was obtained by infrared spectral comparison with the authentic specimen and by its conversion to the corresponding acetate, which had m.p. 156–157° (lit.[15] m.p. 158°) and was identical in all respects with an authentic specimen.

B. From Phenylmagnesium Bromide and Diphenylacetaldehyde.[30]—To a stirred Grignard solution, prepared from 0.70 g. (0.029-g.-atom) of magnesium turnings, 5.00 g. (32.0 mmoles) of bromobenzene, and 10 ml. of ether, was added in a nitrogen atmosphere and at room temperature during the course of 15 min. a solution of 5.00 g. (25.5 mmoles) of diphenylacetaldehyde[27] in 15 ml. of ether. The resulting mixture was heated under reflux for 1 hr. and then cooled in an ice bath while 20 ml. of a saturated solution of ammonium chloride in ice–water was added slowly with stirring. The ether layer was removed and the aqueous phase was extracted twice with 50-ml. portions of ether. The combined ethereal extracts were washed twice with 30-ml. portions of water, dried, and concentrated under reduced pressure to give 6.84 g. of a solid residue. Two recrystallizations of the solid residue from ligroin (b.p. 66–75°) afforded 4.5 g. (64%) of 1,2,2-triphenylethanol (**9**), m.p. 87–88° (lit.[15] m.p. 86–87°). The corresponding acetate, isolated as colorless needles from a 1:1 mixture of benzene–ligroin, had m.p. 155.5–156.0° (lit.[15] m.p. 158°).

It was of interest to determine the mixture melting point of **9** and its isomer **10** since both carbinols have practically the same melting point. A genuine specimen of **10**, prepared from the reaction of phenylmagnesium bromide with deoxybenzoin according to the method of Klages and Heilmann,[17] had m.p. 88–89° (from ligroin), depressed to 83.5–89.0° when mixed with an equal weight of **9**. The infrared spectra in CCl_4 solution of the two carbinols are readily distinguishable.

Reaction of Phenyllithium with 1,1-Diphenylethylene Oxide (6). Formation of 1,1,2-Triphenylethanol (10) and 1,2,2-Triphenylethanol (9).—The reaction in an atmosphere of dry nitrogen of 0.019 mole of ethereal phenyllithium with 4.32 g. (0.022 mole) of 1,1-diphenylethylene oxide was carried out at reflux temperature for 2 hr. as described by Cristol, Douglass, and Meek.[4] The crude reaction product was a straw-colored oil which weighed 4.83 g. Its infrared spectrum (CCl_4 solution) displayed strong absorption in the hydroxyl region at 2.73 μ and revealed the presence of 8% diphenylacetaldehyde, *ca.* 1% benzophenone, and some unchanged epoxide. The identities of the carbonyl-containing components were established by gas chromatography using authentic samples of these compounds for comparison of retention times. Thin layer chromatography (4:1 mixture of hexane–ethyl acetate developer) showed that the crude reaction product contained a large amount of 1,1,2-triphenylethanol (**10**) and a relatively smaller amount of the isomeric carbinol, 1,2,2-triphenylethanol (**9**). Chromatography of a 2.00-g. portion of the oil on a silica gel column (43 cm. × 2.0 cm. diameter) using successively hexane and mixtures of hexane–ethyl acetate of increasing polarity as eluents and thin layer chromatography to monitor the fractions collected, gave five fractions (1–5, in order of appearance).

Biphenyl (1), 83 mg., m.p. 65–68° (lit.[28] m.p. 70°), was identified by a mixture melting point and by infrared spectral comparison with an authentic sample.

Fraction 2 was identified as triphenylethylene, 202 mg., m.p. 64–67° (lit.[17] m.p. 62°); the infrared spectrum of this material was exactly like that of an authentic sample of the ethylene.

The infrared spectrum of fraction 3, 356 mg. of an oil, indicated that it was mainly a mixture of diphenylacetaldehyde and benzophenone.

Fraction 4, identified as 1,1,2-triphenylethanol (**10**), 1.02 g. (47%), m.p. 86–88° (lit.[17] m.p. 88°), melted at 88–89° after one recrystallization from ligroin (b.p. 66–75°). Its infrared spectrum (CCl_4 solution) was indistinguishable from the spectrum of an authentic sample.[17]

Fraction 5, identified as 1,2,2-triphenylethanol (**9**), 52 mg. (2.4%), had m.p. 86.5–87.0° (lit.[15] m.p. 86°) after one recrystallization from a 1:1 mixture of benzene–hexane. The mixture melting point with an authentic sample, whose preparation is described above, was unchanged; both samples had identical infrared spectra in CCl_4 solution.

Carbinol **9** could be isolated more conveniently and in higher yield as its acetate. Thus, heating of the crude reaction mixture (1.70 g.) under reflux for 45 min. with 5 ml. of acetic anhydride gave a straw-colored solution which was poured onto a mixture of ice (15 g.) and water (15 ml.). After the excess anhydride had been hydrolyzed, the resulting oily suspension was extracted twice with 50-ml. portions of ether and the combined ether extracts were washed successively with water (two 50-ml. portions). Concentration of the dried solution under reduced pressure gave an oil which was taken up in 7 ml. of a 1:1 mixture of benzene–hexane, seeded with an authentic sample of the acetate of **9**, and then refrigerated for 4 days. The colorless needles thus obtained weighed 130 mg. (6.2%) and had m.p. 150–155°, which was raised to 155.5–156.5° (lit.[15] m.p. 158°) after one recrystallization from the same solvent mixture. This compound was shown by a mixture melting point determination and infrared spectral comparison to be identical with the acetate derived from the carbinol prepared above by the addition of phenylmagnesium bromide to diphenylacetaldehyde.

The reaction of phenyllithium with 1,1-diphenylethylene oxide was also carried out at room temperature for 24 hr.; the results of this experiment were essentially the same as those realized when the reaction was carried out at reflux temperature for 2 hr.

(30) We are indebted to Mr. F. X. Doyle, S.J., for carrying out this reaction.

Organoboron Compounds. XX. Chemistry of Some 1-Naphthaleneboronic Acids with Substituents in the 8-Position[1]

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The preparation and some properties of naphthalene compounds with a borono group in the 1-position and a benzimidazolyl, borono, or carboxyl group in the 8-position are described.

The 1,8-disubstituted naphthalene compounds have provided a convenient system for investigating reactions of functional groups held close together in a fixed spatial relationship.[4] In the present paper we report the synthesis and characterization of naphthalene compounds which possess a borono group in the 1-position and a benzimidazolyl, borono, or carboxyl group in the 8-position. Unusual chemical properties resulting from the juxtaposition of the functional groups are noted.

Compound I.—The synthesis of 2-(8-borono-1-naphthyl)benzimidazole (I) was patterned after the procedure used for preparing 2-(2-boronophenyl)benzimida-

(1) This research was supported by the Materials Research Center of Northwestern University and by the National Science Foundation. Paper XIX: R. L. Letsinger, "Brown–Nitrogen Chemistry," Advances in Chemistry Series 42, American Chemical Society, Washington, D. C., 1964, p. 1. Paper XVIII: J. D. Morrison and R. L. Letsinger, *J. Org. Chem.*, **49**, 3405 (1964).

(2) Dow Chemical Co. Fellow, 1961–1962.

(3) National Science Foundation Fellow, 1958–1959.

(4) R. L. Letsinger and J. A. Gilpin, *J. Org. Chem.*, **49**, 243 (1964), and earlier papers in the series on *peri*-substituted naphthalene compounds.

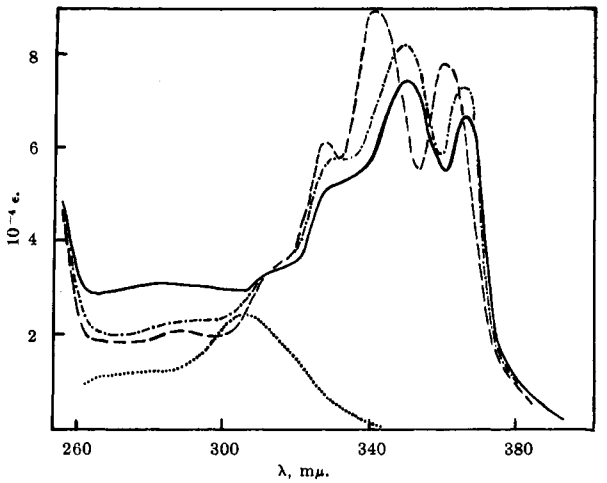


Figure 1.—Ultraviolet absorption spectra of 2-(8-borono-1-naphthyl)benzimidazole in 95% ethanol: (———) neutral solution; (– · – · –) 0.05 *M* in HCl; (– – – –) 0.03 *M* in sodium hydroxide. The spectrum of 2-(1-naphthyl)benzimidazole is indicated for comparison (· · · · ·).

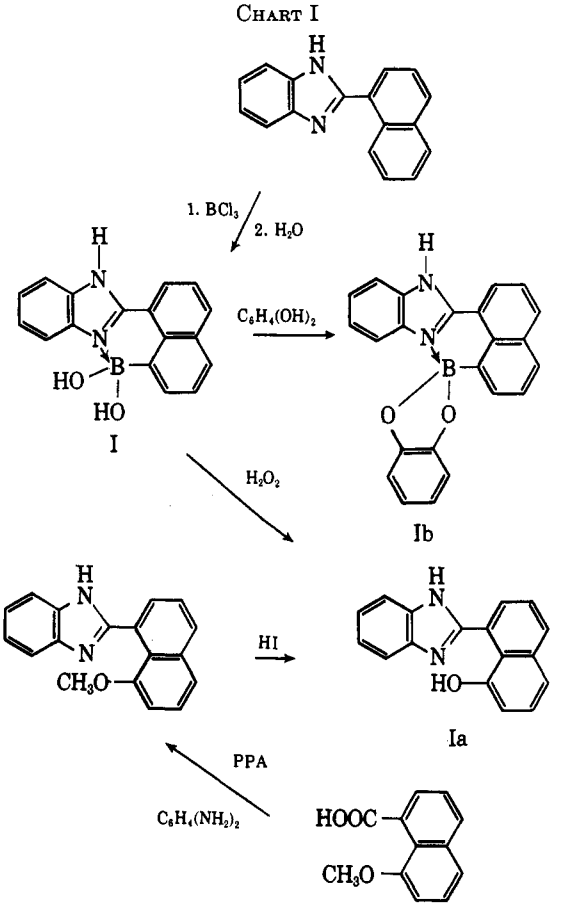
zole.[5] Thus, boron trichloride was passed into a melt of 2-(1-naphthyl)benzimidazole at 310–320° in the absence of an added catalyst. Following hydrolysis, two materials were obtained. One, soluble in ethanol, dimethylformamide, acetic acid, aqueous hydrochloric acid, and aqueous alkali, proved to be the desired 2-(8-borono-1-naphthyl)benzimidazole. It was isolated in 24% yield. The other, insoluble in alcohol and in 10% aqueous sodium hydroxide, appeared to be polymeric and was not identified.[6]

It was then found (see Chart I) that boron could be introduced into 2-(1-naphthyl)benzimidazole much more efficiently by merely warming the imidazole with boron trichloride in benzene. Hydrolysis of the crystalline chloro derivative which precipitated from solution afforded 2-(8-borono-1-naphthyl)benzimidazole in essentially quantitative yield. The remarkable ease and selectivity of this substitution reaction may be attributed to the proximity of the carbon at the 8-position in the naphthyl group and the nitrogen of the imidazole ring and to the general reactivity of the α-position in naphthalene compounds. Under the same conditions 2-phenylbenzimidazole failed to undergo boronation. It is interesting that the yield of I was lower when the reaction was carried out in boiling toluene.

The position at which substitution occurred was established by oxidizing I with hydrogen peroxide to 2-(8-hydroxy-1-naphthyl)benzimidazole (Ia), a compound synthesized independently for comparison from *o*-phenylenediamine and 8-methoxy-1-naphthoic acid. Of further assistance in the characterization of I, which did not melt below 360°, was the preparation of a crystalline, sharp-melting catechol ester derivative (Ib).

The infrared spectrum of I, like that of 2-(2-boronophenyl)benzimidazole,[5] was consistent with a structure possessing a nitrogen–boron coordinate bond. Specifically, absorption was very strong at 8.56 μ (in the related 8-bromo-, 8-methoxy-, and 8-hydroxynaphthyl derivatives absorption was very weak in the 8.35–8.65-μ region), there were no strong bands near 7.5 μ, and absorption in the 3.6–4.2-μ region resembled that of 2-(2-boronophenyl)benzimidazole.[5]

CHART I



Ultraviolet spectra for compound I in neutral, acidic, and basic solutions are presented in Figure 1. In contrast to the case with 1-methyl-2-(2-boronophenyl)benzimidazole[5] and 2-(2-boronophenyl)benzimidazole,[1] changes in the acidity and basicity of the medium had only a small effect upon the spectrum. This fact suggests that the naphthyl and benzimidazole rings in I are coplanar in the acidic and basic solutions.[7] It may therefore be inferred that the boron–nitrogen bond in I is not disrupted under these conditions.

A striking chemical property of 2-(2-boronophenyl)-benzimidazole is the ability to catalyze a reaction between collidine and chloroethanol.[5] This property is associated with the proximity of the benzimidazolyl and borono groups. It is interesting that compound I, in which the boron and nitrogen atoms constitute part of a six-membered ring, also serves as a catalyst in the collidine–chloroethanol reaction. Indeed, I and 2-(2-boronophenyl)benzimidazole proved to be about equally effective in this regard.

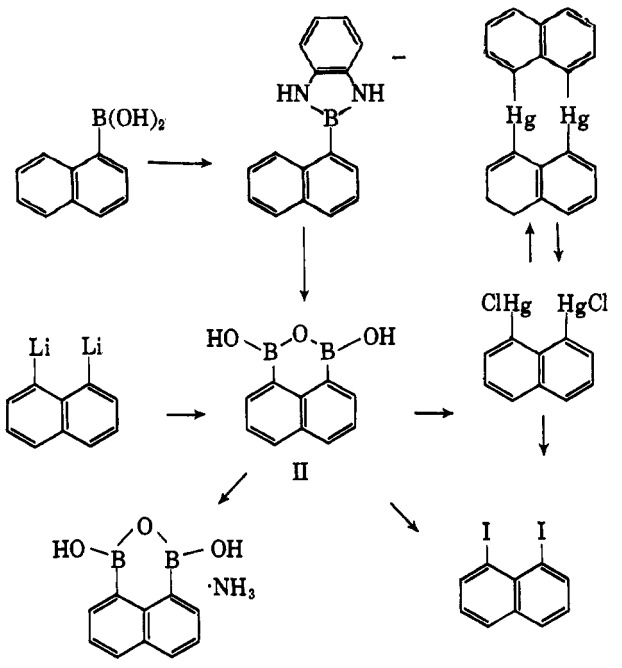
Compound II.—The successful boronation of the 2-arylbenzimidazoles led to development of a novel method for introducing boron selectively into the 8-position of 1-naphthaleneboronic acid. This method utilizes the diazaborole system, which is structurally

(5) R. L. Letsinger and D. B. MacLean, *J. Am. Chem. Soc.*, **85**, 2230 (1963).

(6) This material was unusually resistant to chemical attack. It was not degraded by hydrogen peroxide in either acidic or alkaline solution, by sodium hydroxide in boiling ethanol, or by aqueous silver nitrate. The only chemical degradation achieved was conversion to 2-(1-naphthyl)benzimidazole by the action of concentrated sulfuric acid. The substance may be a product of diboronation.

(7) See ref. 5 and 1 (paper XIX) for a discussion of the effect of conformation on the spectra of 2-arylbenzimidazoles.

CHART II



similar to the benzimidazole group, as a directing agent in the boronation reaction. It also depends upon the fact that diazaboroles can readily be formed from and converted to areneboronic acids.[8] The preparative scheme and the reactions used in characterizing the product are summarized in Chart II.

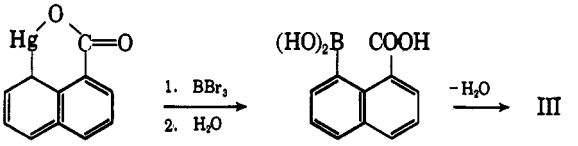
The reaction of 1-naphthaleneboronic acid with *o*-phenylenediamine proceeded smoothly to give the diazaborole,[8] which on treatment with boron tribromide in the presence of aluminum[9] and subsequent hydrolysis yielded a mixture of the diboronic acid and 1-naphthaleneboronic acid. Removal of the latter as an insoluble complex with diethanolamine[10] and dehydration of the remaining diboronic acid afforded compound II in 38% yield.

In an alternate preparative scheme 1,8-dilithionaphthalene, obtained by a metal–halogen exchange reaction between butyllithium and 1,8-dibromonaphthalene,[11] was treated with butyl borate and the product was hydrolyzed. 1,8-Naphthalenediboronic acid was obtained in 71% yield. It readily lost a molecule of water on drying *in vacuo* to give a partial anhydride II. The infrared spectrum of II showed strong absorption at 2.92 μ due to OH and a weaker band at 14.79 μ which may arise from the B–O–B structure.[12] In consideration of the proximity of the boron groups, the heterocyclic partial anhydride formula in Chart II is a reasonable structure for this compound.

Both boron atoms in II could be replaced by I, H, or ClHg by reaction with iodine, phosphoric acid, or mercuric chloride. The most striking effect of bringing two boronic acid groups together in the same molecule was the increase in acidity. Compound II titrated in aqueous alcohol as a monobasic acid with an apparent pK_a of 8.1. Another manifestation of the acidity was the formation of a stable, crystalline adduct with ammonia. In general, ammonium salts of boronic acids decompose readily at room temperature. The relatively high acidity of the HO–B–O–B–OH system may be attributed to the electron-withdrawing effect which one boron exerts upon the other.

Compound II was somewhat more resistant to deboronation than 1-naphthaleneboronic acid. When 1-naphthaleneboronic acid was heated for 12 hr. at 100° with 10% hydrochloric acid and with 10% aqueous sodium hydroxide, it was recovered in 16 and 43% yield, respectively. Under the same conditions the recovery of II was 77 and 86%. It was shown in control experiments that the isolation method employed was essentially quantitative for both compounds.

Compound III.—8-Borono-1-naphthoic acid was obtained by the reaction of boron tribromide with anhydro-8-hydroxymercuri-1-naphthoic acid. Like the diboronic acid it easily lost water to give a partial anhydride III. The position of attachment of the boron atom was verified by conversion of III to 8-bromo-1-naphthoic acid, 8-hydroxy-1-naphthoic acid, and anhydro-8-hydroxymercuri-1-naphthoic acid.



Compound III titrated as a monobasic acid. It was not possible to titrate the $-B(OH)_2$ group even in the presence of mannitol. The most distinctive chemical property of III was the deboronation which occurred in aqueous methanol. The extent of deboronation could be determined by neutralizing the carboxylic acid and then titrating free boric acid with sodium hydroxide in the presence of mannitol. As shown in Table I, (a) compound III lost boron readily when heated in aqueous methanol, and (b) the deboronation reaction was inhibited by either hydrochloric acid or by sodium hydroxide. These results are consistent with the view that the reaction proceeds by attack of a proton on an intermediate in which carboxylate is coordinated to boron (*e.g.*, IIIa).[13]

TABLE I

DEBORONATION OF 8-BORONO-1-NAPHTHOIC ACID[a]

Added reagent	% deboronation
Water	50
Hydrochloric acid	<7
Aqueous sodium hydroxide	<7

[a] In each case 2 ml. of the "added reagent" (water, 10% hydrochloric acid, or 10% aqueous sodium hydroxide) was added to 0.08 g. of the boronic acid in 5 ml. of methanol. The mixture was then refluxed 4.7 hr., cooled, and titrated.

(8) R. L. Letsinger and S. B. Hamilton, *J. Am. Chem. Soc.*, **80**, 5411 (1958).

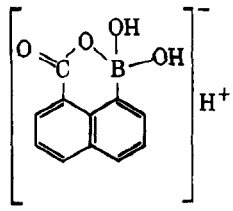
(9) Under the conditions used for boronating the 2-arylbenzimidazoles the yield of diboronic acid was low. The yield was improved by using boron tribromide in the presence of aluminum, an adaptation of a method developed by E. L. Mutterties [*ibid.*, **82**, 4163 (1960)] for introducing boron into aromatic hydrocarbons.

(10) R. L. Letsinger and I. Skoog, *ibid.*, **77**, 2491 (1955). In contrast to the simple areneboronic acids, compound II did not form a crystalline derivative with diethanolamine.

(11) R. L. Letsinger, J. A. Gilpin, and W. J. Vullo, *J. Org. Chem.*, **27**, 672 (1962).

(12) This suggestion is based on the fact that the related cyclic anhydrides of areneboronic acids (boroxines) exhibit a characteristic absorption band in the 680–705-cm.$^{-1}$ region (14.7–14.2 μ): H. R. Snyder, M. S. Konecky, and W. J. Lennarz, *J. Am. Chem. Soc.*, **80**, 3611 (1958).

(13) For a detailed discussion of the mechanism of protodeboronation of areneboronic acids, see K. V. Nahabedian and H. G. Kuivila, *ibid.*, **83**, 2167 (1961).



IIIa

Experimental

The ultraviolet spectra were determined with either a Beckman DK2 or a Cary Model 11 spectrophotometer; the infrared spectra were obtained with a Baird Model AB2 instrument using potassium bromide disks. Analyses were carried out by Miss H. Beck or by the Galbraith Laboratories, Knoxville, Tenn.

2-(8-Borono-1-naphthyl)benzimidazole (I).—To a solution of 1.2 g. (5 mmoles) of 2-(1-naphthyl)benzimidazole[14] in 500 ml. of hot benzene was added 3.0 g. (26 mmoles) of boron trichloride in 20 ml. of benzene. The resulting solution was heated at reflux for 2 hr., during which time yellow crystals formed on the sides of the vessel. Filtration afforded 1.7 g. of crystalline product, which was dissolved in 20 ml. of 10% sodium hydroxide solution. On neutralization with 5 *N* hydrochloric acid at 5°, 1.4 g. (95%) of the borononaphthylbenzimidazole precipitated; λ_{max} 2.90, 3.25, 6.10, 6.29, 6.44, 6.60, 6.82, 7.18, 7.28, 7.67, 8.21, 8.53, 8.81, 9.41, 9.90, 12.03, 12.80, and 13.35 μ. It did not melt below 360° and did not burn completely in an attempted combustion analysis; accordingly, the compound was characterized by means of derivatives. Thus, on warming a solution of 0.29 g. (1 mmole) of the borononaphthylbenzimidazole in 4 ml. of ethanol with 0.11 g. (1 mmole) of catechol in 4 ml. of 1:1 ethanol–benzene for 2 hr. and then cooling the solution, 0.27 g. (75%) of the **catechol ester of 2-(8-borono-1-naphthyl)benzimidazole** was obtained. After two recrystallizations from ethanol it melted at 324–325° (sealed tube).

Anal. Calcd. for $C_{23}H_{15}BN_2O_2$: C, 76.25; H, 4.18; N, 7.74. Found: C, 76.09; H, 4.36; N, 7.82.

The other derivative used in characterizing the borononaphthylbenzimidazole was the product of oxidation with hydrogen peroxide. 2-(8-Borono-1-naphthyl)benzimidazole (0.25 g., 0.87 mmole) was dissolved in a minimum of 10% aqueous sodium hydroxide and then reprecipitated by addition of 10% aqueous sulfuric acid. The resulting gelatinous, acidic suspension was heated to 60° with 1 ml. of 30% hydrogen peroxide, whereupon most of the solid dissolved. The mixture was heated for an additional 5 min. at 60° and filtered while hot. On cooling, the filtrate deposited 0.22 g. (80%) of the sulfate salt of the hydroxynaphthylbenzimidazole.

Anal. Calcd. for $C_{34}H_{24}N_4O_2 \cdot H_2SO_4 \cdot H_2O$: C, 64.14; H, 4.43; N, 8.80. Found: C, 64.75; H, 4.31; N, 8.99.

This salt was dissolved in 4 ml. of pyridine. Addition of water then afforded 0.14 g. (62% based on I) of **2-(8-hydroxy-1-naphthyl)benzimidazole**, m.p. 176–181°. A sample recrystallized from benzene melted at 186.5–187°. The infrared spectrum showed strong absorption at 2.90, 6.48, 7.02, 7.50, 7.80, and 12.10 and a broad band at 13.0–13.5 μ.

Anal. Calcd. for $C_{17}H_{12}N_2O$: C, 78.44; H, 4.65; N, 10.76. Found: C, 78.56; H, 4.88; N, 10.50.

2-(8-Hydroxy-1-naphthyl)benzimidazole from 8-Methoxy-1-naphthoic acid.—A mixture of 1.1 g. (10 mmoles) of *o*-phenylenediamine, 2.0 g. (10 mmoles) of 8-methoxy-1-naphthoic acid, and 15 g. of polyphosphoric acid was heated at 140° for 4 hr. with stirring. The hot reaction mixture was poured into ice and aqueous sodium hydroxide and the pinkish precipitate was filtered off and dried.[15] It was extracted with boiling 6 *N* hydrochloric acid and the extract was cooled and neutralized with alkali. The resulting solid was dissolved in ethyl acetate. Concentration of the ethyl acetate solution afforded a solid, which on recrystallization from benzene yielded 0.35 g. (13%) of **2-(8-methoxy-1-naphthyl)benzimidazole**: m.p. 234–235°; λ_{max} 2.9, 6.21, 6.50, 6.88, 7.10, 7.31, 7.88, 7.95, 8.92, 9.44, 10.25, 12.12, 13.00, and 13.40 μ.

Anal. Calcd. for $C_{18}H_{14}N_2O$: N, 10.21. Found: N, 9.83.

A portion (0.30 g. 11 mmoles) of the methoxynaphthylbenzimidazole was heated with a large excess of 47% hydriodic acid for 5 hr. On cooling, the hydrogen iodide salt of the benzimidazole derivative crystallized out. The mixture was made strongly basic, residual solid matter was filtered off, and the solution was then acidified with sulfuric acid. The resulting sulfate salt was worked up as in the case of the product from the hydrogen peroxide oxidation to yield 0.12 g. (42%) of 2-(8-hydroxy-1-naphthyl)benzimidazole, m.p. 183–184°. Recrystallization from benzene gave a product, m.p. 186–187°, which had an infrared spectrum identical with that for the product obtained by degradation of I. A mixture melting point of the two samples showed no depression (m.p. 186–187°).

Catalysis by I.—Preheated chloroethanol was added at zero time to a mixture of 0.75 mmole of the boron catalyst and 5.0 mmoles of collidine to give a total volume of 10 ml. at 89°. The solution was held at 89° and the rate of liberation of chloride ion was determined by removing aliquots of the solution at suitable intervals and titrating for chloride ion by the Volhard method. As in previous cases,[5] pseudo-zero-order kinetics were obtained until about 5 mmoles of chloride ion had been liberated. The data are summarized in Table II.

TABLE II

CATALYSIS BY BORONOARYLBENZIMIDAZOLES

Boron compound	k_{obsd}, mole l.$^{-1}$ hr.$^{-1}$	$\frac{k_{obsd} - k_{blank}}{[catalyst]}$ hr.$^{-1}$
I	0.0312	0.35
2-(2-Boronophenyl)benzimidazole	0.0302	0.34
None (blank)	0.0050	..

1,8-Naphthalenediboronic Acid from 1,8-Dilithionaphthalene.—To an ether solution of 1,8-dilithionaphthalene, prepared from 3.0 g. (10 mmoles) of 1,8-dibromonaphthalene,[11] at −75° was added dropwise an excess (8.6 ml.) of tri-*n*-butyl borate in 90 ml. of ether. After standing overnight at room temperature the mixture was treated with 2 *N* hydrochloric acid and the layers were separated. Extraction of the ether layer with dilute aqueous sodium hydroxide and acidification of the alkaline extracts afforded 1.6 g. (71% based on dibromonaphthalene) of 1,8-naphthalenediboronic acid as a solid precipitate. On heating, a sample melted at 180–190° but it resolidified and remelted at about 280°. Recrystallization of the product from aqueous ethanol yielded the partial anhydride II as almost white crystals: m.p. 280–285°; λ_{max} (infrared) 2.92, 6.27, 6.63, 7.00, 7.50, 7.92, 8.31, 9.42, 11.30, and 12.73 μ; λ_{max}^{EtOH} (ultraviolet) 228.5 mμ (log ε 4.66), 291 (3.90), 303 (4.05), and 315 (3.93). Titrations of samples of the diboronic acid which had been dried at room temperature gave neut. equiv. 217 ± 7; the calculated value for $C_{10}H_{10}B_2O_4$ is 216. The end point was sharp even though no mannitol was used. The acidity of a solution of the diboronic acid was, however, increased on addition of mannitol. There was no indication of a second acidic group from the titration data. A sample of the partial anhydride obtained from the recrystallization was further dried over P_2O_5 and titrated with aqueous sodium hydroxide. Titration of the compound in aqueous ethanol gave neut. equiv. 199; with the sample in aqueous dimethylformamide, the value was 200. The value calculated for $C_{10}H_8B_2O_3$ is 198. The derivatives described below were prepared from the partial anhydride.

Anal. Calcd. for $C_{10}H_8B_2O_3$: C, 60.7; H, 4.08. Found: C, 54.9[16]; H, 4.28.

Derivatives of Compound II. A. Ammonia Complex.—Ammonia gas was passed through a solution of II (0.30 g., 1.5 mmoles) in anhydrous ether until precipitation ceased. The complex (0.288 g., 88%), isolated by filtration, melted with decomposition at 293–296° in a sealed capillary tube.

(14) 2-(1-Naphthyl)benzimidazole, m.p. 271–272°, was prepared in 60% yield by the method of D. W. Hein, R. J. Alheim, and J. J. Leavitt [*J. Am. Chem. Soc.*, **79**, 427 (1957)].

(15) When higher temperatures (170 or 190°) were used in the reaction, a black precipitate was obtained which was difficult to filter and to purify.

(16) In common with many areneboronic acids, some of the naphthaleneboronic acid derivatives in this series did not undergo complete combustion in the analytical train, as evidenced by appearance of a black boron carbide at the completion of the analysis. Therefore, the carbon analyses may be low and without quantitative significance. The results are reported, however, since the hydrogen values are meaningful.

Anal. Calcd. for $C_{10}H_{11}B_2NO_3$: C, 55.9; H, 5.16; N, 6.5. Found: C, 55.2; H, 5.16; N, 6.3.

B. 1,8-Diiodonaphthalene.—A mixture containing 0.11 g. (0.55 mmole) of II and excess iodine (0.8 g.) in 4 ml. of 15% aqueous potassium hydroxide was allowed to stand at room temperature for 48 hr.[17] After addition of dilute hydrochloric acid and sodium sulfite, the mixture was extracted with ether. On concentration of the ether layer, 1,8-diiodonaphthalene, m.p. 104–107° (lit.[18] m.p. 109°), was obtained in 48% yield (0.085 g.). The melting point was not depressed when the compound was mixed with an authentic sample of diiodonaphthalene.

C. Naphthalene.—A mixture of 0.14 g. (0.71 mmole) of II and 10 ml. of phosphoric acid was warmed on a steam bath for 24 hr. and then poured into water. Extraction with ether, washing the ether layer with aqueous sodium hydroxide, and evaporation of the ether afforded 0.082 g. (97%) of naphthalene, m.p. 75–80°.

D. 1,4,5-Tribromonaphthalene.—A solution of bromine (2.5 ml.) in water saturated with potassium bromide was added to 0.20 g. (1.0 mmole) of II in 15 ml. of acetic acid. After standing 10 min. at room temperature the mixture was poured into water and excess bromine was removed by addition of sodium bisulfite. 1,4,5-Tribromonaphthalene, 0.16 g. (46%), m.p. 70–76°, was isolated by filtration. Recrystallization from ethanol gave a sample melting at 83.5–85° (lit.[19] m.p. 86–87°. Formation of a tribromonaphthalene was not unexpected since 1,8-dibromonaphthalene is brominated under these conditions.

To confirm the structure of the tribromonaphthalene, the 1,4,5-isomer was prepared independently by treating a suspension of 12.1 g. of the silver salt of 4-bromo-1,8-naphthalic acid[20] in 130 ml. of carbon tetrachloride with 2.6 ml. of bromine in 40 ml. of carbon tetrachloride. Isolation as in the case just described gave 2.8 g. (32%) of 1,4,5-tribromonaphthalene, which on recrystallization from ethanol melted at 85–86°. The infrared spectrum was indistinguishable from that of the compound prepared from II.

Anal. Calcd. for $C_{10}H_5Br_3$: C, 32.91; H, 1.38. Found: C, 32.88; H, 1.34.

1,8-Naphthalenediboronic Acid from 1-Naphthaleneboronic acid.—The *o*-phenylenediamine derivative of 1-naphthaleneboronic acid was prepared from the boronic acid by the method of Letsinger and Hamilton.[8] A mixture containing 11.7 g. (0.0048 mole) of this derivative, 0.46 g. (0.017 g.-atom) of aluminum turnings, and several drops of methyl iodide in 40 ml. of chlorobenzene was treated under nitrogen with 7 ml. (0.074 mole) of boron tribromide. The reaction mixture was cooled in a water bath to moderate the initially vigorous reaction. Then, after standing 9 hr. at 52–55°, the mixture was poured cautiously onto ice chips, and several drops of hydrochloric acid was added. The product was taken up in ether and extracted from the ether with dilute aqueous sodium hydroxide. Acidification afforded a precipitate which, as indicated by the infrared spectrum, was a mixture of 1,8-naphthalenediboronic acid and 1-naphthaleneboronic acid. For separation, the crude product was dissolved in warm aqueous ethanol and treated with a solution of 5 ml. of diethanolamine in water. After several minutes of warming on a steam bath the solution deposited white crystals of the diethanolamine derivative of 1-naphthaleneboronic acid: m.p. 238–241° (lit.[10] m.p. 242–243), 1.8 g. (16%). Acidification afforded partially purified 1,8-naphthalenediboronic acid. This material was again subjected to the action of diethanolamine. Acidification of the resulting solution then gave the diboronic acid free from 1-naphthaleneboronic acid, as shown by the absence of bands at 8.5, 8.9, and 12.35 μ in the infrared spectrum. The yield of the diboronic acid was 3.9 g. (38%), and the infrared spectrum was identical with that for the product obtained from 1,8-dilithionaphthalene.

1,8-Bischloromercurinaphthalene.—A sample of the diboronic acid anhydride (0.100 g. 0.50 mmole) prepared from 1-naphthaleneboronic acid was converted to an organomercurial by warming on a steam bath in aqueous ethanol for several minutes with excess mercuric chloride. Crystalline 1,8-bischloromercurinaphthalene separated from the solution: 0.169 g. (56%), m.p. 341–343°.

Anal. Calcd. for $C_{10}H_6Cl_2Hg_2$: C, 20.07; H, 1.01. Found: C, 19.94; H, 1.05.

The same compound (infrared spectrum) was obtained in 89% yield (based on 1,8-dibromonaphthalene used in preparing the lithium derivative) by treating 1,8-dilithionaphthalene[11] with excess mercuric chloride.

On standing at room temperature for 72 hr. with 3 g. of iodine and 1 g. of sodium hydroxide in 26 ml. of water, 0.647 g. of 1,8-bischloromercurinaphthalene yielded 0.0381 g. (93%) of 1,8-diiodonaphthalene, m.p. 105–108°.

Di-1,8-naphthylenedimercury, m.p. 377° dec., was obtained in 94% yield (1.312 g.) by refluxing a mixture of 1,8-bischloromercurinaphthalene (2.5635 g., 4.3 mmoles) and sodium iodide (4.631 g., 31 mmoles) in 100 ml. of 95% ethanol for 50 hr., cooling the mixture, and filtering off the product. For analysis it was recrystallized from dimethylformamide. The most significant peaks in the infrared spectrum were found at 6.75, 11.90, 12.35, and 12.83 μ.

Anal. Calcd. for $C_{20}H_{12}Hg_2$: C, 36.8; H, 1.85. Found: C, 36.0; H, 1.93.

When the dinaphthylenedimercury compound was heated in refluxing acetone with mercuric chloride for 18 hr. it was reconverted to bischloromercurinaphthalene.

8-Borono-1-naphthoic Acid (III).—Boron tribromide (10 ml., 0.106 mole) was added with stirring to a suspension of 12.5 g. (0.0338 mole) of anhydro-8-hydroxymercuri-1-naphthoic acid[21] in 83 ml. of chlorobenzene. The temperature was maintained near 25°. After 15 min. the mixture was poured onto ice and sodium bicarbonate. After the mixture had been washed with ether and filtered, the filtrate was acidified and extracted with ether. On evaporation, 3.4 g. of crude product (contaminated with some naphthoic acid as shown by a band at 12.95 μ in the infrared spectrum) was obtained. Naphthoic acid was removed by careful washing with ether (until the 12.95-μ band was no longer diminished in the spectrum). There remained 2.1 g. (31%) of 8-borono-1-naphthoic acid, m.p. 147–149°. The neutralization equivalent of the sample dried in air at room temperature was 217 ± 1, in good agreement with the value calculated for $C_{11}H_9BO_4$, 216. When the compound was recrystallized from acetone–hexane and dried over P_2O_5 at 56° (2 mm.) for several hours it underwent dehydration to give a product which corresponded to an anhydride: λ_{max}^{EtOH} 230 mμ (log ϵ 4.39) and 314 mμ (log ϵ 3.85). The major absorption bands in the infrared spectrum occurred at 3.10, 5.92, 6.30, 6.67, 7.03, 7.65, 8.08, 9.40, 12.70, and 12.95 μ. 8-Borono-1-naphthoic acid can dehydrate in a variety of ways. The presence of strong absorption at 3.1 μ, characteristic of –BOH, and absence of absorption in the 3.6–4-μ region suggests that water was lost between the boronic acid and carboxyl groups to give HO–B–O–C=O.

Anal. Calcd. for $C_{11}H_7BO_3$: C, 66.72; H, 3.56; neut. equiv., 198. Found: C, 64.3[16]; H, 3.77; neut. equiv., 199.

Derivatives of III. A. 8-Bromo-1-naphthoic Acid.—Compound III (0.1417 g., 0.715 mmole) was added to 1 ml. of bromine in a concentrated aqueous potassium bromide solution. After a few minutes several milliliters of acetic acid were added, excess bromine was reduced by addition of sodium bisulfite, and the organic product was taken up in ether. Extraction of the ether layer with aqueous sodium bicarbonate and acidification of the extracts yielded 0.0702 g. (39%) of 8-bromo-1-naphthoic acid, m.p. 150–170°. A single recrystallization gave white crystals of the bromonaphthoic acid, m.p. 167–173°, identified by the infrared spectrum and a mixture melting point with a sample prepared by the method of Rule, *et al.*[21]

B. 8-Hydroxy-1-naphthoic Acid.—A solution containing 0.1046 g. of III and 4 ml. of 30% hydrogen peroxide in several milliliters of acetic acid was allowed to stand 10 min. at room temperature before it was poured into 30 ml. of water. Extraction with ether, extraction of the ether layer with an aqueous alkaline solution, and acidification of the aqueous portion gave 0.0693 g. (70%) of 8-hydroxy-1-naphthoic acid, m.p. 161–164°. With one recrystallization from ethyl ether–hexane white crystals melting at 168–169.5° were obtained (lit.[22] m.p. 169°).

(17) This is the method used by A. D. Ainley and F. Challenger [*J. Chem. Soc.*, 2171 (1930)] for displacing boron in a boronic acid by iodine.

(18) R. Scholl, C. Seer, and R. Weitzenböck, *Ber.*, **43**, 2202 (1910).

(19) J. Salkind and M. Belikoff, *ibid.*, **66**, 955 (1931).

(20) H. G. Rule and S. B. Thompson, *J. Chem. Soc.*, 1764 (1937).

(21) H. G. Rule, W. Pursell, and R. R. H. Brown, *ibid.*, 168 (1934).

(22) A. Ekstrand, *J. prakt. Chem.*, [2] **38**, 241, 278 (1888).

Major bands in the infrared spectrum were found at 3.00, 5.92, 7.85, 12.20, and 13.20 μ, and the compound gave a violet color with aqueous, alcoholic ferric chloride.

C. Anhydro-8-hydroxymercuri-1-naphthoic Acid.—A solution of 0.0402 g. of III and excess mercuric chloride in aqueous methanol was warmed on a steam bath, until the organomercurial began to precipitate. Filtration and drying afforded the anhydro-8-hydroxymercuri-1-naphthoic acid (0.0266 g., 35%), characterized by the identity of the infrared spectrum with that of an authentic sample.

Heterocyclic Compounds. III. Substituted Barbituric Acids *via* Enamines[1]

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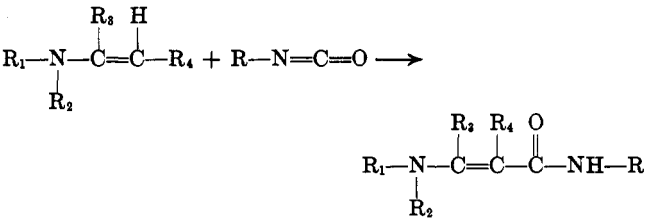
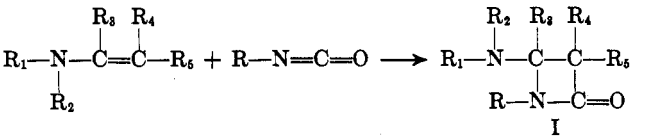
Amino hydrouracils were obtained in good yield from 2 moles of isocyanate and 1 mole of enamine. A new syntheses of substituted barbituric acids was achieved by the acid hydrolysis of this product and subsequent oxidation with chromic acid.

The reaction between enamines and isocyanates has received considerable attention recently. Enamines containing a β-hydrogen add directly to an isocyanate at room temperature to form unsaturated amides.[2,3]

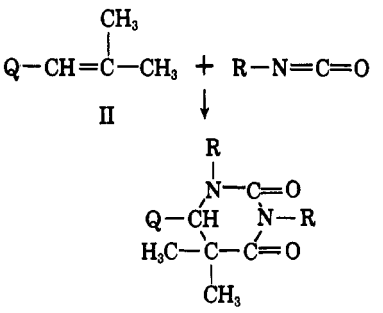


If there is no β-hydrogen on the enamine, a 1:1 addition still occurs at room temperature, and the adduct is a β-lactam[4,5] (I).



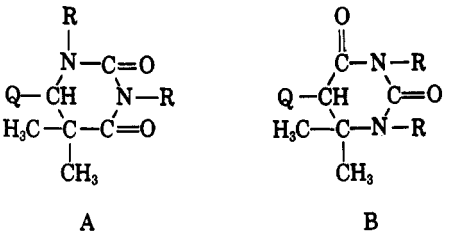
I

We have studied the reaction between β-disubstituted enamines (II) and aryl isocyanates at 120–140°. Under these conditions products were obtained which on the basis of elemental analysis and molecular weight determination were shown to be derived from 2 moles of the aryl isocyanate and 1 mole of the enamine.



III, Q = $(CH_3)_2N$; R = C_6H_5
IV, Q = piperidino; R = C_6H_5
V, Q = piperidino; R = *p*-tolyl
VI, Q = $(CH_3)_2N$; R = α-naphthyl

The spectral data indicated that a cyclic structure was probable for the adducts. The infrared spectrum showed the absence of an N–H group; the carbonyl absorption ruled out a noncyclic amide and suggested a six-membered system. The n.m.r. spectrum was in agreement with either of the possible structures A and B. Specifically, the chemical shift for the singlet proton (*e.g.*, at τ 6.52 for VI) could be accounted for by either structure. The structure A would appear more probable, however, on the basis of the strongly nucleophilic character of the β-position of the enamine.



A B

It seemed possible to distinguish between the two structures by attempting an acid hydrolysis. Structure A contains a nitrogen analog of an acetal and thus should be vulnerable to acid hydrolysis and produce an aldehyde. Structure B, which has the amino function as part of an α-amino acid system, is incapable of leading to an aldehyde by hydrolysis. The acid hydrolysis product of A will no longer be basic and will, therefore, precipitate out of the aqueous acid solution, thus preventing further attack on the amide function. This is precisely what occurred when the hydrolysis was carried out. Compounds III and IV, as expected, gave the same compound VIII when heated under reflux with hydrochloric acid.

The structure A now seemed to be correct and the physical properties of compound VIII further substantiated this conclusion. At room temperature VIII was almost totally in the ring form as evidenced by the spectral data, such as the infrared spectrum, which had a carbonyl pattern very similar to that of III and IV. As the solution was warmed, a small amount of open-chain material was formed as shown by a typical amide absorption at 6.1 μ and an N–H absorption at 2.8 μ. In addition, the warm solution readily reduced Tollens solution, indicating an aldehyde function. When the solution was cooled and allowed to stand for some time, the spectrum slowly returned to that of the

(1) Part I: A. K. Bose and S. Garratt, *Tetrahedron*, **19**, 85, (1963). Part II: A. K. Bose, S. Garratt, and J. Pelosi, *J. Org. Chem.*, **28**, 730 (1963).

(2) (a) G. Berchtold, *ibid.* **26**, 3043 (1961); (b) S. Hunig, K. Hubner, and E. Benzing, *Ber.*, **95**, 926 (1962).

(3) For a brief review of some of this work, see J. Szmuszkovicz, *Advan. Org. Chem.*, **4**, 51 (1963).

(4) M. Perelman and S. Mizsak, *J. Am. Chem. Soc.*, **84**, 4988 (1962).

(5) G. Opitz and J. Koch, *Angew. Chem., Intern. Ed. Engl.*, **2**, 152 (1963).