[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASH.]

An Electrophilic Displacement with Inversion

By Donald S. Matteson and James O. Waldbillig¹

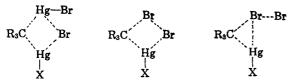
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Both exo- and endo-5-norbornene-2-boronic acid react with mercuric chloride in aqueous acetone to form nortricyclylmercuric chloride in high yields. These reactions involve transannular electrophilic displacement at saturated carbon. The exo isomer, in which the carbon atom from which the boron is displaced undergoes inversion of configuration, reacts hundreds of times faster than the endo isomer, in which the configuration is retained. Analogously, the exo isomer but not the endo yields nortricyclyl 2,4-dinitrophenyl sulfide on treatment with 2,4-dinitrobenzenesulfenyl chloride and pyridine. Unlike previously studied electrophilic displacements, these reactions do not permit direct bonding between the attacking and leaving electrophiles in the transition state. Possible factors causing the unexpected stereochemistry are discussed.

Introduction

Electrophilic displacements at saturated carbon with retention of configuration have been known for a long time. Included in this category are all the familiar intramolecular migrations of alkyl groups to electrondeficient centers, in which geometry requires retention of the configuration of the alkyl group. Intermolecular electrophilic displacements have been studied more recently. Reactive organometallic reagents racemize readily, but some stereospecificity has been found in the carbonation of 2-octyllithium.² Essentially complete retention has been observed in electrophilic displacements of mercury(II) by mercury(II) halides³ and by bromine.⁴

Although it is possible that these electrophilic displacements of mercury(II) truly represent the stereochemistry of the general process free from extraneous influences, it is at least equally likely that nucleophilic properties of the attacking electrophiles intervene.⁴ Linkage of the attacking electrophile to the leaving electrophile through a nucleophilic ligand could lead to a four-center transition state, essentially equivalent to an intramolecular 1,3-migration to an electron-deficient center in its geometry. In bromodemercuration a 1,2-shift of carbon from mercury to bromine is also possible.



The extensive studies of electrophilic displacements by Cram, *et al.*,⁵ have indicated analogous cyclic transition states involving ion pairs for reactions in which there is considerable carbanion character at the site of displacement. Certain solvents not conducive to cyclic transition states lead to considerable net inversion,⁶ but it is not certain how much relation these carbanion reactions have to more concerted electrophilic displacements.

(3) (a) S. Winstein, T. G. Traylor, and C. S. Gardner, *ibid.*, 77, 3741 (1955);
 (b) H. B. Charman, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 2530 (1959).

In view of the foregoing, there was no way of predicting the stereochemistry of a concerted electrophilic displacement with no nucleophilic linkage between the attacking and leaving electrophiles. A transannular electrophilic displacement would separate any nucleophilic ligands on the attacking electrophile from the vicinity of the leaving group and would thus be of considerable theoretical interest, even though it would not be free of possible mechanistic complications of its own. Accordingly, when *exo-* and *endo-5-*norbornene-2-boronic acid became available,⁶ we began investigating the possibility of transannular electrophilic displacements of boron with the aim of determining their stereochemical preference.

Experimental

Dibutyl exo- and endo-5-Norbornene-2-boronates.-The previously described separation of isomers⁶ was improved for preparative use as follows. A slurry of 78 g. of the dibutyl vinylboronate-cyclopentadiene adduct⁶ (60% exo) and 200 ml. of water was distilled under vacuum until the butanol was removed. The boronic acid was extracted with ether and recrystallized twice, yielding 16.5 g. of crude endo-boronic acid. The combined mother liquors were treated with 21 g. of o-phenylenediamine, the water formed was removed as an azeotrope with methylcyclohexane, and the exo-o-phenylenediamine derivative was recrystallized twice from 300 ml. of methylcyclohexane and once from carbon tetrachloride and methylcyclohexane; yield 23 g. The derivative was dissolved in a mixture of 40 ml. of methanol, 10 ml. of water, and 9.5 ml. of hydrochloric acid and the exo-boronic acid crystallized on addition of 100 ml. of water. Esterification with butanol⁶ yielded 23.7 g. of the exo ester, b.p. 67-69° (0.02 mm.). The crude endo acid was recrystallized again from ether and then from methanol-water. Esterification yielded 14 g. of endo-butyl ester, b.p. 54-57° (0.01 mm.). The purities, determined by gas chromatography of the derived dehydron orborneol mixture, 6 were 95% or better.

Nortricyclylmercuric Chloride.-A solution of 4.34 g. (0.017 mole) of 61/39% exo-/endo-dibutyl 5-norbornene-2-boronate in 60 ml. of aqueous 83% acetone was mixed with 4.90 g. (0.017 mole) of mercuric chloride in 30 ml. of acetone and heated on the steam bath until the solution evaporated to about 40%of the original volume. Cooling, filtration, and further concentration to obtain additional crops of crystals yielded 5.4 g. (94%) of nortricyclylmercuric chloride, m.p. 144-146° after recrystallization from acetone-water. Nortricyclylmercuric chloride was also obtained in 80–83 % yields from 94 % endo- and from 73 %exo-5-norbornene-2-boronic acid in smaller scale runs. The infrared spectrum showed bands at 3.28 and 12.45 μ (in Nujol), characteristic of the nortricyclyl group.7 The n.m.r. spectrum in deuteriochloroform was complex but showed no signal in the vinyl proton region. A 3.5-g, sample was brominated in pyridine, 4a yielding 0.1 g. of liquid having an infrared spectrum compatible with impure nortricyclyl bronide, n^{25} D 1.5256, reported⁷ n²⁵D 1.5269. Infrared comparison of our nortricyclyl-

Chem. Soc., 72, 3116 (1950).

 ^{(1) (}a) Abstracted in part from the Ph.D. Thesis of J. O. W. (b) We thank the National Science Foundation for financial support (NSF-G 19906).
 (c) Preliminary communication: J. Am. Chem. Soc., 85, 1019 (1963).

⁽²⁾ R. L. Letsinger, ibid., 72, 4842 (1950).

^{(4) (}a) F. R. Jensen and L. H. Gale, J. Am. Chem. Soc., 82, 148 (1960);
(b) F. R. Jensen, L. D. Whipple, D. K. Wedegaertner, and J. A. Landgrebe. *ibid.*, 82, 2466 (1960);
(c) F. R. Jensen, *ibid.*, 82, 2469 (1960).

⁽⁵⁾ D. J. Cram and L. Gosser, *ibid.*, **85**, 3890 (1963); D. J. Cram and A. S. Wingrove, *ibid.*, **85**, 1100 (1963); and numerous preceding papers by Cram, *et al.*

⁽⁶⁾ D. S. Matteson and J. O. Waldbillig, J. Org. Chem., 28, 366 (1963).
(7) J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, J. Am

mercuric chloride with that prepared by Winstein's group⁸ showed them to be the same.

Anal. Calcd. for C₇H₉HgCl: C, 25.54; H, 2.76; Hg, 60.93; Cl, 10.77. Found:⁹ C, 25.61; H, 2.83; Hg, 61.18; Cl, 10.61.

Approximate Rates of Mercurideboronation.—Two kinds of rate evidence were obtained, recovery of unchanged boronic acid and change in *endo/exo* ratio. Except as otherwise noted, all reactions were carried out at 25° (± 2) in 5:1 acetone-water by volume with the total initial boronic acid (or ester) concentration of 0.39.mole/1. At the end of the reaction period, mercuric salts were precipitated with hydrogen sulfide. The solution was filtered rapidly, concentrated at 20 mm., diluted with a few ml. of water, and extracted with ether. The residue of boronic acid from evaporation of the ether was weighed; its identity was checked by infrared. Alternatively, the boronic acid residue was deboronated with hydrogen peroxide and the *exo/endo* ratio of the derived dehydronorborneols determined by gas chromatography.⁶

From 0.25 g. of 93% endo-5-norbornene-2-boronic acid and an equimolar amount of mercuric chloride, after 26 hr. the recovery of somewhat impure boronic acid was 0.26 g. (104%). In contrast, 0.57 g, of 85% exo-boronic acid under similar conditions yielded crystalline nortricyclylmercuric chloride (not isolated) ina few minutes and after 0.5 hr. yielded 0.22 g. of ether-soluble residue. This residue contained boron (flame test) but infrared examination indicated it was not primarily boronic acid. It was subsequently found that a few per cent of an ether-soluble organomercury by-product accompanies nortricyclylmercuric chloride formation, which may account for the gross impurity in this residue. The endo-boronic acid reacted slowly at reflux; treatment of 2.16 g. (96% endo) with one-half equivalent of mercuric chloride 10 hr. under nitrogen yielded no crystalline nortricyclylmercuric chloride on cooling at 25° but did yield 0.18 \mathbf{g} . (19%) of once-crystallized boric acid and 1.51 \mathbf{g} . (70%) of the unchanged boronic acid. In 20 hr. such reaction mixtures went to within experimental error of completion. In 75% acetone a similar mixture at room temperature for 1370 hr. yielded 32% of crude boric acid and 84% of unchanged crude norborneneboronic acid which was deboronated to boric acid in 75% (62% over-all) yield (theoretical boronic acid recovery for complete reaction, 50%).

Treatment of 85% endo-boronic acid with 50 mole % of mercuric chloride for 27 hr. led to recovery of boronic acid which was over 99% endo. Treatment of 1.08 g. of 76% exo acid with 0.53 g. of mercuric chloride led to boronic acid, 67% exo; theoretical, 68% exo for complete reaction of the mercuric chloride with only the exo isomer. Reaction of 53% endo-boronic ester with 47 mole % of mercuric chloride for 280 min. yielded boronic ester which was 77% endo.

Treatment of a mixture of the butyl esters having an *exo/endo* ratio of 5.83 by weight with an equimolar amount of mercuric chloride at 25° yielded crystalline nortricyclylmercuric chloride within 7 min. After 22 min. the *exo/endo* ratio was 3.01 by the usual analysis,⁶ corresponding to consumption of 48.5% of the *exo* isomer if none of the *endo* reacted.

The reactions were considerably accelerated by calcium carbonate. Stirring 2.00 g. of 95% endo-boronic ester with equimolar mercuric chloride and 1.40 g. of calcium carbonate for 60 min. led to recovery of 0.63 g. (31%) of the starting ester, b.p. $67-70^{\circ}$ (0.1 mm.). A similar experiment except that the reactants were diluted by a factor of two (0.2 M) and the time was 120 min. led to 0.73 g. (37%) of unreacted ester. Treatment of 2 g. of 95% exo-boronic ester with equimolar mercuric chloride and 1.4 g. of calcium carbonate for 15 min. yielded no recoverable boronic ester. At 0.2 M, 2.00 g. of boronic ester having an exo/endo ratio of 5.50 when treated with equimolar mercuric chloride and 1.40 g. of calcium carbonate for 2 min. yielded 0.47 g. (43%) of crude boronic acid having an exo/endo ratio of 2.17, corresponding to reaction of 60% of the exo and none of the endo isomer.

Dibutyl Norbornane-2-boronates.—A solution of 16.4 g. of 61% exo-dibutyl norborneneboronate⁶ in 100 ml. of ethanol was hydrogenated at 2–3-atm. pressure over 2 g. of 10% palladium on charcoal and yielded 14.3 g. of dibutyl norbornaneboronates, b.p. $76-82^{\circ}$ (0.1 mm.), no evidence of unsaturation in the infrared spectrum.

Anal. Calcd. for $C_{15}H_{29}BO_2$: C, 71.43; H, 11.59; B, 4.29. Found: C, 71.72; H, 11.75; B, 4.37.

Treatment of the dibutyl norbornaneboronate mixture with mercuric chloride, each 0.4 M in aqueous 83% acetone, at reflux for 17 hr. under nitrogen yielded only unchanged boronic ester (after re-esterification) and mercuric chloride.

Nortricyclyl 2,4-Dinitrophenyl Sulfide.--- A solution of 3.20 g. of 2,4-dinitrobenzenesulfenyl chloride in 25 ml. of dry pyridine was added dropwise under nitrogen to 3.41 g. of 95% exodibutyl 5-norbornene-2-boronate in 10 ml. of pyridine, stirred, and kept below 50° . After standing overnight the pyridine was distilled at 20 mm. The residue was treated with 1 ml. of water and extracted with two 25-ml. portions of hot benzene. The benzene solution was concentrated to 20 ml., allowed to stand overnight, and filtered to remove disulfide by-product. The benzene-soluble material was crystallized from ethanol, yielding 1.53 g. (38%) of nortricyclyl 2,4-dinitrophenyl sulfide atter suitable reworking of the mother liquors. This reworking included extraction of the residue with 5% sodium hydroxide to free the sulfide from a boronic acid contaminant, which we were unable to purify. After two recrystallizations from ethanol the yield of pure sulfide was 0.93 g., m.p. 142-144.5°, reported¹⁰ m.p. 142.8-144°. An authentic sample¹⁰ was shown to be identical by infrared and mixture m.p. Similar treatment of 98% endodibutyl 5-norbornene-2-boronate with 2,4-dinitrobenzenesultenyl chloride yielded an intractable mixture from which no nortricyclyl 2,4-dinitrophenyl sulfide could be isolated. Treatment of the exo isomer with 2,4-dinitrobenzenesulfenyl chloride in ethylene dibromide under conditions where norbornene yields 10% of the nortricyclyl sulfide¹⁰ led only to an alkali-soluble residue from which no pure organic compound could be isolated.

Results

The approximate rate data are sufficient to show that the reaction of *exo*-5-norbornene-2-boronic acid with mercuric chloride is at least several hundred but not more than a few thousand times faster than that of the *endo* isomer. The faster reaction results in net inversion of the configuration of the carbon atom from which the boron leaves, the slower results in retention.



Essentially quantitative recovery of the endo-boronic acid was obtained after 24 hr. at 0.4 M concentration with 0.4 M mercuric chloride in 83% acetone. Under similar conditions, the exo isomer yielded crystalline nortricyclylmercuric chloride within a few minutes. After 30 min., an attempt to recover the exo acid led to less than 50% recovery of material too impure for certain identification. By mixing the exo isomer with a little endo and determining the change in the exo/endo ratio by gas chromatography of the derived dehydronorborneols,⁶ we were able to show that half of the *exo* isomer reacted in 20-25 min. at 25° when its initial concentration was 0.35 M, that of mercuric chloride, 0.4 M. From recoveries of unreacted starting material, the corresponding "half-life" of the endo isomer appears to be several hours at reflux temperature, several tens of days at room temperature.

Hydrochloric acid, one of the reaction products, inhibits these reactions. Its removal by stirring the reaction mixtures with calcium carbonate accelerated the rate by several tens to hundreds of times, although the pH control by this method was insufficiently accurate to permit any quantitative conclusions. Base catalysis has been previously observed in the reaction

(10) H. Kwart and R. K. Miller, J. Am. Chem. Soc., 78, 5678 (1956).

⁽⁸⁾ We thank Professor Winstein for verifying this identity in advance of publication. Nortricyclylmercuric bromide and acetate: S. Winstein, E. Vogelfanger, and K. C. Pande, Chem. Ind. (London), 2060 (1962).

⁽⁹⁾ Galbraith Laboratories, Knoxville, Tenn.

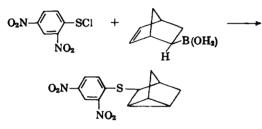
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of benzeneboronic acid with phenylmercuric ion to form diphenylmercury and boric acid.¹¹

Kuivila and Muller reported considerable kinetic complexity in the reaction of phenylmercuric chloride with benzeneboronic acid.¹¹ We expected that our mercuric chloride reactions would not be any simpler. In the hope of obtaining a reaction suitable for kinetic study, we treated the norborneneboronic acids with phenylmercuric nitrate but were only able to isolate an oily material which decomposed to diphenylmercury on standing.

Aliphatic boronic acids are too weak to permit normal pK measurements, but comparison in aqueous 33% glycerol yielded an approximate value of 8.4 for *exo*-norborneneboronic acid, 8.8 for the *endo* isomer.

Attempts were made to find other electrophiles which would react with the norborneneboronic acids in a manner analogous to mercuric chloride. Partial success was obtained with 2,4-dinitrobenzenesulfenyl chloride, which reacted with the *exo* isomer in the presence of pyridine to yield nortricyclyl 2,4-dinitrophenyl sulfide.



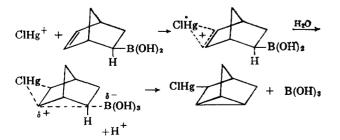
However, under similar conditions the *endo* isomer yielded only an intractable mixture of products.

Other electrophiles tried included sulfuric acid and propionic acid, both of which led to amorphous, intractable products. Aqueous silver ion dissolved the norborneneboronic acids and deposited silver slowly, but the organic product was amorphous polymer.

Discussion

We postulate that the first step of the mercurideboronations is π -complex formation between the double bond and a mercury(II) species, which we illustrate as ClHg⁺, recognizing that the actual species involved may be much more complicated. Oxymercuration of norbornenes provides evidence in favor of this postulate,¹² and the results further indicate that attack by mercury(II) should occur from the *exo* side of the norborneneboronic acid.

The rate-determining step is apparently a transannular electrophilic attack by the olefin-mercury(II) complex on the carbon bearing the boron, which is displaced as boric acid. The acceleration by calcium carbonate and the requirement of a hydroxide ion in the

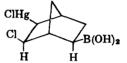


(11) H. G. Knivila and T. C. Muller, J. Am. Chem. Soc., 84, 377 (1962).
 (12) T. G. Traylor and A. W. Baker, *ibid.*, 85, 2746 (1963).

transition state of the analogous deboronation of benzeneboronic acid¹¹ indicate that the boron atom probably abstracts a hydroxide ion from the solvent before or during the transition state.

Good precedents for the transannular displacement mechanism are provided by the bromination of norbornene to bromonortricyclene⁷ and the analogous reaction of norbornene with 2,4-dinitrobenzenesulfenyl chloride.¹⁰ However, because the finding that the electrophilic displacement with inversion is much faster than that with retention was entirely unprecedented and unexpected, we have examined possible alternate mechanisms.

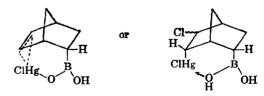
Several details of the postulated mechanism may vary without affecting the essential conclusions. For example, a covalent mercuric chloride adduct with the double bond, analogous to oxymercuration products,¹² might be formed rapidly and reversibly and is of no great concern. However, it might be argued that the



rate-determining step could be solvolysis of chloride ion from this adduct, without involving the carbon-boron bond. Accordingly, we have measured the B^{10}/B^{11} isotope effects in these reactions.¹³ The isotope effects observed, approximately 1.03 for both the *exo* and the *endo* isomer, strongly support the involvement of the boron atom in the rate-determining step.

The isotope effect measurements fail to indicate whether the rate-determining step involves boron-carbon bond breaking, boron-oxygen bond making, or both. However, the relative K_a 's of the boronic acids (in aqueous glycerol) differ by only a factor of 2.5-3. Thus the relative reactivities of the two isomers can hardly be ascribed to boron-oxygen bond formation alone.

Another hypothesis to be considered is the possibility that the reaction of the *endo* isomer is retarded by formation of a relatively stable chelate complex, not possible with the *exo* isomer. This is excluded by experiments in which the *exo* and *endo* isomers were allowed to compete for a limited amount of mercuric chloride without noticeably retarding the rate of reaction of the *exo* isomer.



It was easily shown that the double bond is involved in the rate-determining step of these reactions, since the corresponding saturated compounds, *exo-* and *endo-*2-norbornaneboronic acids, failed to react detectably with mercuric chloride under conditions where the norborneneboronic acids did react. The inertness of saturated boronic acids to mercuric chloride has been previously reported.¹⁴ However, the pos-(13) D. S. Matteson, J. O. Waldbillig, and S. W. Peterson, *ibid.*, **56**, 2781 (1964).

(14) K. Torssell, Acta Chem. Scand., 13, 115 (1959).

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.¹⁵

Extension of this argument to the reaction of 2,4dinitrobenzenesulfenyl 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.¹⁶ 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,^{1c} 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

By D. S. MATTESON, JAMES O. WALDBILLIG,¹ AND S. W. PETERSON Received March 17, 1964

Boron isotope effects in mercurideboronations were determined by measurement of the neutron absorption cross sections of appropriately derived boric acid samples. The $k_{B^{11}}/k_{B^{11}}$ 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 ± 0.005 , and that for the reaction of phenylmercuric nitrate with benzeneboronic acid in refluxing 40% ethanol was 1.021 ± 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^{10} and B^{11} isotopes is convenient for measurements and makes the preparation of labeled compounds unnecessary. Boron is light enough that its isotope effects are readily measureable. 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^{10}/B^{11} ratios are known, including B^{10} neutron absorption,² mass spectrometry,³ and emission or infrared spectroscopy.⁴

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

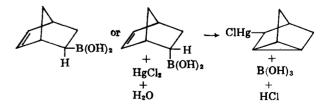
(2) (a) C. M. Judson, U. S. Al. Energy Comm., A-2367 (1946) [Nuclear Sci. Abstr., 11, 11,579 (1957)]; (b) J. E. Hudgens, Jr., L. C. Nelson, R. C. Meyer, and C. Zyskowski, U. S. Al. Energy Comm., NBL-102 (1954) [Chem. Abstr., 55, 18,378 (1961)].

(3) (a) R. M. Abernathey, 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/B 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. Mal'tsev, E. N. Moskvitina, and V. M. Tatevskii, Fis. Sbornik L'vov. Univ., No. 3, 472 (1957) [Chem. Abstr., 56, 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 B¹⁰ to thermal neutrons is 4 \times 10³ barns.⁵ In contrast, B¹¹ and O¹⁶ are practically transparent to thermal neutrons, having scattering cross sections of about 4 barns, while H¹ has an energy-dependent scattering cross section ranging from 20 to 80 barns in the low energy region.⁵ The attenuation of a neutron beam by a boric acid sample thus depends largely on the concentration of B¹⁰ 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.