

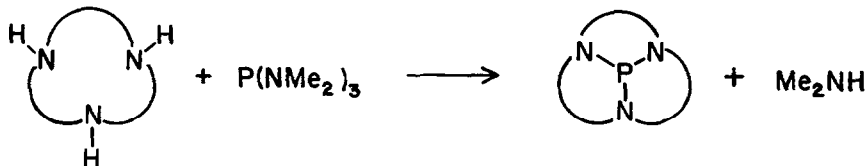
POLYCYCLIC PHOSPHOROUS TRIAMIDES

Thomas J. Atkins

Contribution No. 2522, Central Research and Development Department
E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware 19898

Macrocyclic ring structures have remarkable stabilizing effects on cage compounds derived from them. Recently, stable polycycles containing tetraaminomethane and tetraaminofluorophosphorane moieties have been reported from these laboratories.^{1,2} Our research has pursued the one-step synthesis of the polycycles by "inserting" the central atom into a macrocyclic polyamine via an exchange reaction. This method may be used to prepare tricyclic phosphorous triamides.

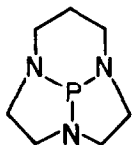
The cage phosphorous triamides $\overset{\sim}{1}$ - $\overset{\sim}{3}$ listed in the table were prepared via the exchange reaction of hexamethyl phosphorous triamide and the appropriate cyclic triamine.^{3,4} By heating stoichiometric amounts of the reactants neat (120°C, 2 hr), or in an inert solvent such as toluene or benzene, dimethylamine was evolved and $\overset{\sim}{1}$ - $\overset{\sim}{3}$ were obtained in good yield. The spectroscopic data are in accord with assigned structures.



The smallest member of this class, the tricyclic phosphorous triamide prepared from 1,4,7-triazacyclononane, could not be isolated. Models indicate the nine-membered ring is too small to accommodate the relatively long phosphorous-to-nitrogen bonds without considerable strain. The linear analog,

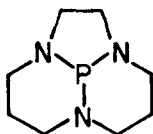
N,N'-dimethyldiethylenetriamine, formed a distillable but unstable product which became a clear glass on standing at room temperature.

Phosphorous Triamide⁵ bp (press.) % Yield δ ³¹P-nmr⁶ δ ¹³C-nmr (J_{P-C})⁶



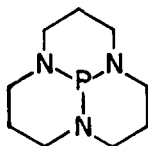
1

84-86° (0.3mm) 92 +111.6 58.1(9)
51.1(6)
45.5(8)
15.3(16)



2

73-75° (0.3mm) 75 +122.7 50.2(10)
49.1(10)
46.4(7)
23.9(8)



3

104-108° (0.6mm) 76 +109.2 49.1(8)
24.3(4)

REFERENCES AND FOOTNOTES

1. J. E. Richman and H. E. Simmons, Tetrahedron, 30, 1769 (1974).
2. J. E. Richman, Tetrahedron Lett., 559 (1977).
3. J. E. Richman and T. J. Atkins, J. Amer. Chem. Soc., 96, 2268 (1974);
H. Koyama and T. Yoshino, Bull. Chem. Soc. Japan, 45, 481 (1972).
4. U.S. 3,996,276.
5. 1: m/e 171.0944; 2: m/e 185.1117; 3: m/e 199.1264.
6. Nmr spectra were obtained in C₆D₆. Chemical shifts are reported in ppm from external 85% H₃PO₄ in benzene (³¹P) or internal TMS (¹³C).
Downfield shifts are reported as positive values.

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