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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILL.]

Arylboronic Acids. VI. Aminoboronic Anhydrides and a New Heterocycle Containing Boron[1,2]

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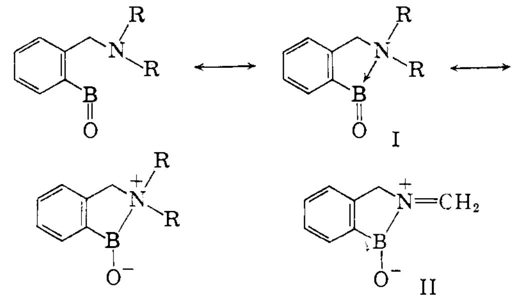
Three *o*-(dialkylaminomethyl)-benzeneboronic anhydrides are shown to be trimeric. Hydration of the corresponding anhydrides, which do not form complexes with pyridine, provides *o*-(N-morpholinomethyl)- and *o*-(dicyclohexylaminomethyl)-benzeneboronic acids. The latter acid shows remarkable stability to acid-catalyzed deboronation as well as dehydration. A new tetracyclic boron-containing heterocycle is reported. The structure of the compound, an *o*-methylene-bridged dihydrobenzoboradiazole, and some of its properties are discussed.

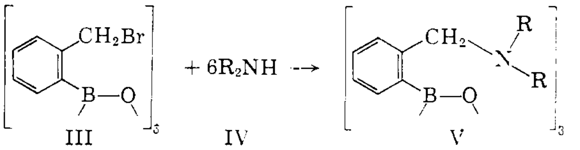
The interactions that may occur between an electron-deficient boron atom and an electron-rich functional group in a suitably substituted organoboron compound are of unusual interest.[4,5] Studies of heteroaromatic compounds such as 9-aza-10-boraphenanthrene have been reported.[6] The heterocycle, an isostere of phenanthrene, shows some aromatic character, with a stability suggestive of the borazoles and unlike that of simple boramides. Similarly, some aromatic character has been ascribed to the 2-substituted-1,3-dihydro-2,1,3-benzoboradiazoles.[7-11] The partial boron-nitrogen double bond character in such compounds is indicated by their enhanced stabilities and their ultraviolet spectra. Boron compounds with hetero atoms other than nitrogen also have been studied.[7,8]



I

II

It seems reasonable to expect that the formation of a trimeric boronic anhydride might be prevented by introducing an electron-rich atom into the molecule at such a point that it could neutralize the deficiency of the boron atom. Thus, the anhydride of an *o*-(dialkylaminomethyl)-benzeneboronic acid might exist as the hetercycle I as a result of resonance among the hypothetical structures shown. The similarity to a structure (II), which has been considered previously[12] for a by-product obtained from *o*-(bromomethyl)-benzeneboronic acid in the Sommelet reaction, is obvious. Several attempts to prepare boronic acids related to I by reaction of the *o*- and *p*-(bromomethyl)-benzeneboronic acids[13] with ammonia and amines[14,15] have been unsuccessful. Failure of the reactions on the *ortho* isomer may have been due to the fact that the basic reagents brought about cyclization to boronophthalide.[16,17] It has been possible to circumvent this cyclization in the replacement of the bromine atom by alkoxyl[16] by operating on the boronic anhydride rather than the acid. In the present work the reaction of *o*-(bromomethyl)-benzeneboronic anhydride with secondary amines was chosen as the most attractive route.



III IV V

$+$

$3R_2NH_2^+Br^-$

VI

Morpholine, dicyclohexylamine and dimethylamine all reacted to give products which appear to exist exclusively as the normal trimeric anhydrides V. Heating the trimers under diminished pressure did not bring about depolymerization; decomposition with the loss of a basic fragment appeared to occur instead. The failure to obtain a stable monomeric anhydride indicates that the amino nitrogen atom in these compounds is not sufficiently basic to satisfy completely the electron demand of the boron atom in structures such as I. The dicyclohexyl-

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[2] Taken in part from the thesis of R. T. Hawkins submitted in partial fulfillment of the requirements for the degree of doctor of philosophy in the Graduate College of the University of Illinois, 1959.

[3] University of Illinois Fellow, 1956–1957; Phillips Petroleum Co. Fellow, 1957–1959.

[4] M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

[5] R. L. Letsinger and S. H. Dandegaonker, THIS JOURNAL, **81**, 498 (1959).

[6] M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

[7] D. Ulmschneider and J. Goubeau, *Ber.*, **90**, 2733 (1957).

[8] M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3076 (1958).

[9] R. L. Letsinger and S. B. Hamilton, THIS JOURNAL, **80**, 5411 (1958).

[10] E. Nyilas and A. H. Soloway, *ibid.*, **81**, 2681 (1959).

[11] H. R. Snyder, R. T. Hawkins and W. J. Lennarz, *ibid.*, **82**, 3053 (1960).

[12] H. R. Snyder, A. J. Reedy and W. J. Lennarz, *ibid.*, **80**, 835 (1958).

[13] H. R. Snyder, M. S. Konecky and W. J. Lennarz, *ibid.*, **80**, 3611 (1958).

[14] K. Torssell, *Arkiv. Kemi*, **10**, 507 (1957).

[15] A. J. Reedy, Thesis, Doctor of Philosophy, University of Illinois, 1957.

[16] W. J. Lennarz, Thesis, Doctor of Philosophy, University of Illinois, 1959.

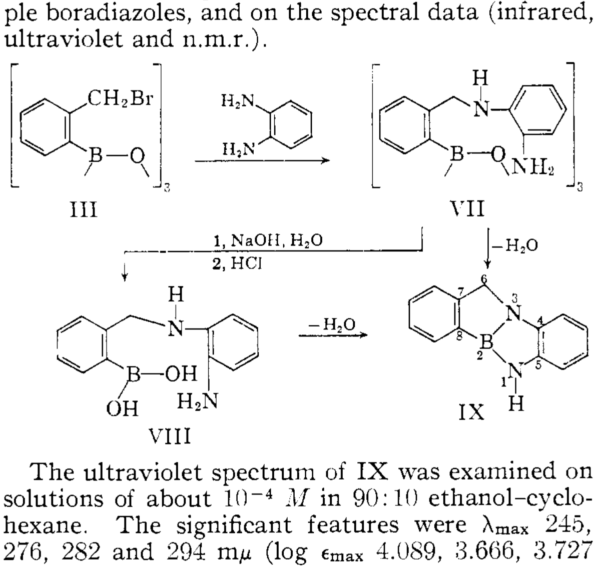
[17] H. R. Snyder and W. J. Lennarz, THIS JOURNAL, **82**, 2172 (1960).

substituted amine was chosen to test whether the bulky groups would favor the existence of the monomer because of steric interference with the boroxole ring of the trimer, but the effect apparently is insufficient. However, the anhydride of *o*-(dicyclohexylaminomethyl)-benzeneboronic acid was so readily hydrolyzed that a satisfactory analytical sample was not obtained. The susceptibility to hydrolysis may well result from steric strain in the anhydride.

The assignment of the trimeric structures to the amino-anhydrides V was made on the basis of a molecular weight measurement on the morpholino compound and on the basis of the presence of a band at about 672 cm.$^{-1}$ in the infrared spectra of all the compounds; a band in this region has been found useful in characterizing ordinary (trimeric) boronic anhydrides.[13,16] Another indication was observed in the formation of a dihydrochloride of the trimeric dimethylamino-anhydride, which precipitated when hydrogen chloride was passed into a benzene solution of the compound. The formation of a dihydrochloride (infrared band at 670 cm.$^{-1}$) suggests that one of the amine groups may be neutralized by interaction with the boroxole ring, interaction of the kind responsible for the formation of boronic anhydride-pyridine complexes.[13] The fact that the amino-anhydrides could not be converted to pyridine complexes supports this interpretation. It would be of interest to determine how many of the amino groups in the anhydrides can be quaternized with active alkyl halides, but, unfortunately, although reactions did occur, pure quaternary salts could not be isolated from treatment of the dimethylamino- and morpholino-anhydrides with methyl iodide, benzyl chloride and triphenylmethyl chloride.

Although the anhydride of *o*-(dicyclohexylaminomethyl)-benzeneboronic acid, as mentioned above, could not be obtained in analytically pure state because of its sensitivity to water, the aminoboronic acid was obtained easily in the pure state. The acid was remarkably stable to dehydration. It did not lose weight at an appreciable rate at 25° and 1 mm. pressure over calcium chloride, and even after 88 hr. at 76° and less than 1 mm. pressure over phosphorus pentoxide only 28% of the theoretical weight loss was observed. The acid also was extraordinarily resistant to acid-catalyzed deboronation.[4,11] Over 80% of a sample of it was recovered after treatment for one hour with refluxing 12% hydrochloric acid; the morpholino analog was completely deboronated by this treatment.

By treatment of *o*-(bromomethyl)-benzeneboronic anhydride with *o*-phenylenediamine and subsequent dehydration of the condensation product, a new heterocyclic system (IX) containing boron was obtained. The substance is a methylene-bridged dihydrobenzoboradiazole for which the name 1,2,3,6 - tetrahydro - 4,5,7,8 - dibenzo - 2,1,3 - boradiazapentalene (numbered as shown in IX) is proposed. As indicated in the reaction scheme, it was obtained directly from the condensation product, presumably VII, by dehydration *via* azeotropic distillation with benzene, or in somewhat better yield (*ca.* 13%) by a preliminary treatment with alkali and water, intended to remove *o*-phenylenediamine present as such or as the hydrobromide and to open the anhydride ring, followed by neutralization and dehydration of the aminoboronic acid, presumably VIII, *via* azeotropic distillation with toluene. The product IX was purified easily by sublimation. Its structure is assigned on the basis of its composition and properties, on the analogy to simple boradiazoles, and on the spectral data (infrared, ultraviolet and n.m.r.).



The ultraviolet spectrum of IX was examined on solutions of about 10^{-4} *M* in 90:10 ethanol-cyclohexane. The significant features were λ_{max} 245, 276, 282 and 294 mμ (log ϵ_{max} 4.089, 3.666, 3.727 and 3.755, respectively). In the presence of a 5-fold excess of hydrogen chloride the maxima found were at 242, 270, 277 and 362 mμ, and after neutralization, filtration and re-examination they were found at 245, 276, 282 and 294 mμ. The same values were found in the presence of 1.25 equivalents of sodium hydroxide. The spectrum resembles that of *o*-phenylenediamine, but is shifted to longer wave lengths and is more intense; it is similar to but somewhat less intense than that of a dihydrobenzoboradiazole,[8] probably as the result of lower double bond character of the boron-nitrogen bonds of the boradiazapentalene. Molecular models indicate that the four rings cannot be coplanar. The infrared spectrum of IX revealed bands at 3420, 1609, 1465, 1362, 1115-1175 and 715-755 cm.$^{-1}$. The absorption at 3420 cm.$^{-1}$ is attributed to the NH, and that at 1609 is tentatively assigned to the aryl-boron linkage. The strong absorption at 1465 cm.$^{-1}$ occurs in the range (about 1500 cm.$^{-1}$) attributed[18] to the boron-nitrogen bond of high double bond character in acyclic systems, and is near absorptions shown by phenyl and mesityl dihydrobenzoboradiazoles.[10,11] The absorption at 1362 cm.$^{-1}$ is near that (1372 cm.$^{-1}$) in phenyldihydrobenzoboradiazole also attributed[10] to a boron-nitrogen bond having double bond character, and that in the 1115-1175 cm.$^{-1}$ region is near that also attributed to the boron-nitrogen bond in the same compound.[10] The absorption at 715-755 cm.$^{-1}$ consists of three sharp peaks occurring in the region characteristic of *o*-disubstituted benzene derivatives, and could result from the presence of two different types of *o*-substitution, as in IX. The low solubility of IX in carbon tetrachloride prevented a complete study of the n.m.r.

[18] K. Niedenzu and J. Dawson, THIS JOURNAL, **81**, 5553 (1959).

spectrum; however, resonance was detected in the regions of aromatic and benzylic protons (ratio, *ca.* 8:2), and no other resonance was observed.

The boradiazapentalene (IX) proved to be slightly soluble in dilute acid, but not in dilute aqueous base, as expected from the spectral (ultraviolet) observations mentioned above. Although it was soluble in concentrated acids, it could not be recovered from these solutions. Its slow oxidation in the air, with the development of color, is similar to that of other dihydrobenzoboradiazoles.[11] Hydrogen peroxide caused rapid color development when added to solutions of IX in dioxane (red color) or ethanol (golden yellow color).

Experimental[19,20]

o-**Tolueneboronic Anhydride.**—*o*-Tolueneboronic acid was prepared from *o*-tolylmagnesium bromide in ether and methyl borate by means of the technique of simultaneous addition.[11] The acid was recrystallized from water and converted to the anhydride by drying initially in a vacuum desiccator and in a vacuum oven until the infrared spectrum indicated substantially no hydroxyl absorption.

o-**(Bromomethyl)-benzeneboronic Anhydride.**—*o*-Tolueneboronic anhydride was brominated according to the procedure of Snyder, Konecky and Lennarz.[13] The bromo-anhydride, obtained in 85% yields from large scale preparations, was sufficiently pure to be used in ensuing reactions without further purification.[21]

o-**(Dimethylaminomethyl)-benzeneboronic Anhydride**—A benzene solution of dimethylamine was prepared by adding solid sodium hydroxide in excess to 20 ml. of a 40% aqueous solution of dimethylamine (8 g., 0.177 mole) and extracting the amine into two 20-ml. portions of benzene. The benzene extracts were combined and dried over solid sodium hydroxide.

The benzene solution of the amine was treated, with agitation at room temperature, with 2.00 g. of *o*-(bromomethyl)-benzeneboronic anhydride (0.00338 mole) over a period of 5 or 10 min. The mixture was stirred for 5 min., allowed to stand one hour, and then concentrated to 15 ml. A precipitate of dimethylamine hydrobromide (0.94 g., 74%) was removed by filtration and washed with cold benzene, and the filtrate and washings were combined and concentrated under reduced pressure to a golden-colored solid. Trituration with ether produced a light tan powder which was collected, washed with ether, and dried. The yield of crude material was 1.77 g.

A portion of the crude material was chromatographed on an alumina column. The solid eluted by chloroform–methanol was recrystallized from toluene and dried at 100° at 0.5 mm. pressure over phosphorus pentoxide, and finally recrystallized from dry pyridine, rinsed with dry ether and dried at 100° and 0.3 mm. pressure. The analytical sample melted at 219–220°.

Anal. Calcd. for $C_{27}H_{36}B_3N_3O_3$: C, 67.13; H, 7.51; N, 8.70. Found: C, 68.12; H, 7.64; N, 8.88.

o-**(Dimethylaminomethyl)-benzeneboronic Anhydride Dihydrochloride.**—A solution of 30 mg. of *o*-(dimethylaminomethyl)-benzeneboronic anhydride in 30 ml. of benzene was saturated with anhydrous hydrogen chloride at room temperature. The suspension was heated to boiling on the hot-plate, cooled to room temperature, and then allowed to stand for 2 hr. The precipitate was removed by filtration, washed well with ether, and dried at 100° and 0.1 mm. pressure over phosphorus pentoxide for 6 hr. to a fine, exceedingly hygroscopic white powder (24 mg., 70%).

Anal. Calcd. for $C_{27}H_{38}B_3Cl_2N_3O_3$: C, 58.33; H, 6.89; N, 7.56. Found: C, 58.96; H, 7.27; N, 7.51.

o-**(N-Morpholinomethyl)-benzeneboronic Anhydride.**—A filtered, warm solution of 4.00 g. (0.00676 mole) of *o*-(bromomethyl)-benzeneboronic anhydride in 60 ml. of benzene was added over a period of 5 min. to a solution of (4.0 g., 0.0519 mole) of morpholine in 20 ml. of benzene. The mixture was stirred 2 min., warmed on the steam-bath for 30 min., and finally chilled in an ice-bath. The amine salt was removed by filtration and the filter pad was washed thrice with cold benzene. A second crop of amine salts separated when the combined filtrate and washings were concentrated. The combined yield of dried amine salt was 3.12 g. or 91.5%.

The combined filtrate and washings were concentrated under reduced pressure on the steam-bath to a sticky, orange oil that crystallized on trituration with ether (2.77 g., 67.2%). The infrared spectrum of the crude amino-anhydride indicated the presence of some of the corresponding boronic acid, some morpholine salts, and other unknown materials.

A portion of the crude amino-anhydride was recrystallized from toluene and dried at 25° and 0.3 mm. pressure overnight. The analytical sample showed a melting point of 220–222° dec.

Anal. Calcd. for $C_{33}H_{42}B_3N_3O_3$: C, 65.06; H, 6.95; B, 5.33; N, 6.90; mol. wt., 609.2. Found: C, 65.65; H, 7.18, B, 5.17; N, 7.09; mol. wt. (ebullioscopic in benzene), 653.

Silver nitrate-catalyzed deboronation of the amino-anhydride yielded N-benzylmorpholine, identified as its picrate, m.p. and mixed m.p. with a known sample, 193–194° (lit.[22] 193.5–195°).

Attempted Formation of a Complex[13] between Pyridine and *o*-**(N-Morpholinomethyl)-benzeneboronic Anhydride.**—To a solution made by dissolving 101 mg. of *o*-(N-morpholinomethyl)-benzeneboronic anhydride (0.166 millimole) in 2.0 ml. of hot toluene was added 14 mg. of pyridine (0.178 millimole, or 107%). The solution was allowed to cool, but precipitation was slow. Accordingly, 2.0 ml. of petroleum ether was added and the mixture was chilled. The recovery of the dry crystals was 57 mg. or 56% identified as the original anhydride by mixed melting point and comparison of the infrared spectra. Under similar conditions, benzeneboronic anhydride gave a complex in high yield.

o-**(N-Morpholinomethyl)-benzeneboronic Acid.**—A solution of the crude amino-anhydride in hot water was treated with charcoal and concentrated on the steam-bath until a little dark oil separated. Both phases deposited crystals when the mixture was cooled. The washed crystals were redissolved in a minimum of hot water, the solution was filtered, and the filtrate was allowed to stand at room temperature. Within 6 days, long needles, up to 10 mm. in length, had begun to separate. A day later, a large crystal, 10 × 4 × 3 mm., had deposited from the solution along with many other clusters of needles and diamond-shaped crystals. The acid showed an indefinite melting point, with loss of water occurring as low as 90°. Analyses indicated the presence of excess morpholine (about 12%).

o-**(Dicyclohexylaminomethyl)-benzeneboronic Acid**—The crude anhydride, obtained in nearly quantitative yield by essentially the same procedure used with the morpholine analog, resisted attempted purification by crystallization or sublimation. It was readily hydrated; despite routine precautions to exclude moisture during recrystallization attempts, mixtures of the acid and the anhydride were invariably obtained, as indicated by analysis and infrared spectrum.

The crude anhydride (*ca.* 6 g.) was dissolved in 30 ml. of hot 95% ethanol and water was added almost to the cloud point. The mixture was boiled, filtered and concentrated to 40 ml. on the hot-plate. The crystals of the acid that separated upon cooling were rinsed sparingly with 95% ethanol. The acid was dried at 27° and 0.5 mm. pressure over calcium chloride for 90 min. The yield was 3.62 g. or 56.8% based on the amine. The infrared spectrum

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[19] All melting points were determined on a calibrated Fisher melting-point block apparatus. Microanalyses were performed by Mr. Josef Nemeth and his associates. Molecular weight determinations were made by Clark Microanalytical Laboratory, Urbana, Ill. Infrared spectra were determined by Mr. Paul McMahon and his associates using a Perkin–Elmer model 21 infrared spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were determined by Mr. J. Chiu using a Cary model 14 spectrophotometer.

[20] Proton magnetic resonance spectra were determined by Mr. B. E. Shoulders using a Varian Associates V-4300-B spectrometer with a hydrogen precession frequency of 40 mc. Assistance in the interpretation of these spectra by Dr. David M. Grant, University of Utah, is gratefully acknowledged.

[21] Some of the bromo-anhydride used in this work was kindly provided by Dr. W. J. Lennarz and Mr. J. R. Kuszewski.

[22] J. P. Mason and M. Zief, THIS JOURNAL, **62**, 1450 (1940).

of the product was essentially the same as that of the analytical sample prepared by two recrystallizations from 95% ethanol (7.6 ml. per g.). The pure acid was dried at 26° and 0.3 mm. over calcium chloride for 3 hr. It showed an indefinite melting point as low as 146° with loss of water.

Anal. Calcd. for $C_{19}H_{30}BO_2N$: C, 72.38: H, 9.59; N, 4.44. Found: C, 72.52; H, 9.40; N, 4.49.

o-(Dicyclohexylaminomethyl)-benzeneboronic Acid Hydrochloride.—A solution of 60 mg. of pure acid in 30 ml. of dry ether was saturated with dry hydrogen chloride. The white powder was removed by filtration, washed copiously with ether, and dried at 25° and 0.1 mm. pressure over calcium chloride for 66 hr. The yield of amine salt was 60 mg. or 89.5%. The hydrochloride showed an indefinite melting point above 134° with loss of water.

The analytical data indicated that the hydrochloride contained excess hydrogen chloride. The results were consistent for a mixture of 98% hydrochloride and 2% hydrogen chloride (2% excess HCl requires C, 63.7; H, 8.77; and Cl, 11.84).

Anal. Calcd. for $C_{19}H_{31}BClO_2N$: C, 64.88; H, 8.88; Cl, 10.08. Found: C, 63.80; H, 8.81; Cl, 11.98.

1,2,3,6-Tetrahydro-4,5,7,8-dibenzo-2,1,3-boradiazapentalene (IX).—A solution of 6.58 g. of recrystallized o-phenylenediamine (61.0 millimoles) in 50 ml. of benzene was warmed and stirred under nitrogen. A solution, prepared by dissolving 3.58 g. of o-(bromomethyl)-benzeneboronic anhydride (6.06 millimoles) in 100 ml. of hot benzene and cooling, was added to the flask over a period of 20 minutes at slightly below reflux temperature. A precipitate appeared immediately and increased in amount. The addition funnel was rinsed with 5 ml. of benzene and the liquid was added to the flask. After 50 min. of stirring, the heating mantle was removed from the flask and the flask was cooled in an ice-bath. To the crude mixture, consisting of a brown solution over a yellow precipitate, was added 4.0 g. of sodium hydroxide dissolved in 30 ml. of water.

The alkaline slurry was stirred 3 min. and then rinsed into a separatory funnel with 50 ml. of water. The aqueous layer was withdrawn and the interfacial material was left with the organic layer. The organic layer was extracted twice with solutions consisting of 0.4 g. of sodium hydroxide, 25 ml. of water and a little sodium chloride, and the extracts were combined with the first water phase. The combined water layers were washed twice with 25 ml. of benzene. The caustic layer was allowed to stand about 1 hr. in the cold.

The caustic extract was neutralized in the cold with concentrated hydrochloric acid to a *p*H of 7.1 as measured by a *p*H meter. The brown solids which separated were collected. The apparent *p*H of the yellow filtrate was 6.5, and no more precipitate appeared at lower *p*H.

The aminoboronic acid was air-dried overnight and then extracted into boiling toluene for about 5 hr., or until no more colored material was being extracted. The dark red solution was concentrated under nitrogen and allowed to cool. The orange crystals (m.p. 215–229°) were removed by filtration, rinsed with cold toluene, and dried briefly in vacuum at room temperature. The yield was 512 mg. or 13.7%. The infrared spectrum was not greatly different from that of the pure product.

The crude boradiazapentalene was recrystallized from benzene to yield silvery-white flakes, very prone to acquire a static charge. The melting point was raised to 239–242°, and the recovery was 85%. The recrystallized boradiazapentalene sublimed readily at 150° and 0.4 mm. pressure. The analytical sample so obtained was very light and fluffy, statically charged, and thus hard to handle. The pure 1,2,3,6-tetrahydro-4,5,7,8-dibenzo-2,1,3-boradiazapentalene melts at 245° with dec.

Anal. Calcd. for $C_{13}H_{11}BN_2$: C, 75.77; H, 5.38; B, 5.25. N, 13.60. Found: C, 75.78; H, 5.29; B, 5.24; N, 13.36;

[CONTRIBUTION FROM THE RICHARD B. WETHERILL LABORATORY OF PURDUE UNIVERSITY]

Hydroboration. IV. A Study of the Relative Reactivities of Representative Functional Groups toward Diborane

BY HERBERT C. BROWN AND W. KORYTNYK[1]

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The relative rates of reduction of a number of representative classes of organic compounds by diborane were established by competition experiments. The results indicate the rates of reaction to decrease in the order: carboxylic acids > olefins > ketones > nitriles > epoxides > esters. Of interest in synthetic chemistry is the marked ease of reduction of the carboxylic acid group, which permits its selective reduction in the presence of the ketone group, and the inertness of the epoxide ring, which permits the complete reduction of a ketone group, or the hydroboration of the carbon–carbon double bond, without significant attack on the epoxide grouping.

Diborane is a powerful reducing agent, capable of reducing many functional groups under exceedingly mild conditions.[2,3] Study of the reaction of typical organic molecules with an excess of diborane gave a rough indication of the relative ease of reduction by this reagent of representative functional groups.[3]

It was observed that aldehydes, ketones, epoxides, nitriles, lactones and azo compounds are reduced rapidly by the reagent, whereas esters react slowly, and acid chlorides and nitro compounds are relatively inert toward the reagent under the experimental conditions. Although the data permitted a rough estimate of the relative reactivities of these groups, it appeared desirable to obtain more quantitative data. It appeared that such data could be obtained by running competitive reductions in which the two components competed for a limited quantity of diborane. Accordingly, we undertook an investigation of such competitive reductions, utilizing vapor phase chromatography (V.P.C.) for analysis of the reaction mixtures.

Results

After preliminary exploration of various procedures, it was decided to examine the reductions in tetrahydrofuran as solvent, utilizing diborane generated externally. The high solubility of diborane in this solvent offered obvious advantages for quantitative work.

In these experiments the reactants were to compete for a limited amount of diborane. Consequently, it appeared desirable to establish the pre-

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(1) American Cyanamid Co. Post-doctorate Fellow at Purdue University, 1958–1959.

(2) H. C. Brown, H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **61**, 673 (1939).

(3) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1135 (1957); H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **82**, 681 (1960).