The Reaction of Trifluoromethylphosphino-compounds with Nitric Oxide

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Nitric oxide has been found to act as an oxidising agent towards the trifluoromethylphosphino-compounds, CF_3PX_2 (X = F, Cl, H, and CF_3), and $(CF_3)_2PX$ (X = F, Cl, H, and $P[CF_3]_2$), reaction occurring in the temperature range 20—100°. The oxidation of $(CF_3)_2PF$ and $(CF_3)_2P \cdot P(CF_3)_2$ gave the new compounds $(CF_3)_2P(\text{:}O)F$ and $(CF_3)_2P(\text{:}O) \cdot O \cdot P(\text{:}O)(CF_3)_2$ respectively.

THE development of the chemistry of trifluoromethyl-substituted phosphine oxides has been hampered by the lack of a general method for the oxidation of the corresponding readily accessible phosphines. Oxidation by nitrogen dioxide of tristrifluoromethylphosphine [1] and dichlorotrifluoromethylphosphine [2] to the corresponding oxides proceeds quantitatively but with chlorobistrifluoromethylphosphine, a complex mixture of products was obtained.[3] Mercuric oxide has also been used for the oxidation of phosphines, although side reactions can occur leading in some cases to poor yields of the desired product.[4]

was thought worthwhile to explore the reaction nitric of oxide with some unco-ordinated trifluoromethylphos-phino-derivatives. The reactions studied and products obtained are summarised in Table 1.

When difluorotrifluoromethylphosphine was allowed to react with nitric oxide at room temperature there was an almost quantitative yield of trifluoromethylphosphonic difluoride, formed according to the equation:

$$CF_3PF_2 + 2NO \longrightarrow CF_3P(\text{:}O)F_2 + N_2O$$

The oxide has been previously prepared [8] in low yield by the reaction of antimony trifluoride on tetrachloro-

TABLE 1

Reaction of trifluoromethylphosphino-compounds with nitric oxide

Reactant	Molar ratio of NO to reactant	$T/°C$	Phosphorus(v) products [a]		Other products [b]
CF_3PF_2	2·04	20	$CF_3P(\text{:}O)F_2$	(98%)	N_2O
$(CF_3)_2PF$	2·09	20	$(CF_3)_2P(\text{:}O)F$	(57%)	N_2O
$(CF_3)_3P$	2·19	80	$(CF_3)_3P(\text{:}O)$	(78%)	N_2, COF_2,
			$(CF_3)_3PO_2\text{-}NO^+$	(12%)	N_2O, NO_2
CF_3PCl_2	2·05	105	$CF_3P(\text{:}O)Cl_2$	(54%)	CF_3NO, $NOCl$,
			$P(O)Cl_3$	(13%)	N_2O, N_2
$(CF_3)_2PCl$	2·28	80	$(CF_3)_2P(\text{:}O)Cl$	(53%)	N_2O, N_2
			$CF_3P(\text{:}O)Cl_2$	(18%)	CF_3NO, COF_2
CF_3PH_2	4·04	20	$CF_3P(\text{:}O)(OH)_2$	(72%)	N_2O, N_2
$(CF_3)_2PH$	2·36	20	$(CF_3)_2P(\text{:}O)OH$	(90%)	N_2O, N_2
$[(CF_3)_2P]_2$	4·15	20	$[(CF_3)_2P(\text{:}O)]_2O$	(76%)	N_2, N_2O

[a] Yields are based on the quantity of phosphine consumed. [b] Products detected in significant amount are listed in order of decreasing abundance. For other products, see Experimental section.

It has been reported that triethyl phosphite [5] and di- and tri-methylphosphine [6] are oxidised by nitric oxide to triethyl phosphate, dimethylphosphinic acid, and tri-methylphosphine oxide respectively. When it was discovered [7] that the complex bis(trifluoromethyl)phos-phido(π-cyclopentadienyl)dicarbonyliron (I), was
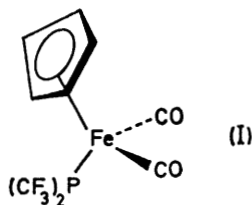
oxidised at room temperature by nitric oxide to the phosphine oxide complex, $(\pi\text{-}C_5H_5)Fe(CO)_2P(\text{:}O)(CF_3)_2$, it

trifluoromethylphosphorane, the oxygen having presumably arisen from water present in the fluorinating agent.

Fluorobistrifluoromethylphosphine reacted in a similar way with nitric oxide to form bistrifluoromethyl-phosphinic fluoride, $(CF_3)_2P(O)F$, but the reaction was incomplete after one week at room temperature. Separation of the phosphine from the product was most easily achieved by allowing the mixture to react with bis(π-cyclopentadienyl)nickel, when the phosphine formed the known [9] complex $Ni[(CF_3)_2PF]_4$, but the acid fluoride was unchanged. The purified phosphinic fluoride was found to liberate only one mole of fluoro-form on treatment with aqueous alkali, so that the basic hydrolysis ceases at the phosphonate stage, as expected from the behaviour of other bistrifluoromethyl-phos-

[1] A. B. Burg and A. J. Sarkis, *J. Amer. Chem. Soc.*, 1965, **87**, 238.
[2] J. E. Griffiths, *Spectrochim. Acta*, 1968, **24**A, 303.
[3] A. B. Burg, *Accounts Chem. Res.*, 1969, **2**, 353.
[4] J. E. Griffiths and A. B. Burg, *J. Amer. Chem. Soc.*, 1960, **82**, 5759; A. B. Burg and I. B. Mishra, *Inorg. Chem.*, 1969, **8**, 1199.

[5] L. P. Kuhn, J. O. Doali, and C. Wellman, *J. Amer. Chem. Soc.*, 1960, **82**, 4792.
[6] M. Halmann and L. Kugel, *J. Chem. Soc.*, 1962, 3272.
[7] R. C. Dobbie, P. R. Mason, and R. J. Porter, unpublished work.
[8] J. E. Griffiths, *Spectrochim. Acta*, 1968, **24**A, 115.
[9] J. F. Nixon, *J. Chem. Soc. (A)*, 1967, 1136.

phinic [10-12] and -thiophosphinic [13,14] derivatives. The [19]F n.m.r. spectrum (see Table 2) showed two distinct areas of absorption, a low-field doublet of doublets caused by coupling of the equivalent fluorine atoms of the trifluoromethyl groups with phosphorus and with the distant fluorine atom, and a high field doublet of septets, assigned to the single fluorine atom. The parameters are similar to those of the thio-analogue, $(CF_3)_2P(S)F$,[14] and to those of a number of other bistrifluoromethyl-phosphinic derivatives (Table 2), confirming the penta-valent formulation rather than the isomeric fluoroxy-structure, $(CF_3)_2P \cdot OF$. The i.r. spectrum of the gas shows $\nu(P=O)$ at 1366 cm^{-1}, $\delta(P=O)$ at 589 cm^{-1}, and an intense band at 907 cm^{-1} [shifted from 850 cm^{-1} in $(CF_3)_2PF$] assigned to the P–F stretching frequency of a phosphorus(v) compound.

TABLE 2

[19]F N.m.r. spectra [a] of some bistrifluoromethylphosphinic derivatives

Compound	$\phi(CF_3)$	$^2J_{FP}$	$\phi(PF)$	$^1J_{FP}$	$^3J_{FF}$
$(CF_3)_2P(\text{:}O)F$	67·9	136	87·5	1189	7·8
$(CF_3)_2P(\text{:}S)F$ [b]	72·3	128·6	94·5	1174·6	1·6
$(CF_3)_2P(\text{:}O)Cl$	70·6	130			
$(CF_3)_2P(\text{:}O)Br$	70·5	126			
$(CF_3)_2P(\text{:}O)NMe_2$	69·8	106			
$[(CF_3)_2P(\text{:}O)]_2O$	70·0	137			

[a] Chemical shifts (ϕ) in p.p.m. from CFCl$_3$; coupling constants (J) in Hz. [b] Data from ref. 14.

Tristrifluoromethylphosphine reacted with nitric oxide at 80° to give the oxide $(CF_3)_3P(\text{:}O)$;[1,11] the other products were nitrogen, nitrous oxide, carbonyl fluoride, and smaller quantities of nitrogen dioxide and trifluoro-nitromethane. There remained in the reaction tube a small amount of a white crystalline solid which was subjected to the action of anhydrous hydrogen chloride. The chief products were nitrosyl chloride and bistri-fluoromethylphosphinic acid,[10] from which it was deduced that the solid was largely $NO^+(CF_3)_2PO_2^-$. A trace of trifluorobistrifluoromethylphosphorane, $(CF_3)_2PF_3$,[15] was also formed, perhaps indicating the presence of another nitrosonium salt as an impurity.

Dichlorotrifluoromethylphosphine and chlorobistri-fluoromethylphosphine did not react with nitric oxide at room temperature but at about 100° each phosphine was totally consumed. The chief products from the dichloro-compound were trifluoromethylphosphonic dichloride $[CF_3P(O)Cl_2]$[16] and phosphoryl chloride, and from the monochlorophosphine, bistrifluoromethylphosphinic chloride $[(CF_3)_2P(\text{:}O)Cl]$,[12] and $CF_3P(\text{:}O)Cl_2$. Nitrogen, nitrous oxide, nitrosyl chloride, and trifluoronitroso-methane were also detected.

Continuing the trend of reduced reactivity as the

heavier halogens become substituents at the phosphorus atom, neither di-iodotrifluoromethylphosphine nor iodo-bistrifluoromethylphosphine reacted with nitric oxide under conditions which succeeded for the chlorides. The use of still more forcing conditions was not investi-gated as the iodo-compounds are known to dispro-portionate at higher temperatures.[17]

It was thought likely that the action of nitric oxide on trifluoromethylphosphine and bistrifluoromethylphos-phine would lead to the formation of some of the known trifluoromethyl-substituted phosphorus acids. At room temperature the secondary phosphine gave bistrifluoro-methylphosphinic acid, $(CF_3)_2P(\text{:}O) \cdot OH$,[10] which prob-ably arises by initial oxidation to $(CF_3)_2P(\text{:}O)H$, followed by the known [12,18] anti-Arbuzov rearrangement to bistrifluoromethylphosphinous acid, $(CF_3)_2P \cdot OH$; further oxidation would produce the phosphinic acid. Trifluoro-methylphosphine was also oxidised by nitric oxide, the chief product being trifluoromethylphosphonic acid, $CF_3P(\text{:}O)(OH)_2$, identified as the dianilinium salt.[10]

Finally, the action of nitric oxide on some compounds containing P–P bonds was studied. Although a mixture of tetrakis(trifluoromethyl)cyclotetraphosphine and pentakis(trifluoromethyl)cyclopentaphosphine failed to react with an excess of nitric oxide at 90°, tetrakistri-fluoromethyldiphosphine, $(CF_3)_2P \cdot P(CF_3)_2$, was com-pletely consumed in a few days at room temperature, adding on three atoms of oxygen to give bistrifluoro-methylphosphinic anhydride, $(CF_3)_2P(\text{:}O) \cdot O \cdot P(\text{:}O)(CF_3)_2$, in high yield. This compound has been mentioned by Burg [3] as being one product of the reaction of chlorobis-trifluoromethylphosphine with nitrogen dioxide, al-though none of its properties has yet been reported. The [19]F n.m.r. spectrum (Table 2) showed a simple doublet ($^2J_{FP}$ 137 Hz), indicating that all the fluorine atoms were chemically equivalent and that $^2J_{FP}$ was very large compared to $^2J_{PP}$ and to $^4J_{FP}$ as the molecule belongs to the $[X_6A]_2$ spin system (X = [19]F; A = [31]P).[19] Further evidence for the structure of the compound was provided by its reactions. The anhydride was stable to chlorine, demonstrating the absence of a P–P bond, whereas with an excess of anhydrous hydrogen chloride, it reacted according to the equation:

$$(CF_3)_2P(\text{:}O) \cdot O \cdot P(\text{:}O)(CF_3)_2 + HCl \longrightarrow$$
$$(CF_3)_2P(\text{:}O) \cdot OH + (CF_3)_2P(\text{:}O)Cl$$
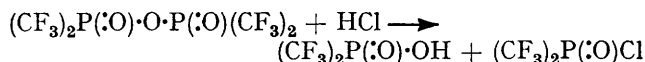
The i.r. spectrum of the phosphinic anhydride, recorded in the vapour phase, gave some evidence for the inter-action of the P=O groups as two bands could be assigned to $\nu(P=O)$ at 1362 and 1345 cm^{-1}, although only one bending vibration was apparent (at 591 cm^{-1}).

[10] H. J. Eméleus, R. N. Haszeldine, and R. C. Paul, J. Chem. Soc., 1955, 563.
[11] R. C. Paul, J. Chem. Soc., 1955, 574.
[12] J. E. Griffiths and A. B. Burg, J. Amer. Chem. Soc., 1962, 84, 3442.
[13] K. Gosling and A. B. Burg, J. Amer. Chem. Soc., 1968, 90, 2011.
[14] R. C. Dobbie, L. F. Doty, and R. G. Cavell, J. Amer. Chem. Soc., 1968, 90, 2015.
[15] W. Mahler, Inorg. Chem., 1963, 2, 230.
[16] J. E. Griffiths, Spectrochim. Acta, 1968, 24A, 303.
[17] F. W. Bennett, H. J. Eméleus, and R. N. Haszeldine, J. Chem. Soc., 1953, 1565.
[18] J. E. Griffiths and A. B. Burg, Proc. Chem. Soc., 1961, 12.
[19] R. K. Harris, Canad. J. Chem., 1964, 42, 2275.

The kinetics of the oxidation of triethyl phosphite by nitric oxide have been examined by Kuhn, Doali, and Wellman [5] who reported that the reaction was first order in phosphite and first order in nitric oxide. A radical mechanism was proposed which invoked the slow formation of $(EtO)_3\dot{P}N{=}O$ or $(EtO)_3\dot{P}ON\colon$ and a similar mechanism is favoured for the reactions now reported. The trifluoromethylphosphino-compounds were oxidised much more slowly than $(EtO)_3P$ or Me_3P and this may be attributed to the very weak basicity of the fluorine compounds. One further point of interest is that the nitrous oxide was partly reduced to nitrogen in most of the experiments described herein.

In summary it appears that nitric oxide will act as a mild oxidant towards trifluoromethyl-substituted phosphines, in some cases requiring more forcing conditions than nitrogen dioxide but never leading to extensive side reactions. A sufficient number of cases has been examined to suggest that the method may be of wider application to the synthesis of oxides from perfluoromethylphosphines with other substituents at phosphorus.

EXPERIMENTAL

The reactions described in this paper were carried out in a vacuum system using standard techniques. I.r. spectra were recorded on a Perkin-Elmer 457 spectrometer and n.m.r. spectra on a Bruker HFX 5 Spectrospin operating at 84·6 MHz for ^{19}F nuclei, using $CFCl_3$ as solvent and standard. Commercial nitric oxide was purified by repeated vacuum fractionation through traps at $-183°$; the resulting nitric oxide was almost colourless in the liquid phase. The trifluoromethylphosphino-compounds were prepared by the literature methods.

Reaction of Trifluoromethylphosphino-compounds with Nitric Oxide.—Difluorotrifluoromethylphosphine.[20] The phosphine (0·270 g, 1·96 mmol) and nitric oxide (0·120 g, 4·00 mmol) reacted at room temperature in a sealed tube (7 d) to give $CF_3P(\colon O)F_2$ (0·296 g, 1·92 mmol), identified by its i.r. spectrum, molecular weight (Found: M, 153) and vapour pressure, a mixture of N_2O and NO (Found: M, 42·2), and a trace of N_2.

Fluorobistrifluoromethylphosphine.[21] When the fluorophosphine (0·292 g, 1·55 mmol) and NO (0·087 g, 3·24 mmol) were allowed to stand at room temperature in a sealed tube there was a slow reaction. After 6 d, vacuum fractionation gave, in order of decreasing volatility, a mixture of N_2O and NO, a mixture of $(CF_3)_2PF$, and another compound suspected to be $(CF_3)_2P(\colon O)F$ (Found: M, 194; 0·238 g together), and a trace of $[(CF_3)_2P]_2O$, all detected by i.r. spectroscopy. The fluorophosphine was removed from the mixture containing it by reaction with $(\pi\text{-}C_5H_5)_2Ni$ (0·101 g, 0·54 mmol) at room temperature (2 d) which yielded $Ni[(CF_3)_2PF]_4$ (0·119 g, 0·15 mmol) as a white crystalline solid and *bistrifluoromethylphosphinic fluoride*, $(CF_3)_2P(\colon O)F$ (0·110 g, 0·54 mmol) (Found: CF_3 liberated on alkaline hydrolysis, 33·3%; m/e 203·9599. C_2F_7OP requires CF_3 liberated on alkaline hydrolysis, 33·8%; m/e 203·9575). I.r. bands were observed in the gas phase at 1366m, 1301w, 1209s, 1161w, 907m, 771w, 750w, 589m, 510m, 472m, and 372m cm^{-1}. The vapour pressure (p) of the liquid between -78

and $-12°$ is given by: $\log_{10}(p/\text{mmHg}) = -1405\,.\,(T/\text{K})^{-1} + 7·90$, giving an extrapolated b.p. of $7°$.

Tristrifluoromethylphosphine.[17] Nitric oxide (0·064 g, 2·14 mmol) and $(CF_3)_3P$ (0·233 g, 0·98 mmol) reacted only to a very slight extent during 2 months at room temperature; in contrast at $80°$ a faint brown colour characteristic of NO_2 was observed in the tube after only 64 h. Vacuum fractionation gave N_2 (ca. 1·0 mmol), a volatile mixture containing COF_2, N_2O, NO, and a trace of CF_3NO_2, and a less volatile fraction in which $(CF_3)_3P(O)$ was found along with some NO_2 (Found: M, 241; 0·85 mmol together). On shaking this fraction with mercury for 5 min, the brown colour disappeared and refractionation gave pure $(CF_3)_3P(\colon O)$ (0·201 g, 0·76 mmol), identified by i.r. spectroscopy and molecular weight (Found: M, 251) and vapour pressure measurements. A white crystalline solid (0·030 g) remaining in the original reaction tube, absorbed anhydrous HCl (0·13 mmol consumed out of 0·49 mmol taken), reacting at ca. $-100°$ to give NOCl (0·007 g, 0·11 mmol), $(CF_3)_2PF_3$ (a trace), and $(CF_3)_2P(\colon O)OH$ (0·024 g, 0·12 mmol) which liberated 1 mole of CF_3H on hydrolysis.

Dichlorotrifluoromethylphosphine.[17] The chloro-compound (0·326 g, 1·91 mmol) and nitric oxide (0·117 g, 3·91 mmol) did not react at room temperature (13 d) but at $100°$ (3 d) a blue-green gas formed in the tube. After a small amount (ca. 0·2 mmol) of nitrogen had been pumped off, the remaining volatile products were separated by vacuum fractionation into a mixture of CF_3NO and N_2O (Found: M, 89; 1·02 mmol together) NOCl (Found: M, 68) (0·035 g, 0·53 mmol), a trace of CF_3NO_2, $CF_3P(\colon O)Cl_2$ (Found: M, 186) (0·192 g, 1·03 mmol), identified by vapour pressure measurements, and $POCl_3$ (Found: M, 153) (0·037 g, 0·24 mmol), the compounds also being identified by their i.r. spectra. A small amount of a white solid (0·011 g), which did not distil from the reaction vessel, was not investigated further.

Chlorobistrifluoromethylphosphine.[17] When $(CF_3)_2PCl$ (0·104 g, 0·51 mmol) and NO (0·035 g, 1·16 mmol) were left in a sealed tube for 1 month the reactants were recovered. After 17 h at $80°$, however, vacuum fractionation gave N_2 (ca. 0·2 mmol), a mixture (0·35 mmol) of NO, N_2O, CF_3NO, COF_2, and CF_3Cl, NOCl (0·002 g, 0·03 mmol), and a mixture of $(CF_3)_2P(O)Cl$ and $CF_3P(O)Cl_2$ (Found: M, 202; 0·36 mmol together), each component of which was identified by i.r. and n.m.r. spectroscopy. Quantitative analysis of the mixture by i.r. and n.m.r. methods showed it to contain 0·060 g (0·27 mmol) of $(CF_3)_2P(\colon O)Cl$ and 0·017 g (0·09 mmol) of $CF_3P(\colon O)Cl_2$.

Di-iodotrifluoromethylphosphine.[17] Nitric oxide (0·052 g, 1·73 mmol) and CF_3PI_2 (0·304 g, 0·86 mmol) were recovered after 8 d at $20°$ and after 24 h at $85°$.

Iodobistrifluoromethylphosphine.[17] The phosphine (0·172 g, 0·58 mmol) and NO (0·035 g, 1·16 mmol) did not react at room temperature (6 d) or at $90°$ (25 h).

Trifluoromethylphosphine.[22] Trifluoromethylphosphine (0·159 g, 1·56 mmol) and NO (0·189 g, 6·30 mmol) reacted at room temperature (68 h) to form a mass of crystals. Vacuum fractionation gave N_2 (ca. 1·0 mmol), N_2O (Found: M, 43·4) (0·097 g, 2·20 mmol), and a small amount (0·012 g) of an unknown trifluoromethylphosphino-compound. The crystalline solid remaining in the tube was slightly impure

[20] V. N. Kulakova, Yu. M. Zinov'ev, and L. Z. Soborovskii, *Zhur. obshchei Khim.*, 1959, **29**, 3957.

[21] A. B. Burg and G. Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198.

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

trifluoromethylphosphonic acid (0·168 g, 1·12 mmol), m.p. 76—78° (lit.,[23] 81—82°), identified by its i.r. spectrum and by its reaction with an excess of aniline (0·5 g) in ethanol (2 ml) to give the di-anilinium salt, whose properties conformed with those reported in the literature.[23]

Bistrifluoromethylphosphine.[22] In a typical reaction a mixture of $(CF_3)_2PH$ (0·029 g, 0·17 mmol) and NO (0·012 g, 0·40 mmol) produced oily drops of a colourless liquid after a few minutes at room temperature. Vacuum fractionation gave some nitrogen, nitrous oxide (0·005 g, 0·12 mmol), excess of $(CF_3)_2PH$ (0·011 g, 0·06 mmol), and bistrifluoromethylphosphinic acid, $(CF_3)_2P(:O)OH$ (0·020 g, 0·10 mmol), identified by i.r. spectroscopy and by the liberation of 1 mole of CF_3H on alkaline hydrolysis.

Tetrakis(trifluoromethyl)cyclotetraphosphine and Pentakis-(trifluoromethyl)cyclopentaphosphine. A mixture of $(CF_3P)_4$ and $(CF_3P)_5$ (0·023 g, 0·23 mmol of CF_3P), produced by the action of mercury on CF_3PI_2,[24] did not react with nitric oxide (0·020 g, 0·67 mmol) at room temperature (5 weeks) or at 90° (40 h).

Tetrakistrifluoromethyldiphosphine.[17] The diphosphine (0·445 g, 1·32 mmol) and nitric oxide (0·165 g, 5·48 mmol) were sealed together and left at room temperature. After 16 h the walls of the tube were covered in a heavy coating of a white solid which slowly disappeared leaving a mobile liquid after a further 3 d. After removal of nitrogen,

vacuum fractionation gave N_2O and NO (1·54 mmol together) (Found: M, 38·4), traces of COF_2 and CF_3NO_2, and *bistrifluoromethylphosphinic anhydride*, $[(CF_3)_2P(:O)]_2O$ (0·387 g, 1·00 mmol) (Found: CF_3 liberated on alkaline hydrolysis, 36·8%; M, 379. $C_4F_{12}O_3P_2$ requires CF_3 liberated on alkaline hydrolysis, 35·8%; M, 386). The new compound melted sharply at −42° to a clear colourless liquid whose vapour pressure at 0° was 8·2 mmHg. The i.r. spectrum of the vapour was recorded in a cell with a thin film of polyethylene over the potassium bromide windows as the compound reacted with alkali halides. Absorption bands occurred at 1362m,sh, 1345s, 1204vs, 1161m,sh, 992m,sh, 967s, 772w, 753w, 591s, 561m,sh, 513m, 462m, and 390m cm⁻¹.

Reactions of Bistrifluoromethylphosphinic Anhydride.—With chlorine. The phosphorus compound (0·154 g, 0·40 mmol) was recovered after being set aside with chlorine (0·030 g, 0·42 mmol) in a small sealed tube for 5 d at room temperature. *With hydrogen chloride.* Anhydrous hydrogen chloride (0·040 g, 1·09 mmol) and the phosphorus compound (0·154 g, 0·40 mmol) reacted at room temperature (42 h) to give HCl (0·0255 g, 0·70 mmol), $(CF_3)_2P(:O)Cl$ (0·089 g, 0·405 mmol) (Found: M, 218) and $(CF_3)_2P(:O)\cdot OH$ (0·077 g, 0·38 mmol), identified by i.r. spectroscopy and by the liberation of 1 mole of CF_3H on alkaline hydrolysis.

[23] F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1954, 3598.

[24] W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, 1958, **80**, 6161.