

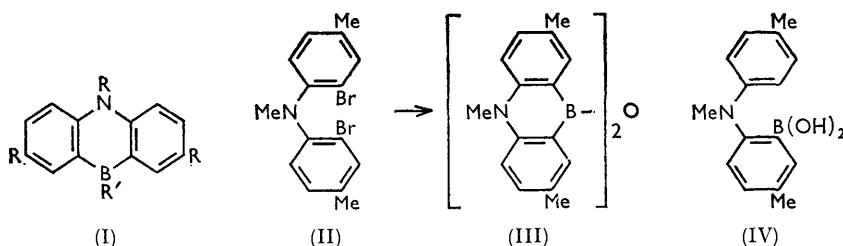
## 75. New Heteroaromatic Compounds. Part IX.\* Some 10,9-Borazaroanthracenes.†

By P. M. MAITLIS.

The preparation and properties of a number of 10-substituted 3,6,9-trimethyl-10,9-borazaroanthracenes are described. It is concluded that less aromatic stabilisation occurs in the hetero-ring here than in the 10,9-borazaro-phenanthrenes.

THE preparation of a number of heteroaromatic molecules containing boron in the ring has been described and some of their properties have been investigated.<sup>1-3</sup> It has been concluded from these that when the boron has oxygen or nitrogen adjacent to it in a six-membered conjugated ring there is considerable stabilisation of that ring owing to the participation in the ground state of structures such as  $^{-+}\text{NH}=\text{B}^{-}\text{H}^{-}$ , and the usual reactivity of the boron is greatly decreased. We therefore investigated systems with non-adjacent heteroatoms in order to find out what effect this has on the stability of the molecule. Derivatives of one such system, 9,10-boroxaroanthracene,<sup>2</sup> have already been reported, but the properties have not yet been fully investigated. Since, however, Dewar and Dietz<sup>1</sup> showed that molecules containing  $-\text{O}\cdot\text{BR}-$  groups are less stabilised than molecules containing  $-\text{NH}\cdot\text{BR}-$  groups it was decided to investigate the 10,9-borazaroanthracenes [9,10-dihydro-9-aza-10-bora-anthracene] (I; R = R' = H).

A simple synthesis of the unsubstituted ring system was not feasible; however, since it has been shown that the presence of a methyl group on the nitrogen in the borazaro-phenanthrenes does not lead to any significant reduction in stability,<sup>3</sup> derivatives of 3,6,9-trimethyl-10,9-borazaroanthracene (I; R = Me) were prepared. The starting material for



these compounds was the readily available 2,2'-dibromo-4,4',N-trimethyldiphenylamine<sup>4</sup> (II).

Treatment of the 2,2'-dilithio-derivative from the amine (II) (prepared by use of butyl-lithium) with butyl orthoborate in ether gave, after hydrolysis, a very low yield (12%) of the cyclic compound (III), together with some of the uncyclised boronic acid

\* Part VIII, *J. Amer. Chem. Soc.*, 1960, **82**, in the press.

† For this nomenclature see *J.*, 1959, 2728.

<sup>1</sup> Dewar, Kubba, and Pettit, *J.*, 1958, 3073, 3076; Dewar and Kubba, *Tetrahedron*, 1959, **7**, 213; Dewar and Dietz, *J.*, 1959, 2728; 1960, 1344.

<sup>2</sup> Davidson and French, *J.*, 1960, 191.

<sup>3</sup> Maitlis and Dewar, *J. Amer. Chem. Soc.*, in the press.

<sup>4</sup> Weitz and Schwechten, *Ber.*, 1927, **60**, 550; Gilman and Zuech, *J. Org. Chem.*, 1959, **24**, 1394.

(IV) (12%); the yield of anhydride was increased to 65% by reaction with butyl metaborate in boiling ether for 1 hr. Using the boron trifluoride-ether complex instead of butyl metaborate gave a low yield.

Evidence for the cyclic structure of the product comes from the elemental analysis, which precludes an uncyclised structure, and the ultraviolet spectrum (Fig. 1). The isoconjugate hydrocarbon is unknown so that no direct comparisons can be made; however, the spectrum of the product resembles those of anthracene- and acridine-type compounds, notably in a strong peak at 382 m $\mu$  ( $\log \epsilon$  3.86) which diphenylamines, *e.g.*, (IV), do not show.

The product, expected to be 10-hydroxy-3,6,9-trimethyl-10,9-borazaroanthracene, is the anhydride (III), as is shown by the carbon analysis, by its insolubility in aqueous sodium hydroxide, and by the absence of a hydroxy peak in the infrared spectrum. The molecular weight found by the Rast method gives an intermediate value (common with compounds of this type), presumably owing to some reaction with the camphor. In ethanolic solution, however, the ethyl ester (I; R = Me, R' = OEt) exists: in 50% aqueous

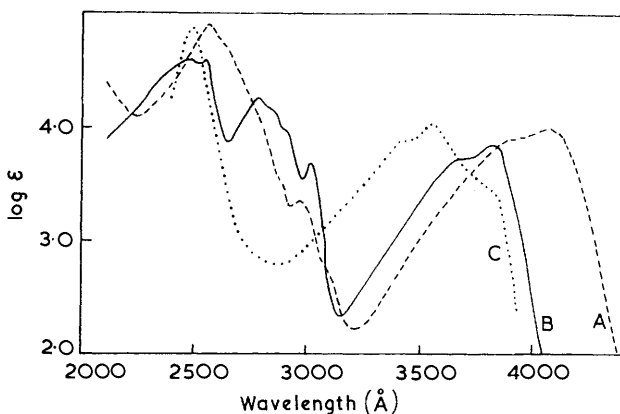


FIG. 1. Spectra of (A) compound (I; R = Me, R' = Ph), (B) compound (III), and (C) acridine, all in ethanol.

ethanol the product shows  $pK_a$  *ca.* 11.2, a value very close to that obtained for the "hydroxy"-borazaro-naphthalene and -phenanthrene.

Treatment of the dilithiodiphenylamine in ether with dibutyl phenylboronate in ether gave a 10% yield of 3,6,9-trimethyl-10-phenyl-10,9-borazaroanthracene (I; R = Me, R' = Ph), which was prepared in better yield (77%) by treating a benzene solution of compound (III) with five mol. of phenylmagnesium bromide in ether. Attempts to make the 10-methyl-, 10-n-butyl-, and 10-t-butyl-borazaroanthracene by the same route from compound (III) all failed, only starting material being isolated. Since in each of these cases reaction occurred it must be concluded that the product was lost during the working-up by aerial oxidation, in spite of attempts to avoid it.

Addition of small amounts of alkali to an ethanolic solution of the *B*-hydroxy- or the *B*-phenyl compound caused an immediate change in the ultraviolet spectrum in which the acridine-like spectrum<sup>5</sup> was replaced by a diphenylamine-type spectrum. This was particularly pronounced in the long-wavelength band which entirely disappears in 5% alkali (Figs. 1 and 2). The effect is reversed in both cases on addition of acid. The changes can be explained only by assuming that in alkali the anthracene-type conjugation is interrupted and an adduct of type (V) is formed. An attempt was made to isolate such an adduct by preparing the ethanolamine derivative\* which might be expected to have a

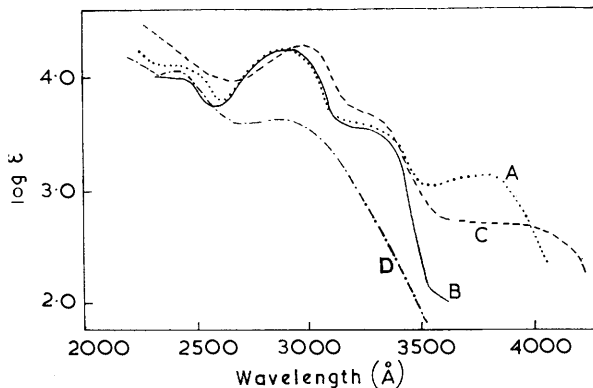
\* Letsinger and Skoog<sup>6</sup> showed that diarylboronic acids form cyclic adducts of this type with ethanolamine in which the boron is tetrahedral and stabilised by back-co-ordination.

<sup>5</sup> Blout and Corley, *J. Amer. Chem. Soc.*, 1947, **69**, 766.

<sup>6</sup> Letsinger and Skoog, *J. Amer. Chem. Soc.*, 1955, **77**, 2491.

spiro-structure (VI). The ethanolamine derivative from compound (III) was prepared and had absorption in the 2.5–3.5  $\mu$  range similar to that of the ethanolamine derivative of diphenylboronous acid; however, the ultraviolet spectrum was identical with that of

FIG. 2. Spectra of compound (III) in ethanol containing (A) 0.5% and (B) 5% of KOH, (C) compound (I; R = Me, R' = Ph) in ethanol containing 0.5% of KOH, and (D) compound (IV) in ethanol.



the compound (III) in both ethanol and cyclohexane, suggesting that, although perhaps in the solid state structure (VI) is important, in solution the amine is too weak a base to co-ordinate on to the boron. 9-Hydroxy-9,10-boroxaroanthracene<sup>2</sup> showed an analogous reversible shift in the ultraviolet spectrum on the addition of alkali (Fig. 3).

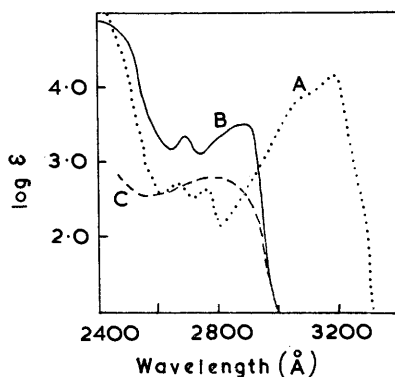
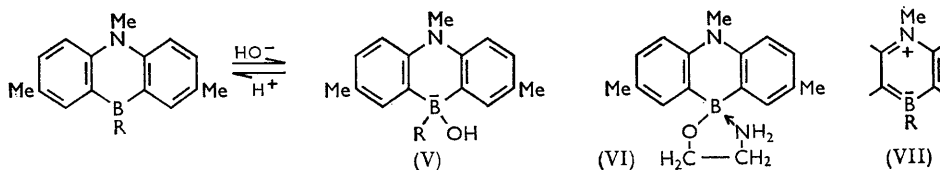


FIG. 3. Spectra of 9-hydroxy-9,10-borazaroanthracene<sup>2</sup> (A) in ethanol and (B) in ethanol containing ~0.2% of NaOH, and (C) *o*-phenoxyphenylboronic acid in cyclohexane.<sup>2</sup>

The anhydride (III) could not be brominated without loss of the boron; with two mol. of bromine in acetic acid it gave an 87% yield of 2,2'-dibromo-4,4',*N*-trimethyldiphenylamine; no boron-containing material could be isolated. Since the borazaroanthracene



(III) is stable in acetic acid under the conditions of the experiment, this must be a case of deboration by bromine<sup>7</sup> rather than by acetic acid<sup>8</sup> followed by bromination.

<sup>7</sup> Kuivila and Easterbrook, *J. Amer. Chem. Soc.*, 1951, **73**, 4629.

<sup>8</sup> Meerwein, Hinz, Majert, and Sönke, *J. prakt. Chem.*, 1936, **147**, 251; Goubeau, Eppele, Ulmschneider, and Lehmann, *Angew. Chem.*, 1955, **67**, 710; Brown and Murray, *J. Amer. Chem. Soc.*, 1959, **81**, 4108.

The properties of the 10,9-borazaroanthracene system as described above lead to the conclusions (1) that the central ring has some aromatic stabilisation as represented by (VII) [this is supported by the stability of compound (III) towards aerial oxidation and by the acridine-type spectrum of both the *B*-hydroxy- and *B*-phenyl-borazaroanthracene] and (2) that this stabilisation is not as great as in molecules where the heteroatoms are adjacent, as in the borazaro-naphthalenes and -phenanthrenes. Three reactions illustrate this.

(a) With alkali compound (III) gives an adduct which does not allow conjugation through the boron, whereas with the naphthalene and the phenanthrene analogues addition of alkali to the *B*-hydroxy-compound causes only a slight bathochromic shift; this would be expected if the anion  $\text{>B}\cdot\text{O}^-$  were formed which had the possibility of existing to some extent as  $\text{>}\bar{\text{B}}=\text{O}$ . That this is not an effect of the methyl group attached to the nitrogen has been shown by the fact that the spectrum of 9,10-dimethyl-10,9-borazarophenanthrene is unchanged on addition of alkali.<sup>3</sup>

(b) Borazaro-naphthalenes and -phenanthrenes containing alkyl groups attached to boron are relatively stable to aerial oxidation and are only slowly oxidised to the hydroxy-compounds in solution. Preparation of the *B*-alkylborazaroanthracenes has not been possible owing to the (presumed) readiness with which they are oxidised, and even the *B*-phenyl compound is slowly oxidised in ethanolic solution to the anhydride (III). This implies that the boron in this molecule is not greatly stabilised by the nitrogen and that for complete stabilisation a further group must be present which can give the boron some back-co-ordinative stability, such as oxygen or a phenyl.

(c) This is the only case hitherto where boron in a heteroaromatic ring is readily removed by a reagent as mild as bromine, and again implies a lack of aromatic stabilisation in the central ring.

This conclusion is not unexpected. Dewar and Lucken<sup>9</sup> showed by nuclear quadrupole resonance studies that conjugative interaction, which is large between chlorine and nitrogen in 2-chloropyridine, is vanishingly small in 4-chloropyridine. By analogy interaction between adjacent nitrogen and boron would be expected to be great, but very much smaller when these atoms are separated by two carbon atoms.

## EXPERIMENTAL

Ultraviolet spectra were determined by a Unicam S.P. 500 spectrophotometer for 95% ethanol and cyclohexane solutions. Microanalyses were by Alfred Bernhardt, Max-Planck-Institut für Kohlenforschung, Mülheim, Germany.

*Bis*-(3,6,9-trimethyl-10,9-borazaro-10-anthryl) Ether.—(a) An ethereal solution of *n*-butyllithium (50 ml., 0.06 mole) was added slowly with stirring to an ice-cold solution of 2,2'-dibromo-4,4',*N*-trimethyldiphenylamine<sup>4</sup> (9.4 g., 0.0255 mole) in ether (50 ml.), under dry, oxygen-free nitrogen. The mixture was stirred at 0° for 2 hr., then *n*-butyl metaborate (3.3 g., 0.03 mole) in ether (30 ml.) was run in slowly. The mixture was allowed to warm to room temperature and then refluxed for 1 hr. 2*N*-Hydrochloric acid (200 ml.) was added, the ethereal layer separated, and the acid layer again extracted with ether. The ether solutions were combined, dried (MgSO<sub>4</sub>), and evaporated, giving a dark oil which on addition of light petroleum (b. p. <40°) gave yellow needles (2.9 g.). Chromatography of the mother liquors on alumina in light petroleum yielded a small amount of starting material (1.7 g., 18%), m. p. and mixed m. p. 101–102°; ether-light petroleum eluted a further 0.2 g. of boron-containing material. The total yield of anhydride was 3.1 g. (65% based on recovered starting material). Crystallisation from benzene-light petroleum (b. p. 100–120°) gave very pale yellow prisms, m. p. 244–245°. Further crystallisation from ether-light petroleum gave colourless material of the same m. p. (Found: C, 79.2; H, 6.7; N, 6.0; B, 5.2%; *M*, 312. C<sub>30</sub>H<sub>30</sub>B<sub>2</sub>N<sub>2</sub>O requires C, 78.95; H, 6.6; N, 6.1; B, 4.8%; *M*, 456).

<sup>9</sup> Dewar and Lucken, *Chem. Soc. Special Publ.*, No. 12, 1958, p. 231.

The *ethanolamine derivative*, obtained by treating the anhydride with ethanolamine in benzene, crystallised in needles, m. p. 223—224° (Found: C, 73.05; H, 7.5; N, 9.95; B, 4.1. C<sub>17</sub>H<sub>21</sub>BN<sub>2</sub>O requires C, 72.85; H, 7.5; N, 10.0; B, 3.9%).

(b) Reaction as above, with half-quantities, but 6.0 g. of butyl orthoborate in ether (30 ml.) and 19 hours' stirring at room temperature, gave a dark oil. With light petroleum this gave first, the anhydride (III) (360 mg., 12%) and then a white solid (400 g.), which on crystallisation from benzene gave 5-methyl-2-(*N*-methyl-*N*-*p*-tolylamino)phenylboronic acid (IV), m. p. 165—166° (Found: C, 70.7; H, 7.2; N, 5.4; B, 4.1. C<sub>15</sub>H<sub>18</sub>BNO<sub>2</sub> requires C, 70.6; H, 7.1; N, 5.5; B, 4.3%).

3,6,9-Trimethyl-10-phenyl-10,9-borazaroanthracene.—(a) The reaction was as described under (b) above except that dibutyl phenylboronate (4.5 g.) in ether (15 ml.) was used in place of the butyl borate. The brown oily product was chromatographed on alumina in light petroleum (b. p. <40°), to give a small amount of boron-free oil (presumably 4,4',*N*-trimethyldiphenylamine); addition of ether to the eluant led to a yellow solid (410 mg., 10%) which crystallised from ether-light petroleum as fluorescent yellow needles, m. p. 114—115°; this was 3,6,9-trimethyl-10-phenyl-10,9-borazaroanthracene (Found: C, 84.6; H, 6.9; N, 4.8; B, 4.0%; *M*, 282. C<sub>21</sub>H<sub>20</sub>NB requires C, 84.85; H, 6.7; N, 4.7; B, 3.7%; *M*, 297).

(b) An ethereal solution (25 ml.) of phenylmagnesium bromide (from bromobenzene, 3.5 g., and magnesium, 0.5 g.) was added with stirring to a solution of the anhydride (III) (1 g.) in benzene (20 ml.). After refluxing for 1 hr. the solution was cooled, hydrolysed with dilute hydrochloric acid, and extracted with ether. The ether extracts were combined, dried, and evaporated. A residue of low-melting yellow solid (1.45 g.) was obtained which on recrystallisation from light petroleum (b. p. 40—60°) gave 3,6,9-trimethyl-10-phenyl-10,9-borazaroanthracene (1.0 g., 77%), m. p. and mixed m. p. 114—115°.

*Bromination of the Anhydride* (III).—A solution of the anhydride (III) (1.7 g.) in glacial acetic acid (20 ml.) was treated with bromine (0.9 ml., 2.2 mol.) in this acid (10 ml.). The solution became bluish-green, then an oil was precipitated that was redissolved by gentle warming on a steam-bath. After 30 min. the solution was poured into a large excess of water and left overnight. The clear supernatant liquid was then decanted (basification gave no more material) and the solid dissolved in benzene, dried, and recovered. Addition of light petroleum (b. p. 100—120°) gave 2,2'-dibromo-4,4',*N*-trimethyldiphenylamine (2.4 g., 87%), m. p. 100—102°, mixed m. p. with synthetic material 101.5—103.5°.

An experiment in which the anhydride (III) was left in hot glacial acetic acid solution for 1 hr. and then precipitated gave no significant quantity of boron-free material.

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