sults were obtained using open sample tubes. The g value was measured only for **6c**, using double cavity technique and potassium nitrosyldisulfonate as a standard, and found to be 2.00432 ± 0.00010.

Treatment of the naphthalene solution of **6c** with Ag_2O at 180° caused a significant increase in esr signal strength. However, when Ag_2O was added to a solution of **6c** in xylene at room temperature, the esr signal (already very weak) was decreased.

To search for triplet-state esr lines, compound **6c** was first heated as a solid to 180° until the single broad esr line had become intense. A scan at high amplification over 10 kG failed to reveal any additional lines. Then, a 10^{-3} M solution of **6c** was dissolved in bis-(α-ethoxyethyl) ether in the quartz sample tube, which was degassed, sealed, and heated to 150° until an intense 1:2:1 esr pattern formed. The solution was chilled to −160° to form a rigid glass and carefully scanned, but only a single line at $g \sim 2$ was observed. A similar experiment using 2-methyltetrahydrofuran glass at −100° also failed to show any additional esr lines.

Acknowledgment. The authors thank the Public Health Service for a grant in support of this research.

Anion Radicals and Neutral Radicals in the Quinocyclopropene–Triquinocyclopropane System

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Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin 53706. *Received April 7, 1969*

Abstract: The deprotonation of bis(*p*-hydroxyaryl)quinocyclopropenes (**1**) to the corresponding dianions is described. The dianions undergo reversible oxidation to stable anion-radicals which are further reversibly oxidized to triquinocyclopropanes (**6**). Electron spin resonance spectra of the anion-radicals indicate that the unpaired electron is fully delocalized over the four-ring system. Direct oxidation of **1** to **6** also proceeds reversibly with formation of small amounts of a neutral monoradical intermediate **2**. Esr spectra of the neutral radicals indicate complete electron delocalization over two aromatic rings and partial delocalization onto the third.

The preceding paper[1] describes the synthesis of bis(*p*-hydroxyaryl)quinocyclopropenes (**1**) and their reversible oxidation to triquinocyclopropanes (**6**). In this paper, the oxidation–reduction reaction will be examined in detail, and evidence for reaction intermediates in this new redox system will be presented.

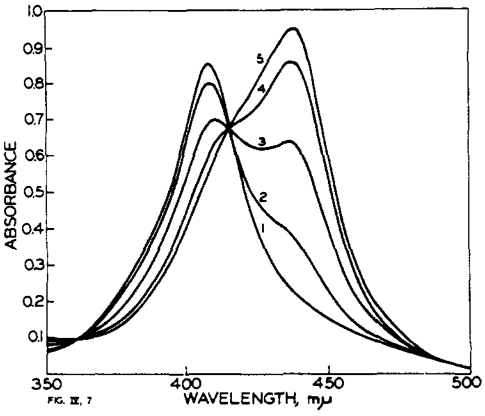

Figure 1. Electronic spectra of **1d** showing its conversion to **4d** upon addition of base: 1, 160 mg (0.24 mmole) of **1d** in 200 ml of methanol; 2, same solution with 1.00 ml of 0.080 M aqueous NaOH added (0.08 mmole); 3, 3.00 ml of base added; 4, 5.00 ml of base added; 5, 6.00 ml (0.48 mmole) of base solution added.

Compounds **1** can be viewed as typical hydroquinones, differing from the latter only in the fact that a third equivalent oxygen atom is present in the oxidized form **6**. As is also the case for all hydroquinones, two pathways for the oxidation of **1** to **6** can be visualized.[2] In neutral or acidic media, oxidation takes place with loss of hydrogen atoms, with possible intermediate formation of a monoradical **2**.

In basic solution, deprotonation of **1** is expected to take place, to yield the monoanion **3** and the dianion **4**. Oxidation of the latter to **6** requires loss of two electrons, which might take place stepwise, leading to possible formation of the intermediate (semiquinone) anion-radical **5**.

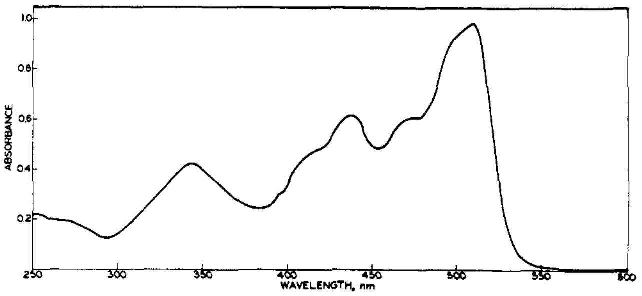

Figure 2. Electronic spectrum of anion-radical **5d**, $\sim 2 \times 10^{-5}$ M in 50% methanol–methylene chloride.

The oxidation–reduction in basic solution, involving formation of the dianions **4**, will be considered first.

Deprotonation of 1a–d. The brightly colored quinocyclopropenes **1a–d** behave as acid–base indicators, undergoing color changes when they are treated with

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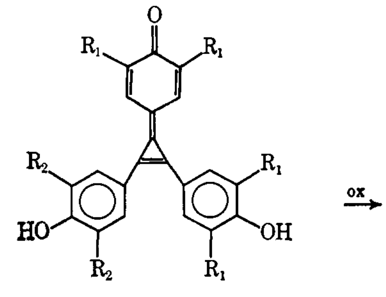
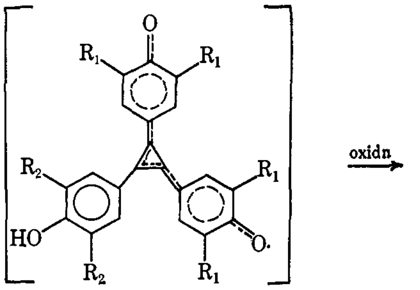
[1] R. West and D. C. Zecher, *J. Amer. Chem. Soc.*, **92**, 155 (1970).

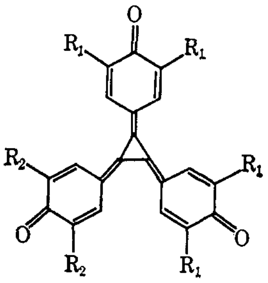
[2] For general discussions of the oxidation of hydroquinones and the intermediates which may be observed see L. Michaelis, *Chem. Rev.*, **16**, 243 (1935); L. Michaelis and S. Granick, *J. Amer. Chem. Soc.*, **70**, 624, 4275 (1948); G. W. Wheland, *Advan. Org. Chem.*, **3**, 176 797 (1966). Possible further complication of the redox systems by dimerization of **2** or **5** has not been considered here, since no evidence for dimerization was observed.



1a, $R_1 = R_2 = i$-Pr
b, $R'_6 = 2i$-Pr,1t-Bu
c, $R' = 1i$-Pr, 2t-Bu
d, $R_1 = R_2 = t$-Bu



2



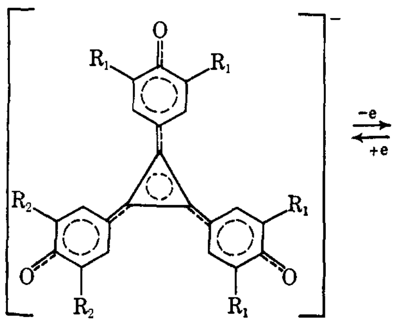
6a, $R_1 = R_1 = i$-Pr
b, $R_1 = i$-Pr; $R_2 = t$-Bu
c, $R_1 = t$-Bu; $R_2 = i$-Pr
d, $R_1 = R_2 = t$-Bu

base and converted to dianions **4**. The deprotonation is reversible, **1a–d** being regenerated when anions **4a–d** are acidified.

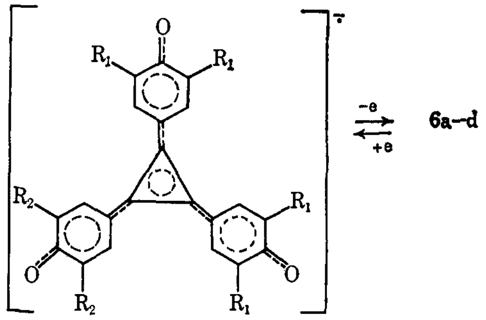
To study the equilibrium quantitatively, a methanolic solution of **1d** was titrated with aqueous NaOH, and the reaction was followed spectrophotometrically. The results given graphically in Figure 1 show clearly the spectrum of the starting material **1d** (λ_{max} 406 nm) and that of the dianion **4d** (λ_{max} 437 nm). All intermediate curves pass through a single isobestic point at 415 nm, indicating that the monoanion **3d** is unstable with respect to **1d** and **4d**. The spectral changes were reversible when the solution containing **4d** was treated with acid.

Attempts to obtain salts of **4d** in pure form were unsuccessful, but the dipotassium salt of **4a** was isolated as a yellow crystalline solid. This salt was water sensitive and unstable, and an elemental analysis was not attempted; the identity of the salt was established by quantitative conversion to **1a** with acid.

The Redox System 4–5–6. The oxidation of a methanol–methylene chloride solution of **4d** with aliquots of aqueous potassium hexacyanoferrate(III) was followed by electronic and electron spin resonance spectroscopy. The reaction proceeds stepwise, with the anion-radical



4a, $R_1 = R_2 = i$-Pr
b, $R_1 = i$-Pr; $R_2 = t$-Bu
c, $R_1 = t$-Bu; $R_2 = i$-Pr
d, $R_1 = R_2 = t$-Bu



5a, $R_1 = R_2 = i$-Pr
b, $R_1 = i$-Pr; $R_2 = t$-Bu
c, $R_1 = t$-Bu; $R_2 = i$-Pr
d, $R_1 = R_2 = t$-Bu

5d being formed and then undergoing further oxidation to **6d**. Study of the oxidation was somewhat complicated by the fact that **6d** partially precipitated from the solution. However, after the addition of 1 equiv of $K_3Fe(CN)_6$, the solution showed only electronic absorption of the anion radical, with λ_{max} 510 nm (Figure 2). The esr spectrum of the solution showed a single broad extremely intense line. The esr signal and electronic absorption due to the anion radical both disappeared as 2 equiv of $K_3Fe(CN)_6$ was added. The results indicate that under the conditions employed the anion-radical **5d** is stable with respect to **4d** and **6d**; that is, that the equilibrium 2(**5d**) $\rightleftharpoons$ **4d** + **6d** lies far to the left.

To study the esr spectra more closely, anion-radicals **5** were prepared in 1,2-dimethoxyethane solution both by oxidation of **4** and reduction of **6**. In the oxidative generation, bis(p-hydroxyaryl)quinocyclopropenes (**1b**, **1d**) were converted to dianions (**4b**, **4d**) by the addition of sodium methoxide, then oxidized with lead dioxide. In the reductive method triquinocyclopropanes **6b**, **6c**, and **6d** were reduced with sodium–potassium alloy. Both methods led to identical esr spectra, but the spectra obtained by reduction were generally better resolved. Sample spectra are shown in Figure 3 and the esr data is summarized in Table I.

Table I. Esr Spectra of Anion Radicals, **5**

Compd	Reagent	Lines	αH, G
6b	Na-K	19	0.43, 1.3
6c	Na-K	13	0.43, 1.3
6d	Na-K	7	0.43
1c	PbO_2, NaOMe	13	0.43, 1.3
1d	PbO_2, NaOMe	7	0.43

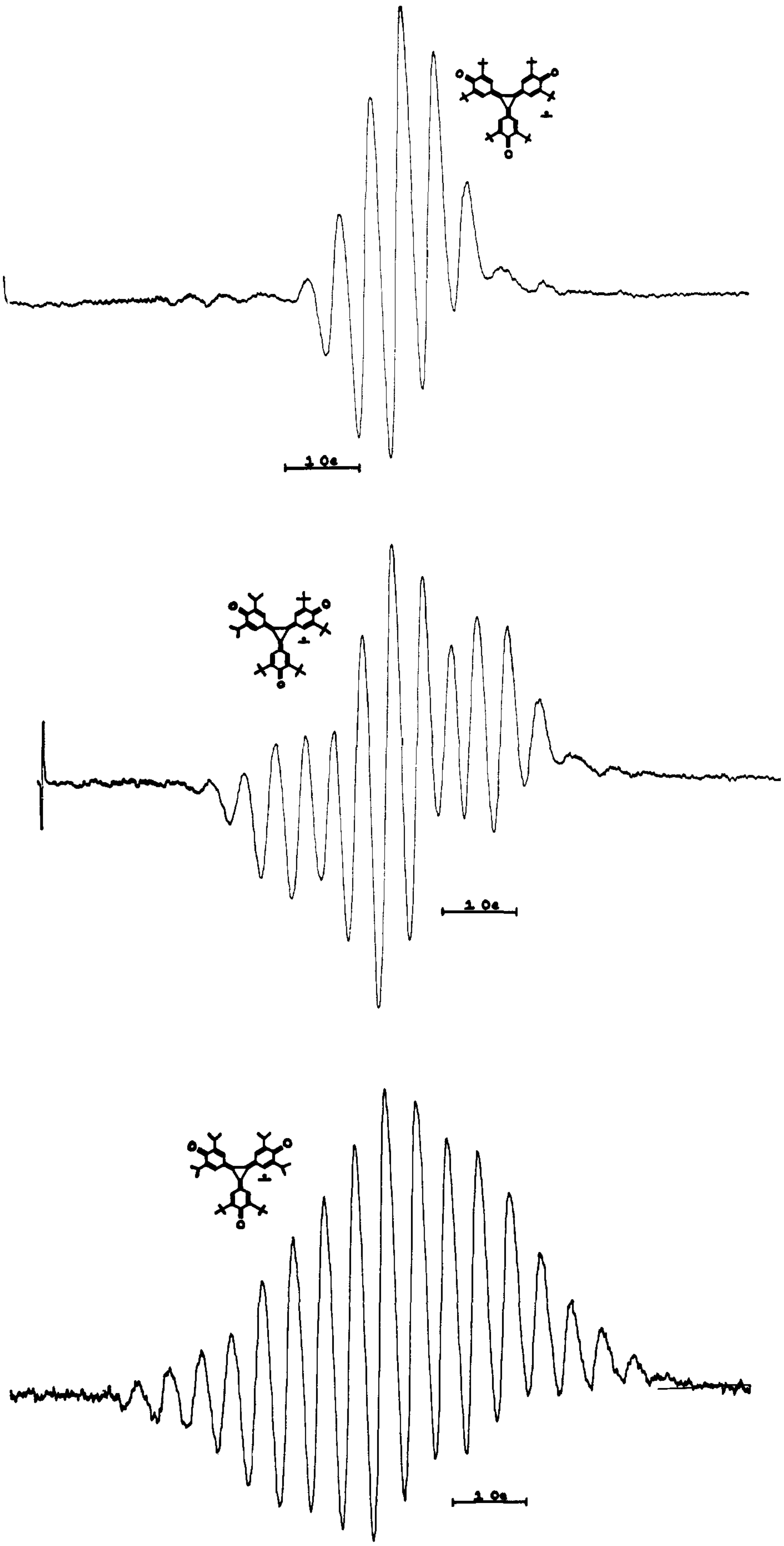


Figure 3. Electron spin resonance spectra of anion-radicals **5b** (below), **5c** (center), and **5d** (above).

The spectrum of **5d** consists of seven lines in the ratio 1:6:15:20:15:6:1, due to coupling with the six equivalent protons in the positions *meta* to oxygen. The spectrum shows decisively that under our experi-

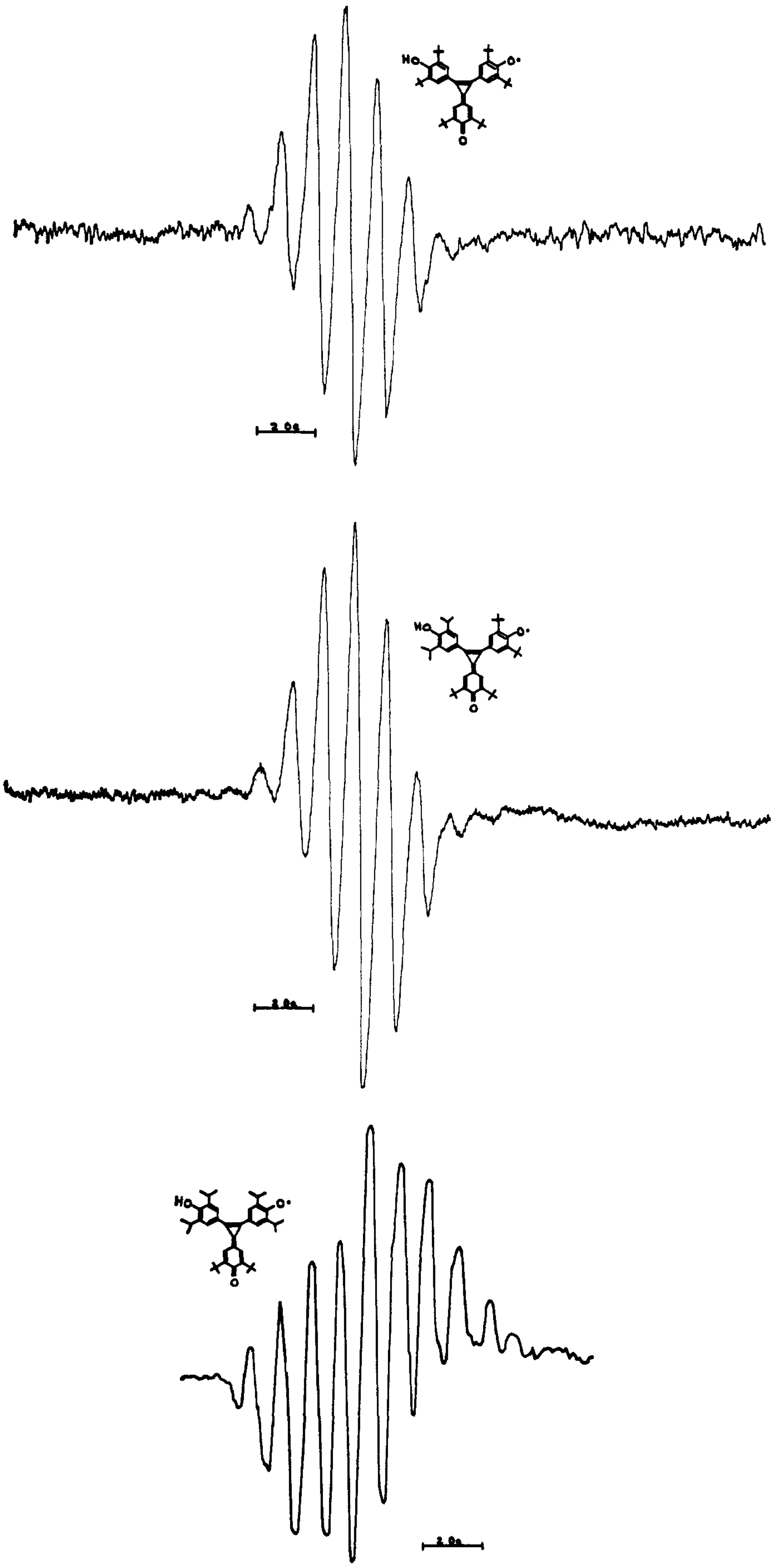


Figure 4. Electron spin resonance spectra of monoradicals **2b** (below), **2c** (center), and **2d** (above).

Table II. Esr Spectra of Monoradicals, **2**

Compd	Oxidizing agent	Solvent	Temp, °C	Lines	α_H, G
1b	Ag_2O	$C_{10}H_8$	90	9	0.94, 1.9
1b	**6b**	$C_{10}H_8$	90	9	0.96, 1.9
1b	Ag_2O	$C_{10}H_8$	170	3	1.6
1c	PbO_2	xylene	40	7	0.98
1c	Ag_2O	$C_{10}H_8$	90	7	0.98
1c	**6c**	$C_{10}H_8$	90	7	0.98
1c	**6c**	$C_{10}H_8$	120	3	1.6
1c	Ag_2O	$C_{10}H_8$	160	3	1.6
1d	PbO_2	Xylene	30	7	1.00
1d	Ag_2O	$C_{10}H_8$	90	7	1.00
1d	**6d**	$C_{10}H_8$	140	3	1.6
1d	Ag_2O	$C_{10}H_8$	190	3	1.6

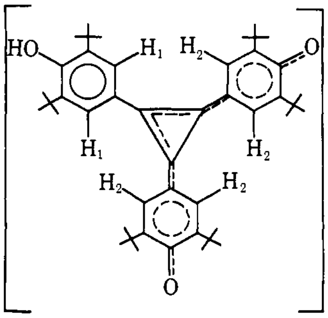
mental conditions the unpaired electron is fully delocalized over the three benzene rings. The experimental value of 0.43 G for the hyperfine splitting constant indicates a spin density of 0.013 at the corresponding carbon atom, if Q is taken as 34 G according to McConnell,[3] or 0.019 assuming $Q = -23.7$.[4] This value is in good agreement with the results of a Hückel MO calculation for unsubstituted triquinocyclopropane, which predicts an electron density of 0.015 at the same carbon atom.[5]

For the anion radicals containing isopropyl groups, additional hyperfine splitting is expected due to coupling with the methine protons. For **5c**, with two isopropyl substituents, a 13-line spectrum is observed (Figure 3, Table I). This spectrum can be rationalized if the reasonable assumption is made that the spin density at the carbons *meta* to oxygen is nearly unchanged when a *t*-butyl is replaced by an isopropyl group. The 13-line spectrum is then accounted for by splitting of the 7 lines due to the ring protons each into a triplet with α_H 1.3 G.[6] The observed relative areas are in good agreement with relative intensities calculated on this basis. If the same hyperfine splitting constants of 0.43 and 1.3 G apply to radical **5b**, a 19-line spectrum would be predicted, exactly as observed (Table I). The inner 17 lines are shown in Figure 3.

The Redox System 1–2–6. The oxidation of the protonated bis(*p*-hydroxyaryl)quinocyclopropenes was also examined by electronic and esr spectroscopy. The electronic spectrum of **1d** changed gradually to that of **6d** when increments of silver(I) oxide were added, but no new bands attributable to a monoradical **2d** were observed. Likewise, a mixture of equimolar amounts of **1d** and **6d** showed only bands due to these two substances and no new bands. These experiments indicate that, just opposite from the anionic case, the monoradical **2d** is unstable with respect to **1d** and **6d**; the equilibrium $2(\mathbf{2d}) \rightleftharpoons \mathbf{1d} + \mathbf{6d}$ lies far to the right.

Although radicals of type **2** were not detected by electronic spectroscopy, they were easily observed by the more sensitive esr technique. Oxidations of **1** were carried out with silver(I) oxide or lead dioxide, in naphthalene or xylene. The results are summarized in Table II, and sample spectra are shown in Figure 4.

Compound **1d** gives on oxidation a 7-line esr spectrum, with relative intensities corresponding to the coefficients of the binomial expansion. This indicates equivalent hyperfine splitting by six equivalent protons, exactly as in the anion-radical **5d**. But in the monoradical **2d** the six ring protons fall into two sets: the two symmetry-equivalent protons (H_1) on the ring bearing the –OH group, and the four protons (H_2) on the two rings bearing nonhydrogenated oxygen atoms. The latter four would be equivalent in esr if the unpaired electron is delocalized over both rings as expected, leading to rapid spin exchange between the two rings. Exchange of the OH proton between the three oxygen atoms at a rate rapid compared to the spin relaxation time would make H_1 equivalent to H_2 in the esr experiment, but such rapid exchange seems most unlikely. Instead, we believe that the hyperfine splitting constants αH_1 and αH_2 are coincidentally nearly equal, both having values very near 1.00 G. Straightforward valence-bond or MO considerations predict that the spin density at the carbon atoms attached to H_1 will be high and perhaps as great as that at the H_2 carbons.



2d

Interesting results were obtained by oxidizing diarylquinocyclopropenes bearing both *t*-butyl and isopropyl groups, **1b** and **1c**. **2c** gives a 7-line esr spectrum nearly identical with that for **2d** (Table II, Figure 4). It is important that *no coupling due to the methine protons of the isopropyl groups is observed.* Our interpretation is that of the two possible radicals, **2c** and **2c***, only **2c** is observed. Both **2c** and **2c*** may originally be formed, but **2c** is expected to be much less reactive because both oxygens bearing the unpaired electron are flanked by *t*-butyl groups. Preferential destruction of **2c***, or hydrogen transfer to **2c*** from **1c**, would eventually leave **2c** as the only radical species present. Coincidental equivalence of spin density at the H_1 and H_2 carbons, as for **2d**, could then give rise to the observed 7-line pattern. This interpretation also requires that the spin density at the carbon atom bearing the isopropyl group in **2c** be very low, in agreement with MO and VB considerations. Note that for **2c**, rapid exchange of the proton between the three oxygens *cannot* explain the results, because a large hyperfine splitting by the methine protons would then be expected.

Oxidation of **1b** leads to the radical **2b**, which is much less stable than **2c** and **2d**, probably because the unpaired electron must now occupy an oxygen atom flanked by isopropyl as well as *t*-butyl groups. A relatively weak esr pattern is therefore observed (Figure 4), consisting of 9 lines which we believe to be

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(3) H. M. McConnell, *J. Chem. Phys.*, 24, 632 (1956).

(4) P. H. Rieger and G. K. Fraenkel, *ibid.*, 37, 2795 (1962)

(5) D. C. Zecher, Ph.D. Thesis, University of Wisconsin, 1967.

(6) A larger hyperfine coupling constant is expected for the isopropyl than for the aromatic protons. In the 2,6-diisopropylphenoxyl radical, for instance, the α_H values for methine and *meta*-aromatic protons are 3.8 and 1.9 G, respectively. See Tables in A. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965, p 80 for this and related examples.

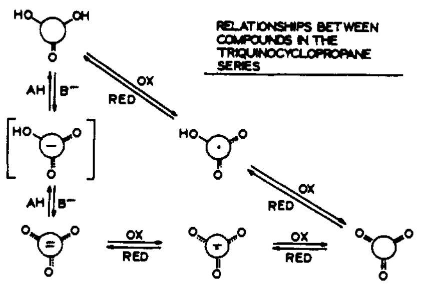
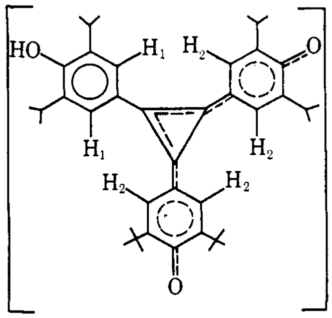
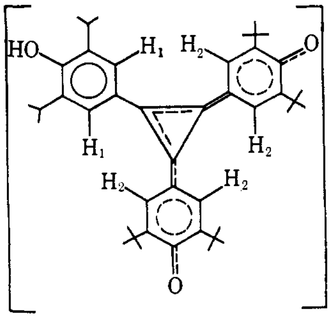


Figure 5. General relationships in the oxidation-reduction reactions involving **1**, **6**, and the intermediates between them. The large circle represents the entire tetracyclic system.

the central lines of an 11-line spectrum. The protons H_1 and H_2 are again assumed to be accidentally degenerate and to have hyperfine coupling constants about equal to those found for the analogous protons in **1c** and **1d**. The observed spectrum can then be accounted for by coupling due to two methine protons with α_H ~1.9 G. Again, the results indicate that **2b** is the stable form of the radical rather than **2b***, since an even larger number of lines would be observed for **2b***.



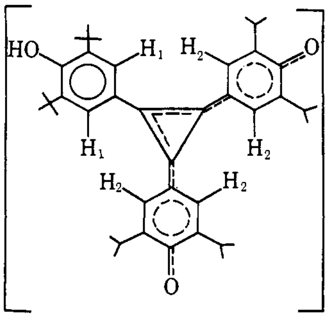
2b



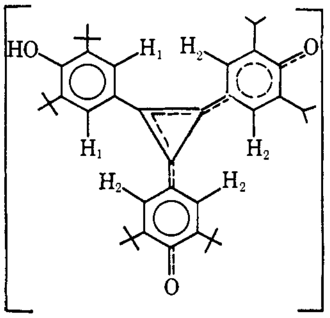
2c

The spectra of the monoradicals **2b–d** persist up to about 100°. At higher temperatures, the spectra decay into the 3-line 1:2:1 spectrum characteristic of the high-temperature decomposition products of the triquinocyclopropanes.[1]

The oxidation–reduction system **1** $\rightleftharpoons$ (**2**) $\rightleftharpoons$ (**6**) is also reversible, for reduction of triquinocyclopropanes under acidic conditions gives **1**. The present state of information about the triquinocyclopropane–bis(*p*-hydroxyaryl)quinocyclopropene system is summarized in general form in Figure 5, where the large circle symbolizes the entire 4-ring carbon skeleton of the molecules. Of the six possible monomeric species, only the monoanion **3** has not been directly observed, although it must actually be present in equilibrium with **1** and **4**. And of the six possible one-electron oxidation–reduction reactions, only one has not yet been observed—the direct one-electron conversion of **2** to **3**.



2b*



2c*

Experimental Section

The diarylquinocyclopropenes **1a–d** and triquinocyclopropanes **6a–d** were synthesized as described in the preceding paper.[1] For general comments on the experimental methods, see ref 7. The esr apparatus is described in ref 1.

Titration of 1d with Sodium Hydroxide. Sodium hydroxide pellets (4 g, 0.1 mol) were dissolved in 4 ml of H_2O, filtered to remove any sodium carbonate impurity, then diluted to 1.0 l with freshly boiled distilled water. Standardization with potassium acid phthalate showed this solution to be 0.080 *M* NaOH.

Diarylquinocyclopropene **1d** (160 mg, 0.24 mmol) dissolved in 200.0 ml of CH_3OH, was added to a 500-ml 3-necked flask, equipped with a magnetic stirring bar and a 10-ml buret. The system was flushed with nitrogen, then stoppered; one of the stoppers was quickly replaced with a rubber septum. The solution was titrated with the standardized NaOH solution. After each addition of base, a 1-ml aliquot was withdrawn by a syringe inserted through the rubber septum, and the electronic spectrum taken in 0.05 in cells. The results of this spectroscopic titration are shown in Figure 1.

Dipotassium Salt of 1a. Tris(3,5-diisopropyl-4-hydroxyphenyl)-cyclopropenium chloride[7] (1.50 g, 2.48 mmol) was dissolved in 75 ml of anhydrous methanol, and 0.5 g (8.9 mmol) of potassium hydroxide was added. The mixture was swirled until all of the base was dissolved and then reduced to low volume (*ca.* 10 ml) by rotary evaporation. Addition of acetonitrile precipitated the product as a yellow solid which was separated by filtration; yield 1.62 g (101%). A portion was recrystallized from acetonitrile to give yellow needles. The infrared spectrum (KBr pellet) in the region 4000–625 cm^{-1} showed absorptions at 2950 (s), 2860 (sh), 1635 (sh), 1590 (s), 1455 (m), 1335 (vs, br), 1140 (m), 1105 (w), 1060 (w), 940 (w), 890 (w), 815 (w), and 785 (m) cm^{-1}. The electronic spectrum in acetonitrile showed maxima at 320 nm (log ϵ 4.50) and 442 (5.03); see Figure 1. Addition of a drop of aqueous perchloric acid to this same solution produced new maxima at 243 nm (log ϵ 4.66), 289 (4.23), 354 (4.84), and 371 (4.89); this spectrum is that of the triarylcyclopropenium starting material,[1] providing good evidence that the yellow solid was indeed the dipotassium salt of **1a**. No attempt was made to obtain an elemental analysis, since this solid appeared to be very sensitive to moisture and decomposed readily.

Titration of the Diarylquinocyclopropene 1d with $K_3Fe(CN)_6$. The following two solutions were prepared: (A) 63.5 mg (0.10

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[7] R. West, D. C. Zecher, and W. Goyert, *J. Amer. Chem. Soc.*, **92**, 149 (1970).

mmol) of the diarylquinocyclopropene **1d** was dissolved in 100.0 ml of benzene (1.0×10^{-3} *M*) and (B) 13.10 mg (0.40 mmol) of $K_3Fe(CN)_6$ and 1.12 g (20 mmol) of KOH were dissolved in 200.0 ml of distilled water (2.0×10^{-3} *M* in $K_3Fe(CN)_6$ and 0.1 *N* in KOH). One milliliter of A was diluted 100 times with benzene and the electronic spectrum was obtained in the visible region (700–400 nm). Twenty milliliters of B was added to the remaining 99.0 ml of A. This mixture was stirred for 30 min; then the benzene layer was separated and washed with water. Again, 1.0 ml of the resulting benzene solution was diluted 100 times with benzene and the visible spectrum taken. An additional 30.0 ml of B was added to the remaining 98 ml of the benzene solution, and treated as above. In the same manner, additional 30, 20, 50, and 50-ml aliquots of B were added to the benzene solution and the visible spectrum taken after each addition.

Of course, the visible spectrum of the original solution, A, showed bands characteristic of **1d**. The spectra obtained from the benzene solution during the titration showed bands characteristic of **1d** and **6d** only. The absorbance at 685 nm was determined after each aliquot of oxidant was added. Since only **6d** absorbs at this wavelength, the observed absorbance was proportional to the amount of **6d** present in solution. The results are shown in Table III.

Table III

Total amount of oxidant added (mol of oxidant/mol of **1d**), ml	Observed absorbance at 685 nm
0 (0)	0
20.0 (0.4)	0.095
50.0 (1.0)	0.190
80.0 (1.6)	0.365
100.0 (2.0)	0.410
150.0 (3.0)	0.415
200.0 (4.0)	0.415

These results show that after 2 molar equiv of oxidant had been added, the reaction was 99% (0.410/0.415) complete. Thus, despite the fact that this must be considered a crude titration, the results show that 100 ml of 2.0×10^{-3} *M* $K_3Fe(CN)_6$ were required to oxidize completely 100 ml of 1.0×10^{-3} *M* **1d**, clearly indicating that the oxidation was a 2-electron process.

Anion-Radical 5 of Triquinocyclopropanes for Esr Studies. A. By Reduction of 6. The preparative technique was similar to that described elsewhere.[8] About 1 mg of the triquinocyclopropane was placed in a 4-mm glass esr sample tube with a side arm. One drop of sodium–potassium alloy was transferred to the side arm and the tube was quickly attached to a vacuum line and evacuated. One milliliter of carefully purified 1,2-dimethoxyethane was then distilled into the sample tube. The Na–K alloy was then distilled from the side arm by carefully heating with a flame so as to form a mirror on the walls of the tube just above the solution level. The tube was then sealed under vacuum and kept at liquid nitrogen temperatures until ready for use. When ready, the anion radical was developed by allowing the solution of the triquinocyclopropane to come in contact with the Na–K alloy mirror at −63° (chloroform slush bath), and then placed immediately into the variable temperature probe of the esr spectrometer set at −60°.

B. By Oxidation of 4. A mixture of the bis(*p*-hydroxyaryl)-quinocyclopropene **1** and lead dioxide was prepared, 3:1 by weight. About 1.5 mg of the mixture was placed in an esr sample tube and 1 ml of 1,2-dimethoxyethane, containing *ca.* 10% of a freshly prepared methanol–sodium methoxide solution, was added. The solution was quickly deoxygenated by flushing with nitrogen, then sealed, and immediately placed in the esr spectrometer set at low temperatures (−20 to −60°).

The observed esr spectra for **5b–d** are given in Figure 3. In each case, the observed relative intensities agreed well with the calculated intensities: **5d**, 6 equivalent hydrogens, $a_H = 0.43$ g, giving 7 lines (1:6:15:20:15:6:1); **5c**, 6 equivalent hydrogens, $a_H = 0.43$ *g*, plus 2 isopropyl methine hydrogens, $a_H = 1.3$, giving 13 lines (1:6:15:22:27:36:42:36:...); **5b**, 6 equivalent hydrogens, $a_H = 0.43$ *g*, plus 4 equivalent isopropyl methine hydrogens, $a_H = 1.3$, giving 19 lines (1:6:15:24:39:66:87:96:114:128:114:...).

g Values were measured for **5b** and **5d**, using double-cavity technique with Fremy's salt, potassium nitrosyldisulfonate, as reference; *g* for Fremy's salt was taken as 2.00550 ± 0.0005. Identical *g* values of 2.00432 ± 0.00010 were obtained for **5b** and **5d**; this value is significantly lower than that for the related 2,5-di-*t*-butylsemiquinone, 2.00464.[9]

Monoradicals (2). A. By Oxidation of 1 with Lead Dioxide. About 1.5 mg of a 3:1 mixture (by weight) of the quinocyclopropene **1** and lead dioxide was placed in an esr sample tube, and 1 ml of *p*-xylene was added. The tube was flushed with nitrogen, sealed, agitated to dissolve and oxidize the sample, and examined in the esr spectrometer.

B. By Oxidation of 1 with Silver (I) Oxide. Six milligrams of a 3:1 mixture of **1** and silver(I) oxide was ground with 2 g of naphthalene in a mortar. About 500 mg of this mixture was then placed in an esr sample tube which was heated to 90° to melt the naphthalene. This method was used to study esr spectra in the temperature range 90–200°. The *g* value for the monoradical of **1d** prepared in this manner was measured to be 2.00417 ± 0.00010.

C. By Comproportionation of 1 and 6. An equimolar mixture of the quinocyclopropene **1** and corresponding triquinocyclopropane **6** was prepared. Six milligrams of the mixture was ground with 2 g of naphthalene and a portion of the resulting powder was placed in the sample tube and heated to form **2**.

In methods B and C, early experiments were carried out with sealed tubes carefully flushed with nitrogen. It was later found that identical results were obtained using unsealed tubes, so some experiments were carried out without special precautions.

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