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NEW HETEROAROMATIC COMPOUNDS—IV[1]

THE NITRATION AND CHLORINATION OF 10-METHYL-10:9-BORAZAROPHENANTHRENE

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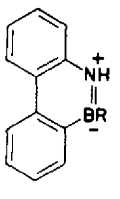
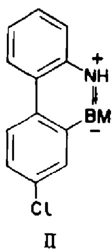
Abstract—10-Methyl- and 10-hydroxy-10:9-borazarophenanthrene have been nitrated with nitric acid in acetic anhydride, and the former compound has been chlorinated with chlorine in acetic acid; the products have been oriented and the proportions of isomers determined quantitatively. The results are shown to be in general agreement with the predictions of MO theory, attack taking place in the 6- and 8-positions. A method for degrading such boron compounds is described, and also the synthesis of 2-, 6-, and 8-chloro-10-methyl-10:9-borazarophenanthrenes as reference compounds. The 6- and 8-amino derivatives of 10-methyl and 10-hydroxy-10:9-borazarophenanthrene have been prepared by reduction of the corresponding nitro derivatives.

In a recent paper[1] we described the preparation of various derivatives (I) of the new heterocyclic system, 10:9-borazarophenanthrene (I; $R = H$). The general properties of these compounds indicated their close resemblance to the corresponding isoconjugate derivatives of phenanthrene; we concluded that they are aromatic, and so best represented by the classical structure (I).

In support of this we have now found that the 10-methyl and 10-hydroxy derivatives (I; $R = Me, OH$) readily undergo nitration or chlorination, without appreciable dealkylation or fission of the boron–nitrogen bond. In view of the theoretical interest of these reactions we have studied them in some detail and determined the orientation of the products formed.



I



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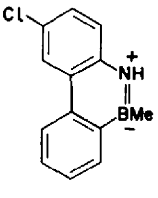

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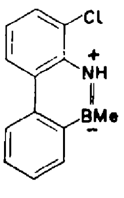

IV

Chlorination of 10-methyl-10:9-borazarophenanthrene (I; $R = Me$) with one molar equivalent of chlorine in acetic acid gave a mixture of chlorination products in 81 per cent yield. This mixture was separated into two components by chromatography. The main component (A) analysed as a chloro derivative of I ($R = Me$); its orientation was determined by synthesis and degradation.

It seemed likely on theoretical grounds (see below) that (A) would be 2-, 6-, or

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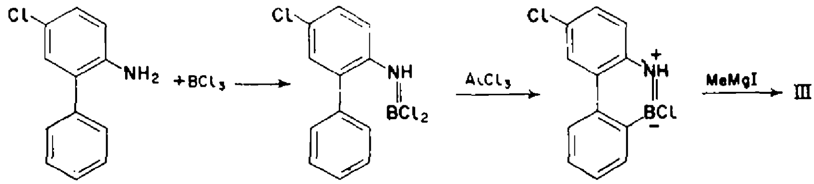
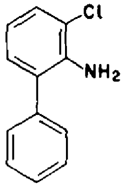
[1] Dewar, Kubba and Pettit, *J. Chem. Soc.* 3073 (1958).

8-chloro-10-methyl-10:9-borazarophenanthrene—i.e. II, III, or IV. These three compounds were synthesized by the method previously described.[1]

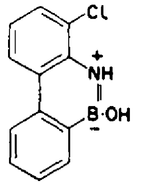


Their U.V. spectra are shown in Fig. 1. Comparison showed A to be the 8-chloro isomer (IV).

Although derivatives of I are unchanged by boiling with alkali or concentrated hydrochloric acid, we found that they could be degraded in good yield to derivatives of 2-aminodiphenyl and boric acid by treatment with cold concentrated sulphuric acid, a reaction analogous to the well-known deboronation of arylboronic acids. Treated in this way, A gave 2-amino-3-chlorodiphenyl (V), confirming it to be IV.



V



VI

The second compound (B), formed in very small amount, was not identified. Its U.V. spectrum resembled closely that of 10-hydroxy-10:9-borazarophenanthrene (Fig. 2); analogy with nitration (see below) suggests that it was probably 8-chloro-10-hydroxy-10:9-borazarophenanthrene (VI). Only one analysis could be carried out, and that gave an apparently erratic result for carbon; carbon analyses for boron compounds are frequently erratic.

The nitration of 10-methyl-10:9-borazarophenanthrene (I; R = Me) was carried out with nitric acid in cold acetic anhydride; a mixture of nitro compounds was obtained in 78 per cent yield. Chromatography separated this into two main components (C), (D), and a minor component (E). All three formed orange-yellow crystalline solids. The U.V. spectra of C and D are shown in Fig. 3; that of E is shown later (Fig. 4).

Attempts were first made to synthesize the three nitro compounds corresponding to II, III, and IV from the appropriate nitroaminodiphenyls; the amines reacted with boron trichloride, but the products could not be cyclized.

Attempts were then made to convert the nitration products to the corresponding chloro derivatives. Reduction with hydrazine hydrate over palladized charcoal gave the three amines in almost theoretical yield, but attempts to convert them to the chloro compounds by the Sandmeyer reaction failed.

Compounds C and D, which analysed well as nitro derivatives of 10-methyl-10:9-borazarophenanthrene, were then degraded with cold concentrated sulphuric acid; C gave 2-amino-3-nitrodiphenyl (VII), while D gave 2-amino-5-nitrodiphenyl (VIII).

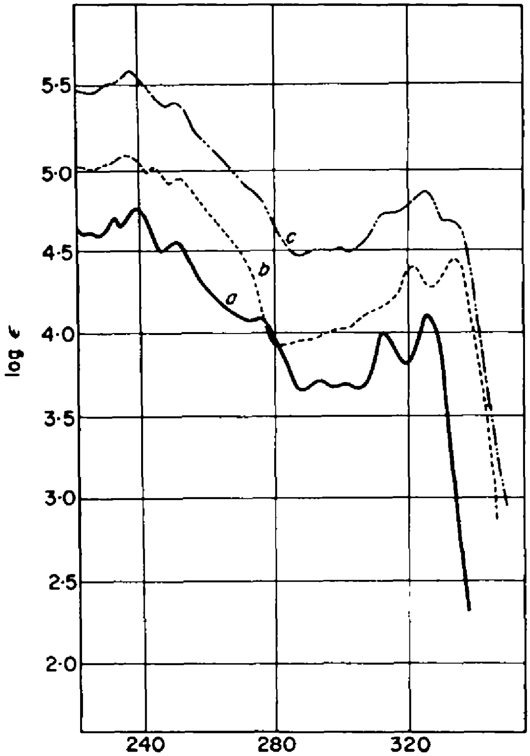


FIG. 1. U.V. spectra of (a) 2-, (b) 6-, and (c) 8-chloro-10-methyl-10:9-borazarophenanthrene. The log ε scale applies to (a); the curves for (b) and (c) are displaced by 0·5 and 1·0 respectively to avoid confusion.

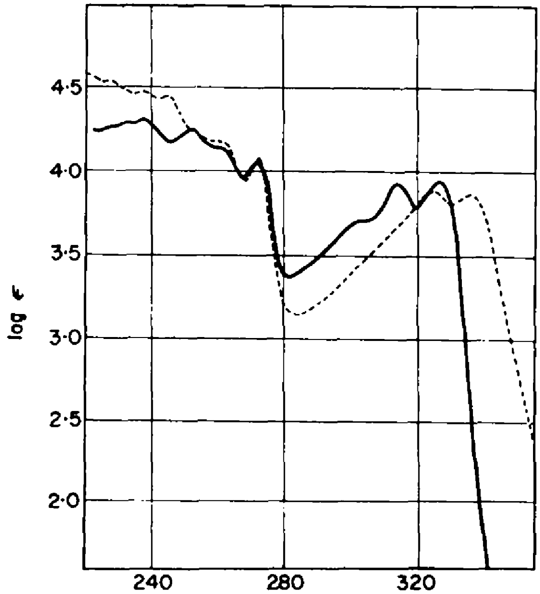
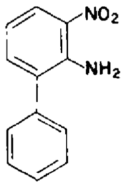
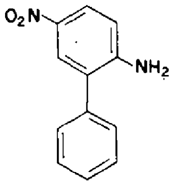


FIG. 2. U.V. spectra of 10-hydroxy-10:9-borazarophenanthrene (———) and the unidentified chlorination product (- - - - -).

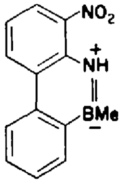
Therefore C was formulated as 8-nitro-10-methyl-10:9-borazarophenanthrene (IX), and D as 6-nitro-10-methyl-10:9-borazarophenanthrene (X).



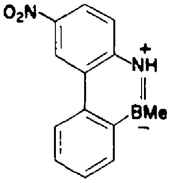
VII



VIII



IX



X

The third component (E) presented difficulties, since at first it gave erratic results on analysis. However, the corresponding amine analysed well as an aminohydroxy-borazarophenanthrene, and the I.R. spectrum of E showed it to contain both NH and OH groups. Moreover, E was degraded by cold concentrated sulphuric acid to VII. We therefore formulated E as 8-nitro-10-hydroxy-10:9-borazarophenanthrene (XI).

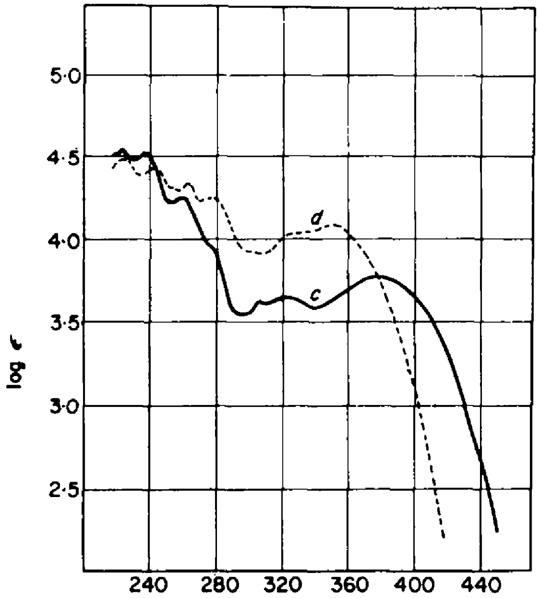
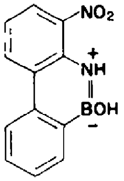
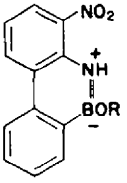


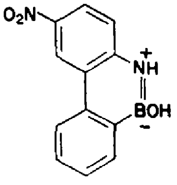
FIG. 3. Spectra of 8-nitro-10-methyl-10:9-borazarophenanthrene (C) (———) and of 6-nitro-10-methyl-10:9-borazarophenanthrene (D) (····).



XI



XII



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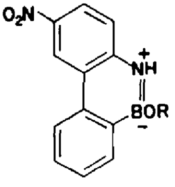


XIV

This structure was confirmed in two ways. First, it was noticed that E was converted to the corresponding methyl and ethyl ethers (XII; R = Me, Et) merely by recrystallization from the corresponding alcohols, and that the ethers were hydrolysed on recrystallization from carbon tetrachloride (presumably by traces of water dissolved in the solvent or adsorbed on the surface of the glass vessels used). It is well known that esters of boric acids are formed and hydrolysed with exceptional ease.

Secondly, we obtained by nitrating 10-hydroxy-10:9-borazarophenanthrene a mixture of mononitro derivatives, separated into two components by extraction with carbon tetrachloride. The soluble component was identical with E, which must therefore be a nitrohydroxyborazarophenanthrene. The insoluble component also analysed as a nitrohydroxyborazarophenanthrene, and it was degraded to VIII by cold concentrated sulphuric acid. It was therefore formulated as 6-nitro-10-hydroxy-10:9-borazarophenanthrene (XIII). Like XI, it was converted to ethers (XIV; R = Me, Et) by crystallization from methanol or ethanol.

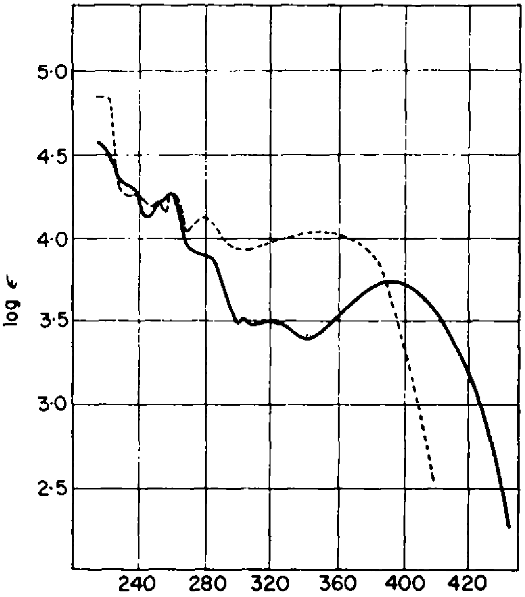
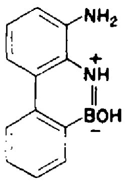


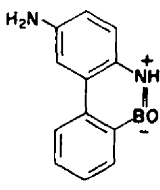
Fig. 4. U.V. spectra of 8-nitro- (———) and 6-nitro(· · · · ·)-10-hydroxy-10:9-borazarophenanthrene.

The U.V. spectra of XI and XIII are shown in Fig. 4.

Both XI and XIII were reduced by hydrazine hydrate over palladized charcoal to the corresponding amines XV and XVI. The UV spectra of the 8- and 6-amino derivatives of 10-methyl and 10-hydroxy-10:9-borazarophenanthrene are shown in Figs. 5 and 6.



XV



XVI

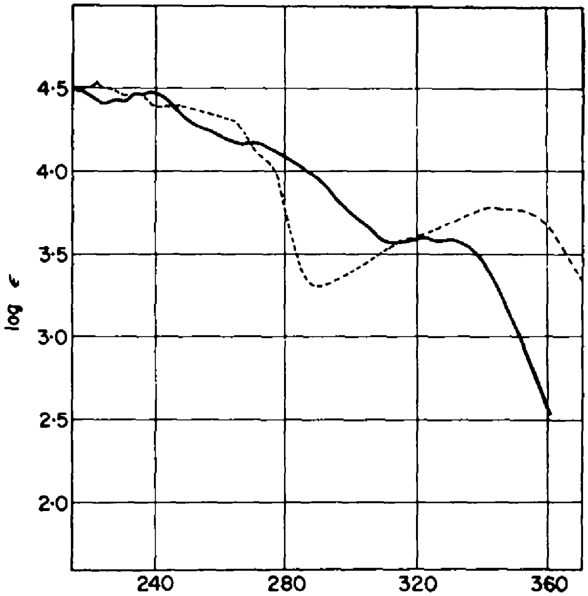


Fig. 5. U.V. spectra of 8- (————) and 6- (·····)-amino-10-methyl-10:9-borazarophenanthrene.

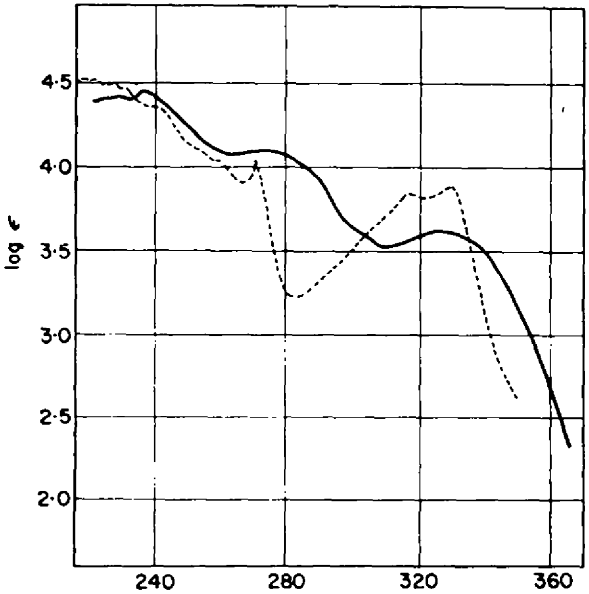


Fig. 6. U.V. spectra of 8- (————) and 6- (···)-amino-10-hydroxy-10:9-borazarophenanthrene.

The formation of XI by nitration of 10-methyl-10:9-borazarophenanthrene involves demethylation; two lines of evidence suggest that demethylation follows nitration. First, we were unable to detect any XIII in the nitration product, although nitration of 10-hydroxy-10:9-borazarophenanthrene gave comparable amounts of XI and XIII; secondly, if the nitration mixture were allowed to stand for a longer period before hydrolysis, the amount of XI in the product increased and the amount of IX decreased. Presumably, the same thing happens in the chlorination of I; (R = Me), VI being formed by oxidation of IV.

TABLE 1. PROPORTIONS OF ISOMERS IN SUBSTITUTION REACTION OF BORAZAROPHENANTHRENE DERIVATIVES

Reaction	6-substitution	8-substitution
Chlorination of (I; R = Me)	0	100
Nitration of (I; R = Me)	34	66
Nitration of (I; R = OH)	33·5	66·5

The proportions of isomers formed in the various reactions is listed in Table 1; the proportion of 8-nitro-10-methyl-10:9-borazarophenanthrene quoted is the sum of the relative yields of IX and XI, since XI is apparently formed by a secondary reaction from IX.

Discussion. Theoretical predictions of orientation in aromatic substitution reactions can be made at various levels of sophistication. In the present state of knowledge a suitable compromise seems to be the simplified MO treatment developed by Longuet-Higgins[2] and by one of us[3] some years ago; this has been shown[4] to account well for the products formed in a variety of substitution reactions of polycyclic aromatic hydrocarbons and heterocycles.

In this treatment, the activation energy for substitution at a given position in a heterocycle is divided into two parts; the first is the activation energy for substitution at the corresponding position in the isoconjugate hydrocarbon; the second measures the modifying effect of the heteroatoms.

Substitution in phenanthrene occurs predominantly[4] in the 9-, 1-, and 3-positions; the 1-, 3-, 6-, and 8-positions in 10:9-borazarophenanthrene should therefore be inherently the more reactive. Nitrogen, being more electronegative than carbon, should deactivate positions of opposite parity to itself;[2] the 9-aza-group should therefore selectively deactivate the 1-, 3-, 5-, and 7-positions. Boron, being less electronegative than carbon, should selectively activate the positions of opposite parity to itself—i.e. the 2-, 4-, 6-, and 8-positions. One would therefore expect substitution in 10:9-borazarophenanthrene to occur predominantly in the 6- and 8-positions—in agreement with our observations (Table 1). These relations are indicated in Fig. 7.

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[2] Longuet-Higgins, *J. Chem. Phys.* **18**, 265, 275, 283 (1950).

[3] Dewar, *J. Amer. Chem. Soc.* **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

[4] Dewar and Maitlis, *J. Chem. Soc.* 2251 (1957).

Predictions of this kind can be put on a semiquantitative basis.[2,3,4] Table 2 lists the relative activation energies so predicted[4] for substitution in 10:9-borazarophenanthrene. The first term gives the activation energy for substitution at the corresponding position in phenanthrene in terms of the carbon–carbon resonance integral β; the second term represents the effect of the nitrogen atom (coulomb term α_N); the third term represents the effect of boron (coulomb term α_B). The experimental evidence[4] indicates that the 4- and 5-positions in phenanthrene are sterically hindered, so that their reactivity is close to that of the 2- and 7-positions; the first term has therefore been arbitrarily set equal to that for 2-substitution.

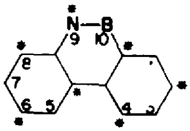

FIG. 7. The starred nitrogen should deactivate positions of opposite parity (i.e. unstarred positions); likewise the unstarred boron should activate the starred positions.

An investigation[4] of nitration in heterocyclic systems suggested that a suitable value for α_N is about 10β; the last column of Table 2 has been calculated on this basis. Boron is less electronegative than carbon; the differences in electronegativity between boron and carbon, and between carbon and nitrogen, are probably comparable. Hence we would expect $\alpha_B \sim -10\beta$; in that case Table 2 indicates that the 6- and 8-positions should be much the most reactive—as observed.

One difficulty remains; on this basis one would expect the 6- and 8-positions to be of comparable reactivity, whereas in practice the 8-position is the more reactive. However, apart from the uncertainty in the value of α_B, two other factors could be important; the inductive effect of the 9-aza nitrogen on the adjacent 8-position, and the possibility that N-nitration or chlorination may occur, followed by an intramolecular rearrangement to the 8-position.

TABLE 2. CALCULATED RELATIVE ACTIVATION ENERGIES FOR SUBSTITUTION IN 10:9-BORAZAROPHENANTHRENE
(the values (b) are calculated with $\alpha_N = 10\beta$)

Position	AF calc (a)	AF calc (b)
1	$1{\cdot}86\beta + 0{\cdot}138\alpha_N + 0{\cdot}046\alpha_B$	$3{\cdot}24\beta + 0{\cdot}046\alpha_B$
2	$2{\cdot}18\beta + 0{\cdot}016\alpha_N + 0{\cdot}048\alpha_B$	$2{\cdot}34\beta + 0{\cdot}048\alpha_B$
3	$2{\cdot}04\beta + 0{\cdot}167\alpha_N + 0{\cdot}056\alpha_B$	$3{\cdot}71\beta + 0{\cdot}056\alpha_B$
4	$2{\cdot}18\beta + 0{\cdot}013\alpha_N + 0{\cdot}038\alpha_B$	$2{\cdot}31\beta + 0{\cdot}038\alpha_B$
5	$2{\cdot}18\beta + 0{\cdot}038\alpha_N + 0{\cdot}013\alpha_B$	$2{\cdot}56\beta + 0{\cdot}013\alpha_B$
6	$2{\cdot}04\beta + 0{\cdot}056\alpha_N + 0{\cdot}167\alpha_B$	$2{\cdot}60\beta + 0{\cdot}167\alpha_B$
7	$2{\cdot}18\beta + 0{\cdot}048\alpha_N + 0{\cdot}016\alpha_B$	$2{\cdot}66\beta + 0{\cdot}016\alpha_B$
8	$1{\cdot}86\beta + 0{\cdot}046\alpha_N + 0{\cdot}0138\alpha_B$	$2{\cdot}32\beta + 0{\cdot}138\alpha_B$

One further point is of interest; the fact that IX is converted to XI under the conditions of nitration, whereas X appears to be stable. This difference must be due to hydrogen bonding between the nitro and imino groups of IX, though it is not obvious why this should labilize the 10-methyl group to oxidative attack.

EXPERIMENTAL

(Microanalyses were carried out by the Microanalytical Laboratory, Imperial College, South Kensington, London S.W.7., and by Alfred Bernhardt, Max-Planck-Institut, Mülheim, Germany. Chromatography was carried out with Peter Spence alumina, type H 100/200 mesh).

2-Chloro-10-methyl-10:9-borazarophenanthrene. A solution of 2-amino-4′-chlorodiphenyl (6 g) in dry benzene (50 ml) was added dropwise with vigorous stirring to one of boron trichloride (3·6 g) in dry benzene (200 ml), and the solution was then boiled under reflux for 7 hr. After removing the solvent, anhydrous aluminium chloride (0·3 g) was added, and the mixture heated to 180° for 6 hr. The resulting 2,10-dichloro-10:9-borazarophenanthrene was taken up in dry benzene (100 ml) and a solution of methylmagnesium iodide (from magnesium, 0·9 g, and methyl iodide, 5·2 g) added slowly with vigorous stirring at 0°. The solution was then boiled under reflux for 1 hr and the product isolated by adding dilute acid and ether; evaporation gave *2-chloro-10-methyl-10:9-borazarophenanthrene*, which crystallized from light petroleum (b.p. 40–60°) in white needles (4·4 g, 65%), m.p. 98–99° (Found: C, 68·7; H, 4·9; N, 6·3; Cl, 15·5; B, 4·5. $C_{13}H_{11}NClB$ requires: C, 68·6; H, 4·8; N, 6·2; Cl, 15·6; B, 4·8%).

6-Chloro-10-methyl-10:9-borazarophenanthrene. Prepared likewise in 70% overall yield from 2-amino-5-chlorodiphenyl, *6-chloro-10-methyl-10:9-borazarophenanthrene* crystallized from light petroleum (b.p. 40–60°) in white needles, m.p. 86–87° (Found: C, 68·6; H, 4·9; N, 6·2; Cl, 15·4; B, 4·7%).

8-Chloro-10-methyl-10:9-borazarophenanthrene. Prepared likewise in 52% overall yield from 2-amino-3-chlorodiphenyl, *8-chloro-10-methyl-10:9-borazarophenanthrene* was obtained as an almost colourless liquid, b.p. 170–175°/0·5–0·6 mm. (Found: C, 68·3; H, 4·8; N, 6·0; Cl, 15·7; B, 4·7%).

Chlorination of 10-methyl-10:9-borazarophenanthrene. Chlorine, prepared from potassium permanganate (4·01 g) and conc. HCl (25·4 ml), was passed slowly into a solution of 10-methyl-10:9-borazarophenanthrene[1] (10 g) in acetic acid (60 ml) at room temp. The solution was then poured into water, neutralized with sodium carbonate, and extracted with ether; evaporation of the ether left a pale brown residue (9·5 g, 81%). A solution of the crude chlorination product (2·35 g) was chromatographed on alumina from benzene, two bands being detected by U.V. fluorescence. The main band gave an oil (1·55 g, 66%), b.p. 170–175°/0·5–0·6 mm. (Found: C, 68·3; H, 4·9; N, 6·0; Cl, 15·8; B, 4·7. $C_{13}H_{11}NClB$ requires: C, 68·6; H, 4·8; N, 6·2; Cl, 15·6; B, 4·8%). The U.V. spectrum was identical with that of 8-chloro-10-methyl-10:9-borazarophenanthrene. Attempts to identify the material (m.p. 182–183°) in the second band were unsuccessful through lack of material. Its U.V. spectrum resembled that of 10-hydroxy-10:9-borazarophenanthrene. Only one analysis could be carried out, and that gave an apparently erratic result for carbon. (Found: C, 64·7; H, 4·2; N, 5·7; Cl, 15·1. $C_{12}H_9ONClB$ requires: C, 62·8; H, 3·9; N, 6·1; Cl, 15·4%).

Degradation of the main chlorination product. The chlorination product (0·5 g) was added to conc H_2SO_4 (20 ml) and left 2 hr at room temp. The solution was then poured into water, basified with sodium hydroxide, and extracted with ether. Removal of the ether left 2-amino-3-chlorodiphenyl (0·25 g, 56%), identified by mixed m.p. of its acetyl derivative.

Nitration of 10-methyl-10:9-borazarophenanthrene. A solution of nitric acid (*d* 1·5, 4·2 g) in acetic acid (20 ml) was added dropwise with vigorous stirring to one of 10-methyl-10:9-borazarophenanthrene (12·1 g) in acetic anhydride (100 ml), the temp being held at 0 ± 2°. After 1 hr the reaction mixture was poured onto water and ice, neutralized with sodium carbonate, and extracted with ether. Evaporation of the dried (Na_2SO_4) extract left a yellowish brown residue. A portion (2·9 g) was chromatographed from benzene on alumina. The first (purple) band was eluted with benzene, giving *8-nitro-10-methyl-10:9-borazarophenanthrene* (1·40 g, 48%), which crystallized from benzene–light petroleum in deep yellow needles, m.p. 165–166°. (Found: C, 65·5; H, 4·8; N, 11·7; B, 4·6. $C_{13}H_{11}O_2N_2B$ requires: C, 65·6; H, 4·6; N, 11·7; B, 4·6%). The second (orange) band, eluted with benzene–chloroform, gave *6-nitro-10-methyl-10:9-borazarophenanthrene* (0·95 g, 33%), which crystallized from benzene–light petroleum in light yellow needles, m.p. 209–210°. (Found: C, 64·1; H, 4·7; N, 11·3; B, 4·4%). The third (dark orange) band was eluted with chloroform, giving *8-nitro-10-hydroxy-10:9-borazarophenanthrene* (0·43 g, 15%) which crystallized from carbon tetrachloride in orange prisms. m.p. 266–267°. (Found: C, 59·8; H, 4,1; N, 11·5; B, 4·2. $C_{12}H_9O_3N_2B$ requires: C, 60·0; H, 3·8; N, 11·6; B, 4·6%). The hydroxy compound gave on recrystallization from ethanol yellow needles of *8-nitro-10-ethoxy-10:9-borazarophenanthrene*, m.p. 125–126°. (Found: C, 62·6; H, 4·8; N, 10·6; OEt, 14·5. $C_{14}H_{13}O_3N_2B$ requires: C, 62·7; H, 4·8; N, 10·4; OEt, 16·8%). Recrystallization from methanol likewise gave yellow needles of *8-nitro-10-methoxy-10:9-borazarophenanthrene*, m.p. 155–156°. (Found: C, 61·3; H, 4·5; N, 10·8; OMe, 11·2. $C_{13}H_{11}O_3N_2B$ requires: C, 61·4; H, 4·3; N, 11·0; OMe, 12·2%).

Degradation of 8-nitro-10-methyl-10:9-borazarophenanthrene. The nitro compound (0·50 g) was added to conc H_2SO_4 (20 ml). After 2 hr at room temp the solution was poured onto ice, basified with sodium hydroxide, and extracted with ether. Evaporation of the ether left 2-amino-3-nitrodiphenyl, which crystallized from light petroleum (b.p. 40–60°) in yellow needles (0·35 g, 78%) m.p. and mixed m.p. 46–47°. The diacetyl derivative crystallized from aqueous ethanol, m.p. and mixed m.p. 87–88°. (Found: C, 64·4; H, 4·8; N, 9·6. Calc. for $C_{16}H_{14}O_4N_2$: C, 64·4; H, 4·7; N, 9·4%).

Degradation of 6-nitro-10-methyl-10:9-borazarophenanthrene. The compound (0·40 g), degraded as above, gave 2-amino-5-nitrodiphenyl, which crystallized from aqueous alcohol in yellow needles (0·30 g, 83%), m.p. and mixed m.p. 125–126°.

Nitration of 10-hydroxy-10:9-borazarophenanthrene. To a stirred solution of the hydroxy compound (6·0 g) in acetic anhydride (85 ml) was added dropwise a solution of fuming nitric acid (*d* 1·5; 2·1 g) in acetic anhydride (10 ml), the temp being kept at 0 ± 2°. After 1 hr the reaction mixture was hydrolysed with ice-cooled water, neutralized, and extracted with ether. Evaporation of the dried (Na_2SO_4) extract gave a yellowish brown mixture of nitro compounds (6·5 g, 88%). The mixture (6·5 g) was extracted with hot carbon tetrachloride (6 × 250 ml); concentration of the extract gave orange crystals of 8-nitro-10-hydroxy-10:9-borazarophenanthrene (4·2 g, 65%), m.p. and mixed m.p. 266–267°. Recrystallization from ethanol gave 8-nitro-10-ethoxy-10:9-borazarophenanthrene, m.p. and mixed m.p. 125–126°. The residue from the carbon tetrachloride extraction crystallized from ethanol in yellow needles (2·1 g 33%), m.p. 172–174°, of *6-nitro-10-ethoxy-10:9-borazarophenanthrene* (Found: C, 62·8; H, 4·9; N, 10·5; OEt, 14·8. $C_{14}H_{13}O_3N_2B$ requires: C, 62·7; H, 4·8; N, 10·4; OEt, 16·8%). On standing in air for 24 hr the compound underwent hydrolysis quantitatively to *6-nitro-10-hydroxy-10:9-borazarophenanthrene*, m.p. 360° (decomp), which was virtually insoluble in non-hydroxylic solvents (Found: C, 59·8; H, 3·9; N, 11·5; B, 4·3. $C_{12}H_9O_3N_2B$ requires: C, 60·0; H, 3·8; N, 11·6; B, 4·6%). The hydroxy compound on recrystallization from methanol gave *6-nitro-10-methoxy-10:9-borazarophenanthrene* as yellow needles, m.p. 237–238°. (Found: C, 61·2; H, 4·4; N, 10·9; OMe, 10·9. $C_{13}H_{11}O_3N_2B$ requires: C, 61·4; H, 4·3; N, 11·0; OMe, 12·2%).

Degradation of 8-nitro-10-hydroxy-10:9-borazarophenanthrene. Degradation of the nitrohydroxy compound (0·5 g) gave 2-amino-3-nitrodiphenyl (0·32 g, 72%), m.p. and mixed m.p. 46–47°, m.p. and mixed m.p. of diacetyl derivative, 87–88°.

Degradation of 6-nitro-10-hydroxy-10:9-borazarophenanthrene. Degradation of the compound (0·5 g) gave 2-amino-5-nitrodiphenyl (0·36 g, 80%), m.p. and mixed m.p. 125–126·5°.

8-Amino-10-methyl-10:9-borazarophenanthrene. Hydrazine hydrate (5 ml) was added dropwise to a boiling solution of 8-nitro-10-methyl-10:9-borazarophenanthrene (1 g) in ethanol containing palladized charcoal (0·1 g, of 10%). After 30 min the solution was cooled, filtered, and evaporated to dryness under reduced pressure, leaving *8-amino-10-methyl-10:9-borazarophenanthrene* which crystallized from light petroleum (b.p. 60–80°) in white needles (0·65 g, 76%) m.p. 137–138°. (Found: C, 75·2; H, 6·7; N, 13·3; B, 5·2. $C_{13}H_{13}N_2B$ requires: C, 75·1; H, 6·2; N, 13·4; B, 5·3%).

6-Amino-10-methyl-10:9-borazarophenanthrene. Prepared likewise from the nitro compound in 69% yield, *6-amino-10-methyl-10:9-borazarophenanthrene* crystallized from light petroleum (b.p. 60–80°) in white needles, m.p. 125–126°. (Found: C, 75·2; H, 6·2; N, 13·6; B, 5·3%).

8-Amino-10-hydroxy-10:9-borazarophenanthrene. Prepared likewise in 74% yield, *8-amino-10-hydroxy-10:9-borazarophenanthrene* crystallized from benzene in white granules, m.p. 195–196°. (Found: C, 68·6; H, 5·2; N, 13·2; B, 4·9. $C_{12}H_{11}ON_2B$ requires: C, 68·6; H, 5·2; N, 13·4; B, 5·2%).

6-Amino-10-hydroxy-10:9-borazarophenanthrene. Prepared likewise in 65% yield, *6-amino-10-hydroxy-10:9-borazarophenanthrene* crystallized from benzene in white granules, m.p. 218–220°. (Found: C, 68·6; H, 5·4; N, 13·2; B, 5·0%).

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