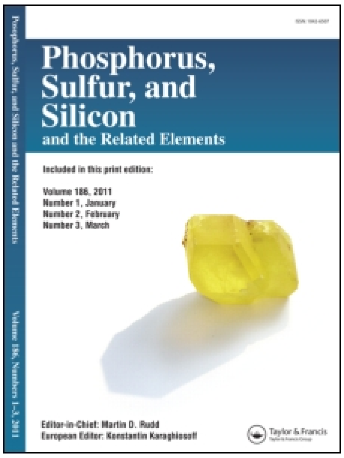

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A NEW CLASS OF PHOSPHORUS-NITROGEN COMPOUNDS

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To cite this Article Holmes, Robert R. and Forstner, James A.(1995) 'A NEW CLASS OF PHOSPHORUS-NITROGEN COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 98: 1, 1 — 2
To link to this Article: DOI: 10.1080/10426509508036936
URL: http://dx.doi.org/10.1080/10426509508036936

Phosphorus, Sulfur, and Silicon, 1995, Vol. 98, pp. 1–2
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A NEW CLASS OF PHOSPHORUS-NITROGEN COMPOUNDS[1]

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(Received August 15, 1960)

The literature shows no successful characterizations of chlorine free phosphorus nitrogen compounds resulting from the reaction of phosphorus trihalides and primary aliphatic amines. However, working with excess methylamine in the absence of solvent below room temperature, we have isolated a crystalline white solid in high yield and report it as the first member of a new class of phosphorus nitrogen compounds.

It has the empirical composition $P_2N_3(CH_3)_3$, m.p. 122.0–122.8°; b.p. 303–304° at 739 mm. *Anal.* Calcd.: C, 24.17; H, 6.08; N, 28.19; P, 41.56. Found: C, 23.92; H, 6.03; N, 28.19; P, 41.32.

Initially it is obtained with the amine hydrochloride from which it is readily separated using dried petroleum ether and working in a nitrogen atmosphere (moisture sensitive). The phosphorus-nitrogen product is purified readily by sublimation, is soluble in a wide variety of organic solvents, initially insoluble in water but slowly dissolves over a period of a few days. No other products are obtained from the reaction, as established by elemental analysis directly on the ether soluble and the ether insoluble fractions.

Infrared measurements in Nujol mulls and in benzene solution were nearly identical showing strong absorptions with rather sharp bands at 2860 cm.$^{-1}$, 2790 cm.$^{-1}$, 1440 cm.$^{-1}$, and 1155 cm.$^{-1}$. The latter band is in the region of the P—N stretching frequency found in the lower membered ring structures in the phosphonitrilic series.[2]

Cryscopic measurements in benzene gave molecular weight results (296 ± 15) in agreement with vapor phase determinations near 200° (313 ± 10, assuming ideal gas behavior) and indicates a molecular formulation $P_4N_6(CH_3)_6$.

N.m.r. measurements on benzene solutions showed one peak, having a one-two-one spin-spin splitting pattern. The latter data indicate equivalent protons each split by two equivalent phosphorus atoms. The chemical shift relative to water, +2.52 p.p.m., is characteristic of a N—CH_3 grouping.[3] In addition the $J_{P—H}$ coupling constant, 16.7 ± 0.6 cps., is in the range characteristic of the P—N—C—H linkage.[4]

The above data strongly indicate a cage structure analogous to that of phosphorus trioxide, P_4O_6, containing a tetrahedral distribution of phosphorus atoms with oxygens strung along the edges, here replaced by six N—CH_3 groups. The latter

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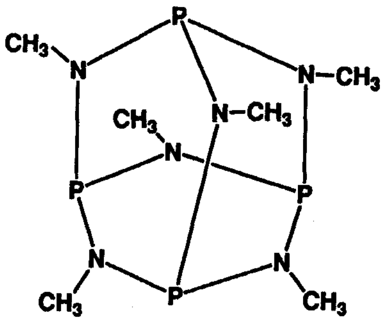

structure is made even more attractive when it is realized that the N—CH$_3$ group is isoelectronic with the oxygen atom.

Chemical data are in agreement with the structural interpretation in that reactions might be expected to proceed toward a phosphorus pentoxide structure, P_4O_{10}, by coördinating the four phosphorus atoms with electron acceptor groups since each phosphorus has an unshared pair in the trioxide structure. Such is the case. Reactions readily occur with boron trichloride just above the melting point of the solid, with oxygen on heating at 170° and with methyl iodide at room temperature.

The main product of the boron trichloride reaction is a clear liquid having a vapor pressure of less than 1 mm. at 30°, soluble in benzene and reacts violently with water. Elemental analysis yielded the composition $P_2N_3(CH_3)_3B_2Cl_8$. The vacuum line reaction corresponded to 4.2 moles of boron trichloride reacting per mole of imide. In addition small amounts of PCl_3 are produced as well as a solid product (presently being characterized). The latter solid must contain a low chlorine to boron ratio since the main product formed (in over 60% yield) contains a boron to chlorine ratio of 1:4.

Experimentally, the reaction proceeds rapidly on melting the crystalline imide in an excess of boron trichloride; the pressure drops abruptly and a clear liquid forms. On heating at 140° in an oven the liquid becomes yellowish and a solid product forms. What may be occurring is an addition of boron trichloride to the phosphorus atoms of the imide followed by a chlorination process. Investigation of the latter substance is currently under way.

The oxygen reaction is complex, yielding a white solid at 170° and some glassy looking material. Preliminary analysis indicates a formulation $P_2N_3(CH_3)_3O_2$ for the white product, that expected for the formation of a phosphorus pentoxide type structure.

The methyl iodide product has been established as $P_4N_6(CH_3)_7I$, a simple 1:1 reaction which proceeds readily at room temperature.

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