visible reaction with the fluoborate VII prepared as above in nitromethane solution. This reaction was not examined further.

Preparation of 2-Deuterio-2-methyl-1,3-dioxolane (XII).—A modified procedure of Claus and Morganthau[22] for the reduction of *ortho* esters was used to reduce 2-methoxy-2-methyl-1,3-dioxolane (IX) with lithium aluminum deuteride. Benzene could not be used as Claus and Morganthau had done since it and the product XII boil at almost exactly the same point. Toluene was found to be unsatisfactory because it formed an azeotropic mixture (~ 1:1) with the product XII which could only be separated by g.p.c. Consequently, 2.36 g. (0.225 equiv. wt.) of lithium aluminum deuteride was added to 26 g. (0.22 mole) of IX in a small reaction flask equipped with stirrer and condenser and cooled in a Dry Ice–acetone-bath. If the mixture is not cooled it becomes violent after about 5 minutes. The cooled mixture is slowly warmed and finally refluxed for 3–4 hours. The product was distilled (Claisen) directly from this mixture to yield 6.0 g. (32%) of 2-deuterio-2-methyl-1,3-dioxolane (XII), b.p. 82–84°; g.p.c. analysis indicated a purity of 96%. The reported[23] boiling point of 2-methyl-1,3-dioxolane is 82°. Before use the deuteriodioxolane XII was purified by preparative scale g.p.c. The n.m.r. was consistent with the assumed structure and no C.2 hydrogen could be detected. Reduction of the methoxydioxolane IX with lithium aluminum hydride gave authentic 2-methyl-1,3-dioxolane as indicated by its infrared, n.m.r. and boiling point; infrared (carbon tetrachloride): 3.31(m), 3.44(m), 4.70(m), 8.88(s), 9.47(s), 11.6(s) μ; n.m.r. (carbon tetrachloride, 1 molar): 6.20 (10), 8.74 (s).

Reaction of Fluoborate VII with 2-Deuterio-2-methyl-1,3-dioxolane (XII).—The fluoroborate VII was prepared as usual on the vacuum line from 1.00 g. (0.008 mole) of silver fluoborate in about 40–50 ml. of sulfur dioxide at about −75°. To this stirred mixture, 1.20 g. (0.013 mole) of deuteriodioxolane (XII) was added all at once and stirring was continued for 4 hours. At the end of this period, 0.97 g. (0.008 mole) of methoxydioxolane (IX) was added and the reaction was worked-up as usual. Warming of the reaction mixture without addition of IX resulted in complete decomposition. Impure 2-methyl-1,3-dioxolenium fluoborate (XI) was obtained in 48% yield (0.67 g.), m.p. 174+° dec. As before, this salt was incompletely soluble in sulfur dioxide. The n.m.r. spectrum of the sulfur dioxide solution revealed about 7% impurity; otherwise, it was identical with authentic material.

Examination of the crude ether-soluble product by g.p.c. indicated the absence of norbornadiene or its possible isomers. Very little volatile material could be detected. However, two very small unresolved peaks appeared at approximately the retention time of 7-methoxynorbornadiene (X), but were insufficient to characterize. Excess dioxolanes IX and XII were, of course, removed in the water wash. The infrared of the crude product was inconclusive, except that the norbornadiene nucleus could not be detected. Claisen distillation gave a wide boiling point range, 100–150° (0.2 mm.), and no identifiable products.

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[22] C. J. Claus and J. L. Morganthau, *J. Am. Chem. Soc.*, **73**, 5005 (1951).

[23] H. J. Dauben, B. Loken and H. J. Ringold, *ibid.*, **76**, 1359 (1954).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Tribenzotalarene; an Unusual Polycyclic Organoboron Compound[1]

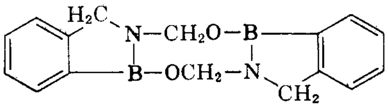
BY MICHAEL J. S. DEWAR, RALPH C. DOUGHERTY[2] AND E. B. FLEISCHER

RECEIVED JULY 16, 1962

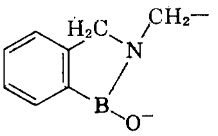
We have shown that the product which Snyder, Reedy and Lennarz obtained by a Sommelet reaction on *o*-bromomethylbenzeneboronic acid[3] is a trimer with the probable structure IV, a tribenzo derivative of talarene (V). The mechanistic implications of the synthesis are discussed and possible use of IV as a clathrate is suggested.

In an attempt to prepare *o*-formylphenylboronic acid by application of the Sommelet synthesis to *o*-bromomethylbenzeneboronic acid, Snyder, Reedy and Lennarz obtained a high melting substance,[3] $(C_8H_8BNO)_n$ (I). They suggested structure II for this compound because it dissolved in dilute acid and was apparently insoluble in water of dilute alkali. Since this structure involves an eight-membered ring which appears from models to be highly strained, and since the evidence for it was by no means conclusive, we decided to reinvestigate the compound.

The material obtained from the Sommelet process did indeed dissolve in dilute acids. However, the material did not dissolve in ethereal solutions of boron trifluoride etherate unless catalytic quantities of ethanol were added. It also dissolved in aqueous alkali if small amounts of ethanol were added to the solution. In several attempts we were unable to recover the original compound from any of the above solutions and changes in the ultraviolet and infrared spectra indicated that it had been destroyed. The solubility behavior of the compound allows no immediate conclusions about the structure, however, since it would be impossible to assess the effect of B–N π-bonding on the donor–acceptor properties of the molecule.



II



III

There can be little doubt from analysis and the method of preparation that I contains the repeating unit III, (C_8H_8BNO). However, the material as obtained by the procedure of Snyder, Reedy and Lennarz analyzed as a monohydrate of the trimer of III, $(C_8H_8BNO)_3 \cdot H_2O$, suggesting that I is at least trimeric. The presence of water of crystallization was confirmed by a strong band in the infrared spectrum at 3655 cm.$^{-1}$ (Fig. 1) and by the fact that anhydrous I, free from this absorption, could be obtained by crystallization from anhydrous solvents or by heating to 150° in a vacuum.

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[1] This work has been supported by a Grant from the National Science Foundation.

[2] Woodrow Wilson Fellow 1960–1961; National Science Foundation Pre-doctoral Fellow 1961–1963.

[3] H. R. Snyder, A. J. Reedy and W. J. Lennarz, *J. Am. Chem. Soc.*, **80**, 835 (1958).

The trimeric structure was confirmed by X-ray studies on a crystal of anhydrous I. Measurement of the crystal unit-cell and density led to a value (440) for the molecular weight in good agreement with that (435) calculated for $(C_8H_8BNO)_3$.

Further evidence was provided by the presence of a strong band in the infrared spectrum at 678 cm.$^{-1}$ (Fig. 1) and by the similarity of the ultraviolet spectrum of I to that of tetralin and by its difference from that of boronophthalide (Table I).

TABLE I

$(C_8H_8BNO)_3$ Ethanol λ_{max}, mμ	log ϵ[a]	Tetralin Isooctane λ_{max}, mμ	log ϵ	Benzoquinuclidine[4] Isooctane λ_{max}, mμ	log ϵ	Boronophthalide Ethanol λ_{max}, mμ	log ϵ
270	2.69	274	2.76	268	2.65	276	3.04
263	2.72	267	2.77	261	2.68	269	3.05
258	2.62	260	2.62			215	3.95

[a] Based on monomer unit.

The infrared spectrum, combined with its trimeric nature, suggests that I is a boroxine derivative; for Snyder, Konecky, and Lennarz[5] have found that boroxines show a strong characteristic absorption at 675–680 cm.$^{-1}$. The ultraviolet spectrum would then indicate that the benzene rings in I are perpendicular to the boroxine ring, the lack of conjugation being due to lack of orbital overlap; a similar situation exists in benzoquinuclidine, the ultraviolet spectrum of which also resembles[4] that of tetralin.

The only reasonable trimeric structure consistent with these observations seems to be the strain-free cage structure IV. This can be regarded as a tribenzo derivative of the parent system for which we suggest the name talarene.[6] Tribenzotalarene would not be expected to show basic or acidic properties since the nitrogen atoms in it are quadricovalent; vigorous treatment with basic or acidic reagents should lead to complete disruption of the central rings.

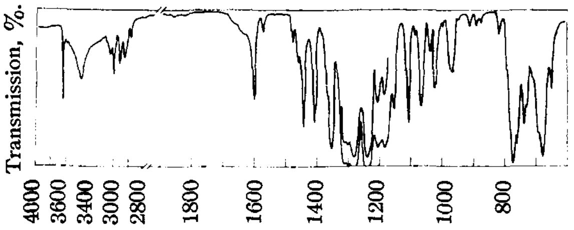
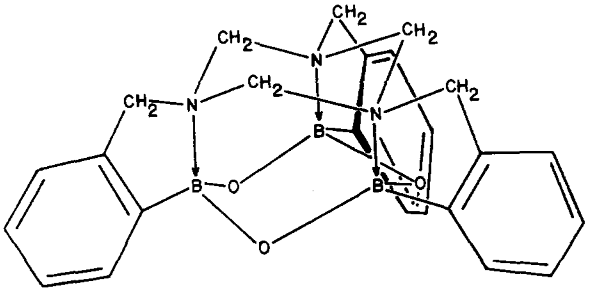
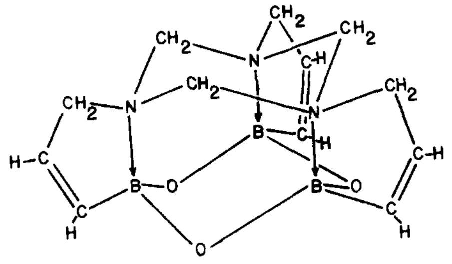


Fig. 1.—Infrared spectrum of tribenzotalarene monohydrate (KBr disk).

Tribenzotalarene (IV) is formed by the Sommelet synthesis when the hydrolysis step is carried out under moderately acid conditions. Stronger acid produces the expected *o*-formylphenylboronic acid, albeit in low yield. *p*-Bromomethylbenzeneboronic acid is reported to give only *p*-formylphenylboronic acid in the Sommelet synthesis. The behavior of *o*- and *p*-bromomethylphenylboronic acid in the Sommelet synthesis may be interpreted in terms of the suggestion[7] that the reaction proceeds by transfer of a hydride ion to the conjugate acid of a Schiff base or to the mesomeric cation which is presumably formed in the acidic hydrolysis of trimeric methyleneamines. The reduction of the basicity of the Schiff's base by intramolecular interaction with the boron atom in the *ortho* isomer would inhibit formation of the conjugate acid, and thus prevent the normal completion of the reaction.



IV



V

Alternatively, the free amine, if it were formed, would not be a good hydride donor for the same reasons.

That the water in the monohydrate shows a nonbonded vibration (3655 cm.$^{-1}$) indicates that it is in a relatively free environment in the crystal structure; yet complete removal of the water requires drastic conditions. This suggests that the water is not merely water of hydration, or trapped by inclusion, but that it may be trapped in the crystal lattice as a clathrate guest. The loose structural similarity between tribenzotalarene and other known clathrates[8] supports this hypothesis; however, no definite statement about the use of tribenzotalarene as a clathrate host can be made until work which is now in progress is completed.

Experimental

Preparation of Tribenzotalarene Monohydrate.—A solution of 25 g. of *o*-tolueneboronic acid, 37.7 g. of N-bromosuccinimide, 2.0 g. of benzoyl peroxide and 320 ml. of dry chloroform was heated under reflux for 3 hours; then 35.6 g. of hexamine in 200 ml. of dry chloroform was added to the hot reaction mixture. The precipitate was separated from the chloroform, and dissolved in 100 ml. of water which contained 1 drop of concentrated hydrochloric acid. This

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(4) Van der Krogt and B. M. Wepster, *Rec. trav. chim.*, **74**, 161 (1955).

(5) H. R. Snyder, M. S. Konecky and W. J. Lennarz, *J. Am. Chem. Soc.*, **80**, 3611 (1958).

(6) We suggest that V be called talarene since we have been unable to devise a systematic name to fit the structure. "Many there be that batten in populous Egypt, well-propped pedants who quarrel without end in the Muses' bird-cage (ταλάρῳ)." Timon of Philus quoted by Anthenaeus, D. 22d, translated by C. B. Gulick, Loeb Classical Library, London, 1928.

(7) S. J. Angyal, D. R. Penman and G. P. Warwick, *J. Chem. Soc.*, 1742 (1953).

(8) A. C. D. Newman and H. M. Powell, *ibid.*, 3747 (1957).

solution was boiled for 1.5 hours during which time a colorless solid separated. This material was the monohydrate, 11.0 g. (42%), m.p. 303–304°. *Anal.* Found: C, 63.8; H, 5.5; N, 9.3. Calcd. for $C_{24}H_{24}B_3N_3O_3 \cdot H_2O$: C, 63.6; H, 5.7; N, 9.3. A dried ($MgSO_4$) ether extract of the mother liquor yielded 1.8 g. (7%) of *o*-formylphenylboronic acid, identified by m.p. (118–120°) and infrared spectrum.

Solubility of II.—Neutralization of a solution of 1 g. tribenzotalarene in 50 ml. of 10% hydrochloric acid left the solution unchanged in appearance. A dried ($MgSO_4$) ether extract of this solution yielded a white solid (less than 100 mg.) which we were unable to characterize. The infrared spectrum of this material was very complicated and contained bands in the carbonyl region indicating that compound I had been destroyed. Several other attempts to recover tribenzotalarene from acidic solutions were similarly unsuccessful. One gram of I slowly dissolved in 25 ml. of 10% potassium hydroxide if catalytic quantities of ethanol were added. Tribenzotalarene (0.5 g.) remained unchanged on treatment with 20 ml. of boron trifluoride etherate; however, immediately after addition of 0.55 ml. of ethanol, solution was complete. Subsequent attempts to recover the same compound from this solution were not successful.

Infrared spectra were recorded on a Beckman I.R.-7 recording spectrophotometer. Ultraviolet spectra were recorded on a Cary model 14 recording spectrophotometer.

For crystallographic determinations tribenzotalarene was recrystallized slowly from dry dimethyl sulfoxide; crystal data: $C_{24}H_{24}B_3N_3O_3$, M = 434.7, orthorhombic, $a = 8.15$, $b = 10.07$, $c = 27.17$ Å., $U = 2230$ Å.^{3} *Dm* 1.31 (by flotation), $Z = 4$, $D_c = 1.30$; absent spectra are: $n00$, $n = 2n+1$; $0k0$, $k = 2n+1$; $00l$, $l = 2n+1$; space group, $p2_12_12_1$. Cu K radiation (Ni filter) single crystal precession photographs.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

New Heteroaromatic Compounds. XVI.[1] Compounds with Heteroatoms at Bridgeheads[2]

BY MICHAEL J. S. DEWAR, CHIKARA KANEKO[3] AND (IN PART) M. K. BHATTACHARJEE

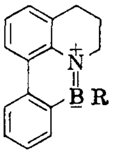
RECEIVED JULY 19, 1962

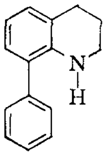
Previous papers of this series have described a number of novel heteroaromatic compounds containing boron atoms as components of six-membered heterocyclic rings. This paper describes the synthesis of several compounds of this type containing heteroatoms at bridgeheads, including 12,11-borazarophenanthrene.

Previous papers of this series have described a number of novel heteroaromatic compounds containing boron atoms as components of six-membered aromatic rings. So far, however, no compound of this type has been described in which one of the heteroatoms occupies the bridgehead between two rings. The purpose of the present investigation was to prepare such compounds.

Our first objective was the synthesis of derivatives of 8,9-trimethylene-10,9-borazarophenanthrene (Ia), partly since this ring system bears an obvious resemblance to that of the apomorphine alkaloids and partly in the hope that suitable 10-substituted derivatives of I might be cyclized to analogs of perylene.

Reduction of 8-phenylquinoline, prepared by an improved procedure, gave 8-phenyltetrahydroisoquinoline (II), which was isolated as its N-acetyl derivative. Reaction of II with boron trichloride, followed by cyclization with aluminum chloride, gave 8,9 - trimethylene - 10 - hydroxy - 10,9-borazarophenanthrene (Ib), isolated as its anhydride. This compound resembled other borazarophenanthrene derivatives[4] in its chemical stability, but differed in that the oxygen could not be replaced by reaction with organometallic reagents.[5] Presumably the boron is sterically hindered by the adjacent methylene and methine groups.


Ia, R = H
b, R = OH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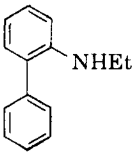
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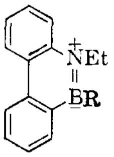
IVa, R = OH
b, R = Me

As a model for the synthesis of I we also prepared 9-ethyl-10-hydroxy-10,9-borazarophenanthrene (I Va) from 2-ethyl-aminobiphenyl (III), in turn prepared by reduction of 2-acetamidobiphenyl with lithium aluminum hydride. Methylmagnesium bromide converted IVa to 9-ethyl-10-methyl-borazarophenanthrene (IVb) which was synthesized independently by ethylation[5] of 10-methyl-10,9-borazarophenanthrene *via* the N-lithio derivative.

We next tried to make the lower homolog V of Ia in the hope that it might undergo dehydrogenation to a pyrroloborazarophenanthrene. The necessary 7-phenyl-2,3-dihydroindole (VI) was readily prepared by reducing 7-phenyloxindole (VII) with lithium aluminum hydride; VII in turn was obtained by cyclization of 2-chloroacetamidobiphenyl with aluminum chloride. However, all attempts to cyclize the adducts of VI with boron trichloride or phenyl dichloroboronite failed. Apparently the change in valence angle due to presence of a five-membered ring is enough to inhibit cyclization.

Our next objective was the preparation of 7,12-dimethyl-7,17-borazarobenz[a]anthracene (VIII) since molecular orbital calculations[6] suggested that

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(1) Part XV, M. J. S. Dewar and R. Dietz, *J. Org. Chem.*, **26**, 3253 (1962).

(2) This work was supported by a Grant from the National Science Foundation.

(3) Present address: Research Institute of Medical and Dental Material, Tokyo Medical and Dental University, Yushima Bunkyo-ku, Tokyo, Japan.

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

(5) *Cf.* M. J. S. Dewar, R. Dietz, V. P. Kubba and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 1754 (1961).

(6) The calculations were carried out with an IBM 7090 digital computer at Bell Telephone Laboratories, using a program written by Dr. L. C. Snyder.