platinum wire working and auxiliary electrodes and a saturated calomel reference electrode. Fast sweep voltammograms (>5 V/s) were recorded with a Tektronix Type RM503 oscilloscope equipped with a Polaroid camera. All solutions were 1 mM in the cyclopropenium salts and 0.1 M in tetrabutylammonium perchlorate in dichloromethane. Sweeps ranged from 0.1 to 50 V/s. The cathodic peak moved slightly toward a positive potential when the sweep rate was decreased. The potential at 85% of the peak height at 50 V/s sweep was read on an oscillograph scale and shown in Table IV.

Zinc Reduction of Tris(*p*-diisopropylaminophenyl)cyclopropenium Fluoroborate (6). To a solution of 0.196 g (0.300 mmol) of **6** in 12 mL of dry acetonitrile, there was added 1.00 g (15.3 mg-atoms) of zinc dust. The mixture was stirred at room temperature under nitrogen for 10 days. The mixture was filtered and washed well with acetonitrile and benzene. The filtrate was evaporated in vacuo to give 0.189 g of orange-brown solid. The acetonitrile extract of this solid gave 0.154 g (78.8% recovery) of unchanged **6**. The solid which did not dissolve in acetonitrile was separated by preparative TLC on silica gel (Merck PF_{254}) with benzene–ether (1:2) as a solvent. The ether extraction of the portion with R_f 0.5 gave 0.012 g of pale yellow solid, which structure was tentatively assigned as hexakis(*p*-diisopropylaminophenyl)benzene (0.010 mmol, 6.5% yield) from the following spectral data: mp >270 °C (no definite melting point observed); IR (KBr) 2980–2800 (m), 1600 (m), 1505 (s), 1460 (w), 1450 (w), 1410 (w), 1380 (m), 1355 (m), 1335 (sh), 1325 (w), 1280 (m), 1260 (m), 1235 (m), 1180 (m), 1150 (m), 1115 (m), 1100 (sh), 1020 (m), 950 (w), 930 (w), 860 (w), 830 (m), 780 (w), 750 (w), 685 cm^{-1} (w); ^1H NMR (CCl_4–$CDCl_3$) δ 6.59 (q, 4 H), 3.46 (septet, 2 H), 0.92 (d, 12 H).

Acknowledgment. This work was supported by Grant MPS74-01345 from the National Science Foundation.

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Alkylidenediquinocyclopropanes. Synthesis and Properties

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Abstract: Reaction of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**4**) with active methylene compounds gives alkylidenecyclopropenes **6a–f** which undergo oxidation to alkylidenediquinocyclopropanes, **5a–f**. The latter are brilliantly colored, strongly dichroic solids, blue or blue-violet in solution but reflecting metallic gold or red. Cyclic voltammetric studies show that **5a–f** are powerful oxidizing agents. The ESR spectra of anion radicals of **5a–f** were studied and compared with the results of Hückel MO calculations.

The triquinocyclopropanes (**1**, R = alkyl), a new class of highly conjugated compounds, were reported several years ago.[1] The oxidation–reduction cycle of **1** with the corresponding quinodiarylcyclopropenes **2** and their anions has been investigated in some detail.[2] Also known is the diquinocyclopropanone **3**[3] in which a carbonyl group replaces one of the quinonoid groups in **1**. Compound **3** somewhat resembles **1** but is unstable, losing carbon monoxide rather rapidly in solution.[3] It is obtained by the oxidation of the diarylcyclopropenone **4**, which is easily available by the reaction of $C_3Cl_3^+$ with 2 equiv of 2,6-di-*tert*-butylphenol.

By the reaction of **4** with active methylene compounds, we have prepared a series of methylenecyclopropene derivatives (**6a–f**) which undergo oxidation to a new family of stable alkylidenediquinocyclopropanes, **5a–f**. The latter compounds are deeply colored, crystalline solids, royal blue or blue-purple

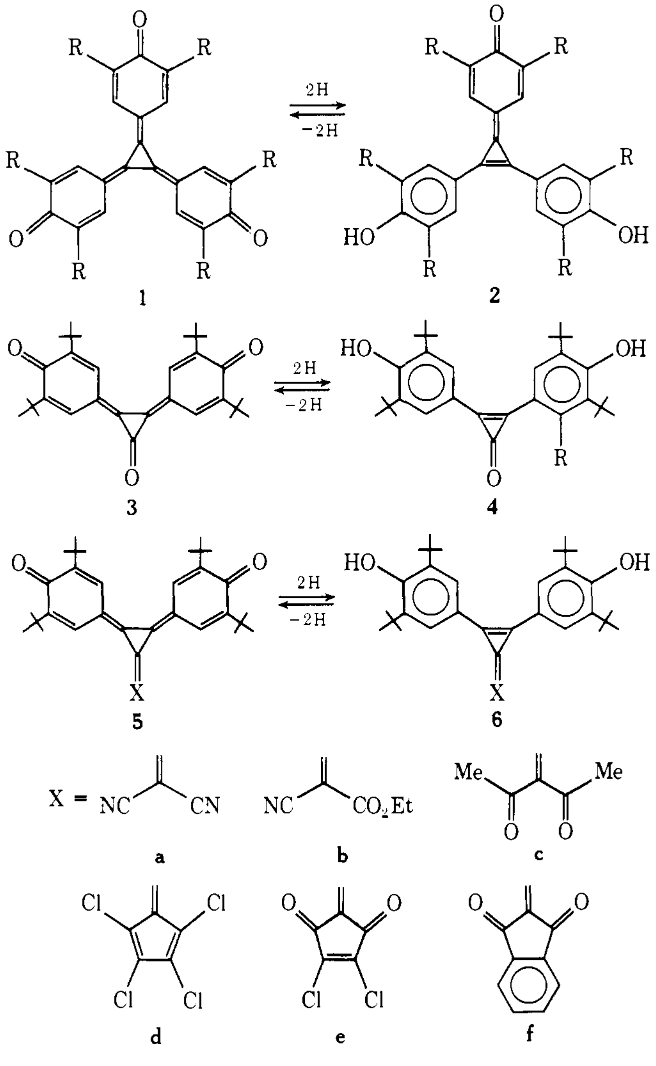
Table I. UV-Visible and Reflectance Spectra of Alkylidenediquinocyclopropanes (5)

Compd	UV-visible (C_6H_6), λ_{max}, nm (log ϵ)	Reflectance, λ_{max}, nm
5a	609 (4.80), 640 (sh) (4.25)	510, 715, 870
5b	591 (4.82), 609 (4.80)	500, 670
5c	608 (4.70)	560, 620, 925
5d	672 (4.60)	400, 650
5e	600 (4.77), 621 (4.75)	525, 625, 655
5f	610 (4.84), 627 (sh) (4.80) 668 (sh) (4.34)	590, 645

in solution, and resembling **1** in having intense low-energy electronic absorption (Table I). But in addition, as a novel property these compounds show pronounced dichroism and a characteristic specular reflectance; **5a**, **5b**, and **5c** appear metallic gold in reflected light whereas **5d**, **5e**, and **5f**, reflect reddish-brown, rather resembling metallic copper.

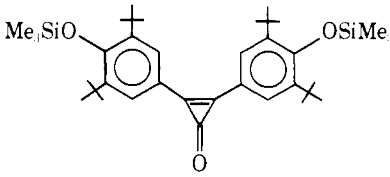
This paper reports syntheses and spectroscopic characteristics of **5** and **6**, together with ESR studies on anion radicals of **5**. Also the oxidation-reduction cycles of **5** with their anions will be described as studied by cyclic voltammetry.

Diarylcyclopropenes (6). Syntheses. Diphenyl- and dipropylcyclopropenones have been reported to react with malononitrile,[4a-c] arylmalononitrile,[4e,f] ethyl cyanoacetate,[4c] and substituted indenes[4d] in refluxing acetic anhydride to give triafulvene and calicene derivatives in rather low yield (3-24%). We carried out the reaction of **4** with a variety of active methylene compounds, i.e., malononitrile, ethyl cyanoacetate, acetylacetone (2,4-pentanedione), 1,2-dichlorocyclopentene-3,5-dione, and indan-1,3-dione, and obtained the condensed products (**6**) in generally higher yields (15-70%).



This reaction is supposed to proceed through the acetoxycyclopropenium ion formed by the action of acetic anhydride upon the cyclopropenone, followed by condensation with active methylene substrates.[6] When this condensation is carried out with **4**, the intermediate diarylacetoxycyclopropenium ion is probably stabilized by the *p*-hydroxyl groups, and this may account for the acceleration of the reaction.

Only with 1,2,3,4-tetrachlorocyclopentadiene was it necessary to carry out the reaction under milder conditions (in methanol), using the silylated compound **7** to avoid reaction



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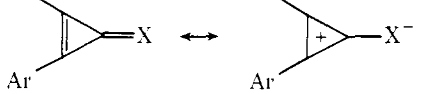
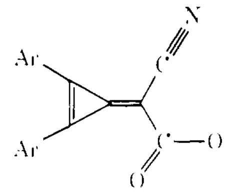
of the hydroxyl groups.[7]

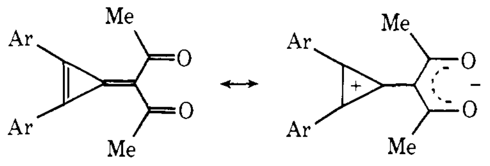
The condensed products **6a-f** are all pale to brilliant yellow crystals exhibiting spectral properties consistent with the assigned structures. In the IR spectrum they all possess a sharp band at ~3600 cm^{-1} (hindered OH) and a weak band at ~1830 cm^{-1} (cyclopropene double bond[4a]). In the NMR spectra the aryl protons appear at relatively low field, consistent with dipolar character in these compounds with the cyclopropene ring bearing some positive charge. The spectrum of **6b** shows quite different shielding for the ortho protons in



the two aryl rings (δ 8.18 and 8.52), indicating restricted rotation around the exocyclic double bond.[9] From comparison with the chemical shift of the aryl protons in **6e** (δ 8.52) and **6f** (δ 8.69), the one appearing at lower field (δ 8.52) is assigned to the aryl proton on the same side as -CO_2Et. This rather large low-field shift found in **6b**, **6e**, and **6f** is probably due to strong deshielding caused by the diamagnetic anisotropy of the carbonyl group which is directed toward the cyclopropene ring.[10] The average conformation of **6b** is, therefore, considered to be[11]



as has been predicted from the dipole moment data for the corresponding diphenyl compound.[4c] This is to be compared with the case of **6c**, in which comparison of the aryl-proton chemical shift suggests its conformation to be as follows:



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This conformation is consistent with the remarkable low-energy shift of the >C=O stretching band (1620 cm^{-1}) in the IR spectrum, indicating a large contribution by the polarized

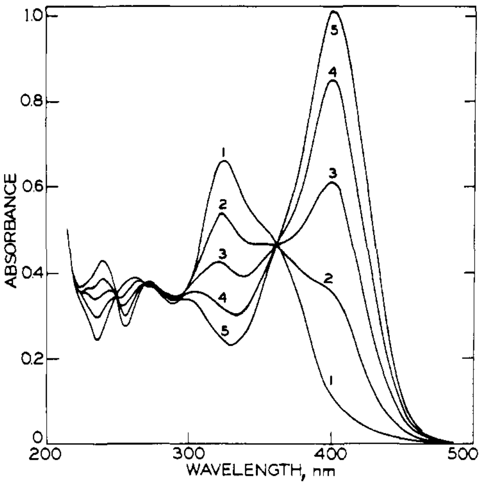


Figure 1. Spectrophotometric titration of diarylcyclopropene **6c** with aqueous NaOH in methanol. Curve 1 is **6c** alone, 1.98×10^{-4} M in methanol. Curve 5 is the same concentration of **6c** in the presence of 4×10^{-4} M NaOH.

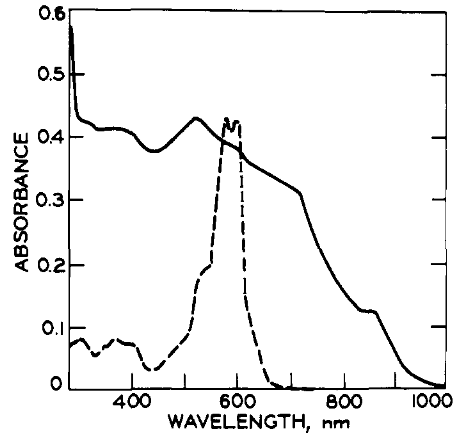


Figure 2. Solid reflectance spectrum (—) and solution absorption spectrum (-----; 7×10^{-5} M in benzene, 1 mm cell) of diquinocyclopropane **5a**.

structure (ii).[12] Likewise, in compounds **6e** and **6f**, the enhanced dipolar character caused by the *p*-hydroxyl group is apparent from the lower energy carbonyl stretching band (IR) and the lower field shift for ortho protons (NMR) than those reported for the corresponding diphenyl compounds.[10]

The UV-visible spectra of all the compounds **6**, except **6d**, exhibited distinctive bathochromic shifts upon changing the solvent from methanol (polar) to cyclohexane (nonpolar) (see Experimental Section). This is again in accord with a large contribution of the ionic dipolar structure to the ground state.[13] Only for **6d** did the UV-visible maxima remain essentially the same in methanol, benzene, and cyclohexane, suggesting that there is little change in dipole moment between the ground and excited states.[14]

Dianion Formation. Methanol solutions of **6a–f** were titrated spectrophotometrically with aqueous NaOH. For all the compounds, 2 molar equiv of NaOH was required for complete change of the spectrum and only one set of isosbestic points was observed as shown in Figure 1 for the representative case **6c**. These results indicate that the neutral compounds **6** are converted directly to the dianions (**8**), the monoanions being unstable with respect to **6** and **8**. This transformation was completely reversible as was indicated by regeneration of **6** by addition of aqueous HCl after each titration.

Alkylidenediquinocyclopropanes (5). Syntheses. Two-phase oxidation of diarylcyclopropenes (**6**) in chloroform with an alkaline solution of potassium ferricyanide afforded the corresponding diquinocyclopropanes (**5**) in excellent yields. For compound **6a** oxidation was also effected by lead dioxide, lead tetraacetate, and *N*-chlorosuccinimide with triethylamine[15] in organic solvents. Two-electron oxidation of the dianion of **6a** (as the sodium salt) with iodine gave a quantitative yield of **5a** as well.

Electronic Spectra. The long-wavelength maxima of compounds **5** lie between 600 and 675 nm (Table I). These absorptions are at lower energy than that for **3** (λ_{max} 542 nm) corresponding to the wider π-conjugation area in **5**. The characteristic metallic appearance of these compounds in the solid state is associated with their reflectance spectra which show even lower energy absorption than the solution spectra except for **5d** (Table I). Among compounds **5** the most remarkable spectrum was obtained from **5a** and **5c**, which exhibit extremely low-energy absorptions at 870 and 925 nm, respectively, as shown in Figure 2 for **5a**.

IR and NMR Spectra. Structures of the alkylidenediquinocyclopropanes **5** were confirmed by their IR and NMR spectra. In the IR spectrum, they all have a strong band near 1600 cm^{-1} characteristic of related quinonoid compounds,[1,3,16] while the OH and cyclopropene absorptions are absent. In the NMR spectra, the *tert*-butyl groups (of **5a, 5d, 5e,** and **5f**) and the quinoidal ortho protons each appear as two different sets of signals. This clearly indicates the existence of exocyclic double bonds which prohibit rotation of quinoidal rings. The rigid planar structure of **5** is especially apparent in compounds **5e** and **5f** from the remarkable low-field shift (δ 8.83 and 9.10, respectively) of the quinoidal protons (which are closer to carbonyl groups). The geometry of these protons, *fixed* very close to the carbonyl groups, apparently causes even larger low-field shifts than in compounds **6e** and **6f**.

Radical Anions. Tetrahydrofuran solutions of **5a–f** were electrolytically reduced and examined by ESR spectroscopy. Strong ESR signals appeared with minimal current and remained unchanged for several hours at room temperature even after the current was cut off, indicating remarkably high stability for the anion radicals (**5a–f**) in solution. The anion radicals of **5c, 5d, 5e,** and **5f** exhibited very similar five-line ESR patterns with relative intensities 1:4:6:4:1, indicating splitting by four nearly equivalent ortho protons, as shown in Figure 3 for **5e**. The observed coupling constants and those predicted by the method of McLachlan[17] using Hückel molecular orbitals (vide infra) and a value of 1.0 for λ are shown in Table II. The observed a_H values show that the spin densities in the diquinoid groups in **5c–f**$^{-}\cdot$ are greater than those in **3**$^{-}\cdot$ and much greater than in **1**$^{-}\cdot$. Thus, the introduction of these electron-withdrawing and π-conjugative substituents (**c–f**) into the diquinocyclopropane ring system seems to have little spin-delocalizing effect. This effect in **5c–f**$^{-}\cdot$ is even somewhat smaller than that of a simple oxo group in **3**$^{-}\cdot$. In **5f** no splitting by the aryl protons of the indandione nucleus was observed, in good agreement with the calculated results (by the Hückel molecular orbital method) which indicate almost zero (0.0002–0.0003) spin densities for the corresponding carbon atoms.

For cyano compounds **5a** and **5b** the ESR spectra were more complicated because of interaction of the unpaired electron with the nitrogen atoms. Compound **5a** exhibited an incompletely resolved 14-line spectrum, which matched reasonably well with a computer-simulated spectrum assuming coupling with four equivalent protons (a_H = 0.59 G) and two equivalent nitrogens (a_N = 0.96 G). The a_H value for the quinoidal protons is slightly smaller than for **5c–f**, consistent with somewhat greater spin delocalization by the dicyanomethylene group than by the other alkylidene substituents. For **5b**, a six- (or possibly eight-) line pattern was observed, but we have been unable to interpret this spectrum to date and it is possible that

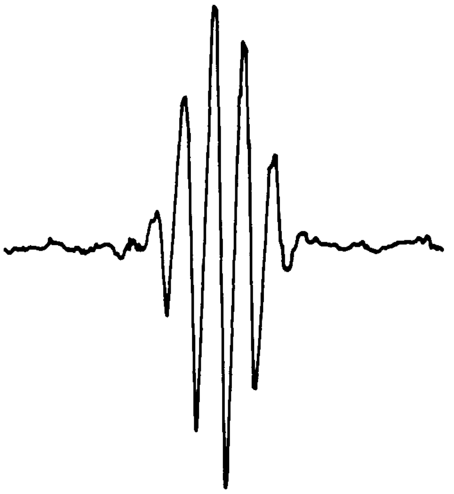


Figure 3. Electron spin resonance spectrum of the anion radical of diquinocyclopropane **5e**, ca. 1×10^{-4} M in tetrahydrofuran.

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

Anion radical	Spin density, ρ calcd	a_H Calcd[a]	a_H Obsd	g value
$\mathbf{5c}^{-}\cdot$	−0.0254	0.76	0.77	2.0053
$\mathbf{5d}^{-}\cdot$	−0.0249	0.75	0.85	2.0052
$\mathbf{5e}^{-}\cdot$	−0.0193	0.58	0.69	2.0054
$\mathbf{5f}^{-}\cdot$	−0.0220	0.66	0.74	2.0054
$\mathbf{1}^{-}\cdot$	−0.014[b]	0.42	0.43[b]	2.0043[c]
$\mathbf{3}^{-}\cdot$	−0.024[b]	0.72	0.63[b]	2.0046[b]

[a] Calculated by using McConnell's equation (ref 18), $a_H = \rho Q$ with $Q = -30$ G. [b] Reference 3. [c] Reference 2.

it is due to a decomposition product rather than to the anion radical $\mathbf{5b}^{-}\cdot$

Cyclic Voltammetry of 5a–f. Hückel molecular orbital calculations on compounds **5a–f** were carried out using the parameters adopted to rationalize the ESR spectra of anion radicals of **1** and **3**.[19] The calculations predict very low energy levels ranging from $\alpha + 0.18\beta$ to $\alpha + 0.21\beta$ for the LUMO in **5a–f**, suggesting that these compounds will be powerful electron acceptors.

To test this prediction the redox characteristics of these compounds were studied by cyclic voltammetry, using 1 mM solution of **5** in dry dichloromethane with tetrabutylammonium perchlorate as a supporting electrolyte. The scan rate ranged from 0.5 to 0.02 V/s. All of the compounds **5a–f** exhibited a well-defined two-wave voltammogram corresponding to two discrete, reversible electron-transfer steps, as is shown in Figure 4 for **5a**. The $E_{1/2}$ values (taken from the average of cathodic and anodic peak potentials) are shown in Table III, together with the values for some commonly known p-benzoquinones for comparison. The remarkably high (positive) values of $E_{1/2}$ indicate the pronounced electron affinity of this series of compounds. The first reduction potentials for **5a–f** are higher than that for chloranil, falling between the values for chloranil and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), and the second reduction potentials are actually more positive than for DDQ. These compounds must therefore be regarded as extremely powerful oxidizing agents.

Finally, an attempt was made to generate the neutral radicals, corresponding to semiquinone radicals, by partial oxidation of alkylidenediarylcyclopropenes **6**.[21] A small amount (2–3 mg) of **6c**, **6d**, or **6e** in toluene was mixed with 0.5 equiv of lead dioxide in an ESR cell, whereupon a deep blue coloration formed immediately due to partial formation of the corresponding **5**. However, the ESR signal was too weak to permit further examination. This result suggests that the equilibrium (1) lies far to the right. The corresponding equilibrium for disproportionation of the anion radical (2) must lie less completely to the right since the anion radicals are easily observable.

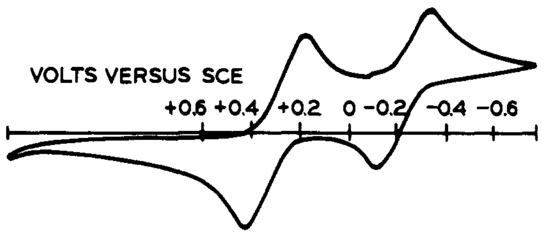
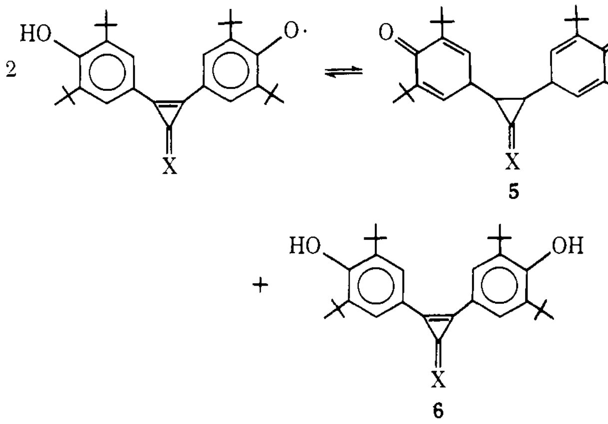


Figure 4. Cyclic voltammogram of diquinocyclopropane **5a**, 1×10^{-4} M in methylene chloride with 0.1 M Bu_4NClO_4, at a Pt wire electrode. Scan rate, 0.50 V/s.

Table III. Reduction-Oxidation Potentials of Alkylidenediquinocyclopropanes (**5**) and p-Quinones in Dichloromethane[a]

Compd	$E_{1/2}$, V vs. SCE 1st wave	2nd wave
5a	+0.30	−0.24
5b	+0.17	−0.32
5c	+0.09	−0.24
5d	+0.25	−0.14
5e	+0.26	−0.25
5f	+0.16	−0.26
p-Benzoquinone	−0.56[b]	−1.38
Chloranil	+0.00[b]	−0.78[b]
DDQ	+0.57[b]	−0.32[b]

[a] **5**, 1×10^{-4} M. Supporting electrolyte: Bu_4NClO_4, 1×10^{-1} M. [b] These data agree well with the polarographic half-wave potentials in acetonitrile reported by Peover (ref 20a) using Et_4NClO_4 as a supporting electrolyte, but not with those reported by Scribner (ref 20b) using $LiClO_4$ as a supporting electrolyte.



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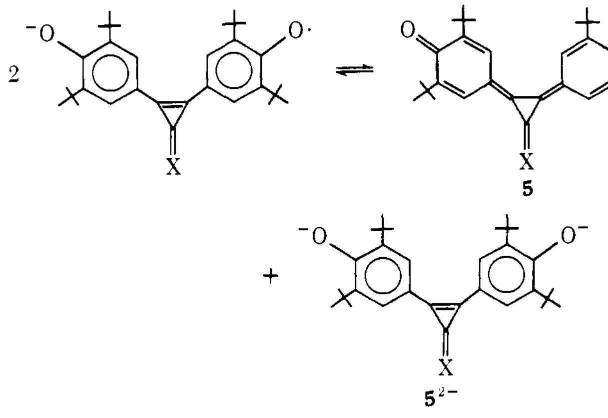

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Experimental Section

General Procedures. Melting points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 237; ^{1}H NMR, JEOL MH-100; ultraviolet-visible and reflectance, Cary 14; mass spectra, CEC Type 21-103C; ESR, Varian 4502-13.

Materials. Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**4**) was prepared as has been reported.[3] 1,2,3,4-Tetrachlorocyclopentadiene and 1,2-dichlorocyclopentene-3,5-dione were prepared according to the method of Roedig and Hörnig.[22] Bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)cyclopropenone was prepared from **4** by the following method. A stirred mixture of 2.58 g (5.58 mmol) of **4** and 2.50 g (12.3 mmol) of bis(trimethylsilyl)acetamide (Aldrich) in 6.5 mL of acetonitrile which had been freshly distilled over P_2O_5 was heated at 60 °C for 10 min. Immediately after **4** went into solution a dense white precipitate formed, which was filtered, washed with dry acetonitrile, and dried under vacuum to give 3.05 g (90.2%) of the bis(siloxyaryl)cyclopropenone as a white powder: mp 180–183 °C dec; IR (KBr) 2960–2860 (m), 1830 (sh), 1815 (s), 1600 (s), 1460 (w), 1430 (m), 1400 (s), 1360 (m), 1330 (s), 1260 (s), 1250–1235 (br, s), 1200 (m), 1120 (m), 920 (m), 895 (m), 875 (s), 850 (s), 780 (w), 650 cm^{-1} (w); NMR (CCl_4) δ 0.47 (s, 18 H), 1.52 (s, 36 H), 7.86 (s, 4 H).

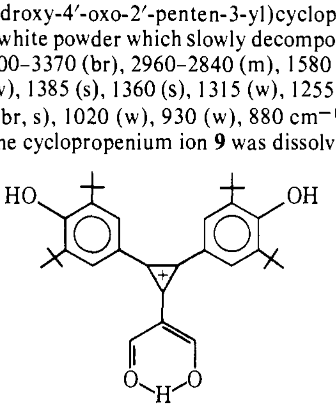
All the other materials were commercially available.

Synthesis of the Diarylcyclopropenes (6). 1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-dicyanomethylenecyclopropene (6a). A mixture of 1.00 g (2.17 mmol) of bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenone (**4**),[3] 0.29 g (4.3 mmol) of malononitrile, and 0.02 g of β-alanine[4c] in 3.0 mL of freshly distilled acetic anhydride was heated to reflux with stirring for 20 min. A white precipitate formed in the reddish-brown solution. The mixture was cooled to room temperature, and the precipitate was collected by filtration and recrystallized from benzene to give 0.62 g (56%) of **6a** as pale yellow needles: mp 280–281 °C dec; IR (KBr) 3560 (m), 2960–2860 (m), 2213 (m), 2197 (m), 1850 (w), 1595 (m), 1490 (s), 1470 (m), 1450 (w), 1410 (s), 1370 (s), 1360 (s), 1310 (m), 1255 (s), 1240 (m), 1200 (w), 1100 (m), 1025 (W(= 925 (w), 900 (w), 890 (sh), 885 (w), 780 (w), 760 (w), 675 (w), 655 (w), 595 cm^{-1} (w); NMR ($CDCl_3$) δ 1.52 (s, 36 H), 5.98 (s, 2 H), 7.91 (s, 4 H); UV-visible λ_{max} (methanol) 233 nm (log ϵ 4.40), 242 (4.34), 252 (4.29), 299 (4.62), 313 (4.57), 368 (4.54), 386 sh) (4.44); λ_{max} (benzene) 381 nm, 400 (sh). For this and the other compounds **6**, only the longest wavelength absorptions will be shown for the UV-visible spectrum in nonpolar solvents. The extinction coefficients are omitted for nonpolar solvents because they are similar to those in polar solvents. Mass spectrum *m/e* 510.32500 (calcd, 510.32462). Anal. Calcd for $C_{34}H_{42}N_2O_2$: C, 79.95; H, 8.29; N, 5.49. Found: C, 80.03; H, 8.32; N, 5.43.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-carboethoxycyanomethylenecyclopropene (6b). A mixture of 3.70 g (8.00 mmol) of **4**, 1.81 g (16.0 mmol) of ethyl cyanoacetate, and 0.02 g of β-alanine in 12.0 mL of freshly distilled acetic anhydride was refluxed for 8 h with stirring under nitrogen atmosphere. To the resulting red solution was added 100 mL of benzene and the mixture was washed twice with 200 mL of water and twice with 200 mL of 10% $NaHCO_3$. After drying ($MgSO_4$), the organic solution was evaporated in vacuo to give 4.6 g of crude mixture which was then chromatographed over a column which was packed with neutral alumina (100 g) at the bottom and with silica gel (115 g) at the top. Elution with 5% ethereal benzene afforded 1.39 g (31.1%) of crude **6b**. Recrystallization from hexane-chloroform gave pale yellow crystals: mp 254–255 °C dec; IR (KBr) 3600 (s), 3090 (w), 2960–2860 (m), 2203 (m), 1840 (w), 1690 (s), 1590 (m), 1490 (s), 1450 (sh), 1410 (s), 1390 (w), 1365 (s), 1325 (m), 1275 (m-s), 1255 (m), 1240 (m), 1200 (w), 1155 (m), 1115 (w), 1080 (s), 890 (w), 810 (w), 760 (m), 640 cm^{-1} (w); NMR ($CDCl_3$) δ 1.35 (t, 3 H), 1.55 (s, 36 H), 4.35 (q, 2 H), 5.96 (s, 1 H), 6.02 (s, 1 H),[23] 8.18 (s, 2 H), 8.52 (s, 2 H); UV-visible λ_{max} (methanol) 233 nm (log ϵ 4.29), 240 (sh) (4.26), 250 (4.18), 302 (4.43), 317 (4.50), 368 (4.42), 388 (sh) (4.29); λ_{max} (cyclohexane) 384 nm, 404 (sh). Anal. Calcd for $C_{36}H_{47}NO_4$: C, 77.52; H, 8.49; N, 2.51. Found: C, 77.43; H, 8.47; N, 2.46.

From successive elution with 50% ethereal benzene, 1.25 g (33.8%) of **4** was recovered.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-diacetylmethylenecyclopropene (6c). A mixture of 4.62 g (10.0 mmol) of **4**, 4.00 g (40.0 mmol) of 2,4-pentanedione, and 0.1 g of β-alanine in 15.0 mL of acetic anhydride was refluxed for 10 h and worked up in the same manner as above. The crude product was dissolved in 12 mL of benzene and stirred with 2.0 mL of concentrated $HClO_4$ at 0 °C. The resulting white precipitate was filtered, washed with benzene, and dried under vacuum to give 1,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(2′-hydroxy-4′-oxo-2′-penten-3-yl)cyclopropenium perchlorate (**9**) as a white powder which slowly decomposes at 160–180 °C: IR (KBr) 3600–3370 (br), 2960–2840 (m), 1580 (m), 1550 (w), 1540 (w), 1440 (w), 1385 (s), 1360 (s), 1315 (w), 1255 (m), 1230 (w), 1195 (w), 1100 (br, s), 1020 (w), 930 (w), 880 cm^{-1} (w). The perchlorate salt of the cyclopropenium ion **9** was dissolved in 10 mL of chloroform and 0.5 mL of triethylamine was added with stirring. The resulting yellow solution was washed with water, dried ($MgSO_4$), and evaporated in vacuo to give 0.79 g (15%) of **6c** as pale yellow crystals after recrystallization from benzene: mp 230–231 °C dec; IR (KBr) 3620 (m), 2960–2850 (m), 1820 (w), 1620 (s), 1590 (s), 1445 (m), 1385 (s), 1355 (s), 1320 (sh), 1305 (m), 1260 (s), 1235 (m), 1190 (m), 1075 (s), 1020 (m), 950 (m), 940 (sh), 915 (w), 890 (m), 780 (m), 720 (w), 680 (w), 625 cm^{-1} (w); NMR ($CDCl_3$) δ 1.50 (s, 36 H), 2.50 (s, 6 H), 5.84 (s, 2 H), 7.96 (s, 4 H); UV-visible λ_{max} (methanol) 239 nm (log ϵ 4.34), 272 (4.28), 324 (4.52), 360 (sh) (4.39), λ_{max} (cyclohexane) 364 nm. Anal. Calcd for $C_{36}H_{48}O_4$: C, 79.37; H, 8.88. Found: C, 79.18; H, 8.91.



ClO_4^-

9

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(2′,3′,4′,5′-tetrachloro-2′,4′-cyclopentadien-1′-ylidene)cyclopropene (6d). A mixture of 6.06 g (10.0 mmol) of bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)cyclopropenone and 4.08 g (20.0 mmol) of 1,2,3,4-tetrachloro-1,3-cyclopentadiene in 140 mL of anhydrous methanol was stirred at 45 ± 5 °C for 1 h to give a yellow solution and then kept at room temperature for 20 h. The resulting yellow precipitate was filtered, washed with hexane, and dried under vacuum to afford 0.70 g (8.8%) of 1,2-bis(3,5-di-*tert*-butyl-4-trimethylsiloxyphenyl)-3-(2′,3′,4′,5′-tetrachloro-2′,4′-cyclopentadien-1′-ylidene)cyclopropene as a bright yellow powder: mp >230 °C (no clear melting point); IR (KBr) 2960–2840 (m), 1825 (w-m), 1585 (m), 1500 (s), 1445 (w-m), 1400 (s), 1385 (m), 1360 (sh), 1340 (s), 1290 (s), 1260 (sh), 1235 (s), 1195 (w), 1115 (w), 1005 (m), 920 (w), 885 (m), 870 (s), 835 (m), 775 (w), 750 (w), 650 cm^{-1} (w); NMR ($CDCl_3$) δ 0.44 (s, 18 H), 1.46 (s, 36 H), 8.16 (s, 4 H).

The filtrate was concentrated to ca. 70 mL by rotary evaporation and then let stand overnight at −20 °C. The resulting yellow crystals (4.30 g) were chromatographed over 100 g of silica gel. Elution with benzene afforded 1.32 g (16.7%) of **6d** as yellow needles after recrystallization from hexane–benzene: mp 240–241 °C dec; IR (KBr) 3600 (m), 2970–2850 (m), 1830 (w), 1590 (m), 1500 (s), 1445 (w), 1410 (s), 1355 (m), 1290 (s), 1250 (m), 1233 (m), 1150 (m), 1110 (w), 1010 (m), 915 (w), 880 (w), 770 (w), 675 cm^{-1} (w); NMR ($CDCl_3$) δ 1.52 (s, 36 H), 5.92 (s, 2 H), 8.07 (s, 4 H); UV-visible λ_{max} (methanol) 244 nm (log ϵ 4.14), 288 (sh) (4.11), 312 (4.19), 360 (4.68); λ_{max} (cyclohexane) 360 nm, λ_{max} (benzene) 362 nm; mass spectrum *m/e* 646.19388 (calcd, 646.19366). Anal. Calcd for $C_{36}H_{42}Cl_4O_2$: C, 66.67; H, 6.53; Cl, 21.87. Found: C, 66.55; H, 6.59; Cl, 21.79.

Successive elution with 30% ethereal benzene gave 2.95 g (63.9%) of **4**.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(3′,4′-dichloro-3′-cyclopentene-2′,5′-dion-1′-ylidene)cyclopropene (6e). A mixture of 1.39 g (3.00 mmol) of **4** and 0.80 g (4.9 mmol) of 1,2-dichloro-1-cyclopentene-3,5-dione in 3.6 mL of acetic anhydride was refluxed for 10 min and then cooled at −20 °C overnight. The resulting precipitate was filtered, washed with ether, and dried under vacuum to give 1.18 g (64.7%) of **6e** as a yellow powder after recrystallization from

CCl_4–$CHCl_3$: mp >290 °C; IR (KBr) 3600 (m), 2950–2860 (m), 1835 (w), 1670 (sh), 1655 (s), 1590 (m), 1490 (s), 1410 (s), 1360 (s), 1325 (s), 1295 (w), 1255 (m), 1240 (s), 1195 (w), 1160 (m), 1137 (m), 1120 (m), 1100 (m), 1055 (m), 930 (w), 920 (w), 880 (w), 855 (w), 810 (m), 770 (w), 690 (w), 640 cm^{-1} (w); NMR ($CDCl_3$) δ 1.56 (s, 36 H), 5.96 (s, 2 H), 8.52 (s, 4 H); UV–visible λ_{max} (methanol) 241 nm ($\log \epsilon$ 4.56), 278 (4.01), 330 (4.64), 362 (4.49), 382 (sh) (4.41); λ_{max} (cyclohexane) 393 nm; mass spectrum *m/e* 608.24600 (calcd, 608.24578). Anal. Calcd for $C_{36}H_{42}Cl_2O_4$: C, 70.92; H, 6.95; Cl, 11.63. Found: C, 70.86; H, 6.80; Cl, 11.88.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(indan-1′,3′-dion-2′-ylidene)cyclopropene (6f). A mixture of 3.00 g (6.50 mmol) of **4**, 1.90 g (13.0 mmol) of 1,3-indandione, and 0.02 g of β-alanine in 8.0 mL of acetic anhydride was refluxed for 2 h. The resulting precipitate was filtered and washed with ether to give 2.82 g (73.5%) of **6f** as pale pink colored crystals after recrystallization from chloroform: mp 295–296 °C dec; IR (KBr) 3596 (s), 2950–2850 (m), 1834 (m), 1653 (s), 1593 (s), 1480 (s), 1409 (m), 1353 (m), 1236 (s), 1197 (w), 1141 (s), 1121 (w), 1020 (w), 922 (m), 875 (m), 810 (w), 771 (w), 749 (w), 730 (m), 672 (w), 644 cm^{-1} (w); NMR ($CDCl_3$) δ 1.60 (s, 36 H), 5.94 (s, 2 H), 7.70 (m, 4 H), 8.69 (s, 4 H); UV–visible λ_{max} (methanol) 210 nm ($\log \epsilon$ 4.61), 232 (4.62), 285 (4.20), 298 (4.21), 364 (4.73); λ_{max} (cyclohexane) 372 nm. Anal. Calcd for $C_{40}H_{46}O_4$: C, 81.32; H, 7.85. Found: C, 81.23; H, 7.82.

Synthesis of the Diquinocyclopropanes (5). 1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-dicyanomethylenecyclopropane (5a). A solution of 1.00 g (3.04 mmol) of potassium ferricyanide in 20 mL of 1 N KOH solution was added to a solution of 0.51 g (1.0 mmol) of **6a** in 20 mL of chloroform. The deep blue two-phase mixture was stirred vigorously at room temperature for 1 h under a nitrogen atmosphere. The organic layer was separated, washed with water, dried ($MgSO_4$), and evaporated in vacuo to give 0.50 g (98%) of **5a** as golden plates after recrystallization from hexane: mp 210–215 °C dec; IR (KBr) 2960–2860 (m), 2227 (w), 2217 (w), 1753 (m), 1600 (s), 1525 (w), 1510 (w), 1470 (s), 1360 (m), 1345 (m), 1260 (w), 1115 (s), 1020 (w), 950 (w), 910 (m), 830 cm^{-1} (w); NMR ($CDCl_3$) δ 1.34 (s, 18 H), 1.38 (s, 18 H), 7.45 (d, J = 2 Hz, 2 H), 7.71 (d, J = 2 Hz, 2 H); UV–visible λ_{max} (benzene) 319 (sh) (3.77), 345 (sh) (3.90), 364 (4.03), 387 (sh) (4.01), 415 (sh) (3.88), 498 (sh) (3.96), 548 (sh) (4.40), 587 (4.79), 609 (4.80), 640 (sh) (4.25); mass spectrum *m/e* 508.31003 (calcd, 508.30897). Anal. Calcd for $C_{34}H_{40}N_2O_2$: C, 80.27; H, 7.93; N, 5.51. Found: C, 80.40; H, 8.09; N, 5.48.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-carboethoxycyanomethylenecyclopropane (5b). In exactly the same manner as above 0.30 g (0.54 mmol) of **6b** was oxidized with excess $K_3Fe(CN)_6$ to give 0.30 g (100%) of **5b** as dark purple plates with golden reflection after recrystallization from hexane–benzene: mp 230–231 °C dec; IR (KBR(296]-2—6] (m), 2215 (w), 1743 (m), 1700 (m), 1585 (s), 1530 (w), 1480 (w), 1455 (m), 1390 (w), 1360 (m), 1250 (s), 1175 (w), 1120 (w), 1090 (s), 1070 (m), 1060 (m), 935 (w), 905 (w), 820 (w), 770 cm^{-1} . (w); NMR ($CDCl_3$) δ 1.40 (s, 36 H), 1.48 (t, 3 H), 4.46 (q, 2 H), 7.56 (br, s, 2 H), 8.06 (d, 1 H), 8.86 (d, 1 H); UV–visible λ_{max} (benzene) 291 nm ($\log \epsilon$ 4.24), 362 (4.01), 550 (sh) (4.45), 591 (4.82), 609 (4.80). Anal. Calcd for $C_{36}H_{45}NO_4$: C, 77.80; H, 8.16; N, 2.52. Found: C, 77.70; H, 8.21; N, 2.46.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-diacetylmethylenecyclopropane (5c). In the same way, $K_3Fe(CN)_6$ oxidation of 0.37 g (0.68 mmol) of **6c** afforded 0.36 g (97%) of **5c** as dark purple plates with golden reflection after recrystallization from hexane: mp 180–190 °C dec; IR (KBr) 2960–2840 (m), 1730 (m), 1685 (s), 1645 (m), 1590 (s), 1540 (w), 1500 (w), 1480 (m), 1450 (m), 1390 (w), 1360 (s), 1255 (m), 1200 (m), 1090 (s), 1025 (m), 930 (m), 895 (m), 820 (w), 750 (s), 630 cm^{-1} (w); NMR ($CDCl_3$) δ 1.40 (s, 36 H), 2.52 (s, 6 H), 7.54 (d, J = 2 Hz, 2 H), 7.86 (d, J = 2 Hz, 2 H); UV–visible λ_{max} (benzene) 296 nm ($\log \epsilon$ 4.13), 357 (4.03), 557 (sh) (4.46), 608 (4.70). Anal. Calcd for $C_{36}H_{46}O_4$: C= 79/66: H, 8.54. Found: C, 79.39; H, 8.50.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-(2′,3′,4′,5′-tetrachloro-2′,4′-cyclopentadien-1′-ylidene)cyclopropane (5d). Similarly oxidation of 0.58 g (0.73 mmol) of **6d** with excess $K_3Fe(CN)_6$ gave 0.57 g (99%) of **5d** as dark purple crystals with reddish copperlike reflectance after recrystallization from hexane: mp 200–210 °C dec; IR (KBr) 2960–2840 (m), 1700 (m), 1590 (s), 1520 (w), 1465 (m), 1450 (m), 1390 (w), 1360 (m), 1270 (s), 1250 (m), 1165 (m), 1120 (w), 1090 (s), 1005 (w), 895 (m), 820 (w), 650 cm^{-1} (w); NMR ($CDCl_3$) δ 1.34 (s, 18 H), 1.37 (s, 18 H), 7.48 (d, J = 2 Hz, 2 H), 7.94 (d, J = 2 Hz, 2 H); UV–visible λ_{max} (benzene) 313 nm ($\log \epsilon$ 4.16), 357 (4.14), 390 (4.10), 672 (4.60). Anal. Calcd for $C_{36}H_{40}Cl_4O_2$: C, 66.88; H, 6.24; Cl, 21.94. Found: C, 66.64; H, 6.40; Cl, 21.75.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-(3′,4′-dichloro-3′-cyclopentene-2′,5′-dion-1′-ylidene)cyclopropane (5e). In the same way oxidation of 0.46 g (0.76 mmol) of **6e** gave 0.45 g (98%) of **5e** as dark purple crystals with reddish reflectance after recrystallization from hexane–benzene: mp 255–260 °C dec; IR (KBr) 2960–2840 (w), 1745 (m), 1680 (s), 1575 (s), 1470 (w), 1440 (w), 1380 (w), 1355 (m), 1250 (w), 1220 (m), 1195 (m), 1120 (m), 1080 (w), 1010 (w), 930 (w), 900 (m), 810 (w), 750 cm^{-1} (w); NMR ($CDCl_3$) δ 1.39 (s, 18 H), 1.45 (s, 18 H), 7.52 (d, J = 2 Hz, 2 H), 8.83 (d, J = 2 Hz, 2 H); UV–visible λ_{max} (benzene) 296 nm ($\log \epsilon$ 4.33), 372 (4.06), 390 (4.05), 420 (sh) (3.95), 550 (sh) (4.36), 600 (4.77), 621 (4.75). Anal. Calcd for $C_{36}H_{40}Cl_2O_4$: C, 71.16; H, 6.64; Cl, 11.67. Found: C, 71.09; H, 6.50; Cl, 11.81.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-(indene-1′,3′-dion-2′-ylidene)cyclopropane (5f). Similarly, oxidation of 0.59 g (1.00 mmol) of **6f** with excess $K_3Fe(CN)_6$ afforded 0.58 g (99%) of **5f** as dark reddish purple crystals after recrystallization from hexane–chloroform: mp 236–238 °C dec; IR (KBr) 2960–2860 (m), 1750 (m), 1677 (s), 1580 (br, s), 1525 (w), 1480 (m), 1450 (m), 1390 (w), 1350 (m), 1325 (m), 1240 (s), 1200 (w), 1160 (m), 1125 (m), 1113 (w), 1090 (m), 1055 (w), 1015 (w), 940 (w), 910 (s), 890 (w), 820 (m), 740 (s), 685 (w), 650 cm^{-1} (w); NMR ($CDCl_3$) δ 1.40 (s, 18 H), 1.50 (s, 18 H), 7.52 (d, J = 2 Hz, 2 H), 7.87 (m, 4 H), 9.10 (d, J = 2 Hz, 2 H); UV–visible λ_{max} (benzene) 290 nm ($\log \epsilon$ 4.30), 307 (4.28), 372 (4.19), 394 (4.15), 423 (4.03), 563 (sh) (4.42), 610 (4.84), 627 (sh) (4.80), 668 (sh) (4.34). Anal. Calcd for $C_{40}H_{44}O_4$: C, 81.60; H, 7.53. Found: C, 81.73; H, 7.60.

Spectrophotometric Titration of 6. The base titration of compounds **6a–f** was carried out by the following general method. To a well-stirred solution of 0.020 mmol of **6** in 100 mL of spectrograde methanol was added 0.10 N aqueous NaOH in 0.10-mL aliquots by the use of micropipet. The UV–visible spectrum was recorded after each addition of the base and the sample solution was returned to the main batch. No spectral change (beyond experimental error) was observed after adding 0.04 mmol of base. After each titration was completed, 0.1 mL of concentrated HCl was added and regeneration of the original spectrum of **6** was observed; UV–visible spectrum for the dianion of **5a**, λ_{max} (methanol) 347 nm ($\log \epsilon$ 4.31), 418 (4.59), 445 (4.63); the dianion of **5b,** λ_{max} (methanol) 228 nm (sh) ($\log \epsilon$ 4.38), 265 (4.25), 300 (4.19), 350 (4.31), 413 (4.64); the dianion of **5c**, λ_{max} (methanol) 262 nm ($\log \epsilon$ 4.30), 300 (4.23), 401 (4.69); the dianion of **5d**, λ_{max} (methanol) 264 nm ($\log \epsilon$ 4.02), 300 (4.16), 417 (4.81); the dianion of **5e,** λ_{max} (methanol) 230 nm ($\log \epsilon$ 4.29), 250 (4.33), 301 (4.22), 406 (4.69); the dianion of **5f,** λ_{max} (methanol) 228 nm ($\log \epsilon$ 4.61), 286 (4.21), 298 (4.28), 326 (4.24), 413 (4.83).

Anion Radicals of 5 Examined by ESR. Electrolytic reduction was carried out for the compounds **5a–f** by the following general procedures. About 3 mg of tetrabutylammonium perchlorate and 1 mg of **5** were placed in an electrolytic ESR cell. A small piece of glass wool was placed between platinum wire electrodes to slow diffusion. After degassing, dry tetrahydrofuran (distilled from $LiAlH_4$, stored over Na–K anthracene) was vacuum distilled into the cell. After three freeze–degas–thaw cycles the cell was sealed and placed in the ESR cavity and a minimal current was passed through the cell to generate the ESR signal. Coupling constants and g values were measured using double-cavity technique with Fremy's salt (potassium nitrosyldisulfonate, g = 2.0057) as reference (Table II). For **5b** an equally spaced pattern of six (or possibly eight) lines was observed, with splitting of 0.75 G, line width 0.35 G, and g = 2.0053. The relative intensities were approximately 1:3:5:5:3:1.

Cyclic Voltammetry. A Princeton Applied Research Model 170 electrochemistry system was used with a three-electrode cell, having platinum-wire working and auxiliary electrodes and a saturated calomel reference electrode. All sample solutions were 1 mM in quinoid compounds with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte in dichloromethane which had been dried and distilled over P_2O_5. For all of compounds **5**, each wave fulfilled the reversibility criteria for the electrode process:[24] the ratio of cathodic and anodic peak currents, i_{pc}/i_{pa}, becomes close to unity as the scan rate is decreased, and a plot of peak current against square root of the scan rate is linear passing through the origin for both cathodic and anodic peaks in each case. For both waves in all the compounds, the separation between cathodic and anodic peaks decreased with slower scan rate reaching the minimal values of 0.08–0.1 V, indicating that the electron transfer is somewhat slower than the completely reversible case with fast electron transfer.[25] From this dependence of the peak separation upon scan rates, the electron transfer rate (k_s) at the platinum-wire electrode surface was calculated to be roughly 5×10^{-3} cm/s for all the compounds **5** using the relationship reported by Nicholson.[25] The detailed cyclic voltammetric data are available as microfilm material.

After this manuscript was written there appeared reports on the synthesis and properties of dianion salts of negatively substituted trimethylenecyclopropanes (TMCP).[27] Although some of the TMCPs were isolated also as neutral species, they seem to be somewhat less stable than the dianions in contrast to the stability of neutral alkylidenediquinocyclopropanes **5** in the present study. However, the compounds **5** can be rather regarded as a link between triquinocyclopropanes **1** and substituted TMCPs from the viewpoint of their structure as well as of the electron affinity: the reduction potentials of **5a** (E_1 − +0.30, E_2 = −0.24 V) lie between those of **1** (E_1 = +0.05, E_2 = −0.33[28] V) and TMCP $(C_6CN)_6$ (E_1 = +1.13 (irreversible), E_2 = +0.34).[27a]

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Supplementary Material Available: Cyclic voltammetric data for 5 (2 pages). Ordering information is given on any current masthead page.

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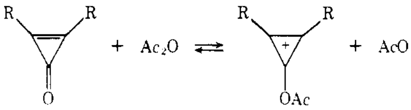
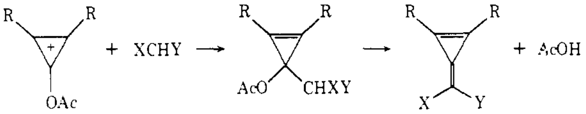
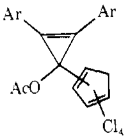
(6) The proposed mechanism is as follows:[4d]



$$AcO^- + XCH_2Y \rightleftarrows AcOH + XCHY$$



(7) The reaction of **6** with 1,2,3,4-tetrachlorocyclopentadiene in acetic anhydride (reflux) gave an unseparable mixture of isomers.



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(19) For quinoidal oxygens: $\alpha_O = \alpha_C + 0.6\,\beta_{CC}$, $\beta_{CO} = 1.2\,\beta_{CC}$ (ref 3). For the other carbonyls and chlorine atoms: $\alpha_O = \alpha_C + \beta_{CC}$, $\beta_{CO} = \beta_{CC}$; $\alpha_{Cl} = \alpha_C + 3.0\,\beta_{CC}$, $\beta_{CCl} = 0.3\,\beta_{CC}$.
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(23) There are two different OH signals at 5.96 and 6.02 ppm because of the difference in magnetic environment around the OH on the aryl group which is on the same side as CN and the OH on the other aryl group. (The exocyclic double bond prevents free rotation of the carboethoxycyanomethylene group.)
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(25) For a typical completely reversible case, the peak separation is expected to be 0.058 V independent of the scan rate (see ref 24).
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