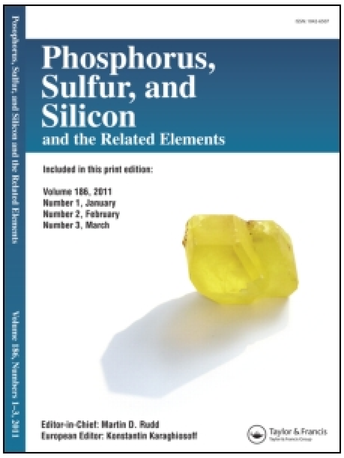

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PREPARATIVE AND N.M.R. STUDIES OF PHOSPHORUS-FLUORINE COMPOUNDS UNDERGOING INTRAMOLECULAR EXCHANGE. PART 2. UNSYMMETRICAL FLUORINATED PHOSPHADIAZETIDINONES

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PREPARATIVE AND N.M.R. STUDIES OF PHOSPHORUS-FLUORINE COMPOUNDS UNDERGOING INTRAMOLECULAR EXCHANGE. PART 2.* UNSYMMETRICAL FLUORINATED PHOSPHADIAZETIDINONES

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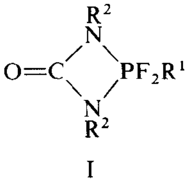
The preparation of fluoro-phosphadiazetidinones, $O{=}C(NMe)(NEt)PF_2R$ (R = Me, Et, Ph), unsymmetrically substituted on nitrogen, from the reaction of tetrafluorophosphoranes with the silyl urea, $O{=}C(NMeSiMe_3)\text{-}(NEtSiMe_3)$ is described. The compounds undergo partial equilibration to the symmetric species, $O{=}C(NMe)_2PF_2R$ and $O{=}C(NEt)_2PF_2R$. Low temperature ^{31}P and ^{19}F n.m.r. spectra indicate changes which are rationalized in terms of variations in the population of energetically different conformers and in the exchange rates between conformers. The conformational differences involved are those arising from pseudorotation at trigonal-bipyramidal phosphorus. Comparable n.m.r. data are also given for some related compounds.

Symmetrical difluorophosphadiazetidinones of the type I have been the subject of previous investigation.[1] Related unsymmetrical compounds of type II have also been reported[1–3] for $R^2 = Me$, $R^3 = Ph$; they



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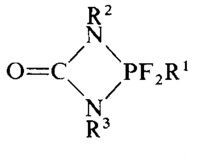
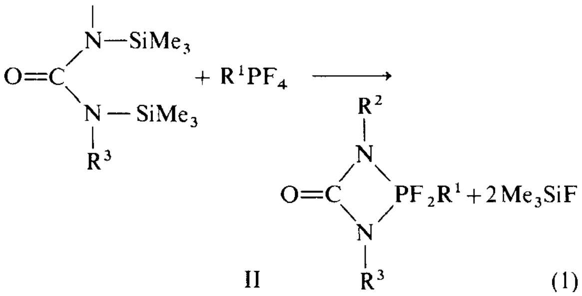


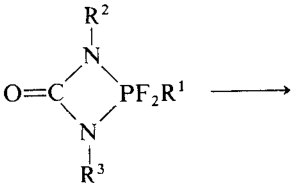
II ($R^2 \neq R^3$)

were prepared by the reaction of a tetrafluorophosphorane with the appropriate silyl urea,[1] as in Eq. (1):



II (1)

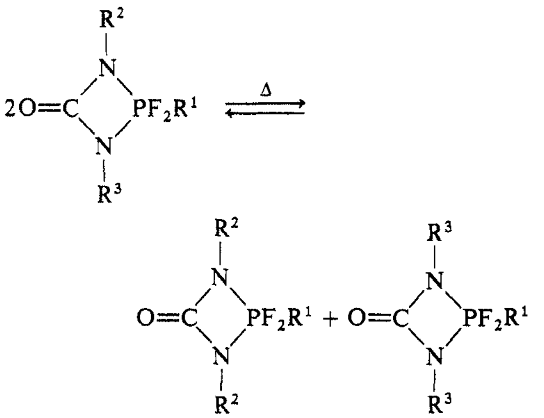
Of the unsymmetrical species only the compounds with $R^1 = R^2 = Me$; $R^3 = Ph$ and $R^1 = Et$; $R^2 = Me$; $R^3 = Ph$ have, hitherto, been isolated in a pure state. Isolation of the pure substances has been difficult in other cases, as a result of a facile decomposition reaction[1,4–7]:



$$R^1P(:O)F_2 + [R^2N{=}C{=}NR^3]_n \quad (2)$$

On the other hand, phosphadiazetidinones with $R^2 = Me$, $R^3 = Et$, and $R^1 = Me$(IIa), Et(IIb) and Ph(IIc), prepared in accord with Eq. (1), have proved to be quite stable and could be obtained in good yield, although not in a completely pure state. While elemental analysis for all the compounds confirms their composition it is concluded from ^{19}F n.m.r. investigations that compounds (IIa)-(IIc) always contain a certain amount of the respective symmetric compounds of the type I, i.e. with both substituents at nitrogen being equal.

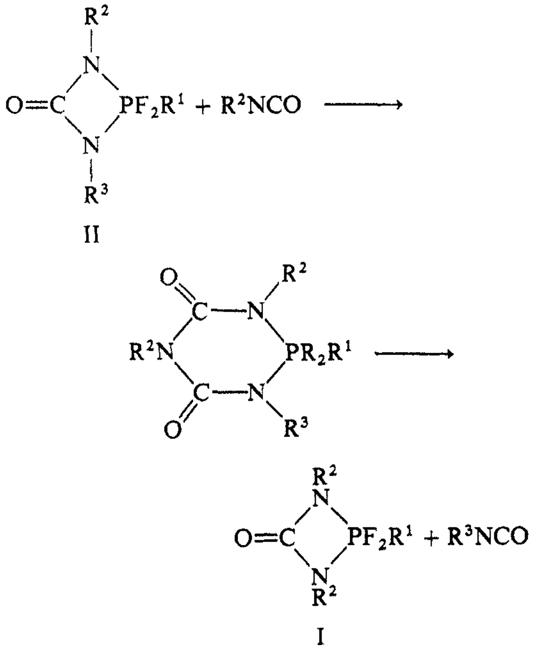
This observation may be rationalised by the assumption of an equilibrium between unsymmetric compounds:



(3)

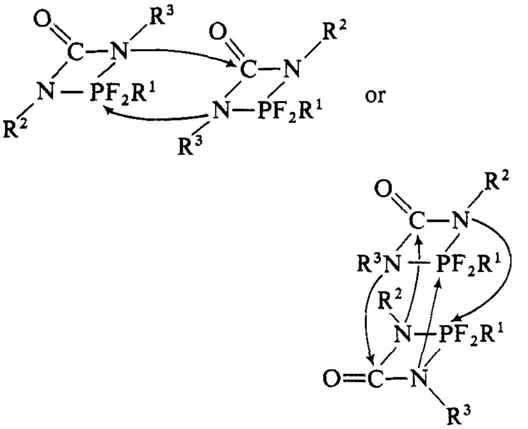
Thus, for compound IIb (i.e. with R^2 = Me; $R^1 = R^3$ = Et) a ratio of IIb: $O{=}C(NMe)_2PF_2Et$: $O{=}C(NEt)_2PF_2Et$ of 20:2:1 was found by the ^{19}F n.m.r. spectrum of the distillate. By this means, the ^{19}F n.m.r. parameters of the hitherto unknown compounds, $O{=}C(NEt)_2PF_2R^1$ (R^1 = Me, Et, Ph) were obtained. The analogous compounds $O{=}C(NMe)_2PF_2R^1$(R^1 = Me, Et, Ph) are known, and the present ^{19}F n.m.r. data are in good agreement with those previously reported.[1–4].

The equilibration, as depicted in Eq. (3) may involve catalytic amounts of isocyanate, and may proceed via a six-membered ring intermediate, i.e.



(4)

Other reaction mechanisms, such as interaction between two molecules of II via a four- or eight-centred transition state (viz. (5)) cannot, however, be excluded.



(5)

The catalytic amounts of isocyanate required in (4) may originate from the preparation of the starting silyl urea, or from the decomposition of the fluorophosphadiazetidinone[1,4,5].

The mass spectra of compounds IIa–IIc were found to exhibit the fragmentation pattern previously described for phosphadiazetidinones,[8] i.e.

$$M]^{+\cdot} \longrightarrow R^1P(:O)F_2\,]^{+\cdot} + R^2N{=}C{=}NR^3$$

and

$$M]^{+\cdot} \longrightarrow R^2N{=}C{=}NR^3]^{+\cdot} + R^1P(:O)F_2$$

In the 12 eV mass spectrum of IIb the fragments

$MeN{=}C{=}NMe]^{+\cdot}$, $MeN{=}C{=}NEt]^{+\cdot}$,

and

$EtN{=}C{=}NEt]^{+\cdot}$

were found in an intensity ratio of 1.3:17.7:1.0, which is in reasonable confirmation of the ^{19}F n.m.r. results mentioned above.

N.M.R. EXPERIMENTS

Phosphorus-31, fluorine-19 and proton n.m.r. spectra were obtained for the three new unsymmetrical compounds, IIa–IIc, and for the symmetrical species I, R^1 = Me, Et, Ph and R^2 = Et, mentioned above. The n.m.r. data, together with values for some related compounds (including new measurements), are given in the tables. The parameters are in general agreement with previous results[1–3] for molecules of these types.

The n.m.r. spectra of difluorophosphadiazetidinones show some features of interest. Symmetrical systems of the type I give spectra which do not change in appearance with temperature, and which indicate that the fluorine nuclei are equivalent. Unsymmetrical compounds of the type II give spectra characteristic of equivalent fluorines at ambient temperature, but the fluorine nuclei become non-equivalent on the n.m.r. time-scale at lower temperatures; not only are there then two distinct values of δ_F, but each is characterised by a different $^1J_{PF}$. This effect enables values of $|^2J_{FF}|$ to be determined, since the low temperature ^{19}F-$\{^1H\}$ and ^{31}P-$\{^1H\}$ spectra are of the ABX type; indeed, since $|\nu_A - \nu_B| \gg |J_{AB}|$, the spectra are of first-order appearance. In the fluorine region increasing the temperature from ca. −70°C first causes line broadening which obscures the splitting due to J_{FF}; then the chemical shift difference becomes averaged, but since this difference is large it is difficult to observe the spectra in the intermediate region and impossible to carry out accurate bandshape analysis. The ^{31}P-$\{^1H\}$ region is more promising, as can be seen from Figure 1. The low temperature spectrum is a quartet. The outer lines are separated by $|J_{AX} + J_{BX}|$ and do not broaden (or significantly shift) as the temperature is varied because they arise from spin states in which the fluorines are $\alpha\alpha$ or $\beta\beta$ and which are therefore invariant to the

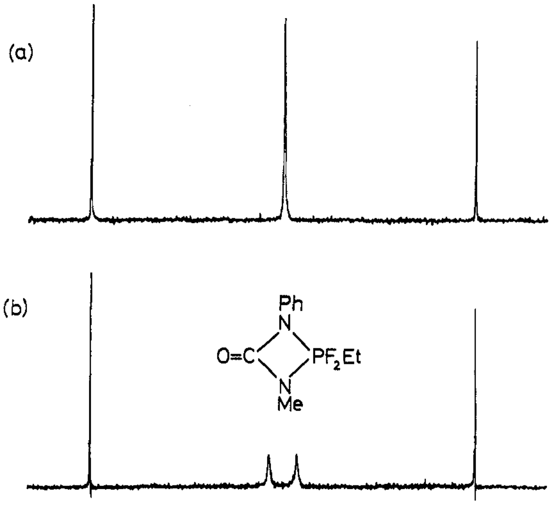


FIGURE 1 40 MHz ^{31}P-$\{^1H\}$ n.m.r. spectrum of compound II (R^1 = Et, R^2 = Me, R^3 = Ph). (a) At ca. 35°C (b) At ca. −50°C.

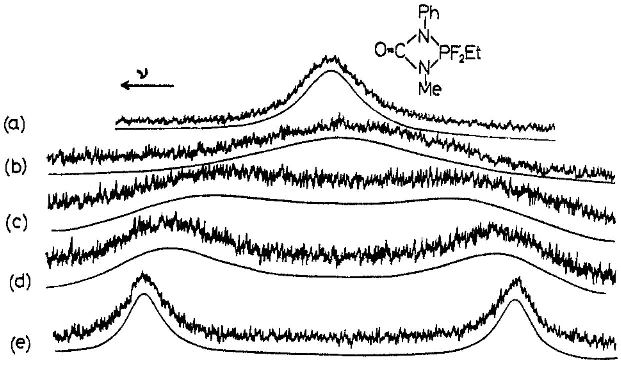


FIGURE 2 A series of observed and calculated 40 MHz ^{31}P-$\{^1H\}$ spectra (central pair of lines only) of compound II (R^1 = Et, R^2 = Me, R^3 = Ph). (a) At −10.5°C, k = 2777 s. (b) At −22.5°C, k = 952 s. (c) At −29.5°C, k = 476 s. (d) At −35.5°C, k = 294 s. (e) At −46°C, k = 71 s. Each observed spectrum results from the co-addition of ca. 12 scans in a Varian 620/i computer.

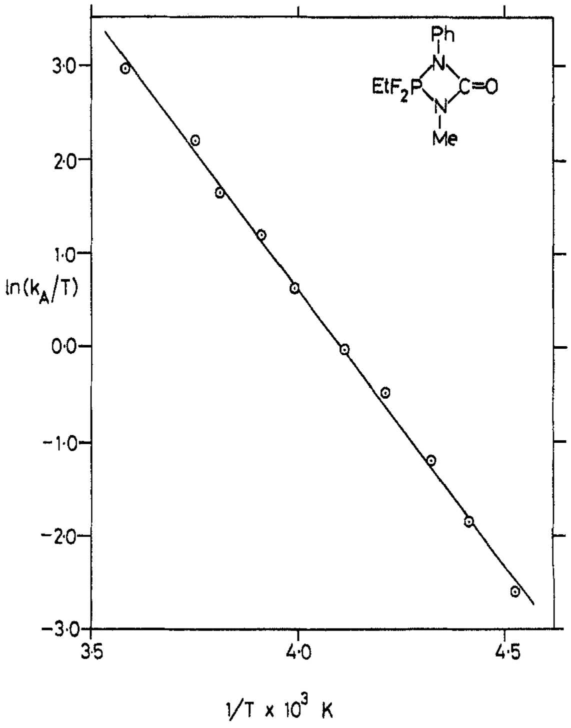


FIGURE 3 Eyring plot to obtain the thermodynamic parameters for the exchange process of compound II, R^1 = Et, R^2 = Me, R^3 = Ph. The rate constant k_A is that for leaving one of the two equivalent sites A and C.

TABLE I

Thermodynamic parameters[a] for pseudorotation in difluorophosphadiazetidinones of structure II

R^1	R^2	R^3	$\Delta G^{\ddagger}_{273}$/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1}K^{-1}
Me	Me	Et	39	50	40
Et	Me	Et	41	43	9
Ph	Me	Et	43	51	30
Me	Me	Ph	[b]46	47	2
			[c]46	47	4
Et	Me	Ph	47	49	9

[a] Using a transmission coefficient $\kappa = \frac{1}{2}$.

[b] From fitting of the spectra by eye.

[c] From iterative computer-fitting of the spectra.

ABX $\rightleftharpoons$ BAX exchange process. The central lines are separated by $|J_{AX} - J_{BX}|$, and these broaden and merge as the temperature is raised. This variation may be treated on a very simple basis, namely as due to exchange between two equally-populated uncoupled sites. The other lines act as markers for the measurement of linewidth in the absence of exchange. On this basis the spectra of compounds with R^2 = Me, R^3 = Ph, R^1 = Me or Et and R^2 = Me, R^3 = Et, R^1 = Me, Et or Ph were computer-simulated and compared by eye with the observed spectra in order to obtain rate constants for the exchange. Figure 2 shows a series of such spectra for II, R^2 = Me, R^3 = Ph, R^1 = Et. The rate constants obtained by this procedure for various compounds of type II were used in Eyring plots (Figure 3 gives an example) to obtain the thermodynamic parameters for the exchange process, which are given in Table I. The chemical shifts and coupling constants are listed in Table II and III, and similar data for symmetrical species of type I are given in Table IV for comparison. Finally, proton n.m.r. data are quoted in Table V for completeness. Table II, III and V also include

TABLE II

Fluorine and phosphorus n.m.r. parameters for unsymmetrical difluorophosphadiazetidinones (II) at ambient probe temperature[a], together with approximate coalescence temperatures[b]

R^1	R^2	R^3	δ_F/p.p.m.	δ_P/p.p.m.	$\lvert{}^1J_{PF}\rvert$/Hz	$T_{C1}^{c,d}$/°C	$T_{C2}^{c,e}$/°C	$T_{C3}^{f,g}$/°C
Me	Me	Et	−60.13[h]	−34.08[f]	921.6[f]	−15	−38	ca. −65
Et	Me	Et	−67.40[h]	−31.13[f]	939.5[f]	−10	−29	ca. −57
Ph	Me	Et	−64.36[h]	−43.70[f]	924.8[f]	+5	−18	ca. −45
Me	Me	Ph	−60.4	−32.8[f]	945[i]	ca. 30		ca. −32
Et	Me	Ph	−68.3[i]	−29.6[f]	885[i]			ca. −25
Ph	Me	Ph[j,k]	−64.3[c,l]	−42.2[m]	931.6[c,l]	+35	+5	

[a] 30–36°C.

[b] Data reported here for the first time are for CH_2Cl_2 solutions, plus a little CCl_3F, except where otherwise stated.

[c] From 56.4 MHz ^{19}F spectra.

[d] Coalescence temperature for the ^{19}F chemical shifts.

[e] Coalescence temperature for the doublets due to J_{FF}.

[f] From 40 MHz ^{31}P-$\{^1H\}$ spectra; likely errors ±0.5 p.p.m. in δ_P and ±0.5 Hz in $^1J_{PF}$.

[g] Coalescence temperature for the ^{31}P-$\{^1H\}$ lines separated by $\Delta(^1J_{PF})$.

[h] From 94.2 MHz ^{19}F spectra.

[i] Ref. 2.

[j] The reaction mixture gives a strong band in the IR absorption spectrum at 1780 cm^{-1}.

[k] All data for this compound were obtained using the reaction mixture plus CH_2Cl_2.

[l] At ca. 80°C.

[m] From 24.3 MHz ^{31}P spectra.

TABLE III

Fluorine and phosphorus n.m.r. parameters for unsymmetrical difluorophosphadiazetidinones (II) at low temperature

			δ_F/p.p.m.		$\lvert{}^1J_{PF}\rvert$(Hz)				
R^1	R^2	R^3	A^{a}	B^{b}	A^{a}	B^{b}	$\lvert J_{FF}\rvert$(Hz)	$\lvert\Delta\delta_F\rvert$(p.p.m.)	$\lvert\Delta{}^1J_{PF}\rvert$(Hz)
Me	Me	Et	-52.0^{c}	-69.0^{c}	896^{c} $893^{d,e}$	942^{c} $945^{d,e}$	50^{c}	17.0^{c}	46^{c} $51.5^{d,e}$
Et	Me	Et	-59.9^{c}	-76.4^{c}	909^{c} $914.4^{d,f}$	954^{c} $962.9^{d,f}$	54^{c}	16.5^{c}	45^{c} $48.5^{d,f}$
Ph	Me	Et	-57.8^{c}	-73.6^{c}	895^{c} $893.1^{d,g}$	944^{c} $949.0^{d,g}$	52^{c}	15.8^{c}	49^{c} $55.9^{d,g}$
Me	Me	Ph	-43.8^{h}	-78.2^{h}	868^{h}	966^{h}	49^{h}	34.4^{h}	98^{h} 145^{d}
Et	Me	Ph	-56.2^{h}	-81.3^{h}	840^{h}	980^{h}	56^{h}	25.1^{h}	140^{h} 139^{d}
Ph	Me	Ph	-53.6^{i}	-78.0^{i}	860^{i}	997^{i}	50^{i}	24.4^{i}	137^{i}

[a] For the fluorine that is preferentially axial.
[b] For the fluorine that is preferentially equatorial.
[c] Measured at 56.4 MHz for a CH_2Cl_2 solution at −60°C.
[d] Measured by ${}^{31}P$-$\{{}^1H\}$ n.m.r. at 40 MHz.
[e] At −92°C.
[f] At −83°C.
[g] At −74°C.
[h] Ref. 2.
[i] Measured at 56.4 MHz for a solution of the reaction mixture in CH_2Cl_2 at −30°C.

results for II, R^1 = Ph, R^2 = Me, R^3 = Ph, presented for the first time; no detailed bandshape studies were carried out in this case.

In addition to the procedure of fitting exchange spectra by eye, attempts were also made to iteratively fit the ${}^{31}P$-$\{{}^1H\}$ spectra of II($R^1 = R^2$ = Me; R^3 = Ph) by computer (varying both the exchange rate constant and ΔJ_{PF}), using a program largely devised by M. Murray.[9] These results are also given in Table I. Problems were encountered because of limits on the allowable digitisation, and it is not suggested that the data are more accurate than the results from "by eye" fitting. In fact, the two methods give very similar results.

TABLE IV

Fluorine and phosphorus n.m.r. parameters for symmetrical difluorophosphadiazetidinones (I)

			δ_F/p.p.m.^{a}		$\lvert{}^1J_{PF}\rvert$/Hz^{a}	
R^1	R^2	δ_P/p.p.m.	high temp.^{b}	low temp.	high temp.^{b}	low temp.
Me	Me	-34.8^{c}	−61.7	-61.9^{d}	918	922^{d}
Et	Me	-32.0^{c}	−68.6	-69.4^{e}	939	936^{e}
Ph	Me	-46.8^{c}	−65.9	-67.2^{e}	928	922^{e}
Me	Et		−58.6	-58.4^{e}	920	921^{e}
Et	Et		−65.7	-66.2^{e}	938	935^{e}
Ph	Et		−62.2	-62.8^{e}	927	919^{e}

[a] Measured at 56.4 MHz.
[b] At ambient probe temperature, ca. 30–32°C, for CH_2Cl_2 solutions.
[c] Ref. 1.
[d] −30°C.
[e] −60°C.

TABLE V

Proton n.m.r. parameters for difluorophosphadiazetidinones[a,b]

Compound			δ_H/p.p.m.							
R^1	R^2	R^3	Ph	NMe	CH_2	CH_3C	PMe	$\lvert {}^3J_{PNCH} \rvert$/(Hz)	$\lvert {}^2J_{PCH} \rvert$/(Hz)	$\lvert {}^3J_{PCCH} \rvert$/(Hz)
Me	Me	Et	—	2.54	3.00[c]	1.00[c]	1.73[d]	17.7[e] 12.0[f]	17.9	—
Et	Me	Et	—	2.55	3.00[c] —	1.00[c] 1.09[g,h]	—	17.0[e] 11.1[f]		26.5
Ph	Me	Et	7.5[i]	2.62	3.10[c]	1.03[c]		18.5[c] 12.0[f]	—	—
Me	Me	Ph		2.75				15.5[f]		
Et	Me	Ph		2.63				15.0[f]		
Ph	Me	Ph	7.1[i,j]	2.79	—	—	—	15.2[f]	—	—

[a] For solutions in CH_2Cl_2 + TMS (except R^1 = Ph, R^2 = Me, R^3 = Ph, which was studied as the reaction mixture +TMS). Data are from 60 MHz work at ca. 31°C.

[b] For the ethyl groups ${}^3J_{HH} \simeq 7.0 - 7.1$ Hz.

[c] NEt.

[d] $\lvert {}^3J_{FPCH} \rvert = 7.0$ Hz.

[e] CH_2.

[f] CH_3

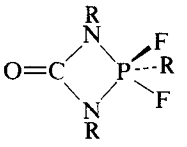
[g] PEt.

[h] $\lvert {}^4J_{FPCCH} \rvert = 1.2$ Hz.

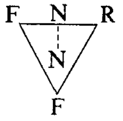
[i] Approximate data.

[j] NPh and PPh.

DISCUSSION



III



IV

The n.m.r. results for phosphadiazetidinones may be understood in terms of a trigonal bipyramidal configuration at phosphorus, with the NR-groups occupying one axial and one equatorial position, as required by the geometry of the ring.† For the difluoro derivatives this forces one fluorine to be equatorial (and one axial), in contrast to the usual situation for unstrained phosphoranes (which have the more electronegative groups preferentially axial). This state of affairs is illustrated by molecular structure III, but is for our purposes more conveniently represented by IV, which shows a view looking along the P···C = O direction; N---N represents the plane of the ring and the triangle connects the remaining substituents at phosphorus. It is apparent that there are four possible stable conformations for molecules of this type (as shown in Figure 4) which are in accord with the principles outlined above.[2] These are labelled A, C, D and F. The nitrogens are distinguished by a prime on one of them, to allow for representation of species II (for which the nitrogen substituents differ). In such a case A and C are equivalent and have the same energy, but they differ in energy from the equivalent pair D and F. From the viewpoint of Figure 4 "pseudorotation" at phosphorus has, indeed, the appearance of a rotation,‡ and its apparent that the exchanges A⇌F

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† It may also be that the preferred situation, with one nitrogen axial and one equatorial, is caused by some other effect, since, surprisingly, some compounds analogous to II but with six-membered rings also have one nitrogen axial and one equatorial to phosphorus, thus showing non-equivalent fluorine nuclei. In contrast to the four-membered ring, in which ring strain may be considered as providing the driving force for the preferred axial/equatorial attachment of the ring, the apparently preferred axial/equatorial attachment of nitrogen at phosphorus is not readily understood in the case of the six-membered ring compounds.

‡ However, this statement is not intended to deny the likelihood that there are additional molecular distortions during such processes as A⇋F; the path actually followed will be that which minimises the energy barrier.

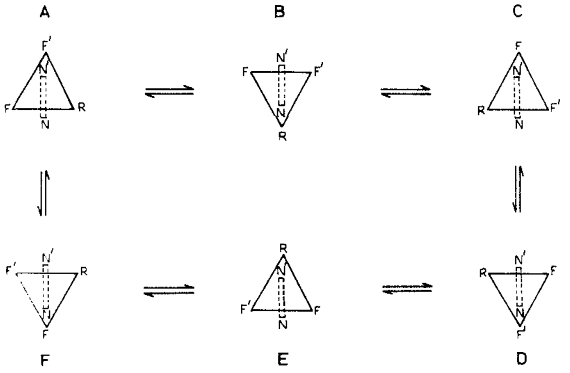


FIGURE 4 Proposed pseudorotation exchange cycle for difluorophosphadiazetidinones.

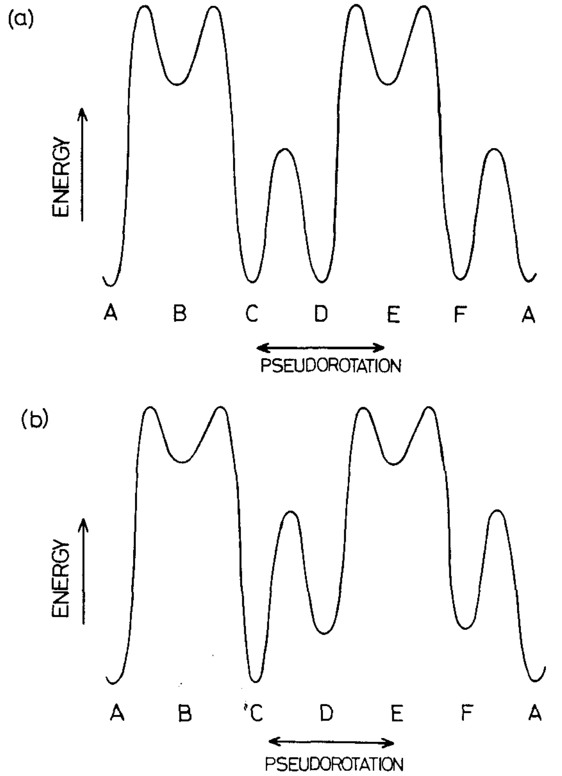
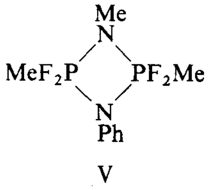


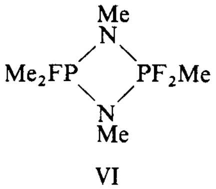
FIGURE 5 Hypothetical pseudorotation energy diagrams for difluorophosphadiazetidinones. (a) Symmetrical compounds (type I). (b) Unsymmetrical compounds (type II). The conformations A to F are as in Figure 4. It is possible that conformations B and E represent energy maxima rather than minima.

and C $\rightleftharpoons$ D are particularly facile since they involve a rotation of only 60° between stable conformations. For symmetrical compounds of type I this suffices to make the two fluorine atoms (and the two substituents at nitrogen) equivalent. This process, therefore, is shown by the invariance of the spectra to be rapid on the n.m.r. time scale at all accessible temperatures, and this is the only dynamic information available from type I compounds. For compounds of type II, however, processes A $\rightleftharpoons$ F and C $\rightleftharpoons$ D are inadequate for making the fluorines equivalent, since one fluorine will still be near NR^2 whereas the other will be near NR^3. However, if processes A $\rightleftharpoons$ C and D $\rightleftharpoons$ F become rapid, the fluorines will be rendered equivalent in this case also. Thus the changes in the observed spectra for type II compounds represent a slowing of the processes A $\rightleftharpoons$ C and D $\rightleftharpoons$ F. On the simple picture of Figure 4 these processes require the intervention of a metastable intermediate with group R^1 axial, thus accounting for the fact that they are slower than processes A $\rightleftharpoons$ F and C $\rightleftharpoons$ D. The pseudorotation energy profiles envisaged for I and II are shown in Figure 5†. It is possible that conformations B and E actually represent energy maxima, rather than metastable minima as illustrated in Figure 5 (see, for example, Ref. 10).

The fluorine non-equivalence for the unsymmetrical compounds has two origins, viz. (i) the intrinsic asymmetry, and (ii) population differences between A and C on the one hand and D and F on the other. For the tetrafluorodiazadiphosphetidine V only origin (i) is present, giving chemical shift non-equivalence (for *gauche* and *trans* isomers)



V



VI

of 5.2 p.p.m. and 4.4 p.p.m. with non-equivalences in $^1J_{PF} + {}^3J_{PF} + {}^3J'_{PF}$ of 12 Hz and 45 Hz, respectively. These values may be contrasted with the appreciably larger data in Table III, showing that population differences are significant for the compounds studied here. The axial-equatorial differences for the trifluorodiazadiphosphetidine VI are 35.95 p.p.m. and 155.6 Hz for δ_F and $^1J_{PF}$, respectively.[11] Thus the compounds of type II with $R^2 = Me$, $R^3 = Ph$ show fluorine non-equivalence of a magnitude which indicates that

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† Figure 11 of Ref. 2 is incorrectly drawn and should be as Figure 5(b) here.

TABLE VI

Fluorine chemical shift non-equivalence[a] as a function of temperature for unsymmetrical difluorophosphadiazetidinones (II)[b]

R^1	R^2	R^3	Temperature/°C	$\|\Delta\delta_F\|$/p.p.m.
Me	Me	Et	−40	15.6
			−50	16.3
			−60	17.0
Et	Me	Et	−40	15.0
			−50	15.6
			−60	16.5
			−70	17.3
Ph	Me	Et	−30	13.9
			−40	14.5
			−60	15.8
Ph[c]	Me	Ph	0	24.5
			−10	24.2
			−20	24.4
			−30	24.4

[a] In all cases the mean values for δ_F do not vary greatly, and they are consistent with the average data obtained above coalescence.

[b] As solutions in CH_2Cl_2, measured at 56.4 MHz.

[c] This compound was studied as the reaction mixture plus CH_2Cl_2.

energy differences between A and F are sufficiently large that there is very little occupancy of one of these conformations, and that the low temperature n.m.r. parameters correspond to nearly pure axial and equatorial situations (with the NPh group axial, for steric and electronic reasons). This accounts for the relative lack of temperature-dependence (Table VI gives data for R^1 = Ph, R^2 = Ph) in values of δ_F and $^1J_{PF}$ below coalescence, which results in reasonable accuracy for the "by eye" bandshape fitting; the non-equivalences in $^1J_{PF}$ were held constant at their low temperature values for all calculations. However, for the compounds with R^2 = Me, R^3 = Et the non-equivalences are smaller, indicating a more balanced population distribution. This is also shown by a tendency for the non-equivalences to increase as the temperature is lowered in the slow exchange region (see Table VI), though it is not always easy to distinguish such changes from the effects of incipient coalescence. Problems arose in the "by eye" bandshape fitting from this origin—the non-equivalences used for $^1J_{PF}$ near the coalescence temperature and above were those actually measured in the lower temperature region; they are therefore liable to error. Variations in ΔJ_{PF} of only a few Hz would significantly affect the derived exchange rates. It is therefore anticipated that the accuracy of the thermodynamic data for these compounds is low, being less than that for the N-phenyl cases. This is almost certainly indicated by the high values of $\Delta S^{\ddagger}$ for two of the compounds (see Table I), since it may be expected that $12 > \Delta S^{\ddagger} \gg 0$ J mol^{-1} K^{-1} (see below). This situation with respect to $\Delta S^{\ddagger} >$ (and $\Delta H^{\ddagger}$) is common in studies of chemical exchange by n.m.r. The principal objects of bandshape fitting must be regarded as obtaining reasonably accurate values of $\Delta G^{\ddagger}$ in the region of coalescence, and extrapolating by a small amount to a common temperature for a range of compounds in order to examine trends in the barriers.

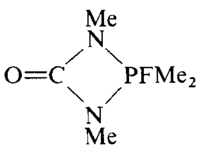
Although variations in the value of $\Delta G^{\ddagger}_{273}$ in Table I are small we feel the trends are significant: the barriers increase for substituents in the order R^1 = Me < Et < Ph. This is in agreement with the variation in the approximate values of coalescence temperatures (see Table II), including the data for the compound R^1 = Ph, R^2 = Me, R^3 = Ph, which is not represented in Table I. Presumably the trends arise from steric and/or electronic factors, which must also be responsible for the energy differences between forms A and C on the one hand and D and F on the other. Gorenstein[12] found that for systems containing five-membered rings the energy of the metastable intermediate was increased by bulky groups in the axial position, though bond-lengths in the trigonal bipyramid are such that substituents on phosphorus do not normally appear to sterically interact with one another, Trippett[10] has also shown that barriers tend to increase with substituent bulk, and comments that it is often assumed that the apical position is more hindered than the equatorial for a trigonal bipyramidal phosphorane. For the four-membered ring systems considered here, molecular models seem to show there is little steric interaction, but it is nonetheless likely that there is a contribution from this source to the trends shown by $\Delta G^{\ddagger}_{273}$. In terms of electronegativity a smaller barrier might be expected for R^1 = Ph than for R^1 = Me or Et, since the axial position required for R^1 in the metastable intermediate will be less unfavourable for the more electronegative aryl group.

The values of $\Delta G^{\ddagger}$ reported by Gorenstein[12] for pseudorotation about phosphorus in systems containing five-membered rings are in the range 40 to 70 kJ mol^{-1}. Trippett[10] reports values from 42 to 61 kJ mol^{-1} for similar systems. Data for diazadiphosphetidines of the type $(RF_2PNME)_2$

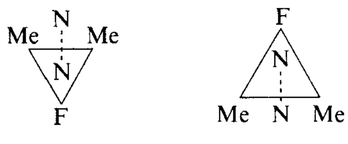
increase[13] from 49 to 80 kJ mol^{-1} as R is increased in bulk from Me to Bu^t; the values for R = Et and R = Ph are equal within experimental error, as is probably the case for the compounds considered here. The effect on the barrier of varying the N-substituents in the diazadiphosphetidine series is not known.

In our procedure for obtaining the thermodynamic parameters for the barrier a transmission coefficient of $\frac{1}{2}$ was used to allow for the fact that an unstable intermediate is envisaged (Figures 4 and 5) which is equally likely to revert to the original conformation as to proceed further to the equivalent form. Such a factor may also be justified (instead of, or as well as, the above argument) if it is felt that the lifetime in the transition state is sufficiently long that deactivation to the two lowest potential minima is equally likely. On the other hand one may argue for a factor of 2 to take account of the two pseudorotation pathways (clockwise and anticlockwise), though the barrier heights are not necessarily the same. When $\kappa = \frac{1}{2}$ is used, as here, the above arguments can probably be used to justify any value of $\Delta S^\ddagger$ between ca. 0 and +12 J mol^{-1} K^{-1}, as mentioned above, but such variations are within experimental error.

It is of interest to note that in principle the NMe resonances of I also provide a possible method of distinguishing rates of pseudorotation, since at slow exchange $A \rightleftharpoons F$ and $C \rightleftharpoons D$ the two P—N bonds are different (the NMe resonances cannot, on the other hand, be affected by $A \rightleftharpoons C$ and $D \rightleftharpoons F$). Such a distinction cannot be realised for I, but is more feasible for VII. In this case there are two equivalent conformers, as shown in VIII(a)



VII



(a) (b)

VIII

and VIII(b), which can, in principle, interchange by pseudorotation processes akin to those of Figure 4. If such an interchange is rapid on the n.m.r. timescale the NMe protons will be equivalent and will be equally coupled to the phosphorus. However, under conditions of slow exchange two NMe bands will be seen, with different splittings due to $^3J_{PH}$ (and also from $^4J_{PH}$). Figure 6 shows that at room temperature pseudorotation (which needs to be through 180°) is slow,† and it remains slow up to at least 100°C. Thus, the barrier to this process is appreciably higher than those obtained for the 120° pseudorotation in compounds of the type II. In terms of a pseudorotation cycle analogous to that of Figure 5 this can only be explained as involving two metastable intermediates, as implied by Figure 7. The fact that barriers to the 180° process are appreciably higher than to the 120° process seems to suggest that conformations B and E of Figure 4 are indeed potential minima rather than maxima (see also Figure 5). The alternative explanation, that apicophilicity of methyl groups depends very heavily on the nature of the other equatorial substituents, seems less likely.

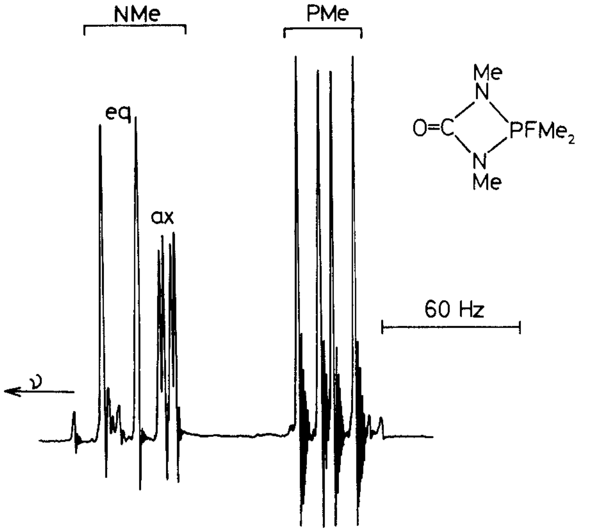


FIGURE 6 60 MHz ^{1}H n.m.r. spectrum of compound VII (benzene solution at ambient probe temperature) to illustrate the non-equivalence of the NMe protons. Minor peaks are due to impurities.

The n.m.r. data we have obtained for VII are as follows:

$\delta_P = -46.4$ p.p.m. $\delta_F = -32.3$ p.p.m.
$\delta_H(\text{PMe}) = 1.26$ p.p.m. $|^2J_{PH}| = 15.3$ Hz
$\delta_H(\text{NMe, eq.}) = 2.74$ p.p.m. $|^3J_{PH}| = 14.3$ Hz
$\delta_H(\text{NMe, ax.}) = 2.40$ p.p.m. $|^3J_{PH}| = 4.8$ Hz
$|^1J_{PF}| = 705$ Hz
$|^3J_{FH}| = 9.6$ Hz
$|^4J_{FH}| < 0.8$ Hz
$|^4J_{FH}| = 1.5$ Hz

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† An early report[1] of n.m.r. data for VII (and for O=C[NMe]$_2$PFPh$_2$) lists only a single NMe chemical shift; this is definitely an error.

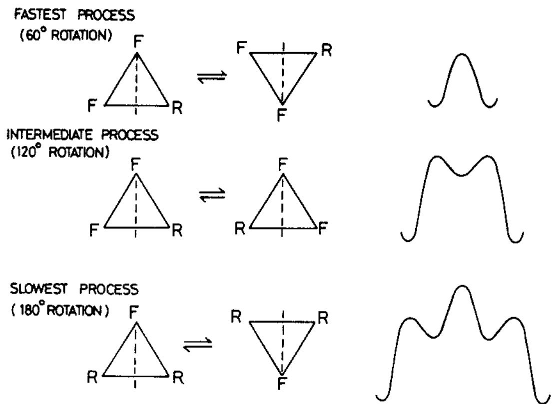

FIGURE 7 Rationalisation of the pseudorotation exchange barriers for fluorophosphadiazetidinones. The plane of the ring, indicated by the dashed line, is regarded as stationary for the purposes of this representation.

The assignment of the NMe resonances is tentative, and relies, especially, on the work by Cavell[14b] on the compound $CH_3(CF_3)_3(NMe_2)P$ for which $^3J(PH)$ is reported to be 13.3 Hz.

EXPERIMENTAL

The usual precautions in handling moisture and/or air-sensitive substances were observed. Solvents were dried by standard procedures. IR spectra were recorded using a Beckman IR 20A instrument.

Preparation of N-Methyl-N'-Ethyl-Bis (trimethylsilyl) Urea

The reaction was conducted in a two-necked flask, fitted with a reflux condenser (topped by a drying tube) and a pressure-equalizing dropping funnel. Ethyl isocyanate (13.6 g; 0.19 mol) was added dropwise with magnetic stirring over 15 min. to 33.6 g (0.19 mol) of heptamethyl-disilazane. The reaction mixture was stirred at 50°/24 h. and was then distilled through a 20 cm Vigreux column, 34.1 g (72 %) of colourless liquid, b.p. 48° (0.9 Torr) being obtained. The infrared spectrum of the pure liquid shows a strong band at 1622 cm^{-1}.
Anal. found: C, 48.9; H, 10.7; N, 11.4. $C_{10}H_{26}N_2OSi_2$ requires C, 48.7; H, 10.6; N, 11.4.

Preparation of P-Methyl-P,P-Difluoro-N-Methyl-N'-Ethyl-Phosphadiazetidinone (IIa)

The urea (9.0 g; 0.036 mol) was placed into a heavy-wall glass tube; the contents of the tube were cooled and 4.45 g (0.036 mol) of $MePF_4$ was condensed in. The tube was sealed while its contents were held at liquid nitrogen temperature. After 24 h. shaking at room temperature the reaction mixture was distilled through a 20 cm Vigreux column, 5.3 g (79 %) of IIa as a colourless liquid, b.p. 44° (1.0 Torr) being obtained. There is a strong absorption band at 1783 cm^{-1} in the infrared spectrum of the pure liquid.
Anal. found: C, 32.8; H, 6.2; N, 15.2. Mol. wt. (mass spect.) 184. $C_5H_{11}F_2N_2OP$ requires: C, 32.6; H, 6.2; N, 15.2. Mol. wt.: 184.13.

Preparation of P-Ethyl-P,P-Difluoro-N-Methyl-N'-Ethyl-Phosphadiazetidinone, (IIb)

As described in the preceding experiment, 11.7 g (0.047 mol) of the urea and 7.4 g (0.054 mol; 14 % excess) of $EtPF_4$ were allowed to react to give 6.0 g (64 %) of (IIb) as a colourless liquid of b.p. 39° (0.3 Torr). IR spectrum (pure liquid): strong absorption at 1785 cm^{-1}.
Anal. found: C, 36.5; H, 6.8; N, 14.0. Mol. wt. (mass spectr.): 198. $C_6H_{13}F_2N_2OP$ requires: C, 36.4; H, 6.6; N, 14.1; Mol. wt. 198.27.

Preparation of P-Phenyl-P, P-Difluoro-N-Methyl-N'-Ethyl-Phosphadiazetidinone, (IIc)

In a round-bottomed flask fitted with a reflux condenser plus drying tube, a mixture of 9.4 g (0.038 mol) of the urea and 7.02 g (0.038 mol) of $PhPF_4$ was stirred for 24 h. at room temperature. Distillation furnished II(c) as a colourless liquid of b.p. 68° (0.05 Torr); yield 8.0 g (85 %). The IR spectrum of the liquid shows a strong absorption at 1787 cm^{-1}.
Anal. found: C, 49.0; H, 5.3; N, 11.4. Mol. wt. (mass spectr.): 246. $C_{10}H_{13}F_2N_2OP$ requires: C, 48.8 H, 5.3; N, 11.4; mol. wt. 246.31.

N.M.R. Measurements

The initial n.m.r. work was carried out using a Varian HA 60A spectrometer at Braunschweig University, operating at 60, 56.4 and 24.3 MHz for ^1H, ^{19}F and ^{31}P, respectively. Later studies on ^1H and ^{19}F were made at 99.9 and 94.2 MHz, respectively with a Varian HA 100 spectrometer at the University of East Anglia. A Schlumberger FSX 3005 frequency synthesizer was used in conjunction with a double-tuned probe for $^{19}F\text{-}\{^1H\}$ work. The $^{31}P\text{-}\{^1H\}$ spectra were obtained at 40.50 MHz using a Varian XL 100 spectrometer (at East Anglia) in either the CW or the FT mode.

In general, solutions in CH_2Cl_2 were used (with some CD_2Cl_2 to provide the ^2H lock signal for the XL-100 work). The detailed studies were carried out with sealed, degassed samples. Chemical shifts are quoted in the tables in p.p.m. with respect to the signals for Me_4Si, $CFCl_3$ and external 85 % H_3PO_4 for ^1H, ^{19}F and ^{31}P respectively. The convention used is that shifts are positive when the sample signal is to high frequency of the reference signal. The ^{31}P shifts from the 40 MHz work were obtained by the indirect method.[11]

The temperatures for the bandshape fitting work were considered accurate to ±2°, whereas those given in Table 6 are probably only accurate to ±4°. The former were calibrated using the standard Varian methanol sample in the ^1H resonance before and after each bandshape was recorded.

The bandshape simulations were carried out using the computer program[15] AXEX which is based on the equation of Hahn, Maxwell and McConnell[16] for exchange between two unequally-populated, uncoupled sites, allowance being made for a common non-exchange linewidth (obtained from the outer $^{31}P\text{-}\{^1H\}$ lines, which are not affected by the exchange). The iterative work with II, $R^1 = R^2 = Me$, $R^3 = Ph$, was done using an adaptation of the program[9] AXEFIT. All computations were carried out with an ICL 1905E computer.

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