SYNTHESIS AND TRANSFORMATIONS OF 2-(2-QUINOLYL)CINCHONINIC ACID

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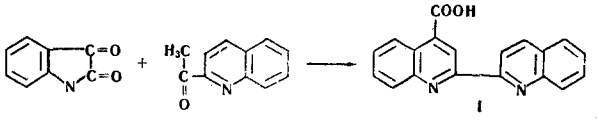
2-(2-Quinolyl)cinchoninic acid was synthesized, decarboxylated, and its isoamyl ester and diethylamide were obtained. The new compounds form colored Cu(I) complexes.

Two-ringed systems with two quinoline rings are known to be complexing agents which have unique specificity for Cu(I) ions. We have developed a simple method for the synthesis of 2-(2-quinolyl)cinchoninic acid (I) from isatin and 2-acetylquinoline and have found that both I and its derivatives – isoamyl ester and diethylamide – form intensely colored Cu(I) complexes. Of interest also is the ease of conversion of I to 2,2'-diquinolyl which, as is well known, is one of the best reagents for copper photometry [1,2].



I

EXPERIMENTAL

General Method for the Preparation of Cu(I) Complexes. A butanol solution of the complexing agent was stirred vigorously with an aqueous solution containing copper nitrate, acetate buffer (pH 6), and hydroxylamine hydrochloride. The butanol solution of the Cu(I) complex was separated and centrifuged, and its spectrum was obtained with an SF-4A spectrophotometer in 1-cm quartz cuvettes.

2-(2-Quinolyl)cinchoninic acid, in contrast to its ester and amide, forms a complex which is soluble not only in alcohol but also in water. In this case, the solution of the complex was obtained by the addition of an aqueous solution of the potassium salt of I to an aqueous solution containing copper nitrate, buffer, and hydroxylamine.

2-(2-Quinolyl)cinchoninic Acid (I). A mixture of 1.47 g (0.01 mole) of isatin and 12 ml of 35% aqueous potassium hydroxide was heated to the boiling point, 2.38 g (0.015 mole) of 2-acetylquinoline was added, and the mixture was heated with gentle refluxing for 1 h. A copious precipitate began to form from the hot solution, and the mixture was converted to a viscous mass on cooling. After steam distillation of the excess 2-acetylquinoline, the solution of the potassium salt of acid I was filtered and acidified with acetic acid. The resulting I was washed with water and reprecipitated to give 80% of a colorless, crystalline powder with mp 265-267° (decomp.). It was quite soluble in aqueous alkali solutions and moderately soluble on heating in organic solvents. Found %: N 9.4. $C_{19}H_{12}N_2O_6$. Calculated %: N 9.3. λ_{max}, nm (ε), Cu(I) complex of acid I: 554 (7400) in butanol, 554 (5400) in water.

2-(2-Quinolyl)cinchoninyl Chloride (II). A total of 3 g (0.01 mole) of I was refluxed for 2 h with 50 ml of thionyl chloride. The thionyl chloride was removed on a water bath, initially at normal pressure and then in vacuo. Compound II was yellow powder which was suitable for subsequent transformations without additional purification. Crystallization from dry benzene gave 94% of yellow needles with mp 230-235° (decomp.). Found %: N 8.9. $C_{19}H_{11}ClN_2O$. Calculated %: N 8.8.

Isoamyl 2-(2-Quinolyl)cinchoninate (III). A mixture of 3.2 g (0.01 mole) of II and 30 ml of isoamyl alcohol was refluxed for 3 h, and the alcohol was removed in vacuo (20 mm) on a boiling-water bath. The

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residual oil was dissolved in 50 ml of boiling ethanol, and hot water was added in small portions to the hot solution until it was slightly turbid. After 24 h the crystals of III were filtered, washed with water, and recrystallized to give 54% of long, colorless plates with mp 69° which were slightly soluble in water and quite soluble in organic solvents on heating. Found %: N 7.6. $C_{24}H_{22}N_2O_2$. Calculated %: N 7.6. UV spectrum of the Cu(I) complex of ester III in butanol: λ_{max} 550 nm (ε 7570).

2-(2-Quinolyl)cinchoninic Acid Diethylamide (IV). A mixture of 3.2 g (0.01 mole) of II and 60 ml of diethylamine was refluxed for 4 h, cooled, and the precipitate of IV was filtered, washed with diethylamine, dried, and crystallized from 50% aqueous ethanol to give 69% of colorless needles with mp 192° which were slightly soluble in water and quite soluble in organic solvents on heating. Found %: N 11.3. $C_{23}H_{21}N_3O$. Calculated %: N 11.2. UV spectrum of the Cu(I) complex of amide IV in butanol: λ_{max} 550 nm (ε 7570).

2,2-Diquinolyl. A total of 1.25 g (0.05 mole) of I was heated at 280-290° for 3 h. The cooled melt was ground into a powder and crystallized twice from isoamyl alcohol to give 50% of a product with mp 192-193°.

LITERATURE CITED

1. J. Hoste, J. Eeckhout, and J. Gillis, Anal. Chim. Acta, 9, 263 (1953).
2. R. Quest, Anal. Chem., 25, 1484 (1953).