shaking with 15-ml. portions of ether. Three and one-half ml. of cold ethyl chlorocarbonate was added to the ether extract and while the solution was stirred mechanically, 2.9 ml. of pyridine was added dropwise. After stirring for 3 min., the ether phase was decanted and concentrated *in vacuo* to a vol. smaller than 3 ml.[16] The 10.5 mmoles of mixed anhydride so obtained, was treated with potassium phosphate as in the first procedure yielding a product of 45% purity in 44% yield. The product was then purified as above except that acetone was used in place of ethanol with a final purity of 92%.

Fluoroacetyl phosphate was prepared by a procedure based on that of Lipmann and Tuttle.[9] Five ml. of fluoroacetyl chloride[17] (approximately 50 mmoles) mixed with 5 ml. of cold anhydrous ether was added dropwise to a homogeneous suspension of 8 g. of silver phosphate (19 mmoles) and 2.75 ml. of 85% phosphoric acid as described[9] for the preparation of acetyl phosphate. After the addition was completed, the bottle was stoppered and shaken vigorously at room temperature for 20 min. to give a milk white viscous suspension. The suspension was cooled to 3° and 20 ml. of cold water (3°) was added followed by careful addition of 30 ml. of cold 4 *N* lithium hydroxide while stirring. The insoluble material was filtered and the ether layer removed in a cold separatory funnel. The water solution was then brought to the first purple shade with *m*-cresol purple by careful addition of 4 *N* lithium hydroxide and the precipitate was removed by filtration and discarded. To the filtrate, cold ($-16°$) 95% ethanol was added to a final ethanol concentration of 23% (v./v.) followed by lithium hydroxide to bring the indicator color back to the first purple shade. The precipitate was filtered off and discarded. To the filtrate, cold ethanol was added slowly with stirring to an ethanol concentration of 85% (v./v.). The precipitate was collected on a buchner funnel, washed with cold ethanol and ether and dried at 3° *in vacuo* over $P_2O_5$. The material obtained was about 50% pure (based on a molecular weight of 170 for dilithium fluoroacetyl phosphate) with a yield of about 12%. An optional purification involved dissolving the material in cold water to give a 10% solution, addition of 4 *N* lithium hydroxide to the purple shade with *m*-cresol purple and repetition of the alcohol precipitation as above. The material was now about 60% pure with a yield of 6% (*i.e.*, a 50% loss during the purification) and contained about equal parts of inorganic phosphate and FAc-P.

**Analytical Methods.**—Acetyl and fluoroacetyl phosphate were analyzed by two modifications of the hydroxamic acid reaction of Lipmann and Tuttle.[18] That of Beinert, *et al.*,[19] (method I) was used when necessary to overcome previously added buffer, while that described by Jones and Lipmann[20] (method II) was employed when small amounts of buffer were present. When converted to the hydroxamic acid, Ac-P gave the same values by both methods. With FAc-P, method I uniformly gave 51% of the value obtained with method II. Accordingly all values obtained by method I with FAc-P have been multiplied by a factor of 1.95. Since this method was used primarily in kinetic studies, the correction is not of primary significance. That the two methods of analysis yield different results with FAc-P may account for the finding by Brady[4] that FAc-CoA gave different values by hydroxamic acid determination and spectrophotometric analysis. Experiments in which various dilutions of hydroxylamine were employed indicated that the reaction with hydroxylamine was quantitative and that the variation depended upon the determination of the formed hydroxamic acid.

Total phosphate was determined according to Fiske and SubbaRow.[21] Inorganic phosphate in the presence of acyl phosphate was determined by dissolving a few mg. of the acyl phosphate preparation in a known volume of ice cold 0.1 *M* tris buffer *p*H 8.1. One aliquot was analyzed for total phosphate while another aliquot was added to 1.5 ml. of ethanolic calcium chloride and the inorganic phosphate determined according to Lipmann and Tuttle.[9] The centrifugation time was 1.5 minutes at 1650 × *g*. The difference between total and inorganic phosphate was taken to be organic phosphate.

The analysis of acyl phosphate by titration was carried out by the following procedure. A sample of acyl phosphate was dissolved in 6 ml. of ice-cold water. Two tenths of a ml. was transferred rapidly to a hydroxylamine solution for hydroxamic acid analysis. A 5.0-ml. aliquot was rapidly brought to the first pink shade by the addition of phenolphthalein and 0.1 *N* NaOH from a micrometer type buret. The solutions were then heated in a steam-bath to obtain complete hydrolysis, 40 min. being allowed for Ac-P and 10 min. for FAc-P. The tubes were cooled, brought to the original volume and titrated with 0.1 *N* NaOH to the original pink color.

**Enzyme Preparations.**—Pig heart acetone powder was prepared according to Kaplan and Lipmann.[22] The dried powder was extracted by making a 10% suspension in 0.02 *M* potassium bicarbonate and centrifuging off the insoluble material at 1650 × *g*.

*E. coli* 4157 (obtained from the National Type Culture Collection) was grown in Kolli flasks or Roux bottles on nutrient agar[23] (Difco) for 18 hr. at 37°. The cells were washed off the agar with 0.4% NaCl, centrifuged, washed with 0.4% NaCl, suspended in a minimal volume of distilled water, lyophilized and stored at $-16°$. The cells were extracted by grinding in a cooled mortar with an equal weight of alumina-A301 (Aluminum Company of America) with gradual addition of buffer (0.02 *M* potassium phosphate *p*H 6.6–0.1 *M* KCl) to give a 5% (w./v.) suspension. The suspension was centrifuged at 23,000 × *g* for 20 minutes and the supernatant fluid was frozen at $-16°$.

BUFFALO, NEW YORK

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[16] In experiments in which the ether vol. was larger than 3 ml., poor yields were obtained.

[17] W. E. Truce, THIS JOURNAL, **70**, 2828 (1948).

[18] F. Lipmann and L. C. Tuttle, *J. Biol. Chem.*, **159**, 21 (1945).

[19] H. Beinert, D. E. Green, P. Hele, H. Hift, R. W. Von Korff and C. V. Ramakrishnan, *ibid.*, **203**, 35 (1953).

[20] M. E. Jones and F. Lipmann, in S. P. Colowick and N. O. Kaplan, "Methods in Enzymology," New York, N. Y., 1955, p. 585.

[21] C. H. Fiske and Y. SubbaRow, *J. Biol. Chem.*, **66**, 375 (1925).

[22] N. O. Kaplan and F. Lipmann, *ibid.*, **174**, 37 (1948).

[23] The *E. coli* cultures were obtained through the courtesy of Dr. E. Witebsky of the Department of Bacteriology and were prepared by Miss Ann Heide.

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[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

# Amine Boranes. I. The Preparation of Pyridine Arylboranes

BY M. FREDERICK HAWTHORNE

RECEIVED JANUARY 29, 1958

The pyridine complexes of a series of arylboranes have been prepared by the lithium aluminum hydride reduction of the corresponding ethyl or *n*-butyl boronates at low temperatures in ethyl ether solution and in the presence of pyridine. These materials are air-stable crystalline solids which exhibit reactions characteristic of the boron–hydrogen bond.

In a preliminary communication[1] the preparation and properties of the pyridine complexes of various aryl- and diarylboranes were described. The present paper presents further data regarding the former compounds.

Although various alkyl derivatives of diborane have been reported in the chemical literature, the

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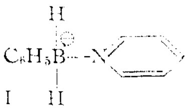
[1] M. F. Hawthorne, *Chemistry & Industry*, **37**, 1242 (1957).

aryl derivatives of diborane have been mentioned only twice. Pace[2] reported the preparation of what he believed to be phenylborane by a route which undoubtedly led to the formation of diethyl phenylboronate. Somewhat later Hurd[3] obtained evidence for the production of this same compound by the reaction of diborane with benzene at elevated temperatures. Most recently Nielson, McEwen and VanderWerf[4] have found that the reduction of phenylboron dichloride with lithium aluminum hydride in tetrahydrofuran at the reflux temperature produces only triphenylborane and diborane. The latter authors considered phenylborane as an intermediate product which rapidly disproportionated to yield the observed products.

Previous to the report[4] of the unsuccessful reduction of phenylboron dichloride with lithium aluminum hydride, the preparation of the pyridine complex of phenylborane was carried out in this Laboratory. Since on an *a priori* basis it appeared likely that any synthetic route designed to yield phenylborane directly would suffer from the probable disproportionation of this material, it seemed most advantageous to prevent this side reaction by carrying out the reduction in the presence of a tertiary amine. The reduction of boron–oxygen bonds rather than boron–halogen bonds was chosen to avoid possible complications which might attend the complexation of boron or aluminum halides with the tertiary amine addend.

At the outset triphenylboroxine was chosen as a model for preliminary study and pyridine was employed as the complexation reagent. It was found that the addition of a pyridine–ethyl ether solution of the boroxine to an excess of lithium aluminum hydride in the same solvent at −70° followed by hydrolysis with water produced pyridine phenylborane (I) in 30% yield. Since the product was not readily hydrolyzed nor air-oxidized this procedure could be carried out with only normal precautions.


I

In order to develop a more successful synthesis of materials of this type, the reduction of diethyl phenylboronate was carried out under similar conditions. The yields of I obtained by this procedure were considerably higher than those obtained previously and eventually reached 75–80% of theory by modification of the experimental procedure.

The several diethyl arylboronates required as starting materials in this study were prepared from the corresponding crude boronic acids by the method of Torssell[5] which employed the azeotropic removal of water from benzene–ethanol solutions of the arylboronic acid. The ester products were carefully purified by distillation. Table I reports the pertinent data for each ester studied.

Table II presents data obtained in the reduction of the esters of Table I and the properties of the corresponding pyridine boranes.

TABLE I

DIETHYL ARYLBORONATES

| Diethyl arylboronate | B.p. °C. | B.p. Mm. | % yield from aryl bromide |
|---|---|---|---|
| Phenyl | 70 | 0.8 | 30 |
| *p*-Tolyl | 82 | 0.8 | 33 |
| *p*-Anisyl | 117 | 1.8 | 32 |
| *o*-Anisyl | 108 | 1.5 | 25 |
| *p*-Chlorophenyl | 145 | 1.5 | 51 |
| α-Naphthyl | 133 | 1.3 | 32 |

In addition to the compounds described in Table II trimethylamine phenylborane (VI, m.p. 69°) and triethylamine phenylborane (VII, m.p. 65°) were prepared by a similar procedure in 28 and 63% yield, respectively.

Additional evidence for the validity of the assumed structures of these new materials is the following: (1) All the borane derivatives gave strong absorption near 4.35 μ in the infrared, the region of B–H band stretching absorption. (2) Hydrolysis in aqueous acetonitrile solution produced phenylboronic acid and two moles of hydrogen per mole of pyridine phenylborane. (3) Silver ion (as perchlorate) was rapidly, though not quantitatively, reduced to silver metal in aqueous acetonitrile solution. (4) Iodine in pyridine is very rapidly reduced to iodide ion in accord with equation 1.

$$C_6H_5BH_2Py + 2I_2 \longrightarrow C_6H_5BI_2 + 2HI + Py \quad (1)$$

In order to test the stability of phenylborane toward disproportionation to diborane and triphenylborane, the reduction of diethyl phenylboronate was carried out in the usual manner but in the absence of a tertiary amine. The resulting product mixture was warmed to zero degrees and maintained at that temperature for 20 minutes. The addition of pyridine to this "aged" solution followed by the usual work up procedure afforded pyridine phenylborane in 44% yield. It thus appears as though phenylborane is relatively stable toward disproportionation when dissolved in diethyl ether containing lithium and aluminum alkoxides, an observation which contrasts strongly with the observations of Nielson, McEwen and VanderWerf.[4]

## Experimental

The experimental procedures for the preparation of all diethyl arylboronates and pyridine arylboranes were essentially identical and are illustrated for the case of diethyl phenylboronate and pyridine phenylborane. The esters were prepared by a modification of the method of Torssell.[5]

**Diethyl Phenylboronate.**—A solution of phenylmagnesium bromide was prepared from 12.0 g. of magnesium and 78 g. (0.50 mole) of bromobenzene in 250 ml. of ethyl ether. This solution was added dropwise under nitrogen and with vigorous stirring to a solution of 52 g. (0.50 mole) of pure methyl borate in 250 ml. of ether at −78°. After the addition the reaction mixture was warmed to room temperature by allowing the coolant to evaporate overnight. The mixture was then cooled to 0° and 2 *N* hydrochloric acid added to dissolve the magnesium salts. The ethereal solution was separated, washed three times with water, dried over magnesium sulfate and the solvent removed by vacuum evaporation to yield 30.5 g. (50%) of crude phenylboronic acid, m.p. 196°.

The crude acid (0.25 mole), 160 g. of dry benzene and 70 g. of absolute ethanol were distilled slowly with a spinning band column of 30 theoretical plates to remove the ternary water–alcohol–benzene azeotrope boiling at 64°. The temperature then was raised slowly to 80° and the residual benzene almost completely removed. The pressure now was lowered to 0.8 mm. and after a small forerun 27 g. (0.15 mole

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(2) E. Pace, *Atti accad. Lincei*, **10**, 193 (1929).

(3) D. T. Hurd, THIS JOURNAL, **70**, 2053 (1948).

(4) D. R. Nielson, W. E. McEwen and C. A. VanderWerf, *Chemistry & Industry*, **37**, 1069 (1957).

(5) K. Torssell, *Acta Chem. Scand.*, **8**, 1779 (1954).

TABLE II

PYRIDINE ARYLBORANES

| | Ar in $ArBH_2Py$ | M.p., °C. | Yield, % | Formula | Analyses, % Calcd. C | H | B | Found C | H | B |
|---|---|---|---|---|---|---|---|---|---|---|
| I | Phenyl | 80–83 | 78 | $C_{11}H_{12}BN$ | 78.16 | 7.16 | 6.40 | 77.78 | 7.13 | 6.63 |
| II | *p*-Tolyl | 63–65 | 34 | $C_{12}H_{14}BN$ | 78.73 | 7.70 | 5.91 | 78.16 | 7.73 | 5.85 |
| III | *p*-Anisyl | 78–79 | 61 | $C_{12}H_{14}BNO$ | 72.40 | 7.09 | 5.44 | 72.20 | 7.16 | 5.30 |
| IV | *o*-Anisyl | 55–56 | 38 | $C_{12}H_{14}BNO$ | 72.40 | 7.09 | 5.44 | 72.25 | 7.06 | 5.33 |
| VI | *p*-Chlorophenyl | 61–62 | 51 | $C_{11}H_{11}BNCl$ | 64.92 | 5.45 | 5.32 | 64.66 | 5.49 | 5.27 |
| V | α-Naphthyl | 140–141 | 24 | $C_{16}H_{14}BN$ | 82.23 | 6.44 | 4.94 | 81.59 | 6.83 | 5.19 |

or 30%) of diethylphenylboronate was collected at 70°. The other diethyl arylboronates which were prepared by this method are presented in Table I.

**Pyridine Phenylborane** (I).—Two and one-half grams of lithium aluminum hydride was dissolved in 500 ml. of dry ether at reflux and under dry nitrogen. The resulting solution was cooled to −70° and 10 ml. of dry pyridine added in one portion. Diethyl phenylboronate (17.7 g., 0.10 mole) dissolved in 70 ml. of ether next was added slowly with vigorous stirring under dry nitrogen. The addition required about one hour. The cooling bath then was removed and the reaction mixture allowed to warm slowly to room temperature with stirring. A solution of 5 ml. of pyridine and 12 ml. of water was prepared and added dropwise with cooling by an ice-bath. The sludge was removed by vacuum filtration and the filtrate concentrated in vacuum. The crystalline residue of pyridine phenylborane (13 g. or 77%) was recrystallized from ethyl ether–pentane at 0° to yield material melting at 83–85°. Table II presents the data obtained in analogous reductions.

**Trimethylamine Phenylborane** (VI).—Six grams (0.035 mole) of diethyl phenylboronate was dissolved in 40 ml. of dry ether and added under nitrogen during the course of one hour to a solution of 1.0 g. of lithium aluminum hydride and 10 g. of trimethylamine in 200 ml. of dry ether at −70°. After the addition the reaction mixture was warmed to 0° and poured onto 200 g. of ice and water. The ether layer was separated, dried over magnesium sulfate and concentrated to 20 ml. in vacuum. The resulting concentrated solution was cooled to −70° and 1.5 g. (28%) of trimethylaminephenylborane separated as white crystals, m.p. 68–69°. The infrared spectrum of this material gave B–H stretching bands at 4.35 μ and the material rapidly reduced a dilute silver nitrate solution to produce a silver mirror.

*Anal.* Calcd. for $C_9H_{16}BN$: C, 72.52; H, 10.82; B, 7.26. Found: C, 72.30; H, 11.0; B, 7.15.

**Triethylamine phenylborane** (VII) was prepared in the same manner as was trimethylamine phenylborane (VI) except 10 g. of triethylamine was substituted for the trimethylamine. Concentration of the ether solution of product afforded 4.2 g. (63%) of triethylamine phenylborane, m.p. 64–65°, which similarly reduced silver nitrate to silver metal and exhibited B–H stretching at 4.35 μ in the infrared.

*Anal.* Calcd. for $C_{12}H_{22}BN$: C, 75.41; H, 11.60; B, 5.66. Found: C, 75.62; H, 11.30; B, 5.31.

**Reaction of Pyridine Phenylborane** (I) **with Aqueous Acetonitrile.**—A solution of 3.35 g. ($1.98 \times 10^{-2}$ mole) of pure I was refluxed with 7 ml. of water and 25 ml. of acetonitrile. The evolved hydrogen was measured with a wet test meter and amounted to 900 ml. (S.T.P.) or a yield of 100%.

The hydrolysate was poured into 200 ml. of water and extracted three times with 50-ml. portions of ether. The ether extract was washed with water, dried over magnesium sulfate and the solvent removed in vacuum. The residue (2.2 g.) melted at 210–212° (lit.[5] 214–216°) and gave an infrared spectrum identical with that of phenylboronic acid. Recovery of phenylboronic acid amounted to 92% of theory.

**Reaction of Silver Perchlorate with Pyridine Phenylborane** (I).—To a solution of 4.0 g. of silver perchlorate dissolved in 10 ml. of water was added with stirring a solution 1.7 g. ($1 \times 10^{-2}$ mole) of I dissolved in 20 ml. of acetonitrile. The mixture was stirred for two hours and then filtered with a tared sintered glass funnel. The collected silver weighed 1.45 g. (70% of theory for two gram atoms of silver produced per mole of I) when washed and dried.

The filtrate was poured into 200 ml. of water and extracted three times with 50-ml. portions of ether. The ether extract was washed with water, dried over magnesium sulfate and evaporated to dryness in vacuum to yield 0.6 g. (50% of theory) of phenylboronic acid which was identified by infrared spectrum.

**Reduction of Iodine by Pyridine Phenylborane** (I).—Pyridine phenylborane (169 mg.) was dissolved in 10 ml. of dry pyridine in a 10-ml. volumetric flask. Several 1.00-ml. aliquots of this solution were titrated in 15 ml. of 80:20 (volume) pyridine–water with an 0.020 *M* solution of iodine in pyridine. The end-point was detected by the slight yellow coloration of excess iodine. The reproducible titer was 9.20 ml. which corresponds to 92% reaction as described by equation 1. The low titer may possibly be due to the decomposition of a small amount of the borane by reaction with the produced pyridinium ion.

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[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

# Amine Boranes. II. The Preparation of Pyridine Diarylboranes

BY M. FREDERICK HAWTHORNE

RECEIVED JANUARY 29, 1958

The low temperature reduction of butyl, ethyl and β-aminoethyl diarylborinates with lithium aluminum hydride in diethyl ether containing pyridine produced modest yields of pyridine diarylboranes. Several such compounds have been prepared and their properties are described. An attempt to prepare pyridine α-naphthylphenylborane was unsuccessful.

In the previous paper of this series[1] the preparation of pyridine arylboranes ($ArBH_2 \cdot Py$) were described. As a logical extension of this work the preparation of pyridine diarylboranes was carried out by an essentially identical path, *i. e.*, the low temperature lithium aluminum hydride reduction of esters of diarylborinic acids in the presence of pyridine.

$$Ar_2BOR \xrightarrow[Py]{LiAlH_4} Ar_2B\overset{\ominus}{H}\text{-}\overset{\oplus}{Py}$$

This paper describes the synthesis and general chemical properties of several of these compounds

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[1] M. F. Hawthorne, THIS JOURNAL, **80**, 4291 (1958).