phenylhydrazine hydrochloride. The filtrate was extracted with three 20-ml. portions of methylene chloride. After the combined methylene chloride extracts were washed with water, sodium carbonate solution, and water again, the methylene chloride solution was dried over sodium sulfate. Removal of the methylene chloride *in vacuo* gave 3.0 g., of a cloudy oil which was largely a mixture of IV, methylphenylcarbinol (V), and the phenylhydrazone of IV (VI). Extraction of this oil with ethanol, left behind 120 mg. of crude VI. Recrystallization of VI from ether–ethanol gave 62 mg. (0.30 mmole, 1.2%) of white crystals melting at 104–106° (lit.[14] m.p. 105°). Molecular distillation of the ethanol-soluble material gave 2.2 g. of a clear oil and 270 mg. of tarry residue. Gas phase chromatography (retention time for authentic material and product IV, 5 min. 10 sec.; authentic and product alcohol V, 8 min. 20 sec.; both at 158° and under the column conditions described under Materials) indicated that the ratio of IV to alcohol V to unknown volatiles was 1.5:1.4:0.13. The yields were, therefore, 1.1 g. (9.2 mmoles, 36%) of IV; 1.0 g. (8.2 mmoles, 32%) of alcohol V, $[\alpha]^{25}D$ + 1.8° (*c* 1.1, ethanol), lit.[15] $[\alpha]D$ +43.4°, collected from gas phase chromatography; and *ca.* 4% of unidentified volatiles.

When equimolar portions of borane I and acetophenone were similarly mixed, but worked up under neutral conditions (*i.e.*, water hydrolysis and Florisil chromatography), 21% of alcohol V, $[\alpha]^{25}D$ −1.9° (*c* 1.8, ethanol), and 6.9% of acetophenone were isolated.

An infrared spectrum of the solid labile intermediate (m.p. 77–84° dec.) before hydrolysis indicated no carbonyl peak.

Boric acid was also identified as a product in the aqueous solutions of these runs.

B. Benzophenone.—Borane I (553 mg., 4.53 mmoles) was stirred for 2 days with benzophenone (1.43 g., 7.85 mmoles) in 30 ml. of methylene chloride at 25–30°, as described for the reduction of acetophenone. After hydrolysis, 1.71 g. (m.p. 40–55°) of methylene chloride soluble product was isolated. Treatment of this oily solid product with ethanol, and filtration of the ethanol-insoluble crystals, gave 212 mg. (0.78 mmoles, 10%) of the phenylhydrazone of benzophenone (VII) (m.p. 133–136°). Recrystallization of the crude VII from ethanol gave 113 mg. (0.42 mmoles, 5.4%) of white needles, m.p. 136–138° (lit.[14] m.p. 137–138°). Fractional crystallization from hexane of the ethanol-soluble material, gave 806 mg. (4.4 mmoles, 56%) of white needles of benzhydrol, m.p. 66–68° (lit.[16] m.p. 67.5–68°).

When a 2.8-fold molar excess of benzophenone was similarly treated with borane I and worked up as in the acetophenone runs (either acidic or neutral hydrolysis may be used), with the exception that silica gel chromatography was used for the separation of the methylene chloride-soluble products, 12% of phenylhydrazone VII, and 35% of benzhydrol were isolated.

The reaction of a 1:1 molar ratio of benzophenone with borane I in the absence of solvent, gave similar results. Essentially similar products also were obtained under argon or air atmospheres.

C. *p*-Quinone.—Borane I (1.00 g., 8.20 mmoles) dissolved in 20 ml. of methylene chloride was treated with 1.78 g., 16.5 mmoles, of *p*-quinone dissolved in 20 ml. of methylene chloride as described for the reduction of acetophenone. The reaction was almost complete after 2 hr. After 1 day at 25–30°, the solution was hydrolyzed and worked up in the manner described for benzophenone to give 995 mg. (9.05 mmoles) of crude hydroquinone, m.p. 159–163°. Recrystallization from ether–hexane gave 275 mg. (2.50 mmoles) of hydroquinone, m.p. 172° (lit.[17] m.p. 172°).

D. Benzaldehyde, a twofold molar excess, dissolved in tetrahydrofuran was treated for 1 day at 25° with borane I, hydrolyzed and worked up as described for acetophenone to give benzyl alcohol (43%) and the phenylhydrazone of benzaldehyde (10%) m.p. 153–155° (lit.[18] m.p. 154.5–155.5°). The gas phase chromatography retention time of product and authentic benzyl alcohol was 4 min. 30 sec. at 103°, under the column conditions described under Materials.

E. Cinnamaldehyde (437 mg., 3.31 mmoles) dissolved in 5 ml. of ether, was added to borane I (411 mg., 3.37 mmoles) dissolved in 15 ml. of ether at 25°. The solution was stirred for 3 hr., after which hydrolysis and work-up as described for acetophenone gave 57% of cinnamyl alcohol, m.p: 32–33° (lit.[19] m.p. 33°), and 15% of the phenylhydrazone of cinnamaldehyde.

F. Benzoyl chloride and equimolar portions of borane I were stirred in dry ether at 25° for 3 days. After hydrolysis and work-up, 10% of benzyl alcohol was isolated. Other products were unreacted benzoyl chloride, benzoic acid, and 2-benzoylphenylhydrazine, m.p. 166–168° (lit.[20] m.p. 168°).

G. *trans*-Stilbene (1.33 g., 7.39 mmoles) in 25 ml. of tetrahydrofuran was heated under reflux with 905 mg. (7.42 mmoles) of borane I for 2 weeks. After oxidation with 20% basic hydrogen peroxide, the reaction mixture was worked up by the procedure of Hawthorne.[4] Isolated were 682 mg. (3.79 mmoles, 51.3%) of *trans*-stilbene, m.p. 123–124° (lit.[21] m.p. 125°) and 421 mg. (2.3 mmoles, 31%) of crude *trans*-stilbene (m.p. 118–121°). Also isolated was 108 mg. of a brown oil which did not contain 1,2-diphenylethanol, as indicated by thin layer chromatography.

Ethyl benzoate and borane I (equimolar portions) were stirred in ether at 25° for 1 day. Ethyl benzoate, whose infrared spectra was identical with starting ethyl benzoate, was recovered in 95% yield.

Benzoic acid and **nitrobenzene** likewise were recovered virtually unchanged when heated under reflux for 5 days with borane I in tetrahydrofuran.

Reaction of N-Bromosuccinimide with Borane I.—N-Bromosuccinimide (765 mg., 4.31 mmoles) dissolved in 15 ml. of methylene chloride, was added dropwise to 581 mg. (4.76 mmoles) of borane I dissolved in 20 ml. of methylene chloride containing 1 ml. of pyridine, over a 30 min. period at 0°, while the solution was being stirred. Gas evolution was noted during the reaction period. After 1 hr., the white, crystalline precipitate (VIII) was filtered and washed with dry methylene chloride. The dried VIII (m.p. 179–181° dec.) weighed 379 mg. (1.3 mmoles, 30%). Crystals of VIII decomposed in aqueous or basic solution with the liberation of pyridine and a gas. The product VIII was soluble in ethanol and insoluble in ether, hexane, methylene chloride, and acetone.

Anal. Calcd. for $C_{11}H_{16}BBrN_3O$: C, 44.49; H, 5.43; Br, 26.91; N, 14.15. Found: C, 44.47; H, 4.97; Br, 26.84; N, 14.02.

Infrared spectrum (KBr): 3430 (mbr), 3205 (m), 3000 (s), 2940 (sbr), 2730 (w), 2715 (w), 2680 (w), 2635 (w), 2465 (m), 2425 (m), 2380 (w), 1638 (m), 1602 (m), 1498 (m), 1461 (s), 1450 (w), 1374 (m), 1347 (w), 1319 (m), 1243 (w), 1218 (w), 1174 (m), 1164 (s), 1121 (m), 1060 (w), 1025 (w), 1012 (w), 952 (w), 929 (w), 893 (w), 813 (w), 772 (m), 760 (m), 695 (m), 593 (w), and 502 (mw) $cm.^{-1}$ principal peaks.

Hydrolysis of VIII with an excess of 3 *N* hydrochloric acid, gave pyridinium hydrochloride and phenylhydrazine hydrochloride.

Acknowledgment.—We wish to thank Mr. John A. Sousa for his help and useful advice in the spectral work. We also thank Dr. George Thomas, Dr. Joseph Bornstein, and Dr. M. K. Wilson for their helpful suggestions. Analyses were done by Mr. Carmine DiPietro, molecular weight determinations by Dr. Wenzel E. Davidson, and the gas chromatographic analyses was done with the help of Dr. Warren V. Sherman.

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The Preparation of 2-Arylimidazo[4,5-*b*]pyridines

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Some 2-arylimidazo[4,5-*b*]pyridines have been mentioned in the literature,[1] but it would appear from the

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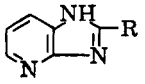
TABLE I

2-SUBSTITUTED IMIDAZO[4,5-*b*]PYRIDINES



R	M.p., °C.	Yield, %	Ultraviolet absorption spectra[a] λ_{max}	log ϵ_{max}	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found
C_6H_5	291–293[b]	65	234	3.96	$C_{12}H_9N_3$	73.83	73.78	4.65	4.58	21.53	21.69
			307	4.47							
			319	4.43							
3-$CH_3C_6H_4$	240–241	78	237	3.92	$C_{13}H_{11}N_3$	74.62	74.78	5.30	5.44	20.08	20.27
			307	4.47							
			319	4.32							
4-$CH_3C_6H_4$	261–262	90	238	4.02	$C_{13}H_{11}N_3$	74.62	74.38	5.30	5.40	20.08	20.20
			307	4.52							
			321	4.37							
4-ClC_6H_4	361[c]	61	...	...	$C_{12}H_8ClN_3$	62.75	62.98	3.51	3.60	18.30	18.50
4-FC_6H_4	219[d]	61	...	...	$C_{12}H_8FN_3$	67.90	68.00	3.78	3.71	19.61	19.62
2-$H_2NC_6H_4$	337–338[e]	43	250	4.11	$C_{12}H_{10}N_4$	68.55	68.39	4.79	4.81	26.65	26.61
			294	4.09							
			305	4.16							
			355	4.10							
2-Thienyl	273–274[f]	41	256	3.90	$C_{10}H_7N_3S$	59.68	59.60	3.51	3.46	20.88	20.76
			324	4.41							
			340	4.24							
$C_6H_5CH{=}CH{-}$	205–207[g]	...	265	3.90	$C_{14}H_{11}N_3$	75.99	76.18	5.01	5.01	19.00	18.87
			335	4.52							
3-$ClC_6H_4CH{=}CH$	246–247[h]	31	...	...	$C_{14}H_{10}ClN_3$	65.76	65.82	3.94	3.72	16.43	16.36
3-Pyridylvinyl	256–257	43	255	4.02	$C_{13}H_{10}N_4$	70.25	69.93	4.52	4.65	25.21	25.19
			335	4.58							
4-Pyridylvinyl	254–255	75	255	3.86	$C_{13}H_{10}N_4$	70.25	70.01	4.52	4.53	25.21	25.30
			336	4.50							

[a] In methanol. [b] Lit.[1] m.p. 235–238°. [c] Calcd.: Cl, 15.44. Found: Cl, 15.36. [d] Calcd.: F, 8.91. Found: F, 8.91. [e] Lit.[1] m.p. 174–175°. [f] Calcd.: S, 15.93. Found: S, 16.27. [g] Lit.[1] m.p. 197–198°. [h] Calcd.: Cl, 13.87. Found: Cl, 13.88.

reported melting points and mode of preparation that the products which were obtained did not correspond to the assigned structures. The authors claimed to have obtained 2-phenylimidazo[4,5-*b*]pyridine, m.p. 235–238°, and the 2-*o*-aminophenyl analog, m.p. 175°, by heating 2,3-diaminopyridine (under unstated conditions) with benzoic anhydride and anthranilic acid, respectively. We have found that heating 2,3-diaminopyridine with benzoic anhydride at 180° for 2 hr. yielded 2,3-dibenzamidopyridine, m.p. 222–223°, as the only identifiable product. Similar treatment with anthranilic acid gave only a salt of anthranilic acid and 2,3-diaminopyridine, m.p. 180–182°. However, the cyclized products were readily obtained by condensing the diamine and the aromatic acid in polyphosphoric acid.[2] In this way, the 2-phenyl derivative, m.p. 291–293°, and the 2-*o*-aminophenyl derivative, m.p. 337–338° (Table I), were obtained in fair yields.

Polyphosphoric acid was a convenient condensing agent for the preparation of the aryl, pyridylvinyl, and thienyl derivatives listed in Table I. However, some difficulty was experienced in purification of the 2-styryl analog; accordingly, 2,3-diaminopyridine was refluxed with acetic anhydride in the expectation of obtaining the 2-methyl derivative[3,4] for subsequent reaction with benzaldehyde to yield the 2-styryl derivative.[5]

The reaction with acetic anhydride gave 2,3-diacetamidopyridine, m.p. 169–171°, rather than the cyclized compound; however, treatment of the diacetamido derivative with benzaldehyde at 190° gave 2-styrylimidazo[4,5-*b*]pyridine, m.p. 204–206°.

Ultraviolet spectral data for some of the compounds prepared in this work are given in Table I.

Experimental

All melting points are corrected. Analyses were performed by the Microanalytical Laboratories of Abbott Laboratories, North Chicago, Ill.

2-Phenylimidazo[4,5-*b*]pyridine.—A mixture of benzoic acid (3.66 g., 0.03 mole) and 2,3-diaminopyridine (3.27 g., 0.03 mole) in polyphosphoric acid (30 ml.) was stirred at 175° for 2 hr. The solution was cooled, diluted with water (200 ml.), and filtered clear. Neutralization of the filtrate gave the crude product, m.p. 289–293°, yield 3.8 g. (65%). Recrystallization from methanol raised the melting point to 291–293°.

The other compounds listed in Table I were prepared by the same general procedure. The reaction temperature in the case of the 2-thienyl derivative was 125°; for the others, the temperature range was 175–250°. The products are all amphoteric, and in some cases purification could be effected by solution in 10% sodium hydroxide and reprecipitation.

Treatment of 2,3-Diaminopyridine with Benzoic Anhydride.—2,3-Diaminopyridine (1.1 g.) was heated with benzoic anhydride (2.3 g.) at 180° for 2 hr., and the reaction mixture was then extracted with chloroform. Evaporation of the chloroform extract and crystallization of the residue from ethanol gave 2,3-dibenzamidopyridine, m.p. 222–223°, yield 0.6 g. (38%).

Anal. Calcd. for $C_{19}H_{15}N_3O_2$: C, 71.91; H, 4.76; N, 13.24. Found: C, 71.44; H, 4.50; N, 13.46.

Treatment of 2,3-Diaminopyridine with Anthranilic Acid.—A mixture of 2,3-diaminopyridine (1.1 g.) and anthranilic acid

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(1.4 g.) was heated at 180° for 2 hr. The dark brown solid was crystallized twice from methanol, giving colorless prisms melting at 180–182°, yield 0.8 g. (32%). The water-soluble product analyzed for $C_{12}H_{14}N_4O_2$, corresponding to a 1:1 salt of the two starting materials.

Anal. Calcd. for $C_{12}H_{14}N_4O_2$: C, 58.52; H, 5.73; O, 12.99. Found: C, 58.76; H, 5.90; O, 12.55.

2-Styrylimidazo[4,5-*b*]pyridine.—2,3-Diaminopyridine (5.0 g.) was refluxed in acetic anhydride (40 g.) for 2 hr.; the solution was then evaporated to dryness. The residue was dissolved in water (20 ml.), potassium carbonate (4 g.) was added, and the mixture was extracted with chloroform. The extract was dried and evaporated and the residue was crystallized from ethanol to give 2,3-diacetamidopyridine, m.p. 169–171°, yield 3.8 g. (43%).

Anal. Calcd. for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 56.02; H, 5.45; N, 21.76.

A mixture of 2,3-diacetamidopyridine (1.33 g., 0.01 mole) and benzaldehyde (1.06 g., 0.01 mole) was heated at 190° for 2 hr. The residue was crystallized from ether, giving 0.9 g. (41%), m.p. 190–195°. Recrystallization from ethanol raised the melting point to 205–207°.

Organoboron Compounds. XVIII. Bifunctional Binding of Water by the *cis*-1,2-Cyclopentanediol Ester of 8-Quinolineboronic Acid

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It has been shown that 8-quinolineboronic acid is a polyfunctional catalyst for the hydrolysis of 2-chloroethanol and 3-chloropropanol in N,N-dimethylformamide solutions containing water and collidine,[2] and that the reaction of 8-quinolineboronic acid with the isomeric 2-chloroindanols and 2-chloro-1,2-diphenylethanols is highly stereoselective.[3] These properties of 8-quinolineboronic acid and similar compounds[4,5] were attributed to the cooperative action of intramolecular boron and nitrogen atoms.[2-5] The present paper reports spectroscopic evidence for a related manifestation of synergetic activity by boron and nitrogen, the binding of water and phenol by the *cis*-1,2-cyclopentanediol ester of 8-quinolineboronic acid.

The infrared spectrum of a saturated solution of water in carbon tetrachloride is shown in Fig. 1 (spectrum B). The absorption bands at about 3700 and 3610 cm.$^{-1}$ have been assigned to the two fundamental O–H stretching modes of the monomeric water molecules in such solutions.[6] Infrared spectra of dilute solutions (10^{-4} to $10^{-3}M$) of the *cis*-1,2-cyclopentanediol ester of 8-quinolineboronic acid (I) in dry carbon tetrachloride were transparent in the O–H stretching region (*e.g.*, spectrum A in Fig. 1). The spectra of

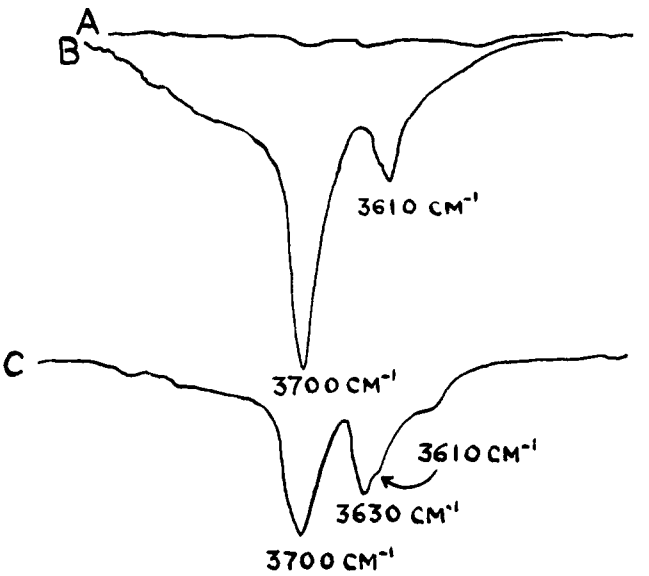

Fig. 1.—The effect of I on the spectrum of water in carbon tetrachloride: A, the spectrum of I (2×10^{-3} *M*) in dry CCl_4; B, the spectrum of water in CCl_4; C, the spectrum of water in CCl_4 containing I (2×10^{-3} *M*). Spectra are recorded as per cent transmittance *vs.* linear frequency (cm.$^{-1}$). Frequencies are ±2 cm.$^{-1}$

dilute solutions of I in wet carbon tetrachloride, however, exhibited three absorption bands, the two associated with water in carbon tetrachloride plus a new absorption at about 3630 cm.$^{-1}$ (*e.g.*, spectrum C in Fig. 1).

The intensity of the absorption at 3630 cm.$^{-1}$ increased as the concentration of I in wet carbon tetrachloride was increased from 3.2×10^{-4} to 3×10^{-3} *M*. Below a concentration of 3.2×10^{-4} *M* absorption at 3630 cm.$^{-1}$ was not significant, and the spectrum was that of water in carbon tetrachloride. Increasing the concentration of I from 3.2×10^{-4} to 1.2×10^{-3} *M* caused a decrease in the intensity of the 3700-cm.$^{-1}$ band and the appearance of the 3630-cm.$^{-1}$ band. At an ester concentration of about 3×10^{-3} *M* the 3700- and 3630-cm.$^{-1}$ bands were of approximately equal intensity. Increasing the concentration of I from 3×10^{-3} to 5×10^{-3} *M* produced no detectable change in the solution spectrum in the O–H stretching region.[7]

The spectrum of a dilute solution of I in D_2O-saturated carbon tetrachloride exhibited a band at about 2665 cm.$^{-1}$. This band was not present in the spectrum of a dilute solution of I in dry carbon tetrachloride nor was it present in the spectrum of CCl_4 saturated with D_2O.[8]

In contrast to these results it was found that the spectrum of water in carbon tetrachloride was not altered when the solution contained, as added reagents, pyridine (3×10^{-3} *M*), the *cis*-1,2-cyclopentanediol ester of benzeneboronic acid (3×10^{-3} *M*), a mixture

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(7) The intensity of C–H stretching bands in the 3050–2850-cm.$^{-1}$ region of the spectrum provided a qualitative means of observing the increasing ester concentration. These bands were evident at concentrations less than 3.2×10^{-4} *M* and became more intense as the ester concentration was increased.

(8) The spectrum of CCl_4 saturated with D_2O had absorption bands centered at 2745 (strong) and 2630 cm.$^{-1}$ (weak). These represent the fundamental O–D stretching modes of unassociated D_2O. A very weak band observed at about 2685 cm.$^{-1}$ is probably due to O–D stretching absorption in HOD, while another very weak absorption at about 3650 cm.$^{-1}$ is most likely that due to O–H stretch in HOD.