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THE REACTION OF TRIAMINOPHOSPHINES WITH PERFLUOROKETONES. THE SO-CALLED TRISDIMETHYLAMINODIFLUOROMETHYLENEPHOSPHORANE

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Mark[2] reported that the reaction of trisdimethylaminophosphine, (TA), with α-trifluoroacetophenone, (TFA), gave *trisdimethylaminodifluoromethylenephosphorane*, (I), $[(CH_3)_2N]_3PCF_2$ in 60% yield. He assigned the value of +65 ppm to the ^{31}P nmr shift of I, relative to H_3PO_4, and stated that "the structure seems to be the first example of a pentacovalent phosphorus compound with an actual phosphorus-carbon double bond (d-p overlap)" . The ylide structure I was based also on ^{19}F and ^{1}H nmr data and on infrared and mass spectrometry[2].

Several observations led us to question the ylide structure I. (1) The related ylide $[(CH_3)_2N]_3PC(CO.R)(R)$ had $\delta^{31}P = -63$ ppm[3]. Even accepting some of the rationalizations offered by Mark[2], such an effect of the fluorines on the shift was puzzling. (2) The elemental analysis of I was questionable. (3) The mass spectral data was scanty. Mark stated that "spectrometry indicated the following peaks: 179, 154 (abundant), 139, 135, 110 (abundant), 44 (abundant)" ; and that "the abundance of peak 154 indicates the ready detachment of trimethylamine from the ylide I" . (4) The ylide I was said[2] to be unreactive toward benzaldehyde, when the former was "pure" , but reactive if "impure" . We had observed a rapid reaction of the related ylide $(C_6H_5)_3PCBr_2$ with benzaldehyde[4].

We have now found that the major product, about 40%, of the reaction of TA with TFA was difluorotrisdimethylaminophosphorane, (II), a new substance. The physical properties given below, and the nmr data summarized in Table 1, agreed with those reported by Mark[2] for the ylide I. Table 1 includes data for two known trifluorobisdialkylaminophosphoranes[5,6]. The data suggest that the fluorines of II are in axial positions in a trigonal bipyramid, and that the molecule is, probably, stereochemically rigid[7]. The ^1H nmr was similar at -60°.

The major product, about 50%, of the reaction of TA with hexafluoroacetone, (HFA) was also the phosphorane II. In addition, we isolated ca. 10% of the amidate IV, $[(CH_3)_2N]_3PO$, $\delta^{31}P$ = -22 ppm, and ca. 30% of the fluoridate V, $[(CH_3)_2N]_2P(O)F$ $\delta^{31}P$ = -40 ppm, J_{PF} = 975 cps. The reaction was run at 30° and at -70° with analogous results.

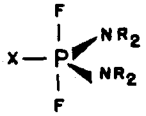
The phosphorane II was also prepared in 60% yield from TA and sulfur tetrafluoride. This shows the absence from II of the carbon atom that distinguishes it from ylide I.

$$[(CH_3)_2N]_3P + CF_3.CO.R \longrightarrow [(CH_3)_2N]_3PF_2,\ (II) \leftarrow SF_4 + [(CH_3)_2N]_3P$$

Experimental. Equimolar amounts of TA and of TFA were reacted at 30° in benzene. A fraction with b.p. 32-34° (2 mm) was obtained in 55% yield after distillations from a 12-in and a 24-in spinning band column. Only the nmr signals due to II were observable (Table 1). However, the mass spectral data showed that the liquid contained an estimated 75% of II, plus six other components in detectable concentrations. One of these was a diamino-imidophosphorofluoridate, III. The amidate IV, and the fluoridate V were also present. There seemed to be traces of the ylide I, and of an analog of it, VI, with a fluorine in place of an amino group; their concentrations could not be estimated. Most of these substances, including II, were very sensitive to moisture. Two further distillations of the liquid gave phosphorane II of estimated 95+% purity, by mass spectrometry; b.p. 35° (3 mm); n_D^{25} 1.4190, d^{25} 1.0604; anal. found: C, 36.1; H, 9.2; N, 21.3; F, 18.7; P, 15.4; mol. wt. 193 (cryoscopic in benzene). $C_6H_{18}N_3F_2P$ requires: C, 35.8; H, 8.9; N, 20.9; F, 18.9; P, 15.4; mol. wt. 201.

The IR spectrum[8] was examined from 80 to 4000 cm^{-1}. The bands at 107 and 740 cm^{-1} are attributed to the axial bending and the asym. stretching modes of the PF_2, respectively. In Cl_3PF_2[9] these were at 122 and 678 cm^{-1}.

Table 1. NMR Shifts, in ppm, of Fluoroaminophosphoranes. δP vs H_3PO_4. δF vs CF_3COOH. J, cps. [a]This work. [b]Ref. 2. [c]Ref. 5. [d] Ref. 6



NMR	X = $N(CH_3)_2$[a] R = CH_3	Lit.[b]	X = F R = C_2H_5	X = F R = CH_3
δP	+65.7	+65.5	+63.7[c]	....
δF(ax)	-25.1	-25.2	-17.0[c]; -11.8[d]	-17.3[d]
δF(eq)	none	none	-9.0[c]; -3.6[d]	+1.4[d]
$J_{F(ax)P}$	700	705	758[c]; 753[d]	752[d]
$J_{F(eq)P}$	none	none	890[c]; 876[d]	871[d]
τH	7.40	7.36	....	7.35[d]
J_{HP}	10.5	10.8	....	11[d]
$J_{HF(ax)}$	2.8	2.9	....	2.8[d]

Table 2. Assignment of peaks in the Mass Spectrum[a] of the Liquid Boiling at 32-34° (2.5 mm)[b] Obtained from the Reaction of Trisdimethylaminophosphine with α,α,α-Trifluoroacetophenone (1:1 mole ratio), in Benzene at 30°, Difluorotrisdimethylaminophosphorane, II, is the Major Constituent (Estimated Concentration 75%).

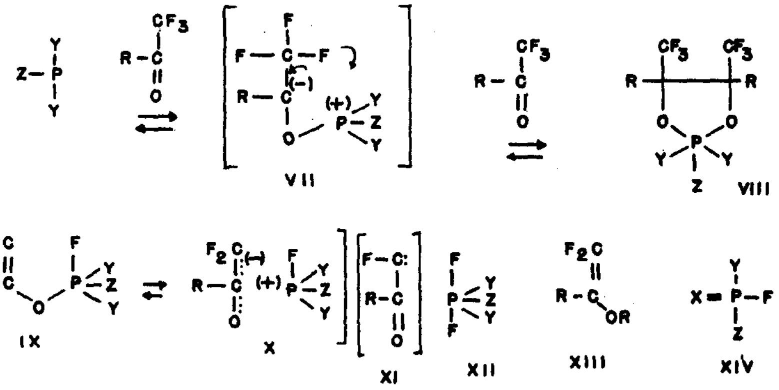
N°	Probable Structure	Parent Mass	Masses of Associated Fragment-ions
II	$[(CH_3)_2N]_3PF_2$[c]	201	182^d, 157^e, 141^f, 138^f, 113^f, 112^g, 94^h, 69^i
III	$[(CH_3)_2N]_2P(NCH_3)F$	167	
IV	$[(CH_3)_2N]_3PO$	179	135^e
V	$[(CH_3)_2N]_2P(O)F$	154	153^j, 110^e
I	$[(CH_3)_2N]_3P{=}CF_2$	213	212^j, 211, 210
VI	$[(CH_3)_2N]_2(F)P{=}CF_2$	188	187^j, 186, 185
	$[(CH_3)_2N]_3P$	163	119^e

[a] A limited application of the method given by S. Meyerson, *Anal. Chem.*, *31*, 174 (1959) led to partial spectra attributed to the seven components listed. Peaks so identified as arising wholly from a single component are listed here. An intense peak at mass 44 assigned to the $(CH_3)_2N^+$ ion evidently contains contributions from several components. In the case of the phosphorane II, the *phosphoranyl radical* (cf. Ref. 4a) is lost in the formation of this ion. [b] After distillations from 12-in. and 24-in. spinning band columns. [c] Repeated distillations of II gave small amounts of a substance which showed a parent peak at 219 and a fragment-ion peak at 175. This substance disappeared after several days; it probably is $[(CH_2F)(CH_3)N][(CH_3)_2N]_2PF_2$. [d] Loss of F atom from parent ion. [e] Loss of $(CH_3)_2N$. [f] Loss of CH_4, F, and $(CH_3)_2N$, respectively, from the 157-ion. [g] Loss of H from 113. [h] Loss of $(CH_3)_2N$ from 138-ion. [i] Loss of $(CH_3)_2N$ from 113-ion. [j] Loss of H.

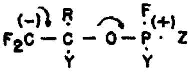
Trialkyl phosphites and trisdimethylaminophosphine attacked the carbonyl-oxygen of vicinal polycarbonyl compounds[10]. The phosphites[11a] and the aminophosphine[11b], however, added to the carbonyl-carbon of aliphatic monoaldehydes. Phosphite, phosphonites and phosphinites, as well as triphenylphosphine gave 2:1 adducts, VIII, with hexafluoroacetone (HFA)[10]. These were formed via the 1:1 adducts VII; i.e., the presence of the fluorine atoms directed the phosphorus to the oxygen of the monoketone.

The pyrolysis of the HFA-triphenylphosphine adduct, VIII (R CF$_3$; Y Z C$_6$H$_5$), gave mostly HFA and the phosphine, and some difluorotriphenylphosphorane[12], XII (^{31}P +58.1 ppm; triplet, J$_{PF}$ 659 cps) and oxide (C$_6$H$_5$)$_3$PO. Pyrolysis of the HFA-triethyl phosphite adduct, VIII (R CF$_3$; Y Z OC$_2$H$_5$) gave mostly the fluoridate XIV (Y Z OC$_2$H$_5$; X O) and the phosphate (C$_2$H$_5$O)$_3$PO, in a 3:1 mole ratio. Part of the fluoridate XIV resulted from the intermediate difluorotriethoxyphosphorane, XII; part of XIV was formed in a reaction that produced also the perfluoroethoxypropene XIII.

The products listed in Table 2 can be derived similarly.



The phosphorane II is XII ($Y = Z = N(CH_3)_2$), and can originate, together with XI, from IX or X *via* the 1:1 adduct VII. The imidfluoridate III is XIV ($Y = Z = N(CH_3)_2$; $X = NCH_3$), and could result from X by oxygen attack on a methyl group, or from XII by the loss of CH_3F. The amidate IV can form in several ways: from VII, VIII or IX, or by the hydrolysis of XII (II). The fluoridate V is XIV ($Y = Z = N(CH_3)_2$; $X = O$), and can result from IX *via* XV; or IX may be converted into XIV intramolecularly. The fluoridate V may be also a product of the hydrolysis of XII (II). The ylides I and VI may result from the recombination of X at carbon to give $R.CO.CF_2.P(FY_2Z)$, followed by carbon-carbon fission.



$$\overset{(-)}{F_2C} - \underset{Y}{\overset{R}{C}} - O - \underset{Y}{\overset{F}{P}}{}^{(+)} \cdot Z$$

(XV)

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