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

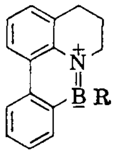
RECEIVED JULY 19, 1962

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.

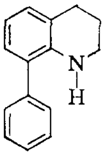
Previous papers of this series have described a number of novel heteroaromatic compounds containing boron atoms as components of six-membered aromatic rings. So far, however, no compound of this type has been described in which one of the heteroatoms occupies the bridgehead between two rings. The purpose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

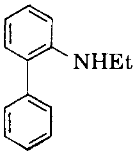
Reduction of 8-phenylquinoline, prepared by an improved procedure, gave 8-phenyltetrahydroisoquinoline (II), which was isolated as its N-acetyl derivative. Reaction of II with boron trichloride, followed by cyclization with aluminum chloride, gave 8,9 - trimethylene - 10 - hydroxy - 10,9-borazarophenanthrene (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.



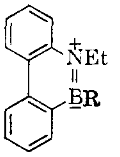
Ia, R = H
b, R = OH



II



III



IVa, R = OH
b, R = Me

As a model for the synthesis of I we also prepared 9-ethyl-10-hydroxy-10,9-borazarophenanthrene (IVa) 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-methylborazarophenanthrene (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).

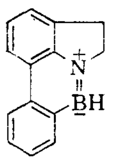
(2) This work was supported by a Grant from the National Science Foundation.

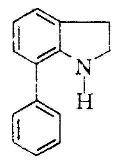
(3) Present address: Research Institute of Medical and Dental Material, Tokyo Medical and Dental University, Yushima Bunkyo-ku, Tokyo, Japan.

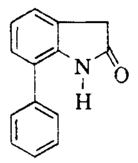
(4) M. J. S. Dewar, V. P. Kubba and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

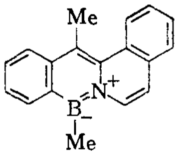
(5) *Cf.* M. J. S. Dewar, R. Dietz, V. P. Kubba and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 1754 (1961).

(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.


V

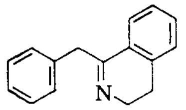

VI

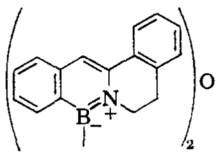

VII

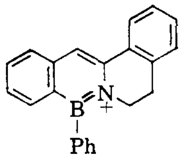

VIII

this might be an even more potent carcinogen than its carbon analog, judging by the criterion suggested by Pullman and Pullman.[7]

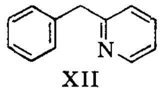
When the adduct from boron trichloride and 1-benzyl-3,4-dihydroisoquinoline (IX) was heated with aluminum chloride and the product hydrolyzed with water, a moderate yield of bis-(7,17-borazaro-5,6-dihydro-7-benz[a]anthryl) ether (X) was obtained. This interesting reaction involves an unusual prototropic shift. We also obtained 7-phenyl-7,17-borazaro-5,6-dihydrobenz[a]anthracene (XI) by heating IX with phenyl dichloroboronite, no catalyst being needed in this case.

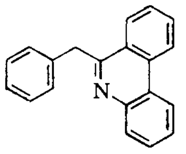

IX

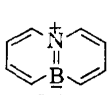

X


XI

This ring system proved much less stable than other borazaro analogs of hydrocarbons. On standing in moist air, or on recrystallization from moist solvents, XI was converted to an insoluble high-melting solid which could not be recrystallized and attempts to dehydrogenate X or XI were unsuccessful. It seems likely that the completely aromatic system in VIII would be even less easily formed and even more susceptible to hydrolysis; this conclusion seems to be supported by the fact that the adducts of α-benzylpyridine (XII) or 10-benzylphenanthridine (XIII) with boron trichloride or phenyl dichloroboronite could not be cyclized even under drastic conditions. The 10-benzylphenanthridine was prepared from 2-(N-phenylacetylamino)-biphenyl with phosphorus pentoxide.


XII


XIII

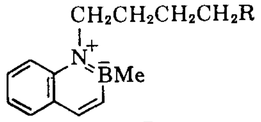

XIV

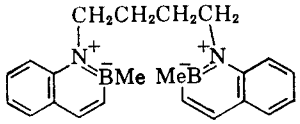
The final investigation was directed to the synthesis of benzo derivatives of 10,9-borazaronaphthalene (XIV), where both heteroatoms are at the bridgeheads of aromatic rings. Very few aromatic compounds are known with heteroatoms in such bridgehead positions and their physical and chemical properties should be of considerable interest.

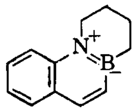
Alkylation[8] of 2-methyl-2,1-borazaronaphthalene[9] by treating the N-lithio derivative with 1,4-dibromobutane gave 1-(4-bromo-1-butyl)-2-methyl-2,1-borazaronaphthalene (XVa). The bromide apparently underwent partial dehydrobromination during distillation since the product gave low bromine analyses and was unsaturated. Its structure was indicated by the simultaneous formation of 1,4-bis-(2-methyl-2,1-borazaro-1-naphthyl)-butane (XVI) and by conversion to the morpholine derivative XVb. When XVa was treated with magnesium it underwent cyclization to 1,2,3,4-tetrahydro-12,11-borazarophenanthrene (XVII), presumably by elimination of methylmagnesium bromide from the intermediate Grignard reagent XVc. We first obtained XVII as an oil which appeared from mass spectrometric analysis[9a] to contain XVII (mass no. 183) and 1-butyl-2-methyl-2,1-borazaronaphthalene (XVIII) (mass no. 199) in the ratio 3.5:1. On further purification, XVII was obtained as a low melting solid which analyzed correctly. These results suggest that XVII is formed by the reversible reaction

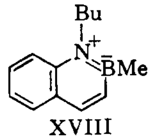
$$\text{XVc} \rightleftharpoons \text{XVII} + \text{MeMgBr}$$

When the reaction mixture was decomposed with water, the XVc was converted to XVII.


XVa, R = Br
b, R = -N O
c, R = MgBr


XVI

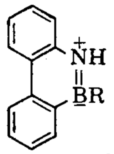

XVII

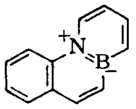

XVIII

The formation of XVII is analogous to the conversion of 10-methyl-10,9-borazarophenanthrene (XIXa) to 10-phenyl-10,9-borazarophenanthrene (XIXb) with phenyllithium.[10] In that case the driving force was an increase in total bond energy in the process

$$\text{XIXa} + \text{PhLi} \longrightarrow \text{XIXb} + \text{MeLi}$$

Here the driving force is an increase in translational entropy when a single molecule of XVc is replaced by two molecules, one of XVII and one of methylmagnesium bromide.


XIXa, R = Me
b, R = Ph


XX

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(7) A. Pullman and B. Pullman, "Cancérisation par les substances chimiques et structure moleculaire," Maisson et Cie, Paris, 1955.

(8) M. J. S. Dewar and V. P. Kubba, work in course of publication.

(9) M. J. S. Dewar and R. Dietz, *J. Chem. Soc.*, 2728 (1959).

(9a) We are very grateful to Dr. S. Meyerson, American Oil Co., Whiting, Ind., for the mass spectrometric analysis.

(10) M. J. S. Dewar and P. M. Maitlis, *J. Am. Chem. Soc.*, **83**, 187 (1961).

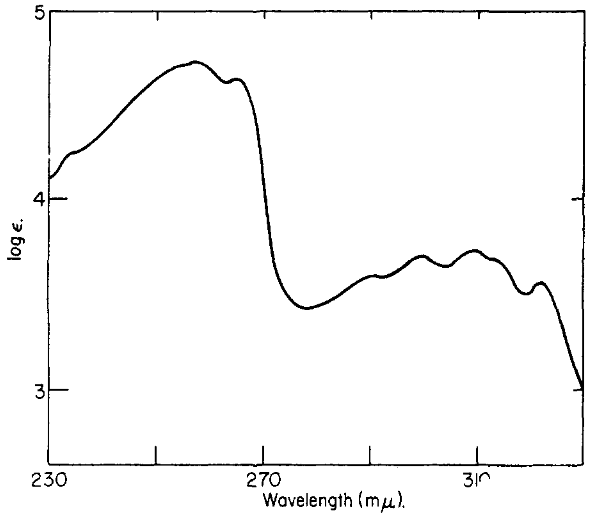

Fig. 1.—Ultraviolet spectrum of XVII (———) in ethanol.

Dehydrogenation of XVII over palladized charcoal at 300° in the presence of hexene as hydrogen acceptor gave 12,11-borazarophenanthrene (XX) as a white crystalline solid in about 30% yield. The structure of XX followed from analysis and from the similarity of its ultraviolet spectrum (Fig. 1) to those of derivatives of 10,9-borazarophenanthrene.[4] Both show a strong characteristic band in the 320 mμ region.

Preliminary studies indicate that XX is a stable aromatic compound, comparable in stability with the other aromatic boron compounds we have made. This is also indicated by its formation in reasonable yield from XVII by dehydrogenation at 300°. A detailed study of its chemical and physical properties will be reported later.

Experimental

8-Phenylquinoline.—Concentrated sulfuric acid (110 g.) was added slowly with vigorous stirring to a mixture of 2-aminobiphenyl (45 g.), anhydrous glycerol (92 g.) and arsenic pentoxide (43 g.) at 100–120°. The mixture was then heated to 130–150° for 7 hours and the 8-phenylquinoline isolated by basification, ether extraction and distillation, b.p. 180° (2.5 mm.), 36 g. The use of nitrobenzene as oxidizing agent as recommended by La Coste and Sorger[11] gave much inferior yields. The picrate crystallized from ethanol in yellow needles, m.p. 150–152°. Möhlou and Berger[12] reported m.p. 210° but quoted no analysis of their material.

Anal. Calcd. for $C_{21}H_{16}N_4O_7$: C, 58.1; H, 3.2. Found: C, 58.2; H, 3.5.

8-Phenyl-1,2,3,4-tetrahydroisoquinoline.—Sodium (39 g.) was added gradually to a solution of 8-phenylquinoline (35 g.) in ethanol (700 ml.) and the mixture then boiled under reflux for 90 minutes. Evaporation of the alcohol and isolation with water and benzene gave crude 8-phenyl-1,2,3,4-tetrahydroisoquinoline (II) (22 g.). The N-acetyl derivative, after chromatography from benzene on alumina, crystallized from petroleum ether–benzene as white needles, m.p. 122–124°.

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.0; H, 6.8; N, 5.6; mol. wt., 251. Found: C, 81.2; H, 6.9; N, 5.8; mol. wt. (Rast), 256.

Bis-(8,9-trimethylene-10,9-borazaro-10-phenanthryl)-Ether.—Crude X (10 g.) in benzene (50 ml.) was added dropwise to a stirred solution of boron trichloride (10 g.) in benzene (250 ml.). After distilling the solvent, the residue was stirred with aluminum chloride (1 g.) at 190° for 3 hours. The product was extracted with benzene, washed with water, and chromatographed on alumina, giving **bis-(8,9-trimethylene-10,9-borazaro-10-phenanthryl) ether** (anhydride of Ib) which crystallized from acetone in pale yellow prisms, m.p. 237–240° (0.8 g.). The low carbon analysis suggests that the product may have contained a little unchanged IX; this difficulty often arises with compounds of this type.

Anal. Calcd. for $C_{30}H_{28}N_2B_2O$: C, 79.7; N, 5.7; N, 6.2; B, 4.8; mol. wt., 446. Found: C, 78.1; H, 5.7; N, 6.0; B, 4.5; mol. wt. (Rast), 400.

2-Ethylaminobiphenyl.—An ethereal solution of 2-acetamidobiphenyl (3 g.) was added dropwise to a stirred suspension of lithium aluminum hydride (2 g.) in ether. After 2 hours the excess hydride was decomposed with hydrated sodium sulfate and the ether solution washed and evaporated. The residue of 2-ethylaminobiphenyl (III), 2.3 g., was converted to its **hydrochloride** which crystallized from acetone in white prisms, m.p. 151–155°.

Anal. Calcd. for $C_{14}H_{16}NCl$: C, 71.9; H, 6.9. Found: C, 72.0; H, 6.8.

Bis-(9-ethyl-10,9-borazaro-10-phenanthryl) Ether.—Prepared in the same way as IIb from 2-ethylaminobiphenyl (8 g.), the **borazarophenanthryl ether** (anhydride of IVa) crystallized from acetone in white prisms, m.p. 183–184° (5.0 g.).

Anal. Calcd. for $C_{28}H_{26}N_2B_2O$: C, 78.5; H, 6.1. Found: C, 78.7; H, 6.3.

9-Ethyl-10-methyl-10,9-borazarophenanthrene.—Methylmagnesium bromide (12 ml. of 3 *M* solution in ether) was added to IVa (1 g.) in ether (100 ml.) and the mixture boiled under reflux for 2 hours. Hydrolysis, evaporation and chromatography from benzene–petroleum ether (b.p. 60–65°) gave **9-ethyl-10-methyl-10,9-borazarophenanthrene (IVb)** (0.71 g.) which crystallized from petroleum ether (b.p. 30–35°) in prisms, m.p. 60–62°.

Anal. Calcd. for $C_{15}H_{16}NB$: C, 81.5; H, 7.2. Found: C, 81.6; H, 7.3.

The same compound (m.p. and mixed m.p.) was obtained by treating 9-lithio-10-methyl-10,9-borazarophenanthrene with ethyl iodide or diethyl sulfate.[10]

2-N-Chloroacetylaminobiphenyl.—Chloroacetyl chloride (12 g.) was added gradually to a cold stirred solution of 2-aminobiphenyl (40 g.) in benzene (200 ml.). The next day the solution was washed with acid and evaporated, giving the **amide** (21 g.) which crystallized from ether in white prisms, m.p. 101–103°.

Anal. Calcd. for $C_{14}H_{12}NOCl$: C, 68.4; N, 4.9; N, 5.7. Found: C, 68.6; H, 5.1; N, 5.6.

7-Phenyloxindole.—A mixture of 2-chloroacetylaminobiphenyl (10 g.) and aluminum chloride (20 g.) was heated 1 hour at 220°. After isolation with water and benzene and crystallization from acetone, the **7-phenyloxindole (VII)** was chromatographed on alumina from methylene chloride–methanol (1:1), forming small prisms, m.p. 227–230°.

Anal. Calcd. for $C_{14}H_{11}NO$: C, 80.4; H, 5.7; N, 6.7. Found: C, 80.2; H, 5.4; N, 6.9.

7-Phenyl-2,3-dihydroindole.—A solution of XIII (0.5 g.) in tetrahydrofuran (100 ml.) was added to a suspension of lithium aluminum hydride (1.5 g.) in ether (50 ml.) and the mixture boiled overnight under reflux. The resulting **7-phenyl-2,3-dihydroindole (VI)** was isolated as its **hydrochloride** which crystallized from acetone in white needles, m.p. 260–262° (sintering at 220°), 0.44 g.

Anal. Calcd. for $C_{14}H_{14}NCl$: C, 80.4; H, 5.3; N, 6.7. Found: C, 80.2; H, 5.4; N, 6.9.

The free base had m.p. 80–82°.

Bis-(7,17-borazaro-5,6-dihydro-7-benz[a]anthryl) Oxide.—A solution of 1-benzyl-3,4-dihydroisoquinoline[13] (IX) (4 g.) in benzene was added dropwise to a cold stirred solution of boron trichloride (7 g.) in benzene. The mixture was boiled under reflux for 4 hours and then evaporated under reduced pressure. The residue was heated with aluminum chloride (0.5 g.) with stirring at 180–185° for 3 hours, cooled, and treated with ice-cold hydrochloric acid and benzene. The residue (2.3 g.) from evaporation of the benzene layer was chromatographed from benzene on magnesium oxide. The main fraction crystallized from acetone in

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(11) W. La Coste and S. Sorger, *Ann.*, **230**, 1 (1885).

(12) R. Möhlou and R. Berger, *Ber.*, **26**, 2004 (1893).

(13) A. Pictet and F. W. Kay, *ibid.*, **42**, 1973 (1909).

prisms (0.8 g.), m.p. 196–198°, of **bis-(7,17-borazaro-5,6-dihydro-7-benz[a]anthryl) oxide (X)**. The carbon analyses were consistently low, probably due to partial hydration.

Anal. Calcd. for $C_{32}H_{26}N_2B_2O$: C, 80.7; H, 5.5; N, 5.9; mol. wt., 476. Found: C, 79.9; H, 5.8; N, 5.8; mol. wt. (Rast), 400.

7-Phenyl-7,17-borazaro-5,6-dihydrobenz[a]anthracene.—A solution of IX (4.6 g.) and phenyl dichloroboronite (7.4 g.) in decalin (50 ml.) was boiled under reflux with stirring for 3 hours after the initially formed complex had dissolved and then evaporated under pressure. The residue was treated with ice–cold potassium hydroxide solution (30%) and ether and the ether layer washed with hydrochloric acid, dilute alkali, and water, then dried and evaporated. The oily residue (1.8 g.) was chromatographed from benzene on alumina. The main fraction (480 mg.) crystallized from dry petroleum ether–benzene in almost colorless prisms, m.p. 178–180°, of **7-phenyl-7,17-borazaro-5,6-dihydrobenz[a]anthracene (XI)**.

Anal. Calcd. for $C_{22}H_{18}NB$: C, 86.0; H, 5.9; N, 4.6. Found: C, 85.6; H, 6.1; N, 4.7.

On exposure to moist air the compound changed to a white insoluble powder, m.p. 305–307°. The same product was obtained by elution of the chromatographic column with methylene chloride.

10-Benzylphenanthridine.—A mixture of 2-phenylacetylamino-biphenyl (10 g.) phosphorus pentoxide (10 g.) and xylene (100 ml.) was boiled overnight and the solid residue then decomposed with strong potash solution. Isolation with ether gave **10-phenylphenanthridine (XIII)** (4.5 g.) which crystallized from methanol in needles, m.p. 109°–110°.

Anal. Calcd. for $C_{20}H_{15}N$: C, 89.2; H, 5.6; N, 5.2. Found: C, 89.1; H, 5.5; N, 5.4.

1-(4-Bromo-1-butyl)-2-methyl-2,1-borazaronaphthalene and 1,4-Bis-(2-methyl-2,1-borazaro-1-naphthyl)-butane.—A solution of methyllithium prepared from lithium (5.5 g.) and methyl iodide (40 g.) in dry ether was added dropwise to one of 2-methyl-2,1-borazaronaphthalene[9] (18 g.) in dry benzene with vigorous stirring at 20° until a permanent yellow color appeared. The resulting solution was added gradually to a solution of freshly distilled 1,4-dibromobutane (110 g.) in boiling benzene (200 ml.) and the mixture boiled 12 hours under reflux. After cooling and hydrolysis (dilute hydrochloric acid), the benzene layer was evaporated and the residue fractionated under reduced pressure. Fraction 1, b.p. 150–180°/(0.9 mm.) consisted of unchanged starting material (5 g.). Fraction 2 (10.5 g.), b.p. 190–195°/(0.7 mm.) consisted of 1-(4-bromo-1-butyl)-2-methyl-2,1-borazaronaphthalene (XVa) apparently contaminated by unsaturated products containing less bromine. The residue from the distillation crystallized from acetone in white needles (0.2 g.), m.p. 157–158° of **1,4-bis-(2-methyl-2,1-borazaro-1-naphthyl)-butane (XVI)**.

Anal. Calcd. for $C_{20}H_{26}N_2B_2$: C, 77.6; H, 7.4; N, 8.2. Found: C, 77.7; H, 7.6; N, 8.2.

1-(4-N-Morpholino-1-butyl)-2-methyl-2,1-borazaronaphthalene.—A solution of crude IV (2 g.) and morpholine (3 g.) in ethanol (100 ml.) was boiled under reflux for 24 hours then evaporated under reduced pressure and the residue treated with ether and 40% sodium hydroxide solution. Evaporation of the ether gave **1-(4-N-morpholino-1-butyl)-2-methyl-2,1-borazaronaphthalene (XVb)** as a pale yellow oil (1.2 g.), b.p. 190–195°(0.7 mm.), n^{26}D 1.5689.

Anal. Calcd. for $C_{18}H_{25}N_2BO$: C, 71.9; H, 8.8; N, 9.8; B, 3.8. Found: C, 71.9; H, 9.0; N, 9.7; B, 4.0.

1,2,3,4-Tetrahydro-12,11-borazarophenanthrene.—Magnesium (3 g.) was added to a solution of crude IV (3 g.) in dry ether (200 ml.) with cooling (ice-bath). After 2 hours at room temperature the solution was boiled overnight under reflux, cooled, hydrolyzed with cold dilute hydrochloric acid and the ether layer dried (sodium sulfate) and evaporated. Fractionation of the residue in a bulb tube gave a colorless oil (1.6 g.), b.p. 150–155° (0.5 mm.) which crystallized on standing in a refrigerator, forming white needles, m.p. 26–28°, of **1,2,3,4-tetrahydro-12,11-borazarophenanthrene (XVII)**.

Anal. Calcd. for $C_{14}H_{14}NB$: C, 78.8; N, 7.8; N, 7.7; B, 5.9; mol. wt., 207. Found: C, 78.3; H, 8.0; N, 7.5; B, 5.6; mol. wt. (mass spec.), 207.

12,11-Borazarophenanthrene.—A mixture of VII (90.3 mg.), palladized charcoal (0.25 g., 10% Pd) and 1-hexene (1 ml.) was heated overnight in a sealed tube at 290–300° and the cold residue extracted with ether. Evaporation of the ether and chromatography from petroleum ether (b.p. 60–65°) benzene gave **12,11-borazarophenanthrene (XVIII)** (67 mg.) which crystallized from petroleum ether (b.p. 30–35°) in long white needles, m.p. 75–77°.

Anal. Calcd. for $C_{12}H_{10}NB$: C, 80.54; H, 5.59. Found: C, 80.57; H, 5.53.

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Rearrangements of Benzeneazotribenzoylmethane and its Derivatives. Structural Reassignments[1]

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The coupling of benzenediazonium ion with tribenzoylmethane anion gives a product I which had previously been thought to be an O-azo compound A. It has now been found to be benzeneazotribenzoylmethane (B). The red rearrangement product II, obtained by heating the azo compound I, had been assigned the structure B. It has now been found to be the enol benzoate, α-benzeneazo-β-benzoyloxybenzalacetophenone. The enol benzoate II is converted with zinc and acetic acid to 2-benzoyl-3-phenylindole (XII). Catalytic reduction of the enol ester II gives benzamidodibenzoylmethane (XIV). Bromination of tribenzoylmethane in chloroform, carried out in order to prepare bromotribenzoylmethane as previously reported, gave instead bromodibenzoylmethane. Mesityleneazotribenzoylmethane, instead of undergoing the thermal rearrangements observed with the unsubstituted compound I, gives 5,7-dimethylindazole (XVIII) when heated either alone or in dioxane solution.

Dimroth and Hartmann,[3] in 1907, reported that the anion of tribenzoylmethane reacts with benzenediazonium ion in buffered aqueous solution to give a yellow product (I) assigned the structure A, which would result from a coupling reaction at an oxygen atom. Evidence for structure A was provided primarily by the observation that the substance I reverted readily to benzenediazonium ion. Thus, with cold ethereal hydrogen chlo-

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(2) Roger Adams Fellow, 1958–1959. National Science Foundation Fellow, 1959–1961.

(3) O. Dimroth and M. Hartmann, *Ber.*, **40**, 2404, 4460 (1907); **41**, 4012 (1908).