vacuum. This drying is necessary, otherwise, a hygroscopic product is obtained. Further crystallization was performed by using absolute alcohol-ether mixture (1:10). After filtering, the product was dried at 100° and 1 mm., m. p. 152-153°; $(\alpha)^{25}{}_{\rm D} + 210.22°$ (*c*, 0.7064%; water).

Anal. Calcd. for $C_{27}H_{36}O_6N_2$: C, 66.64; H, 7.87; N, 5.76. Found: C, 66.41; H, 7.63; N, 5.69.

Summary

A novel application of an optically active quaternary ammonium hydroxide for resolution purposes has been demonstrated by separating the levo-rotatory α-hydroxy-β,β-dimethyl-γ-butyrolactone from its enantiomorph.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Inner Complexes of Phenylazo-phenanthrol, -retenol, and -chrysenol

BY HELMUT M. HAENDLER AND GEORGE McP. SMITH

The product formed by the action of phenylhydrazine on 9,10-phenanthrenequinone was first reported as the phenylhydrazone by Zincke,[1] and the analogous retenequinone compound was also reported as the phenylhydrazone by Bamberger and Grob.[2] "Phenanthrenequinone phenylhydrazone" was later characterized by Auwers[3] as an *o*-hydroxy azo compound on the basis of its chemical reactions, particularly those with acyl phenylhydrazines. More recently, Auwers[4] has summarized the evidence for the formulation of this type of compound as an ortho-hydroxy azo type.

Consequently, in connection with our recently published work on the inner complexes of ortho-hydroxy azo dyes,[5] it was decided to study the possible formation of copper inner complexes of phenyl-azo-phenanthrol, -retenol, and -chrysenol as compared to the previously prepared inner complexes of the naphthol series. Comparison of absorption spectra of both organic compounds and inner complexes should serve as further evidence for the existence of the ortho-hydroxy azo form.

Comparison of the spectra (Fig. 1) of phenylazophenanthrol, phenylazoretenol, phenylazochrysenol and their copper inner complexes with the spectra of 1-phenylazo-2-naphthol and its copper inner complex indicated strongly that all the organic compounds and complexes were structurally similar to those reported.[5] The structure thus appears to be, in all probability, the *o*-hydroxy azo type rather than the quinone phenylhydrazone type. In addition, the chemical and physical behavior of compounds and complexes is extraordinarily similar in both series.

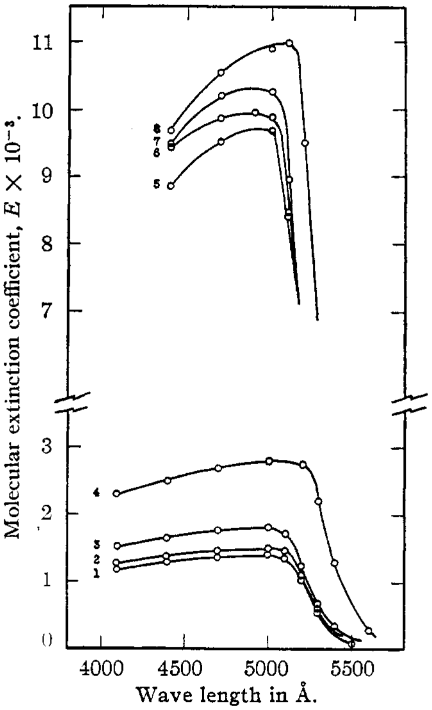

Fig. 1.—Absorption spectra of: 1, 1-phenylazo-2-naphthol; 2, 9-phenylazo-10-phenanthrol; 3, 9(10)-phenylazo-10(9)-retenol; 4, 5(6)-phenylazo-6(5)-chrysenol; 5, 1-phenylazo-2-naphtholato-copper; 6, 9-phenylazo-10-phenanthrolato-copper; 7, 9(10)-phenylazo-10(9)-retenolato-copper; 8, 5(6)-phenylazo-6(5)-chrysenolato-copper.

Experimental

9-Phenylazo-10-phenanthrol.—The azo compound was prepared from phenanthrenequinone and phenylhydrazinium chloride by the method of Auwers[3]; m. p. 162°.

9(10)-Phenylazo-10(9)-retenol.—This had been prepared originally by the violent reaction between phenylhydrazine and retenequinone,[2] but the following modification was found more satisfactory. To a solution of 5.25

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(1) Zincke, *Ber.*, **16**, 1564 (1883).

(2) Bamberger and Grob, *ibid.*, **34**, 539 (1901).

(3) Auwers, *Ann.*, **378**, 214 (1911).

(4) Auwers, *ibid.*, **505**, 283 (1938).

(5) Haendler with Smith, THIS JOURNAL, **62**, 1669 (1940).

g. of retenequinone in 35 ml. of hot glacial acetic acid was added gradually 2.9 g. of phenylhydrazinium chloride. The dark red solution was refluxed for ten minutes, cooled, filtered, and the red residue washed with alcohol and water till the washings were neutral. The crude product was crystallized from ligroin; b. p. 90–120°; bright orange crystals; m. p. 159–160.5°; yield, 60% of theoretical.

5(6)-Phenylazo-6(5)-chrysenol.—This compound, previously unreported, was prepared by the gradual addition of 5.8 g. of phenylhydrazinium chloride to a solution of 10.25 g. of chrysenequinone in 525 ml. of hot glacial acetic acid. The mixture, which foamed considerably at first, was refluxed for fifteen minutes, cooled, filtered, and the crude product crystallized from xylene; bright red matted crystals; m. p. 219–220°; yield, 50% of theoretical.

Anal.[6] Calcd. for $C_{24}H_{16}ON_2$: N, 8.04. Found: N, 7.98, 8.08.

9-Phenylazo-10-phenanthrolato-copper(II).—Two grams of cupric acetate was dissolved in 30 ml. of water and 30 ml. of 95% ethyl alcohol added. The solution was added dropwise to a hot, nearly saturated solution of 3.0 g. of 9-phenylazo-10-phenanthrol in *ca.* 200 ml. of alcohol. After twelve hours, the brown micro-crystals were filtered, washed with alcohol, and crystallized from xylene. The purified product was best washed with petroleum ether: green crystals with metallic luster; red-brown when powdered.

Anal. Calcd. for $(C_{20}H_{13}ON_2)_2Cu$: Cu, 9.7. Found: Cu, 9.6.

9(10)-Phenylazo-10(9)-retenolato-copper(II).—One g. of cupric acetate was dissolved in 15 ml. of water and 15 ml. of acetone added. One and three-quarters grams of 9(10)-phenylazo-10(9)-retenol was suspended in 50 ml. of 95% ethyl alcohol and 100 ml. of acetone added. The cupric acetate solution was added dropwise to the hot retenol solution and the crystals removed after twelve hours. The crude complex was crystallized from a ligroin–benzene mixture; deep brown crystals.

Anal. Calcd. for $(C_{24}H_{21}ON_2)_2Cu$: Cu, 8.3. Found: Cu, 8.5.

5(6)-Phenylazo-6(5)-chrysenolato-copper(II).—One g. of cupric acetate was dissolved in 60 ml. of lukewarm absolute alcohol and the filtered solution added slowly to a boiling solution of 1.75 g. of 5(6)-phenylazo-6(5)-chrysenol in 125 ml. of toluene. The mixture was refluxed for thirty minutes after addition of all the cupric acetate. The crystals were filtered after twelve hours, washed with petroleum ether, and crystallized from nitrobenzene; black crystals with a faint green luster.

Anal. Calcd. for $(C_{24}H_{15}ON_2)_2Cu$: Cu, 8.4. Found: Cu, 8.6.

Absorption Spectra.—The visual absorption spectra were measured with the Coleman Regional Spectrophotometer.[5] The azo compounds were dissolved in xylene and compared with the pure solvent. The spectra of the phenanthrolato- and retenolato-copper complexes were also measured in xylene solution, but the naphtholato- and chrysenolato-copper complexes were measured in xylene, nitrobenzene = 23, 2 (by volume), compared to the pure mixture.

Summary

1. Several *o*-hydroxy azo compounds related to phenanthrol have been prepared.

2. The copper inner complexes of these *o*-hydroxy azo compounds have been prepared in the crystalline state.

3. The absorption spectra of the azo compounds and of the inner complexes have been measured and compared with the spectra of corresponding compounds of the naphthol series.

4. The similarity in chemical behavior and in absorption spectra indicates identical structure for the phenanthrol, retenol, chrysenol, and naphthol compounds, with *o*-hydroxy azo structure rather than quinone hydrazone.

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(6) Micro-Dumas analysis by Ronald A. Henry.