

sibility that the rate-determining step is the formation of norbornenylmercuric chloride, which then rearranges rapidly to nortricyclylmercuric chloride, is not entirely ruled out if one is willing to invoke some sort of transannular participation of the double bond in the direct electrophilic displacement step. A precedent of sorts is the reported reaction of mercuric chloride with benzylboronic acid.<sup>15</sup>

Extension of this argument to the reaction of 2,4-dinitrobenzenesulfonyl chloride with *exo*-5-norbornene-2-boronic ester seems far-fetched. Although we were unable to prove that the *endo* isomer reacts more slowly than the *exo* to form nortricyclyl 2,4-dinitrophenyl sulfide, failure to obtain any of this product from the *endo* isomer is at least in agreement with our postulated mechanism. In view of the moderate yield and considerable by-product formation with the *exo* isomer, failure of the *endo* isomer to produce any nortricyclyl compound is the expected result, assuming that alternate reaction paths available to the two isomers have comparable rates for each.

(15) E. Khotinsky and M. Melamed, *Ber.*, **42**, 3090 (1909).

Our conclusion that inversion is preferred over retention in certain kinds of transannular electrophilic displacements in the norbornyl-nortricyclyl system has been independently reached by Nickon, *et al.*, in a recent study of homoketonization.<sup>16</sup> In basic solution, transfer of a hydrogen ion from solvent to carbon opened the cyclopropane ring with inversion of the carbon configuration. In acid, ring opening occurred with retention, perhaps because hydrogen ion can complex with the cyclopropane ring and thus attacks from the inner side.

We are pursuing further investigations to determine whether electrophilic displacements generally occur with inversion in the absence of direct bonding between the attacking and leaving electrophilic groups, or whether the norbornyl system is peculiar. We have briefly outlined a theoretical rationalization for inversion being favored under certain circumstances,<sup>1c</sup> but there is insufficient evidence to justify further speculation at present.

(16) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Am. Chem. Soc.*, **85**, 3713 (1963).

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## Isotope Effects in Mercurideboronations Measured by Neutron Absorption

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Boron isotope effects in mercurideboronations were determined by measurement of the neutron absorption cross sections of appropriately derived boric acid samples. The  $k_{B^{10}}/k_{B^{11}}$  ratio for the reaction of mercuric chloride with *exo*-5-norbornene-2-boronic acid in 83% acetone at 25° to form nortricyclylmercuric chloride was 1.033, that for the *endo* isomer in refluxing 75% acetone 1.027, both  $\pm 0.005$ , and that for the reaction of phenylmercuric nitrate with benzeneboronic acid in refluxing 40% ethanol was  $1.021 \pm 0.009$ .

Boron offers some uniquely advantageous properties for the study of isotope effects in carbon-metal bond cleavages. Organoboron compounds, especially boronic acids and esters, are stable and isolable, yet reactive enough to permit electrophilic displacement of the boron atom under mild conditions. The natural mixture of B<sup>10</sup> and B<sup>11</sup> isotopes is convenient for measurements and makes the preparation of labeled compounds unnecessary. Boron is light enough that its isotope effects are readily measurable. Organoboron compounds are easily degraded to derivatives suitable for determinations of isotopic composition. In contrast, all other metallic elements would be inconvenient to work with and, except for lithium and beryllium, their isotope effects would be exceedingly small.

Several methods of measuring B<sup>10</sup>/B<sup>11</sup> ratios are known, including B<sup>10</sup> neutron absorption,<sup>2</sup> mass spectrometry,<sup>3</sup> and emission or infrared spectroscopy.<sup>4</sup>

(1) Abstracted in part from the Ph.D. Thesis of J. O. W.

(2) (a) C. M. Judson, *U. S. At. Energy Comm.*, **A-2367** (1946) [*Nuclear Sci. Abstr.*, **11**, 11,579 (1957)]; (b) J. E. Hudgens, Jr., L. C. Nelson, R. C. Meyer, and C. Zyskowski, *U. S. At. Energy Comm.*, **NBL-102** (1954) [*Chem. Abstr.*, **55**, 18,378 (1961)].

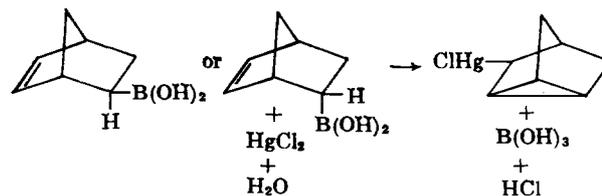
(3) (a) R. M. Abernathy, *U. S. At. Energy Comm.*, **IDO-14503** (1960) [*Chem. Abstr.*, **54**, 11,833 (1960)]; (b) G. H. Palmer, D. F. Dance, and K. L. Aitken, *At. Energy Res. Estab. (Gr. Brit.)*, **GP/E 1994** (1956) [*Chem. Abstr.*, **50**, 16,540 (1956)]; (c) Kiichi Hoshino, *Rikagaku Kenkyushu Hokoku*, **35**, 99 (1959) [*Chem. Abstr.*, **54**, 20,364 (1960)].

(4) (a) B. V. L'vov and V. I. Mosichev, *At. Energy (U.S.S.R.)*, **10**, 279 (1961) [*Chem. Abstr.*, **56**, 6864 (1962)]; (b) A. A. Maltsev, E. N. Moskvitina, and V. M. Tatevskii, *Fiz. Sbornik L'vov. Univ.*, No. 3, 472 (1957) [*Chem. Abstr.*, **55**, 23,109 (1961)].

Only the first two methods are likely to yield accurate enough results for isotope effect measurements. Equipment for measuring neutron absorption was readily available to us.

The cross section of B<sup>10</sup> to thermal neutrons is  $4 \times 10^3$  barns.<sup>5</sup> In contrast, B<sup>11</sup> and O<sup>16</sup> are practically transparent to thermal neutrons, having scattering cross sections of about 4 barns, while H<sup>1</sup> has an energy-dependent scattering cross section ranging from 20 to 80 barns in the low energy region.<sup>5</sup> The attenuation of a neutron beam by a boric acid sample thus depends largely on the concentration of B<sup>10</sup> and the absorption of monochromatic neutrons follows the well-known exponential law.

We were particularly interested in the isotope effect in the reaction of *exo*- and *endo*-5-norbornene-2-boronic acid with mercuric chloride to yield nortricyclylmer-



(5) D. J. Hughes and R. B. Schwartz, "Neutron Cross Sections," 2nd Ed., BNL 325, U. S. Govt. Printing Office, Washington, D. C., 1958; D. J. Hughes, B. A. Magurno, and M. K. Brussel, "Neutron Cross Sections," 1st suppl., 1960.

TABLE I  
 ISOTOPE EFFECTS FROM BORIC ACID CROSS SECTIONS

Reactants	Boric acid cross sections, barns			Isotope effect, $k_{B^{10}}/k_{B^{11}}$
	From starting material	From recovered boronic ester	Formed in deboronation	
<i>exo</i> -Norboreneboronic ester and HgCl <sub>2</sub>	685	678	697	1.032
		669	685	1.027
	681	682	705	1.039
		669	689	1.034
	Av. 683 ± 2	675 ± 6	694 ± 7	1.033 ± 0.004
<i>endo</i> -Norboreneboronic ester and HgCl <sub>2</sub>	672	661	680	1.032
	683	680	694	1.024
		672	687	1.025
	Av. 678 ± 5	671 ± 7	687 ± 5	1.027 ± 0.003
	662	667	672	1.008
Benzeneboronic ester and PhHgNO <sub>2</sub>	666	666	679	1.022
	686	675	685	1.017
		668	690	1.037
	Av. 671 ± 10	669 ± 3	682 ± 6	1.021 ± 0.009

curic chloride.<sup>6</sup> The *exo* isomer reacts much faster than the *endo*. We wished to rule out the possibility that the rate-determining step might not directly involve the boron atom.

After establishing that this reaction does have a B<sup>10</sup>/B<sup>11</sup> isotope effect, we thought it desirable to measure the isotope effect in an ordinary mercurideboronation for which the mechanism had been thoroughly studied. The reaction of basic phenylmercuric perchlorate with benzeneboronic acid in aqueous ethanol to yield diphenylmercury<sup>7</sup> was chosen; we substituted the commercially available basic nitrate for the perchlorate.

Because of the rapid air oxidation of dry samples of the norborneneboronic acids we used the stable butyl esters. In aqueous acetone these would be in equilibrium with the boronic acid.

### Experimental

**Boric Acid Samples.**—A solution of 5.00 g. (0.02 mole) of 95% *exo*-dibutyl norborneneboronate<sup>8</sup> and 2.71 g. (0.01 mole) of mercuric chloride in 50 ml. of aqueous 83% acetone was allowed to stand 1 hr. under nitrogen at 25–30°, then saturated with hydrogen sulfide, and filtered. Most of the solvent was evaporated at 20 mm. and the boronic acid was extracted with ether. Concentration of the aqueous phase yielded the boric acid formed in the reaction, 0.3–0.5 g. crude, 0.2–0.35 g. once recrystallized from water. The ethereal boronic acid solution was either concentrated to yield the boronic acid or treated with butanol to yield the ester, 2.4–2.9 g. after distillation, identity checked by infrared. The boronic acid or ester was deboronated with excess alkaline hydrogen peroxide, the organic products were removed by extraction with ether, and the borate solution was acidified with sulfonic acid ion-exchange resin. The yield of boric acid after one or two recrystallizations from water was 0.2–0.4 g.

Dibutyl *endo*-norborneneboronate was similarly treated, except that 75% acetone was used as the solvent in the tabulated runs (Table I) and the solution was refluxed 24 hr. under nitrogen to complete the reaction.<sup>6</sup>

The reaction of 5.00 g. of dibutyl benzeneboronate with 3.39 g. of basic phenylmercuric nitrate in 500 ml. of aqueous 40% ethanol buffered with 4.44 g. of sodium carbonate and 1.17 g. of sodium bicarbonate yielded 3.66 g. of crystalline diphenylmercury after 6 hr. at room temperature. The solution was treated with 5 g. of sodium hydroxide and concentrated to 100 ml. at 20 mm., acidified with sulfonic acid ion-exchange resin. Subsequent work-up was analogous to that used for the norborneneboronic acids.

**Boric Acid Pellets.**—The samples of boric acid derived from a mercurideboronation reaction were all dried at one time in a vacuum desiccator about 1 hr. (until the pressure dropped to 0.1

mm.) at room temperature. About 180 mg. of boric acid was ground to powder by shaking 1 min. in a dental amalgamator. The powder was pressed into a pellet at 10<sup>4</sup> p.s.i. (700 kg./cm.<sup>2</sup>) for 3–4 min. in an evacuated Beckman 5020 0.5-in. die. In preliminary experiments (not tabulated with the results) we used the metal retaining rings commonly used for potassium bromide pellets for infrared spectra, but we found that the superior mechanical properties of boric acid made the rings unnecessary. The pellets were weighed accurately. After the neutron absorbance had been determined, the boric acid content of each pellet was determined by titration with standard base in the presence of mannitol. The weight and titration values normally agreed to ±0.1% average deviation within a set of pellets prepared at the same time, except where a pellet was considerably discolored by impurities. Data from impure pellets were discarded. Sets prepared on different days might differ by 0.3% in boron concentration, presumably because of different degrees of dehydration.

**Neutron Transmittance Measurements.**—The incident neutron beam gave a count rate of 1.15 × 10<sup>6</sup> neutrons/cm.<sup>2</sup>-min. and was essentially monochromatic at 1.37 Å. The content of fast neutrons not stopped by cadmium was about 1%. The neutron beam intensities were measured with a boron trifluoride proportional counter. The beam was collimated by passing through a pair of 5-mm.-diameter holes drilled in plugs of boron carbide powder cemented with epoxy resin and mounted 8 cm. apart. The boric acid pellets were mounted in a close-fitting well in an aluminum disk and held in place with a retaining ring prepared by cutting a Beckman 16579 ring (the kind used for holding potassium bromide pellets). The aluminum disk was threaded to screw firmly into the beam collimator and hold the pellets perpendicular to the beam. The I<sub>0</sub>/I values were determined by counting the neutrons through the collimator with and without the boric acid pellet in place, per standard number of counts on the monitor counter ahead of the collimator. Neutron counts of 5 × 10<sup>5</sup> were normally used (random counting error ±0.15%), which required counting times of about 5 min. The response of the counter was essentially linear in the region of measurement.

### Results

The isotope effects were calculated for the difference in cross sections, Δσ, between the boric acid formed in a given reaction and that derived by hydrogen peroxide deboronation of the recovered boronic ester or acid. Measured boric acid cross sections to 1.37 Å. neutrons are listed in Table I, together with the ratio of rate constants  $k_{B^{10}}/k_{B^{11}}$  calculated from each pair of boric acid samples. Table I also includes measured cross sections of boric acid derived from the untreated starting boronic esters, which were not used in the calculations but serve as a check of validity of the measurements.

**Calculations.**—If the reaction is first-order in boronic acid

$$k_{B^{10}}/k_{B^{11}} = \log ([B_o^{10}]/[B_r^{10}]) / \log ([B_o^{11}]/[B_r^{11}]) \quad (1)$$

(6) D. S. Matteson and J. O. Waldbillig, *J. Am. Chem. Soc.*, **85**, 1019 (1963); **86**, 2778 (1964).

(7) H. G. Kuivila and T. C. Muller, *ibid.*, **84**, 377 (1962).

(8) D. S. Matteson and J. O. Waldbillig, *J. Org. Chem.*, **28**, 366 (1963).

where the  $[B_o]$ 's and  $[B_r]$ 's are the initial and final molar concentrations, respectively, of the boronic acid reactant containing the given isotope in the reaction mixture. Since  $[B_o^{10}] = [B_r^{10}] + [B_i^{10}]$ , where  $[B_i^{10}]$  is the final molar concentration of  $H_3B^{10}O_3$

$$[B_o^{10}]/[B_r^{10}] = ([B_r^t]\sigma_r + [B_i^t]\sigma_i)/[B_r^t]\sigma_r \quad (2)$$

where  $[B_r^t] = [B_r^{10}] + [B_r^{11}]$ , etc., and  $\sigma_r$  is the absorption cross section due to  $B^{10}$  in the recovered boronic ester,  $\sigma_i$  that due to  $B^{10}$  in the boric acid generated in the reaction. We estimated the scattering cross section of boric acid to be 140 barns from the scattering cross sections of water, oxygen, and boron at 1.37 Å.<sup>5</sup> The average total cross section of all the boric acid samples in runs 1-7 (Table I) was about 680 barns. Subtraction of the scattering cross section leaves about 540 barns, which agrees within experimental deviations<sup>5</sup> with the absorption cross section of natural boron, 565 barns from the graph<sup>5</sup> at 0.044 e.v. (1.37 Å.). We ran our reactions to half completion ( $[B_r^t] = [B_i^t]$ ). Assuming that variations in the absolute magnitude of  $\sigma$  were not significant, we employed an approximation using  $\Delta\sigma$ .

$$[B_o^{10}]/[B_r^{10}] \cong 1 + (540 + \Delta\sigma/2)/(540 - \Delta\sigma/2) \quad (3)$$

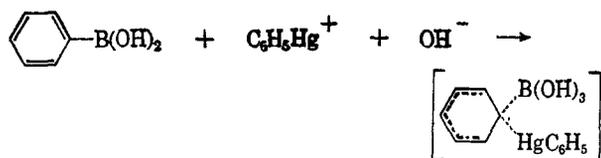
Assuming that the average  $B^{10}$  abundance was 19.8%, deriving the  $B^{11}$  values by difference, and substituting eq. 3 into eq. 1 yielded this approximate numerical relationship, essentially linear in the region of interest.

$$k_{B^{10}}/k_{B^{11}} \cong 1 + 0.00168\Delta\sigma$$

#### Discussion

From the usual assumptions,<sup>9</sup> the theoretical maximum for  $k_{B^{10}}/k_{B^{11}}$  is about 1.05-1.06. The measured values, 1.02-1.03, are thus of the expected magnitude.

Several factors may be involved in these isotope effects and some caution is called for in the interpretation. The reaction of benzenboronic acid with phenylmercuric ion evidently involves a hydroxide ion bonded to boron in the transition state.<sup>7</sup>



Possible factors involved include kinetic effects of carbon-boron bond breaking and boron-oxygen bond making, as well as the equilibrium effect of boron-oxygen bond formation. This equilibrium effect can be large; dissociation of the  $B^{11}F_3$ -dimethyl ether complex is favored over that of the  $B^{10}$  compound by 1.027.<sup>10</sup>

(9) J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 71-72.

However, this effect ought to be smaller with boronic acids, where weaker bonds than B-F are involved. Mechanisms involving this equilibrium but not carbon-boron bond breaking in the transition state seem inconsistent with other data.<sup>6,7</sup> A concerted process in which the carbon-boron bond is broken as the boron-oxygen bond is formed is one possibility; reversible boron-oxygen bond formation prior to rate-determining carbon-boron bond breaking is another.<sup>6</sup>

**Errors.**—Inspection of Table I (as well as preliminary data omitted from the tabulation) reveals that the random deviations in the isotope effects calculated from each run of a set are much smaller than the over-all random deviations in the boric acid cross sections. This is not unreasonable, since boric acid samples dried at different times showed about three times the variation in boron content by titration as the average deviation within an identically prepared set. In addition, reaction times were too short for 100% reaction of mercuric chloride, and variations in the reaction times would affect the absolute value of the cross sections more than the difference between a pair.

The two major random error sources are probably the statistical neutron counting error,  $\pm 0.15\%$  or 1 barn per pellet, and the uncertainty in pellet weight and boron concentration,  $\pm 0.1\%$ . Together these account for a random error of  $\pm 3$  barns between paired pellets, or to  $\pm 0.005$  in  $k_{B^{10}}/k_{B^{11}}$ , which is in agreement with the observations.

Recrystallization of reagent grade boric acid ( $693 \pm 5$  barns, five determinations) four times from water did not change the cross section significantly (683 and 693 barns found). Concentration of acetone-water solutions yielded negligible boric acid in the distillate on titration. Thus, isotope fractionation in preparation of the boric acid samples is probably negligible.

**Advantages of Method.**—Boric acid is the most easily obtained direct product of deboronations. It is easily purified and prepared for the simple and rapid neutron absorption measurements. The inherent accuracy seems competitive with mass spectrometry. Corrosion problems may be encountered with boron trifluoride in mass spectrometers,<sup>3b,c</sup> although methyl borate has been used.<sup>3a</sup> The relatively large samples required are a disadvantage of the neutron absorption method, although a tenfold reduction might be possible if there were need for it.

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(10) D. A. McCaulay, *U. S. At. Energy Comm.*, **A-2357** (1945) [*Nuclear Sci. Abstr.*, **11**, Abstr. No. 8556 (1957)].