ing a light yellow colored salt, m.p. 188–192° after losing gas from 150–170°.

An ionic chlorine analysis indicates this material to be the trihydrochloride salt.

Anal. Calcd. for $C_{23}H_{42}N_3Cl_3$; Cl^-, 22.70. Found: Cl^-, 22.33.

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LINCOLN, NEB.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

New Heteroaromatic Compounds. VII. Chloro and Bromo Derivatives of 10-Hydroxy-10,9-borazarophenanthrene

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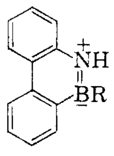
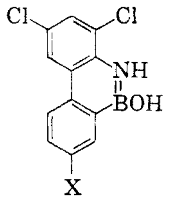
Chlorination or bromination of 10-hydroxy-10,9-borazarophenanthrene gave the 6,8-dichloro or dibromo derivatives. Further chlorination of 6,8-dichloro-10-hydroxy-10,9-borazarophenanthrene gave the 2,6,8-trichloro derivative. Syntheses of the ethers from 2- and 6-chloro-10-hydroxy-10,9-borazarophenanthrene are described.

In a previous paper[1] we reported the nitration and chlorination of 10-methyl-10,9-borazarophenanthrene (Ia) and the nitration of 10-hydroxy-10-9-borazarophenanthrene (Ib). We have now examined the chlorination and bromination of Ib.

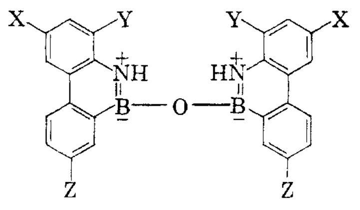
Chlorination of Ib with two moles of chlorine at room temperature gave, in good yield, a dichloro derivative which was shown to be 6,8-dichloro-10-hydroxy-10,9-borazarophenanthrene (IIa) by degradation to 3,5-dichloro-2-aminodiphenyl with cold concentrated sulfuric acid.[1]



Ia. R = Me
Ib. R = OH



IIa. X = H
IIb. X = Cl



IIIa. X = Y = H, Z = Cl
IIIb. X = Cl, Y = Z = H
IIIc. X = Y = Z = Cl
IIId. X = Y = Br, Z = H

When the chlorination was repeated with one mole of chlorine, IIa remained the sole isolable product. All attempts to obtain monochloro derivatives failed, even when less than one mole of chlorine was used. Since we had hoped to obtain a mixture of monochloro derivatives we began work on the synthesis of possible isomers; 2- and 6-chloro-10-hydroxy-10,9-borazarophenanthrene were readily obtained by hydrolysis of the corresponding 10-chloro derivatives[1] and isolated as their anhydrides, IIIa and IIIb, respectively. Since no monochloro derivatives could be obtained from Ib and since the necessary starting material (2-amino-3-chlorodiphenyl) is inaccessible we did not synthesise the 8-chloro derivative.

Chlorination of Ib with three moles of chlorine at a higher temperature gave 2,6,8-trichloro-10-hydroxy-10,9-borazarophenanthrene (IIb) which on standing at room temperature lost water to form the corresponding ether (IIIc). The structure of IIIc was indicated by its synthesis from IIIa by chlorination.

Bromination of Ib with two moles of bromine in acetic acid gave 6,8-dibromo-10-hydroxy-10,9-borazarophenanthrene which was isolated as the corresponding ether (IIId). The structure of IIId was shown by degradation to 2-amino-3,5-dibromodiphenyl with concentrated sulfuric acid and by synthesis from 2-amino-3,5-dibromodiphenyl by the method previously described.[2] The ultraviolet absorption spectra of these compounds in 95% ethanol solution are indicated in Table I.

DISCUSSION

Theory suggests[1] that the 8-position in 10,9-borazarophenanthrene should be the most reactive towards electrophilic substitution, followed closely by the 6-position. This was shown to be the case for nitration of Ia and Ib while chlorination of Ia gave almost exclusively the 8-chloro derivative. Here we have shown that the 6- and 8-positions of Ib are also the most reactive for chlorination and bromination.

The effect of a −E substituent (such as hydroxyl)

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(1) M. J. S. Dewar and Ved P. Kubba, *Tetrahedron*, 7, 213 (1959).

(2) M. J. S. Dewar, V. P. Kubba, and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

TABLE I

ULTRAVIOLET ABSORPTION

Compound	λ_{max}	Log ϵ_{max}	λ_{min}	Log ϵ_{min}
IIa	222	4.5489	214	4.4693
	234	4.6240	224	4.5448
	242	4.5550	238	4.4593
	268	4.0355	264	4.0254
	276	4.0648	272	3.9428
	326	3.8739	294	3.2138
	338	3.8661	332	3.8114
			350	2.7908
IIb	218	4.5077	216	4.4926
	224	4.5325	220	4.5031
	228	4.5395	226	4.5204
	282	4.1388	276	4.0762
	328	3.9183	298	3.4516
	342	3.9333	336	3.8881
			356	2.9160
IIIa	220	4.8607	216	4.8511
	226	4.8644	222	4.8511
	230	4.8700	228	4.8607
	266	4.3910	262	4.3533
	276	4.4154	270	4.2913
	316	4.2150	286	3.7031
	328	4.2354	320	4.1598
			340	2.9761
IIIb	220	4.8665	216	4.8488
	224	4.8524	222	4.8488
	238	4.7949	234	4.7866
	244	4.7700	242	4.7652
	272	4.4056	268	4.2679
	324	4.1928	284	3.4897
	336	4.2073	330	4.1425
			348	3.3259
IIId	222	4.8599	216	4.8349
	236	4.8711	226	4.8501
	268	4.3861	266	4.3738
	278	4.3897	274	4.2800
	326	4.1877	294	3.4830
	340	4.2171	332	4.1457
			350	3.3980

on the reactivity of an alternant hydrocarbon (such as phenanthrene) should be similar to that of replacing the corresponding ring carbon atom by a less electronegative atom (such as boron). Introducing a hydroxyl group into the 10-position of phenanthrene should therefore accelerate electrophilic substitution in the 2-, 4-, 6-, and 8-positions.[3] The 6- and 8-positions in 10-hydroxy-10,9-borazarophenanthrene should therefore be much the most reactive, the difference between them and the other positions being even greater than for 10,9-borazarophenanthrene itself.

Calculation[1] suggests that the 2- and 4-positions should be the next in reactivity, the former probably being the more reactive. (This should definitely be so if, as seems likely, the difference in electronegativity between B^- and C is similar to that between C and N^+). Since the 4-position in phenanthrene seems to be sterically hindered to substitution[4] and since the orientational effects of the hydroxyl in Ib should be similar to those of the boron, we can predict with assurance that the 2-position in Ib should be the third in reactivity. It is therefore satisfactory that further chlorination of IIa gave the 2,6,8-trichloro derivative (IIb).

We had hoped to compare the reactivities of the 6- and 8-positions of Ib to chlorine by determining the proportions of monochloro derivatives formed by chlorination. We were, however, unable to isolate any monochloro derivatives from the reactions; even when a deficiency of chlorine was used the dichloro derivative (IIa) was the sole isolable product. This was surprising; for the monochloro derivatives of Ib must be less reactive to electrophiles than Ib itself, and Ia can be readily monochlorinated. The only reasonable explanation seems to be that the reactivity of Ib is so great that the chlorination does not take place homogeneously. The chlorination was carried out by bubbling chlorine into a solution of Ib in acetic acid; if under these conditions both Ib and its monochloro derivatives react sufficiently rapidly with chlorine, the reation could be diffusion-controlled. The material in a layer of solution round each bubble of chlorine would then be completely chlorinated, the rest being unaffected. This explanation seems reasonable, for theory suggests that the 6- and 8-positions in Ib should be much the most reactive, and also much more reactive than the corresponding positions in Ia. It seems quite feasible that Ib should undergo a diffusion-controlled chlorination to IIa, while under similar conditions Ia reacts normally to give a monochloro derivative in good yield.

EXPERIMENTAL

Bis(2-chloro-10,9-borazaro-10-phenanthryl) ether (IIIa). A solution of 2-amino-4′-chlorodiphenyl (3.5 g.) in dry benzene (50 ml.) was added dropwise with vigorous stirring to one of boron trichloride (2.8 g.) in dry benzene (250 ml.) and the mixture boiled under reflux for 4 hr. After removing the solvent, anhydrous aluminum chloride (0.5 g.) was added and the mixture heated to 190° for 3 hr. The resulting 2,10-dichloro-10,9-borazarophenanthrene was taken up in ether and washed with water. Evaporation of the dried organic layer gave IIIa which crystallized from benzene in light brown needles (2.8 g., 75%) m.p. 192–193°.

Anal. Calcd. for $C_{24}H_{16}ON_2Cl_2B_2$: C, 65.3; H, 3.6; N, 6.4; Cl, 16.1. Found: C, 65.2; H, 3.9; N, 6.6; Cl, 16.0.

Bis(6-chloro-10,9-borazaro-10-phenanthryl) ether (IIIb) was prepared likewise in 69% over-all yield from 2-amino-5-chlorodiphenyl; the compound was crystallized from benzene in light brown prisms, m.p. 205–206°.

Anal. Calcd. for $C_{24}H_{16}ON_2Cl_2B_2$: N, 6.4; Cl, 16.1. Found: N, 6.6; Cl, 16.0.

6,8-Dichloro-10-hydroxy-10,9-borazarophenanthrene (IIa). Chlorine, prepared from potassium permanganate (2.14 g.) and concd. hydrochloric acid (13.3 ml.) was passed slowly into a solution of Ib (3.3 g.) in glacial acetic acid at room temperature. The solution was then poured into water, neutralized with sodium carbonate, and extracted with ether. Evaporation of the ether left crude IIa (3.35 g., 76%), which was chromatographed on Peter Spence alumina, type

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[3] M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 *et seq.* (1952).

[4] M. J. S. Dewar and E. W. T. Warford, *J. Chem. Soc.*, 3570 (1956).

H, 100/200 mesh, from benzene/chloroform. Only one band could be detected by ultraviolet fluorescence; elution of this gave IIa which crystallized from benzene in needles, m.p. 263–264°.

Anal. Calcd. for $C_{12}H_8ONCl_2B$: N, 5.3; Cl, 26.9. Found: N, 5.2; Cl, 26.2.

Degradation of 6,8-dichloro-10-hydroxy-10,9-borazarophenanthrene. The chloro compound (0.5 g.) was added to concd. sulfuric acid (25 ml.). After 3 hr. at room temperature the solution was poured on ice, made basic with sodium hydroxide, and extracted with ether. Evaporation of the ether left 2-amino-3,5-dichlorodiphenyl which crystallized from aqueous alcohol in white needles (0.27 g., 60%), m.p. and mixed m.p. 50–51°.

2,6,8-Trichloro-10-hydroxy-10,9-borazarophenanthrene (IIb). Chlorine, prepared from potassium permanganate (3.92 g.) and concd. hydrochloric acid (24.4 ml.), was passed slowly into a solution of Ib (4.0 g.) in glacial acetic acid at 90–100°. The solution was poured into water, neutralized with sodium carbonate, and extracted with ether. Evaporation of the ether gave IIb which crystallized from benzene in white needles (4.9 g., 80%), m.p. 283–284°.

Anal. Calcd. for $C_{12}H_7ONCl_3B$: C, 48.3; H, 2.3; N, 4.7; Cl, 35.7. Found: C, 48.6; H, 2.3; N, 4.5; Cl, 35.9.

Bis(2,6,8-trichloro-10,9-borazaro-10-phenanthryl) ether (IIIc). (a) Chlorination of IIIa (2.0 g.) as above with chlorine prepared from potassium permanganate (1.3 g.) and concd. hydrochloric acid (10 ml.) gave IIIc (1.6 g., 61%) which, after crystallization from benzene, melted at 285–286°. (b) The same compound was obtained by allowing IIb to stand in air for 8 weeks at room temperature.

Anal. Calcd. for $C_{24}H_{12}ON_2Cl_6B_2$: N, 4.8; Cl, 36.7. Found: N, 4.6; Cl, 36.8.

Bis(6,8-dibromo-10,9-borazaro-10-phenanthryl) ether (IIId). (a) Bromine (4.8 g.) in glacial acetic acid (15 ml.) was added to a solution of Ib (3.0 g.) in glacial acetic acid (100 ml.) at 50°. After 2 hr. at 80° water was added and the crude dibromo compound (4.3 g., 80%) collected and crystallized from acetic acid, m.p. 295–296°. (b) The dibromo compound was synthesized as above from 2-amino-3,5-dibromodiphenyl (2.5 g.) by successive treatment with boron trichloride and aluminum chloride, the yield of material, melting point, and mixed melting point 295°, being 1.6 g. (61%).

Anal. Calcd. for $C_{24}H_{14}ON_2Br_4B_2$: N, 4.1; Br, 46.5. Found: N, 4.2; Br, 46.4.

CHICAGO 37, ILL.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

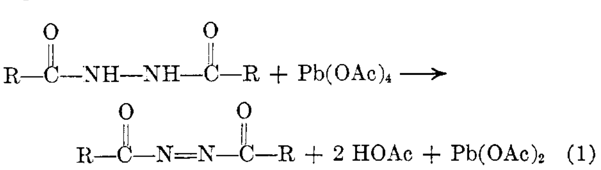
The Oxidation of 2,3-Dihydrophthalazine-1,4-dione with Lead Tetraacetate. Phthalazine-1,4-dione and 1,4-Dihydropyridazino[1,2-*b*]-phthalazine-6,11-dione

ROBERT A. CLEMENT

Received March 16, 1960

Evidence is presented that the oxidation of 2,3-dihydrophthalazine-1,4-dione (phthalhydrazide) with lead tetraacetate produces, as the initial and unstable product of oxidation, phthalazine-1,4-dione. By taking advantage of its extraordinary reactivity as a dienophile, this compound was intercepted with butadiene as 1,4-dihydropyridazino[1,2-*b*]phthalazine-6,11-dione, the structure of which was firmly established.

We have found[1] that the oxidation of diacyl hydrazides with lead tetraacetate according to equation 1 is a convenient method for the prepara-



$$R{-}\overset{O}{\overset{\|}{C}}{-}NH{-}NH{-}\overset{O}{\overset{\|}{C}}{-}R + Pb(OAc)_4 \longrightarrow R{-}\overset{O}{\overset{\|}{C}}{-}N{=}N{-}\overset{O}{\overset{\|}{C}}{-}R + 2\,HOAc + Pb(OAc)_2 \quad (1)$$

tion of diacyl diimides, generally superior to the methods heretofore employed.[2] However, when the reaction was applied to 2,3-dihydrophthalazine-1,4-dione (I) (phthalhydrazide), the expected product, phthalazine-1,4-dione(II), was not isolated. Contrary to our experience with other diacyl hydrazides, gas was evolved during the oxidation and the initially highly-colored solution[3] became quite colorless during the isolation procedure.

This paper is concerned with the results of an examination of the reaction of I with lead tetraacetate and provides evidence that the initial product of oxidation is, indeed, the expected diimide II which, however, is too unstable to be isolated or even to be preserved in solution. In the course of the investigation, there were prepared 1,4-dihydropyridazino[1,2-*b*]phthalazine-6,11-dione (III) and 1,2,3,4-tetrahydropyridazino-[1,2-*b*]phthalazine-6,11-dione (IV), representatives of a heterocyclic ring system which, to the best of our knowledge, has not previously been described. Some of the transformations involved in this study are summarized in Fig. 1.

RESULTS

When the oxidation of 2,3-dihydrophthalazine-1,4-dione (I) with one mole of lead tetraacetate was carried out in acetonitrile, there was obtained, initially, a lime-green solution which very rapidly deposited a fine, white, amorphous solid and which

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[1] Unpublished results, this laboratory.

[2] E. Mohr, *J. prakt. Chem.*, II, **70**, 281 (1904); R. Stolle *Ber.*, **45**, 273 (1912); L. Horner and W. Naumann, *Ann.*, **587**, 93 (1954); J. E. Leffler and W. B. Bond, *J. Am. Chem. Soc.*, **78**, 335 (1956).

[3] Diacyl hydrazides are intensely colored, generally red in solution.