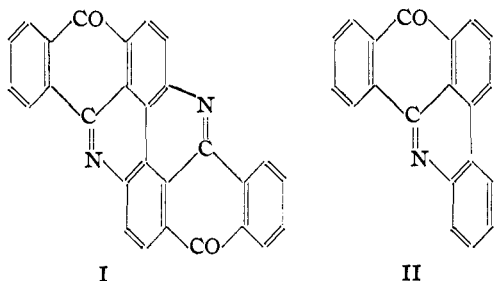


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## Benzo-semiflavanthrene. I. Reduction

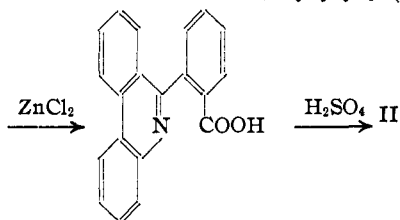
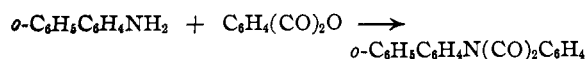
BY C. FREDERICK KOELSCH

The researches of Scholl and his collaborators<sup>1</sup> have cleared up to a large extent the constitutions of the vat dye flavanthrene (I) and of its reduction products. The chemistry of these substances is, however, quite involved. For example Scholl has obtained from flavanthrene nine different reduction products, of which six exist in two forms: one form non-hydrated, the other containing a molecule of water "in a very firm atomically bound condition."



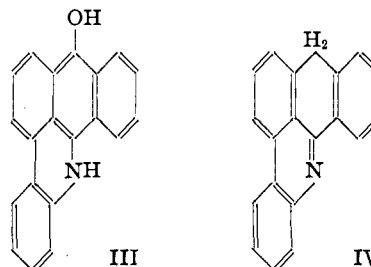
Doubtless still more can be learned about this type of quinone imine by a study of related substances whose structures are less complex. To this end, the substance (II) has been prepared; the name benzo-semiflavanthrene is proposed for this compound to indicate its relation to flavanthrene. Incidentally, benzo-semiflavanthrene appears to hold little promise as a dye, since the color it imparts to fabrics is a very pale yellow.

The preparation of benzo-semiflavanthrene, illustrated by the accompanying formulas, is easily carried out. Each reaction gives a single product in a good yield.



Two reduction products have been obtained from benzo-semiflavanthrene: the dihydro compound (III), and a desoxy compound, probably (IV).

(1) Scholl and Mansfield, *Ber.*, **43**, 1734 (1910), and previous papers.



The reduction product (III), a violet-black substance, separates directly in a crystalline condition when benzo-semiflavanthrene is boiled with alkaline hydrosulfite. It is only weakly acidic and is little soluble in aqueous sodium hydroxide. In such a solution, or dissolved in organic solvents, it is readily oxidized to benzo-semiflavanthrene by air; however, it is quite stable in the solid state. It cannot be acylated, for when it is boiled with acetic anhydride or treated with benzoyl chloride in pyridine, or even when it is boiled with aqueous hydrochloric acid it undergoes disproportionation to benzo-semiflavanthrene and the desoxy compound (IV).

This desoxy compound, a deep red-brown substance, is most readily obtained by the acid reduction of benzo-semiflavanthrene. It, too, is sensitive to air even when dissolved in dilute aqueous hydrochloric acid. Nitrous acid also reconverts it into benzo-semiflavanthrene.

None of the reduction products so far isolated has shown any tendency to form a stable hydrate.

The investigation is being continued.

## Experimental

***o*-Xenylphthalimide.**—A mixture of 100 g. of *o*-aminobiphenyl with 88 g. of phthalic anhydride is heated at 200° for ten minutes. The product (175 g.), crystallized from acetic acid, forms colorless prisms that melt at 165–166°.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{15}\text{O}_2\text{N}$ : C, 80.3; H, 4.35. Found: C, 80.3; H, 4.41.

***o*-(9-Phenanthridyl)-benzoic Acid.**—An intimate mixture of 175 g. of *o*-xenylphthalimide with 350 g. of zinc chloride is heated rapidly to 275° and kept at this temperature for one minute; no reaction takes place at lower temperatures and longer heating results in considerable decomposition. The melt is stirred into much water, and the insoluble product is purified by dissolving in 5% aqueous soda and treatment with charcoal. The acid is precipitated by dilute hydrochloric acid as a fine powder which is pure enough for most purposes; yield, 135 g. Recrystal-

lized from ethyl acetate, in which it is very difficultly soluble, it forms colorless prisms that melt at 268–270° with decomposition.

*Anal.* Calcd. for  $C_{20}H_{13}O_2N$ : C, 80.3; H, 4.35. Found: C, 80.3; H, 4.38.

The methyl ester obtained from the acid with methanol and sulfuric acid forms prisms from benzene that melt at 150–151°.

*Anal.* Calcd. for  $C_{21}H_{15}O_2N$ : C, 80.5; H, 4.8. Found: C, 80.0; H, 4.77.

Distilled with copper acetate (1 g.) *o*-(9-phenanthridyl)-benzoic acid (5 g.) gives 9-phenylphenanthridene (3.5 g.) which melts at 104–106° alone or mixed with a sample of the substance prepared according to the method of Pictet and Hubert.<sup>2</sup>

**Benzo-semiflavanthrene.**—Ninety grams of *o*-(9-phenanthridyl)-benzoic acid is stirred into 450 ml. of concd. sulfuric acid and the solution is heated for two hours at 160°. The product is isolated by pouring into water. After drying and crystallizing from xylene there is obtained 45 g. of pure benzo-semiflavanthrene which melts at 221–223°.

*Anal.* Calcd. for  $C_{20}H_{11}ON$ : C, 85.4; H, 3.96. Found: C, 85.3; H, 3.96.

**The Reduction Product (III).**—A suspension of 2 g. of benzo-semiflavanthrene in 50 ml. of *N* sodium hydroxide is treated with 4 g. of sodium hydrosulfite, and the mixture is boiled in an inert atmosphere for thirty minutes. Fifteen ml. of acetic acid is added, the precipitate is filtered, washed well with water and dried for a short time at 100°. The product forms black-violet needles that melt at 197°.

*Anal.* Calcd. for  $C_{20}H_{13}ON$ : C, 84.7; H, 4.6. Found: C, 84.8; H, 4.46.

The hydroxyamine is little soluble in boiling *N* sodium hydroxide and is completely extracted from the violet solution thus formed by toluene. This solution and the deep

red solution in alcohol rapidly become yellow on exposure to air, and deposit yellow needles of benzo-semiflavanthrene. With an excess of acetic anhydride, the reduction product dissolves to give a red solution which becomes deep brown on boiling and deposits benzo-semiflavanthrene, even when air is excluded. From the brown solution, the desoxy compound can be precipitated by dilution with water. A similar result is obtained when the deep red solution of the hydroxyamine in pyridine is treated with benzoyl chloride.

**The Desoxy Compound (IV).**—A mixture of 1.5 g. of benzo-semiflavanthrene, 5 ml. of hydrochloric acid and 35 ml. of acetic acid is boiled until all of the solid is dissolved. A solution of 3.5 g. of stannous chloride in 5 ml. of hydrochloric acid and 10 ml. of acetic acid is added in one portion, and the boiling is continued until the yellow-green precipitate has become black (thirty minutes to one hour). This black tin double salt is filtered, washed well with acetic acid and water, and boiled for five minutes with 50 ml. of 0.5 *N* sodium hydroxide, excluding air. The red-brown desoxy compound is quite readily attacked by air, even when dry, and in a capillary tube has the same melting point as benzo-semiflavanthrene. Freshly prepared, it is completely soluble in 10% hydrochloric acid; on keeping, even in an evacuated desiccator, it is oxidized, becoming yellow and insoluble in dilute acid. Concordant analytical results could not be obtained. Found: C, 87.5 to 88.2; H, 4.5 to 4.7.  $C_{20}H_{12}N$  requires: C, 89.8; H, 4.87.

### Summary

This paper reports the preparation of benzo-semiflavanthrene, a quinone imine related in structure to the vat dye flavanthrene. Some experiments on the reduction of the substance are described.

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(2) Pictet and Hubert, *Ber.*, **29**, 1183 (1896).

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## Studies in the *peri*-Naphthindene Series. I. The Condensation of $\beta$ -Naphthol with Cinnamic Acid

BY C. FREDERICK KOELSCH

Comparatively few derivatives of *peri*-naphthindene have been investigated, but the reactions of these few indicate that the chemistry of this system is quite different from that of the at first sight related indene system.<sup>1</sup> In the present series of papers, the syntheses and reactions of *peri*-

(1) Compare, *e. g.*, the ease of formation, stability and basicity of *peri*-naphthindone [Cook and Hewett, *J. Chem. Soc.*, 368 (1934)] with the unknown, presumably easily polymerizable indone, whose derivatives are not basic; the tendency to enolize of 8-phenyl-*peri*-naphthindandione-7,9 [Cesaris, *Gazz. chim. ital.*, **42**, II, 453 (1912)] with the tendency to ketonize of 2-phenylindandione-1,3 [Hantzsch, *Ann.*, **392**, 286 (1912)]; the action of phenylmagnesium bromide on benzanthrone [Allen and Overbaugh, *This Journal*, **57**, 740 (1935)] with its action on fluorenone [Ullmann and v. Wurstemberger, *Ber.*, **37**, 73 (1904)].

naphthindene derivatives will be examined with special reference to the analogous procedures in the indene series.

Phenol reacts with cinnamic acid in the presence of sulfuric acid to give 3,4-dihydro-4-phenylcoumarin.<sup>2</sup> It is now shown that  $\beta$ -naphthol and cinnamic acid behave similarly forming 3,4-dihydro-4-phenyl-5,6-benzocoumarin (I).<sup>3</sup> This lactone is easily hydrolyzed and methylated to give

(2) Liebermann and Hartmann, *Ber.*, **24**, 2586 (1891).

(3) The present paper is published in its incomplete form to avoid duplication, a recent article by Miller and Robinson [*J. Chem. Soc.*, 1535 (1934)] having announced a projected investigation of the condensation of  $\alpha,\beta$ -unsaturated carbonyl compounds with phenols.