Synthesis and Reactions of a Tetraquinocyclobutane

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Thermal dimerization of the cumulene 5 yields the bright purple tetraquinocyclobutane 3, which is reduced by benzopinacol to the diaryldiquinocyclobutene 4. Reduction of 3 electrolytically or by the dianion of 4 gives a stable anion radical whose electron spin resonance spectrum indicates that the unpaired electron is fully delocalized over the five-ring system. Direct oxidation of 4 proceeds through a neutral monoradical intermediate 9. The ESR spectrum of 9 indicates odd-electron delocalization over three aromatic rings.

The properties of triquinocyclopropanes 1 and their reduction products, diarylquinocyclopropenes (2), have been reported earlier.¹ This paper describes the synthesis and chemistry of four-membered ring analogs to these compounds: the tetraquinocyclobutane 3 [tetrakis(3,5-di-*tert*butyl-4-oxo-2,5-cyclohexadien-1-ylidene)cyclobutane] and the diaryldiquinocyclobutene 4.



Compound 3 is obtained by thermal dimerization of the diquinoethylene $5.^2$ When heated in cyclooctane for 3-4 hr,



5 disappears completely and work-up of the reaction mixture yields 25% of 3 as sparkling purple crystals.³ The tetraquinocyclobutane structure is related to those of 4-radialenes, many of which can similarly by synthesized by dimerization of cumulenes.^{4,5}

In organic solvents 3 gives brilliant purple solutions which show complex electronic spectra in the visible and ultraviolet region (Figure 1). The spectrum of 3 is rather similar to that of the triquinocyclopropanes $1,^1$ but the visible absorptions occur at higher energy for 3.

Molecular models indicate that a planar conformation is possible for 1 but not for 3, and X-ray crystal structure determinations on both compounds confirm this deduction.^{6,7} Compound 1 (R = tert-butyl) is almost planar with an average angle of twist of the six-membered rings of 5.5°. In contrast 3 exists in a propeller-like conformation with an average twist angle of 36°. The central four-membered ring is also distorted from planarity.

As would be expected from the high symmetry of the molecule, the infrared spectrum of 3 is quite simple, showing only ten medium and intense bands, and the ¹H NMR spectrum shows only two singlets in the expected 9:1 ratio.

Although it is stable indefinitely as a solid and in hydrocarbon solutions, 3 reacts with nucleophiles. Solution in methanol results in the addition of 1 mol of methanol to 3. Similarly, if 3 is dissolved in wet N,N-dimethylformamide a water adduct is isolated. Based on ¹H NMR evidence the most likely structures for these adducts are 6a, b. The ex-



pected 1:1:1:1 ratio of *tert*-butyl resonances is observed in the ¹H NMR of the methanol adduct in deuteriobenzene, while the water adduct shows a 2:1:1 pattern.

Although triquinocyclopropanes are reduced to diarylquinocyclopropenes by hydroquinone,¹ 3 does not react at all with hydroquinone. Other conventional reduction techniques (e.g., Zn-HCl, Zn-HOAc) fail because of the reactivity of 3 and 4 with nucleophiles. However, when 3 is refluxed with a slight excess of benzopinacol in cyclooctane the desired diaryldiquinocyclobutene 4 is formed as a bright orange solid. The ¹H NMR of 4 (C_6D_6) shows three types of tert-butyl protons in a 2:1:1 ratio (Figure 2) consistent with the assigned structure. The ¹H NMR spectrum also rules out the possibility of reduction diagonally across the ring to give a bicyclobutane structure, since this would be expected to give two resonances of equal intensity in the tert-butyl region. Although quite stable in the solid state, 4 is oxidized back to 3 by atmospheric oxygen if left in solution for a few hours. This diaryldiquinocyclobutene also exhibits the sensitivity to nucleophiles observed for 3. A gradual change in the electronic spectrum occurs when 4 is dissolved in methanol, the final spectrum showing λ_{max} 460 nm (ϵ 3.87 \times 10⁴). No attempt was made to determine the exact structure of the methanol adduct(s).

The diarylquinocyclopropene analogous to 4, compound 2 (R = tert-butyl), has its electronic absorption at 413 nm in benzene but shows a blue shift to 406 in acetonitrile. This suggests that the ground state of 2 is more polar than



Figure 1. Electronic spectrum of tetraquinocyclobutane 3, 0.1 mM in cyclohexane.

the excited state and is evidence for the importance of the resonance contribution of the cyclopropenium cation in the ground state, as pictured below. The absence of a similar



solvent shift in the spectrum of 4 is evidence that the cyclobutenyl cation or cyclobutadienyl dication does not contribute significantly to the ground state of 4, or anyway no more than to the excited state.

The diaryldiquinocyclobutene 7 was reported⁸ while our work with diaryldiquinocyclobutene 4 was in progress. Compound 7 was synthesized by oxidative dimerization of





Figure 2. Proton magnetic resonance spectrum of 4 in C_6D_6 .

acetylene 8 and appears to have properties similar to those of 4. Compound 7 also reacts with alcohols to form "asymmetric adducts in which alcohol molecules seem to have reacted at one of the double bonds of the molecule".⁸

Deprotonation of 4 to Its Dianion. Spectrophotometric titrations with various bases were attempted in order to convert 4 to its dianion. In acetonitrile with aqueous sodium hydroxide as base, the isosbestic point was lost after about 1 equiv had been added, indicating that reaction was occurring rather than simple deprotonation. Titration with potassium tert-butoxide was similarly unsuccessful. However, when the hindered bicyclic amine, 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN), was used as the base in dry tetrahydrofuran, simple deprotonation was observed to give the turquoise-colored dianion (Figure 3). All intermediate curves pass through two isosbestic points at 522 and 300 nm, implying that the monoanion is not stable with respect to the dianion under the conditions used. To complete the deprotonation an amount of DBN in excess of the theoretical 2 equiv was required, showing qualitatively that 4 is not a very strong acid.

The Anion Radical of 3. Electrolytic reduction of 3 to its anion radical was carried out in tetrahydrofuran (THF). The reduced solution gave an ESR spectrum shown in Figure 4. The nine-line pattern indicates splitting by eight equivalent quinonoid protons, showing that the odd electron is completely delocalized over the four six-membered rings. Delocalization was similarly observed for the analogous triquinocyclopropane anion radical⁹ as well as for the anion radicals of the related diquinoethylene and diquinocyclopropanone.¹⁰ The proton hyperfine splitting constant, 0.43 G, is accounted for by molecular orbital calculations discussed in the accompanying paper.¹⁰ The anion radical of 3 is stable for several days and can be exposed at least briefly to air without decomposition. If degassing is carried out after such exposure, the original nine-line pattern is observed.

To confirm that the species observed by electrolytic reduction of 3 was the anion radical, a solution of 3 plus the same volume of an equimolar solution of the dianion of 4 (prepared by DBN deprotonation) were mixed. The resulting solution showed exactly the same nine-line ESR pattern. The electronic spectrum showed no absorptions due to 3 or the dianion of 4 but gave a new maximum at 615 nm which can be assigned to the anion radical.

The Monoradical of 4. While the anion radical of 3 and the dianion of 4 should be redox intermediates in the tetraquinocyclobutane system under basic conditions, the expected intermediate under neutral conditions would be the monoradical 9 (the protonated anion radical). Two methods were employed to generate 9 in the ESR cavity, both



Figure 3. Spectrophotometric titration of 4 with DBN in THF solvent. Curve 1 shows the spectrum of pure 4. Curve 8 shows the spectrum of 4 in the presence of excess DBN sufficient to convert 4 almost completely to the dianion.



Figure 4. ESR spectrum of the anion radical of 3, showing splitting by eight equivalent protons.

involving partial oxidation of 4. When 4 was treated with PbO_2 in xylene, no signal was observed below 90°, when a weak multiplet appeared. The signal intensity increased as the temperature was raised to 135°, and decreased to the previously observed level when the temperature was lowered. Radical 9 was also generated from 4 in melted naph-



thalene using an equivalent amount of 3 as oxidant. The same pattern and reversible temperature effect was observed up to 180° (Figure 5). These results indicate that 3



Figure 5. ESR spectrum of monoradical 9 formed by comproportionation of 3 and 4, at 100 and 180° in melted naphthalene.

and 4 undergo reversible comproportionation to 9 as shown below. The weakness of the signal shows that the equilibrium lies very far toward 3 and 4 at moderate temperatures.



The ESR spectrum of 9 is a seven-line pattern, with the two outermost lines partially obscured by noise (Figure 5). This indicates hyperfine splitting by six equivalent protons, i.e., delocalization over three of the benzenoid rings. Resonance structures can be drawn (see below) consistent



with delocalization of the odd electron over three (and not four) rings, but only two of the rings are equivalent. Evidently accidental equivalence accounts for the equal splitting by six protons and the odd-electron density is too small in the fourth ring to cause observable splitting.

Scheme I summarizes the intermediates in the $3 \rightleftharpoons 4$ redox systems and the relationships between them.

Scheme I



Experimental Section

General Procedures. Hydrocarbon and ether solvents were freshly distilled from Na-K alloy or LiAlH₄, respectively, before use. Combustion analyses were performed by Alfred Bernhardt, Engelskirchen, West Germany. All melting points are uncorrected.

Spectra were recorded by means of the following instruments: infrared, Perkin-Elmer 457 or Beckman IR-33; proton NMR, Varian A-60A or Jeol JNM-MH-100; mass spectra, AEI-MS 902 at 70 eV; ultraviolet-visible, Cary 14; ESR, Varian 4502-13. ESR electrolysis experiments were carried out using a 300-V battery source with the current kept at <0.1 μ A. The g values of all observed radicals were measured using double-cavity technique and potassium nitrosyldisulfonate (Fremy's salt) as a standard.

Synthesis of Tetraquinocyclobutane 3. Compound 5 (0.30 g, 0.70 mmol) in 20 ml of cyclooctane was heated to boiling under nitrogen for 3.5 hr. The cyclooctane was vacuum distilled to a volume of 1-2 ml, 10-15 ml of dry hexane was added, and the solution was filtered through a sintered glass funnel and washed with 5-10 ml of hexane. This solution was concentrated to about 10 ml and cooled. Two crops of crystals were collected in good purity, totaling 51 mg (17%). Mother liquors from several such syntheses were combined and chromatographed on Florisil eluting with hexane and hexane-ether mixtures to yield further product after recrystallization (to about 25% total yield): mp 267°; ¹H NMR (CDCl₃) δ 1.33 (72 H), 7.45 (8 H); ir (CHCl₃) 2950 (s), 2850 (s), 1630 (m, br), 1450 (s), 1357 (m, doublet), 1260 (m), 1110 (m), 1018 (m), 915 (w, sh), 910 (m), 865 cm⁻¹ (m); uv-visible λ_{max} (cyclohexane) 240 nm (log \$\epsilon 4.07), 280 (4.03), 325 sh (4.18), 371 sh (4.82), 389 (4.87), 455 (4.03), 485 (4.28), 535 (4.48), 570 (4.50), 595 (4.35). Calcd for C60H80O4: m/e 864.6056. Found: 864.6056.

Anal. Calcd for $C_{60}H_{80}O_4$: C, 83.28; H, 9.33; 0, 7.40. Found: C, 83.13; H, 9.30; O, 7.42.

Methanol Adduct of 3 (6a). 3 (100 mg) was dissolved in 100 ml of anhydrous methanol and refluxed for 3 hr. Evaporation of methanol followed by ¹H NMR of the crude solid in deuteriobenzene showed essentially quantitative conversion. Recrystallization from dry hexane gave red-purple crystals: mp 175°; ¹H NMR (C₆D₆) δ 1.25 (18 H), 1.31 (18 H), 1.35 (18 H), 1.41 (18 H), 3.05 (3 H), 4.91 (1 H), 7.70–7.78 (8 H); ir (CHCl₃) 3618 (w) and 1600 cm⁻¹ (vs); uv-visible λ_{max} (CHCl₃) 227 nm (log ϵ 4.26), 285 (4.23), 303 sh (4.04), 352 sh (4.29), 370 sh (4.56), 389 (4.71), 538 (very broad, 4.47).

Anal. Calcd for $C_{61}H_{84}O_5{:}$ C, 81.63; H, 9.45; O, 8.92. Found: C, 81.48; H, 9.54; O, 8.98 (diff).

H₂O Adduct of 3 (6b). A solution of 54 mg of 3 in 35 ml of N,N-dimethylformamide and 0.5 ml of H₂O was heated to 120° for 0.5 hr, then stirred at room temperature for several days. TLC showed essentially quantitative conversion of 3 to the deep bluepurple 6b. Ether was added and the solution was washed with water several times, dried (MgSO₄), filtered, and evaporated. Recrystallization from hexane-ether gave sparkling irridescent purple crystals: ¹H NMR (C₆D₆) δ 1.26 (36 H), 1.28 (18 H), 1.63 (18 H), 6.92 (8 H), 7.25 (1 H), 8.07 (1 H); ir (CHCl₃) 3618 (w), 1582 cm⁻¹ (vs); uv-visible λ_{max} (CHCl₃) 300 nm (log ϵ 4.11), 335 (4.33), 563 sh (4.76), 587 (4.82).

Anal. Calcd for $C_{60}H_{82}O_5$: C, 81.58; H, 9.36; O, 9.06. Found: C, 81.45: H, 9.26; O, 8.93.

Attempted Dimerization of 10. At present 3 is the only tetraquinocyclobutane known. Repeated attempts were made to dimerize diquinoethylene 10,¹¹ but decomposition invariably occurred



without formation of the desired tetraquinocyclobutane. Reactions were monitored by TLC and were allowed to proceed until complete decomposition was observed. Except for the melting point tube experiment, the reactions were carried out in red-tinted glassware to minimize contact with light. None of the following methods gave any indication of tetraquinocyclobutane formation: (1) melting solid 10; (2) thermolysis of 10 in a sealed melting point capillary in dry decalin; (3) thermolysis of 10 in refluxing benzene in the presence of a small amount of PbO₂; (4) thermolysis of 10 in refluxing cyclooctane in the presence of a small amount of hydroquinone; and (5) thermolysis of 10 in refluxing cyclooctane in the presence of a catalytic amount of AlCl₃.

Reduction of 3 to 4. Compound 3 (365 mg, 0.42 mmol) and 157 mg (0.46 mmol) of benzopinacol were refluxed in 80 ml of dry cyclooctane under nitrogen for 45 min. About half the solvent was distilled off just above room temperature under vacuum. The reaction was allowed to cool and settle overnight. After the addition of 10–15 ml of dry hexane, the orange precipitate (257 mg, 70%) was collected under nitrogen, washed with 15 ml of dry hexane, and al-

lowed to dry overnight. The product gave the following spectral data: ¹H NMR (C₆D₆) § 1.28 (36 H), 1.30 (18 H), 1.51 (18 H), 5.16 (2 H), 7.37 (4 H), 7.67 (2 H), 7.86 (2 H); ir (CCl₄) 3600, 3550, 1600, 1580 cm⁻¹; mass spectrum m/e 866 (M⁺), 851, 824, 809, also minor peaks at 884 (M + H₂O), 890 (3 + 2H₂O); uv-visible λ_{max} (CCl₄) 265 nm (log e 3.51), 387 (4.63), 404 sh (4.56), 440 sh (4.41). Calcd for C60H82O4: m/e 866.6213. Found: 866.6206.

Electron Spin Resonance Experiments. Anion Radical of 3. A few milligrams of 3 with a small amount of $(n-Bu)_4N+ClO_4^-$ was placed in an electrolytic cell. A small piece of glass wool was placed between the electrodes to slow diffusion. The cell was evacuated and THF (distilled from LiAlH₄, stored over Na-K anthracene) was distilled into the cell. The solution was degassed twice and the cell was placed in the ESR cavity. A minimal current was passed through the cell and scanning was begun.

The best spectrum was obtained by electrolytic reduction at room temperature of a sample which had been reduced several times before, and observation at 0° using the line-sharpening technique devised by Glarum.¹² The spectrum showed $a_{\rm H} = 0.33$ G and g = 2.0054, with a ratio of line intensities 70:55.6:28.3:9.1 (calcd for nine lines 70:56:29:8).

Monoradical of 4 (9). 3 as Oxidizing Agent. 3 (8.2 mg), 8.7 mg of 4 (1:1 molar ratios), and 2 g of naphthalene were ground together in a mortar and pestle and a small amount of this mixture was placed in an ESR cell. The cell was twice alternately evacuated and flushed with nitrogen, leaving 1 atm of nitrogen in the cell. (A previous experiment showed this technique was necessary to prevent loss of resolution and signal level.) No signal from this solid mixture was evident at room temperature or until it melted at about 90°. A weak five- or seven-line pattern was then observed and better resolved with the line-sharpening technique devised by Glarum.¹² The signal level increased (reversibly) with temperature up through 180°. The sample was opened to the air momentarily at 140 and 170° (with no loss of signal) to prevent undue build-up of pressure.

PbO₂ as Oxidizing Agent. 4 (6 mg) and 2 mg of PbO₂ were weighed together and manually mixed with a spatula. Approximately ½ of this mixture was placed in an ESR cell with about 1 ml of dry xylene. The cell was degassed twice and then nitrogen was added. A weak signal (like the signal observed with 3 as oxidizing agent) was observed at 90°. As the temperature was increased, the signal level increased reversibly up to 135° (bp of xylene 137-140°).

In both this experiment and the previous one, $a_{\rm H} = 1.17$ G, g =2.0051, with a ratio of line intensities 20:14.5:5.7:1.2 (calcd for seven lines, 20:15:6:1).

Base Titrations of 4. NaOH-CH₃CN Titration. A 0.04 N NaOH solution and a 300-ml solution of 52 mg of 4 in CH₃CN were used; 0.5-ml aliquots of base were added to the CH₃CN solution of 4, and samples were withdrawn for uv-visible spectrum and returned after each addition. After the addition of about 1 equiv, the isosbestic point was lost and the spectrum changed, indicating that reaction had taken place.

Potassium tert-Butoxide-THF Titration. A solution of 20.3 mg of 4 in 300 ml of dry THF was titrated with a solution of 122.2 mg of potassium tert-butoxide in 100 ml of dry THF, as previously described. After addition of about 1 equiv of base the isosbestic was again lost. Evidently 4 also reacts with tert-butyl alcohol.

DBN-THF Titration. A solution of 22.7 mg of 4 in 300 ml of dry THF was titrated with 21.6 mg of DBN in 100 ml of THF using the same procedure. This time the isosbestic points at 522 and 300 nm persisted throughout the titration. After 2 equiv of base had been added, the new dianion peak stopped growing appreciably but the absorption due to 4 continued to diminish slightly after each addition even after five times the theoretical amount was added. The dianion has λ_{max} 640 nm (log ϵ 4.80), 393 (3.41), 370 (3.43). After standing overnight, the solution gave an altered spectrum, e.g., the main band was weaker and appeared at 630 nm instead of 640 nm indicating that the DBN-H⁺ salt of the dianion is not indefinitely stable.

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Registry No.-3, 34879-70-4; 3 radical ion, 55255-32-8; 4, 55255-35-1; 5, 14106-40-2; 6a, 55281-78-2; 6b, 55255-36-2; 9, 55255-37-3; 10, 55255-31-7.

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Synthesis of Heterofulvenes—Derivatives of 9-Alkylenexanthenes by the Friedel-Crafts Reaction, Accompanied by Halide Exchange

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11-Chloro- and 11-bromo-9-alkylenexanthenes can be prepared from aromatic ethers and 2-haloacyl chlorides in the presence of aluminum halides. In some cases, halide exchange occurs between the haloacyl compounds and the aluminum halides. Occasionally, intermediate ketones are obtained and can be transformed to the final products by heating with phosphorus oxychloride or polyphosphoric acid. 9-Methylenexanthenes can be similarly synthesized.

9-Alkylenexanthenes, such as 13, are π -isoelectronic with the corresponding thioxanthenes and dibenzoheptafulvenes,^{1,2} and consequently are of both biological and theoretical interest. In fact, it has been suggested that the 9alkylenexanthenes are more "heptafulvenic" in nature than the dibenzoheptafulvenes.^{3,4} Only one general approach to the synthesis of these olefins exists to date, namely, the reaction of xanthen-9-one with Grignard reagents, followed by dehydration.⁵ However, this and the Wittig reaction⁶

were found unsatisfactory for the preparation of 9-methylenexanthene.

We would like to report a convenient procedure for the synthesis of 9-alkylenexanthenes, such as 13 or 25, using the aluminum halide catalyzed condensation of aromatic ethers 1-4 and acyl chlorides⁷ illustrated in Scheme I. This approach is especially suited for the preparation of 11-chloro- and 11-bromo-9-alkylenexanthenes 13-23. Halide exchange between the 2-haloacyl compounds 5-9 or 12 and