on the *m/e* 172 peak. However, the P − 15 peak of 2-*n*-propylquinoline was found not to be changed in intensity due to the presence of such dimeric products.

Sample A: *m/e* (rel intensity) 346 (5), 343 (5), 341 (3), 340 (7), 326 (4), 325 (8), 202 (8), 201 (26), 200 (84), 175 (8), 174 (29), 173 (100), 172 (32), 171 (71), 159 (8), 158 (24), 157 (0), 156 (0), 145 (16), 144 (47), and 131 (3).

Sample B: *m/e* (rel intensity) 340 (6), 339 (0), 338 (19), 324 (6), 323 (16), 200 (6), 199 (13), 198 (75), 196 (19), 172 (19), 171 (100), 170 (81), 159 (0), 158 (0), 157 (0), 156 (28), 143 (81), 132 (22), and 129 (6).

Thus, it is noteworthy that sample C shows peaks <171 at *m/e* (rel intensity) 170 (35), 158 (13), 157 (13), 156 (11), 145 (11), 144 (41), 143 (24), 131 (2), 130 (2), and 129 (0).

All three samples were then individually subjected to fractional distillation and the MS analyses repeated at 15 eV on the isolated 2-*n*-propylquinolines.

Sample A: *m/e* (rel intensity) 173 (7), 172 (4), 171 (4), 158 (9), 157 (2), 156 (2), 145 (22), 144 (100), 143 (35).

Sample B: *m/e* (rel intensity) 171 (12), 170 (2), 169 (2), 157 (2), 156 (8), 144 (18), 143 (100), 142 (4).

Sample C: *m/e* (rel intensity) 173 (4), 172 (5), 171 (5), 170 (2), 158 (10), 157 (10), 156 (10), 145 (18), 144 (80), 143 (100), 142 (8).

Photochemical Reaction of 2-Allyl-1,2-dihydroquinoline. A 4.2-g sample (25 mmol) in 200 ml of freshly distilled and deoxygenated benzene was irradiated in a photochemical reactor equipped with low-pressure mercury vapor lamps (254 nm) for a period of 24 hr. After removal of the solvent, a NMR analysis showed the presence of 60% quinoline, 20% 2-*n*-propylquinoline, and 20% starting material.

Acknowledgment. The authors express their gratitude to the National Cancer Institute of the U.S. Public Health Service for support of this research under Grant CA-10743.

Registry No.—**3a,** 55570-22-4; **3b,** 55570-23-5; **4a,** 1613-34-9; **4b,** 1613-32-7; **5b,** 55570-24-6; **6b,** 55570-25-7; **7,** 55570-26-8; **10,** 55570-27-9; **11,** 38178-76-6; **16,** 38178-79-9; **17b,** 38178-81-3; **17b** free base, 33538-26-0; **18,** 491-35-0; **21,** 55570-28-0; 2,4-dichloroquinoline, 703-61-7; 4-*n*-propylquinoline, 20668-44-4; 2-methylquinoline, 91-63-4; allyl chloride, 107-05-1; quinoline, 91-22-5; vinyl chloride, 75-01-4; 2-vinylquinoline, 772-03-2; 2-deuterioquinoline, 15793-81-4; 2-(2-deuterioethyl)quinoline, 55570-29-1; phenyllithuim, 591-51-5; 2,4-dideuterioquinoline, 55570-30-4; phenyl chloride, 108-09-7; 4-allyl-2-methylquinoline, 38178-77-7; 4-allyl-2-methyl-1,2-dihydroquinoline, 38178-78-8; *cis*-2-methyl-4-*n*-propyl-1,2,3,4-tetrahydroquinoline, 55570-31-5; *trans*-2-methyl-4-*n*-propyl-1,2,3,4-tetrahydroquinoline, 55570-32-6; *trans*-2-propenylquinoline, 55570-33-7.

References and Notes

(1) This contribution is part III of the series "Rearrangements of Heterocyclic Compounds". Part II: J. J. Eisch, H. Gopal, and D. A. Russo, *J. Org. Chem.*, **39**, 3110 (1974). Part I: *J. Organomet. Chem.*, **38**, 209 (1972).
(2) M. Florkin and E. H. Stotz, Ed., "Comprehensive Biochemistry", Vol. 14, Elsevier, Amsterdam, 1966, pp 1–98.
(3) (a) H. Gilman, J. J. Eisch, and T. S. Soddy, *J. Am. Chem. Soc.*, **81**, 4000 (1959); (b) *ibid.*, **79**, 1245 (1957).
(4) D. Bryce-Smith, *2nd Int. Symp. Organomet. Abstr.*, 83 (1965).
(5) J. J. Eisch and R. L. Harrell, Jr., unpublished studies.
(6) T. Agawa and S. I. Miller, *J. Am. Chem. Soc.*, **83**, 449 (1961).
(7) Cf. J. Kolc and R. S. Becker, *J. Am. Chem. Soc.*, **91**, 6513 (1969), and *J. Chem. Soc., Perkin Trans. 2*, 17 (1972), for the photochemical ring opening and thermal closure of 1,2-dihydroquinolines.
(8) J. J. Eisch and D. R. Comfort, *J. Organomet. Chem.*, **43**, C17 (1972).
(9) J. M. Patterson, J. D. Ferry, J. W. de Haan, and M. R. Boyd, *J. Am. Chem. Soc.*, **97**, 360 (1975).
(10) Cf. ref 3b and references cited therein.
(11) E. J. Zobian, W. S. Kelley, and H. C. Dunathan, *J. Org. Chem.*, **29**, 584 (1964).
(12) K. Ziegler and H. Zeiser, *Justus Liebigs Ann. Chem.*, **485**, 174 (1931).
(13) J. J. Eisch and R. M. Thompson, *J. Org. Chem.*, **27**, 4171 (1962).
(14) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, pp 141–144.
(15) J. J. Eisch and R. L. Harrell, Jr., *J. Organomet. Chem.*, **21**, 21 (1970).
(16) (a) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966); (b) J. J. Eisch and C. K. Hordis, *ibid.*, **93**, 2974 (1971); (c) J. J. Eisch and S.-G. Rhee, *ibid.*, **96**, 7276 (1974).
(17) H. Gilman and J. H. McGlumphy, *Bull. Soc. Chim. Fr.*, **43**, 1322 (1928).
(18) M. S. Kharasch and C. F. Fuchs, *J. Org. Chem.*, **9**, 359 (1944).
(19) D. Seyferth and M. A. Weiner, *Org. Synth.*, **41**, 30–33 (1961).
(20) H. Normant, *Adv. Org. Chem.*, **2**, 37–38 (1960).
(21) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).
(22) T. E. Young and E. D. Amstutz, *J. Am. Chem. Soc.*, **73**, 4773 (1951).
(23) J. Metzger, H. Larive, E.-J. Vincent, and R. Dennilauler, *Bull. Soc. Chim. Fr.*, 46 (1967).
(24) H. Gilman and C. G. Gainer, *J. Am. Chem. Soc.*, **69**, 877 (1947).
(25) L. G. S. Brooker and L. A. Smith, *J. Am. Chem. Soc.*, **59**, 67 (1937).
(26) R. Delaby and J. Hiron, *Bull. Soc. Chim. Fr.*, **47**, 1395 (1930).

Diquinocyclopropanones, Diquinoethylenes, and the Anion-Radical and Free-Radical Intermediates in Their Formation[1]

Robert West,* David C. Zecher, Sandra K. Koster, and David Eggerding

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

Received February 24, 1975

Reaction of trichlorocyclopropenium tetrachloroaluminate with 2 equiv of hindered phenols followed by hydrolysis leads to bis(hydroxyaryl)cyclopropenones (**1**). These are converted upon oxidation to diquinocyclopropanones (**2**), which lose carbon monoxide spontaneously, forming diquinoethylenes (**4**). When photolyzed, compounds **1** lose carbon monoxide, giving bis(hydroxyaryl)acetylenes (**3**), which can be oxidized reversibly to **4**. The free-radical and anion-radical intermediates in the oxidation of **1c** to **2c** and **3c** to **4c** have been studied by electron spin resonance spectroscopy. The hyperfine splitting constants for the anion radicals of **2c**, **4c**, and related quinonoid compounds are rationalized by molecular orbital calculations.

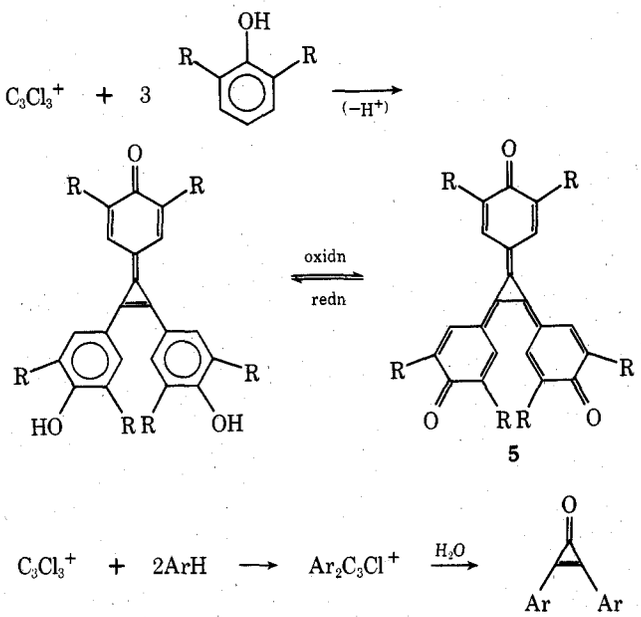
The triquinocyclopropanes (**5**), brilliant blue dye-like compounds, are obtained by reaction of trichlorocyclopropenium tetrachloroaluminate with 2,6-disubstituted phenols followed by deprotonation and oxidation.[2] The reaction of $C_3Cl_3^+$ with aromatic hydrocarbons can also be controlled so that only two of the three chlorine atoms are replaced. The product of this reaction, after hydrolysis, is a diarylcyclopropenone.[3]

This paper reports the reaction of 2,6-dialkylphenols with $C_3Cl_3^+$, leading to bis(hydroxyaryl)cyclopropenones **1a–c**. These compounds undergo oxidation to bright purple diquinocyclopropanones, **2**. The latter can be reduced back to **1** if the reduction is carried out immediately, but if **2a–c** are allowed to stand in solution they spontaneously lose carbon monoxide to give the cumulene derivatives **4a–c**. These are magenta-colored solids (λ_{max} 486 nm), which we term diquinoethylenes.

The stability of diquinoethylenes depends on the alkyl groups: **4c** (R = *tert*-butyl) is stable and unreactive, **4b** (R = isopropyl) is isolable but reacts with water, and **4a** (R =

Table I
Calculated Odd-Electron Spin Densities at the Hydrogen-Bearing Carbon of the Anion Radical of 4c

	h					
k	0.4	0.5	0.6	0.8	1.0	1.2
0.8		+0.001		+0.031		+0.059
1.0	−0.009		+0.005		+0.034	
1.1		−0.004			+0.028	
1.2			0.000	+0.012		
1.3	−0.012		−0.002		+0.018	
1.4			−0.005			



methyl) was so reactive that it could not be isolated and was detected only by its uv spectrum in solution.

Diquinoethylenes can also be obtained from **1a–c** by a second pathway. A known reaction of cyclopropenones is photolytic decarbonylation to acetylenes.[4] Photolysis of **1a–c** yields bis(hydroxyaryl)acetylenes, **3a–c**. These can be converted to the corresponding diquinoethylenes by a reversible oxidation.

Within this series of compounds one observes two separate oxidation–reduction systems differing by the loss of carbon monoxide from the three-membered ring. For both systems oxidation and reduction involves transfer of two

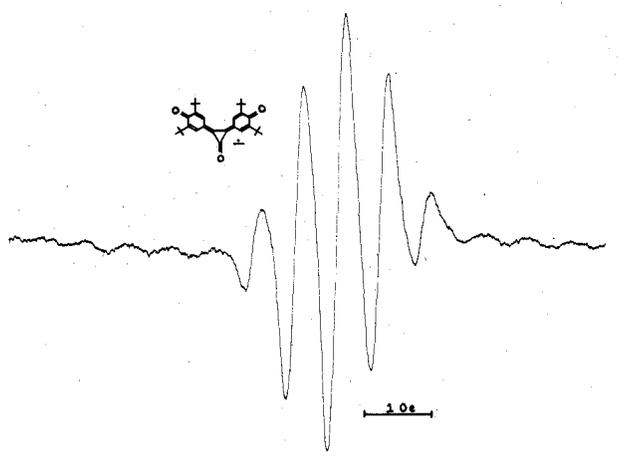


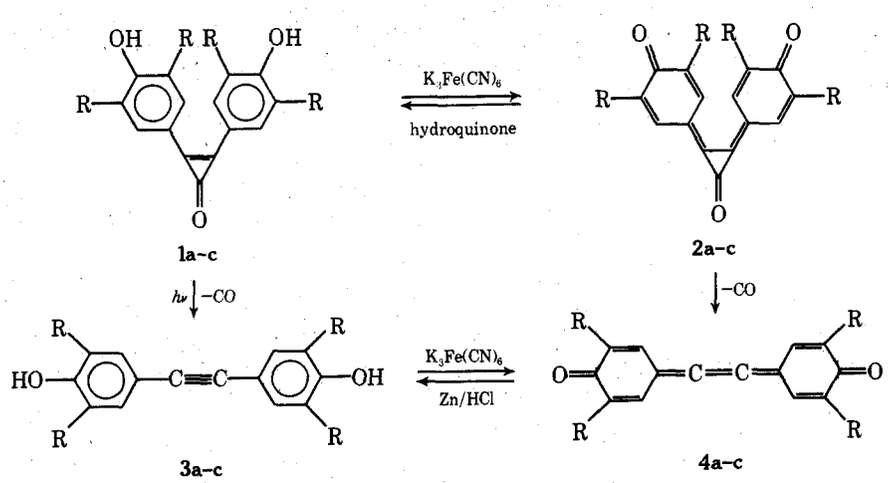
Figure 1. Electron spin resonance spectrum of anion radical of diquinocyclopropanone **2c**.

electrons between diamagnetic products. However, as with the triquinocyclopropanes,[5] paramagnetic one-electron intermediates in the redox reactions can be detected and studied by electron spin resonance spectroscopy. Because the compounds with R = *tert*-butyl were the most stable, the intermediates were studied mostly for the **1c–2c** and **3c–4c** systems.

Anion Radicals. Under basic conditions, intermediate anion radicals might be formed either by reduction of **2c** and **4c** or oxidation of the dianions of **1c** and **3c**, respectively.

Treatment of the diquinocyclopropanone **2c** with Na–K alloy in 1,2 dimethoxyethane at −60° produced an anion radical which gave the ESR spectrum shown in Figure 1, a five-line pattern with relative intensities 1:4:6:4:1 indicating hyperfine splitting by four equivalent protons, with a splitting constant of 0.63 G. The same anion radical showing an identical ESR spectrum was also generated by oxidation of the diarylcyclopropenone **1c** with PbO_2 in the presence of base.

Treatment of the diquinoethylene **4c** with Na–K alloy gave a single strong line with no detectable hyperfine splitting. The same ESR signal was obtained when **4c** was reduced electrolytically in THF. A single line was observed at all temperatures from −80 to 30° indicating that the hyperfine splitting constant for the ring protons must be <0.04 G. This very small value is surprising because all related species show sizable hyperfine splitting for the protons on carbon atoms meta to oxygen.[5–7]

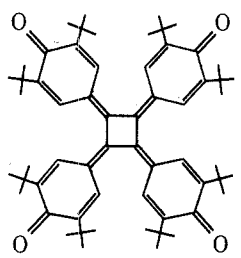


a, R = CH_3
b, R = $CH(CH_3)_2$
c, R = $C(CH_3)_3$

Table II
Calculated and Observed Hyperfine Splitting Constants (Gauss) for Anion Radicals

Registry no.	Anion radical	ρ calcd	a_H calcd, $Q = -24$	a_H calcd, $Q = -28$	a_H obsd	Ref
55281-77-1	4c$^{\cdot-}$	0.000	0.00	0.00	<0.04	This work
34470-38-1	5$^{\cdot-}$	−0.014	0.34	0.39	0.43	5
55255-32-8	6$^{\cdot-}$	−0.012	0.29	0.34	0.33	6
55255-33-9	2c$^{\cdot-}$	−0.024	0.58	0.67	0.63	This work
55255-34-0	7$^{\cdot-}$	−0.025	0.60	0.70	0.71	7

In order to see if this result could be rationalized theoretically, molecular orbital calculations were carried out first for the anion radical from **4c** and then for all of the related species whose ESR spectra have been determined. These include the anion radicals of diquinocyclopropanone **2c**, hexa-*tert*-butyltriquinocyclopropane (**5**, R = *t*-Bu),[5] octa-*tert*-butyltetraquinocyclobutane (**6**),[6] and tetra-*tert*-butyl-1,2-diquinocyclobutanedione (**7**).[7] Odd electron spin



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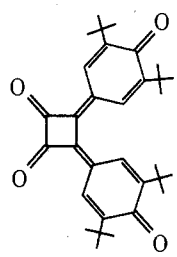

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densities (ρ) at the hydrogen-bearing carbons were calculated by the method of McLachlan[8] using Hückel molecular orbitals and a value of 1.0 for λ. Spin densities were converted to coupling constants by McConnell's equation,[9] $a_H = Q\rho$, using McLachlan's value of −24 G for Q.

In the Hückel calculations, the coulomb and resonance integrals, α_c and β_{cc}, were assumed to be identical for all carbon atoms and carbon–carbon π bonds. The coulomb integrals for oxygen atoms, α_O, and the resonance integrals for the carbon–oxygen π-bonds, β_{CO}, were related to α_c and β_{cc} in the usual way (eq 1 and 2). Frequently h and k for

$$\alpha_O = \alpha_C + h\beta_{CC} \quad (1)$$

$$\beta_{CO} = k\beta_{CC} \quad (2)$$

carbon–oxygen double bonds are taken to be 1.0, but other values have been used.[10] The odd-electron spin densities at the hydrogen-bearing carbons of the anion radical of **4c** were calculated for values of h from 0.4 to 1.2 and of k from 0.8 to 1.4, as shown in Table I. The values $h = 0.6$ and $k = 1.2$ gave a very low spin density consistent with the experimental result.

These latter values were then used to calculate the spin densities at the appropriate carbons of the other compounds. The calculated coupling constants agreed with the observed values for the anion radicals of **5** and **6** but not for **2c** and **7**. However, if the values $h = 1.0$ and $k = 1.0$ were used for the cyclopropanone and cyclobutanedione oxygens of **2c** and **7** along with the values $h = 0.6$ and $k = 1.2$ for the quinonoid oxygens, good agreement with the experimental data was obtained. The calculated and observed coupling constants are shown in Table II. Even better agreement between calculated and observed data is obtained if a value of $Q = -28$ G is used. This value is within the range of −20 to −30 G suggested by McLachlan.[8]

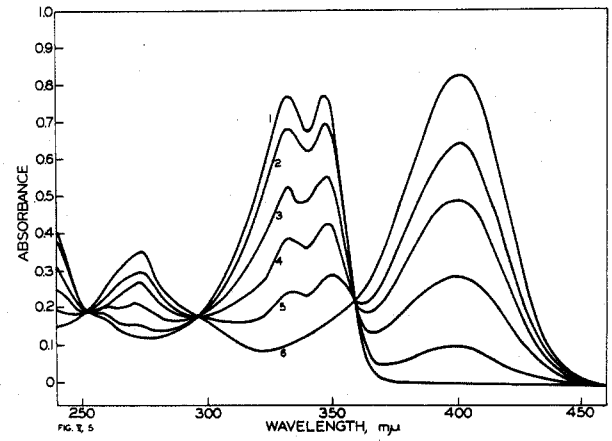
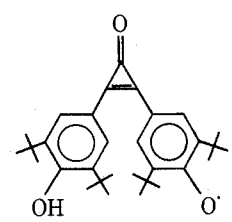


Figure 2. Spectrophotometric titration of dihydroxydiarylcyclopropenone **1c** with aqueous NaOH in methanol. Curve 1 is **1c** alone, 0.00120 *M* in methanol. Curve 6 the same concentration of **1c** in the presence of 0.00240 *M* NaOH.

Dianions. To obtain the dianion of the dihydroxydiarylcyclopropenone **1c**, a methanolic solution of **1c** was titrated with aqueous NaOH and titration was followed by ultraviolet–visible spectroscopy (Figure 2). Only one set of isosbestic points was observed, indicating that the cyclopropenone was converted directly to the corresponding dianion.

The diarylacetylene **3c** reacted very slowly with NaOH, so a spectroscopic titration similar to that described above for **1** was not performed. However, addition of excess base to **3c** in methanol gave a solution which showed a new electronic absorption maximum at 455 nm, probably due to the corresponding dianion.

Monoradicals. Neutral oxidation of cyclopropenone **1c** (or neutral reduction of **2c**) should proceed through the radical **8** (note that **8** is the protonated form of the anion radical). Similarly, neutral oxidation of **3c** or reduction of **4c** should proceed through the radical **9.** To generate these



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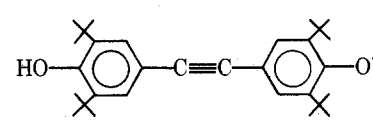

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radicals the diarylcyclopropenone **1c** and the diarylacetylene **3c** were treated with traces of Ag_2O or PbO_2 and the ESR spectra were recorded (Figure 3). The nine-line pattern observed for **8** is in good agreement with that predicted for splitting by two sets of two equivalent protons, with coupling constants of 0.72 and 1.86 G. Likewise the seven-line pattern observed for **9**, with relative intensities of 1:2:3:4:3:2:1, is attributable to two sets of two equivalent protons having coupling constants of 0.93 and 1.86 G. The two spectra are therefore consistent with those expected for the monoradicals **8** and **9**, respectively. In both cases, it is assumed that the larger splitting is caused by the aromatic protons of the phenoxyl ring, while the smaller splitting is due to the two aromatic protons of the ring bearing the hydroxyl group.

The principal splittings of 1.86 G observed for **8** and **9** are almost twice those observed for the corresponding monoradical **10** in the triquinocyclopropane series, which shows $a_H = 1.00$ G. This is consistent with delocalization of the unpaired electron over two equivalent rings in the triquinocyclopropane radical **10**, and restriction of the un-

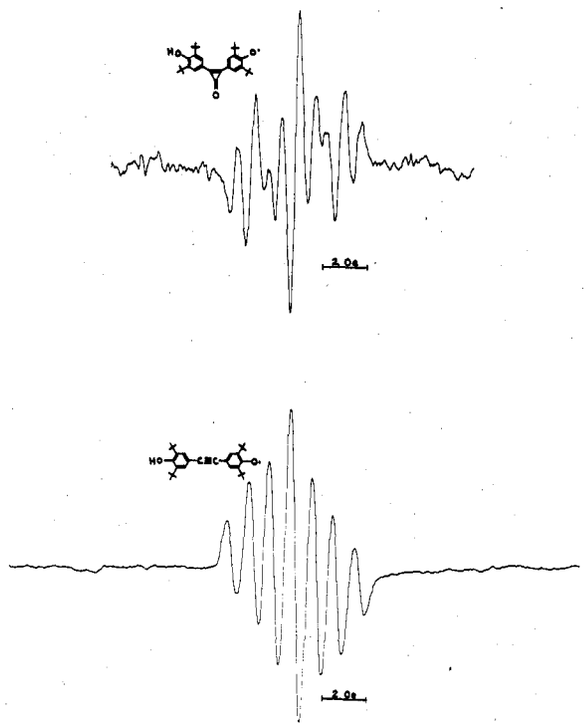
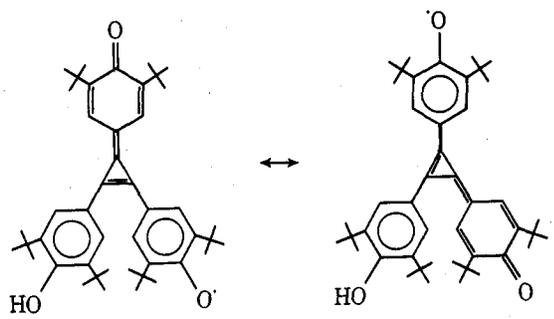


Figure 3. ESR spectra of monoradicals 8 (above) and 9 (below).

paired electron mainly to one six-membered ring in 8 and 9.



10

Experimental Section

General Procedures. All syntheses were carried out using purified grades of commercially available starting materials. Combustion analyses were performed by Alfred Bernhardt Laboratories, Mülheim, Germany, and Galbraith Laboratories, Knoxville, Tenn. Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer-237; proton NMR, Varian A-60 or A-60A; ultraviolet–visible, Cary 14; mass spectra, CEC Type 21-103C; ESR, Varian 4502-13. Infrared spectra reported are Fluorolube–Nujol mull composites unless otherwise specified.

Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (1c). Aluminum chloride (10 g, 0.075 mol) was added to 13.4 g (0.075 mol) of tetrachlorocyclopropene in 10 ml of dichloromethane under nitrogen. The slurry was stirred and heated at reflux until pronounced thickening indicated the formation of the $C_3Cl_3^+AlCl_4^-$ salt. The reaction mixture was cooled to −15° and another 10 ml of dichloromethane was added followed by dropwise addition of 30.9 g (0.15 mol) of 2,6-di-*tert*-butylphenol in 75 ml of dichloromethane, while the temperature of the reaction was maintained at −10 to −5°. The mixture was stirred for 1 hr at −5° and then 100 ml of water was added. The organic layer was separated, dried, filtered, and evaporated. Addition of 100 ml of diethyl ether induced cystallization and 22.2 g (64%) of white **1c** was collected: mp 215° dec; ir 1840 (s), 1590 (s), 1415 (m), 1345 (s), 1295 (w), 1255 (m), 1230 (m, sh), 1195 (w), 1085 (br, m), 1020 (w, sh), 920 (w), 890 (w, sh), 885 (m), 775 (w), 720 cm^{-1} (w); ^1H NMR (CF_3COOH) δ 1.60 (36 H), 4.10 (2 H), 8.07 (4 H); uv–visible λ_{max} (CH_3CN) 236 nm (log ε 4.26), 326 (4.40), 344 (4.36).

Anal. Calcd for $C_{31}H_{42}O_3$: C, 80.51; H, 9.09; O, 10.40. Found: C, 80.32; H, 9.30; O, 10.24.

Compounds **1a** (R = methyl) and **1b** (R = isopropyl) were prepared by similar procedures using 2,6-dimethylphenol and 2,6-diisopropylphenol in 100 and 82% yield, respectively.

Bis(3,5-dimethyl-4-hydroxyphenyl)cyclopropenone (1a): mp 268° dec; ir 1840 (s), 1600 (s), 1560 (s), 1495 (m), 1375 (vs), 1335 (vs), 1265 (s), 1210 (vs), 1120 (m), 1105 (m), 1025 (m), 990 (w), 950 (vs), 935 (vw), 890 (m), 875 (sh, w), 860 cm^{-1} (sh, w); ^1H NMR (CF_3COOH) δ 2.42 (12 H), 4.07 (2 H), 7.78 (4 H); uv–visible λ_{max} (CH_3OH) 237 nm (log ε 4.33), 332 (4.57), 347 (4.58).

Anal. Calcd for $C_{19}H_{18}O_3$: C, 77.55; H, 6.12. Found: C, 77.42; H, 6.21.

Bis(3,5-diisopropyl-4-hydroxyphenyl)cyclopropenone (1b): mp 209–211° dec; ir 3200 (m, v br), 2960 (m), 2920 (m, sh), 2870 (m), 1850 (s, sh), 1835 (vs), 1705 (w), 1595 (vs), 1560 (vs), 1460 (s), 1430 (s), 1370 (vs), 1335 (s), 1305 (vs, br), 1260 (s), 1200 (vs, br), 1145 (s), 1105 (m), 1045 (m), 1025 (w), 955 (vw), 935 (m), 885 (m), 820 (vs), 775 (w), 745 cm^{-1} (w); ^1H NMR (CF_3COOH) δ 1.44 (d, 24 H, J = 7 Hz), 3.38 (septet, 4 H, J = 7 Hz), 4.10 (s, 2 H), 7.97 (s, 4 H); uv–visible λ_{max} (CH_3OH) 239 nm (log ε 4.35), 333 (4.57), 348 (4.58).

Anal. Calcd for $C_{27}H_{34}O_3$: C, 79.80; H, 8.38. Found: C, 79.33; H, 8.51.

Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene (3c). A solution of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**1c**, 131 mg, 0.283 mmol) in 10 ml of benzene was irradiated for 2 hr in a quartz vessel using a Hanovia mercury arc source. The benzene was removed by rotary evaporation, leaving 120 mg (98%) of crude light brown **3c**. A portion of this material was recrystallized twice from cyclohexane and sublimed at 220° (0.5 Torr) to give colorless solid **3c**: mp 256–259° dec; ir 3625 (w), 2950–2850 (s), 1440 (vs), 1390 (m), 1360 (m), 1300 (w), 1240 (s), 1195 (m), 1150 (m), 1120 (w), 1025 (w), 985 (w), 920 (vw), 880 (s), 790 (m), 760 cm^{-1} (m); uv–visible λ_{max} (CH_3CN) 295 nm (log ε 4.65), 302 sh (4.48), 314 (4.53).

Anal. Calcd for $C_{30}H_{42}O_2$: C, 82.94; H, 9.69. Found: C, 82.98; H, 9.68.

The syntheses of acetylenes **3a,b** from cyclopropenones **1a,b** were carried out in similar fashion except that methanol and 2-propanol were used as solvents, respectively. Acetylene **3a** was isolated in 24% yield after purification and **3b** in 5.4% yield.

Bis(3,5-dimethyl-4-hydroxyphenyl)acetylene (3a): mp 209–210° dec; ir 3425 (s, br), 2960–2860 (m), 1595 (w), 1485 (s), 1440 (m), 1320 (s), 1260 (w), 1235 (m), 1205 (s), 1170 (s), 1040 (m), 1025 (m), 970 (w), 945 (m), 880 (m), 870 (s), 770 (w), 725 cm^{-1} (w); uv–visible λ_{max} (CH_3CN) 294 nm (log ε 4.58), 302 sh (4.49), 312 (4.51).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.20; H, 6.77. Found: C, 81.04; H, 6.93.

Bis(3,5-diisopropyl-4-hydroxyphenyl)acetylene (3b): mp 148–152° dec; ir 1465 (vs), 1375 (m), 1360 (m), 1335 (m), 1305 (s), 1285 (s), 1250 (m), 1235 (m), 1200 (s), 1180 (m), 1150 (s), 1125 (w), 1105 (w), 1070 (w), 980 (w), 935 (w), 880 (s), 815 (vw), 785 (m), 760 cm^{-1} (m); uv–visible λ_{max} (CH_3CN) 294 nm (log ε 4.55), 302 sh (4.47), 313 (4.50).

Anal. Calcd for $C_{26}H_{34}O_2$: C, 82.54; H, 9.00. Found: C, 81.90; H, 8.79.

Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-cyclopropanone (2c) and Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)ethylene (4c). A solution of 11.6 g (0.025 mol) of **1c** in 1 l. of benzene was added to 1 l. of 0.1 *M* aqueous KOH containing 21.4 g (0.065 mol) of $K_3Fe(CN)_6$. The organic layer was immediately separated, washed with water to remove excess oxidizing agent, dried, filtered, and evaporated as quickly as possible to give a purple solid, whose infrared spectrum indicated the presence of **2c** contaminated with 15–20% **4c**: ir (Nujol mull) 1810 (m), 1590 cm^{-1} (vs); uv–visible λ_{max} (benzene) 542 nm.

Anal. Calcd for $C_{31}H_{40}O_3$: C, 80.86; H, 8.70; O, 10.44. Found: C, 80.12; H. 8.86; O, 10.14 (corrected for 1.9% residue).

No attempt was made to recrystallize this solid because of its instability in solution, although once isolated **2c** appeared to be stable. If work-up of the reaction mixture was delayed for 45 min and the benzene solution was allowed to stand over drying agent for several hours the product isolated was **4c** in a yield of 9.06 g (84%), after washing with acetonitrile to remove most impurities: ir (Nujol mull) 1620 (w), 1595 cm^{-1} (vs); ^1H NMR (CCl_4) δ 1.33 (s, 36 H), 7.00 (s, 4 H); uv–visible λ_{max} (benzene) 486 nm (log ε 5.08).

Anal Calcd for $C_{30}H_{40}O_2$: C, 83.33; H, 9.26. Found: C, 83.17; H, 9.34.

During oxidation of **1a** and **1b** in benzene solution, intense absorptions were observed due to **2a** and **2b** at 514 and 543 nm, respectively. However, these products were not isolated. After a short time these absorptions were replaced by those of **4a** and **4b**

at λ_{max} 476 and 486 nm. Compound **4a** could not be isolated but oxidation of **1b** under aprotic conditions allowed isolation of **4b.**

Preparation of Bis(3,5-diisopropyl-4-oxo-2,5-cyclohexadien-1-ylidene)ethylene (4b). To a solution of 5.0 g (0.0123 mol) of **1b** in 600 ml of dry benzene was added 10 g of $MgSO_4$ and approximately 5 g of PbO_2. The mixture was stirred under nitrogen for 2 days. Filtration under nitrogen followed by removal of solvent by vacuum distillation (0°, 1 Torr) left a quantitative yield of **4b** by ^1H NMR. Recrystallization from dichloromethane–acetonitrile gave red-purple crystals: ir 2970–2860, 1630 (m), 1585 (vs), 1520 (w), 1365 (m), 1285 (m), 1260 (w), 1220 (m), 1105 (w), 1075 (m), 960 (vw), 945 (m), 935 (w), 915 (m), 865 (vw), 815 (m), 805 (sh), 790 cm^{-1} (w); ^1H NMR (CCl_4) δ 1.17 (d, J = 6.5 Hz, 12 H), 3.10 (septet, J = 6.5 Hz, 2 H), 6.78 (s, 4 H); uv–visible λ_{max} (benzene) 486 nm (log ϵ 5.02).

Anal. Calcd for $C_{26}H_{32}O_2$: C, 82.95; H, 8.51. Found: C, 83.07; H, 8.53.

Oxidation of Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene (3c). A solution of **3c** (0.190 g, 0.440 mmol) in 50 ml of benzene was swirled for 15 min with an aqueous solution containing 1.00 g (3.00 mmol) of $K_3Fe(CN)_6$ and 1.0 g of KOH. The red-brown benzene layer was separated, washed with water, dried ($MgSO_4$), filtered, and evaporated, leaving 0.17 g (91%) of crude maroon solid which was recrystallized from dichloromethane–acetonitrile to give **4c.**

The same procedure applied to acetylenes **3a,b** gave solutions whose uv–visible maxima at 476 and 486 nm, respectively, indicated the presence of the desired diquinoethylenes **4a,b,** but work-up resulted in decomposition.

Reduction of the Diquinoethylene 4c. A solution of 0.3 g (0.7 mmol) of diquinoethylene **4c** in 200 ml of benzene was treated with excess powdered zinc and acetic acid. The solution was stirred vigorously until it had changed from red-brown to light yellow, then filtered free of excess zinc and washed with water to extract the excess acetic acid. The benzene layer was separated, dried ($CaCl_2$), filtered, and stripped of solvent by rotary evaporation. The residue was crystallized from cyclohexane to give 0.20 g (0.46 mmol, 66%) of a white solid, identified as bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)acetylene (**3c**) by comparison of its physical properties with those given above for **3c.**

Reduction of the Diquinocyclopropanone (2c). A benzene solution of the diquinocyclopropanone **2c,** showing maxima at 486 and 542 nm (the 486-nm band due to decomposition to the diquinoethylene **4c**), was treated with excess hydroquinone. The new electronic spectrum showed maxima at 327, 346, and 486 nm, indicating that diquinocyclopropanone **2c** had been reduced to diarylcyclopropenone **1c** (327, 346 nm) while the diquinoethylene **4c** remained unaffected.

Base Titration of 1c. To a solution of **1c** (110 mg, 0.24 mmol) in 200 ml of methanol was added 0.08 M aqueous NaOH in 1-ml aliquots. The uv–visible spectrum was determined (Figure 2) and the spectrum sample was returned to the titration mixture after each addition of base. Isosbestic points were observed at 251, 295, and 359 nm throughout the titration, indicating that the cyclopropenone was converted directly to the dianion, which has λ_{max} 400 nm (log ϵ 4.61).

Preparation of Anion Radicals and Monoradicals for ESR Studies. Anion Radical of 2c. The anion radical of the diquinocyclopropanone **2c** was prepared both by reduction of **2c** with Na–K alloy in vacuo at −60° in 1,2-dimethoxyethane and by oxidation of **1c** with PbO_2 in the presence of base. A mixture of **1c** and PbO_2 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% 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 at −60°.

Either method of generation gave the same ESR spectrum (Figure 1), consisting of five lines with relative intensities 1:4:6:4:1 with a_H = 0.63 G and g = 2.0046.

Anion Radical of 4c. The chemical reduction of **4c** was carried out as described for the reduction of **2c.** For electrolytic reduction, about 1 mg of **4c** with a few milligrams of $(n\text{-}Bu)_4N^+ClO_4^-$ was placed in an electrolytic cell. A small piece of glass wool was placed between the electrodes to slow diffusion. The cell was evacuated and tetrahydrofuran (distilled from $LiAlH_4$, stored over Na–K anthracene) was distilled into the cell. The solution was degassed twice and the cell was placed in the ESR cavity at −80°. A minimal current was passed through the cell and scanning was begun. A single strong line was soon observed, whose sharpness and apparent stability did not vary from −80° to room temperature, g = 2.0056. The same spectrum was obtained by chemical reduction of **4c.**

Monoradical of 1c. About 1.5 mg of a 3:1 mixture (by weight) of the cyclopropenone **1c** and PbO_2 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. The spectrum (Figure 3) consists of nine lines with a_H (2 H) = 0.72 G, a_H (2 H) = 1.86 G.

Monoradical of 3c. Six milligrams of a 3:1 mixture of **3c** 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. The ESR spectrum of the monoradical, shown in Figure 3, consists of seven lines with ratio of intensities 1:2:3:4:3:2:1 with a_H (2 H) = 0.93 G and a_H (2 H) = 1.86 G.

Acknowledgment. This work was supported by Grant GP32081 from the National Science Foundation.

Registry No.—**1a,** 25361-96-0; **1b,** 25361-97-1; **1c,** 14106-41-3; **1c** free radical, 55255-27-1; **2c,** 15331-04-1; **3a,** 55255-28-2; **3b,** 55255-29-3; **3c,** 14106-39-9; **3c** free radical, 55255-30-6; **4b,** 55255-31-7; **4c,** 14106-40-2; tetrachlorocyclopropene, 6262-42-6; 2,6-di-*tert*-butylphenol, 128-39-2.

References and Notes

(1) Part of this work was previously reported in a communication: D. C. Zecher and R. West, *J. Am. Chem. Soc.*, **89,** 153 (1967).
(2) R. West and D. C. Zecher, *J. Am. Chem. Soc.*, **92,** 155 (1970).
(3) R. West, D. C. Zecher, and W. Goyert, *J. Am. Chem. Soc.*, **92,** 149 (1970).
(4) G. Quinkert, K. Opitz, W. Wiersdorff, and J. Weinlich, *Tetrahedron Lett.*, 1863 (1963).
(5) R. West and D. C. Zecher, *J. Am. Chem. Soc.*, **92,** 161 (1970).
(6) Following paper in this issue: S. K. Koster and R. West.
(7) S. K. Koster and R. West, in press.
(8) A. D. McLachlan, *Mol. Phys.*, **3,** 233 (1960).
(9) H. M. McConnell and D. B. Chestnut, *J. Chem. Phys.*, **28,** 107 (1958).
(10) A. Streitwelser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, pp 117–122.