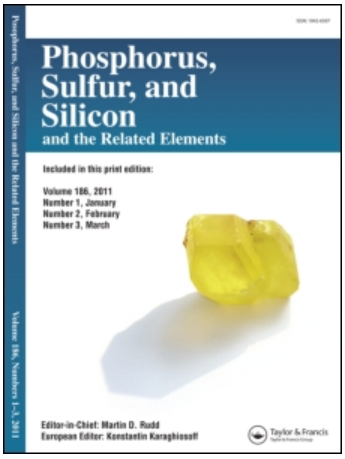

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PREPARATION AND NMR STUDY OF PHOSPHORUS-FLUORINE COMPOUNDS UNDERGOING INTRAMOLECULAR EXCHANGE. PART 1.[1] BENZYLMETHYLAMINOFLUORO-PHOSPHORANES

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PREPARATION AND NMR STUDY OF PHOSPHORUS-FLUORINE COMPOUNDS UNDERGOING INTRAMOLECULAR EXCHANGE. PART 1.[1] BENZYLMETHYLAMINOFLUORO-PHOSPHORANES

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The preparation is described of a series of benzylmethylamino-substituted fluorophosphoranes of general formula $PhCH_2(Me)NPF_{4-n}R_n$ (where R = Me, Ph; n = 0, 1, 2) from the cleavage of the silicon-nitrogen bond in benzyl-methylamino-trimethylsilane by fluorophosphoranes. The structures of the new compounds are deduced from ^1H, ^{19}F and ^{31}P nmr data. Variable temperature spectra give information about intramolecular exchange processes, and a detailed study was made of benzylmethylamino-diphenyldifluorophosphorane and of the corresponding 2-methyl-piperidyl compound.

INTRODUCTION

The cleavage reaction of the silicon-nitrogen bond in aminosilanes by fluorophosphoranes of the type R_nPF_{5-n} (where R = alkyl, aryl; n = 0, 1, 2) has proved to be a facile method for the preparation of amino-substituted phosphorus-fluorine compounds.[2-25] In general the reactions are characterized by mono-substitution, and the formation of a strong silicon-fluorine bond (as opposed to the weaker phosphorus-fluorine bond) is believed to provide the driving force of such reactions. Interest has arisen concerning the preparation of fluorophosphoranes containing asymmetric amino groups, and the compounds thus prepared have been shown to have interesting stereochemical properties resulting from the restriction of the P–N bond rotation.[17,18,21,26-28]

The reaction of primary amines with fluorophosphoranes affords aminofluorophosphoranes in which the asymmetry is due to the presence of a primary amine group;[29-33] a silicon-nitrogen cleavage reaction on $MeNHSiMe_3$ was employed[21] for the preparation of $MeNHPF_4$. Asymmetric secondary amino groups have been introduced to fluorophosphoranes by the reaction of the silicon-nitrogen compound with the respective fluorophosphoranes[17,18] in which methyl-substituted piperidyl groups were employed.

Our interest was directed towards the preparation of aminofluorophosphoranes containing an acyclic asymmetric secondary amino group and the investigation of their nmr properties. A detailed comparison of the variable temperature ^{19}F spectra of one of these compounds with those of the corresponding previously reported cyclic methyl-substituted piperidyl fluorophosphorane was carried out. The acyclic system studied was the benzylmethylamino group.

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TABLE I

Benzylmethylamino-substituted alkyl (or aryl) fluorophosphoranes

Compound	Reactants: phosphorane n[a]/mol	BMAS[b]/mol	Reaction conditions time/hr (temp./°C).	Yield/%	bp/°C (press./mm Hg)	Analysis calc. (found) C	H	F	N	P
$PhCH_2(Me)NPF_4$	PF_5 0.06	0.06	48 (−78)	72	78 (8.0)	42.3	4.4		6.2	
					109 (10.0)	(42.9)	(4.2)		(6.4)	
$[PhCH_2(Me)N]_2PF_3$	PF_5 0.03	0.06	48 (−78)	97[c]	[c]	[d]				
$[PhCH_2(Me)N]_2PF_3$	$PhCH_2(Me)NPF_4$ 0.017	0.017	1 (100)[e]	36[f]	*ca.* 230–240[f] (0.005)	[d]				
$PhCH_2(Me)NPF_3Ph$	$PhPF_4$ 0.05	0.05	1 (90)	96	116 (0.05)	58.9	5.3	20.0		10.9
						(57.2)	(5.5)	(20.0)		(11.1)
$PhCH_2(Me)NPF_3Me$	$MePF_4$ 0.23	0.23	12 (30)	88	42.5 (0.25)	48.4	5.9	25.5	6.3	13.9
					81 (3.0)	(48.9)	(6.0)	(25.2)	(6.3)	(13.6)
$PhCH_2(Me)NPF_2Ph_2$	Ph_2PF_3 0.05	0.05	8 (150)	73	146 (0.05)	69.9	5.8	11.1		9.1
						(69.0)	(6.0)	(11.1)		(10.4)
$PhCH_2(Me)NPF_2Me$	Me_2PF_3 0.13	0.13	24 (130)	52	62 (0.7)	54.8	7.4		6.4	
						(54.9)	(7.4)		(6.5)	

[a] Number of moles of phosphorane.
[b] Benzylmethylaminotrimethylsilane.
[c] This compound was thermally unstable and could not be purified by distillation. The yield is calculated on the quantity left over after trimethylfluorosilane had been removed under vacuum.
[d] Characterised by nmr spectroscopy.
[e] Vigorous reaction on combination of reactants (temperature rose to 140°C).
[f] Decomposition of the compound was observed during distillation and is reflected in the low yield and the approximate nature of the bp given.

RESULTS AND DISCUSSION

The cleavage reaction of benzylmethylaminotrimethylsilane by fluorophosphoranes proceeds with the formation of trimethylfluorosilane and the corresponding benzylmethylamino-substituted fluorophosphoranes, according to the equation,

$$PhCH_2(Me)NSiMe_3 + R_nPF_{5-n} \longrightarrow PhCH_2(Me)NPF_{4-n}R_n + Me_3SiF$$

(where R = Me, Ph; n = 0, 1, 2)

Contrary to normal expectation it was found that bis-(benzylmethylamino) trifluorophosphorane could be prepared under conditions similar to those employed for the preparation of the monosubstituted derivatives. It was prepared either by the reaction of phosphorus pentafluoride with two equivalents of the silylamine, or by the reaction of the monosubstituted tetrafluorophosphorane with the silylamine.

$$2\ PhCH_2(Me)NSiMe_3 + PF_5 \longrightarrow \left(PhCH_2(Me)N\right)_2PF_3 + 2Me_3SiF$$

$$PhCH_2(Me)NSiMe_3 + PhCH_2(Me)NPF_4 \longrightarrow \left(PhCH_2(Me)N\right)_2PF_3 + Me_3SiF$$

Both reactions proceed at low temperatures and are exothermic. Preparation of the analogous bis(dialkylamino)trifluorophosphoranes is carried out at 150°C over an extended period.[19]

Table I lists the fluorophosphoranes prepared. The benzylmethylaminotetra- and tri-fluorophosphoranes as well as the dimethyldifluorophosphorane are all colourless liquids and the diphenyldifluorophosphorane is a white crystalline solid. Their stability to hydrolysis is comparable to other fluorophosphoranes.[2]

Both the tetra- and tri-fluorophosphoranes show a tendency under the influence of heat to rearrange to ionic isomers, as has been observed for other aminofluorophosphoranes,[2,34-36] the rearrangements proceeding according to the equations,[37]

$$2R_2NPF_4 \longrightarrow [(R_2N)_2PF_2]^+[PF_6]^-$$

$$2R^1_2NPF_3R^2 \longrightarrow [(R^1_2N)_2PFR^2]^+[R^2PF_5]^-$$

Formation of ionic products was also observed upon prolonged storage of samples at room temperature, but the compounds could be kept for indefinite periods at low temperatures. The difluorophosphoranes, however, show no tendency to rearrange even on heating for prolonged periods.

All the compounds were characterized by ^1H, ^{19}F, ^{31}P nmr spectroscopy and elemental analysis.

NUCLEAR MAGNETIC RESONANCE DATA

Tables II, III and IV list the ^{19}F, ^{31}P and ^1H nmr data, respectively.

The room temperature ^{31}P nmr data are consistent with trigonal bipyramidal structures in every case, in which the amino group, phenyl and methyl groups occupy equatorial sites.[2,38] The ^1H nmr data are also consistent with such a formulation. Interesting features are to be seen in the ^{19}F variable temperature spectra.

Previous low temperature nmr studies on compounds of the type R_2NPF_4 (R = Me, Et, Ph)[2,39,40] have shown that the simple 1 : 1 doublet in the ^{19}F nmr spectrum of these molecules at room temperature changes to a more complex spectrum at low temperatures. At room temperature intramolecular positional exchange of fluorine atoms occurs, thus inducing magnetic equivalence of fluorine atoms; this process has been labelled "pseudo-rotation."[41] The spectrum may be rationalized in terms of trigonal bipyramidal geometry, thus indicating that the molecule has reverted from a non-rigid pseudo-rotating form to a more rigid form within the time-scale of the nmr technique. This was found to be the case for the methylpiperidyl-substituted tetrafluorophosphoranes previously reported[17,18] and for the benzylmethylaminotetrafluorophosphorane reported here. The corresponding trifluorophosphoranes all show distinct axial and equatorial fluorine atom environments even at room temperature.

TABLE II

Variable temperature ^{19}F nmr data for benzylmethylaminofluorophosphoranes[a]

Compound	Temp./°C	δ_F/ppm[b,c]		$\lvert^1J_{PF}\rvert$/Hz[c]		$\lvert^2J_{FF}\rvert$/Hz[c]	
$PhCH_2(Me)NPF_4$	+30	av[d]	−65.5	av[d]	850		
	−80[e]	F^1	−55.8	PF^1	779	F^1, eq av[f]	64
		F^2	−58.4	PF^2	779	F^2, eq av[f]	72
		eq av[f]	−72.2	eq av[f]	915		
$(PhCH_2(Me)N)_2PF_3$	+30	ax av[g]	−54.4	ax av[g]	753	F^3, ax av[g]	47
		F^3	−68.8	PF^3	870		
$PhCH_2(Me)NPF_3Ph$	+30	ax av[g]	−41.0	ax av[g]	828	F^3, ax av[g]	53
		F^3	−66.4	PF^3	966		
	−50[e]	F^1	−40.8	PF^1	823	F^1F^2	14
		F^2	−43.2	PF^2	821	F^1F^3	55
		F^3	−65.6	PF^3	961	F^2F^3	56
$PhCH_2(Me)NPF_3Me$	+30	ax av[g]	−27.6	ax av[g]	812	F^3, ax av[g]	54
		F^3	−66.6	PF^3	962		
	−60[e]	F^1	−26.9	PF^1	808	F^1F^3	49
		F^2	−29.2	PF^2	800	F^2F^3	58
		F^3	−65.5	PF^3	957	F^1F^2	not resolved
$PhCH_2(Me)NPF_2Ph_2$	+30[h]	ax av[g]	−38.4	ax av[g]	711		
	−80[e,i]	F^1	−37.1	PF^1	708		
		F^2	−40.0	PF^2	711		
$PhCH_2(Me)NPF_2Me_2$	+30	ax av[g]	−15.2	ax av[g]	653		
	−120[j]	F^1	−14.4	PF^1	655		
		F^2	−16.8	PF^2	652		

[a] All values refer to neat liquids except where stated.
[b] Measured relative to $CFCl_3$ as internal standard; the negative sign indicates the reference resonates to high-frequency of the sample.
[c] F^1 and F^2 refer to axial fluorines; F^3 refers to equatorial fluorine.
[d] Average of all four fluorines (equivalent at ambient probe temperature).
[e] In toluene.
[f] Average for the two equatorial fluorines (equivalent even at −80°C).
[g] Average for the two axial fluorines (equivalent at ambient probe temperature).
[h] Spectra obtained at 30°C for a supercooled liquid sample.
[i] Further low temperature data are given in Table V.
[j] In methylcyclohexane. The spectrum was obtained using a Bruker HFX-90 spectrometer operating at 84.67 MHz.

Nmr investigations carried out on organothio-substituted fluorophosphoranes[42-46] and asymmetric aminofluorophosphoranes containing primary amine groups[21,29-33] showed that as the temperature was decreased a non-equivalence of the axial fluorine atoms was induced, which was attributed to a decrease in rotation about the P-heteroatom bond, with the P-heteroatom group sited preferentially in the axial plane of the trigonal bipyramid. Similar results were obtained for the methylpiperidyl-substituted compounds[17,18] and for the benzylmethylaminofluorophosphoranes.

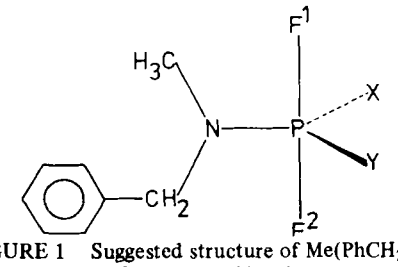
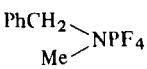
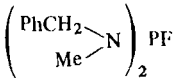
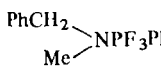
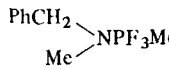
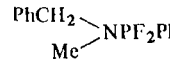
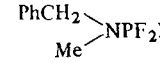


FIGURE 1 Suggested structure of $Me(PhCH_2)NPF_{4-n}R_n$ (where n = 0, 1, 2; R = Me, Ph) at low temperature. For the various compounds studied X = F^3, Y = F^4; X = F^3, Y = Me or Ph; X = Y = Me or Ph. The individual assignments of F^1 and F^2 have not been linked to the chemical shifts and coupling constants in Table II.

TABLE III

^{31}P Nmr data for benzylmethylaminofluorophosphoranes[a]

Compound	δ_P/ppm[b]	$\lvert^1J_{PF}\rvert$/Hz[c]	Multiplicity[d]
	−69.2	850	quintet
	−66.2	753 (ax) 868 (eq)	doublet of triplets
	−53.3	828 (ax) 966 (eq)	doublet of triplets
	−36.8	812 (ax) 962 (eq)	doublet of triplets
	−55.1	711	triplet
	−27.4	653	triplet

[a] All values refer to neat liquids at room temperature.
[b] Phosphorus chemical shifts were measured relative to 85% H_3PO_4 as external standard, the negative sign indicates the reference resonates to high-frequency of the sample.
[c] ax = axial; eq = equatorial.
[d] Due to (P, F) coupling.
[e] Spectrum run on a super-cooled liquid sample.

The ^{19}F nmr spectrum of benzylmethylaminotetrafluorophosphorane[46] shows a 1 : 1 doublet at room temperature (characteristic of all tetrafluorophosphoranes). However, the low-temperature ^{19}F spectrum indicated a 1 : 1 : 2 arrangement of non-equivalent fluorine atoms. We conclude that both pseudo-rotation of the PF_4 entity and rotation about the P–N bond are slowed down sufficiently to be within the nmr timescale. The twenty-line spectrum can be rationalized in terms of the structure shown in Figure 1 (with X = Y = F). Since non-equivalence of the axial fluorine atoms is not observed in the low temperature ^{19}F nmr spectra of compounds containing symmetric amino groups, we conclude from our observations that the amino group must be "frozen" with the alkyl groups on the opposite sides of the equatorial plane of the trigonal bipyramid. If both substituents were below or both above the equatorial plane of the trigonal bipyramid (on the nmr timescale) the axial fluorine atoms should be non-equivalent even in the case of a symmetrically-substituted amino group. However, methylpiperidyl-substituted tetrafluorophosphoranes exhibit non-equivalent *equatorial* fluorine atoms[17,18] at low temperatures, indicating that the amino group is positioned in the equatorial plane of the trigonal bipyramid. This observation was explained by the steric hindrance of the large piperidyl group being less in the equatorial plane than in the axial plane.

The tri- and di-fluorophosphoranes exhibit the expected patterns for trigonal bipyramidal molecules. Upon lowering the temperature the axial fluorine atoms become non-equivalent, and a more complex pattern is observed. Once again a decrease in P–N bond rotation contributes to the observations made. The observed spectral patterns can again be rationalized in terms of the structure shown in Figure 1 (X = F; Y = Me, Ph; or X = Y = Me, Ph). The corresponding methylpiperidyl-substituted tri- and di-fluorophosphoranes also show magnetic non-equivalence of axial fluorine atoms,[17,18] consistent with a structure in which the amino group is situated in the axial plane. In such cases the steric hindrance appears to be less in the axial plane than in the equatorial one.

The high energy barrier to rotation about the P–N bond is presumably caused[47] mainly by $d\pi$-$p\pi$ bonding between P and N, although this effect should be considerably reduced in the presence of other strongly π-bonding elements, such as fluorine, on phosphorus. By the latter argument compounds containing P–F bonds should not be susceptible to "freezing" rotation about the P–N bond at low temperatures, though this is clearly contrary to the experimental evidence. The second feature affecting the barriers is steric crowding in the transition state (relative to the ground state). Steric considerations presumably also need to be invoked to explain the difference in ground state stability observed between the methylpiperidyl- and benzylmethylaminotetrafluorophosphoranes.

Of course there are other factors influencing the conformation of the compounds under discussion, viz. inversion at nitrogen, internal rotation about N–C bonds (for the benzylmethyl compounds), ring inversion (for the methylpiperidyl compounds), and, in appropriate cases, internal rotation about P–C bonds. None of these is likely to affect the present discussion, but it may be noted that for methylpiperidyltetrafluorophosphorane all four fluorines should be non-equivalent if P–N internal rotation and phosphorus pseudorotation are slow on the nmr timescale, regardless of the rates of other processes and irrespective as to whether the N–C bonds are in the axial or

TABLE IV

Room temperature ^{1}H Nmr data for benzylmethylaminofluorophosphoranes[a]

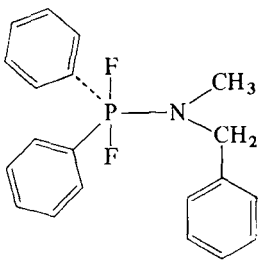
Compound	δ_H/ppm[b]	$\lvert J_{PH}\rvert$/Hz[c]	$\lvert J_{FH}\rvert$/Hz[d,e]	Multiplicity
$PhCH_2(Me)NPF_4$	CH_3N 2.55	11.5	2.5	doublet of quintets
	CH_2N 4.08	15.0		broad doublet
	Ph–C ~ 7.16			broad singlet
$[PhCH_2(Me)N]_2PF_3$	CH_3N 2.60	11.0	3.0 (ax)	doublet of doublets of
			3.0 (eq)	triplets
	CH_2N 4.10	14.0		broad doublet
	Ph–C ~ 7.18			broad singlet
$PhCH_2(Me)NPF_3Ph$	CH_3N 2.73	11.0	3.0 (ax)	doublet of doublets of
			3.0 (eq)	triplets
	CH_2N 4.24	13.5		broad doublet
	Ph–C ~ 7.16			broad singlet
	Ph–P ~ 7.61			complex multiplet
$PhCH_2(Me)NPF_3Me$	CH_3P 1.58	20.0[f]	12.5 (ax)[g]	doublet of doublets of
			1.5 (eq)[g]	triplets
	CH_3N 2.66	10.5	3.0 (ax)	doublet of doublets of
			3.0 (eq)	triplets
	CH_2N 4.16	13.5		broad doublet
	Ph–C ~ 7.21			broad singlet
$PhCH_2(Me)NPF_2Ph_2$[h]	CH_3N 3.2	10.0	3.0	doublet of triplets
	CH_2N 4.75	12.0		broad doublet
	Ph–C ~ 7.55			broad singlet
	Ph–P ~ 8.06			complex multiplet
$PhCH_2(Me)NPF_2Me_2$	CH_3P 1.89	17.5[f]	13.0	doublet of triplets
	CH_3N 3.01	10.0	3.0	doublet of triplets
	CH_2N 4.62	12.0		broad doublet
	Ph–C ~ 7.22			broad singlet

[a] All values refer to neat liquids except where stated.
[b] Proton chemical shifts were measured relative to tetramethylsilane as internal standard.
[c] $\lvert^3J_{PH}\rvert$ except where otherwise stated.
[d] ax = axial; eq = equatorial.
[e] $\lvert^4J_{FH}\rvert$ except where otherwise stated.
[f] $\lvert^2J_{PH}\rvert$/Hz.
[g] $\lvert^3J_{FH}\rvert$/Hz.
[h] Spectrum run using a dichloromethane solution (*ca.* 50%).

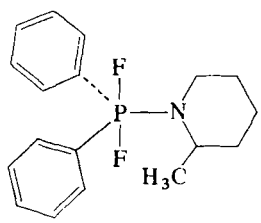
equatorial planes of the P atom. Presumably the methyl substituent on the piperidyl ring is actually too far, even when in the 2-position, from the axial fluorines to induce a chemical shift difference for the methylpiperidyltetrafluorophosphoranes. However, it is clear that there are ambiguities inherent in the results, and the conclusions drawn here and in the earlier papers[17,18] are not definitive, though they appear to be the most likely explanation for the results.

THE BARRIER TO INTERNAL ROTATION ABOUT THE P–N BOND

In order to characterize further the exchange processes involved, benzylmethylaminodiphenyldifluorophosphorane (**I**) was chosen for detailed study, since in this case P–N internal rotation is the only process involved. For purposes of comparison a detailed investigation of this process was also carried out for α-methylpiperidyldiphenyldifluorophosphorane (**II**).



I



II

The ^{19}F-{^1H} spectra of both compounds at −100°C are of the ABX type, where $X \equiv {}^{31}P$, whereas the effective spin system at room temperature is A_2X. Thus the P–N internal rotation process may be represented in nmr terms as mutual exchange of the type ABX ⇌ BAX. The effects of the X nucleus can be entirely taken into account by invoking subspectral principles.[48] Thus the fluorine region can be interpreted in terms of two ab subspectra with parameters.

(i) $\nu_a = \nu_A + \frac{1}{2}J_{AX}$; $\nu_b = \nu_B + \frac{1}{2}J_{BX}$; $J_{ab} = J_{AB}$ and

(ii) $\nu_a = \nu_A - \frac{1}{2}J_{AX}$; $\nu_b = \nu_B - \frac{1}{2}J_{BX}$; $J_{ab} = J_{AB}$ respectively.

The two subspectra are well separated due to the large magnitude of $^1J_{PF}$, and the exchange can be treated as due to two independent processes of the type ab ⇌ ba with a common rate constant, and effective chemical shift differences $\Delta\nu_{ab} = \nu_A - \nu_B + \frac{1}{2}(J_{AX} - J_{BX})$ in one case and $\Delta\nu_{ab} = \nu_A - \nu_B - \frac{1}{2}(J_{AX} - J_{BX})$ in the other. In fact for all the subspectra $|\Delta\nu_{ab}| > |^2J_{FF}|$ so that the low temperature spectra are first order in appearance. As the temperature is raised lines broaden, and the splitting due to $^2J_{FF}$ is obscured. Further increase in temperature results in a coalescence of the a and b signals, the coalescence temperatures for the low frequency subspectra being *ca.* −65°C and *ca.* −50°C for **I** and **II** respectively. The relevant nmr data are listed in Table V. It was found that the values of $\Delta\nu_{ab}$ varied appreciably with temperature, so that in order to obtain accurate rate constants it was necessary to evaluate this temperature-dependence. This was done over a range of *ca.* 30° below the coalescence temperature. Figure 2 shows a typical plot for $\Delta\nu_{ab}$ *vs. T.* Extrapolation was used to obtain suitable values of $\Delta\nu_{ab}$ for use in the region where exchange affected the nmr spectra. The extrapolation procedure was checked by comparing the mean shifts, $(\nu_a + \nu_b)/2$, extrapolated to temperatures well above coalescence with the observed values.

Exchange rates were obtained by fitting the observed ^{19}F-{^1H} bandshapes for both subspectra over a temperature range of *ca.* 50°C for each compound. In most cases fitting by eye to a set of spectra simulated by the computer program[49] ABSHAPE was employed.

TABLE V

Variable temperature nmr data for compounds **I** and **II** at −110°C

		I	**II**
δ_F/ppm[a,b]	A	−40.21	−36.67
	B	−37.18	−34.24
Δ^{ν}_{ab}/Hz	(i)[d]	280.2	225.3
	(ii)[e]	291.0	233.3
$\lvert^2J_{FF}\rvert$/Hz		20.2	9.5
$\lvert^1J_{PF}\rvert$/Hz[b,c]	A	708.9	677.3
	B	719.4	685.5

[a] From the resonance due to $CFCl_3$. The shifts are negative when to low frequency of the reference signal. At *ca.* +35°C the averaged values of δ_F are −37.92 ppm (**I**) and −37.41 ppm (**II**).

[b] A is the low frequency fluorine, B is the high frequency fluorine.

[c] At *ca.* +35°C the averaged values of $|^1J_{PF}|$ are 719.2 Hz (**I**) and 702.9 Hz (**II**).

[d] Low frequency subspectrum.

[e] High frequency subspectrum.

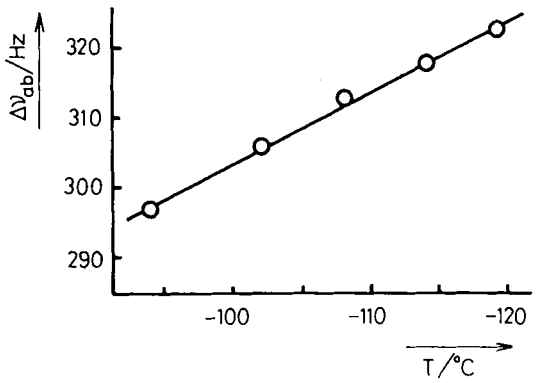


FIGURE 2 Change of subspectral chemical shift difference, $\Delta\nu_{ab}$, with temperature well below coalescence for the low frequency subspectrum of compound I.

Some spectra were digitized using a d-Mac pencil follower and then iteratively fitted using the program[49] ABEX; the pre-exchange lifetimes obtained by this method were within the error limits of the ones derived from the non-iterative approach. For the iterative cases the chemical shift difference $\Delta\nu_{ab}$ was allowed to vary, but the iterated result was always very close to the extrapolated value used in the non-iterative method. The linewidth of the room temperature spectrum (i.e. well above coalescence) was used to obtain a value for an effective T_2, which was kept constant in all the calculations. Some observed and computed spectra are shown in Figure 3.

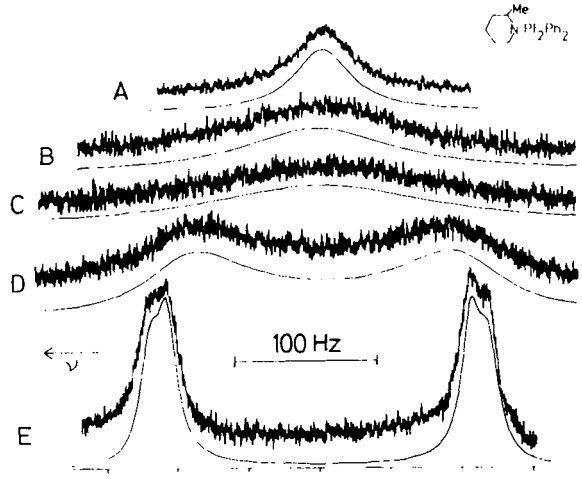


FIGURE 3 ^{19}F-{^1H} experimental and computed nmr band-shapes for the low frequency subspectrum of compound II. A. −27°C, τ = 0.34 ms; B. −39°C, τ = 0.84 ms; C. −44°C, τ = 1.1 ms; D. −55°C, τ = 3.7 ms; E. −80°C, τ = 25 ms. The parameter τ is the mean lifetime in the two (equivalent) configurations, that is $1/2k$, where k is the pseudo-first-order rate constant.

A few drops of $(Me_3Si)_2NMe$ were added to the solutions studied to check whether traces of H_2O or HF have any effect on exchange rates. Since no effect was found it is concluded that intermolecular exchange is not occurring so that the process studied is entirely intramolecular.

The pre-exchange lifetimes (inverse rate constants) were used in Eyring plots to calculate the thermodynamic activation parameters, a transmission coefficient of 1 being assumed. The parameters found are given in Table VI, and the Eyring plot for II is shown in Figure 4. Data for $\Delta G^{\ddagger}$ are listed at a common temperature of 210 K for both compounds; this is in the region of coalescence. Values of $\Delta G^{\ddagger}$ reported[47,50,51] in the literature for P–N internal rotation are in the same region as those given in Table VI.

The difference in $\Delta G^{\ddagger}$ values for I and II at 210 K, which is marginally outside probable experimental error, may be partly due to the π-bonding ability of the two amines involved and partly due to steric effects. The donor ability of the lone pair on nitrogen

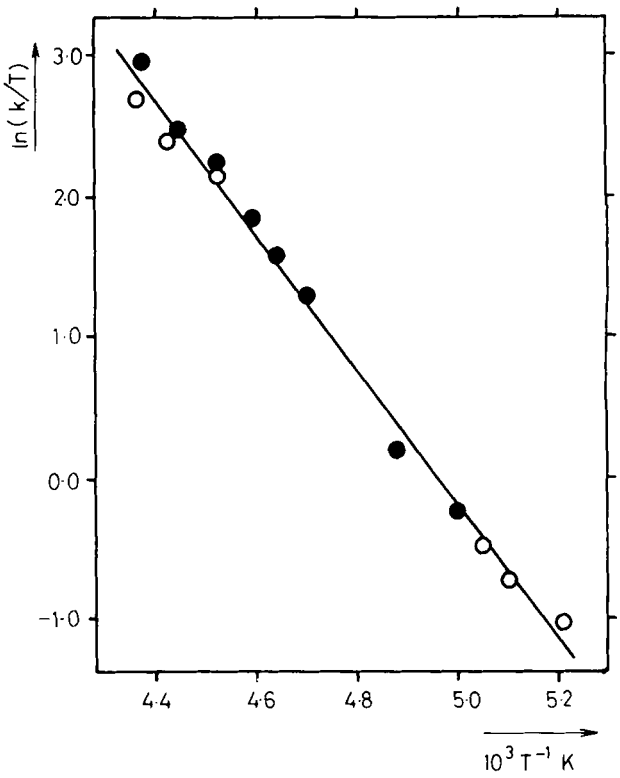


FIGURE 4 Eyring rate plot for P–N internal rotation in compound I. The open circles refer to the high frequency subspectrum. The filled circles are for the low frequency subspectrum.

TABLE VI

Thermodynamic parameters for P–N internal rotation in compounds I and II[a]

Compound	$\Delta G^{\ddagger}_{210}$[b]/kJ mol^{-1}	$\Delta H^{\ddagger}$[c]/kJ mol^{-1}	$\Delta S^{\ddagger}$[c]/J mol^{-1} K^{-1}
I	41 (9.8)	39 ± 6 (9.4)	−8 ± 12 (−2)
II	44 (10.4)	37 ± 4 (8.8)	−29 ± 12 (−7)

[a] Derived using K = 1. Data in kcal mol^{-1} ($\Delta G^{\ddagger}_{210}$ and $\Delta H^{\ddagger}$) or cal mol^{-1} K^{-1} ($\Delta S^{\ddagger}$) are given in brackets.
[b] Probably accurate to ± 2 kJ mol^{-1}.
[c] The errors listed are from the Eyring plot linearity only. True errors may therefore be larger.

can be roughly correlated with the pK_a value of the relevant amine. The pK_a of piperidine (11.1) is higher[52] than that of R_2NH (10.9), and therefore the piperidyl nitrogen should be more involved in π-bonding than the benzylmethylamine nitrogen. Moreover the α-methylpiperidyl compound (II) should have more steric interaction with the phenyl groups in the transition state than the benzylmethylamino compound. Both effects would tend to make $\Delta G^{\ddagger}$ for II higher than for I, as observed. For benzylmethylaminodimethyldifluorophosphorane, $PhCH_2(CH_3)NPF_2(CH_3)_2$, fluorine non-equivalence was found only below −100°C, i.e. the barrier to P–N internal rotation is lower than for I. This may again be attributed to the two effects mentioned above; the acidity of the phosphorus is reduced by the inductive effect of the methyl groups, and steric crowding in the equatorial plane is reduced compared to that from the phenyl groups.

As is usual in nmr bandshape studies of exchange, the data for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are substantially less accurate than those for $\Delta G^{\ddagger}$ in the coalescence region, especially as there is the possibility of systematic errors. It is encouraging that the values of $\Delta S^{\ddagger}$ are relatively low, though that for II is higher than expected and may indicate a systematic error. Since internal rotation may occur in two opposite senses, one might expect a contribution to $\Delta S^{\ddagger}$ of $R \ln 2 = 5.8$ J mol^{-1} K^{-1}. An alternative hypothesis is that promotion to the activated state might be followed by deactivation to either the original conformation or the other rotamer;† this suggests a contribution to $\Delta S^{\ddagger}$ of −5.8 J mol^{-1} K^{-1}. Thus values of $\Delta S^{\ddagger}$ indicate that the second hypothesis above is the more likely to be correct. Other contributions to $\Delta S^{\ddagger}$ are expected to be small.

† A similar contribution is given if it is supposed that there is a metastable intermediate with the nitrogen substituents in the equatorial plane of the phosphorus.

The results show that this appears to be the case for I but not for II. Indeed, the larger result for $\Delta S^{\ddagger}$ in II causes the value of $\Delta H^{\ddagger}$ to be less for II than for I, in contrast to $\Delta G^{\ddagger}_{210}$. The errors given in Table VI do not permit such a reversal to be established definitively and, indeed, we believe it is not likely to be true. The main achievement of bandshape analysis for I and II lies in the ability to obtain $\Delta G^{\ddagger}$ near coalescence with a relatively high accuracy.

EXPERIMENTAL

The nmr data reported in Tables II, III and IV were obtained using Varian Associates 60 MHz HA/HR-60 and JEOL HCL-60 spectrometers. The Varian instrument was fitted with an external frequency generator to enable measurement of ^{19}F nmr spectra by the extended lock technique. Sealed capillaries containing 85% phosphoric acid solution were used as an external reference for the phosphorus spectra, fluorotrichloromethane was used as an internal standard for all the fluorine spectra, and tetramethylsilane as internal reference for all the proton spectra. The low temperature spectra were run in toluene or methylcyclohexane solution.

The detailed variable temperature ^{19}F-{^1H} nmr experiments on I and II were carried out at 94.155 MHz using a Varian HA 100 spectrometer, in conjunction with a Schlumberger FSX 3005 frequency synthesizer (providing the 100 MHz ^1H irradiation), a Hewlett-Packard 3722A noise generator and a double-tuned probe as described previously.[53] The samples were dissolved in vinyl chloride, with some $CFCl_3$ added to provide a ^{19}F field/frequency lock and reference signal. The solutions were made up in 5 mm O.D. tubes using a vacuum line; these were sealed in the degassed state. For the study of the variation of $\Delta\nu_{ab}$ with T a thermocouple was used to monitor the temperature;[54] for the bandshape studies the temperature was calibrated using[54] the ^{19}F chemical shift difference in a sample of 10% $(CFCl_2)_2$, 10% $(CF_2Br)_2$ and 80% butyl benzene.

The usual precautions required in handling moisture-sensitive phosphorus compounds were observed. Organic solvents were dried by standard procedures. Nmr samples were prepared in an atmosphere of dry nitrogen or dry argon.

Benzylmethylaminotrimethylsilane was prepared from the reaction of trimethylchlorosilane (108.5 g; 1.0 mole) with benzylmethylamine (121.0 g; 1.0 mole) in the presence of triethylamine (101.0 g; 1.0 mole) as acid acceptor in diethylether (1.0 l) as solvent. The triethylammonium chloride was removed by filtration and the filtrate distilled to remove the ether. The higher boiling fraction was distilled under vacuum affording a colourless liquid of bp 52–54°C/0.05 mm. The yield was 76%. Anal. calcd. for $C_{11}H_{19}SiN$: C, 68.4; H, 9.8; N, 7.3. Found: C, 68.2; H, 9.7; N, 7.3%. The compound was also characterized by its ^1H nmr spectrum:

$\delta(SiMe_3) = 0.10$ ppm; $\delta(CH_2N) = 2.28$ ppm;
$\delta(CH_3N) = 3.76$ ppm; $\delta(Ph) = 6.12$ ppm

Phosphorus pentafluoride was purchased from U.S. Agrichemicals. The synthesis of the fluorophosphorane precursors used has been reported in the literature[55,56] and the preparation of methylpiperidyl-substituted fluorophosphoranes has been reported elsewhere.[17,18]

Preparation of Benzylmethylaminofluorophosphoranes

The following examples of the syntheses of tetra-, tri- and di-fluorophosphoranes illustrate the procedures used in the preparation of all the benzylmethylaminofluorophosphoranes. In all the cases the amount of trimethylfluorosilane formed was determined and invariably corresponded to a quantitative or nearly quantitative yield, assuming the cleavage of one P–F bond per molecule of the original fluorophosphorane. Data pertinent to the preparation of these compounds, including analyses, are listed in Table I. The relevant nmr data are listed in Tables II, III, and IV.

Benzylmethylaminotetrafluorophosphorane

Phosphorus pentafluoride (7.6 g; 0.06 mole) was condensed onto benzylmethylaminotrimethylsilane (11.6 g; 0.06 mole) *in vacuo* in a glass reaction tube at −196°C. The tube was sealed and left in a dry-ice/acetone bath at −78°C for two days. The tube was then opened, trimethylfluorosilane (5.8 g; 96%) was allowed to evaporate at room temperature into a trap held at −78°C and the remaining liquid was distilled under reduced pressure from a 25 ml flask. Benzylmethylaminotetrafluorophosphorane (9.8 g; 72%) was obtained as a colourless liquid of bp 78°C/8.0 mm. The liquid was stored at low temperature in a Teflon vial.

Benzylmethylaminophenyltrifluorophosphorane

Benzylmethylaminotrimethylsilane (9.6 g; 0.05 mole) was added dropwise with stirring to phenyltetrafluorophosphorane (9.2 g; 0.05 mole) at 50°C. An exothermic reaction was observed, the temperature rising to about 70°C. After the mixture had been heated at 90°C for a further 1.0 hr the reaction appeared to be complete. A total of 4.0 g (96%) of gas was collected in a −78°C trap and was identified as trimethylfluorosilane. Distillation of the residue under vacuum from a 25 ml flask yielded benzylmethylaminophenyltrifluorophosphorane (12.9 g; 96%) as a colourless liquid of bp 116°C/0.05 mm.

Benzylmethylaminodiphenyldifluorophosphorane

Benzylmethylaminotrimethylsilane (9.6 g; 0.05 mole) was added dropwise to stirred diphenyltrifluorophosphorane (12.1 g; 0.05 mole) at 50°C. No reaction took place and the reaction mixture was heated at 150°C for 8.0 hr, in which time a volatile product collected in a trap at −78°C. This was identified as trimethylfluorosilane (4.0 g; 96%). Distillation of the residue *in vacuo* from a 25 ml flask afforded benzylmethylaminodifluorophosphorane (12.4 g; 73%) as a colourless oil, of bp 146°C/0.05 mm, which subsequently solidified affording a white crystalline product of mp *ca.* 72°C (measured in a sealed capillary). The compound was further purified by sublimation at 100°C/0.05 mm using a water-cooled probe and affording white needle-like crystals.

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