New Stable Phenoxy Radicals. The Oxidation of Hydroxystilbenes

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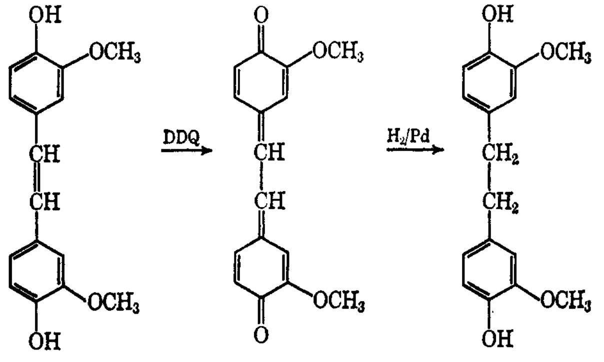
Dehydrogenation of 3,5-disubstituted 4-hydroxystilbenes with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) or alkaline potassium ferricyanide leads to new bisquinone methides which in solution spontaneously dissociate into their monomeric phenoxy radical precursors. Methoxy substitution is found to enhance the homolytic cleavage reaction. The 2,6-disubstituted 4-β-styrylphenoxy radicals are characterized by ultraviolet and electron spin resonance spectroscopy. Oxidation of 2-hydroxy-3-methoxystilbene results in the formation of dimethoxydi-β-styryldiphenoquinone.

Although the field of phenol oxidation has received continuous attention during the past 50 years, little seems to be known about the dehydrogenation of hydroxystilbenes.[1] The oxidation of 4,4′-dihydroxystilbenes has been reported to give the corresponding stilbene quinones.[2] Thus, for instance, dehydrogenation of 4,4′-dihydroxy-3,3′-dimethoxystilbene **1** with either lead tetraacetate[3] or 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[4] at room temperature gives 3,3′-dimethoxystilbene quinone **2** whose structure is confirmed by its catalytic reduction to 4,4′-dihydroxy-3,3′-dimethoxybibenzyl **3**.



1 **2** **3**

The oxidation of monohydroxystilbenes apparently has not been reported previously. We found in a preliminary experiment that the known[5] 2-hydroxy-3-methoxystilbene **4** is readily oxidized with chromic acid[6] to give the crystalline dimethoxydi-β-styryldiphenoquinone **5** (probably as a mixture of *cis–trans* isomers), which forms intensely purple solutions. The structure of **5** is based on its ultraviolet and visible spectrum which is similar to that of known diphenoquinones (see Figure 1). Reduction of **5** with hydrazine hydrate gives colorless bisphenol **6** which is easily reoxidized and whose structure is supported by elemental analysis and molecular weight.

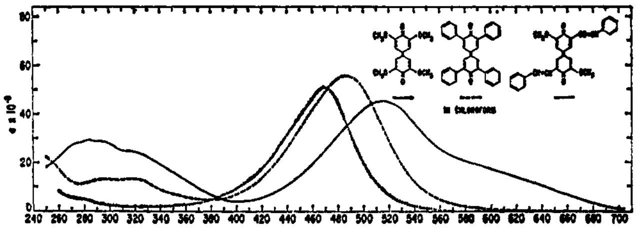
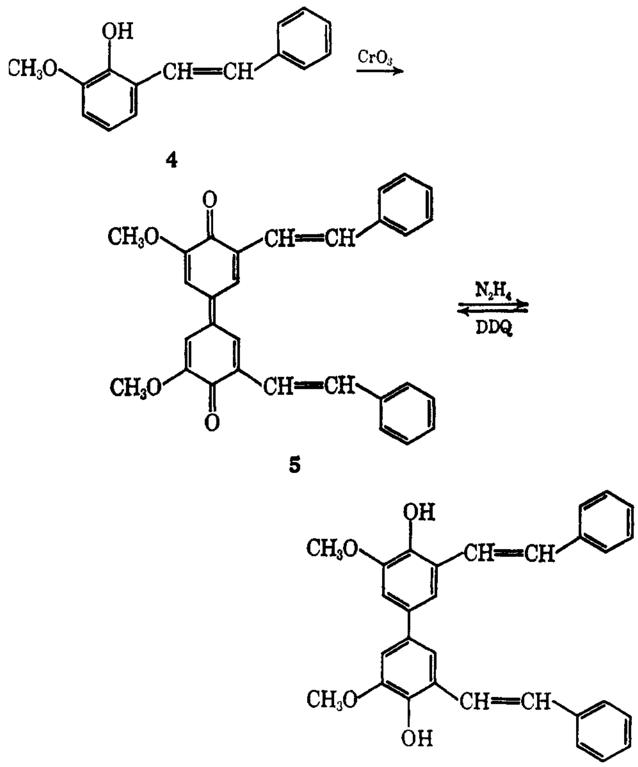


Figure 1.



4

5

6

It appeared interesting to study the oxidation of 3,5-disubstituted 4-hydroxystilbenes **7** since their corresponding phenoxy radicals **8** conceivably could be more stable than other 2,4,6-trisubstituted phenoxy radicals[7] because of the resonance effect of the β-styryl group.

The preparation of the 3,5-disubstituted 4-hydroxystilbenes[8] involved the reaction of benzylmagnesium

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(1) For a recent review on the oxidation of phenols, see H. Musso in "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 1.

(2) H. v. Euler and E. Adler in "The Svedberg, 1884–1944" (Memorial Volume), Uppsala, Sweden, 1944, p 246.

(3) E. Adler and S. Häggroth, *Svensk Papperstidn.*, **53**, 321 (1950).

(4) *Cf.* H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

(5) E. Adler and K. Lundquist, *Acta. Chem. Scand.*, **17**, 13 (1963).

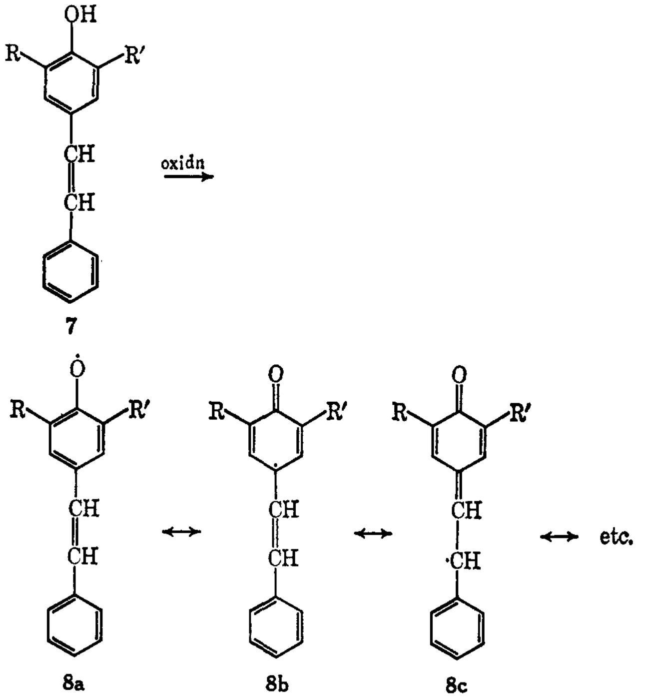
(6) Other oxidants such as DDQ or active MnO$_2$ seemed to give a mixture of products.

(7) For a recent review of phenoxy radicals, see E. Altwicker, *Chem. Rev.* **67**, 475 (1967).

(8) *Cf.* H. P. Kaufmann, *Ann.*, **433**, 237 (1923).

Table I
The Preparation of
3,5-Disubstituted 4-Hydroxystilbenes

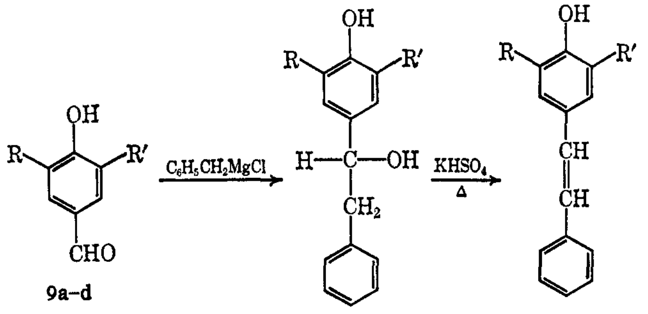
	R	R'	Yield of **10**, %	Yield of **7**, %
a	*t*-Butyl	*t*-Butyl	79	81
b	Methyl	Methyl	78	86
c	Allyl	Methoxy	40	74
d	Methoxy	Methoxy	51	78



7

8a **8b** **8c**

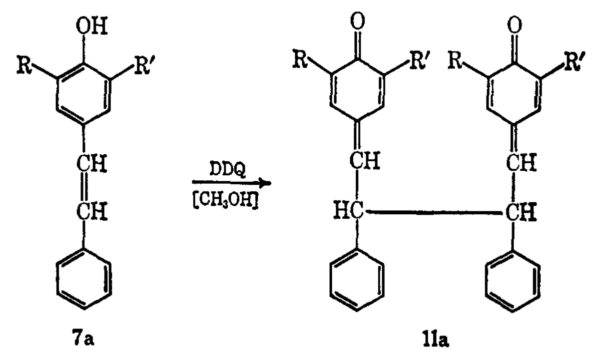
chloride with known 3,5-disubstituted 4-hydroxybenzaldehydes **9** to give the secondary alcohols **10** which were then dehydrated in the presence of potassium hydrogen sulfate. The results on the synthesis of the 3,5-disubstituted 4-hydroxystilbenes **7** are summarized in Table I.



9a–d **10a–d** **7a–d**

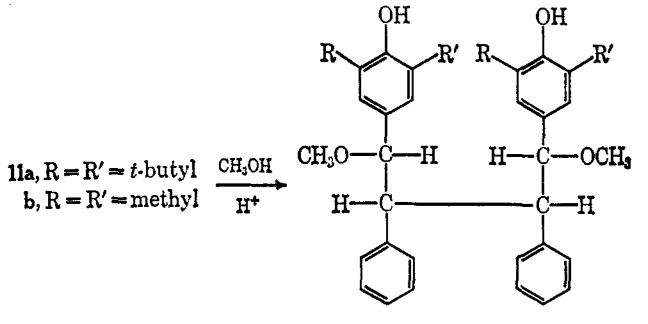
Results and Discussion

The oxidation of 3,5-di-*t*-butyl-4-hydroxystilbene **7a** with 2,3-dichloro-5,6-dicyanobenzoquinone in methanol at room temperature proceeds rapidly to give a yellow crystalline product (71% yield) for which spectroscopic data (ir, nmr), elemental analysis, and molecular weight are in agreement with dehydro dimer **11a**. The bisquinone methide structure of **11a** is supported by the acid-catalyzed reaction with methanol leading to a bisphenol for which elemental analysis, molecular weight, and spectroscopic data (ir, nmr) are in excellent agreement with structure **12a**.



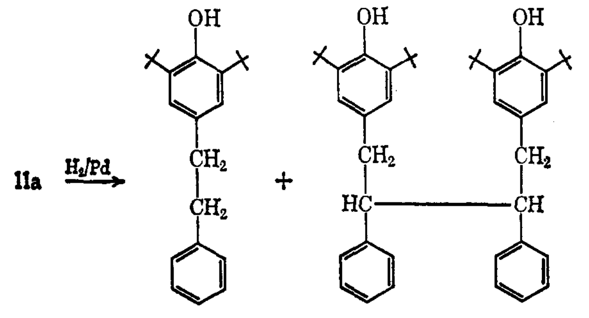
7a **11a**

R = R' = *t*-butyl



12a, R = R' = *t*-butyl
b, R = R' = methyl

Crystalline bisquinone methide **11a** appears to be quite stable since no changes have been observed in samples which have been stored at room temperature for more than 18 months. However, evidence for an unprecedented equilibrium in solution between a dimeric bisquinone methide[9] and its monomeric radical precursors was found in the behavior of **11a** toward reducing agents. Thus, upon treatment with sodium iodide in a chloroform–acetic acid mixture, bisquinone methide **11a** liberates 1 molar equiv of iodine and regenerates 3,5-di-*t*-butyl-4-hydroxystilbene **7a**. Catalytic reduction of **11a**, using Pd/C catalyst in ethyl acetate, gives 3,5-di-*t*-butyl-4-hydroxybibenzyl **13** in 75% yield, and in only 2.4% yield the dimeric reduction product **14**. Obviously, the rate of reduction of phenoxy radical **8** is much greater than that of bisquinone methide **11a**.



13, 75% **14**, 2.4%

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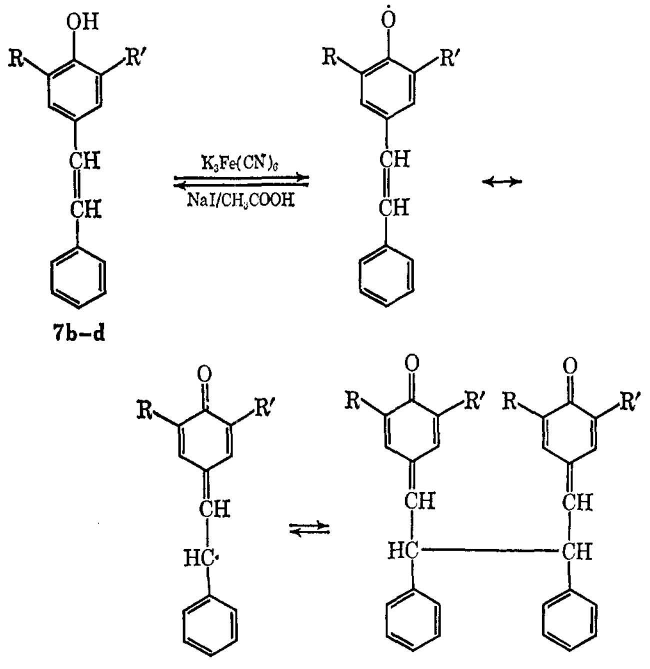
[9] The oxidation of 3,5-di-*t*-butyl-4-hydroxycinnamates had been reported to give bisquinone methides which do not dissociate into free radicals. *Cf.* E. Müller, R. Mayer, H.-D. Spanagel, and K. Scheffler, *Ann.*, **645**, 53 (1961).

In agreement with the chemical indications for a spontaneous homolytic cleavage reaction, solutions of **11a** in chloroform indeed are found to be paramagnetic, giving rise to an esr spectrum (see Figure 2) consistent[10] with the assigned structure of 2,6-di-*t*-butyl-4-β-styrylphenoxy radical (**8**, R = R′ = *t*-butyl). By comparison with diphenylpicrylhydrazyl (DPPH), a 2.5 × 10^{-4} *M* solution of **11a** was found to be approximately 5 × 10^{-6} *M* in free radical.

The oxidation of 3,5-dimethyl-4-hydroxystilbene **7b**, 3-allyl-4-hydroxy-5-methoxystilbene **7c**, and 3,5-dimethoxy-4-hydroxystilbene **7d** with alkaline potassium ferricyanide gives the crystalline bisquinone methides **11b–d** (see Table II) with similar chemical properties as those described for *t*-butyl compound **11a**. For example, bisquinone methide **11b** undergoes acid-catalyzed addition of methanol to give bisphenol **12b**. Spontaneous homolytic dissociation of **11b–d** at room temperature is indicated by the generation of 2,4,6-tri-*t*-butylphenoxy radical upon addition of 2,4,-6-tri-*t*-butylphenol. Treatment of **11d** with sodium iodide at room temperature results in the rapid formation of 1 molar equiv of iodine and regeneration of 3,5-dimethoxy-4-hydroxystilbene **7d**.



7b–d

11b–d

TABLE II

THE OXIDATION OF 4-HYDROXYSTILBENES

7, 11	R	R′	Yield of 11,%
b	Methyl	Methyl	94
c	Allyl	Methoxy	84
d	Methoxy	Methoxy	69

Solutions of bisquinone methides **11b–d** are found to be paramagnetic at room temperature. Surprisingly, however, dimethoxy compound **11d** which is pale green is paramagnetic even in its crystalline state, indicating partial dissociation into free radicals. In solution, **11d** gives rise to an esr spectrum which is similar to that of the *t*-butyl analog. Quantitative determination of spin by comparison with DPPH revealed that a 2.5 × 10^{-4} *M* solution of **11d** in chloroform was 5 × 10^{-5} *M* in 2,6-dimethoxy-4-β-styrylphenoxy radical. This corresponds to a tenfold increase of free radicals as compared with the amount of free 2,6-di-*t*-butyl-4-β-styrylphenoxy radicals measured under identical conditions.

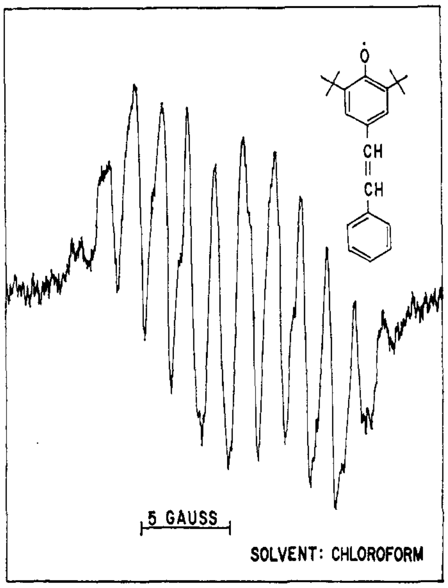


Figure 2.

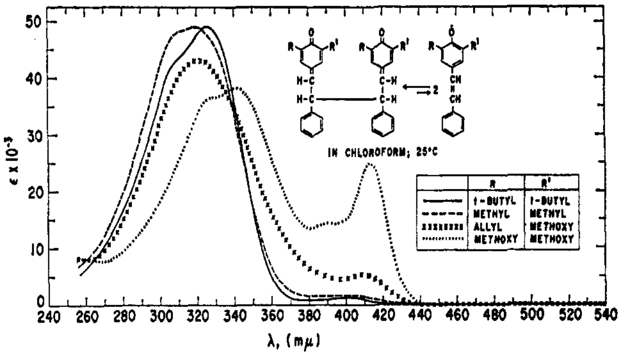


Figure 3.

The results of the ultraviolet spectroscopic investigation of bisquinone methides **11** are in excellent agreement with the esr spectroscopic findings. Phenoxy radicals are known to exhibit a characteristic ultraviolet absorption spectrum with generally three maxima around 320, 380, and 400 mμ, respectively.[11] On the other hand, alkyl-substituted quinone methides have been found to show one symmetric absorption maximum between 289 and 322 mμ.[12] The main absorption maximum in the spectrum of **11a** due to the quinone methide chromophore is found at 326 mμ (see Figure 3). An additional absorption maximum which we attribute to the 2,6-di-*t*-butyl-4-β-styrylphenoxy radical is found at 400 mμ. The reported short wavelength maximum typical of phenoxy radicals is apparent as a pronounced shoulder around 315 mμ. The generally weakest absorption maximum of phenoxy

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(10) The twelve-line spectrum is explained by coupling of the unpaired electron with the benzylic hydrogen atom and the *ortho and para* hydrogen atoms of the phenyl substituent.

(11) E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).

(12) L. J. Filar and S. Winstein, *Tetrahedron Lett.*, No. 25, 9 (1960).

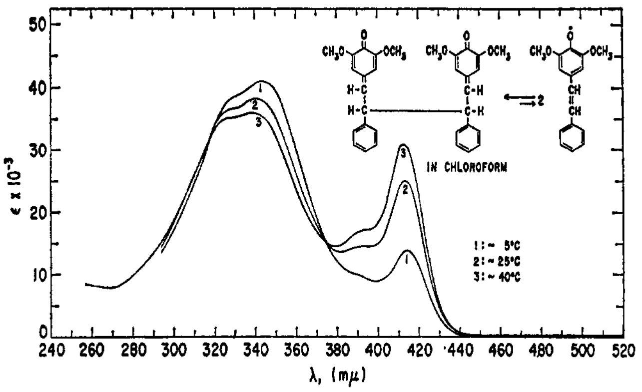

Figure 4.

radicals around 380 mμ may be indicated by the broadness of the long wavelength maximum.

The increased concentration of free 2,6-dimethoxy-4-β-styrylphenoxy radicals in solutions of bisquinone methide **11d** is obviously reflected by the increased absorbance of the long wavelength maximum at 420 mμ and the pronounced shoulders at 330 and 390 mμ, while the absorption due the quinone methide chromophore at 340 mμ is found decreased (see Figure 3). Upon heating, the phenoxy radical absorption increases at the expense of the bisquinone methide absorption. Cooling the solution of **11d** has the reverse effect. The appearance of two isosbestic points (see Figure 4) suggests that these spectral changes indeed are due to changes in the equilibrium between the bisquinone methide and 2,6-dimethoxy-4-β-styrylphenoxy radical.

Based on the ultraviolet spectrum of bisquinone methide **11b**, the concentration of 2,6-dimethyl-4-β-styrylphenoxy radicals is about the same as that of 2,6-di-*t*-butyl-4-β-styrylphenoxy radicals. Compared with bisquinone methides **11a** and **11b**, an approximately threefold increase of radical concentration is indicated by the absorbance of the long wavelength maximum in the spectrum of bisquinone methide **11c**. These findings suggest that the degree of dissociation of bisquinone methides **11** into the phenoxy radicals depends on the electronic nature of the substituents rather than on their steric influence. A similar enhancing effect of the methoxy substituent on the generation of phenoxy radicals from quinol ethers[13] and quinone ketals[14] has only recently been reported. It is worth noting, however, that a spontaneous dissociation of dimeric bisquinone methides into their monomeric phenoxy radical precursors has not been observed previously.

Experimental Section

Melting points were determined on a hot-stage microscope and are not corrected. Analyses were carried out by A. Bernhardt, Mülheim (Germany), and by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Molecular weights were determined by thermoelectric measurement.

3,3'-Dimethoxystilbenequinone (2).—DDQ (227 mg, 1 mmol) was added to a stirred suspension of 4,4'-dihydroxy-3,3'-dimethoxystilbene[15] (272 mg, 1 mmol) in absolute ethanol (5 ml). After 30 min of stirring the deep red reaction product was removed by filtration and washed with absolute ethanol: yield, 150 mg (55%); mp 195–205° (depending on the rate of heating). When the reaction was repeated on a 2-mmol scale, the yield of **2** was 72%, mp 202–206° (lit.[3] mp 210°, unsharp). The ir spectrum of **2** did not show any absorption in the OH region but showed a strong band at 1610 cm^{-1} (in KBr). *Anal.* Calcd for $C_{16}H_{14}O_4$ (270.27): C, 71.10; H, 5.22. Found: C, 70.93; H, 5.26.

Catalytic Reduction of 3,3'-Dimethoxystilbenequinone (3).—3,3'-Dimethoxystilbenequinone (135 mg, 0.5 mmol) was suspended in ethyl acetate (5 ml) and hydrogenated in the presence of Pd/C (10%) catalyst (100 mg). The hydrogen uptake after 50 min was 225 ml. Filtration and evaporation of the solvent gave 118 mg (91%) of 3,3'-dimethoxy-4,4'-dihydroxybibenzyl, mp 158° (lit.[16] mp 158°). The melting point was unsharp (as reported), probably because the compound is autoxidized at elevated temperature to give the stilbene. The structure of **3** is fully supported by its nmr spectrum.

3,3'-Dimethoxy-5,5'-di-β-styryldiphenoquinone (5).—A solution of chromic acid (1.8 g) in acetic acid (15 ml) and pyridine (15 ml) was added dropwise to a stirred solution of 2-hydroxy-3-methoxystilbene[5] (2.26 g) in acetic acid (25 ml). The reaction mixture was then diluted with acetic acid (40 ml) and water (40 ml). Since the crystalline precipitate was difficult to remove by filtration, the suspension was subjected to centrifugation. The precipitate thus obtained was washed four times with ethanol and separated each time by centrifugation: yield, 980 mg (43%) of deep green shiny crystals; mp 210–213° dec. The ir spectrum of **5** shows a strong split absorption of 1605/1625 cm^{-1}. Diphenoquinone **5** is essentially insoluble in ethanol or methanol, but dissolves with a deep purple color in chloroform. *Anal.* Calcd for $C_{30}H_{24}O_4$ (448.49): C, 80.33; H, 5.39. Found: C, 80.21; H, 5.31.

4,4'-Dihydroxy-3,3'-dimethoxy-5,5'-di-β-styrylbiphenyl (6).—Hydrazine hydrate (2 ml) was added dropwise to a stirred solution of 3,3'-dimethoxy-5,5'-di-β-styryldiphenoquinone (350 mg) in chloroform (80 ml) and methanol (40 ml). The reaction mixture rapidly turned light yellow and a colorless crystalline precipitate formed. Filtration and recrystallization by dissolving in boiling chloroform and adding methanol gave 330 mg (94%) of colorless crystals, mp 241–242°. The ir spectrum of the compound shows an OH absorption at 3420 cm^{-1} (in KBr). *Anal.* Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82; mol wt, 450.51. Found: C, 79.79; H, 5.85; mol wt (in acetone), 494.

Oxidation of 4,4'-Dihydroxy-3,3'-dimethoxy-5,5'-di-β-styrylbiphenyl.—DDQ (56 mg, 0.25 mmol) was added to a stirred suspension of **6** (113 mg, 0.25 mmol) in methanol (5 ml). As the DDQ dissolved, a dark green crystalline precipitate formed. Stirring was continued for 15 min. Filtration and recrystallization of the residue by dissolving in boiling chloroform and adding methanol gave 100 mg (88%) of green crystals, mp 210–213°. The ir spectrum of the product was completely identical with that of diphenoquinone **5** obtained by oxidation of 2-hydroxy-3-methoxystilbene with chromic acid.

3,5-Di-*t*-butyl-4-hydroxystilbene (7a).—A mixture of 1-[3,5-di-*t*-butyl-4-hydroxyphenyl]-2-phenylethanol **10a** (3.26 g, 10 mmol) and potassium hydrogen sulfate (410 mg) was kept for 10 min at 185–190°. The reaction mixture was then dissolved in a little ethanol and filtered in order to remove the inorganic material. Dilution of the filtrate with little water gave colorless crystals: yield, 2.5 g (81%); mp 91–93°. *Anal.* Calcd for $C_{22}H_{28}O$: C, 85.66; H, 9.15; mol wt, 308.44. Found: C, 85.48; H, 9.03; mol wt (in benzene), 310.

Stilbenes 7b–d were prepared in the same manner as described for **7a**: dehydration temperature 150–155°; yields are shown in Table I.

3,5-Dimethyl-4-hydroxystilbene (7b) had mp 140–143°. *Anal.* Calcd for $C_{16}H_{16}O$ (224.29): C, 85.68; H, 7.19. Found: C, 86.09; H, 7.45.

3-Allyl-4-hydroxy-5-methoxystilbene (7c) had mp 103–104°. *Anal.* Calcd for $C_{18}H_{18}O_2$ (266.32): C, 81.17; H, 6.81. Found: C, 80.91; H, 6.70.

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[13] L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 5619 (1967); M. A. DaRooge and L. R. Mahoney, *J. Org. Chem.*, **32**, 1 (1967); J. Petranek, J. Pilar, and D. Doskocilova, *Tetrahedron Lett.*, 1979 (1967).

[14] J. D. Fitzpatrick, C. Steelink, and R. E. Hansen, *J. Org. Chem.*, **32**, 625 (1967). *Cf.* also C. Steelink and R. E. Hansen, *Tetrahedron Lett.*, 105 (1966).

[15] H. Richtzenhain and C. V. Hofe, *Ber.*, **72**, 1890 (1939).

[16] W. Manchot and C. Zahn, *Ann.*, **345**, 315 (1906).

3,5-Dimethoxy-4-hydroxystilbene (7d) had mp 123–124°. *Anal.* Calcd for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29; mol wt, 256.29. Found: C, 74.92; H, 6.49; mol wt (in benzene), 256.

1-[3,5-Di-*t*-butyl-4-hydroxyphenyl]-2-phenylethanol (10a).—3,5-Di-*t*-butyl-4-hydroxybenzaldehyde (9.36 g, 40 mmol) dissolved in ether (1500 ml) was allowed to react with benzylmagnesium chloride prepared from benzyl chloride (35 g) and magnesium (7 g) in ether (200 ml). After 5 hr of refluxing the reaction mixture was acidified with aqueous acetic acid. The ether layer was separated and dried over sodium sulfate. After evaporation of the solvent the residue was subjected to vacuum distillation at about 0.2-mm pressure and a bath temperature of 100° in order to remove the by-product bibenzyl. The oily residue was treated with pentane to give colorless crystals which were recrystallized from boiling pentane: yield 10.5 g (79%); mp 77–79°. *Anal.* Calcd for $C_{22}H_{30}O_2$: C, 80.93; H, 9.26; mol wt, 326.42. Found: C, 80.75; H, 9.23; mol wt (in benzene), 323.

Compounds **10b–d** were prepared in the same manner as described for **10a**. Yields are shown in Table I.

1-[3,5-Dimethyl-4-hydroxyphenyl]-2-phenylethanol (10b) had mp 122–130°. *Anal.* Calcd for $C_{16}H_{18}O_2$ (242.30): C, 79.31; H, 7.49. Found: C, 79.18; H, 7.41.

1-[3-Allyl-4-hydroxy-5-methoxyphenyl]-2-phenylethanol (10c) had mp 101°. *Anal.* Calcd for $C_{18}H_{20}O_3$ (284.34): C, 76.03; H, 7.09. Found: C, 76.22; H, 7.29.

1-[3,5-Dimethoxy-4-hydroxyphenyl]-2-phenylethanol (10d) had mp 117–118°. *Anal.* Calcd for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61; mol wt, 274.30. Found: C, 69.83; H, 6.66; mol wt (in chloroform), 280.

Oxidation of 3,5-Di-*t*-butyl-4-hydroxystilbene (11a).—DDQ (568 mg, 2.5 mmol) was added to a stirred suspension of 3,5-di-*t*-butyl-4-hydroxystilbene (1.54 g, 5 mmol) in methanol (10 ml). As the DDQ dissolved a yellow crystalline precipitate formed. Filtration after 5 min gave 1.10 g (71%) of yellow crystals, mp 202–204°. Recrystallization by dissolving in a little chloroform and adding methanol raised the melting point to 207–209°. *Anal.* Calcd for $C_{44}H_{54}O_2$: C, 85.94; H, 8.85; mol wt, 614.87. Found: C, 85.75; H, 8.87; mol wt (in benzene), 610.

Oxidation of 3,5-Dimethyl-4-hydroxystilbene (11b).—A solution of 3,5-dimethyl-4-hydroxystilbene (2.24 g, 10 mmol) in benzene (200 ml) was added dropwise under nitrogen to a stirred solution of potassium ferricyanide (16.5 g) and potassium hydroxide (3 g) in water (150 ml). After 10 min of stirring, the benzene layer was separated, washed with water, shaken with sodium sulfate, filtered, and evaporated to give a pale yellow crystalline residue. It was washed with methanol and removed by filtration to give 2.1 g (94%) of yellow crystals, mp 134–135°. Recrystallization by dissolving in warm benzene, adding methanol, and evaporating part of the solvent did not raise the melting point. *Anal.* Calcd for $C_{32}H_{30}O_2$ (466.56): C, 86.06; H, 6.77. Found: C, 86.12; H, 6.84.

Oxidation of 3-Allyl-4-hydroxy-5-methoxystilbene (11c).—A solution of 3-allyl-4-hydroxy-5-methoxystilbene (1.07 g, 4 mmol) in benzene (125 ml) was added under nitrogen to a stirred solution of potassium ferricyanide (6.6 g) and potassium hydroxide (1.2 g) in water (60 ml). After 5 min, additional benzene was added and the benzene layer was separated, washed with water, shaken with sodium sulfate, and filtered. Evaporation of the solvent *in vacuo* gave an oily residue which crystallized upon treatment with methanol. The yield of yellow crystalline product was 0.9 g (84%), melting between 126 and 129° dec. *Anal.* Calcd for $C_{36}H_{34}O_4$: C, 81.48; H, 6.46; mol wt, 530.63. Found: C, 81.76; H, 6.41; mol wt (in benzene), 521.

Oxidation of 3,5-Dimethoxy-4-hydroxystilbene (11d).—A solution of 3,5-dimethoxy-4-hydroxystilbene (512 mg, 2 mmol) in benzene (15 ml) was added dropwise under nitrogen to a stirred solution of potassium ferricyanide (3.3 g) and potassium hydroxide (0.6 g) in water (30 ml). A colorless crystalline precipitate formed immediately, and stirring was continued for 15 min. The reaction product was then removed by filtration, dried, and recrystallized by dissolving in little chloroform and adding methanol, and passing a stream of nitrogen through the green solution: yield 350 mg (69%) of light green to yellow crystals; mp 180–185° dec (the substance turns deep red upon heating). The ir spectrum (in KBr) shows a strong absorption band at 1645 cm^{-1} (shoulder at 1625 cm^{-1}). *Anal.* Calcd for $C_{32}H_{30}O_6$: C, 75.25; H, 5.92; mol wt, 510.56. Found: C, 75.15; H, 5.99; mol wt (in chloroform), 446.

Acid-Catalyzed Addition of Methanol to 11a (12a).—Bisquinone methide **11a** (154 mg, 0.25 mmol) was dissolved in a mixture of ether (10 ml) and methanol (10 ml) acidified with a trace of HCl vapor. As the yellow color of the solution faded, a colorless crystalline precipitate formed. Filtration gave 110 mg (65%) addition product **12a**, mp 257–259°. *Anal.* Calcd for $C_{46}H_{62}O_4$: C, 81.37; H, 9.20; mol wt, 678.96. Found: C, 81.20; H, 9.36; mol wt (in benzene), 680.

Acid-Catalyzed Addition of Methanol to 11b (12b).—Bisquinone methide **11b** (446 mg, 1 mmol) was added to methanol (10 ml) which was acidified with a trace of HCl vapor. As the bisquinone methide dissolved, a colorless precipitate formed. After 2 hr of stirring the reaction mixture was filtered to give 400 mg (78%) of colorless crystalline product, mp 294–295°. Recrystallization from boiling methanol raised the melting point to 296–300°. *Anal.* Calcd for $C_{34}H_{38}O_4$ (510.64): C, 79.97; H, 7.50. Found: C, 80.21; H, 7.36.

Reduction of 11a with Sodium Iodide.—A solution of sodium iodide (100 mg) in acetic acid (10 ml) was added to a solution of bisquinone methide **11a** (154 mg, 0.25 mmol) in chloroform (10 ml). The reaction mixture was kept at 50° for 30 min and the liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution (5 ml, corrected). The slightly reddish chloroform layer was separated and the aqueous layer was extracted once more with little chloroform. Evaporation of the combined chloroform solutions gave 90 mg (60%) of colorless crystalline residue, mp 89–92°. The mixture melting point with 3,5-di-*t*-butyl-4-hydroxystilbene was not depressed.

Reduction of 11d with Sodium Iodide.—Bisquinone methide **11d** (255 mg, 0.5 mmol) was added to a solution of sodium iodide (300 mg, 2 mmol) in acetic acid (10 ml). The reaction mixture was shaken for 10 min. The liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution (10 ml, corrected) and the colorless precipitate which formed during the titration was removed by filtration: yield 176 mg (69%) of 3,5-dimethoxy-4-hydroxystilbene, mp 120–122°. The mixture melting point with authentic material was not depressed.

Catalytic Reduction of Bisquinone Methide 11a (13, 14).—Bisquinone methide **11a** (500 mg, 0.815 mmol), dissolved in ethyl acetate (20 ml), was reduced in the presence of Pd/C (10%) catalyst (300 mg). The hydrogen uptake (60 ml, 2.67 mmol) stopped after 80 min. Filtration and evaporation of the filtrate *in vacuo* gave an oily residue which crystallized upon treatment with a little aqueous methanol. The crystalline product was removed by filtration and subjected to vacuum sublimation at about 0.1 mm pressure and a bath temperature of 65°: yield of colorless crystalline **13**, 380 mg (75%); mp 56°. *Anal.* Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74; mol wt, 310.49. Found: C, 85.21; H, 9.85; mol wt (acetone), 291.

The sublimation left a small amount of a colorless crystalline residue which was recrystallized from boiling methanol: yield 12 mg (2.4%); mp 218–221°. *Anal.* Calcd for $C_{44}H_{58}O_2$ (618.94): C, 85.39; H, 9.45. Found: C, 85.29; H, 9.53.

Registry No.—**5**, 19566-69-9; **6**, 19566-70-2; **7a**, 19566-71-3; **7b**, 19566-72-4; **7c**, 19566-73-5; **7d**, 19566-74-6; **10a**, 19566-75-7; **10b**, 19566-76-8; **10c**, 19566-77-9; **10d**, 19566-78-0; **11a**, 19594-77-5; **11b**, 19566-82-6; **11c**, 19566-83-7; **11d**, 19566-84-8; **12a**, 19566-79-1; **12b**, 19566-80-4; **13**, 15017-98-8; **14**, 19566-68-8.

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