ference between the quartet and doublet may be small.

Let us now turn to the magnetic coupling between the randomly oriented quartet molecules in the frozen glass. Intermolecular magnetic coupling observed in the CH_2Cl_2 glass is found to be antiferromagnetic with negative Weiss constant $\Theta = -110$ K, obtained from the intercept of the temperature axis in Figure 7. Since the Weiss constant is very large and negative, the antiferromagnetic coupling between neighboring molecules is strong. Such strong coupling is unusual for organic molecules; therefore, TDAB is very interesting as an organic ferro- or rather antiferromagnetic material. This strong intermolecular coupling may, however, be attributable to the superexchange interaction[29] involving BF_4^- anions. We must also note that the intermolecular magnetic coupling is normally dependent on the molecular packing and crystalline forms, as has been seen in the case of *p*-nitrophenyl nitronyl nitroxides.[9] Moreover, in these materials, the intermolecular magnetic coupling is known to be ferromagnetic, while it is antiferromagnetic in the crystals of phenyl and *m*-nitrophenyl nitronyl nitroxides.[8] The difference in the magnetic coupling among these members has been explained on the basis of π-electron delocalization and spin polarization, which are considerably dependent on the type of substituent and the crystalline form. It is therefore important to examine the magnetic properties of the crystals of TDAB families mixed with various anions in order to achieve quantitative spin control.

Conclusion

We have analyzed the molecular and the crystal structures of TDAB and have observed the quartet state of TDAB. The observed ESR spectrum of the cationic radicals, which are rigidly held but randomly oriented with respect to the magnetic field in CH_2Cl_2 glass, agreed well with the theoretical prediction for a quartet spin state. The temperature dependence of the intensity for the $\Delta m_s = \pm 1$ transition confirmed that the quartet is the ground state. Although organic molecules with multiplet ground states, such as carbenes and nitrenes, have been prepared, these types of species are only observable under irradiation at low temperatures. In contrast to these species, the cationic triradical of TDAB is stable under vacuum or nitrogen atmosphere even at room temperature. This material is therefore of interest as an example of a novel type of organic magnetism. The stability of this radical is probably attributable to the presence of heteroatoms in the π-conjugation as seen in the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. A particularly unique feature of TDAB is that the observed intramolecular ferromagnetic interaction operates among the cationic radicals. This is the first observation of a high-spin state ($S = {}^3/_2$) for such a cationic radical. The present ferromagnetic interaction might provide important information about the still unknown chemical nature of the organic ferromagnetic material poly(1,3,5-triaminobenzene).[1] In this case, however, the intermolecular magnetic coupling of TDAB in the CH_2Cl_2 glass has turned out to be strongly antiferromagnetic. Therefore, examination of the role of counteranions may be necessary for an understanding of the stability of this cationic triradical and the observed intermolecular magnetic coupling.

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Supplementary Material Available: Tables of positional parameters, thermal parameters, distances, angles, and least-squares planes and a stereoview of the unit cell of TDAB (14 pages). Ordering information is given on any current masthead page.

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Cyclopropanones from the Oxidation of Hindered [4]- and [5]-Cumulenes with Epoxidation Reagents

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Abstract: The oxidation of *tert*-butyl-substituted [5]-cumulene **4** with epoxidizing agents was shown to give sequentially formed conjugated cyclopropanones **15** and **11**. The more stable cyclopropanone **11** was isolated and shown to add carboxylic acids to give allenyl ketones of type **5** and to thermally and photochemically lose carbon monoxide to give the [4]-cumulene **6**. The oxidation of **4** with peracids leads directly to allenyl ketones **5** as isolated products. Hydrolysis of **5a** produced the novel furofuran **9**. The oxidation of the hindered [4]-cumulene **6** gave conjugated cyclopropanone **19**, which underwent chemical transformations similar to those of **11**. These oxidations are rationalized in terms of hypothetical cumulene oxide intermediates that rapidly isomerize to the observed cyclopropanones.

As an extrapolation of our long-standing interest in the epoxidation chemistry of allenes,[1] we recently reported on the reaction of butatriene **1** with peracids to give methylenecyclopropanone **2**.[2,3] This was shown to proceed via an unstable intermediate, whose low-temperature ^1H and ^{13}C NMR spectra suggested the triene oxide structure **3**. We now confirm this assignment by an FT-IR experiment which clearly shows a transient allene band at 1998 cm^{-1} that rapidly accumulates and then disappears during the course of the conversion of **1** to **2** by *m*-chloroperbenzoic acid (mCPBA); see Scheme I.

The observation of cumulene oxide **3** prompted an extension of our studies to the oxidation of hexapentaene **4**, the most readily available higher homologue of **1**.[4] Reaction of **4** with 3 equiv of mCPBA in $CHCl_3$ generated a modest yield (26%) of a

(1) (a) Crandall, J. K.; Conover, W. W.; Komin, J. B.; Machleder, W. H. *J. Org. Chem.* **1974**, *39*, 1723. (b) Crandall, J. K.; Batal, D. J.; Sebesta, D. P.; Lin, F. *J. Org. Chem.* **1991**, *56*, 1153. (c) For reviews of allene oxide chemistry, see: Stang, P. J. The Chemistry of Functional Groups, Supplement E: *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulfur Analogs*; Patai, S., Ed.; Wiley: New York, 1980; pp 859-879. L'Abbe, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 276.

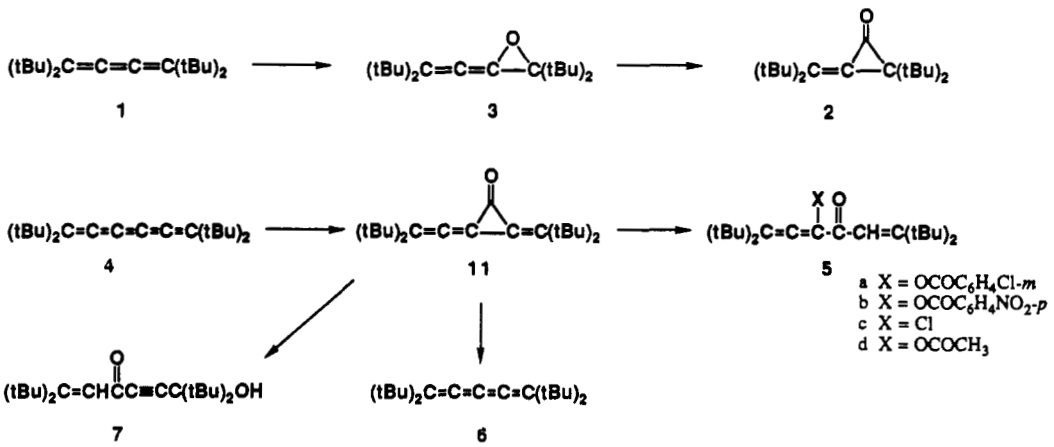
(2) Crandall, J. K.; Salazar, G. E.; Watkins, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 4338.

(3) For a related study, see: Ando, W.; Hayakawa, H.; Tokitoh, N. *Tetrahedron Lett.* **1986**, *27*, 6357.

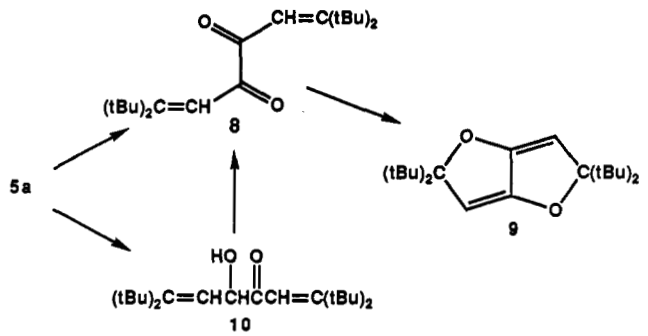
(4) Negi, T.; Kaneda, T.; Mizuno, H.; Toyoda, T.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2398. Hartzler, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 4527.

0002-7863/92/1514-5998$03.00/0

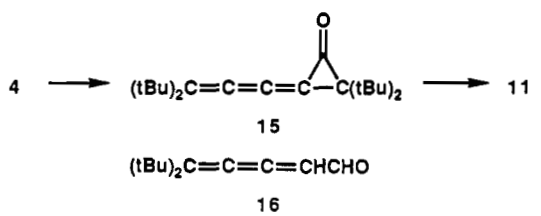
Scheme I



Scheme II



Scheme III



crystalline compound assigned as allenic ketone **5a**, on the basis of its characteristic spectroscopic properties. Small amounts of pentatetraene **6**[5] and alkynyl ketone **7** were also obtained. *p*-Nitroperbenzoic acid gave the analogous *p*-nitrobenzoate **5b**. Hydrolysis of **5a** with KOH in aqueous DME was performed with the goal of securing α-diketone **8** in order to substantiate structure **5a**. However, this process led to an unanticipated new compound which was ultimately shown by X-ray crystallography to possess the furofuran structure **9**.[6] Reduction of allenic ketone **5a** with $LiAlH_4$ generated ketol **10**, but attempted MnO_2 oxidation of **10** to **8** resulted once again in furofuran **9** (see Scheme II). This suggests that diketone **8** spontaneously undergoes a facile ring closure to **9**. The mechanism and generality of this intriguing transformation warrant further study.

With a view to the observation of precursors of allenyl ketones **5**, the behavior of pentaene **4** with 1 equiv of the neutral, nonnucleophilic oxidant dimethyldioxirane[7] was examined. After several minutes, preparative TLC separation (in the absence of light) provided methylenevinylidenecyclopropanone **11** as an orange solid in 25% yield. This previously unknown variety of conjugated cyclopropanone is a complicated member of the radialene class of compounds.[8] This cyclopropanone was, as expected, quite reactive.[9] Thus, solid **11** was completely decarbonylated to **6** upon brief exposure to sunlight or upon warming in a melting point capillary, which caused the orange color of **11** to disappear at ca. 72 °C with the formation of white, crystalline tetraene **6**. An acetone solution of **11** at room temperature in the dark also slowly loses carbon monoxide to give **6** (50% conversion after 0.5 h). Allenyl ketone **5a** was obtained by reaction of **11** with *m*-chlorobenzoic acid, fully consistent with **11** as the source of this product in oxidations using mCPBA. Treatment of **11** with HCl likewise gave allenyl chloride **5c**, whereas incorporation of acetic acid into a reaction of cumulene **4** with dimethyldioxirane cleanly produced the corresponding acetate **5d**.

Since an unstable cumulene oxide intermediate was suspected as the initial product of the oxidation of **4**, this transformation was subjected to close spectroscopic scrutiny. Thus, following a reaction of **4** with 1 equiv of mCPBA in $CHCl_3$ at room temperature by FT-IR analysis clearly demonstrated the intervention of an intermediate which displayed bands at 2045 and 1782 cm^{-1}. This species achieved maximum concentration after 6 min, before being further converted into cyclopropanone **11**. A similar experiment in $CDCl_3$ in an NMR tube was arrested after 6 min by cooling to −30 °C to give a mixture that was stable for over an hour and which consisted of starting pentaene **4** (45%), cyclopropanone **11** (12%), and a major new species (43%) with *tert*-butyl signals at δ 1.34, 1.32, and 1.16 in a 1:1:2 ratio. The ^{13}C NMR spectrum showed peaks at δ 204.8, 164.4, 163.7, 156.9, 105.3, and 59.7 not attributable to other reactants and products and, therefore, assigned to this intermediate. Warming to room temperature resulted in the disappearance of the ^1H NMR peaks of the intermediate and subsequently those for **11**. After several hours the product mixture consisted of tetraene **6** (9%), allenyl ketone **5a** (60‰), and starting pentaene **4** (29%).

Surprisingly, the data for the intermediate species are not consistent with any of the three possible cumulene oxide structures **12–14**, particularly the number of types of *tert*-butyl substituents. The observation of three different *tert*-butyl groups by NMR, and IR bands for a cumulene unit[10] at 2045 and a strained-ring carbonyl at 1782 cm^{-1}, suggests that the unstable intermediate is 3,3-di-*tert*-butyl-2-(3-*tert*-butyl-4,4-dimethylpenta-1,2-dienylidene)cyclopropanone (**15**). Analysis of the ^{13}C NMR spectrum provides support for this formulation, although the observation

(5) Tokitoh, N.; Suzuki, T.; Ando, W. *Tetrahedron Lett.* **1989**, *30*, 4271.

(6) Heterocyclic structures similar to **9** have been claimed in the literature, but subsequent reinvestigation has resulted in revision of these assignments; see: Bohlmann, F. *Chem. Ber.* **1961**, *94*, 1104. A full description of the X-ray determination of **9** is provided in the supplementary material.

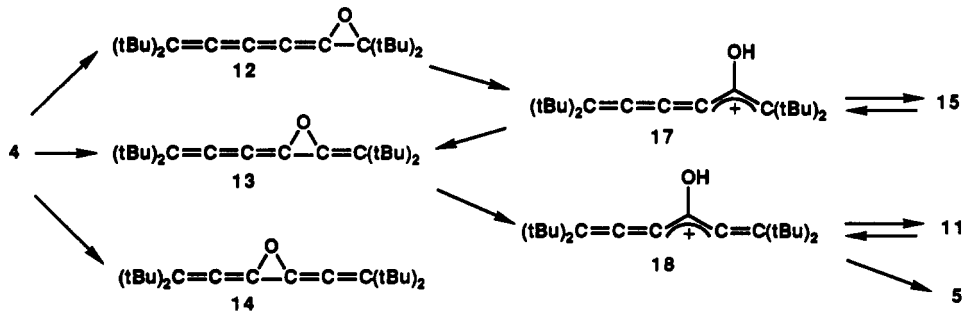
(7) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847. For recent reviews on dioxiranes, see: Murray, R. W. *Chem. Rev.* **1989**, *89*, 1187. Adam, W.; Curci, R.; Edwards, J. O. *Acc. Chem. Res.* **1989**, *22*, 205.

(8) Kobrich, G.; Heinemann, H.; Zundorf, W. *Tetrahedron*, **1967**, *23*, 565. Iyoda, M.; Tanaka, S.; Otani, H.; Nose, M.; Oda, M. *J. Am. Chem. Soc.* **1988**, *110*, 8494.

(9) For a review of cyclopropanone chemistry, see: Wasserman, H. H.; Berdahl, D. R.; Lu, T. *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; pp 1455–1532.

(10) Conjugated cumulenes typically show strong IR absorptions in the range 2030–2070 cm^{-1}. For representative examples, see: Kosower, E. M.; Sorensen, T. S. *J. Org. Chem.* **1963**, *28*, 687. Vo-Quang, L.; Battioni, P.; Vo-Quang, Y. *Tetrahedron* **1980**, *36*, 1331.

Scheme IV



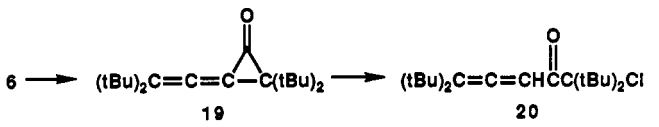
of all three exocyclic cumulene carbons in the chemical-shift range of δ 155–165 was initially of some concern. This interpretation requires that conjugation through the cumulene system shift the carbon most remote from the carbonyl group substantially downfield relative to a simple butatriene. An NMR study of trienyl aldehyde **16** demonstrates that the magnitude of this effect is quite reasonable, since the remote cumulene carbon in model **16** is found at δ 162, almost 30 ppm downfield from the corresponding carbon of butatriene **1**.[11] Thus, we conclude that two cyclopropanones are involved as unstable intermediates in the oxidation of **4**; cyclopropanone **15** is formed initially, but it readily rearranges to the more stable isomer **11** (Scheme III).

Although no definite evidence has been obtained to support the intermediacy of a cumulene oxide in this process, experience with the lower cumulenes strongly suggests that such a species precedes cyclopropanone **15**. If so, its isomerization must be exceedingly facile. Epoxide **12**, which has only one exocyclic double bond, is the most likely candidate for this putative intermediate. Acid-catalyzed opening of **12** to hydroxyallyl cation **17** generates a suitable precursor of cyclopropanone **15**, which can be formed by electrocyclic closure of **17**.[12] This kinetic cyclopropanone could be interconverted with its more stable isomer **11** by leakage from equilibrating ion **17** to isomeric hydroxyallyl cation **18**. This interconversion can be visualized to proceed via oxygen bridging to give cumulene oxide **13** (or its protonated version), followed by the alternate ring cleavage to **18**. Cyclization of cation **18** leads to cyclopropanone **11** in a straightforward manner. In the presence of carboxylic acid, equilibrating cation **18** is captured in a slower process which provides the stable allenyl ketones of structure **5**. Cumulene oxide **13** could, in principle, be the initial intermediate, but the observed partitioning between kinetic and thermodynamic cyclopropanones seems less probable to us. Furthermore, both steric effects and product-strain considerations ought to disfavor epoxidation at this site. Likewise, symmetrical cumulene oxide **14** is a reasonable precursor of **11** and **5** via cation **18**, but it is not logically connected with cyclopropanone **15** by a much faster process. Consequently, we propose that **12** is a first, fleeting intermediate in these oxidative conversions to cyclopropanones (see Scheme IV).

The isolation of tetraene **6** provided the opportunity to examine briefly the oxidation chemistry of this less readily available cumulene. Thus, reaction of **6** with 1 equiv of mCPBA gave vinylidenecyclopropanone **19** as a relatively stable yellow solid in 57% yield. No other products were observed in significant amounts. Furthermore, careful monitoring of the oxidation of **6** by FT-IR and low-temperature ^{1}H NMR spectroscopy failed to provide evidence of an intermediate. Once again, the suspected cumulene oxide must isomerize to **19** very rapidly. Cyclopropanone **19** slowly decarbonylated to **1** upon exposure to sunlight, and treatment with HCl gave allenyl ketone **20** (Scheme V).

Finally, oxidation of pentaene **4** with 5 equiv of mCPBA in $CDCl_3$ at room temperature in the absence of light for 1.5 h resulted in the complete conversion of starting material to a

Scheme V



mixture of allenyl ketone **5a** (40%), tetraene **6** (20%), vinylidenecyclopropanone **19** (20%), triene **1** (5%), and methylenecyclopropanone **2** (5%). Consequently, a cascading sequence of epoxidation, rearrangement, and decarbonylation reactions must occur under these conditions.

In conclusion, several unprecedented cyclopropanone systems have been obtained from the oxidation of higher cumulenes. These transformations are suggested to proceed via unstable cumulene oxides that rapidly undergo the allene oxide–cyclopropanone rearrangement.[1]

Experimental Section

General. Infrared (IR) spectra were determined as thin films between NaCl disks or as solutions in $CDCl_3$ using a Perkin-Elmer Model 298 grating spectrometer, an IBM IR/30 FT-IR spectrometer system with DTGS detector, or a Mattson Galaxy 4020 FT-IR instrument. ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on $CDCl_3$ solutions, unless otherwise specified, using a Varian XL-300 instrument at 300 MHz, a Varian VXR-400s at 400 MHz, or a Bruker AM-500 at 500 MHz. ^{13}C NMR were normally recorded on $CDCl_3$ solutions using a Varian VXR-400s spectrometer at 100 MHz or a Bruker AM-500 at 125 MHz. Mass spectra (MS) were obtained on a Kratos MS 80 RFAQQ spectrometer using chemical (CI) or electron-impact (EI) ionization. Exact-mass measurements are reported for the (M + 1) or (M) peak unless otherwise specified. Melting points were determined on a Thomas-Hoover Unimelt apparatus or a Fisher-Johns melting point apparatus. UV/vis spectra were recorded on a Hewlett-Packard 8450A diode array spectrophotometer. Analytical gas chromatography (GC) was performed using a Varian 3700 instrument fitted with a 50-m × 0.2-mm HP5 column, a flame ionization detector, and a Hewlett-Packard Model 3390-A integrator. Preparative thin-layer chromatography (TLC) was performed on Kieselgel 60 F-254 silica gel on 10- × 20-cm plates of 0.25-mm thickness unless otherwise indicated.

Oxidation of 1 with mCPBA. FT-IR Experiment. To a solution of 6.6 mg (0.039 mmol) of recrystallized mCPBA in 0.5 mL of CH_2Cl_2 was added 8.8 mg (0.032 mmol) of **1** in 0.5 mL of CH_2Cl_2. An aliquot of the mixture was immediately placed into an IR solution cell and FT-IR spectra were taken at intervals of 3 min. A peak at 1998 cm^{-1} attributed to **3** was observed to appear, reach maximum intensity at about 15 min, and diminish and disappear after 1 h. The reaction progress was monitored by observing changes in the mCPBA and *m*-chlorobenzoic acid peaks. A peak at 1785 cm^{-1} attributed to **2** appeared after 10 min.[13]

Oxidation of 4 with 1 Equiv of mCPBA. To a solution of 13.6 mg (0.08 mmol) of mCPBA in 2 mL of CH_2Cl_2 at 0 °C under nitrogen was added 22 mg (0.073 mmol) of **4** in 3 mL of CH_2Cl_2. After 1 h, the mixture was warmed to room temperature and stirred for 18 h. A few drops of tetramethylethylene was added to consume excess mCPBA. The reaction mixture was washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. Flash chromatography on silica gel (230–400 mesh) afforded several mixed fractions; the first fraction was rechromatographed to afford **4** plus a small amount of 3,7-di-*tert*-butyl-2,2,8,8-tetramethyl-3,4,5,6-nonatetraene (**6**), which was recrystallized from ethanol as colorless needles: mp 100–100.5 °C (lit.[5] mp 97–98 °C); IR 2062, 1479, 1362, 1208 cm^{-1}; ^{1}H NMR δ 1.23 (s); ^{13}C NMR δ 171.2,

(11) For comparison, **1** shows: ^{13}C NMR δ 158.3, 134.7, 38.9, 32.4.

(12) Although it seems likely to us that these processes are acid-catalyzed, the involvement of the zwitterions corresponding to **17** and **18** cannot be excluded.

(13) Representative spectra are given in the supplemental material.

128.6, 124.3, 37.3, 29.7; UV (hexane) λ_{max} (ϵ) 336 (473), 307 (645), 256 (30900), 232 (118400); MS (CI) *m/z* (rel intensity) 288 (31), 231 (24), 175 (67), 119 (46), 69 (100).

Oxidation of 4 with 3 Equiv of mCPBA. A solution of 603 mg (2 mmol) of **4** and 1.03 g (6 mmol) of mCPBA in 75 mL of CH_2Cl_2 was stirred at room temperature under nitrogen in the dark. After 2.25 h, a few drops of tetramethylethylene was added. The pale green reaction mixture was washed twice with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. Flash chromatography on silica gel using 9:1 hexane/ether as an eluant provided 240 mg (26%) of 6-(3-chlorobenzoyloxy)-3,8-di-*tert*-butyl-2,2,9,9-tetramethyl-3,6,7-decatrien-5-one (**5a**) as a pale yellow solid: mp 112–114 °C; IR 1927, 1740, 1663, 1599, 1482, 1393, 1366, 1288, 1250, 1190 cm^{-1}; ^1H NMR δ 8.12 (s, 1), 8.03 (d, J = 8 Hz, 1), 7.55 (d, J = 8 Hz, 1), 7.40 (t, J = 8 Hz, 1), 6.25 (s, 1), 1.36 (s, 9), 1.33 (s, 18), 1.26 (s, 9); ^{13}C NMR δ 201.0, 190.3, 168.0, 163.5, 137.2, 134.5, 133.2, 131.4, 130.3, 129.7, 128.4, 125.6, 122.5, 39.9, 38.8, 37.6, 32.9, 31.7, 31.6; MS (EI) *m/z* (rel intensity) 415 (21), 167 (100), 139 (97), 111 (46), 83 (32); exact mass 415.204; calcd for $C_{25}H_{32}O_3Cl$ (M − *t*-Bu), 415.2042.

An early fraction contained a mixture of **4** and **6** which was not separated. The column was washed with ether and the residue was submitted to preparative TLC using hexane–ether (1:1) as eluant to provide 8 mg (1%) of 3,8-di-*tert*-butyl-8-hydroxy-2,2,9,9-tetramethyl-3-decen-6-yn-5-one (**7**) as a white crystalline solid: mp 71–72 °C; IR 3620, 2200, 1650, 1605, 1477, 1392, 1369 cm^{-1}; ^1H NMR δ 5.97 (s, 1), 2.03 (s, 1), 1.33 (s, 9), 1.23 (s, 9), 1.17 (s, 18); ^{13}C NMR δ 182.2, 165.8, 125.4, 96.0, 85.9, 80.7, 41.1, 38.7, 38.3, 32.2, 31.0, 27.9; MS (CI) *m/z* (rel intensity) 277 (11), 261 (100), 221 (68), 179 (28), 137 (34), 111 (35); exact mass 277.217; calcd for $C_{18}H_{29}O_2$ (M − *t*-Bu), 277.2167.

Reaction of 5a with KOH. A solution of 94 mg (0.2 mmol) of **5a** and 116 mg (2.2 mmol) of KOH in 11 mL of 2:1 dimethoxyethane/water and 1 mL of ether was stirred at room temperature for 48 h. The reaction mixture was extracted with ether and the combined extracts were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. Flash chromatography over silica gel using 4:1 hexane/ether as an eluant provided 22 mg (32%) of 2,2,5,5-tetra-*tert*-butyl-2,5-dihydrofuro[3,2-*b*]furan (**9**) as white crystals; mp 163–165 °C; IR 3110, 1662, 1488, 1397, 1371, 1049 cm^{-1}; ^1H NMR (CCl_4) δ 4.54 (s, 1), 1.06 (s, 18); ^{13}C NMR (CCl_4) δ 158.5, 113.5, 88.4, 41.8, 29.2; MS (CI) *m/z* (rel intensity) 277 (27), 221 (77), 207 (33), 167 (100), 139 (17), 127 (28), 111 (48); exact mass 277.217; calcd for $C_{18}H_{29}O_2$ (M − *t*-Bu), 277.2167.

Reduction of 5a. To a slurry of 220 mg of $LiAlH_4$ in 15 mL of ether was added 30.8 mg (0.065 mmol) of **5a** in 10 mL of ether under nitrogen. After stirring for 1 h at room temperature, 0.2 mL of water, 0.3 mL of 10% NaOH solution, and 0.6 mL of water were added sequentially. The mixture was filtered through Celite, which was washed with $CHCl_3$. The filtrate was dried ($MgSO_4$) and concentrated. The resulting mixture was separated by TLC using $CHCl_3$ as eluant to give 4 mg (19%) of 3,8-di-*tert*-butyl-6-hydroxy-2,2,9,9-tetramethyl-3,7-decadien-5-one (**10**) as white crystals: mp 52–53 °C; IR 3450, 3022, 1686, 1608, 1484, 1396, 1370, 1218, 1053, 1017 cm^{-1}; ^1H NMR δ 6.08 (s, 1), 5.24 (dd, J = 11, 4 Hz, 1), 5.08 (d, J = 11 Hz, 1), 3.96 (d, J = 4 Hz, 1), 1.42 (s, 9), 1.30 (s, 9), 1.20 (s, 9), 1.19 (s, 9); ^{13}C NMR δ 206.6, 169.9, 160.2, 121.9, 121.5, 75.2, 40.0, 39.1, 38.6, 37.6, 34.4, 32.5, 31.6, 31.3; MS (CI) *m/z* (rel intensity) 319 (1), 167 (100), 111 (35), 83 (55), 69 (14); exact mass 319.298; calcd for $C_{22}H_{39}O$ (M − OH), 319.3001.

Oxidation of 10 with MnO_2. A solution of 18 mg (0.05 mmol) of **10** in 2 mL of CH_2Cl_2 was stirred at room temperature with 62 mg (0.75 mmol) of activated MnO_2 for 18 h. Preparative TLC using $CHCl_3$ as an eluant afforded 8.1 mg (46%) of **9**.

Oxidation of 4 with Dimethyldioxirane. A solution of 28 mg (0.09 mmol) of **4** in 5 mL of CH_2Cl_2 was stirred with 3 mL (0.24 mmol) of dimethyldioxirane solution[7] in the dark for 5 min. The reaction mixture was concentrated to give an orange solid, which was taken up in a small amount of CCl_4 and submitted to TLC with pentane as eluant. The material on the baseline was extracted into ether and concentrated to give 14 mg (38%) of 2-(2-*tert*-butyl-3,3-dimethyl-1-butenylidene)-3-(1-*tert*-butyl-2,2-dimethylpropylidene)cyclopropanone (**11**) as orange crystals: mp 72–75 °C (dec); IR 1913, 1782, 1552, 1480, 1381, 1366, 1210 cm^{-1}; ^1H NMR δ 1.37 (s, 9), 1.30 (s, 9), 1.21 (s, 18); ^{13}C NMR δ 190.8, 177.6, 159.9, 125.7, 115.2, 93.7, 41.3, 40.2, 37.1, 32.0, 31.5, 30.7; UV/vis (hexane) λ_{max} (ϵ) 416 (217), 337 (8600), 314 (7800), 256 (16000), 233 (57800).

Preparation of 5a by Dimethyldioxirane Oxidation of 4. To a stirred solution of 222 mg (0.75 mmol) of **4** in 10 mL of CH_2Cl_2 under nitrogen in the dark at room temperature with 2 g of solid K_2CO_3 was added 12 mL (0.2 mmol) of dimethyldioxirane solution. After 1 h, the mixture was filtered and concentrated to give a red-orange solid: IR 1912, 1781, 1553 cm^{-1}. The solid was dissolved in 10 mL of CH_2Cl_2, and 120 mg (0.75 mmol) of *m*-chlorobenzoic acid in 15 mL of CH_2CL_2 was added. The mixture was stirred at room temperature for 18 h and concentrated to give a green solid. This material was dissolved in ether, washed twice with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. Flash column chromatography on silica gel using 9:1 hexane–ether as eluant afforded 44 mg of a solid shown by GC to be a 1:1 mixture of **4** and **6** and 40 mg (11%) of **5a**.

Photolysis of 11. A few crystals of **11** in a capillary tube were exposed to sunlight for 5 min. Afterwards, it was observed that the crystals had become colorless and had a mp of 85–93 °C. Analysis by GC showed only **6**.

Thermolysis of 11. A few crystals of **11** in a capillary tube were warmed in a melting point apparatus. The crystals turned from orange to colorless at 72–75 °C and went on to melt at 85–93 °C. Analysis by GC showed only **6**.

Treatment of 11 with Dimethyldioxirane. A solution of 3 mg (0.01 mmol) of **11** in 1 mL of acetone was stirred with 0.5 mL (0.04 mmol) of dimethyldioxirane solution in the dark at room temperature for 45 min. ^1H NMR showed peaks only for **11** and **6** in a 1:1 ratio. A similar solution of **11** was stirred without oxidant in the dark at room temperature for 45 min. ^1H NMR showed only peaks for **11** and **6** in a 1:1 ratio.

Reaction of 11 with HCl. A solution of 22 mg (0.07 mmol) of **11** in 10 mL of CH_2Cl_2 was stirred at room temperature with HCl gas bubbling in for 5 min. The orange color completely disappeared. The mixture was concentrated and the residue was submitted to preparative TLC using CH_2Cl_2 as eluent to give 14 mg (58%) of 3,8-di-*tert*-butyl-6-chloro-2,2,9,9-tetramethyl-3,6,7-decatrien-5-one (**5c**) as a colorless solid: mp 73–74 °C; IR 1918, 1665, 1603, 1480, 1392, 1367, 1161, 655 cm^{-1}; ^1H NMR δ 6.14 (s, 1), 1.30 (s, 9), 1.27 (s, 18), 1.22 (s, 9); ^{13}C NMR δ 206.7, 190.7, 166.3, 133.8, 123.2, 108.5, 39.7, 38.8, 37.4, 32.8, 31.7, 31.4; MS (CI) *m/z* (rel intensity) 353 (4), 296 (42), 239 (51), 168 (100), 139 (82), 111 (19); exact mass 353.261; calcd for $C_{22}H_{38}ClO$, 353.2611.

Oxidation of 4 with Dimethyldioxirane in the Presence of Acetic Acid. A solution of 120 mg (0.4 mmol) of **4** in 5 mL of CH_2Cl_2 and 10 mL of acetic acid was stirred at room temperature with 10 mL of a dimethyldioxirane solution for 3 h. The mixture was concentrated, dissolved in ether, washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The solid residue was dissolved in ether and recrystallized by slow evaporation of solvent. The resulting crystals were washed with cold acetone to give 94 mg (63%) of 6-acetoxy-3,8-di-*tert*-butyl-2,2,9,9-tetramethyl-3,6,7-decatrien-5-one (**5d**) as colorless crystals: mp 117–118 °C; IR 1927, 1752, 1661, 1601, 1468, 1393, 1368, 1217, 1190 cm^{-1}; ^1H NMR δ 6.18 (s, 1), 2.23 (s, 3), 1.34 (s, 9), 1.29 (s, 18), 1.24 (s, 9); ^{13}C NMR δ 201.2, 190.7, 168.8, 167.6, 136.4, 125.5, 122.7, 39.8, 38.7, 37.6, 32.9, 31.7, 31.6, 20.6; MS (CI) *m/z* (rel intensity) 319 (21), 263 (14), 221 (20), 167 (100), 111 (50). Anal. Calcd for $C_{24}H_{40}O_3$: C, 76.53; H, 10.71. Found: C, 76.48; H, 10.73.

Oxidation of 4 with mCPBA. FT-IR Experiment. A solution of 10.5 mg (0.06 mmol) of mCPBA in 0.25 mL of CH_2Cl_2 was added to 13 mg (0.043 mmol) of **4** in 0.25 mL of CH_2Cl_2. An aliquot was placed immediately into an IR solution cell and observed by FT-IR at intervals of 2–3 min. A strong peak at 2045 cm^{-1} was observed immediately, reached a maximum in about 5 min, and then diminished and disappeared over about 45 min. Spectrum analysis by subtraction of known components also identified a very high intensity peak at 1782 cm^{-1}, which appeared and receded in concert with the other peak. The reaction progress was monitored by observing changes in the mCPBA and *m*-chlorobenzoic acid peaks. It was also observed that a peak at 1910 cm^{-1}, attributed to cyclopropanone **11**, appeared and disappeared over the course of the reaction. At the end of the reaction, peaks for **5a** were observed, as well as a peak for **6** at 2062 cm^{-1}.[13]

Oxidation of 4 with mCPBA. ^1H NMR Experiment. The reaction of 15 mg (0.05 mmol) of **4** and 11.5 mg (0.065 mmol) of mCPBA in 1 mL of $CDCl_3$ in an NMR tube was observed by 500-MHz ^1H NMR at a probe temperature of 21 °C. Spectra were taken at intervals of 3–5 min until little further change was observed (80 min). The intensity of the singlets at δ 1.34, 1.32, and 1.16 (ratio 1:1:2) increased with time, maximized after 6–10 min, then diminished. After 80 min, they were no longer evident. Peaks at δ 1.39, 1.32, and 1.24 attributed to **11** disappeared after exposure to sunlight. The final spectrum was dominated by signals from **5a**, **4**, and **6**. An aliquot of the reaction mixture taken when the intermediate was most abundant showed IR 2045 and 1782 cm^{-1}.[13]

Oxidation of 4 with mCPBA. Low-Temperature ^{13}C NMR Experiment. The reaction of 29 mg of **4** and 36 mg of mCPBA in 1.5 mL of $CDCl_3$ in an NMR tube was observed by ^1H NMR at 21 °C until the peaks at δ 1.34, 1.32, and 1.16 comprised 43% of the reaction mixture by integration. The mixture was cooled to −30 °C and a ^{13}C NMR spectrum was recorded. After 2 h of data accumulation, an ^1H NMR spectrum showed that the intermediate was still 40% of the mixture. The

^{13}C NMR spectrum showed peaks at δ 204.8, 164.4, 163.7, 156.9, 105.3, 59.7, 41.8, 41.5, 37.8, 31.5, 31.4, and 30.1 attributed to **15**.[13]

Oxidation of 4 with *p*-Nitroperbenzoic Acid. Low-Temperature ^{13}C NMR Experiment. To a solution of 23.1 mg (0.077 mmol) of **4** in 0.35 mL of $CDCl_3$ in an NMR tube was added 14.5 mg (0.079 mmol) of *p*-nitroperbenzoic acid in 0.15 mL of THF-d_8 and 0.25 mL of $CDCl_3$. After 5 min at room temperature, the mixture was cooled to −30 °C. The ^1H NMR spectrum showed peaks at δ 1.34, 1.32, and 1.13 for the transient material (15% of the reaction mixture by integration) and those for **11** (9%). The ^{13}C NMR spectrum showed the same peaks attributed to **15** in the previous experiment.

Following the reaction, the solution was concentrated and the residue was triturated with acetone to give 3,8-di-*tert*-butyl-2,2,9,9-tetramethyl-6-(4-nitrobenzoyloxy)-3,6,7-decatrien-5-one (**5b**) as a crystalline solid: mp 170–172 °C; IR 1927, 1740, 1663, 1603, 1530, 1479, 1348, 1188, 1090 cm^{-1}; ^1H NMR δ 8.31 (s, 4), 6.26 (s, 1), 1.36 (s, 9), 1.33 (s, 18), 1.26 (s, 9); ^{13}C NMR δ 200.7, 190.0, 168.6, 162.9, 150.7, 137.8, 135.1, 131.4, 125.7, 123.5, 122.3, 39.9, 38.8, 37.7, 32.9, 31.7, 31.6; MS (EI) *m/z* (rel intensity) 426 (12), 370 (11), 203 (15), 167 (100), 150 (46), 111 (57), 83 (56); exact mass 426.226; calcd for $C_{25}H_{32}NO_5$ (M − *t*-Bu), 426.2280.

Oxidation of 4 with 5 Equiv of mCPBA. To a solution of 14.3 mg (0.048 mmol) of **4** in 1 mL of $CHCl_3$ at room temperature in the dark was added 46.1 mg (0.27 mmol) of mCPBA. After 1.5 h, ^1H NMR indicated the presence of **5a** (40%), **6** (20%), **19** (20%), **1** (5%), and **2** (5%).

5-*tert*-Butyl-6,6-dimethylhepta-2,3,4-trienal (16). The method of Kosower was used.[10] To a solution of 3 g (36.6 mmol) of freshly distilled *cis*-1-methoxy-1-buten-3-yne in 40 mL of dry THF at −40 °C under N_2 was added 14 mL (35 mmol) of 2.5 M *n*-butyllithium in hexane. After 1 h, 4.25 g (30 mmol) of di-*tert*-butyl ketone was added, and the mixture was allowed to warm slowly to room temperature and stirred for 16 h. Water was added and the organic layer was separated and washed sequentially with saturated $NaHCO_3$ solution and 10% HCl solution, dried ($MgSO_4$), and concentrated. Flash chromatography on silica gel using 9:1 pentane–ether as eluant afforded 1.14 g (20%) of **16** as a viscous yellow liquid: IR 2723, 2057, 1670, 1477, 1447, 1392, 1105 cm^{-1}; ^1H NMR δ 9.40 (d, *J* = 8 Hz, 1), 5.90 (d, *J* = 8 Hz, 1), 1.33 (s, 9), 1.30 (s, 9); ^{13}C NMR δ 189.8 (dd, *J* = 176, 2 Hz, C1), 183.2 (s, C4), 161.7 (m, *J* = 4 Hz, C5), 152.9 (d, *J* = 7.3 Hz, C3), 104.0 (dd, *J* = 172, 27 Hz, C2), 40.5 (m, *J* = 3.5 Hz), 39.8 (*m*, *J* = 3.5 Hz), 31.5 (qm, *J* = 126, 4.5 Hz), 31.4 (qm, *J* = 126, 4.5 Hz); MS (EI) *m/z* (rel intensity) 193 (35), 136 (100), 121 (62), 109 (63), 93 (30), 91 (64); exact mass 191.160; calcd for $C_{13}H_{21}O$, 193.1592.

A brown crystalline solid, identified as (*Z*)-3-*tert*-butyl-7-methoxy-2,2-dimethylhept-6-en-4-yn-3-ol, was also collected: mp 42.5–45 °C; IR 3449, 2209, 1634, 1472, 1385, 1100, 1035 cm^{-1}; ^1H NMR δ 6.31 (d, *J* = 6.4 Hz, 1), 4.59 (d, *J* = 6.4 Hz, 1), 3.81 (s, 3), 2.01 (s, 1), 1.25 (s, 18); ^{13}C NMR δ 156.0, 96.2, 85.3, 81.8, 79.8, 60.2, 41.6, 28.8; MS (EI) *m/z* (rel intensity) 224 (1), 208 (8), 167 (100), 109 (62), 107 (23), 81 (53); exact mass 224.179; calcd for $C_{14}H_{24}O_2$, 224.1776.

Oxidation of 6 with mCPBA. A solution of 13.4 mg (0.047 mmol) of **6** in 1 mL of $CHCl_3$ was stirred at room temperature with 10 mg (0.058 mmol) of mCPBA for 1 h. The reaction mixture was washed with saturated $NaHCO_3$ solution and concentrated. Preparative TLC using pentane as eluant provided 8.2 mg (57%) of 3,3-di-*tert*-butyl-2-(2-*tert*-butyl-3,3-dimethyl-1-butenylidene)cyclopropanone (**19**) as bright yellow crystals: mp 77–79 °C; IR 1918, 1786, 1478, 1366, 1215, 1096, 1002 cm^{-1}; ^1H NMR δ 1.27 (s, 1), 1.19 (s, 1); ^{13}C NMR δ 203.8, 192.6, 123.8, 87.5, 58.6, 37.7, 36.9, 32.5, 30.4; MS (EI) *m/z* (rel intensity) 276 (48), 219 (31), 163 (37), 135 (79), 121 (91), 91 (100); exact mass 276.278; calcd for $C_{20}H_{36}$ (M − CO), 276.2816.

Photolysis of 19. A small sample of **19** in $CDCl_3$ in an NMR tube was exposed to sunlight for 30 min. ^1H NMR showed that 30% of the sample had been converted to **1**. The remainder was starting material.

Treatment of 19 with HCl. To a solution of 8.2 mg (0.027 mmol) of **19** in 5 mL of $CHCl_3$ was added 1 mL of concentrated HCl. The yellow color disappeared in seconds. The organic layer was separated, dried ($MgSO_4$), and concentrated. Preparative TLC using 5:1 pentane–ether as eluant afforded 3 mg (31%) of 3,7-di-*tert*-butyl-3-chloro-2,2,8,8-tetamethylnona-5,6-dien-4-one (**20**): IR 1923, 1660, 1476, 1366, 1216, 778 cm^{-1}; ^1H NMR δ 7.09 (s, 1), 1.33 (s, 18), 1.30 (s, 18); MS (EI) *m/z* (rel intensity) 340 (1), 215 (1), 213 (4), 179 (100), 151 (32), 123 (33), 95 (18); exact mass 340.258; calcd for $C_{21}H_{37}ClO$, 340.2532.

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Supplementary Material Available: Spectra for reactive intermediates **3** and **15** and complete X-ray data for **9** (14 pages); listing of structure factors (3 pages). Ordering information is given on any current masthead page.