

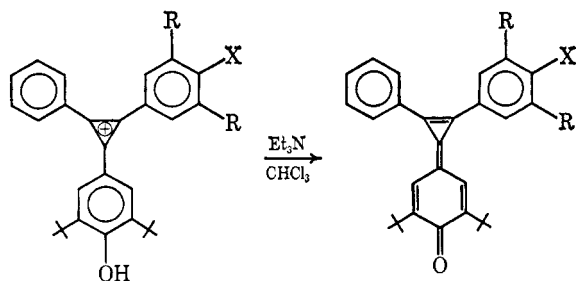
## Diarylquinocyclopropenes and Triquinocyclopropanes

Robert West and David C. Zecher

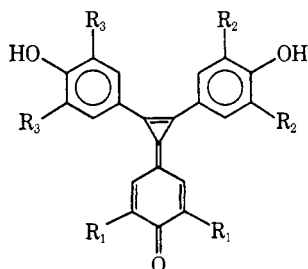
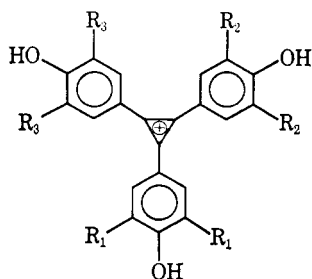
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**Abstract:** Several triarylquinocyclopropenium ion salts bearing *p*-hydroxyl groups on the aromatic rings have been converted by treatment with bases to diarylquinocyclopropenes (**1a,b**, **2a-f**); these revert to triarylquinocyclopropenium ions upon reprotonation. Tris(*p*-hydroxyaryl)cyclopropenium ions yield bis(*p*-hydroxyaryl)quinocyclopropenes which upon oxidation form 3-radialene derivatives, the triquinocyclopropanes **6b-f**. Compounds **6b-f** are purplish blue solids whose stabilities increase with steric hindrance around the oxygen atoms; their nmr spectra indicate that rotation of the aromatic rings does not take place at room temperature. The electron spin resonance and thermal decomposition of **6b-f** were studied, and their electronic structure is discussed.

**Diarylquinocyclopropenes.** In the accompanying paper,<sup>1</sup> we report the reaction of phenols with diarylchloro-, aryldichloro-, or trichlorocyclopropenium ions to give triarylquinocyclopropenium ion salts bearing one, two, or three *p*-hydroxyl substituents, respectively. These cyclopropenium ion salts lose a phenolic hydrogen atom upon treatment with bases, forming diarylquinocyclopropenes (**1a, b**, **2a-c**).

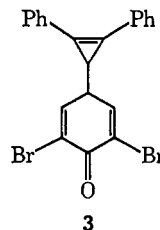
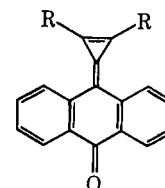


**1a**, R = X = H  
**b**, R = *t*-Bu, X = OH



**2**  
**2a**, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = Me  
**b**, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = *i*-Pr  
**c**, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = *t*-Bu  
**d**, R<sub>x</sub> = R<sub>y</sub> = *t*-Bu; R<sub>z</sub> = Me  
**e**, R<sub>x</sub> = R<sub>y</sub> = *t*-Bu; R<sub>z</sub> = *i*-Pr  
**f**, R<sub>x</sub> = *t*-Bu; R<sub>y</sub> = R<sub>z</sub> = *i*-Pr

Quinocyclopropenes, as a class, are relatively new. Only two were known when our experiments were carried out, the dibromo compound **3** reported in 1963 by Kende,<sup>2</sup> and the anthraquinone derivative **4a** reported in 1965 by Föhlisch and Bürgle.<sup>3</sup> In later research simultaneous with ours, the latter two workers also prepared the dipropyl analog **4b**, and compound **1a**.<sup>4</sup> The properties of our **1a** agree fully with those reported by Föhlisch and Bürgle.<sup>4,5</sup>

**3**

**4a**, R = Ph  
**b**, R = *n*-Pr

All of our diarylquinocyclopropenes were brightly colored solids, the color varying from yellow for **2b** to maroon for **1a**. They showed no definite melting points, but instead underwent a series of color changes beginning about 190° and decomposed completely above 250°. The compounds all showed weak cyclopropene C=C stretching bands at 1800–1825 cm<sup>-1</sup> in the infrared. Detailed spectra for **1a,b** and **2a-c** are given in the Experimental Section. Compounds **2d-f** appeared to be mixtures of isomers, and so were not studied in detail except as their oxidation products (*vide infra*).

The electronic spectra of these compounds are recorded in Table I. As shown, they all contain an intense maximum near 406 nm which is primarily responsible for their color. Note also that the electronic spectrum of **2c**, listed in several different solvents, shows a bathochromic shift from polar to nonpolar solvents. A solvent effect of this type can be explained as resulting from a transition to an excited state that is less polar than the ground state.<sup>6</sup> This provides strong evidence

(2) A. S. Kende, *ibid.*, **85**, 1882 (1963). In agreement with Kende, who was unable to obtain unsubstituted diphenylquinocyclopropene, we were not able to isolate stable quinocyclopropenes lacking substituents *ortho* to the quinonoid oxygen atom. Unsuccessful attempts were made starting with each of the three ions, [(*p*-HOC<sub>6</sub>H<sub>4</sub>)<sub>n</sub>Cs-(C<sub>6</sub>H<sub>5</sub>)<sub>3-n</sub>]<sup>+</sup> where *n* = 1–3.

(3) B. Föhlisch and P. Bürgle, *Tetrahedron Lett.*, 2661 (1965).

(4) B. Föhlisch and P. Bürgle, *Ann. Chem.*, **701**, 67 (1967).

(5) These workers have also reported synthesis of the related quinotropyliene compounds; see B. Föhlisch, P. Bürgle, and D. Krockenberger, *Angew. Chem. Intern. Ed. Engl.*, **4**, 972 (1965).

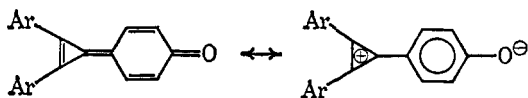
(6) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954); E. M. Kosower, *J. Amer. Chem. Soc.*, **80**, 3253 (1958).

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

Table I. Electronic Spectra of Some Diarylquinocyclopropenes

Compd	Color	Solvent	$\lambda$ , nm (log $\epsilon$ )			
1a	Maroon	CH <sub>3</sub> CN	275 (4.47),	383 (4.67),	403 (4.85)	
1b	Red	CH <sub>3</sub> CN		367 (4.37),	385 (4.61),	405 (4.85)
2a	Yellow-orange	CH <sub>3</sub> OH	256 (4.14),	325 (4.38)		404 (4.73)
2b	Yellow	CH <sub>3</sub> OH	260 (4.23),	316 (4.35),	328 (4.42),	406 (4.87)
2c	Orange-red	CH <sub>3</sub> OH	273 (4.13),	315 (4.31),	325 (4.33),	406 (4.86)
2c		CH <sub>3</sub> CN	310 (4.40),	323 (4.42),	386 (4.56),	406 (4.86)
2c		C <sub>6</sub> H <sub>6</sub>	310 (4.49),	324 (4.45),	391 (4.70),	413 (4.90)

that the ground state of the diarylquinocyclopropenes is dipolar and therefore that an ionic form with "cyclopropenium ion" character makes a strong contribution.<sup>7</sup>



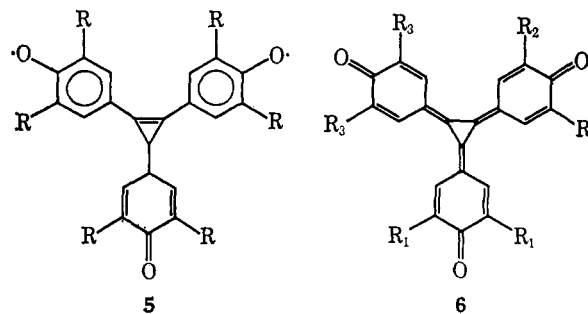
The solubility of these quinocyclopropenes was also consistent with a high polarity, in that they were most soluble in polar solvents such as methanol. The high molecular weight compounds, **2b** and **2c**, proved to be slightly more soluble in polar solvents than the lower molecular weight **2a**, perhaps because intermolecular hydrogen bonding is more significant for **2a**, with only methyl groups flanking the quinoidal oxygen, than for **2b** or **2c** in which the quinoidal oxygen is flanked by much bulkier and sterically interfering groups.<sup>8</sup>

Because of the low solubility of the quinocyclopropenes in usual solvents, the proton nmr spectrum was determined only for **1a**. This showed multiplets at  $\tau$  1.92 and 2.33, as well as a singlet at  $\tau$  8.55 (*t*-butyl protons). The spectrum of each compound was however determined in trifluoroacetic acid. As expected, in this highly acidic solvent the compounds all gave spectra identical with those of the cyclopropenium ions from which they were derived.<sup>1</sup> Treatment of compounds **1a,b** and **2a-c** with hydrogen bromide in ether or with aqueous perchloric acid in benzene also regenerated the corresponding triarylcyclopropenium bromides or perchlorates in good yields.

It is interesting that the diarylquinocyclopropenes were apparently generated merely upon high dilution of the corresponding triarylcyclopropenium ion salts in acetonitrile. Solutions of these salts (chlorides, bromides, or perchlorates) at  $10^{-3}$  M in acetonitrile showed only bands for the cyclopropenium ions,<sup>1</sup> but when the same solutions were diluted to  $10^{-5}$ – $10^{-6}$  M, characteristic maxima for the diarylquinocyclopropenes appeared.

**Triquinocyclopropanes.**<sup>9</sup> Oxidation of the bis(*p*-hydroxyaryl)quinocyclopropenes, **2a-f**, was attempted in order to obtain stable, delocalized biradicals of type **5**. Oxidation of **2a-f** either in aqueous or non-aqueous media leads to purple colored crystalline compounds which are easily reduced back to the diarylquinocyclopropenes with hydroquinone. Magnetic and esr studies show however that the products are paired electron species. From spectral evidence to be dis-

cussed below, the novel triquinocyclopropane structures **6a-f** are proposed for these compounds.



- 6a, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = Me  
 b, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = *i*-Pr  
 c, R<sub>1</sub> = R<sub>2</sub> = R<sub>3</sub> = *t*-Bu  
 d, R<sub>1</sub> = R<sub>2</sub> = *t*-Bu; R<sub>3</sub> = Me  
 e, R<sub>1</sub> = R<sub>2</sub> = *t*-Bu; R<sub>3</sub> = *i*-Pr  
 f, R<sub>1</sub> = *i*-Pr; R<sub>2</sub> = R<sub>3</sub> = *t*-Bu

For preparative purposes, it is most convenient to generate triquinocyclopropanes not from **2a-f** but from the corresponding tris(*p*-hydroxyaryl)cyclopropenium salts.<sup>1</sup> When the latter are dissolved in benzene and treated with excess alkaline aqueous potassium hexacyanoferrate(III) solution, deprotonation and oxidation occur simultaneously, and the benzene layer turns deep blue. Separation of the layers and evaporation of the benzene produces **6b-f** (but not **6a**) in good yield.

In accordance with the zero dipole moment predicted for the triquinocyclopropane structure, compounds **6b-f** are soluble in nonpolar solvents (benzene, CCl<sub>4</sub>) and insoluble in polar solvents (methanol, acetone). This behavior is just the reverse of that for the highly polar **2a-c**. The infrared spectra of **6b-f** are very simple, also suggesting a highly symmetrical structure. For instance, that for **6c**, shown in Figure 1, has only six bands of moderate or strong intensity in the region from 600–2500 cm<sup>-1</sup>, at 1590, 1465, 1720, 1090, and 900 cm<sup>-1</sup>, in addition to C–H stretching modes at 2860–2960 cm<sup>-1</sup>.<sup>10</sup> A band near 1600 cm<sup>-1</sup> has been observed in the ir spectrum of related quinonoid compounds.<sup>11</sup> No bands are found in regions characteristic for OH stretching or cyclopropane C=C.<sup>12</sup>

(10) For comparison, the corresponding diarylquinocyclopropene **2c** and triarylcyclopropenium ion show 16 and 18 medium to strong bands in the region 625–2000 cm<sup>-1</sup>.

(11) E. R. Altwicker, *Chem. Rev.*, **67**, 475 (1967).

(12) Although the intensity and position of cyclopropane C=C infrared bands depend heavily on the nature of the ring substituents (for example, G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **83**, 1003 (1961), and **85**, 99 (1963), list infrared bands for a number of alkylcyclopropane derivatives), the lack of any bands for **6b-f** in the range 2000–1640 cm<sup>-1</sup> clearly shows that these compounds at least do not possess a C=C absorption similar to that earlier assigned to the diarylquinocyclopropenes, **2b-f**, at 1800–1825 cm<sup>-1</sup>.

(7) This same conclusion was reached for simple methylenecyclopropane derivatives and for calicenes. For example, see W. M. Jones and R. S. Pyron, *J. Amer. Chem. Soc.*, **87**, 1608 (1965).

(8) B. G. Somers and H. S. Gutowsky, *ibid.*, **85**, 3065 (1963).

(9) The synthesis of these compounds was previously reported in a communication: D. C. Zecher and R. West, *ibid.*, **89**, 152 (1967).

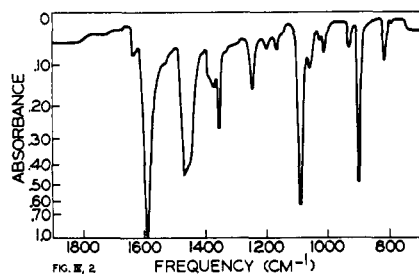


Figure 1. Infrared spectrum of **6c**. Composite of mulls in Nujol and fluorocarbon oil.

The proton nmr spectra for the triquinocyclopropanes provide the strongest evidence for the proposed structures. Data in Table II show that for compounds **6b** and **6c**, all of the alkyl groups and all of the aromatic protons are equivalent. Highly significant structural information can be obtained from the alkyl portions of the nmr spectra of the compounds containing different kinds of alkyl groups, **6d-f**. The spectrum for the compound with four *t*-butyl and two isopropyl groups, **6e**, shows a doublet for the isopropyl methyl protons (split by the methine hydrogen), and two chemically shifted *t*-butyl resonances (Figure 2). The result shows that exocyclic double bonds are present in **6e**, for if they were not, the *t*-butyl groups would become equivalent by rotation. In agreement with this interpretation, the spectrum of **6f** shows the two *t*-butyl groups to be equivalent and the isopropyl methyl protons to be chemically dissimilar (Figure 2). The spectrum for **6d** is also consistent, showing two dissimilar sets of *t*-butyl groups. For all three compounds, rotation of the aromatic rings about the bond joining them to the cyclopropane ring must be slow compared to the proton spin relaxation time.

The electronic spectra of these compounds are of outstanding interest. Data for **6b-f** are given in Table II, and the spectrum of **6c** is shown in Figure 3. All of the compounds have remarkably similar spectra, consisting of a series of six strong bands at nearly the same wavelengths for each compound. The strongest absorption in the spectra falls at very long wavelength, in the near infrared at about 770 nm (37 kcal/mol). This band must result from a highly allowed  $\pi \rightarrow \pi^*$  transition lying at relatively low energy.

When the hexamethyl compound **2a** or the corresponding cyclopropenium ion was oxidized in benzene with potassium hexacyanoferrate, a blue solution was produced which decomposed within minutes to a yellow one. The triquinocyclopropane **6a** was never isolated, but its existence in solution was indicated by the electronic spectrum, which showed bands at 305, 317, 387, 628, 692, and 772 nm, very similar to those for **6b-f** (Table II). With the unalkylated tris(*p*-hydroxyphenyl)cyclopropenium ion, similar oxidation failed to produce even a blue color. Any triquinocyclopropane formed in the latter reaction must decompose instantly.

The stabilities of the isolable compounds **6b-f** also varied significantly depending on the nature of the alkyl substituents. The temperature at which rapid decomposition ensues increases with increasing steric hindrance around oxygen, from 133° for **6b** to 280° for **6c**, the compound with six *t*-butyl groups. When

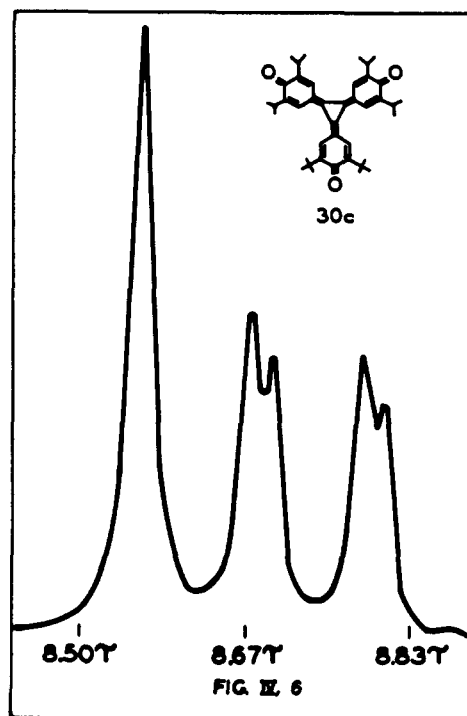
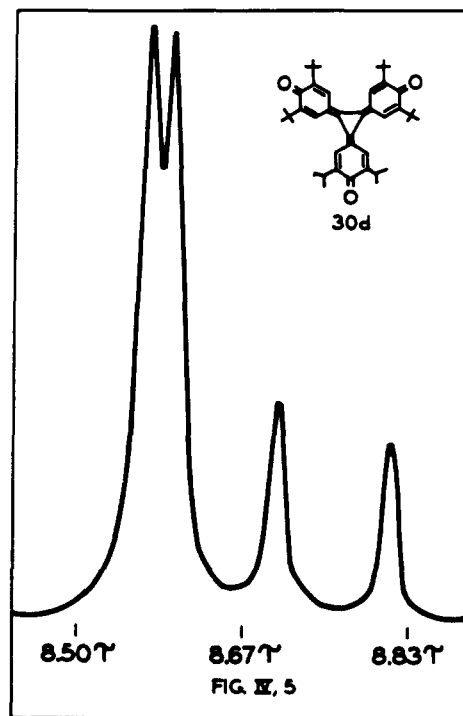


Figure 2. Proton nmr for triquinocyclopropanes **6e** (above) and **6f** (below), in carbon tetrachloride solution. The methyl region only is shown.

**6b** was heated to 133°, it formed a red-brown solid which was shown by infrared, electronic, and nmr spectroscopy to be essentially the quinocyclopropene **2b**. Recrystallization of the red-brown solid gave pure **2b**, which could be oxidized again to **6b**. Similar observations were made for the thermal decomposition products of other triquinocyclopropanes. Thus the

Table II. Spectral Data for Triquinocyclopropanes

Compd	Electronic		Proton nmr, $\tau^a$			Esr		Temp, °C		
	$\lambda_{\max}$ (log $\epsilon$ )		$H_{ar}$	$R_1R_2$	$R_1$	Lines, rel int	$a_H, Oe$			
6b	307 (4.13), 317 (4.15), 390 (4.59), 630 (4.36), 692 (4.62), 776 (4.66)		2.52 (S)	6.70 (SP; $J = 7$ cps) 8.75 (D; $J = 7$ cps)		1:2:3:4:3:2:1		1.5	90	
6c	307 (4.13), 316 (4.15), 390 (4.62), 625 (4.43), 685 (4.68), 769 (4.71)		2.50 (S)	8.60 (S)		1:2:1		1.5	180	
6d	304 (4.10), 314 (4.11), 388 (4.59), 619 (4.38), 684 (4.64), 768 (4.67)		2.50 (S)	8.60 (S), 8.63 (S)		7.87 (S)		1:2:1	1.6	100
6e	307 (4.20), 315 (4.20), 391 (4.60), 625 (4.37), 688 (4.63), 772 (4.67)		2.50 (S)	8.58 (S), 8.61 (S)		6.83 (SP; $J = 7$ cps) 8.77 (D; $J = 7$ cps)		1:2:1	1.6	100
6f	306 (4.23), 317 (4.24), 390 (4.66), 627 (4.38), 690 (4.65), 770 (4.70)		2.50 (S)	8.57 (S)		6.72 (M) 8.73 (D; $J = 7$ cps) 8.75 (D; $J = 7$ cps)				

<sup>a</sup> S = singlet, D = doublet, SP = septet, M = multiplet.

predominant mode of thermal decomposition of these substances leads ultimately to reduction.

Compound **6b** also was found to decompose slowly at room temperature, with a half-life of about 1 week. Preliminary observations indicate that at least some of the other triquinocyclopropanes also decompose at room temperature, but at much slower rates. However, compounds **6b-f** are very much more stable than the other known compounds incorporating the 3-radialene structure; trimethylenecyclopropane<sup>13</sup> itself and tris(isopropylidene)cyclopropane.<sup>14</sup>

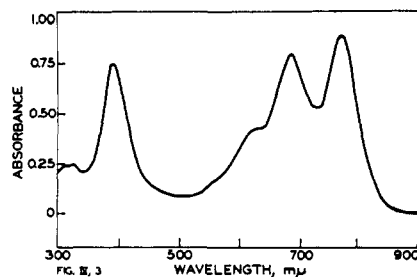


Figure 3. Electronic spectrum of **6c**,  $1.5 \times 10^{-5}$  M in benzene.

**Electron Spin Resonance Spectra.** To study the decomposition of triquinocyclopropanes more closely and also to search for possible thermally-populated triplet-state species, the esr spectra of **6b-e** were investigated under various conditions. As solids, these compounds all showed only an extremely weak, broad ( $\sim 25$  G) signal near  $g = 2$ . This may be, but is not certainly, due to a very small concentration of molecules in the diradical (triplet) state. The signal strength increased slowly with increasing temperature, then sharply increased in the vicinity of the decomposition temperature (Table II). When the sample was cooled the signal decreased but still was several times as intense as that for the original compound at room temperature. Heating above the decomposition temperature also led to a decrease in signal strength.

The same kind of variation of esr signal strength with temperature was observed for **6b-d** dissolved in melted naphthalene (above  $90^\circ$ ), but these solutions showed hyperfine splitting (Table II, Figure 4). The

(13) E. A. Korko, *J. Amer. Chem. Soc.*, **87**, 5518 (1965); P. A. Waitkus, L. I. Peterson, and G. W. Griffin, *ibid.*, **88**, 181 (1966).

(14) G. Köbrich and H. Heinemann, *Angew. Chem. Intern. Ed. Engl.*, **4**, 594 (1965).

compounds containing *t*-butyl groups, **6c**, **d**, and **e**, all gave the same 1:2:1 pattern with a hyperfine splitting of 1.5–1.6 G, but **6b** which contains only isopropyl groups gave a seven-line pattern, with relative intensities 1:2:3:4:3:2:1 (Figure 4).

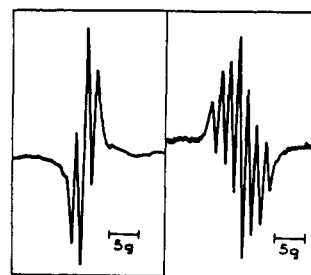


Figure 4. ESR spectra of triquinocyclopropanes **6c** (left) and **6b** (right) in melted naphthalene.

Several attempts were made to detect the " $\Delta m = 2$ " and additional " $\Delta m = 1$ " lines, characteristic of triplet-state molecules.<sup>15</sup> The triquinocyclopropanes were heated to develop a strong esr signal in bis(2-ethoxyethyl)ether solution and then cooled to  $-160^\circ$  to form a rigid glass, in which triplet lines should be detectable. No signal was found other than a single broad line at  $g = 2$ .

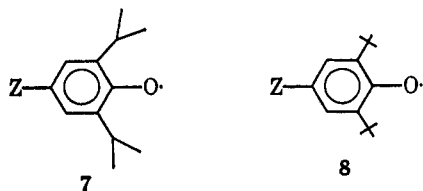
Uncoupling of one pair of electrons to form a diradical of type **5**, followed by proton abstraction to give a quinocyclopropane seems a reasonable mechanism for the decomposition of triquinocyclopropanes. However, **5** is most unlikely to be the species responsible for the esr spectra in naphthalene solution. In **5** the unpaired electrons would be expected to be delocalized over the aromatic rings. They would then interact equally with six aromatic hydrogens and a seven-line hyperfine pattern would be observed.<sup>16,16a</sup> Even if the electrons were somehow localized on the individual

(15) These designations are conventional despite the fact that  $m_s$  is not a satisfactory quantum number for the spin states. For a discussion see A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row Publishers, Inc., New York, N. Y., 1967, Chapter 8, p 115–131.

(16) Broadening of the hyperfine lines is also possible if the spin and exchange interactions are of comparable size; see S. M. Weissman, *J. Chem. Phys.*, **29**, 1189 (1958); R. M. Dupeyre, H. Lemaire, and A. Rassat, *J. Amer. Chem. Soc.*, **87**, 16 (1965); (a) Radicals derived from **5** by capture of a hydrogen atom on one oxygen are also excluded as the source of the observed esr signal. These radicals have been prepared and show quite different spectra; see R. West and D. C. Zecher, *ibid.*, **92**, 161 (1970).

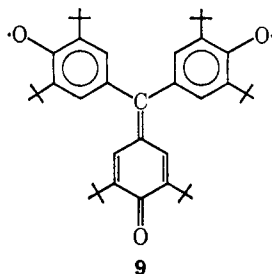
aromatic rings, dipolar spin correlation should give rise to a typical triplet esr spectrum.<sup>17</sup>

The spectra seem instead to be those of monoradicals with the unpaired electron localized on a single ring, or possibly biradicals in which the electrons are so far apart that spin correlation is negligible. The esr spectra for **6b** and **6c-e** can be reasonably attributed to phenoxy radicals of types **7** and **8**, respectively, where the structure of Z is unknown. **7** and **8** could



be formed either by cleavage or polymerization of the diradical **5**. The hyperfine splitting of 1.5–1.6 G for **8** is consistent with that for known radicals of this type where Z is alkyl which give  $a_H$  from 1.6 to 2.0 G for the aromatic protons *meta* to oxygen.<sup>18</sup> In **7**, the observed seven-line pattern can be explained by coupling of the unpaired electron with the methine proton of the isopropyl groups and the *meta* protons with hyperfine constants of 3.0 and 1.5 G, respectively. The corresponding coupling constants of the 2,6-diisopropyl phenoxy radical (**7** where Z = H) are 3.8 and 1.9 G.<sup>18</sup> Our explanation requires also the reasonable assumption that the phenoxy radicals **8** containing *t*-butyl flanking groups be more stable than those with isopropyl or methyl groups, since the spectrum of **8** is obtained from the mixed compounds **6e** and **6f** as well as from **6c**. Only **6b**, which contains no *t*-butyl groups, gives the diisopropylphenoxy type spectrum of **7** (Figure 4).

**Electronic Structure.** The triquinocyclopropanes are analogous to the biradical **9** prepared by Yang and Castro,<sup>19</sup> except that the central carbon atom is replaced by a cyclopropane ring in **6a-f**. The triplet ground state for **9** has been studied by esr spectroscopy,<sup>20</sup> and justified by detailed molecular orbital calculations.<sup>21</sup>



While no such full theoretical treatment has yet been carried out for **6a-f**, we have done a simple Hückel  $\pi$ -electron calculation for the unsubstituted triquinocyclopropane system. The molecule is calculated to have a singlet ground state. The energy levels are closely spaced, and the lowest unfilled orbital is predicted to lie only 0.24 eV above the highest filled level.

(17) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948); E. Wasserman, L. C. Snyder, and W. A. Yager, *ibid.*, **41**, 1763 (1964).

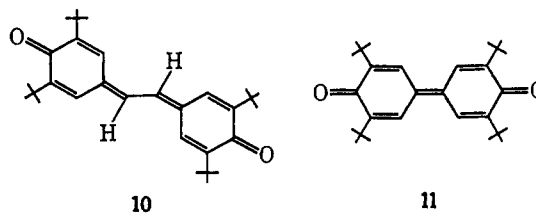
(18) A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965, p 80.

(19) N. C. Yang and A. J. Castro, *J. Amer. Chem. Soc.*, **82**, 6308 (1960).

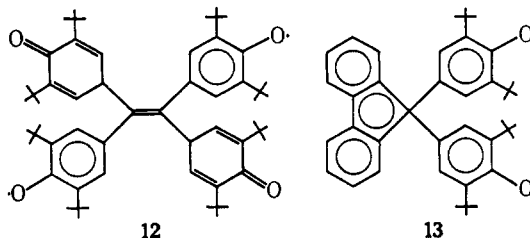
(20) R. Kreilick, *J. Chem. Phys.*, **43**, 308 (1965).

(21) D. Kearns and S. Ehrenson, *J. Amer. Chem. Soc.*, **84**, 739 (1962).

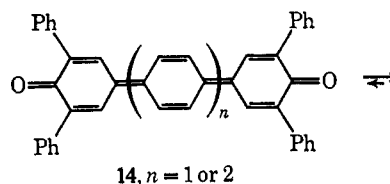
The esr measurements on highly purified samples of **6c** allow us to place an upper limit on the proportion of diradical molecules at room temperature of 1 in **10**.<sup>6</sup> The other molecules **6b-f** behave similarly and all must have singlet ground states, in agreement with the MO calculations. Other molecules for which diradical structures can be written, but which also prove to have singlet ground states include **10**<sup>22</sup> and **11**.<sup>23</sup> In these molecules, as in **6b-f**, adoption of the paired electron quinonoid form takes place in spite of the loss of aromatic resonance energy for two benzene rings which would be present in the diradical form.



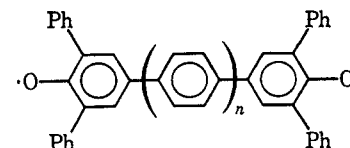
Most phenoxy compounds which exist as stable biradicals are ones for which no reasonable quinonoid structure can be written. Besides Yang and Castro's biradical,<sup>19,21</sup> these include digalvinoxyl **12** and the triplet species **13**, both studied by Chandross.<sup>24,25</sup> This



criterion is not determinative, however, for Dimroth and his coworkers have recently shown<sup>23</sup> that extended systems for which the quinonoid structures **14** can be written give very strong esr signals, and so probably exist substantially in the diradical form **15**. In this connection it will be of interest to prepare more extended compounds related to **6a-f**, and research on these is now under way.



14,  $n = 1$  or  $2$



15,  $n = 1$  or  $2$

## Experimental Section<sup>26</sup>

**Diarylquinocyclopropanes (1a, b, 2a-c).** Most of the diarylquinocyclopropanes were prepared by treatment of the corresponding triarylquinocyclopropanium chlorides<sup>1</sup> in a suitable solvent (usually

(22) C. R. Bohn and T. W. Campbell, Jr., *J. Org. Chem.*, **22**, 458 (1957).

(23) K. Dimroth, W. Umbach, and K. H. Blöcher, *Angew. Chem.*, **75**, 860 (1963).

(24) E. A. Chandross, *J. Amer. Chem. Soc.*, **86**, 1263 (1964).

(25) E. A. Chandross and R. Kreilick, *ibid.*, **86**, 117 (1964).

(26) For general comments on experimental methods see ref 1.

chloroform) with triethylamine. For example, compound **2b** was prepared in 40% yield by adding 1.5 g of tris(3,5-diisopropyl-4-hydroxyphenyl)cyclopropenium chloride to 100 ml of a 50% chloroform-water mixture; no attempt was made to completely dissolve the salt. Approximately 2 ml of triethylamine was added and the mixture shaken. Most of the original salt appeared to dissolve by this treatment, then a new precipitate formed which floated on top of the aqueous layer. This was filtered and recrystallized from methanol-acetonitrile-water to give the product as bright yellow needles.

Compound **2a** was prepared by dissolving tris(3,5-dimethyl-4-hydroxyphenyl)cyclopropenium chloride in the minimum amount of methanol and adding triethylamine dropwise, causing **3a** to precipitate.

The diarylquinocyclopropenes were often prepared without the actual isolation of the corresponding triaryl cyclopropenium salts, simply by adding triethylamine to the reaction mixture in the final stages of the synthesis of the triaryl cyclopropenium chlorides.

The products, recrystallized from methanol or acetonitrile, were highly colored solids; see Table I. Some were observed to darken on exposure to light, so they were ordinarily stored in the dark.

The electronic spectra of **1a,b** and **2a-c** are recorded in Table I. The proton nmr spectra were taken in trifluoroacetic acid, and were identical with those for the corresponding triaryl cyclopropenium ion precursors. The infrared spectra and elemental analysis for the pure compounds **1a,b** and **2a-c** are given below.

Compound **1a** showed infrared bands at 3615 (w), 2950 (m), 2910 (sh), 2870 (sh), 1850 (w), 1810 (m), 1600 (s), 1555 (w), 1495 (vs), 1470 (vs), 1440 (vs), 1350 (vs), 1330 (vs), 1255 (s), 1230 (m), 1200 (m), 1150 (m), 1110 (m), 1015 (w), 910 (m, doublet), 895 (m), 810 (w), 780 (w), 760 (m), 720 (w), and 680 (m)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{27}\text{H}_{46}\text{O}_2$ : C, 85.06; H, 8.81; O, 6.13. Found: C, 85.30; H, 8.71; O, 5.90.

Compound **1b** showed infrared bands at 2950 (m), 2920 (sh), 2870 (sh), 1820 (m), 1605 (s), 1570 (m), 1500 (vs), 1480 (vs), 1445 (vs), 1355 (vs), 1330 (vs), 1250 (w), 1170 (w), 1120 (w), 1010 (vw), 900 (s), 815 (vw), 780 (w), 760 (m), and 670 (m)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{29}\text{H}_{50}\text{O}$ : C, 88.32; H, 7.61; O, 4.07. Found: C, 88.29; H, 7.54; O, 4.48.

Compound **2a** showed infrared bands in the 2000–625  $\text{cm}^{-1}$  region at 1825 (w), 1600 (vs), 1425 (m, br), 1375 (vs, br), 1325 (vs, br), 3 strong peaks between 1260–1230, 1175 (vs, br), 1105 (s), 1030 (m), 995 (s), 955 (m), 930 (m), 890 (m), 775 (m), 745 (w), and 725 (m)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{27}\text{H}_{26}\text{O}_3$ : C, 81.40; H, 6.54; O, 12.06. Found: C, 81.21; H, 6.56; O, 12.23 (diff).

Compound **2b** exhibited infrared bands in the 2000–625  $\text{cm}^{-1}$  region at 1825 (w), 1590 (s), 1570 (m), 1490 (w), 1450 (m), 1370 (vs), 1330 (s), 1295 (s), 1275 (s, br), 1240 (s), 1210 (s), 1170 (s), 1130 (s,sh), 1105 (s), 1090 (s,sh), 1070 (s), 1050 (s, br), 930 (m), 890 (m), 880 (m), 860 (m), 810 (m), 785 (m), and 730 (m)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{30}\text{H}_{50}\text{O}_3$ : C, 82.68; H, 8.84; O, 8.48. Found: C, 82.22; H, 8.36; O, 9.42 (diff).

Compound **2c** showed infrared bands at 1830 (w), 1605 (m), 1560 (w), 1470 (vs), 1455 (sh), 1420 (s), 1390 (s), 1365 (vs), 1340 (vs), 1270 (s), 1255 (sh), 1215 (m), 1170 (m, br), 1100 (m, br), 1030 (w), 935 (m), 900 (w), 830 (vw), 800 (w), 760 (vw), and 740 (w)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{45}\text{H}_{62}\text{O}_3$ : C, 83.08; H, 9.54; O, 7.38. Found: C, 82.82; H, 9.60; O, 7.32.

**Treatment of the Diarylquinocyclopropenes with Hydrogen Bromide.** The reaction described below exemplifies the general reaction of the diarylquinocyclopropenes with hydrogen bromide. **2c** (2.0 g 3.1 mmol) was dissolved in a minimum amount of diethyl ether. Hydrogen bromide was slowly bubbled into the resulting orange solution. The solution became colorless, and the product, tris(3,5-di-*n*-butyl-4-hydroxyphenyl)cyclopropenium bromide, precipitated. This was filtered and dried, giving 1.3 g (58%) of the bromide as a white solid, which was identified by comparison of its spectral data with that of an authentic sample.

**Treatment of the Diarylquinocyclopropenes with Perchloric Acid.** The reaction described below is typical. **1b** (0.80 g, 2.0 mmol) was dissolved in a minimum amount of benzene, then shaken vigorously with 10 ml of 10%  $\text{HClO}_4$ . A precipitate formed when the resulting mixture was cooled to 0°. This was filtered to give 0.84 g (85%) of a white solid which was identified as diphenyl(3,5-di-*n*-butyl-4-hydroxyphenyl)cyclopropenium perchlorate from its melting point and infrared spectrum, which were identical with those of the known compound.<sup>1</sup>

**Triquinocyclopropanes 6b-f.** These compounds were prepared in 80–90% yields by treatment of a benzene solution of the ap-

propriate triaryl cyclopropenium chlorides with excess potassium ferricyanide in 0.1 *N* KOH, as described here for the preparation of **6b**. Tris(3,5-diisopropyl-4-hydroxyphenyl)cyclopropenium chloride (3.0 g, 5.0 mmol) was added to 500 ml of benzene. To this solution was added 6.0 g (18.3 mmol) of potassium ferricyanide in 1 l. of 0.1 *N* KOH and the resulting 2-layer system was stirred vigorously for 15 min. The benzene layer, now deep blue-green in color, was separated from the aqueous layer, then washed with water until free of excess potassium ferricyanide (yellow). After drying and filtering the benzene solution, the solvent was removed under vacuum leaving a crude blue solid. This was washed with acetonitrile and filtered to give 2.5 g (88%) of the triquinocyclopropane **6b**. Recrystallization from methylene chloride-acetonitrile afforded fine sparkling blue-purple crystals.

The triquinocyclopropane **6c** was prepared not only by the above procedure, but also by treating the diarylquinocyclopropene **2c** with  $\text{Ag}_2\text{O}$ ,  $\text{PbO}_2$ , or aqueous alkaline  $\text{K}_3\text{Fe}(\text{CN})_6$ , then working up as described above.

The proton nmr spectra were determined in  $\text{CCl}_4$  using tetramethylsilane as an internal standard; data are given in Table II. In every case the nmr peak areas corresponded to the number of protons calculated on the basis of the assignments in Table II. Electronic spectra were determined using a Cary Model 14 spectrometer, on approximately  $10^{-5}$  *M* solutions in benzene; data are also given in Table II. The infrared spectral data and elemental analyses are given below.

The infrared spectrum of **6b** in the region 4000–625  $\text{cm}^{-1}$  showed bands at 2970 (m), 2930 (m, sh), 2910 (m, sh), 2860 (m), 1630 (w), 1590 (vs), 1550 (m), 1490 (m), 1465 (s), 1380 (m), 1370 (m), 1220 (w), 1200 (m), 1130 (s), 1105 (m), 1075 (s), 935 (w), 915 (w), 895 (s), 855 (w), and 815 (w)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{39}\text{H}_{48}\text{O}_3$ : C, 82.96; H, 8.52; O, 8.52. Found: C, 82.83; H, 8.73; O, 8.44 (diff).

The infrared spectrum of **6c** in the region 4000–2000  $\text{cm}^{-1}$  showed C–H stretching bands at 2960 (m), 2910 (sh), and 2860 (sh)  $\text{cm}^{-1}$ ; the region 2000–625  $\text{cm}^{-1}$  is shown in Figure 1. *Anal.* Calcd for  $\text{C}_{48}\text{H}_{60}\text{O}_3$ : C, 83.33; H, 9.26; O, 7.41. Found: C, 83.19; H, 9.19; O, 7.62 (diff).

Compound **6d** showed infrared bands at 2955 (m), 2920 (m), 2860 (m), 1630 (w), 1590 (s, sh), 1585 (vs), 1540 (m), 1480 (m), 1445 (m), 1355 (m), 1250 (m), 1205 (m), 1115 (m), 1090 (s), 1060 (w), 1025 (vw), 1010 (w), 935 (w), 895 (s), 880 (w), and 815 (w)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{39}\text{H}_{48}\text{O}_3$ : C, 82.96; H, 8.52; O, 8.52. Found: C, 83.03; H, 8.68; O, 8.29 (diff).

Compound **6e** exhibited infrared bands at 2950 (s), 2920 (s), 2865 (s), 1590 (s), 1545 (m, sh), 1450 (m), 1355 (m), 1245 (w), 1185 (w), 1090 (s), 1075 (s, sh), 1030 (m, br), and 900 (m)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{48}\text{H}_{56}\text{O}_3$ : C, 83.23; H, 9.03; O, 7.74. Found: C, 83.04; H, 9.12; O, 7.84 (diff).

Compound **6f** showed infrared bands at 2960 (m), 2920 (sh), 2870 (m), 1590 (vs), 1550 (w, sh), 1485 (m), 1465 (m), 1360 (w), 1200 (w), 1130 (m), 1105 (s), 1075 (s), 1035 (m), 935 (w), 900 (m), and 815 (w)  $\text{cm}^{-1}$ . *Anal.* Calcd for  $\text{C}_{41}\text{H}_{52}\text{O}_3$ : C, 83.11; H, 8.78; O, 8.11. Found: C, 83.05; H, 8.83; O, 8.09 (diff).

**Treatment of the Triquinocyclopropanes with Hydroquinone.** Treatment of blue-green solutions of the triquinocyclopropanes with hydroquinone resulted in orange solutions. The electronic spectra of these solutions indicated that the products were diarylquinocyclopropenes, by comparison with the spectra listed in Table I.

One preparatory reaction was performed, so as to leave no doubt that the triquinocyclopropanes were indeed being reduced to diarylquinocyclopropenes. Triquinocyclopropane **6c** (0.40 g, 0.62 mmol) was dissolved in 400 ml of benzene. To this, excess hydroquinone (about 1 g) in 200 ml of water was added, and the mixture was stirred vigorously until the benzene layer had changed from blue-green to orange-red (about 30 min). The benzene layer was separated, washed several times with water, dried, and finally stripped to low volume under vacuum. Acetonitrile was added forming an orange precipitate. This was collected and dried, giving 0.35 g (87%) of product, which was identified as the diarylquinocyclopropene **2c** by comparison of its spectral data with that described earlier. In a semiquantitative experiment followed by visible absorption spectroscopy, it was shown that the addition of 5.5 mg (0.05 mmol) of hydroquinone to 32.0 mg (0.05 mmol) of the triquinocyclopropane **6c** caused complete reduction to the diarylquinocyclopropene **2c**.

**Electron Spin Resonance.** A Varian V-4502 spectrometer with 9-in. magnet was used for the esr studies. The spectra in naphthalene (Table II, Figure 3) were obtained on  $2 \times 10^{-3}$  *M* solutions. Some of the samples were degassed and sealed, but equivalent re-

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  $2.00432 \pm 0.00010$ .

Treatment of the naphthalene solution of **6c** with  $\text{Ag}_2\text{O}$  at  $180^\circ$  caused a significant increase in esr signal strength. However, when  $\text{Ag}_2\text{O}$  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  $180^\circ$  until the single broad esr line had become intense. A scan at high amplification over 10 kG failed to reveal any addi-

tional lines. Then, a  $10^{-3} M$  solution of **6c** was dissolved in bis-( $\alpha$ -ethoxyethyl) ether in the quartz sample tube, which was degassed, sealed, and heated to  $150^\circ$  until an intense 1:2:1 esr pattern formed. The solution was chilled to  $-160^\circ$  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  $-100^\circ$  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<sup>1</sup> 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.

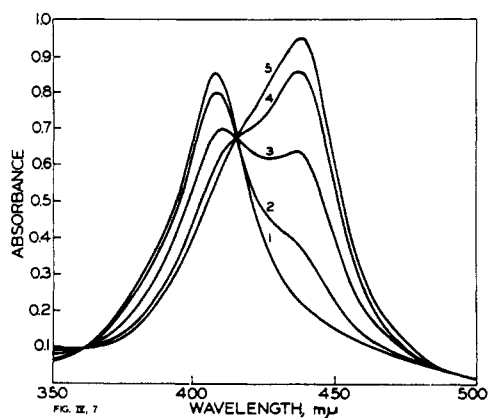


Figure 1. Electronic spectra of **1d** showing its conversion to **4d** upon addition of base: 1, 160 mg (0.24 mmole) of **1d** in 200 ml of methanol; 2, same solution with 1.00 ml of 0.080 *M* aqueous NaOH added (0.08 mmole); 3, 3.00 ml of base added; 4, 5.00 ml of base added; 5, 6.00 ml (0.48 mmole)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

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

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**.

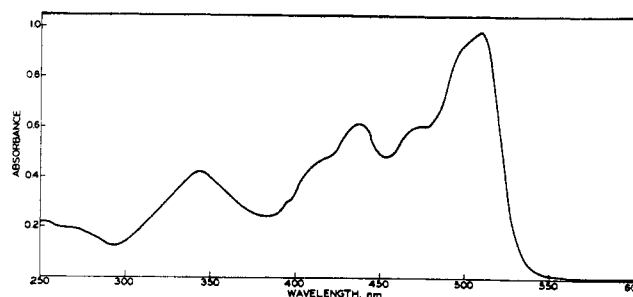


Figure 2. Electronic spectrum of anion-radical **5d**,  $\sim 2 \times 10^{-5} M$  in 50% methanol-methylene chloride.

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

(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.