and 102 mequiv of hydride ion there was obtained crude **aniline** which was converted into the **phenylthiourea derivative** in 64.5% yield by treatment with phenyl isothiocyanate:[16] mp 155–156°;[17] nmr ($CDCl_3$) δ 7.53 (s, 10, aromatic H) and 8.40 (s, 2, NH).

Similarly treating 1.90 g (17.4 mmol) of phenylhydroxylamine with 120 mequiv of hydride ion and keeping the reaction mixture 20 hr at ambient temperatures resulted in the evolution of 33.74 mmol of hydrogen.

Hydrolyzing the reaction mixture at 0° by the cautious addition of 4 ml of water followed by 10 ml of 20% hydrochloric acid and refluxing for 1 hr gave an additional 68.10 mmol of hydrogen. The total amount of hydrogen evolved was 101.84 mmol, indicating that 1.04 equiv of hydride ion per mole of hydroxylamine was consumed in the reduction.

Registry No.—Diborane, 16970-81-3; 2,2-nitronitrosopropane, 5275-46-7; 1,1-nitronitrosocyclohexane, 14296-14-1; 1-nitropropanal oxime, 19519-78-9; 1,1-chloronitrosocyclophexane, 695-64-7.

Acknowledgment.—We wish to extend our appreciation to the Office of Naval Research for financial support of this work.

(16) N. D. Cheronis and J. B. Entrikin, "Identification of Organic Compounds," Interscience Publishers, New York, N. Y., 1963.
(17) H. Fry, *J. Amer. Chem. Soc.*, **35**, 1539 (1913).

New Synthesis of 1,2-Phenanthrenequinone

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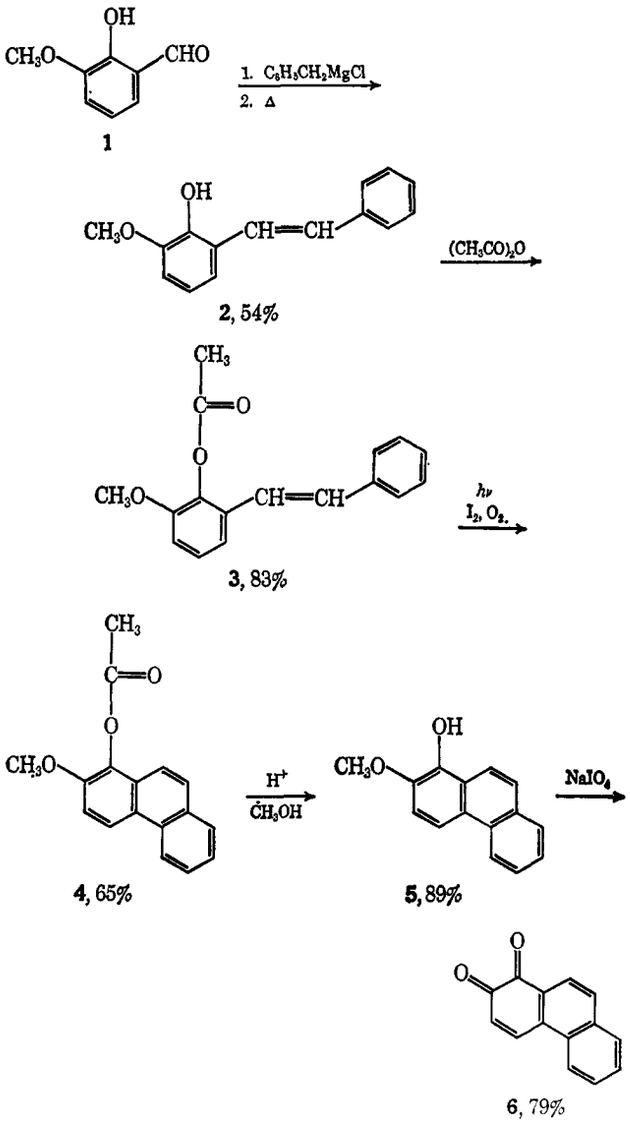
The synthesis of 1,2-phenanthrenequinone described by Fieser[1] in 1929 involves the sulfonation of phenanthrene, separation of phenanthrene-2-sulfonic acid *via* its barium salt, and alkali fusion to give 2-phenanthrol. Coupling with diazotized sulfanilic acid followed by reduction leads to 1-amino-2-phenanthrol which upon oxidation with chromic acid yields 1,2-phenanthrenequinone. According to a more recent procedure, 2-phenanthrol can be converted directly into 1,2-phenanthrenequinone by oxidation with potassium nitrosodisulfonate, but no yield has been reported.[2] The optimal yield of 2-phenanthrol from phenanthrene, however, appears to vary between 13 and 20%.[3,4]

We have now found that 1,2-phenanthrenequinone can easily be prepared from *o*-vanillin according to a reaction sequence outlined in Scheme I. The previously described reaction of benzyl magnesium chloride with *o*-vanillin (**1**) followed by dehydration gives 2-hydroxy-3-methoxystilbene (**2**).[5] Photolysis of its acetate **3** leads to 1-acetoxy-2-methoxyphenanthrene (**4**). Acid catalyzed hydrolysis gives 1-hydroxy-2-methoxyphenanthrene (**5**) which upon oxidation with sodium periodate[6] yields 1,2-phenanthrenequinone (**6**) in a high state of purity. It was characterized by its reduction to 1,2-dihydroxyphenanthrene, which in turn was converted into the diacetate.

SCHEME I
THE SYNTHESIS OF 1,2-PHENANTHRENEQUINONE FROM *o*-VANILLIN



Interestingly, the synthesis of 1-hydroxy-2-methoxyphenanthrene (**5**) has been accomplished a few years ago by the following classical route.[7] Elbs persulfate oxidation of 2-phenanthrol led to 2-hydroxy-1-phenanthryl sulfate. Methylation with diazomethane followed by acid-catalyzed hydrolysis gave **5** in an over-all yield of about 2.8%. According to the new procedure, the over-all yield of **5** based on *o*-vanillin, however, is approximately 25%. The preparative usefulness of the photochemical route to phenanthrols is thus apparent.

Experimental Section

Melting points were taken on a hot-stage microscope and are not corrected. All analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

The photolysis was carried out in an immersion well apparatus.[8]

(1) L. F. Fieser, *J. Amer. Chem. Soc.*, **51**, 1896 (1929).
(2) B. Lukowczyk, *J. Prakt. Chem.*, **8**, 372 (1959).
(3) L. F. Fieser, *J. Amer. Chem. Soc.*, **51**, 2460 (1929).
(4) W. O. Foye, M. Weitzenhoff, and A. M. Stranz, *J. Amer. Pharm. Assoc., Sci. Ed.*, **41**, 312, (1952).
(5) E. Adler and K. Lundquist, *Acta Chem. Scand.*, **17**, 13 (1963).
(6) E. Adler, I. Falkehag, and B. Smith, *ibid.*, **16**, 529 (1962).
(7) P. Sims, *Biochem. J.*, **84**, 558 (1962).
(8) H. D. Becker, *J. Org. Chem.*, **32**, 2115 (1967).

The preparation of 2-hydroxy-3-methoxystilbene **2** is described here since neither experimental details nor any yields have been reported previously.

2-Hydroxy-3-methoxystilbene (2).—A solution of *o*-vanillin (12.5 g) in ether (500 ml) was added slowly to a stirred ether solution (100 ml) of benzyl magnesium chloride (from 7 g of Mg). The resulting suspension was refluxed for 4 hr and then acidified with a mixture of acetic acid (30 ml) and water (100 ml). The ether layer was separated, and the aqueous layer was extracted three times with 100 ml of ether. Drying of the ether solution over sodium sulfate and evaporation of the solvent gave an oil which was subjected to distillation at about 1-mm pressure and a bath temperature of 120° to remove the by-product bibenzyl. The oily residue was then mixed with potassium hydrogen sulfate (1 g) and heated for 30 min to 160–170°. Vacuum distillation at about 0.5-mm pressure and a bath temperature of 180–200° gave a colorless to light yellow distillate that crystallized in the receiver. It was triturated with pentane and filtered to give 10 g (54%) of colorless crystals, mp 86–87° (lit.[5] 86–87°).

2-Acetoxy-3-methoxystilbene (3).—A solution of 2-hydroxy-3-methoxystilbene **2** (6.4 g, 28.3 mmol) in acetic anhydride (40 ml) and pyridine (1 ml) was heated for 5 min to 100° and then kept at room temperature overnight. Decomposition of the acetic anhydride with methanol and evaporation of the solvent gave a colorless crystalline residue which was recrystallized from boiling methanol. The yield was 6.3 g (83%), mp 112–113°.

Anal. Calcd for $C_{17}H_{16}O_3$ (268.30): C, 76.10; H, 6.01. Found: C, 76.00; H, 5.99; mol wt (benzene), 261.

1-Acetoxy-2-methoxyphenanthrene (4).—A solution of 2-acetoxy-3-methoxystilbene **3** (1.34 g, 5 mmol) and iodine (50 mg) in benzene (400 ml) was irradiated (Corex filter, 450-W Hanovia, oxygen) for 70 min. Vacuum evaporation gave a crystalline residue which was recrystallized from a chloroform–methanol mixture. The yield was 720 mg (54%), mp 192–193° (lit.[7] mp 185°).

Anal. Calcd for $C_{17}H_{14}O_3$ (266.28): C, 76.67; H, 5.30. Found: C, 76.92; H, 5.19; mol wt (in benzene), 258.

The irradiation was also carried out in a quartz apparatus in cyclohexane solution. The yield thus could be increased to 65%; however, the immersion well had to be cleaned repeatedly since the product tended to crystallize at the immersion well, thus impairing the light absorption.

1-Hydroxy-2-methoxyphenanthrene (5).—A solution of 1-acetoxy-2-methoxyphenanthrene **4** (665 mg, 2.5 mmol) in a mixture of chloroform (30 ml) and methanol (30 ml) containing concentrated hydrochloric acid (4 ml) was refluxed for 2 hr. Vacuum evaporation of the solvent gave a crystalline residue which was recrystallized from petroleum ether (bp 30–60°) or aqueous methanol. The yield was 500 mg (89%), mp 120–121° (lit.[7] mp 113°).

Anal. Calcd for $C_{15}H_{12}O_2$ (224.25): C, 80.33; H, 5.39. Found: C, 80.14; H, 5.35; mol wt (in benzene), 209.

1,2-Phenanthrenequinone (6).—A warm solution (50°) of sodium metaperiodate (2.5 g, 11.7 mmol) in 50% aqueous acetic acid (40 ml) was added to a stirred solution of 1-hydroxy-2-methoxyphenanthrene **5** (1.12 g, 5 mmol) in acetic acid (100 ml). 1,2-Phenanthrenequinone precipitated in form of beautiful red needle-shaped crystals. Stirring was continued for 30 min. The reaction mixture was then diluted with water (50 ml) and filtered to give 825 mg (79%) of 1,2-phenanthrenequinone, mp 215° dec (lit.[1] mp 216°). Recrystallization from aqueous acetic acid did not raise the melting point.

Anal. Calcd for $C_{14}H_8O_2$ (208.20): C, 80.76; H, 3.87. Found: C, 80.44; H, 3.91.

1,2-Dihydroxyphenanthrene.—A solution of sodium dithionite (2 g) in water (50 ml) was added to a stirred suspension of 1,2-phenanthrenequinone (300 mg) in chloroform (50 ml). After 1 hr of stirring the chloroform was removed from the colorless reaction mixture by evaporation *in vacuo*. Filtration gave 300 mg (99%) of silver gray crystals, melting between 174 and 178° (with darkening). Sublimation at 0.1-mm pressure (bath temperature 120–150°) gave a colorless crystalline sublimate, melting at 178–180° (with darkening) (lit.[9] mp 178°).

Anal. Calcd for $C_{14}H_{10}O_2$ (210.22): C, 79.98; H, 4.79. Found: C, 79.82; H, 4.96.

1,2-Diacetoxyphenanthrene.—1,2-Dihydroxyphenanthrene was acetylated with acetic anhydride in the presence of pyridine. The diacetate was recrystallized from aqueous methanol to give needle-shaped crystals, mp 153–154° (lit.[10] mp 147°).

Anal. Calcd for $C_{18}H_{14}O_4$ (294.29): C, 73.46; H, 4.80. Found: C, 73.38; H, 4.77.

(9) L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, **53**, 792 (1931).

Registry No.—**3**, 19551-00-9; **4**, 19551-02-1; **5**, 19551-03-2; **6**, 573-12-6; 1,2-dihydroxyphenanthrene, 19551-04-3; 1,2-diacetoxyphenanthrene, 19551-05-4.

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(10) E. Mosettig and A. Burger, *ibid.*, **55**, 2981 (1933).

Oxidative Trimerization of 2,4-Diphenylphenol

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The oxidation of 2,4-disubstituted phenols with common one-electron oxidants generally leads to 2,2′-dihydroxydiphenyl compounds which often undergo further oxidation.[1] For example, oxidation of 2,4-di-*t*-butylphenol gives 2,2′-dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl which is rapidly converted into a spiroquinol ether by an intramoleclar oxidative coupling reaction.[2] The oxidation of 2,4-diphenylphenol apparently has not been reported previously.

We have now found that 2,4-diphenylphenol (**1**) (see Scheme I) is easily oxidized with alkaline potassium ferricyanide to give the yellow crystalline dioxepin **2** which was isolated in 54% yield. The dioxepin structure is supported by elemental analysis, molecular weight determination, and the following data and chemical transformations.

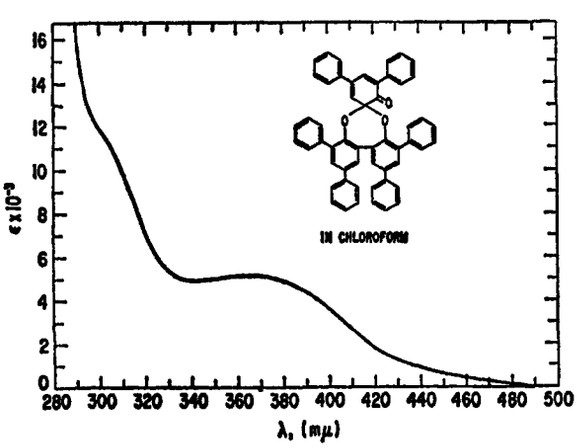

Figure 1.

(1) For a recent review, see H. Musso in "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, Inc., New York, N. Y., 1957, p 1.

(2) E. Müller, R. Mayer, B. Narr, A. Rieker, and K. Scheffler, *Ann.*, **645**, 25 (1961).