EXPERIMENTAL

2-Aminoethyl Bis(*o*-vinylphenyl)borinate. The general procedure described previously for the preparation of the vinylbenzeneboronic acids was employed (*1*). A solution of *o*-vinylphenylmagnesium bromide, prepared from 18.3 grams (0.10 mole) of freshly distilled *o*-bromostyrene and 2.43 grams (0.10 gram-atom) of magnesium in 50 ml. of tetrahydrofuran, was added (at a rate of about 1 drop per second) to a solution of 10.4 grams (0.045 mole) of butyl borate in 50 ml. of ether, cooled to −70° C. After addition was complete, the reaction mixture was allowed to warm to 25° C. during a 6-hour period.

After hydrolysis, the combined ether extracts were treated with 4.3 grams (0.07 mole) of 2-aminoethanol, and the resultant mixture was allowed to remain at room temperature for 12 hours. Ethanol (25 ml.) was then added, and the solvents were removed in vacuo. A copious white solid separated which was collected on a suction filter and washed with water. The air-dried material weighed 10.9 grams (79%). The product was recrystallized from ethanol to give white needles, m. p. 176–178° C. Two additional recrystallizations from 85% ethanol afforded material melting at 177.5–178° C. (All melting points reported herein are uncorrected.) Anal. Calcd. for $C_{18}H_{20}BNO$: C, 78.00; H, 7.27; N, 5.05. Found: C, 77.88; H, 7.18; N, 4.84.

2-Aminoethyl Bis(*m*-vinylphenyl)borinate. This compound was prepared in a manner analogous to that described for the ortho isomer. The Grignard reagent, prepared from 9.15 grams (0.05 mole) of freshly distilled *m*-bromostyrene and 1.22 grams (0.05 gram-atom) of magnesium in 35 ml. of tetrahydrofuran, was added to 5.20 grams (0.023 mole) of butyl borate in 50 ml. of ether, cooled to −70° C.

Isolation of the product was accomplished in the same manner as for the ortho isomer. The air-dried solid weighed 5.47 grams (81%), m. p. 156–161° C. The product was recrystallized 3 times from 85% ethanol, which afforded white needles, m. p. 163.5–164° C. Anal. Calcd. for $C_{18}H_{20}BNO$: C, 78.00; H, 7.27; N, 5.05. Found: C, 78.09; H, 7.56; N, 4.84.

2-Aminoethyl Bis(*p*-vinylphenyl)borinate. A procedure analogous to that described for the preparation of the ortho isomer was employed. A solution of *p*-vinylphenylmagnesium chloride, prepared from 13.9 grams (0.10 mole) of freshly distilled *p*-chlorostyrene and 2.43 grams (0.10 gram-atom) of magnesium in 50 ml. of tetrahydrofuran, was allowed to react with 10.4 grams (0.045 mole) of butyl borate in 50 ml. of ether, cooled to −70° C.

Isolation of the product was effected as described for the ortho isomer. The solid ester weighed 8.0 grams (58%) and melted at 170–175° C. Three recrystallizations from aqueous ethanol afforded white needles, m. p. 186.5–187° C., [(*2*), m. p. 181–182° C.]. The product was difficult to free from polymeric material which separated from solution with the monomer. Anal. Calcd. for $C_{18}H_{20}BNO$: C, 78.00; H, 7.27; N, 5.05. Found: C, 75.95; H, 7.23; N, 4.85.

Three attempts to repeat the above experiment failed. In one instance, a small amount of 2-aminoethyl bis(*p*-vinylphenyl)borinate was isolated (in addition to polymeric material) which, after four recrystallizations from 80% ethanol, melted at 188.5–189.5° C. Found: C, 77.92; H, 7.01; N, 4.85.

Hydrolysis of 2-Aminoethyl Bis(*o*-vinylphenyl)borinate. 2-Aminoethyl bis(*o*-vinylphenyl)borinate, (2.77 grams, 0.01 mole), was suspended in 50 ml. of aqueous methanol (50% by volume), and the mixture was acidified to a pH of 2 (Hydrion paper) with hydrochloric acid. The mixture was warmed slightly; when the pH of the solution reached 6, the solution was diluted to 200 ml. with water and then extracted with three 50-ml. portions of ether. The extracts were combined and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, using a rotary evaporator, to give a yellow oil which could not be induced to crystallize. The liquid weighed 2.21 grams (94%) and had a phenolic odor. The infrared spectrum of this material was consistent with that of monomeric bis-(*o*-vinylphenyl)borinic acid.

Hydrolysis of 2-Aminoethyl Bis(*m*-vinylphenyl)borinate. In the manner described for the ortho isomer, 2.77 grams (0.01 mole) of 2-aminoethyl bis(*m*-vinylphenyl)borinate was hydrolyzed to the acid. During removal of the solvent, 0.34 gram of polymeric material separated, which was isolated by suction filtration. The remaining solution afforded an oily residue which weighed 1.76 grams (75%). This material possessed a phenolic odor and exhibited an infrared spectrum consistent with that for the free acid. Attempts to purify the product were unsuccessful.

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Solubilities of Indigo and the Dienophilic Behavior of Furan Towards Dehydroindigo

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SOLUBILITIES OF INDIGO in several organic solvents are listed in Table I. In these determinations, 10 cc. of the solution that was saturated at its boiling point with indigo was evaporated, and the residue was weighed. The numbers in the table represent grams solidus 100 cc. of solution saturated at the boiling point.

These solubilities were determined in an unsuccessful effort to find some solvent for testing indigo as a dienophile in the Diels-Alder reaction. In addition to the findings of Table I, it was established that the solubility of indigo in molten phenanthrene (140°) was practically zero.

Many investigations have demonstrated the reactivity of furan as a diene in the Diels-Alder reaction, but there is no unequivocal record of its participation as a dienophile.

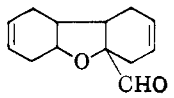
Solubility data are listed for indigo in several solvents. Furan adds to dehydroindigo and in so doing seems to function as a dienophile. Indigo and analogous compounds do not participate in Diels-Alder reactions, 1,1′-oxalyl-5,7,5′,7′-tetrabromoindigo is reported.

Table I. Solubilities of Indigo

Solvent	Temp., ° C.	Indigo, G/100 cc
Furfural	161	1.78
Dimethylformamide	153	0.26
Nitrobenzene	211	0.20
Furan	32	0.137
Acetone	56	0.026
Pyridine	115	0.024
Ethyl acetate	77	0.014
Benzene	80	0.008
Chloroform	61	0.006
Ethyl ether	34	0.004
Toluene	110	0.002
Hexane	69	0.000

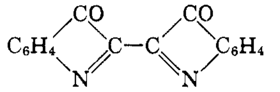
Furfural, in its reaction with 1,3-butadiene, is probably functioning as a dienophile (*2*):

$2C_4H_6 + C_4H_3O{-}CHO \longrightarrow$

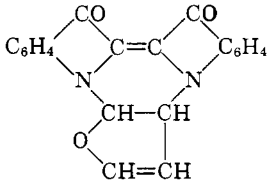


Addition of two moles of hexachlorocyclopentaidiene to one of furan at 140–180° for 100–300 hours has been reported (*3*). It was not established with certainty whether furan in this reaction behaved as a diene or dienophile but the latter was favored.

We have found that furan reacts with dehydroindigo (I) to yield *N,N′*-(2,3-furylene)indigo (II), a 1:1 adduct. In this reaction, it would appear that furan participates as a dienophile. Evidence supporting structure II, other than its synthesis, is the analysis and the color change in passing from I to II.



I



II

Dehydroindigo is an oxidation product of indigo, yellow in color in contrast to the deep color of indigo. The change of I into II is accompanied by a marked deepening of color from yellow to violet red, as would be expected by inspection of the structure of II. It contains the same chromophore as indigo. Also supporting structure II is the fact that the compound paralleled indigo in failing to react with molten anthracene.

It had been established earlier in this study that indigo, *N,N′*-oxalylindigo (*1*), and 1,1′-oxalyl-5,7,5′,7′-tetrabromoindigo, a new compound, all failed to react with anthracene even under forcing conditions. Additionally, indigo is unreactive towards cyclopentadiene, either in four days at room temperature or four days in a sealed tube at 206°.

The inertness of indigo towards anthracene or cyclopentadiene deserves brief comment. These latter two compounds react readily with maleic anhydride in the diene synthesis. Indigo and its congeners resemble maleic anhydride in having the necessary $-CO-\underset{|}{C}=\underset{|}{C}-CO-$ grouping in its structure for this reaction but they differ in having amino substituents at the two central carbons of this grouping, thus promoting a much larger resonance stabilization.

The formation of II from dehydroindigo is obviously related to the formation of *N,N′*-(phenylethylene)indigo (*5*) from styrene and dehydroindigo.

EXPERIMENTAL

***N,N′*-(2,3-Furylene)indigo.** A mixture of 3.3 grams of dehydroindigo, (*4*), containing a little indigo, and 50 cc. of furan was left for 9 days. It was shaken occasionally. Filtration removed 3.0 grams of unused dehydroindigo. The brown-red filtrate was diluted with an equal volume of ligroin. During an hour 0.06 gram of violet-red crystals separated, m.p. 170–171°. Another 0.1 gram of this product was obtained by concentrating the filtrate. This substance formed pink-red solutions in acetone, methanol, or ether. It was insoluble in water. It dissolved in concentrated sulfuric acid to form a deep green-blue color. *Anal.* (by H. Beck). Calcd. for $C_{20}H_{12}N_2O_3$: N, 853. Found: N,8.43. Found: N, 8.43.

1,1′-Oxalyl-5,7,5′,7′-tetrabromoindigo. Tetrabromoindigo (4.4 grams), dry pyridine (22 cc.) and oxalyl chloride (4.3 grams added portionwise) were mixed and set aside for 10 days. Then 100 cc. of dilute hydrochloric acid was added. The brown residue, after washing with water, alcohol and ether, was extracted with 100 cc. of hot nitrobenzene. The first black substance to separate from the filtrate was discarded, then 0.2 gram of brownish yellow solid gradually appeared; m.p. 336–340° with sublimation. It became dark red when added to concentrated sulfuric acid, in contrast to tetrabromoindigo which yielded a blue solution. It turned blue-violet when added to concentrated ammonium hydroxide (tetrabromoindigo, no change). *Anal.* (by H. Beck). Calcd. for $C_{18}H_4Br_4N_2O_4$: C, 34.21; H, 0.64. Found: C, 34.46; H, 0.81.

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