

with a mechanical stirrer was placed 0.411 g (0.00189 mol) of enol ether 18 in 3 mL of freshly distilled bromoform and 0.020 g of Cetrimide. To this was added 3 mL of 33% aqueous sodium hydroxide dropwise over a 15-min period. The resulting two-phase mixture was vigorously stirred for 34 h at ambient temperature. Workup as in method A gave 0.715 g of a brown oil which on Florisil (elution with 20% dichloromethane–80% pentane) gave 0.507 g (69% yield) of crystalline material identical with that produced by method A.

Bromoeneone 20. A solution of silver tetrafluoroborate was prepared along the lines of Birch and Keeton.¹⁹ To 4.6 g of 37–40% aqueous hydrofluoroboric acid in a 10-mL Erlenmeyer flask equipped with a magnetic stirrer was slowly added 0.506 g (0.00218 mol) of silver oxide in small portions. The black silver oxide dissolved to give a clear pale gray solution, which was stirred an additional 10 min. At this time the silver tetrafluoroborate solution was slowly added to a 50-mL round-bottomed flask equipped with a magnetic stirrer and containing a solution of 0.850 g (0.00218 mol) of dibromocyclopropane 19 in 15 mL of ethanol. The mixture was stirred at reflux for 2 h. During the course of the reaction, silver bromide was formed as a granular precipitate. The solution was cooled to room temperature and transferred to a 125-mL Erlenmeyer flask and made alkaline (cautiously) with solid sodium carbonate. The solution was filtered to remove silver salts and the filtrate extracted with dichloromethane. The combined organic layers were washed with water until neutral and then dried. Evaporation of the solvent gave 0.640 g of a brown oil which was chromatographed on Florisil. Elution with 20% dichloromethane–80% pentane gave 0.572 g (89% yield) of bromoeneone 20 as a pale yellow oil: IR (neat) 1645 cm^{-1} (conjugated >C=O); NMR (CCl_4) δ 1.31 (s, 6 H), 2.41 (d, 2 H, $J = 5.5$ Hz), 3.71 (s, 3 H), 6.40–7.50 (m, 3 H), and 6.89 ppm (t, 1 H, $J = 5.5$ Hz); low resolution mass spectrum, parent peak: (m/e) = 204 (^{79}Br) and 206 (^{81}Br).

9,9-Dimethyl-2-methoxy-5-benzosuberone (1). A 25-mL round-bottomed flask was charged with 0.471 g (0.0016 mol) of bromoeneone 20. To this were added 0.150 g of 5% palladium on charcoal catalyst and 0.20 g of sodium carbonate, followed by 10 mL of benzene. The mixture was magnetically stirred as it was hydrogenated at room temperature and pressure for 8 h. At this time, the reaction mixture was filtered to remove the catalyst and excess sodium carbonate. The filtrate was evaporated at reduced pressure to give a yellow oil, which upon chromatography on Florisil (50% dichloromethane–50% pentane) gave 0.320 g (92% yield) of ketone 1. This material was identical with that obtained from the direct oxidation of benzosuberone 2 with chromium trioxide in aqueous acetic acid.

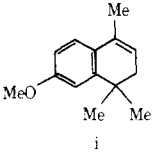
When 7.63 g (0.035 mol) of enol ether 18 was subjected to the sequence $18 \rightarrow 19 \rightarrow 20 \rightarrow 1$ using the same molar ratios and conditions, but not isolating the intermediate products, a yield of 6.33 g of ketone 1 was produced after column chromatography as above. This represents a yield of 83% from enol ether 18 (or 66% from tetralone 2).

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Registry No.—1, 65275-82-3; 2, 23203-51-2; 3, 4521-28-2; 4, 20637-08-5; 5, 4586-90-7; 6, 23203-50-1; 7, 65275-83-4; 8, 65275-77-6; 9, 65275-78-7; 10, 21336-18-5; 11, 6500-65-8; 15, 65275-79-8; 16, 13587-99-0; 17, 64746-51-6; 18, 65275-80-1; 19, 65354-45-2; 20, 65275-81-2; methylolithium, 917-54-4; methyltriphenylphosphonium iodide, 2065-66-9; bromoform, 75-25-2.

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- (4) Exocyclic olefin 8 isomerizes to endocyclic olefin i on contact with acid or on attempted distillation or chromatography.



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- (5) McMurry has noted minor changes in product distribution upon the addition of AgBF_4 ; see ref 2.
- (6) These ratios were determined by integration of the NMR spectrum of the crude reaction product. Integration of the aromatic proton ortho to the carbonyl function in ketone 1 ($\delta = 7.29$ ppm) relative to the remaining aromatic protons (no absorption past $\delta = 7.00$ ppm) gave the reported ratios.
- (7) Some conditions which failed were sodium dichromate–acetic acid in benzene both at room temperature and at reflux, and chromium trioxide in pyridine.
- (8) Compound 10 was prepared from 6-methoxy-1-tetralone (Aldrich Chemical Co.) by a completely analogous route to that used for the preparation of compound 9 (see Scheme II). The yields of the individual steps were very similar in each case.
- (9) Starting material disappeared after 36 h at room temperature but only a 52% yield of 11 was realized.
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Synthesis and Novel Physical Properties of a Biphenoquinocyclopropane

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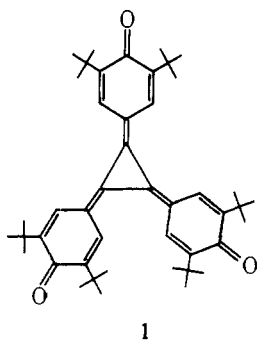
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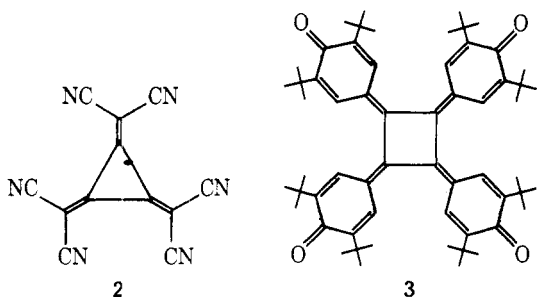
The synthesis and physical properties of 1-(3,5-di-*tert*-butyl-4-hydroxy-4'-biphenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropane (8) are described. Upon oxidation with either PbO_2 or alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ 8 yields two major products. One of the products is tentatively identified as the fully quinoid system 4, which displays a λ_{max} well into the near-infrared at 1300 nm. The other oxidation product is identified as the biradical 10. The dianion of 8 can be electrochemically oxidized in an ESR cell to yield an anion radical identical with that obtained upon electrochemical reduction of 10.

The quinocarbons (polyquinocycloalkanes) represent a class of radialenes in which each exocyclic double bond comprises either the ylidene linkage of a 4-oxo-2,5-cyclohexa-

dien-1-ylidene moiety or a carbonyl group. Since the synthesis of the first quinocarbon, triquinocyclopropane 1,¹ a number of other quinocarbons and related radialenes have been re-

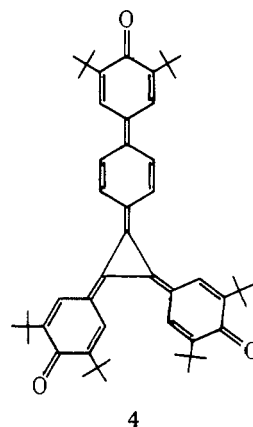


ported.²⁻⁵ Among the more noteworthy advances in this area are the syntheses of hexacyanomethylenecyclopropane **2**⁶ and tetraquinocyclobutane **3**.³



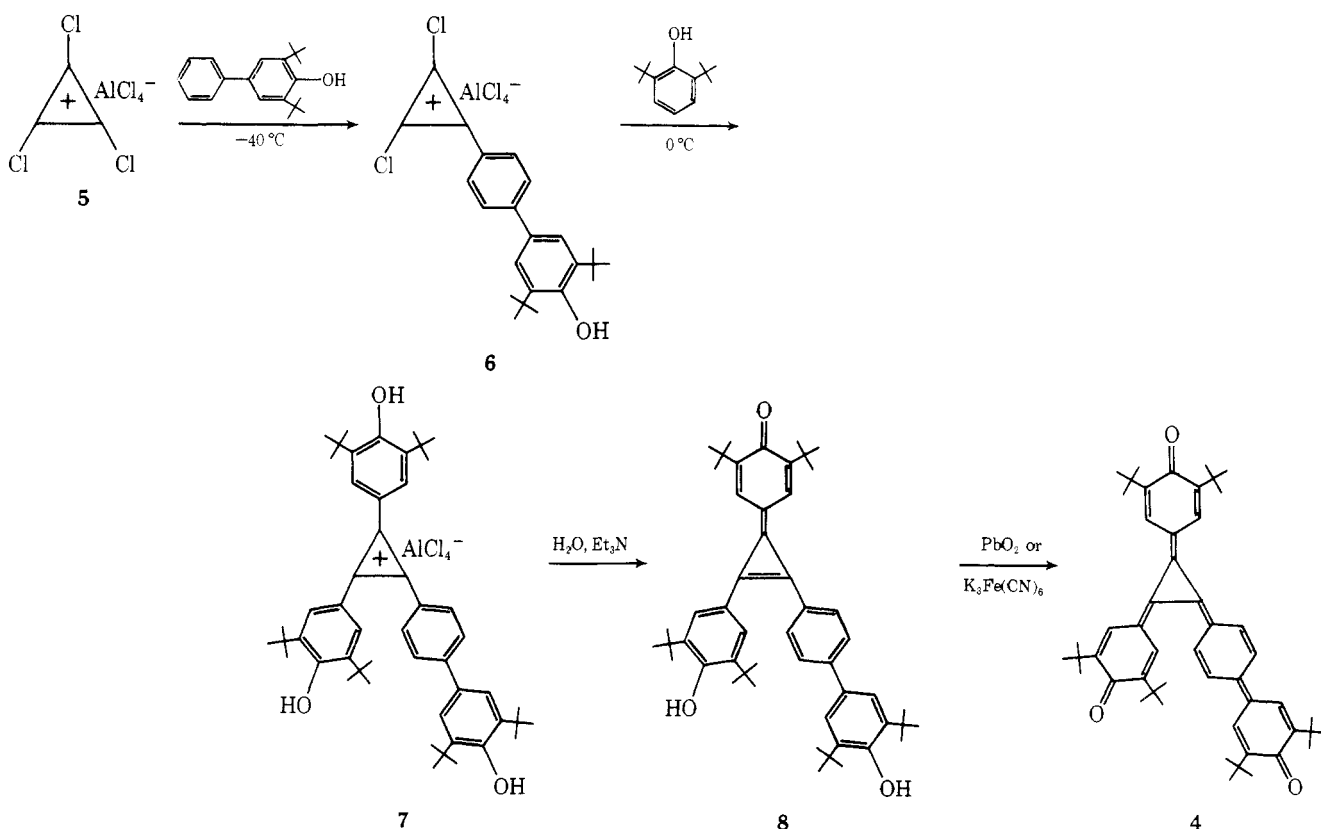
Recent interest in the possible uses of the highly conjugated, brightly colored quinocarbons as dyes, organic semiconductors, photographic materials, and charge-transfer salts has stimulated our endeavors to design and synthesize molecules having potentially useful electronic and magnetic properties. Since triquinocyclopropane **1** has an extremely intense electronic absorption in the near-infrared at about 770 nm ($\log \epsilon$ 4.71),¹ we have directed our efforts toward the syntheses and investigation of the physical properties of molecules with even

lower energy first electronic transitions. In this report we describe results of attempts to synthesize the biphenocyclopropane compound **1,2-bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-(3,5-di-*tert*-butyl-4-oxobiphen-4'-ylidene)cyclopropane (**4**).**



Based on analogy to the straightforward preparation of triquinocyclopropane **1**,¹ we employed the synthetic route outlined in Scheme I. 2,6-Di-*tert*-butyl-4-phenylphenol (1 equiv), prepared by the method of Koser and Pirkle,⁷ was slowly added to trichlorocyclopropenium aluminate at -40°C . The reaction was allowed to warm slowly to 0°C , and 2 equiv of 2,6-di-*tert*-butylphenol was added to generate the triaryl cyclopropenium aluminate **7**. An attempt to first generate the 1,2-bis(2,6-di-*tert*-butyl-4-hydroxyphenyl)-3-chlorocyclopropenium aluminate followed by addition of the 2,6-di-*tert*-butyl-4-phenylphenol proved unsuccessful. Apparently the 2,6-di-*tert*-butyl-4-phenylphenol is unreactive towards electrophilic attack by diarylcyclopropenium ion. Similar behavior has been observed upon the attempted addition of other unactivated aromatics, such as benzene, to diarylcyclopropenium salts.⁸ Hydrolysis of **7** followed by

Scheme I



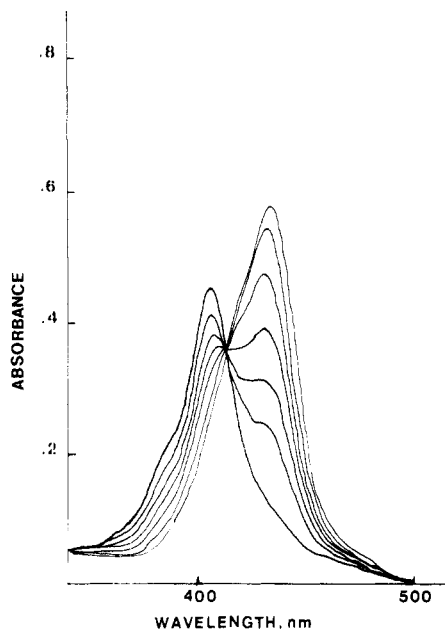
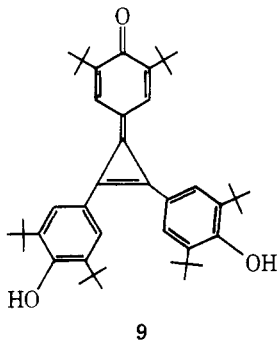


Figure 1. Electronic spectra of 8 (1×10^{-4} M MeOH) showing the conversion to its dianion upon titration with 3.34×10^{-4} N NaOH.

treatment with triethylamine produced 8 in about 30% yield after column chromatography.

The ^1H NMR spectrum of 8 displays two *tert*-butyl absorbances with intensity ratios of 2:1. This pattern is attributed to hydrogen exchange between the 3,5-di-*tert*-butyl-4-hydroxyphenyl and the 3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadiene moieties. Apparently the 1-(3,5-di-*tert*-butyl-4-hydroxybiphenyl) substituent does not participate in this hydrogen exchange since two distinct hydroxyl ^1H NMR absorbances of equal intensity (one sharp and one broad) are observed. Similar hydrogen exchange is observed for the diarylquinocyclopropane precursor to 1, compound 9, which



shows only one *tert*-butyl absorbance in its ^1H NMR spectrum.⁹ The aryl region of the ^1H NMR spectrum of 8 shows the expected pattern of two singlets in a 2:1 intensity ratio as well as a doublet of doublets (4 H, $J_1 = 11.0$, $J_2 = 1.7$ Hz).

The orange-red colored 8 has λ_{max} 405 nm ($\log \epsilon$ 4.65) in methanol, closely paralleling that of 1, λ_{max} 406 nm ($\log \epsilon$ 4.86).¹ Compound 8 also shows a bathochromic shift from polar to nonpolar solvents (λ_{max} 413 nm in cyclohexane), which suggests a dipolar ground state with significant cyclopropenium ion character. A spectrophotometric titration of 8 using sodium hydroxide in methanol was performed (Figure 1). All intermediate curves passed through one set of isosbestic points, implying that the monoanion is unstable with respect to the dianion under the titration conditions. The dianion has λ_{max} 432 nm ($\log \epsilon$ 4.77).

The infrared spectrum of 8 shows the characteristic 1822-cm^{-1} absorbance from the carbon-carbon double-bond

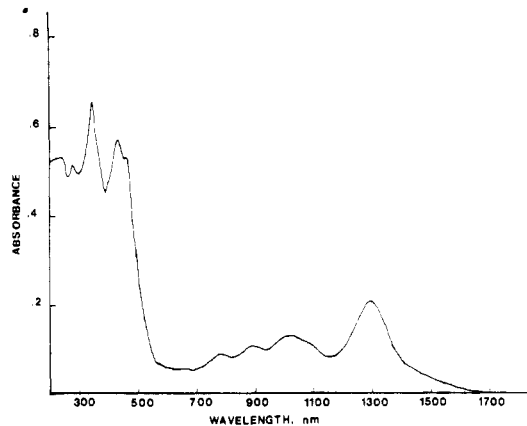


Figure 2. Electronic spectra of freshly oxidized 8 in CCl_4 (4.3×10^{-5} M).

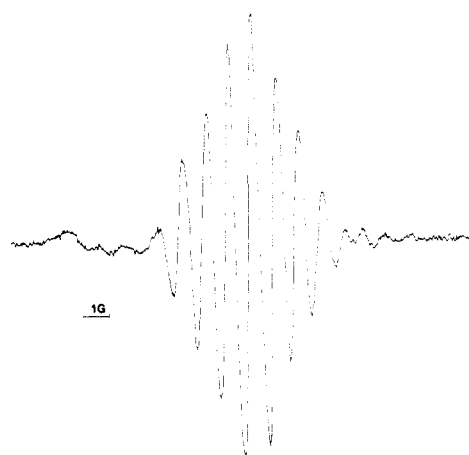


Figure 3. Electronic spin resonance spectrum of the biradical 10 in toluene at room temperature. The spectrum was obtained by PbO_2 oxidation of 8.

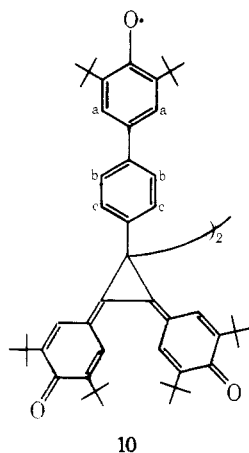
stretch of cyclopropenes. An intense band near 1600 cm^{-1} , attributed to the quinoid group, is also observed.

Further structural proof of 8 includes conversion to its ionic perchlorate salt by treatment with perchloric acid. The infrared spectrum of the perchlorate salt shows an intense 1365-cm^{-1} band, characteristic of cyclopropenium ions, as well as the 1070-cm^{-1} broad band from O_4Cl^- . The 1822-cm^{-1} stretching is no longer present.

Upon oxidizing 8 with an excess of either PbO_2 or alkaline $\text{K}_3\text{Fe}(\text{CN})_6$, we observed absorptions well into the near-infrared at 1300 nm, 1030, 880 sh, and 770 sh (Figure 2). The 1300-nm absorption represents an extremely low-energy first electronic transition. However, all four of the long wavelength absorptions decayed at room temperature, following first-order kinetics ($\tau_{1/2} = 92$ min).

The oxidized solution displays a strong nine-line signal in the ESR spectrum (Figure 3), whose intensity remains constant as the near-infrared absorptions decay. In addition to the low-energy absorption bands, the oxidized solution also displays λ_{max} at 467 nm, 434, 347, and 283. After the 1300-nm absorption has disappeared, only the 467-nm band remains, implying that it is from the paramagnetic species.

Our interpretation of these observations is that the fully quinoid structure 4, having λ_{max} 1300 nm, is produced upon oxidation of 8 and this compound decomposes via an unspecified route. Assuming the extinction coefficient of 4 to be similar to that of triquinocyclopropane ($\log \epsilon$ 4.71), 4 is formed in about 10% yield. The paramagnetic species is probably best represented as the biradical dimer 10.



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The ESR signal can be simulated as the central nine lines of an 11-line pattern from a pentet of triplets with respective coupling constants of 1.78 and 0.80 G and a line width of 0.25 G, $g = 2.0039$. The pentet arises from coincidentally equivalent couplings with the four a and b protons (see structure 10) and the triplet from the two c protons. This spectrum closely parallels that of the 2,6-di-*tert*-butyl-4-phenylphenoxyl radical, which has analogously equal a and b proton splittings of 1.77 G and c splitting of 0.88 G.¹⁰

A sample of 8 was oxidized with excess alkaline $K_3Fe(CN)_6$ in chloroform; after removal of the oxidizing agent and solvent, a polycrystalline black solid was isolated. The magnetic susceptibility (μ) of this solid was $1.10 \mu_B$, based on moles of starting material 8. This μ is consistent with the dimer biradical 10 and rules out any possible monomeric biradical structure which would have a predicted μ of $3.46 \mu_B$. (The deviation of the observed μ ($1.10 \mu_B$) from the theoretical value for 10 of $1.73 \mu_B$ can be accounted for by the uncorrected possible diamagnetic impurities from the decomposition products of 4 and the relatively large diamagnetic correction necessary for 10.)

The absence of a sharp O-H stretching band in the IR spectrum of 10 suggests that it is fully oxidized. Further proof that no monoradical of 8 is present was obtained by treatment of 8 with less than 0.25 equiv of PbO_2 . A complicated and uninterpretable ESR spectrum is obtained, presumably from overlap of the signals from the two possible monoradicals of 8.

While any discussion of the nature of the immediate precursor to 10 can only be speculative, several important inferences should be emphasized. 10 must be formed from rapid dimerization of an oxidized form of compound 8. The oxidized form of 8 is most likely either the singlet state quinoid structure 4, the triplet state of 4, or a biradical. Oxidations carried out at $-70^\circ C$ followed by low-temperature ESR experiments failed to show any signals other than those observed for 10. No enhanced ESR signal intensity was observed during the decay of 4 at any temperature. 4 decays with first-order kinetics and consequently cannot be an immediate precursor to 10; however, it could cross to a triplet state or biradical which dimerizes. Considering the relatively small proportion of 4 which is detected upon oxidation of 8, it is most reasonable to assume that the primary source of 10 is from rapid dimerization of short-lived triplet or biradical species, which are formed concomitantly with 4.

The biradical 10 can be cleaved by electrochemical reduction in an ESR cell to yield the corresponding anion radical. The ESR spectrum shows the central 11 lines of a 13-line pattern (Figure 4). The spectrum can be simulated assuming two sets of pentets with respective coupling constants of 1.62 and 0.81 G and a line width of 0.25 G, $g = 2.0045$. The same anion radical spectrum was generated by electrochemical

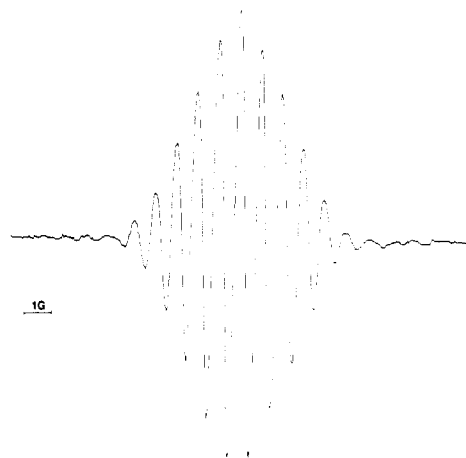
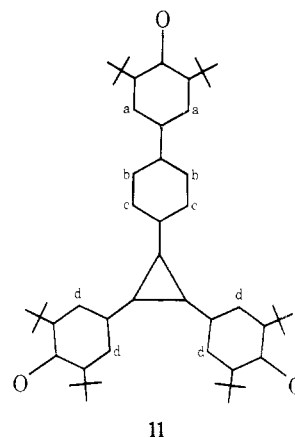


Figure 4. Electronic spin resonance spectrum of the radical anion 11 in CH_2Cl_2 at room temperature. The spectrum was obtained by electrolytic oxidation of the dianion of 8.

oxidation of the dianion of 8 in an ESR cell. The anion radical spectrum suggests complete delocalization of the unpaired electron over the conjugated π system. McLachlan-type Hückel molecular orbital calculations¹¹ are in agreement with the major pentet arising from interaction of the unpaired electron with the coincidentally equivalent four a and b protons (see structure 11) and the minor pentet arising from in-



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teraction with the four equivalent d protons. The calculations predict interaction with the c protons to be negligible. This spin delocalization closely parallels the anion radicals of triquinocyclopropane 1 and other quinocarbons which also show the unpaired electron to be completely delocalized throughout the conjugated π system.^{1,4,5}

Experimental Section

General Procedures. All syntheses were performed using purified grades of commercially available starting materials. Combustion analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Spectra were recorded by means of the following instruments: IR, Perkin-Elmer 237; 1H NMR, Jeol MA-100; UV-vis near-infrared, Cary 14; ESR, Varian 4502-B.

1-(3,5-Di-*tert*-butyl-4-hydroxy-4'-biphenyl)-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropane (8). Trichlorocyclopropenium aluminate (5) was generated by the rapid addition of 5.34 g (0.030 mol) of tetrachlorocyclopropene to a slurry of 3.99 g (0.030 mol) of $AlCl_3$ and 5 mL of methylene chloride. After the initial exothermicity, the reaction was heated at $60^\circ C$ for 15 min as a beige paste formed. An additional 10 mL of methylene chloride was added, and the reaction was cooled to $-40^\circ C$. The monoarylcyclopropenium aluminate 6 was formed by the addition of 8.46 g (0.030 mol) of 2,6-di-*tert*-butyl-4-phenylphenol in 10 mL of methylene chloride over the course of 1 h while maintaining the reaction temperature at $-40^\circ C$. After the addition was completed, the reaction was allowed to

warm to -20°C for 30 min, to -10°C for 30 min, and then to 0°C for 30 min. The triarylcyclopropenium aluminate **7** was formed by the rapid addition of 12.36 g (0.060 mol) of 2,6-di-*tert*-butylphenol in 10 mL of methylene chloride at 0°C . After the addition was completed, the reaction was allowed to warm to room temperature over the course of 1 h. At this time the reaction mixture was poured into 200 mL of ice water, and 5 mL of triethylamine was added. Chloroform (50 mL) was added, and the organic and aqueous phases were separated. The organic phase was thoroughly washed with water and dried over MgSO_4 . After filtration and solvent evaporation, the crude burgundy residue was chromatographed on 360 g of silica gel ($\text{CHCl}_3\text{-CCl}_4$, 1:1) to isolate 6.54 g (30.0%) of **8** as a red powder, mp $135\text{-}139^{\circ}\text{C}$ dec. A small amount of the tautomer of **8** was also present, and it can be converted entirely to **8** by acid catalysis and warming at 50°C for 30 min. Analytical samples of **8** were obtained by additional preparative TLC on silica gel (Skelly B-diethyl ether, 1:1): $^1\text{H NMR}$ (CDCl_3) δ 1.26 (s, 18 H), 1.41 (s, 36 H), 5.22 (s, 1 H), 5.34 (s, 1 H, broad), 7.26 (s, 2 H), 7.52 (s, 4 H), 7.93 (d of d, 4 H, $J = 11.0, 1.7$ Hz); IR (CHCl_3) 3622 m, 2960 s, 2875 m, 1822 m, 1600 s, 1483 s, 1432 s, 1357 s, 1330 s, 1156 m, 906 m, 886 w cm^{-1} ; UV-vis (MeOH) 405 nm ($\log \epsilon$ 4.65), 385 sh (4.34), 310 (4.06), 265 (4.12); UV-vis (cyclohexane) 413 nm ($\log \epsilon$ 4.83), 392 (4.79), 371 (4.55), 3.15 (4.56), 275 (4.57).

Anal. Calcd for $\text{C}_{51}\text{H}_{66}\text{O}_3$: C, 84.24; H, 9.16; O, 6.60. Found: C, 84.10; H, 9.01; O, 6.89.

Perchlorate Salt of 8. A 1.00-g amount of **8** was dissolved in 5 mL of benzene and treated with 2.5 mL of 60% HClO_4 . After 10 min a light green precipitate was filtered off and thoroughly washed with water followed by Skelly B. This material was precipitated from CH_3CN -diethyl ether to give 0.35 g of a light yellow powder, mp $171\text{-}175^{\circ}\text{C}$ dec. This perchlorate could be converted back to **8** by treatment with triethylamine in a chloroform-water mixture: $^1\text{H NMR}$ (acetone- d_6) δ 1.57 (s, 18 H), 1.67 (s, 36 H), 3.16 (s, 3 H, broad), 7.72 (s, 2 H), 8.47 (s, 4 H), 8.47 (d of d, 4 H, $J = 9.0, 2.0$ Hz); IR (CHCl_3) 3600 m, 2960 s, 1590 s, 1365 s, 1332 m, 1070 s, broad, 720 m, 660 w, 620 w cm^{-1} ; UV (MeOH) 360 nm ($\log \epsilon$ 4.79), 232 (4.09).

Titration of 8 to Its Dianion. A solution of 14.5 mg (0.020 mmol) of **8** in 200 mL of spectroquality MeOH was titrated with 3.34×10^{-4} N NaOH. Base was added to the solution of **8** in 2-mL aliquots. Aliquots were withdrawn for each UV-vis spectrum and returned after each reading. An isosbestic point was observed at 412 nm throughout the titration. The dianion has λ_{max} 432 nm ($\log \epsilon$ 4.77), 318 (4.08), and 254 (4.08); see Figure 1. After the dianion was completely formed, it was converted back to the original full intensity spectrum of **8** by the addition of 1 equiv of aqueous HCl.

Oxidation of 8. PbO_2 and alkaline $\text{K}_3\text{Fe}(\text{CN})_6$ oxidations of **8** were performed by adding at least a fourfold excess of oxidizing agent to a solution of **8** in a variety of different solvents, including toluene, methylene chloride, chloroform, and carbon tetrachloride. PbO_2 was

always centrifuged from the oxidized solution, and $\text{K}_3\text{Fe}(\text{CN})_6$ oxidations were always thoroughly washed with water. **4**: UV-vis near-infrared (CCl_4) λ_{max} 1300 nm, 1030, 880, 770, 434, 347. No extinction coefficients were calculated since the exact amount of **4** in solution was not determined.

Electron Spin Resonance Experiments: Biradical 10. In a typical ESR experiment 2 mg of **8** was placed in the bottom of an ESR cell and 6 mg of PbO_2 was placed in a side arm in the cell. Degassed solvent (either toluene, 2-methyl THF, or methylene chloride) was vacuum transferred into the bottom of the degassed cell. The solution of **8** was mixed with the PbO_2 in the side arm just prior to recording the spectrum. The spectrum in Figure 3 was obtained at room temperature: $a_{\text{H}} = 0.88$ G; $g = 2.0039$.

Anion Radical of 8. The dianion of **8** was generated from 2 mg of **8** and an excess of DBU in dichloromethane. A small amount of (*n*-Bu) N^+ClO_4^- was added to the solution which was transferred to an electrochemical ESR cell. A small piece of glass wool was placed between the electrodes to slow diffusion, and the cell was degassed. A minimal current was passed through the cell to develop a strong signal: $a_{\text{H}} = 0.81$ G; $g = 2.0045$. An identical spectrum was generated by starting with the biradical prepared from **8** and excess PbO_2 in dichloromethane followed by electrochemical reduction.

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Registry No.—**5**, 10438-65-0; **6**, 65276-06-4; **7**, 65276-08-6; **8**, 65276-77-9; **8** perchlorate, 65276-78-0; tetrachlorocyclopropene, 6262-42-6; 2,6-di-*tert*-butyl-4-phenylphenol, 2668-47-5; 2,6-di-*tert*-butylphenol, 128-39-2.

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Synthesis and Physical Properties of a Quinoiminocyclopropane

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The syntheses and physical properties of two quinoiminocyclopropanes, **1a** and **1b**, are described. These brightly colored, extensively conjugated quinoid compounds display an intense λ_{max} at 539 nm ($\log \epsilon$ 4.85). The anion radicals of **1a** and **1b** were generated electrochemically in an ESR cell, and their spectra show the unpaired spin density to be primarily localized in the quinoimine ring. Cyclic voltammetry shows that **1a** and **1b** are relatively strong oxidizing agents, each having $E_{1/2}$ values of +0.075 and -0.505 V.

In light of the interesting physical properties of tris-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropane (**2**)^{1,2} and other related quinocarbons,³⁻⁶ we wished to observe the effect of replacing one of the 4-oxo moieties of **2** with a different heteroatom group, the imino substituent. In this paper we report the synthesis and characterization of the first quinoiminocyclopropanes, **1a** and **1b**.

Although quinomonoimines and -diimines have been known for many years, their study has been hampered by their sensitivity to light, water, and air.⁷ In addition to our primary objective of synthesizing a new quinocarbon, we hoped our approach would also offer a novel route to sterically hindered, less labile quinomonoimine compounds.

Synthesis. The syntheses of **1a** and **1b** are accomplished