# Conformation and Stereodynamics of 2-Dialkylamino-1,3-dioxa- and 3-Methyl-1,3-oxaza- 2-phospholanes. A Carbon-13 Nuclear Magnetic Resonance and Theoretical MNDO Investigation.

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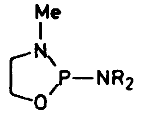
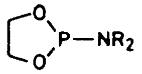
Rotation around the exocyclic P–NR$_2$ bond in the title compounds (R = Me, Et, and Pr$^i$) has been frozen on the $^{13}$C n.m.r. time-scale at −100 to −150 °C. The exocyclic PNC coupling constants confirm that the preferred conformation has one NR group eclipsing the phosphorus lone pair and the other lying over the face of the ring; this geometry is also supported by MNDO SCF MO calculations. The P–NR$_2$ rotational barriers, which lie in the range 6.0—9.2 kcal mol$^{-1}$, increase in the sequence 1,3-dioxa- < 1,3-oxaza- < 1,3-diazaphospholane and also with increasing size of the NR group. MNDO calculations of the barrier height reproduce the former sequence. The cyclic POC and PNC coupling constants are discussed in relation to the ring conformation, and some $^{15}$N n.m.r. data are reported.

The conformation of compounds containing P–N and P–O bonds has been the subject of a large number of investigations. Trivalent phosphorus compounds of this type are usually air sensitive liquids which are not readily amenable to *X*-ray structural analyses, hence the majority of investigations have employed either $^1$H n.m.r., photoelectron spectroscopy or electron diffraction. Recently it has become evident that $^{13}$C n.m.r. can provide considerable conformational information on these compounds as phosphorus(III)–carbon coupling constants are markedly dependent on the local molecular geometry.[1–8] Low temperatures can be used in appropriate cases to freeze out conformational averaging processes and provide more informative n.m.r. parameters. The present report is concerned with a variable temperature $^{13}$C n.m.r. study of oxaza- and dioxa-phospholanes, (1) and (2), bearing an exocyclic dialkylamino substituent on the phosphorus(III) atom.



(1)

a; R = Me
b; R = Et
c; R = Pr$^i$



(2)

a; R = Me
b; R = Et
c; R Pr$^i$

At temperatures between ambient and −70 °C a single set of $^{13}$C n.m.r. signals was observed for the exocyclic NR$_2$ group in series (1) and (2) compounds and the carbon–phosphorus coupling constants are conformationally averaged values (Table 1). The two-bond PNC couplings which lie in the range 10—22 Hz were shown to be positive in sign by off-resonance $^1$H irradiation experiments. These couplings, and the smaller three-bond couplings, are similar to those measured in 2-dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes[5] and 4-substituted 2-dimethylamino-1,3,2-dioxaphospholanes[3] at ambient temperature. On cooling the sample below −100 °C, rotation about the exocyclic P–N bond was slowed sufficiently to observe separate signals for the non-equivalent *N*-alkyl groups (Figure 1). The observation of non-equivalent *N*-alkyl groups in series (2) compounds (X = Y = O) establishes that the ground-state conformation is (**3a**) and not (**3b**). Furthermore, the PNC couplings were markedly different and, as in diazaphospholanes[5,8] and some acyclic aminophosphorus(III) compounds,[1,2,4] the alkyl groups *syn* to the phosphorus lone pair has a large positive PNC coupling whereas a smaller negative $^2J_{\text{PNC}}$ value is associated with an *anti* NR group. The close similarity in the n.m.r. spectra of series (1) and (2) compounds indicates that the former series also adopt conformation (**3a**).

Semiempirical MNDO molecular orbital calculations on the dimethylamino compounds (**1a**) and (**2a**), with complete optimisation of all bond lengths and angles, gave the geometries listed in Table 2. The optimised geometry of (**1a**) is depicted in Figure 2 and the structure of (**2a**) is very similar (Table 2). The bisected arrangement about the exocyclic PN bond corresponds with that indicated by the low temperature n.m.r. experiments, *viz.* one NR group eclipses the phosphorus lone pair and the other is directed over the face of the phospholane ring and *anti* to the phosphorus lone pair (**3a**). The MNDO geometries about the exocyclic nitrogens in (**1a**) and (**2a**) are coplanar (sum of the bond angles = 359.3 and 360.0°, respectively), though the n.m.r. data do not distinguish between a planar nitrogen and a rapidly inverting pyramidal arrangement. The calculated geometry about the cyclic nitrogen in (**1a**) deviates only slightly from planarity (sum of the bond angles = 358.2°). The $^2J_{\text{PNC}}$ value for the methyl group on this cyclic nitrogen is *ca.* 25 Hz (Table 1) consistent with it being *gauche* to the phosphorus lone pair, *i.e.*, φ between 30 and 60°.[4,5]

The reduced magnitude of $^2J_{\text{PNC}}$ for the *syn* methine carbon in (**1c**) and (**2c**) (+27 Hz), compared with the analogous $^2J_{\text{PNC}}$ values in the dimethyl and diethyl analogues (+45 to +50 Hz), parallels the situation in 1,3,2-diazaphospholanes.[5] It has been suggested that this effect is associated with the di-isopropylamino moiety adopting the propeller-like conformation (**4**) to minimise non-bonded interactions.[5] This conformational proposal has recently been supported by arguments based on the chemical shift of the methine carbons in this and other di-isopropylamino compounds.[9] Additionally, the comparatively large value (15.6 Hz) of the three-bond PNCC coupling for the downfield set of CMe$_2$ groups in (**2c**) probably arises from the *syn* isopropyl group in conformation (**4**) owing to a 'through space' coupling effect[2,10] involving the adjacent phosphorus lone pair.

Turning to the cyclic carbons, the two-bond POC coupling constants in the dioxa series (**2**) have similar magnitude to those

Table 1. $^{13}C$ N.m.r. data for 2-dialkylamino-3-methyl-1,3,2-oxazaphospholanes and 2-dialkylamino-1,3,2-dioxaphospholanes[a]

| | | Exocyclic NC | | Exocyclic NCC | | Ring $OCH_2$ | | Ring $NCH_2$ | | Ring NMe | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | $T$/°C | $\delta_C$/ p.p.m. | $^2J_{PNC}$[b]/ Hz | $\delta_C$/ p.p.m. | $^3J_{PNCC}$/ Hz | $\delta_C$/ p.p.m. | $^2J_{POC}$[b]/ Hz | $\delta_C$/ p.p.m. | $^2J_{PNC}$/ Hz | $\delta_C$/ p.p.m. | $^2J_{PNC}$[b]/ Hz |
| (1a) | −68 | 36.3 | +17.1 | | | 68.8 | −10.4 | 51.7 | ±1.8 | 32.9 | +24.4 |
| | —150 | 34.5, 38.3 | —9.2, +44.6 | | | 69.2 | *ca.* −10 | 51.6 | | 33.4 | +24.4 |
| (1b) | −65 | 38.7 | +19.5 | 15.3 | 2.9[c] | 67.9 | −11.0 | 51.3 | ±1.2[c] | 32.8 | +24.4 |
| | −132 | 36.3, 40.0 | −9.1, +47.0 | 14.4, 16.0 | *d* | 68.1 | *ca.* −10 | 51.2 | | 33.1 | +23.8 |
| (1c) | −20 | 44.6 | +9.2 | 24.9, 25.0 | 6.1, 10.5 | 66.9 | −11.6 | 51.1 | <2 | 32.7 | +26.2 |
| | −100 | 43.0, 45.5 | +26.9, −7.9 | *e* | *e* | 67.1 | −10.4 | 50.8 | | 32.9 | +25.6 |
| (2a) | −60 | 35.4 | +20.1 | | | 65.4 | −8.5 | | | | |
| | −145 | (33.7, 37.1)[f] | (−8, +50)[f] | | | 65.4 | −8.5 | | | | |
| (2b) | −70 | 38.2 | +21.4 | 15.1 | 2.4 | 65.0 | −8.5 | | | | |
| | −152 | 35.9, 39.2 | (−8),[f] +50 | 14.3, 15.2 | *d* | 65.0 | −8.5 | | | | |
| (2c) | −60 | 45.4 | +10.7 | 25.1 | 7.8 | 64.9 | −8.8 | | | | |
| | −124 | 44.0, 46.0 | +27.3, −6.8 | 22.2, 27.8 | 0, 15.6 | 64.9 | −8.8 | | | | |

[a] Spectra were recorded in $CHClF_2$ solution except for (**1c**) where the solvent was $CHCl_2F$. Digital resolution 0.61 Hz. [b] The sign of $^2J_{PC}$ (relative to $^3J_{PH}$ which was assumed to be positive) were determined by off-resonance $^1H$ irradiation experiments on (**1a**), (**1c**), and (**2c**) and inferred by analogy for the remaining homologues. [c] The coupling constant quoted was determined at ambient temperature in [$^2H_6$]benzene (digital resolution 0.25 Hz) as it was not resolved at low temperature. [d] The coupling was not resolved due to considerable line broadening at low temperature. [e] Signal overlap prevented assignment (4 non-equivalent methyl doublets). [f] Estimated values by analogy with other compounds in the series as the slow exchange limit could not be attained. These values afforded good agreement between calculated and observed bandshapes at coalescence.

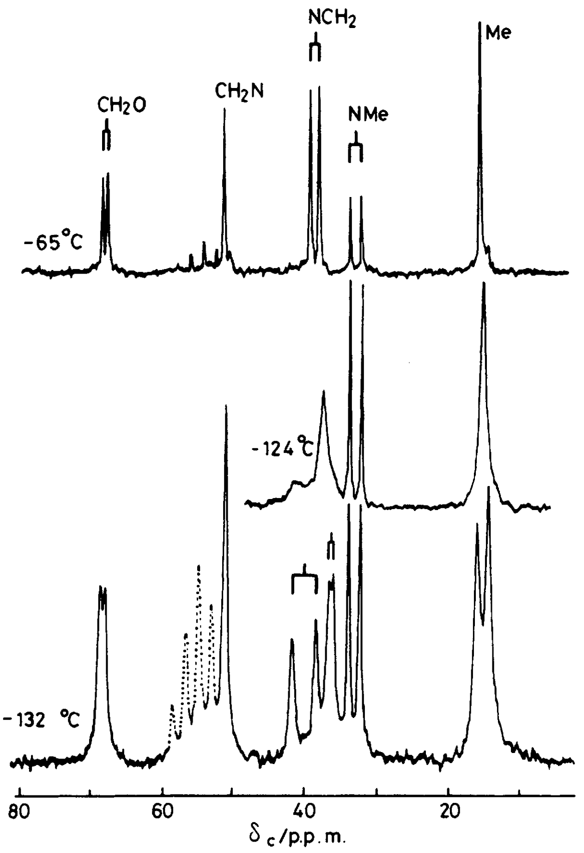
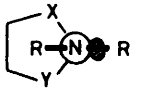
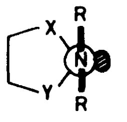


Figure 1. $^{13}C$ N.m.r. spectra of (**1b**) at various temperatures in $CHClF_2$ solution (the multiplet at 55 δ arises from *ca.* 12% [$^2H_2$]dichloromethane added for locking purposes)



(3a)



(3b)

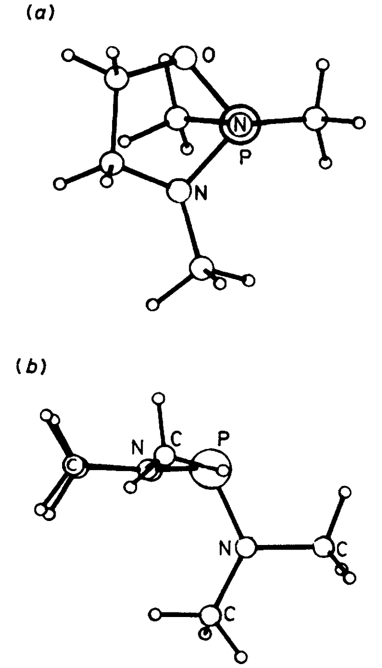


Figure 2. Optimised MNDO geometry for (**1a**) viewed as projections down the exocyclic P–N bond (*a*) and the $CH_2$–$CH_2$ bond (*b*).

reported previously for this type of compound,[3,6] though the sign of this coupling is now shown to be negative similar to the cyclic $^2J_{PNC}$ in 2-dialkylamino-1,3-dimethyl-1,3,2-diazaphospholanes.[5] A negative $^2J_{POC}$ is therefore associated with a conformation in which the C–O bond has a dihedral angle of *ca.* 120—150° with respect to the phosphorus lone pair (Figure

**Table 2.** Optimised MNDO parameters for (**1a**) and (**2a**)

| Parameter | Compound (**1a**) | Compound (**2a**) |
|---|---|---|
| Heat of formation (kcal mol$^{-1}$) | −103.11 | −150.90 |
| Dipole moment (D) | 1.33 | 0.97 |
| Ionisation energy (e.v.) | 9.58 | 9.95 |
| Bond lengths (Å): *exo* P–N | 1.660 | 1.652 |
| cyclic P–N | 1.673 | |
| cyclic P–O | 1.611 | 1.621 |
| cyclic N–CH$_2$ | 1.455 | |
| ring N–CH$_3$ | 1.446 | |
| *syn* N–CH$_3$ | 1.456 | 1.457 |
| *anti* N–CH$_3$ | 1.452 | 1.453 |
| cyclic O–CH$_2$ | 1.395 | 1.392 |
| cyclic C–C | 1.560 | 1.572 |
| C–H | 1.113—1.120 | 1.112—1.119 |
| Bond angles (°) *exo* NPN | 105.9 | |
| *exo* OPN | 104.7 | 105.1 |
| cyclic OPN | 94.3 | |
| cyclic OPO | | 94.8 |
| *syn* PNC | 113.7 | 113.9 |
| *anti* PNC | 128.8 | 129.5 |
| cyclic PNC | 114.0 | |
| ring PNC | 123.2 | |
| cyclic POC | 116.9 | 115.3 |
| *exo* CNC | 116.8 | 116.6 |
| ring CNC | 121.0 | |
| cyclic NCC | 105.9 | |
| cyclic OCC | 108.7 | 107.0 |
| Dihedral angle (°) $\varphi_{PN}$[a] | 90.8 | 89.9 |

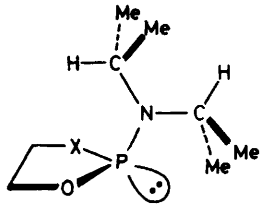
[a] $\varphi_{PN}$ is the dihedral angle between the axes of the phosphorus and nitrogen lone pairs (defined using the 'dummy atom' facility in MNDO).

2), and the size of this coupling is almost identical to the analogous $^{2}J_{PNC}$ in the diazphospholanes.

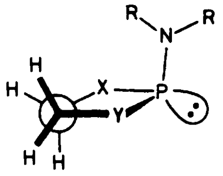
The near zero cyclic PNC couplings observed in the oxaza compounds (**1**) contrast with the $^{2}J_{PNC}$ values of *ca.* −9 Hz in the diaza analogues.[5] This difference might result from electronic factors, but conformational factors should also be considered. Thus it is unlikely that the dioxa- or oxaza-phospholane rings are coplanar as indicated by the MNDO calculations (Figure 2)* since $^{1}$H n.m.r. analysis of the vicinal proton couplings in dioxa- and oxaza-phospholanes points to a staggered arrangement around the XCH$_2$–CH$_2$Y system.[3,12] Hence the cyclic POC and PNC couplings in the symmetrical dioxa and diaza compounds will be a 1 : 1 average of those in the rapidly interconverting staggered conformers (**5a**) and (**5b**) where X = Y = O or NMe. However, these conformers are of unequal energy in the unsymmetrical oxaza compounds (X = NMe, Y = O), therefore the time averaged orientation of the CH$_2$–N and CH$_2$–O bonds relative to the phosphorus lone pair will differ from that in the diaza and dioxa compounds. On this basis the more positive value of the cyclic $^{2}J_{PNC}$ in the oxaza compounds would tend to suggest that the preferred conformation is (**5a**) where X = NMe and Y = O, since the CH$_2$–N–P–lone pair dihedral angle in this conformation is closer to 90° than the 180° (*anti*) orientation usually associated with a significantly negative $^{2}J_{PNC}$. Similarly if (**5a**) were indeed the preferred conformation of the oxazaphospholane ring, one might expect a larger negative cyclic $^{2}J_{POC}$ in these compounds since the CH$_2$–Y bond (Y = O) is oriented closer to the *anti* arrangement, and the dihedral angle is not reduced by time averaging as in the symmetrical dioxa compounds. The cyclic POC couplings in the oxaza series (**1**) are *ca.* 2.5 Hz more negative than those in series (**2**) though the difference is somewhat less than that expected from the above analysis.† An alternative rationalisation of the differing cyclic PNC coupling constants in the oxaza and diaza compounds in terms of differing contributions *via* the three-bond route (POCC and PNCC, respectively) seems less likely as the ring carbons in the dioxa- and diaza-phospholanes show almost identical couplings to the phosphorus (−8.5 to −9.2 Hz).‡

**Table 3.** Dynamic $^{13}$C n.m.r. data for exocyclic PN bond rotation

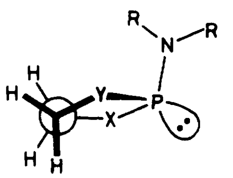
| Compound | Observed signals | $T$/°C | $k$/s$^{-1}$ | $\Delta G^{\ddagger}$/ kcal mol$^{-1}$ |
|---|---|---|---|---|
| (**1a**) | NMe | −139 | 115 | 6.4 |
| (**1b**) | NCH$_2$ | −124 | 119 | 7.1 |
| | NCH$_2$C$\mathit{H}_3$ | −129 | 42 | 7.2 |
| (**1c**) | NCH | −83 | 122 | 9.2 |
| | NCH(C$\mathit{H}_3$)$_2$ | −83 | 104 | 9.2 |
| (**2a**) | NMe | −145 | 150 | 6.0 |
| (**2b**) | NCH$_2$ | −138 | 201 | 6.2 |
| (**2c**) | NCH | −93 | 161 | 8.5 |
| | NCH(C$\mathit{H}_3$)$_2$ | −93 | 171 | 8.5 |



(**4**)



(**5a**)



(**5b**)

The rate constants for rotation around the exocyclic P–NR$_2$ bond, determined by analysis of the R group bandshapes in the region of maximum exchange broadening, are given in Table 3 together with the derived free energies of activation ($\Delta G^{\ddagger}$). In some cases the site exchange rates were determined from both the α and β carbon resonances, and the resulting $\Delta G^{\ddagger}$ values are equal within the precision of the measurements. In both series the rotational barrier increases in the sequence R = Me < Et < Pr$^{i}$ as found previously in 2-dialkylamino-1,3,2-diazaphospholanes[5,8] and in acyclic aminophosphorus compounds.[13–16] This trend is probably mainly steric in origin, though there might also be a contribution from inductive effects of the more branched alkyl groups enhancing π-type donation from nitrogen to phosphorus. Comparison of the PN rotational

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* It is known that MNDO has the tendency to underestimate ring puckering, thus cyclopentane is incorrectly predicted to be planar, see ref. 11.

† This suggestion is tentative since the precise behaviour of $^{2}J_{POC}$ (and $^{2}J_{PNC}$) in the dihedral angle range 90—180° is not clearly established. Previous work has indicated that $^{2}J_{POC}$ is *ca.* ±2 Hz for lone pair dihedral angles of 60 and 180°.[6]

‡ A fortuitous cancellation of unequal contributions *via* the three-bond route by differences in the two-bond contributions of precisely equal size but opposite sign in the dioxa and diaza compounds cannot be excluded.

**Table 4.** Comparison of experimental and calculated PN rotational barriers for various 2-dialkylaminophospholanes

| | Experimental $\Delta G^{\ddagger}$ (kcal mol$^{-1}$) | | | Calculated MNDO (kcal mol$^{-1}$) |
|---|---|---|---|---|
| Phospholane | Pr$^i$ | Et | Me | Me |
| 1,3-Diaza | 10.1[a] | 8.1[a] | 7.0 | 5.2[b] |
| 1,3-Oxaza (1) | 9.2 | 7.1 | 6.4 | 4.4 |
| 1,3-Dioxa (2) | 8.5 | 6.2 | 6.0 | 3.2 |

[a] Data taken from ref. 5. [b] See ref. 17.

**Table 5.** $^{15}N$ N.m.r. data for 2-dialkylamino-3-methyl-1,3,2-oxazaphospholanes[a]

| | *endo* | | *exo* | |
|---|---|---|---|---|
| Compound | $\delta_A$/p.p.m. | $^1J_{PN}$/Hz | $\delta_N$/p.p.m. | $^1J_{PN}$/Hz |
| (1a) | −344.0 | 51.3 | −324.1 | 89.1 |
| (1b) | −345.0 | 51.9 | −292.8 | 90.9 |
| (1c) | −352.1 | 50.0 | −274.1 | 94.0 |

[a] Spectra were recorded in [$^2H_6$]benzene; digital resolution 0.6 Hz; reference external Me$^{15}NO_2$.

barriers for the three series of phospholanes (Table 4) indicates a marked decrease in the sequence 1,3-diaza > 1,3-oxaza > 1,3-dioxa. This trend could also be rationalised in terms of steric effects. Thus the exocyclic *N*-alkyl groups must pass the ring *N*-methyl groups in the transition state for PN rotation (**3b**). The barrier therefore decreases as the ring NMe groups are replaced by oxygen. However, electronic factors involving possible effects of the ring heteroatoms on the degree of $\pi$-bonding in the exocyclic P–N bond may also contribute.

The exocyclic PN rotational potentials were also calculated by MNDO for the 2-dimethylamino compounds with complete optimisation of all geometric variables (except $\varphi_{PN}$) along the rotational co-ordinate.[17] Although the theoretical potential barriers are somewhat lower than the measured $\Delta G^{\ddagger}$ values for the dimethylamino compounds (Table 4), the barrier trend diaza > oxaza > dioxa is reproduced. The transition state for PN rotation occurs, as expected, when the nitrogen and phosphorus lone pair axes are collinear (**3b**), *i.e.*, a 90° twist from the ground state (**3a**) where these axes are orthogonal.

$^{15}N$ N.m.r. spectra were recorded for series (**1**) compounds, and the chemical shifts and $^{15}N$–$^{31}P$ coupling constants are listed in Table 5. The lower field doublet was assigned to the exocyclic nitrogen on the basis that this signal was more sensitive to changes in the *N*-alkyl group. This assignment is confirmed by the $^1J_{PN}$ values of the high field signal, which are in the usual range for cyclic nitrogens in azaphospholanes (*ca.* 50 Hz).[5,18,19] The exocyclic $^{15}N$–$^{31}P$ coupling constants in series (**1**) compounds are much larger than their endocyclic counterparts. This '*exo* effect' has been previously observed in 2-dialkylamino-1,3,2-diazaphospholanes and is probably a consequence of the differing conformations around the exo- and endo-cyclic PN bonds.[5] The PN conformation could influence $^1J_{PN}$ either directly owing to electronic changes or indirectly by accompanying changes in the geometry at nitrogen. CNDO/2 FPT calculations[20] on a model system have indicated that the one-bond $^{15}N$–$^{31}P$ coupling constant decreases markedly as the geometry at nitrogen changes from trigonal to pyramidal. Other *ab initio* MO calculations on acyclic aminophosphines suggest that the nitrogen tends to become more pyramidal as the dihedral angle $\varphi_{PN}$ deviates from the usually preferred value of *ca.* 90°.[21] Geometric constraints in series (**1**) compounds cause the endocyclic $\varphi_{PN}$ to deviate from 90°. The MNDO calculations (Figure 2) do show that the cyclic nitrogen is not coplanar, though the deviation from planarity is small.

## Experimental

2-*Dialkylamino*-3-*methyl*-1,3,2-*oxazaphospholanes* (**1a**—**c**).—The appropriate dialkylaminophosphorodichloridite, $R_2NPCl_2$ (0.2 mol) in dry ether (60 cm$^3$) and a separate mixture of 2-methylaminoethanol (15.0 g, 0.2 mol) and anhydrous triethylamine (40.5 g, 0.4 mol) in dry ether (50 cm$^3$) were simultaneously added dropwise over a 2 h period to 400 cm$^3$ of dry ether at 0 °C contained in a 1 l 3-necked flask fitted with a mechanical stirrer. When precipitation of the triethylamine hydrochloride was complete, the solution was filtered, concentrated, and the residue distilled *in vacuo* to afford the product. The dimethylamino compound (**1a**) had b.p. 85 °C at 3.5 mmHg (lit.,[22] 66—68 °C at 16 mmHg), the diethylamino analogue (**1b**) had b.p. 91—94 °C at 2.6 mmHg (lit.,[23] 88—90 °C at 3 mmHg), and the di-isopropylamino analogue (**1c**) had b.p. 43—45 °C at 0.2 mmHg (Found: $M^+$, 204.1388. $C_9H_{21}N_2OP$ requires *M*, 204.1391); *m*/*z* 204 (12%), 189 (3), 161 (8), 147 (6), 120 (4), and 104 (100); $\delta_H$ ($CDCl_3$) 1.16 (6 H, d, $^3J_{HCCH}$ 6.7 Hz, 2 Me), 1.23 (6 H, d, $^3J_{HCCH}$ 6.7 Hz, 2 Me), 2.59 (3 H, d, $^3J_{PNCH}$ 11.1 Hz, N-Me), 2.8—3.8 (4 H, m, $NCH_2$ + 2NCH), and 2.1 (2 H, m, $OCH_2$).

2-*Dialkylamino*-1,3,2-*dioxaphospholanes* (**2a**—**c**).—These compounds were prepared by the reaction of 2-chloro-1,3,2-dioxaphospholane (0.2 mol) with the appropriate dialkylamine (0.4 mol) in dry ether at 0 °C.[24] The dimethylamino compound (**2a**) had b.p. 43—45 °C at 0.5 mmHg (lit.,[25] 61—62 °C at 11 mmHg), the diethylamino analogue (**2b**) had b.p. 77 °C at 4 mmHg (lit.,[24] 98.7—99.1 °C at 25 mmHg), and the di-isopropylamino analogue (**2c**) had b.p. 57—60 °C at 0.2 mmHg (lit.,[26] 79.5—80.5 °C at 8.5 mmHg).

*N.m.r. Studies.*—The $^{13}C$ n.m.r. spectra were recorded at 15.0 MHz on a JEOL FX-60 instrument, and the probe temperature was measured as described previously.[16] Exchange-mediated spectra were analysed interactively using the multi-site INMR program[16] mounted on a Data General Nova/4 computer coupled with a Hewlett-Packard 2649C graphics terminal.

Components of spin-coupled multiplets were treated in the computations as separate sites with the appropriate relative intensity (all $^{13}C$ spectra are first order). The $^{15}N$ spectra were recorded at 18.24 MHz on the Bruker WB-180 spectrometer at PCMU, Harwell.

*MNDO Calculations.*—The molecular orbital calculations were performed on the CDC 7600 computer at the Manchester University Regional Centre *via* the link to Birmingham University. The MNDO program (QCPE No. 353)[27] was modified to include the phosphorus parameters proposed by Dewar *et al.*[28]

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