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POLYAMINOPHOSPHORANES III.[1] P(III) - P(V) Tautomerism in Four Nitrogen Cage Phosphoranes

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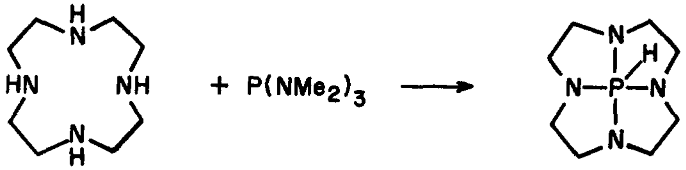
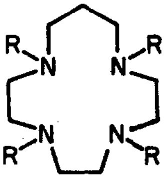
We recently reported the preparation of the novel cyclen phosphorane **2** by the exchange reaction of 1,4,7,10-tetraazacyclododecane (**1**)[3] and hexamethylphosphorous triamide.[1] In our studies on the synthesis of new polycyclic compounds *via* the direct "insertion" of a central atom into a macrocyclic polyamine, we wished to examine the conformational constraints imposed by the macrocyclic ring in greater detail. We therefore prepared a series of polycyclic tetraaminophosphorus compounds to examine the effect of ring size on the P(III) - P(V) tautomerism.



1 **2**

We prepared the series of four nitrogen, 12- to 16-membered macrocycles **3a** - **6a**, by condensation of sodium salts of the respective *p*-toluenesulfonamides with the appropriate ditosylates.[3] Hydrolysis of **3a** - **6a** in concentrated sulfuric acid gave amines **3b** - **6b** in good (60 - 90%) yield.[4]

The reactions of **3b** - **6b** with hexamethylphosphorous triamide proceeded smoothly at 120° in 2 - 3 hr.[5] The products listed in the table were obtained in high yield by distillation of the reaction mixture and were characterized by their analytical and spectral properties. The ^{31}P - nmr chemical shifts



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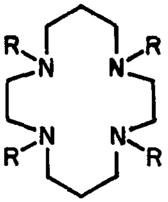

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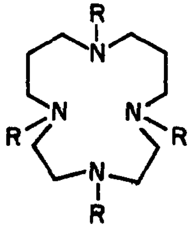

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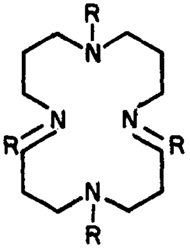

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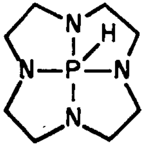
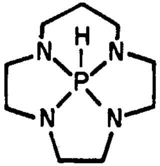
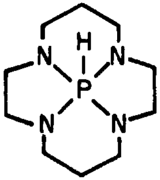
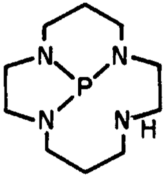
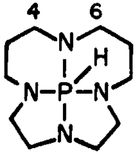
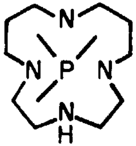
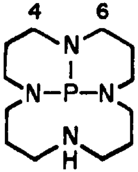
a. R = $SO_2C_7H_7$
b. R = H

clearly distinguishes phosphorous triamide [P(III): δ + 104 to +116 ppm] from tetraaminophosphorane [P(V): δ - 53 to - 61 ppm][4] tautomers. Additionally, the products existing predominantly as the phosphorane had infrared absorptions in the 4.4 - 4.7 μ (ν_{P-H}) region. Mass spectral analysis confirmed the elemental compositions.

When 1 and 3b were reacted with hexamethylphosphorous triamide, we found (within nmr detection limits) only the phosphorane tautomers, 2[1] and 7[7], respectively. 6b gave only the corresponding tricyclic phosphorous triamide 10. However, a dramatic tautomer preference was observed when the isomeric tetraazacyclotetradecanes 4b and 5b were used; 4b gave a mixture in which the phosphorane tautomer 8a[8] predominated, whereas 5b gave predominantly the isomeric P(III) tautomers 9b. Examination of models of 8a and 9a discloses very little difference in steric requirements. The isomers differ by only one-atom connection. When two 6-membered rings are adjacent, as in 9a or 10, the relatively long phosphorus-nitrogen bond accentuates a modest steric repulsion between the eclipsed hydrogens of C_4 and C_6 in the phosphorane tautomer that is slightly relieved in the more flexible P(III) tautomers. This repulsion is absent in compounds with two fused 5-membered rings or a 5- and 6-membered ring fusion, as in 2, 7, and 8.

Macrocylic polyamines provide the entropic advantage necessary to prepare monomeric tetraamino phosphorus polycycles from hexamethylphosphorous triamide and can provide the appropriate bonding geometry to form phosphorane tautomers The P(III)- P(V) tautomerism is delicately balanced in these polycycles and small changes in bonding configuration can dramatically change the product structure.

TETRAAMINOPHOSPHOROUS COMPOUNDS

Compound		Yield(%)	bp(pressure)	^{31}P-nmr^{6}	^{13}C-nmr^{6}
2 		88	mp 112-115°	-54.5	45.0
7 		83	92°(0.3 mm)	-61.1	47.4 44.0 47.1 25.0 44.6
8 a: 	b: 	80	subl.60-70° (0.3 mm)	a: -53.1 (82%) b: +111.9 (18%)	
9 a: 	b: 	80	106-110° (0.3 mm)	a: -53.0 (12%) b: +111.6, + 112.9, +115.5 (88%)	
10 		94	126-135° (0.2 mm)	+104.8	49.7 44.9 47.0 28.0 46.7 24.3

REFERENCES AND FOOTNOTES

1. For the previous paper in this series, see J. E. Richman and T. J. Atkins, Tetrahedron Lett., ,(1978).
2. Current address, Department of Chemistry, University of Idaho, Moscow, Idaho 83843.
3. J. E. Richman and T. J. Atkins, J. Amer. Chem. Soc., **96**, 2268(1974); T. J. Atkins, J. E. Richman and W. F. Oettle, Org. Syn., in press.
4. **3b**: 1,4,7,10-Tetraazacyclotridecane; **4b**: 1,4,8,11-tetraazacyclotetradecane; **5b**: 1,4,7,11-tetraazacyclotetradecane; **6b**: 1,5,9,13-tetraazacyclohexadecane.
5. U.S. 4,038,312.
6. ^{31}P-nmr spectra were obtained in C_6D_6 and are reported in ppm from external H_3PO_4, ^{13}C-nmr spectra (C_6D_6) are reported in ppm from internal TMS. Downfield shifts are assigned positive values.
7. The ir spectrum showed an absorption at 4.43μ (ν_{PH}), the ^1H-nmr showed a 1H doublet (J = 609 Hz) at δ 7.11 in $CDCl_3$, corresponding to the ^{31}P-nmr doublet (J = 606 Hz).
8. The ^1H-nmr spectrum (220 MHz in C_6D_6/TMS) of 8a showed a 1H doublet (J = 549 Hz) at δ 5.84, corresponding to the ^{31}P-nmr doublet (J = 547 Hz).

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