Nuclear Magnetic Resonance Studies of Pseudo-rotation in some Unsymmetrical Diazadiphosphetidines

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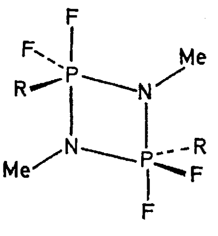
Summary Variable temperature ^{19}F n.m.r. spectra of some novel diazadiphosphetidines are consistent with concerted pseudo-rotation at the two phosphorus atoms.

The structure of the tetrafluorodiazadiphosphetidines, $(RPF_2NMe)_2$, in the solid state has been demonstrated to be as in (I), with the two R groups on opposite sides of the ring plane.[1] Evidence for a less stable *gauche*-isomer has been found by n.m.r. investigations,[2] the exchange between the two forms being rapid on the n.m.r. time scale above *ca.* 20 °C (for R = Me, Et, Ph). In these cases the *trans*-isomer is only slightly more stable than the *gauche*, the equilibrium ratio being between 1 : 1 and 1 : 3 (the latter for R = Ph).

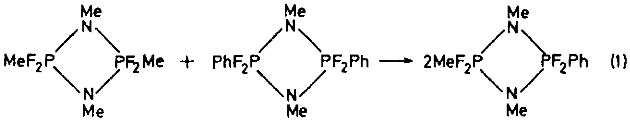


(I)

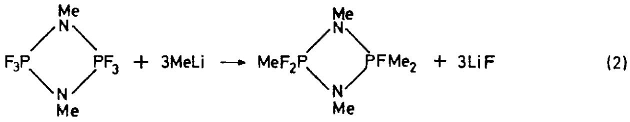
We have synthesized[3] a series of novel diazadiphosphetidines which are unsymmetrical either at phosphorus or at nitrogen, *via* reactions of the types (1)—(3).

The n.m.r. spectra of such compounds (II—IV) are of particular interest. In all fluorodiazadiphosphetidines so far described the fluorine atoms for each isomer are all chemically equivalent on the n.m.r. time scale, even at −80 °C. This makes the determination of (F,F) coupling constants difficult, although those values which have been obtained show a remarkable sensitivity to stereochemistry. We have now examined several compounds for which the lack of symmetry causes fluorine atoms to be chemically non-equivalent. It is assumed, in the discussion below, that the immediate environment of the nitrogen atoms is planar or that there is rapid inversion at nitrogen throughout the temperature range studied (the former hypothesis appears the more likely, in view of *X*-ray studies[1]).

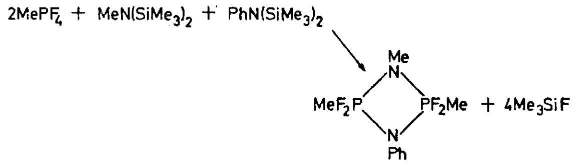
Thus compound (II) shows, at room temperature and above, ^{19}F n.m.r. spectra corresponding to an $AB[XY]_2$ spin system (A,B ≡ P, X,Y ≡ F, ignoring the effects of coupling to protons), from which the following data could be obtained: $\phi_{F(X)}$ 57·8 p.p.m., $|J_{PF(X)}|$ 891 Hz (PF$_2$Me group), $\phi_{F(Y)}$ 62·1 p.p.m., $|J_{PF(Y)}|$ 891 Hz (PF$_2$Ph group), $|J_{PP}|$ 79 Hz (from ^{31}P resonance). Below −20 °C the spectra of two such systems were observed, corresponding to the *trans*- and *gauche*-isomers. This behaviour is similar to that observed for the symmetrical compounds,[2] the coalescence temperature (*ca.* 0 °C) indicating that the energy barrier to the exchange is also similar.



(II)



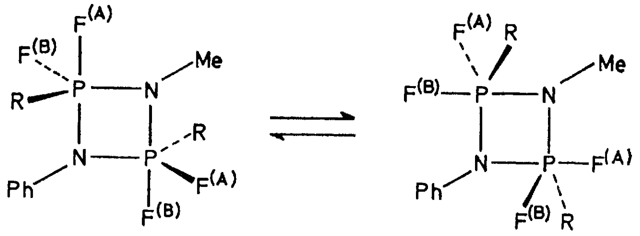
(III)



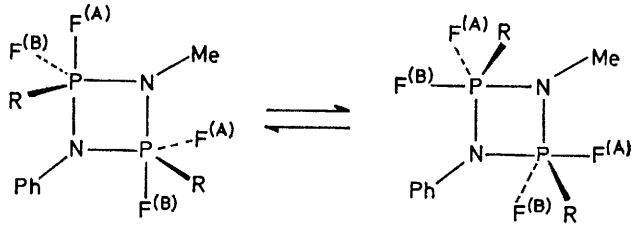
(IV)

Compound (III) shows a more striking temperature dependence in that the two fluorine atoms attached to the same phosphorus atom, which at room temperature are chemically equivalent, become chemically non-equivalent below −40 °C. The large differences in the chemical shifts (ϕ_A 34·7 p.p.m., ϕ_B 72·3 p.p.m.) and coupling constants ($|J_{PF(A)}|$ 816 Hz, $|J_{PF(B)}|$ 974 Hz) indicate that all exchange at the PF$_2$Me group is slow on the n.m.r. time scale. Since in other diazadiphosphetidines containing PF$_2$Me groups exchange between axial and equatorial fluorine atoms is fast[2] even at −80 °C the slow exchange in (III) must be due to the rigidity arising from the PFMe$_2$ group, where the fluorine atom preferentially occupies the axial site. This establishes clearly the concerted nature of the exchange processes at the two phosphorus atoms in the symmetrical systems, and allows for the first time the determination of n.m.r. parameters for fluorine atoms in axial and equatorial positions [F(A) is axial and F(B) is equatorial, $|^2J_{FF}|$ 57 Hz] in diazadiphosphetidines, as opposed to average parameters for fast exchange.

A further effect of asymmetry is found in compound (IV), which shows at room temperature chemically equivalent fluorine atoms (ϕ_F 53·1 p.p.m., $|N_{PF}|$† 904 Hz). On cooling to −60 °C, not only are the *gauche*- and *trans*-isomers observed [*cf.* compound (II)], but in each isomer the two fluorine atoms on each phosphorus are chemically non-equivalent. The n.m.r. data are as follows: *gauche*-isomer, $\phi_{F(A)}$ 48·1 p.p.m., $\phi_{F(B)}$ 53·3 p.p.m., $|N_{PF(A)}|$ 924 Hz, $|N_{PF(B)}|$ 912 Hz, $|N_{F(A)F(B)}|$ 53 Hz: *trans* $\phi_{F(A)}$ 53·3 p.p.m., $\phi_{F(B)}$ 57·7 p·m., $|N_{PF(A)}|$ 912 Hz, $|N_{PF(B)}|$ 867 Hz, $|N_{F(A)F(B)}|$ 53 Hz. The chemical shifts and coupling constants of both types of fluorine atoms in both isomers are characteristic of averaged axial and equatorial environments [*cf.* parameters for (III)]. These observations can be explained by assuming that rapid exchange is occurring between structures a and b of (V) [and (VI)]. The asymmetry of the ring results in different n.m.r. parameters for the two fluorines on each phosphorus, though each undergoes rapid exchange between axial and equatorial positions.



(Va) *trans*-isomer (Vb)



(VIa) *gauche*-isomer (VIb)

A more detailed analysis of the low temperature spectra, and band-shape studies to obtain activation energies for the pseudo-rotation are currently being undertaken.

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† N_{AX} refers, as is usual for symmetrical compounds, to the sum of the short-range and long-range (A,X) coupling constants.

[1] J. W. Cox and E. R. Corey, *Chem. Comm.*, 1967, 123.

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

[3] O. Schlak and R. Schmutzler, unpublished work.