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.

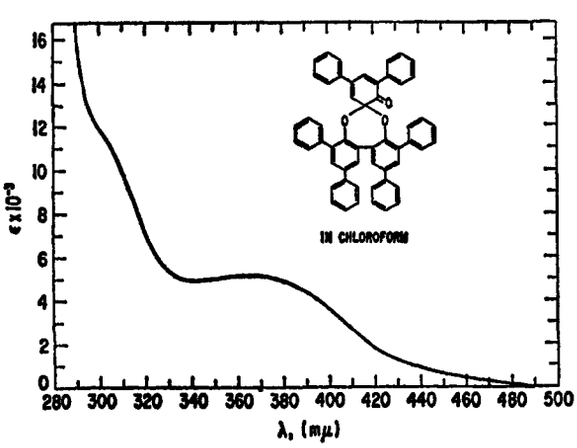
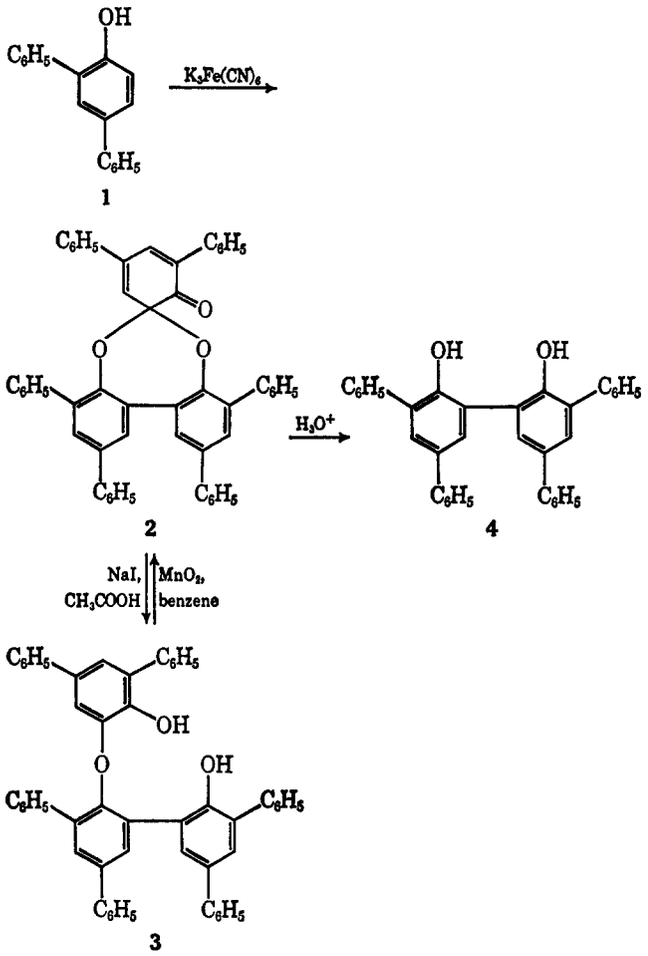


Figure 1.

(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).

SCHEME I



The ultraviolet and visible spectrum of **2** (see Figure 1) is indicative of the 2,4-cyclohexadienone system.[3] The infrared spectrum shows no absorption in the hydroxyl region but exhibits a carbonyl band at 1693 cm^{-1} (in KBr). Upon treatment with sodium iodide in acetic acid the trimer is reduced to give a quantitative yield of the colorless crystalline bisphenol **3** which was characterized by its diacetate. Oxidation of bisphenol **3** with active manganese dioxide[4] in benzene results in an intramolecular coupling reaction regenerating dioxepin **2** in excellent yield. The quinone ketal structure and the diphenyl linkage in the trimeric oxidation product of 2,4-diphenylphenol is confirmed by the acid-catalyzed hydrolysis which leads to 2,2′-dihydroxy-3,3′,5,5′-tetraphenylbiphenyl (**4**). No attempt has been made to isolate and characterize any products deriving from the 3,5-diphenyl-*o*-benzoquinone, the second fragment of the hydrolysis reaction.

The formation of **5** can be interpreted in terms of oxidative C–C coupling of **1** to give **4** which then undergoes intermolecular oxidative C–O coupling with **1** to give **3**, the direct precursor of dioxepin **2**.

Dioxepin formation has been observed recently in the oxidation of alkoxyphenols.[5,6] Although numerous 2,4-dialkylphenols have been studied previously, only the dehydrogenation of 2-methyl-4-*t*-butylphenol with either silver[7] oxide or $CuCl_2$ in the presence of pyridine[8] has been reported to give a dioxepin. In that case, the dioxepin formation was considered to be a deviation in phenol oxidation.[7] The isolation of **2** suggests that other examples of deviation may be found as the interest in phenol oxidation continues.

(3) For a recent review, see A. J. Waring, *Advan. Alicyclic Chem.*, **1**, 129 (1966).

(4) J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. N. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1094 (1952).

Experimental Section

Melting points were determined on a hot-stage microscope. Analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Molecular weights were determined by thermoelectric measurement.

2,4,8,10,4′,6′-Hexaphenyldibenzo[*d,f*][1,3]dioxepin-6-spiro-2′-cyclohexa-3′,5′-dien-2-one (2).—A solution of potassium ferricyanide (33 g) and potassium hydroxide (6 g) in water (300 ml) was added over a 5-min period to a stirred solution of 2,4-diphenylphenol (12.3 g) in benzene (500 ml) under nitrogen. A colorless precipitate formed, but dissolved again as stirring was continued. After 15 min the green benzene layer was separated, washed with water and dried over sodium sulfate. Evaporation of the benzene *in vacuo* gave a green oily residue which crystallized upon treatment with acetone. Filtration gave 6.6 g (54%) of yellow crystals, mp 255–258°.

Anal. Calcd for $C_{54}H_{36}O_3$: C, 88.50; H, 4.95; mol wt, 732.78. Found: C, 88.37; H, 4.89; mol wt, 732 (M^+).

From the acetone filtrate no other products but polymeric methanol insoluble material could be isolated. Slow addition of 2,4-diphenylphenol to the alkaline potassium ferricyanide solution decreased the yield of the trimer considerably and increased the yield of polymeric material.

Reduction of Dioxepin 2 with Sodium Iodide (3).—A mixture of **2** (1.22 g, 1.55 mmol) in chloroform (50 ml) and sodium iodide (3 g) in acetic acid (120 ml) was refluxed for 30 min. The chloroform was then evaporated *in vacuo* and the liberated iodine was reduced by dropwise addition of 0.1 *N* sodium thiosulfate solution. The colorless crystalline precipitate thus obtained was dried overnight *in vacuo* at 60°: yield 1.20 g (98%); mp 159–162°. The substance was dissolved in hot acetic acid (75 ml) and filtered through cellulose powder in order to remove a trace of insoluble material. Addition of a little water to the hot filtrate gave a colorless crystalline precipitate having the same melting point as the crude reduction product. The substance was dried overnight *in vacuo* at 110°.

Anal. Calcd for $C_{54}H_{38}O_3$: C, 88.25; H, 5.21; mol wt, 734.90. Found: C, 87.99; H, 5.05; mol wt, 734 (M^+).

The nmr spectrum of **3** (in $CDCl_3$) indicates two different hydroxy groups by singlets at τ 4.7 and 4.2 ppm.

Oxidation of Reduction Product 3.—A suspension of active MnO_2 (2.5 g) in a solution of reduction product **3** (250 mg) in benzene (50 ml) was shaken for 2 hr. Evaporation of the filtrate *in vacuo* gave a glassy yellow residue which crystallized upon trituration with little acetone: yield 230 mg (92%); mp 252–255°; mmp with authentic **2** gave no depression.

Acetylation of Reduction Product 3.—Reduction product **3** (488 mg, 0.66 mmol) was acetylated with hot acetic anhydride in the presence of pyridine. The diacetate was recrystallized from a boiling chloroform–methanol mixture to give 480 mg of colorless crystals, mp 212–213°.

Anal. Calcd for $C_{58}H_{42}O_5$ (818.98): C, 85.06; H, 5.17. Found: C, 84.74; H, 5.19.

The nmr spectrum of the diacetate (in $CDCl_3$) indicates two different acetyl groups by singlets at τ 8.2 and 8.3 ppm.

Acid-Catalyzed Hydrolysis of Dioxepin 2 (4).—A solution of **2** (732 mg, 1 mmol) in a mixture of chloroform (20 ml), methanol (10 ml), and concentrated hydrochloric acid (2 ml) was refluxed for 18 hr. Most of the chloroform was then removed by distillation. The residual light yellow solution gave a colorless crystalline precipitate when most of the solvent had evaporated at room temperature: yield 210 mg (43%); mp 188–190°. Recrystallization from a boiling chloroform–methanol mixture raised the melting point to 189–192°.

(5) D. F. Bowman, F. R. Hewgill, and B. R. Kennedy, *J. Chem. Soc., C*, 2274 (1966); see also other papers of that series by F. R. Hewgill and coworkers.

(6) J. C. Pew and W. J. Connors, unpublished results cited by J. M. Harkin in "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Batterysb, Ed., Marcel Dekker, Inc., New York, N. Y., 1957, p 243.

(7) D. F. Bowman and F. R. Hewgill, *Chem. Commun.*, 471 (1968).

(8) W. W. Karpow and M. L. Khydekel, *Zh. Org. Khim.*, **4**, 861 (1968).

Anal. Calcd for $C_{36}H_{26}O_2$: C, 88.13; H, 5.34; mol wt, 490.57. Found: C, 87.92; H, 5.47; mol wt (in dioxane), 495.

Registry No.—**1**, 6093-03-4; **2**, 19550-96-0; **3**, 19550-98-2; **3** (diacetate), 19550-99-3; **4**, 19550-97-1.

Acknowledgment.—The author is very much indebted to Drs. A. S. Hay and J. R. Ladd for providing the 2,4-diphenylphenol.

Decabromopentacyclo-[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one

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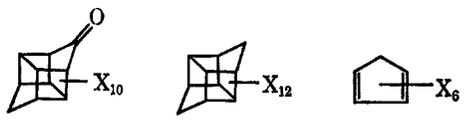
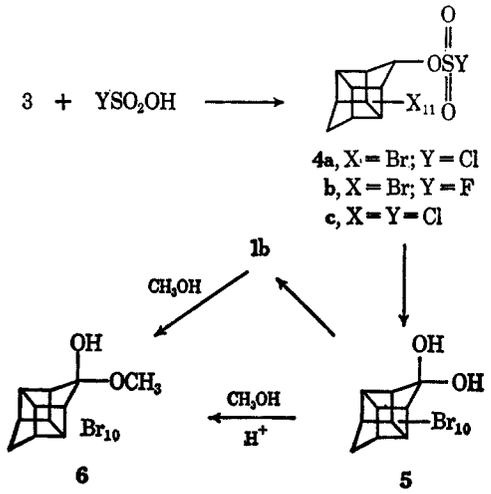
Despite many investigations of the chemistry of decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one (**1a**) and its derivatives,[2,3] the synthesis of the analogous bromine compound has not been reported in the literature, although the synthesis of the parent bromocarbon, dodecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane (**2b**), has been described.[4,5] Recent interest in the synthesis and reactions of hexabromocyclopentadiene[6] (**3b**) prompts us to report our results on the reaction of **3b** with fluoro- and chlorosulfonic acids. This investigation has led to the successful syntheses of the first derivatives of **2b**.



1 **2** **3**

a, X = Cl
b, X = Br

Hexabromocyclopentadiene (**3b**) and excess fluorosulfonic acid were stirred and heated at 60–80° for about 2 hr. The reaction mixture was cooled to room temperature or less, filtered, and product washed with water, dried, and recrystallized from ether–methanol to give a white solid, mp >310° dec. The elucidation of the structure of the product as the fluorosulfate ester of undecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-ol (**4b**) follows unmistakably from the elemental analyses and spectral data. The mass spectrum had a parent peak at *m/e* 1088 (^{79}Br) and the ^{19}F nmr spectrum showed a singlet at −51.2 ppm from $CFCl_3$ in good agreement with the proposed structure. The infrared spectrum did not show carbon–hydrogen or double bond absorption but the $-SO_2-$ symmetric and antisymmetric stretching modes were present at 1259 and 1438 cm^{-1}, respectively. Recent work on the structural elucidation



4a, X = Br; Y = Cl
b, X = Br; Y = F
c, X = Y = Cl

6 **5**

of the products from the reaction of **3a** with the chlorosulfonic acids provides further support for the strucure of **4b**.[7] With chlorosulfonic acid, **3b** yields the corresponding ester, **4a**. Sulfur trioxide, which will effect the synthesis of **4c** from **3a**,[8] cannot be substituted for fluoro- or chlorosulfonic acid in the reaction with hexabromocyclopentadiene. Apparently, bromide ion is formed in the reaction and oxidized by the sulfur trioxide and complete decomposition of the starting material is observed.

Hydrate **5** of the title compound was prepared from either **4a** or **4b**. From the fluorosulfate ester **4b**, aqueous alkali is required to effect the hydrolysis, whereas chlorosulfate ester **4a** is hydrolyzed readily by dissolution in 10% aqueous acetone.[9,10] Ketone hydrate **5** is readily dehydrated at elevated temperatures and reduced pressure to the title compound **1b**. The dehydration may be followed by the disappearance of the hydroxyl stretching modes in the 3600-cm^{-1} region of the infrared spectrum and by the appearance of the strong carbonyl stretching mode at 1798 cm^{-1}, a reasonable frequency for the caged ketone.[11] Hemiketal **6** was prepared from either dissolution of **1b** in methanol or by recrystallization of **5** from methanol containing a trace of mineral acid.

Experimental Section

Infrared spectra were obtained with a Beckman IR-9 spectrometer. The mass spectra were obtained on a CEC-21-110B (Direct Probe) instrument. The isotope peaks observed match the relative abundances calculated for the naturally occurring isotopes.

Hexabromocyclopentadiene (**3b**) was prepared by the method of Straus.[12] Recrystallization from hexane or methanol yielded a product melting at 86.5–88°.

Fluorosulfonic Acid, Undecabromopentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]-decan-5-yl Ester (**4b**).—Hexabromocyclopentadiene (25 g, 0.046

(1) To whom inquiries should be addressed.
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(6) P. T. Kwitowski and R. West, *J. Amer. Chem. Soc.*, **88**, 4541 (1966); **90**, 4697 (1968).
(7) (a) Y. Okaya and A. Bednowitz, *Acta Cryst.*, **22**, 111 (1967); (b) R. G. Pews, *Can. J. Chem.*, in press.
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(9) The facile hydrolysis of **4a** compared to **4b** is in good agreement with the order of reactivity of toluenesulfonyl halides with nucleophilic reagents. The order of reactivity toward diethylamine in benzene at 25° is I > Br > Cl ≫ F.[10]
(10) L. M. Litvinenko, A. F. Popov, and A. M. Borovenski, *Reaktsii Sposobnost. Organ. Soedin., Gos. Univer.*, **3**, 93 (1966); *Chem. Abstr.*, **66**, 115190 (1966).
(11) The carbonyl stretching mode of the caged ketone **1a** in KBr is 1810 cm^{-1}: G. W. Griffin and A. K. Price, *J. Org. Chem.*, **29**, 3192 (1964).
(12) F. Straus, L. Kollek, and W. Heyn, *Ber.*, **63B**, 1868 (1930).