1,7-Bis-(ω-acetoxy-*n*-butyl)-octamethyltetrasiloxane, compound 13, 62 g. (0.12 mole), 9% yield. *Anal.* Calcd. for $C_{20}H_{46}Si_4O_7$: Si, 22.0; sapn. equiv., 256; *MR*D, 136.0. Found: Si, 22.0; sapn. equiv., 253; *MR*D, 135.7.

1,9-Bis-(ω-acetoxy-*n*-butyl)-decamethylpentasiloxane, compound 14, 36 g. (0.06 mole), 5% yield. *Anal.* Calcd. for $C_{22}H_{52}Si_5O_8$: Si, 24.0; sapn. equiv., 293; *MR*D, 154.7. Found: Si, 24.2; sapn. equiv., 293; *MR*D, 154.4.

1,11-Bis-(ω-acetoxy-*n*-butyl)-dodecamethylhexasiloxane, compound 15, 8.1 g. (0.01 mole), 1% yield. *Anal.* Calcd. for $C_{24}H_{58}Si_6O_9$: Si, 25.55; sapn. equiv., 330; *MR*D, 173.3. Found: Si, 25.59; sapn. equiv., 331; *MR*D, 173.3.

By a procedure similar to that described above, bis-(γ-acetoxypropyl)-tetramethyldisiloxane, compound 7 (499 g., 1.5 moles), was equilibrated with octamethylcyclotetrasiloxane (148 g., 0.5 mole), in the presence of 14.5 ml. of concentrated sulfuric acid and gave: Bis-(γ-acetoxypropyl)-tetramethyldisiloxane, compound 7, 142 g., 28% recovery based on the amount of starting diester.

1,5-Bis-(γ-acetoxypropyl)-hexamethyltrisiloxane, compound 8, 76 g., 12.5% yield. *Anal.* Calcd. for $C_{16}H_{36}Si_3O_6$: Si, 20.6; sapn. equiv., 204; *MR*D, 108. Found: Si, 20.8; sapn. equiv., 205; *MR*D, 108.

1,7-Bis-(γ-acetoxypropyl)-octamethyltetrasiloxane, compound 9, 28 g., 4% yield. *Anal.* Calcd. for $C_{18}H_{42}Si_4O_7$: Si, 23.3; sapn. equiv., 241; *MR*D, 127. Found: Si, 23.6; sapn. equiv., 246; *MR*D, 127.

1,9-Bis-(γ-acetoxypropyl)-decamethylpentasiloxane, compound 10, 8 g., 1% yield. *Anal.* Calcd. for $C_{20}H_{48}Si_5O_8$: Si, 25.2; sapn. equiv., 278; *MR*D, 145. Found: Si, 24.9; sapn. equiv., 278; *MR*D, 145.

Physical Properties.—Boiling points were determined in a modified Cottrell apparatus.[14] The boiling points at 39 mm. given in Table I for compounds 1–10 are taken from vapor pressure *vs.* temperature plots covering the range 15–100 mm. Boiling points for compounds 10–15 were determined at 39 mm.

Refractive indices were determined with an Abbe refractometer. Densities were measured with pycnometers of about 5-ml. capacity. Viscosities were determined in Cannon–Fenske viscometers.[15]

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[14] D. Quiggle, C. O. Tongberg and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

[15] M. R. Cannon and M. R. Fenske, *ibid.*, **10**, 297 (1938).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Organoboron Compounds. V. The Preparation of an Unsymmetrical Diarylborinate[1]

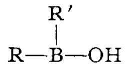
BY ROBERT L. LETSINGER AND NATHANIEL REMES

RECEIVED NOVEMBER 19, 1954

The preparation and some properties of aminoethyl phenyl-α-naphthylborinate and aminoethyl di-α-naphthylborinate are described.

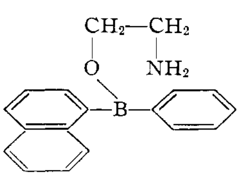
The limited range of known organoboron compounds is well illustrated by the fact that no unsymmetrical borinic acids (I, $R \neq R'$) have been described. With the development of practical procedures for isolating and characterizing the symmetrical borinic acids,[2] however, the synthesis of such compounds seemed feasible. We therefore undertook to make a compound of this class, phenyl-α-naphthylborinic acid. An aromatic borinic acid was selected for investigation since it was expected to be more stable and less prone to disproportionation than an unsymmetrical aliphatic borinic acid.

Butyl benzeneboronate was treated with an equimolar amount of α-naphthylmagnesium bromide in an ether solution at −60 to −70°. After acid hydrolysis, the organic layer was warmed to distil the ether and then mixed with ethanolamine dissolved in alcohol and water. A white precipitate, II, assigned the structure, β-aminoethyl phenyl-α-naphthylborinate, separated (75% yield) from the solution. The ethanolamine served, therefore, as an agent to remove the borinic acid selectively from the other organoboron compounds present in the reaction mixture. In another experiment this borinate also was prepared (80% yield) from the alternate pair of reagents, phenylmagnesium bromide and butyl α-naphthaleneboronic acid.



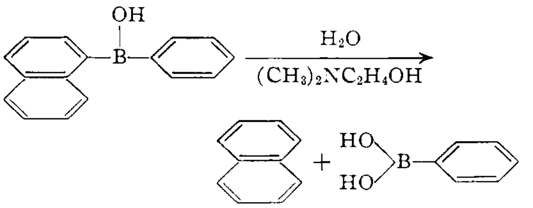
$$\begin{array}{c} R' \\ | \\ R\text{—}B\text{—}OH \end{array}$$

I



II

Compound II was a high melting solid (m.p. 228°) stable indefinitely in air at room temperature. In this respect it differed markedly from the unsymmetrical alkylborines.[3] With dilute hydrochloric acid it hydrolyzed rapidly to an oil, no doubt phenylnaphthylborinic acid, which could be re-esterified with ethanolamine, or converted to the β-aminoisobutyl ester (92% yield from the aminoethyl ester) with 2-amino-2-methyl-1-propanol. An attempt to prepare a solid ester with β-dimethylaminoethanol was unsuccessful. Instead of forming the derivative, the borinic acid partially decomposed with the formation of naphthalene. At steam-bath temperatures, the cleavage reaction was virtually quantitative within ten minutes (reaction 1); naphthalene and benzeneboronic acid were isolated from this reaction in yields of 86 and 82%, respectively.



(1)

Melnikov found that diarylborinic acids reacted with bromine to give aryl bromides and boric acid.[4]

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[1] Presented at the 126th Meeting of the American Chemical Society in New York, September, 1954. A portion of this material appeared in a preliminary publication, THIS JOURNAL, **76**, 4047 (1954).

[2] R. L. Letsinger and I. Skoog, *ibid.*, **77**, 2491 (1955); **76**, 4147 (1954).

[3] T. Parsons and D. Ritter, *ibid.*, **76**, 1710 (1954).

[4] H. Melnikov, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 636 (1936); *C. A.*, **30**, 5571 (1936).

In agreement with these results, we obtained bromobenzene and bromonaphthalene from a reaction of phenylnaphthylborinic acid with bromine in aqueous acetic acid. The carbon boron bonds in II were cleaved by hot aqueous zinc chloride and by hydrogen peroxide; naphthalene was isolated from the former reaction, and α-naphthol from the latter.

If aminoethyl phenylnaphthylborinate were to disproportionate, the aminoethyl esters of diphenylborinic acid and dinaphthylborinic acid could be formed. An equimolar mixture of these two esters would analyze the same and give the same degradation products as the unsymmetrical borinate. In order to test the possibility that such a disproportionation had occurred, aminoethyl diphenylborinate and aminoethyl dinaphthylborinate were prepared. The former compound has been described previously.[2] It was found, however, that some improvement in the yield could be realized by eliminating a distillation and an ammonia precipitation step from the original procedure. With this simplification, the ester was isolated in 67% yield from a reaction of phenylmagnesium bromide with butyl borate. Aminoethyl dinaphthylborinate was similarly obtained (58% yield) from naphthylmagnesium bromide and butyl borate. The melting points of these compounds and the melting point of a mixture of the two were 190, 205 and 170–185°, respectively. These data, in conjunction with the methods for preparing II, with the analytical data and with the degradation reactions show that compound II was indeed aminoethyl phenyl-α-naphthylborinate.

Acid hydrolysis converted aminoethyl dinaphthylborinate to dinaphthylborinic acid, a solid which melted at 105–106°. This acid decomposed when heated above 120° to naphthalene and an oxide which, on addition of water, yielded naphthaleneboronic acid.

Experimental Part

Aminoethyl Diphenylborinate.—Phenylmagnesium bromide (1.05 moles in 500 ml. of an ether solution) was added dropwise over a period of 1.5 hours to a well-stirred solution of butyl borate (115 g., 0.5 mole) in ether at Dry Ice temperature. The mixture was left for 10 hours, during which it warmed to room temperature, then hydrolyzed with dilute hydrochloric acid. The ether layer was mixed with 250 ml. of 75% ethanol and 42.7 g. of ethanolamine. After this solution had been warmed on the steam-bath for a short time, the ester precipitated; weight 109 g., m.p. 182–185°. Recrystallization from aqueous alcohol yielded 64 g. (67%) of the purified ester as fine white needles, m.p. 190–192°.

Aminoethyl Di-α-naphthylborinate.—Naphthylmagnesium bromide (207 g., 1.0 mole) in 350 ml. of ether was added to 29.2 g. (1.2 g. atoms) of magnesium in 500 ml. of ether at a rate so as to maintain a gentle reflux. During the addition, some of the Grignard reagent precipitated. It was dissolved by the addition of 300 ml. of benzene to the mixture. The resulting clear, brown solution was then added over a five-hour period to 125 g. (0.5 mole) of butyl borate in 300 ml. of ether at about −60°. After the mixture had stood overnight, it was hydrolyzed and the organic layer separated and mixed, with external cooling, with 42.7 g. of ethanolamine. The resulting precipitate was washed with 200 ml. of warm 50% water and ethanol; weight of product, 94.5 g. (58%), m.p. 205–206°. This material was further purified by liberating the borinic acid by shaking the ester with ether and hydrochloric acid, and then reprecipitating the ester from alcohol and water with ethanolamine. The melting point of the material thus obtained was still 205–206° (a variation of a few degrees could be made by heating the sample rapidly) and the neutralization equivalent determined by acid titration was 328; the value calculated for $C_{22}H_{20}ONB$ was 325. In one experiment a sample of the borinate was obtained which melted at 191–193°. This material also had a neutralization equivalent of 328, and the boron analysis[5] was 3.20 and 3.30%, as compared to a calculated value of 3.33%. The melting point of this sample gradually increased over a period of several weeks, and both this material and the sample melting at 205–206° became tan colored after standing in air for a few months. Neither aminoethyl diphenylborinate nor II showed discoloration on standing.

Dinaphthylborinic Acid.—A small sample of the aminoethyl ester was hydrolyzed by warming it with 50% methanol–water acidified with hydrochloric acid. When this solution was poured into ice-water a white solid separated, which after recrystallization and drying over 65% sulfuric acid melted at 105–106°. The neutralization equivalent of this borinic acid, determined by titration with alkali in the presence of mannitol, was found to be 290; the value calculated for dinaphthylborinic acid, 282. A portion (0.087 g.) of the acid was reconverted to the aminoethyl ester with ethanolamine in alcohol–water in 74% yield.

Pyrolysis of Dinaphthylborinic Acid.—A sample of the borinic acid (0.50 g.) was heated for six hours at 120–130° in an atmosphere of nitrogen in a side arm test-tube fitted with a cold finger condenser. Naphthalene, 0.22 g. (97%), m.p. 80–81°, sublimed during this heating period. The residue was dissolved in ether, extracted with 10% sodium hydroxide, and acidified. Naphthaleneboronic acid, m.p. 194–196°, 0.2 g. (66%), separated from the solution.

Aminoethyl Phenyl-α-naphthylborinate (II). **(a)**.—α-Naphthylmagnesium bromide (0.049 mole) in about 20 ml. of ether and 3 ml. of benzene was added dropwise to a cold solution (−60°) of butyl benzeneboronate (11.70 g., 0.05 mole, b.p. 102–105° at 2 mm.) in 100 ml. of ether. After the mixture had stood overnight at room temperature it was hydrolyzed with dilute hydrochloric acid. The ether layer was then separated and the ether evaporated. Ethanol (125 ml.), water (20 ml.) and finally ethanolamine (6 ml.) were then added to the residue. The white ethanolamine ester which separated from the solution weighed 10.1 g. (75% yield), m.p. 226–228°. The neutralization equivalent of the crude ester was 284. After a recrystallization from acetone–water, the ester melted at 228–229°.

Anal. Calcd. for $C_{18}H_{18}ONB$: B,[5] 3.93; neut. equiv., 275. Found: B, 3.93, 3.74; neut. equiv., 275.

In another experiment, the ethanolamine ester, m.p. 221–223°, was obtained in 88% yield from a reaction of 0.146 mole of naphthylmagnesium bromide with 0.15 mole of butyl benzeneboronate.

(b).—Butyl naphthaleneboronate (b.p. 170–174° at 1 mm., $n^{27}\text{D}$ 1.5322) was prepared by the distillation of naphthaleneboronic acid with butanol. To 28.4 g. (0.1 mole) of this ester was added 392 ml. of 0.097 *N* phenylmagnesium bromide in ether. The reaction conditions and the method of working up the product were the same that were used in part a. A 90% yield (24 g.) of aminoethyl phenylnaphthylborinate, m.p. 221–222°, was isolated.

β-Aminoisobutyl Diarylborinates.—β-Aminoethyl phenyl-α-naphthylborinate (1.5 g.) was shaken with ether and 6 *N* hydrochloric acid. After all the solid had disappeared, the ether layer was evaporated on a steam-bath and the residual borinic acid mixed with 20 ml. of alcohol and with water just short of the amount to cause turbidity. A solution of 1 ml. of 2-amino-2-methylpropanol in 1 ml. of alcohol was added. After ten minutes the white precipitate was filtered off, washed with alcchol and ether and dried in a vacuum oven. The aminoisobutyl phenylnaphthylborinate thus obtained weighed 1.43 g. (87%) and melted at 199–200°. The neutralization equivalent, determined by titration with hydrochloric acid, was 305; the value calculated for $C_{20}H_{22}ONB$, 303. By addition of water to the filtrate from the borinate, an additional 0.082 g. of the ester (m.p. 195–197°) was obtained, making the total yield 92%.

β-Aminoisobutyl di-α-naphthylborinate (m.p. 208–210°; neutralization equivalent found 355, calculated 353) was prepared similarly from β-aminoethyl dinaphthylborinate. The mixed melting point taken with these two esters showed a depression of only a few degrees at most. The melting points of all of these naphthalene derivatives vary somewhat

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[5] Boron analysis by J. Thoburn.

with the rate of heating. With very slow heating, they melt a few degrees lower (1–4°).

Cleavage of Phenylnaphthylborinic Acid with Dimethylaminoethanol.—A 0.500-g. sample of aminoethyl phenylnaphthylborinate (prepared from butyl naphthaleneboronic acid as described in procedure b) was shaken with ether and 6 *N* hydrochloric acid until all of the solid had dissolved. The ether layer was then evaporated on a steam-bath and a solution of 2 ml. of β-dimethylaminoethanol in 2 ml. of 95% ethanol was added to the residue. After this solution had been warmed on a steam-bath for ten minutes. 25 ml. of water was added over a period of five minutes while the flask was still on the steam-bath. A milky, white solid separated and on cooling it coagulated to an easily filtered precipitate, which after drying weighed 0.200 g. (86%) and was shown to be naphthalene by its melting point (79–80°) and a mixed melting point determination with commercial naphthalene. The filtrate from the naphthalene was clear. Acidification and ether extraction yielded 0.181 g. (82%) of benzeneboronic acid, m.p. 209–215°. The melting point was not depressed when the sample was mixed with pure benzeneboronic acid, but it was depressed over 40° when the sample was mixed with naphthaleneboronic acid.

This cleavage reaction proceeded even at room temperature. Thus a 0.500-g. sample of the aminoethyl borinate treated as described above except that the mixture was maintained at room temperature gave a 19% yield of naphthalene. In this case dilute sodium hydroxide was added to the reaction mixture after the addition of water in order to dissolve unreacted borinic acid. From a similar reaction at room temperature for which the water and sodium hydroxide were added within a few seconds after the dimethylaminoethanol had been added, no naphthalene was obtained. Only a slight turbidity remained after addition of the sodium hydroxide. It is apparent therefore that the naphthalene formed during the treatment with dimethylaminoethanol and not before the addition of this reagent.

A 0.500-g. sample of aminoethyl phenylnaphthylborinate was heated for 10 minutes on a steam-bath with 2 ml. of ethanolamine and 2 ml. of alcohol. The ester did not dissolve in this solution. After cooling, it was filtered off and dried; weight of recovered ester, 0.471 g. (94%). Therefore the ethanolamine did not cleave the carbon boron bond in this compound as did dimethylaminoethanol. The insolubility of the aminoethyl ester in the reaction mixture may be responsible for the lack of reaction.

Cleavage of Phenylnaphthylborinic Acid by Bromine.—A modification of the bromine degradation described by Kuivila and Soboczenski[6] was employed. Phenyl-α-naphthylborinic acid, obtained as an oil by the acid hydrolysis of 4.99 g. (0.018 mole) of the ethanolamine ester (prepared from butyl benzeneboronate, procedure a), was mixed with 25 ml. of 3.3 *M* acetic acid containing 3.2 g. (0.08 mole) of sodium fluoride and 4.92 g. (0.06 mole) of sodium acetate. A solution of 16.0 g. (0.1 mole) of bromine and 14.4 g. of potassium bromide in 50 ml. of 3.3 *M* acetic acid was added over a two-hour period to the stirred, refluxing solution. The resulting mixture was refluxed for an additional 30 minutes, cooled and treated with sodium sulfite to remove unreacted bromine. It was then made alkaline and steam distilled for 30 minutes. The steam-volatile distillate was taken up in 20 ml. of petroleum pentane and 3 ml. of ether, dried over potassium carbonate, and distilled. A 68% yield (1.92 g.) of bromobenzene, b.p. 149–164°, $n^{27.4}_{D}$ 1.5528, was obtained. The higher boiling residue amounted to 1.08 g. This residue was combined with the organic material obtained by steam distilling the original reaction mixture for an additional 30 minutes, and redistilled. There was obtained 1.8 g. of α-bromonaphthalene, b.p. 153–156° at 27 mm., n^{30}_{D} 1.6442. The identity of the bromobenzene and bromonaphthalene was established by a comparison of their spectra with the infrared spectra of authentic samples of these compounds. From the residue there was isolated 0.17 g. of a solid (m.p. 67–70°) which after recrystallization melted at 74–76°. This melting point was not depressed when the sample was mixed with pure 1,4-dibromonaphthalene (m.p. 82–85°) prepared by the bromination of α-bromonaphthalene.

Cleavage of II with Other Reagents.—To 0.5 g. of the borinate (prepared by procedure a) suspended in 10 ml. of 50% alcohol was added 5 ml. of 30% hydrogen peroxide. After a few minutes the mixture began to warm up spontaneously, and the solid ester became a liquid. On cooling, the oil resolidified, was filtered (weight 0.1 g., m.p. 88–90°), and recrystallized from ethanol-water. The melting point of the compound thus obtained (m.p. 92°) was not depressed when the sample was mixed with α-naphthol.

From the distillate of a steam distillation of a solution of 1 g. of the borinate and 2 g. of zinc chloride in 20 ml. of water was isolated naphthalene, which after recrystallization weighed 0.28 g. (49% yield). The first crop of the crystals from the recrystallization melted at 80–81°, and the third crop, at 79–80°. Mixed melting points with naphthalene showed no depression. In the absence of the zinc chloride the cleavage was very slow. Thus the steam distillation of the ester in dilute hydrochloric acid yielded only a trace of naphthalene and the aminoethyl borinate was recovered in 75% yield after the solution had been made basic.

EVANSTON, ILLINOIS

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[6] H. G. Kuivila and E. J. Soboczenski, THIS JOURNAL, **76**, 2575 (1954).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

Organoboron Compounds. IV.[1] Aminoethyl Diarylborinates

BY ROBERT L. LETSINGER AND IVAN SKOOG

RECEIVED NOVEMBER 1, 1954

A practical procedure has been developed for the preparation of aminoethyl diphenylborinate. This involves the reaction of phenylmagnesium bromide with butyl borate at low temperature, isolation of butyl diphenylborinate as a complex with ammonia, and conversion of the ammonia complex to the aminoethyl ester with ethanolamine. Aminoethyl bis-(*p*-bromophenyl)-borinate was prepared by similar techniques. Solid derivatives of arylboronic acids may be obtained by esterifying them with diethanolamine.

The diarylborinic acids represent an important class of organoboron compounds since projected syntheses for a variety of complex types of arylboron compounds involve them as intermediates. Yet no satisfactory procedure for preparing and characterizing these substances has been described. Several diarylborinic acids have been reported[2]; however, the isolation procedures were generally poor, the yields were low or unspecified, and in some cases there were marked divergences in the properties reported for a particular compound. The status of the parent member of the

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[1] This material was presented at the meeting of the American Chemical Society in New York, September, 1954. For paper III in the series see THIS JOURNAL, **76**, 4047 (1954), and paper II, *ibid.*, **76**, 4147 (1954).

[2] (a) A. Michaelis, *Ber.*, **27**, 244 (1894); (b) A. Michaelis and E. Richter, *Ann. Chem.*, **315**, 26 (1901); (c) W. Konig and W. Scharrnbeck, *J. prakt. Chem.*, **128**, 153 (1930); (d) N. N. Melnikov and M. S. Robilsbaya, *J. Gen. Chem., USSR*, **8**, 1768 (1938); *C. A.*, **33**, 4970 (1930); (e) N. N. Melnikov, *J. Gen. Chem., U.S.S.R.*, **6**, 636 (1936); *C. A.*, **30**, 5571 (1936).