Quinone Dehydrogenation. III.[1] The Oxidation of 2,4-Di-*t*-butylphenol

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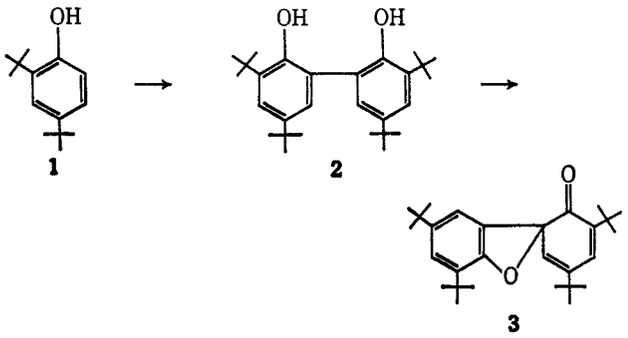
Received October 4, 1968

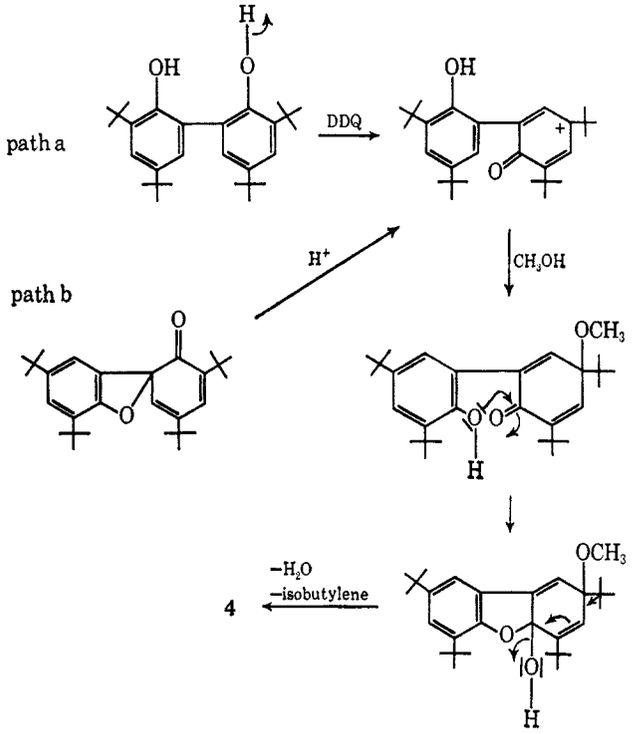
The oxidation of 2,4-di-*t*-butylphenol with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in methanol leads to 2-methoxy-4,6,8-tri-*t*-butyldibenzofuran and a tetra-*t*-butyl-substituted benzofuranoxepinone. A sequence of one-electron and two-electron transfers to DDQ is proposed for this unusual dehydrogenation reaction. The preparation and isolation of a stable benzofuranoxepinoxy radical is described.

The oxidation of 2,4-di-*t*-butylphenol **1** with common one-electron oxidizing agents results in the formation of 2,2′-dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl (**2**) which is rapidly further oxidized to the spiroquinol ether **3**.[2,3] Similar spiroquinol ethers are known to be formed by intramolecular oxidative coupling of other bisphenols.[4]



We have now investigated the dehydrogenation of 2,4-di-*t*-butylphenol with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) since it appeared desirable to substantiate the recently[5] proposed one-electron mechanism of phenol–DDQ interaction by further examples of oxidative coupling.

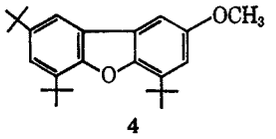
SCHEME I



Results and Discussion

The oxidation of 2,4-di-*t*-butylphenol with DDQ in methanol solution proceeds smoothly at room temperature, giving 2,3-dichloro-5,6-dicyanohydroquinone ($DDQH_2$) and approximately equal amounts of two products which precipitate from the reaction mixture and which can be separated by fractional crystallization. The same product mixture is obtained by oxidation of 2,2′-dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl[6] (**2**) with DDQ in methanol, indicating that the first step of an apparent sequence of reactions probably is that of the expected C–C coupling of phenol **1**.

The structure of one component of the product mixture, a colorless crystalline compound, was readily determined as that of 2-methoxy-4,6,8-tri-*t*-butyldibenzofuran (**4**) on the basis of its C and H analysis, molecular weight, and ir, nmr, and uv spectrum. The latter is strikingly similar to that of 2,4,6,8-tetra-*t*-butyldibenzofuran (Figure 1). The assignment of the methoxy group into the 2 position is based on literature data on the chemical shift of *t*-butyl groups in the nmr spectra of dibenzofurans.[7]



The methoxytri-*t*-butyldibenzofuran **4** became the major product when the oxidation of **1** or **2** with DDQ (molar ratio 1:2 or 1:1, respectively) was carried out in acidified methanol. It appeared conceivable that the introduction of the methoxy group into the reaction product was the result of a heterolytic oxidation of **2** (path a, Scheme I). However, the methoxytri-*t*-butyldibenzofuran **4** is also formed in the absence of DDQ in an acid-catalyzed reaction of the spiroquinol ether **3** with methanol (path b, Scheme I). Thus, the

(1) For part II of this series, see H.-D. Becker, *J. Org. Chem.*, **30**, 989 (1965).

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

(3) E. C. Horswill and K. U. Ingold, *Can. J. Chem.*, **44**, 269 (1966).

(4) 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., 1967, p 1.

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

(6) We found in the course of this study that 2,2′-dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl is easily prepared in excellent yield by oxidation of 2,4-di-*t*-butylphenol with chloranil at 200° (see Experimental Section).

(7) F. R. Hewgill and D. G. Hewitt, *J. Chem. Soc., C*, 726 (1967).

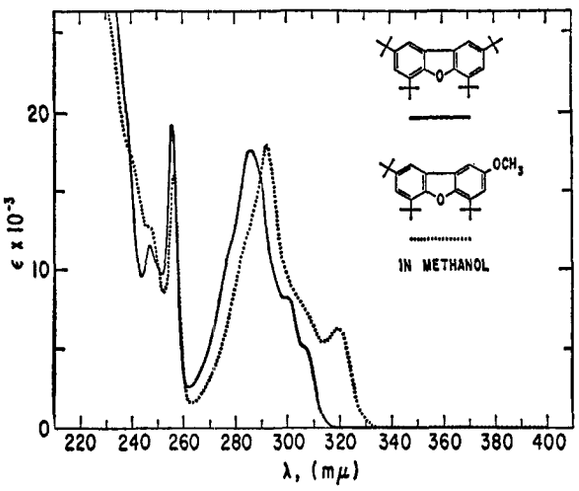
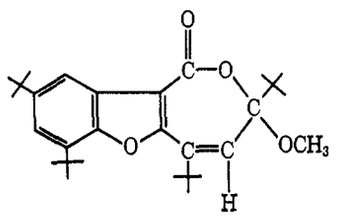


Figure 1.

around 260 mμ attributed to the aromatic system and one broad maximum around 355 mμ attributed to the α,β,γ,δ-unsaturated carbonyl system. The ir spectrum of **5** (in KBr) shows a carbonyl absorption at 1760 cm^{-1}



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typical of esters or lactones. (Two recently synthesized β,γ,δ,ε-unsaturated ε-lactones show a carbonyl absorption at 1770 and 1772 cm^{-1}, respectively.)[9] The pseudoester structure—and thus the position of the

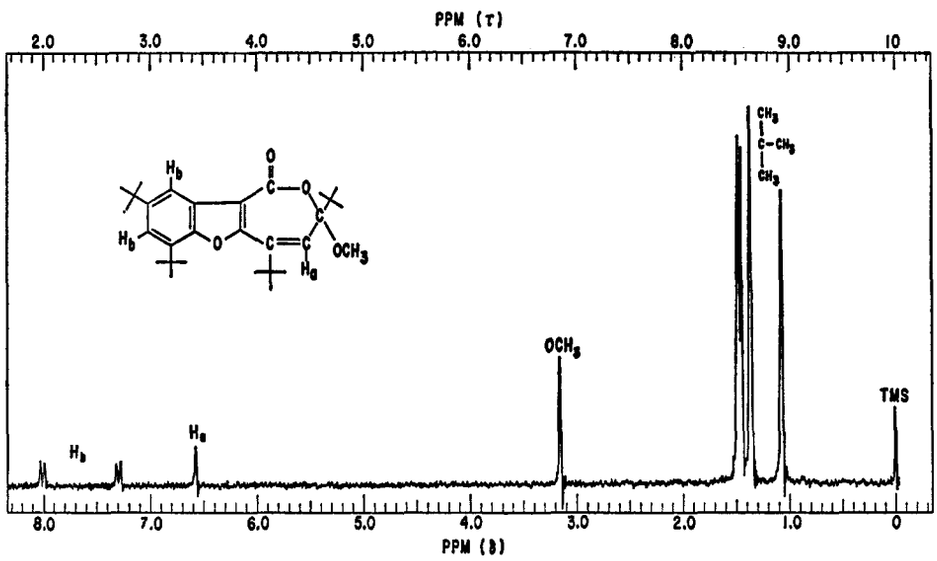


Figure 2.

formation of **4** does not necessarily involve a two-electron oxidation. Most likely, it is the result of a nucleophilic attack[8] of solvent onto the charge-transfer complex of DDQ with spiroquinol ether **3**, which in turn is formed by intramolecular homolytic oxidative coupling of bisphenol **2**.

The second product from the oxidation of 2,4-di-*t*-butylphenol, a yellow crystalline substance, analyzed for $C_{29}H_{42}O_4$. It was also formed as the major product (isolated in 85–88% yield) of the reaction of 2 mol of DDQ with 1 mol of spiroquinol ether **3** in 96% methanol. No reaction, however, was observed in absolute methanol. Based on the following evidence, we propose the benzofuranoxepinone structure **5** for this reaction product.

The nmr spectrum of **5** (Figure 2) reveals four different *t*-butyl groups, one methoxy group, one olefinic proton (3.4 ppm), and two aromatic (*meta*) protons coupling with each other (J_{ab} = 3 cps). The uv spectrum of **5** (Figure 3) shows two narrow maxima

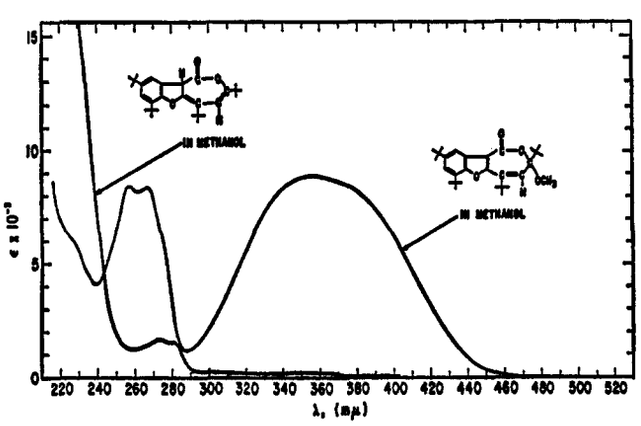


Figure 3.

methoxy group—is confirmed by the transesterification experiment with ethanol which gives the ethoxy compound **6**.

(8) Nucleophilic displacement reactions in spiroquinol ethers have been observed earlier; see F. R. Hewgill and B. R. Kennedy, *ibid.*, 362 (1966).

(9) M. Foá, L. Cassar, and M. Tacchi Venturi, *Tetrahedron Lett.*, 1357 (1968).

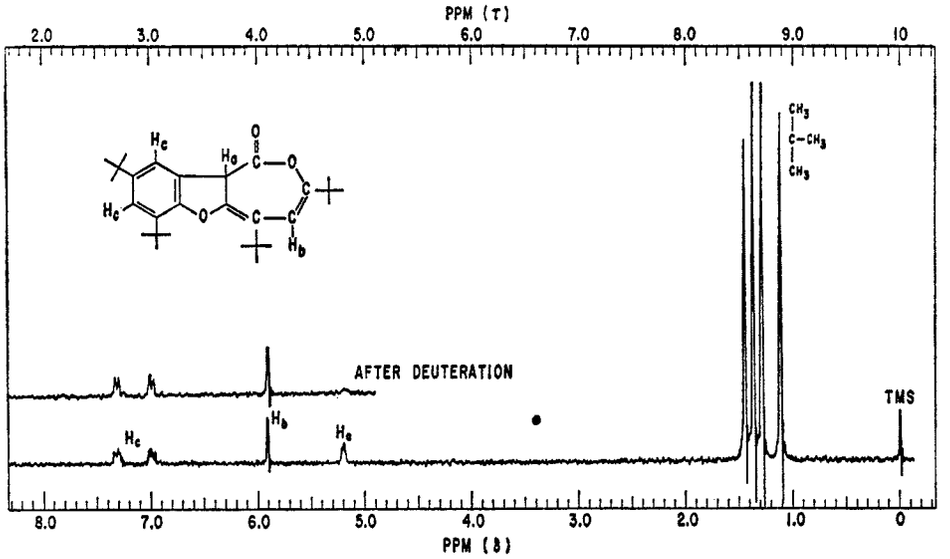
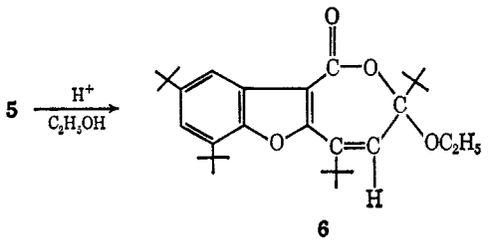


Figure 4.



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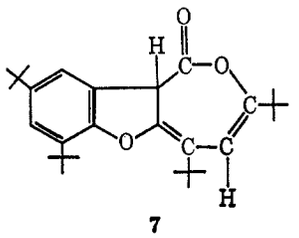
Though compound **5** resists catalytic hydrogenation (Pd–C), it liberates 1 mol of iodine upon treatment with sodium iodide in acetic acid and gives a colorless product which is also obtained by reaction of **5** with zinc and hydrochloric acid. The colorless "reduction" product is also formed by reaction of 1 mol of DDQ with spiroquinol ether **3** in 96% methanol. Structure **7** is assigned to this new compound on the basis of elemental analysis, molecular weight, and the following evidence.



7

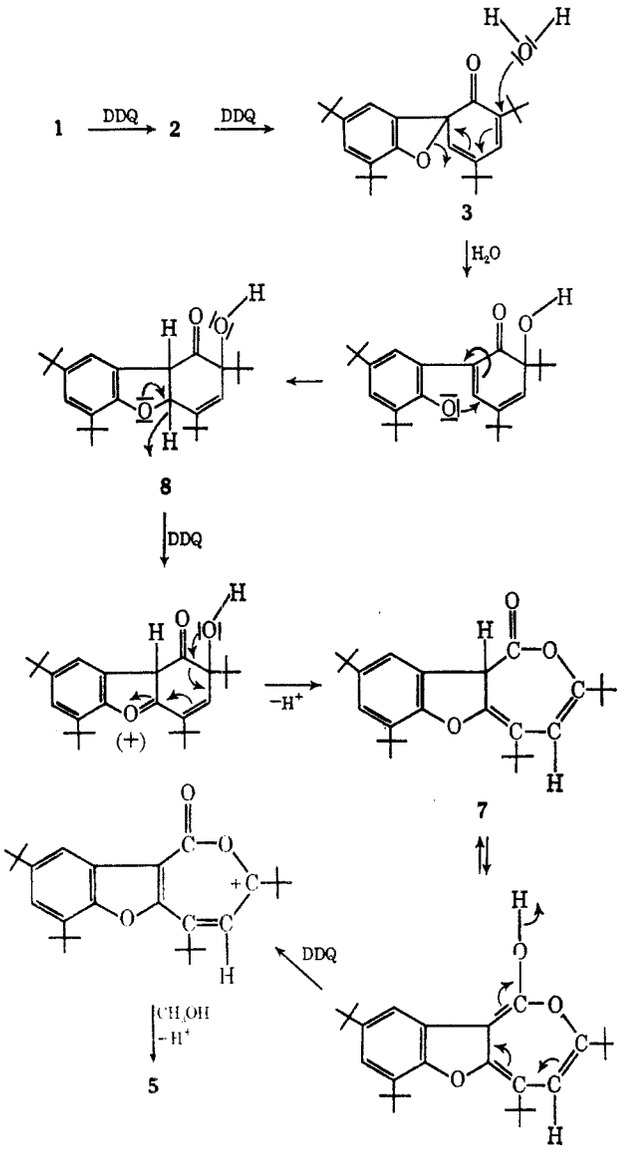
The nmr spectrum of **7** (Figure 4) reveals the reductive removal of the methoxy group from compound **5** and shows the presence of four different *t*-butyl groups, one olefinic proton (H_b, 4.08 ppm), and one proton (H_a) at 4.8 ppm which couples with the two aromatic *meta* protons. The proton with the chemical shift of 4.8 ppm can be exchanged for deuterium by deuteration with D_2O, preferably in the presence of pyridine. Deuteration restores normal *meta* coupling of the aromatic protons and thus confirms the position of H_a in compound **7**. The uv spectrum of **7** (see Figure 3) indicates the presence of the aromatic system and the disappearance of the α,β-unsaturation of the carbonyl group. No absorption is observed above 300 mμ when the uv spectrum of **7** is measured in ether solution. This finding suggests that the low absorption between 300 and 400 mμ observed in the more polar solvent may be due to the presence of small amounts of enolized **7**. However, the ir spectrum of **7** (in KBr) does not show any absorption in the hydroxyl region but exhibits a split carbonyl absorption at 1789–1815 cm^{-1}. Oxidation of the "reduction" product **7** with DDQ (1 mol) in methanol smoothly regenerates the original methoxy compound **5**.

The reaction of DDQ with 2,4-di-*t*-butylphenol leading to compound **5** apparently involves many steps. Based on the experiments described above, we would like to propose the following mechanism for the formation of **5** (see Scheme II).

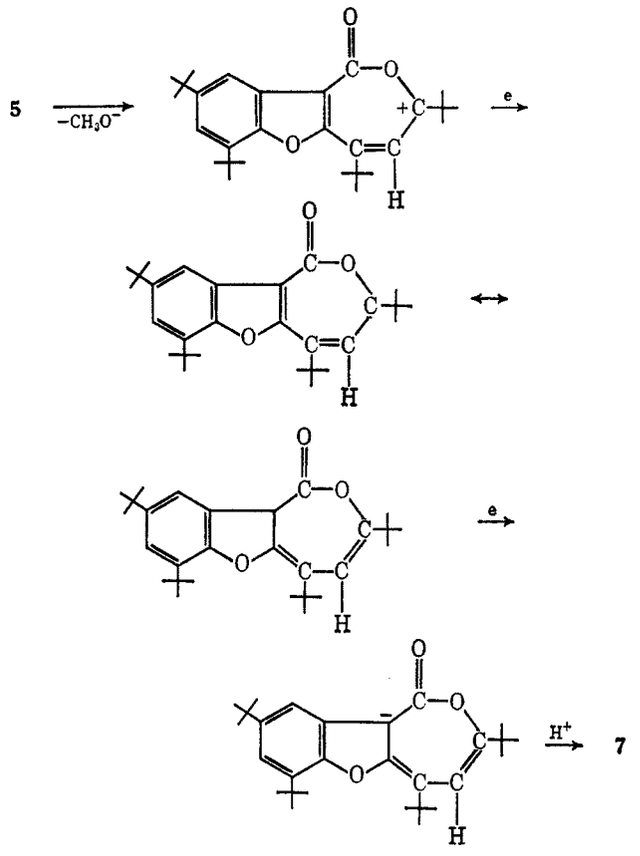
DDQ reacts with 2,4-di-*t*-butylphenol to give $DDQH_2$ and the C–C coupled dehydro dimer **2**. Oxidation of **2** by DDQ then leads to the spiroquinol ether **3** and $DDQH_2$. Both reactions are typical one-electron oxidations. The next step apparently involves nucleophilic attack of water onto the spiroquinol ether *via* its charge-transfer complex with DDQ to give the α-hydroxy ketone **8**. Over-all two-electron oxidation, depicted as hydride-ion abstraction by DDQ from the α-ether carbon atom of **8** results in the lactonization to give the "reduction" product **7**. Also the final step of the reaction sequence involves an over-all two-electron oxidation formulated as hydride-ion abstraction reaction by DDQ from enolizable **7** to give a resonance-stabilized carbonium ion which reacts with the solvent to give the benzofuranoxepinone **5**.

Evidence for the existence of the proposed carbonium ion is found in the formation of deep purple solutions of **5** in strong acids. Furthermore, the double-bond migration which accompanies the reductive removal of the methoxy group in benzofuranoxepinone **5** is well explained by two successive one-electron reductions of the carbonium ion (Scheme III). During the reaction of **5** with zinc and hydrochloric acid the radical stage formulated in Scheme III actually is indicated by the appearance of a transient deep green color. Also, we have been able to produce the radical by carrying out a one-electron oxidation of the "reduction" product **7**. Thus, oxidation of **7** with active manganese dioxide

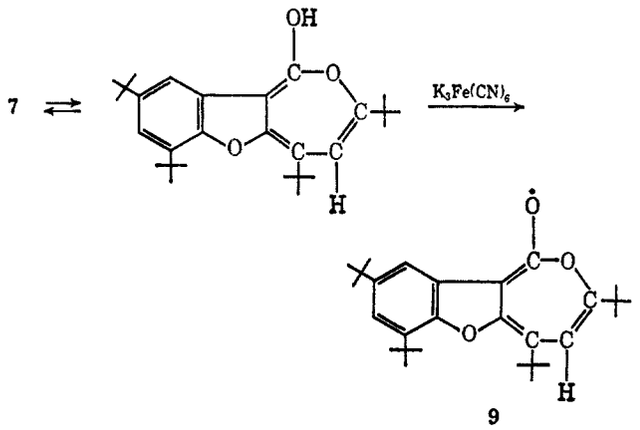
Scheme II



Scheme III



and/or 2,4,6-tri-*t*-butylpenoxy radical in benzene gives the deep blue [λ_{max} 700 mμ ($\epsilon \approx 10000$)] stable free radical **9** which we have isolated in the form of its



crystalline dimer. The first derivative esr spectrum of the benzofuranoxepinoxy radical **9** (Figure 5A) appears as an overlapping pair of doublets, as confirmed by the second derivative spectrum shown in Figure 5B.

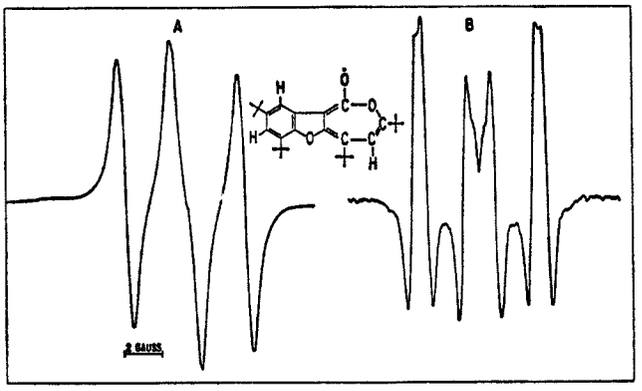
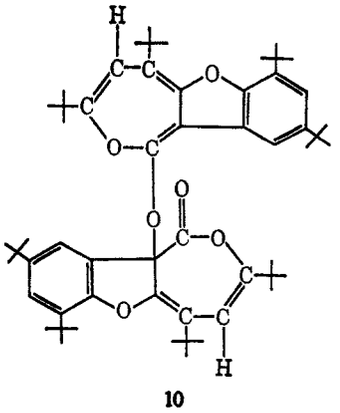


Figure 5.

The structure of the radical dimer probably is that of a carbon–oxygen coupled product **10** since the ir spectrum exhibits the carbonyl absorption at 1812



10

cm^{-1}, similar in position to that of the "reduction" product **7**.

The results presented in this paper are in agreement with the earlier[5] proposed homolytic mechanism for the oxidation of phenols by DDQ. The only oxidation reactions requiring a heterolytic mechanism are those of the nonphenolic intermediates **7** and **8**. Since we have demonstrated the existence of the benzofuranoxepinoxy radical, however, even these reactions may occur in a sequence of two one-electron transfers to DDQ.

Experimental Section

DDQ was recrystallized from methylene chloride. Absolute methanol was commercial grade. It was generally used without further drying. All oxidation reactions were carried out in screw cap bottles under nitrogen. Melting points were taken on a hot-stage microscope and are not corrected. Analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Molecular weights were determined by thermoelectric measurements in solvents specified in each case.

Oxidation of 2,4-Di-*t*-Butylphenol with Chloranil (2).—Chloranil (1.23 g, 5 mmol) was dissolved in warm 2,4-di-*t*-butylphenol (4.12 g, 20 mmol) and the deep red solution was heated for 5 min to 200–230°. The solution by then had turned light orange. The reaction mixture was triturated with about 10 ml of methanol, diluted with a few drops of water and filtered, yielding 1.64 g (80%) of bisphenol **2**, mp 196–198° (lit.[2] mp 194.5–195.5°). Evaporation of the filtrate and treatment of the residue with chloroform (20 ml) gave 1.18 g (95%) of tetrachlorohydroquinone, mp 236°.

Oxidation of 2,4-Di-*t*-butylphenol with DDQ.—DDQ (3.41 g, 15 mmol) was added to a solution of 2,4-di-*t*-butylphenol (1.54 g, 7.5 mmol) in methanol (20 ml, Baker Grade Absolute). The deep green reaction mixture was shaken for 24 hr. Filtration gave 900 mg of a yellow crystalline material, which was analyzed by nmr and found to consist of a mixture of **4** and **5** in the ratio of about 1:1. The ratio, however, has been found to vary, probably depending on the amount of water present in the methanol used. The separation of the two products is described in the following experiment.

Oxidation of 2,2′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl (2) with DDQ.—A suspension of bisphenol **2** (2.05 g, 5 mmol) and DDQ (2.50 g, 11 mmol) in methanol (15 ml) was shaken for 16 hr. Filtration gave 1.7 g of a yellow crystalline mixture of two products (nmr analysis) melting between 145 and 160°. The filtrate after evaporation of solvent and treatment of the residue with benzene gave 2.32 g (92%) of $DDQH_2$.

Separation of the two components of the product mixture was originally accomplished by fractional crystallization from much methanol in which the benzofuranoxepinone **5** is slightly less soluble than the dibenzofuran **4**. A more effective separation was achieved in the following way. The product mixture (1.25 g) was dissolved in boiling methanol (150 ml) and heated with zinc powder and few milliliters of concentrated hydrochloric acid. When the boiling solution turned colorless and part of the solvent had evaporated, it was filtered (hot). Upon cooling to room temperature, 350 mg of 2-methoxy-4,6,8-tri-*t*-butyldibenzofuran (**4**) crystallized from the filtrate and was removed by filtration. Addition of a little water to the filtrate gave 850 mg of a crystalline product (**7**), mp 125–130°, which was still contaminated with dibenzofuran **4**. It was suspended in methanol (25 ml) and oxidized by shaking for 16 hr with DDQ (425 mg). The yellow crystalline precipitate of **5** thus obtained was recrystallized from a mixture of chloroform and methanol: yield 750 mg, mp 193–195°.

2-Methoxy-4,6,8-tri-*t*-butyldibenzofuran (4). A. By Reaction of 2,2′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyldiphenyl with DDQ in the Presence of HCl.—DDQ (681 mg, 3 mmol) was added to a suspension of bisphenol **2** (1.23 g, 3 mmol) in methanol (10 ml) containing concentrated hydrochloric acid (0.1 ml). The green reaction mixture was shaken for 12 hr. A very light yellow crystalline precipitate (840 mg, mp 150–160°) was then removed by filtration. Recrystallization from a hot mixture of chloroform and methanol gave 680 mg (62%) of colorless crystals: mp 162–163°; nmr data (ppm in τ), 8.56 (s, 9), 8.42 (s, 9), 8.38 (s, 9), 6.08 (s, 3), 3.0 (d, J_{ab} = 2.5 cps, 1), 2.7 (d, J_{ab} = 2.5 cps, 1), 2.55 (d, J_{ab} = 2 cps, 1), 2.2 (d, J_{ab} = 2 cps, 1).

Anal. Calcd for $C_{25}H_{34}O_2$ (366.52): C, 81.92; H, 9.35. Found: C, 82.06; H, 9.30; mol wt (in chloroform), 346.

B. By Reaction of Spiroquinol Ether 3 with Acidified Methanol.—A suspension of **3** (380 mg, 0.43 mmol) in methanol (4 ml) containing 1 drop of concentrated hydrochloric acid was shaken for 15 hr. The colorless precipitate in the reaction mixture was removed by filtration. The yield was 135 mg (40%), mp 158–161°. Recrystallization from hot methanol gave 110 mg (32%) of colorless crystals, melting between 162 and 163°. The mixture melting point with methoxytri-*t*-butyldibenzofuran (**4**) obtained under A was not depressed.

Benzofuranoxepinone 5. A. By Reaction of Spiroquinol Ether 3 with DDQ in Aqueous Methanol.—A suspension of spiroquinol ether **3** (2.05 g, 5 mmol) in a solution of DDQ (2.27 g, 10 mmol) in 96% aqueous methanol (24 ml) was shaken for 2 hr. The originally dark brown reaction mixture (exothermic reaction) turned orange and a yellow crystalline precipitate had formed within 20 min. It was removed by filtration and recrystallized by dissolving in little chloroform and adding methanol: yield 1.91 g (84%); mp 193–195°.

Anal. Calcd for $C_{29}H_{42}O_4$ (454.63): C, 76.61; H, 9.31. Found: C, 76.46; 76.80; H, 9.20; 9.26; mol wt, 429 (in chloroform), 432 (in benzene); mass$^+$, 454.

B. By Oxidation of 7 with DDQ.—DDQ (565 mg, 2.5 mmol) was added to a suspension of **7** (1.06 g, 2.5 mmol) in methanol (10 ml). The reaction mixture was shaken overnight and the yellow crystalline precipitate was then removed by filtration: yield 1.0 g (88%); mp 192–194°. A mixture melting point with **5** obtained under A was not depressed.

Reaction of 3 in Absolute Methanol.—Spiroquinol ether **3** (2.04 g, 5 mmol) was added to a solution of DDQ (2.27 g, 10 mmol) in *freshly dried and distilled absolute methanol* (20 ml) under nitrogen. After 2 hr the deep brown reaction mixture was still clear. Upon addition of 2 drops of water dissolved in 1 ml of methanol a yellow crystalline material precipitated after 1 min and the reaction mixture turned light orange. Filtration gave 1.87 g (82.5%) of **5**, mp 192–194°. A mixture melting point with **5** obtained under A was not depressed.

Transesterification of 5 with Ethanol (6).—A solution of **5** (454 mg, 1 mmol) in absolute ethanol (50 ml) containing concentrated sulfuric acid (0.3 ml) was refluxed for 5 hr. Evaporation of the solvent *in vacuo* left a yellow oily residue which was dissolved in ether (100 ml). The ether solution was washed with aqueous bicarbonate solution. Evaporation of the ether *in vacuo* gave a yellow oily residue which gave yellow crystals upon treatment with little methanol, melting between 138 and 140°. The yield was 350 mg (75%).

Anal. Calcd for $C_{30}H_{44}O_4$ (468.65): C, 76.88; H, 9.46. Found: C, 76.69; H, 9.34.

The ir spectra (in KBr) of the methoxy compound and the ethoxy compound are essentially identical. However, the nmr spectrum of the transesterified product showed the presence of the ethoxy group instead of the methoxy group.

Benzofuranoxepinone 7. A. By Reduction of 5 with Zinc–HCl.—A solution of **5** (1.14 g, 2.5 mmol) in a chloroform–methanol mixture (10:25 ml) containing zinc powder (1 g) and concentrated hydrochloric acid (3 ml) was boiled for 20 min. By then the originally yellow solution had turned transiently deep green and finally colorless. Filtration and partial evaporation of the solvent *in vacuo* gave colorless crystals which were recrystallized from hot aqueous methanol: yield 1.0 g (91%); mp 130–132°.

Anal. Calcd for $C_{28}H_{40}O_3$ (424.60): C, 79.20; H, 9.50. Found: C, 79.47; H, 9.47; mol wt, 407 (in chloroform).

B. By Reduction of 5 with Sodium Iodide.—A solution of **5** (454 mg, 1 mmol) and sodium iodide (500 mg) in acetic acid (100 ml) was boiled for 25 min. After the solution had cooled to room temperature the liberated iodine was titrated with 0.1 *N* sodium thiosulfate solution (20 ml). The colorless crystalline precipitate thus obtained was removed by filtration: yield 400 mg (94%); mp 130–131°. A mixture melting point with the reduction product obtained under A was not depressed.

C. By Reaction of Spiroquinol Ether 3 with 1 Mol of DDQ.—A suspension of **3** (510 mg, 1.25 mmol) in a solution of DDQ (285 mg, 1.25 mmol) in methanol (10 ml) was shaken for 13 hr. From the light yellow reaction mixture 12 mg of **5**, mp 192–193°, were removed by filtration. Evaporation of the filtrate left a light yellow crystalline residue which was washed with a little

cold methanol to give 200 mg (38%) of **7**, mp 130–132°. A mixture melting point with reduction product obtained under A was not depressed.

Benzofuranoxepinoxy Radical (9–10).—A solution of 2,4,6-tri-*t*-butylphenol (262 mg, 1 mmol) and benzofuranoxepinone **7** (424 mg, 1 mmol) in benzene (30 ml) was added under nitrogen to a stirred solution of potassium ferricyanide (3.3 g) and potassium hydrixide (0.6 g) in water (30 ml). Stirring was continued for 15 min. The deep blue benzene layer was then quickly separated, washed twice with water, shaken with sodium sulfate, and evaporated *in vacuo*. The green, partially crystalline residue was triturated with about 20 ml of methanol and stirred for few minutes. Filtration gave a light blue to green crystalline residue (150 mg, 35%), melting around 130° dec.

Anal. Calcd for $C_{56}H_{78}O_6$ (846.60): C, 79.40; H, 9.30. Found: C, 79.28, 79.46; H, 9.24, 9.43.

Compound **10** forms deep blue solutions in chloroform.

The oxidation was also carried and in the absence of 2,4,6-tri-*t*-butylphenol, giving the oxidation product in only 2.5% yield.

Anal. Found: C, 79.19; H, 9.17.

Esr Measurement.[10]—The benzofuranoxepinoxy radical **9** was generated by dissolving dimer **10** in benzene. It can also be generated by dissolving **7** (5 mg) in benzene (5 ml) containing 1 drop of pyridine, and adding activated MnO_2 (50 mg). Filtration under nitrogen through a sintered-glass funnel gave a deep blue filtrate which was used for the esr experiment.

Spectra.[11]—Infrared spectra were taken on a Perkin-Elmer grating ir spectrophotometer, Model 521. Ultraviolet spectra were recorded on a Cary spectrophotometer, Model 14. The uv spectrum of radical **9** was obtained by dissolving **10** (8.46 mg) in chloroform (100 ml) under nitrogen. Proton magnetic resonance spectra were taken in $CDCl_3$ on a Varian A-60 instrument.

Registry No.—**1**, 96-76-4; **4**, 19566-63-3; **5**, 19566-64-4; **6**, 19566-65-5; **7**, 19566-66-6; **10**, 19566-67-7.

Acknowledgment.—The author is very much indebted to Dr. A. S. Hay for providing the spiroquinol ether **3**. Part of this work was carried out during the author's stay, 1966–1967, at the Department of Chemistry, Chalmers University of Technology, Gothenburg, Sweden. The author is very much indebted to Professor Adler for his kind hospitality.

(10) The author is indebted to Mr. Kobayashi of JEOLCO, Inc., for recording the esr spectra during a demonstration of the JEOLCO JES-ME-1X esr spectrometer. Thanks are also due to Dr. A. Factor of this laboratory for discussions concerning the spectrum.

(11) Thanks are due to Miss Dorothy McClung for measuring all uv and ir spectra.

Quinone Dehydrogenation. IV.[1] One-Electron Oxidations with 2,3-Dichloro-5,6-dicyanobenzoquinone

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Received October 4, 1968

The dehydrogenation by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) of a variety of phenolic compounds is described. Substituted 4-hydroxytriphenylmethanes are found to be easily oxidized to give stable quinone methides in high yields. A new mechanism for the disproportionation of 4-alkyl-substituted phenoxy radicals is discussed. Dehydrogenation of substituted 4,4′-dihydroxytetraphenylmethanes results in an intramolecular coupling reaction leading to bispirodienones in excellent yields. Several addition reactions of DDQ are described. A quinone ketal capable of undergoing homolytic dissociation is obtained by addition of 3,4,5-trimethoxyphenol to DDQ. 2,6-Dichlorophenol and DDQ react to give 2,3-dicyano-4,4′-dihydroxy-5,5′,6-trichlorodiphenyl ether. DDQ was found to add, together with methanol, to 1,1-diphenylethylene. 2,3-Dichloro-5,6-dicyanohydroquinone bisdiphenyl methyl ether is formed in high yield from DDQ and diphenylmethane. The reaction of methanol with DDQ results in the displacement of one cyano group to give 2-cyano-5,6-dichloro-3-methoxybenzoquinone. Diazomethane reacts with DDQ to give a spiroepoxydienone. A one-electron mechanism for the oxidation and addition reactions involving dissociation of a substrate–quinone charge-transfer complex into radical ions is discussed.

2,3-Dichloro-5,6-dicyanobenzoquinone (henceforth abbreviated DDQ) in methanol solution was recently found to be a powerful oxidant for phenols[1–3] and enols.[4] However, contrary to the common concept of quinone dehydrogenation involving a hydride-ion transfer reaction,[5,6] all products observed in these oxidations could have been formed in one-electron processes.

In view of the general interest in reactions of DDQ[6] it appeared desirable to extend the quinone dehydrogenation to phenolic compounds of structural types not previously investigated. We have now applied DDQ for the oxidation of substituted α,α-diphenyl-*p*-cresols (4-hydroxytriphenylmethanes), substituted 4,4′-dihydroxytetraphenylmethanes, and phenols having either a free *ortho* or *para* position. To gain a better understanding of the dehydrogenation mechanism, the reaction of DDQ with some hydrocarbons was included in this investigation.

Results and Discussion

A. Quinone Methide Formation.—Several substituted *p*-cresols **1** have previously[2] been found to react with DDQ in methanol solution, giving the corresponding carbonyl compounds **6**. The unstable

(1) For part III of this series, see H.-D. Becker, *J. Org. Chem.*, **34**, 1198 (1969).

(2) H.-D. Becker, *ibid.*, **30**, 982 (1965).

(3) The oxidation of phenols by DDQ has also been under investigation by E. Adler and R. Wettstrom (unpublished work, private communication by Professor Adler); see R. Wettstrom, *Svensk Kem. Tidskr.*, **75**, 429 (1963) (abstract of talk).

(4) H.-D. Becker, *J. Org. Chem.*, **30**, 989 (1965).

(5) L. M. Jackman in "Advances in Organic Chemistry: Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p 329. *Cf.* B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 1847 (1967).

(6) For a comprehensive review of DDQ and its reactions, see D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153 (1967).