sity = 1.60 g./ml.; ethyl iodide, density = 1.92 g./ml.; and ethylene bromide, density = 2.17 g./ml.

In order to achieve complete solution of the HBO_2(c,I) in 20 to 30 minutes for calorimetric experiments, it was necessary to crush the sample to pass a No. 200 standard sieve and use 2*N* sodium hydroxide solution at 40° as the calorimetric solution. The calorimetric samples were placed in spherical glass ampoules and heated at 100° for about 30 minutes to drive off adsorbed moisture. The ampoules then were sealed under vacuum and weighed.

The solution calorimeter consisted of a vacuum-jacketed, Pyrex-glass vessel having a capacity of about 500 ml. of solution. A metal cap supported a platinum resistance thermometer, a glass stirrer, a precision immersion heater used in electrical calibrations, and a glass sample-holder. Electrical calibrations were made on the initial systems.

In four experiments, samples of HBO_2(c,I), 0.3 to 0.4 g. (prepared by the second method described above), reacted with 2 *N* sodium hydroxide at 40°; the corrected temperature rise was approximately 0.1° and the mean heat of reaction, $\Delta H(40^\circ) = -27.44 \pm 0.042$ kj./mole. Similarly, four experiments with 1.5 to 1.8 g. of H_3BO_3(c) produced a temperature rise of a little more than 0.2° and $\Delta H(40^\circ) = -21.46 \pm 0.02$ kj./mole. The uncertainties are twice the standard deviation of the mean.

The difference in the heats of reaction at 40° is -5.98 ± 0.05 kj./mole or -1.429 ± 0.011 kcal./mole. We estimate a thermal coefficient, $\Delta C_p \sim -10$ cal./deg. mole, which gives -1.28 kcal./mole for the difference in the heats of reaction at 25°. By using $\Delta Hf^\circ = -68.317$ kcal./mole for the heat of formation of liquid water,[2] and $\Delta Hf^\circ = -262.16$ kcal./mole for H_3BO_3(c),[3] we obtain $\Delta Hf^\circ_{(298.15)} = -192.56 \pm 0.33$ kcal./mole for HBO_2(c,I).

[2] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," NBS Circular 500, U. S. Government Printing Office, Washington 25, D. C., 1952.

[3] W. H. Evans, E. J. Prosen, and D. D. Wagman, "Thermochemistry and Thermodynamic Functions of Some Boron Compounds," in "Thermodynamic and Transport Properties of Gases, Liquids, and Solids," Y. S. Touloukian, editor, McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 226.

NATIONAL BUREAU OF STANDARDS MARTHADA V. KILDAY
WASHINGTON, D. C. EDWARD J. PROSEN

RECEIVED SEPTEMBER 12, 1960

A NEW CLASS OF PHOSPHORUS-NITROGEN COMPOUNDS[1]

Sir:

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.

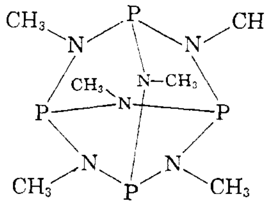
Initially it is obtained with the amine hydrochloride from which it is readily separated using dried petroleum ether and working in a nitrogen atmosphere (moisture sensitive). The phosphorus-nitrogen product is purified readily by sublimation, is soluble in a wide variety of organic solvents, initially 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 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 tri-

[1] Supported in part by the Office of Ordnance Research, U. S. Army.

[2] H. J. Emeleus and A. G. Sharpe, ed., "Advances in Inorganic Chemistry and Radiochemistry," Vol. I, Academic Press Inc., New York, N. Y., 1959, p. 372.

[3] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 272.

[4] Pople, *et al.*, *ibid.*, p. 351.

oxide 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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RECEIVED AUGUST 15, 1960

THE SYNTHESIS OF PRODIGIOSIN

Sir:

We wish to report the synthesis, and concomitant proof of structure, of prodigiosin, the red pigment of *Serratia marcesens*. This pigment has been of much interest since first it provided the excuse for religious excesses.[1] It also has considerable antibiotic activity, although high toxicity precludes the use of prodigiosin itself.[2]

The first degradative work reported[3] on prodigiosin, $C_{20}H_{25}ON_3$, established its gross features; *viz.*, the presence of three pyrrole nuclei (pyrrole, 3-methoxypyrrole and 2-methyl-3-amylpyrrole) joined in some manner with the aid of a single bridging carbon. On the basis of this work Wrede, in 1933,[3b] proposed structures I and III for prodigiosin, later favoring III without any further experimental data. A pyrryldipyrrylmethene structure did not appear again in the literature until very recently.[4,5]

Of paramount importance to the structure elucidation of prodigiosin is the structure of a substance $C_{10}H_{10}O_2N_2$, isolated[6] from a mutant strain and shown by biosynthetic experiments[6] and condensation with 2-methyl-3-amylpyrrole[5] to be a precursor of prodigiosin. If the tripyrrylmethene structure III for prodigiosin were correct, this precursor would be a methoxy-2,2′-dipyrryl ketone, while a pyrryldipyrrylmethene structure, I or II, would require the precursor to be a methoxy-2,2′-bipyrrole aldehyde. It was found, by synthesis of 4-methoxy-2,2′-dipyrryl ketone,[7] that the ultraviolet absorption of this type compound is sufficiently different from that reported[5,6] for prodigiosin precursor to rule out a dipyrryl ketone structure. This in turn eliminates a tripyrrylmethene structure for prodigiosin. Isolation of pyrrole-2-carboxamide from oxidation of prodigiosin and the precursor[5] provided strong evidence for 2,2′-linked pyrrole rings, and coupled with n.m.r. data led to the proposal[5] of structures I and IV for prodigiosin, with I being favored.

We considered either of the pyrryldipyrrylmethenes I and II as most likely for prodigiosin. The precursor should then be a methoxy-2,2′-bipyrrole aldehyde. No existing methods for synthesizing bipyrroles appeared applicable to such a compound. However, condensation of Δ^1-pyrroline with pyrrole to give 2-(2′-pyrrolidinyl)-pyrrole has been reported recently,[8] and dehydrogenation of this compound readily gave 2,2′-bipyrrole (V), m.p. 187° (found: C, 72.5; H, 6.1 N, 21.4; mol. wt., 128). To apply this method to the preparation of the 2,2′-bipyrrole VI, we require the unknown ethyl 3-methoxypyrrole-2-carboxylate. Condensation of the sodium salt of ethyl N-ethoxycarbonylglycinate with diethyl ethoxymethylenemalonate gave diethyl 3-hydroxypyrrole-2,4-dicarboxylate, m.p. 121° (found: C, 52.9; H, 5.7; N, 6.0; OC_2H_5, 39.3) which with diazomethane formed diethyl 3-methoxypyrrole-2,4-dicarboxylate, m.p. 83° (found: C, 55.0; H, 6.3; N, 5.9; OR, 3.03/241). Hydrolysis of the diester with concd. sulfuric acid gave 2-ethoxycarbonyl-3-methoxypyrrole-4-carboxylic acid, m.p. 178° dec. (found: C, 50.9; H, 5.2; equiv. wt., 214) which on heating above its melting point, decarboxylated to ethyl 3-methoxypyrrole-2-carboxylate, m.p. 94° (found: C, 56.7; H, 6.8). This selective hydrolysis of the β-ester is common in the pyrrole series[9] and was verified by alkaline hydrolysis of the diester to 4-ethoxycarbonyl-3-

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