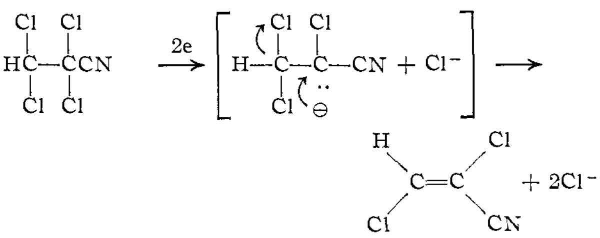
respond to changes in "*h*" as expected for diffusion-controlled processes. Similar results were obtained for propiolamide (Table I).

2,2,3,3-Tetrachloropropionitrile (2,2,3,3-CN).—This compound was of particular interest inasmuch as it was believed that it would be reduced exclusively to the *trans*-2,3-AN as



Reduction of *trans*-2,3-dichloroacrylonitrile should then proceed as above (e). One should, therefore, obtain a 2e wave at ~0.4 v., a 4e wave at −1.21 v. (*trans*-2,3-dichloroacrylonitrile → acrylonitrile), and a 2e wave at −1.95 v. (reductive saturation of acrylonitrile). This is precisely the polarogram obtained (Fig. 3). The wave heights observed (uncorrected for $t^{1/6}$ changes) were: W_1 = 1.41 μA., W_2 = 2.04 μA. and W_3 = 0.92 μA.

Acknowledgment.—The authors wish to express their appreciation to members of the Stamford Laboratories staff and others for their helpful suggestions on various aspects of this investigation. We are particularly grateful to Mr. E. F. Williams for cryoscopic data, Dr. J. E. Lancaster for n.m.r. studies, and to the Infrared and Microanalytical Laboratories for their contributions.

STAMFORD, CONN.

[CONTRIBUTION FROM KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Reaction of Trimethoxyboroxine with Aromatic Grignard Reagents. A New Synthesis of Borinic Acids[1]

BY THOMAS P. POVLOCK AND WILLIAM T. LIPPINCOTT[2]

RECEIVED APRIL 23, 1958

A study of the reactions of trimethoxyboroxine with nine aromatic Grignard reagents is reported. Borinic acids, isolated as their aminoethyl esters, are obtained in yields of 21–63%. Low yields of boronic acids also are obtained. Studies of the effect of temperature, the ratio of reactants and the influence of some steric and electrical factors in the Grignard reagent on the yield of borinic acid are reported and discussed.

Arylborinic acids probably were first prepared in 1894 by Michaelis[3] who hydrolyzed diphenylchloroborane. Physical constants have been reported for only a few borinic acids.[4] Most of these have been prepared by the action of a Grignard reagent with an alkyl borate.[4c,d,e] However, Letsinger recently has revived interest in these compounds, and, in addition to developing an excellent method for the preparation of solid derivatives,[5] has prepared the first mixed borinic acid[6] and the first tricyclic borinic acid.[7] Lappert and co-workers[8a] recently have reported good yields of dibutylborinic anhydride from the reaction of a Grignard reagent with boron trifluoride. Considerably more information is available concerning boronic acids.[8b]

The reactions of trimethoxyboroxine with phenyl, *o*-, *m*- and *p*-tolyl, *p*-anisyl, *p*-biphenyl, *p*-chlorophenyl, mesityl and α-naphthyl Grignard reagents have been carried out in ether solution. The reaction proceeds at all temperatures between −60 and 35°. Products are principally borinic acids with low yields of boronic acids. The reaction may be represented by the equation

$$6\text{ArMgBr} + (\text{CH}_3\text{OBO})_3 \longrightarrow 3(\text{Ar})_2\text{B—O—MgBr} + 3\text{CH}_3\text{OMgBr}$$

A study of the effect of temperature and ratio of reactants has been made with phenylmagnesium bromide. Maximum yields of borinic acids are obtained at 25° with a 9–1 mole ratio of Grignard reagent to boroxine. The yields obtained under these conditions range from 21 to 63% based on the boroxine and are, in most cases, approximately double those obtained by the reaction of a Grignard reagent with an alkyl borate.[4c,d,e] The borinic acids were isolated as their aminoethyl esters and identified by comparing the melting points, neutralization equivalents and elemental analyses of these esters with reported or calculated values. Boronic acids were identified by elemental analyses and by the melting points of their anhydrides.

Experimental

General Procedure.—Grignard reagents were prepared from the corresponding bromobenzenes by the method of Allen and Converse.[9] Trimethoxyboroxine, prepared from methyl borate and boric anhydride by the method of Goubeau and Keller,[10] was dissolved in ether and added to each Grignard reagent. The reaction of the boroxine with phenylmagnesium bromide illustrates the procedure followed.

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[1] Presented to the College of Arts and Sciences, Michigan State University in partial fulfillment of the requirements for the degree, Master of Science.

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[3] A. Michaelis, M. Behrens, J. Robinson and W. Geisler, *Ber.*, **27**, 244 (1894); *J. Chem. Soc.*, 190 (1894).

[4] (a) H. I. Schlesinger, L. Horvitz and A. B. Burg, THIS JOURNAL, **58**, 407 (1936); (b) A. L. Borisov, *Izvest. Akad. Nauk S.S.R., Otdel. Khim. Nauk*, 402 (1951); *C. A.*, **46**, 2995d (1952); (c) N. N. Mel'nikkov, *J. Gen. Chem. (U.S.S.R.)*, **6**, 636 (1936); (d) N. N. Maelnikov and M. S. Rokitskaya, *ibid.*, **8**, 1768 (1938); *C. A.*, **33**, 4969 (1939); (e) W. Konig and W. Scharrnbeck, *J. prakt. Chem.*, **128**, 153 (1930).

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

[6] R. L. Letsinger and N. Remes, *ibid.*, **77**, 2489 (1955).

[7] R. L. Letsinger and I. Skoog, *ibid.*, **77**, 5176 (1955).

[8] (a) W. Gerrard, M. F. Lappert and R. Schaffermar, *J. Chem. Soc.*, 3828 (1957); (b) M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

[9] C. F. H. Allen and S. Converse, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 226.

[10] J. Goubeau and H. Keller, *Z. anorg. Chem.*, **267**, 1 (1951).

TABLE I

YIELDS, MELTING POINTS, NEUTRALIZATION EQUIVALENTS AND ANALYSES OF AMINOETHYL BORINATES

Aminoethyl borinate	Yield,[b] %	M.p., °C. obsd.	Neut. equiv.		Analyses, %							
					Found				Calculated			
			Obsd.	Calcd.	C	H	N	B	C	H	N	B
Diphenyl	62.4	189[a]	225.3	225	74.67	7.36	6.22	4.80	74.63	7.15	6.22	4.88
Di-*o*-tolyl-	59.3	181–181.5	255	253	75.62	8.36	5.46	4.33	75.90	7.91	5.53	4.34
Di-*m*-tolyl-	60.3	180–181	256	253	75.37	8.09	5.43	4.40	75.90	7.91	5.53	4.34
Di-*p*-tolyl-	33.0	186–187	251	253	75.60	8.32	5.27	4.40	75.90	7.91	5.53	4.34
Di-*p*-anisyl-	38.0	173–174	287	285	67.43	7.21	4.75	3.82	67.30	7.02	4.91	3.85
Di-*p*-biphenyl-	41.7	217–218	381	377	79.95	6.30	3.69	2.92	82.75	6.36	3.71	2.92
Di-*p*-chlorophenyl-	21.5	223–224	292	294	...	..	..	3.72	...	..	..	3.67
Di-α-naphthyl-	62.0	202–203	326.5	325	80.84	6.39	4.01	3.35	81.20	6.15	4.31	3.38

[a] Literature value 190°.[6] [b] At 25° with a 9:1 mole ratio of Grignard reagent to boroxine.

The phenylmagnesium bromide was prepared in the presence of 200 ml. of ether and filtered into a 1-l. three-necked flask containing 100 ml. of ether and equipped with a stirrer, dropping funnel and a parallel side arm holding a reflux condenser and a thermometer. The condenser and dropping funnel were protected from moisture with $CaCl_2$ drying tubes. The contents of the flask were cooled to 25° by placing the flask in a water-bath. Analysis[11] showed that 0.398 mole of phenylmagnesium bromide had been prepared. To this solution, 7.7 g. (0.044 mole) of trimethoxyboroxine (a 9 to 1 ratio of Grignard reagent to boroxine) dissolved in 150 ml. of anhydrous ether was added dropwise over a period of two hours while the temperature was maintained between 24 and 26° by adding ice to the water-bath. After the addition of boroxine, the reaction was stirred for three hours at the same temperature; 40 ml. of concentrated HCl in 300 ml. of water was used to hydrolyze the reaction mixture. The ether layer was separated, washed twice with 100-ml. portions of water and heated on a steam-bath to remove the ether; 100 ml. of water was added to the resultant oil and the mixture was heated on a steam-bath for 15 minutes to remove the boronic acid that had dissolved in the ether. The oil was separated from the water and diluted to 250 ml. with ether. The water layer was evaporated and a 4% yield of boronic acid was obtained. A solution of 8 ml. of ethanolamine in an equal volume of water[6] was added to the ether solution and the mixture was stirred until the precipitate ceased to form. This solid was filtered, washed with three 50-ml. portions of water, dried and recrystallized from ethanol. The yield of ester, based on boroxine was 19.0 g., 62.4%. A summary of the yields of the other borinates prepared in the same manner is given in Table I.

Purification of Boronic Acids.—Phenyl-, *o*-, *m*- and *p*-tolyl-, *p*-anisyl- and *p*-biphenylboronic acids, isolated from the reaction mixture as previously described, were recrystallized three times from water. Mesityl- and α-naphthylboronic acids were recrystallized three times from benzene. The observed melting points of the anhydrides of these acids are all in excellent agreement with literature values. Mesityl boronic anhydride, previously not reported, melts 170–171°.

Analysis of Products.—Neutralization equivalents of the aminoethyl borinates were determined using a procedure of Stone[12] for the estimation of total amines. Samples of each of the esters ranging from 0.4 to 0.9 g. (20 meq.) were weighed, dissolved in isopropyl alcohol and titrated with standard HCl in isopropyl alcohol to a sharp decrease in *p*H as determined by a Beckman model G *p*H meter equipped with a glass and a calomel electrode. Neutralization equivalents of the aminoethylborinates prepared in this study are given in Table I.

Elementary Analyses.—Boron analyses, obtained by following a procedure of Johnson,[13] and carbon and hydrogen and N micro-analyses, performed by Micro-Tech Laboratories, Skokie, Ill., are given in Table I.

Results and Discussion

The effect of temperature on the yield of borinic acid was studied by carrying out the reaction with phenylmagnesium bromide in a 9 to 1 mole ratio of Grignard reagent to boroxine at five temperatures. The temperatures and the corresponding yields, based on the boroxine, are: −60°, 11.2%; 6°, 18.4%; 16°, 42.6%; 25°, 62.4%; 35°, 51.7%.

The effect of varying the ratio of reactants was studied by carrying out the reaction with phenylmagnesium bromide at 25° at four different mole ratios. The ratios of Grignard reagent to boroxine and the corresponding yields, based on the boroxine, are: 3:1, 15.7%, 6:1, 52.6%; 9:1, 62.4%; 12:1, 44.4%.

Reversing the order of adding reactants, *i.e.*, adding the Grignard reagent to the boroxine, and using a 2:1 mole ratio of phenylmagnesium bromide resulted in a sixfold increase in the yield of boronic acid compared to the "normal" reaction. The yield of borinic acid under these conditions was 13%, approximately the same as that obtained in the normal procedure.

Substituting tri-*n*-butoxyboroxine for the methoxy compound resulted in a decrease in the yield of borinic acid from 62.5 to 35.0%.

The effect of electron-donating or -withdrawing substituents in the Grignard reagent is reflected in the yields of borinates obtained from reactions involving seven Grignard reagents. The aryl portion of the Grignard reagent and the corresponding yields, based on boroxine, are: phenyl, 62.4%; α-naphthyl, 62.0%; *m*-tolyl, 60.3%; *p*-biphenyl, 41.7%; *p*-anisyl, 38.0%; *p*-tolyl, 33.0%; *p*-chlorophenyl, 21.5%. In these cases, the yields of borinates are decreased by both electron-donating and electron-withdrawing substituents.

The influence of some steric factors in the Grignard reagent is apparent from the results obtained when *p*-tolyl, *o*-tolyl, α-naphthyl and mesityl Grignard reagents are employed in the reaction. The yields (*p*-tolyl, 33.0%; *o*-tolyl, 59.3%; α-naphthyl, 62.0%; mesityl, 0.00%) indicate that substitution of a single carbon atom in the *o*-position increases the yield of borinic acid, whereas blocking both *o*-positions with methyl groups apparently prevents formation of this acid. No reaction between mesitylmagnesium bromide and the boroxine was detected after increasing the reaction

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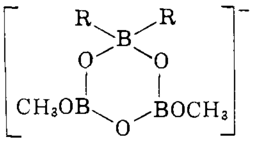
[11] L. F. Fieser, "Experiments in Organic Chemistry," second edition, D. C. Heath and Co., New York, N. Y., 1941, pp. 407–408.

[12] K. G. Stone, "Determination of Organic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 169.

[13] H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938).

time fivefold. A 5% yield of mesitylboronic acid was obtained from this reaction after 24 hours.

The results give some insight into the path of the reaction. Of especial significance is the tendency for the boron atom to acquire two aryl groups rather than three in the presence of a large excess of Grignard reagent. This apparently reflects the high stability of the boroxine ring, and when coupled with the well-known fact that in processes of this type the introduction of one hydrocarbon onto the boron atom facilitates attack by a second molecule of the Grignard reagent,[4] suggests an intermediate of the type



Several observations support this suggestion. The first is the fact that a 16% yield of borinic acid was obtained at a 3:1 mole ratio of Grignard reagent to boroxine. This ratio provides sufficient Grignard reagent so that one aryl group is available for each boron atom. Similarly, a 13% yield of borinic acid was obtained when the Grignard reagent in a 2:1 mole excess was added to the boroxine—conditions which should strongly favor boronic acid formation. In both of these cases, appreciable disubstitution on boron atoms occurred, but no trisubstitution was detected. This constitutes significant evidence for the anion-type intermediate.

A third observation of possible significance is the fact that yields of borinic acids never exceeded 63%. This may be fortuitous, or it may mean that only two of the three boron atoms of the boroxine can be used in borinic acid formation. This could be related to the solubility of the intermediate. It is conceivable that once two boron atoms of the boroxine acquire a pair of aryl groups, the intermediate may precipitate from solution. A white precipitate having approximately the composition of the intermediate is formed during the reaction.

Finally, it is likely that the boroxine ring is stable until the reaction mixture is hydrolyzed with acid. Otherwise, considerable quantities of triarylboranes would be expected among the products. Only traces of these compounds have been obtained from reactions at 35°.

LANSING, MICH.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

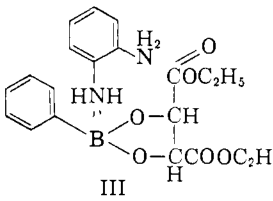
Organoboron Compounds. VIII. Dihydrobenzoboradiazoles[1]

BY ROBERT L. LETSINGER AND STEPHEN B. HAMILTON

RECEIVED MAY 5, 1958

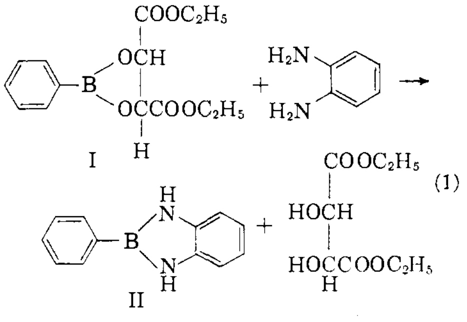
Phenylenediamine reacts with boronic acids and esters to form substituted dihydrobenzoboradiazoles, representatives of a new class of heterocyclic compounds. These substances serve as good derivatives for the characterization of the boronic acids. Boradiazole formation from phenylenediamine and the ethyl tartrate ester of benzeneboronic acid is rapid in benzene solution at room temperature.

In the course of investigating the manner in which complex formation involving boron can affect organic reactions, we examined the reaction of *o*-phenylenediamine with the ethyl tartrate ester of benzeneboronic acid (I). Molecular models indicated that in the amine complex (III), should it form, the second amino group of phenylenediamine would be close to the carbethoxyl group. It was of interest to see whether amide formation would be accelerated as a consequence.



III

o-Phenylenediamine and Compound I did react readily in refluxing toluene solution. The product, m.p. 215–216°, was not, however, the expected amide. On the basis of the analysis, molecular weight, infrared spectrum and hydrolysis data it was assigned structure II, 2-phenyl-1,3-dihydro-2,1,3-benzoboradiazole. As such, it is the first example of this heterocyclic ring system.



Compound II hydrolyzes very rapidly in dilute acids solutions to give benzeneboronic acid and phenylenediamine. In neutral solution hydrolysis is much slower. With hydrogen chloride in toluene it forms a dihydrochloride. There was no evidence for B–N cleavage by hydrogen chloride to give phenyldichloroborane, even for a reaction carried out for eight hours in refluxing toluene. By contrast, hydrogen chloride converted methylaminodimethylborane to dimethylchloroborane and methylamine hydrochloride (a two-hour reaction

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[1] For paper VII see R. L. Letsinger and J. R. Nazy, *J. Org. Chem.*, **23**, 914 (1958). This work was supported by the National Science Foundation.