

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.²

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 β -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.¹ 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. Wursterberger, *Ber.*, **37**, 73 (1904)].

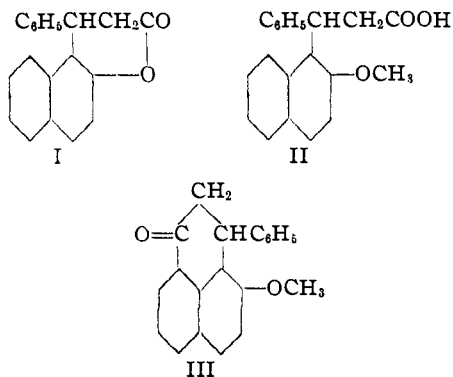
naphthindene derivatives will be examined with special reference to the analogous procedures in the indene series.

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

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

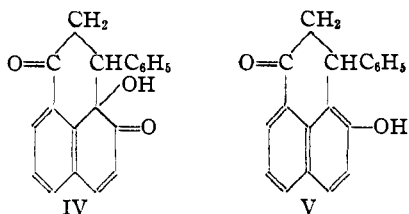
(3) The present paper is published in its incomplete form to avoid duplication, a recent article by Miller and Robinson [*J. Chem. Soc.*, 1535 (1934)] having announced a projected investigation of the condensation of α,β -unsaturated carbonyl compounds with phenols.

β -phenyl- β -(2-methoxynaphthyl-1)-propionic acid (II), whose chloride, treated with aluminum chloride, is cyclized to 6-methoxy-7-phenyl-7,8-dihydro-9-keto-*peri*-naphthindene (III).



In view of the results of Cook and Hewett,¹ who obtained 9-keto-*peri*-naphthindene and not the corresponding 7,8-dihydro compound by the cyclization of β -(naphthyl-1)-propionic acid, it was at first believed that in the present cyclization also hydrogen had been lost. This belief was strengthened by: (a) the yellow color of the product (III), (b) the non-reactivity of it toward phenylmagnesium bromide⁴ and (c) the non-formation of a benzal derivative. However, analyses of the ketone (III), its oxime, its demethylation product and its oxidation product indicate that these substances are all dihydro compounds.⁵

The most remarkable reaction of the ketone III is its behavior on oxidation with chromic acid. It is thus converted into a compound which must be 6,9-diketo-7-phenyl-6a-hydroxy-6,6a,7,8-tetrahydro-*peri*-naphthindene (IV) since this oxidation product is easily reduced by alkaline hydrosulfite to (V), the demethylation product of (III).⁸



Experimental

3,4-Dihydro-4-phenyl-5,6-benzocoumarin.—A mixture of 250 g. of β -naphthol, 250 g. of cinnamic acid, 700 ml. of acetic acid and 300 ml. of sulfuric acid is boiled for one

(4) The forced reaction will be described in a later paper.

(5) Compare the cyclization of β -(2-methoxynaphthyl-1)-propionic acid, Barger and Starling, *J. Chem. Soc.*, **99**, 2033 (1911).

(6) Compare the oxidation of 1-methylnaphthol-2. Bargellini and Silvestri, *Gazz. chim. ital.*, **37**, II, 412 (1907).

hour and then poured into water. The resinous precipitate is washed with hot water and boiled with dilute sodium carbonate, enough of the salt being added to cause the red substance to become green. The insoluble material is washed, distilled under reduced pressure and crystallized from alcohol. There is obtained 125–130 g. of the lactone which forms colorless prisms that melt at 115–116°.

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_4$: C, 83.1; H, 5.1. Found: C, 83.2; H, 5.3.

β -Phenyl- β -(2-methoxynaphthyl-1)-propionic Acid (II).—The lactone (120 g.) is dissolved in 400 ml. of 10% sodium hydroxide by boiling. The solution is cooled and 40 ml. of methyl sulfate is added slowly with stirring. The methylation is completed by boiling for two minutes, cooling, adding more sodium hydroxide (20 g.) and methyl sulfate (20 ml.). The solution is boiled a short time and cooled; the difficultly soluble sodium salt is filtered and decomposed with hydrochloric acid. The precipitate is crystallized from acetic acid, giving 95–100 g. of the methoxylated acid which forms colorless prisms that melt at 168–170°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_3$: C, 78.4; H, 5.9. Found: C, 77.9; H, 6.0.

6-Methoxy-7-phenyl-7,8-dihydro-9-keto-*peri*-naphthindene (III).—The methoxylated acid (80 g.) and phosphorus pentachloride (60 g.) are added to 280 ml. of benzene and boiled for five minutes. The solution is cooled and 45 g. of aluminum chloride is added in portions. After boiling a few minutes, the mixture is hydrolyzed and the benzene is removed with steam. The residue is crystallized from acetic acid, giving 66 g. of pale yellow needles that melt at 144–145°. The compound is insoluble in hot sodium hydroxide, and gives a bright red color with sulfuric acid.

Anal. Calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_2$: C, 83.3; H, 5.55. Found: C, 83.1; H, 5.65.

The oxime, obtained by boiling the ketone with hydroxylamine hydrochloride in alcohol for two hours, melts at 207–211°.

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}$: C, 79.2; H, 5.6. Found: C, 79.4; H, 5.7.

6-Hydroxy-7-phenyl-7,8-dihydro-9-keto-*peri*-naphthindene (V).—A mixture of 2 g. of the methoxy ketone, 15 ml. of acetic acid and 5 ml. of 40% hydrobromic acid is boiled for three hours. Ether and water are added, the phenol is extracted from the ether with dilute sodium hydroxide, distilled at 20 mm. and crystallized from dilute acetic acid. The compound forms bright yellow needles that sinter at 185° and melt at 191–193°. Its solution in dilute caustic soda is orange-brown.

Anal. Calcd. for $\text{C}_{19}\text{H}_{14}\text{O}_2$: C, 83.2; H, 5.1. Found: C, 83.3; H, 5.1.

6,9-Diketo-7-phenyl-6a-hydroxy-6,6a,7,8-tetrahydro-*peri*-naphthindene (IV).—The methoxy ketone (10 g.) in acetic acid (75 ml.) is treated with 20 g. of chromic acid in dilute acetic acid. When the vigorous reaction is over, the mixture is poured into water and extracted with ether. Sodium carbonate removes very little acidic product; the neutral product is crystallized from dilute ethanol, when it forms bright yellow needles (3.6 g.) that melt with gas evolution at 105–110°.

Anal. Calcd. for $C_{19}H_{14}O_3 + H_2O$: C, 74.0; H, 5.2. Found: C, 73.7; H, 5.4.

The quinol also separates from dilute methanol or dilute acetic acid in needles that contain water. From toluene it is obtained in the form of pale tan prisms which are solvent free and melt at 160–163° with darkening.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.6; H, 4.8. Found: C, 78.4; H, 4.7.

Boiling with sodium hydroxide transforms the quinol into an amorphous brown substance. On boiling with alkaline sodium hydrosulfite it gives a clear orange-brown solution from which acids precipitate the hydroxy com-

pound (V), identified by mixed melting point and by its conversion to the methoxy ketone (III) on methylation with methyl sulfate and alkali.

Summary

The condensation of β -naphthol with cinnamic acid yields a dihydrocoumarin which has been converted into a *peri*-naphthindene derivative. Some reactions of this latter substance are described.

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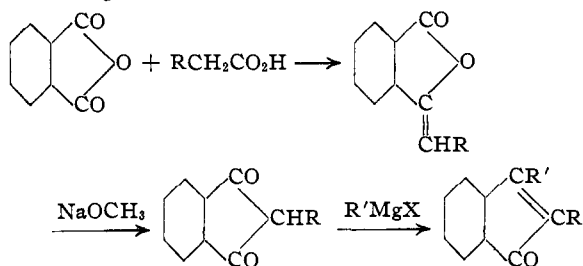
Some Applications of the Rosenmund-v. Braun Nitrile Synthesis

BY C. FREDERICK KOELSCH

When an aromatic bromide is heated in a sealed tube with water, sodium cyanide and cuprous cyanide, the halogen is replaced by carboxyl.¹ Hydrolysis of the intermediate nitrile may be avoided by omitting the water and sodium cyanide, this procedure making the use of a sealed tube or an autoclave unnecessary.² The importance of this reaction has been demonstrated in a recent synthesis of phenanthrene-9-carboxylic acid.³

In the present research the reaction has been applied to the preparation of some derivatives of 2,3-diphenylindone, and the cyano group has been introduced into each of the three benzenoid rings of this compound. Likewise it has been found that β,γ,γ -triphenylacrylonitrile and β -phenyl- γ -diphenyleneacrylonitrile are readily obtainable from the corresponding vinyl bromides. However, when α -*p*-bromophenyl- β,β -diphenylvinyl bromide is heated with cuprous cyanide under the usual conditions, it is completely resinified; at lower temperatures it is recovered unchanged.

The halogenated indones were prepared by the following series of reactions, the last step of the se-



(1) Rosenmund and Struck, *Ber.*, **52**, 1749 (1919).

(2) Von Braun and Manz, *Ann.*, **488**, 111 (1931).

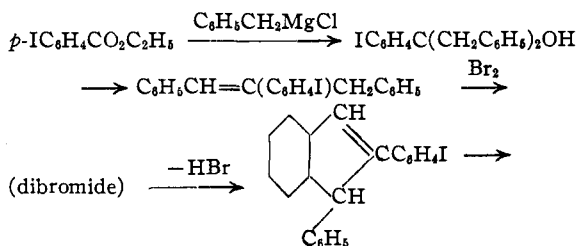
(3) Mosettig and van de Kamp, *This Journal*, **54**, 3334 (1932).

ries constituting a hitherto undescribed diarylindone synthesis.

When 4-bromophthalic anhydride was used, a mixture of benzal bromophthalides was obtained which was converted quantitatively into 1,3-diketo-2-phenyl-5-bromoindane. This with phenylmagnesium bromide gave an easily separable mixture of the isomeric 5- and 6-bromodiphenylindones; thus enolization of this unsymmetrical β -diketone involves either of the carbonyl groups.

It is noteworthy that although solid 2-phenylindandione is obtainable in only the white keto form,⁴ the halogenated derivatives of this substance prepared in this research were each easily obtainable in two forms: by crystallization from non-polar solvents in a white modification (keto), and from polar solvents in a violet-black modification (enol).

The structure of 5-bromo-2,3-diphenylindone was proved by oxidation to the known 4-bromo-2-benzoylbenzoic acid, and that of 2-*p*-iodophenyl-3-phenylindone by a separate synthesis according to the scheme⁵



(4) Hantzsch, *Ann.*, **392**, 286 (1912).

(5) Compare Orechhoff, *Ber.*, **47**, 89 (1914); Ruggli, *Ann.*, **414**, 125 (1917).