carbonate solution, was obtained 6.52 g. (56%) of IIb as colorless plates, m.p. 128–129°. An analytical sample, obtained by recrystallization from methanol, melted at 131–132°.

Anal. Calcd. for $C_{19}H_{13}FO_2$: C, 78.1; H, 4.5; F, 6.5. Found: C, 78.0; H, 4.5; F, 6.3.

o-(α-5-Fluoro-1-naphthylethyl)benzoic acid (IIIb). A mixture of 10.27 g. of IIb 20.6 g. of zinc dust, 206 ml. of formic acid and 21 ml. of water was refluxed for 12 hr. After dilution with 500 ml. of water the solids were collected and extracted with 300 ml. of 2% sodium hydroxide solution. After removal of insoluble materials, acidification afforded 10.15 g. of almost colorless IIIb. Recrystallization from benzene-Skellysolve B (1:1) gave 9.74 g. (94%) of IIIb as white needles, m.p. 160–161°. An analytical sample, obtained by recrystallization from benzene–Skellysolve B, melted at 161–162°.

Anal. Calcd. for $C_{19}H_{15}FO_2$: C, 77.5; H, 5.2; F, 6.5. Found: C, 77.9; H, 5.3; F, 6.4.

Reduction of IIb by the alkaline zinc dust method[10] afforded IIIb in 70% yield.

o-(α-5-Fluoro-1-naphthylethyl)acetophenone (IVb). Just as in the case of IIIa→IVa above described, 10.64 g. of IIIb was converted into 6.40 g. of crude IVb, m.p. 81–83°. Recrystallization from ethanol gave 6.10 g. (57%) of colorless prisms of IVb, m.p. 83–84°. An analytical sample, obtained by recrystallization from ethanol, melted at 84–85°.

Anal. Calcd. for $C_{20}H_{17}FO$: C, 82.1; H, 5.9; F, 6.5. Found: C, 82.1; H, 6.0; F, 6.3.

From the acid fraction, 2.96 g. (28%) of IIIb, m.p. 155–156°, was recovered.

4'-Fluoro-9,10-dimethyl-1,2-benzanthracene (Vb). A mixture of 6.10 g. of the methyl ketone, IVb, and 100 g. of polyphosphoric acid was heated with stirring at 85–90° for 1 hr. The reaction mixture was diluted with ice water and the yellow solid which precipitated was collected, washed with water, and dried. By chromatography in benzene–Skellysolve B (1:1) over alumina, there was obtained 5.27 g. (92%) of Va, as faintly colored plates, m.p. 97–98°. Further purification by chromatography afforded pure hydrocarbon, m.p. 97.5–98.0°.

Anal. Calcd. for $C_{20}H_{15}F$: C, 87.6; H, 5.5; F, 6.9. Found: C, 87.6; H, 5.6; F, 6.7.

3-Methyl-3-(4-fluoro-1-naphthyl)phthalide (IIc). To a stirred solution of 15.24 g. of o-(4-fluoro-1-naphthoyl)benzoic acid,[2] Ic, in 380 ml. of ether, was added dropwise 56 ml. of 3.0*N* methylmagnesium bromide in ether. After 2 hr. of refluxing, the mixture was decomposed with dilute hydrochloric acid. From the neutral fraction, freed of acids by washing with potassium carbonate, was obtained 13.45 g. (88%) of colorless plates, m.p. 126–130°. By recrystallization from ethanol, there was obtained 12.10 g. (79%) of IIc as colorless plates, m.p. 134–136°. An analytical sample, obtained by recrystallization from ethanol, melted at 143–144°, with little loss. Evidently, the lower melting form was polymorphic with the higher melting form.

Anal. Calcd. for $C_{19}H_{13}FO_2$: C, 78.1; H, 4.5; F, 6.5. Found: C, 78.2; H, 4.7; F, 6.4.

o-(α-4-Fluoro-1-naphthylethyl)benzoic acid (IIIc). A mixture of 5.10 g. of IIc, 10.2 g. of zinc dust, 100 ml. of 90% formic acid, and 10 ml. of water was refluxed for 12 hr. After isolation as described for IIIb there was obtained 5.05 g. of almost colorless IIIc. Recrystallization from benzene-Skellysolve B (1:1) gave 4.50 g. (88%) of IIIc as white needles, m.p. 163–164°.

Anal. Calcd. for $C_{19}H_{15}FO_2$: C, 77.5; H, 5.2; F, 6.5. Found: C, 77.8; H, 5.3; F, 6.2.

o-(α-4-Fluoro-1-naphthylethyl)acetophenone (IVc). Just as in the case of IIIa–IVa above described, 9.03 g. of IIIc was converted into 7.50 g. of IVc, colorless plates, m.p. 131–133°. Recrystallization from ethanol gave 7.10 g. (79%) of IVc, m.p. 133–134°. An analytical sample, obtained by recrystallization from ethanol, melted at 134–135°.

Anal. Calcd. for $C_{20}H_{17}FO$: C, 82.1; H, 5.9; F, 6.5. Found: C, 81.9; H, 5.9; F, 6.3.

From the acid fraction, 0.43 g. of IIIc, m.p. 161–163°, was recovered.

3-Fluoro-9,10-dimethyl-1,2-benzanthracene (Vc) A mixture of 6.00 g. of the methyl ketone (IVc) and 110 g. of polyphosphoric acid was heated with stirring at 85–90° for 1.5 hr. The reaction mixture was diluted with ice water and the hydrocarbon was extracted with ether. Chromatography in benzene–Skellysolve B under nitrogen over alumina afforded 3.70 g. (66%) of slightly yellow plates, m.p. 88–91°. By further chromatography, there was obtained 3.30 g. (59%) of pure Vc, as faintly colored plates, m.p. 92.5–93.0°. The purification must be carried out under nitrogen and/or in absence of sunlight to avoid formation of a peroxide which is apparently formed more easily from Vc than from Va or Vb.

Anal. Calcd. for $C_{20}H_{15}F$: C, 87.6; H, 5.5; F, 6.9. Found: C, 87.6; H, 5.6; F, 6.7.

3-Fluoro-9,10-dimethyl-1,2-benzanthracene peroxide. The compound, Vc (0.60 g.) was dissolved in benzene–Skellysolve B (1:1) and chromatographed over alumina with no precautions to exclude air or light. The eluate was evaporated to yield 0.54 g. of colorless plates, m.p. 91–150°. By fractional recrystallization from benzene–Skellysolve B (1:1), there was obtained 0.41 g. of the peroxide, m.p. near 206°, with decomposition.

Anal. Calcd. for $C_{20}H_{15}FO_2$: C, 78.4; H, 4.9; F, 6.2. Found: C, 78.2; H, 4.8; F, 6.3.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEMPLE UNIVERSITY]

Substituted 1,10-Phenanthrolines, XII. Benzo and Pyrido Derivatives[1]

EMIL KOFT AND FRANCIS H. CASE

Received June 22, 1961

The synthesis of the following fused ring compounds is described—benzo [*b*]- and[*f*][1,10]phenanthrolines and the 5,6,-7,8-tetrahydro derivative of the latter; pyrido [3,2-*f*][1,7]phenanthroline; quino[8,7-*b*][1,10] phenanthroline.

It has been shown by analytical tests that 5,6-dimethyl-(I) and diethyl-1,10-phenanthroline, previously prepared in this laboratory, are sensitive reagents for the detection of Fe(II). The object of the present work was to provide 1,10-phenanthrolines with six-membered rings fused across the 5 and 6 positions.

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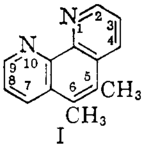
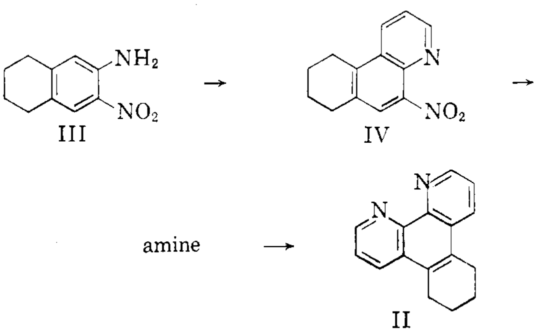
(1) This work was supported by a grant from the Committee on Research and Publications of Temple University.

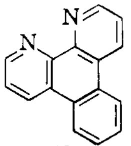


I

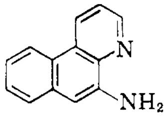
The synthesis of 5,6,7,8-tetrahydrobenzo[*f*][1,10]phenanthroline (II) was accomplished through the following series of conversions: 2-amino-3-nitro-5,6,7,8-tetrahydronaphthalene (III) (prepared from 2-acetyl-5,6,7,8-tetrahydronaphthalene by a series of reactions described in the literature[2]) was converted by a Skraup reaction to 5-nitro-7,8,9,10-tetrahydrobenzo[*f*]quinoline (IV). After reduction to the amine another Skraup reaction yielded II.



Benzo[*f*][1,10]phenanthroline (V) was prepared by a modified Skraup[3] reaction on 5-aminobenzo[*f*]quinoline (VI), prepared by Barnum and Hamilton[4] in a series of reactions starting with 2-amino-3-naphthoic acid.

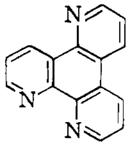


V

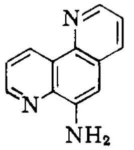


VI

For the preparation of pyrido[3,2-*f*][1,7]phenanthroline (VII) one approach would be a Skraup reaction on 5-amino-1,10-phenanthroline, which we prepared from the nitro derivative.[5] However, a more promising method proved to be the use of a Skraup reaction on 6-amino-1,7-phenanthroline (VIII), previously prepared by a series of reactions from 5-amino-8-hydroxyquinoline.[6]

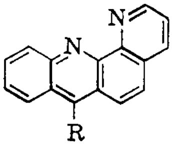


VII

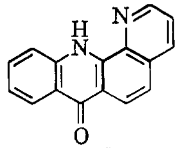


VIII

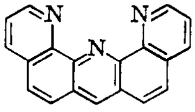
Of the three possible benzo-1,10-phenanthrolines, the benzo-*c* isomer has previously been described[7] and the *f*-isomer appears in this paper. We have also prepared the *b*-isomer (IX) by hydrogenation of 7-chlorobenzo[*b*][1,10]phenanthroline (X), previously obtained from *o*-chloroanthranilic acid and 8-aminoquinoline.[8] We have prepared X by reduction of 4-nitroacridone[9] to the amino derivative followed by a Skraup reaction forming benzo[*b*][1,10]phenanthrolin-7[12*H*]-one (XI) and treatment of this with a phosphorus pentachloride–phosphoryl chloride mixture. By reduction of the above aminoacridone to the aminoacridine, followed by a Skraup reaction, IX was also obtained.



IX; R = H
X; R = Cl



XI



XII

With the object of preparing quino[8,7-*b*][1,10]phenanthroline (XII), 4,5-diaminoacridine[10,11] was subjected to a double Skraup reaction. As this was at first unsuccessful, a similar reaction was successfully run on the corresponding diaminoacridone[10,11] yielding the quinophenanthrolinone. However, this could not be reduced either by zinc, or by sodium in amyl alcohol. Furthermore, it could not be converted to a chloride with phosphoryl

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(2) J. H. von Rij, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **70**, 236 (1951).

(3) H. L. Yale and J. Bernstein, *J. Am. Chem. Soc.*, **70**, 254 (1948).

(4) E. R. Barnum and C. S. Hamilton, *J. Am. Chem. Soc.*, **64**, 540 (1942).

(5) G. F. Smith and F. W. Cagle, *J. Org. Chem.*, **12**, 781 (1947).

(6) R. D. Howarth and W. O. Sykes, *J. Chem. Soc.*, 311 (1944).

(7) F. H. Case, *J. Org. Chem.*, **21**, 1069 (1956).

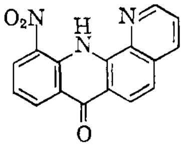
(8) J. Dobson and W. Kermack, *J. Chem. Soc.*, 150 (1946).

(9) G. R. Clemo, W. H. Perkin, and R. Robinson, *J. Chem. Soc.*, 1770 (1924).

(10) A. Goldberg and W. Kelly, *J. Chem. Soc.*, 597 (1947).

(11) E. R. Klein and F. N. Lahey, *J. Chem. Soc.*, 1418 (1947).

chloride. Attempts to cyclize the double condensation product of 4,5-diaminoacridine with ethylethoxymethylene malonate were also unsuccessful. By condensing 8-aminoquinoline with the potassium salt of 2-bromo-3-nitrobenzoic acid[12] and cyclizing the resulting acid we prepared 11-nitrobenzo[*b*][1,10]phenanthrolin-7[12*H*]-one (XIII) which was reduced to the amine. This, however, could not be reduced to the acridine, although it yielded the previously described quinophenanthrolinone in a Skraup reaction.



XIII

Recently we have prepared XII by a double Skraup reaction on 4,5-diaminoacridine, in which *m*-nitrobenzenesulfonic acid was used as the oxidizing agent instead of arsenic acid.

EXPERIMENTAL[13]

5-Nitro-7,8,9,10-tetrahydrobenzo[f]quinoline. A mixture of 18 g. (0.094 mole) of 2-amino-3-nitro-5,6,7,8-tetrahydronaphthalene, 15 g. (0.066 mole) of arsenic pentoxide 37.6 g. of concentrated sulfuric acid, and 7 ml. of water was heated to 100° with stirring. Thirty-six grams (0.37 mole) of glycerol was added in 10 minutes, the temperature rising to 110°. The reaction mixture was slowly heated to 135–140° and maintained at that temperature for 2 hr. It was then cooled, poured on ice, and neutralized with 30% sodium hydroxide solution. The black precipitate (14 g.) was removed by filtration. The aqueous solution was extracted with boiling benzene which was then used to extract the precipitate. Treatment of the benzene with Darco followed by concentration and addition of petroleum ether precipitated 10 g. of material melting at 150–155°. Crystallization from benzene-hexane yielded 8 g. (37.4%) of product melting at 161.5–162.5°.

Anal. Calcd. for $C_{13}H_{12}N_2O_2$: C, 68.40; H, 5.30. Found: C, 68.42; H, 5.27.

5-Amino-7,8,9,10-tetrahydrobenzo[f]quinoline. The nitro compound (14.5 g.) and stannous chloride dihydrate (43.1 g.) were dissolved in 800 ml. of ethanol and refluxed for 3 hr. The excess alcohol was removed by distillation and the residue made alkaline with sodium hydroxide solution. Extraction with ether followed, and on removal of the ether, the residue was crystallized from hexane; yield, 7.3 g. (58%), melting point 83–84.5°.

Anal. Calcd. for $C_{13}H_{14}N_2$: C, 78.76; H, 7.12. Found: C, 78.60; H, 7.22.

5,6,7,8-Tetrahydrobenzo[f]1,10-phenanthroline. A mixture of 8.3 g. (0.041 mole) of 5-amino-7,8,9,10-tetrahydrobenzo[*f*]quinoline, 3 ml. of water, 9 ml. of concentrated sulfuric acid, and 6.66 g. (0.029 mole) of arsenic pentoxide was heated with stirring to 100°. After addition of 16 g. (0.17 mole) of glycerol the temperature was gradually raised to 140° where it was maintained for two hours. The reaction mixture was then poured on cracked ice and made alkaline with 30% sodium hydroxide solution. The aqueous portion was decanted from the tarry residue and extracted three times with hot benzene. The benzene was then used to extract the dried residue. Treatment of the benzene extracts with Darco and concentration of the benzene solution yielded 3.3 g. of crude product melting at 210–212°. Crystallization from benzene yielded 2.1 g. (21.4%) melting at 218–219.5°.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02. Found: C, 81.92; H, 6.03.

Benzo[f]1,10-phenanthroline. A mixture of 5 g. of 5-aminobenzo[*f*]quinoline, (0.026 mole), 6.8 g. of arsenic acid (0.05 mole), and 38 ml. of 85% phosphoric acid was heated with stirring to 100°. Freshly distilled acrolein (6.6 g., 0.11 mole) was slowly added at this temperature. The reaction was maintained at 99–101° for 30 min., then poured on ice, and made alkaline in the cold with excess of solid potassium hydroxide. The solid precipitating was separated by filtration and dried. The aqueous solution was extracted with hot benzene which was used to extract the solid material. The benzene solution was treated with Darco, and on concentration yielded 1.5 g. of semisolid material. Crystallization from benzene yielded 0.9 g. (15.2%) of product melting at 180–181°.

Anal. Calcd. for $C_{16}H_{10}N_2$: C, 83.45; H, 4.38. Found: C, 83.47; H, 4.34.

5-Amino-8-hydroxyquinoline hydrosulfate. Sulfanilic acid was coupled with 72.5 g. (0.5 mole) of 8-hydroxyquinoline according to the directions of Fischer and Renouf.[14] The following procedure was found to be more convenient than that originally described for the reduction. The moist azo compound was transferred to a 3-l. beaker containing 88.2 g. (22 moles) of sodium hydroxide dissolved in 500 ml. of water. Sodium hydrosulfite (25 g.) was added, and after frothing subsided, 207 g. (total moles, 1.1) of additional reducing agent was added at once. After heating to 70° and allowing to cool, the solids were filtered, washed with cold 1% sodium hydrosulfite solution, and finally with a little ice water. The precipitate was then stirred into a cold dilute sulfuric acid solution and the precipitated sulfate filtered off. One crystallization from water yielded 35 g. (28%). The free base liberated from the above salt melted at 142–143°.

Pyrido[3,2-f][1,7]phenanthroline. A mixture of 6.5 g. of 6-amino-1,7-phenanthroline,[6] (0.033 mole), 2.3 ml. of water, 7 ml. of concentrated sulfuric acid, and 5.3 g. of arsenic pentoxide was heated in a stirred reaction flask to 100°. Glycerol (12.1 g., 0.132 mole) was added in 10 min. and the mixture slowly heated to 140° where it was maintained for 3 hr. The partially cooled reaction mixture was poured on ice, neutralized with 30% sodium hydroxide solution, and the aqueous phase decanted from the resulting tar. The aqueous solution and the tarry residue were extracted repeatedly with hot benzene. The benzene solution was treated with Darco and concentrated, yielding 3 g. of crude product. Crystallization from water yielded 1.2 g. (15.7%) of product melting at 199–200°.

Anal. Calcd. for $C_{15}H_9N_3$: C, 77.90; H, 3.92. Found: C, 77.81; H, 4.10.

5-Amino-1,10-phenanthroline. To a solution of 34 g. of stannous chloride dihydrate in 250 ml. of ethanol was added 11 g. of 5-nitro-1,10-phenanthroline,[5] and the mixture refluxed for 4 hr. After removal of most of the ethanol, the mixture was made alkaline with sodium hydroxide, and the precipitate removed by filtration and dried. On crystallization from ethanol, 33 g. of product was obtained melting at 259–260°.

Anal. Calcd. for $C_{12}H_9N_3$: C, 73.85; H, 4.62. Found: C, 73.80; H, 4.28.

4-Aminoacridone. A mixture of 21.3 g. of 4-nitroacridone,[9] 150 ml. of concentrated hydrochloric acid, and 90 g. of stannous chloride dihydrate was heated for 3 hr. on the steam bath. It was then made strongly alkaline, the precipitate removed by filtration, and dried. In this way there was obtained 18.5 g. of crude product, m.p. 347–348° (dec.).

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(12) *Org. Syntheses,* **7,** 12 (1927).

(13) All melting points reported are uncorrected.

(14) P. Fischer and E. Renouf, *Ber.,* **17,** 1643 (1884).

A pure sample, crystallized from ethanol, melted at 355° (dec.) [lit.,[15] 355° (dec.)].

Benzo[b][1,10]phenanthrolin-7[12H]-one. A mixture of 28.4 g. of crude 4-aminoacridone, 19.2 g. of arsenic acid hemihydrate, 43.2 ml. of concentrated sulfuric acid, and 14.4 ml. of water was heated to 100°. To the stirred mixture 52.8 g. of glycerol was then added during 10 min., the temperature rising to 110°. The mixture was then heated at 130–140° for 2.5 hr. The cooled contents of the flask were made alkaline, and the precipitate removed by filtration and dried. Repeated extraction with chloroform, followed by crystallization of the residue from methyl cellosolve yielded 17.5 g. of product melting at 271–272° (lit.[8] 273°).

7-Chloro-benzo[b][1,10]phenanthroline A mixture of 6 g. of benzo[*b*][1,10]phenanthrolin-7[12*H*]-one, 60 ml. of phosphoryl chloride, and 15 g. of phosphorus pentachloride was refluxed for 5–6 hr. It was then poured on ice, made alkaline with dilute ammonium hydroxide, the precipitate removed by filtration, and dried. Extraction with benzene yielded 5.2 g. of crude product, m.p. 160°. Crystallization from benzene afforded a pure specimen, m.p. 163–164° (lit.[8] 165°).

4-Aminoacridine. As the reduction[9] of 4-nitroacridone to 4-aminoacridine did not give good results, the following procedure was used. To a stirred mixture of 16 g. of crude 4-aminoacridone, 192 ml. of 95% ethanol, 13 ml. of water and 16 g. of sodium bicarbonate at 60–70° was added 70.4 g. of 5% sodium amalgam during four hours. Heating was then continued for one hour at reflux. The mixture was then poured on ice, the precipitate removed by filtration and dried. Extraction with petroleum ether yielded 7 g. of product melting at 103° (lit.[9] 105–106°). In another run, the melting point of the product was 113–114° (lit.[9] 114° for the acridan). For use in the subsequent Skraup reaction both forms could be used, as the acridan would be oxidized.

Benzo[b][1,10]phenanthroline. Method A. A mixture of 3.5 g. of 7-chloro-benzo[*b*][1,10]phenanthroline, 2 g. of 10% palladium on charcoal, 120 ml. of 95% ethanol, and 10 ml. of 10% potassium hydroxide was shaken for 3 hr. under 30 lb. pressure of hydrogen. Absorption of one pound was noted. After removal of the catalyst by filtration and evaporation to dryness, the residue was extracted with benzene. The residue from the removal of the benzene was heated one hour on the steam bath with a solution of 1 g. of potassium dichromate in 30 ml. of glacial acetic acid and 6 ml. of water, to oxidize any acridan formed. The mixture was poured on ice, made alkaline, the precipitate removed by filtration, and dried. The residue from benzene extraction was crystallized from ethanol-water, yielding 1.1 g., m.p. 113° (dec.). A sample heated at 100° for two hours melted at 136–138°.

Anal. Calcd. for $C_{16}H_{10}N_2 \cdot 2H_2O$: C, 72.17; H, 5.30. Found: C, 72.73; H, 5.21. After 24-hr. heating at 100°, Calcd. for $C_{16}H_{10}N_2$: C, 83.44; H, 4.38. Found: C, 83.03; H, 4.34.

Method B. To a stirred mixture of 13 g. of 4-aminoacridine, 19 g. of arsenic acid hemihydrate, and 67 ml. of 85% phosphoric acid warmed to 100° was added 10 ml. of acrolein at such a rate that the temperature did not rise more than 1°. Heating was continued for 1 hr. at 110°. The mixture was then made alkaline with potassium hydroxide solution, the precipitate removed by filtration, and dried. The residue from extraction with benzene was crystallized from ethanol-water, yielding 1.3 g., m.p. 113° (dec.). This was shown by mixed melting point to be identical with the product prepared in *Method A.*

Quino[8.7-b][1,10]phenanthrolin-7(14H)-one. A mixture of 15.2 g. of crude 4,5-diamino acridone,[10,11] 19.2 g. of arsenic acid hemihydrate, 43.2 ml. of concentrated sulfuric acid, and 14.4 ml. of water was heated to 100°. To the stirred mixture 52.8 g. of glycerol was added during 10 min., the temperature rising to 110°. The mixture was then heated at 130–140° for three hours. The cooled contents of the flask were made alkaline, and the precipitate removed by filtration and dried. Repeated extraction with chloroform, followed by crystallization of the residue from dimethyl formamide, yielded 6.1 g. (30.5%) of product melting at 325–326°.

Anal. Calcd. for $C_{19}H_{11}ON_3$: C, 76.77; H, 3.70. Found: C, 76.67; H, 3.67.

4,5-Bis(β-dicarbethoxyvinylamino)acridine. A mixture of 25 g. of ethylethoxymethylene malonate and 11.5 g. of 4,5-diaminoacridine was heated on the steam bath for 3 hr. The solid which separated on cooling was crystallized from benzene, yielding 15 g. of product melting at 183°. On heating in Dowtherm this compound did not yield any identifiable product.

Anal. Calcd. for $C_{29}H_{31}N_3O_8$: C, 63.39; H, 5.65. Found: C, 63.46; H, 5.73.

3-Nitro-2-(8'-quinolylamino)benzoic acid. A mixture containing the dry potassium salt made by neutralizing 24.6 g. of 2-bromo-3-nitrobenzoic acid,[12] 7.2 g. of anhydrous potassium carbonate, 20 g. of 8-aminoquinoline, 0.5 g. of copper powder, and 100 ml. of *n*-butyl alcohol was heated under reflux at 120° for 3 hr. After cooling, the precipitate was removed by filtration, washed with acetone, and dried. It was then dissolved in about 2 l. of hot water, filtered to remove impurities, cooled, and acidified with hydrochloric acid. The resulting precipitate was removed by filtration, dried (15.5 g.), and used in the next step. A sample, crystallized from ethanol-water, melted at 205–206°.

Anal. Calcd. for $C_{16}H_{11}N_3O_4$: C, 62.14; H, 3.56. Found: C, 62.55; H, 3.46.

11-Nitrobenzo[b][1,10]phenanthrolin-7[12H]-one. A 15.5-g. sample of the above acid was added to 120 ml. of concentrated sulfuric acid, and heated for 2 hr. on the steam bath. The mixture was poured on ice and the precipitate removed by filtration. It was then stirred with dilute ammonium hydroxide to remove unchanged acid. Recrystallization from dimethylformamide yielded 10.5 g. of acridone melting at 275–276°.

Anal. Calcd. for $C_{16}H_9N_3O_3$: C, 65.98; H, 3.19. Found: C, 65.81; H, 2.94.

Quino[8,7-b][1,10]phenanthroline. In an apparatus provided with stirrer and reflux condenser, a mixture of 7 g. of 4,5-diaminoacridine, 20 ml. of concentrated sulfuric acid, 7 ml. of water, and 16 g. of *m*-nitrobenzenesulfonic acid was heated to 100°. Glycerol (25 g.) was then added slowly, keeping the temperature below 140°. After 2-hr. heating at this temperature the mixture was made alkaline with sodium hydroxide, and the precipitate dried and extracted with chloroform. The chloroform solution was eluted through a column of activated alumina, the impurities being removed in the first fraction. Removal of solvent and crystallization from benzene yielded 1.7 g. (16.0%), m.p. 258°. The pure product melts at 259–260°. The product, which was a dihydrate, was dried at 110° *in vacuo* before analysis.

Anal. Calcd. for $C_{19}H_{11}N_3$: C, 81.12; H, 3.94. Found: C, 80.57; H, 4.05. Dihydrate: Calcd. for $C_{19}H_{11}N_3 \cdot 2H_2O$: C, 71.92; H, 4.73; N, 13.25. Found: C, 71.82; H, 4.68; N, 13.19.

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(15) F. Ullmann, *Ann.*, **355**, 329 (1907).