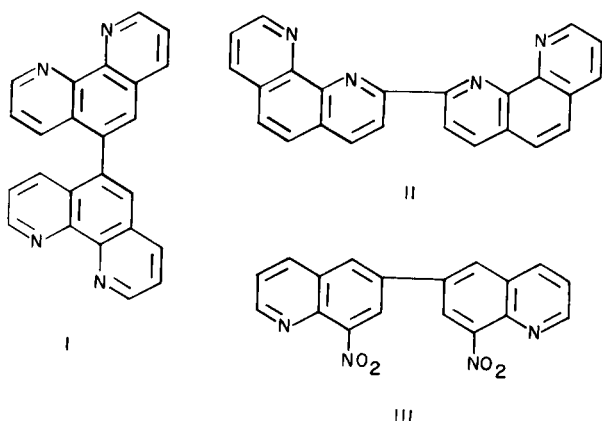


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The Synthesis of 2,2 and 5,5 -Bi(1,10-phenanthroline) (I)

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The well-known chelating ability of 1,10-phenanthroline and its derivatives for Fe(II) and Cu(I) have prompted the synthesis of 5,5'-bi(1,10-phenanthroline) (I) and 2,2'-bi(1,10-phenanthroline) (II).



The preparation of I was achieved by first subjecting 3,3'-dinitrobenzidine to a Skraup reaction, which yielded 8,8'-dinitro-6,6'-biquinoline (III). Reduction to the diamine followed by a second Skraup reaction produced the desired product. Earlier attempts to prepare I by treating 5-bromo-1,10-phenanthroline with copper were unsuccessful.

The preparation of II was accomplished by heating 2-chloro-1,10-phenanthroline (2) with copper powder.

EXPERIMENTAL

3,3' Dinitrobenzidine.

The following modification of the original procedure (3) was used: Bis *p*-toluenesulfonyl benzidine (4) (30 g.) was added slowly to 150 ml. of concentrated nitric acid keeping the temperature between 40 and 50°. The mixture was then poured on ice and filtered. After washing with water the precipitate was crystallized from aqueous dimethylformamide. The yield was 27 g. (76.1%) of product melting at 215° (the pure compound melts at 220°). The above material was hydrolyzed by dissolving it in 250 ml. of concentrated sulfuric acid, heating for two hr. on the steam bath, and pouring into ice water. The yield was 14.0 g. of product melting at 270° (lit. (3) 275°).

8,8' Dinitro-6,6'-Biquinoline (III).

A mixture of 16.6 g. of 3,3'-dinitrobenzidine, 17.6 g. of arsenic acid, 40 ml. of concentrated sulfuric acid and 13 ml. of water, was heated in a stirred reaction flask to 100°. Glycerol (48.4 g.) was added during 10 min. and the mixture heated at 130-140° for 2 hr. The contents of the flask were then poured on ice, neutralized with sodium hydroxide, and the precipitate collected by filtration. After drying it was extracted in a Soxhlet apparatus with chloroform. Removal of chloroform and crystallization from aqueous dimethylformamide yielded 4.4 g. (21.0%) of material melting at 353-354°. An analytical sample, crystallized from the same solvent, melted at 356-357°.

Anal. Calcd. for C₁₈H₁₀N₄O₄: C, 62.43; H, 2.89. Found: C, 62.28; H, 3.04.

8,8'-Diamino-6,6'-Biquinoline.

To a solution of 60 g. of stannous chloride dihydrate in 500 ml. of ethanol was added 11.7 g. of 8,8'-dinitro-6,6'-biquinoline (III), and the mixture refluxed for 5 hr. After removal of the ethanol, the mixture was made strongly alkaline with sodium hydroxide solution, diluted with water and filtered. The dried precipitate, after crystallization from ethanol, weighed 7.5 g. (77.6%). It melted at 197°. An analytical sample, crystallized from the same solvent, melted at 201-202°.

Anal. Calcd. for C₁₈H₁₄N₄: C, 75.52; H, 4.90. Found: C, 75.75; H, 5.17.

5,5'-Bi(1,10-phenanthroline) (I).

In an apparatus provided with stirrer and reflux condenser, a mixture of 9.6 g. of 8,8'-diamino-6,6'-biquinoline, 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 solution, and the precipitate removed by filtration, dried, and extracted with chloroform. Removal of chloroform and crystallization from ethanol yielded 3.9 g. (32.5%) of product melting at 336-337°. An analytical sample, crystallized from the same solvent, melted at 340-341°.

Anal. Calcd. for C₂₄H₁₄N₄: C, 80.45; H, 3.92. Found: C, 80.24; H, 4.05.

2,2'-Bi(1,10-phenanthroline) (II).

To 3.4 g. of 2-chloro-1,10-phenanthroline heated to 200° in a test tube provided with a stirrer, was added gradually 5 g. of copper powder. The temperature was then raised to 230°, where it was maintained for 1.5 hr., during which time the mixture hardened. After cooling, the hard cake was powdered, suspended in a saturated potassium cyanide solution, and allowed to stand overnight. After filtration and washing with water the dried precipitate was extracted with chloroform and the chloroform solution eluted over a column of activated alumina, the impurities being removed in the first fractions. Evaporation and crystallization from chloroform yielded 0.7 g. (24.6%) of product melting at 365-366°. The pure monohydrate, crystallized from the same solvent, melts at 370°.

Anal. Calcd. for C₂₄H₁₄N₄·H₂O: C, 76.60; H, 4.26; N, 14.90. Found: C, 76.48; H, 4.55; N, 15.11.

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