

Attempted Synthesis of a Stable, Quintet, Tetraphenoxy Tetraradical: Facile Rearrangement of a Substituted Bicyclobutane

Kraig K. Anderson, David A. Shultz, and Dennis A. Dougherty*

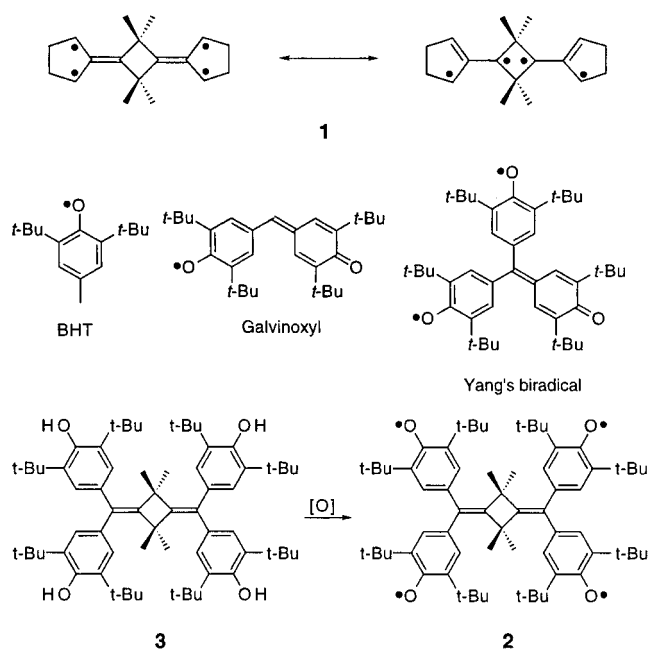
Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125

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The preparation of tetraphenol **3** and its attempted oxidation to tetraradical **2** are described. Tetraphenoxy **2** was envisioned as a more stable analog of the previously reported, quintet tetraradical **1**. However, EPR studies on **3** and model compounds and crystallographic characterization of the product from oxidation of **3** suggest that **2** is not a viable target. Apparently, **2** or an intermediate in the multistep oxidation path leading to it undergoes a ring closure to a bicyclobutane. The bicyclobutane, in turn, undergoes a surprisingly facile rearrangement to the analogous butadiene structure.

The preparation of room-temperature stable, high-spin organic polyradicals is intrinsically interesting and challenging and plays an important role in long-range efforts toward organic magnetic materials.¹ Previously, this group has described a quintet tetraradical (**1**) that incorporates both trimethylenemethane (TMM) and cyclobutanediyl aspects in its resonance structures.^{2,3} The generation of **1** is nontrivial, however, requiring the construction and photolysis in solid matrix of an appropriate bisdiazene precursor. Additionally, tetraradical **1** is not stable in fluid media. Inspired by stable radicals such as BHT, galvinoxyl,^{4–16} and Yang's biradical,^{17–21} we anticipated that the tetraphenoxy radical, **2**, obtained by oxidation of tetraphenol **3**, might be stable and more

easily generated than the (magnetically) topologically equivalent tetraradical **1**.



It also seemed possible that tetraradical **2** could close to form substituted bicyclobutane biradical **4**, by analogy with observations of Hünig et al. in similar closed-shell systems.^{22–26} If so, it might be possible to observe “magneto-optical switching” between the ring-opened tetraradical **2** and the ring-closed biradical **4**, a process this group has demonstrated previously^{27–30} with the triplet biradical **5**.

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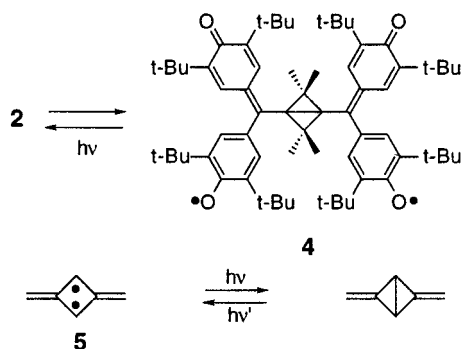
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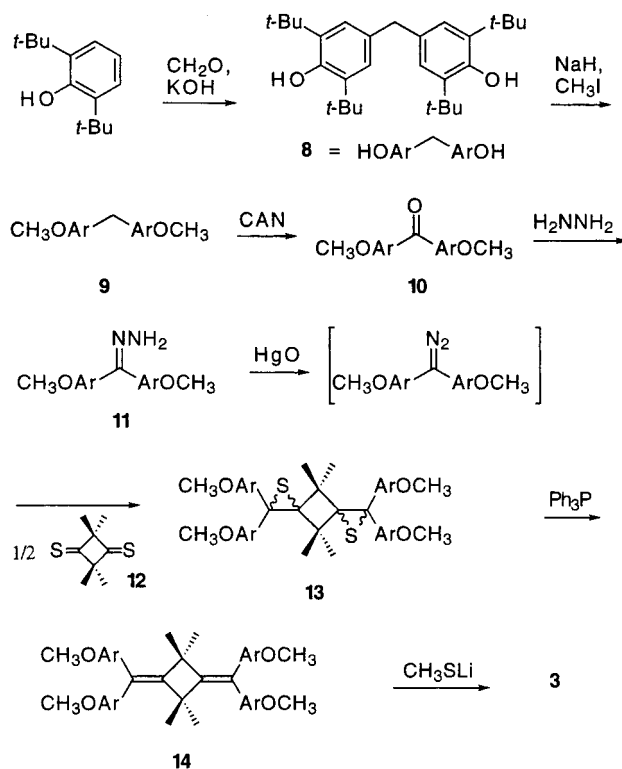
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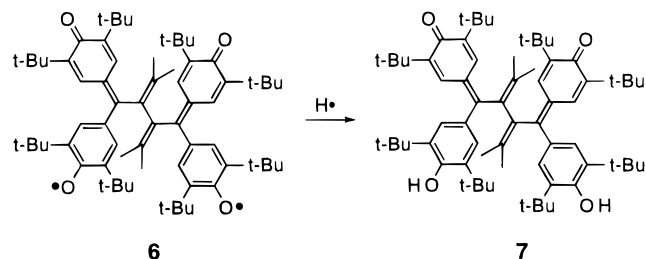
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Scheme 1. Synthesis of Tetraphenol 3



We now report that the major isolated product from the oxidation of **1** is the bisgalvinoxyl **6**, indicating the formation of bisgalvinoxyl **6**. These products signal a rearrangement that must involve an unstable bicyclobutane intermediate such as **4**. While the bicyclobutane-to-butadiene rearrangement is known, it occurs for unsubstituted bicyclobutane at $\sim 200^\circ\text{C}$ ³¹ and for Hünig's substituted bicyclobutanes at $\sim 40^\circ\text{C}$.^{22–26} In the present system, however, it occurs readily at room temperature and may occur at temperatures as low as -78°C —a remarkable rate enhancement.



Target Structures and Synthetic Strategies

Tetraphenol **3** was obtained on a multigram scale in 7% overall yield (based on 2,6-di-*tert*-butylphenol) as shown in Scheme 1. Bisphenol **8** was obtained in 64% yield by coupling 2,6-di-*tert*-butylphenol with CH_2O using KOH in 2-propanol.³² The phenol was protected as a methyl ether, giving bisanisole **9** in 36% yield.³³ Despite the low yield and the subsequent difficulty of deprotection, this step was necessary, as other protecting groups did not survive the rest of the sequence. Bisanisole **9** was then oxidized with $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ to give benzophenone **10** in 74% yield.³⁴ Formation of hydrazone **11** in 95% yield was accomplished with anhydrous H_2NNH_2 .^{35,36} In the key step,^{22,35–38} the substituted diazomethane, prepared *in situ* by oxidation of **11** with activated mercuric oxide,³⁹ was added to 2,2,4,4-tetramethylcyclobutanedithione (**12**) to give bisepisulfide **13** in 75% yield on the basis of hydrazone **11**. Desulfurization was accomplished by reflux with triphenylphosphine to give

tetraanisole **14** in 95% yield.²² In the final step, heating the tetraanisole at 85°C in a 1.5 M CH_3SLi /HMPA solution for 10 days removed the methyl ether protecting groups, giving tetraphenol **3** in 60% yield.⁴⁰ Tetraphenol **3** is a white solid, sparingly soluble in THF, benzene, and chlorinated solvents, and apparently immune to significant air oxidation, even when heated to 360°C in a melting point apparatus.

Phenols **15** and **19** (see Schemes 2 and 3) were designed and synthesized to help explain some of the initially puzzling oxidation/EPR results of phenol **3**. Their syntheses were straightforward. Both are white solids, freely soluble in most organic solvents, but sensitive to oxygen—a sample of white powder turned yellow after a few minutes in air.

Results and Discussion

A variety of chemical oxidants, including $\text{K}_3\text{Fe}(\text{CN})_6$, I_2 , activated nickel peroxide, 2,3-dichloro-5,6-dicyanobenzoquinone, PbO_2 , and AgO , were used in this study.^{17–21,41} Representative experimental⁴² and computer-simulated⁴³ EPR spectra are shown in the figures. We begin with a description of the reference compounds **15** and **19**.

The room-temperature EPR spectrum obtained from phenol **15** (Figure 1) upon oxidation with PbO_2 is composed of 15 lines and is 28 G wide. Computer simulation⁴³ of hyperfine splitting produced a similar, though not precisely superimposable, spectrum, by considering two meta hydrogens, $a_{\text{H}} = 1.7\text{ G}$, and six allylic

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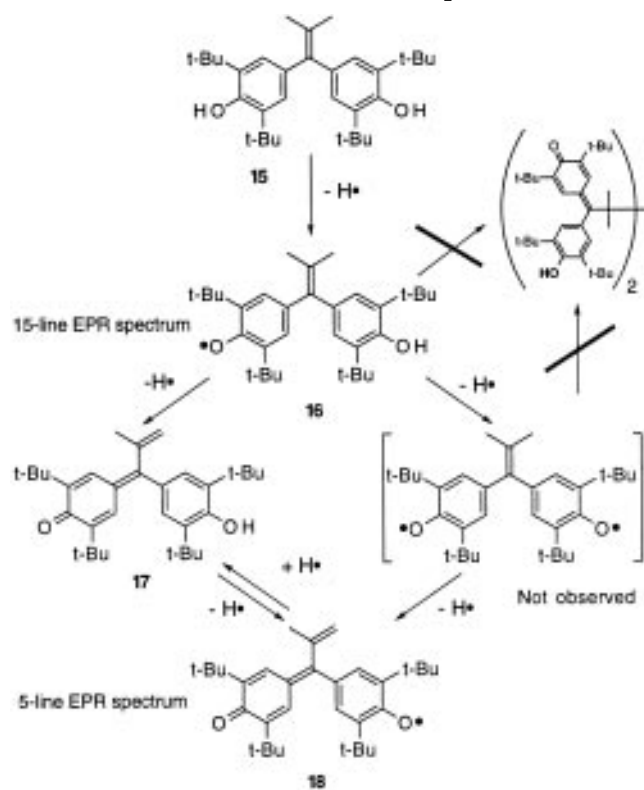
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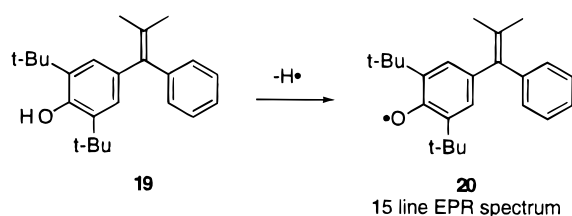
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Scheme 2. Oxidation of bisphenol 15



Scheme 3. Oxidation of 19



hydrogens, $a_H = 3.1$ G.⁴⁴ Aromatic couplings in the 1.6–1.9 G range are indicative of simple phenoxyl radicals. Frozen matrix spectra at 77 K gave a single line 17.5 G wide (not shown, see Figure 7 for representative spectrum), with no sign of a $\Delta m_S = 2$ transition or any other indications of higher than a doublet spin state.

The behavior of phenol 15 upon oxidation with $K_3Fe(CN)_6$ under basic, biphasic conditions was more complex. Aliquots of the organic layer were separated after 5–10 min of oxidation and frozen at 77 K until spectra were taken. These gave spectra similar to those from the PbO_2 oxidation. However, samples taken after 30 min of oxidation gave a 5-line spectrum (Figure 2), consistent with a galvinoxyl-type doublet radical split by four meta hydrogens, $a_H = 1.35$ G.^{4–16} The spectrum in frozen matrix was composed of a single line 10.9 G wide, with no sign of a $\Delta m_S = 2$ transition or any other indications of higher than a doublet spin state. Samples that generated the 15-line spectrum did not transform into the 5-line spectrum when isolated from the oxidant. The behavior of phenol 15 upon oxidation with AgO was similar. Room-temperature spectra taken after 1 h exhibited the 15-line spectrum, which transformed over 24 h (in contact with the oxidant) into a 5-line spectrum (not shown).

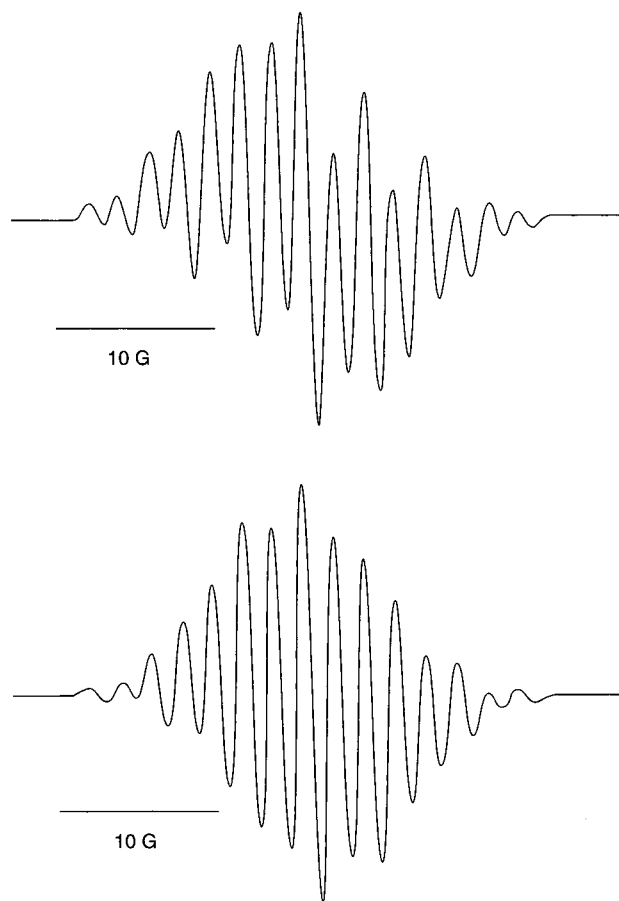


Figure 1. EPR Spectra (15-line). Top: **15** oxidized by PbO_2 . The spectrum is centered at 3400 G. Bottom: computer simulation⁴³ using 2H, $a_H = 1.7$ G, and 6H, $a_H = 3.1$ G.⁴⁴

Phenoxyl radical **16** (Scheme 2), obtained by partial oxidation of phenol **15**, is the likely source of the observed 15-line spectrum. The 5-line galvinoxyl-type spectrum obtained after prolonged oxidation could be due to either a dimer or to galvinoxyl **18**. Since the only galvinoxyl isolated after the reaction is **17**, which generates the previously observed 5-line spectrum upon reoxidation, the original 5-line spectrum is assigned to **18**. One possible path from **15** to **18** involving disproportionation (not shown) is contradicted by the fact that the 15-line phenoxyl spectrum does not transform into the 5-line spectrum in the absence of oxidant. This suggests that oxidation of the second phenol is necessary for abstraction of one of the allylic hydrogens or occurs after the galvinoxyl intermediate is generated. No evidence of triplet spin was observed, nor any hyperfine that could be assigned to a biradical. Thus, if a biradical were produced, it is either a strong ground state singlet or has a short lifetime. This leaves two possible mechanisms: formation of the biradical which rapidly loses an allylic hydrogen or loss of an allylic hydrogen from **16** to give the galvinoxyl **17** which is then further oxidized. The room-temperature EPR spectra from phenol **19** (Figure 3) upon oxidation with either PbO_2 or AgO are identical and consist of 26 G wide, 15-line spectra that are similar to the 15-line spectra obtained from oxidation of **15**. Computer simulation⁴³ of hyperfine splitting showed that a similar, though not precisely superimposable spectrum could be generated from two meta hydrogens, $a_H = 1.6$ G, and six allylic hydrogens, $a_H = 2.9$ G.⁴⁴ Frozen matrix spectra at 77 K gave a single line 20.5 G wide. The

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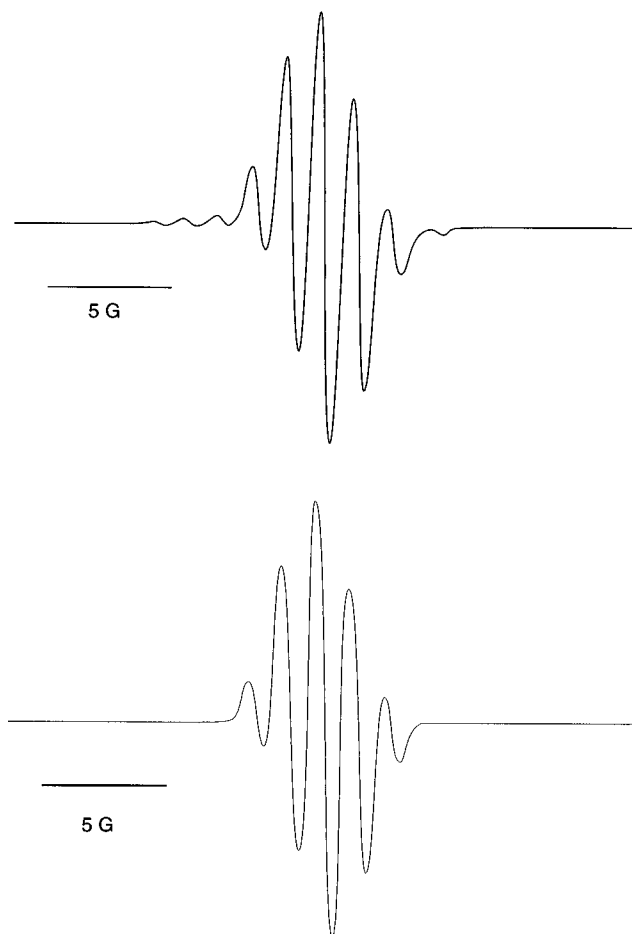


Figure 2. EPR spectra (5-line). Top: **15** after 30 min biphasic $\text{K}_3\text{Fe}(\text{CN})_6/\text{NaOH}$ oxidation. The spectrum is centered at 3400 G. Bottom: computer simulation⁴³ using 4H, $a_{\text{H}} = 1.35$ G.⁴⁴

behavior of phenol **19** upon oxidation with $\text{K}_3\text{Fe}(\text{CN})_6$ under basic, biphasic conditions⁴¹ is again more complex. Aliquots of the organic layer were separated after 5–10 min of oxidation and frozen at 77 K until spectra were taken. These gave a 15-line, 26 G wide spectrum at room temperature that was qualitatively identical to those produced by the PbO_2 and AgO oxidations. However, room-temperature samples taken after 45 min of oxidation gave weak, broadened 3-line spectra (not shown) consistent with a phenoxyl doublet radical split by two meta hydrogens, $a_{\text{H}} = 1.9$ G.⁴⁴ Samples that generated the 15-line spectrum did not transform into the 3-line spectrum when isolated from the oxidation reaction.

Clearly, phenoxyl radical **20**, obtained by oxidation of phenol **19** (Scheme 3), is the source of the 15-line spectrum, with the unpaired electron being split by the two meta hydrogens and the six allylic hydrogens. The latter indicates that spin density is not localized completely to the phenoxyl ring. The weak 3-line spectrum observed after prolonged biphasic oxidation with $\text{K}_3\text{Fe}(\text{CN})_6$ is likely due to a decomposition product of **20**. The 77 K EPR spectrum consists of a simple doublet signal, as expected.

Initial attempts to oxidize tetraphenol **3** under a wide variety of conditions were frustrating. Oxidation either alone in 2-methyl-THF or after exposure to base (biphasic with aqueous KOH, organolithiums, metal hydrides, or pyridine solvent) gave room-temperature spectra composed of 3 lines (Figure 4) consistent with an isolated phenoxyl doublet radical split by two meta hydrogens,

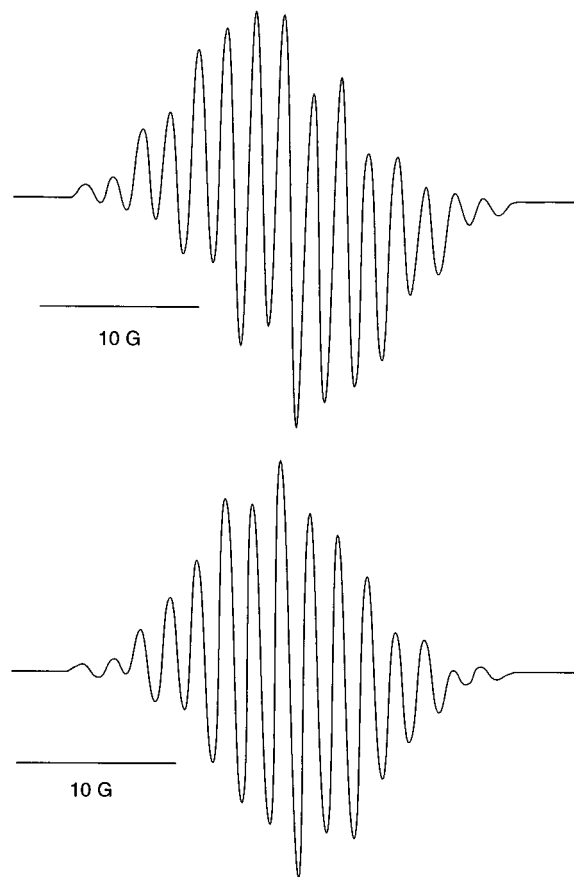


Figure 3. EPR spectra (15-line) from phenol **19**. Top: **19** oxidized by PbO_2 . The spectrum is centered at 3400 G. Bottom: computer simulation⁴³ using 2H, $a_{\text{H}} = 1.6$ G, and 6H, $a_{\text{H}} = 2.9$ G.⁴⁴

$a_{\text{H}} = 1.7$ G.⁴⁴ Frozen matrix spectra at 77 K are composed of a single line 7.2 G wide, with no sign of a $\Delta m_s = 2$ transition.

Unsuccessful attempts to perform hydrogen–deuterium exchange on the phenolic protons of **3**, even while using strong bases, suggested that the anions of **3** were much less soluble than those of model compounds **15** and **19**. The use of a milder base with a soluble organic counterion, tetrabutylammonium hydroxide,^{45,46} showed immediate results. Tetrabutylammonium hydroxide was able to solublize **3** in many solvents. The concomitant rapid development of a deep blue color suggested that deprotonated **3** was easily air-oxidized, as are **15** and **19** when exposed to more conventional bases. Further experiments with tetrabutylammonium hydroxide demonstrated that all four phenol protons of **3** could be exchanged for deuterium or trimethylsilyl groups.

Oxidation of **3** with varying amounts of I_2 in the presence of stoichiometric or excess amounts of tetrabutylammonium hydroxide/MeOH showed markedly different behavior from attempts without this base (Figure 5). At less than 1 equiv of oxidant, the room-temperature EPR spectrum displays the same isolated phenoxyl spectrum as before. Between 1 and 3 equiv, the simple 3-line spectrum is again exhibited, but other lines are beginning to emerge. At slightly more than 4 equiv, a 5-line spectrum is observed, consistent with a galvinoxyl-

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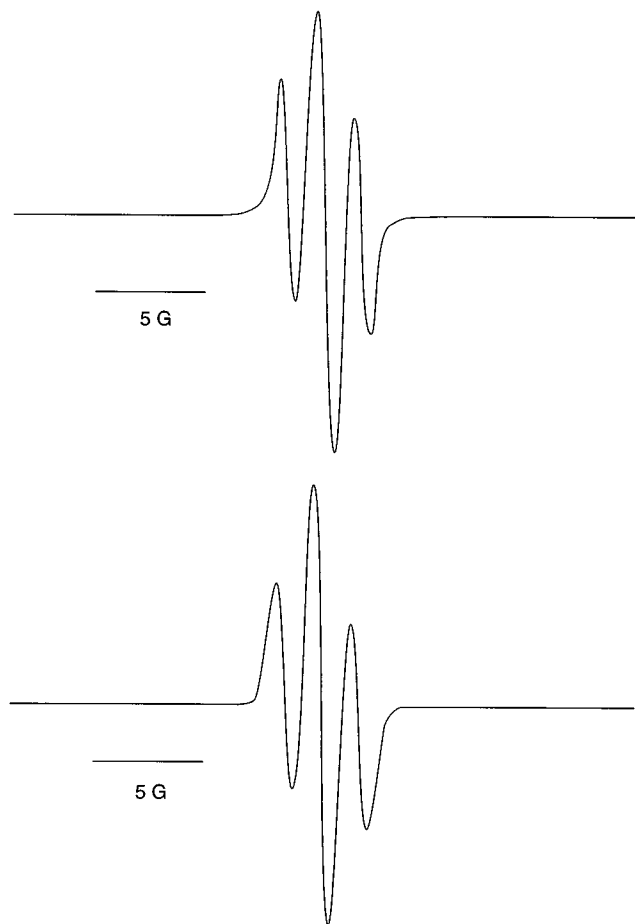


Figure 4. Typical EPR spectra obtained by oxidation of tetraphenol **3** without tetrabutylammonium hydroxide. Top: **3** oxidized by AgO. The spectrum is centered at 3400 G. Bottom: computer simulation⁴³ using $2H$, $a_H = 1.7$ G.⁴⁴

type radical split by four meta hydrogens.^{4–16,44} Addition of a large excess of I_2 resulted in a weakened spectrum with 3 prominent lines (Figure 6), similar to that observed in the overoxidation of **15** and **19**. The smaller shoulders in this spectrum indicate the presence of another species exhibiting 5 lines. Spectra at 77 K for these samples indicated only a doublet spin state (Figure 7). Oxidation of **3** with excess amounts of strong oxidants (AgO , PbO_2) led to no EPR signal although reaction did occur, as evidenced by the appearance of a deep blue color.

We were greatly encouraged by the iodine oxidations, despite the fact that the 77 K spectra (Figure 7) indicated only a doublet spin state, since we thought it possible that this signal was due to a bicyclobutane species such as **4**. If this were the case, it might be possible to break the central bond of the bicyclobutane by irradiation. Exposure of the EPR sample to a variety of wavelengths, however, did not change the 77 K spectra.

Anticipating possible rearrangement of the bicyclobutane at elevated temperatures,^{22–26,31} the base-assisted oxidation was conducted on a preparatory scale in a dry ice bath and at reduced temperature in the EPR cavity. Both yielded results essentially identical to the room-temperature studies.

The product from quenching either the low-temperature or room-temperature oxidation of tetraphenol **3** gave a complicated 1H NMR spectrum (Figure 8), no doubt due in part to the number of rotomers possible. Some

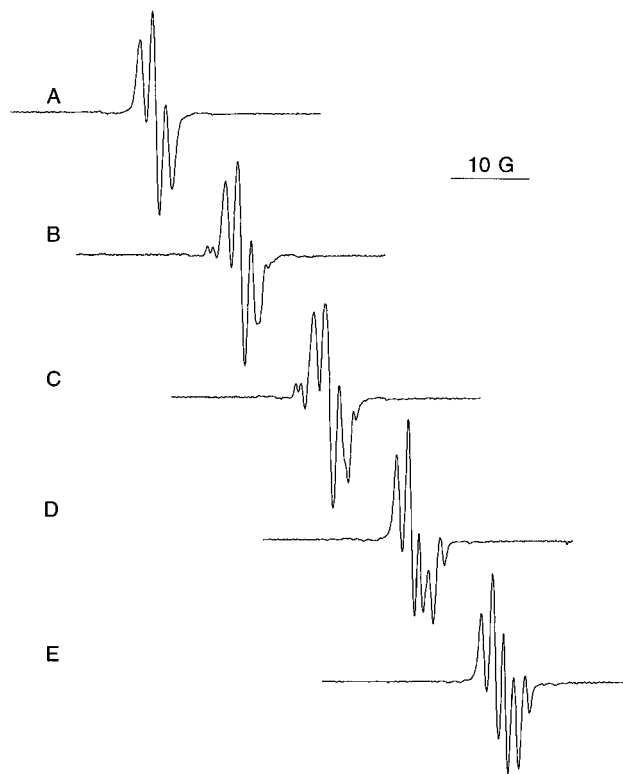


Figure 5. Tetraphenol **3** and excess tetrabutylammonium hydroxide after n equiv of oxidant: **A**, $n < 1$; **B**, $n = 1$; **C**, $n = 2$; **D**, $n = 3$; **E**, $n > 4$. The spectra are centered at 3400 G.

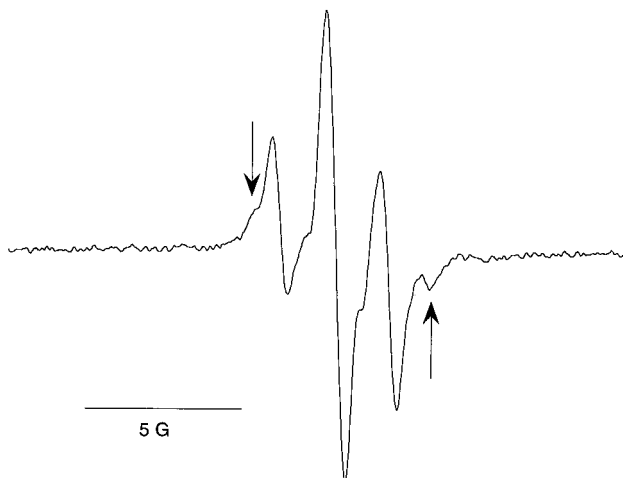


Figure 6. Tetraphenol **3**, excess tetrabutylammonium hydroxide, and excess I_2 . The spectrum is centered at 3475 G.

coalescence could be seen in toluene- d_8 at 100 °C. A spectrum taken in LiOD/acetone- d_6 showed only six singlets. Both the base treatment and the variable temperature behavior were reversible.

None of these spectra nor IR, UV/vis, or mass spectrometry allowed us to readily distinguish between the two likely products: the bicyclobutane bisgalvinol derived from **4** or the diene bisgalvinol **7**. A single crystal of the product, recrystallized from methanol, was submitted to X-ray analysis, definitively assigning the structure to the ring-opened bisgalvinol **7** (Figure 9). Though Hünig's substituted bicyclobutanes are reported to ring-open in hot, polar solvents,^{22–26} the methanol recrystallization is not responsible for the rearrangement here since unheated product displays the same NMR spectra.

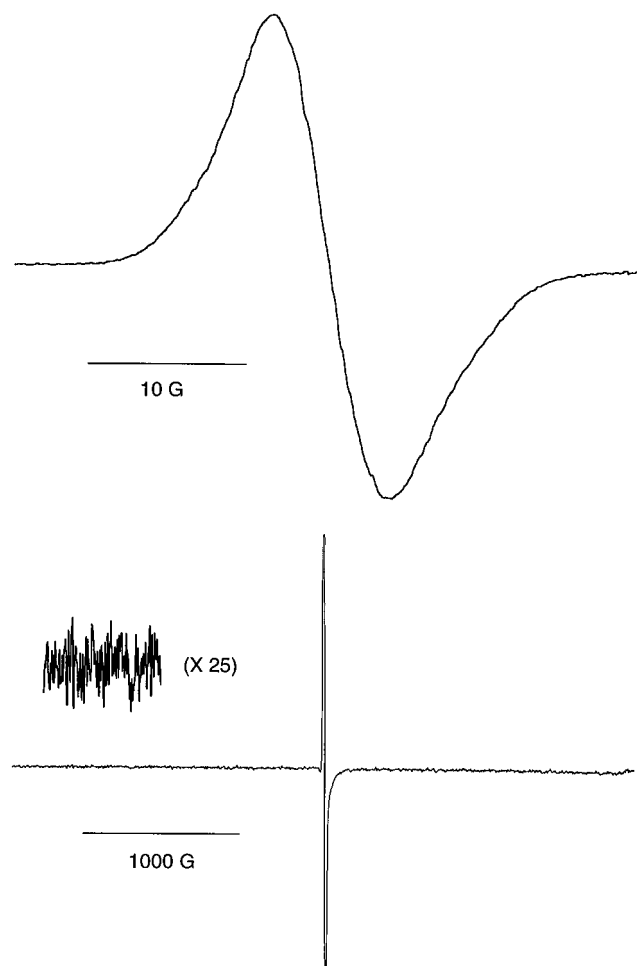


Figure 7. Representative spectra for all 77 K EPR-active species—actual sample is that of Figure 5a. Top: 40 G scan. Bottom: 4000 G scan. Note lack of signal in $\Delta m_S = 2$ region at half-field. The spectrum is centered at 3282 G.

The EPR spectra of purified **7** are interesting. Partial oxidation results in a 5-line spectrum (Figure 10) with $a_H = 1.4$ G, characteristic of a monogalvinoxyl (this splitting is identical to that seen in Figure 5E). For the biradical, it might be expected that $J \gg a_H$, in which case the triplet would be split by all eight aryl protons, resulting in 9 lines with splitting equal to $\frac{1}{2}a_H$ of the monoradical or ~ 0.7 G.^{5,6,8,47} Full oxidation of **7**, however, results in a 5-line spectrum with broadened, unequally spaced lines (Figure 11). This behavior is consistent with J modulation.^{48,49} In a biradical such as **6**, J could be modulated by conformational changes, leading to selective line broadening. In **6**, lines at $\pm \frac{3}{2}a_H$ and $\pm \frac{1}{2}a_H$ from the center (lines 2, 4, 6, and 8 of the 9-line spectrum) are broadened so much that they are not resolved, leaving the observed 5-line spectrum. These 5 lines should have the same splitting as the monoradical, but overlap with the broadened lines causes their apparent positions to shift toward the center. The inner pair experience nearly balanced overlap from the two pairs of broadened lines, resulting in only a slight shift, while the outer pair

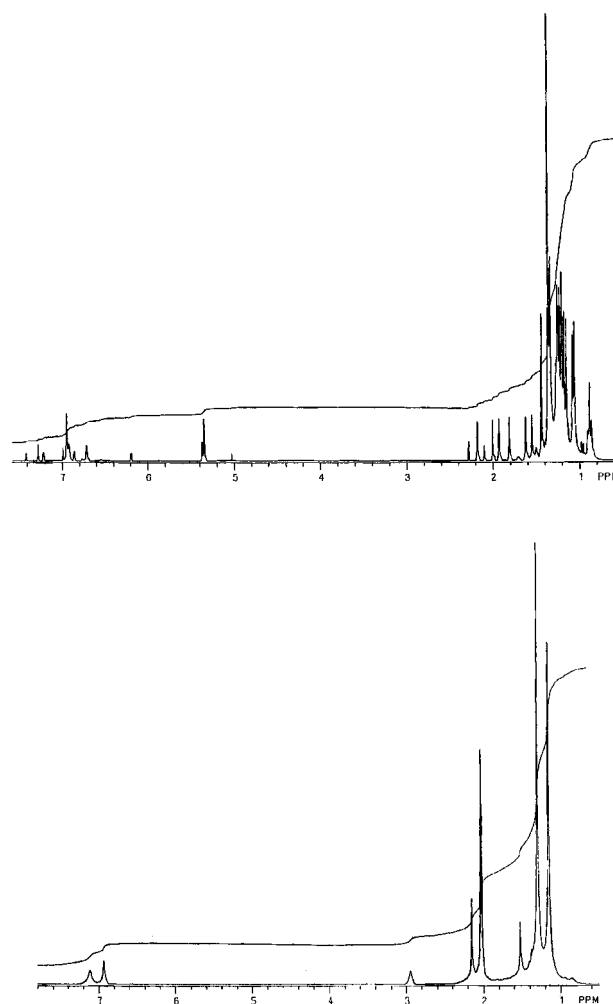


Figure 8. ^1H NMR spectra (300 MHz) of bisgalvinoxyl **7**. Top: **7** in CDCl_3 . Bottom: **7** with slight excess of LiOD in acetone- d_6 .

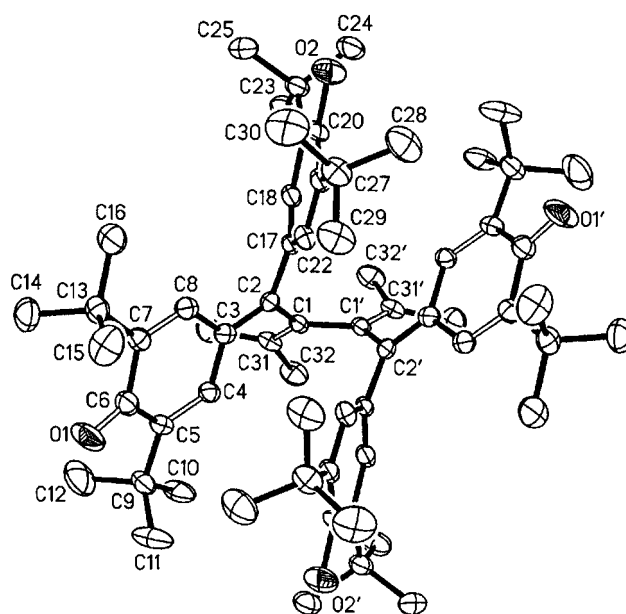


Figure 9. X-ray structure of bisgalvinoxyl **7**.

overlaps with only one pair of broadened lines, resulting in the observed splitting of 1.15 G.

Spectra taken at 77 K for these samples show that the partially oxidized sample has a strong doublet signal (not

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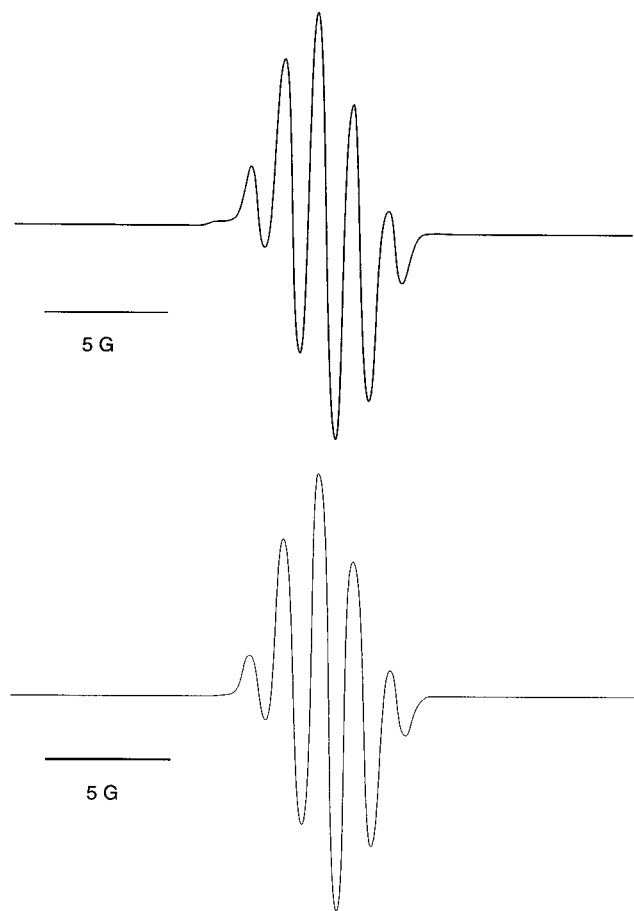


Figure 10. EPR spectra (5-line) from partial oxidation of bisgalvinol **7**. Top: **7** oxidized by PbO_2 . The spectrum is centered at 3400 G. Bottom: computer simulation⁴³ using $4H$, $a_H = 1.4$ G.⁴⁴

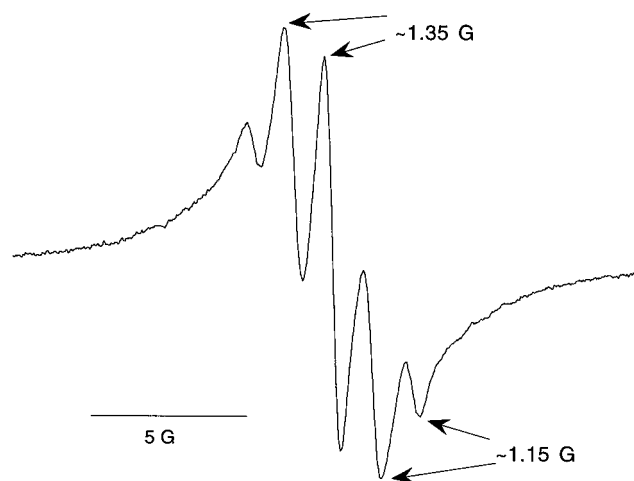
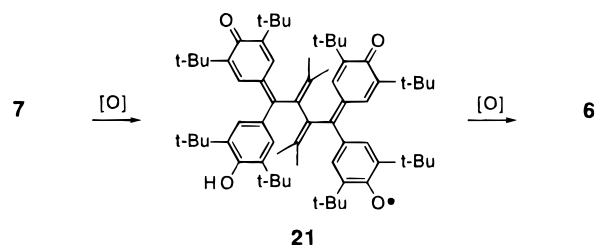


Figure 11. EPR spectra (5-line) from bisgalvinol **7**, fully oxidized by PbO_2 . The spectrum is centered at 3475 G. Note the unequal splitting and broadened lines compared to the monogalvinoxyl in Figure 10.

shown) whereas the exhaustively oxidized sample exhibits no signal. The original spectrum for each returns upon warming to room temperature. Thus, we assign Figure 11 to thermally populated triplet bisgalvinoxyl **6** and Figure 10 to monoradical **21** (Scheme 4).

In the oxidation of **3** (Figure 5), it seems that little **6** is produced by 4 equiv of I_2 , although Figure 5E is not just pure monogalvinoxyl as seen in Figure 10. Closer

Scheme 4. Oxidation of **7**



examination of the spectrum obtained with a large excess of I_2 (Figure 6) reveals shoulders whose spacing corresponds with the outer peaks of **7**'s biradical spectrum. In the preparative-scale oxidation of **3**, four spots are observed by TLC as the oxidant is added; one due to unreacted **3**, one to product **7**, one to an unidentified, possibly polymeric product, and one to unidentified base line residue. The unidentified components do not give an EPR signal upon oxidation. Thus we conclude that Figure 6 is a combination of the 5-line spectrum due to biradical **6** and a 3-line spectrum due to an unstable, phenoxyl-type decomposition product.

The exact sequence of events from cyclobutane tetraphenol **3** to butadiene **7** is unclear. It is certain, however, that a bicyclobutane structure must lie along the pathway. The bicyclobutane-to-butadiene rearrangement is well-known, and it is firmly established that the 2–3 bond of the butadiene originates from the central bond of the bicyclobutane.⁵⁰ Also, it is well-established that there is no direct path from a 1,3-cyclobutanediyl to a butadiene.⁵¹ The only issue is the timing of the oxidation, ring-closure, and rearrangement steps.

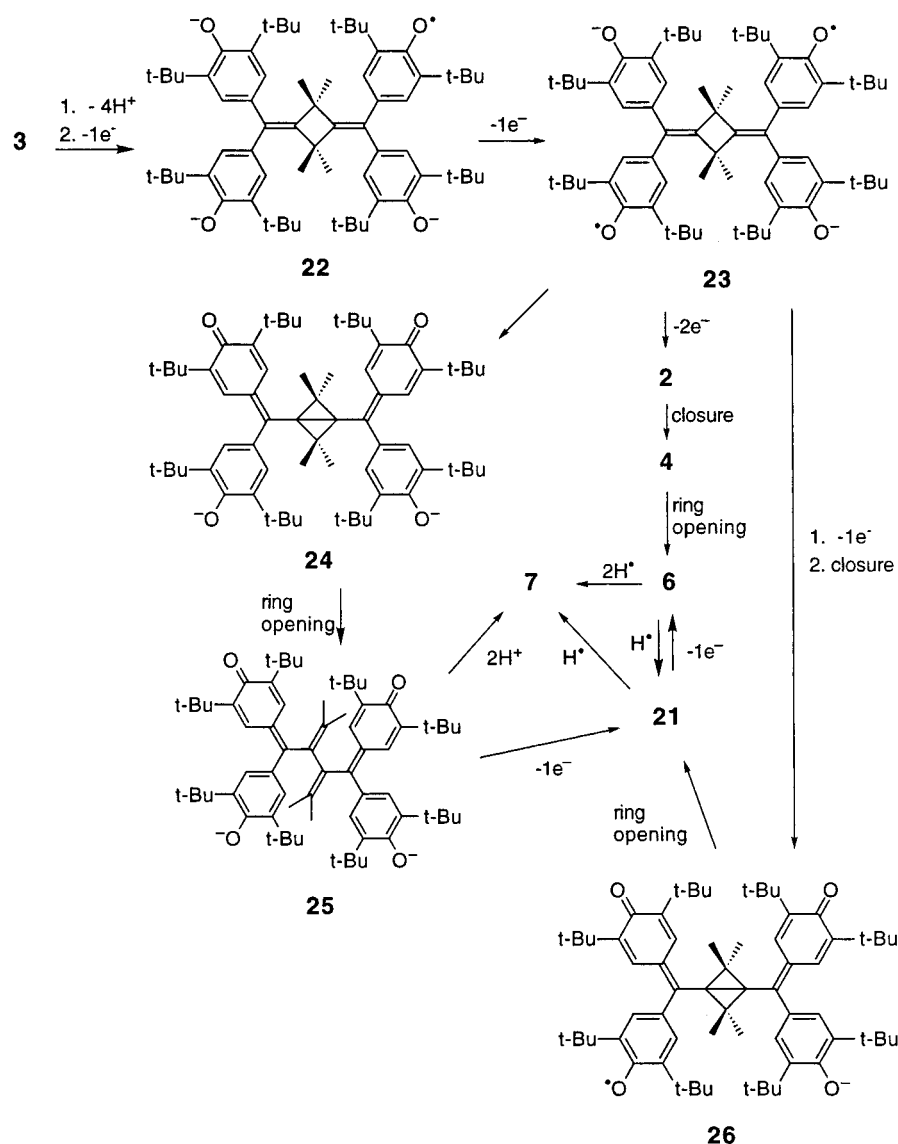
The pathway we favor is shown in Scheme 5. Tetraphenol **3** is deprotonated and undergoes a series of oxidations to monoradical **22** and biradical **23**, one or both of which is responsible for the initial 3-line, phenoxyl-type EPR spectrum. A key intermediate is a bicyclobutane such as **4**, **24**, or **26**. These then undergo the bicyclobutane-to-butadiene ring-opening rearrangement. Several possibilities are suggested by the fact that the monoradical spectrum is prominent at medium levels of oxidant. One possibility is that **24** rearranges, producing **25**, the dianion of **7**; the oxidant which was not consumed in the first two steps or in one of the other side reactions reacts with this to produce **21**. Or, monoradical **26** rearranges to **21**, with the excess oxidant again consumed by side reactions. Alternatively, after **4** rearranges to **6**, the side reactions or solvent may donate hydrogen to **6**, producing **21**. In any of these scenarios, further oxidation generates **6** and the unidentified 3-line decomposition product, as seen in Figure 6.

Hünig has established that sterics can accelerate the bicyclobutane-to-butadiene rearrangement,^{22–26} and considerations of space filling models show that bicyclobutanes derived from **2** are more crowded than the Hünig systems. Whether this additional crowding is enough to account for the bicyclobutane's facile rearrangement is unclear; however, comparison with model compounds **15** and **19** shows that even such simple chemistry as H–D exchange is strongly influenced by the presence of the tetramethylcyclobutane unit. Additionally, the tendency of these compounds to be overoxidized, the known

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Scheme 5. Paths from 3 to 7



reactivity of bicyclobutanes to halogens,³¹ and the presence of the tetrabutylammonium hydroxide/MeOH reagent may also affect stability. Concerning the viability of tetraradical **2**, if it is formed in this sequence it apparently closes readily to bicyclobutane **4**. While this possibility was considered from the outset, the facile rearrangement of **4** was not anticipated.

Conclusions

The current work sought the preparation of tetraphenoxy radical **2**, a potentially more stable version of the previously reported quintet tetraradical **1**. On the basis of EPR observations from model compounds **15** and **19**, and the X-ray structure determination of the product from oxidation of tetraphenol **3**, we conclude that the target **2** is most likely not observable. Instead, **2**, or an intermediate on the path to it, closes to a bicyclobutane such as **4**, which undergoes a surprisingly facile rearrangement to produce, ultimately, butadiene derivative **7**.

Experimental Section

2,6-Di-*tert*-butylphenol, benzophenone hydrazone, and isobutyrophenone were commercially available. Compounds **8**,³² **9**,³³

12,^{22,52} and 2,6-di-*tert*-butylanisole⁵³ are known and were prepared as referenced. Compound **10**⁵⁴ is known but was prepared³⁴ as described. Reactions were run under an atmosphere of dry argon using oven-dried glassware. General experimental and analytical techniques have been reported previously.⁵⁵ EPR spectra were obtained using a Varian E-Line Century Series spectrometer ($\nu \approx 9.52$ GHz) and an IBM-Brüker E200SRC spectrometer ($\nu \approx 9.77$ GHz). EPR samples were generally prepared in 2-methyl-THF, vacuum transferred from sodium benzophenone ketyl in the strict absence of oxygen. Some EPR samples were prepared in other solvents such as THF, toluene, benzene, or Et₂O. All samples were carefully degassed on a vacuum line by the freeze-pump-thaw method. A liquid nitrogen-filled finger dewar was used for spectra taken at 77 K.

Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)methanone (10).^{34,54} A mixture of **9**³³ (35.0 g, 0.0773 mol) and Ce(NH₄)₂(NO₃)₆ (170 g, 0.309 mol) in glacial AcOH (800 mL) was heated to 95 °C. After 3 h, the mixture was poured onto ice and extracted with Et₂O. The combined extracts were neutralized, dried, and reduced to a solid. The glassy orange residue was recrystallized from MeOH to give **10** (26.7 g, 0.0572 mol) in

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74% yield as pale yellow crystals: GC/MS, 50–250 °C, 10 °C/min, m/z 466 (M^+) at 24.1 min; ^1H NMR, CDCl_3 , $\delta = 1.42$ ppm, s, 36H; 3.76, s, 6H; 7.43, s, 4H; FTIR, KBr, $\nu = 1655$ cm^{-1} (C=O); mp = 165–167 °C (lit.⁵² mp 165 °C).

Bis(3,5-di-*tert*-butyl-4-methoxyphenyl)methylhydrazone (11).^{35,36} Anhydrous H_2NNH_2 (2.8 mL, 0.087 mol), **10** (4.08 g, 0.00874 mol), and a few drops of glacial AcOH were added to absolute EtOH (100 mL). After being refluxed for 12 h, the mixture was cooled to room temperature and the solvent removed. Recrystallization from MeOH gave diarylhydrazone **11** (3.99 g, 0.00831 mol) in 95% yield as pale yellow crystals: GC/MS, 50–250 °C, 10 °C/min, m/z 480 (M^+) at 28.0 min; ^1H NMR, CDCl_3 , $\delta = 1.38$ ppm, s, 18H; 1.44, s, 18H; 3.71, s, 3H; 3.77, s, 3H; 5.2 broad s, 2H; 7.20, s, 2H; 7.43, s, 2H; FTIR, NaCl, $\nu = 1590$ cm^{-1} (C=N).

Bisepisulfide 13.^{22,35–38} A mixture of **11** (2.59 g, 0.00539 mol), freshly activated HgO (2.85 g, 0.0132 mol), NaSO_4 (1.22 g, 0.00862 mol), 5 drops of saturated KOH/absolute EtOH solution, and Et_2O (100 mL) was stirred under a drying tube for 45 min. The intensely purple mixture was vacuum filtered through a fine glass sinter. The purple residue after solvent removal was presumably bis(3,5-di-*tert*-butyl-4-methoxyphenyl)diazomethane (see Scheme 1: TLC, violet spot at R_f 0.7, no stain, 33% Et_2O /petroleum ether; FTIR, NaCl, $\nu = 2031$ (N=N), 1590, (C=N) cm^{-1}). This residue (2.58 g, 0.00539 mol) and **12**^{22,52} (0.464 g, 0.00269 mol) were added to Et_2O (50 mL). Slight warming and gas evolution was observed. Upon stirring overnight, the color went from deep purple to light gold. The solid precipitated by cooling to 0 °C was collected by vacuum filtration and washed with a minimum of cold Et_2O . Drying gave bisepisulfide **13** (2.17 g, 0.00202 mol) in 75% yield as a white powder: 90 MHz ^1H NMR, CDCl_3 , $\delta = 0.46$, ppm, s, 3H; 0.66, s, 3H; 0.95, s, 3H; 1.21, s, 3H; 1.40, s, 72H; 3.61, s, 12H; 7.74, s, 8H. Anal. Calcd for $\text{C}_{70}\text{H}_{104}\text{O}_4\text{S}_2$: C, 78.30; H, 9.76; S, 5.97. Found: C, 78.03; H, 10.01; S, 5.87.

Activation of HgO.³⁹ Mercury(II) oxide (5.0 g, 0.023 mol) was dissolved, with stirring, in concentrated HClO_4 . After the mixture was cooled in an ice bath, 50% NaOH was added dropwise until the mixture was basic. The orange precipitate was collected by vacuum filtration and dried to give activated HgO (4.9 g, 0.023 mol).

1,3-Bis(bis(3,5-di-*tert*-butyl-4-methoxyphenyl)methyl-ene)-2,2,4,4-tetramethylcyclobutane (14).²² Bisepisulfide **13** (1.35 g, 0.00126 mol) and triphenylphosphine (0.66 g, 0.0025 mol) were added to 100 mL of benzene and refluxed for 48 h. The residue after solvent removal was boiled for 10 min in 50 mL of a 1:1 solution of CCl_4 and 95% EtOH. After removing this solvent, the residue was washed with 95% EtOH and dried to give tetraanisole **14** (1.21 g, 0.00120 mol) in 95% yield as a white powder: HRMS, found MW = 1008.7924, calcd MW = 1008.7935, for $M^+ = \text{C}_{70}\text{H}_{104}\text{O}_4$; ^1H NMR, CDCl_3 , $\delta = 0.97$ ppm, s, 12H; 1.44, s, 72H; 3.74, s, 12H; 6.95, s, 8H; ^{13}C NMR, CDCl_3 , $\delta = 27.7, 32.2, 35.5, 49.6, 64.2, 127.1, 136.4, 136.9, 142.2, 154.3, 157.8$ ppm; mp > 360 °C. Anal. Calcd for $\text{C}_{70}\text{H}_{104}\text{O}_4$: C, 83.28; H, 10.38; O, 6.34. Found: C, 83.39; H, 10.26; O, 6.29.

1,3-Bis(bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl-ene)-2,2,4,4-tetramethylcyclobutane (3).⁴⁰ Under an argon atmosphere, 9.6 mL (0.014 mol) of 1.5 M $\text{CH}_3\text{SLi/HMPA}$ was added to tetraanisole **14** (1.21 g, 0.00120 mol). (Note: O_2 and H_2O must be rigorously excluded.) The mixture was heated to 85 °C. Because the final product cannot be easily purified from methoxy intermediates, the reaction was run until no methoxy compounds were visible by TLC (removal of each methyl results in spots at successively lower R_f s), although this resulted in some product decomposition. After 10 d, the reaction, which had turned green, was quenched with H_2O (10 mL), stirred for 5 min, and then stirred for 1 h with concentrated HCl (20 mL) to destroy the HMPA. The mixture was extracted with CH_2Cl_2 , dried, filtered, and reduced to a solid. The residue was washed on a fine glass sinter with 500 mL each of boiling H_2O and boiling CH_3CN . Drying gave tetraphenol **3** (0.686 g, 0.000719 mol) in 60% yield as a white powder: TLC, blue grey spot at R_f 0.25, molybdate stain, 5% EtOAc/petroleum ether; HRMS, FAB, found MW = 952.731600, calcd MW = 952.730862 for $M^+ = \text{C}_{66}\text{H}_{96}\text{O}_4$; ^1H NMR, d_8 -THF, $\delta = 0.97$ ppm, s, 12H; 1.37 ppm, s, 72H; 5.90 ppm, s, 4H; 7.11

ppm, s, 8H; ^{13}C NMR, d_8 -THF, $\delta = 28.5, 31.1, 35.3, 50.6, 126.1, 135.3, 137.1, 138.5, 153.3, 155.0$; FTIR, NaCl, $\nu = 3641, 3618$ (sharp, OH) cm^{-1} ; UV/vis, $\lambda_{\text{max}} = 241$ nm; mp > 360 °C. Anal. Calcd for $\text{C}_{66}\text{H}_{96}\text{O}_4$: C, 83.14; H, 10.15; O, 6.71. Found: C, 83.25; H, 10.21; O, 6.24.

Preparation of 1.5 M $\text{CH}_3\text{SLi/HMPA}$.⁴⁰ Under an argon atmosphere, 125 mL of HMPA was distilled from BaO (75 °C, 0.4 Torr) onto LiH (4.58 g, 0.576 mol). This mixture was cooled with an ice bath, and CH_3SH (35.3 mL, 0.188 mol, collected at –78 °C) was added via cannula. After being stirred at room temperature for 12 h, the mixture was vacuum filtered through a Schlenk line fine glass sinter. The concentration (1.50 ± 0.01 M) was determined by titration with 0.1501 M potassium hydrogen phthalate.

Bisgalvinol 7.^{4–16,41} Tetraphenol **3** (0.287 g, 0.000301 mol) was stirred in benzene (50 mL) and purged thoroughly with argon. A solution of $\text{Bu}_4\text{NOH/MeOH}$ (1.0 M, 3.6 mL, 0.0036 mol) was added, and the mixture was allowed to stir until **3** had dissolved completely, about 5 min. A solution of I_2 in benzene (0.0301 M, 20.3 mL, 0.000612 mol) was added via syringe, resulting immediately in a dark blue-purple color. The reaction was stirred for an additional 10 min and then quenched by carefully adding half-saturated NH_4Cl (20 mL). The organic layer was dried and reduced to a brown solid. The residue was purified by column chromatography using 1–10% Et_2O /petroleum ether as eluant to give bisgalvinol **7** (0.237 g, 0.249 mmol) in 83% yield as a bright orange solid. A portion of this was recrystallized from MeOH for X-ray analysis:⁵⁸ HRMS, FAB, found MW = 952.731600, calcd MW = 952.730862, for $MH^+ = \text{C}_{66}\text{H}_{96}\text{O}_4$; ^1H NMR (see also Figure 8), acetone- d_6 with slight excess of LiOD, $\delta = 1.15$ ppm, s, 36H; 1.30, s, 36H; 1.52, s, 6H; 2.16, s, 6H; 6.93, s, 4H; 7.11, s, 4H; FTIR, NaCl, $\nu = 3636$ (sharp, OH) 1602 (C=O) cm^{-1} ; UV/vis, neutral, $\lambda_{\text{max}} = 395$ nm, $\epsilon = 36$ 950; dianion, $\lambda_{\text{max}} = 602$ nm, $\epsilon = 110$ 830; mp = 175–176 °C. Anal. Calcd for $\text{C}_{66}\text{H}_{96}\text{O}_4$: C, 83.32; H, 9.96; O, 6.73. Found: C, 83.02; H, 10.07; O, 6.79.

1,1-Dimethyl-2,2-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)-ethylene.^{56,57} Benzophenone **10** (2.17 g, 0.00465 mol) was dissolved in THF (50 mL) and cooled to 0 °C. To this was added isopropylmagnesium chloride (2.0 M, 2.3 mL, 0.0047 mol). After the solution was stirred for 2 h at room temperature, the reaction was cooled with an ice water bath and quenched by carefully adding H_2O (10 mL), and the alcohol intermediate was dehydrated by adding concentrated HCl (10 mL). This mixture was extracted with Et_2O , dried, filtered, and reduced to a solid. Recrystallization of the residue from MeOH gave the bisanisole precursor to **15** (2.06 g, 0.00418 mol) in 92% yield as white crystals: GC/MS, 50–250 °C, 10 °C/min, m/z 492 (M^+) at 22.4 min; ^1H NMR, CDCl_3 , $\delta = 1.33$ ppm, s, 36H; 1.81, s, 6H; 3.63, s, 6H; 6.94, s, 4H; ^{13}C NMR, CDCl_3 , $\delta = 23, 33, 37, 65, 129, 130, 138, 143, 158$ ppm.

1,1-Dimethyl-2,2-bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)-ethylene (15).⁵⁴ Ethanethiol (2.3 mL, 0.044 mol) was added to a stirred suspension of NaH (1.15 g, 0.0479 mol) in DMF (75 mL). After the bubbling ceased, 1,1-dimethyl-2,2-bis(3,5-di-*tert*-butyl-4-methoxyphenyl)ethylene (see above, 1.48 g, 0.00318 mol) was added and the mixture was heated to 100 °C for 2 days. The reaction, which had turned dark brown, was quenched by carefully adding H_2O (10 mL), stirred for 5 min, and stirred for 1 h with 6 M HCl (100 mL). The mixture was poured into H_2O , extracted with Et_2O , dried, and reduced to a solid. Recrystallization of the residue from MeOH gave bisphenol **15** (0.753 g, 0.00162 mol) in 51% yield as air-sensitive white microcrystals (these slowly turned yellow even in a glovebox): GC/MS, 50–250 °C, 10 °C/min, m/z 464 (M^+) at 23.8 min; ^1H NMR, CDCl_3 , $\delta = 1.41$ ppm, s, 36H; 1.81, s, 6H; 5.06, s, 2H; 6.96, s, 4H; ^{13}C NMR, CDCl_3 , $\delta = 22.9, 30.5, 24.4, 108, 126.3, 129.5, 134.7, 151.5$ ppm. Anal. Calcd for

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(58) The author has deposited atomic coordinates for structure **7** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

$C_{32}H_{48}O_2$: C, 82.70; H, 10.41; O, 6.89. Found: C, 81.61; H, 10.47; O, 6.63.

Galvinoxol 17.^{4–16,41} Bisphenol **15** (0.155 g, 0.000 333 mol), $K_3Fe(CN)_6$ (0.384 g, 0.00117 mol), and a few pellets of KOH were added to a flask containing H_2O (10 mL) and benzene (10 mL). The mixture was purged carefully with argon and then stirred vigorously. Within seconds a dark blue color appeared and the reaction turned opaque by 1 min. After 30 min, the color was brown-gold, and the aqueous layer was removed. The organic layer was washed with aqueous pH 7 buffer (1.20 mol of KH_2PO_4 and 1.60 mol of K_2HPO_4 dissolved in 1 L of H_2O), dried, and reduced to a brown solid. This residue was redissolved in benzene (10 mL), and an excess of 1,4-cyclohexadiene (0.5 mL, 0.005 mol) was added. The dark brown solution was carefully degassed and then heated in an oil bath at 65 °C for 1 h, at which point the color had changed to light red-orange. The solvent was removed and the residue pumped on at <0.1 Torr for 24 h. The residue was then redissolved in hexane and purified on a Chromatatron (Harrison Research) using 1% Et_2O in hexane. The fractions containing product, which were still impure, were reduced to a solid and then recrystallized from petroleum ether to give 0.103 g (67%) of fine yellow crystals: TLC, visibly yellow spot at R_f 0.4, no stain, 5% $EtOAc$ /petroleum ether: HRMS, DCI/ NH_3 , found MW = 463.356700, calcd MW = 463.357606, for $MH^+ = C_{32}H_{47}O_2$; 1H NMR, $CDCl_3$, δ = 1.33 ppm, s, 18H; 1.42, s, 9H; 1.44, s, 9H; 1.73, s, 3H; 5.07, s, 1H; 5.19, s, 1H; 5.28, s, 1H; 7.41, s, 2H; 7.51, s, 1H; 7.75, s, 1H; ^{13}C NMR, $CDCl_3$, δ = 23.4, 29.7, 30.2, 30.5, 34.5, 35.4, 102.6, 120.3, 127.8, 128.4, 132.0, 135.5, 144.8, 146.2, 146.9, 155.2, 160.4, 186.7 ppm; FTIR, NaCl, ν = 3635 (sharp, OH), 1604 (C=O) cm^{-1} ; UV/vis, λ_{max} = 387 nm; mp = 175–176 °C. Anal. Calcd for $C_{32}H_{46}O_2$: C, 83.06; H, 10.02; O, 6.92. Found: C, 82.74; H, 10.01; O, 6.51.

1,1-Dimethyl-2-(3,5-di-*tert*-butyl-4-methoxyphenyl)-2-phenylethylene.^{56,57} *tert*-Butyllithium (1.7 M in hexanes, 19.7 mL, 0.033 mol) was added to a solution of 4-bromo-2,6-di-*tert*-butylanisole⁵³ (5.00 g, 0.0167 mol) in THF (75 mL), all cooled by a dry ice/acetone bath. After 1 h of stirring, isobutyrophenone (2.49 mL, 0.0167 mol) was added. The reaction was stirred at –78 °C for 1 h more, and then the temperature was allowed to rise to 0 °C. Hydrolysis of the alcohol intermediate was accomplished by adding HCl (6 M, 100 mL). The resulting mixture was extracted with Et_2O , neutralized, dried, and reduced to an oil. Upon standing overnight, the oil crystallized to give product (2.75 g, 0.00784 mol) in 47% yield as large colorless crystals: GC/MS, 50–250 °C, 10 °C/min, m/z 350 (M^+) at 20.3 min; 1H NMR, $CDCl_3$, δ = 1.43 ppm, s, 18H; 1.83, s, 3H; 1.87, s, 3H; 3.72, s, 3H; 7.03, s, 2H; 7.25–7.45, m, 5H; ^{13}C NMR, $CDCl_3$, δ = 22.8, 32.3, 35.8, 64.2, 107.4, 125.9, 127.8, 128.3, 129.9, 130.3, 137.3, 137.8, 142.4, 143.9, 157.7 ppm.

1,1-Dimethyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-phenylethylene (19).⁵⁴ Ethaneethiol (1.9 mL, 0.025 mol) was added to a stirred suspension of NaH (0.70 g, 0.029 mol) in DMF (50 mL). After the bubbling ceased, the anisole derivative prepared above (1.25 g, 0.00358 mol) was added and the mixture was heated to 100 °C for 12 h. The reaction, which had turned dark brown, was quenched by carefully adding H_2O (10 mL), stirred for 5 min, and stirred for 1 h with 6 M HCl (100 mL). The mixture was poured into H_2O , extracted with Et_2O , and dried, and the solvent was removed. Recrystallization from MeOH gave **19** (0.759 g, 0.00226 mol) in 63% yield as air-sensitive white microcrystals: GC/MS, 50–250 °C, 10 °C/min, m/z 336 (M^+) at 20.0 min; 1H NMR, $CDCl_3$, δ = 1.43 ppm, s, 18H; 1.83, s, 3H; 1.86, s, 3H; 5.02, s, 1H; 6.98, s, 2H; 7.25–7.45, m, 5H. Anal. Calcd for $C_{24}H_{32}O$: C, 85.66; H, 9.59; O, 4.75. Found: C, 85.50; H, 9.53; O, 4.91.

General Procedure for Biphasic $K_3Fe(CN)_6$ Oxidations.⁴¹ Under an argon atmosphere, a solution of phenol (10^{-3} – 10^{-4} M, 5 mL) in Et_2O and excess $K_3Fe(CN)_6$ were added to a dilute solution of NaOH (5 mL, ca. 1 M). After the solution was stirred for a desired length of time, a 0.5 mL aliquot of the ether solution was transferred into an EPR tube. The ether was removed under vacuum and replaced with about 0.5 mL of 2-methyl-THF.

General Procedure for Heterogeneous Oxidations. A solution of argon-purged phenol in THF, toluene, or benzene (10^{-3} – 10^{-5} M, 0.5 mL), an excess of solid oxidant, and (optionally) tetrabutylammonium hydroxide/MeOH were added to an EPR tube. The mixture was agitated and allowed to settle before measurement. Alternatively, the phenol solution, oxidant, and base (if added) were stirred vigorously in an oxygen-free drybox and filtered through glass wool into an EPR tube.

General Procedure for Iodine/Tetrabutylammonium Hydroxide Oxidations. Under an argon atmosphere, solutions of a phenol (10^{-3} – 10^{-5} M), tetrabutylammonium hydroxide/MeOH, and iodine/THF were added to EPR tubes. The deep blue solutions were then carefully degassed by the freeze/pump/thaw method.

Acknowledgment. We thank the National Science Foundation for support of this work. We thank Dr. Joseph Ziller (U.C., Irvine) for the X-ray crystal structure determination.

Supporting Information Available: Details of the X-ray structure of **7** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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