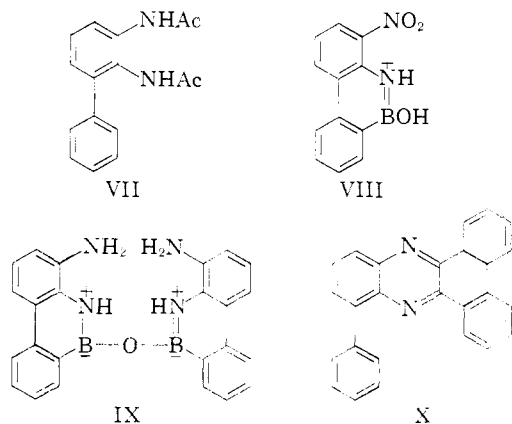


Fig. 1.—Infrared spectrum of XIa.

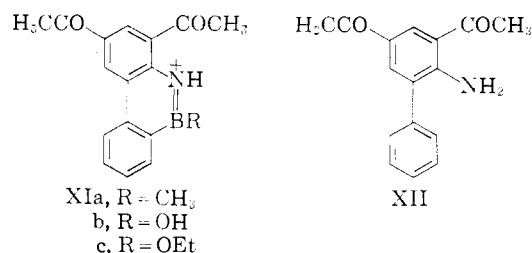
6-nitro-10-hydroxy-10,9-borazarophenanthrene² (V) to 2-amino-5-nitrobiphenyl (VI) followed by reduction and acetylation.

Crystallization of the hydroxy compound IIIb from alcohol gave the corresponding ethyl ether IIIc, a common reaction in 10-hydroxyborazarophenanthrenes.²

We also prepared 2,3-bisacetamidobiphenyl (VII) which differed from the degradation product in two different ways, starting with 8-nitro-10-hydroxy-10,9-borazarophenanthrene² (VIII). In the first route, VIII was deboronated to 2-amino-3-nitrobiphenyl, followed by reduction and acetylation; in the second, VIII was reduced to bis-(8-amino-10,9-borazaro-10-phenanthryl) oxide (IX) followed by deboronation and acetylation. The structure of IX was indicated by these reactions, by analysis and by lack of a hydroxyl bond in the infrared spectrum; it is interesting that IX did not undergo self-condensation by interaction of the amino groups with the boric anhydride function. The structure of the 2,3-diaminobiphenyl was confirmed by preparation of the phenazine X.



No other monoacetyl derivative seemed to be present in the product from Ia or Ib, although a careful search was made by chromatography for the expected² 8-isomer. The only other product in each case was a compound which appeared to be the 6,8-diacetyl derivative XIa or XIb. Both compounds gave on degradation with sulfuric acid at 150° the same product which appeared to be 2-amino-3,5-diacetyl biphenyl (XII). Attempts to degrade XIa or XIb by the Schmidt reaction failed to give any identifiable product.



The structures XI and XII were assigned from the following considerations. (a) All three compounds must be diacetyl derivatives, from elementary analysis and from the presence of each infrared spectrum of a double carbonyl peak (*cf.* Fig. 1). The infrared spectra of II, IIIa, and IIIb showed single peaks in this region. Moreover acetylation of Ib with two moles of acetyl chloride gave XIb as the sole product in 84% yield. (b) One of the acetyl groups must surely have been *para* to nitrogen since monoacetylation of I gave exclusively the 6-acetyl derivatives III. (c) The second acetyl groups could not have been attached to nitrogen since XIa showed strong NH absorption in the infrared at 3.1 μ (Fig. 1) and since the degradation product XI was different from 2-acetamido-5-acetyl biphenyl, formed by acetylating II. (d) A Schmidt reaction on XIa gave an intractable product from which benzoic acid was obtained by permanganate oxidation; this indicates that the ring adjacent to boron in XI was unsubstituted.

Therefore, XIa and XIb must have been the 5,6-6,7- or 6,8-diacetyl derivatives of I. The two former structures are out of the question since two acetyl groups could not possibly have been introduced into adjacent positions by a Friedel-Crafts reaction. Therefore, XIa, XIb must have been the 6,8-diacetyl derivatives.

This formulation is also supported by theoretical considerations (see below) and by the failure of the Schmidt reaction to give a simple product. If the acetyl groups had been in different rings, Schmidt degradation should have given an easily isolated aminobisacetamidodiphenyl. Degradation of a 6,8-diacetyl-10,9-borazarophenanthrene could well have followed a more complex course due to the presence of an *o*-aminoacetophenone grouping. The formulation is also supported by the ultraviolet spectra (see below).

Crystallization of XIb from alcohol gave the ethyl ether XIc.

Discussion

These reactions are of interest for two reasons. First, the deboronation of III and XI required surprisingly drastic conditions; complete deboronation of XIb took place only after heating with concentrated sulfuric acid to 150° for 5 minutes. These are without question the most acid-resistant boron compounds yet described.

Secondly, the formation of a homoannular diacetyl derivative as a major product of a Friedel-Crafts reaction using *one* mole of acid chloride is very surprising and probably unique. It implies that further acetylation of a monoacetyl derivative must take place at a rate at least comparable with the first step, whereas introduction of an acetyl

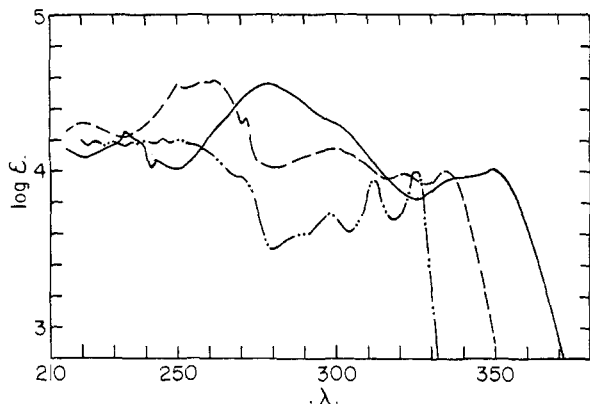


Fig. 2.—Ultraviolet spectra of: Ia, ····; IIIa, - - - -; XIa, ———.

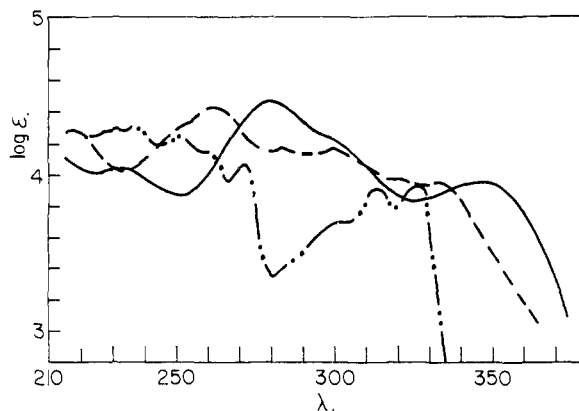


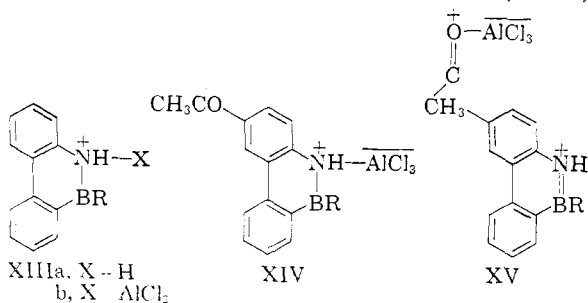
Fig. 3.—Ultraviolet spectra of: Ib, ····; IIIb, - - - -; XIb, ———.

group into an aromatic ring usually deactivates that ring to any further acetylation. The situation here is made even stronger by the absence of any isomer other than III in the monoacetyl fraction; if the diacetyl derivatives were 6,*x*-substituted, it seems extraordinary that appreciable amounts of the *x*-monosubstituted borazarophenanthrenes should not have been formed.

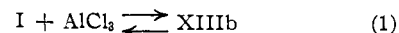
There are only two possible explanations: Either (a) monoacetylation takes place almost exclusively in the 6-position to give a product which acetylates further in the *x*-position much faster than I itself *x*-acetylates; or (b) I does acetylate initially to some extent in the *x*-position, but the product undergoes further acetylation in the 6-position, faster than I itself 6-acetylates.

A simple kinetic analysis indicates that the second alternative is extremely unlikely. In the acetylation of Ib, 98% of the starting material was accounted for as IIIb, XIb or unchanged Ib. If explanation b were correct, this would imply that the *x*-acetyl derivative acetylates at least a hundred times faster in the 6-position than does Ib itself, which seems out of the question. Explanation a merely requires the reactivity of IIIb in the 8-position to be comparable with that of Ib in the 6-position. The 8-position of IIIb is moreover known to be highly reactive since we obtained an excellent yield of the diacetyl derivative XIb by acetylating Ib in the cold with just two moles of acetyl chloride.

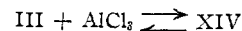
The unusual reactivity of IIIb in the 8-position can be explained in the following way. Derivatives I of 10,9-borazarophenanthrene certainly show some basicity since the deboration in sulfuric acid almost certainly involves a preliminary protonation of nitrogen to form an ion (XIIIa)



in which the boron-containing ring is no longer aromatic. This being the case, one would certainly expect I to coordinate with aluminum chloride in carbon disulfide to form the complex XIIIb. In this the nitrogen atom has a covalency of four and therefore cannot activate the adjacent ring to electrophilic substitution. The reaction



will, however, be reversible and the small amount of I present in equilibrium should react rapidly with acetyl chloride in presence of aluminum chloride. The fact that attack takes place in the 6- rather than the 8-position, unlike nitration,² is not surprising; Friedel-Crafts reactions seem to be very prone to steric hindrance by groups *ortho* to the point of attack. The acetylation product III will also form a similar complex (XIV) with aluminum chloride; but since the 6-acetyl group will reduce the basicity of the nitrogen, the equilibrium



will lie much further over to the left-hand side. (This effect will be further accentuated by the fact that the 6-acetyl group will itself combine with aluminum chloride, forming XV.) Here again the complex XIV is deactivated and only III can undergo further acetylation; but in this case the concentration of the reactive species III will be much greater. Therefore, although the 6-acetyl group will have a deactivating effect making the reactivity of III less than that of I, this may be balanced by the greater concentration of III in the reaction mixture. Therefore, further acetylation of III may compete with monoacetylation of I.

Ultraviolet Spectra.—The ultraviolet spectra of these compounds are interesting; Fig. 2 compares the spectra of Ia, IIIa and XIa, and Fig. 3 those of Ib, IIIb and XIb. Each acetyl group produces a marked bathochromic shift. This would be expected if the acetyl groups were *ortho*, *para* to nitrogen, both on theoretical grounds and from analogy with the corresponding 6- and 8-nitro derivatives²; groups in the other ring should have a much smaller effect. These results therefore provide further evidence for the structures of the diacetyl derivatives. Note that the wave length

shifts from acetyl are considerably less than those from nitro²; this would be expected since acetyl has much the weaker +E effect.

Experimental

Acetylation of 10-Methyl-10,9-borazarophenanthrene (Ia).—Anhydrous aluminum chloride (3.5 g., 1 mole) and a solution of acetyl chloride (2.05 g., 1 mole) in carbon disulfide (25 ml.) were added gradually at room temperature with vigorous stirring to a solution of 10-methyl-10,9-borazarophenanthrene (5.0 g., 1 mole) in carbon disulfide (400 ml.). After 6 hours the mixture was poured into water, acidified and extracted with methylene chloride. Evaporation of the dried (Na_2SO_4) extract left a residue (5.7 g.) which was separated by chromatography from benzene on alumina into unchanged Ia (1.51 g., 30.2%) and a monoacetyl derivative IIIa (2.58 g., 42.4%). Elution of the column with chloroform then gave a diacetyl derivative XIa (1.25 g., 17.4%). The monoacetyl derivative crystallized from 95% alcohol in light yellow plates, m.p. 164–165°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{BNO}$: C, 76.6; H, 6.0; N, 6.0. Found: C, 76.5; H, 6.2; N, 6.0.

The diacetyl derivative crystallized from 95% alcohol in white needles, m.p. 205–207°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{BNO}_2$: C, 73.6; H, 5.7; N, 5.1. Found: C, 73.5; H, 5.9; N, 5.2.

Degradation of the Monoacetyl Derivative IIIa to 2-Amino-6-acetylphenyl (II).—A solution of IIIa (1 g.) in concentrated sulfuric acid (20 ml.) was heated to 100°, cooled, left overnight, poured into water, basified and extracted with ether. Evaporation of the ether left 2-amino-6-acetylphenyl (II) (0.66 g., 73%) which crystallized from aqueous alcohol in pale green needles, m.p. 141–142°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}$: C, 79.6; H, 6.1. Found: C, 79.5; H, 6.3.

Degradation of IIIa to 2,5-Bisacetamidobiphenyl (IVb).—A mixture of IIIa (2.65 g., 1 mole), concentrated sulfuric acid (20 ml.) and chloroform (30 ml.) was stirred at room temperature while sodium azide (1.46 g., 2 moles) was gradually added. After 30 minutes the temperature was raised to 45° for 2 hours and the mixture then poured into water, basified and extracted with ether. Evaporation of the dried extract gave 2-amino-5-acetamidobiphenyl (IVa) (2.0 g., 80%) which crystallized from benzene in white needles, m.p. 133–134°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{14}\text{N}_2$: C, 74.3; H, 6.1. Found: C, 74.3; H, 6.2.

Acetylation gave 2,5-bis-acetamidobiphenyl, m.p. and mixed m.p. 158–159°. The infrared spectrum was also identical with that of an authentic specimen.

Degradation of the Diacetyl Derivative XIa to 2-Amino-3,5-diacetylphenyl (XII).—A solution of XIa (1 g.) in concentrated sulfuric acid (20 ml.) was heated to 150° then cooled, kept overnight, poured into water, basified and extracted with ether. Evaporation of the dried extract gave 2-amino-3,5-diacetylphenyl (XII) (0.54 g., 59%) which crystallized from aqueous alcohol in deep green needles, m.p. 179–180°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{NO}_2$: C, 75.8; H, 5.9. Found: C, 76.1; H, 6.1.

Degradation of XIa to Benzoic Acid.—A mixture of XIa (2.0 g., 1 mole), concentrated sulfuric acid (20 ml.) and chloroform (30 ml.) was stirred at room temperature while sodium azide (1.9 g., 2 moles) was added gradually. Next day the solution was poured into water, basified and extracted with methylene chloride; evaporation of the extract gave a gummy product (1.0 g.) which was suspended in water and oxidized by the gradual addition at room temperature of a solution of potassium permanganate (6 g.) in water (75 ml.). After a further 2 hours the mixture was poured into water, acidified and steam distilled; ether extraction of the distillate gave benzoic acid, m.p. and mixed m.p. 120°.

Acetylation of 10-Hydroxy-10,9-borazarophenanthrene (Ib).—The reaction was carried out as above using a solu-

tion of Ib (7.0 g., 1 mole) in carbon disulfide (800 ml.), a solution of acetyl chloride (2.8 g., 1 mole) in carbon disulfide (25 ml.), and aluminum chloride (5.0 g., 1 mole). The crude reaction product was extracted with methylene chloride; chromatography of the residue from alcohol on alumina gave the diacetyl derivative XIb (1.78 g., 17.8%).

The methylene chloride extract was evaporated and the residue extracted in a Soxhlet with petroleum ether (b.p. 60–80°). Evaporation of the extract gave unchanged Ib, m.p. 169° (2.27 g., 32.6%). The residue from the Soxhlet was chromatographed from alcohol on alumina giving IIIb (4.05 g., 47.6%).

The monoacetyl derivative IIIb was converted to the ethyl ether IIIc by crystallization from alcohol, forming white needles, m.p. 210–211°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{BNO}_2$: C, 72.4; H, 6.1; N, 5.3. Found: C, 72.7; H, 6.1; N, 5.4.

The ether was hydrolyzed by standing overnight in dilute hydrochloric acid to IIIb, which crystallized from aqueous alcohol in colorless needles, m.p. 233–235°.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{BNO}_2$: C, 70.9; H, 5.1; N, 5.9. Found: C, 70.5; H, 5.4; N, 5.8.

The diacetyl derivative XIb crystallized from alcohol as its ethyl ether XIc, colorless needles, m.p. 258–260°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{BNO}_3$: C, 70.4; H, 5.8; N, 4.6. Found: C, 70.6; H, 6.2; N, 4.9.

Hydrolysis with dilute hydrochloric acid gave XIb which crystallized from aqueous alcohol in small needles, m.p. > 350°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{BNO}_3$: C, 68.8; H, 5.0; N, 5.0. Found: C, 68.6; H, 5.5; N, 5.1.

Degradation of IIIb to II.—This reaction was carried out in exactly the same way as the corresponding degradation of IIIa, giving the same product II (70% yield), m.p. and mixed m.p. 141–142°.

Degradation of XIb to XII.—The degradation of XIb (1 g.) by sulfuric acid (20 ml.) at 150° was not complete in less than 5 minutes, by which time extensive oxidation of XII had taken place. The product was identical with that from the corresponding degradation of XIa.

Acetylation of Ib with Two Moles of Aluminum Chloride.—Acetylation of Ib as before, but using twice as much acetyl chloride, gave the diacetyl derivative XIb (8.35 g. 83.5%) as the sole isolable product.

Synthesis of 2,5-Bis-acetamidobiphenyl (IVb).—Degradation of 6-nitro-10-hydroxy-10,9-borazarophenanthrene⁽²⁾ (V) with sulfuric acid gave 2-amino-5-nitrobiphenyl (VI) which was reduced with hydrazine hydrate and palladized charcoal to 2,5-diaminobiphenyl (over-all yield 85%); acetylation gave 2,5-bis-acetamidobiphenyl which crystallized from aqueous alcohol in white leaflets, m.p. 158–160°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$: N, 10.5. Found: N, 10.7.

Synthesis of 2,3-Bis-acetamidobiphenyl (VII).—The synthesis was carried out as above, starting with 8-nitro-10-hydroxy-10,9-borazarophenanthrene⁽²⁾ (VIII), in 80% over-all yield. The diacetyl derivative VII crystallized from alcohol in white plates, m.p. 192.5–193.5°.

Anal. Calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$: C, 71.6; H, 6.0; N, 10.5. Found: C, 71.7; H, 5.7; N, 10.4.

Bis-(10-amino-10,9-borazaro-10-phenanthryl) Ether (IX).—Hydrazine hydrate (40 ml.) was added dropwise to 8-nitro-10-hydroxy-10,9-borazarophenanthrene (VIII) (5 g.) and palladized charcoal (0.4 g.) in boiling alcohol (150 ml.). After 3 hours reflux the solution was filtered and evaporated, leaving bis-(10-amino-10,9-borazaro-10-phenanthryl) ether (IX) (2.92 g., 70%) which crystallized from benzene, m.p. 240–242°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{20}\text{B}_2\text{N}_4\text{O}$: C, 71.6; H, 5.0. Found: C, 71.6; H, 5.3.

Degradation with cold concentrated sulfuric acid gave 2,3-diaminobiphenyl (75% yield), identified as its diacetyl derivative, m.p. and mixed m.p. 192.5–193.5°, and as the phenyl dibenzophenazine derivative X, m.p. 218–220°.

Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{N}_2$: N, 8.4. Found: N, 7.9.