

8. *I. Langmuir*: Science 54, (1921) 65.
9. *F. F. Martens* and *F. Grünbaum*: Ann. Phys. 12, (1903) 984.
10. *T. Millner*: J. Hungarian Chem. Soc. 4, (1949) 224.
11. *L. C. Pauling*: J. Am. Chem. Soc. 53, 1391 (1931). The nature of the Chemical Bond. 1949 New York.
12. *M. L. Schultz* and *E. F. Lilek*: J. Am. Chem. Soc. 64, (1943) 2748, 71, 1418 (1949).
13. *Sigwick*, and *Bailey*: Proc. Roy. Soc. 144, (1934) 521.
14. *J. E. Stanworth*: J. Soc. Glass Techn. 32, (1948) 224.
15. *P. F. Váradi*: Acta Chem. Phys. Univ. Szeged, (1949) 175. Doctorate thesis Szeged, (1949) 2.

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## The structure of the complexes formed by cobaltous chloride with absolute organic solvents, according to an analysis of light-absorption curves plotted in the visible spectrum

By GEORGE VARSÁNYI

### *Introduction.*

According to Hantzsch, also Donnan and Basett, as well as Dirking, the blue colour of cobalt complexes is related to a coördination number of four, viz., there is no blue cobalt complex with a coördination number of six. The two complexes can be described by the formulae  $\text{CoCl}_2\text{L}_2$  and  $\text{CoCl}_2\text{L}_4$  respectively, as chlorine is situated in the coördination belt of the complex.

On the basis of research performed earlier in the Institute of Inorganic Chemistry of the University of Szeged, the view expressed above had to be rejected. My own research appears to substantiate this rejection, as the existence of blue cobaltous chloride complexes with a coördination number of six can be regarded as proven, on the basis of spectrophotometric analysis of anhydrous cobaltous chloride in various organic solvents and the application of suitable methods of calculation.

In order to investigate the problem, I have observed the visible-light absorption of anhydrous cobaltous chloride in methyl-, ethyl-, propyl-, butyl-, and amylalcohol, as well as pyridine. A considerable part of my investigation consists of the measurements performed on cobaltous chloride dissolved in a mixture of pyridine and ethylalcohol, the alcohol of the highest dipolemoment, and those performed in the two latter solvents both pure and mixed in the presence of excess chlorine.

In obtaining my data I have used the König—Martens—Grünbaum photometer.

I have plotted the absorption spectrum of the solution of anhydrous cobaltous chloride in ethylalcohol at a con-

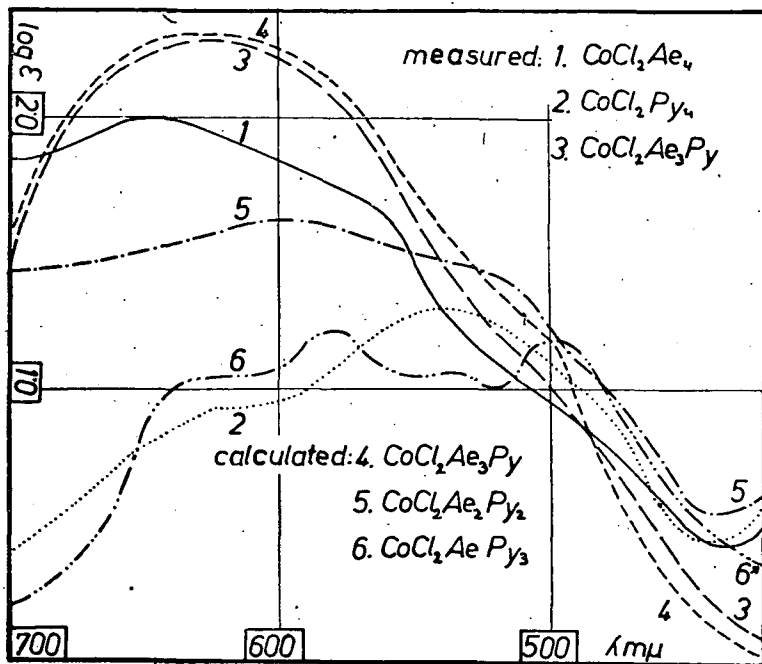
centration of 0,00966 moles, in pyridine at the same concentration (Fig. 1, curves 1. and 2.), also in a mixed solvent of ethylalcohol and pyridine, containing 0,25, 0,5, 0,75, 1, 1,5 2, 3, 5, 8, 10, 15, 20, 30, 50, and 80% of pyridine.

*Method of calculation.*

If a solution contains a mixture of two compounds, the extinction-curve of the mixture can be computed for each wave-length, provided, the relative concentration of the two compounds is known:

$$c_1 \varepsilon_1 + c_2 \varepsilon_2 = \varepsilon \quad (1)$$

As we are dealing with molar extinction coefficients,  $c_1 + c_2 = 1$ .



The experimentally obtained extinctions of the curve plotted for a mixture of solvents containing 0,25% pyridine greatly differed from the calculated values, and particularly at 6240 A, as well as other wave-lengths the solution absorbed to an extent unparalleled by the spectra of either the pure alcoholic or the pure pyridinic solution at any wave-length. (Curve 3.) As I was convinced by a control experiment that in a 0,3% pyridine-alcohol mixture the extinction decreased near the maximum, two facts became plain. One is the presence of a well-defined intermediate ( $\text{CoCl}_2\text{Ae}_m\text{Py}_n$ ), the other is that the mixture with the most stable intermediate contains no more than 0,25% of pyridine, because the main structural characteristic of the intermediate was its large extinction, which decreased after 0,25%.

If there is only one intermediate present, it should be possible to compute the curves for cobaltous chloride dissolved in all other mixtures from the curves of the intermediate and the pure

pyridinic solution. I have calculated the extinctions of 14 curves in 8 loci of each and I have compared them with the experimental results. This showed that on increasing the concentration of pyridine the curves diverged systematically from the calculated data, so there must be a second, possibly also a third intermediate. This fact excludes the possibility of the coördination number being four, as no meaning can be attached to the existence of two intermediates in a coördination of four.

Let us suppose that there is only one intermediate at some given concentration ratio. If its curve were known, the curves to the left of it could be computed by the means of its left limiting curve, and those to the right of it by means of the right one. Applying equation (I) four times:

$$\begin{aligned} \epsilon_1 x + (1-x)\epsilon_x &= \epsilon_2 & \text{Unknowns: } \epsilon'_x, \epsilon_x, x \text{ and } y. \\ \epsilon'_1 x + (1-x)\epsilon'_x &= \epsilon'_2 \\ \epsilon'_4 y + (1-y)\epsilon'_y &= \epsilon'_3 \\ \epsilon_4 y + (1-y)\epsilon_x &= \epsilon_3 \end{aligned} \quad (I)$$

$\epsilon_1$  and  $\epsilon'$  are the extinctions of the left limiting curve at wavelengths of  $\lambda$  and  $\lambda'$  respectively,  $x$  is the proportion in which the compound represented by the left limiting curve is present in the solution represented by the immediately adjacent curve,  $\epsilon_x$  and  $\epsilon'_x$  are the extinctions of the sought intermediate, also at wavelength of  $\lambda$  and  $\lambda'$  respectively,  $\epsilon_2$  and  $\epsilon'_2$  are the extinctions of the curve adjacent to the left limiting one,  $y$  is the proportion in which the compound represented by the right limiting curve is present in the solution represented by the immediately adjacent curve,  $\epsilon_3$  and  $\epsilon'_3$  are the extinctions of this adjacent curve at wavelengths of  $\lambda$  and  $\lambda'$  respectively.

As a result of this calculation I obtained a curve which didn't resemble any among the series of curves, and when I tried to verify the other curves by means of computation from the curve of the supposed intermediate, I found again great incongruences. Therefore it is plain that there must be more than two intermediates between the pure alcoholic and the pure pyridinic complex.

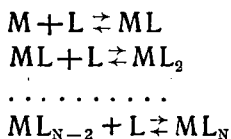
The extinctions now had to be examined in three different loci, but still the number of equation was too small compared with the number of unknowns. I had to select at random a curve between those of the two intermediates and use its extinctions as data at the three wavelengths. The set-up of the system of equations is completely analogous with that of system (I):

$$\begin{aligned} \epsilon_1 x + (1-x)\epsilon_x &= \epsilon_2 & \text{Unknowns: } \epsilon_x, \epsilon'_x, \epsilon''_x, \epsilon_y, \epsilon'_y, \epsilon''_y, x, y \text{ and } z. \\ \epsilon'_1 x + (1-x)\epsilon'_x &= \epsilon'_2 \\ \epsilon''_1 x + (1-x)\epsilon''_x &= \epsilon''_2 \\ \epsilon_3 y + (1-y)\epsilon_y &= \epsilon_4 \\ \epsilon'_3 y + (1-y)\epsilon'_y &= \epsilon'_4 \\ \epsilon''_3 y + (1-y)\epsilon''_y &= \epsilon''_3 \\ \epsilon_x z + (1-z)\epsilon_y &= \epsilon_3 \\ \epsilon'_x z + (1-z)\epsilon'_y &= \epsilon'_3 \\ \epsilon''_x z + (1-z)\epsilon''_y &= \epsilon''_3 \end{aligned} \quad (II)$$

By computation I obtained the two curves (curves 4. and 5.), which fitted the series exactly. One fitted between the curves of the solutions containing 1,5 and 2% of pyridine respectively, the other between those of the solutions containing 8 and 10%. Having made control calculations for the other curves by using as limiting curves in each case two of the curves of the three intermediates and the pure pyridine solution, I obtained remarkably good congruencies with the experimental data. On a scale of  $\log \epsilon$  the incongruency nowhere surpassed 0,02.

*Computation of the real extinction curves of the intermediates.*

I have obtained, on a purely theoretical basis, most valuable data pertaining to the three intermediates in a mixture of ethyl-alcohol and pyridine without excess chlorine. I found the starting point for these calculations in Bjerrum's „Metal ammine formation in aqueous solution“. The reaction-equations he starts from describe a process whereby a central nucleus puts on a radical, after which fresh radicals are added to a preformed central grouping:



The equilibrium constants for these equations can be stated as follows:

$$\begin{aligned} K_1 &= \frac{[ML]}{[M][L]} \\ K_2 &= \frac{[ML_2]}{[ML][L]} \\ &\dots\dots\dots \\ K_N &= \frac{[ML_N]}{[ML_{N-1}][L]} \end{aligned}$$

By the means of the equilibrium constants the average number of radicals bound per molecule can be stated:

$$\bar{n} = \frac{[ML] + 2[ML_2] + \dots + N[ML_N]}{[M] + [ML] + [ML_2] + \dots + [ML_N]}$$

However:

$$\begin{aligned} [ML] &= K_1[M][L] \\ [ML_2] &= K_2[ML][L] = K_1K_2[M][L]^2 \\ &\dots\dots\dots \end{aligned}$$

$$[ML_N] = K_N[ML_{N-1}][L] = K_1K_2\dots K_N[M][L]^N$$

Introducing these quantities and simplifying numerator and denominator by  $[M]$ , we obtain:

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + \dots + NK_1K_2\dots K_N[L]^N}{1 + K_1[L] + K_1K_2[L]^2 + \dots + K_1K_2\dots K_N[L]^N} \quad (2)$$

The mutual relations of the equilibrium constants can be characterized by consideration of statistical probability. Let  $N$  be the number of the radicals which can be put on, and  $n$  the quantity

of radicals bound in a single complex, then we find that the probability of the complex putting on another radical is proportional to  $N-n$ , and the probability of it releasing one is proportional to  $n$ . The equilibrium constants, then, are respectively proportional to the following quantities:

$$\frac{1}{N}, \frac{2}{N-1}, \dots, \frac{N-n}{n+1}, \frac{N-n+1}{n}, \dots, \frac{N-1}{2}, \frac{N}{1}$$

Hence the ratio of the two equilibrium constants can be written as:

$$\frac{K_n}{K_{n+1}} = \frac{N-n+1}{n} \frac{n+1}{N-n} \quad (3)$$

Actually, Bjerrum states this expression has to be multiplied in every case by a factor of  $k^2$ , the numerical value of which depends upon the mechanism of the reaction:

In my case this function proved to be acceptable because although it is a process not putting on, but of exchanging radicals, still, as the pyridine molecule has a greater dipole moment, the resistance of the alcohol molecules can be expressed by the factor  $k^2$ .

As the first intermediate was found below 0,25%, the second between 1,5 and 2%, and the third between 8 and 10%, the conditions are fulfilled if and only if  $k=1,68$ .

On the basis of the obtained data the equilibrium constants themselves could be calculated:

$$K_1 = 116,7, \quad K_2 = 15,5, \quad K_3 = 2.442, \quad K_4 = 0,3244$$

Now the actual absorption curve of the intermediates can be calculated, considering also the presence of all five complexes in the solution. The proportion in which each complex is represented in the solution with a stable intermediate can be calculated from the following system of equations:

$$\frac{[ML]}{[M][L]} = K_1, \quad \frac{[ML_2]}{[ML][L]} = K_2, \quad \frac{[ML_3]}{[ML_2][L]} = K_3, \quad \frac{[ML_4]}{[ML_3][L]} = K_4,$$

$$[M] + [ML] + [ML_2] + [ML_3] + [ML_4] = C_{Co} \quad (III.)$$

In the case of the individual intermediates:

	CoCl <sub>2</sub> Ae <sub>3</sub> Py	CoCl <sub>2</sub> Ae <sub>2</sub> Py <sub>2</sub>	CoCl <sub>2</sub> AePy <sub>3</sub>
CoCl <sub>2</sub> Ae <sub>4</sub>	0,2203	0,0109	0,0001
CoCl <sub>2</sub> Ae <sub>3</sub> Py	0,5719	0,2113	0,0109
CoCl <sub>2</sub> Ae <sub>2</sub> Py <sub>2</sub>	0,1971	0,5448	0,1984
CoCl <sub>2</sub> AePy <sub>3</sub>	0,0107	0,2212	0,5719
CoCl <sub>2</sub> Py <sub>4</sub>	0,0001	0,0119	0,2190
	1,0001	1,0001	1,0003

Relative to a certain wavelength the following system of equations can be set up:

$$0,2203 \varepsilon_1 + 0,5719 \varepsilon_x + 0,1971 \varepsilon_y + 0,0107 \varepsilon_z + 0,0001 \varepsilon_6 = \varepsilon_2$$

$$0,0109 \varepsilon_1 + 0,2112 \varepsilon_x + 0,5448 \varepsilon_y + 0,2212 \varepsilon_z + 0,0119 \varepsilon_6 = \varepsilon_3$$

$$0,0001 \varepsilon_1 + 0,0209 \varepsilon_x + 0,1984 \varepsilon_y + 0,5719 \varepsilon_z + 0,2190 \varepsilon_6 = \varepsilon_4$$

$\epsilon_1$  being the extinction of the pure alcohol solution,  $\epsilon_2$  the extinction of the first intermediate,  $\epsilon_3$  that of the second one,  $\epsilon_4$  that of the third one,  $\epsilon_5$  that of the pure pyridine solution.  $\epsilon_x^2, \epsilon_y, \epsilon_z$  are the three unknown quantities: the actual extinctions of the intermediates at the wavelength considered.

All in all, by means of equation system (II) I have only drawn the limits of those solvent concentration ratio at which the intermediates are stable, all other results have been discarded later. This calculus can be applied to any solvent concentration ratio but as in that case the concentration of free radicals is unknown, the average number of bound radicals has to be computed from equation (2), the knowledge of which enables us to calculate  $[L]$ :

$$[L] = C_{py} - C_{co}^{\bar{n}}$$

After this it is possible to compute from equation system (III) in what proportion the individual complexes are represented at the concerned concentration ratio. What's more, the extinctions can be computed from equation (1).

I performed this calculus for some loci on some curves, and obtained quite as satisfactory a congruency with experimental data as when I had calculated on the basis of the presence of only two intermediates. This is as it should be, as the curves obtained from equation system (II) were equilibrium curves, so that I had taken into account the presence of every complex indirectly, even though I hadn't done so directly.

*The case of one or two intermediates.*

The actual absorption curve of a single intermediate cannot be computed on a purely theoretical basis. This is the reason why:

Though the „equilibrium curve“ of the intermediate has been computed on the basis of equation system (I) and limits of the concentration ratio within which the intermediate complex is stable have been ascertained, still there are difficulties in calculating  $k$

and  $K$ . ( $K$  is just an abbreviation meaning  $\sqrt{\frac{2N}{N-2} K_1 k}$ ). From equation (3):

$$\frac{K_1}{K_2} = 4k_2; \frac{K_1}{2k} = 2K_2k = K; K_1 = 2Kk; K_2 = \frac{K}{2k}$$

Substituting this into the formula expressing the average number of bound radicals relative to the solution in which the intermediate is stable:

$$\frac{2Kk[L + 2K^2[L]^2]}{1 + 2Kk[L + K^2[L]^2]} = 1$$

We now have one equation with three unknowns. The number of unknowns can be reduced by one if we narrow the concentration interval experimentally until the last experimental curve coincides with the curve computed on the basis of equation system (I). So we determine  $[L]$  experimentally:

$$[L] = C_{py} - C_{co}$$

We still have two unknowns,  $k$  and  $K$ , but  $K$  can be computed from (4):

$$2K^1[L]^2 = 1 + K^2[L]^2K = \frac{1}{[L]} \quad (5)$$

$k$  however can be nowise expressed by the means of a single equation containing  $[L]$  without obtaining an identity:

$$\frac{[ML]}{[M][L]} = K_1 = 2Kk; \quad \frac{[ML_2]}{[M][L]} = K_2 = \frac{K}{2k}$$

$$\frac{[ML_2]}{[M][L]} = K^2 \text{ According to (5): } M[L_2] = [M]$$

Therefore, in the solution, in which the single intermediate is stable, the concentrations of the two limit compounds are equal.

Approaching to the problem from another angle, let us express  $[ML]$  as a function of radical concentration:

$$[ML] = 2Kk[M][L] \quad (6)$$

$[L] = Cx - cy$ , where only complex  $ML_2$  can exist, i.e. the pure pyridine solvent expressed in molar concentration,  $x$  is vol. % divided by 100, that is, a real fraction,  $c$  is the concentration of cobaltous chloride,  $y$  is the average number of bound radicals. Because:

$$[ML] + [M] + [ML_2] = [ML] + 2[M] = c$$

$$[ML] = 2Kk(Cx - cy) \frac{c - [ML]}{2}$$

$$[ML] = \frac{Kkc(Cx - cy)}{1 + Kk(Cx - cy)}$$

We know  $[ML]$  is as its maximum when the concentration equals that of the solution containing a stable intermediate, which we have determined experimentally. The problem, then, is a maximum-minimum type one:

$$[ML]' = \frac{Kkc(C - cy)'}{1 + 2Kk(Cx - cy) + K^2k^2(Cx - cy)^2}$$

The fraction can equal 0 only if either the numerator equals 0, or the denominator equals  $\infty$ . The denominator does not equal  $\infty$ . Therefore the numerator must be 0:

$$y' = \frac{C}{c}$$

$y'$  can be computed from the formula expressing the average number of bound radicals, which also contains the value of  $k$ , which we seek:

$$y = \frac{2Kk(Cx - cy) + 2K^2(Cx - cy)^2}{1 + 2Kk(Cx - cy) + K^2(Cx - cy)^2}$$

$$y' = \frac{2KkCy + 2K^2Cy(Cx - cy) - 2KkC - 4K^2C(Cx - cy)}{1 + 2Kk(Cx - 2cy) + K^2[(Cx - cy)^2 - 2cy(Cx - cy)] + 2Kkc + 4K^2c(Cx - cy)} = \frac{C}{c}$$

Explicating the equation for  $k$  we obtain:

$$k = \frac{2K^2Ccy(Cx - cy) + K^2C[(Cx - cy)^2 - 2cy(Cx - cy)]}{2KC(Cx - 2cy) + 2KCcy}$$

Where function  $[ML]$  has its maximum, i. e. where the intermediate is stable, the average number of bound radicals,  $y = 1$ . The value of  $x$  has been determined experimentally, so the formula can be simplified thus:

$$k = \frac{+2K^2Cc(Cx - c) + K^2C[(Cx - c)^2 - 2c(Cx - c)]}{2KC(Cx - 2c) + 2KCC}$$

As  $k$  entered our formulae by splitting  $k^2$  into its denominators, i. e.  $(+k)(-k)$ , its absolute value can be substituted. On the right everything is known,  $k$  can be calculated.

Now it is possible to determine the equilibrium constants and by comparing (5) and (6), the participation ratio of the individual complexes at the solvent concentration ratio determined experimentally:

$$[ML] = 2k[M]$$

Hence:

$$[M]:[ML]:[ML_2] = 1:2k:1$$

We now have an equation with only one unknown for every wavelength, by the means of which the actual extinction curve of the intermediate can be computed:

$$\frac{1}{2+2k} \varepsilon_1 + \frac{2k}{2+2k} \varepsilon_2 + \frac{1}{2+2k} \varepsilon_3 = \varepsilon_2$$

where  $\varepsilon_1$  is the extinction of one limiting curve,  $\varepsilon_3$  is that of the other one and  $\varepsilon_2$  is that of the equilibrium curve.

In the case of two intermediate, the problem can be solved more easily by determining the values of  $[L_1]$  and  $[L_2]$  experimentally by boxing. We obtain two equations with two unknowns. After this the computation proceeds in a manner analogous to that used in the case of three intermediates.

### Summary.

I have investigated the absorption spectra of anhydrous cobaltous chloride in various organic solvents. I have proved the existence of the complexes  $\text{CoCl}_2\text{Ae}_4$ ,  $\text{CoCl}_2\text{Ae}_3\text{Py}$ ,  $\text{CoCl}_2\text{Ae}_2\text{Py}_2$ ,  $\text{CoCl}_2\text{AePy}_3$ ,  $\text{CoCl}_2\text{Py}_4$  and thereby the existence of a blue cobalt complex with a coordination number of six.

The calculus I have published is applicable in other cases too, but one must take care to enter into the computation a number of wavelengths which exceeds by one the expected number of intermediate, to find an experimental curve between each pair of intermediates, and the number of unknowns must be  $(n+1)^2$ , if  $n$  is the number of expected intermediates.

I have performed this work in the Institute of General and Physical Chemistry at the University of Szeged.



## References.

1. J. Bjerrum: Metal Ammine Formation an Aqueous Solution Copenhagen (1941).
2. H. Dirking: Z. anorg. allg. Chem. 223. (1937) 321.
3. J. Groh: Z. anorg. allg. Chem. 146. (1927) 305, 166. (1929) 237.
4. A. Hantzsch: Z. anorg. allg. Chem. 159. (1927) 2 91.
5. F. G. Donnan and H. Bassett: J. Chem. Soc. London 81. (1902) 939.
6. A. Kiss and M. Gerendás: Z. physik. Chem. A. 180. (1937) 117. A. Kiss and M. Richter: Z. physik. Chem. A. 187. (1940) 211.
7. W. R. Brode: J. Amer. Chem. Soc. 53. (1931) 2457.
8. A. Kiss: Acta Chem. mineral. physica Univ. Szeged. 7. (1939) 119.

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## The Reaction of Aryl-thio-glycolic acid chlorides with sodium azide

By JÓZSEF KISS and ELEMÉR VINKLER

The reaction between acid chlorides and sodiumazide is known since a long time in the literature.<sup>1</sup> The formed azide decomposes readily with evolution of nitrogen and rearranges into the corresponding isocyanate. This reaction proceeds very easily particularly in the case of the aliphatic acid-azides. The isocyanate compounds react readily, e. g. with water and yield primary amino-compounds on evolving carbon dioxide.

According to the as yet not published results of E. Vinkler the phenyl-thio-glycolic acid azide (II. a.) recovered at the reaction between phenyl-thio-glycolic acid chloride (I. a.) and sodium azide is spontaneously converted into phenyl thiomethyl isocyanate (III. a.). This compound could be separated in the form of a solution which can readily be distilled. In consequence of its great reactivity it reacts with various agents, e. g. with water and is converted into N, N'-bis-(phenyl-thiomethyl)-carbamide (V. a.). If it is allowed to stand in an open vessel for several days the isocyanate yields the same carbamide derivative.

The purpose of this paper is to study to what an extent the various aryl radicals exert an influence on the reactivity of the isocyanate synthesized from aryl-thiomethyl-glycolic chlorides. In the following experiments the conversion of  $\beta$ -naphtyl- and p-tolyl-thio glycolic acid which had formed as intermediates was investigated. To enable the synthesis of these substances p-methyl-thiophenol<sup>2</sup> and thio- $\beta$ -naphtol were prepared from the suitable sulfochloride in phosphorus acid through reduction with potassium iodide in the presence of red phosphorus.

This method enabled the preparation of thio- $\beta$ -naphtol in a far better yield and under far simpler experimental conditions than