3$
(Log $P = 5.6743 + 1.75 \log T - 0.004T - 2420/T$)
($t_{760} = 152°$; Trouton constant = 21.8 eu)

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

Nmr Spectra. The proton nmr spectrum of $(CH_3)_3CSPCH_3CF_3$ was recorded by the A-60 instrument at maxium scale-expansion showing δ 1.19 ppm downfield of TMS (by substitution) for the *t*-butyl group (J_{HCCP} = 0.92 cps). The PCH_3 protons appeared as a doublet of quartets with total area one-third that of *t*-butyl; δ 1.21; J_{HCP} = 7.67 cps; J_{HCPCF} = 0.38 cps. By analogy, the PCH_3 protons of $CH_3SPCH_3CF_3$ belong to the doublet at δ 1.32 (J_{HCP} = 7.1 cps), leaving to the mercapto group the doublet at δ 2.11 ppm, with J_{HCSP} = 12.6 cps. By this fairly reasonable assignment, it seems that the sulfur linkage increases the coupling, just as oxygen often does.[7]

The ^{19}F spectra (measured upfield from Cl_3CF, by substitution) showed for $CH_3SPCH_3CF_3$ δ 62.0 ppm and J_{FCP} = 64 cps, and for $(CH_3)_3CSPCH_3CF_3$ δ 21.1 ppm and J_{FCP} = 65 cps. The ^{31}P spectrum of $CH_3SPCH_3CF_3$ showed δ 113 ppm upfield of $P(OCH_3)_3$. It was too complex and poorly resolved for a recheck of J_{PCF}.

The Arbuzov Reactions. The conversion of $CH_3SPCH_3CF_3$ to $(CH_3)_2CF_3PS$ by methyl iodide was insignificant during 35 hr at 63°, 8 hr at 105°, or 18 hr under ultraviolet irradiation at 25°; but nearly 35% conversion occurred during 6 months at 25°. An unknown side reaction consumed an equal amount of the original $CH_3SPCH_3CF_3$.

For the identification of the product $(CH_3)_2CF_3PS$, this compound was made also by direct addition of sulfur (70.8 mg) to $(CH_3)_2CF_3P$ (0.193 mmol), first only during 2.5 hr at 100° (for a 22% yield), and then during 7 hr at 150° to bring the yield to 0.190 mmol, or 98.5%. The second experiment (4 hr at 150°) employed 86.3 mg of sulfur and 1.150 mmol of $(CH_3)_2CF_3P$, giving a 94.7% yield of $(CH_3)_2CF_3PS$. The product melted in the range 49.9–50.0° after purification by high-vacuum fractional condensation at −50°.

The molecular weight of $(CH_3)_2CF_3PS$ was determined at 81° (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 $(CH_3)_2CF_3PS$

Solid: $\log P = 11.9842 - 3551/T$

t, °C	27.05	32.30	37.28	42.60	47.23
P_{obsd}, mm	1.43	2.23	3.51	5.47	7.95
P_{calcd}, mm	1.43	2.28	3.51	5.47	7.95

Liquid: $\log P = 6.8204 + 1.75 \log T - 0.005T - 2783/T$
($t_{760} = 163°$; Trouton constant = 22.7 eu; mp 49.2°)

t, °C	49.90	55.00	60.15	65.45	71.05	83.50
P_{obsd}, mm	9.63	12.67	16.52	21.74	28.53	50.20
P_{calcd}, mm	9.59	12.65	16.56	21.64	28.42	50.18

The formula $(CH_3)_2CF_3PS$ was confirmed by basic hydrolysis (10% NaOH, 5 hr, 100°) giving a 99.1% yield of HCF_3, and by a quantitative abstraction of sulfur (30 days, 135°).

$$\begin{array}{lcccccc} & \mathrm{(CH_3)_2CF_3PS} & + & \mathrm{(CH_3)_3P} \longrightarrow & \mathrm{(CH_3)_2CF_3P} & + & \mathrm{(CH_3)_3PS} \\ \text{mmol:} & 0.149 & & 0.149 & 0.148 & & 0.147 \\ & \underline{-0.001} & & & & & \\ & 0.148 & & & & & \end{array}$$

The product $(CH_3)_2CF_3P$ was identified by its molecular weight (129.6 *vs.* calcd 130.1), volatility, and infrared spectrum. The product $(CH_3)_3PS$ was identified by its melting point (155.5–155.7°), proton nmr spectrum, and infrared spectrum.[10]

The compound $(CH_3)_2CF_3PS$, unlike $(CH_3)_3PS$, failed to form any adduct with CH_3I (6 hr, 25°). Also, like its precursor $CH_3SPCH_3CF_3$, it failed to form a BF_3 adduct. Its nmr spectra in CS_2 solution showed protons at δ 1.86 ppm downfield of TMS (J = 14.3 cps)

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

and ^{19}F at 104.7 ppm upfield of Cl_3CF (J = 85.5 cps). The fine structure of these doublets was not observed.

The classical Arbuzov reaction

$$\mathrm{(CH_3)_3CSPCH_3CF_3 + CH_3I \longrightarrow (CH_3)_2CF_3PS + (CH_3)_3CI}$$

was observed by means of the proton nmr spectrum, showing less intensity for CH_3I as the $(CH_3)_3CI$ singlet and the $(CH_3)_2CF_3PS$ doublet of quartets appeared and increased. The extent of reaction was about 6% after 31 hr at 63°, 30% after a further 6 hr at 100°, and not more than 60% after 23 hr at 103°. Significant amounts of nonvolatile by-products now had appeared.

Hydrogen Chloride Cleavages. The cleavage of $CH_3SPCH_3CF_3$ by HCl (3.3 volumes) to form CH_3SH and CH_3CF_3PCl (reversing the original synthesis) was about 70% complete after 10 hr at 25°.

The compound $(CH_3)_3CSPCH_3CF_3$ with a small excess of HCl reacted during 19 hr at 25° to a limited extent which did not increase appreciably during 13 hr at 100°. The products $(CH_3)_3CSH$ and CH_3CF_3PCl passed a U-trap at −65° and condensed at −130° (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

$$\mathrm{(CH_3)_3CSPCH_3CF_3 + HCl \rightleftarrows (CH_3)_3CSH + CH_3CF_3PCl}$$

and no appreciable side reactions. Apparently the reverse process could be used efficiently for making $(CH_3)_3CSPCH_3CF_3$, without the use of an amine to remove HCl.

Of special interest here was the absence of any trace of CH_3CF_3HPS from either cleavage; there was no analogy to the formation of CH_3CF_3HPO from HCl and $(CH_3)_3COPCH_3CF_3$. However, it was possible to obtain evidence for the existence of CH_3CF_3HPS in relation to the study of $(CH_3CF_3P)_2S$, next described.

Thiobis(methyltrifluoromethylphosphine)

Synthesis and Characterization. The formation of the thiobisphosphine $(CH_3CF_3P)_2S$ in two experiments is described (with respective millimole quantities) as follows.

$$\begin{array}{cccccc}
\mathrm{2CH_3CF_3PCl} & + \ \mathrm{H_2S} & + \ \mathrm{2(CH_3)_3N} & \longrightarrow & \mathrm{(CH_3CF_3P)_2S} & + \ \mathrm{2(CH_3)_3NHCl} \\
1.032 & 0.511 & 1.022 & & 0.506 & \ldots \\
0.878 & 0.435 & 0.868 & & 0.427 & \ldots
\end{array}$$

In both experiments, the components were warmed very slowly from −78 to 25°. 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 $(CH_3CF_3P)_2$. This thermal decomposition could be observed during months of storage at 25°. A pure sample, heated at 100° for 34 hr, was 5% decomposed to form a nonvolatile solid presumed to be the diphosphine disulfide $(CH_3CF_3PS)_2$, and the corresponding formation of $(CH_3CF_3P)_2$ 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 $(CH_3CF_3P)_2S$, which was further confirmed by the molecular weight (263.2 *vs.* calcd 262.1) and hydrolysis by 10% NaOH to give a 98% yield of HCF_3 (after 22.5 hr at 120°). Yet further proof of the formula came from the process (with millimole quantities)

$$\begin{array}{ccccccc}
\mathrm{(CH_3CF_3P)_2S} & + & \mathrm{(CH_3)_3P} & \longrightarrow & \mathrm{(CH_3CF_3P)_2} & + & \mathrm{(CH_3)_3PS} \\
0.319 & & 0.431 & & 0.318 & & 0.321 \\
 & & \underline{-0.108} & & & & \\
 & & 0.323 & & & &
\end{array}$$

which was completed during 19.5 hr at 82°. The resulting $(CH_3CF_3P)_2$ was identified by its infrared spectrum, volatility (4.0 mm at 0°),[2] and molecular weight (231 *vs.* calcd 230), and the $(CH_3)_3PS$ by its melting point, infrared spectrum, and proton nmr spectrum, as before.

Although such experiments established the purity of the product $(CH_3CF_3P)_2S$ 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° began to melt between −45.7 and −42.7° and was all melted at −33°, but the same sample, after 1 hr at −45°, melted in the range −33.6 to −27.5°. The digestion at −45° 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 $(CH_3CF_3P)_2S$ was normal, as indicated by the data of Table VI.

Table VI. Volatility of $(CH_3CF_3P)_2S$
($\log P = 7.8113 + 1.75 \log T - 0.0065T - 2888/T$)
(t_{760} = 154.3°; Trouton constant = 21.7 eu)

t, °C	43.17	48.30	55.47	62.30	68.65
P_{obsd}, mm	10.01	13.32	19.58	27.63	37.52
P_{calcd}, mm	10.01	13.34	19.55	27.63	37.52

Cleavage by Methyl Iodide. The Arbuzov-like reaction

$$\mathrm{(CH_3CF_3P)_2S + CH_3I \longrightarrow (CH_3)_2CF_3PS + CH_3CF_3PI}$$

was investigated by heating the reactants (0.213 mmol of each) in a sealed tube. There was no change during 4 hr at 50°, but after 30 hr at 100°, 0.103 mmol of CH_3I 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 CH_3CF_3PI. Allowing for the impurities, this would represent all of the consumed CH_3I. The other product, $(CH_3)_2CF_3PS$, could not be isolated from the unused $(CH_3CF_3P)_2S$, but the latter could be destroyed by heating with CH_3I in large excess (3 hr, 153°), forming mostly a black tar, but permitting the isolation of 5.3 mg (0.033 mmol) of $(CH_3)_2CF_3PS$. This was clearly identified by its infrared spectrum.

The Quest for Methyltrifluoromethylphosphine Sulfide. Our attempts to isolate the phosphine sulfide CH_3CF_3-

Table VII. Comparison of Infrared Spectra

Suggested Assignment	CH_3CF_3PF	$CH_3OP{}^{CH_3}_{CF_3}$	$(CH_3)_3COP{}^{CH_3}_{CF_3}$	$CH_3SP{}^{CH_3}_{CF_3}$	$(CH_3)_3CSP{}^{CH_3}_{CF_3}$	$(CH_3CF_3P)_2S$	${}^{H}_{O}P{}^{CH_3}_{CF_3}$	${}^{D}_{O}P{}^{CH_3}_{CF_3}$	$(CH_3)_2P{}^{CF_3}_{O}$	$(CH_3)_2P{}^{CF_3}_{S}$
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) R 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_3 asymm. 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)	1476 (1.0) 1425 (1.7) 1398 (2.2)	1436 } (1.8) 1429 }	1478 (1.4) 1463 (2.0) 1429 (1.5) 1397 (0.6)	1426 (3.2)	1420 (0.69) 1381 (0.35)	1411 (1.2)	1432 (1.6) 1378 (0.44)	sh 1434 (0.9) sh 1429 (1.6) sh 1424 (1.5) 1420 (1.7) sh 1410 (1.0)
CH_3 symm. deformation (or P=O stretching)	1298 (0.9)	1371 (0.16) 1299 } (0.7) 1295 } sh 1277 } (0.3) sh 1268 }	1375 (6.5) 1292 (1.0) 1252 (3.0)	R 1331 (0.7) Q 1326 (0.8) P 1322 (0.7) R 1302 (0.4) Q 1299 (0.5) P 1294 (0.4)	1371 (3.8) 1300 (0.6) ?1222 (0.5)	1298 (1.1) 1275 (0.4)	1313 } (9.4) 1308 } 1284 (9.2) 1279 (9.7)	1312 } (6.1) 1308 } 1278 (6.6)	R 1322 (3.6) Q 1316 (7.6) P 1309 (4.5) R 1280 (4.7) Q 1273 (8.1) P 1266 (4.7)	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) 1134 (44)	1187 (26) 1128 (98)	1175 (18) 1143 (20) 1125 } (25) 1120 }	1176 (25) 1141 (26) 1119 } (38) 1116 }	1174 (38) 1144 (41) 1125 (67)	sh 1217 (14) 1211 } (22) 1205 } 1172 (25) 1153 } (28) 1147 }	sh 1215 (11) 1209 } (17) 1204 } 1172 (18) 1146 (21)	R 1218 (7.1) Q 1213 (11.1) P 1208 (9.3) 1162 (11) 1133 (11)	1207 (20) 1168 (17) 1131 (16)
C-O stretching	. . . . .	1057 (9.1) 1051 (8.1)	954 (27)	. . . . .	. . . . .	. . . .	. . . . .	. . . .	. . . .	. . . .
CH_3 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) 875 (8.4)	965 (0.4) 901 (2.2) 885 (2.8)	901 (2.8) 887 (4.2)	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) 906 (2.1)	R 935 (2.8) Q 928 (3.7) P 923 (2.9) 907 (2.9)	954 (9.4) sh 924 (8.8) 921 (9.8)
P-F stretching	808 (8)	. . . . .	. . . .	. . . . .	. . . .	. . . .	. . . . .	R 891 (2.4) Q 883 (3.3) P 880 (1.8)	sh 901 (2.3) 875 (4.9)	
CH_3 wagging ?	. . . . .	. . . . .	811 (1.5)	. . . . .	. . . .	. . . .	856 (1.6)		869 (7.2)	860 (2.3) 852 (2.7)
CF_3 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)	819 (6.6) 798 (1.9)	819 (2.3) 778 (2.9)	836 (0.7) 749 (1.5)	761 (8.1) (mainly P=S)
$P-CH_3$ 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)	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)	R 622 (3.9) Q 616 (5.8) P 610 (3.7)
CF_3 asymm. 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)	. . . . .	. . . . .		
$P-CF_3$ 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	R 447 (5.1) Q 441 (8.0) P 435 (5.0)	R 415 (2.0) Q 409 (2.8) P 402 (1.6)
CF_3 rocking or CH_3 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_2S reaction of CH_3CF_3PCl, with or without trimethylamine, and the cleavage of $(CH_3CF_3P)_2S$ by H_2S. In no case could we separate the desired compound from the similarly volatile $(CH_3CF_3P)_2S$, but the proton and ^{19}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_3CF_3PCl and 1.807 mmol of H_2S, 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_2S); now $(CH_3CF_3P)_2S$ was clearly recognized as a major product, both by its characteristic infrared peaks and by its complex proton and ^{19}F nmr spectra. Another product, having nearly the same total intensity of proton nmr absorption, and not separable by distillation methods, showed proton and ^{19}F nmr spectra strictly consistent with CH_3CF_3HPS. For CH_3, there was a doublet of doublets centered at δ 2.08 ppm downfield of TMS, with $J_{HCP} = 15.5$ and $J_{HCPH} = 4.9$ cps; and for H–P there was a complex doublet centered at δ 7.39 ppm, with $J_{HP} = 487$ cps and total intensity one-third that for CH_3. The ^{19}F spectrum was a doublet of doublets centered at 72.3 ppm upfield of Cl_3CF, with $J_{FCP} = 93.9$ and $J_{FCPH} = 4.7$ cps.

A second approach employed CH_3CF_3PCl and H_2S, with $(CH_3)_3N$ 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_3CF_3HPS and $(CH_3CF_3P)_2S$. However, a trace of CH_3CF_3PH (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.

$$2CH_3CF_3HPS \longrightarrow CH_3CF_3PH + CH_3CF_3PS_2H$$

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_3CF_3HPS, with a much smaller proportion of $(CH_3CF_3P)_2S$; 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_3CF_3PSH exists in a rapidly established equilibrium with CH_3CF_3HPS, and would be volatile enough for slow delivery through the −78° column under high vacuum. Then upon warming to 25°, reversal would occur.

$$2CH_3CF_3PSH \xrightarrow{\text{fast}} 2CH_3CF_3HPS \overset{\text{slow}}{\rightleftharpoons} (CH_3CF_3P)_2S + H_2S$$

In a third approach, the cleavage of $(CH_3CF_3P)_2S$ by H_2S was attempted in a sealed tube at 100° (20 hr). The 0.203-mmol sample of the thiobisphosphine consumed 0.204 mmol of H_2S (from the 2.249-mmol sample), but the chief volatile product was 0.167 mmol of CH_3CF_3PH (mol wt 117.8 *vs.* calcd 116; confirmed by the infrared spectrum). It would have formed by the disproportionation of CH_3CF_3HPS, yielding an equal amount of $CH_3CF_3PS_2H$, but this hypothetical compound could not be isolated from a fraction containing $(CH_3CF_3P)_2S$ (infrared-identified). On standing at 25°, this fraction slowly formed a nonvolatile solid, while evolving traces of H_2S and CH_3CF_3PH (0.009 and 0.012 mmol, respectively).

In sum, then, it is clear that the phosphine sulfide CH_3CF_3HPS exists well enough but equilibrates fairly soon with H_2S and $(CH_3CF_3P)_2S$, and a very small component may be CH_3CF_3PSH. More slowly, its disproportionation yields CH_3CF_3PH and probably more than one other product.

Infrared Spectra

The vapor-phase infrared spectra of ten new CH_3CF_3P compounds were recorded by means of the Beckman IR7 instrument, calibrated to 1 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 (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, P═O stretching and CH_3 symmetric deformation occur at similar frequencies, and some of the strong peaks in the C—F stretching region may be 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 CH_3CF_3PF, the 808-cm^{-1} band (5 cm^{-1} wide at the peak) could represent coupling of P–F stretching with CH_3 rocking, leaving exact assignments uncertain in this region. Very weak peaks at 2355, 2295, 2255, 1996, 1880, and 1605 cm^{-1} represent overtones and combinations.

For $CH_3OPCH_3CF_3$, combinations and overtones were seen at 2322 (0.2), 2247 (0.2), 2095 (0.1), 1800 (0.2), and probably 577 (0.09) cm^{-1}. For $(CH_3)_3COPCH_3CF_3$, combinations appeared at 1765 (0.2) and 1637 (0.4) cm^{-1}, and a peak at 489 (0.2) cm^{-1} was not assigned. Similarly, $(CH_3)_3CSPCH_3CF_3$ showed peaks at 575 (0.8) and 460 (0.14) cm^{-1}, omitted from Table VII for lack of assignment.

The recorded spectrum for $(CH_3CF_3P)_2S$ 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 $(CH_3)_2CF_3PO$, an overtone at 2352 (0.05) and a combination at 1995 (0.15) cm^{-1} were observed.

Mass Spectra

The mass spectra of $(CH_3)_2CF_3PO$, $(CH_3)_3COPCH_3CF_3$, and CH_3CF_3HPO were recorded in detail, with fluorocarbon calibration of the M-66 instrument. The full record is to be found in the original dissertation.[1]

Miscellaneous Nmr Spectra

Beyond the nmr spectra already listed for seven compounds, the results shown in Table VIII also were recorded. The δ values were measured in ppm, for protons downfield from TMS, for F, upfield from Cl_3CF, and for P, upfield from $P(OCH_3)_3$.

Table VIII. Nmr Comparison of Chloro and Iodo Phosphines

	CH_3CF_3PCl		CH_3CF_3PI	
	δ	J	δ	J
^1H	1.44	10.4 HCP	2.28	11.2 HCP
		0.51 HCPCF		0.36 HCPCF
^{19}F	112	. . .	144	60.4 FCP
^{31}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}P–^{31}P coupling constant were obtained in 13 complexes of the type *cis-* and *trans-*$(OC)_4ML_2$ (where M = Cr, Mo, or W), *trans-*$(OC)_3FeL_2$, and *cis-* and *trans-*PdL_2X_2 (where X = Cl or I) in which L = $P(CH_3)_3$, $P[N(CH_3)_2]_3$, or $P(OCH_3)_3$. The signs and magnitudes of $\delta(^{31}P)$, $\delta(^{13}C)$, $^3J_{PH}$, $^5J_{PH}$, $^2J_{PC}$, $^4J_{PC}$, and $^1J_{CH}$ and their relationship to the ^{31}P–^{31}P couplings ($^2J_{PP}$) are presented and discussed. The *cis* zerovalent group VI complexes have negative $^2J_{PP}$ values in all cases. The rest of the complexes possess positive $^2J_{PP}$ 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. D_{4h} and 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-*$(OC)_4Mo[P(CH_3)_3]_2$ is a function of the electron distribution among these atoms and therefore such couplings ($^2J_{PP}$) should reflect some aspects of the nature of phosphorus–metal bonding. Since our original reports[2] on estimating values of $^2J_{PP}$ from

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