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

HANS-DIETER BECKER

General Electric Research and Development Center, Schenectady, New York 12301

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).

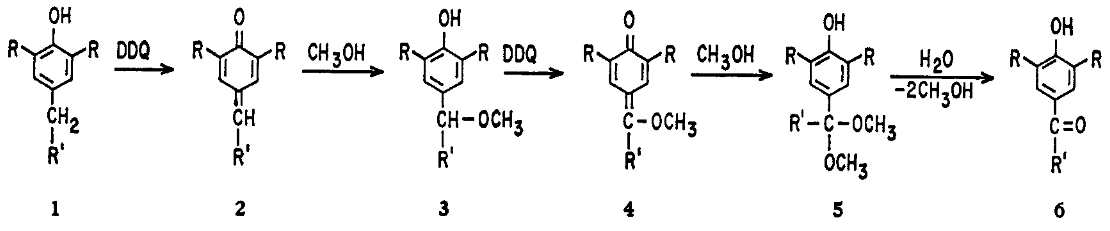
[3] The oxidation of phenols by DDQ has also been under investigation by E. Adler and R. Wettstrom (unpublished work, private communication by Professor Adler); see R. Wettstrom, *Svensk Kem. Tidskr.*, **75**, 429 (1963) (abstract of talk).

[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).

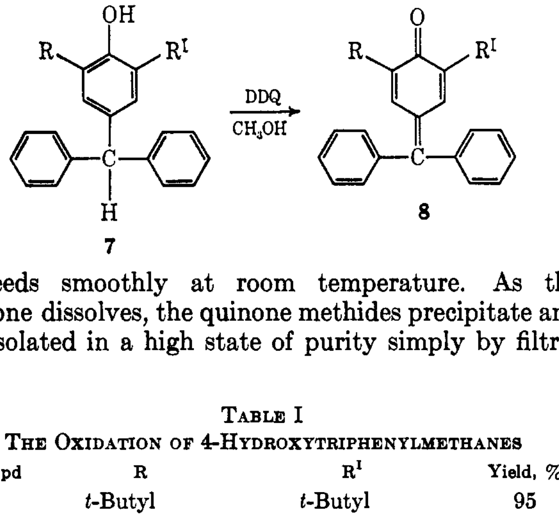
SCHEME I



a. R = CH_3; R' = H
b. R = t-BUTYL; R' = H
c. R = t-BUTYL; R' = OCH_3
d. R = H; R' = PHENYL

quinone methides **2** and **4** were postulated as intermediates[2,7] (Scheme I).

We have now found that quinone methides are the stable end products in the reaction of DDQ with 4-hydroxytriphenylmethanes.[8] Addition of DDQ (1 mol) to a methanol solution of 4-hydroxytriphenylmethanes **7a**–**7f** (1 mol) leads to quinone methides **8a**–**8f** in yields of 73–95% (see Table I). The reaction proceeds smoothly at room temperature. As the quinone dissolves, the quinone methides precipitate and are isolated in a high state of purity simply by filtration.

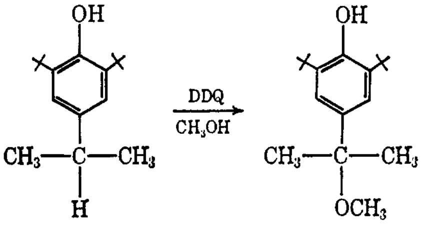


7 **8**

TABLE I
THE OXIDATION OF 4-HYDROXYTRIPHENYLMETHANES

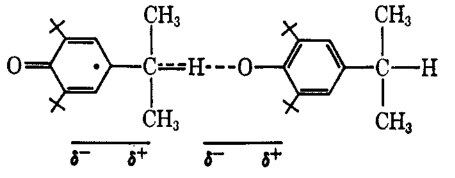
Compd	R	R^I	Yield, %
8a	*t*-Butyl	*t*-Butyl	95
8b	*t*-Butyl	Phenyl	90
8c	Cyclohexyl	Cyclohexyl	95
8d	Isopropyl	Isopropyl	73
8e	Methyl	Phenyl	86
8f	Phenyl	Phenyl	88

The α,α-diphenyl substitution was found to be essential for the formation of stable quinone methides by oxidation of *p*-cresols with DDQ. In accordance with Scheme I, the reaction of DDQ with 2,6-di-*t*-butyl-4-isopropylphenol (**9**) in methanol leads to 2,6-di-*t*-butyl-4-dimethylmethoxymethylphenol (**10**) which was isolated in 71% yield. The slowly fading blue color observed when small quantities of DDQ are added to excess **9** in methanol under nitrogen may be due to 2,6-di-*t*-butyl-4-isopropylphenoxy radicals which undergo spontaneous disproportionation into **9** and the corresponding quinone methide susceptive to nucleophilic attack by methanol.



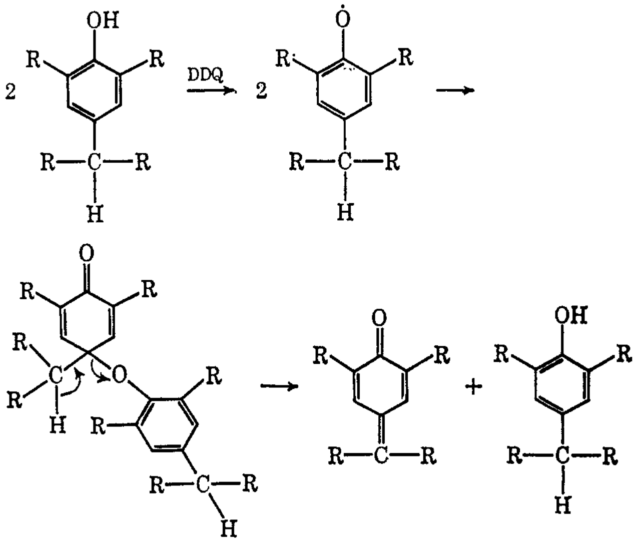
9 **10**

The disproportionation of *p*-alkyl-substituted phenoxy radicals[9] into parent phenol and quinone methide has frequently been observed in phenol dehydrogenation. However, little seems to be known about the mechanism of this oxidation–reduction reaction. In a comprehensive study, Cook and Norcross showed that the disproportionation of 2,6-di-*t*-butyl-4-isopropylphenoxy radicals follows second-order kinetics.[10] They suggested that the reaction proceeds *via* a head-to-tail complex **11** of two phenoxy radicals.



11

We believe, however, that the precursor of the parent phenol and the quinone methide is better represented by the quinol ether structure **12**. This suggestion is



12

---

(7) W. Brown, J. W. A. Findlay, and A. B. Turner, *Chem. Comm.*, 10 (1968); see also A. B. Turner and H. J. Ringold, *J. Chem. Soc., C*, 1720 (1968).

(8) H.-D. Becker, *J. Org. Chem.*, **32**, 2943 (1967).

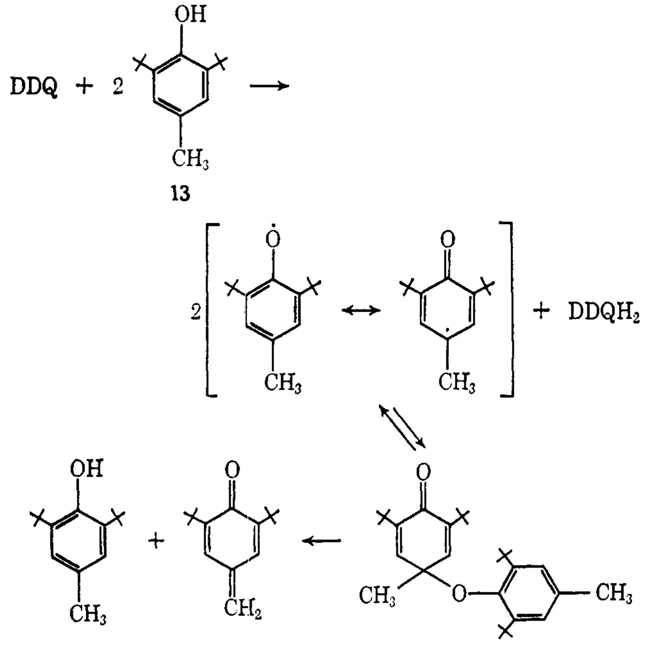
(9) The subject of phenoxy radicals has been treated in a recent comprehensive review article; see E. R. Altwicker, *Chem. Rev.*, **67**, 475 (1967).

(10) C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **81**, 1176 (1959).

TABLE II
THE OXIDATION OF 4,4′-DIHYDROXYTETRAPHENYLMETHANES

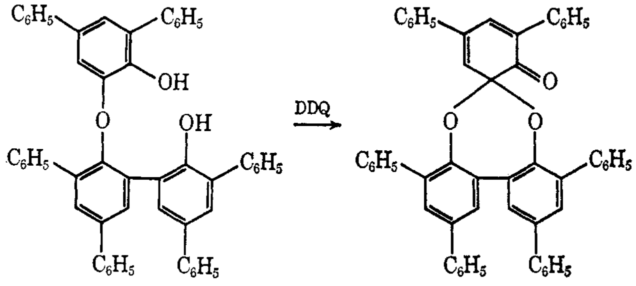
						18			Anal, %			
									Calcd		Found	
Compd	R	R^I	R^{II}	R^{III}	R^{IV}	Mp, °C	Yield, %	Formula (mol wt)	C	H	C	H
17a	*t*-Butyl	*t*-Butyl	H	*t*-Butyl	*t*-Butyl	257–258	98	$C_{41}H_{50}O_2$ (574.86)	85.67	8.77	85.62	8.64
17b	*t*-Butyl	*t*-Butyl	Br	*t*-Butyl	*t*-Butyl	245–246	96	$C_{41}H_{49}BrO_2$ (653.77)	75.40	7.55	75.22	7.58
17c	*t*-Butyl	*t*-Butyl	Cl	*t*-Butyl	*t*-Butyl	252–254	95	$C_{41}H_{49}ClO_2$ (609.31)	80.82	8.11	80.52	8.24
17d	*t*-Butyl	*t*-Butyl	$COOCH_3$	*t*-Butyl	*t*-Butyl	244–245	95	$C_{43}H_{52}O_4$ (632.85)	81.60	8.28	81.62	8.33
17e	*t*-Butyl	*t*-Butyl	H	*t*-Butyl	Phenyl	208–209	84	$C_{43}H_{46}O_2$ (594.80)	86.82	7.80	86.87	7.88
17f	*t*-Butyl	*t*-Butyl	H	Phenyl	Phenyl	185–190	91	$C_{45}H_{42}O_2$ (614.79)	87.91	6.89	87.72	6.94

supported by our finding that oxidation of 2,6-di-*t*-butyl-4-methylphenol (**13**) with DDQ gives 2,6-di-*t*-butyl-4-methylphenoxy radicals which dimerize to give the quinol ether **14** high yield.[2,11] In solution as well as the solid state, **14** spontaneously disproportionates at room temperature, giving equimolar amounts of 2,6-di-*t*-butyl-4-methylphenol and the corresponding quinone methide. After much controversy, other workers indeed have shown that the diappearance of 2,6-di-*t*-butyl-4-methylphenoxy radicals also follows second-order kinetics.[12] Thus, it seems likely that the intermolecular oxidation–reduction reaction of phenoxy radicals deriving from *p*-cresols proceeds according to the quinol ether mechanism[13] rather than *via* a radical complex. There is no ultraviolet (uv) spectroscopic evidence[2] for a significant concentration of phenoxy radicals (λ_{max} at 320 mμ[12]) during the disproportionation of **14** (λ_{max} at 280 mμ) in solution, suggesting that the reaction may be described in terms of a heterolytic process as indicated in structure **12**.



B. Intramolecular Coupling Reactions.—Suitable bisphenols give spirodienones by heterogeneous oxidation with alkaline potassium ferricyanide or metal oxides.[14–16] We have now found that such bisphenols also undergo intramolecular coupling by oxidation with DDQ.

Upon treatment with an equimolar amount of DDQ in methanol solution, bisphenol **15** is converted into the dioxepin **16**[17] in high yield.



15 **16**

DDQ was also found to be a powerful oxidant for bisphenols deriving from tetraphenylmethane which have only recently[18,19] become available. The oxidation of 4,4′-dihydroxytetraphenylmethanes **17a–17f** (see Table II) proceeds rapidly at room temperature in methanol solution to give bispirodienones **18a–18f** in excellent yield and a high state of purity. The yellow to brown bispirodienones precipitate from the reaction mixture as the quinone dissolves. The infrared (ir) and uv spectra of **18** (see Figure 1) are in full agreement with the bispirodienone structure assigned to the oxidation products. As reported previously[16] for **18a**, no evidence was found that the tetra-*t*-butyl-substituted bispirodienones **18b–18d** are in equilibrium with their corresponding diradicals. Solutions of bispirodienones **18e** and **18f** in chloroform containing 2,4,6-tri-*t*-butylphenol, however, turn blue-green upon

---

[11] It is worth noting that the oxidation of 2,6-bistrimethylsilyl-4-methylphenol has recently been reported to give the corresponding quinol ether; see G. A. Razuvaev, I. L. Khrzhanovskaia, N. S. Vasileiskaia, and D. V. Muslim, *Dokl. Akad. Nauk SSSR*, **177**, 600 (1967).

[12] E. J. Land and G. Porter, *Trans. Faraday Soc.*, **57**, 1885 (1961).

[13] *Cf.* H.-D. Becker, *J. Org. Chem.*, **29**, 3068 (1964); see also L. R. Mahoney and M. A. DaRooge, *J. Amer. Chem. Soc.*, **89**, 5619 (1967).

[14] (a) E. A. Chandross and R. Kreilick, *ibid.*, **85**, 2530 (1963); (b) E. A. Chandross and R. Kreilick, *ibid.*, **86**, 117 (1964).

[15] A. Rieker, H. Kaufmann, R. Mayer, and E. Muller, *Z. Naturforsch.*, **19b**, 558 (1964).

[16] H.-D. Becker, *J. Org. Chem.*, **32**, 2115 (1967).

[17] H.-D. Becker, *ibid.*, in press.

[18] H.-D. Becker, *ibid.*, **32**, 2124 (1967).

[19] H.-D. Becker, *ibid.*, **32**, 2131 (1967).

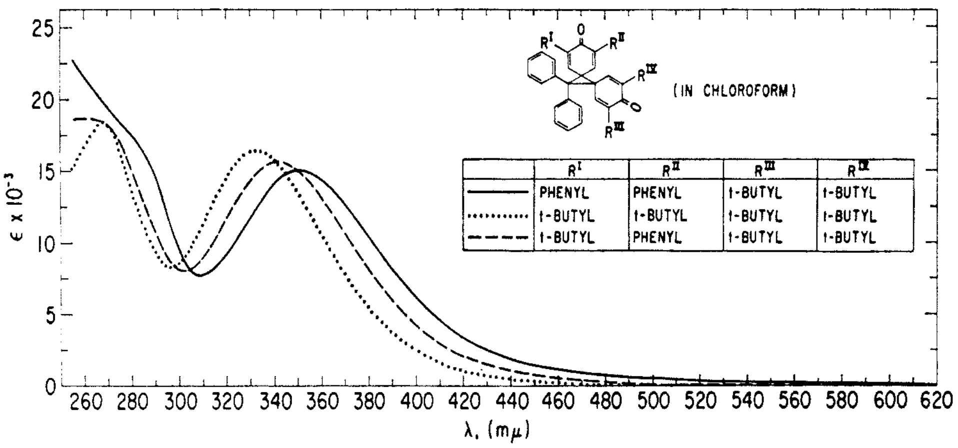
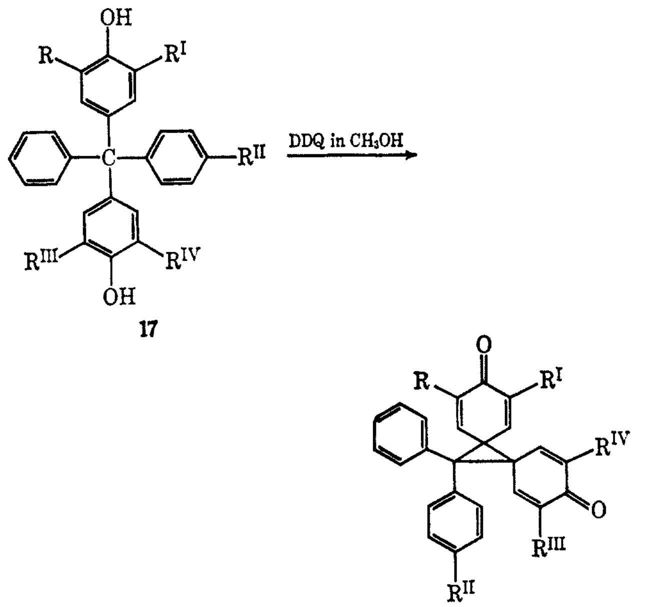


Figure 1.

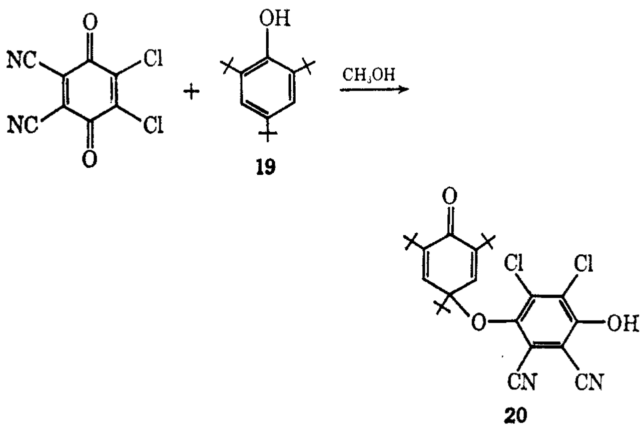
heating, indicating that diradicals may be formed from **18** at elevated temperature.



17

18

C. Addition Reactions of DDQ.—DDQ reacts with 2,4,6-tri-*t*-butylphenol **19** to give the quinol ether **20**.[2]



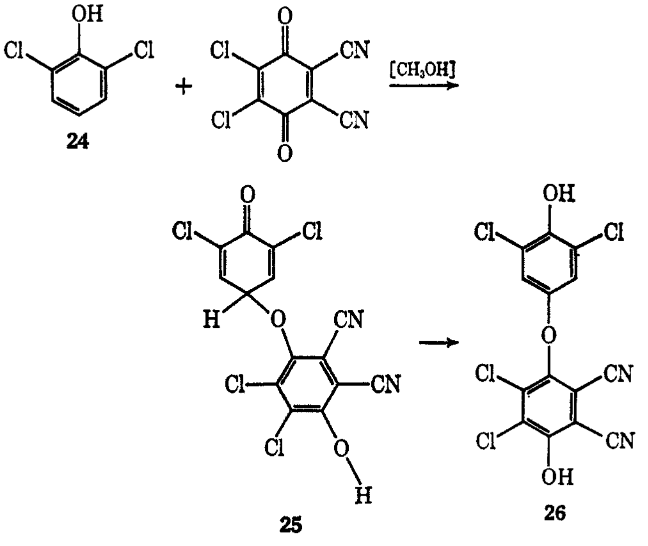
19

20

The result of mixed coupling does not seem surprising since 2,4,6-tri-*t*-butylphenoxy radicals do not dimerize because of steric hindrance. We have now found, however, that DDQ can undergo a similar coupling reaction even with such phenols for which oxidative dimerization by either C–C or C–O coupling is structurally possible.

Addition of DDQ to a methanol solution of 3,4,5-trimethoxyphenol **21** (see Scheme II) gives (*via* a deep colored transient assumed to be a charge-transfer complex) a colorless crystalline product which precipitates from the reaction mixture in excellent yield. The quinone ketal structure **22** for the 1:1 adduct is supported by its ir spectrum which shows a broad hydroxyl absorption (in KBr) around 3000 and a carbonyl band at 1665 cm^{-1}. The compound readily dissociates into free radicals at room temperature, forming deep purple paramagnetic solutions in chloroform and acetone. Chemical evidence for the quinone ketal structure is found in the acid-catalyzed hydrolysis of **22** which gives DDQH$_2$ (97%) and 2,6-dimethoxy-*p*-benzoquinone (**23**, 98%).

Another example of adduct formation was found in the reaction of DDQ with 2,6-dichlorophenol (**24**). In this case, however, the primary addition product **25** cannot be isolated but it tautomerizes to give the 4,4′-dihydroxydiphenyl ether (**26**). Since the final product itself is a phenol and thus subject to further dehydrogenation, the yield of **26** increases significantly when the DDQ/2,6-dichlorophenol ratio is decreased (see Table III).



24

25

26

SCHEME II

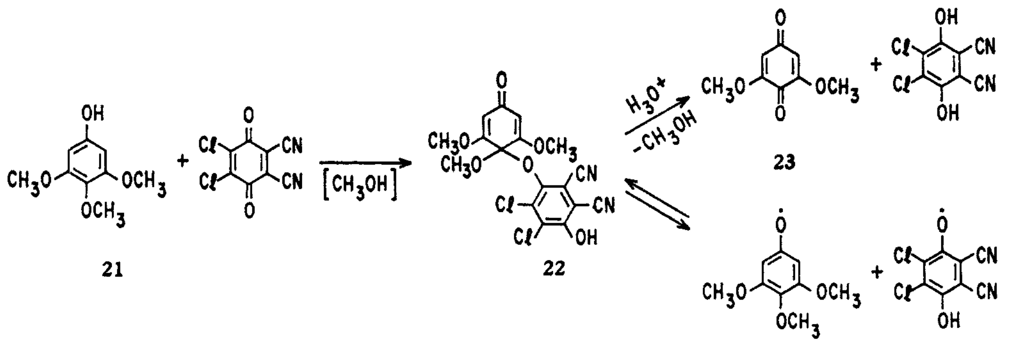


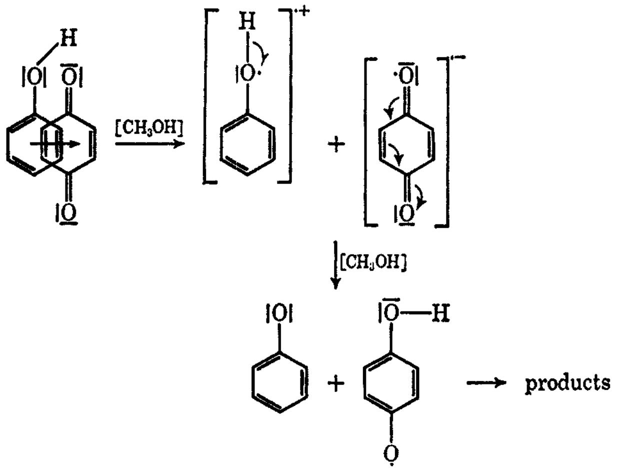
TABLE III
THE EFFECT OF DDQ/PHENOL RATIO ON THE PRODUCT YIELD

DDQ, mmol	2,6-Dichlorophenol, mmol	CH_3OH, ml	Time, hr	Yield, %
2	2	4	72	32
20	40	40	48	64
20	80	40	48	76

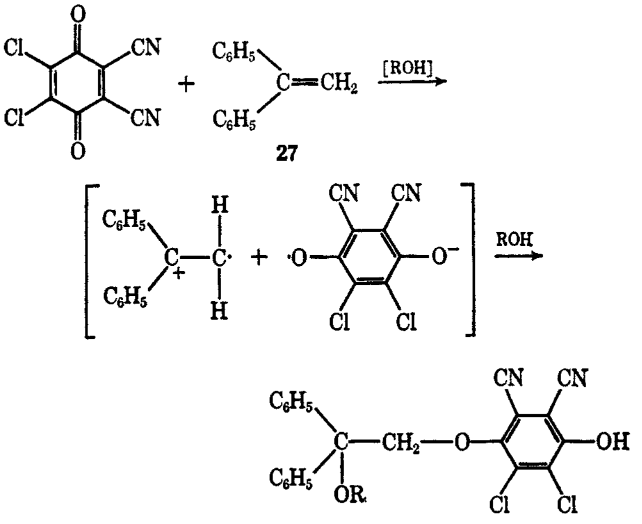
The DDQ–phenol adducts **20**, **22**, and **26** are of particular interest since their formation according to the common concept of quinone dehydrogenation could be described in terms of a hydride-ion transfer reaction followed by collapse of the resulting ion pair. We have previously suggested, however, that the primary step in the reaction of DDQ with phenols consists in the formation of a charge-transfer complex which can undergo homolytic dissociation. It is worth noting that since we made this proposal the formation of radical ions by dissociation of charge-transfer complexes of high-potential quinones and suitable electron donors has indeed been established for polar solvents such as methanol.[20] It has been suggested subsequently that the formation of radical ions results from a chemical reaction between the neutral donor–acceptor complex and the polar solvent.[21]

Applying this concept to the reaction of phenols with DDQ, dissociation of the phenol–quinone charge-transfer complex followed by transfer of a proton from the radical cation to the radical anion would give the phenoxy radical and the DDQH· radical (see Scheme III). These two radicals may then combine to give "DDQ–phenol adducts" or they may undergo further independent reactions giving rise to typical phenol oxidation products and $DDQH_2$.

SCHEME III



In order to obtain more evidence for the proposed one-electron oxidation by DDQ we have investigated its reaction with 1,1-diphenylethylene (**27**) under conditions similar to those applied in the oxidation of phenols. Addition of DDQ to 1,1-diphenylethylene (molar ratio 1:1) in methanol under nitrogen at room temperature gives a deep brown solution from which a colorless crystalline material precipitates. The main product, isolated in 82% yield, was found to be the DDQ–olefin–methanol adduct **28** (R = CH_3).



28, 29

Its structure is based on elemental analysis, molecular weight, and spectroscopic data (ir and nmr). A second product was isolated in only 2.8% yield. Its elemental analysis and molecular weight are in agreement with an adduct consisting of 1 mol of DDQ, 2 mol of 1,1-diphenylethylene, and 2 mol of methanol. The structure of the adduct was not determined. The ir spectrum shows a strong band at 1720 cm^{-1}, but neither an OH nor a CN absorption.

The reaction of DDQ with 1,1-diphenylethylene in ethanol smoothly leads to a DDQ–olefin–ethanol adduct for which elemental analysis, molecular weight, and spectroscopic data (ir and nmr) are in agreement with structure **29** (R = C_2H_5).

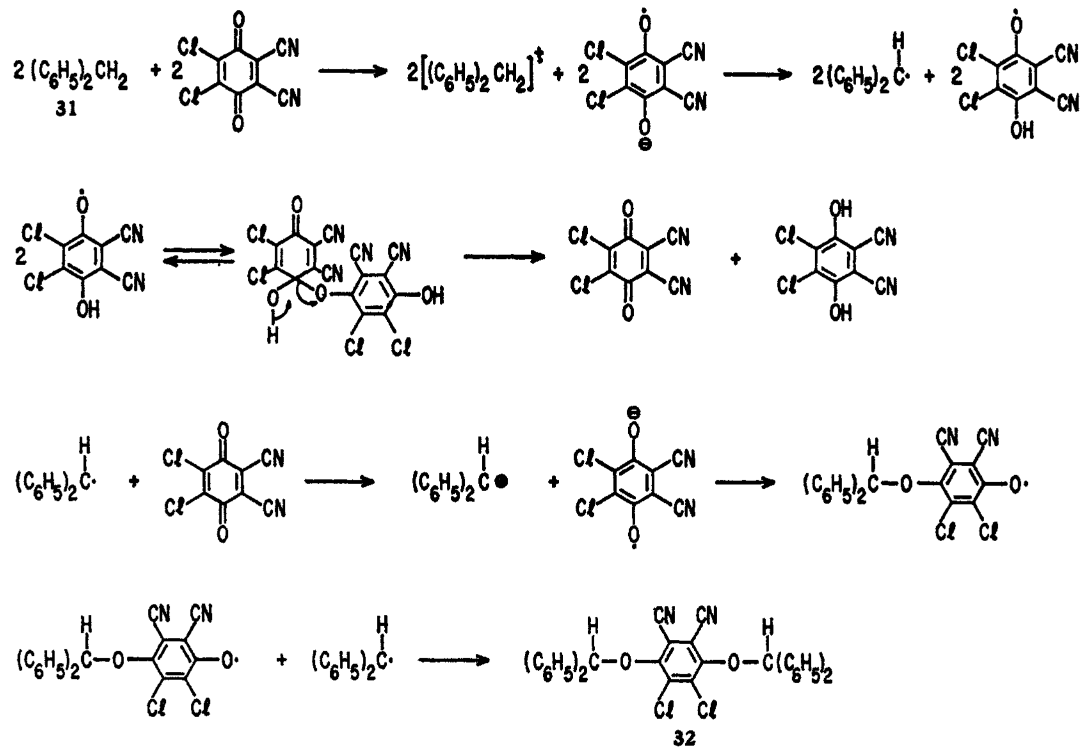
We consider the formation of **28** and **29** as interesting and significant with regard to the one-electron *vs.* two-electron mechanism. Obviously, hydride-ion abstraction from 1,1-diphenylethylene appears improbable

---

[20] P. H. Emslie, R. Foster, and T. J. Thomson, *Rec. Trav. Chim.*, **83**, 1311 (1964).

[21] K. M. C. Davis and M. C. R. Symons, *J. Chem. Soc.*, 2079 (1965).

SCHEME IV



while charge-transfer complex formation and one-electron transfer is conceivable.[22] The transient deep color observed during the reaction is indicative of a charge-transfer complex which, according to the mechanism outlined above, dissociates in alcohol solution to give the diphenylethylene radical cation and the semiquinone radical anion. Their combination followed by reaction with the alcohol would lead to the observed products **28** and **29**, respectively. The combination of the radical-ion pair presumably is favored by a solvent cage.

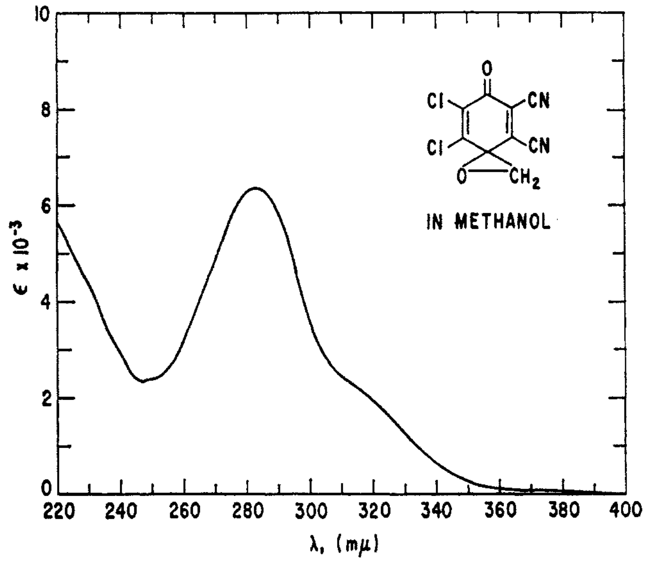
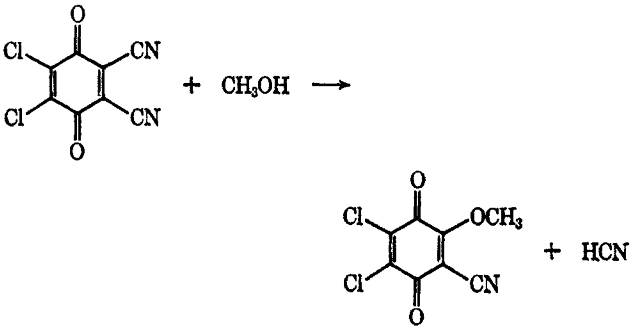


Figure 2.

The results obtained with 1,1-diphenylethylene prompted us to extend the dehydrogenation by DDQ to diphenylmethane. Oxidation of diphenylmethane with tetra-*t*-butyldiphenoquinone at 260° had previously been reported to result in the formation of 1,1,2,2-tetraphenylethane.[23]

An attempt to bring about the dehydrogenation of diphenylmethane by DDQ at room temperature in methanol solution was not successful. Interestingly, however, the product isolated from this reaction mixture derived from the nucleophilic displacement of a cyano group in DDQ by methanol. The resulting 2-cyano-5,6-dichloro-3-methoxybenzoquinone (**30**) also forms when solutions of DDQ in methanol are kept overnight at room temperature.



30

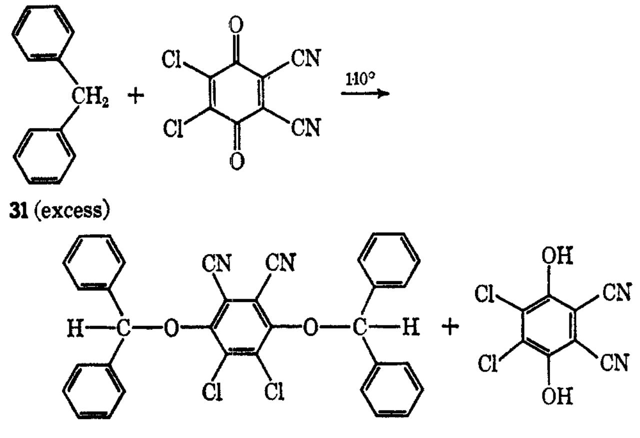
In the absence of any solvent, diphenylmethane (**31**) was found to react smoothly with DDQ at elevated

---

[22] An example of one-electron transfer from a substituted 1,1-diphenylethylene by a radical cation has recently been reported by C. E. H. Bawn, F. A. Bell, and A. Ledwith, *Chem. Comm.*, 599 (1968).

[23] A. S. Hay, *Tetrahedron Lett.*, 4241 (1965). The oxidative coupling of phenols by diphenoquinones has been reported recently by R. G. R. Bacon and O. J. Stewart, *Chem. Comm.*, 977 (1967).

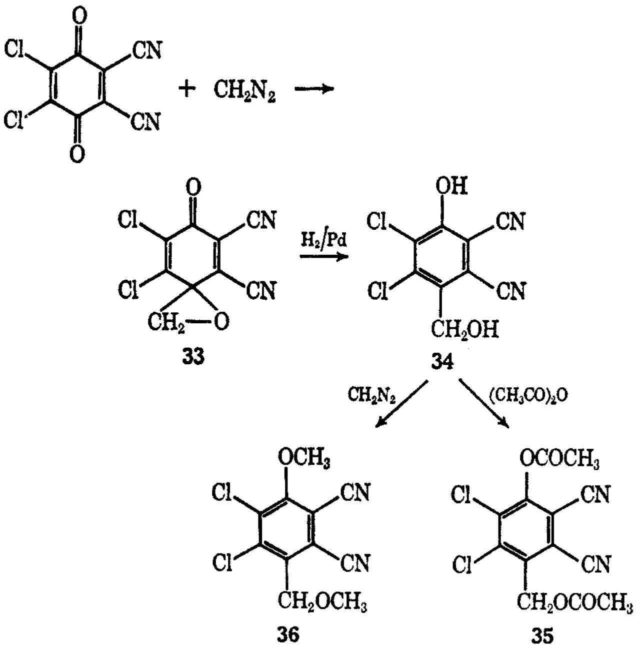
temperature, yielding $DDQH_2$ (100%) and its bis-diphenylmethyl ether (**32**, which was isolated in 83% yield).



Similar hydroquinone ethers have been obtained previously by reaction of alkyl-substituted benzenes with DDQ.[24] However, their formation has always been described in terms of a hydride-ion mechanism, although it is well known that alkyl radicals do undergo addition reactions to quinones.[25] Thus, triphenylmethyl radicals add to the oxygen of benzoquinone to give the bistriphenylmethyl ether of hydroquinone.[26a] Therefore, the formation of any 2,3-dichloro-5,6-dicyanohydroquinone bisalkyl ether probably can also be described in terms of a one-electron mechanism, as exemplified in Scheme IV for the formation of **32**. This mechanism does not imply that DDQ reacts as a diradical, but we suggest that bond formation between DDQ and the diphenylmethyl radical is preceded by electron transfer.[26b] A disproportionation mechanism is proposed for the formation of $DDQH_2$.

The typical quinone rather than diradical behavior of DDQ also is evident in its reaction with diazomethane[27] which leads to the spiroepoxydienone **33**. The structure of **33** is supported by its ir spectrum showing a carbonyl band at 1710–1720 cm^{-1} (in KBr), by its uv spectrum (Figure 2), and by its catalytic reduction to 2,3-dichloro-5,6-dicyano-4-hydroxybenzyl alcohol (**34**). The reduction product was characterized by its diacetate **35** and its dimethyl ether **36**.

We conclude from the results obtained in the course of this investigation that reactions of DDQ with phenols are well explained by one-electron oxidation processes. Furthermore, addition reactions of DDQ to hydrocarbons to give hydroquinone ethers do not necessarily involve hydride-ion abstraction but may be the result of a one-electron transfer.



Experimental Section

2,3-Dichloro-5,6-dicyanobenzoquinone was purchased from Arapahoe Chemicals, Boulder, Colo. All DDQ used was recrystallized from methylene chloride. Absolute methanol was commercial grade. Oxidations were carried out in screw-cap bottles under nitrogen. All melting points were taken on a hot-stage microscope. Molecular weights were determined by thermoelectric measurement in solvents as indicated in each case. Analyses were carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

Quinone Methides 8 (Standard Procedure).—DDQ (1 mmol) was added to a solution of 4-hydroxytriphenylmethane **7** (1 mmol) in methanol. The reaction mixture was shaken for time periods as indicated in Table IV. In all cases the mixture melting point with authentic[16,28] samples was not depressed.

TABLE IV

THE DEHYDROGENATION OF 3,5-DISUBSTITUTED 4-HYDROXYTRIPHENYLMETHANES

Compd	R	R^1	CH_3OH, ml	Time, hr	Yield of **8**, %
7a	*t*-Butyl	*t*-Butyl	10	0.2	95
7b	*t*-Butyl	Phenyl	5	8	90
7c	Cyclohexyl	Cyclohexyl	10	0.5	95
7d	Isopropyl	Isopropyl	5	0.5	73
7e	Methyl	Phenyl	5	8	86
7f	Phenyl	Phenyl	10	20	88

Oxidation of 2,6-Di-*t*-butyl-4-isopropylphenol with DDQ to Give 10.—2,6-Di-*t*-butyl-4-isopropylphenol (1.24 g, 5 mmol) was added to a solution of DDQ (1.135 g, 5 mmol) in methanol (5 ml) under nitrogen. After 24 hr the partly crystalline reaction mixture was evaporated *in vacuo* and the essentially colorless residue was triturated with benzene. Filtration gave 1.06 g (93%) of $DDQH_2$. The benzene filtrate was evaporated to dryness and the residue thus obtained was treated with a little aqueous methanol. Filtration gave 1.13 g (81%) of crude 2,6-*t*-butyl-4-dimethylmethoxymethylphenol. Recrystallization from pentane gave 990 mg (71%) of colorless crystals, mp 106–108° (lit.[29] 106.5–108.5°).

Dioxepin 16.—DDQ (113 mg, 0.5 mmol) was added to a stirred suspension of **15** (367 mg, 0.5 mmol) in methanol (10 ml). Filtration after 10 hr gave 320 mg of crude precipitated oxidation product, mp 245–250°. Recrystallization from a boiling acetone–chloroform mixture gave 285 mg (78%) of

---

[24] R. Foster and I. Horman, *J. Chem. Soc., B*, 1049 (1966). For other examples of ether formation, see ref 6.

[25] A. F. Bickel and W. A. Waters, *J. Chem. Soc.*, 1764 (1950).

[26] (a) J. Schmidlin, J. Wohl, and H. Thommen, *Ber.*, **43**, 1293 (1910); (b) *Cf.* K. A. Bilevitch, N. N. Bubnov, and O. Yu. Okhlobystin, *Tetrahedron Lett.*, 3465 (1968).

[27] *Cf.* B. Eistert and L. Klein, *Chem. Ber.*, **101**, 391 (1968), and earlier papers of that series, especially B. Eistert and G. Bock, *ibid.*, **92**, 1247 (1959).

[28] H.-D. Becker, *J. Org. Chem.*, **32**, 2943 (1967).

[29] C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **78**, 3797 (1956).

dioxepin **16**, mp 250–252°. The mixture melting point with authentic[17] **16** was not depressed.

Oxidation of 4,4′-Dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane with DDQ to Give 18a.—DDQ (277 mg, 1 mmol) was added to a suspension of 4,4′-dihydroxy-3,3′,5,5′-tetra-*t*-butyltetraphenylmethane (576 mg, 1 mmol) in methanol (10 ml). After 6 hr of shaking, the precipitated bispirodienone was removed by filtration. The yield was 560 mg (98%), mp 257–258°. The mixture melting point with authentic[16] material was not depressed.

Spirodienones 18b–18f were prepared in the same manner as that described for **18a**. Their uv data are summarized in Table V.

TABLE V

THE ULTRAVIOLET SPECTRA OF BISPIRODIENONES 18 (IN METHANOL)

	Max_1		Max_2	
Compd	λ, mμ	$\epsilon \times 10^{-3}$	λ, mμ	$\epsilon \times 10^{-3}$
18a	333	16.5	268	18.5
18b	332	16.2	268	20.2
18c	332	16.5	268	19.7
18d	330	16.2	258	26
18e	341	15.7	260	18.7
18f	350	15.0	255	16.3

Addition of DDQ to 3,4,5-Trimethoxyphenol (22).—DDQ (908 mg, 4 mmol) was added to a solution of 3,4,5-trimethoxyphenol (736 mg, 4 mmol) in methanol (15 ml) agitated with a stream of nitrogen. As the DDQ dissolved, a colorless to light yellow crystalline precipitate formed. Filtration yielded a very light yellow material which was washed with little cold acetone to give 1.3–1.4 g (79–85%) of colorless addition product. The compound decomposes without melting above 100°.

Anal. Calcd for $C_{17}H_{12}Cl_2N_2O_6$: C, 49.66; H, 2.94; Cl, 17.24; N, 6.81; mol wt, 411.20. Found: C, 49.39; H, 3.12; Cl, 17.30; N, 6.80.

Acid-Catalyzed Hydrolysis of Quinone Ketal *22*.—A suspension of the quinone ketal **22** (1.23 g, 3 mmol) in a mixture of methanol (20 ml) and concentrated hydrochloric acid (3 ml) was stirred for 5 min. Vacuum evaporation of the solvents and treatment of the solid residue with boiling chloroform left 650 mg of $DDQH_2$ (97%) undissolved. The filtrate was evaporated to dryness and the solid residue was washed with methanol to give 495 mg (98%) of 2,6-dimethoxybenzoquinone, mp 258–259°.

Anal. Calcd for $C_8H_8O_4$: C, 57.14; H, 4.80; mol wt, 168.14. Found: C, 56.85; H, 4.79.

Addition of DDQ to 2,6-Dichlorophenol (26).—DDQ (4.54 g, 20 mmol) was added to a solution of 2,6-dichlorophenol (13.04 g, 80 mmol) in methanol (40 ml), agitated with a stream of nitrogen. The dark brown solution was kept in a closed flask for 24 hr. The colorless precipitate was then removed from the light yellow solution by filtration. The yield was 5.14 g. An additional 0.8 g of **26** was isolated from the partly evaporated filtrate. The total yield was 5.94 g (76%), mp 260° dec. Recrystallization from hot methanol or vacuum sublimation [220° (1 mm)] raised the melting point to 262° dec.

Anal. Calcd for $C_{14}H_4Cl_4N_2O_3$: C, 43.12; H, 1.03; Cl, 36.36; N, 7.18; mol wt, 390.01. Found: C, 43.14; H, 1.02; Cl, 36.10; N, 7.30; mol wt, 409 (in dioxane).

Reaction of DDQ with 1,1-Diphenylethylene in Methanol to Give 28.—A solution of DDQ (2.27 g, 10 mmol) and 1,1-diphenylethylene (1.8 g, 10 mmol) in absolute methanol (10 ml) placed in a screw-cap bottle was shaken for 24 hr. The colorless crystalline precipitate that had formed was removed by filtration (3.8 g) and boiled in 50 ml of methanol, leaving 180 mg (2.8%) of a crystalline substance, mp 298–300°, undissolved.

Anal. Calcd for $C_{38}H_{30}Cl_2N_2O_4$: C, 70.25; H, 4.66; Cl, 10.92; N, 4.31; mol wt, 649.14. Found: C, 70.04; H, 4.60; Cl, 11.07; N, 4.46; mol wt, 652 (in chloroform).

From the hot filtrate 3.4 g of colorless **28** separated at room temperature. The substance was vacuum dried [50° (1 mm)] for 3 hr, mp 187–188° dec, yield 77%.

Anal. Calcd for $C_{23}H_{16}Cl_2N_2O_3$: C, 62.89; H, 3.67; Cl, 16.14; N, 6.38; mol wt, 439.30. Found: C, 62.91; H, 3.82.

From the original methanol filtrate 114 mg of $DDQH_2$ was isolated.

Reaction of DDQ with 1,1-Diphenylethylene in Ethanol to Give 29.—The reaction was carried out in the same manner as that described above. Filtration yielded 2.85 g (63%) of colorless crystals, mp 180° dec.

Anal. Calcd for $C_{24}H_{18}Cl_2N_2O_3$: C, 63.59; H, 4.00; Cl, 15.64; N, 6.18; mol wt, 453.33. Found: C, 63.60; H, 4.02; Cl, 15.53; N, 6.20; mol wt, 451 (in chloroform).

2-Cyano-5,6-dichloro-3-methoxy-1,4-benzoquinone (30).—A solution of 2,3-dichloro-5,6-dicyanobenzoquinone (2.27 g, 10 mmol) in absolute methanol (10 ml) was kept standing in a dark closed flask for 48 hr. The yellow crystalline precipitate was removed by filtration. The yield was 350 mg (15%), mp >220° dec. Recrystallization from boiling methanol raised the melting point to 225–226° dec.

Anal. Calcd for $C_8H_3Cl_2NO_3$: C, 41.41; H, 1.30; Cl, 30.56; N, 6.04; mol wt, 232.03. Found: C, 41.44; H, 1.55; Cl, 30.56; N, 6.21; mol wt, 237 (in benzene).

Reaction of DDQ with Diphenylmethane (32).—A deep red solution of DDQ (5.68 g, 25 mmol) in diphenylmethane (50 ml, 300 mmol) was kept at 110° under nitrogen agitation for 15 min. As the red color disappeared, a colorless precipitate $DDQH_2$ formed. The reaction mixture was cooled to room temperature and filtered through a sintered-glass funnel, leaving 2.75 g (100%) of $DDQH_2$ undissolved.

The light orange filtrate was subjected to vacuum distillation at about 1-mm pressure and a bath temperature of 120°, thus removing the excess diphenylmethane. The light pink residue was washed with little methanol and recrystallized by dissolving in little warm benzene and adding ether. The yield was 5.8 g (83%) of colorless needle-shaped crystals, mp 189–190° dec.

Anal. Calcd for $C_{34}H_{22}Cl_2N_2O_2$: C, 72.72; H, 3.95; N, 4.99; mol wt, 561.48. Found: C, 72.86; H, 4.12; N, 4.93; mol wt, 561 (in chloroform).

Reaction of DDQ with Diazomethane (33).—An ether solution of diazomethane was added dropwise to a solution of DDQ (1.135 g) in benzene (75 ml) until the yellow color due to the quinone disappeared. At that point a colorless crystalline precipitate formed. It was removed by filtration and recrystallized from boiling methanol under addition of little water. The yield was 1.12 g (93%), mp ~250° dec.

Anal. Calcd for $C_9H_2Cl_2N_2O_2$: C, 44.85; H, 0.84; mol wt, 241.03. Found: C, 44.96; H, 0.96; mol wt, 239 (in acetone).

Catalytic Reduction of DDQ–CH_2 Adduct 33 (35 and 36).—Spiroepoxydienone **33** (482 mg, 2 mmol) was hydrogenated with Adams catalyst (15 mg) in acetone (6 ml). After 2 hr, when 55 ml of hydrogen (120% of theory) had been absorbed, the reaction mixture was filtered. The crystalline product obtained after evaporation of the solvent had mp 160–175° dec. Since it was difficult to recrystallize, it was methylated with diazomethane in ether solution to give 300 mg (55%) of the dimethyl ether of 2,3-dichloro-5,6-dicyano-4-hydroxybenzyl alcohol, mp 122–124°.

Anal. Calcd for $C_{11}H_8Cl_2N_2O_2$: C, 48.74; H, 2.97; mol wt, 271.10. Found: C, 49.05; H, 3.18; mol wt, 250 (in acetone).

The diacetate of 2,3-dichloro-5,6-dicyano-4-hydroxybenzyl alcohol was prepared by dissolving the reduction product of **33** in acetic anhydride containing a few drops of concentrated sulfuric acid. The yield was 300 mg (46%), mp 163–164°.

Anal. Calcd for $C_{13}H_8Cl_2N_2O_4$: C, 47.73; H, 2.47; mol wt, 327.13. Found: C, 47.61; H, 2.60; mol wt, 312 (in acetone).

Registry No.—DDQ, 84-58-2; **18a**, 13145-52-3; **18b**, 19566-50-8; **18c**, 19566-51-9; **18d**, 19566-52-0; **18e**, 19566-53-1; **18f**, 19566-54-2; **22**, 19566-55-3; **23**, 530-55-2; **26**, 19566-56-4; **28**, 19566-57-5; **29**, 19566-58-6; **30**, 19566-59-7; **32**, 19566-60-0; **33**, 19566-61-1; **35**, 19566-62-2; **36**, 19556-79-7.