

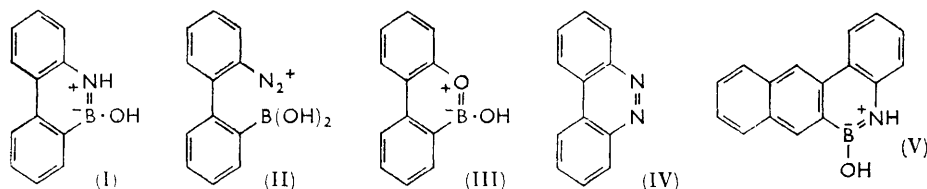
### 411. A New Route to Polycyclic Benzocinnolines.

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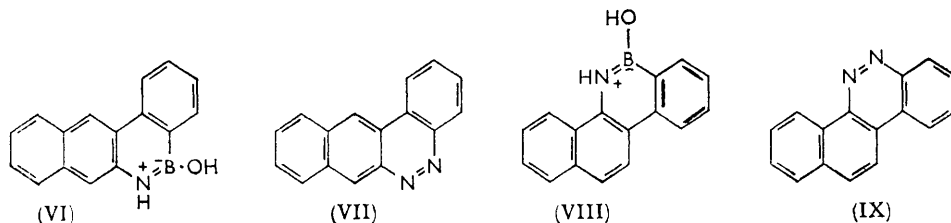
Polycyclic borazaro-compounds (dihydroazabora-compounds) can be converted into diazoarylboronic acids by diazotization. The diazonium salts undergo internal diazo-coupling with elimination of boric acid and formation of a polycyclic cinnoline derivative. These reactions provide a new and convenient route to such compounds.

POLYCYCLIC cinnoline derivatives are of interest as potential carcinogens.<sup>1</sup> We here report a new synthesis of such compounds which seems likely to be of general utility.

Dewar and Maitlis<sup>2</sup> found that 10-hydroxy-10,9-borazarophenanthrene (9,10-dihydro-9-aza-10-boraphenanthren-10-ol) (I) was converted into the diazonium salt (II) by treatment with nitrous acid in acetic acid, and that 10-hydroxy-10,9-boroxarophenanthrene (9,10-dihydro-9-oxa-10-boraphenanthren-10-ol) (III) was obtained when the diazonium solution was poured into boiling water. We have now found that if the solution of the salt (II) is set aside in the cold after addition of sodium acetate, internal coupling takes place and benzo[*c*]cinnoline (IV) is formed in almost theoretical yield.



Similar treatment of 6-hydroxy-6,5-borazarobenz[*a*]anthracene (V) or its isomer (VI) gave the previously unknown dibenzo[*c,g*]cinnoline (VII), the structure of which is established by its formation from both these compounds. In these reactions it is often convenient to use the methyl ethers of the borazaro-compounds, these being hydrolyzed immediately in the conditions used.



We have also converted 6-hydroxy-6,5-borazarochrysenes (VIII) into dibenzo[*c,h*]cinnoline (IX) but here the yield was much less, presumably owing to some steric effect of the *peri*-hydrogen atom. In this case it was also found essential to carry out the diazotization in the absence of mineral acid. The product (IX) was identified by comparison with an authentic sample prepared by electrolytic reduction of 1-nitro-2-*o*-nitrophenylanthralene; we found this procedure preferable to the use of lithium aluminium hydride as recommended by Corbett and Holt<sup>12</sup> although our yield was somewhat less.

Since the borazaro-compounds are prepared by Friedel-Crafts cyclization<sup>3</sup> of the adducts of aromatic amines with boron trichloride, these reactions provide a method for converting such amines into polycyclic cinnolines. This route has the advantage of requiring only one functional group where the  $-N=N-$  bridge is to be formed, whereas previous

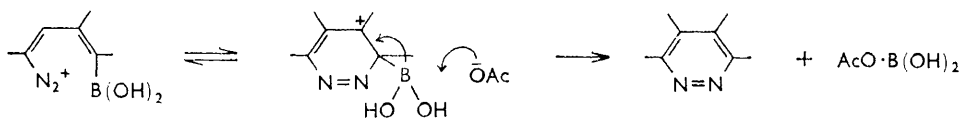
<sup>1</sup> Braithwaite and Holt, *J.*, 1959, 3025.

<sup>2</sup> Dewar and Maitlis, *Chem. and Ind.*, 1960, 1626.

<sup>3</sup> Dewar, Kubba, and Pettit, *J.*, 1958, 3073.

methods needed two, *viz.*, reduction of dinitro-derivatives,<sup>4</sup> oxidation of diamines,<sup>5</sup> or azine formation.<sup>6</sup>

The cyclization in our synthesis involves electrophilic displacement of boric acid by a diazonium group. Displacements of boric acid from arylboronic acids by other electrophilic reagents are known.<sup>7</sup> The cyclization takes place only in presence of a base (sodium acetate), suggesting that the diazonium salt undergoes reversible isomerization to a carbonium-ion form and that the rate-determining step is the removal of boric acid from this by the action of the base, as in certain of the deboronations studied by Kuivila and his collaborators.<sup>8</sup>



### EXPERIMENTAL

**10-Methoxy-10,9-borazarophenanthrene (9,10-Dihydro-10-methoxy-9-aza-10-boraphenanthrene).**—A mixture of 10-hydroxy-10,9-borazarophenanthrene<sup>3</sup> (19.5 g.) and anhydrous methanol (400 ml.) was boiled under reflux for 3 hr., concentrated to 50 ml., and kept overnight at  $-20^{\circ}$ . The precipitate was collected and the treatment with methanol repeated, giving 10-methoxy-10,9-borazarophenanthrene (10.2 g., 49%) which crystallized from methanol (charcoal) in needles, m. p.  $94.5-96.5^{\circ}$  (Found: C, 74.6; H, 5.9; N, 6.8.  $C_{13}H_{12}BNO$  requires C, 74.7; H, 5.8; N, 6.7%).

**Benzo[c]cinnoline.**—Concentrated hydrochloric acid (5 ml.) was added to a solution of 10-methoxy-10,9-borazarophenanthrene (0.84 g.) in hot acetic acid (10 ml.). The mixture was diazotized with stirring at  $4-5^{\circ}$  with a concentrated solution of sodium nitrite (0.30 g.). After 1 hr. a cold solution of sodium acetate (14 g. of trihydrate) in water (30 ml.) was added slowly, at  $<8^{\circ}$ , and 1 hr. later the cooling-bath was removed. Next day the precipitate of crude benzo[c]cinnoline (0.70 g., 98%), m. p.  $145-149^{\circ}$ , was collected. Recrystallization from ethanol raised the m. p. to  $155^{\circ}$  (lit.,<sup>9</sup>  $156^{\circ}$ ). The ultraviolet spectrum in methylcyclohexane was identical with that reported by Badger and Walker.<sup>10</sup>

**Dibenzo[c,g]cinnoline.**—(a) *From 5-methoxy-5,6-borazarotetraphene (5,6-dihydro-5-methoxy-6-aza-5-borachrysene).* The reaction was carried out as above, with 5-methoxy-5,6-borazarotetraphene<sup>11</sup> (1 g.) in acetic acid (20 ml.) and the previous quantities of the other reagents. The crude precipitate (0.92 g.; m. p.  $187^{\circ}$ ) was chromatographed in benzene on alumina, the column being eluted with 1:19, and later 1:9, ethyl acetate-benzene. Evaporation of the solvent gave pure dibenzo[c,g]cinnoline (0.52 g., 57%) which crystallized from methanol in yellow needles, m. p.  $221-221.5^{\circ}$  (Found: C, 83.4; H, 4.3; N, 12.4.  $C_{14}H_{10}N_2$  requires C, 83.45; H, 4.4; N, 12.2%).  $\lambda_{\max}$ . ( $\log_{10} \epsilon$  in parentheses) 415 (3.25), 393 (3.34), 373 (3.25), 357 (3.93), 340 (3.96), 325 (3.83), 295 (4.67), 285 (4.76), 265 (4.47), 254 (4.60), and 222 (4.42), with shoulders at 276 (4.61), 247 (4.54), and 236  $\mu$  (4.40) (solvent, methyl cyclohexane).

(b) *From 6-methoxy-6,5-borazarotetraphene.*<sup>11</sup> The reaction was carried out as above, giving dibenzo[c,g]cinnoline (0.46 g., 50%) identical with that obtained as under (a) (m. p. and mixed m. p., ultraviolet and infrared spectra).

**Dibenzo[c,h]cinnoline.**—(a) *From 1-nitro-2-o-nitrophenylnaphthalene.* A solution of 1-nitro-2-o-nitrophenylnaphthalene in ethanol (250 ml.) was reduced electrolytically at  $78^{\circ}$ , with saturated sodium carbonate solution in the anode compartment, a nickel cathode, and a lead anode. The dibenzo[c,h]cinnoline was precipitated with water and chromatographed in

<sup>4</sup> Braithwaite, Holt, and Hughes, *J.*, 1958, 4073.

<sup>5</sup> Corbett and Holt, *J.*, 1961, 3695.

<sup>6</sup> *E.g.*, Benndorf and Sorns, *Monatsh.*, 1937, **64**, 167.

<sup>7</sup> Melnikov, *J. Gen. Chem. U.S.S.R.*, 1936, **6**, 636; 1938, **8**, 1766; Ainley and Challenger, *J.*, 1930, 2171; Challenger and Richards, *J.*, 1934, 405; Michaelis and Becker, *Ber.*, 1882, **15**, 180; Torssell, *Arkiv Kemi*, 1957, **10**, 507.

<sup>8</sup> See Kuivila and Muller, *J. Amer. Chem. Soc.*, 1962, **84**, 377, and references therein.

<sup>9</sup> Täuber, *Ber.*, 1891, **24**, 3085.

<sup>10</sup> Badger and Walker, *J.*, 1956, 123.

<sup>11</sup> Dewar and Poesche, unpublished work.

benzene on alumina, with elution by ethyl acetate-benzene (first 1:19, then 1:9). Evaporation of the solvent gave dibenzo[*c,h*]cinnoline (35%; cf. 300%,<sup>12</sup> 63%<sup>13</sup>) which crystallized from ethanol in yellow needles, m. p. 196—197° (lit.,<sup>12</sup> 190°) (Found: C, 83.6; H, 4.6. Calc. for C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>: C, 83.45; H, 4.4%).

(b) *From 6-methoxy-6,5-borazarochrysene.* Sodium nitrite (0.30 g.) was added slowly to a vigorously stirred solution of the chrysene derivative<sup>11</sup> (1 g.) in acetic acid (20 ml.) and propionic acid (10 ml.) at 5°. The mixture was stirred for 2 hr. at 5° and then overnight at room temperature. After evaporation the residue was chromatographed as above, giving dibenzo[*c,h*]cinnoline, identical with the preceding sample.

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<sup>11</sup> Corbett and Holt, *J.*, 1960, 3650.

<sup>13</sup> Corbett, Thesis, Reading, 1961.