

was collected by centrifugation, washed with 100 ml. of 80% ethanol and dried *in vacuo* over KOH. The yield was 258 mg. Fractions 102-112, containing about 225  $\mu$ moles of pentose in 259 ml. were adjusted to pH 6.5 with 1.5 ml. of saturated KOH solution and the barium salts precipitated with 1 ml. of *M* barium acetate and 300 ml. of ethanol. The precipitate, washed and dried as described for peak II, weighed 142 mg.

**Analytical Data.**—Aliquots of the dried barium salts were dissolved in dilute acid and analyzed for pentose, total organic phosphorus and acid labile phosphorus. On the basis of pentose content the products were approximately 80% pure: peak III, ribose 5-pyrophosphate:  $C_5H_8O_{11}Ba_2P_2$ ; pentose calcd. 29.3%, found 24.2%; peak IV, ribose 5-triphosphate:  $C_5H_8O_{11}Ba_3P_3$ ; pentose calcd. 22.7%, found 18.2%.

The results of phosphate analyses are shown in Table I. Very little inorganic phosphorus was present in either fraction and the ratios of organic phosphorus and acid labile phosphorus were consistent with the presence of pyrophosphate and triphosphate esters. The esters consumed 3.5 and 3.0  $\mu$ moles of periodate, respectively, per  $\mu$ mole of pentose which is consistent with esterification in the 5-position only. Paper chromatography in the solvent of Paladini and Leloir<sup>12</sup> separates ribose 5-phosphate ( $R_f = 0.52$ ) from the pyrophosphate ester ( $R_f = 0.42$ ) and triphosphate ester ( $R_f = 0.33$ ). The compounds were in the expected positions relative to one another, when compared with the corresponding uridine and adenosine derivatives.

TABLE I  
RATIO OF PHOSPHORUS TO PENTOSE IN THE BARIUM SALTS

Analysis <sup>a</sup>	Ribose 5-pyrophosphate		Ribose 5-triphosphate	
	$\mu$ moles per ml.	Molar ratio	$\mu$ moles per ml.	Molar ratio
Pentose	19.0	1.0	15.3	1.0
Inorganic phosphorus	0.9	..	1.3	..
Acid labile phosphorus <sup>b</sup>	18.2	0.96	29.3	1.92
Total organic phosphorus	40.0	2.10	48.3	3.15

<sup>a</sup> These analyses were carried out on solutions of the potassium salt obtained by dissolving the barium salt in dilute acetic acid and adding a slight excess of  $K_2SO_4$ . <sup>b</sup> Hydrolyzed by heating for 10 minutes at 100° in *N*  $H_2SO_4$ .

**Enzymatic Tests.**—The activity of ribose 5-pyrophosphate and ribose 5-triphosphate with spinach phosphoriboisomerase is shown in Table II. On the basis of the cysteine carbazole reaction<sup>13,14</sup> these esters appear to be converted to ribulose 5-pyrophosphate and ribulose 5-triphosphate since no inorganic phosphate was formed. However, the reaction products have not been isolated. The relative rates of reaction compared with ribose 5-phosphate were

(12) A. Paladini and L. Leloir, *Biochem. J.*, **51**, 426 (1952).

(13) Z. Dische and E. Borenfreund, *J. Biol. Chem.*, **192**, 583 (1951).

(14) B. Axelrod and R. Jang, *ibid.*, **209**, 847 (1954).

TABLE II

RATE OF REACTION WITH PHOSPHORIBOISOMERASE	
Substrate	Ketopentose formed <sup>a</sup>
Ribose 5-phosphate	10,000
Ribose 5-pyrophosphate	1,000
Ribose 5-triphosphate	395

<sup>a</sup> The incubation mixtures (0.7 ml.) contained 2.2  $\mu$ moles of substrate, 2  $\mu$ moles of cysteine, 70  $\mu$ moles of tris-(hydroxymethyl)-aminomethane buffer, pH 7.0 and phosphoriboisomerase. After 10 min. at 38° ketopentose was estimated by the cysteine-carbazole test<sup>13</sup> as modified by Axelrod and Jang.<sup>14</sup> In the case of ribose 5-pyrophosphate and ribose 5-triphosphate, 10  $\mu$ g. of protein was used; with ribose 5-phosphate the quantity of enzyme was 0.1  $\mu$ g. The enzyme solution contained 12 mg. of protein per ml. The quantity of ketopentose formed is calculated as  $\mu$ moles formed per ml. of enzyme in 10 minutes at 38°.

TABLE III

HYDROLYSIS OF RIBOSE PYROPHOSPHATE BY INOSINE DIPHOSPHATASE

Time, min.	Substrate	Inorganic phosphate formed, $\mu$ moles
30	Ribose pyrophosphate	0.25
85	Ribose pyrophosphate	.45
150	Ribose pyrophosphate	.50
346	Ribose pyrophosphate	.50
30	Inosine diphosphate	.40

<sup>a</sup> The incubation mixture (0.09 ml.) contained 0.035 ml. of 0.035 *M* veronal-acetate, pH 7, containing 0.004 *M*  $MgCl_2$ , 0.02 ml. of 0.15% albumin, 0.005 ml. of 0.33 *M* glutathione containing 0.002 *M* sodium ethylenediamine tetraacetate, 3.6  $\mu$ grams of purified inosine diphosphatase,<sup>4</sup> and 0.6  $\mu$ mole of ribose pyrophosphate or inosine diphosphate. Incubation was at 37.5°. Analysis for inorganic phosphate was by the method of Fiske and Subbarow.<sup>11</sup> In the absence of enzyme, less than 0.01  $\mu$ mole of inorganic phosphate was formed in 100 minutes with either substrate.

1.0 and 0.3%, respectively. In these experiments on prolonged incubation, approximately one-third of the ribose pyrophosphate and ribose triphosphate added was converted to ketopentose as measured by the cysteine-carbazole reaction.

As shown in Table III, ribose 5-pyrophosphate is cleaved by inosine diphosphatase.

The following enzyme systems were found to be inactive with either or both ribose 5-pyrophosphate and ribose 5-triphosphate: yeast hexokinase,<sup>8</sup> muscle myokinase<sup>15</sup> and phosphoribulokinase.<sup>3</sup> In the latter case, the determination was carried out in the presence of phosphoriboisomerase.

(15) S. P. Colowick and H. M. Kalckar, *ibid.*, **148**, 117 (1943).

BETHESDA, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES AND THE DEPARTMENT OF BIOCHEMISTRY, YALE UNIVERSITY]

## The Preparation and Metal Complexing of 2-(2'-Pyridyl)-10-hydroxybenzo[h]quinoline-4-carboanilide

BY THOMAS C. BRUCE<sup>1</sup>

RECEIVED AUGUST 3, 1956

A new type of chelating agent 2-(2'-pyridyl)-10-hydroxybenzo[h]quinoline-4-carboanilide (I) has been prepared and its solution complexes examined. In methanol, I formed 1:1 complexes which exhibited a relative order of stability:  $Cu^{II} > Ni^{II} > Co^{II} > Zn^{II} > Mn^{II} > Mg^{II}$ .

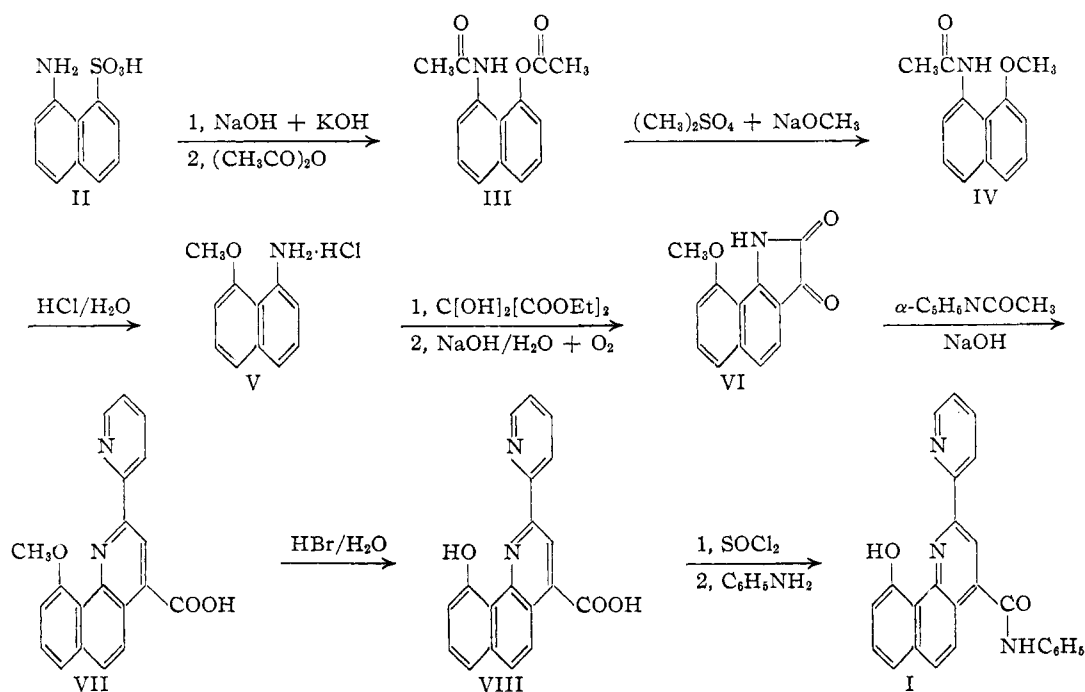
A chelating agent (I), combining the essential features of the extensively studied 8-hydroxy-

quinoline<sup>2</sup> and 2,2'-bipyridyl<sup>3</sup> systems, has been synthesized and examined as to its complexing with

(1) Lilly Postdoctoral Fellow in the Natural Sciences administered by the National Research Council, 1954-1955.

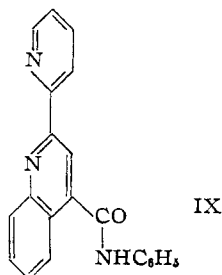
(2) J. P. Phillips, *Chem. Revs.*, **56**, 271 (1956).

(3) F. P. Dwyer and E. C. Gyarfas, *ibid.*, **54**, 959 (1954).



$\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$  and  $\text{Mg}^{\text{II}}$ . The conversions which led to I are shown in the diagram. The transformation of II to V has been reported previously, but the details of the literature method were found to be inadequate. Revised procedures for the alkaline fusion of II and subsequent conversions leading to V are included in the Experimental section, as is an improved synthesis of  $\alpha$ -pyridyl methyl ketone. For the preparation of VII a ratio of base to VI larger than that normally employed in Pfitzinger reactions is essential.

For spectroscopic examination, compound I was dissolved in a small amount of hot 1-butanol and made up to volume with methanol. The absorption maximum of I at  $390 \text{ m}\mu$  was decreased in the presence of metal salts with the appearance of new maxima at longer wave length (Fig. 1). From continuous variation studies<sup>4</sup> (Fig. 2) it was found that I forms 1:1 complexes with  $\text{Cu}^{\text{II}}$ ,  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$ . The normal chelate compounds of 8-hydroxyquinoline have the formulas<sup>2</sup>  $\text{M}(\text{C}_9\text{H}_6\text{NO})_n$ , in which  $n$  is the valence of the metal M, and 2,2'-bipyridyl<sup>3</sup> generally forms complexes of the formulas  $\text{M}(\text{C}_{10}\text{H}_8\text{N}_2)_{2-3}(\text{X}^-)_n$ . The formation of only 1:1 complexes by I may be due to steric factors since 2-(2'-pyridyl)-cinchoninic acid anilide (IX) forms complexes containing only 1 or 2 molecules of chelating agent (Table I, see also p. 994 of ref. 3).



(4) P. Job, *Compt. rend.*, **180**, 928 (1925).

In solution equimolar in I and metal salt (Fig. 1) the order of suppression of the  $390 \text{ m}\mu$  peak and increase in intensity of the absorbance at longer

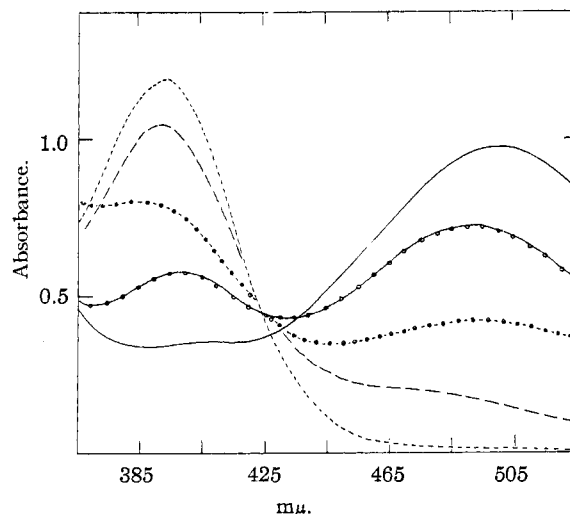


Fig. 1.—Spectra of I (---), I and  $\text{Cu}^{\text{II}}$  (—), I and  $\text{Ni}^{\text{II}}$  (—●—●—●—), I and  $\text{Co}^{\text{II}}$  (—●—●—●—) and I and  $\text{Zn}^{\text{II}}$  (—). The concentration of all reactants were at  $1.25 \times 10^{-4} \text{ M}$ . and the solvent was 10% 1-butanol in methanol (v./v.).

wave length was:  $\text{Cu}^{\text{II}} > \text{Ni}^{\text{II}} > \text{Co}^{\text{II}} > \text{Zn}^{\text{II}} > \text{Mn}^{\text{II}}$  and  $\text{Mg}^{\text{II}} = 0$ . In the presence of a great excess of metal to I, suppression of the  $390 \text{ m}\mu$  peak and increase in intensity of absorbance at longer wave length followed the same order as before, with the exception that  $\text{Zn}^{\text{II}}$  brought about the most intense absorption. Chelation with  $\text{Mn}^{\text{II}}$  but not  $\text{Mg}^{\text{II}}$  was now detectable. The absorbance vs. wave length curves were found to be much the same whether the chloride or the nitrate salts were employed. From these results as well as

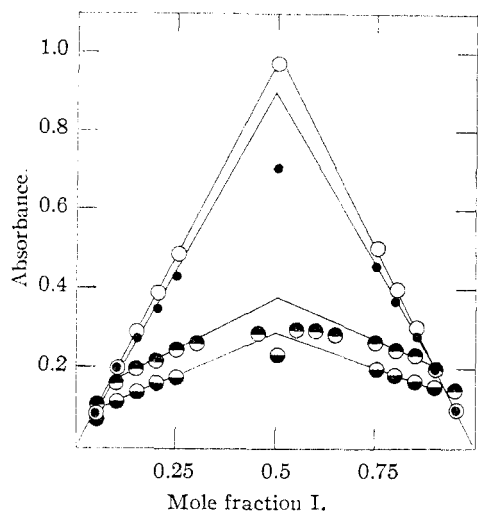


Fig. 2.—Continuous variation study of I with  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$  and  $\text{Co}^{\text{II}}$ : O,  $\text{Cu}^{\text{II}}$  at 500  $\text{m}\mu$ ,  $c\ 2.5 \times 10^{-4}\ M$ ; ●,  $\text{Zn}^{\text{II}}$  at 460  $\text{m}\mu$ ,  $c\ 2.5 \times 10^{-4}\ M$ ; ●,  $\text{Ni}^{\text{II}}$  at 490  $\text{m}\mu$ ,  $c\ 2.5 \times 10^{-4}\ M$ ; ●,  $\text{Co}^{\text{II}}$  at 490  $\text{m}\mu$ ,  $c\ 1.25 \times 10^{-4}\ M$ . Solvent was 10% 1-butanol in methanol (v./v.).

from the deviation from linearity of the mole fraction vs. absorbance curves, at ratios of reactants of 1.0, it may be inferred that the stability of the chelates of I decreases in the order:  $\text{Cu}^{\text{II}} > \text{Ni}^{\text{II}} > \text{Co}^{\text{II}} > \text{Zn}^{\text{II}} > \text{Mn}^{\text{II}} > \text{Mg}^{\text{II}}$ . The extent of the bathochromic shift of the 390  $\text{m}\mu$  peak of I which is brought about by chelation also follows this order. However, as noted previously, the intensity of absorbance is greatest in the case of the complex formed with  $\text{Zn}^{\text{II}}$ . The relative stabilities of the chelates of 8-hydroxyquinoline and 2,2'-bipyridyl also follow this same general order.<sup>2,3</sup>

TABLE I

CONTINUOUS VARIATION STUDIES WITH IX IN METHANOL

Metal ion <sup>c</sup>	$\text{m}\mu$	Ratio of IX to $\text{M}^{\text{II}}$ ( $p$ )
$\text{Cu}^{\text{II}}$	337	1.6, <sup>a</sup> 1.5 <sup>b,d</sup>
$\text{Ni}^{\text{II}}$	373	2.1 <sup>a</sup>
$\text{Co}^{\text{II}}$	363	1.0, <sup>a</sup> 1.1 <sup>a</sup>
$\text{Zn}^{\text{II}}$	364	1.0 <sup>a,d</sup>

<sup>a</sup>  $c = 5 \times 10^{-4}\ M$ . <sup>b</sup>  $c = 2.5 \times 10^{-4}\ M$ . <sup>c</sup> As metal chloride. <sup>d</sup> A value of  $p = 1.0$  for  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  would agree with the elemental analysis of the  $\text{Cu}^{\text{II}}$  and  $\text{Zn}^{\text{II}}$  complexes of IX, as prepared from methanol (see Experimental).

### Experimental<sup>5</sup>

**O-Methyl-*peri*-naphtholamine Hydrochloride (V).**—One hundred and twenty grams each of potassium hydroxide and sodium hydroxide were added to 200 ml. of water in a vessel prepared by shaping 0.005 gage sheet copper around a 1-l. beaker. The contents of the copper container were heated to 100° when 40 g. (0.18 mole) of *peri*-naphthylaminesulfonic acid<sup>6</sup> was added. With intermittent stirring the contents of the copper beaker were heated to 225–230° at a rate commensurate with the frothing of the reaction mixture. The reaction mixture was held at this temperature, with intermittent stirring, until such time that the fusion mixture acquired the characteristics of a cherry-red solution overlaid by a black froth (the entire operation requiring about 7 hr.). The froth was ladled into a thick-walled 1-l. flask and allowed to cool.

To the cooled fusion product there was added dropwise a solution of 100 ml. each of acetic acid and acetic anhydride.

(5) All melting points are uncorrected. The analyses were performed by Miss Heather King of U.C.L.A.

(6) Eastman product.

When the reaction had subsided 100 ml. of additional acetic anhydride was added and the mixture refluxed for 1 hr., cooled somewhat and poured into 1.5 l. of water. After several hours the crude O,N-diacetyl-*peri*-aminonaphthol (III) was collected at the pump and dried *in vacuo* over sodium hydroxide and calcium chloride.

Without purification the crude product was suspended in 250 ml. of absolute methanol containing 6.8 g. (0.176 mole) of sodium methoxide. Solution was completed with gentle heating and there was added dropwise 12 ml. (0.128 mole) of methyl sulfate. After refluxing for 4 hr. the addition of sodium methoxide and methyl sulfate were repeated and the reaction mixture refluxed for an additional 4 hr. The solvent was aspirated off and the residue triturated with benzene. The benzene solution was washed with 10% potassium carbonate solution and dried over anhydrous potassium carbonate. The solution was next passed through a 4"  $\times$  1" alumina column, which was subsequently washed with two column volumes of dry benzene. The combined filtrate and washings were aspirated to dryness and the crude O-methyl-N-acetyl-*peri*-aminonaphthol (IV) recrystallized from acetone (6.0 g., 15.5%), m.p. 130–131° (lit.<sup>7</sup> 128°).

The product IV without further purification was refluxed with 6 *N* hydrochloric acid (10 ml. for each gram of IV) for 10 hr. Upon cooling silvery needles of V precipitated. After collecting and drying, there was obtained 5.24 g. (overall yield 13.9%).

**$\alpha$ -Pyridyl Methyl Ketone.**—Ethyl  $\alpha$ -picolinate was obtained from  $\alpha$ -picolinic acid hydrochloride<sup>8</sup> by the general Fischer esterification technique (200 g. of picolinic acid hydrochloride (1.18 moles), 16 ml. of concentrated sulfuric acid and 1.5 l. of absolute ethanol (41.2 moles) yielded 147 g. (90%) of ethyl  $\alpha$ -picolinate, b.p. 99–100°, at a bath temperature of 125° and 1.6 mm. (lit. 240–241° at 760 mm.<sup>9</sup>).

Sixty-eight ml. (0.50 mole) of the ester, prepared as above, was added dropwise, with vigorous shaking, to a fine suspension of 44 g. (0.815 moles) of sodium methoxide in 700 ml. of dry benzene and 140 ml. (1.77 moles) of commercially anhydrous ethyl acetate. The ensuing exothermic reaction was accompanied by the solution of the sodium methoxide and the concomitant appearance of an orange color. The orange color quickly faded and within a few minutes the entire mass solidified. The reaction mixture was allowed to cool, 250 ml. of concentrated hydrochloric acid added and the suspension heated to reflux with intermittent shaking. After 4 hr. reflux the contents of the flask were cooled, the organic layer separated from the aqueous phase and neutralized with solid sodium carbonate. The aqueous and organic suspension were filtered and the inorganic salts and the aqueous filtrate were both thoroughly washed with ether to remove residual ketone. The organic phase and the ether washings were combined and dried over anhydrous sodium carbonate. After the removal of solvent, over steam, the residue was distilled (b.p. 42.5° at a bath temp. of 60–80° and 2.2 mm., lit.<sup>10</sup> 187–190° at 760 mm.). In this manner there was obtained 46.8 g. (77.5%) of  $\alpha$ -methyl pyridyl ketone (lit.<sup>8</sup> 50% of theory).

**8-Methoxybenz[*g*]indoline-2,3-dione (VI).**—To 120 ml. of glacial acetic acid, contained in a round-bottom flask fitted with reflux condenser and calcium chloride drying tube, there was added 3.2 g. (0.015 mole) of V. The flask was warmed gently until solution of V was complete and then 2.88 g. (0.016 mole) of diethyl mesoxalate<sup>11</sup> was added. After 1 hr. of refluxing all solvent was removed at the aspirator and the residual tar washed several times with 1 *N* hydrochloric acid and taken up in 200 ml. of 5% potassium hydroxide solution by shaking. A slow stream of air was passed through the solution for 8 hr. and the resultant yellow solution acidified to congo red with hydrochloric acid. After 1 hr. of refrigeration the crude product was filtered off and dried over calcium chloride *in vacuo*. After recrystallization from boiling pyridine, VI (1.8 g., 57%) was obtained as brown needles which reflect red, m.p. 272–273°. After several further recrystallizations from a 1:1 mixture of pyridine and ethanol the melting point remained unchanged.

(7) Fr. Fichter and R. Gageur, *Ber.*, **39**, 3331 (1906).

(8) A. W. Singer and S. M. McElvain, *THIS JOURNAL*, **57**, 1136 (1935).

(9) R. Camps, *Arch. Pharm.*, **240**, 345 (1902).

(10) H. G. Kolloff and J. H. Hunter, *THIS JOURNAL*, **63**, 492 (1941).

(11) A. W. Dox, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 266.

*Anal.* Calcd. for  $C_{18}H_{13}O_3N$ : C, 68.72; H, 3.99. Found: C, 68.86; H, 4.15.

**2-(2'-Pyridyl)-10-methoxybenzo[h]quinoline-4-carboxylic Acid (VII).**—A solution of 1.4 g. (0.0066 mole) of VI in 60 ml. of 5% aqueous potassium hydroxide solution and 90 ml. of 95% ethanol was brought to reflux when there was added 7.3 g. (6.7 ml., 0.061 mole) of  $\alpha$ -pyridyl methyl ketone. Refluxing was continued for 24 hr.; the solvent was removed under vacuum and the residual tar repeatedly extracted with hot 2% aqueous potassium hydroxide solution (chilling each time to solidify the tar so that the aqueous phase could be easily decanted) until the extract no longer gave a precipitate when acidified with acetic acid (care being taken not to add excess acid, otherwise unreacted VI precipitates). The suspension of crude product was heated on a steam-bath, refrigerated and the product collected at the pump. By this procedure there was obtained between 1.13 g. and 1.80 g. of VII (52–83% yield), m.p. 225°. An analytical sample was prepared by successive recrystallization from a large volume of glacial acetic acid by addition of water and by reprecipitation of the acid from a dilute solution of sodium hydroxide by acidification with acetic acid (charcoal), followed by drying at 100° over phosphorus pentoxide at 1 mm., m.p. 236–237°.

*Anal.* Calcd. for  $C_{20}H_{14}O_3N_2$ : C, 72.72; H, 4.27; N, 8.48. Found: C, 72.68; H, 3.80; N, 8.67.

The hydrochloride was prepared by allowing the analytical sample to equilibrate with hydrogen chloride gas, whereupon the yellow color of the base turned to the orange of the hydrochloride. The sample was found to revert from orange to yellow on heating to 211–216° and to sinter with decomposition and sublimation at 332–342°.

*Anal.* Calcd. for  $C_{20}H_{14}O_3N_2Cl$ : C, 65.49; H, 4.12; N, 7.63; Cl, 9.67. Found: C, 65.4; H, 4.1; N, 7.85; Cl, 9.97.

**2-(2'-Pyridyl)-10-hydroxybenzo[h]quinoline-4-carboxylic Acid (VIII).**—VII (2.3 g., 0.007 mole) was refluxed for 8 hr. with 20 ml. of 48% aqueous hydrobromic acid containing 1 ml. of hypophosphorous acid. The reaction mixture was diluted with water, chilled and the crude precipitate collected at the pump. The dark colored material was treated with hot dilute potassium hydroxide for 10 minutes and filtered. The precipitate was next suspended in water, made slightly acidic with acetic acid and again collected. After crystallization from boiling pyridine (charcoal) there was obtained, as yellow needles, 1.49 g. (67.5%) of material melting at 350–351°.

*Anal.* Calcd. for  $C_{19}H_{12}O_3N$ : C, 77.14; H, 3.87. Found: C, 77.36; H, 4.13.

**2'-(2'-Pyridyl)-10-hydroxybenzo[h]quinoline-4-carboanilide (I).**—One hundred mg. of VIII (0.00032 mole) was refluxed for 2 hr. with 7 ml. of anhydrous benzene containing

0.45 ml. (0.0023 mole) of thionyl chloride. The reaction mixture was chilled, and 1.4 ml. of aniline (0.052 mole) dissolved in 5 ml. of anhydrous benzene was added. After refluxing for an additional half-hour the mixture was chilled and poured into water. All solvent was evaporated by a stream of air and the amorphous yellow material collected and washed with dilute acetic acid. The product was then extracted with portions of boiling, dilute potassium carbonate solution until the extract remained colorless. The residue was dissolved in boiling dimethylformamide, the solution filtered hot, allowed to cool and once again filtered. The product was recovered by diluting the hot solution with water until just cloudy and then allowing to cool. After collecting and washing with water and dilute acetic acid and drying over calcium chloride, 86 mg. (70%) of a yellow material which melted at 300–301° with decomposition was obtained. For analysis the compound was dried for 5 hr. at 180° over phosphorus pentoxide at 1 mm.

*Anal.* Calcd. for  $C_{25}H_{17}O_3N_2$ : N, 10.71. Found: N, 10.56.

**Anilide of 2-(2'-Pyridyl)-cinchoninic Acid (IX).**—2-(2'-Pyridyl)-cinchoninic acid<sup>12</sup> was refluxed with excess thionyl chloride until all solid material had dissolved. Excess solvent was removed under vacuum and the residue warmed with an excess of aniline. After washing with dilute acetic acid the product was recrystallized from ethanol, methanol and acetone, m.p. 238°.

*Anal.* Calcd. for  $C_{21}H_{16}ON_2$ : N, 12.93. Found: N, 13.20.

The  $Cu^{II}$  and  $Zn^{II}$  chelates of IX were prepared by mixing dilute solutions of the metal halide and IX in methanol, collecting the precipitate and washing with large volumes of methanol, then drying at 100° over phosphorus pentoxide at 1 mm.

*Anal.* Calcd. for  $C_{21}H_{16}ON_2CuCl_2$ : C, 54.85; H, 3.29; Cl, 15.42. Found: C, 54.64; H, 3.52; Cl, 14.90.

*Anal.* Calcd. for  $C_{21}H_{16}ON_2ZnCl_2$ : C, 54.63; H, 3.28; Cl, 15.36. Found: C, 54.63; H, 3.57; Cl, 15.4.

**Continuous Variation Studies.**—Stock solutions of the metallic chlorides or nitrates (analytical grade) and the chelating agent were prepared and aliquots mixed in the proper ratios. Absorption measurements were made at selected wave lengths. Absorbance values were obtained by subtracting the absorbance for zero complexation from the observed readings, all measurements being carried out with a Beckman DU spectrophotometer. Formulas were determined from a plot of absorbance against the mole fraction of chelating agent employed (Fig. 2).

(12) S. P. Massie, *Iowa State Coll. J. Sci.*, **21**, 41 (1946).

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Quinol Imide Acetates. IV. The Reactions of 2,4-Dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide Acetate

By ROGER ADAMS AND EDWIN L. DEYOUNG<sup>1</sup>

RECEIVED SEPTEMBER 19, 1956

2,4-Dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate is formed by oxidation with lead tetraacetate of 2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene. The quinol imide adds hydrogen chloride, hydrogen bromide and acetic acid with formation of 3-substituted 2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalenes. On the other hand, hydrogen cyanide gives 2-acetoxy-1-cyano-2,4-dimethyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene, which with alkali is converted to 2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene and by acid to 1,1'-dicyano-4,4'-dimethyl-2,2'-dinaphthobenzyl ether. Lead tetraacetate converts 4-methyl-1-*p*-toluenesulfonamidonaphthalene to 4-methyl-*p*-naphthoquinol-*p*-toluenesulfonimide acetate.

### Benzoquinol imide acetates<sup>2</sup> and *o*-benzoquinol

(1) An abstract of part of a thesis submitted by Edwin L. DeYoung to the Graduate College of the University of Illinois, 1956, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy. Minnesota Mining and Manufacturing Co. Fellow, 1953–1956.

(2) R. Adams and K. R. Brower, *THIS JOURNAL*, **78**, 4770 (1956).

imide diacetates<sup>3</sup> have been shown to undergo many of the addition reactions typical of the quinone mono- and di-imides. Similar studies on

(3) R. Adams, E. J. Agnello and R. S. Colgrove, *ibid.*, **77**, 5617 (1955).