

## Derivatives of Acetamide containing Difluorophosphino-groups

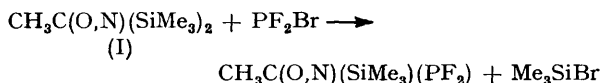
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Bis(trimethylsilyl)acetamide reacts with an equimolar proportion of  $\text{PF}_2\text{Br}$  at  $-80^\circ\text{C}$  to give  $\text{CH}_3\text{C}(\text{OSiMe}_3)\text{:NPF}_2$ . With an excess of  $\text{PF}_2\text{Br}$ , the initial product at  $-80^\circ\text{C}$  is  $\text{CH}_3\text{C}(\text{OPF}_2)\text{:NPF}_2$ ; at temperatures above  $-40^\circ\text{C}$  there is a slow rearrangement to give a mixture of  $\text{CH}_3\text{C}(\text{OPF}_2)\text{:NPF}_2$  and  $\text{CH}_3\text{CON}(\text{PF}_2)_2$ . All these  $\text{PF}_2$  derivatives of acetamide decompose slowly at room temperature to give acetonitrile and either  $\text{PF}_2\text{OSiMe}_3$  or  $(\text{PF}_2)_2\text{O}$ . They have been characterised by  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  n.m.r. and by i.r. spectroscopy. There was no evidence for fast exchange of  $\text{PF}_2$  groups between N and O sites.

BIS(TRIMETHYLSILYL)ACETAMIDE, (I), has proved to be an important silylating agent.<sup>1</sup> The n.m.r. and i.r. spectra indicate that the compound should not be described as an amide, but rather as an oxyimine, with one trimethylsilyl group bound to nitrogen and one to oxygen.<sup>2</sup> There is exchange of trimethylsilyl groups between the two sites that is rapid on the  $^1\text{H}$  n.m.r. time-scale at room temperature but at low temperature is slow enough to allow observation of two separate resonances in the  $\text{Me}_3\text{Si}$  region.<sup>2</sup> In the past we have synthesised a range of new compounds containing  $\text{PF}_2$  groups by exchange between  $\text{PF}_2\text{Br}$  and silyl, germyl, and stannyl derivatives,<sup>3,4</sup> and as part of this programme we have investigated the reaction between  $\text{PF}_2\text{Br}$  and (I). We hoped that the use of  $^{31}\text{P}$  and  $^{19}\text{F}$  n.m.r. spectroscopy would enable us to characterise any products relatively easily, and would also afford a way of investigating any possible exchange processes over a range of possible timescales.

### RESULTS

The  $^{31}\text{P}$  and  $^{19}\text{F}$  n.m.r. spectra of a solution containing equimolar proportions of  $\text{PF}_2\text{Br}$  and (I) at  $-80^\circ\text{C}$  showed that all the  $\text{PF}_2\text{Br}$  initially added was rapidly consumed; the  $^1\text{H}$  n.m.r. spectrum established that  $\text{Me}_3\text{SiBr}$  was liberated. Only one  $^{31}\text{P}$  resonance was observed from the products: this showed the wide triplet coupling associated with a  $\text{PF}_2$  group. The proton resonance spectrum of the purified reaction product shows two sharp singlets with the relative intensities 1:3. These spectra are most easily explained if we suppose that one trimethylsilyl group has been exchanged for  $\text{PF}_2$ , giving a product containing one  $\text{PF}_2$  group and one trimethylsilyl group bound to the amide function:



The  $^{31}\text{P}$  chemical shift of the product (see Table 1) is consistent with P bound to N rather than O, and varies with temperature as found in related derivatives known to contain  $\text{PF}_2\text{N}$  groups;<sup>4</sup> furthermore, the lines in the  $^{31}\text{P}$  spectrum are somewhat broadened, presumably as a result of interaction with the quadrupole moment of  $^{14}\text{N}$ . This broadening is often observed in  $\text{PF}_2\text{N}$  compounds,<sup>4</sup> but not in derivatives containing  $\text{PF}_2$  bound to O.<sup>5</sup> The line-widths increased slightly when the temperature was reduced, and this line did not split, so we do not believe that the broadening is due to an exchange process. We therefore

conclude that  $\text{PF}_2$  is bound to N in our product. The i.r. spectrum (see Table 2) shows no strong band in the region associated with C=O groups, but a weak band at  $1590\text{ cm}^{-1}$  which can be associated with a C=N- unit in the molecule, and so we formulate (II) as  $\text{CH}_3\text{C}(\text{OSiMe}_3)\text{:NPF}_2$ .

The n.m.r. spectra of (II) show no evidence of exchange involving  $\text{PF}_2$  groups, such as additional line-broadening, at temperatures up to  $30^\circ\text{C}$ . However, at room temperature the compound decomposes over a period of hours, forming  $\text{Me}_3\text{SiOPF}_2$  and  $\text{CH}_3\text{CN}$ .

TABLE 1

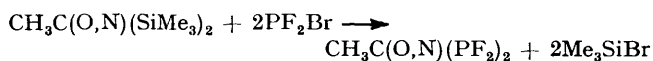
N.m.r. parameters for  $\text{PF}_2$  derivatives of acetamide (Italic values were obtained from solutions in  $\text{CDCl}_3$ ; others from solutions in  $\text{C}_6\text{D}_6\text{-C}_7\text{H}_8$ )

Compound	$\delta$ (P)/ p.p.m.		$\delta$ (F)/ p.p.m.	$\delta$ ( $\text{CH}_3\text{C}$ )/ $^1J$ (PF)/ p.p.m. Hz	
	213 K	273 K	273 K	273 K	273 K
(IIIa): $\text{OPF}_2$	158.5	155.2	-63.8	1.86 <sup>a</sup>	1 248
N $\text{PF}_2$	121.2	121.4	-56.3	2.33	1 340
(IIIb)	151.7	148.5	-65.7		1 269
(IV)	145.3	146.0 <sup>b</sup>	-69.4	2.39	1 297
	nm <sup>*</sup>	144.1 <sup>c</sup>	-72.8	2.15	1 235

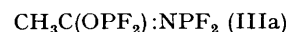
<sup>a</sup>  $\delta$  (H) ( $\text{Me}_3\text{Si}$ ) = 0.31 p.p.m. <sup>b</sup>  $\delta^2J$ (PP) = 32.7; <sup>3</sup> $J$ (PF) = +34.9; <sup>4</sup> $J$ (PH) = 4.5; <sup>5</sup> $J$ (FH) = 0.9 Hz. <sup>c</sup>  $\delta$ (NH) = 7.0 p.p.m.; <sup>3</sup> $J$ (FH) = 4.2; <sup>4</sup> $J$ (PH) = 2.4; <sup>5</sup> $J$ (FH) = 0.4 Hz.

\* Not measured.

If a three-fold molar excess of  $\text{PF}_2\text{Br}$  was taken initially, the  $^1\text{H}$  resonance spectrum of the product at  $-80^\circ\text{C}$  showed that the only compound present containing the  $\text{Me}_3\text{Si}$  group was  $\text{Me}_3\text{SiBr}$ . It is evidence that both  $\text{Me}_3\text{Si}$  groups were eliminated from (I) by exchange:

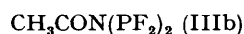


Two different triplet resonances were observed in the  $^{31}\text{P}$  spectrum at  $-80^\circ\text{C}$ ; the large triplet couplings showed that both were due to  $\text{PF}_2$  groups. One set of triplet lines were substantially broader than the other, and its chemical shift corresponded to that expected from  $\text{PF}_2\text{N}$  compounds: the other triplet was sharper, and the associated chemical shift was in keeping with that expected from a  $\text{PF}_2$  group bound to O. We conclude that the initial product of the reaction, (IIIa), contains one  $\text{PF}_2$  group bound to N and the other bound to O:



In keeping with this conclusion, the  $^{19}\text{F}$  spectrum showed two doublets, the splittings corresponding to those in the two triplets from the  $^{31}\text{P}$  spectrum. There were no significant changes in the  $^{31}\text{P}$  or the  $^{19}\text{F}$  spectra as the sample

was allowed to warm from  $-80$  to  $-40$  °C; none of the lines broadened, though the chemical shift of the  $\text{PF}_2\text{N}$ -phosphorus nucleus changed somewhat. At  $-20$  °C, new peaks began to appear in both  $^{31}\text{P}$  and  $^{19}\text{F}$  spectra, and after half an hour at room temperature the n.m.r. spectra indicated that there was about three times as much of the new material as of (IIIa). The new species showed a single set of  $\text{PF}_2$  resonances in both the  $^{31}\text{P}$  and  $^{19}\text{F}$  spectra. The peaks were somewhat broadened, particularly in the  $^{31}\text{P}$  spectrum. Second-order effects could clearly be distinguished, implying that at least two  $\text{PF}_2$  groups were bound to the same heteroatom; the spectra clearly resembled those obtained from  $(\text{PF}_2)_2\text{NH}$ , and could be analysed approximately on the assumption that the spin system was of the form  $(\text{AX}_2)_2\text{Q}$ . These observations, together with the  $^{31}\text{P}$  chemical shift (in the region characteristic of  $\text{PF}_2\text{N}$ ) show that the new species is an isomer of (IIIa) in which both  $\text{PF}_2$  groups are bound to nitrogen:



The  $^1\text{H}$  resonance spectrum of pure compound (III) at room temperature does not give much information but shows a complicated line pattern due to very small and slightly different coupling constants of the two isomers which have almost identical chemical shift values as well. When the

TABLE 2  
I.r. spectra of  $\text{PF}_2$  derivatives of acetamide

(II)	Frequencies ( $\text{cm}^{-1}$ ) (IIIa/b) mixture		Assignments *
	Vapour	Liquid film	
2 975m	2 980w	2 980w	$\nu_{\text{CH}}$
2 920w			
1 700w, br		1 704w, br	$? 2 \times 855$
	1 660vw	1 655mw	$\nu_{\text{CO}}$
1 590w		1 605w	$\nu_{\text{C-N}}$
1 425w			$\delta_{\text{CH}_3}$ (asym)
1 270s			$\delta_{\text{CH}_3\text{Si}}$ (sym)
		1 259mw	
1 120w			
	1 080m	1 090mw	$\nu_{\text{POC}}$
		1 045mw	
1 042vs			$\nu_{\text{SiOC}}$
	980vs	980vs	$\nu_{\text{PNC}}$
862vs.	855vs, br	855vs, br	$\nu_{\text{PF}}$ and (?) $\rho_{\text{CH}_3\text{Si}}$
815s			
	680m	680ms	
	520m	521m	$\delta_{\text{PF}_2}$
		468mw	

v = Very; br = broad; s = strong; m = medium intensity; w = weak.

\* D. E. C. Corbridge, *Topics Phosphorus Chem.*, 1971, **6**, 235.

solution was cooled again to  $-50$  °C and kept at that temperature for some time, the relative intensities of peaks due to (IIIa) and (IIIb) remained unchanged; there was no evidence of exchange between the two forms at any temperature we studied. The molar proportions of (IIIa) and (IIIb) did not change if the solution was left at room temperature for a long time; slow decomposition led to the formation of  $(\text{PF}_2)_2\text{O}$  and  $\text{CH}_3\text{CN}$ . The n.m.r. parameters are given in Table 1.

It proved possible by low-temperature fractionation to obtain samples of (II) and of (IIIa/b) whose i.r. spectra were free of peaks due to  $\text{Me}_3\text{SiBr}$ . The spectra help to confirm that the structures we propose are correct. The spectrum of (II) contains peaks due to  $\text{Me}_3\text{Si}$  groups, but no strong band that can be assigned to  $\nu(\text{CO})$ ; the spectrum of (IIIa/b) contains a band in the region associated with  $\nu(\text{CO})$ ,

but no strong bands assignable to  $\text{Me}_3\text{Si}$  groups. The observed frequencies, with tentative assignments, are given in Table 2. We have also recorded the mass spectrum of the equilibrium mixture of (IIIa/b). We were able to detect a weak peak due to the molecular ion, together with peaks due to  $\text{CH}_3\text{CN}^+$ ,  $(\text{PF}_2)_2\text{O}^+$ , and  $\text{PF}_2\text{O}^+$ .

Treatment of (IIIa/b) with water gave a white solid whose  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{31}\text{P}$  n.m.r. spectra led us to identify it as  $\text{CH}_3\text{CONHPF}_2$  (IV) which was also formed in traces when  $\text{PF}_2\text{Br}$  reacted with  $\text{CH}_3\text{CONH}_2$ . It too decomposed slowly at room temperature. Reaction between acetamide and  $\text{PF}_2\text{Br}$  led to the formation of traces of (IV), together with large quantities of white solid; however, no derivatives of acetamide containing  $\text{PF}_2$  groups could be detected among the products of reaction between  $\text{PF}_2\text{NH}_2$  and acetyl chloride. There was no reaction between  $\text{PF}_2\text{Br}$  and bis-(trimethylsilyl)trifluoroacetamide at temperatures up to  $+80$  °C.

## DISCUSSION

It is clear from these results that although amide-type derivatives in which  $\text{PF}_2$  groups are bound to the amide function can be obtained, they do not show exchange of  $\text{PF}_2$  groups between O and N sites that is fast on the n.m.r. timescale at room temperature, as would be analogous to the exchange of  $\text{Me}_3\text{Si}$  groups between O and N sites in the silylamides. The initial exchange between (I) and  $\text{PF}_2\text{Br}$  involves the trimethylsilyl group that is bound to N. At least with respect to  $\text{PF}_2\text{Br}$  the two trimethylsilyl groups show quite different reactivities and there is no evidence that in (II) the remaining trimethylsilyl group spends any of its time bound to N rather than O. If fast exchange of  $\text{Me}_3\text{Si}$  between O and N does occur in (II) under the conditions of our experiments, either it must be so fast that even at  $-80$  °C the spectrum observed is of the time-averaged environment, or the equilibrium must lie very heavily on the side of the form with  $\text{Me}_3\text{Si}$  bound to O. The slow transformation of (IIIa) into a mixture of (IIIa) and (IIIb) indicates that some kind of isomerisation between (IIIa) and (IIIb) occurs that is slow at or just below room temperature, and the constancy of the composition of the mixture of (IIIa) and (IIIb) over a period of time implies that some sort of equilibrium is reached. We obtained no evidence for fast exchange of  $\text{PF}_2$  groups between O and N sites in (III). Despite the initial formation of  $\text{PF}_2\text{N}$  rather than  $\text{PF}_2\text{O}$  species, the decomposition products contain  $\text{PF}_2\text{O}$  rather than  $\text{PF}_2\text{N}$  bonds; this presumably reflects the thermodynamic stability of the other decomposition product acetonitrile. The thermal instability of all  $\text{PF}_2$  amides is noteworthy. The absence of any reaction between  $\text{PF}_2\text{Br}$  and  $\text{CF}_3\text{C}(\text{O},\text{N})(\text{SiMe}_3)_2$  may well be associated with the electron-withdrawing properties of the  $\text{CF}_3$  group, and implies that exchange of  $\text{PF}_2$  for  $\text{Me}_3\text{Si}$  is associated with electrophilic attack at the amide function.

## EXPERIMENTAL

Volatile compounds were handled in standard vacuum apparatus, fitted with greased glass or greaseless polyfluoro

ethylene (Sovirel) taps; involatile compounds that were sensitive to air or moisture were handled in a glove-box made by Vacuum Atmospheres. The mass spectrum was obtained using an AEI MS902 spectrometer. I.r. spectra were recorded in the range 4 000–350  $\text{cm}^{-1}$  by means of a Beckman IR11 double-beam spectrometer, and Raman spectra with a Cary 83 instrument fitted with an argon ion laser. Proton and  $^{19}\text{F}$  n.m.r. routine spectra were recorded by means of a Varian Associates EM 360 spectrometer, and  $^{19}\text{F}$  and  $^{31}\text{P}$  spectra were obtained by means of a Varian Associates XL100 spectrometer operating in the FT mode. Compound (I) was obtained commercially and  $\text{PF}_2\text{Br}$  was prepared by an established method.<sup>6</sup>

*Reactions in N.M.R. Tubes.*—Compound (I) (0.4 mmol) was introduced into an n.m.r. tube in a glove-box; solvent (20%  $\text{C}_6\text{D}_6$  and 80% toluene) was distilled into the tube on the vacuum-line, followed by the appropriate amount of  $\text{PF}_2\text{Br}$ . The tube was kept at 77 K until the spectrum was to be recorded, when the sample was allowed to warm to the desired temperature in the n.m.r. probe.

*Preparation of Compound (II).*—In a typical experiment, compound (I) (3.0 mmol) and  $\text{PF}_2\text{Br}$  (3.0 mmol) were allowed to mix in an ampoule fitted with a greaseless tap at room temperature (30 min). Repeated fractional distillation and condensation in the vacuum system gave a sample of (II) whose  $^1\text{H}$  resonance and i.r. spectrum showed the absence of  $\text{Me}_3\text{SiBr}$  and whose  $^{19}\text{F}$  and  $^{31}\text{P}$  spectra corresponded with those obtained from a similar reaction that was allowed to occur in toluene in an n.m.r. tube. Compound (II) was not very volatile *in vacuo* (v.p. = 20 mmHg\* at 293 K); over a period of hours at room temperature it decomposed to  $\text{CH}_3\text{CN}$  and  $\text{Me}_3\text{SiOPF}_2$  (both identified spectroscopically).<sup>7</sup>

*Preparation of Compound (III).*—Compound (I) (5.0 mmol) and  $\text{PF}_2\text{Br}$  (15.0 mmol) were allowed to react at room temperature in an ampoule fitted with a greaseless tap. Repeated fractional distillation and condensation in a vacuum system gave a sample of (IIIa/b) whose i.r. spectrum contained no peaks characteristic of  $\text{Me}_3\text{Si}$  groups. The i.r. and Raman spectra of this sample were recorded; the n.m.r. spectra corresponded with those obtained from the product of a similar reaction in an n.m.r. tube. On standing for several hours at room temperature, the compound

\* Throughout this paper: 1 mmHg  $\approx$  13.6  $\times$  9.8 Pa.

decomposed slowly into  $\text{CH}_3\text{CN}$  and  $(\text{PF}_2)_2\text{O}$  (both identified spectroscopically).<sup>6</sup>

*Reaction of Compound (III) with Water.*—Compound (III) (4.0 mmol) and  $\text{H}_2\text{O}$  (2.0 mmol) were allowed to react together in an ampoule to whose side was sealed an n.m.r. tube. A white solid soon formed at room temperature. Volatile materials were removed,  $\text{CDCl}_3$  and  $\text{Me}_4\text{Si}$  were distilled into the tube, and the solution sealed in the n.m.r. tube. The spectra established that the product was  $\text{CH}_3\text{CONHPPF}_2$ ; the n.m.r. parameters are given in Table 1.

*Reaction of  $\text{PF}_2\text{Br}$  with  $\text{CH}_3\text{CONH}_2$ .*—Dried acetamide (0.8 mmol) was allowed to react with  $\text{PF}_2\text{Br}$  (0.4 mmol) at room temperature in  $\text{CDCl}_3$ . A substantial amount of white fluffy solid was formed immediately. The n.m.r. spectrum of the product showed that a small amount of  $\text{CH}_3\text{CONHPPF}_2$  had been formed.

*Reaction of  $\text{PF}_2\text{NH}_2$  with  $\text{CH}_3\text{COCl}$ .* When  $\text{PF}_2\text{NH}_2$  (1.50 mmol) was allowed to react with  $\text{CH}_3\text{COCl}$  (1.00 mmol) at room temperature white and pale yellow solids were formed. The only volatile material recovered was  $\text{PF}_3$  (0.4 mmol) and a mixture of  $\text{PF}_2\text{NH}_2$  and  $\text{CH}_3\text{COCl}$  (0.9 mmol in all). When  $\text{PF}_2\text{NH}_2$  (1.00 mmol),  $\text{CH}_3\text{COCl}$  (1.10 mmol), and  $\text{Me}_3\text{N}$  (1.00 mmol) were allowed to react together, the volatile material recovered was a mixture of  $\text{PF}_2\text{NH}_2$  and  $\text{CH}_3\text{COCl}$  (0.65 mmol).

*Reaction of  $\text{CF}_3\text{CON}(\text{SiMe}_3)_2$  with  $\text{PF}_2\text{Br}$ .*—Mixing of these two reagents in varying concentrations, at temperatures of up to 323 K, led only to the recovery of starting materials.

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#### REFERENCES

- 1 L. Birkhofer and A. Ritter, *Angew. Chem.*, 1965, **77**, 414.
- 2 W. Kantlehner, W. Kugel, and A. Brederbeck, *Chem. Ber.*, 1972, **105**, 2264.
- 3 E. A. V. Ebsworth, D. J. Hutchison, and D. W. H. Rankin, unpublished work.
- 4 D. E. J. Arnold, E. A. V. Ebsworth, H. F. Jessep, and D. W. H. Rankin, *J.C.S. Dalton*, 1972, 1681.
- 5 J. F. Nixon, *Adv. Inorg. Chem. Radiochem*, 1970, **13**, 363.
- 6 J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Synth.*, 1967, **10**, 154.
- 7 R. G. Cavell, R. D. Leary, A. R. Sanger, and A. J. Tomlinson, *Inorg. Chem.*, 1973, **12**, 1374.