Derivatives of Acetamide containing Difluorophosphino-groups

By **E. A. V. Ebsworth, David W. H. Rankin, Wolfgang Steger,** and (in part) **John G. Wright,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

Bis(trimethylsilyl)acetamide reacts with an equimolar proportion of PF_2Br at −80 °C to give $CH_3C(OSiMe_3){:}NPF_2$. With an excess of PF_2Br, the initial product at −80 °C is $CH_3C(OPF_2){:}NPF_2$; at temperatures above −40 °C there is a slow rearrangement to give a mixture of $CH_3C(OPF_2){:}NPF_2$ and $CH_3CON(PF_2)_2$. All these PF_2 derivatives of acetamide decompose slowly at room temperature to give acetonitrile and either PF_2OSiMe_3 or $(PF_2)_2O$. They have been characterised by ^1H, ^{19}F, and ^{31}P n.m.r. and by i.r. spectroscopy. There was no evidence for fast exchange of PF_2 groups between N and O sites.

BIS(TRIMETHYLSILYL)ACETAMIDE, (I), has proved to be an important silylating agent.[1] 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.[2] There is exchange of trimethylsilyl groups between the two sites that is rapid on the ^1H n.m.r. timescale at room temperature but at low temperature is slow enough to allow observation of two separate resonances in the Me_3Si region.[2] In the past we have synthesised a range of new compounds containing PF_2 groups by exchange between PF_2Br and silyl, germyl, and stannyl derivatives,[3,4] and as part of this programme we have investigated the reaction between PF_2Br and (I). We hoped that the use of ^{31}P and ^{19}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}P and ^{19}F n.m.r. spectra of a solution containing equimolar proportions of PF_2Br and (I) at −80 °C showed that all the PF_2Br initially added was rapidly consumed; the ^1H n.m.r. spectrum established that Me_3SiBr was liberated. Only one ^{31}P resonance was observed from the products: this showed the wide triplet coupling associated with a 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 PF_2, giving a product containing one PF_2 group and one trimethylsilyl group bound to the amide function:

$$\underset{\text{(I)}}{CH_3C(O,N)(SiMe_3)_2} + PF_2Br \longrightarrow CH_3C(O,N)(SiMe_3)(PF_2) + Me_3SiBr$$

The ^{31}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 PF_2N groups;[4] furthermore, the lines in the ^{31}P spectrum are somewhat broadened, presumably as a result of interaction with the quadrupole moment of ^{14}N. This broadening is often observed in PF_2N compounds,[4] but not in derivatives containing PF_2 bound to O.[5] The linewidths 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 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 1 590 cm^{-1} which can be associated with a $C{=}N^-$ unit in the molecule, and so we formulate (II) as $CH_3C(OSiMe_3){:}NPF_2$.

The n.m.r. spectra of (II) show no evidence of exchange involving PF_2 groups, such as additional line-broadening, at temperatures up to 30 °C. However, at room temperature the compound decomposes over a period of hours, forming Me_3SiOPF_2 and CH_3CN.

TABLE 1

N.m.r. parameters for PF_2 derivatives of acetamide (Italic values were obtained from solutions in $CDCl_3$; others from solutions in C_6D_6–C_7H_8)

Compound	δ (P)/ p.p.m.		δ (F)/ p.p.m.	δ (CH_3C)/ p.p.m.	^1J(PF)/ Hz
	213 K	273 K	273 K	273 K	273 K
	158.5	155.2	−63.8	1.86 [a]	1 248
(IIIa): OPF_2	121.2	121.4	−56.3	*2.33*	1 340
NPF_2	151.7	148.5	−65.7		1 269
(IIIb)	145.3	146.0 [b]	−69.4	*2.39*	1 297
(IV)	nm *	144.1 [c]	−72.8	*2.15*	1 235

[a] δ (H) (Me_3Si) = 0.31 p.p.m. [b] δ^2J(PP) = *32.7*; ^3J(PF) = +34.9; ^4J(PH) = *4.5*; ^5J(FH) = *0.9* Hz. [c] δ(NH) = 7.0 p.p.m.; ^3J(FH) = *4.2*; ^4J(PH) = *2.4*; ^5J(FH) = *0.4* Hz.

* Not measured.

If a three-fold molar excess of PF_2Br was taken initially, the ^1H resonance spectrum of the product at −80 °C showed that the only compound present containing the Me_3Si group was Me_3SiBr. It is evidence that both Me_3Si groups were eliminated from (I) by exchange:

$$CH_3C(O,N)(SiMe_3)_2 + 2PF_2Br \longrightarrow CH_3C(O,N)(PF_2)_2 + 2Me_3SiBr$$

Two different triplet resonances were observed in the ^{31}P spectrum at −80 °C; the large triplet couplings showed that both were due to PF_2 groups. One set of triplet lines were substantially broader than the other, and its chemical shift corresponded to that expected from PF_2N compounds: the other triplet was sharper, and the associated chemical shift was in keeping with that expected from a PF_2 group bound to O. We conclude that the initial product of the reaction, (IIIa), contains one PF_2 group bound to N and the other bound to O:

$$CH_3C(OPF_2){:}NPF_2 \text{ (IIIa)}$$

In keeping with this conclusion, the ^{19}F spectrum showed two doublets, the splittings corresponding to those in the two triplets from the ^{31}P spectrum. There were no significant changes in the ^{31}P or the ^{19}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 PF_2N-phosphorus nucleus changed somewhat. At −20 °C, new peaks began to appear in both ^{31}P and ^{19}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 PF_2 resonances in both the ^{31}P and ^{19}F spectra. The peaks were somewhat broadened, particularly in the ^{31}P spectrum. Second-order effects could clearly be distinguished, implying that at least two PF_2 groups were bound to the same heteroatom; the spectra clearly resembled those obtained from $(PF_2)_2NH$, and could be analysed approximately on the assumption that the spin system was of the form $(AX_2)_2Q$. These observations, together with the ^{31}P chemical shift (in the region characteristic of PF_2N) show that the new species is an isomer of (IIIa) in which both PF_2 groups are bound to nitrogen:

$$CH_3CON(PF_2)_2 \text{ (IIIb)}$$

The ^1H 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 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 $(PF_2)_2O$ and CH_3CN. The n.m.r. parameters are given in Table 1.

TABLE 2

I.r. spectra of PF_2 derivatives of acetamide

(II)	Frequencies (cm^{-1}) (IIIa/b) mixture		Assignments *
Vapour	Vapour	Liquid film	
2 975m	2 980w	2 980w	ν_{CH}
2 920w			
1 700w, br		1 704w, br	?2 × 855
	1 660vw	1 655mw	ν_{CO}
1 590w		1 605w	$\nu_{C=N}$
1 425w			δ_{CH_3} (asym)
1 270s			δ_{CH_3Si} (sym)
		1 259mw	
1 120w			
	1 080m	1 090mw	ν_{POC}
		1 045mw	
1 042vs			ν_{SiOC}
	980vs	980vs	ν_{PNC}
862vs.	855vs, br	855vs, br	ν_{PF} and (?) ρ_{CH_3Si}
815s			
	680m	680ms	
518mw	520m	521m	δ_{PF_2}
		468mw	

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

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

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 Me_3SiBr. The spectra help to confirm that the structures we propose are correct. The spectrum of (II) contains peaks due to Me_3Si groups, but no strong band that can be assigned to ν(CO); the spectrum of (IIIa/b) contains a band in the region associated with ν(CO), but no strong bands assignable to Me_3Si 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 CH_3CN^+, $(PF_2)_2O^+$, and PF_2O^+.

Treatment of (IIIa/b) with water gave a white solid whose ^1H, ^{19}F, and ^{31}P n.m.r. spectra led us to identify it as $CH_3CONHPF_2$ (IV) which was also formed in traces when PF_2Br reacted with CH_3CONH_2. It too decomposed slowly at room temperature. Reaction between acetamide and PF_2Br led to the formation of traces of (IV), together with large quantities of white solid; however, no derivatives of acetamide containing PF_2 groups could be detected among the products of reaction between PF_2NH_2 and acetyl chloride. There was no reaction between PF_2Br and bis(trimethylsilyl)trifluoroacetamide at temperatures up to +80 °C.

DISCUSSION

It is clear from these results that although amide-type derivatives in which PF_2 groups are bound to the amide function can be obtained, they do not show exchange of 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 Me_3Si groups between O and N sites in the silylamides. The initial exchange between (I) and PF_2Br involves the trimethylsilyl group that is bound to N. At least with respect to PF_2Br 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 Me_3Si 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 Me_3Si 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 PF_2 groups between O and N sites in (III). Despite the initial formation of PF_2N rather than PF_2O species, the decomposition products contain PF_2O rather than PF_2N bonds; this presumably reflects the thermodynamic stability of the other decomposition product acetonitrile. The thermal instability of all PF_2 amides is noteworthy. The absence of any reaction between PF_2Br and $CF_3C(O,N)(SiMe_3)_2$ may well be associated with the electron-withdrawing properties of the CF_3 group, and implies that exchange of PF_2 for Me_3Si 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 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}F n.m.r. routine spectra were recorded by means of a Varian Associates EM 360 spectrometer, and ^{19}F and ^{31}P spectra were obtained by means of a Varian Associates XL100 spectrometer operating in the FT mode. Compound (I) was obtained commercially and PF_2Br was prepared by an established method.[6]

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% C_6D_6 and 80% toluene) was distilled into the tube on the vacuum-line, followed by the appropriate amount of PF_2Br. 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 PF_2Br (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 ^1H resonance and i.r. spectrum showed the absence of Me_3SiBr and whose ^{19}F and ^{31}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 CH_3CN and Me_3SiOPF_2 (both identified spectroscopically).[7]

Preparation of Compound (III).—Compound (I) (5.0 mmol) and PF_2Br (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 Me_3Si 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 decomposed slowly into CH_3CN and $(PF_2)_2O$ (both identified spectroscopically).[5]

Reaction of Compound (III) with Water.—Compound (III) (4.0 mmol) and H_2O (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, $CDCl_3$ and Me_4Si were distilled into the tube, and the solution sealed in the n.m.r. tube. The spectra established that the product was $CH_3CONHPF_2$; the n.m.r. parameters are given in Table 1.

Reaction of PF_2Br *with* CH_3CONH_2.—Dried acetamide (0.8 mmol) was allowed to react with PF_2Br (0.4 mmol) at room temperature in $CDCl_3$. A substantial amount of white fluffy solid was formed immediately. The n.m.r. spectrum of the product showed that a small amount of $CH_3CONHPF_2$ had been formed.

Reaction of PF_2NH_2 *with* CH_3COCl. When PF_2NH_2 (1.50 mmol) was allowed to react with CH_3COCl (1.00 mmol) at room temperature white and pale yellow solids were formed. The only volatile material recovered was PF_3 (0.4 mmol) and a mixture of PF_2NH_2 and CH_3COCl (0.9 mmol in all). When PF_2NH_2 (1.00 mmol), CH_3COCl (1.10 mmol), and Me_3N (1.00 mmol) were allowed to react together, the volatile material recovered was a mixture of PF_2NH_2 and CH_3COCl (0.65 mmol).

Reaction of $CF_3CON(SiMe_3)_2$ *with* PF_2Br.—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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* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

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