TABLE II

PYRIDINE ARYLBORANES

Ar in ArBH$_2$Py		M.p., °C.	Yield, %	Formula	Analyses, %					
					Calcd.			Found		
					C	H	B	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. (1.98×10^{-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. (1×10^{-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.

HUNTSVILLE, ALABAMA

[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.

$$\mathrm{Ar_2BOR} \xrightarrow[\mathrm{Py}]{\mathrm{LiAlH_4}} \mathrm{Ar_2\overset{\ominus}{B}H\text{-}\overset{\oplus}{Py}}$$

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).

TABLE I

THE PREPARATION AND PROPERTIES OF PYRIDINE DIARYLBORANES

Ar in $Ar_2BH·Py$	Ester reduced	Yield, %	M.p., °C.	Carbon, %		Hydrogen, %		Boron, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
Phenyl (I)	Ethyl	73	106–107	83.29	83.02	6.58	6.85	4.41	4.43
p-Tolyl (II)	*n*-Butyl	41	110–113	83.53	83.51	7.38	7.54	3.96	4.08
p-Anisyl (III)	β-Aminoethyl	64	109–110	74.77	74.83	6.61	6.79	3.55	3.57
p-Chlorophenyl (IV)	*n*-Butyl	32	103–104	65.02	65.09	4.49	4.60	3.45	3.36
p-Bromophenyl (V)	Ethyl	43	122–124	50.67	51.05	3.50	3.96	2.69	2.81

and, in addition, an unsuccessful attempt to prepare an amine diarylborane containing a tetrahedral and asymmetric boron atom (ArAr′BH-Py).

In order to obtain a simple method for the preparation of pyridine diarylboranes, ethyl diphenylborinate was prepared by the azeotropic distillation of diphenylborinic acid,[2] ethanol and benzene and reduced with lithium aluminum hydride in the presence of pyridine as previously described[1] for the preparation of pyridine arylboranes. Pyridine diphenylborane (I) was obtained in 73% yield as a white crystalline solid which melted at 106–107° and which was stable in the air.

The extension of this preparative method to other pyridine diarylboranes was limited by the difficulty of preparing the required diarylborinate esters. This limitation was in part overcome by the finding that when necessary the required diarylborinic acid could be isolated from Grignard reaction mixtures[3] as the β-aminoethyl ester, a technique developed and successfully employed by Letsinger and Skoog.[2] In two of the six systems reported here it was found to be expedient to reduce directly the β-aminoethylborinate esters. In this manner pyridine di-(*p*-anisyl)-borane was prepared in moderate yield as was the apparently unstable pyridine α-naphthylphenylborane (*vide infra*). In two of the remaining four systems this latter type of reduction was unpromising and the β-aminoethyl esters were converted to the corresponding ethyl esters *via* the borinic acid and azeotropic esterification. These were the di-(*p*-bromophenyl)- and diphenylborinic acid systems. In the two remaining cases it was found that the *n*-butyl esters could be obtained either by careful fractionation of the crude Grignard product or by azeotropic esterification of the crude acids followed by fractionation. In this manner *n*-butyl di-(*p*-tolyl)-borinate and *n*-butyl di-(*p*-chlorophenyl)-borinate were prepared, respectively. Table I sets forth the data pertinent to the reduction of these esters to the corresponding pyridine diarylboranes.

Since an amine diarylborane which has an asymmetric and tetrahedral boron atom would be of interest for further stereochemical and mechanism studies, an attempt was made to prepare pyridine α-naphthylphenylborane (VI) from the stable β-aminoethyl α-naphthylphenylborinate.[4] A crystalline material was obtained by the usual procedure which exhibited B–H and O–H stretching in the infrared and which rapidly reduced silver ion to silver metal. However, on attempted recrystallization from ethyl ether this material evolved hydrogen readily and the recovered solid showed no B–H stretching in its infrared spectrum. It thus appears as though the isolated solid was badly contaminated with the corresponding borinic acid and that this particular pyridine borane is inordinately sensitive to protolytic decomposition. This enhanced instability could well be due to steric crowding of the three large groups attached to the tetrahedral boron atom and might thus represent an excellent example of B-strain[5] since expulsion of hydride would lead to a planar trigonal boron atom.

With regard to general chemical properties the pyridine diarylboranes were found to be closely analogous to the pyridine arylboranes. Examples of similarity are: (1) the rapid though not quantitative reduction of silver ion to silver metal in aqueous acetonitrile, (2) the presence of B–H stretching at 4.35 μ in the infrared spectrum, (3) rapid and quantitative reduction of iodine to iodide ion in aqueous pyridine (20:80 by volume) and (4) hydrolysis in aqueous acetonitrile to produce one mole of hydrogen and one mole of diarylborinic acid per mole of pyridine diarylborane. Kinetic measurements presented in the following paper of this series show that pyridine diphenylborane is many times more reactive toward hydrolysis than is pyridine phenylborane.

$$Ar_2BH·Py + I_2 \longrightarrow Ar_2BI + HI + Py$$

Quantitative concentration *vs.* time measurements proved that pyridine diphenylborane and pyridine phenylborane would not reduce ketones such as 2-octanone nor aldehydes such as isobutyraldehyde in acetonitrile solution at room temperature. However, addition of isobutyryl chloride to a diethyl ether solution of either of these amine boranes resulted in a reaction from which isobutyraldehyde could be isolated in modest yield as its 2,4-dinitrophenylhydrazone derivative. Although a new method for the preparation of aldehydes from acid chlorides would be an attractive goal, the low efficiency of these reductions and the rather involved preparation of the amine boranes militates against the synthetic usefulness of this method.

Experimental

Ethyl Diphenylborinate.—To 40.0 g. (0.18 mole) of β-aminoethyl diphenylborinate (prepared by the method of Letsinger and Skoog) and dissolved in a minimum of 50:50 acetone–methanol was added 20 ml. of concentrated hydrochloric acid followed by sufficient water to cause separation of layers. The mixture was extracted with ether, the ether layer washed well with water, dried over magnesium sulfate and evaporated under reduced pressure to yield an oil. The oily residue was dissolved in 100 g. of absolute ethanol and 220 g. of benzene and azeotropically distilled with a

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(2) R. L. Letsinger and I. Skoog, THIS JOURNAL, **77**, 2491 (1955).

(3) All diarylborinic acid derivatives were prepared by the reaction of two equivalents of the proper Grignard reagent with one equivalent of tri-*n*-butyl borate as described by Letsinger and Skoog (ref. 2).

(4) R. L. Letsinger and N. Remes, THIS JOURNAL, **77**, 2489 (1955).

(5) That this great reactivity is probably not electronic in origin is illustrated by the results of the following paper of this series.

spinning-band column of approximately 40 plates efficiency. After the slow removal of ternary azeotrope (b.p. 64°) the excess benzene and ethanol were distilled rapidly and the residual oil fractionated at 0.5 mm. to yield 26.5 g. (0.13 mole) of ethyl diphenylborinate boiling at 100°. The yield is 73% of theory.

Pyridine Diphenylborane (I).—Lithium aluminum hydride (5.0 g.) was dissolved in 500 ml. of anhydrous ether by refluxing under nitrogen. The resulting solution was cooled to −70° and 50 ml. of pyridine added in one portion. To this solution was added slowly with stirring at −70° a solution of 25 g. (0.12 mole) of ethyl diphenylborinate dissolved in 100 ml. of dry ether. After the addition the mixture was stirred and allowed to warm to 0°, whereupon a solution of 10 ml. of pyridine and 25 ml. of water was added with cooling. The mixture was immediately filtered, and the precipitate washed well with ether. The combined ether solution was washed three times with ice-water, separated, dried over magnesium sulfate and evaporated under reduced pressure at −10°. The crystalline residue was dissolved in a small quantity of benzene (45°), a small volume of ether was added, and then dry pentane to produce turbidity. The solution now was cooled slowly to 0°, whereupon large crystals of pyridine diphenylborane (15 g. or 0.061 mole) melting at 106–107° were deposited. The yield amounted to 51% of theory.

β-Aminoethyl Di-(*p*-anisyl)-borinate.—Ninety-two grams of *p*-bromoanisole (0.5 mole) was converted to the Grignard reagent in 350 ml. of dry ether and 12 g. of magnesium turnings under nitrogen. This solution was added slowly to 58 g. of tri-*n*-butyl borate dissolved in 500 ml. of ether under nitrogen and at −70°. The addition required about three hours. After the addition the solution was allowed to warm to room temperature overnight with stirring and the magnesium salts decomposed with a slight excess of dilute hydrochloric acid. The ethereal layer was separated, washed well with water, dried over magnesium sulfate, and distilled under reduced pressure. The portion boiling between 150–200° at 0.5 mm. was collected and weighed 36.4 g. This fraction was dissolved in 75 ml. of ethanol, and 15 ml. of ethanolamine in 30 ml. of water was added. The solution was heated on the steam-bath for ten minutes, cooled and filtered to obtain 10.0 g. of white crystals melting at 168–170°, yield 14%.

Anal. Calcd. for $C_{16}H_{20}BO_3N$: C, 67.38; H, 7.07. Found: C, 67.57; H, 7.16.

A small amount of this ester was treated with dilute hydrochloric acid and converted to di-(*p*-anisyl)-borinic acid, m.p. 107°.

Pyridine Di-(*p*-anisyl)-borane (II).—Six grams (0.021 mole) of β-aminoethyl di-(*p*-anisyl)-borinate dissolved in 50 ml. of pyridine was added slowly to a solution of 3.0 g. of lithium aluminum hydride in 50 ml. of ether and 100 ml. of pyridine. The addition was carried out under nitrogen and at −70°. The mixture was stirred at −20° for one hour following the addition and slowly warmed to 0°. A solution of 15 ml. of water and 5 ml. of pyridine was added, the mixture filtered and the ether layer washed three times with ice-water. The washed ethereal solution was dried over magnesium sulfate and the solvent removed under reduced pressure at −10° to yield crystalline material. The crude product was recrystallized from benzene–ether–pentane to yield 4.1 g. (64%) of pyridine di-(*p*-anisyl)-borane melting at 109–110°.

Butyl Di-(*p*-chlorophenyl)-borinate.—The Grignard reagent prepared from 184 g. (1.0 mole) of *p*-bromochlorobenzene and 24 g. of magnesium turnings in 400 ml. of ether was added slowly under nitrogen to a solution of 116 g. (0.5 mole) of tri-*n*-butyl borate dissolved in 1000 ml. of dry ether. The addition was carried out with vigorous stirring at −70°. The Grignard formed two layers and both layers were used. After the addition the mixture was allowed to warm to room temperature while standing overnight. The magnesium salts were decomposed with dilute hydrochloric acid, the ether layer washed with water, dried over magnesium sulfate and evaporated to an oil in vacuum. The residual oil was distilled at 1 mm. and the fraction boiling between 150 and 180° collected (85 g.). This material was dissolved in 500 ml. of 1-butanol and the mixture slowly distilled with a spinning band column to remove the 1-butanol–water azeotrope. The excess butanol was similarly removed and the residue fractionated at 0.7 mm. Twenty-nine grams of di-*n*-butyl (*p*-chlorophenyl)-boronate was obtained at 118° and 30 g. of *n*-butyl di-(*p*-chlorophenyl)-borinate was collected at 156°. The latter fraction was redistilled to 0.5 mm. to yield 21.5 g. of ester boiling at 150° (15.5% of theoretical).

Anal. Calcd. for $C_{16}H_{17}BOCl_2$: C, 62.58; H, 5.58; B, 3.52. Found: C, 61.61; H, 5.68; B, 3.49.

Pyridine Di-(*p*-chlorophenyl)-borane (III).—Six grams (0.022 mole) of *n*-butyl di-(*p*-chlorophenyl)-borinate was dissolved in 50 ml. of dry ether and added slowly to a solution of 2.0 g. of lithium aluminum hydride in 200 ml. of ether containing 10 ml. of pyridine. The addition was carried out at −70° as before and the mixture was warmed to 0° with stirring following the addition. To the reaction mixture was added a solution of 5 ml. of water and 10 ml. of pyridine followed by filtration and water washing of the ether layer. The ethereal solution of product was dried over magnesium sulfate and the ether removed in vacuum. The oily residue was dissolved in a very small amount of benzene and pentane added to produce turbidity. The solution was cooled to −70° and 2.2 g. (32%) of impure product melting at 100–101° was collected. Recrystallization from an identical solvent mixture produced analytically pure material melting at 103–104°.

Ethyl Di-(*p*-bromophenyl)-borinate.—Twenty-six grams (0.068 mole) of crude β-aminoethyl di-(*p*-bromophenyl)-borinate prepared as previously described[2] was treated with excess dilute hydrochloric acid in the presence of 1000 ml. of ether. The ether layer was washed well with water, dried over magnesium sulfate and the ether removed by vacuum. The oily residue was azeotropically distilled with 65 g. of absolute ethanol and 150 ml. of benzene. Following the removal of water and excess solvent the residue was distilled at 0.25 mm. with a spinning band column to yield 10.5 g. (0.029 mole) of pure ethyl di-(*p*-bromophenyl)-borinate boiling at 160°. The yield amounted to 42.7%.

Anal. Calcd. for $C_{14}H_{13}BOBr_2$: C, 45.70; H, 3.56. Found: C, 45.86; H, 3.20.

Pyridine Di-(*p*-bromophenyl)-borane (IV).—Nine grams (0.024 mole) of ethyl di-(*p*-bromophenyl)-borinate was reduced by the procedure described above for reduction of butyl di-(*p*-chlorophenyl)-borinate. The product weighed 4.2 g. before recrystallization (43%). Recrystallization from benzene–pentane gave 2.6 g. of product melting at 122–124°.

***n*-Butyl Di-(*p*-tolyl)-borinate.**—One-hundred and seventy-one grams (1.0 mole) of *p*-bromotoluene was converted to the Grignard reagent with 23 g. of magnesium in 500 ml. of dry ether under nitrogen. The resulting solution was added slowly at −70° to 115 g. (0.50 mole) of tri-*n*-butyl borate in 500 ml. of ether. Vigorous stirring was maintained. After standing overnight the mixture was worked up by the addition of just enough dilute hydrochloric acid to dissolve the magnesium salts followed by a rapid water washing of the ethereal layer. The organic layer was dried over magnesium sulfate and distilled under reduced pressure. The fraction boiling at 125–185° at 2.5 mm. was collected (78 g.) and redistilled with a spinning band column at 0.6 mm. Two fractions were obtained after a small amount of low boiling material was removed. Di-*n*-butyl *p*-tolylboronate (15.3 g.) was collected at 110° and the desired product, *n*-butyl di-(*p*-tolyl)-borinate (35 g.) was obtained at 138°, yield 26%.

Anal. Calcd. for $C_{18}H_{23}BO$: C, 81.21; H, 8.71; B, 4.06. Found: C, 80.95; H, 8.49, B, 3.90.

Pyridine Di-(*p*-tolyl)-borane (V).—Six grams (0.023 mole) of *n*-butyl di-(*p*-tolyl)-borinate was reduced in the same manner as ethyl di-(*p*-chlorophenyl)-borinate. The crystalline residue, 2.6 g. or 41%, was recrystallized from benzene–pentane to yield 2.1 g. of analytically pure material melting at 110–113°.

Pyridine α-Naphthylphenylborane (VI).—β-Aminoethyl α-naphthylphenylborinate (8.0 g. or 0.029 mole) prepared by the method of Letsinger and Remes[4] was slurried with 50 ml. of dry pyridine and added in one portion to 2.0 g. of lithium aluminum hydride in 100 ml. of dry ether maintained at −20°. The mixture was stirred at that temperature for one hour and then warmed to 0°. The mixture was worked up by the addition of 10 ml. of water in 20 ml. of pyridine and then filtration. The ethereal solution of products was washed three times with ice-water and dried over magnesium sulfate. Removal of the ether at reduced pressure and in the cold afforded about 4 g. of oily product which was dissolved immediately with gassing in a small amount of warm benzene and dry ether and cooled to −70°. A crystalline material separated which displayed both B–H and strong O–H stretch in the infrared. The material melted over an indefinite range and smelled strongly of pyridine. Repeated recrystallization afforded 2.5 g. of an unidentified mixture having no B–H stretch but very strong O–H stretch in the infrared. Since the recrystallization procedure employed here was identical with that employed with the other members of the series it must be concluded that pyridine α-naphthylphenylborane is extremely sensitive to traces of moisture.

Reaction of Silver Ion with Pyridine Diphenylborane (I).—To 2.45 g. (0.01 mole) of pyridine diphenylborane dissolved in 10 ml. of acetonitrile was added a solution of 5.0 g. of silver perchlorate in 2 ml. of water and 10 ml. of acetonitrile. After standing at room temperature for two hours the solution was filtered with a tared fritted glass funnel. The silver was washed well with water, ethanol and ether and weighed 0.65 g. which corresponds to 0.6 equivalent of silver per mole of borane. The low yield is no doubt due to the competing hydrolysis and protolysis of borane by water and produced perchloric acid. All other pyridine diarylboranes gave similar qualitative reactions.

Hydrolysis of Pyridine Diphenylborane (I).—To 4.91 g. (0.02 mole) of pyridine diphenylborane dissolved in 60 ml. of acetonitrile was added 5 ml. of water and the solution brought to the reflux temperature in a closed system connected to a wet test meter. Gas was evolved steadily and amounted to 95% of the theoretical amount after correction to S.T.P. The resulting acetonitrile solution was flooded with 300 ml. of water and extracted with two 100-ml. portions of ether. The combined ether extracts were washed with water, dried over magnesium sulfate and the solvent removed in vacuum. The colorless residual oil weighed 4.1 g. and had an infrared spectrum identical with diphenylborinic acid prepared by the acidification of β-aminoethyl diphenylborinate or by the hydrolysis of phenylboron dichloride.

Reaction of Pyridine Diphenylborane (I) **with Iodine**.—A solution of 245 mg. (1 mmole) of pyridine diphenylborane was prepared in 10 ml. of pyridine. One-ml. aliquots were diluted to 10 ml. with 4:1 pyridine–water and titrated to a yellow iodine end-point with an 0.020 *M* solution of iodine in pyridine. Each aliquot required 4.90 ml. of iodine solution and indicated that the borane was 98% pure if one mole of borane reacts with one mole of iodine.

Reduction of Isobutyryl Chloride with Pyridine Diphenylborane (I).—To 5.3 g. (0.050 mole) of pure isobutyl chloride dissolved in 50 ml. of dry ether was added 12.2 g. (0.050 mole) of pure pyridine diphenylborane (I). The solution was refluxed for five hours with magnetic stirring and cooled to room temperature. An unidentified solid was removed by filtration and the ethereal filtrate combined with 200 ml. of ethanol, 20 ml. of water, 4.0 g. of 2,4-dinitrophenylhydrazine and 2 ml. of concentrated hydrochloric acid. The mixture was heated and stirred for one hour on the steam-bath, flooded with one liter of water and filtered. The precipitated solid was extracted with methylene chloride, the methylene chloride solution concentrated to 20 ml. and placed on a small chromatographic column packed with acid-washed alumina and methylene chloride. The first bright yellow band was collected separately, the solvent evaporated and the residue recrystallized from ethanol-water to yield 6.3 g. or a 50% yield of isobutyraldehyde 2,4-dinitrophenylhydrazone, m.p. 173–176°.[6] Further recrystallization afforded crystals meeting at 181–182°

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(6) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 188, reported m.p. of 182°

HUNTSVILLE, ALABAMA

[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, AND THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

Amine Boranes. III. Hydrolysis of Pyridine Diphenylborane and the Mechanism of Hydride Transfer Reactions

BY M. FREDERICK HAWTHORNE AND EDWARD S. LEWIS

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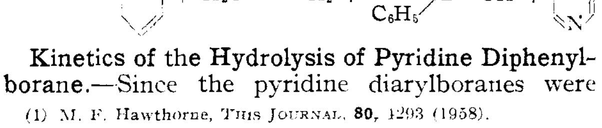
The hydrolysis of pyridine diphenylborane and pyridine diphenylborane-d_1 have both been studied kinetically with water and deuterium oxide in acetonitrile solution. Similarly the hydrolyses of four additional pyridine di-(*p*-x-phenyl)-boranes have been examined and the Hammett treatment applied. It is shown that the results are consistent with a non-linear transition state involving electrophilic attack of a water proton on the electrons of the B-H bond, and it is proposed that electrophilic attacks on bonds to hydrogen are generally of this type.

Pyridine diarylboranes are unique among known arylborane derivatives in that they contain only one B–H bond per molecule and they are therefore well suited for kinetic studies which would examine the chemistry of that bond. Among the simplest of these reactions is the hydrolysis of the B–H bond to produce hydrogen and a B–OH species. Since the hydrolysis of the pyridine diarylboranes was shown[1] to be quantitative and to produce hydrogen and the corresponding boronous acid, this reaction was chosen for study.



Kinetics of the Hydrolysis of Pyridine Diphenylborane.—Since the pyridine diarylboranes were found to be stable in pure acetonitrile, this solvent was employed in the kinetic study. A reaction temperature of 39.90 ± 0.05° was chosen since at this temperature all the compounds examined gave conveniently rapid reactions. The analytical method employed for the determination of the instantaneous concentration of remaining amine borane was based on the previously described[1] titration of hydridic hydrogen with iodine in pyridine solution.

The addition of water to acetonitrile solutions of pyridine diphenylborane produced a rapid second-order reaction, first order both in water and amine borane. The range of water concentration was 0.46 to 4.16 *M* while the pyridine diphenylborane was either 0.05 or 0.10 *M* at low and at high water concentrations, respectively. By using these excess quantities of water the observed reactions were pseudo first-order over-all and were followed to 85%

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(1) M. F. Hawthorne, THIS JOURNAL, **80**, 1293 (1958).