was added,[10] and the mixture was allowed to reflux for 4 hr. The solution, after refluxing, gave a positive test for active oxygen with potassium iodide–starch test paper. The methanol was removed by evaporation at reduced pressure in a flash evaporator, and a light yellow-green oil with a pungent odor was obtained. Distillation of the crude oil (18.2 g.) under vacuum in a spinning-band column yielded 8.6 g. of light yellow oil boiling at 139–146° (12 mm.). The total yield of distilled methyl *o*-acetylbenzoate was 48%. The infrared spectrum indicates that this keto ester exists mainly in the cyclic lactol form.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.64; sapon. equiv., 178. Found: C, 67.21, 67.29; H, 5.38, 5.55; sapon. equiv., 178.

o-Acetylbenzoic acid (IV). A sample of distilled methyl *o*-acetylbenzoate (3.0 g., 0.0169 mole) was weighed into a 50-ml. round-bottom flask, sodium hydroxide (1.0 g., 0.025 mole) in 20 ml. of water was added, and the mixture refluxed for 30 min. Upon cooling, the now black solution was acidified with concentrated hydrochloric acid. A red-yellow oil separated, which after crystallizing overnight was filtered, washed with water, and dried in a vacuum desiccator. The yield of crude *o*-acetylbenzoic acid, which melted at 84–104° and had a neutral equivalent of 174, was 2.2 g. (80%). Pure *o*-acetylbenzoic acid is reported to melt at 114–115°[7] and to have a neutral equivalent of 164. The crude product was identified by comparison of its infrared spectrum with that of an authentic sample obtained from the Aldrich Chemical Co.

Attempted preparation of o-acetylbenzaldehyde. A solution of 1-methylnaphthalene (0.1 mole) in 200 ml. of methanol was cooled to −40°, and then 2.0 mole-equivalents of ozone were passed through the solution. The ozone uptake was not quantitative. After flushing with oxygen, the total solution was found to contain 164 mmoles of active oxygen (theory = 200 mmoles). The cold solution was transferred into a 500-ml. Erlenmeyer flask and recooled to −40°. Solid sodium iodide (60 g., 0.4 mole) and 5 ml. of glacial acetic acid were added slowly with stirring. An exothermic reaction occurred, and the solution was warmed to 0°. After about 1 hr., the solution was allowed to warm to room temperature and the liberated iodine reduced with 20% aqueous sodium thiosulfate solution (about 200 ml.). The methanol was then removed by evaporation on a steam bath under an air blast. The resulting aqueous solution was extracted with three 50-ml. portions of ether, and the combined extracts were dried (sodium sulfate) and evaporated under reduced pressure in a flash evaporator. Evaporation yielded 10.7 g. of orange-red oil. The infrared spectrum showed a hydroxyl band at 2.9 μ and a doublet carbonyl band at 5.7 μ and 6.0 μ.

Although the viscous oil appeared to decompose gradually at room temperature, it decomposed rapidly to a tar-like material when heated. Attempts to form derivatives gave either no reaction or mixtures that could not be separated. A Clemmensen reduction also did not lead to any identifiable product.

Phthalaldehydic acid (VI). A suspension of 2-methylnaphthalene (14.2 g., 0.1 mole) in 100 ml. of methanol was treated with 2.0 mole-equivalents of ozone at a temperature of −40°. The ozone uptake was not quantitative, and the reaction vessel was shaken intermittently to allow undissolved 2-methylnaphthalene to come into more intimate contact with the gas stream. After flushing with oxygen, the solution was transferred into a 500-ml. round-bottom flask and evaporated under reduced pressure until most of the methanol had been removed. At this stage, 30 ml. of distilled water and 20 ml. of glacial acetic acid were added, and the mixture was allowed to reflux for 1 hr. After the solution was refluxed, it gave a negative test for peroxides with potassium iodide–starch test paper. The water and acetic acid were removed by evaporation under reduced pressure, and the residual oil was treated with 100 ml. of 7% aqueous sodium bicarbonate solution and warmed on a steam bath for 30 min. After cooling, insoluble neutral material was removed by extraction with ether. Upon acidification of the bicarbonate solution with concentrated hydrochloric acid, a viscous, red oil separated. The oil was extracted with ether (100 ml.), and the ether extract was evaporated to dryness to yield 9.0 g. (60% yield) of very crude phthalaldehydic acid, which was identified by its infrared spectrum. Recrystallization from benzene yielded 0.6 g. (4% yield) of white solids that melted at 89–94° and had a neutral equivalent of 150. Pure phthalaldehydic acid reportedly melts at 97°[11] and has a neutral equivalent of 150. The infrared spectrum of the crystalline material was identical with that of an authentic sample obtained from the Dow Chemical Co.

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Deboronation: Formation of Phenylboronic Anhydride from Diphenyl Hydroxyborane in the Presence of Amides[1]

Howard K. Zimmerman[2]

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The deboronation of aryl groups in aryldihydroxyboranes and diaryl hydroxyboranes has been known for many years.[3,4] Normally the deboronating agent is of a kind which may generally be considered an oxidizing agent (*e.g.*, hydrogen peroxide bromine or chlorine), and since the boron-containing product is usually in an apparently higher oxidation state (*viz.* boric acid from phenyl dihydroxyborane, or phenyl dihydroxyborane from diphenyl hydroxyborane than before the reaction, such processes are frequently regarded as oxidations. During the past decade, Kuivila and his students[5]) have studied the aryl dihydroxyboranes and their deboronations quite extensively from this viewpoint.

We have recently found evidence that a deboronation of an aryl group in diphenyl hydroxyborane can occur under clearly nonoxidizing conditions when the compound is allowed to reflux in an or-

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ganic solvent in the presence of an amide. When phthalimide is used in place of the amide, it is recovered in 92.5% yield, and there is an 11% conversion of the boron compound to phenylboronic anhydride. In order to eliminate the possibility that a factor other than the amide might be responsible for the observed results, diphenyl hydroxyborane was also subjected to the same treatment alone in toluene, leading to the recovery in 44% yield of bis(diphenylboron oxide. No phenylboronic anhydride was found.

These observations suggest that the crucial property required of a deboronating agent may be its Lewis base character rather than any oxidizing power *per se*. This implies that the key step in deboronation is the incipient *reducing* effect produced by the coordination of the Lewis base at the boron atom, and that subsequent steps in the mechanism are more or less incidental, important though they may be on occasion from the preparative standpoint. Such an initial coordination step seems rather well established as a necessary part of the mechanism of deboronation in the aryl dihydroxyboranes[5] by means of relatively powerful nucleophilic agents. The efficiency of weakly nucleophilic reagents such as amides in accomplishing deboronation of a diaryl hydroxyborane indicates that the diaryl compounds are considerably more reactive under such attack than are the monoaryl ones. It also suggests a means for carrying out selective deboronations.

EXPERIMENTAL

Acetamide (0.8 gm.) was added with 450 ml. of toluene to the diphenyl hydroxyborane from hydrolysis of 3.0 gm. of *B,B*-diphenyl boroxazolidine,[6] and the mixture was azeotropically distilled to a residue of 3–5 ml., from which there crystallized overnight 1.3 gm. of phenylboronic anhydride, m.p. 214–216°, after recrystallization from carbon tetrachloride.[7] The product was further characterized by preparing from it the *N*-ethyl-*B*-phenyl diptych boroxazolidine.[8]

Benzamide (1.6 gm.) was added, with 200 ml. of toluene, to the diphenyl hydroxyborane from 3.0 gm. of *B,B*-diphenyl boroxazolidine, and the mixture azeotropically distilled to about 5–7 ml. from which crystallized 1.85 gm. of white product. This product contained a carbon tetrachloride-soluble fraction which crystallized to give phenylboronic anhydride (mixed m.p. which authentic phenylboronic anhydride undepressed), and a water-crystallizable fraction which gave an undepressed mixed m.p. with authentic benzamide.

Phthalimide (1.3 gm.), with 200 ml. of toluene was added to diphenyl hydroxyborane from 2.0 gm. of *B,B*-diphenyl boroxazolidine and azeotropically distilled to 25–30 ml., from which 1.2 g. of phthalimide crystallized in plates on cooling, m. 234–235°. The filtrate was concentrated under vacuum to 3–5 ml. and cooled to give 0.1 gm. of phenylboronic anhydride.

B,B-Diphenyl hydroxyborane (3.0 gm.), in 160 ml. of toluene, was distilled to a residue of 3–5 ml. which, after 4 hours gave 1.0 gm. of white crystalline product which melted at 116–118° after recrystallization from carbon tetrachloride, in good agreement with the melting point of bis(diphenylboron)oxide.[9]

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Preparation of *N,N*-Dialkyl-*N'*-(2-dialkylaminoethyl)benzamidines

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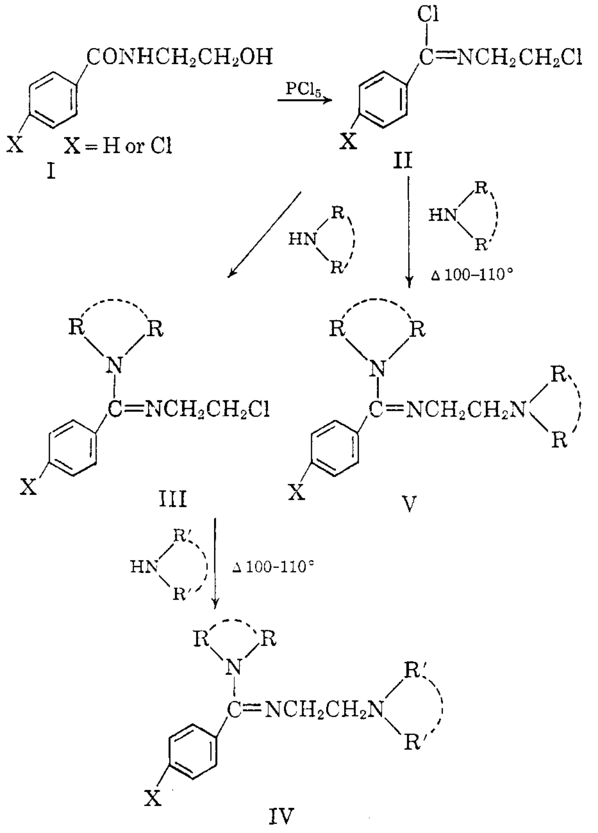
In the course of work carried out in these laboratories to synthesize compounds of interest as pharmaceuticals, we have prepared some benzamidines which exhibit diuretic activity of an order approximately equal to that of theophylline.[2]



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[2] Of the compounds listed in Table I, Nos. 4, 14, and 16 gave the greatest diuretic response in dogs. The authors wish to thank William B. McKeon, Jr., of our pharmacology division for the diuretic screening.