The deprotonation and rearrangement of N-methyl methylphosphazinium quaternary salts: a novel synthetic route to cyclic azaphosphorins

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The N-methyl methylphosphazinium salts (NPMe₂)₃⁺·MeI and N₃P₃Ph₂Me⁺·Me can be deprotonated by a variety of bases to yield the novel azaphosphorins Me₂₋₋₋₋(NHMe)P₃N₋₋₋₋CH (n = 3, 4) and Me(NHMe)Ph₄PₓN₃CH, formed by a rearrangement in which the methylated nitrogen atom is displaced from the PN ring by the initially produced exocyclic methylene group. The ¹H nmr spectra of the azaphosphorins indicate a rapid proton exchange between the endocyclic carbon and the exocyclic nitrogen, which can be slowed by the addition of an auxiliary base. When KO-t-Bu reacts with the quaternary salts, nucleophilic attack competes with proton removal, and the linear oxides (NHMe)(PMe₂)ₙPMe₂O (n = 2–4) have been isolated from these reactions. The azaphosphorins Me₂₋₋₋₋(NHMe)PₓNₓ₋₋₋₋CH (n = 3, 4) are hydrolysed in aqueous ethanol to give the cyclic oxides Me₂₋₋₋₋(O)PₓNₓ₋₋₋₋CH, and react with methyl iodide by a proton transfer reaction to give the hydroiodides Me₂₋₋₋₋(NHMe)PₓNₓ₋₋₋₋CH-HI. Their reaction with benzylo chloride leads to the derivatives Me₆(NHMe)PₓNₓ₋₋₋₋COPh and Me₇(NMeCOPh)ₓPₓNₓ₋₋₋₋COPh, the initial substitution on carbon being that of the primary basic centre. Model calculations of π-electron energies suggest that both the azaphosphorin rearrangement and the proton exchange reactions depend on the relative orbital electronegativity of the ring and exocyclic atoms, the less electronegative atom being more stable in the endocyclic position.


Les sels de N-méthyl méthylphosphazénium (NPMe₂)₃⁺·MeI et N₃P₃Ph₂Me⁺·Me peuvent être déprotonnés par une variété de bases conduisant à de nouvelles azaphosphorines Me₂₋₋₋₋(NHMe)P₃N₋₋₋₋CH (n = 3, 4) et Me(NHMe)Ph₄PₓN₃CH, formées par réarrangement, où l’atome d’azote méthylé est déplacé du cycle PN par le groupe méthylé éxocyclique formé initialement. Le spectre rnm ¹H des azaphosphorines indique un échange rapide de protons entre le carbone endocyclique et l’azote exocyclique, qui peut être ralenti par l’addition d’une base auxiliaire. Lorsque le KO-t-Bu réagit avec les sels quaternaires, une attaque nuclo-\mphi le concurrence l’abstraction du proton et il résulte de ces réactions des oxydes linéaires (NHMe)(PMe₂)ₙPMe₂O (n = 2–4). Les azaphosphorines Me₂₋₋₋₋(NHMe)PₓNₓ₋₋₋₋CH (n = 3, 4) sont hydrolysées dans l’éthanol aqueux pour conduire aux oxydes cycliques Me₂₋₋₋₋(O)PₓNₓ₋₋₋₋CH, et elles réagissent avec l’iodure de méthyle par une réaction de transfert de protons pour conduire aux hydroiodures Me₂₋₋₋₋(NHMe)PₓNₓ₋₋₋₋CH-HI. Elles réagissent avec le chlorure de benzyle pour conduire aux dérivés Me₆(NHMe)PₓNₓ₋₋₋₋COPh et Me₇(NMeCOPh)ₓPₓNₓ₋₋₋₋COPh; la substitution initiale sur le carbone indique que celui-ci est le premier centre basique. Des calculs modeles des énergies pour les électrons-π suggèrent que tant le réarrangement des azaphosphorines que les réactions d’échange de protons dépendent de l’électronegativité relative des orbitales du cycle et des atomes exocycliques, l’atome le moins électronegatif étant plus stable en position endocyclique.

Introduction

The formation of carbonian from methylphosphazenes by their reaction with strong bases (1) parallels the acidic behaviour of simple alkylphosphine oxides (2) and exemplifies the many chemical similarities that exist between cyclic phosphazen (X₂PN)ₙ and simple phosphoryl compounds XₐPO. In a further study of the acidic properties of the methylphosphazenes,

we have investigated the reaction of N-methyl methylphosphazinium salts (NPMe₂)₃⁺·MeI with bases (3). As expected, these salts can be deprotonated by a variety of bases, as such phosphonium salts as Me₃P(NMe₂)₂⁺X⁻ (4). However, the final products of such reactions indicate the occurrence of an unusual skeletal rearrangement, thereby illustrating that although many properties of phosphazen correspond to those of mononuclear phosphorus compounds, certain chemical features are di-
rectly related to their cyclic structure. The reaction leads to several new azaphosphorin derivatives.

Results
Reactions of Quaternary Methylphosphazenium Salts with Bases

We have used chiefly the bases potassium tert-butoxide (KO-t-Bu) and sodium hexamethyldisilylamide. Both are appreciably soluble in hydrocarbons, which are the most convenient media for achieving a clean separation of the products, and both have been used successfully in the deprotonation of phosphonium salts (5–8). The reaction with the silylamide is the simpler. In boiling octane or toluene, NaN(SiMe₃)₂ reacts smoothly with the quaternary iodides N₃P₃Me₆·MeI and gem-N₃P₃Ph₂Me₂·MeI, (I, R = Me, Ph) removing a proton from one of the P-methyl groups adjacent to the quaternized nitrogen atom. The final products are not the expected ylids, but rather the novel azaphosphorins 4 (a, R = Me; b, R = Ph), formed from the ylids by a rearrangement in which the methylated nitrogen atom is displaced from the ring, the resulting exocyclic imine (3) then tautomerizing to give the aromatic amine form 4. An exactly analogous reaction occurs with N₄P₄Me₆·MeI (5), to give the azaphosphorin 8.

Potassium tert-butoxide reacts both as a base, removing a proton from an exocyclic group, (as in Scheme 1), to form an azaphosphorin, and as a nucleophile attacking a phosphorus atom adjacent to the quaternized nitrogen atom, to form a linear oxophosphazene. The products obtained from the reactions of the monoquaternary salts (NPMe₂)₃·MeI and the diquaternary salt (NPMe₂)₆·2MeSO₃F with KO-t-Bu collectively demonstrate both possibilities, and indicate that the relative importance of the two processes is strongly dependent on the size and charge of the cyclic phosphazenium cation.

In the reaction of (NPMe₂)₃·MeI with KO-t-Bu, proton abstraction does not occur. Instead, the tert-butoxide ion effects a nucleophilic attack on phosphorus, and cleaves the PN skeleton (Scheme 2). The subsequent elimination of isobutene or (less probably) an ether (9, 10) then produces the novel linear oxophosphazene (NHMe)(PMe₂N)₂PMe₂O (9) in high yield (92%). The reaction of the tetrameric salt (NPMe₂)₄·MeI with KO-t-Bu shows a marked contrast to the one just described. Nucleophilic attack of tert-butoxide ion still occurs, to give the open chain oxide (NHMe)(PMe₂N)₂PMe₂O·Me (10) but the yield of this product is low (~5%). The principal product (~80%) is the cyclic azaphosphorin 8, formed presumably by a deprotonation reaction and a phosphazene–azaphosphorin rearrangement. The reaction of the diquaternary ion [(NPMe₂)₄·2Me]²⁺ with KO-t-Bu reflects the effect of an increase in charge on the tetrameric ring. Nucleophilic attack on phosphorus now predominates, the only product of the reaction, the linear oxophosphazene...
(NHMe)(PMe₂N)PMe₂O (11), indicating that ring cleavage occurs twice.

**Spectra and Structures**

The structures of the azaphosphorins 4 and 8 have been established spectroscopically (see Table 1 for numerical details). The $^1$H nmr spectrum of 4b in benzene (Fig. 1a) shows the expected features, the resonances of the MeP, the MeN, the NH, and the CH protons all being clearly distinguishable. The N-methyl signal is similar in position and appearance to the equivalent resonance in $N_3P_3(NHMe)_6$ ($\delta_{NH}(NMe) = 2.57$ ppm (11)), for which no $^1$H-$^1$H coupling is observed. The chemical shift of the CH proton is close to that found in other phosphorins (12, 13), and as such is at lower field than in C-alkyl ylids $R_3P=CHR'$ ($\delta_{CH}(CH) = -0.5$ to $-1.0$ ppm (14)) in which the anionic nature of the ylidic carbon atom has a large shielding effect on the CH proton. It is at higher field than in those ylids which are stabilized by electron withdrawing substituents on carbon (e.g. $\delta_{CH}(CH)$ in $Ph_3P=CHC(O)Me$ is 3.68 ppm (15)).

The lack of resolution of the CH resonance into the expected triplet is explicable in terms of a rapid proton exchange between nitrogen and carbon, a process which has already been observed for methylene diphosphine dioxides in the presence of aniline (16), and which, in the present case, corresponds to the tautomeric change between the imine and amine forms 3 and 4. Similar effects have been observed elsewhere; the sulphur ylid 12 has been shown to exist in solution in two tautomeric forms (17), and the azaphosphorin $MeS(NPPh_3)_2CH$ (13), whose broad CH singlet at $\delta_{CH} 1.6$ ppm is not resolved into the expected triplet even at $-30^\circ$C (13), may well undergo a similar exchange.

In the present system, proton transfer is believed to be promoted by traces of acid, as is found for simple ylids (13, 14, 18, 19) and, as in

<table>
<thead>
<tr>
<th>TABLE 1. $^1$H nmr parameters and vibrational frequencies of azaphosphorin derivatives</th>
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<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>$\delta$(MeN)</td>
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<tr>
<td>$\delta$(MeP)</td>
</tr>
<tr>
<td>$\delta$(MeP)</td>
</tr>
<tr>
<td>$\delta$(MeP)</td>
</tr>
<tr>
<td>$\nu$(N—H)</td>
</tr>
<tr>
<td>$\nu$(C—N)$^d$</td>
</tr>
<tr>
<td>$\nu$(P—N)</td>
</tr>
</tbody>
</table>

* $\delta$(ppm) in C₆D₆, reference internal tetramethylsilane. J(PH) (Hz) in parentheses.
* $^a$(cm$^{-1}$) from Nujol mull spectra, assignments tentative.
* No $^1$H-$^1$H coupling observed (at ambient temperature).
* $^c$ unresolved multiplet.
* $^d$phenyl $\sim 7.0$-8.0 ppm.
* $^e$Assignment confirmed by ir spectrum of $Me_2(NHCD_3)P,N,CH, v(N—C)1037$ cm$^{-1}$, cf. $v(N—C)$ in $MeNH_2$, 1044 cm$^{-1}$, $CD_3NH_2$, 973 cm$^{-1}$ (52, 53).
* $^f$Assignment confirmed by ir spectrum of $Me_2(NHCD_3)P,N,CH, v(N—C)1037$ cm$^{-1}$, cf. $v(N—C)$ in $MeNH_2$, 1044 cm$^{-1}$, $CD_3NH_2$, 973 cm$^{-1}$ (52, 53).
* $^g$(CH) = 1.23, $^h$(NH) = 1.76 ppm (broad singlets).
ylids (19), can be suppressed by the addition of an auxiliary base. For example, the $^1$H nmr spectrum of 4b in pyridine (Fig. 1b) is better resolved than the same spectrum run in benzene (Fig. 1a), and shows clearly the $^1$H-$^1$H coupling in the NHMe group and also the $^1$H-$^{31}$P coupling of the CH proton.

The corresponding methyl derivative 4a is more basic, sufficiently so to decompose chloroform, and proton exchange from carbon to nitrogen is consequently more rapid. Its $^1$H nmr spectrum in benzene (Fig. 1c and d) shows no NH or CH signals, even when pyridine is added. The other structural features, however, are observed; the resonances of the PMe group, the two inequivalent PMe$_2$ groups, and the NMe group are readily distinguished. The NH and CH resonances are also absent from the $^1$H nmr spectrum of the corresponding eight-membered ring compound 8 but, for all the azaphosphorins listed in Table 1, the presence of the NHMe group is confirmed by the observation of a

$^2$The dependence of the chemical shifts of the NH and CH resonances on the nature of the solvent, and on temperature, is noteworthy. Further work is required to relate this dependence to the imine-amine equilibrium.
v(N—H) band in their infrared spectra. Its frequency (~3200 cm⁻¹) is similar to the value found for it in N-alkyl phosphoramidates (20). The high values of v(N—C) indicate a single rather than a double exocyclic PN bond. In N-alkylphosphoramidates, for example, v(N—C) is found in the region of 1020–1220 cm⁻¹ (20), whilst in N-methyl phosphinimines (21, 22), its value is much lower (848 cm⁻¹ in Ph₃PNMe (21)).

The ¹H and ³¹P nmr spectra (Table 2) of the compounds NHMe(PMe₃)₂PMe₃O (n = 1, 2, 3) indicate an open chain structure, since all the phosphorus atoms, and PMe₃ protons, are inequivalent. Shielding of the phosphorus atoms is expected to decrease with increasing distance from oxygen, because of the polarization of charge towards the more electronegative end of the molecule, and, as in the analogous phenyl compounds (23), the δₚ values are so assigned. Hydrogen bonding is indicated for all the compounds listed in Table 2 by the low value of ν(P=O) (1170 cm⁻¹ in Me₃PO (24)).

Reactions of Azaphosphorins

The chemical properties of the azaphosphorins reported here are primarily those of a strong base but, depending on the position of the equilibrium between the imine and amine tautomeric forms, the compounds can be regarded as being related either to phosphorus ylids R₃PCHR' or to imines R₃PNR'. In some respects their behaviour is similar to that of λ₅-phosphorins (25); they do not, for example, react with molecular oxygen (as do simple ylids (26, 27)), nor do they undergo the Wittig reaction, the P=C bond being insufficiently polar. In the reaction of 4a and 8 with aqueous ethanol, the exocyclic P—N bond is broken rather than the endocyclic P=C bond, to give the cyclic oxides 14, 15; the ready loss of the exocyclic methylenimino group from these molecules is in contrast to the hydrolytic stability of aminophosphazenes. In related molecules, cleavage of the P=C bond can occur, as in the hydrolysis of the azaphosphorin MeC(NPPh₃)₂CH (12). Both reaction paths are exemplified in the hydrolysis of the di-imine PhN=PPh₂CH₂PH₂=P—NPh. In basic solution, the expected diphosphine dioxide is produced, but acidic hydrolysis results in the cleavage of a central P—C bond, and the formation of the simple oxides MePh₂PO and (NHPPh)Ph₂PO (28). The course of the reaction
Table 3. $^1$H nmr parameters$^a$ of cyclic phosphazene oxides 14, 15

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$(CH$_2$)</th>
<th>$\delta$(MeP)</th>
<th>$\delta$(Me$_2$P$^b$)</th>
<th>$\delta$(Me$_2$P$'$)$^b$</th>
<th>$\delta$(Me$_2$P$''$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>1.95(13.5)$^c$</td>
<td>1.96(13.5)</td>
<td>1.61(14.0)</td>
<td>1.48(15.0)$^d$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>2.11(13.5)</td>
<td></td>
<td>1.53(15.0)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>2.31(12.5)</td>
<td>1.94(13.0)</td>
<td>1.63(14.0)</td>
<td>1.54(13.0)$^e$</td>
<td>1.47(14.0)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.56(14.0)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$(ppm), CDCl$_3$, reference internal TMS. $J$(PH) (Hz) in parentheses.
$^c$Ring positions of P, P', P'' uncertain.
$^d$ABXY pattern partially obscured by P-methyl resonances; $J$(PH) values approximate. $J$(H$_1$,H$_2$) = 13.5 Hz.
$^e$Inequivalent geminal methyl groups displaying second order coupling.
$^f$Inequivalent geminal methyl groups.

evidently depends sensitively on the conditions used.

Like their parent azaphosphorins, the oxides 14, 15 can be represented by either of two tautomeric forms 16a, b. However, the appearance of

![Diagram of 16a and 16b]

characteristic methylene signals in their $^1$H nmr spectra (Table 3), and the absence of a $\nu$(O—H) band from their infrared spectra, indicates that the equilibrium favours the oxide structure 16b.

In the six-membered ring, the methylene protons are magnetically inequivalent, as expected, and give rise to an AB proton coupling pattern. In the eight-membered ring, the two protons are accidentally equivalent, and give rise to a simple triplet (Fig. 2).

Unlike other azaphosphorins (12), and simple ylids R$_3$PCHR$'$ (14, 29–32), which react with methyl iodide to give C-methylated phosphonium salts, the azaphosphorins reported here react to give the corresponding C-hydroiodides, 17 and 18 (X = I). Presumably the initial

![Diagram of 17 and 18]

methylation is immediately followed by a proton transfer reaction with a second mole of azaphosphorin (eq. 3), as is found in the alkylation of

Fig. 2. $^1$H nmr spectra of the phosphazene oxide 15 (100 MHz, CDCl$_3$); (A) direct, (B) $^{31}$P decoupled.

phosphinimines (33). Protonation on carbon rather than on nitrogen is confirmed by the $^1$H nmr spectra (Table 4) of the salts, which show a characteristic AB proton coupling pattern for the inequivalent methylene protons. The presence of a positive charge on the rings further facilitates the interpretation of their spectra; the charge distribution is less uniform than in the neutral compounds, and the various signals are better separated, as is illustrated in Fig. 3, which shows the $^1$H nmr spectra of 17 (X = I).
Table 4. $^1$H nmr parameters$^a$ of the azaphosphorin hydrohalides 17, 18

<table>
<thead>
<tr>
<th>Parameter</th>
<th>17 (R = Me)</th>
<th>18</th>
<th>17 (R = Ph)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X = I</td>
<td>X = Cl</td>
<td>X = I</td>
</tr>
<tr>
<td>$\delta$(MeN)</td>
<td>2.65(13.5)</td>
<td>2.63(13.5)</td>
<td>2.62(13.0)</td>
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<tr>
<td>$J$(HH)</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>$\delta$(HN)</td>
<td>5.85</td>
<td>6.03</td>
<td>4.24</td>
</tr>
<tr>
<td>$\delta$(MeP)</td>
<td>1.99(13.0)</td>
<td>1.99(13.5)</td>
<td>1.96(13.5)</td>
</tr>
<tr>
<td>$\delta$(MeP)$^c$</td>
<td>1.86(13.5)</td>
<td>1.79(14.0)$^d$</td>
<td>1.79(13.5)</td>
</tr>
<tr>
<td>$\delta$(MeP)$^e$</td>
<td>1.58(14.0)</td>
<td>1.53(14.0)</td>
<td>1.53(13.5)$^d$</td>
</tr>
<tr>
<td>$\delta$(MeP)$^f$</td>
<td></td>
<td></td>
<td>1.49(13.5)</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)(H$_4$)$^a$</td>
<td>3.74(15.0, 11.0)</td>
<td>4.09(14.0, 11.0)</td>
<td>3.75(15.5, 12.5)</td>
</tr>
<tr>
<td>$\delta$(CH$_3$)(H$_4$)$^a$</td>
<td>2.78(13.5, 13.5)</td>
<td>2.27(14.0, 13.5)</td>
<td>3.05(15.5, 12.5)</td>
</tr>
<tr>
<td>$J$(H$_4$H$_4$)$^a$</td>
<td>15.5</td>
<td>15.0</td>
<td>15.5</td>
</tr>
</tbody>
</table>

$^a$$\delta$(ppm), CDC$_2$, reference internal TMS; $J$(PH) (Hz) in parentheses.

$^b$Phenyl region omitted.

$^c$Relative positions of P, P', P'' uncertain.

$^d$Inequivalent methyl groups on same phosphorus atom.

$^e$ABXY pattern, partially obscured; $J$(PH) approximate.

$^f$J(PH) not assigned. In CD$_3$CN, $H_{ax}$ equivalent, $\delta = 3.44$ ppm, $J$(PH): 13.0 Hz.

$^g$In Hz.

The appearance and position of the resonance of the N-methyl protons is similar to that found in aminophosphonium salts (34), exhibiting both $^{31}$P-$^1$H and $^1$H-$^1$H coupling. However, the addition of one drop of D$_2$O to a solution of 17 ($X = I$) in CDCl$_3$ brings about the immediate collapse of $^1$H-$^1$H couplings, and the loss of the NH resonance (Fig. 3B), indicating that proton exchange between the solvent and the exocyclic nitrogen is rapid. The methylene protons are expected to be less acidic, and their exchange with protic solvents is consequently slower, but the effect is nonetheless observable. When 17 ($X = I$) is dissolved in D$_2$O, the methylene resonance appears as a simple triplet which, upon allowing the solution to stand, becomes less intense and finally vanishes (after about 2 h).

In the reaction of the azaphosphorins with methyl iodide, the neutral product 20 cannot be isolated. It apparently undergoes a second methylation and proton transfer reaction, the overall yield of hydroiodide being such that 3 mol of azaphosphorin are converted into 2 mol of hydroiodide. In order to determine the position of primary substitution on the azaphosphorin ring (carbon or nitrogen), the reactions of 4a and 8 with benzoyl chloride have been examined. In the case of the eight-membered ring, the reaction yields the C-benzoyl derivative 22. The reaction of the six-membered ring is more vigorous and, as with its reaction with methyl iodide, cannot be stopped at the first stage. Instead, the initially formed C-benzoyl derivative reacts with a second mole of benzoyl chloride, to give the N-benzoyl C-benzoyl compound 21.

As in the case of their parent azaphosphorins, the $^1$H nmr spectra of the benzoylated derivatives 21 and 22 (Table 5) reveal very little separation of the P-methyl resonances, thereby indicating
the uniformity of the charge distribution within the ring. For the tetrameric compound, $^1$H-$^1$H coupling in the NHMe group is now observed (as it is in simple N-methyl amides); proton exchange is obviously suppressed by the low basicity of the nitrogen. The shielding of the N-methyl protons in 21 ($\delta_{\text{H}}(\text{NMe}) = 2.50$ ppm) is greater than in N-methyl benzamidile ($\delta_{\text{H}}(\text{NMe}) = 3.40$ ppm, CDCl$_3$, reference internal TMS), suggesting that the diffusion of lone pair density from nitrogen to phosphorus is limited.

The infrared spectra of these compounds are too complex to allow a detailed interpretation, but their carbonyl stretching frequencies (Table 5) are well isolated and easily identified. For both the six- and the eight-membered ring, the low value of the carbonyl frequency is similar to that found in other acylated ylids (35-37), and reflects the extent to which resonance such as that depicted in eq. 4 weakens the C–O double bond. The lower frequency found in the six-
TABLE 5. $^1$H nmr parameters$^a$ and carbonyl stretching frequencies$^b$ of azaphosphorin benzoyl derivatives 21, 22

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta$(MeN)</th>
<th>$\delta$(MeP)</th>
<th>$\delta$(Me$_2$P)$^c$</th>
<th>$\nu$(C—O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>2.50(9.0)</td>
<td>1.70(15.0)</td>
<td>1.64(13.5), 1.60(13.0)</td>
<td>1502</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.55(13.5), 1.48(13.0)</td>
<td>1642</td>
</tr>
<tr>
<td>22</td>
<td>2.46(14.0)$^d$</td>
<td>$^e$</td>
<td>$^e$</td>
<td>1530</td>
</tr>
</tbody>
</table>

$^a$\(\delta\)(ppm), CDCl$_3$, reference internal TMS; $^b$\(\nu\)(PH) (Hz) in parentheses.
$^c$No equivalent methyl groups.
$^d$\(\nu\)(N—NMe) = 5.5 Hz; \(\delta\)(PH) = 2.70 ppm.
$^e$Unresolved PMe, PMe$_2$ multiplet near \(\delta = 1.55\) ppm.

membered ring suggests that electron release onto the C-benzoyl group is greater for that ring size. The amide carbonyl frequency of 17 (1642 cm$^{-1}$) is similar to that found in simple tertiary amides (e.g. \(\nu\)(C—O) in PhCONMe$_2$ is 1640 cm$^{-1}$ (38), and in PhCONMePh$^3$ is 1653 cm$^{-1}$). In these latter compounds, the presence of an N-phenyl group increases \(\nu\)(C—O), the competitive electron withdrawing effect of the aromatic ring reducing the influence of the ionic form Ph—N$^+$=C—O$^-$(40). The relatively low value of the amide carbonyl frequency in 17 is consistent with the \(^1\)H nmr evidence indicating that conjugative interactions between phosphorus and the exocyclic nitrogen are limited.

**Discussion**

\(N\)-Ethyl phosphazenium salts (41), like their pyridine analogues, react with bases to yield the neutral compound and ethylene. Such an elimination reaction is not possible for the \(N\)-methyl compounds, and their principal reactions with bases are deprotonation and nucleophilic attack. In the pyridine series, a 2-methyl group is deprotonated to give a methide, which is alkylated on carbon rather than on nitrogen, thereby conserving ring aromaticity (42). When an electron-withdrawing substituent is present in the 2- (or 4-) position, the susceptibility of the molecule to nucleophilic attack at these positions is increased, and, in basic solutions, such salts are hydrolysed to pyridones (42), the stability of which is enhanced by the strength of the carbonyl bond.

In the reactions reported here, deprotonation and nucleophilic attack both occur, but the balance between them is determined by the reagent and by the ring size. Open chain oxides are produced when KO-t-Bu is used, primarily because the elimination of isobutene or dibutyl ether allows the formation of a strong phosphoryl bond. The size of the ring has a marked effect on the relative yield of cyclic and linear products. The \(^31\)P nmr shifts of (NPMe)$_2$$_3$ (43) suggest that the partial positive charge on the phosphorus atoms adjacent to the \(N\)-methyl group is greater in the six-membered ring compound, nucleophilic attack and the formation of the linear oxide being thereby promoted, as found.

Deprotonation of the \(N\)-methyl methylphosphazenium salts occurs, as expected, at the 2-position, and the consequent rearrangement is probably aided by the electrophilic character of the phosphorus atoms adjacent to the alkylated nitrogen atom. Although the detailed mechanism is unknown, it seems likely to involve a four-centre interaction (as shown) similar to that of the Wittig reaction.$^4$ A related mechanism has been suggested (44) for the base catalyzed rearrangement of (Me$_3$PCSiMe$_2$)$_2$, in which a

$^3$Present work, CC1$_3$ solution; Nujol mull; cf. 1641 cm$^{-1}$ (39).

$^4$The possibility that the reaction is bimolecular, so reducing strain in the transition state, has been suggested by a referee, and cannot at present be excluded.
methylenegroup enters the ring. A rearrangement in the opposite sense, but also involving a 4-centre mechanism, occurs during the ammonolysis of bis(diphenylphosphino)methane in carbon tetrachloride to give \((\text{MePPh}_2\text{NPPh}_2\text{NH}_2)\text{Cl}\) (12), and may account for the apparent migration of a methyl group during the chloramination of bis(diphenylphosphino)methylamine, which yields the salt \([\text{NHMePPh}_2\text{NPPh}_2\text{NH}_2]\text{Cl}\) (45).

In the latter two examples, the driving force of the reaction is probably the formation of the resonance stabilized \((\text{P}==\text{N}==\text{P})^+\) cation. The phosphazene-azaphosphorin system is more complicated, in that both a cyclic \(\pi\)-system and an exocyclic \(\pi\)-bond are involved, but we can nevertheless understand the rearrangements that take place by simple model calculations of the \(\pi\)-energy changes. The three related molecular forms are shown in Fig. 4 which shows how the \(\pi\)-electron energies of the three forms depends on the assumed Coulomb parameter of carbon. Isomer \(a\) is the exocyclic ylid 6 formed by the deprotonation of the quaternary cation, \(b\) is the product of its direct rearrangement to an exo-imide 7, and \(c\) results from the further proton migration to give the azaphosphorin 8. Form \(c\) is unique in restoring the cyclic delocalization of the initial quaternary compound 5.

Although the energetic advantage of the delocalization may be important, the calculations show that it may be outweighed by a high localized \(\pi\)-energy in an exocyclic bond in \(a\) or \(b\).

The general result is that the exocyclic position is favoured for the more electronegative atom. To take the extreme cases first, if \(\alpha_c < -1\), (the value for nitrogen), \(a\) is the most stable form, and no rearrangement would be expected. On the other hand, if \(\alpha_c < -0.7\) (approximately), rearrangement should take place, but should stop at the exo-imide stage \(b\). In both cases the molecule is stabilized by a strong exocyclic \(\pi\)-bond. For intermediate values of \(\alpha_c\), the situation is more interesting. The azaphosphorin \(c\) is now slightly more stable than the exo-ylid \(a\), because cyclic delocalization is now possible; if localized bonds are assumed, the azaphosphorin is never favoured over the exo-ylid. In terms of the simple model used, it is therefore possible to understand the azaphosphorin rearrangement as being driven by the increase of \(\pi\)-energy arising from the displacement of the more electronegative atom from the ring, and reinforced by the attainment of cyclic delocalization.\(^5\)

Although the results of Fig. 4 are qualitative, the assumed parameters are realistic enough to show that the energy differences between the three forms are likely to be small, and it is not surprising that proton transfer between the endocyclic carbon and endocyclic nitrogen atoms of the azaphosphorins is fast enough to cause a collapse of the \(^{31}\text{P}-^1\text{H}\) coupling of the CH signal. The results have another application. Since oxygen is more electronegative than nitrogen, the introduction of an exocyclic phosphoryl group in the cyclic oxophosphazenes 14, 15 alters the equilibrium in favour of exocyclic \(\pi\)-bonding, lowering the energy of the exo-imide \(b\) without direct effect on the energies of \(a\) and \(c\). It is consistent with this result that rapid proton

\(\text{Fig. 4. } \pi\)-Electron energies (eV, arbitrary zero) of the three isomers shown, as a function of the assumed Coulomb parameter of carbon. The values of \(\alpha_c(2\text{ eV})\) and \(\alpha_c (-1\text{ eV})\) used are not critical, but have been found useful for the description of other properties of \((\text{NPM}_{2})\). All resonance parameters were taken to be \(-1\text{ eV}\), independent of overlap, in both out-of-plane and in-plane \(\pi\)-systems.

\(^5\)In a reaction which is apparently similarly dependent on relative electronegativity, 2-arylaminoxyrrylum chlorides can be deprotonated to pyranimines, which then rearrange to pyridones in a reaction closely analogous to the azaphosphorin rearrangement described above. The corresponding reaction of the thiapyrrylum iodides stops at the thiapyraniline stage (51).
migration is not observed in the cyclic oxophos-
phazenes described above. The general concepts
are further supported by the structures of the phos-
phazenes N₅P₅Ph₅(OH) and N₅P₅Ph₅(OH)₂
(non-geminal) for which hydroxy- rather than
oxy-structures have been suggested (46, 47).

From the present point of view, the potential
tautomerism equilibrium is that between forms b
and c of Fig. 4, N being substituted for CH in the
ring, and O for NCH₃ in the exocyclic position.
The increased electronegativity of the ring atom
would tend, following the diagram, to stabilize the
cyclical delocalized form c. The energy balance is
sensitively dependent on the relative
electronegativities of the relevant atoms.
The same feature is found in pyridine chemistry;
2- and 4-hydroxy pyridines normally exist in the
pyridone form, but when the oxygen is replaced
by a less electronegative atom, as in 2-amino-
pyridine, the aromatic amino-form, rather than
the exocyclic imide, is the more stable.

Experimental

Sodium metal, hexamethyldisilazane, methyl iodide,
and benzoyl chloride were commercial products. Potas-
sium tert-butoxide and methyl fluorosulphate were also
obtained commercially. The former was purified by
sublimation in vacuo, the latter by distillation under
nitrogen. Hexane and octane were of reagent grade.

Quaternary Salts

The monouaternary salts (NPMe₂)⁺ MeI were prepared by the reaction of the neutral methylenophos-
phazenes with methyl iodide (43). The preparation of the
salt (NPMe₂)₄ 2MeCl by the reaction of Me₄PCl and
MeNH₂.HCl has already been reported (48); the diquaternary salt (NPMe₂)₄ 2MeSO₃F used here was prepared by treating (NPMe₂)₄ MeI with two equivalents of
Me₂SO₃F used here was prepared by treating (NPMe₂)₄ MeI with two equivalents of
Me₂SO₃F in acetonitrile solution. The product was pre-
cipitated quantitatively from the solution by the addition
of diethyl ether, and purified by recrystallization from
acetonitrile: mp 231-233°C; 1H nmr spectrum (6, CDCl₃,
int. TMS), 2.84 (6H, triplet, J₉ = 11.5 Hz), 1.95
(24H, doublet, J₉ = 13.7 Hz); ir spectrum v(P=N)
1275, 1330 cm⁻¹; v(C-N), 1220, 1260 cm⁻¹; v(C=O)
1700 cm⁻¹. Anal. calcd. for C₁₀H₁₂N₄F₄O₂P₄: C 52.7, H
8.5, N 10.6; found: C 52.9, H 5.0, I 20.4, N 6.8.

Reaction of (NPMe₂)₄ MeI with Na(NiMe₂)²

Sodium (0.20 g, 8.7 mmol) was added to a slurry of
(NPMe₂)₄ MeI (3.54 g, 8.0 mmol) in 200 ml octane.
About 0.5 ml of HN(NiMe₂)₂ was injected into the
reaction mixture at the reflux temperature, and, to
compensate for possible losses by evaporation, again at 24 h
intervals to a total reaction time of 72 h. The mixture
was cooled and filtered and the solvent distilled from the
filtrate to leave a white solid, which was purified by
sublimation at ~130°C/0.01 Torr and recrystalization
from hot hexane to give colourless hygroscopic prisms of
8 (2.21 g, 7.0 mmol, 88%); mp 104-105°C. Anal. calcd. for
C₉N₂6Ni₄P₄: C 34.3, H 8.6, N 17.8; found C 34.4, H
8.5, N 17.6.

Reaction of (NPMe₂)₄⋅ MeI with Na(NiMe₂)²

In a similar reaction, sodium (0.35 g, 15.3 mmol) and
(NPMe₂)₄ MeI (5.11 g, 13.9 mmol) were allowed to react with HN(NiMe₂)₂ in octane (200 ml). After 96 h, the
mixture was filtered and the solvent distilled from the
filtrate to leave a white solid, which was purified by
sublimation at ~130°C/0.01 Torr and recrystalization
from hot hexane to give colourless hygroscopic plates of
8 (2.68 g, 11.2 mmol, 80%); mp 140-142°C. Anal. calcd. for
C₉N₂6Ni₄P₄: C 35.15, H 8.4, N 17.6; found C 35.4, H
8.5, N 17.6.

Reaction of Me₅P₄N₃P₃Me₂ with Na(NiMe₂)²

Sodium (0.06 g, 2.6 mmol), Me₅P₄N₃P₃ MeI (1.34 g,
2.2 mmol) dried as before to remove EtOH and HN-
(NiMe₂)₂ were allowed to react together in 60 ml boiling
toluene for 24 h. The mixture was filtered and the solvent
distilled off. The residual white solid was purified by
recrystallization from benzene-octane to give colourless
prisms of 46 (0.95 g, 2.0 mmol, 93%); mp 147-149°C. Anal. calcd. for
C₂₇H₂₉N₃P₃: C 65.9, H 5.55, N 8.65; found: C 65.9, H
5.5, N 8.65.

Reaction of (NPMe₂)₄ MeI with KO-t-Bu

Finely powdered (NPMe₂)₄ MeI (3.00 g, 6.8 mmol)
was added to a slurry of KO-t-Bu (0.84 g, 7.4 mmol) in
100 ml hexane, and the mixture heated under reflux for
24 h. The solvent was distilled from the filtered solution to
leave a white solid (1.82 g) which was sublimed at
~130°C/0.01 Torr on to a water cooled cold finger. The
sublimate (8) was recrystallized from hot hexane (1.71 g,
5.4 mmol, 80%) and identified by comparison of its ir
spectrum with that of an authentic sample, and by its
mp, 104-105°C. The residual oil in the sublimation vessel
solidified into a white solid, which was purified by
recrystallization from hot hexane to give colourless
hygroscopic crystals of 10 (0.11 g, 0.33 mmol, 5%); mp
72-74°C. Anal. calcd. for C₉H₂₈N₄O₄P₄: C 32.5, H 8.5,
N 16.9; found C 32.6, H 8.6, N 16.9.

Reaction of (NPMe₂)₄ MeI with KO-t-Bu

Similarly, (NPMe₂)₄ MeI (1.38 g, 3.8 mmol) was
allowed to react with a slurry of KO-t-Bu (0.50 g, 4.5 mmol) in 50 ml boiling hexane. After 24 h, the mixture was filtered and the solvent removed from the filtrate to leave a colourless oil. Sublimation of this oil at 184°C yielded a white hygroscopic solid (0.89 g, 3.4 mmol, 93%), which was recrystallized as colourless plates by cooling a concentrated solution of it in pentane to -23°C; mp 73-75°C. Anal. calcd. for C16H18N2O2P: C 35.4, H 8.9, N 15.4; found: C 35.2, H 8.9, N 15.4.

Reaction of Azaphosphorins 4a, 8
In separate experiments, samples of 4a and 8 (0.3-0.4 g) were dissolved in 25 ml of a 50/50 ethanol-water mixture. After 24 h, the solution was removed at room temperature in vacuo to leave a white solid. Recrystallization from benzene of the solid from 4a gave colourless hygroscopic blocks of 14, mp 184-186°C. Anal. calcd. for C16H18N2O2P: C 32.7, H 8.6, N 13.4; found: C 32.6, H 8.5, N 16.0.

Hydrolysis of Azaphosphorins 4a, 8
In a similar experiment, a slurry of KO-t-Bu (1.30 g, 11.6 mmol) and (NPMe2)·2MeSO3F (2.70 g, 5.1 mmol) was heated to reflux in 60 ml hexane. After 24 h, the solution was decanted from the pasty residue and the solvent distilled off to yield a white solid, which was recrystallized from hot hexane to give colourless feather-like crystals of 11 (0.93 g, 5.0 mmol, 50%); mp 73-75°C. Anal. calcd. for C16H18N2O2P: C 33.0, H 8.9, N 15.4; found: C 33.3, H 8.9, N 15.25.

Reactions of Azaphosphorins 4a, 8, with Methyl Chloride
The addition of an excess of methyl chloride to a solution of 4a (1.04 g, 4.33 mmol) in ether resulted in the precipitation of the hydroiodide 17 (R = Me) (0.45 g, 1.64 mmol) and 18 (0.43 g, 1.0 mmol). The neutral products of the transylidation reactions could not be isolated. The air-stable crystalline hydroiodides were recrystallized from acetonitrile-toluene: 17 (R = Me), mp 194-195°C. Anal. calcd. for C16H18N2O2P: C 27.4, H 7.7, N 12.7; found: C 27.4, H 7.7, N 12.6. The mixture was filtered, leaving the hydrochloride of 17 (0.26 g, 0.59 mmol), which was recrystallized from 5 ml boiling hexane to give colourless octane as colourless blocks: (dec.) 181-184°C. Anal. calcd. for C16H18N2O2P: C 36.4, H 6.3, N 9.4; found: C 36.1, H 6.2, N 9.6.

In another experiment, a solution of benzoyl chloride (0.12 g, 0.9 mmol) in 10 ml ether was added dropwise to a stirred solution of the azaphosphorin 8 (0.56 g, 1.8 mmol) in 50 ml ether. A fine white precipitate was immediately formed. After 3 h the mixture was filtered, and the hygroscopic solid recrystallized from acetonitrile-benzene to give small colourless cubes of the hydrochloride of 18 (0.25 g, 0.7 mmol): mp 193-195°C. Anal. calcd. for C16H18N2O2P: 3.08, H 7.8, N 16.0; found: C 3.09, H 7.7, N 15.9. The solvent was distilled from the filtrate to leave a yellow oil which, on drying in vacuo, solidified to a yellow, air stable powder. Recrystallization of this solid from hot hexane yielded yellow mica-like plates of the benzoyl derivative 22: mp 133-134°C. Anal. calcd. for C16H18N2O2P: C 46.0, H 7.2, N 13.4; found: C 45.7, H 7.3, N 13.1.

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