agent and which was maintained until the mixture was hydrolyzed. The percentage yield is based upon the crude product. In all cases the purity of the crude acid seemed to be the same, since the melting points were nearly the same.

Reaction of Boron Trichloride with Organomercury Compounds.—The organomercury compound (0.05 mole) was suspended in 500 ml. of chlorobenzene in a three-necked, round-bottomed flask equipped with a stirrer, a Dry Ice–acetone condenser attached to a mercury pressure relief valve, and an inlet tube which extended below the level of the solvent. The inlet tube was connected through a mercury trap[20] to a tank of boron trichloride. Boron trichloride was bubbled into the mixture until the boron trichloride tank had decreased in weight the amount desired for the reaction. After stirring for the desired length of time, the mixture was filtered to remove the mercuric chloride and the filtrate was hydrolyzed by the slow addition of ice. The hydrolysis appeared to be catalyzed by hydrogen chloride and so once started was autocatalytic. The rate of hydrolysis could be controlled only by the amount of water added. The acid which was formed was extracted with 250 ml. of 10% potassium hydroxide in four portions. The aqueous solution was washed with 100 ml. of ether and then acidified. The cream colored solid which separated was filtered and recrystallized from water.

The results of several reactions are summarized in Table II.

TABLE II

REACTION OF BORON TRICHLORIDE WITH ORGANOMERCURY COMPOUNDS

ArM	Excess BCl_3, %	Reacn. time, hr.[a]	Yield, %[b]
$(C_6H_5)_2Hg$	100	0.5	70.5
$(C_6H_5)_2Hg$	100	0	55.0
$(C_6H_5)_2Hg$	50	2.5	52.0
$(C_6H_5)_2Hg$	50	3	57.0
$(C_6H_5)_2Hg$	200	6	70.0
p-$ClHgC_6H_4OH$[c]	100	10	0.0[d]
p-$CH_3COOHgC_6H_4NH_2$	100	10	0.0[e]
p-$ClHgC_6H_4COOH$	100	4	0.0[f]
p-$ClHgC_6H_4COOH$[g]	1000	12	0.0[f]

[a] This represents the time after the addition of the boron trichloride was complete. [b] The yield is based upon the recrystallized boronic acid. [c] Used 0.2 mole of organomercury compound. [d] There was separated 54% of phenol and 92% of mercuric chloride. [e] Isolated nearly 100% of mercuric chloride. [f] Recovered the starting mercury compound quantitatively. [g] This reaction was run at 120°.

AMES, IOWA

---

[20] This trap served to remove any chlorine which was present in the boron trichloride as well as to allow the rate of addition to be observed carefully.

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

Aryl Boronic Acids. II. Aryl Boronic Anhydrides and their Amine Complexes[1]

BY H. R. SNYDER, MILTON S. KONECKY[2] AND W. J. LENNARZ

RECEIVED FEBRUARY 1, 1958

The change of an arylboronic acid to its anhydride, which sometimes occurs when the acid is simply warmed in an anhydrous solvent, can be detected by examination of the infrared absorption spectrum of the sample. As a result of the change, the hydroxyl absorption band of the acid disappears and a new absorption near 700 cm.$^{-1}$, characteristic of the anhydride, appears. The bromination of *p*-tolueneboronic acid in carbon tetrachloride is found to produce a mixture of *p*-bromomethylbenzeneboronic acid and its anhydride. The yield in the bromination is increased by prior conversion of *p*-tolueneboronic acid to its anhydride. The formation of complexes between arylboronic anhydrides and amines is studied further, and the use of the complexes in the purification of the boronic acids is suggested.

The syntheses of boronic acid analogs of azo dyes,[3a,b,4] diaminoacridine dyes[5] and certain amino acids[6] are of interest because the substances may be of use in the boron-disintegration therapy of brain tumors proposed by Kruger.[7] In this therapy, tumor cells are destroyed by the dissipation of the high energy of products resulting from the neutron-induced disintegration of the boron isotope 10 which has been localized within the neoplasm in the form of some suitable organic derivative.

In the course of recent studies in this Laboratory devoted to the synthesis of these boronic acid analogs, the ease with which aryl boronic acids form the corresponding anhydrides, a phenomenon noted by Gilman, *et al.*,[8] for *o*-hydroxybenzeneboronic acid, has been observed. With the objective of developing a criterion for distinguishing a boronic acid and its anhydride from each other and from mixtures of both, the infrared spectra of several aryl boronic acids and the corresponding anhydrides were studied.

As a result of this study a region of absorption, invariably strong and sharp, between 680 and 705 cm.$^{-1}$ has been empirically assigned to the aryl boronic anhydride structure. This absorption is absent from the spectrum of a pure aryl boronic acid, while the infrared absorption attributed to the hydroxyl group of a boronic acid is not detected in the spectrum of a pure anhydride. The infrared spectrum of a mixture of an acid and anhydride exhibits both of these absorption bands in diminished intensity. Table I shows the region of absorption in the infrared for the hydroxyl group of the boronic acid together with the position of the anhydride band for the corresponding anhydride. The absorption band which invariably occurs near 1350 cm.$^{-1}$ with both aryl boronic acids

---

[1] Part of this work was supported by a grant [AT(11-1)-314] from the Atomic Energy Commission.

[2] Texas Co. Fellow, 1956–1957.

[3] (a) H. R. Snyder and C. Weaver, THIS JOURNAL, **70**, 232 (1948); (b) H. R. Snyder and S. L. Meisel, *ibid.*, **70**, 774 (1948).

[4] H. Gilman, L. Santucci, D. Swayampati and R. Ranck, *ibid.*, **79**, 2898 (1957).

[5] M. S. Konecky, Thesis, Doctor of Philosophy, University of Illinois, 1958.

[6] H. R. Snyder, A. J. Reedy and W. J. Lennarz, THIS JOURNAL, **80**, 835 (1958).

[7] P. G. Kruger, *Radiation Research*, **3**, 1 (1955).

[8] H. Gilman, L. Santucci, D. Swayampati and R. Ranck, THIS JOURNAL, **79**, 3077 (1957).

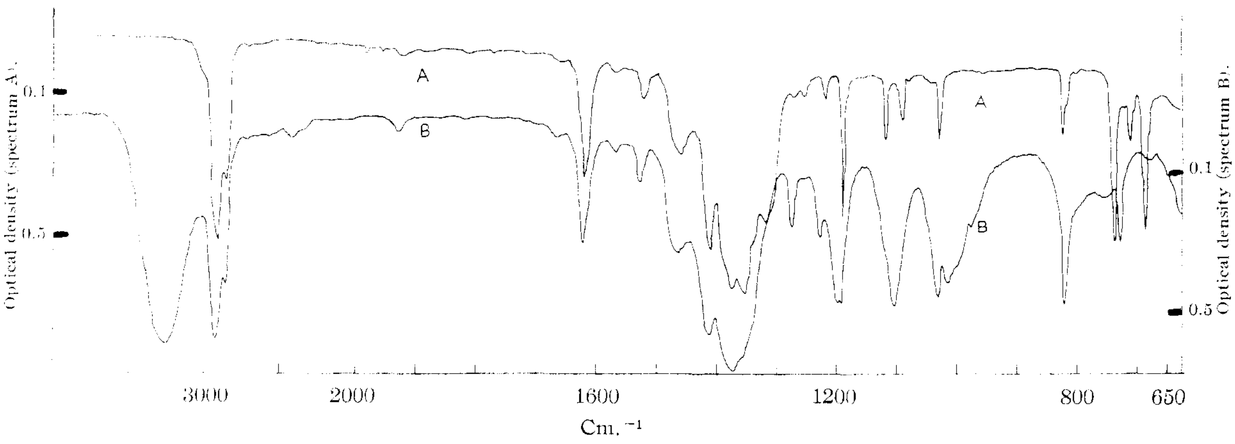


Fig. 1.—Infrared spectra of tolueneboronic anhydride (A) and tolueneboronic acid (B).

and anhydrides appears to be the most reliable criterion for the presence of the boron–oxygen linkage. The position of this absorption band for each boronic acid is also given in Table I. The infrared spectra of *p*-tolueneboronic acid and anhydride are reproduced in Fig. 1.[9]

TABLE I

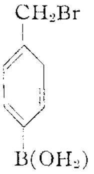
SELECTED INFRARED ABSORPTION BANDS OF ARYL BORONIC ACIDS AND THE CORRESPONDING ANHYDRIDES[a]

Aryl boronic acid	OH band, cm.$^{-1}$	Anhydride band, cm.$^{-1}$	BO band, cm.$^{-1}$[b]
Benzeneboronic	3250	690(sh.)	1355
p-Tolueneboronic	3250	685	1355
o-Tolueneboronic	3340(3260sh.)	685	1350
Mesityleneboronic[c]	3300	705	1350
p-Ethylbenzeneboronic	3250	680	1350(broad)
p-Vinylbenzeneboronic[d]	3400	700	1350
ω-Bromo-*p*-tolueneboronic	3310	690	1350

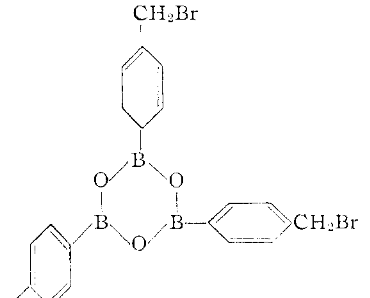
[a] All infrared spectra obtained from Nujol mulls. [b] For the acids only. [c] R. T. Hawkins, unpublished studies. [d] W. J. Lennarz, unpublished studies.

The formation of an anhydride from the corresponding aryl boronic acid by the heating (or even gentle warming) of the acid in an anhydrous solvent appears to be a general phenomenon. Benzeneboronic acid, *p*-tolueneboronic acid and *p*-vinylbenzeneboronic acid have been observed to undergo dehydration to the anhydrides when warmed or heated under reflux in anhydrous carbon tetrachloride or chloroform. If a large enough sample of the boronic acid is heated in the solvent, a layer of water is detectable. If the water is removed by azeotropic distillation or by filtration of the solution through absorbent cotton, the conversion of the acid to the anhydride is complete. This latter observation was made in connection with the preparation of ω-bromo-*p*-tolueneboronic acid (I) and ω,ω-dibromo-*p*-tolueneboronic acid according to the method of Torssell.[10]

Torssel effected the preparation of these two bromoboronic acids by the mono- and dibromination of *p*-tolueneboronic acid with N-bromosuccinimide in carbon tetrachloride, but the composition reported did not agree with that calculated for these acids. When this preparation of I was repeated (on a scale fourfold larger than employed by Torssell), a visible layer of water was present in the reaction mixture. Since the presence of water would be expected to decrease the yield, the water was removed by filtration of the carbon tetrachloride solution of the tolueneboronic acid through absorbent cotton before the addition of N-bromosuccinimide. The infrared spectrum in Nujol of the product from this bromination exhibited no significant absorption in the OH– region and showed a sharp absorption band near 690 cm.$^{-1}$ (the anhydride band). Thus the compound isolated was actually the ω-bromo-*p*-tolueneboronic anhydride (II).



I



II

When this bromination was undertaken with *p*-tolueneboronic anhydride instead of the acid, a "crude" product was obtained in larger yield and with a higher melting point than that reported by Torssell for the product after one recrystallization from carbon tetrachloride. The infrared spectrum of this product from the anhydride is essentially identical to that of the product obtained from the boronic acid.

A larger yield of ω,ω-dibromo-*p*-tolueneboronic anhydride than that reported was also obtained

---

(9) Since this was written L. Santucci and H. Gilman have reported [THIS JOURNAL, **80**, 193 (1958)] on an examination of the infrared spectra of 25 aromatic boronic acids and anhydrides. They indicate the best criterion for the boronic acid–anhydride interchange to be the disappearance of a band at 9.7–9.8 μ (1025 cm.$^{-1}$), found in all the acids, upon conversion to the anhydrides. In our experience, two bands often were observed in this region in the spectra of the acids and only one in those of the anhydrides (see Fig. 1). Although our collection of samples for study has been limited, it appears to us that the use *of the band near 700 cm.*$^{-1}$ as an indication of the presence of the anhydride is probably safer, especially in detecting the anhydride in the presence of its acid.

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

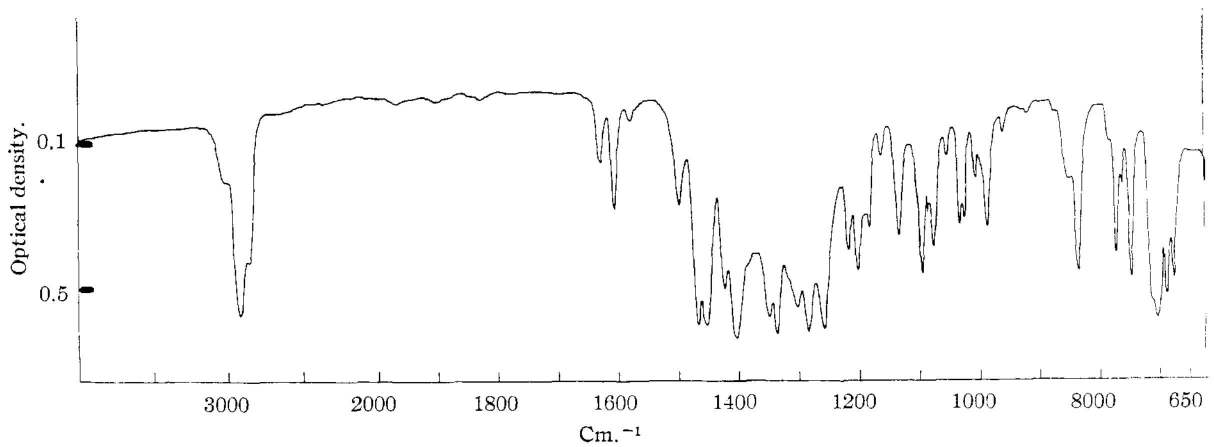


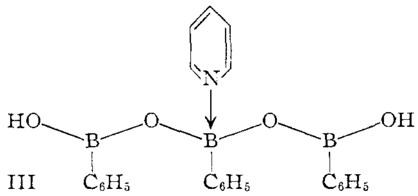
Fig. 2.—Infrared spectrum of pyridine–benzeneboronic anhydride complex.

when the water layer was removed before reaction of the tolueneboronic acid with N-bromosuccinimide. It should be pointed out that intentional removal of the water before initiating the reaction in these brominations is not necessary in order to obtain the anhydride as the product, especially on the scale on which Torssell executed these preparations. Most of the water is removed from the reaction mixture by steam distillation with carbon tetrachloride; the water is not returned to the reaction mixture since it clings to the glass surface of the reflux condenser and the reaction flask.

The infrared spectrum of the reaction product obtained from the monobromination of *p*-tolueneboronic acid with bromine in carbon tetrachloride at room temperature, a method of bromination developed in this Laboratory,[6] shows that the product is a mixture of the acid I and the anhydride II.

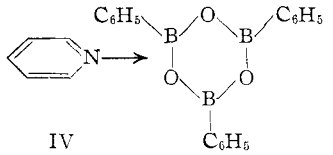
These results re-emphasize a point in boronic acid chemistry which is often overlooked. Since the conversion of the free acid to the anhydride is often very easily accomplished, the presence of the boronic anhydride and the consequences which may result from it should be considered in any reaction of a boronic acid which entails the use of anhydrous conditions.

Another example of the ease of anhydride formation was found in a different phase of these investigations. Yabroff and Branch in 1933 prepared a complex by the reaction of pyridine with benzeneboronic acid in ether.[11] These investigators postulated structure III for this complex.

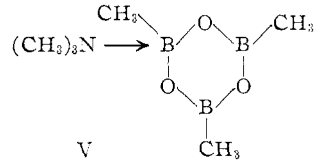


III

When the preparation of this complex was repeated according to the method of Yabroff and Branch, the infrared spectrum of the product (see Fig. 2) failed to exhibit significant absorption in the OH– region. Moreover it exhibited intense absorption near 690 cm.$^{-1}$. The composition found by microanalyses was in agreement with the structure of the pyridine–benzeneboronic anhydride complex (IV). Thus, the dehydration of the acid



IV



V

occurred during the formation of the complex under the very mild conditions involved in the partial evaporation of ether from the solution of the acid and pyridine.

The finding that the complex is related to the anhydride is not surprising, in view of the discovery by Burg[12] in 1940 that methaneboronic anhydride forms 1:1 complexes with amines and ammonia. Structures of the type illustrated by V were suggested for these substances. As was to be expected, the complex IV was more conveniently prepared from benzeneboronic anhydride, rather than the acid, and pyridine. Attempts to prepare a complex containing more than one molecule of pyridine were unsuccessful; only IV was obtained. Burg[12] detected a 2:1 complex with ammonia and methaneboronic anhydride, but the high dissociation pressure of the second ammonia molecule made it appear that it was held by hydrogen bonding to the first ammonia molecule and not by coördination to one of the boron atoms. The fact that only one nitrogen atom can bond to the anhydride molecule suggests that in the bonding the entire boroxole ring functions as an electron-deficient unit. This possibility is being studied further.

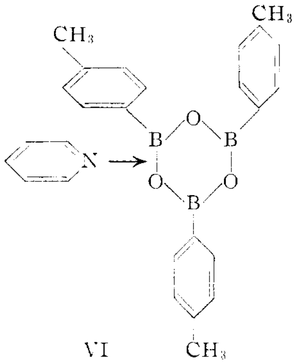
In two experiments designed to explore the scope of the complex formation, the pyridine–*p*-tolueneboronic anhydride complex (VI) and the morphol-

---

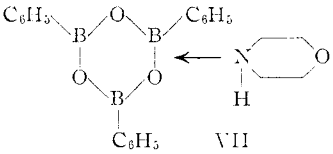
[11] D. Yabroff and G. Branch, This Journal, **55**, 1633 (1933).

[12] A. B. Burg, *ibid.*, **62**, 2228 (1940).

ine–benzeneboronic anhydride complex (VII) were prepared.



VI



VII

After these survey reactions were completed, attention was then directed to the acridine series. The preparation of a similar type of complex from acridine and benzeneboronic anhydride was attempted, but under the conditions employed no reaction occurred. This result is not unexpected since the ring nitrogen atom of acridine is more sterically hindered to the approach of bulky acidic groups than that of pyridine. It then became of interest to endeavor to prepare a complex from 3,6-diaminoacridine and benzeneboronic anhydride. The synthesis was successful, and the composition found indicated that two anhydride molecules were complexed per molecule of the diamine in this complex VIII. The formation of a complex with a primary amine thus was demonstrated.

An interesting property of these amine–boronic anhydride complexes is the ease with which analytically pure samples are obtained. With most of the complexes, the products as isolated from the reaction mixtures were analytically pure. This property of the complexes suggested a practical application—the preparation of an analytical sample of either an amine or a boronic anhydride *via* the corresponding complex. In a test of this proposal, an analytical sample of benzeneboronic anhydride was obtained by decomposition of the pyridine–benzeneboronic anhydride complex (IV) with boiling water, followed by thermal dehydration of the benzeneboronic acid produced; similarly, the decomposition of the 3,6-diaminoacridine–benzeneboronic anhydride complex (VIII) with base produced an analytically pure sample of 3,6-diaminoacridine.

Experimental[13]

ω,ω-Dibromo-*p*-tolueneboronic Anhydride.—The method of preparation was essentially that of Torssell,[10] but a modification in which the bromination was run with tolueneboronic anhydride instead of the acid resulted in an improved yield. A mixture of 17 g. of *p*-tolueneboronic acid and 612 ml. of reagent grade carbon tetrachloride was brought to reflux on a steam-bath in a round-bottomed flask equipped with condenser and drying tube. The acid dissolved and a layer of water floated on the surface of the solution. The hot solution was filtered through a glass column which had been filled with absorbent cotton to remove the water. To the filtered solution was added 46.2 g. of N-bromosuccinimide, which had been recrystallized from water and dried, and 0.4 g. of benzoyl peroxide. The mixture was heated under reflux on a steam-bath, and a 200-watt, unfrosted, incandescent bulb was placed adjacent to the reaction flask. After 2.5 hours, the flask was removed from the steam-bath, and the succinimide was removed by rapid filtration of the hot reaction mixture. Almost immediately, white crystals formed in the filtrate. The filtrate was cooled at 4° for several hours, and the white solid was collected by filtration and washed first with 50 ml. of carbon tetrachloride then with low-boiling petroleum ether. The filtrate was reserved. The solid (24 g., 69%) decomposed at 155–170° (k) (lit.[10] dec. at 160–170°).

The filtrate was reduced in volume to *ca.* 20 ml. by evaporation of the solvent in an air-stream, and the resultant solid was collected by filtration and washed with petroleum ether. This material (9.6 g.) which decomposed at 160–170° (k), was combined with the rest of the product, and the total yield was 96% (lit.[10] 84% calculated for acid as product). This product was used directly to prepare *p*-formylbenzeneboronic acid, and the yield (66%) was about the same (63%) as that reported by Torssell.

ω-Bromo-*p*-tolueneboronic Anhydride.—A mixture of 14.9 g. of *p*-tolueneboronic anhydride, 22.2 g. of recrystallized N-bromosuccinimide, 0.3 g. of benzoyl peroxide and 650 ml. of reagent grade carbon tetrachloride was heated under reflux on a steam-bath for one hour. A 200-watt, unfrosted, incandescent bulb was placed adjacent to the reaction flask. The succinimide was removed by rapid filtration of the hot reaction mixture through a coarse, fluted, filter paper. Immediately, white crystals formed in the filtrate. When cooled to room temperature, the white precipitate was collected by suction filtration and dried. The solid (19.7 g., 79%) melted at 170–176° (lit.[10] 165–168° after recrystallization of crude product from carbon tetrachloride). Evaporation of the filtrate in an air-stream resulted in the isolation of more white crystals (3.6 g., 14%) which melted at 147–155°.

Pyridine–Benzeneboronic Anhydride Complex.—A stock solution of pyridine in ether was prepared by dissolution of 2.80 g. of reagent grade pyridine in anhydrous ether to give a total volume of 100 ml. Of this solution a 10-ml. aliquot, which contained 0.28 g. of pyridine, was added to 1.10 g. of benzeneboronic anhydride in a conical flask, and the mixture was immediately swirled. Complete solution of the anhydride occurred rapidly, and precipitation of the white, crystalline complex followed immediately. The flask was stoppered and allowed to stand for *ca.* one hour. The crystals were then collected by suction filtration and were rinsed in succession with anhydrous ether and low-boiling petroleum ether. The crystals (0.95 g., 69%) melted at 154–156°. Without further purification the product was submitted for microanalysis.

Anal. Calcd. for $C_{23}H_{20}NO_3B_3$: C, 70.68; H, 5.16; N, 3.58. Found: C, 70.47; H, 5.08; N, 3.67.

Attempted Preparation of a Polypyridine–Benzeneboronic Anhydride Complex.—A 10-ml. aliquot, which contained 0.791 g. of pyridine, of an ether solution of pyridine was added to 0.94 g. of benzene-boronic anhydride. The anhydride dissolved rapidly, but no immediate precipitation of the complex occurred. After a few minutes clear, colorless crystals began to form slowly. After several hours, the crystals were collected by suction filtration, washed in succession with ether and petroleum ether, and dried. The infrared spectrum of this product was identical to that of the 1:1 pyridine–benzeneboronic anhydride complex.

Pyridine–*p*-Tolueneboronic Anhydride Complex.—A 10-ml. aliquot, which contained 0.237 g. of pyridine, of an ether solution of pyridine was added to 1.06 g. of *p*-tolueneboronic anhydride in a conical flask. The mixture was swirled to effect solution. No precipitate separated, even after several hours. The solution was filtered by gravity filtration, and the filtrate was reduced in volume to *ca.* 5 ml. by gentle evaporation on a water-bath. The white, crystalline complex immediately precipitated. The precipitate was collected by suction filtration and was rinsed in succes-

---

(13) Melting-point determinations followed by the symbol (k) were made on a Kofler micro-stage melting-point apparatus. All other melting-point determinations were uncorrected capillary tube determinations.

sion with anhydrous ether and low-boiling petroleum ether. The crystals (0.64 g., 49.3%) decomposed at 143–145°. The filtrate deposited an additional amount of product which weighed 0.33 g. (25%) and decomposed at 137–145°. The product with the higher decomposition point was submitted directly for microanalysis.

Anal. Calcd. for $C_{26}H_{26}NO_3B_3$: C, 72.13; H, 6.06; N, 3.24. Found: C, 71.95; H, 5.98; N, 2.98.

Morpholine–Benzeneboronic Anhydride Complex.—A 10-ml. aliquot, which contained 0.26 g. of morpholine, of an ether solution of technical grade morpholine was added to 0.94 g. of benzeneboronic anhydride. The anhydride dissolved, but no precipitation occurred. After the solution was filtered by gravity filtration and the filtrate was reduced in volume to *ca.* 5 ml. on a water-bath, the complex separated in clumps of white needles. The white needles were collected by suction filtration and were rinsed with ether and petroleum ether. The crystals (0.68 g., 58%) melted at 183–187°. The filtrate deposited an additional amount of product which weighed 0.17 g. (14.5%) and melted at 165–171°. An analytical sample was prepared by one recrystallization of the higher melting crystals from ether. The analytical sample melted at 188–189°.

Anal. Calcd. for $C_{22}H_{24}NO_4B_3$: C, 66.25; H, 6.07; N, 3.51. Found: C, 66.44; H, 6.32; N, 3.49.

Attempted Preparation of an Acridine–Benzeneboronic Anhydride Complex.—A 15-ml. aliquot, which contained 0.54 g. of acridine, of an ether solution of acridine was added to 0.94 g. of benzeneboronic anhydride in a conical flask. A precipitate was always present in the flask. Thus it was not possible to distinguish between insolubility of the anhydride in the acridine solution and dissolution of the anhydride in the solution accompanied by simultaneous precipitation of the complex. After several hours, the precipitate was collected by suction filtration, and washed with ether and petroleum ether. The infrared spectrum of this precipitate was essentially identical with that of benzeneboronic anhydride.

3,6-Diaminoacridine–Benzeneboronic Anhydride Complex.—The 3,6-diaminoacridine used in this reaction was prepared by treatment of the sulfate salt (Eastman Kodak Co., practical grade) with excess base and crystallization of the free amine from dimethylformamide. A mixture of 0.32 g. of 3,6-diaminoacridine and 40 ml. of tetrahydrofuran was heated to reflux on a steam-bath to effect solution. The solution was filtered rapidly while hot to remove a minute amount of insoluble material. The filtrate was added to 0.90 g. of benzeneboronic anhydride. Within a few minutes the anhydride dissolved completely to give an orange-red solution which exhibited an intense green fluorescence. The solution was reduced in volume to *ca.* 12 ml. on a steam-bath. A small amount of amorphous, colored material which deposited upon cooling was removed from the solution by filtration. When the filtrate was further reduced in volume to *ca.* 2–3 ml., a red precipitate separated on cooling. The red precipitate was collected by suction filtration and washed in succession with tetrahydrofuran and anhydrous ether. These ether washes removed the red color and left a brilliant yellow, crystalline product on the filter. The yellow crystals were rinsed with petroleum ether. These crystals (0.32 g., 25%) melted at 252–255°. Additional highly colored material deposited in the filtrate, but no attempt was made to isolate more of the product. The yellow crystals were submitted for microanalysis without further purification.

Anal. Calcd. for $C_{49}H_{41}N_3O_6B_6$: C, 70.66; H, 4.96; N, 5.05. Found: C, 70.66; H, 5.00; N, 5.10.

Preparation of Analytical Samples *via* Complexes. A. Benzeneboronic Anhydride.—Ten milliliters of water was added to 0.27 g. of the pyridine–benzeneboronic anhydride complex in a conical flask and the mixture was boiled on a hot-plate. The complex gradually dissolved in the boiling water, and then the volume of solution was reduced to *ca.* 3 ml. The flask was stoppered and allowed to stand overnight; white crystals of benzeneboronic acid deposited. The crystals were collected by suction filtration, dried in a vacuum desiccator over calcium chloride, and then converted to benzeneboronic anhydride in an oven at 105° for 17 hours. The product was submitted for microanalysis without further purification.

Anal. Calcd. for C_6H_5OB: C, 69.43; H, 4.85. Found: C, 69.52; H, 4.96.

B. **3,6-Diaminoacridine.**—Ten ml. of 2 *N* sodium hydroxide solution was added to *ca.* 150 mg. of the 3,6-diaminoacridine–benzeneboronic anhydride complex, and the mixture was allowed to stand for one or two hours. The complex appeared to decompose, and a yellow solid deposited in the dark brown solution. The yellow solid was collected by suction filtration and rinsed well with water. The solid was dried in an oven at 105° overnight and submitted for microanalysis without further purification.

Anal. Calcd. for $C_{13}H_{11}N_3$: C, 74.63; H, 5.31; N, 20.09. Found: C, 74.36; H, 5.07; N, 20.07.

URBANA, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Formation of Linear Polymers from Diene Monomers by a Cyclic Polymerization Mechanism. I. The Structure of Poly-(diallylammonium Halides)[1,2]

BY GEORGE B. BUTLER, ALLAN CRAWSHAW AND W. LAMAR MILLER

RECEIVED JANUARY 13, 1958

Two of the soluble, linear polymers obtained from monomers of the general formula $[(CH_2{=}CHCH_2)_2NR_2]^+Br^-$ have been degraded by well-known methods. Both poly-(diallylammonium bromide) and poly-(diallyldimethylammonium bromide) have given products resulting from the cleavage of piperidinium bromide rings present in the structures. The results confirm the structure previously proposed for these polymers.

Polymerization of diallylammonium halides of the general formula $[(CH_2{=}CHCH_2)_2NR_2]^+X^-$ leads to soluble linear polymers.[3] To explain the formation of such polymers, a chain propagation mechanism was proposed which involved alternate intramolecular and intermolecular growth steps. The resultant polymer structure consisted of a linear chain of recurring N-substituted piperidinium halide units alternating along the chain with methylene groups. The polymers appeared to contain a small amount of residual unsaturation, suggesting the occurrence of occasional pendant allyl groups along the polymer chains. In more recent work, extensive purification has afforded polymers in which no unsaturation could be detected. It appears, therefore, that the proposed

---

(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract number AF 18(603)-116. Reproduction in whole or in part is permitted for any purpose of the United States government.

(2) This paper was presented before the Division of Polymer Chemistry, American Chemical Society, New York, N. Y., September, 1957.

(3) G. B. Butler and R. J. Angelo, THIS JOURNAL, **79**, 3128 (1957).