

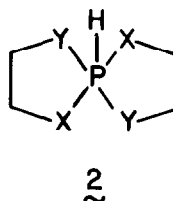
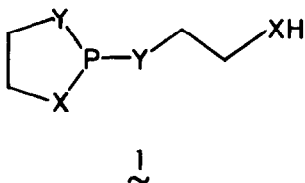
POLYAMINOPHOSPHORANES II.<sup>1</sup> CYCLEN PHOSPHORANE -

A NOVEL P(V) TAUTOMER

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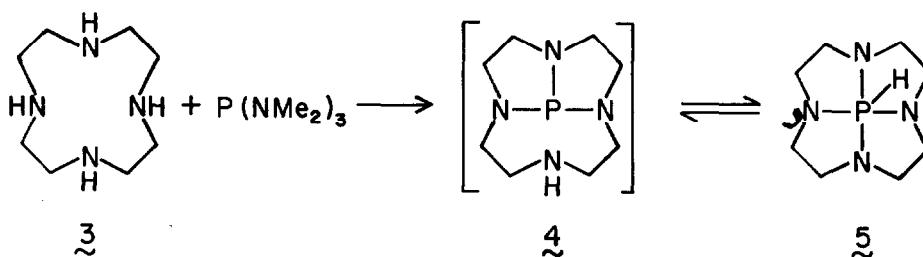
Both trivalent and pentavalent derivatives of phosphorous have been known for a long time. Recent work of Burgada<sup>3</sup> has shown that the compounds obtained from ethylene glycols and phosphorous derivatives can exist either as trivalent phosphorous(III), e.g., 1, or pentavalent phosphorous(V) tautomers, e.g., 2. The equilibrium between 1 and 2 is highly dependent on the heteroatom and substitution in the ethylene bridges.<sup>4,5</sup> The equilibrium 1a  $\rightleftharpoons$  2a



- a; X = Y = O
- b; X = NH, Y = O
- c; X = Y = NH

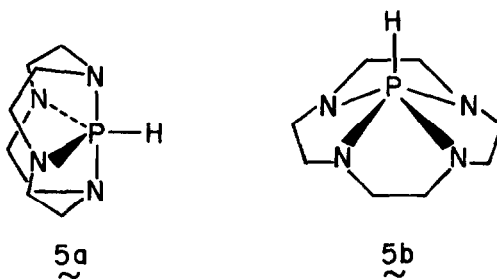
heavily favors the phosphorane, 2a, whereas the equilibrium 1b  $\rightleftharpoons$  2b is delicately balanced and suitable substitution on the ethylene bridge can lead to a preponderance of either tautomer. Phosphorus forms stronger bonds with oxygen than with nitrogen; thus, 1b is the observed P(III) tautomer. No reports of phosphoranes from simple ethylene diamine derivatives, e.g., 2c have been found.

For some time, we have been investigating the direct, one-step synthesis of polycyclic compounds from macrocyclic polyamines. An appropriately substituted atom can be directly "inserted" into the center of a macrocyclic polyamine via an exchange reaction. We have reported the preparation of polycycles containing tetravalent carbon,<sup>6</sup> trivalent<sup>7</sup> and pentavalent<sup>1,7c</sup> phosphorus moieties. Because the pentavalent cyclen fluorophosphorane and the polycyclic triaminophosphorous compounds were readily prepared, we wanted to test whether a four-nitrogen macrocycle would undergo the simple exchange reaction to form a P(III) or P(V) derivative. We therefore reacted stoichiometric amounts of 1,4,7,10-tetraazacyclododecane( $\tilde{3}$ )<sup>8</sup> and hexamethylphosphorous triamide. After heating the mixture for 2 hr at 120°, dimethylamine evolution had ceased and a white, crystalline, modestly air-stable compound was obtained in 83% yield.<sup>9</sup>



Spectral characterization of the product indicated the phosphorane tautomer  $\tilde{5}$  predominated rather than the tricyclic phosphorous triamide,  $\tilde{4}$ .<sup>7a</sup> A strong and characteristic P-H stretch appeared in the infrared spectrum of  $\tilde{5}$  at 4.29 $\mu$ , and P-H coupling was present in the <sup>1</sup>H- and <sup>31</sup>P-nmr spectra. The <sup>31</sup>P-nmr spectrum of  $\tilde{5}$  exhibited a doublet ( $J = 621$  Hz) at -54.5 ppm;<sup>10,11</sup>. No signal was detected for  $\tilde{4}$ . The <sup>31</sup>P-decoupled <sup>1</sup>H-nmr spectrum of  $\tilde{5}$  had a one proton absorption at  $\delta_{\text{H}} = 6.88$  and a 16 hydrogen symmetrical AA'BB' multiplet for the methylene protons with  $\delta_{\text{H}_A} = 3.03$  and  $\delta_{\text{H}_B} = 2.83$ ;  $J_{\text{AA}'} = 6.4$  Hz,  $J_{\text{BB}'} = 6.4$  Hz,  $J_{\text{AB}'} = 5.6$  Hz, and  $J_{\text{AB}} = -8.7$  Hz. In the undecoupled <sup>1</sup>H-nmr spectrum, the phosphorane hydrogen appeared as a doublet ( $J = 628$  Hz) and the methylene protons as a dissymmetric multiplet because  $\text{H}_A$  and  $\text{H}_B$  have different phosphorus coupling constants. The <sup>13</sup>C-nmr spectrum of  $\tilde{5}$  exhibited a doublet at 45.0 ppm ( $J_{\text{PC}} = 8.8$  Hz).<sup>11</sup> The mass spectrum of  $\tilde{5}$  had a strong parent peak at  $m/e$  200.1226, and an M-1 peak at 199 (94%).

The  $^1\text{H}$  and  $^{13}\text{C}$ -nmr data are consistent with either a time-averaged spectrum of a rapidly pseudo-rotating trigonal bipyramidal structure, 5a, or the eclipsed square pyramidal structure, 5b. Both models have a "sidedness," i.e., the hydrogens syn to the P-H bond must differ from the hydrogens anti. In 5a the hydrogens on carbon adjacent to the axial nitrogen differ from those on carbon adjacent to the equatorial nitrogen. However, pseudorotation of this model brings the equatorial nitrogens into the axial positions and converts  $\text{H}_A$  into  $\text{H}_{A'}$ , and makes the carbons equivalent. Whether either 5a or 5b is an adequate representation is not known. Based on the similarity of the proton coupling constants,<sup>12</sup> we suspect the structure to be similar to that of cyclen fluorophosphorane.<sup>1,13</sup>



The remarkable "macrocycle effect"<sup>14</sup> stabilizes the 1:1 "insertion" product as the polycyclic tetraaminophosphorane 5. We were unable to identify a 1:1 product when the linear analogue of 5, N, N'-dimethyltriethylenetetra-amine, was treated with hexamethylphosphorous triamide.

#### ACKNOWLEDGMENT

Phosphorus decoupled nmr spectra were obtained and analyzed by G. S. Reddy.

#### REFERENCES AND FOOTNOTES

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9. The reaction can be carried out by refluxing the reactants in toluene or directly heating the mixture. The concentrated reaction product was taken up into boiling hexane, decanted from insoluble oil and crystallized (mp. 112-115°) by slow cooling to -78°. Anal. Calcd for  $C_8H_{17}N_4P$ : C, 47.99; H, 8.56; N, 27.98. Found: C, 48.15; H, 8.64; N, 28.03.
10. This absorption is characteristic for pentavalent phosphoranes. Typical phosphorane absorptions appear at -47 to -67 ppm, whereas the corresponding trivalent tautomers appear at +135 to +147 ppm. The polycyclic phosphorous triamides had absorptions at +109 to +122 ppm.<sup>7a</sup>
11. Nmr spectra were obtained in  $C_6D_6$ .  $^{31}P$ -nmr data are reported in ppm from external  $H_3PO_4$ ,  $^1H$ - and  $^{13}C$ -nmr data are from internal TMS. Following standard conventions, downfield shifts are assigned positive values.
12. G. S. Reddy and J. E. Richman, unpublished results.
13. R. C. Gearhart, L. J. Guggenberger, and J. E. Richman, unpublished results.
14. The term "macrocycle effect" has found wide use in describing the enhanced stability of metal complexes of cyclic ligands over their acyclic counterparts. For example, see F.P.Hing and D.W.Margerum, Inorg. Chem., 13, 2941 (1974).

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