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 ($CHCl_3$–CCl_4, 1:1) to isolate 6.54 g (30.0%) of **8** as a red powder, mp 135–139 °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}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 ϵ 4.65), 385 sh (4.34), 310 (4.06), 265 (4.12); UV–vis (cyclohexane) 413 nm (log ϵ 4.83), 392 (4.79), 371 (4.55), 3.15 (4.56), 275 (4.57).

Anal. Calcd for $C_{51}H_{66}O_3$: 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 171–175 °C dec. This perchlorate could be converted back to **8** by treatment with triethylamine in a chloroform–water mixture: ^{1}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 ϵ 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 ϵ 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 $K_3Fe(CN)_6$ 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 $K_3Fe(CN)_6$ 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_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_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.

Acknowledgment. We are sincerely grateful to Mr. Cliff Feldmann for performing magnetic susceptibility measurements. This work was supported by Grants CHE74-01345A02 and CHE76-80374 from the National Science Foundation and by a grant from the 3M Company.

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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Received September 23, 1977

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 ϵ 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-cy-clohexadien-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

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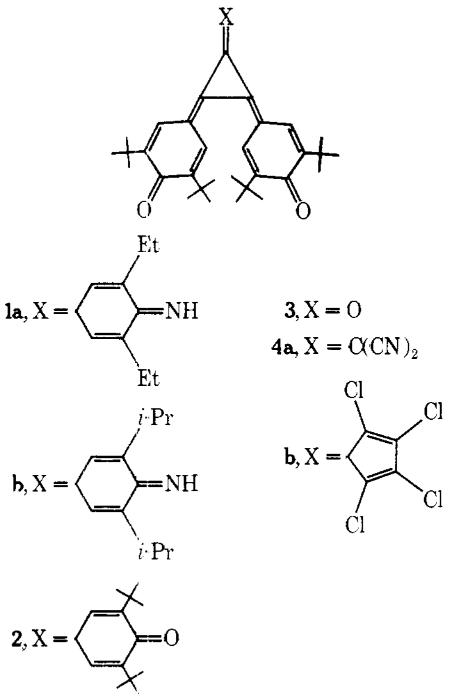


by the sequence depicted in Scheme I. The appropriate 2,6-dialkyl-substituted aniline is treated with 1-chloro-2,3-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)cyclopropenium aluminate (**5**)[8] followed by hydrolysis and treatment with triethylamine to yield a mixture of the isomeric quinocyclopropenes **6** and **7** in 60–70% isolated yield. The lead dioxide oxidation of **6** and **7** to the stable quinoiminocyclopropane **1** is effected in quantitative yield.

Analytical samples of both **6** and **7** can be isolated by dry column chromatography. The ^{1}H NMR spectra of **7a** and **7b** clearly show *tert*-butyl absorbances with the expected 2:1:1 intensity ratios. While the alkyl portion of the ^{1}H NMR spectra of **6a** and **6b** is not clearly resolved, two types of *tert*-butyl absorbances with the anticipated 1:1 intensity ratios can be discerned. **6** and **7** display medium intensity IR absorbances at 1870 and 1845 cm^{-1}, respectively; these bands are characteristic for the quinodiarylcyclopropene C=C bond stretch.[1]

The fully oxidized quinoiminocyclopropanes **1a** and **1b** display ^{1}H NMR absorbances from four magnetically nonequivalent *tert*-butyl groups, indicating that N–H inversion is slow on the ^{1}H NMR time scale. Consistent with slow N–H inversion, the aryl region of the ^{1}H NMR spectra for these compounds shows four broad[10] doublet[11] absorbances and one sharper absorbance with relative intensities of 1:1:1:1:2. The two quinoid hydrogens furthest away from the imino function are coincidentally equivalent and give rise to the singlet absorbance.

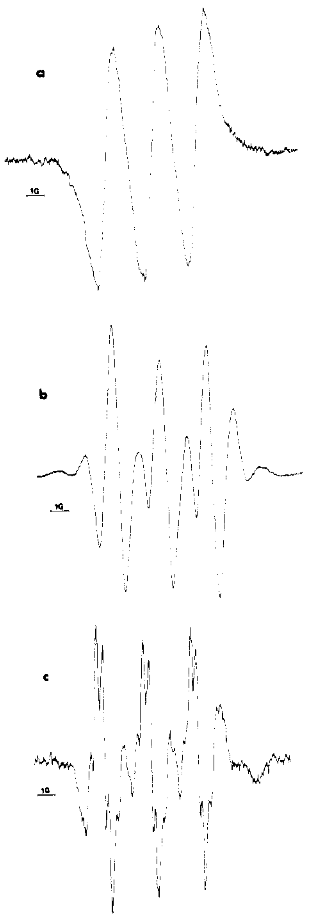
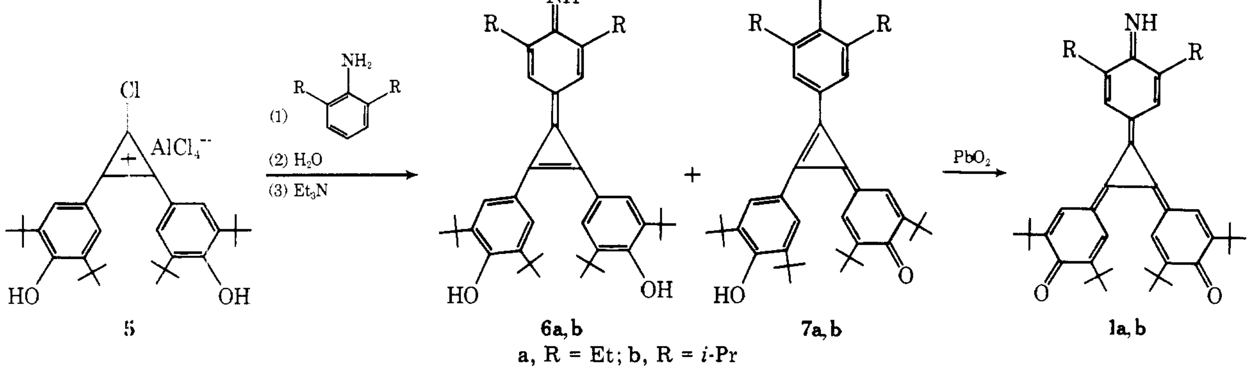


Figure 1. Electron spin resonance of the anion radical of **1a** with decreasing (a → c) modulation. The spectra were obtained by electrolytic reduction of **1a** in dichloromethane.

Physical Properties. One of the more striking physical properties of the quinocarbons is their intense color in solution. These extensively π-conjugated systems have electronic transitions in the visible and near-infrared region with extremely large extinction coefficients. For example, triquinocyclopropane **2** has λ_{max} 770 nm (log ϵ 4.71),[1] diquinocyclopropanone **3** has λ_{max} 542 nm (log ϵ 5.08),[4] and the diquinodicyanomethylenecyclopropane **4a** has λ_{max} 640 nm (log ϵ 4.25).[6] Like the other quinocarbons, **1a** and **1b** are brilliantly colored in solution (violet), having λ_{max} 539 nm (log ϵ 4.85).

The radical anions of **1a** and **1b** were electrochemically generated in an ESR cell. Each anion spectrum initially displayed three lines of equal intensity: a = 2.64 G; g = 2.0027 (Figure 1a). Utilizing the line-sharpening technique described by Glarum,[9] each of the three lines was shown to be split into doublets of equal intensity to give a six-line pattern, a = 1.35

Scheme I



5 **6a,b** **7a,b** **1a,b**

a, R = Et; b, R = *i*-Pr

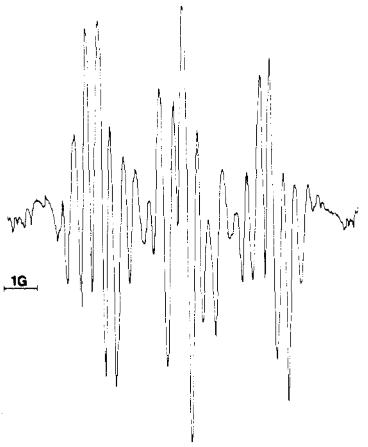
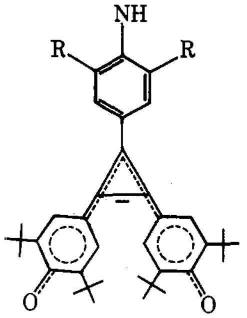


Figure 2. Electron spin resonance of the anion radical of **1b**. The spectrum was obtained by electrolytic reduction of **1b** in dichloromethane.

G (Figure 1b). Each of the doublets of the anion radical spectrum of **1b** has further couplings of about 0.30 G, splitting each doublet peak into a six-line pattern (Figure 1c). Similar fine structure in the spectrum of **1a** shows each doublet to be split into an eight-line pattern, a = 0.41 G, with approximate relative intensities of 1:4:6:5:5:6:4:1 (Figure 2).

These spectra are consistent with the major triplet splitting arising from coupling with the nitrogen nucleus and the doublets from coupling with the imino hydrogen. The six-line fine structure of **1b** is attributed to the coupling of the unpaired electron with the two methine hydrogens of the isopropyl groups, further splitting each line into nonoverlapping sets of triplets. Similarly, the fine structure of **1a** arises from the splitting of each line of the sextet by the four equivalent methylene hydrogens of the ethyl substituents to give partially overlapping pentets having predicted intensities of 1:4:6:5:5:6:4:1.

The ESR spectra suggest that the anion radical of **1** can be represented by structure **10**. The unpaired electron appears to be primarily localized on the nitrogen nucleus, with the negative charge delocalized mainly over the more electron-withdrawing aryloxy groups. Since no coupling from the meta hydrogens of the quinoid rings is observed (0.1-G couplings would be discernible), the spin density at these positions must be very small. The triquinocyclopropane anion radical **2**, in which the unpaired electron is delocalized over three *equivalent* quinoid rings, displays couplings of 0.43 G from the quinoid hydrogens.[2] Diquinocyclopropanone **3** and diquinotetrachlorocyclopentadien-1-ylidenecyclopropane **4b**, which contain *more* strongly electron-withdrawing substituents than the quinoid group, have anion radicals with quinoid hydrogen couplings of 0.63 and 0.85 G, respectively.[6] The larger coupling constants for these two compounds are consistent with greater localization of the negative charge on the electron-withdrawing carbonyl and tetrachlorocyclopentadiene substituents, with consequently greater spin density on the quinoid groups.



10

The coupling constants of the anion radicals of **2**, **3**, **4b**, and other quinocarbons have been accurately predicted by the method of McLachlan,[10] using Hückel molecular orbitals as reported elsewhere.[2,6] Similar calculations on **1** show very little spin density for the quinoid meta positions, in agreement with the negligible coupling from the hydrogens at these positions. The quinoiminocyclopropanes are the first quinocarbons which contain a more electron-releasing substituent than the quinoid group; a further test of our explanation awaits the synthesis and study of other such quinocarbons.

Cyclic voltammetry of **1a** and **1b** displays well-defined reversible voltammograms having two waves of similar height, corresponding to two discrete one-electron transfers to form the respective radical anions and dianions. For both **1a** and **1b**, $E_{1/2}$ values of −0.075 and −0.505 V were recorded. The quinocarbons in general have high positive values for $E_{1/2}$, suggesting their potential use as organic oxidizing agents. The $E_{1/2}$ values of **1a** and **1b** are not as positive as values reported for other quinocarbons; for example, triquinocyclopropane **2** has $E_{1/2}$ values of +0.05 and −0.33 V, and 1,2-bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-3-dicyanomethylenecyclopropane (**4a**) has $E_{1/2}$ values of +0.30 and −0.24 V.[11] The more positive $E_{1/2}$ values of **2** and **4a** reflect the greater electron affinities of the quino and dicyanomethylene substituents relative to the quinoimino group.

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; ^{1}H NMR, Jeol MH-100; UV–vis, Cary 14; MS, CEC 21-103C; ESR, Varian 4502-B; cyclic voltammetry, PAR Model 170 electrochemistry system.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(3,5-diethyl-4-imino-2,5-cyclohexadien-1-ylidene)cyclopropene (6a) and 1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-(3,5-diethyl-4-aminophenyl)-3-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropene (7a). Tetrachlorocyclopropene (1.78 g, 0.010 mol) was added to 1.33 g (0.010 mol) of aluminum chloride slurried in 3 mL of dichloromethane under nitrogen. After initial exothermicity the reaction was stirred for 15 min at 60 °C, forming a brown paste. The slurry was diluted with 10 mL of dichloromethane and cooled to −40 °C. At this point 4.12 g (0.020 mol) of 2,6-di-*tert*-butylphenol in 15 mL of dichloromethane was added dropwise over the course of 30 min while maintaining the temperature at −40 °C. The mixture was allowed to warm to −20 °C for 30 min and then to 0 °C for 30 min, forming a brownish-green solution. 2,6-Diethylaniline (1.49 g, 0.010 mol) in 5 mL of dichloromethane was rapidly added, and the reaction was warmed to room temperature and brought to reflux for 4 h. After cooling the mixture to room temperature and diluting with 20 mL of chloroform, 15 mL of water was added dropwise with stirring, followed by the addition of 2 mL of triethylamine. The organic layer was separated, washed with water and a saturated aqueous sodium chloride solution, and then dried over $MgSO_4$. After filtration and solvent removal the remaining orange residue was triturated with hot benzene and 1.4 g of a yellow powder consisting mostly of **6a** with some **7a** was filtered off. The filtrate was concentrated and chromatographed on silica gel (benzene–diethyl ether, 9:1) to give 2.9 g of a yellow powder consisting mostly of **7a** with some **6a** present. The combined product represents a yield of 70.0%. Analytical samples of **6a** and **7a** were obtained by dry column chromatography on silica gel (hexane–diethyl ether, 1:1). **6a:** ^{1}H NMR (THF-d_8) δ 1.17–1.41 (multiplet, 24 H), 1.61 (s, 18 H), 2.79 (q, 4 H, broad), 7.21–7.33 (multiplet, 7 H, broad), 7.81 (s, 2 H); IR (KBr) 3600 m, sh, 3400 w, broad, 3040 m, 2950 s, 2870 s, 1870 m, 1585 s, 1453 m, 1380 s, 1310 s, 1190 m, 1135 m, 975 m, 924 m, 890 w, 776 m, 750 w cm^{-1}; UV (MeOH) 420 nm (log ϵ 4.59), 330 (4.12), 280 (4.36).

Anal. Calcd for $C_{41}H_{55}NO_2$: C, 82.91; H, 9.34; N, 2.36; O, 5.39. Found: C, 82.85; H, 9.27; N, 2.41; O, 5.47.

7a: ^{1}H NMR (CCl_4) δ 1.12 (t, 6 H), 1.32 (s, 18 H), 1.35 (s, 9 H), 1.48 (s, 9 H), 2.61 (q, 2 H), 7.00 (multiplet, 5 H, broad), 7.24 (s, 2 H), 7.43 (d, 2 H, broad); IR ($CHCl_3$) 3600 m, 3300 w, broad, 3200 w, broad, 2960 s, 2867 m, 1845 m, 1590 s, 1560 s, 1350 s, 1290 s, 909 s, 890 m, 639 m, 629 m cm^{-1}; UV (MeOH) 430 nm (log ϵ 4.49), 320 (4.36); MS Calcd for $C_{41}H_{55}NO_2$, 593.42327; MS Obsd, 593.42387.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(3,5-diisopropyl-4-imino-2,5-cyclohexadien-1-ylidene)cyclopropene (6b) and 1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-(3,5-diisopropyl-4-aminophenyl)-3-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropene (7b). These compounds were synthesized and purified by the method described for **6a** and **7a**.

6b: ^{1}H NMR (Me$_2$SO-d_6 and CDCl$_3$, 1:1) δ 1.04–1.24 (multiplet, 30 H), 1.48 (s, 18 H), 3.16 (septet, 2 H, broad), 6.96 (s, 2 H), 7.08–7.36 (multiplet, 5 H, broad), 7.62 (s, 2 H); IR (KBr) 3600 m, sh, 3400 w, broad, 3050 m, 2950 s, 2860 s, 1870 m, 1587 s, 1460 s, 1380 s, 1300 s, 1190 s, 1140 m, 972 m, 925 m, 890 m, 860 w, 877 m, 850 m cm^{-1}; UV (MeOH) 420 nm (log ϵ 4.54), 330 (4.07), 280 (4.26); MS Calcd for $C_{43}H_{59}NO_2$, 621.45457; MS Obsd, 621.45350.

Anal. Calcd for $C_{43}H_{59}NO_2$: C, 83.04; H, 9.56; N, 2.25; O, 5.15. Found: C, 82.80; H, 9.42; N, 2.20; O, 5.58.

7b: ^{1}H NMR (CDCl$_3$) δ 1.07 (d, 12 H), 1.25 (s, 18 H), 1.31 (s, 9 H), 1.47 (s, 9 H), 3.21 (septet, 2 H), 4.23 (s, 3 H, broad), 7.07 (s, 2 H), 7.09 (s, 2 H), 7.43 (d, 2 H, broad); IR (CHCl$_3$) 3610 m, sh, 3300 w, broad, 3200 w, broad, 2955 s, 2860 s, 1845 m, 1590 s, 1560 s, 1460 s, 1365 s, 1325 m, 1150 s, 1130 s, 908 s, 890 m, 638 m, 630 m cm^{-1}; MS Calcd for $C_{43}H_{59}NO_2$, 621.45457; MS Obsd, 621.45364.

Anal. Calcd for $C_{43}H_{59}NO_2$: C, 83.04; H, 9.56; N, 2.25; O, 5.15. Found: C, 83.06; H, 9.48; N, 2.14; O, 5.32.

1-(3,5-Diethyl-4-imino-2,5-cyclohexadien-1-ylidene)-2,3-bis-(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropane (1a). In a typical preparation, 0.200 g (0.3 mmol) of the combined mixture of **6a** and **7a** was slurried in 30 mL of benzene in an Erlenmeyer flask under a nitrogen atmosphere. To this slurry was added 0.200 g of lead dioxide, and the reaction mixture was stirred for 30 min. The lead dioxide was then filtered from the brilliant purple solution and the solvent was removed, leaving a metallic golden solid. The product was chromatographed on silica gel (hexane–ethyl ether, 9:1), giving **1a** in quantitative yield: ^{1}H NMR (CCl$_4$) δ 0.92–1.16 (multiplet, 15 H), 1.34 (s, 9 H), 1.40 (s, 9 H), 1.42 (s, 9 H), 2.40 (q, 4 H, broad), 6.18 (d, 1 H, broad), 6.92 (s, 3 H), 7.19 (d, 1 H, broad), 7.24 (d, 1 H, broad), 7.44 (d, 1 H, broad); IR (CHCl$_3$) 2963 s, 2880 w, 1750 m, 1610 s, 1600 s, 1485 m, 1410 m, 1365 m, 1255 m, 1093 s, 905 w, 881 w cm^{-1}; UV (cyclohexane) 539 (log ϵ 5.84), 500 sh (4.25), 280 (4.17); MS Calcd for $C_{41}H_{53}NO_2$, 591.40762; MS Obsd, 591.40682.

1-(3,5-Diisopropyl-4-imino-2,5-cyclohexadien-1-ylidene)-2,3-bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclopropane (1b). 1b was synthesized and purified by the method described for **1a**: ^{1}H NMR (CCl$_4$) δ 0.92 (s, 9 H), 1.08 (d, 6 H), 1.16 (d, 6 H), 1.33 (s, 9 H), 1.38 (s, 9 H), 1.40 (s, 9 H), 2.96 (septet, 2 H, broad), 6.26 (d, 1 H, broad) 7.14 (s, 3 H), 7.30 (d, 1 H, broad), 7.40 (d, 1 H, broad), 7.60 (d, 1 H, broad); IR (CHCl$_3$) 2965 s, 2878 w, 1750 m, 1610 sh, 1593 s, 1484 m, 1409 m, 1364 m, 1254 m, 1093 s, 905 w, 881 w, 810 w cm^{-1}; UV (cyclohexane) 539 nm (log ϵ 4.85), 500 sh (4.57), 280 (4.17).

Anal. Calcd for $C_{43}H_{57}NO_2$: C, 83.04; H, 9.24; N, 2.25; O, 5.47. Found: C, 83.09; H, 9.33; N, 2.14; O, 5.44.

Cyclic Voltammetry. A PAR 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 compound with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte in dichloromethane.

Electron Spin Resonance. About 2 mg of the quinoid compound and a small amount of tetrabutylammonium perchlorate were placed in an electrolytic ESR cell. A small piece of glass wool was placed between the electrodes to slow diffusion, and approximately 0.25 mL of dichloromethane was added as solvent. The cell was thoroughly degassed, and a minimal current necessary for a satisfactory signal was passed through the cell. Identical g values of 2.0027 were obtained for the anion radicals of **1a** and **1b**. The ESR spectra of the anion radicals of **1a** and **1b** are shown in Figures 1 and 2 and are described in the text.

Acknowledgment. We wish to thank Mr. John Jorgensen for stimulating discussions throughout the course of this work. This work was supported by Grants CHE74-01345A02 and CHE76-80374 from the National Science Foundation and by a grant from the 3M Company.

Registry No.—**1a,** 65276-72-4; **1b,** 65338-73-0; **6a,** 65276-73-5; **6b,** 65276-74-6; **7a,** 65276-75-7; **7b,** 65276-76-8; tetrachlorocyclopropene, 6262-42-6; 2,6-di-*tert*-butylphenol, 128-39-2; 2,6-diethylaniline, 579-66-8.

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Synthesis of Morphinandienones, a Dihydrophenanthrone, and Pummerer's Ketones by Anodic Coupling[1]

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Received September 22, 1977

Anodic oxidations of several 1-benzyltetrahydroisoquinolines, laudanosine derivatives, were performed at platinum in acetonitrile containing sodium bicarbonate. Morphinandienones, flavinantine derivatives, were obtained in high yield. Oxidation of 4,4′-dimethoxy-2-methylbibenzyl anodically or with VOF_3 produced a dihydrophenanthrone. The anodic oxidation of several 4-alkylphenols to the corresponding Pummerer's ketones has been investigated, and improved yields are reported using aqueous acetonitrile as solvent and a carbon anode.

We have been interested for some time in the synthetic utility of anodic reactions which couple together activated aromatic rings. In this paper we explore three aspects of such anodic couplings. The first is an intramolecular coupling which produces morphinandienones. An improved procedure which gives very high yields is reported, and several approaches to compounds with the morphine substitution pattern are discussed. Second, the intramolecular coupling of 4,4′-dime-

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