Phosphorus–Fluorine Chemistry. Part XXXV.[1] Unsymmetrical 1,3-Diaza-2,4-diphosphetidines of Zwitterionic Structure

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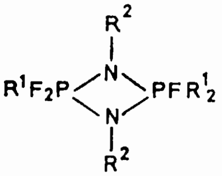
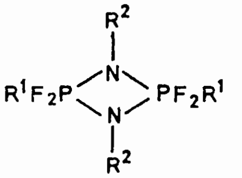
The reactions of 2,2,2,4,4,4-hexafluoro-1,3-dimethyl-1,3-diaza-2,4-diphosph(v)etidine with *NN'*-dilithio-*NN'*-dimethylethylenediamine, and of the 1,3-t-butyl analogue with t-butyl-lithium gave rise to zwitterionic species, involving tetra- and hexa-co-ordinate phosphorus atoms, instead of the products of normal nucleophilic substitution in which phosphorus retains co-ordination number five. The zwitterionic structure of these products has been established by ^{1}H, ^{19}F, and ^{31}P n.m.r. spectroscopy. Mass spectroscopy has shown that decomposition into monomeric phosphine imides, which is characteristic of 1,3-diaza-2,4-diphosph(v)etidines, does not occur in the case of the zwitterionic compounds.

According to n.m.r. studies by Harris *et al.*[2,3] the five-co-ordinate phosphorus atoms in the dimeric fluorophosphine imide (1a; $R^1 = F$, $R^2 = Me$) have identical environments; the structure of this compound has also been deduced from vibrational spectra [4,5] and from an electron diffraction study.[6] From the variation of the ^{19}F n.m.r. spectra of compounds of types (1a and b) it was concluded [3,7] that a concerted pseudorotation process is taking place.



(1a)



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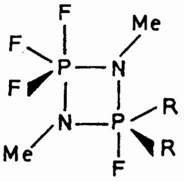
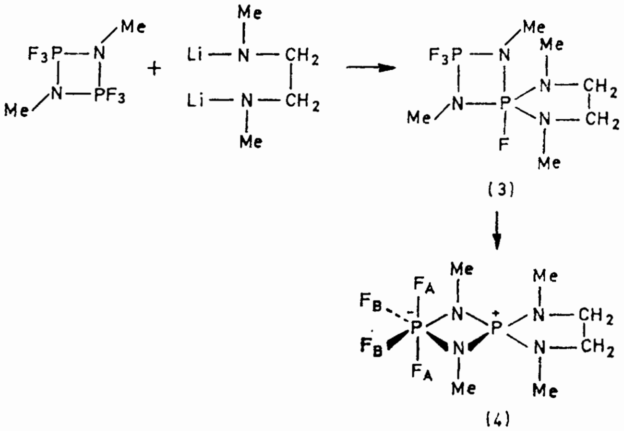
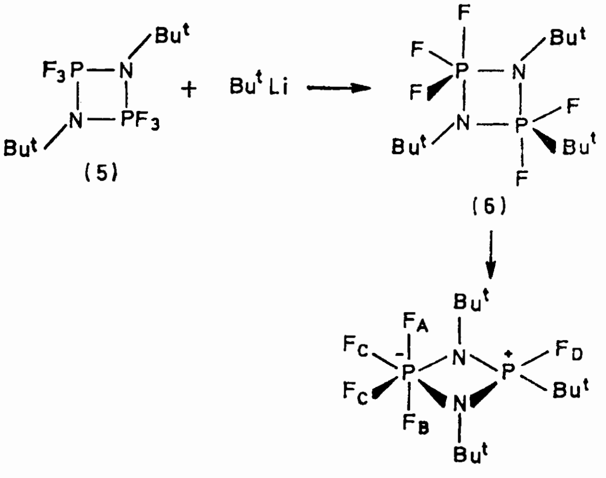


(2)

In order to gain further insight into this phenomenon, we wished to study the pseudorotation process in unsymmetrical compounds of type (2). The synthesis of such compounds was attempted from the diazadiphosphetidine (1a; $R^1 = F$, $R^2 = Me$) and *NN'*-dilithio-*NN'*-dimethylethylenediamine. We believe that the expected compound (3) was formed as an intermediate, but the actual product obtained, in nearly quantitative yield, was apparently (4), the n.m.r. data for which indicate a zwitterionic structure.

We also wished to investigate the influence of bulky t-butyl groups on the pseudorotation processes, and efforts were made to prepare suitable compounds. However, from the reaction of the hexafluorodiazadiphosphetidine (5) with t-butyl-lithium the expected product (6) was not isolated, although its intermediate formation is assumed. Instead, the zwitterionic compound (7) was obtained.





(7)

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[1] Part XXXIV, K. P. John, R. Schmutzler, and W. S. Sheldrick, *J.C.S. Dalton*, 1974, 1841.

[2] R. K. Harris and C. M. Woodman, *Mol. Phys.*, 1966, **10**, 437.

[3] R. K. Harris, J. R. Woplin, R. E. Dunmur, M. Murray, and R. Schmutzler, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 44.

[4] A. J. Downs, *Chem. Comm.*, 1967, 628.

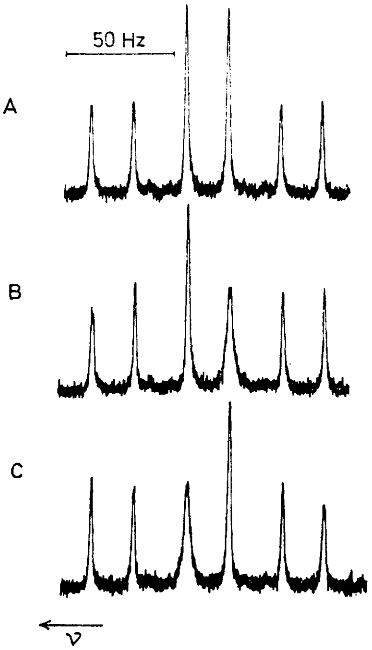
[5] M. P. Yagupski, *Inorg. Chem.*, 1967, **6**, 1770.

[6] A. Almenningen, B. Andersen, and E. E. Astrup, *Acta Chem. Scand.*, 1969, **23**, 2179.

[7] O. Schlak, R. Schmutzler, R. K. Harris, and M. Murray, *J.C.S. Chem. Comm.*, 1973, 23.

Characterization of compounds (4) and (7) as zwitterions depended heavily on interpretation of their n.m.r. spectra, which were investigated in detail, particularly in the case of (4); mass spectroscopy was also employed.

N.m.r. Spectra of Compound (4).—The ^{19}F and ^{31}P n.m.r. spectra of compound (4) were examined under conditions of proton-noise decoupling using the frequency-sweep mode. Multi-scan averaging by a Varian 620/i computer was used for the ^{31}P spectra (up to 10 scans). The spectra could be interpreted on a first-order basis in terms of structure (4), and assignment was straightforward, except for the choice between fluorine nuclei A and B. A decision in this respect was made by using the results for compound (7), where the distinction between fluorine nuclei in the plane of the P_2N_2 ring and those perpendicular to it is clear, since geometrical influences render the latter non-equivalent. The relative signs of the coupling constants were determined by heteronuclear multiple resonance experiments, by using population (nuclear Overhauser) and tickling effects.[8] Thus the relative signs of $^1J_{PF_B}$ and $^2J_{PP}$ were obtained by observing the fluorine spectrum in the B region (without proton decoupling) while irradiating the P^+ region of the phosphorus spectrum. The other experiments of this type were: (*a*) observation of F_B (without proton decoupling) while irradiating P^-, giving the relative signs of $^2J_{PP}$ and $^3J_{PF_B}$ as shown in the Figure; a similar experiment, involving irradiation of different P^- lines, gave the relative signs of $^1J_{PF_A}$ and $^2J_{FF}$; (*b*) observation of F_B under triple-resonance conditions (tickling F_A and noise-decoupling all the protons); this gave the relative signs of $^3J_{PF_B}$ and $^3J_{PF_A}$, and of $^1J_{PF_B}$ and $^1J_{PF_A}$. The results are given in the Table.



^{19}F Spectrum (B region, low frequency half) of zwitterion (4) at 94·1 MHz, illustrating the determination of relative signs of $^2J_{PP}$ and $^3J_{PF_B}$: A, single resonance spectrum; B and C, ^{19}F-{^{31}P} spectra obtained while irradiating the P^- region with low power. The P^- region may be described as a triplet of triplets of doublets. Spectra B and C were obtained while irradiating the low and high frequency members, respectively, of the two most intense lines. Each experiment should affect one member of the most intense pair of ^{19}F lines shown. The small effect on another ^{19}F line in each case is probably due to the presence of a weaker ^{31}P resonance near the one being irradiated

^{19}F and ^{31}P N.m.r. parameters for the zwitterions (4) and (7) [a-d]

δ_F	−49·83 [(4)A]	−75·93](4)B]	
	−26·94 [(7)B]	−61·17 [(7)B]	−72·55 [(7)D]
	−24·30 [(7)A]		
$^1J_{PF}$ [f]	−744·0 [(4)A]	−789·0 [(4)B]	
	771·1 [(7)A]	822·0 [(7)C]	1227·6 [(7)D] [g]
	842·6 [(7)B]		
$^3J_{PF}$	+6·3 [(4)A]	+19·5 [(4)B]	
	14·8 [(7)A]	16·5 [(7)C]	4·3 [(7)D]
	11·7 [(7)B]		
J_{FF}	−44·5 [(4)]		37·3 [AD]
	52·0 [(7)AC]	<0·5 [(7)AB]	2·0 [BD]
	63·8 [(7)BC]		2·0 [CD]
δ_P [h]	−151·6 [(4)P⁻]	33·4 [(4)P⁺]	
	−139·0 [(7)P⁻]	68·5 [(7)P⁺]	
$^2J_{PP}$	+107·5 [(4)]	54·4 [(7)]	

[a] Errors in chemical shifts estimated at ±0·01 p.p.m. for ^{19}F and ±0·2 p.p.m. for ^{31}P. The larger error for the ^{31}P measurements arises from drifts in the master oscillator. The coupling constants are in Hz, with errors *ca.* ±0·5 Hz. [b] The compound is indicated in brackets, together with information about the nuclei involved. For δ_F, $^1J_{PF}$, and $^3J_{PF}$ the three columns are for fluorine nuclei perpendicular to the plane of the P_2N_2 ring, in the plane, and on P^+, respectively. [c] The assignment of the A and B fluorines for (7) is tentative (see text). [d] The data on coupling constants for (7) are without sign information. [e] With respect to the resonance of $CFCl_3$: positive when the sample resonance is at the higher frequency. [f] Sign assumed.[16] [g] Value from ^{19}F measurements. [h] With respect to 85% H_3PO_4; positive when the sample resonance is at the higher frequency.

Proton spectra (HA-60A instrument) showed an ' apparent ' triplet of triplets for the MeN groups of the P_2N_2 ring with δ_H 2·4 p.p.m. $|^3J_{PH}|$ 15·0 and $|^4J_{FH}|$ *ca.* 1 Hz. The ' triplet ' structure is a result of couplings with the phosphorus atoms which, in spite of the different co-ordination numbers (four and six), are nearly equal. For the MeN groups of the five-membered ring a doublet with δ_H 2·6 p.p.m. and $|^3J_{PH}|$ 11·0 Hz, and for the ethylene grouping a doublet with δ_H 3·2 p.p.m. and $|^3J_{PH}|$ 10·0 Hz, were observed. Dichloromethane was used as internal reference; the δ_H values were obtained by adding 318 Hz to the shifts from CH_2Cl_2.

N.m.r. Spectra of Compound (7).—These spectra were obtained as for (4). The fluorine region showed four different doublets, each having further fine structure. The two high-frequency doublets (assigned to F_A and F_B) have about the same combined intensity as the doublet at medium frequency (F_C) and about twice the intensity of the doublet at lowest frequency (F_D). According to our structural proposal, F_A and F_B in (7) are non-equivalent; therefore, the high-frequency resonances are assigned to these fluorine atoms. The relative assignment of resonances to F_A and F_B is not simple. However, if one assumes that the P_2N_2 ring, owing to substituent influences, is not completely planar, but

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[8] R. A. Hoffman and S. Forsen, *Progr. N.M.R. Spectroscopy*, 1966, **1**, 15.

puckered so that F_A and F_D approach one another, the large value of $^4J_{FF}$ (37·3 Hz) for *one* of the fluorine nuclei bonded to P^- (namely F_A) may be explained on the basis of a ' through-space ' effect; it is for this reason that the assignment of the F_A resonance was made as given in the Table. However, in the case of cyclotriphosphazatrienes similar reasoning fails, since $|^4J_{FF}(cis)| < |^4J_{FF}(trans)|$.[9] Molecular models for (7) show that the molecule is subject to severe steric crowding; a departure from planarity for the P_2N_2 ring reduces steric interactions and does, indeed, bring F_A and F_D close together.

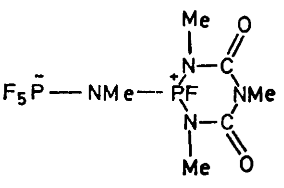
The ^{31}P spectrum showed a doublet with fine structure at high frequency and an approximate quintet with fine structure at lower frequency. The δ_P values observed [+68·5 ($^1J_{PF_D}$ 1228 Hz) and −139·0 p.p.m. (with $|^1J_{PF}|$ 771 and 843 Hz)] are in accord with the assumption of one tetra- and one hexa-co-ordinate phosphorus atom. The ^{19}F and ^{31}P n.m.r. parameters for (7) are given in the Table.

The ^1H spectrum of (7) consisted of a broad singlet (δ_H 1·55 p.p.m.) for the Bu^{t}N groups, and a doublet of doublets at δ_H 1·4 p.p.m. ($|^3J_{PH}|$ 20·5 and $|^4J_{FH}|$ 2·0 Hz) for the PBu^t group. The ^1H shift values were calculated from shifts relative to internal C_6H_6 by adding 442 Hz.

DISCUSSION

The analyses of the ^{19}F and ^{31}P spectra, together with the data in the Table, fully confirm the structures (4) and (7) as far as the fluorine and phosphorus atoms are concerned. The proton spectra are also consistent with the proposed structures.

The ^{19}F and ^{31}P chemical shifts and coupling constants fall in the appropriate ranges [including considerations of signs for coupling constants in (4)]. For (4) the difference between $^3J_{PF}$ values for the two types of fluorine atom is substantial, but both these coupling constants are positive (in some instances, for example in certain diazadiphosphetidines,[3,10] $^3J_{PF}$ can be negative). The differences between the analogous types of $^3J_{PF}$ for (7) are much less marked but only the magnitudes are known. The value of $|^3J_{PF_D}|$ is considerably less than that of the other $|^3J_{PF}|$ for (7). The value of $|^2J_{PP}|$ for (4) is large; the present results are, of course, the first reports of J_{PP} in zwitterions [except the value of 46 Hz, sign unknown, given in a Ph.D. thesis [11] for (8)], but some other values of $|^2J_{PP}|$ through nitrogen are also large, and the sign has been shown to be positive in the few cases where it has been determined.[12-14] The value of $|^2J_{PP}|$ is substantially smaller for (7) than for (4), possibly because the ring may be no longer planar. The magnitudes of $^2J_{FF}$ [and the sign in the case of (4)] for *cis*-fluorine nuclei are also in agreement with the literature results.[10,15,16] It is perhaps surprising that $^2J_{FF}$ between the *trans*-fluorine atoms in (7) is too small to be detected, but there do not appear to be any reports in the literature of a comparable coupling. The assignment of chemical shifts to F_A and F_B in (4) [and similarly for (7)] is surprising in view of predictions based on δ_F values found for $[PF_6]^-$ (*ca.* −71)[17] and $[Me_2NPF_5]^-$ (−66·9 and −54·2 for the equatorial and axial fluorine nuclei, respectively).[18] Presumably the distortions induced by the four-membered ring are responsible for the reversal of expectations in regard to the shifts.



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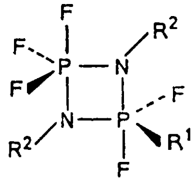

(9)

^{19}F N.m.r. parameters of (4) observed at −60° with the HA-60A spectrometer were nearly identical with room temperature values, and it was concluded that the molecule, unlike the starting diazadiphosphetidine, is rigid on the n.m.r. time-scale. The ^{19}F n.m.r. spectra of (7) at +60° and −60° are practically identical with the room temperature spectrum, and it is concluded that this molecule also is rigid on the n.m.r. time-scale.

With regard to the stereochemistry of (4) it is supposed that the two rings are perpendicular to each other, and that two fluorine atoms are situated in the plane of each ring. In the case of (7) there is substantial distortion from the ideal geometry, as shown by the large difference between the values of $^4J_{FF}$ (and $^1J_{PF}$) for the fluorine nuclei A and B. This presumably arises from the steric effect of the t-butyl groups, though the effects are surprisingly large. The steric influence of the t-butyl group on the reaction of (5) with Bu^{t}Li [and therefore, by inference, the steric effect in compound (6)] is apparently pronounced; it is believed to promote rearrangement of the diazadiphosphetidines, giving rise to zwitterionic products such as (7). In this connection it should be noted that compounds of type (9) ($R^1 = R^2 =$ Me, or $R^1 =$ OMe, $R^2 =$ Me, or $R^1 =$ Bu^t, $R^2 =$ Me) are stable and show no tendency to rearrange.

Apart from that of ref. 11, there are only two literature reports on compounds [(10) and (11)] related to (4) and (7);[19,20] moreover in these cases the positive charge is not on phosphorus, but on either carbon [19] or nitrogen.[20]

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[9] R. K. Harris, M. I. M. Wazeer, P. Clare, and D. B. Sowerby, unpublished work.

[10] R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912.

[11] R. E. Dunmur, Ph.D. Thesis, University of Loughborough, 1970.

[12] M. L. Heffernan and R. F. M. White, *J. Chem. Soc.*, 1961, 1282.

[13] F. Heatley and S. M. Todd, *J. Chem. Soc. (A)*, 1966, 1152.

[14] I. A. Nuretdinov, V. V. Negrebetskii, A. Z. Yankelevich, A. V. Kessenikh, E. I. Loginova, L. K. Nikonorova, and N. P. Grechkin, *Doklady Chem.*, 1971, **196**, 161.

[15] W. McFarlane, J. F. Nixon, and J. R. Swain, *Mol. Phys.*, 1970, **19**, 141.

[16] H. Dreeskamp, C. Schumann, and R. Schmutzler, *Chem. Comm.*, 1970, 671.

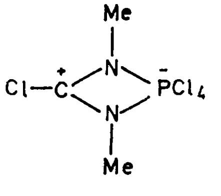
[17] G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, 1970, **25b**, 1199.

[18] S. C. Peake and R. Schmutzler, *J. Chem. Soc. (A)*, 1970, 2364.

[19] P. B. Hormuth and H. P. Latscha, *Z. anorg. Chem.*, 1969, **369**, 59.

[20] K. Utvary and W. Czysch, *Monatsh.*, 1972, **103**, 1048.

Mass Spectra of Compounds (4) *and* (7).—The fragmentation patterns of the zwitterionic compounds (4) and (7) show characteristic differences, as a function of the different substituents. The electron impact-induced decomposition with formation of the monomeric phosphine imides, which is characteristic of both symmetrically and unsymmetrically substituted 1,3-diaza-2,4-diphosphetidines,[21] is not observed for these compounds. The preferred mode of breakdown of the four-membered ring in (4) involves loss of PF_4, and a second pathway, found by observation of the corresponding transition signals, commences *via* loss of MeN from the P_2N_2 ring (Scheme 1a).



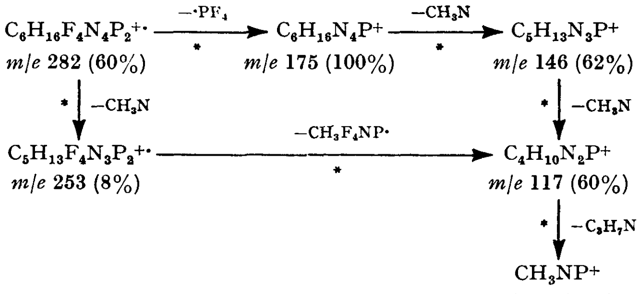
(10)

$(F_3PNMe)_4$

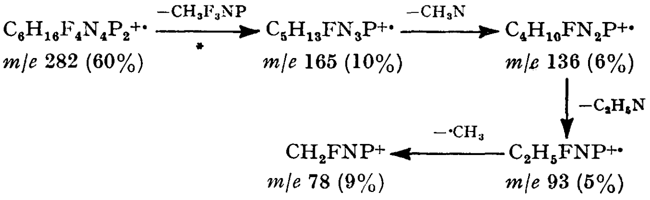
(11)

The formation of $C_5H_{13}FN_3P^{+\cdot}$ (*m/e* 165) involves the transfer of fluorine. Further fragmentation of this ion can be formulated as shown in Scheme 1b.

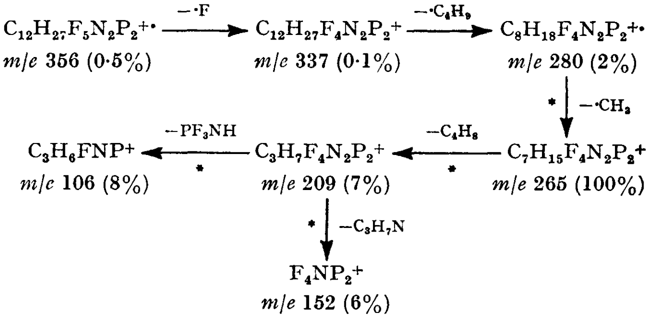
As for (4), in the case of compound (7) a decomposition pathway is followed parallel to the fragmentation of the original zwitterion (Scheme 2a) which includes migration of fluorine. For the two processes, the sequences indicated in Schemes 2a and b are proposed.



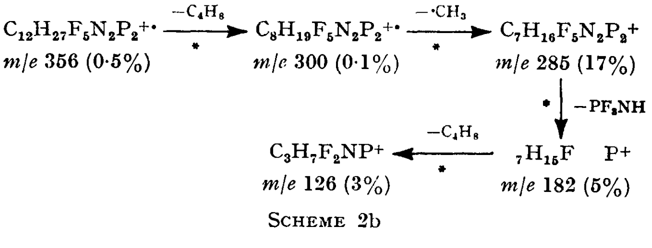
Scheme 1a



Scheme 1b



Scheme 2a



Scheme 2b

EXPERIMENTAL

The usual precautions required in handling moisture-sensitive products were observed.

Preparation of the Zwitterionic Compound (4).—n-Butyllithium (5·47 g, 0·0844 mol) (36·5 g of a 15% solution in hexane) was added at solid carbon dioxide temperature to a solution of *NN'*-dimethylethylenediamine (3·77 g, 0·0428 mol) in ether (100 ml). The mixture was then allowed to warm to room temperature. The resultant suspension was cooled to solid carbon dioxide temperature while 2,2,2,4,4,4-hexafluoro-1,3-dimethyl-1,3-diaza-2,4-diphosph(v)etidine (10·0 g, 0·042 mol)[22] in ether (20 ml) was added dropwise with stirring during 0·5 h. The mixture was then stirred at room temperature for 24 h, and the precipitate was filtered off. Evaporation left an off-white solid (9·7 g, 0·034 mol, 80%), which was purified by repeated sublimation [130° (bath) at 0·05 mmHg] or column chromatography (polyamide powder with benzene as eluant). Both methods furnished the pure *product* (4), m.p. 179—180° (Found: C, 25·4; H, 5·6; N, 19·8. $C_6H_{16}F_4N_4P_2$ requires C, 25·5; H, 5·7; N, 19·8%).

Preparation of the Zwitterionic Compound (7).—t-Butyllithium (10·12 g, 0·158 mol) (67·5 g of a 15% solution in hexane) was added dropwise with stirring and cooling (solid carbon dioxide; internal temperature between −80 and −40° during 0·5 h to a solution of 2,2,2,4,4,4-hexafluoro-1,3-di-t-butyl-1,3-diaza-2,4-diphosph(v)etidine[23] (33·5 g, 0·105 mol) in ether (700 ml). The mixture was then allowed to warm to room temperature; even after a subsequent 24 h under reflux no precipitate was formed. The solvent was then removed, and the residue was sublimed directly; yield 11·0 g (0·0317 mol, 30%). Purification through sublimation (75° at 0·2 mmHg), by recrystallization from benzene, or through column chromatography (polyamide powder; benzene as eluant) furnished the *product* (7), m.p. 99—101° (Found: C, 40·5; H, 7·5; N, 8·0. $C_{12}H_{27}F_5N_2P_2$ requires C, 40·5; H, 7·6; N, 7·9%).

2,2,4,4-Tetrafluoro-1,2,3,4-tetra-t-butyldiazaphosphetidine, which might also be expected as a product, was not observed.

N.m.r. Spectra.—Three spectrometers were used: (*a*) a Varian HA-60A instrument operating at 24·3, 56·4, and 60 MHz for ^{31}P, ^{19}F, and ^{1}H, respectively, (*b*) a Varian HA-100 spectrometer operating at 94·155 MHz for ^{19}F,

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[21] I. K. Gregor and O. Schlak, unpublished work.

[22] (*a*) R. Schmutzler, *Chem. Comm.*, 1965, 19; (*b*) R. Schmutzler, *J.C.S. Dalton*, 1973, 2687.

[23] J. J. Harris and B. Rudner, *J. Org. Chem.*, 1968, **33**, 1392.

and (*c*) a Varian XL-100 instrument operating at 40·5 MHz for ^{31}P in the continuous-wave mode only. The HA-100 and XL-100 spectrometers were both equipped with facilities for heteronuclear double resonance, including noise decoupling. The HA-60A was used for ^{31}P and ^{19}F spectra for an initial investigation only, but the data reported here are from work with the HA-100 and XL-100 instruments.

For the ^{19}F and ^{31}P spectra the sample was dissolved in 1 : 1 CH_2Cl_2–CD_2Cl_2 and some $CFCl_3$ was added to serve as a reference and locking substance for the ^{19}F work. The deuterium resonance signal of CD_2Cl_2 was used as a locking and a reference substance for the ^{31}P spectrum. The absolute ^{31}P resonance frequencies, scaled so that the ^{1}H resonance of tetramethylsilane occurs at exactly 100 MHz,[24] are 40,482,092 (4) and 40,483,511 Hz (7) for P^+ and 40,474,602 Hz (4) and 40,475,113 Hz (7) for P^-. The chemical shifts of ^{31}P quoted in the Table were obtained using a value [24] of 40,480,740 Hz for 85% H_3PO_4. The sample used for these experiments was degassed and sealed in a 5 mm (o.d.) tube. The spectra were obtained at ambient probe temperature.

The ^{1}H spectra of both compounds were determined on undegassed samples. For compound (4) dichloromethane was employed as a solvent and reference; benzene was used in both capacities in the case of compound (7).

Mass Spectra.—These were obtained on the following instruments: A.E.I. MS9; A.E.I. MS902 (Data System DS 30), and Varian MAT 731 (Data System 100). A direct inlet system (ionizing energy 70 eV) was employed.

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[4/408 *Received*, 1*st March*, 1974

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[24] W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**,135.