Degradation and Synthesis of the Molecular Complex.—When a sample of the molecular complex (m.p. 177–177.5°) was dissolved in warm benzene and the solution was cooled, white crystals melting at 211–212° were obtained. This product did not depress the melting point when admixed with samples of *sym*-tetraphenylethane (m.p. 211–212°). The benzene filtrate, from which *sym*-tetraphenylethane had been removed, was evaporated to dryness and the residue was recrystallized from ethanol. Benzophenone azine, m.p. 162–164°, was obtained.

Separate solutions containing equimolar amounts of benzophenone azine and *sym*-tetraphenylethane in ethanol were mixed and the resulting solution was cooled. Yellow crystals, m.p. 177–177.5°, were obtained. A mixed melting point of this product and the molecular complex described above was 177–177.5°.

Anal. Calcd. for $C_{52}H_{42}N_2$: C, 89.9; H, 6.09. Found: C, 89.9; H, 5.85.

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2-Bromophenanthridone

BY W. L. MOSBY

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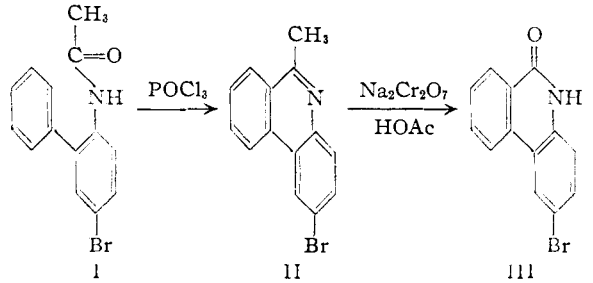
In 1935, Walls[1] recorded the preparation of 2-bromophenanthridone (III) by the cyclization of 2-acetamido-5-bromobiphenyl (I) and oxidation of the resulting 2-bromo-6-methylphenanthridine (II).

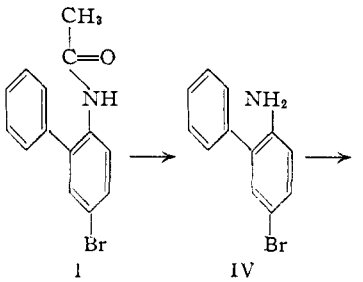


I II III

Walls described III (after recrystallization from nitrobenzene) as yellow needles which decomposed at 302° after previous sintering.

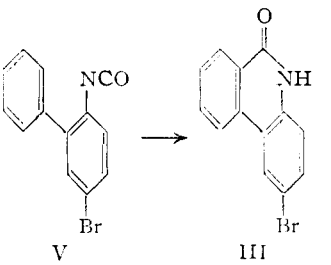
In the course of preparing some phenanthridone derivatives we found that treatment of phenanthridone in acetic acid with bromine resulted in a nearly quantitative yield of a monobromo derivative. The product recrystallized from nitrobenzene in white fluffy needles, m.p. 323.5–324.5°. This product was thought to be the 4- or, more likely, the 2-bromo derivative (III).

In view of the discrepancy in melting points, and as there appeared to be no reason to expect III to have the yellow color ascribed to it by Walls, an unambiguous synthesis of III was effected.



I IV

(1) L. P. Walls, *J. Chem. Soc.*, 1405 (1935).



V III

The melting point of this product agrees with that of the product obtained by the bromination of phenanthridone, and a mixed melting point shows no depression. It would thus seem quite well established that the two are identical, and that the product described by Walls was impure.

Since slight modifications in the preparation of 2-biphenylyl isocyanate described by Fraenkel-Conrat and Olcott,[2] and in the cyclization of this to phenanthridone described by Butler,[3] have resulted in nearly quantitative yields, an over-all yield of 92–93% of III from 2-aminobiphenyl may be attained. It is of interest that, contrasted with the nitration of phenanthridone,[4] bromination shows no evidence of the formation of the 4-substituted isomer.

Experimental[5]

2-Biphenylyl Isocyanate.—A solution of 300 g. of 2-aminobiphenyl in 500 ml. of toluene was added slowly with stirring under reflux to a solution of 700 g. of phosgene in 2000 ml. of toluene. A crystalline precipitate formed. The mixture was stirred and refluxed for five hours, then allowed to stand overnight. The resulting clear brown solution was stripped of solvent and distilled *in vacuo* to give 345 g. of product (99.7% yield), b.p. 92–94° (1 mm.) (lit.[2] b.p. 100° (0.5–1.0 mm.)).

Phenanthridone.—In a 2-liter, 3-necked flask equipped with addition funnel, solid addition tube, reflux condenser and stirrer, was placed 1000 ml. of chlorobenzene. While the flask was cooled in ice to keep the temperature of the reaction mixture at about 30°, 244 g. (1.25 moles) of 2-biphenylyl isocyanate and 175 g. (1.30 moles) of powdered anhydrous aluminum chloride were added at approximately equivalent rates. When the reactants had been added the mixture was stirred with continued cooling for a half hour, then for a few minutes at room temperature. The mixture was filtered; the solid was washed with a little chlorobenzene and dried overnight at room temperature. The dry product was hydrolyzed by beating in a Waring Blendor with warm very dilute hydrochloric acid. The slurry was filtered; the solid was rebeaten with methanol and refiltered, washed with methanol and dried. The yield of pure white phenanthridone, m.p. 291.5–293° (lit.[3] 292.5–293.5°), was 233 g. (95.5%).

A. **2-Bromophenanthridone by Bromination. 2-Bromophenanthridone (III).**—To a stirred, refluxing solution of 19.5 g. (0.10 mole) of phenanthridone in 200 ml. of glacial acetic acid was added dropwise a solution of 17.6 g. (0.11 mole) of bromine in 50 ml. of glacial acetic acid over a period of about 1.5 hours. After a short induction period, a copious evolution of hydrogen bromide (trap!) was evident, and a white precipitate began to form. When all of the bromine had been added, the mixture was stirred and refluxed until the orange bromine color was no longer noticeable (about 20 minutes), then poured into water and filtered. The white filter cake was washed well with water

(2) H. Fraenkel-Conrat and H. S. Olcott, THIS JOURNAL, **66**, 845 (1944).

(3) J. M. Butler, *ibid.*, **71**, 2578 (1949).

(4) A. J. Nunn, K. Schofield and R. S. Theobald, *J. Chem. Soc.*, 2797 (1952).

(5) The author wishes to thank Mr. O. E. Sundberg, Miss I. H. Prokul and Mrs. R. Cran for the microanalyses. All melting points were taken in commercially available soft glass capillaries, using Anschütz thermometers and a Hershberg apparatus.

and dried. The yield of crude product, m.p. 320.5–323.0°, was 27.25 g. (99.2%). Recrystallization from about 200 ml. of nitrobenzene gave 25.17 g. (91.5%) of white fluffy needles, m.p. 323.5–324.5°.

Anal. Calcd. for $C_{18}H_8BrNO$: C, 56.9; H, 2.92; N, 5.11; Br, 29.1. Found: C, 57.3; H, 2.97; N, 5.14; Br, 28.8.

B. 2-Bromophenanthridone by Cyclization. 2-Acetamido-5-bromobiphenyl (I).—The acetylation of 2-aminobiphenyl was conducted in benzene solution using acetic anhydride. On recrystallization from cyclohexane the product melted at 118.5–120.5° (lit.[6] m.p. 121°). Bromination of the acetyl derivative in acetic acid followed by recrystallization of the product from cyclohexane gave I, m.p. 128–129° (lit.[6] 130°).

2-Bromophenanthridone (III).—A mixture of 30 g. of I, 200 ml. of ethanol and 25 ml. of 48% hydrobromic acid was refluxed for 1 hour, then 100 ml. of solvent was allowed to distill. The residue was diluted with water, made basic with ammonium hydroxide and extracted well with ether. The ethereal extracts were dried ($MgSO_4$) and stripped of solvent, giving 25.1 g. of 2-amino-5-bromobiphenyl (IV), a pale pinkish-tan oil which crystallized readily on seeding (a seed was obtained by triturating a drop of oil with ligroin while cooling in Dry Ice). It was used directly in the next step.

A solution of 24.8 g. (0.10 mole) of 2-amino-5-bromobiphenyl (IV) in 100 ml. of toluene was added slowly to a solution of 50 g. (0.50 mole) of phosgene in 150 ml. of toluene, whereupon a white precipitate formed. The mixture was refluxed 1.5 hours and the clear pinkish-tan solution was stripped of solvent giving a quantitative yield of crude 5-bromo-2-biphenylyl isocyanate (V). It was used in the next step without distillation.

The isocyanate V was dissolved in 100 ml. of chlorobenzene and this solution was added dropwise with stirring to a suspension of 20.0 g. (0.15 mole) of powdered anhydrous aluminum chloride in 100 ml. of chlorobenzene. The mixture was warmed gently, then cooled and filtered. The white filter cake was washed with benzene and dried, then decomposed with cold dilute hydrochloric acid and filtered. The product was washed well with hot water, then methanol, and dried. The yield of crude product was 21.1 g. (77% from I). A sample recrystallized from nitrobenzene formed fluffy white needles, m.p. 323.0–324.0°. No noticeable depression in the melting point occurred with a mixture of this material and the product obtained by the bromination of phenanthridone.

Anal. Calcd. for $C_{13}H_8BrNO$: C, 56.9; H, 2.92; N, 5.11; Br, 29.1. Found: C, 57.0; H, 2.82; N, 5.13; Br, 29.1.

(6) H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, 89 (1927).

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A New Method of Purifying α,β,γ,δ-Tetraphenylporphine

BY J. H. PRIESTHOFF AND C. V. BANKS

RECEIVED OCTOBER 15, 1953

α,β,γ,δ-Tetraphenylporphine is prepared by the reaction of pyrrole with benzaldehyde in a sealed tube. Aronoff and Calvin[1] prepared the free-base porphine by this method. Ball, Dorough and Calvin[2] found the yield could be increased to about 10% if the zinc complex salt was prepared. The zinc was subsequently removed by the action of 6 *N* hydrochloric acid.

Although it was reported that the reaction product could be filtered and purple, crystalline tetraphenylporphine obtained, this was found not to be the case in any one of the twenty reactions carried out in this Laboratory. The product of the reaction was a black, tarry mass and could not be filtered. Although the tarry by-product could be extracted with acetone and crystalline zinc tetraphenylporphine obtained, about 5 g. of the complex were lost per liter of acetone used. Therefore, a new method was developed in which the zinc complex was decomposed with acid and the free-base-tar solution chromatographed on activated alumina (Aluminum Company of America, Grade F-20). The free-base eluate was concentrated and chromatographed on Magnesol (Westvaco Chemicals, S. Charleston, West Virginia; dry cleaning grade), yielding pure tetraphenylporphine.

Experimental

Zinc tetraphenylporphine was prepared by the method of Ball, Dorough and Calvin,[2] involving reaction of 5 ml. of pyrrole, 10 ml. of benzaldehyde, 10 ml. of pyridine and 5 g. of zinc acetate in a special Carius tube or bomb of about 40-ml. capacity (2.4 × 10 cm.). Nitrogen was bubbled through the reactants for one-half hour before the bomb was sealed. The bomb size was later increased to about 400-ml. capacity (5.0 × 20 cm.) with appropriate increase in the quantity of reactants.

The bomb was placed in a pipe jacket which was then sealed with caps and placed in an oven at 200° for 48 hours. After cooling to room temperature, the bomb was removed from the pipe jacket, opened, and the contents washed into a beaker with sufficient chloroform to ensure complete dissolution. An equal volume of 6 *N* hydrochloric acid was added to the beaker and the mixture stirred vigorously for two hours. The acidic solution was then neutralized with ammonium hydroxide.

The entire contents of the beaker were poured into a special U-tube, Fig. 1. The stirrer (A) forced the water through the chloroform solution and the wash water drained off at (C). The flow of water and the speed of stirring were carefully regulated to obtain optimum washing. If the stirring is too fast, the chloroform solution will be carried through the overflow with the water; if it is too slow, the method is inefficient. The washing time for a run made in a 400-ml. bomb was from 4 to 6 hours.

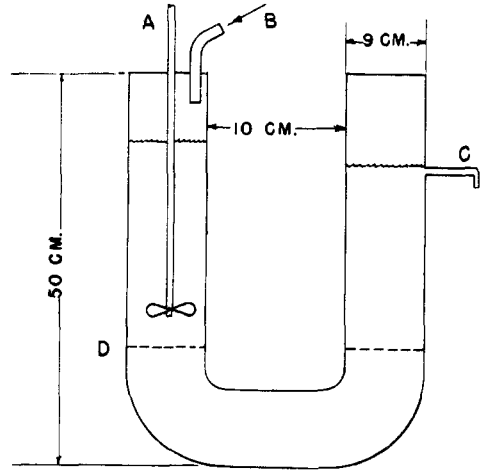

Fig. 1.—Apparatus for washing chloroform solution of TPP: A, stirrer; B, water inlet; C, water outlet; D, level of chloroform.

The chloroform solution was separated from the water and chromatographed on a column (8 × 63 cm.) of activated alumina. The column was packed by tapping the sides of the column with the hand while the alumina was being introduced. Throughout the developing and eluting procedures the flow rates were maintained at 40 to 50 ml. per

(1) S. Aronoff and M. Calvin, *J. Org. Chem.*, **8**, 205 (1943).

(2) R. H. Ball, G. D. Dorough and M. Calvin, THIS JOURNAL, **68**, 2278 (1946).