EXPERIMENTAL

The preparation and properties of the nitro compounds, α-nitroesters, and nitrate esters have been described previously.[8]

The infrared absorption spectra were determined with a Perkin Elmer Model 21 spectrophotometer. In all cases the pure liquid was employed.

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Preparation of *o,o'*-Dihydroxyazo Compounds[1,2]

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A number of *o,o'*-dihydroxyazo compounds were desired in an investigation of the fluorescence of metal chelates. Some of these could not be made by standard coupling procedures because of unfavorable directing influences. A new procedure for the preparation of symmetrical azo compounds has been published by Bogoslovskii,[4] but he did not report the preparation of any compounds containing *o*-hydroxy groups. When Bogoslovskii's procedure was used for the preparation of *o*-hydroxyazo compounds the product was found to be isolable as the stable copper chelate. The compounds prepared and the procedures used are detailed below.

EXPERIMENTAL

2,2'-Dihydroxyazobenzene (I). The catalyst stock solution was prepared as follows: Copper(II) sulfate pentahydrate (28.5 g.) was dissolved in 100 ml. of hot water. The solution was cooled and treated with concentrated ammonium hydroxide until the formation of the soluble ammonia complex was complete. This was reduced to the colorless copper(I) solution with 7 g. of hydroxylamine hydrochloride in 20 ml. of water just before use.

For the preparation of the diazonium mixture concentrated hydrochloric acid was added dropwise to 250 ml. of a solution of 11.0 g. of *o*-aminophenol and 7.0 g. of sodium nitrite in 5% sodium hydroxide until a positive reaction was observed with starch-iodide paper. The temperature was kept below 10° during this reaction. The diazonium mixture was added rapidly to the catalyst solution which was stirred constantly. Excessive foaming was prevented with ether. The mixture was allowed to stand for about one hour, stirred occasionally, and then was collected on a filter. The brown copper chelate isolated was found to be identical with that of Drew and Landquist.[5] This chelate was mixed with 500 ml. of concentrated hydrochloric acid and warmed gently. The mixture then was diluted with an equal volume of ice-water and filtered. The product was recrystallized three times from benzene to give a 53% yield of yellow-orange needles which melted at 172–172.7° (Lit.[6] 172°). The yield was increased to 78% by continuous liquid-liquid extraction of the diluted hydrochloric acid mixture with ether.

Anal. Calc'd for $C_{12}H_{10}N_2O_2$: C, 67.3; H, 4.71; N, 13.08. Found: C, 67.17; H, 4.54; N, 13.40.

2,2'-Dihydroxy-5,5'-dimethylazobenzene (II). 2-Nitro-4-methylphenol was prepared by the method of Neunhoeffer and Kolbel.[7] This was reduced to the amine in 69% yield by hydrogenation in dioxane with Raney nickel at room temperature. The copper chelate of II was prepared in the same manner as that of I. A solution of 5.5 g. of the chelate in 100 ml. of commercial ether was treated with hydrogen sulfide for 15 minutes. The mixture was filtered with Celite to remove the copper(II) sulfide and the ether was removed by evaporation. The product was recrystallized from petroleum ether (60–80°) with Norit to give a 28% yield of yellow needles, m.p. 219–220°.

Anal. Calc'd for $C_{14}H_{14}N_2O_2$: C, 69.5; H, 5.82; N, 11.56. Found: C, 69.34; H, 6.00; N, 11.60.

2,2'-Dihydroxy-4,4'-dimethylazobenzene (III). 2-Nitro-5-methylphenol was prepared by the method of Staedel,[8] and reduced to the amine as by Proskouriakoff and Titherington.[9] The copper chelate of III was prepared in the same manner as that of I. A concentrated hydrochloric acid solution of 10.0 g. of the chelate was boiled gently for about 10 minutes. The product separated as a black oily mass on top of the deeply colored hydrochloric acid. The mixture was cooled, and after 200 ml. of ice-water was added it was filtered with Celite. The dried mass then was extracted with benzene in a Soxhlet extractor. The product was crystallized from the extract and then from petroleum ether (90–100°) to give a 40% yield of bright yellow needles, m.p. 223–224°.

Anal. Calc'd for $C_{14}H_{14}N_2O_2$: C, 69.5; H, 5.82; N, 11.56. Found: C, 69.64; H, 5.93; N, 11.92.

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