these exaltations in the moment to changes in the bond angles in $[(C_6H_5)_3P]_2NiBr_2$, such that they become more nearly tetrahedral. This explanation is entirely untenable since (a) although the bond angles in $[(C_6H_5)_3P]_2NiBr_2$ have not been reported, those in $[(C_6H_5)_3P]_2NiCl_2$ are reported by Venanzi to be very near to 109°,[13] and (b) regardless of the exact bond angles, the vast difference in the two kinds of ligands may be expected to cause a quenching of most of the considerable orbital moment expected in a tetrahedral nickel(II) complex with true T_d symmetry. We believe that the most likely explanation of Matsunaga's results is that under the conditions (long heating) required for formation of the "solvates," quaternization of the phosphine occurs so that the compounds are actually $[(C_6H_5)_3(tert\text{-}C_4H_9)P][(C_6H_5)_3PNiBr_3]$ and $[(C_6H_5)_4P]_2[NiBr_4]$. In fact, Reppe and Schweckendiek imply that a compound analogous to the former can be prepared from $[(C_6H_5)_3P(C_4H_9?)]Br$, $(C_6H_5)_3P$ and $NiBr_2$.

Our investigations of this class of compounds are continuing. We thank the U. S. Atomic Energy Commission for financial support under Contract No. AT(30-1)-1965.

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[13] L. M. Venanzi, *J. Inorg. Nucl. Chem.*, **8**, 141 (1958).

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A NEW HEXABORANE

Sir:

Recent studies of the mass spectra of the boranes indicate the probable existence of a hexaborane with a minimum of twelve hydrogen atoms. The compound may be the hexaborane-12 originally described but subsequently withdrawn by Stock.[1] The presence of hexaborane-12 might account for the erroneous vapor pressure measurements attributed to hexaborane-10.[2] Specifically, Stock reported the vapor pressure of hexaborane-10 as 7.2 mm. at 0° whereas we found it to be 11.85 mm.[3]

The two hexaboranes differ widely in thermal stability; at room temperature B_6H_{10} is fairly stable,[3] whereas the new hexaborane decomposes very rapidly—hence making its identity elusive until now. Actually it was not until we observed a discrepancy in vapor pressure values and the reasonable stability of purified hexaborane-10 as contrasted to previous reports that we realized there was an unknown compound accounting for these differences.

To determine the identity of this unknown compound, we prepared a sample for mass spectroscopic analysis by subjecting diborane to an electric discharge[4] and then making a gross separation of products by pumping the more volatile compounds from the sample. The sample was maintained cold until introduced into a CEC Model 21-103 mass spectrometer for analysis, which revealed the presence of the new hexaborane. The severe heat treatment used in our previous work[3] for purifying hexaborane-10 would have completely destroyed this new hexaborane.

A comparison in the *m/e* 65–78 range of the polyisotopic mass spectrum of pure hexaborane-10[3] (cut-off at *m/e* 76) and that of the new hexaborane (labeled B_6H_{12}) contaminated by hexaborane-10 is given in Table I. Additionally, the new hexaborane spectrum is contaminated by about 3% heptaborane (assuming equal sensitivity of the dominant peaks) and a trace of octaborane. As indicated below, the peaks at *m/e* 77 and 78 are real, and are part of a parent grouping of peaks in the B_6 range that cannot be attributed to B_6H_{10}. This together with the sharp cut-off at *m/e* 78 leaves no question of the existence of another hexaborane, which may be either hexaborane-12, or possibly hexaborane-14. Precedent for the latter is found in the case of tetraborane-10 and pentaborane-11 since the mass spectra of both these compounds cut off at two mass units lower than their corresponding molecular weights.

TABLE I

COMPARISON OF POLYISOTOPIC MASS SPECTRA OF HEXABORANES

m/e	Relative intensities B_6H_{12}[a]	Relative intensities B_6H_{10}[3]	*m/e*	Relative intensities B_6H_{12}[a]	Relative intensities B_6H_{10}[3]
78	7.3	..	71	100	100
77	11.0	..	70	75.5	79.4
76	34.8	22.6	69	54.1	57.7
75	43.5	34.1	68	41.8	44.0
74	60.7	48.2	67	39.0	41.5
73	63.5	49.4	66	32.4	35.4
72	93.6	86.9	65	18.8	20.7

[a] Includes contaminants of hexaborane-10, heptaborane (*ca.* 3%), and octaborane (trace amount).

That the peaks at *m/e* 77 and 78 cannot be due to contamination by compounds other than boranes is inferred from the fact that the polyisotopic spectrum can be reduced to a monoisotopic one on the basis of $B_6H_x^+$ with only negligible residues. If effective peak heights at both *m/e* 77 and 78, or *m/e* 77 alone, were reduced by as much as 5%, negative residues would occur in the monoisotopic spectrum. The possibility that *m/e* 78 could be due entirely to contamination cannot be eliminated by this method; however, the carefully controlled experimental work leads us to believe that there is no non-borane contaminant present.

The possibility that the peaks at *m/e* 77 and 78 are due primarily to heptaborane was eliminated by "stripping" the heptaborane contribution (based on principal peaks at *m/e* 83 or 87)[5] from

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[1] A. Stock and W. Siecke, *Ber.*, **57**, 566 (1924).

[2] A. Stock and E. Kuss, *ibid.*, **56**, 789 (1923).

[3] S. G. Gibbins and I. Shapiro, *J. Chem. Phys.*, **30**, 1483 (1959).

[4] W. V. Kotlensky and R. Schaeffer, THIS JOURNAL, **80**, 4517 (1958).

[5] In our studies we have observed repeatedly the mass spectra of two heptaboranes. One of these (principal peak at *m/e* 83) is similar to that reported recently[6]; the other has a dominant peak at *m/e* 87. Contamination by *ca.* 15% octaborane prevents a precise determination of the cut-off peak of the heptaboranes. If the octaborane is the same as that reported,[7] then the cut-off must be at least as high as *m/e* 92, corresponding to heptaborane-15. Regardless of the lack of precision associated with the mass spectrum of either heptaborane, we feel that only an extremely small error is introduced when this mass spectrum is used to strip 3% heptaborane from hexaborane-12 at *m/e* 77 and 78.

[6] R. W. Schaefer, K. H. Ludlum and S. E. Wiberley, THIS JOURNAL, **81**, 3157 (1959).

[7] I. Shapiro and B. Keilin, *ibid.*, **76**, 3864 (1954).

the mixture at mass numbers greater than m/e 76. The heptaborane contribution to m/e 78 was only 10% and to m/e 77, only 8% of the observed peak heights.

From the monoisotopic mass spectrum, the $B_6H_{10}^+$ and $B_6H_8^+$ species of hexaborane-12 are relatively more abundant than those of hexaborane 10. Hexaborane-12 resembles hexaborane-10 in that it has no $B_5H_{11}^+$ or $B_5H_{10}^+$ species.

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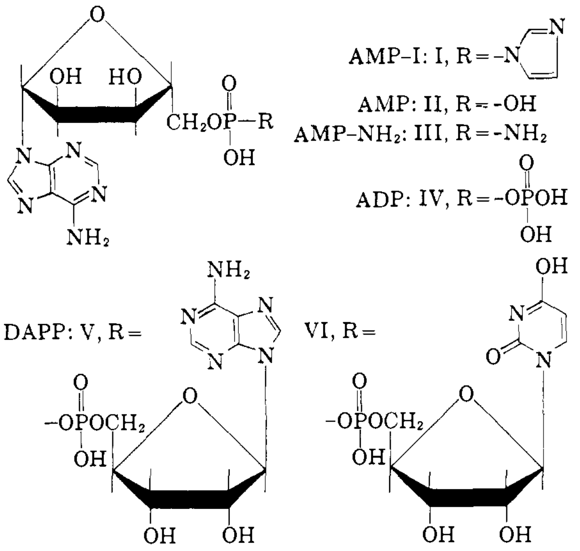
THE PREPARATION OF ADENOSINE-5' IMIDAZOL-1-YLPHOSPHONATE AND ITS REACTIONS WITH NUCLEOPHILES. A NOVEL SYNTHESIS OF NUCLEOTIDE COENZYMES

Sir:

The imidazole ring of a histidine moiety is implicated in the binding or catalytic activity of esterases, proteases, carbohydrases, etc.[1] Enzyme-ATP complexes have been suggested as intermediates in transphosphorylation,[2] and an imidazol-1-ylphosphonate[3] has been suggested[4] as an example of this type of complex. Imidazolylphosphonates, such as imidazol-1-ylphosphonic acid, imidazol-1,3-diyldiphosphonic acid and phenyl imidazol-1-ylphosphonate have been shown to be phosphorylating agents.[4,5,6]

Adenosine-5' imidazol-1-ylphosphonate (AMP-I, I) was chosen as a model for reaction with nucleophiles to provide information bearing on the nature of transphosphorylation. In addition, these reactions exemplify a novel, facile synthesis of nucleotide coenzymes.

Imidazolium AMP-I[7] is prepared readily in anhydrous dimethylformamide by reaction of the imidazolium salt of adenosine-5' phosphate (AMP, II) with 1,1'-carbonyldiimidazole (CDI).[8,9] With equimolar quantities of AMP monohydrate and CDI, the products found by paper chromatography are AMP-I in major amount, unchanged AMP, and P^1,P^2-di-(adenosine-5') pyrophosphate (DAPP, V). With 2–4 moles of CDI to one mole of AMP monohydrate, conversion to AMP-I is nearly quantitative. On Whatman No. 1 paper AMP-I has R_f = 0.43[10] in isopropyl alcohol–ammonia–water (7:1:2), in which solvent it is partly solvolyzed to adenosine-5' phosphoramidate (AMP-NH_2, III), R_f = 0.20.



When imidazolium AMP-I (from one mole of AMP monohydrate and 2 moles of CDI) is allowed to react with AMP monohydrate and the reaction mixture is chromatographed on Dowex-1 (formate), 57% of colorless crystalline DAPP (V) sesquihydrate,[11] m.p. 184–189°, is obtained (Calcd. for $C_{20}H_{26}N_{10}O_{13}P_2 \cdot 1.5H_2O$: C, 34.2; H, 4.16; N, 19.9; P, 8.81. Found: C, 34.3; H, 4.20; N, 20.2; P, 8.49, 8.37), homogeneous by the criteria of paper chromatography in two solvent systems and by paper electrophoresis. Uridine-5' phosphate and AMP-I give P^1-(adenosine-5') P^2-(uridine-5') pyrophosphate (VI), 0.84 as electrophoretically mobile as P^1,P^2-di-(uridine-5') pyrophosphate on Whatman 3MM paper in *p*H 4.8 acetate buffer.[12]

Imidazolium AMP-I (from one mole of AMP monohydrate and 3 moles of CDI), aqueous ammonia, dimethylformamide and *tert*-butyl alcohol, kept at 92° for 11 hours, give AMP-NH_2 (III), isolated in 86% yield as the colorless crystalline 1,3-dicyclohexylguanidinium salt solvated with water and dimethylformamide, m.p. 207–210° dec. (Calcd. for $C_{10}H_{15}N_6O_6P \cdot C_{13}H_{25}N_3 \cdot H_2O \cdot C_3H_7NO$: C, 47.3; H, 7.47; N, 21.2; P, 4.69. Found: C, 47.4; H, 7.25; N, 21.6, 21.3; P, 4.93), which, when recrystallized from aqueous acetone, gives the unsolvated salt, m.p. 236–238° dec.[10]

With excess 85% phosphoric acid at −10 to −20°, imidazolium AMP-I (from equal moles of AMP monohydrate and CDI) is converted to adenosine-5' pyrophosphate (ADP, IV), isolated in 25% yield as the yellow crystalline acridinium salt,[13] m.p. 216–217° dec. (Calcd. for $C_{10}H_{15}N_5O_{10}P_2 \cdot C_{13}H_9N$: C, 45.6; H, 3.99; N, 13.9; P,

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(1) For a review and leading references see E. A. Barnard and W. D. Stein, *Advances in Enzymol.*, **20**, 51 (1958).

(2) M. B. Hoagland, *Biochim. et Biophys. Acta*, **16**, 288 (1955).

(3) "Imidazolylphosphonate," rather than "phosphoimidazole"[5] or "phosphoroimidazole"[10]; *cf.* report of the A.C.S. Nomenclature, Spelling and Pronunciation Committee, *Chem. Eng. News*, **30**, 4515 (1952).

(4) J. Baddiley, J. G. Buchanan and R. Letters, *J. Chem. Soc.*, 2812 (1956).

(5) T. Rathlev and T. Rosenberg, *Arch. Biochem. and Biophys.*, **65**, 319 (1956).

(6) H. A. Staab, H. Schaller and F. Cramer, *Angew. Chem.*, **71**, 736 (1959).

(7) AMP, imidazole and dicyclohexylcarbodiimide were reported[10] to give an unstable solid tentatively identified as a mixture of AMP-I and AMP.

(8) H. A. Staab, *Ann.*, **609**, 75 (1957).

(9) After completion of the work described here, H. A. Staab, *et al.*,[6] reported the preparation of imidazol-1-ylphosphonic acid and phenyl imidazol-1-ylphosphonate by the reaction of the appropriate phosphate with 1,1'-carbonyldiimidazole.

(10) R. W. Chambers and J. G. Moffatt, THIS JOURNAL, **80**, 3752 (1958).

(11) An amorphous tetrahydrate is described by S. M. H. Christie, D. T. Elmore, G. W. Kenner, A. R. Todd and F. J. Weymouth, *J. Chem. Soc.*, 2947 (1953).

(12) G. W. Kenner, C. B. Reese and A. R. Todd, *ibid.*, 546 (1958).

(13) T. Wagner-Jauregg, *Hoppe-Seyler's Z. physiol. Chem.*, **239**, 188 (1936).