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## Isomeric Bis(Vinylphenyl)borinic Acids

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**The synthesis of bis(*o*-, *m*-, and *p*-vinylphenyl)borinic acids, isolated as their 2-aminoethyl esters, is reported. The bis(*o*- and *m*-vinylphenyl)borinic acids were obtained as uncrystallizable oils by hydrolysis of their esters. The para isomer could not be isolated in monomeric form.**

THE AUTHORS described, in a recent paper (1), the synthesis of the isomeric vinylbenzeneboronic acids and now wish to report the synthesis of the corresponding bis(*o*-, *m*-, and *p*-vinylphenyl)borinic acids.

Both bis(*o*-vinylphenyl)borinic acid and the corresponding meta isomer were prepared by allowing 2 moles of *o*(or *m*)-vinylphenylmagnesium bromide to react with 1 mole of butyl borate at low temperature. The reaction mixture was hydrolyzed with dilute hydrochloric acid, and the product was isolated from the ethereal solution as the 2-aminoethyl ester. This method of isolation was more advantageous than attempts to isolate the free acid.

Both esters were readily hydrolyzed in the presence of dilute hydrochloric acid, yielding the free acids as viscous oils which could not be induced to crystallize. All attempts to dehydrate the acids led to polymer formation exclusively.

An initial attempt to synthesize bis(*p*-vinylphenyl)borinic acid by the method employed for the ortho and meta isomers met with remarkable success; a 58% yield of the crude 2-aminoethyl ester was obtained, which melted at 170-175°C. This result could not be repeated, however; only polymeric material was isolated in each additional attempt. However, when hydrolysis was effected with an aqueous solution of ammonium chloride, a 35% yield of the ester was obtained. Alternately, this ester could be obtained (35%) by treating the reaction mixture with an excess of 2-aminoethanol rather than with aqueous ammonium chloride. No attempt was made to isolate the free acid.

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## 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  $-70^{\circ}\text{C}$ . After addition was complete, the reaction mixture was allowed to warm to  $25^{\circ}\text{C}$ . 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.  $176\text{--}178^{\circ}\text{C}$ . Two additional recrystallizations from 85% ethanol afforded material melting at  $177.5\text{--}178^{\circ}\text{C}$ . (All melting points reported herein are uncorrected.) Anal. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{BNO}$ : 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  $-70^{\circ}\text{C}$ .

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.  $156\text{--}161^{\circ}\text{C}$ . The product was recrystallized 3 times from 85% ethanol, which afforded white needles, m. p.  $163.5\text{--}164^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{BNO}$ : 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  $-70^{\circ}\text{C}$ .

Isolation of the product was effected as described for the ortho isomer. The solid ester weighed 8.0 grams (58%) and melted at  $170\text{--}175^{\circ}\text{C}$ . Three recrystallizations from aqueous ethanol afforded white needles, m. p.  $186.5\text{--}187^{\circ}\text{C}$ . [(2), m. p.  $181\text{--}182^{\circ}\text{C}$ .]. The product was difficult to free from polymeric material which separated from solution with the monomer. Anal. Calcd. for  $\text{C}_{18}\text{H}_{20}\text{BNO}$ : 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  $188.5\text{--}189.5^{\circ}\text{C}$ . 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 (Hydron 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 ( $140^{\circ}$ ) 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.