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.

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

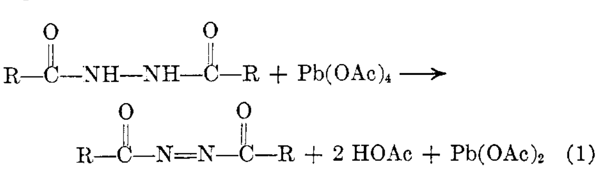
The Oxidation of 2,3-Dihydrophthalazine-1,4-dione with Lead Tetraacetate. Phthalazine-1,4-dione and 1,4-Dihydropyridazino[1,2-*b*]-phthalazine-6,11-dione

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 preparation 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.



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

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.

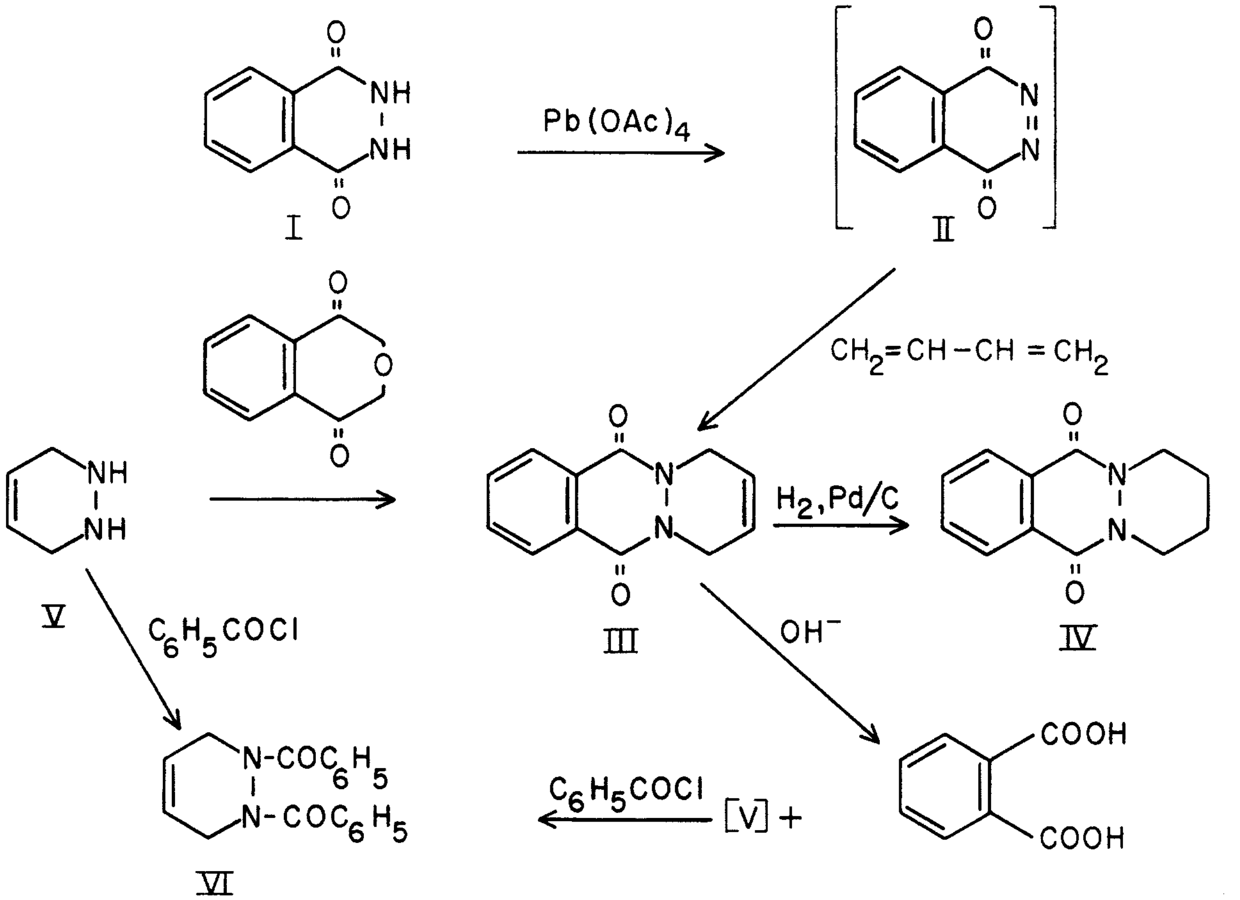
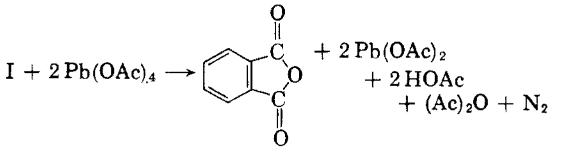


Fig. 1. Some transformations with 2,3-dihydrophthalazine-1,4-dione

became colorless in the course of a few hours. The amorphous solid was an intractable substance which was insoluble in all common solvents and which decomposed, usually explosively, when heated. Although this material could not be purified, it yielded an approximate analysis for phthalazine-1,4-dione (II) and in view of its intractable nature and its lack of color it was formulated as a polymer $(II)_n$ of that compound. Closer inspection of the reaction mixture revealed the presence, in roughly equivalent amounts, of phthalic anhydride and unchanged I. At this point it appeared that oxidation of I was proceeding, simultaneously, according to Equations 2 and 3, that II was responsible for the color of the solution, and that because of its instability, II was being removed rather rapidly according to Equation 4 to form the polymer $(II)_n$.

$$I + Pb(OAc)_4 \longrightarrow II + 2\,HOAc + Pb(OAc)_2 \qquad (2)$$



$$I + 2\,Pb(OAc)_4 \longrightarrow C_6H_4(CO)_2O + 2\,Pb(OAc)_2 + 2\,HOAc + (Ac)_2O + N_2 \qquad (3)$$

$$n\,II \longrightarrow (II)_n \qquad (4)$$

Confirmation of the validity of equation 3 was obtained in the oxidation of I with two moles of lead tetraacetate. Phthalic anhydride and nitrogen gas were produced in essentially quantitative yield.

In view of the certain reactivity of II as reflected by Equation 4, and in view of the known reactivity of diacyl diimides as dienophiles,[4,5] it seemed feasible to attempt the interception of II with butadiene. In fact, when butadiene was added to the clear green solution, the green color disappeared immediately and there was produced 1,4-dihydropyridazino[1,2-*b*]phthalazine-6,11-dione (III), the structure proof for which is outlined below. III was produced in an amount roughly equivalent to that of the polymer $(II)_n$ formed from the green solution in the absence of butadiene, and the amounts of unchanged I and phthalic anhydride obtained in the two experiments were also roughly equivalent. These observations indicated that III and $(II)_n$ were derived from an identical precursor which most likely was II and which was responsible for the green color.

When the oxidation was carried out with buta-

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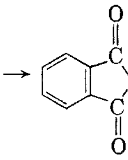
(4) P. Baranger and J. Levisalles, *Bull. soc. chim. France*, 704 (1957).

(5) O. Diels, J. H. Blom, and W. Koll, *Ann.*, **443**, 242 (1925); O. Diels and K. Alder, *Ann.*, **450**, 237 (1926); O. Diels, S. Schmidt, and W. Witte, *Ber.*, **71**, 1186 (1938); K. Alder and H. Niklas, *Ann.*, **585**, 81 (1954).

diene present from the start, III was obtained in a 90% yield. This result showed, beyond doubt, that the initial product of oxidation is II as defined by Equation 2. Because of its instability, however, II disappears according to equations 4 and 5, reaction by the latter route consuming additional oxidant and, with a molar amount of oxidant, requiring one mole of I to remain unchanged for each mole of phthalic anhydride produced. The reactivity of II as a dienophile, however, is greater than its reactivities according

$\mathrm{II} + \mathrm{Pb(OAc)_4} \rightarrow$



$+ \mathrm{Pb(OAc)_2} + \mathrm{(Ac)_2O} + \mathrm{N_2}$ (5)

to Equations 4 and 5, and in the presence of butadiene, II is intercepted by butadiene essentially as rapidly as it is formed.

The structure of III is of some interest since it is a representative of the heretofore-unknown pyridazino[1,2-*b*]phthalazine heterocyclic ring system. As expected from its structure, III readily absorbed one mole of hydrogen to yield a dihydro derivative which is formulated as 1,2,3,4-tetrahydropyridazino[1,2-*b*]phthalazine-6,11-dione (IV). The structure of III was proved by an alternative synthesis from phthalic anhydride and 1,2,3,6-tetrahydropyridazine (V). Further confirmation of structure III was obtained by its hydrolysis to phthalic acid and V, identified as its derivative, 1,2-dibenzoyl-1,2,3,6-tetrahydropyridazine (VI).

The extraordinary reactivity of phthalazine-1,4-dione (II) as a dienophile is worthy of note. Its reaction with butadiene was instantaneous even at 0° and at a concentration of *ca.* 0.05*M*. The reaction of II with other dienes is currently under investigation as is the possiblity that it may undergo reaction with simple olefins by 1,2-cycloaddition.

EXPERIMENTAL[6]

Oxidation of 2,3-dihydrophthalazine-1,4-dione (I) *with lead tetraacetate. A. With one mole of lead tetraacetate.* To a slurry of I[7] (4.59 g., 28.4 mmoles) and purified acetonitrile[8] (150 ml.) in a flask provided with a loose-fitting stopper and cooled in an ice bath, was added lead tetraäcetate[9] (12.6 g., 28.4 mmoles), and the heterogeneous mixture was stirred magnetically. As reaction proceeded, some gas was evolved, the solution became thick with precipitated lead acetate, and the color of the solution changed from golden brown to lime green. At the end of 1.33 hr. a test for lead tetraacetate was negative,[10] and the reaction mixture was immediately filtered and the filter cake washed with 50 ml. of acetonitrile to give an off-white precipitate and a clear, intense green filtrate.

The precipitate was stirred vigorously with 100 ml. of 1*N* nitric acid, filtered, and washed with water. It was then suspended in 100 ml. of water, and sufficient 2*N* sodium hydroxide was added to dissolve most of the precipitate and to bring the solution to *p*H 10. The solution was then filtered and the filtrate was added to a mixture of 25 ml. of glacial acetic acid and 25 ml. of water. The resulting precipitate was isolated by filtration and, after being dried at 110°, amounted to 1.41 g. (8.70 mmoles) of unchanged I, identified by its infrared spectrum.

The clear green filtrate from the initial filtration became cloudy with precipitate within 3 min., and after 3 hr. the solution was virtually colorless and had deposited a fine, white, amorphous precipitate which was collected by centrifugation and amounted to 0.71 g. [4.44 mmole of phthaloyl units on the basis of polymer $(\mathrm{II})_n$]. The analytical sample was prepared by washing this material with 100 ml. of acetonitrile and possessed absorption in the infrared (potassium bromide pellet) at 1700 (broad, carbonyl) and 1595 (carbonyl-conjugated unsaturation) cm^{-1}. It was insoluble in all the common organic solvents and in water, and decomposed in the range, 190–290°, usually explosively.

Anal. Calcd. for $(\mathrm{C_8H_4N_2O_2})_n$: N, 17.50. Found: N, 16.01.

The mother liquors from the isolation of the polymer $(\mathrm{II})_n$ were evaporated to dryness under reduced pressure and the gummy residue was sublimed at 100° and 1 mm. to yield 1.46 g. (9.74 mmoles) of phthalic anhydride, m.p. 125–131°, identified by the criteria of mixture melting point and infrared spectral comparison.

B. With two moles of lead tetraacetate. A slurry of I (0.47 g., 2.90 mmoles) in 40 ml. of acetonitrile was placed in a flask which was provided with a magnetic stirrer and a dumping arm which contained 2.60 g. (5.87 mmoles) of lead tetraacetate. The flask was attached to a manometric system which was flushed with nitrogen and maintained at atmospheric pressure and 28°. Reaction was initiated by dumping the lead tetraacetate into the acetonitrile solution. As reaction proceeded, the solution changed color from golden brown to green to colorless. After 1.5 hr. there was no further change in volume which, after correction for the partial pressure of acetonitrile and reduction to S.T.P., amounted to 68 ml. (103% of theory according to Equation 3).

The solution was then filtered and the filtrate was evaporated to dryness under reduced pressure. The residue was sublimed at 100° and 1 mm. to yield 0.41 g. (95% of theory according to Equation 3) of phthalic anhydride, m.p. 123–131°, identified by the criteria of mixture melting point and infrared spectral comparison.

C. With one mole of lead tetraacetate and subsequent addition of butadiene. The reaction was run as in *A* with 4.86 g. (30.0 mmoles) of I, 150 ml. of acetonitrile, and 13.3 g. (30.0 mmoles) of lead tetraacetate. Unchanged I, isolated and identified as in *A*, amounted to 1.56 g. (9.63 mmoles).

Immediately after filtration and before any precipitate had appeared, the clear green filtrate from the removal of unchanged I and lead acetate was stirred while a stream of butadiene was directed onto the solution. Within *1 min.* after initiation of the operation (within 3 min. after filtration) the solution had become colorless and a white pre-

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[6] Melting points were determined on a calibrated Fisher-Johns block. Infrared spectra were recorded on a Perkin-Elmer Model 21 Infrared Spectrophotometer. We are indebted to Mr. W. Saschek of this Department for the analyses.

[7] H. D. K. Drew and H. H. Hatt, *J. Chem. Soc.*, 16 (1937).

[8] A. R. Ronzio and W. B. Cook, *Org. Syntheses*, Coll. Vol. III, 72 (1955).

[9] J. C. Bailar, Jr., *Inorg. Syntheses*, 1, 47 (1939).

[10] To test for lead tetraacetate, *ca.* 0.1 ml. of the reaction mixture was added to *ca.* 5 ml. of dilute sulfuric acid, swirled for 1 min., and then poured into an aqueous solution of potassium iodide and starch. If lead tetraacetate (at this point, lead dioxide) were present, the characteristic deep blue color of the iodine-starch complex appeared. It was necessary to destroy II with aqueous acid prior to addition to the iodide-starch solution, as it oxidizes iodide to iodine, instantly. In fact, all diacyl diimides we have tested give an intense blue color when added directly to an acidic solution of potassium iodide and starch.

cipitate had appeared. The reaction mixture was immediately connected to the water aspirator, and solvent was removed at reduced pressure to yield a white solid which was suspended in 100 ml. of water and stirred while the solution was adjusted to *p*H 10 with 2*N* sodium hydroxide. Filtration gave a pale orange solid which was stirred vigorously for 1 hr. in a mixture of 50 ml. of water and 5 ml. of glacial acetic acid and then filtered to yield, after being dried at 110°, 1.30 g. (6.08 mmoles) of 1,4-dihydropyridazino[1,2-*b*]-phthalazine-6,11-dione (III), which possessed an infrared spectrum indistinguishable from that of the analytical sample described below.

The basic filtrate from the initial isolation of III was concentrated to *ca.* 30 ml. and adjusted to *p*H 0 with concd. nitric acid. The buff-colored precipitate that appeared was isolated by filtration and, after being air dried, amounted to 1.26 g. (7.60 mmoles) of phthalic acid, identified by its infrared spectrum and its neutralization equivalent (required, 83; found, 85).

D. With one mole of lead tetraacetate in the presence of butadiene. *1,4-Dihydropyridazino[1,2-b]phthalazine-6,11-dione* (III). To a slurry of I (4.05 g., 25.0 mmoles), butadiene (11.0 g.), and acetonitrile (125 ml.) in a flask equipped with a loose-fitting stopper and cooled in an ice bath, was added lead tetraacetate (11.0 g., 24.8 mmoles); the mixture was stirred magnetically. As reaction proceeded, the solution became thick with precipitate, but at no time was there visible a green color. At the end of 1.75 hr., solvent was removed from the reaction mixture under reduced pressure and the residue was stirred vigorously and in succession with 100 ml. of water, 100 ml. of 0.1*N* nitric acid, 100 ml. of 0.1*N* sodium hydroxide, and 100 ml. of water, being isolated by filtration after each operation. The final filtration afforded a tan solid which, after being dried at 110°, amounted to 4.82 g. (90%) of III and which possessed an infrared spectrum indistinguishable from that of the analytical sample. The analytical sample of III was obtained as fine white needles, m.p. 272–275° dec. (sealed capillary), after two recrystallizations from acetic acid–water, and possessed absorption in the infrared (3% in chloroform) at 1627 (carbonyl) and 1604 (carbonyl-conjugated unsaturation) cm^{-1}.

Anal. Calcd. for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71. Found: C, 67.36; H, 4.88.

Hydrogenation of 1,4-dihydropyridazino[1,2-b]phthalazine-6, 11-dione (III). *1,2,3,4-Tetrahydropyridazino[1,2-b]phthalazine-6,11-dione* (IV). A slurry of III (0.149 g.) in glacial acetic acid (45 ml.) was hydrogenated in the presence of 10% palladium-on-charcoal (0.10 g.), the reduction in volume corresponding to 99% of theory for the absorption of 1 mole of hydrogen and being attained in 15 min. The reaction mixture was filtered, the filtrate was evaporated to dryness under reduced pressure, and the residue was crystallized from water to yield 0.124 g. (82%) of IV as white swords, m.p. 146°. The analytical sample was obtained, after two more crystallizations from water, as white swords, m.p. 145.5–146.5°, or as very fine white needles, m.p. 156.0–156.5°. An intimate mixture of the two forms melted at 156.0–156.5°, and occasionally the lower-melting form resolidified to remelt at 156.0–156.5°. In the infrared (1% in chloroform) IV possessed absorption at 1648 (carbonyl) and 1607 (carbonyl-conjugated unsaturation) cm^{-1}.

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.60. Found: C, 66.75; H, 5.60.

1,2,3,6-Tetrahydropyridazine (V). This material was prepared as previously described,[4] b.p. 88–91°/50 mm., n_D^{25} 1.5126 (lit.[4] b.p. 68.5°/20 mm.). *1,2-Dibenzoyl-1,2,3,6-tetrahydropyridazine* (VI) was prepared from V and benzoyl chloride in pyridine and, after recrystallization from ethanol-water, melted at 162.5–164.0° (lit.[4] m.p. 160.5°) and possessed absorption in the infrared (5% in chloroform) at 1673 and (a shoulder) 1650 (carbonyl) cm^{-1}.

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52. Found: C, 74.02; H, 5.89.

1,4-Dihydropyridazino[1,2-b]phthalazine-6,11-dione (III) *from phthalic anhydride and 1,2,3,6-tetrahydropyridazine* (V). A mixture of phthalic anhydride (2.96 g., 20.0 mmoles) and V (1.68 g., 20.0 mmoles) in 50 ml. of water, 7 ml. of concd. hydrochloric acid, and 3 ml. of ethanol (to control foaming) was heated under reflux for 11 hr. At the end of this time the reaction mixture was cooled and filtered and the tan solid collected was washed with 50 ml. of water. This material, after being dried at 110°, amounted to 3.31 g. (77%) of III and possessed an infrared spectrum indistinguishable from that of the analytical sample described above.

Hydrolysis of 1,4-dihydropyridazino[1,2-b]phthalazine-6,11-dione (III). A mixture of III (2.14 g., 10.0 mmoles, as obtained in *D*) and potassium hydroxide (4.0 g., 71 mmoles) in 25 ml. of water was heated under reflux for 20.5 hr. At the end of this time, the homogeneous solution was extracted with ten 50-ml. portions of methylene chloride and the aqueous layer was preserved for further treatment. The combined methylene chloride extracts were dried over potassium carbonate, filtered, and evaporated under reduced pressure to yield 0.56 g. of a pale yellow residue which possessed an amine-like odor. This residue was dissolved in pyridine (25 ml.), benzoyl chloride (3.00 g.) was added, and the mixture was stirred at room temperature for 3.5 hr. At the end of this time, the reaction mixture was poured into 400 ml. of water and stirred vigorously until the odor of benzoyl chloride was no longer noticeable. Filtration yielded a tan solid which, after being dried at 110°, amounted to 0.90 g. (31%) of VI, m.p. 152–160°, identified by mixture melting point and infrared spectral comparison with authentic VI described above.

The aqueous layer preserved after the methylene chloride extractions was acidified to *p*H 0 with concd. hydrochloric acid and the precipitate which appeared was filtered and air dried to yield 0.86 g. (52%) of phthalic acid, identified by its infrared spectrum and its neutralization equivalent (required, 83; found, 84).

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