

NEW HETEROAROMATIC COMPOUNDS—XIII¹

REACTIONS OF 10-SUBSTITUTED 9-ETHOXYCARBONYL-10:9-BORAZAROPHENANTHRENES

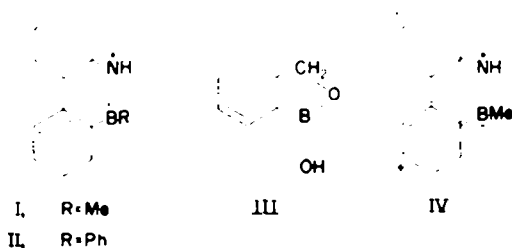
M. J. S. DEWAR and P. M. MAITLIS²
George Herbert Jones Laboratory, University of Chicago

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Abstract—10-Ethoxycarbonyl derivatives of 10:9-borazarophenanthrenes have been prepared by reaction of the 10-lithio derivatives with ethyl chloroformate. Unlike the parent compounds they are rapidly oxidized by air to products in which the BN bond is broken. These reactions suggest that the stability of the present compounds to oxidation and hydrolysis must be due to resonance stabilization. A measurement of the dipole moment of 10-methyl-10:9-borazarophenanthrene by Professor R. Huisgen and his collaborators is reported.

PREVIOUS papers of this series have described a number of novel heterocyclic boron compounds isoconjugate with normal aromatic hydrocarbons. These compounds showed much greater stability than previously described organic compounds of boron and this was taken as evidence for aromaticity. Two lines of evidence have suggested however, that this may not be the case and that the resonance effects in such compounds may be small.

In the first place Professor R. Huisgen has informed³ us that one of these compounds, 10-methyl-10:9-borazarophenanthrene (I), has a very low dipole moment (0.16 ± 0.02D), suggesting that the contribution of dipolar resonance structures such as (I) must be small. Secondly Snyder and his collaborators⁴ have reported that the cyclic boric ester (III) is very resistant to hydrolysis, suggesting that the stability of our compounds might be due merely to their cyclic structure.



If the stability of compounds such as (I) is due to aromaticity, the stability should be reduced by structural changes which destroy the resonance in the boron-containing rings. This could be effected in (I) by attaching +E substituents to nitrogen or -E

¹ Part XII: M. J. S. Dewar and R. Dietz, previous paper.

² Present address: Department of Chemistry, Cornell University, Ithaca, New York

³ Details are given in a note at the end of this paper at Professor Huisgen's request.

⁴ H. R. Snyder, A. J. Reedy, and W. J. Lennarz, *J. Amer. Chem. Soc.* **80**, 835 (1958); W. J. Lennarz and H. R. Snyder, *Ibid.* **82**, 2172 (1960).

substituents to boron; for the resonance interaction between nitrogen and a +E substituent (e.g. acyl) should reduce the availability of the p-electrons of nitrogen for bonding to boron, while -E substituents (e.g. hydroxy) attached to boron should reduce its tendency to accept electrons from nitrogen. We therefore decided to examine the properties of 9-acyl derivatives of 10:9-borazarophenanthrene.

In a previous paper of this series we reported⁵ that the 9-lithio derivatives (V), (VI) of 10-methyl-(I) and 10-phenyl-(II) 10:9-borazarophenanthrene reacted with dimethyl

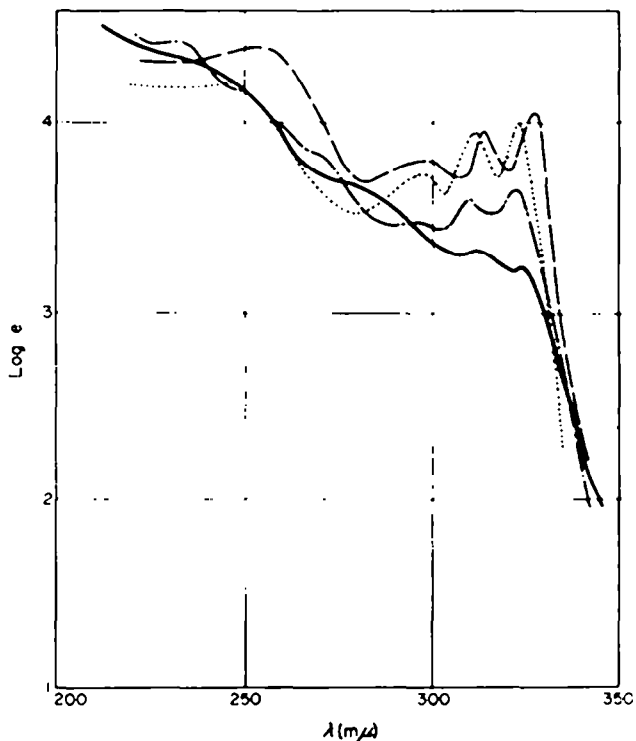


FIG. 1. Comparison of the ultraviolet spectra of 10:9-borazarophenanthrene (IX) (—); (X) (— —); (I) (- - -); (II) (.....).

sulphate to form the corresponding 9-methyl derivatives (VII), (VIII). We have found that the 9-lithio derivatives react likewise with ethyl chloroformate giving the corresponding urethanes (IX) (X).

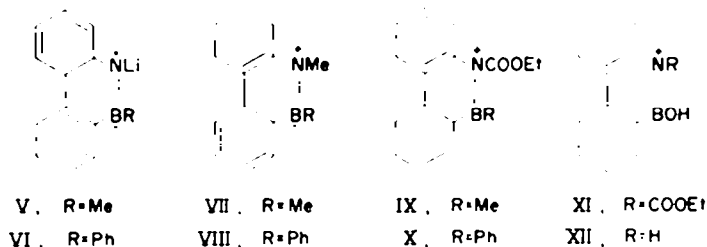
These were reasonably stable compounds, being unaffected by small amounts of alkali or acid in alcoholic solution, and their ultraviolet spectra showed a close similarity to those of the parent compounds (I) or (II) (Fig. 1). Hydrolysis with alkali regenerated (I) or (II) by decarboxylation of intermediate carbamic acids.

However the urethanes (IX), (X) were rapidly oxidized on exposure to air unlike the parent compounds (I), (II), or their 9-methyl derivatives (VII), (VIII). The liquid 10-methylurethane (IX) gave a solid oxidation product (A). The crystalline 10-phenylurethane (X) was stable in air but an ethereal solution underwent oxidation to

⁵ M. J. S. Dewar and P. M. Maitlis, *J. Amer. Chem. Soc.* **83**, 187 (1961).

phenol and the same product (A) that had been obtained from (IX). Clearly the oxidation must have led to loss of the methyl or phenyl group from boron.

The oxidation product (A) was clearly closely related to 10-hydroxy-9-ethoxycarbonyl-10:9-borazarophenanthrene (XI) since it contained the correct amount of



ethoxyl and it was readily hydrolyzed by alkali to 10-hydroxy-10:9-borazarophenanthrene (XII). However, the ultraviolet spectrum (Fig. 2) no longer showed the

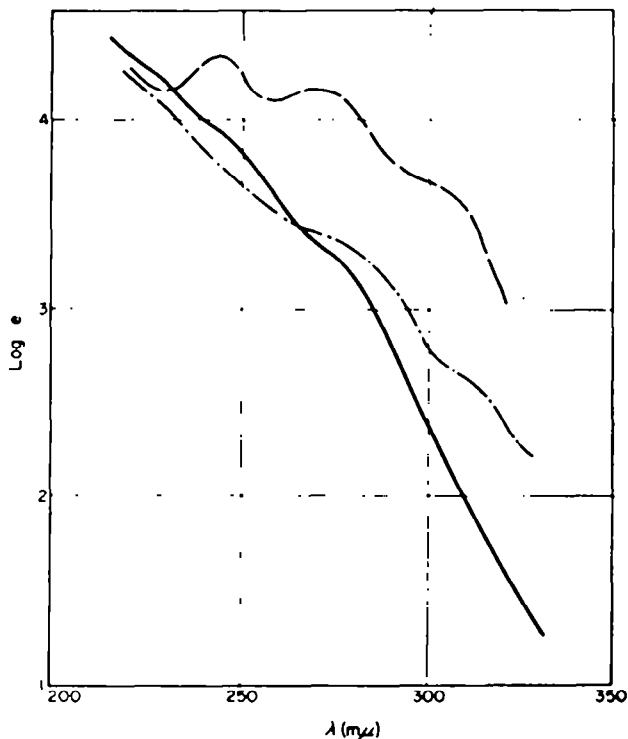
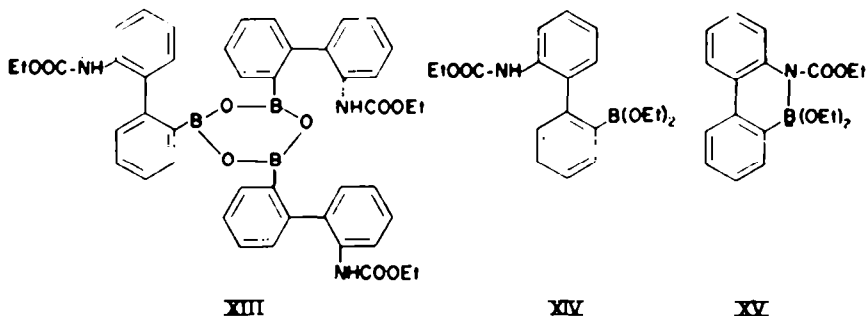


FIG. 2. Comparison of the ultraviolet spectra of (A) in 95% ethanol (— —) and in 95% ethanol containing sodium hydroxide (— · —) with that of 2-methylbiphenyl-2-carboxamide (— —).

absorption in the 320 $m\mu$ region characteristic of 10:9-borazarophenanthrene derivatives; indeed it showed no peaks at all above 225 $m\mu$, rising steadily from 330 $m\mu$ (log E, 2.25) to 225 $m\mu$ (log E, 4.46) through a series of shallow inflections. This type of spectrum is characteristic of a sterically hindered diphenyl, with an auxochromic

group attached to one ring; 2-methylbiphenyl-2'-carboxamide shows a spectrum very similar⁶ to that of (A).

This strongly suggested that (A) no longer had an intact B-N bond, a conclusion supported by the infrared spectrum which showed a very broad NH band at 2.97μ and a carbonyl band at 5.9μ ; absorption of this type is characteristic of a urethane. The 9-ethoxycarbonyl derivatives (IX), (X) showed carbonyl absorption at 5.75μ ; here the conjugative interaction between nitrogen and carbonyl is less than in a normal urethane since the nitrogen forms part of an aromatic ring. The infrared spectrum of (A) also showed a single peak at 7.45μ , presumably due to B-O stretching, and also a strong band at 14.4μ analogous to that observed⁷ in arylboronic anhydrides. This evidence suggests that (A) was 2'-ethoxycarbonamido-2-biphenylboronic anhydride (XIII) which presumably forms the corresponding ethyl ester (XIV) in alcoholic solution. This formulation was further supported by the appearance of definite peaks (Fig. 2) in the ultraviolet spectrum at $250-260 m\mu$ when alkali was added to the alcoholic solution; peaks in this region are characteristic⁸ of an unhindered biphenyl, suggesting that alkali brings about a cyclization of (VI) to the planar ion (VII).



Similar ions were probably formed when (A) dissolved in aqueous alkali; (A) was precipitated unchanged from such solutions by acidification. Moreover (A) reacted with O-phenylenediamine in the manner typical⁹ of arylboronic anhydrides to form the diazborole derivative (XVI) which had a strong carbonyl band at 5.8μ .

One aspect of (A) proved puzzling. The strength of the NH and CO bands in the infrared (KBr disc) varied greatly in different samples and the analyses were erratic. We eventually found that prolonged drying in a vacuum at 214° (just below the melting point) gave material (B) which showed no absorption in the regions normally characteristic of imino or carbonyl groups and which analyzed for (XIII) less half a molecule of water per biphenyl residue. This indicated that (XIII) must have undergone dehydration. The most likely structure for the product is the *bis* carbomethoxy-anhydride structure (XVII). The lack of a normal carbonyl band in the infrared can be ascribed to internal coordination to (XVIII) (cf. the preceding paper). Models indicate that the chelate structure (XVIII) should be almost unstrained. The formation of (XVIII) from (XIII) is easily understood; most preparations are evidently mixtures of

⁶ R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds* No. 181. John Wiley, New York (1951).

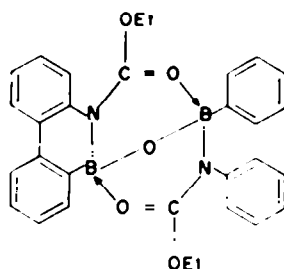
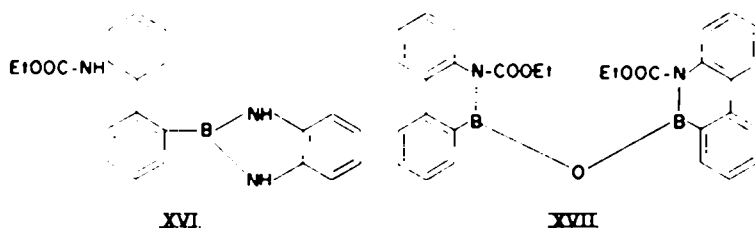
⁷ H. R. Snyder, M. S. Konecky and W. J. Lennarz, *J. Amer. Chem. Soc.* **80**, 3611 (1958).

⁸ cf. C. H. Beaver, D. M. Hall, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.* 854 (1952); G. H. Beaver and D. M. Hall, *Ibid.* 4638 (1956).

⁹ cf. R. L. Letsinger and S. B. Hamilton, *J. Amer. Chem. Soc.* **80**, 5411 (1958).

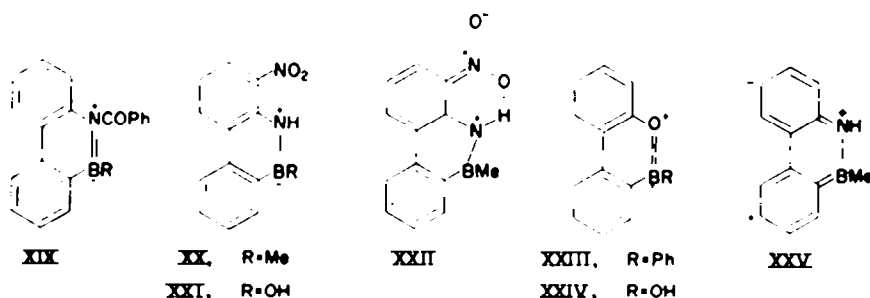
the two. Fresh material that had been only gently dried gave very strong imino and carbonyl absorption and its analysis corresponded closely to (XIII).

The structure of (XIII) was further indicated by a synthesis from 10-hydroxy-10:9-borazarophenanthrene (XII) by treatment with slightly more than two moles of phenyllithium, followed immediately by an excess of ethyl chloroformate. If (XII) is



allowed to stand with an excess of phenyllithium the hydroxyl is replaced by phenyl giving (II); reactions of this kind are also effected¹⁰ by the action of Grignard reagents on (XII).

We also examined the reactions of benzoyl chloride with the 9-lithio derivatives (V) and (VI). In each case the same high-melting product was formed, suggesting



that the methyl or phenyl group had been lost during the reaction. The reaction product was insoluble in all solvents (except concentrated sulfuric acid which destroyed it) and the infrared spectrum (KBr disc) showed the carbonyl absorption at 6.1μ characteristic of aromatic amides together with a very broad NH band. Analogy suggests that the product was a mixture of benzamido derivatives analogous to the urethanes (XIII) and (XVII), formed by oxidative demethylation or dephenylation of intermediate 10-benzoyl derivatives (XIX). All attempts to isolate (XIX) failed; unless

¹⁰ M. J. S. Dewar, R. Dietz, Ved P. Kubba and A. R. Lepley, *J. Amer. Chem. Soc.* In press (1961).

strong resonance interactions in the central ring. The resistance to oxidation is therefore strong evidence that compounds of this type are aromatic.

The relation between (IVc) and (V) is interesting. Any 10-hydroxy-10:9-borazaphenanthrene (XVI) is isomeric with an arylboron oxide (XVII), the trimer of which is an arylboronic anhydride (XVIII).

The relative heats of formation of (XVI) and (XVIII) will depend on their total bond energies and resonance energies; if the former could be estimated, one might be able to draw conclusions concerning the resonance energy of (XVI) from the relative stabilities of (XVI) and (XVIII). Unfortunately this is not possible since the B-N bond energy is known only in borazine derivatives where there is an uncertain correction for the resonance energy of the borazine ring; the experimental evidence suggests that (XVI) is normally the more stable form, but that introduction of π E substituents on the nitrogen atom makes (XVIII) more stable. Such substituents should decrease the resonance energy of (XVI), but not that of (XVIII).

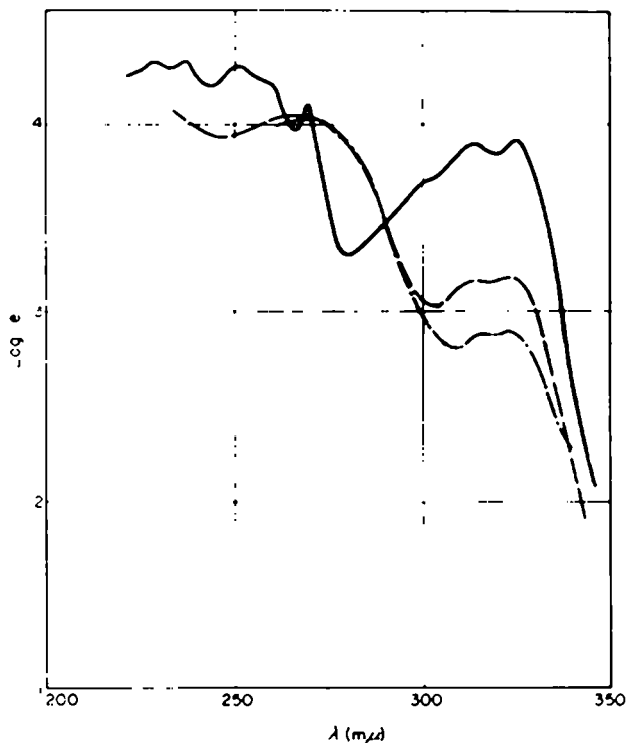


Fig. 3. Comparison of the ultraviolet spectra of XII in 95% ethanol (—) and in a mixture of 95% ethanol with concentrated hydrochloric acid, either 1:5 v/v (---) or 1:10 v/v (- · - · -).

The reactions of borazaphenanthrenes with acid are interesting. Derivatives with a free NH group seem to undergo protonation in acid without rupture of the central ring; this is indicated in the ultraviolet spectrum by the disappearance of the typical borazaphenanthrene bands in the 320 $m\mu$ region and the appearance of the strong maximum round 260 $m\mu$ characteristic of a planar unhindered biphenyl (cf. Fig. 3). The urethanes (IX), (X) also undergo protonation in strong acid, but the

ultraviolet spectrum now loses all its structure (Fig. 4), showing the characteristics of a sterically hindered biphenyl. This must mean that the central ring of (IV) undergoes rupture under these conditions. Presumably protonation takes place first on the carbonyl oxygen. This increases the +E activity of the group to such an extent that the central ring loses all its aromatic character and so undergoes hydrolysis. The urethane must have remained intact during the time that it took to measure the

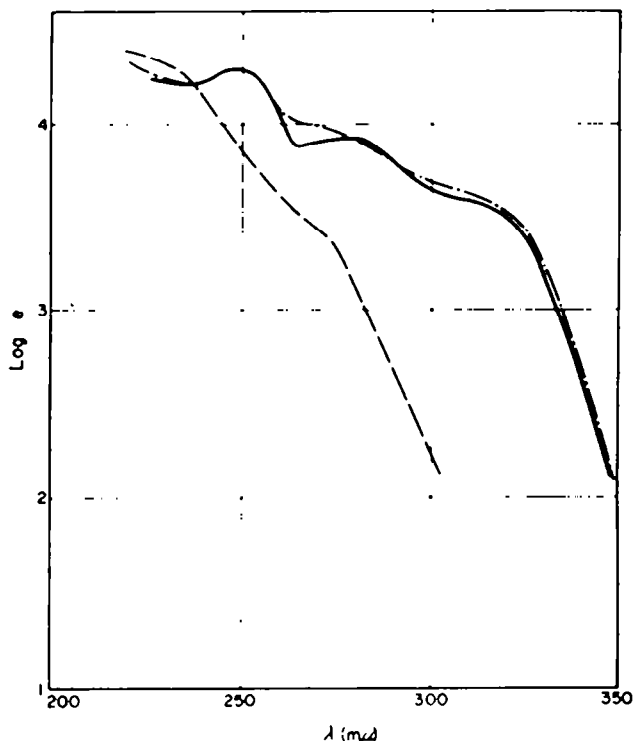


FIG. 4. Comparison of the ultraviolet spectra of X in alkaline ethanol (—) and in a mixture of 95% ethanol with concentrated hydrochloric acid, 1:5 v/v (---), with that of IX in alkaline ethanol (- - -).

spectrum since hydrolysis would have led to ring closure to 10-phenyl-10:9-borazarophenanthrene which like the 10-hydroxy derivative forms salts in which the central ring is intact.

EXPERIMENTAL

The infrared spectra were measured on a Grubb-Parsons double beam spectrophotometer; ultraviolet spectra in 95% ethanol on a Unicam S.P. 500 spectrophotometer. The ultraviolet spectra in strong acid were carried out on ethanolic solutions of the B-hydroxy compounds which were diluted with concentrated hydrochloric acid (1:5 for the 9.0 N and 1:10 for the 9.8 N solutions). The microanalyses were carried out by Alfred Bernhardt, Mülheim, Germany; molecular weights were determined in naphthalene since camphor did not give reliable results.

9-Ethoxycarbonyl-10-methyl-10:9-borazarophenanthrene (IVb). A solution of 10-methylborazarophenanthrene^{2a} (7.0 g; 0.0363 mole) in benzene (30 ml) was titrated under nitrogen with an ethereal solution of methyl lithium (it required 34 ml (0.048 mole) of a solution containing 0.5 g active lithium per 50 ml). The end-point of the titration was marked by the appearance of a stable bright yellow colour.³ The solution was stirred for 5 min and then a benzene solution of dry, freshly distilled ethyl

chloroformate (5.5 g in 20 ml) was added; the color disappeared immediately and the solution was refluxed for one hour. It was then cooled, hydrolyzed with dilute hydrochloric acid and ether-extracted. The ethereal solution was dried, and the solvent distilled (last traces of ethyl chloroformate being removed under vacuum), to leave an oil which did not solidify on cooling. The oil distilled at 160°/0.3 mm to give, after a small fore-run of starting material, 9-ethoxycarbonyl-10-methyl-10:9-borazarophenanthrene (9.6 g, 80%), n_D^{25} 1.6188 (Found: C, 72.37; H, 5.78; N, 5.33; B, 4.41% M, 268. $C_{18}H_{14}O_2NB$ requires: C, 72.45; H, 6.04; N, 5.28; B, 4.09%; M, 265).

9-Ethoxycarbonyl-10-phenyl-10:9-borazarophenanthrene IVa. A solution of 10-phenylborazarophenanthrene²⁴ (5.0 g, 0.0196 mole) in benzene (20 ml) was titrated with ethereal phenyllithium [it required 15 ml (0.0215 mole) of a solution containing 0.5 g. active lithium per 50 ml]. A benzene solution of ethyl chloroformate (4.0 g. in 10 ml) was added, the color disappeared and the solution was refluxed for one hour. It was worked up as previously described to give a brown liquid which solidified on cooling. Crystallization from ether-light petroleum (b.p. 40-60°) gave 9-ethoxycarbonyl-10-phenyl-10:9-borazarophenanthrene (2.6 g) m.p. 116-117°. The mother liquors were chromatographed on alumina and eluted first with ether to give 10-phenylborazarophenanthrene (0.5 g) and then with chloroform to give more ethoxycarbonylphenylborazarophenanthrene (0.7 g) m.p. 113-115°. The total yield was 3.3 g (51%) (Found: C, 76.1; N, 5.48; B, 3.15% M, 320,206. $C_{21}H_{18}O_2NB$ requires C, 77.06; H, 5.50; N, 4.28 B, 3.32%; M, 356).

2-(N-ethoxycarbonyl) aminodiphenyl-2'-boronic anhydride (Compound A). A solution in benzene (30 ml) of 10-hydroxy-10:9-borazarophenanthrene (4.2 g, 0.0227 mole), which had been thoroughly dried under high vacuum, was titrated with the ethereal phenyllithium (it required 35 ml (0.05 mole) of a solution containing 0.5 g active lithium in 50 ml) till a stable yellow color had been obtained. During the addition nearly all the solid dissolved initially but was reprecipitated towards the end. Ethyl chloroformate in benzene (4.0 g, in 10 ml) was added very quickly; the solution cleared and was refluxed for one hour. The reaction was worked up as described above, to give a solid which gave, on crystallization from benzene-light petroleum b.p. 100-120°, 2-(N-ethoxycarbonyl) aminodiphenyl-2'-boronic anhydride, m.p. 215-220° (3.1 g, 51%). The freshly prepared material had strong C=O and N-H bands and had the following analysis: (Found: C, 67.90; H, 5.17; N, 5.53; B, 4.05; OEt, 17.15%; M, 703. (IV), ($C_{18}H_{14}O_2NB$), requires: C, 67.41; H, 5.24; N, 5.24; B, 4.06; OEt, 16.85%; M, 800).

(V), ($C_{18}H_{14}O_2NB$)₂ requires: C, 69.78; H, 5.04; N, 5.43; B, 4.26; OEt, 17.45%; M, 516].

A sample which had been dried at 214°/0.2 mm and which had m.p. 220-221° and showed only weak carbonyl and N-H absorption in the infrared had analysis; (Found: C, 69.26; H, 4.88; N, 5.44 B, 4.26%).

This latter sample was presumably mainly in the form of the cyclic compound (IX) whereas the fresh sample was mainly present as (V). Samples which had been vacuum dried under milder conditions showed intermediate analyses.

A mixture of compound (A) (130 mg) and *o*-phenylenediamine (60 mg) was dissolved in benzene (50 ml, b.p. 100-120°) and the solution was evaporated until the volume remaining was about 5 ml. On cooling it deposited white crystals (80 mg; 46%) of the *o*-phenylenediamine derivative of 2-(N-ethoxycarbonyl)aminodiphenyl-2'-boronic anhydride (IV), m.p. 156-157°. (Found: C, 70.06; H, 5.29; N, 11.51%. $C_{21}H_{18}O_2N_2B$ requires: C, 70.58; H, 5.61; N, 11.76%).

2-(N-Benzoyl)aminodiphenylboronic anhydride. 10-Phenyl-10:9-borazarophenanthrene (2.3 g, 0.009 mole) dissolved in benzene (20 ml) was titrated with ethereal phenyllithium (0.012 M) and freshly distilled benzoyl chloride (2.5 g) in benzene (15 ml) added. The solution turned deep red and was refluxed for 75 min. It was then worked up rapidly as previously described to give a crude, red, boron-containing solid. This red color was removed by washing with solvent to leave a white amorphous solid m.p. above 300° (2.8 g, 96%). This solid was unaffected by all organic solvents and by hot concentrated solutions by both alkali and acids with the exception of concentrated sulfuric acid in which it dissolved (however on dilution and basification, no product could be isolated). This material was presumably the 2-(N-benzoyl)aminodiphenylboronic anhydride (X) mixed with some

* It is necessary to carry out all the operations in which ethereal solutions are exposed to air very rapidly; even on standing in air for a few minutes solutions of the ethoxycarbonyl compound turn brown due to oxidation.

of the cyclic compound (XI). [Found: C, 78.61; H, 4.63; N, 5.01; B, 3.50%. ($C_{21}H_{14}O_2NB_2$)(X) requires: C, 78.0; H, 4.33; N, 4.33; B, 3.36%. ($C_{21}H_{14}O_2NB_2$)(XI) requires: C, 80.2; H, 4.14; N, 4.46; B, 3.46%]. It was not possible to determine either the molecular weight of the substance or the ultraviolet spectrum because of the great insolubility of the compound. The infrared spectrum showed a carbonyl band (6.1μ), an N-H band (2.93μ) and a band at 7.05μ which is presumably the B-O band. An exactly similar reaction starting from 10-methylborazarophenanthrene (2.0 g) gave the above material (identical infrared spectra) in 60% yield (2.0 g).

The hydrolyses of 10-methyl-(IVb) and 10-phenyl-(IVa) 9-ethoxycarbonyl-10:9-borazarophenanthrene and 2-(N-ethoxycarbonyl)aminodiphenyl-2'-boronic anhydride Compound (A). 10-Methyl-9-ethoxycarbonyl-10:9-borazarophenanthrene (IVb) (1.4 g) was dissolved in ethanol (10 ml) and added to a solution of a sodium hydroxide (3 g) in water (30 ml) and the solution refluxed overnight. On cooling, 10-methyl-10:9-borazarophenanthrene (0.8 g) m.p. $99-100^\circ$, mixed m.p. with authentic material $101-102^\circ$). Acidification followed by ether extraction gave additional 0.1 g (total yield 88%). 10-Phenyl-9-ethoxycarbonyl-10:9-borazarophenanthrene (IVa) (0.5 g) was hydrolyzed in the same way to give 10-phenyl-10:9-borazarophenanthrene (0.15 g, 39%; m.p. $106-107^\circ$, mixed m.p. with authentic material, $107-108^\circ$). Alkaline hydrolysis of 2-(N-ethoxycarbonyl)aminodiphenylboronic anhydride (compound, 0.95 g) under the above conditions gave 10-hydroxy-10:9-borazarophenanthrene (0.6 g, 88%), infrared spectrum identical with that of an authentic sample. The melting point is not a reliable guide to the purity of this material; different samples with very similar infrared spectra had m.ps. from $128-130^\circ$ to $181-182^\circ$ (lit. 170°)¹⁸. This probably reflects changes in the hydration of the material since the high m.p. form was only obtained after vigorous vacuum drying at 170° .

Aerial oxidation of 10-phenyl- and 10-methyl-9-ethoxycarbonyl-10:9-borazarophenanthrene (IV). 10-Phenyl-9-ethoxycarbonyl-10:9-borazarophenanthrene (0.5 g) was dissolved in ether (20 ml) and the solution left standing in a loosely stoppered flask at room temperature until all the ether had evaporated (48 hr). A brownish crystalline solid remained which was washed with ether and filtered to give compound (A) (0.35 g, 85%; m.p. and mixed m.p. with authentic material $215-220^\circ$). The filtrate was evaporated down to dryness and the residue sublimed onto a cold finger to give a small amount of oil which gave a purple spot test with ferric chloride, identical with that given by a sample of phenol, and had an infrared spectrum (in carbon tetrachloride solution) which was identical with that of phenol. An analogous experiment with 10-methyl-9-ethoxycarbonyl-10:9-borazarophenanthrene (0.95 g) which was left standing for five days under the above conditions gave 0.2 g (20% of compound (A), m.p. $215-220^\circ$) the remainder being recovered as starting material.

Acknowledgements—The work described here was carried out at Queen Mary College, University of London. We wish to thank British Petroleum Ltd. for the award of a Fellowship (to P. M. M.) and Mr. P. Cook for determining the infrared spectra.

DIE BESTIMMUNG DES DIPOLMOMENTS DES 10-METHYL- 10:9-BORAZAROPHENANTHRENS

R. HUISGEN, I. UGI, I. ZEIGLER und H. HUBER
Institut für Organische Chemie der Universität München

Das Dipolmoment des 10-methyl-10:9-borazarophenanthrens wurde nach der früher beschriebenen Methode¹⁹ gemessen und errechnet; Lösungsmittel Reinstbenzol.

Bestimmung der Dielektrizitätskonstante:

Molenbruch des Gelosten (γ) $\times 10^3$ 0 2.2271 4.5345 6.6697 9.4374

Dielektrizitätskonstante (ϵ) 2.2726 2.2774 2.2823 2.2869 2.2927

Daraus ergibt sich: $\left(\frac{\partial \epsilon}{\partial \gamma}\right)_{\gamma=0} = 2.125$.

¹⁹ R. Huisgen und H. Walz, *Chem. Ber.* **89**, 2616 (1956); R. Huisgen und H. Ott, *Tetrahedron* **6**, 253 (1959).

Vor und nach der Messung wurde das Gerät mit Butyrolacton getestet.

Dichte-Bestimmung: $\left(\frac{\partial d}{\partial \gamma}\right)_{\gamma \rightarrow 0}$ ergab sich zu 0.481

Die Auswertung erfolgte nach Hedestrand.¹⁴ Für die Molrefraktion wurde ein Näherungswert von 61.30 verwendet, dem Bindungsrefraktionen von Vogel und Mitarbeiter¹⁵ zu Grunde gelegt wurden.

Daraus ergibt sich: $\mu \rightarrow 0.16 \pm 0.02$ D.

¹⁴ G. Hedestrand, *Z. Phys. Chem.* **B2**, 428 (1949).

¹⁵ A. J. Vogel, W. T. Cresswell, G. H. Jeffery und J. Leicester. *J. Chem. Soc.* 514 (1952).