

## Some Reactions of Bis(trifluoromethyl)phosphines, -phosphine Oxides, and -phosphine Sulfides with Alcohols and Mercaptans. Preparation, Characterization, and NMR Spectra of a Homologous Series of Esters and Thioesters

RONALD G. CAVELL,\* A. ALAN PINKERTON, WILLIAM SIM, and ADRIAN J. TOMLINSON

Received March 16, 1979

The esters  $(CF_3)_2POR$  and thioesters  $(CF_3)_2PSR$  ( $R = CH_3, C_2H_5, CH(CH_3)_2,$  and  $C(CH_3)_3$ ) of trivalent phosphorus have been synthesized. Previously unknown esters in the series have been characterized and NMR parameters of all the above esters recorded. Synthesis of phosphinous esters and thioesters is aided by the presence of amine which is mandatory in the case of the reaction of *tert*-butyl alcohol with  $(CF_3)_2PCl$ . In the absence of amine,  $(CF_3)_2PCl$  reacted with *tert*-butyl alcohol to give  $(CF_3)_2P(O)C(CH_3)_3$  and HCl. Separate reactions showed that  $(CF_3)_2POC(CH_3)_3$  reacted with HCl to yield  $(CF_3)_2POH$  and  $(CH_3)_3CCl$  and that  $(CF_3)_2POH$  and  $(CH_3)_3CCl$  reacted to form  $(CF_3)_2P(O)C(CH_3)_3$  and HCl. These reactions provide a basis for the detailed understanding of the reaction of  $(CF_3)_2PCl$  and related systems with *tert*-butyl alcohol. The oxy- and thioesters of pentavalent phosphorus,  $(CF_3)_2P(O)OR$ ,  $(CF_3)_2P(O)SR$ ,  $(CF_3)_2P(S)OR$ , and  $(CF_3)_2P(S)SR$  ( $R = CH_3, C_2H_5, CH(CH_3)_2$ ), were prepared by reactions analogous to those used to prepare the phosphinous esters; however, the competitive reaction of salt formation with amines in the case of the *tert*-butyl and, to a lesser extent, methyl esters requires use of alternate synthetic routes. In the case of *tert*-butyl esters, isobutene was also obtained in addition to the amine salt due to the instability of the *tert*-butylammonium salt. The *tert*-butyl thioester  $(CF_3)_2P(S)SC(CH_3)_3$  was obtained from *tert*-butyl iodide and the appropriate phosphorus acid salt,  $(CF_3)_2PS_2^-$ . In contrast the dioxo and oxythioesters could not be prepared in this way. NMR parameters are recorded for all esters of pentavalent phosphorus and the new esters of pentavalent phosphorus have been characterized. Separate reaction of the esters of pentavalent phosphorus with trimethylamine gave  $R'(CH_3)_3N^+(CF_3)_2PXY^-$  ( $X, Y = O, S$ ) salts. In the case of esters of trivalent phosphorus, only  $(CF_3)_2POCH_3$  formed a 1:1 adduct with trimethylamine which may be the salt  $(CH_3)_4N^+(CF_3)_2PO^-$ . NMR parameters of the *tert*-butylphosphine oxide  $(CF_3)_2P(O)C_4H_9$  are also given.

### Introduction

A number of homologous oxyesters and thioesters of trivalent and pentavalent bis(trifluoromethyl)phosphorus acids were required in our continuing study of (trifluoromethyl)-phosphorus chemistry. The extension of previously utilized synthetic procedures to analogous systems illustrates subtle variations in the behavior of different members of a homologous series.

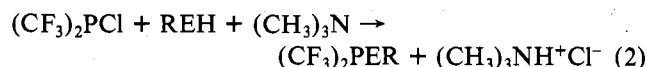
### Results and Discussion

(A) **Esters of Bis(trifluoromethyl)phosphinous and -thio-phosphinous Acids.** The reaction of an alcohol with bis(trifluoromethyl)chlorophosphine follows, in general, eq 1.



Ethanol,<sup>1</sup> methanol,<sup>2</sup> and now 2-propanol react smoothly and cleanly to give good yields of the phosphinous ester. The new compounds have been characterized. NMR data are given in Table I and IR data in Table II.

While the lower mercaptans react similarly,<sup>3-5</sup> the reactions are slow even at moderately elevated temperatures<sup>3,4</sup> and only partial conversion occurs. The methyl thioesters are not readily cleaved by hydrogen halides, so the incomplete conversion does not seem to be due to the existence of an equilibrium.<sup>4</sup> Yields of the thioester are greatly improved (and separation problems reduced) by the addition of an equimolar quantity of tertiary amine.<sup>3,4</sup> The general reaction described by eq 2, previously

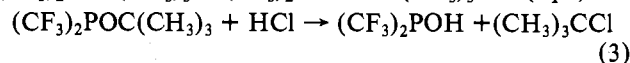


used to prepare methyl thio-<sup>3,4</sup> and *tert*-butyl thioesters, has now been successfully extended to the preparation of new isopropyl and ethyl thioesters. Methoxy- and *tert*-butoxy-phosphinous esters have also been prepared in good yield according to eq 2. The results are summarized in Tables III and IV. NMR data are given in Table I and IR data in Table II.

In contrast to the  $C_1$ - $C_3$  alcohols, the reaction of  $(CF_3)_2PCl$  with only *tert*-butyl alcohol at 70 °C does not follow eq 1. The products are  $(CF_3)_2POH$  and  $(CF_3)_2P(O)C(CH_3)_3$  (in an

approximate 1:1 molar ratio),  $(CH_3)_3CCl$ , and HCl. The desired *tert*-butylphosphinous ester can be made either by the reaction described by eq 2 or by the reaction of  $(CF_3)_4P_2$  and *tert*-butyl alcohol,<sup>2</sup> and comparison of properties clearly indicates that the product of the reaction of  $(CF_3)_2PCl$  with only *tert*-butyl alcohol is  $(CF_3)_2P(O)C_4H_9$ , the *tert*-butylphosphine oxide isomer. It is interesting to note that the equimolar mixture of  $(CF_3)_2POH$  and  $(CF_3)_2P(O)C(CH_3)_3$  obtained here and in the model experiments outlined below is not separable by vacuum distillation techniques which suggests the existence of a complex, perhaps arising from hydrogen bonding interactions. The vapor pressure behavior and the difficulties in handling  $(CF_3)_2POH$  have been attributed to hydrogen bonding.<sup>2</sup> The mixture is, however, readily separated by the formation of a base adduct with  $(CF_3)_2POH^2$  from which the uncomplexed phosphine oxide can be distilled under vacuum.

Separate experiments were done to clarify the anomalous behavior of *tert*-butyl alcohol. Under conditions similar to those used for the alcoholysis we find that HCl converts  $(CF_3)_2POC(CH_3)_3$  to  $(CF_3)_2POH$  and  $(CH_3)_3CCl$  (eq 3). It



is worth noting here that  $CF_3(CH_3)POC(CH_3)_3$  reacts similarly with HCl to yield the isomeric phosphine oxide  $C-F_3(CH_3)P(O)H^6$  indicating that the phosphinous acid structure is stable only when there are two  $CF_3$  substituents on phosphorus.

Another experiment showed that  $(CF_3)_2POH$  and  $(C-H_3)_3CCl$  react readily to form the *tert*-butylphosphine oxide and HCl (eq 4). Heating a pure sample of  $(CF_3)_2POC(CH_3)_3$



showed that it did not rearrange or decompose at temperatures similar to those involved in the above reactions. Thermal stability of this compound to 67 °C has been previously demonstrated.<sup>2</sup>

Finally the role of HCl in the formation of the rearranged product is clearly shown by the reaction of  $(CF_3)_2PCl$  and *tert*-butyl alcohol in the presence of a molar equivalent of

Table I. NMR Data<sup>a</sup>

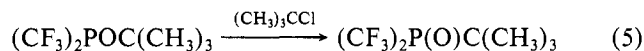
	$\phi_F$	$^2J_{FP}$ , Hz	$\tau_{CH_3}$	$\tau$ other protons	$J_{PCH_3}$ , Hz	$J_{PCH_x}$ , Hz	$^3J_{HH}$ , Hz	$^5J_{FH}$ or $^6J_{FH}$ , Hz
(CF <sub>3</sub> ) <sub>2</sub> POCH <sub>3</sub>	64.4	86.1	6.08		12.4			0.5
(CF <sub>3</sub> ) <sub>2</sub> POCH <sub>3</sub> <sup>5</sup>	66.2	85.1	6.53		12.7			0.5
(CF <sub>3</sub> ) <sub>2</sub> POC <sub>2</sub> H <sub>5</sub>	65.0	87.2	8.56	5.85 (CH <sub>2</sub> )	n.o. <sup>b</sup>	9.8	7.0	0.3
(CF <sub>3</sub> ) <sub>2</sub> POC <sub>2</sub> H <sub>5</sub> <sup>1,3</sup>	65.3	86.6	8.66	5.87 (CH <sub>2</sub> )	n.r. <sup>b</sup>	9.9	6.87	n.r.
(CF <sub>3</sub> ) <sub>2</sub> POCH(CH <sub>3</sub> ) <sub>2</sub>	65.6	88.0	8.57	5.64 (CH)	n.o.	7.8	6.2	0.2
(CF <sub>3</sub> ) <sub>2</sub> POC(CH <sub>3</sub> ) <sub>3</sub>	65.9	88.3	8.64		n.o.			0.2
(CF <sub>3</sub> ) <sub>2</sub> PSCH <sub>3</sub> <sup>4</sup>	56.7	78.4	7.48		14.9			0.5
(CF <sub>3</sub> ) <sub>2</sub> PSCH <sub>2</sub> CH <sub>3</sub> <sup>c</sup>	57.1	79.4	8.50	7.03 (CH <sub>2</sub> )	0.5	14.6	7.3	n.o.
(CF <sub>3</sub> ) <sub>2</sub> PSCH(CH <sub>3</sub> ) <sub>2</sub> <sup>d</sup>	57.0	80.3	8.51	6.61 (CH)	n.o.	6.7	6.7	n.o.
(CF <sub>3</sub> ) <sub>2</sub> PSC(CH <sub>3</sub> ) <sub>3</sub>	56.7	81.2	8.41		1.1			n.o.
(CF <sub>3</sub> ) <sub>2</sub> P(O)OCH <sub>3</sub> <sup>5</sup>	73.3	120.0	6.28		11.1, 10.8			0.37, 0.5
(CF <sub>3</sub> ) <sub>2</sub> P(O)OCH <sub>2</sub> CH <sub>3</sub>	73.5	121.8	8.87	5.99 (CH <sub>2</sub> )	<0.5	9.0	7.5	<0.5
(CF <sub>3</sub> ) <sub>2</sub> P(O)OCH(CH <sub>3</sub> ) <sub>2</sub>	72.4	118.3	8.73	5.08 (CH)	<0.5	7.0	5.85	<0.5
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>3</sub>	70.6	109.0	7.30		13.4			0.6
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>2</sub> CH <sub>3</sub> <sup>c</sup>	71.1	108.5	8.73	7.01 (CH <sub>2</sub> )	<0.5	14.0	7.1	<0.5
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH(CH <sub>3</sub> ) <sub>2</sub>	71.3	107.8	8.32	5.90 (CH)	n.o.	11.9	7.2	n.o.
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>3</sub>	71.6	116.5	5.90		13.7			0.4
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>2</sub> CH <sub>3</sub>	72.0	116.3	8.79	5.81 (CH <sub>2</sub> )	<0.5	12.2	7.55	<0.5
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH(CH <sub>3</sub> ) <sub>2</sub>	72.6	114.1	8.54	4.80 (CH)	n.o.	10.8	6.3	n.o.
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH <sub>3</sub>	70.0	104.5	7.43		17.4			0.6
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH <sub>2</sub> CH <sub>3</sub>	70.4	103.7	8.79	7.07 (CH <sub>2</sub> )	<0.5	18.5	7.4	<0.5
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH(CH <sub>3</sub> ) <sub>2</sub>	70.5	103.0	8.66	6.38 (CH)	<0.5	14.8	6.7	<0.5
(CF <sub>3</sub> ) <sub>2</sub> P(S)SC(CH <sub>3</sub> ) <sub>3</sub>	70.7	103.4	8.46		1.65			~0
(CF <sub>3</sub> ) <sub>2</sub> P(O)CH <sub>3</sub> <sup>5</sup>	72.4	99.0	8.20		15.6			0.83, 0.78
(CF <sub>3</sub> ) <sub>2</sub> P(O)C(CH <sub>3</sub> ) <sub>3</sub>	64.7	84.7	8.48		17.3			0.8

<sup>a</sup> Where a reference is given for a particular compound, the NMR data given is that given in the literature. All other values were obtained in the present study. The chemical shifts of <sup>19</sup>F ( $\phi$ ) are relative to internal CCl<sub>3</sub>F with positive values denoting resonance to high field. <sup>1</sup>H chemical shifts are given relative to Me<sub>4</sub>Si ( $\tau = 10.0$ ). <sup>b</sup> n.o. = not observed; n.r. = not reported. <sup>c</sup>  $^3J_{PH} = 2^3J_{HH}$  gives a six-line spectrum for the CH<sub>2</sub> group with intensities 1:3:4:4:3:1 as observed. <sup>d</sup>  $^3J_{PH} = ^3J_{HH}$  gives an eight-line spectrum with the intensity ratio 1:7:21:35:35:21:7:1 of which only the central six lines are observed (with intensities 1:3:5:5:3:1).

trimethylamine, according to eq 2 (R = *t*-Bu, E = O), which gives the desired trivalent ester in good yield. Thus, removal of free HCl as the ammonium salt allows the reaction to proceed normally to yield the phosphinous ester.

The reaction of just *tert*-butyl alcohol with (CF<sub>3</sub>)<sub>2</sub>P(O)Cl may proceed initially according to eq 1, followed by cleavage of the phosphinous ester by free HCl according to eq 3, followed in turn by the formation of the phosphine oxide and HCl according to eq 4. Removing free HCl with the amine blocks the cycle and yields the phosphinous ester.

A less likely explanation of the formation of the phosphine oxide in the reaction of (CF<sub>3</sub>)<sub>2</sub>P(O)Cl with *tert*-butyl alcohol is an Arbuzov-like rearrangement of (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub> catalyzed by *tert*-butyl chloride (eq 5). However the presence

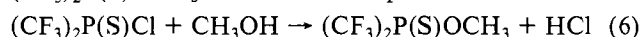


of (CF<sub>3</sub>)<sub>2</sub>POH in the alcoholysis reaction requires the involvement of a reaction such as that described by eq 3. Furthermore, we find that the process described by eq 5 does not occur when an equimolar ratio of the ester and *tert*-butyl chloride is heated for several hours at 70 °C. Methyl iodide is apparently a better catalyst for the rearrangement of the phosphinous ester giving<sup>2</sup> 77% conversion to (CF<sub>3</sub>)<sub>2</sub>P(O)C(CH<sub>3</sub>)<sub>3</sub> (which is not the normal Arbuzov product) after 2 h at 70 °C. We find that no rearrangement of (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub> occurs when it is treated with an equimolar quantity of CH<sub>3</sub>I for several weeks at room temperatures; thus elevated temperatures and an alkyl iodide seem to be required to achieve the rearrangement.

Although not investigated in detail, the reaction of (CF<sub>3</sub>)<sub>2</sub>P(O)Cl with benzyl alcohol alone proceeds similarly to that of *tert*-butyl alcohol, forming reasonable yields of (CF<sub>3</sub>)<sub>2</sub>POH. In this case the products are more readily separated and we have used this reaction as a convenient preparative route to (CF<sub>3</sub>)<sub>2</sub>POH.

As a general procedure, the addition of amine to the reaction mixture is most suitable for the synthesis of phosphinous oxyesters of higher homologues or the thioesters. While the methoxyphosphinous ester can be successfully synthesized in the presence of amine, it also forms the adduct (CH<sub>3</sub>)<sub>3</sub>N·(CF<sub>3</sub>)<sub>2</sub>POCH<sub>3</sub> (which can be formulated as the salt (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>(CF<sub>3</sub>)<sub>2</sub>PO<sup>-</sup>). This adduct formation is not strongly competitive with the primary synthesis of the ester. In the case of the pentavalent oxy- and thioester systems, discussed in more detail below, this adduct (or salt) formation is more often competitive with the ester synthesis.

**(B) Esters of Bis(trifluoromethyl)phosphinic Acids.** Methanol reacts smoothly with (CF<sub>3</sub>)<sub>2</sub>P(S)Cl at either 70 °C or at room temperature to give a good yield of the oxyester (CF<sub>3</sub>)<sub>2</sub>P(S)OCH<sub>3</sub> in accord with eq 6.



In contrast, the analogous reaction of (CF<sub>3</sub>)<sub>2</sub>P(O)Cl with methanol alone gave only a low yield<sup>5</sup> of (CF<sub>3</sub>)<sub>2</sub>P(O)OCH<sub>3</sub> probably as a result of the secondary reaction of the ester with HCl. Notably CH<sub>3</sub>Cl was observed in the products.<sup>5</sup> Likewise *tert*-butyl alcohol reacts with (CF<sub>3</sub>)<sub>2</sub>P(O)Cl giving (CH<sub>3</sub>)<sub>3</sub>CCl and HCl in less than quantitative yields along with involatile mixtures of (CF<sub>3</sub>)<sub>2</sub>P compounds which cannot be transferred in the vacuum system. Both systems can be understood by reference to the reaction of *tert*-butyl alcohol and (CF<sub>3</sub>)<sub>2</sub>P(O)Cl discussed above. *tert*-Butyl mercaptan reacts with (CF<sub>3</sub>)<sub>2</sub>P(O)Cl in the absence of amine to give only involatile products which have not been characterized. (CF<sub>3</sub>)<sub>2</sub>P(S)Cl did not react with 2-propanol in the absence of trimethylamine. We did not investigate the reactions of the remaining alcohols and mercaptans with (CF<sub>3</sub>)<sub>2</sub>P(E)Cl (E = O, S) in the absence of an amine because of the smooth reactions achieved in the presence of trimethylamine.

Ethanol, 2-propanol, ethyl mercaptan, and 2-propyl mercaptan react, in the presence of an equivalent molar quantity

Table II. IR Data for New Compounds<sup>a,b</sup>

(CF <sub>3</sub> ) <sub>2</sub> - POCH(CH <sub>3</sub> ) <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> - PSC <sub>2</sub> H <sub>5</sub>	(CF <sub>3</sub> ) <sub>2</sub> - PSCH(CH <sub>3</sub> ) <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(O)OC <sub>2</sub> H <sub>5</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(O)OCH- (CH <sub>3</sub> ) <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)- OCH <sub>3</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)OC <sub>2</sub> H <sub>5</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)OCH- (CH <sub>3</sub> ) <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SC <sub>2</sub> H <sub>5</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SCH- (CH <sub>3</sub> ) <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SC <sub>2</sub> H <sub>5</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SCH- (CH <sub>3</sub> ) <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SC <sub>2</sub> H <sub>5</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SCH- (CH <sub>3</sub> ) <sub>2</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SC <sub>2</sub> H <sub>5</sub>	(CF <sub>3</sub> ) <sub>2</sub> - P(S)SCH- (CH <sub>3</sub> ) <sub>2</sub>	assign	
2988 m	2994 m, sh	2975 m, sh	3010 w, sh	2995 m	3022 m	3002 w, sh	2990 m	3000 w, sh	2985 w, sh	2995 w, sh	2995 w, sh	2995 w, sh	2985 w, sh	2995 w, sh	2995 w, sh	} νC-H	
2942 w	2988 m	2968 m	2995 m	2948 w	2965 m	2990 m	2950 w	2980 w	2975 w	2975 m	2975 m	2980 w	2975 w	2975 m	} νC-H		
2910 w	2970 m	2930 m	2947 w	2887 w	2905 w	2943 w	2885 w	2944 w	2940 w	2930 w	2940 w	2944 w	2940 w	2930 w			} νC-H
2885 w	2942 w	2912 w	2930 w, sh	2887 w	2860 w	2918 w	2880 w	2885 w	2920 w, sh	2910 w	2920 w, sh	2885 w	2920 w, sh	2910 w			
2250 w	2220 w	2250 w	2890 w	2915 w	2878 w	2880 w	2880 w	2880 w	2880 w	2875 w	2880 w	2880 w	2880 w	2875 w		} νC-H	
1465 w	1460 w	1458 w	1450 w	1460 w	1460 w	1482 w	1465 m	1462 w	1468 w	1478 w	1468 w	1462 w	1468 w	1458 m	} δCH <sub>3</sub> , νCO		
1388 m	1455 w, sh	1390 w	1400 w	1393 m	1390 w	1450 w	1392 m	1387 w	1463 w	1458 m	1463 w	1387 w	1463 w	1400 w			} δCH <sub>3</sub> , νCO
1357 m	1435 w, sh	1374 w	1377 w	1369 w	1377 w	1398 m	1358 w	1290 w	1377 w	1372 m	1377 w	1290 w	1377 w	1372 m			
1344 m	1386 w, sh	1381 w	1295 w	1324 vs	1293 s	1303 w	1140 m	1267 w	1255 w	1282 w	1255 w	1267 w	1255 w	1282 w		} δCH <sub>3</sub> , νCO	
1222 s	1266 m	1254 m	1325 s	1226 vs	1194 vs	1197 m, sh	1217 s	1203 vs	1203 vs	1202 vs	1203 vs	1203 vs	1203 vs	1202 vs	} νP-O		
1172 vs	1200 vs	1196 vs	1212 s	1213 vs	1188 vs	1180 vs	1188 vs	1186 vs	1185 vs	1185 vs	1185 vs	1186 vs	1185 vs	1185 vs			} νP-O
1142 s	1191 vs, sh	1158 vs	1188 vs	1190 vs	1144 m	1144 m	1168 vs, sh	1170 vs	1168 vs	1161 vs	1168 vs	1170 vs	1168 vs	1161 vs			
1110 s	1162 vs	1125 vs	1140 s	1139 vs	1140 m	1142 s	1140 s	1142 s	1140 s	1140 s	1140 s	1142 s	1140 s	1140 s		} νP-O	
1000 m, sh	1155 vs, sh	1126 vs	1028 vs	1104 m	1046 s	1031 vs	1001 s	970 w	1060 m	1060 m	1060 m	970 w	1060 m	1060 m	} νP-O		
979 s	968 w	1055 m	968 m	1004 w	1059 w	971 m	899 m	899 m	899 m	899 m	899 m	899 m	899 m	899 m			} νP-O
881 m	745 w	746 w	779 w	763 m	750 w	750 w	809 s	770 s	770 s	770 s	770 s	770 s	770 s	770 s			
761 m	648 w	618 w	764 w	763 m	618 s	610 s	754 m	728 s	732 s	725 s	732 s	728 s	732 s	725 s		} νP-O	
567 m	559 m	563 s	590 s	590 s	552 m	557 m	688 m	640 w	638 w	638 w	638 w	640 w	638 w	638 w	} δ(e)CF <sub>3</sub>		
542 w	524 m	530 m	513 m	515 s	531 m	533 w	553 m	575 s	578 s	572 m	578 s	575 s	578 s	572 m			} δ(a)CF <sub>3</sub>
460 s	451 s	449 s	513 m	460 w	501 s	505 m	496 s	478 m	482 m	523 m	482 m	478 m	482 m	523 m			
	451 s	449 s	513 m	460 w	501 s	505 m	496 s	478 m	482 m	476 m	482 m	478 m	482 m	476 m		} νP-S	
	392 w	431 m	448 w	448 w	446 m	465 w	446 m	465 w	446 m	428 w	446 m	465 w	446 m	428 w	} νP-CF <sub>3</sub>		
	392 w	431 m	448 w	448 w	446 m	465 w	446 m	465 w	446 m	428 w	446 m	465 w	446 m	428 w			} νP-CF <sub>3</sub>

<sup>a</sup> All frequencies in cm<sup>-1</sup>. <sup>b</sup> Abbreviations: s = strong, m = medium, w = weak, v = very, sh = shoulder, ν = stretch, δ = bend, a = asymmetric, e = symmetric.

**Table III.** Synthesis of Esters from  $(CF_3)_2P(E)Cl^a$ ,  $REH^b$ , and  $(CH_3)_3N$ 

product	amt of $(CF_3)_2P(E)Cl^a$ taken, mmol	amt of $REH^b$ taken, mmol	amt of $(CH_3)_3N$ taken, mmol	yield of product, mmol %
$(CF_3)_2POCH_3^e$	0.42	0.41	c	0.36 (88)
$(CF_3)_2POC(CH_3)_3^e$	0.53	0.54	0.56	0.45 (85)
$(CF_3)_2PSCH_2CH_3^e$	2.76	2.80	2.83	2.66 (96)
$(CF_3)_2PSCH(CH_3)_2^e$	1.41	1.42	c	1.31 (93)
$(CF_3)_2P(O)OCH_2CH_3^f$	1.49	1.55	1.59	0.97 (65)
$(CF_3)_2P(O)OCH(CH_3)_2^f$	2.08	2.03	1.98	1.86 (94)
$(CF_3)_2P(O)SCH_3^e$	0.65	0.65	0.65	0.36 (55)
$(CF_3)_2P(O)SCH_2CH_3^f$	1.78	1.75	1.67	1.44 (86)
$(CF_3)_2P(O)SCH(CH_3)_2^e$	1.24	1.36	1.34	0.93 (75)
$(CF_3)_2P(S)OCH_2CH_3^f$	2.00	1.95	1.95	1.56 (80)
$(CF_3)_2P(S)OCH(CH_3)_2^e$	0.97	0.97	1.00	0.85 (88)
$(CF_3)_2P(S)SCH_2CH_3^f$	3.15	3.15	3.19	2.08 <sup>d</sup> (66)
$(CF_3)_2P(S)SCH(CH_3)_2^f$	1.83	1.86	1.83	1.39 (76)

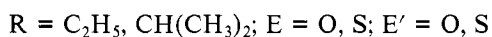
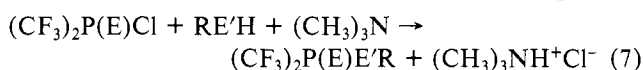
<sup>a</sup> E = O, S, or nothing as in product—no reorganization. <sup>b</sup> E = O or S as in product—no reorganization, R as in product. <sup>c</sup> Slight excess over that required for 1:1:1 ratios taken. <sup>d</sup> Contaminated with  $(CF_3)_2PSCH_2CH_3$ . <sup>e</sup> Method a(i). <sup>f</sup> Method (ii).

**Table IV.** Synthesis of Esters from  $ROH^a$  and  $(CF_3)_2P(E)Cl^b$ 

product	amt of $ROH^a$ taken, mmol	amt of $(CF_3)_2P(E)Cl^b$ taken, mmol	yield of product, mmol	yield of HCl, mmol
$(CF_3)_2POCH(CH_3)_2$	0.41	0.41	0.39	0.44 <sup>c</sup>
$(CF_3)_2P(S)OCH_3^d$	1.86	1.91	1.63	1.65

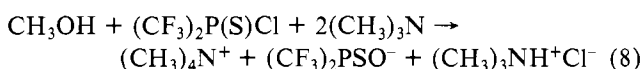
<sup>a</sup> R as in product. Reactions done at 70 °C. <sup>b</sup> E = S or nothing as in product—no reorganization. <sup>c</sup> Also contained a trace of volatile fluorocarbon. <sup>d</sup> Similar results were obtained by a room-temperature reaction.

of trimethylamine, with  $(CF_3)_2P(O)Cl$  or  $(CF_3)_2P(S)Cl$  to give good yields of the predicted esters according to eq 7, and

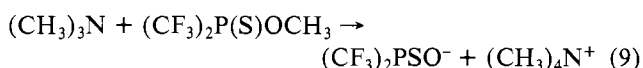


spectral properties of the products indicate that no rearrangement occurs during synthesis. Mixed phosphoryl thioesters or thiophosphoryl oxyesters of the  $C_2$ – $C_3$  series can be efficiently prepared by this method.

The reaction of methanol with  $(CF_3)_2P(S)Cl$  in the presence of trimethylamine gives only solid products along with the consumption of 2 mol of base as the result of the formation of the tetramethylammonium salt<sup>7</sup> of  $(CF_3)_2PSO^-$ .



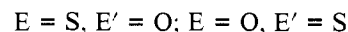
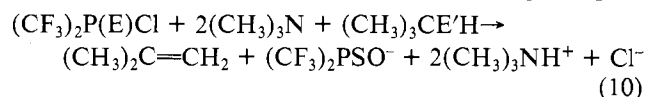
The acid,  $(CF_3)_2PSOH$ ,<sup>7</sup> can be liberated from this salt by sulfuric acid. Presumably the methyl ester is formed initially in a reaction obeying eq 7 but subsequent rapid attack by trimethylamine on this ester gives the ammonium salt. A separate experiment showed that the desired methoxy ester reacts rapidly with trimethylamine to form the salt.



The isopropyl ester reacts similarly with  $(CH_3)_3N$  to form the ammonium salt  $(CH_3)_2PSO^-$  but this reaction is noticeably slower than those of the methoxy and *tert*-butoxy esters so, in this case, the amine-assisted alcoholysis (eq 7) gives a reasonable yield of the ester. Similar slow salt formation in

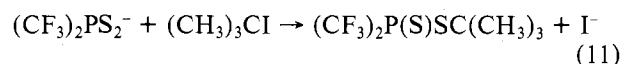
the case of higher homologous mercaptans likewise permits isolation of reasonable yields of the desired esters in the presence of amine.

Reaction of *tert*-butyl alcohol with  $(CF_3)_2P(S)Cl$  or *tert*-butyl mercaptan with  $(CF_3)_2P(O)Cl$  in the presence of trimethylamine results in the consumption of 2 mol of  $(CH_3)_3N$  but with the evolution of isobutene along with the formation of the ammonium salt of  $(CF_3)_2PSO^-$  according to eq 10.



This reaction probably proceeds through the initial formation of the predicted *tert*-butyl oxyester by a reaction obeying eq 7. Subsequent removal of the *tert*-butyl group by trimethylamine gives the salt. Isobutene is formed along with a second equivalent of  $(CH_3)_3NH^+$  because of the instability of the  $(CH_3)_3NC(CH_3)_3^+$  cation. A separate attempt to form this ion from  $(CH_3)_3N$  and  $(CH_3)_3Cl$  gave only isobutene and  $(CH_3)_3NH^+I^-$ , independently demonstrating the instability of this cation.

Because of these secondary reactions (eq 9 and 10) the *tert*-butyl oxy- and thioesters of pentavalent bis(trifluoromethyl)oxy and -thio acids cannot be obtained from *tert*-butyl alcohol or mercaptan. Successful synthesis of the *tert*-butyl thioester of bis(trifluoromethyl)dithiophosphinic acid  $(CF_3)_2P(S)SC(CH_3)_3$  is achieved by the reaction of *tert*-butyl iodide with a salt of the acid:



The analogous dioxo or oxythioesters, however, have not been obtained pure by this or any other route (vide infra). The  $(CF_3)_2PO_2^-$  salt does not react with *tert*-butyl iodide, presumably because the parent acid is a stronger<sup>8</sup> acid than  $PH_3$ . Although the  $(CF_3)_2PSO^-$  salt does react, the product is an intractable oily residue which has some NMR signals in agreement with those expected for  $(CF_3)_2P(S)OC(CH_3)_3$  plus additional NMR signals arising from a smaller amount of another compound which do not appear to be those of the isomer  $(CF_3)_2P(O)SC(CH_3)_3$  and must be ascribed to an unknown impurity. The intractable nature of the products hinders further examination of the system.

Treatment of the *tert*-butyl dithioester,  $(CF_3)_2P(S)SC_4H_9$ , with trimethylamine (vide infra) results in the formation of isobutene, confirming the validity of eq 10.

Alternate routes to the unavailable *tert*-butyl esters, such as the oxidation of  $(CF_3)_2PSC(CH_3)_3$  to  $(CF_3)_2P(O)SC(CH_3)_3$  with  $H_2O$ ,  $(CH_3)_3NO$ ,  $N_2O_4$ , pyridine *N*-oxide, and dry air, proved unsuccessful as was an attempt to prepare  $(CF_3)_2P(S)OC(CH_3)_3$  by sulfur oxidation of  $(CF_3)_2POC(CH_3)_3$ .

**(C) Properties of the Esters.** Alkaline hydrolyses<sup>8,9</sup> and synthetic methods confirm the trivalent character of the esters derived from the parent phosphinous acids  $(CF_3)_2PEH$  (E = O, S) and the pentavalent character of those esters derived from parent pentavalent phosphinic acids; however, in the latter case the yields of fluoroform were somewhat higher than expected for typical pentavalent  $(CF_3)_2P$  compounds and it appears that hydrolysis proceeds slowly to remove the second  $CF_3$  group from the anion in these esters in contrast to the usual<sup>7-12</sup> hydrolytic stability of pentavalent phosphorus compounds containing one  $CF_3$  group. The anionic products were characterized by NMR spectroscopy<sup>9</sup> and the results are summarized in Table V. One notable result is the evolution of isobutene in the alkaline hydrolysis of  $(CF_3)_2P(S)SC(CH_3)_3$ .

The only definitive base adduct formed by trivalent phosphorus esters is the 1:1 adduct obtained in 72% yield from

Table V. Alkaline Hydrolysis of Esters

ester	amt of ester taken, mmol	amt of CF <sub>3</sub> H obtained, mmol	other identified products <sup>a</sup>
(CF <sub>3</sub> ) <sub>2</sub> POCH(CH <sub>3</sub> ) <sub>2</sub>	0.280	0.550	ni <sup>b</sup>
(CF <sub>3</sub> ) <sub>2</sub> POC(CH <sub>3</sub> ) <sub>3</sub>	0.217	0.440	ni
(CF <sub>3</sub> ) <sub>2</sub> PSCH(CH <sub>3</sub> ) <sub>2</sub>	0.562	1.060	ni
(CF <sub>3</sub> ) <sub>2</sub> PSCH <sub>2</sub> CH <sub>3</sub>	0.277	0.561	ni
(CF <sub>3</sub> ) <sub>2</sub> P(O)OCH <sub>2</sub> CH <sub>3</sub>	0.611	0.615	CF <sub>3</sub> PO <sub>3</sub> <sup>2-</sup>
(CF <sub>3</sub> ) <sub>2</sub> P(O)OCH(CH <sub>3</sub> ) <sub>2</sub>	0.662	0.783	CF <sub>3</sub> PO <sub>3</sub> <sup>2-</sup>
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>3</sub>	0.417	0.427	CF <sub>3</sub> PO <sub>3</sub> <sup>2-</sup> , S <sup>2-</sup>
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>2</sub> CH <sub>3</sub>	0.612	0.708	CF <sub>3</sub> PO <sub>3</sub> <sup>2-</sup> , S <sup>2-</sup>
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH(CH <sub>3</sub> ) <sub>2</sub>	0.536	0.563	ni
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>3</sub>	0.712	0.847	CF <sub>3</sub> PSO <sub>2</sub> <sup>2-</sup> , trace CH <sub>3</sub> OH
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>2</sub> CH <sub>3</sub>	0.454	0.477	CF <sub>3</sub> PSO <sub>2</sub> <sup>2-</sup> , trace S <sup>2-</sup>
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH(CH <sub>3</sub> ) <sub>2</sub> (i)	0.186	0.340	(CF <sub>3</sub> ) <sub>2</sub> PSO <sup>-</sup> (CF <sub>3</sub> ) <sub>2</sub> PSO <sub>2</sub> <sup>2-</sup> , S <sup>2-</sup> CF <sub>3</sub> PSO <sub>2</sub> <sup>2-</sup> , S <sup>2-</sup> , trace CH <sub>3</sub> SH
(ii)	0.258	0.399	
(iii)	0.86	0.50	
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH <sub>3</sub>	0.342	0.397	CF <sub>3</sub> PSO <sub>2</sub> <sup>2-</sup> , S <sup>2-</sup> , trace CH <sub>3</sub> SH
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH <sub>2</sub> CH <sub>3</sub>	0.523	0.669	CF <sub>3</sub> PSO <sub>2</sub> <sup>2-</sup> , S <sup>2-</sup>
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH(CH <sub>3</sub> ) <sub>2</sub>	0.448	0.590	CF <sub>3</sub> PSO <sub>2</sub> <sup>2-</sup> , S <sup>2-</sup> , trace (CH <sub>3</sub> ) <sub>2</sub> CHSH and some unreacted (CF <sub>3</sub> ) <sub>2</sub> P(S)SCH(CH <sub>3</sub> ) <sub>2</sub>
(CF <sub>3</sub> ) <sub>2</sub> P(S)SC(CH <sub>3</sub> ) <sub>3</sub>	0.481	0.380	CF <sub>3</sub> PS <sub>2</sub> O <sup>2-</sup> , isobutene (0.288 mmol)

<sup>a</sup> Neutral molecules listed were identified as constituents of gas-phase condensate after separation from CF<sub>3</sub>H. CF<sub>3</sub>P anions in the residual solution were identified by <sup>19</sup>F NMR<sup>9</sup> and other species by qualitative tests. <sup>b</sup> ni = not investigated.

Table VI. Reactions of Esters with Trimethylamine

ester	amt of ester taken, mmol	amt of (CH <sub>3</sub> ) <sub>3</sub> N taken, mmol	amt of ester recovered, mmol	amt of (CH <sub>3</sub> ) <sub>3</sub> N recovered, mmol	amt of ester used, mmol	amt of (CH <sub>3</sub> ) <sub>3</sub> N used, mmol	anionic product	notes
(CF <sub>3</sub> ) <sub>2</sub> POCH <sub>3</sub>	0.410	0.466	0.113	0.164	0.297	0.302	(CF <sub>3</sub> ) <sub>2</sub> PO <sup>-</sup>	<i>a</i>
(CF <sub>3</sub> ) <sub>2</sub> POC(CH <sub>3</sub> ) <sub>3</sub>	0.305	0.397	0.291	0.456 <sup>b</sup>				
(CF <sub>3</sub> ) <sub>2</sub> PSCH <sub>3</sub> <sup>c</sup>	0.299	0.410	0.295	0.407	0.004	0.003	<i>g</i>	
(CF <sub>3</sub> ) <sub>2</sub> PSC(CH <sub>3</sub> ) <sub>3</sub> <sup>c</sup>	0.200	0.395	0.188	0.427 <sup>d</sup>				
(CF <sub>3</sub> ) <sub>2</sub> P(O)OCH <sub>2</sub> CH <sub>3</sub>	0.339	0.415	0.0	0.061 <sup>h</sup>	0.339	0.354	(CF <sub>3</sub> ) <sub>2</sub> PO <sub>2</sub> <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(O)OCH(CH <sub>3</sub> ) <sub>2</sub>	0.388	0.602	0.0	0.217 <sup>h</sup>	0.388	0.385	(CF <sub>3</sub> ) <sub>2</sub> PO <sub>2</sub> <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>3</sub>	0.272	0.341	0.0	0.085	0.272	0.255	(CF <sub>3</sub> ) <sub>2</sub> PSO <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>2</sub> CH <sub>3</sub>	0.383	0.436	0.0	0.051	0.383	0.385	(CF <sub>3</sub> ) <sub>2</sub> PSO <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH(CH <sub>3</sub> ) <sub>2</sub>	0.202	0.254	0.03	0.088	0.175	0.166	(CF <sub>3</sub> ) <sub>2</sub> PSO <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>3</sub>	0.656	0.993	0.0	0.402	0.656	0.591	(CF <sub>3</sub> ) <sub>2</sub> PSO <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>2</sub> CH <sub>3</sub>	0.396	0.551	0.0	0.093 <sup>h</sup>	0.396	0.458	(CF <sub>3</sub> ) <sub>2</sub> PSO <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH(CH <sub>3</sub> ) <sub>2</sub>	0.298	0.412	0.0	0.098	0.298	0.314	(CF <sub>3</sub> ) <sub>2</sub> PSO <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH <sub>3</sub>	0.273	0.356	0.036 <sup>e</sup>	0.152	0.242 <sup>f</sup>	0.203	(CF <sub>3</sub> ) <sub>2</sub> PS <sub>2</sub> <sup>-</sup>	
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH <sub>2</sub> CH <sub>3</sub>	0.491 <sup>i</sup>	0.668	0.055 <sup>i</sup>	0.192	0.436	0.476	(CF <sub>3</sub> ) <sub>2</sub> PS <sub>2</sub> <sup>-</sup>	<i>j</i>
(CF <sub>3</sub> ) <sub>2</sub> P(S)SCH(CH <sub>3</sub> ) <sub>2</sub>	0.428	0.551	0.303	0.432	0.125	0.119	(CF <sub>3</sub> ) <sub>2</sub> PS <sub>2</sub> <sup>-</sup>	<i>j</i>
(CF <sub>3</sub> ) <sub>2</sub> P(S)SC(CH <sub>3</sub> ) <sub>3</sub>	0.627	0.797	0.139	0.136	0.488	0.661	(CF <sub>3</sub> ) <sub>2</sub> PS <sub>2</sub> <sup>-</sup>	<i>k</i>

<sup>a</sup> Identified by reaction with (i) HCl to give (CF<sub>3</sub>)<sub>2</sub>POH and with (ii) H<sub>2</sub>O to give CF<sub>3</sub>P(H)O<sub>2</sub><sup>-</sup> + CF<sub>3</sub>H. <sup>b</sup> Product obtained also contained (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub>. <sup>c</sup> Reaction carried out at 70 °C for 24 h. <sup>d</sup> Contained a trace of (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub>. <sup>e</sup> Recovered material was (CF<sub>3</sub>)<sub>2</sub>PSCH<sub>3</sub>. <sup>f</sup> Calculated from weight of ester consumed, assuming that the (CF<sub>3</sub>)<sub>2</sub>PSCH<sub>3</sub> impurity did not react with (CH<sub>3</sub>)<sub>3</sub>N. <sup>g</sup> Insufficient product to identify. <sup>h</sup> Contains a little CF<sub>3</sub>H. <sup>i</sup> Contains a little (CF<sub>3</sub>)<sub>2</sub>PSCH<sub>2</sub>CH<sub>3</sub>. <sup>j</sup> Almost insoluble in water. <sup>k</sup> Isobutene evolved (0.483 mmol).

trimethylamine and (CF<sub>3</sub>)<sub>2</sub>POCH<sub>3</sub>. This compound has previously been reported to be inert to trimethylamine.<sup>2</sup> This adduct is analogous to that formed by (CF<sub>3</sub>)<sub>2</sub>POH and trimethylamine which has been formulated<sup>2</sup> as R<sub>3</sub>NH<sup>+</sup>OP(CF<sub>3</sub>)<sub>2</sub><sup>-</sup>. Treatment of our (CH<sub>3</sub>)<sub>3</sub>N·(CF<sub>3</sub>)<sub>2</sub>POCH<sub>3</sub> adduct with HCl liberated (CF<sub>3</sub>)<sub>2</sub>POH<sup>2</sup> in keeping with the formulation of this adduct as a quaternary ammonium salt but further attempts to characterize this solid product and to obtain definitive evidence in support of the species (CF<sub>3</sub>)<sub>2</sub>PO<sup>-</sup> have not been successful. The analogous methyl thioester (CF<sub>3</sub>)<sub>2</sub>PSCH<sub>3</sub> gives a very small amount of product which may contain the salt (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>(CF<sub>3</sub>)<sub>2</sub>PS<sup>-</sup>. We suspect, however, that this phosphinous thioester does not form an adduct with trimethylamine because (CF<sub>3</sub>)<sub>2</sub>PSH is a weak acid<sup>3,4</sup> and we would not expect a strong tendency to salt formation. (CF<sub>3</sub>)<sub>2</sub>PSH does form a quantitative solid adduct with trimethylamine from which (CF<sub>3</sub>)<sub>2</sub>PSH is readily recovered.<sup>4</sup>

All of the pentavalent esters react with trimethylamine to form salts as expected. Yields of salt are virtually quantitative

with oxyacid esters and thioesters with small alkyl groups. Esters containing large thioalkyl groups also form salts but these reactions are not quantitative. The results are summarized in Table VI. Of interest is the reaction of (CF<sub>3</sub>)<sub>2</sub>P(S)SC(CH<sub>3</sub>)<sub>3</sub> with trimethylamine which gave isobutene presumably on account of the instability of the (CH<sub>3</sub>)<sub>3</sub>CN<sup>-</sup>(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> ion as discussed above.

The *tert*-butylphosphinous esters (CF<sub>3</sub>)<sub>2</sub>PEC(CH<sub>3</sub>)<sub>3</sub> (E = O, S) did not react with trimethylamine.

**(D) Spectroscopic Studies and Structural Considerations.** Infrared and NMR spectroscopic studies of all products in the mixed oxythio system (shown in Tables I and II) show that all products have the structure expected from metathetical reaction of substitution at the halogen by the ester moiety without rearrangement during the reaction. Thus thio-phosphoryl and phosphoryl functions are preserved in these reactions and not interconverted. Attempted interconversions of thiophosphoryl oxyesters to phosphoryl thioesters were not very instructive. Two samples of (CF<sub>3</sub>)<sub>2</sub>P(S)OCH<sub>3</sub> rearranged

to  $(\text{CF}_3)_2\text{P}(\text{O})\text{SCH}_3$  after 3 days at 100 °C but a third sample did not rearrange under the same conditions.  $\text{CH}_3\text{I}$  did not cause the rearrangement of  $(\text{CF}_3)_2\text{P}(\text{S})\text{OCH}_3$  at room temperature. Clearly the phosphoryl form is the more stable of the forms in the thermodynamic sense; however, the thiophosphoryl isomer appears to be capable of prolonged existence in the absence of substances which catalyze the rearrangement. We do not know the identity of the apparent catalyst and clearly further study is warranted.

NMR parameters for homologous series of bis(trifluoromethyl)phosphines, -phosphoryl, and -thiophosphoryl compounds are given in Table I. The parameters are consistent<sup>4,5,9,10,13,14</sup> with the structures given. As expected,  $\tau$  values for  $\text{CH}_3$  or  $\text{CH}_2$  groups directly attached to oxygen are different from those attached to sulfur.<sup>14</sup> The apparently accidental relationship between  $^3J_{\text{PH}}$  and  $^3J_{\text{HH}}$  which produces a six-line spectrum for the  $\text{CH}_2$  group bound to phosphorus through sulfur is notable and not mirrored in the oxyester series. Our data for  $(\text{CF}_3)_2\text{POC}_2\text{H}_5$  are in essential agreement with that reported elsewhere<sup>13</sup> except that an equal intensity distribution between the two halves of the methylene quartet is found in our spectra, possibly because our measurements were made at 60 and 100 MHz and are therefore not affected by the second-order contributions which appear to be responsible for the intensity distribution observed<sup>13</sup> at lower field strengths (40 MHz).

One notable feature of the NMR data is the close similarity of chemical shift and  $^2J_{\text{PF}}$  parameters of  $(\text{CF}_3)_2\text{POC}(\text{CH}_3)_3$  and the isomer  $(\text{CF}_3)_2\text{P}(\text{O})\text{C}(\text{CH}_3)_3$ .<sup>2</sup> The two compounds, which have notably different volatility and are easily separated, are characterized principally by the large P-H coupling observed in the directly bound *tert*-butyl compound (17.3 Hz) in contrast to the near zero value of the four-bond P-H coupling in the P-O-C( $\text{CH}_3$ )<sub>3</sub> unit. Couplings of this type are usually small and the result is not unexpected.<sup>14</sup> The isomers  $(\text{CF}_3)_2\text{P}(\text{O})\text{CH}_3$ <sup>5</sup> and  $(\text{CF}_3)_2\text{POCH}_3$ <sup>5</sup> are more readily distinguished by NMR spectroscopy since  $\tau(\text{CH}_3)$ ,  $\phi(\text{CF}_3)$ , and both  $^2J_{\text{PF}}$  and  $J_{\text{PH}}$  are larger in the former compound in keeping with the presence of a pentavalent phosphorus atom.

## Experimental Section

Standard vacuum techniques with Pyrex glass apparatus were employed throughout. Stopcocks were lubricated with Apiezon "N" grease. Gas-phase IR spectra were recorded with Perkin-Elmer 337, 457, or 421 or Beckman IR11 instruments using 9-cm gas cells with KBr windows. NMR spectra were obtained with Varian A56/60 or Varian HA-100 instruments. Proton spectra were measured at 60 or 100 MHz on 15% solutions in  $\text{CCl}_3\text{F}$  with chemical shifts given relative to tetramethylsilane. Fluorine spectra were measured at 56.4 MHz on the same solutions with chemical shifts given relative to  $\text{CCl}_3\text{F}$ . Vapor pressures were measured with a glass spiral microtensimeter<sup>15</sup> by using the null point technique with both ascending and descending temperature. Reactions were carried out in sealed Pyrex glass tubes.

**Materials.** The alcohols employed were reagent grade materials dried over sodium metal under vacuum before use. Mercaptans were used as supplied.

The (trifluoromethyl)phosphorus compounds  $(\text{CF}_3)_2\text{PCl}$ ,<sup>16</sup>  $(\text{CF}_3)_2\text{P}(\text{O})\text{Cl}$ ,<sup>2,17</sup>  $(\text{CF}_3)_2\text{P}(\text{S})\text{Cl}$ ,<sup>10,11</sup> and  $(\text{CF}_3)_2\text{PP}(\text{CF}_3)_2$ <sup>12</sup> and the acids  $(\text{CF}_3)_2\text{PS}_2\text{H}$ ,<sup>10,11</sup>  $(\text{CF}_3)_2\text{PSOH}$ ,<sup>7</sup> and  $(\text{CF}_3)_2\text{PO}_2\text{H}$ <sup>8</sup> were obtained by literature methods. Salts of the acids were prepared by reaction of the acids with dry  $\text{NaOCH}_3$ . The previously known esters  $(\text{CF}_3)_2\text{POCH}_3$ ,<sup>2</sup>  $(\text{CF}_3)_2\text{POC}_2\text{H}_5$ ,<sup>1,2</sup>  $(\text{CF}_3)_2\text{POC}(\text{CH}_3)_3$ ,<sup>2</sup>  $(\text{CF}_3)_2\text{PS-CH}_3$ ,<sup>3,4</sup>  $(\text{CF}_3)_2\text{PSC}(\text{CH}_3)_3$ ,<sup>4</sup> and  $(\text{CF}_3)_2\text{P}(\text{S})\text{SCH}_3$ <sup>11</sup> were also prepared by literature methods.  $(\text{CF}_3)_2\text{POC}(\text{CH}_3)_3$  was also obtained from the reaction of  $(\text{CF}_3)_2\text{PCl}$  with  $(\text{CH}_3)_3\text{COH}$  in the presence of  $(\text{CH}_3)_3\text{N}$  as in Table III.

**Preparation of Esters. (a) From Chlorophosphorus Derivatives in the Presence of Trimethylamine.** (i) A general synthetic procedure was used for the preparation of the majority of the phosphinous esters and thioesters from halogenophosphorus derivatives. Equal molar quantities of chlorophosphorus compound, the alcohol or mercaptan,

and trimethylamine were combined in a sealed Pyrex ampule of about 30-cm<sup>3</sup> capacity and allowed to warm slowly from -78 °C to room temperature. The reaction was generally fast below room temperature and usually gave high yields (but see below). The volatile products were fractionated under vacuum through a series of cooled traps with the desired product generally collected at -63 °C. The compounds synthesized by this procedure with quantities used are given in Table III.

(ii) A variation of the above method was used in some cases to improve yields of esters of low volatility. The reactions were carried out as described above except that a reaction vessel of 250-cm<sup>3</sup> capacity (with a separate side arm into which the trimethylamine was condensed before reaction) was used. The products were separated as described and quantities involved are given in Table III.

(b) **From Chlorophosphorus Derivatives in the Absence of Trimethylamine.** Equal molar quantities of chlorophosphorus compound and alcohol were combined in a 30-cm<sup>3</sup> sealed tube and heated at 70 °C for 24 h. Separation of the volatile materials as described above (a(i)) gave, in some cases, the desired product and HCl. The compounds synthesized by this method with quantities used are given in Table IV.

(c) **From Tetrakis(trifluoromethyl)diphosphine.**<sup>2</sup>  $(\text{CH}_3)_2\text{CHOH}$  (0.72 mmol) and  $(\text{CF}_3)_2\text{PP}(\text{CF}_3)_2$  (0.71 mmol) were allowed to react for 4 days in a sealed tube at room temperature followed by 7 h at 70 °C. Vacuum fractionation gave  $(\text{CF}_3)_2\text{POCH}(\text{CH}_3)_2$  (0.70 mmol).  $(\text{CF}_3)_2\text{PH}$  was also observed in the volatile products.

(d) **Preparation of *tert*-Butyl Esters from  $(\text{CH}_3)_3\text{Cl}$  and Acid Salts.** (i) **Preparation of  $(\text{CF}_3)_2\text{PS}_2\text{C}(\text{CH}_3)_3$ .**  $(\text{CF}_3)_2\text{PS}_2\text{H}$  (0.504 g, 2.15 mmol) and pentane (Na-dried, ~3 mL) were condensed into a flask on the vacuum system containing sodium methoxide (0.112 g, 2.08 mmol) and allowed to react for 1 h with stirring to give a viscous oil which was insoluble in pentane. All volatile materials were removed and  $(\text{CH}_3)_3\text{Cl}$  (0.373 g, 2.03 mmol) was added to the residual oily material whereupon a solid was formed. After 18 h of reaction at room temperature the volatile product was removed and identified as  $(\text{CF}_3)_2\text{PS}_2\text{C}(\text{CH}_3)_3$  (0.457 g, 1.57 mmol, 78% yield). In a similar experiment, the yield of ester after allowing 1 h reaction time was ~68%.

(ii) **Attempted Preparation of  $(\text{CF}_3)_2\text{PO}_2\text{C}(\text{CH}_3)_3$ .** Reaction of  $(\text{CF}_3)_2\text{PO}_2\text{H}$  (0.541 g, 2.68 mmol) and  $\text{NaOCH}_3$  (0.138 g, 2.56 mmol) in pentane followed by removal of pentane and other volatile products and then treatment of the residual solid product with  $(\text{CH}_3)_3\text{Cl}$  (0.444 g, 2.41 mmol) for 24 h at room temperature gave unchanged  $(\text{CH}_3)_3\text{Cl}$  (0.439 g, 2.38 mmol, 99% recovery) as the only volatile product.

(iii) **Reaction of  $(\text{CF}_3)_2\text{PSO}^-\text{Na}^+$  with  $(\text{CH}_3)_3\text{Cl}$ .**  $(\text{CF}_3)_2\text{P}(\text{S})\text{OH}$  (0.451 g, 2.07 mmol),  $\text{NaOCH}_3$  (0.112 g, 2.07 mmol), and dry (with Na) pentane (~1 mL) were stirred at room temperature for 20 h to form a colorless oil insoluble in pentane. All volatile materials were removed in vacuo leaving an off-white solid.  $(\text{CH}_3)_3\text{Cl}$  (0.399 g, 2.16 mmol) and dry pentane (~2 mL) were added to the solid and the mixture was stirred. The solid was initially transformed into an oil which was then converted into an insoluble white solid after 1-2 h. Separation of the volatile products gave 0.129 g of a pale yellow liquid which was collected in a cold trap at -45 °C. NMR spectra of this liquid indicated that it was a mixture of at least two components, including signals attributable to  $(\text{CF}_3)_2\text{P}(\text{S})\text{OC}(\text{CH}_3)_3$  (approximately 66% of the mixture according to the NMR spectrum). The NMR parameters ( $\phi_{\text{F}}$  72.7,  $^2J_{\text{FP}}$  = 116 Hz) are typical of  $(\text{CF}_3)_2\text{P}(\text{S})\text{OR}$  compounds as opposed to  $(\text{CF}_3)_2\text{P}(\text{O})\text{SR}$  compounds and this provides the principal evidence for the identification of this product as the *tert*-butoxy ester. Another compound in the mixture (~33%) gave rise to  $^{19}\text{F}$  signals ( $\phi_{\text{F}}$  70.0,  $^2J_{\text{FP}}$  = 113 Hz). The  $^1\text{H}$  spectrum of this mixture showed one prominent species ( $\tau$  8.43,  $^4J_{\text{HP}}$  = 1.35 Hz) which can be associated with a compound containing phosphorus and this is reasonably assigned to the *tert*-butoxy ester. No evidence for another isomer of the *tert*-butyl derivative of phosphorus was provided by the  $^1\text{H}$  spectrum; hence the  $^{19}\text{F}$  parameters of the minor component are likely due to a  $(\text{CF}_3)_2\text{P}$  compound which does not contain a *tert*-butyl group. A trace impurity was also observed in the  $^{19}\text{F}$  spectrum ( $\phi_{\text{F}}$  73.0,  $^2J_{\text{FP}}$  = 115 Hz).

**Characterization of New Compounds. (a) Alkaline Hydrolysis.** The compounds were hydrolyzed by allowing them to react with 5 mL of 10% NaOH solution in a sealed tube at room temperature for 2 days. The quantities used and the amounts of fluoroform obtained are listed in Table V. Results of vapor pressure measurements are given in Tables VII and VIII.

Table VII. Volatility of Some of the New Compounds Prepared

compound	range studied, °C	A <sup>a</sup>	B <sup>a</sup>	T <sub>b</sub> , °C	ΔH <sub>v</sub> , cal mol <sup>-1</sup>	ΔH <sub>v</sub> /T <sub>b</sub>
(CF <sub>3</sub> ) <sub>2</sub> POCH(CH <sub>3</sub> ) <sub>2</sub>	0-50	7.98	1840	88	8420	23.3
(CF <sub>3</sub> ) <sub>2</sub> PSCH(CH <sub>3</sub> ) <sub>2</sub>	15-60	8.10	2079	125	9520	23.9
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>3</sub>	-10-60	7.95	1835	89	8400	23.2
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH(CH <sub>3</sub> ) <sub>2</sub>	0-70	7.10	1710	132	7820	19.3
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>3</sub>	20-70	6.99	1767	157	8080	18.8
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH(CH <sub>3</sub> ) <sub>2</sub>	15-70	7.65	2042	155	9340	21.8

<sup>a</sup> Constants for the equation  $\log P_{\text{mm}} = A - B/T$ .

Table VIII. Vapor Pressure Data for New Compounds

(CF <sub>3</sub> ) <sub>2</sub> POCH(CH <sub>3</sub> ) <sub>2</sub>							
t, °C	0.0	7.6	10.8	14.9	25.0	35.4	40.6
p, mm (obsd)	17.3	26.9	31.3	39.4	64.9	103.5	128.9
p, mm (calcd) <sup>a</sup>	17.5	26.7	31.6	39.1	64.3	103.8	130.3
(CF <sub>3</sub> ) <sub>2</sub> PSCH(CH <sub>3</sub> ) <sub>2</sub>							
t, °C	16.8	23.0	29.0	35.4	46.0	56.2	59.1
p, mm (obsd)	8.5	11.9	16.7	22.9	39.1	61.6	69.1
p, mm (calcd) <sup>a</sup>	8.6	12.1	16.7	23.1	38.7	61.7	70.0
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH <sub>3</sub>							
t, °C	-5.9	0.0	7.9	15.5	26.3	36.1	49.8
p, mm (obsd)	12.1	17.0	26.1	38.7	65.6	102.9	186.0
p, mm (calcd) <sup>a</sup>	12.1	17.0	26.2	38.9	66.0	103.2	184.3
(CF <sub>3</sub> ) <sub>2</sub> P(S)OCH(CH <sub>3</sub> ) <sub>2</sub>							
t, °C	0.0	12.2	25.0	37.9	50.5	54.0	55.4
p, mm (obsd)	6.9	12.4	22.8	40.7	64.6	75.1	78.8
p, mm (calcd) <sup>a</sup>	6.9	12.8	23.2	40.5	65.7	74.9	78.8
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH <sub>3</sub>							
t, °C	22.7	29.3	36.1	39.1	44.2	49.2	57.1
p, mm (obsd)	10.4	13.8	19.3	21.3	27.1	31.8	43.6
p, mm (calcd) <sup>a</sup>	10.4	14.0	18.9	21.4	26.4	32.2	43.5
(CF <sub>3</sub> ) <sub>2</sub> P(O)SCH(CH <sub>3</sub> ) <sub>2</sub>							
t, °C	17.4	24.2	30.0	43.5	52.7	59.7	65.5
p, mm (obsd)	4.1	6.0	8.5	16.2	24.0	32.4	41.7
p, mm (calcd) <sup>a</sup>	4.2	6.0	8.2	15.8	24.1	32.6	41.5

<sup>a</sup> Pressures calculated from the equation  $\log P_{\text{mm}} = A - B/T$  by using coefficients given in Table VII.

(b) **Reaction with Trimethylamine.** All the esters were allowed to react with a small excess of trimethylamine for 24 h in a sealed tube at room temperature. The quantities taken, quantities recovered, and hence quantities involved in salt formation and identifications of the salts are listed in Table VI. The identity of the residual salts was established by NMR spectroscopy.<sup>7</sup>

**Reactions of (CF<sub>3</sub>)<sub>2</sub>P(E)Cl with *tert*-Butyl Alcohol and Mercaptan.**

(a) **Reaction of (CF<sub>3</sub>)<sub>2</sub>P(O)Cl with (CH<sub>3</sub>)<sub>3</sub>COH.** (CF<sub>3</sub>)<sub>2</sub>P(O)Cl<sup>12,17</sup> (0.228 g, 1.03 mmol) and (CH<sub>3</sub>)<sub>3</sub>COH (Na-dried, 0.092 g, 1.24 mmol) were allowed to react for 3 days at room temperature whereupon colorless and yellow immiscible liquids had formed. Vacuum fractionation then gave a small amount of an unidentified oil of low volatility which trapped at -63 °C, (CH<sub>3</sub>)<sub>3</sub>CCl (0.039 g, 0.42 mmol, 39%) trapped at -116 °C, and a mixture (0.025 g) which trapped at -196 °C and which consisted principally of HCl along with some (CH<sub>3</sub>)<sub>3</sub>CCl and traces of other unidentified constituents. All the (CF<sub>3</sub>)<sub>2</sub>P containing products were retained in the involatile oily residues which decomposed, becoming deep red and more viscous, on heating.

(b) **Reactions of (CF<sub>3</sub>)<sub>2</sub>P(O)Cl with (CH<sub>3</sub>)<sub>3</sub>CSH.** (CF<sub>3</sub>)<sub>2</sub>P(O)Cl<sup>12,17</sup> (0.108 g, 0.49 mmol), (CH<sub>3</sub>)<sub>3</sub>N (0.061 g, 1.03 mmol), and (CH<sub>3</sub>)<sub>3</sub>CSH (0.047 g, 0.52 mmol) were allowed to react while slowly warming from -78 °C to room temperature over 2 days. Vacuum fractionation gave (CH<sub>3</sub>)<sub>3</sub>CSH (0.003 g, 0.03 mmol), (CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub> (0.026 g, 0.47 mmol), and (CH<sub>3</sub>)<sub>3</sub>N (0.007 g, 0.12 mmol). The latter constituent was removed from the mixed volatile products by treatment with H<sub>3</sub>PO<sub>4</sub> and refractionation. The involatile salt which remained in the reaction tube was identified as (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>(CF<sub>3</sub>)<sub>2</sub>PSO<sup>-</sup> by NMR spectroscopy.<sup>7</sup>

A similar experiment using 1 molar equiv of (CH<sub>3</sub>)<sub>3</sub>N resulted in the consumption of all of the (CH<sub>3</sub>)<sub>3</sub>N and gave a mixture of the same products and unreacted starting material.

Reaction in the absence of (CH<sub>3</sub>)<sub>3</sub>N proceeded at 70 °C to give mainly involatile material which was not characterized.

In the presence of dimethylamine (0.046 g, 1.03 mmol), *tert*-butyl mercaptan (0.086 g, 0.95 mmol) and (CF<sub>3</sub>)<sub>2</sub>P(O)Cl<sup>12,17</sup> (0.210 g, 0.95 mmol) gave only (CF<sub>3</sub>)<sub>2</sub>P(O)N(CH<sub>3</sub>)<sub>2</sub><sup>17</sup> (0.105 g, 0.46 mmol) and unreacted starting material.

(c) ***tert*-Butyl Alcohol with (CF<sub>3</sub>)<sub>2</sub>P(S)Cl.** (i) *tert*-Butyl alcohol (0.034 g, 0.46 mmol), (CF<sub>3</sub>)<sub>2</sub>P(S)Cl<sup>10,11</sup> (0.12 g, 0.51 mmol), and (CH<sub>3</sub>)<sub>3</sub>N (0.059 g, 1.00 mmol) were allowed to react as described above for 24 h. Analysis of the volatile products as described above gave (CH<sub>3</sub>)<sub>3</sub>COH (0.011 g, 0.15 mmol), (CF<sub>3</sub>)<sub>2</sub>P(S)Cl (0.037 g, 0.15 mmol), (CH<sub>3</sub>)<sub>3</sub>N (0.016 g, 0.28 mmol), and (CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub> (0.013 g, 0.23 mmol). The involatile salt produced was identified as (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>(CF<sub>3</sub>)<sub>2</sub>PSO<sup>-</sup>.

In a similar experiment, 1 molar equiv of (CH<sub>3</sub>)<sub>3</sub>N reacted in the same manner to consume all the (CH<sub>3</sub>)<sub>3</sub>N and gave similar products.

(ii) *tert*-Butyl alcohol (0.028 g, 0.37 mmol), (CF<sub>3</sub>)<sub>2</sub>P(S)Cl (0.105 g, 0.44 mmol), and (CH<sub>3</sub>)<sub>2</sub>NH (0.038 g, 0.87 mmol) were allowed to react as above. Vacuum fractionation gave mainly (CF<sub>3</sub>)<sub>2</sub>P(S)N(CH<sub>3</sub>)<sub>2</sub><sup>10,11</sup> and excess (CH<sub>3</sub>)<sub>3</sub>COH.

**Attempted Oxidation of Phosphino Esters.** (a) The *tert*-butylphosphino ester (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub> (0.103 g, 0.42 mmol), sulfur (0.016 g, 0.49 mmol), and a trace of Al<sub>2</sub>Cl<sub>6</sub> did not appear to react at 70 °C. After heating of the mixture for 3 days at 150 °C, vacuum fractionation gave only (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub>.

A similar reaction in the absence of Al<sub>2</sub>Cl<sub>6</sub> did not proceed below 165 °C. After 12 h at 165 °C the major product was a black involatile tar.

(b) (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub> (0.047 g, 0.18 mmol) and HgO (0.047 g, 0.22 mmol) did not react at room temperature; after 20 h at 70 °C a mixture of (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub> and (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub> resulted.

(c) (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub> (0.047 g, 0.18 mmol) and excess resublimed (CH<sub>3</sub>)<sub>3</sub>NO reacted during 18 h at room temperature to give (CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>N as the only volatile products.

(d) (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub> (0.043 g, 0.17 mmol) and N<sub>2</sub>O<sub>4</sub> (0.009 g, 0.10 mmol) reacted rapidly at room temperature to give some solid and excess (CF<sub>3</sub>)<sub>2</sub>PSCH(CH<sub>3</sub>)<sub>2</sub>. No oxidized volatile product was observed and the nature of the solid was not investigated.

(e) (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub> (0.53 g, 0.21 mmol) and excess resublimed pyridine *N*-oxide did not react at room temperature. After 24 h at 70 °C vacuum fractionation gave (CH<sub>3</sub>)<sub>2</sub>C=CH<sub>2</sub> and unreacted (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub>. The involatile material contained the (CF<sub>3</sub>)<sub>2</sub>PSO<sup>-</sup> ion (identified by NMR spectroscopy).<sup>7</sup>

(f) (CF<sub>3</sub>)<sub>2</sub>PSC(CH<sub>3</sub>)<sub>3</sub> (0.025 g, 0.10 mmol) and air (dried by passage through -196 °C traps) containing 0.2 mmol of oxygen did not react during 16 h at room temperature.

**Reaction of Methanol with (CF<sub>3</sub>)<sub>2</sub>P(S)Cl in the Presence of Trimethylamine.** Equimolar portions of (CF<sub>3</sub>)<sub>2</sub>P(S)Cl,<sup>10,11</sup> CH<sub>3</sub>OH, and (CH<sub>3</sub>)<sub>3</sub>N reacted rapidly below room temperature to form a white solid containing the ions (CH<sub>3</sub>)<sub>4</sub>N<sup>+</sup>, (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>, Cl<sup>-</sup>, and (C-F<sub>3</sub>)<sub>2</sub>PSO<sup>-</sup>.<sup>7</sup> The only volatile products were excess (CF<sub>3</sub>)<sub>2</sub>P(S)Cl and CH<sub>3</sub>OH.

**Reaction of (CF<sub>3</sub>)<sub>2</sub>P(S)Cl with Sodium Methoxide.** Caution: An equimolar mixture of (CF<sub>3</sub>)<sub>2</sub>P(S)Cl<sup>10,11</sup> and solid sodium methoxide exploded on warming to room temperature.

**Isomerization of (CF<sub>3</sub>)<sub>2</sub>P(S)OCH<sub>3</sub>.** One sample of (CF<sub>3</sub>)<sub>2</sub>P(S)OCH<sub>3</sub> heated at 100 °C for 2 days largely rearranged to (CF<sub>3</sub>)<sub>2</sub>P(O)SCH<sub>3</sub>. A second sample in CFCl<sub>3</sub> solution did not rearrange during 3 days at 100 °C; however, a third, fresh, sample of ester in CFCl<sub>3</sub> solution completely isomerized during 3 days at 100 °C.

A sample of (CF<sub>3</sub>)<sub>2</sub>P(S)OCH<sub>3</sub> in CFCl<sub>3</sub> solution remained unchanged in the presence of CH<sub>3</sub>I during 3 weeks at room temperature.

**Reaction of (CF<sub>3</sub>)<sub>2</sub>PCI with (CH<sub>3</sub>)<sub>3</sub>COH.** (CF<sub>3</sub>)<sub>2</sub>PCI<sup>16</sup> (0.288 g, 1.41 mmol) and (CH<sub>3</sub>)<sub>3</sub>COH (0.107 g, 1.45 mmol) were allowed to react at 70 °C for 18 h. Vacuum fractionation gave (CH<sub>3</sub>)<sub>3</sub>CCl (0.095 g, 1.03 mmol), HCl (0.018 g, 0.49 mmol), (CF<sub>3</sub>)<sub>2</sub>PCI (0.007 g, 0.03 mmol), and a fraction of low volatility (0.215 g) analyzed by NMR spectroscopy as a 1:1 mixture of (CF<sub>3</sub>)<sub>2</sub>P(O)C(CH<sub>3</sub>)<sub>3</sub> and (CF<sub>3</sub>)<sub>2</sub>POH<sup>2</sup> (approximately 0.50 mmol each). Complete mass balance was not achieved. A portion of this mixture (0.144 g, 0.34 mmol) was allowed to react with (CH<sub>3</sub>)<sub>3</sub>N (0.0324 g, 0.55 mmol) for 10 min at room temperature whereupon subsequent vacuum separation gave (C-F<sub>3</sub>)<sub>2</sub>P(O)C(CH<sub>3</sub>)<sub>3</sub><sup>2</sup> (0.073 g, 0.30 mmol).

**Reaction of (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub> with HCl.** (CF<sub>3</sub>)<sub>2</sub>POC(CH<sub>3</sub>)<sub>3</sub> (0.108 g, 0.45 mmol) and HCl (0.45 mmol) were heated at 70 °C for 20 h. Vacuum fractionation gave (CF<sub>3</sub>)<sub>2</sub>POH<sup>2</sup> (0.017 g, 0.09 mmol), (CH<sub>3</sub>)<sub>3</sub>CCl (0.030 g, 0.33 mmol), (CF<sub>3</sub>)<sub>2</sub>PCI<sup>13</sup> (0.002 g, 0.01 mmol), HCl (0.005 g, 0.14 mmol), and a 1:1 mixture (analyzed by NMR

spectroscopy) of  $(CF_3)_2POH^2$  and  $(CF_3)_2P(O)C(CH_3)_3^2$  (0.067 g, 0.16 mmol of each component).

**Reaction of  $(CF_3)_2POH$  with  $(CH_3)_3Cl$ .**  $(CF_3)_2POH^2$  (0.101 g, 0.54 mmol) was allowed to react with excess  $(CH_3)_3CCl$  for 4 days at 70 °C. Vacuum fractionation gave a mixture of  $(CF_3)_2POH$  and  $(CF_3)_2P(O)C(CH_3)_3$  (0.094 g), HCl (0.015 g, 0.41 mmol), and unreacted  $(CH_3)_3Cl$ .

**Thermal Stability of  $(CF_3)_2POC(CH_3)_3$ .** A sample of  $(CF_3)_2P-OC(CH_3)_3$  was quantitatively recovered unchanged after heating at 70 °C for 5 h.

**Treatment of  $(CF_3)_2POC(CH_3)_3$  with  $(CH_3)_3CCl$ .** A sample of  $(CF_3)_2POC(CH_3)_3$  (~1 mmol) was combined with an equal molar quantity of  $(CH_3)_3CCl$  in a 5-mm o.d. NMR tube. Examination by  $^1H$  and  $^{19}F$  NMR spectroscopy after 2 days at room temperature showed that no detectable rearrangement had occurred. The mixture was heated to 70 °C for 2 days but again, according to the NMR spectra, no rearrangement had occurred.

**Treatment of  $(CF_3)_2POC(CH_3)_3$  with  $CH_3I$ .** Approximately equimolar quantities of  $(CF_3)_2POC(CH_3)_3$  (~1 mmol) and  $CH_3I$  showed no sign of rearrangement after 2 weeks at 25 °C according to NMR spectroscopy.

**Reaction of  $(CF_3)_2PCl$  with Benzyl Alcohol.**  $(CF_3)_2PCl^{16}$  (0.190 g, 0.93 mmol) and benzyl alcohol (0.14 g, 1.3 mmol) were heated at 70 °C for 4 h. Vacuum fractionation gave  $(CF_3)_2POH^2$  (0.115 g, 0.62 mmol) and an oil of low volatility which was not identified.

**Reaction of  $(CH_3)_3CI$  with  $(CH_3)_3N$ .**  $(CH_3)_3CI$  (0.295 g, 1.61 mmol) and  $(CH_3)_3N$  (0.096 g, 1.60 mmol) reacted slowly at room temperature, and rapidly at 100 °C. Vacuum fractionation after 24 h of reaction at 100 °C gave  $(CH_3)_2C=CH_2$  (0.071 g, 1.27 mmol) and a trace of starting materials. The NMR spectrum of the white involatile salt showed only signals due to  $(CH_3)_3NH^+I^-$ .

**Acknowledgment.** We thank the National Research Council of Canada for financial support of this work.

**Registry No.**  $(CF_3)_2POCH_3$ , 684-25-3;  $(CF_3)_2POC_2H_5$ , 1692-49-5;  $(CF_3)_2POCH(CH_3)_2$ , 71009-82-0;  $(CF_3)_2POC(CH_3)_3$ , 4571-88-4;  $(CF_3)_2PSCH_2CH_3$ , 71009-83-1;  $(CF_3)_2PSCH(CH_3)_2$ , 71009-84-2;  $(CF_3)_2PSC(CH_3)_3$ , 1733-46-6;  $(CF_3)_2P(O)OCH_2CH_3$ , 71009-85-3;

$(CF_3)_2P(O)OCH(CH_3)_2$ , 71009-86-4;  $(CF_3)_2P(O)SCH_3$ , 71009-87-5;  $(CF_3)_2P(O)SCH_2CH_3$ , 71009-88-6;  $(CF_3)_2P(O)SCH(CH_3)_2$ , 71009-89-7;  $(CF_3)_2P(S)OCH_3$ , 71040-58-9;  $(CF_3)_2P(S)OCH_2CH_3$ , 71009-90-0;  $(CF_3)_2P(S)OCH(CH_3)_2$ , 71009-91-1;  $(CF_3)_2P(S)SCH_3$ , 18799-79-6;  $(CF_3)_2P(S)SCH_2CH_3$ , 71009-92-2;  $(CF_3)_2P(S)SCH(CH_3)_2$ , 71009-93-3;  $(CF_3)_2P(S)SC(CH_3)_3$ , 71009-94-4;  $(CF_3)_2P(O)C(CH_3)_3$ , 71040-59-0;  $(CF_3)_2PP(CF_3)_2$ , 2714-60-5;  $(CF_3)_2PS_2H$ , 18799-75-2;  $(CH_3)_3CI$ , 558-17-8;  $(CF_3)_2P(S)OH$ , 35814-49-4;  $(CF_3)_2P(S)OC(CH_3)_3$ , 71009-95-5;  $(CF_3)_2P(O)Cl$ , 646-71-9;  $(CH_3)_3NH^+(CF_3)_2PSO^-$ , 71009-96-6;  $(CF_3)_2P(O)N(CH_3)_2$ , 3331-12-2;  $(CF_3)_2P(S)Cl$ , 18799-82-1;  $(CF_3)_2P(S)N(CH_3)_2$ , 18799-80-9;  $(CF_3)_2PCl$ , 650-52-2;  $(CF_3)_2POH$ , 359-65-9;  $(CH_3)_2CHOH$ , 67-63-0;  $(CH_3)_3COH$ , 75-65-0;  $(CH_3)_3CCl$ , 513-36-0;  $(CH_3)_3CSH$ , 75-66-1;  $(CH_3)_2C=CH_2$ , 115-11-7;  $CH_3OH$ , 67-56-1;  $CH_3CH_2SH$ , 75-08-1;  $(CH_3)_2CHSH$ , 75-33-2;  $CH_3CH_2OH$ , 64-17-5;  $CH_3SH$ , 74-93-1;  $(CH_3)_3N$ , 75-50-3; benzyl alcohol, 100-51-6.

## References and Notes

- (1) H. J. Emel us and J. D. Smith, *J. Chem. Soc.*, 375 (1959).
- (2) J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **84**, 3442 (1962).
- (3) K. Gosling and A. B. Burg, *J. Am. Chem. Soc.*, **87**, 2113 (1965).
- (4) R. G. Cavell and H. J. Emel us, *J. Chem. Soc.*, 5825 (1964).
- (5) A. B. Burg and I. B. Mishra, *Inorg. Chem.*, **8**, 1199 (1969).
- (6) A. B. Burg and D. K. Kang, *J. Am. Chem. Soc.*, **92**, 1901 (1970).
- (7) A. A. Pinkerton and R. G. Cavell, *J. Am. Chem. Soc.*, **93**, 2384 (1971).
- (8) H. J. Emel us, R. N. Haszeldine, and R. C. Paul, *J. Chem. Soc.*, 563 (1955).
- (9) A. A. Pinkerton and R. G. Cavell, *Inorg. Chem.*, **10**, 2720 (1971).
- (10) R. C. Dobbie, L. F. Doty, and R. G. Cavell, *J. Am. Chem. Soc.*, **90**, 2015 (1968).
- (11) K. Gosling and A. B. Burg, *J. Am. Chem. Soc.*, **90**, 2011 (1968).
- (12) F. W. Bennett, H. J. Emel us, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).
- (13) K. J. Packer, *J. Chem. Soc.*, 960 (1963).
- (14) J. W. Emsley, J. Feeny, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy", Pergamon, London, 1965.
- (15) R. Couper and D. R. Stranks, "Techniques of Inorganic Chemistry", Vol VI, H. B. Jonassen and A. Weissberger, Eds., Wiley, New York, 1966, p 6.
- (16) A. B. Burg and J. F. Nixon, *J. Am. Chem. Soc.*, **86**, 356 (1964).
- (17) A. B. Burg and A. J. Sarkis, *J. Am. Chem. Soc.*, **87**, 238 (1965).

Contribution from the Department of Chemistry,  
University of Massachusetts, Amherst, Massachusetts 01003

## Transition-Metal Eight-Coordination. 13. Synthesis, Characterization, and Crystal and Molecular Structure of the Schiff-Base Chelate Bis(*N,N'*-disalicylidene-1,2-phenylenediamino)zirconium(IV) Benzene Solvate

RONALD D. ARCHER,\* ROBERTA O. DAY, and MARVIN L. ILLINGSWORTH

Received February 21, 1979

As part of our program to elucidate eight-coordinate complexes and their polymeric counterparts we have isolated and structurally characterized the model Schiff-base chelate bis(*N,N'*-disalicylidene-1,2-phenylenediamino)zirconium(IV),  $Zr(dsp)_2$ , as the benzene solvate  $Zr(dsp)_2 \cdot 2.5C_6H_6$ . The synthesis involves a condensation between tetrakis(salicylaldehydato)zirconium(IV),  $Zr(sal)_4$ , and *o*-phenylenediamine, a method which also allows the synthesis of analogous coordination polymers. The  $Zr(dsp)_2$  unit is an eight-coordinate dodecahedral species with nitrogen donors in the dodecahedral A position and oxygen donors in the B positions in accord with theoretical predictions. The chelating ligands span the *mm* edges. The Zr-O bonds average 2.10  , which is appreciably shorter than the Zr-N distance of 2.43  . The donor atoms are in an almost perfect dodecahedral array with the trapezoidal planes intersecting at 89.2 , even though the chelating ligands are quite puckered from these planes. The  $Zr(dsp)_2 \cdot 2.5C_6H_6$  solvate crystallizes in the space group  $P\bar{1}$  with  $Z = 2$ ,  $a = 13.037$  (4)  ,  $b = 13.669$  (6)  ,  $c = 14.500$  (2)  ,  $\alpha = 98.81$  (2) ,  $\beta = 116.47$  (2) , and  $\gamma = 92.78$  (3) .

## Introduction

The monomeric Schiff-base chelate bis(*N,N'*-disalicylidene-1,2-phenylenediamino)zirconium(IV),  $Zr(dsp)_2$ , has been synthesized and characterized as a model for analogous polymers, which have been prepared<sup>1</sup> as part of a program to develop tractable, thermally stable coordination polymers

containing nonrigid metal centers. The molecular structure of the benzene solvate has been determined by means of single-crystal X-ray diffraction analysis in order to learn the detailed disposition of two quadridentate Schiff-base ligands about a  $d^0$  metal ion. Previous structural studies<sup>2</sup> with this ligand for lower coordination numbers have shown that the ligand can coordinate in either a planar or a nonplanar fashion.