6d: ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 3.50 (s, 2 H), 7.20 (s, 5 H); IR (Nujol) 1780 cm^{-1}.

6e: ^{1}H NMR (CCl_4) δ 1.19 (d, 6 H, J = 7.5 Hz), 1.29 (s, 9 H), 2.62 (sep, 1 H, J = 7.5 Hz); IR (film) 1780 cm^{-1}.

***t*-BuOK-Catalyzed Reaction of *tert*-Butyl Peroxy Esters 6.** A solution of **6** (5 mmol) in dry pentane (10 mL) was added dropwise in 30 min to a vigorously stirred solution of *t*-BuOK (20 mmol) in dry DMF (20 mL) containing dry pentane (6 mL) at −60 to −78 °C under nitrogen atmosphere. The mixture was stirred at the same temperature for 4 h and neutralized with dilute HCl (pH ca. 8). The resulting mixture was then evaporated under a reduced pressure at 40 °C to dryness. The residue was further acidified with dilute HCl and extracted with ether. The extract was dried (Na_2SO_4) and evaporated to givbe a colorless oily residue. Products were isolated by the following workup. Compound **7a** was obtained by direct distillation of the residue. The residues from **6b–e** were treated with diazomethane, and **7b–e** and other carboxylic acids were isolated as their methyl esters by means of gas chromatography followed by distillation. The methyl esters of the C_3 and C_4 carboxylic acids were identified with authentic samples. Acetic acid from **6a** was not isolated, but its formation was confirmed by ^{1}H NMR spectrum of the reaction mixture obtained from **6a**.

7a: bp 95 °C (4 mmHg); ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 3.96 (s, 2 H); IR (film) 1735 cm^{-1}. Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.42; H, 9.25.

Methyl ester of 7b: colorless oil; bp 100 °C (6 mmHg); ^{1}H NMR (CCl_4) δ 1.17 (s, 9 H), 1.26 (d, 3 H, J = 7.0 Hz), 3.71 (s, 3 H), 4.13 (q, 1 H, J = 7.0 Hz); IR (film) 1755 cm^{-1}. Anal. Calcd for $C_8H_{16}O_3$: C, 59.98; H, 10.07. Found: C, 59.83; H, 9.88. **7b**: ^{1}H NMR (CCl_4) δ 1.21 (s, 9 H), 1.34 (d, 3 H, J = 7 Hz), 4.09 (q, 1 H, J = 7 Hz).

Methyl ester of 7c: colorless oil; bp 55 °C (4 mmHg); ^{1}H NMR (CCl_4) δ 0.95 (t, 3 H, J = 7 Hz), 1.13 (s, 9 H), 1.55 (q, d, 2 H, J = 7, 6 Hz), 3.66 (s, 3 H), 3.77 (t, 1 H, J = 6 Hz); IR (film) 1755 cm^{-1}. Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 61.79; H, 10.49. **7c**: ^{1}H NMR (CCl_4) δ 0.95 (t, 3 H, J = 7.5 Hz), 1.20 (s, 9 H), 1.60 (q, d, 1 H, J = 7.5, 6 Hz), 3.88 (t, 1 H, J = 6 Hz).

Methyl ester of 7d: colorless oil; bp 95 °C (3 mmHg); ^{1}H NMR (CCl_4) δ 1.26 (s, 9 H), 3.70 (s, 3 H), 5.11 (s, 1 H), 7.2–7.6 (m, 5 H); IR (film) 1755 cm^{-1}. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.98; H, 8.21. **7d**: ^{1}H NMR (CCl_4) δ 1.20 (s, 9 H), 4.97 (s, 1 H), 7.0–7.5 (m, 5 H).

Methyl (*o*-*tert*-butoxyphenyl)acetate: colorless oil; ^{1}H NMR (CCl_4) δ 1.37 (s, 9 H), 3.45 (s, 2 H), 3.56 (s, 3 H), 6.6–7.2 (m, 4 H). Anal. Calcd for $C_{13}H_{18}O_3$ (as a mixture with the *p*-isomer): C, 70.24; H, 8.16. Found: C, 70.24; H, 8.41.

Methyl (*p*-*tert*-butoxyphenyl)acetate: colorless oil; ^{1}H NMR (CCl_4) δ 1.32 (s, 9 H), 3.48 (s, 2 H), 3.65 (s, 3 H), 6.7–7.3 (m, 4 H).

Registry No. **1a**, 62926-71-0; **1b**, 62926-72-1; **1c**, 62926-73-2; **1d**, 62926-74-3; **1e**, 62926-75-4; **1f**, 62926-76-5; **1g**, 62955-68-4; **1h**, 62926-77-6; **1i**, 87100-48-9; **2a**, 62926-78-7; **2a** methyl ester, 87100-49-0; **2b**, 62926-79-8; **2c**, 62926-80-1; **2d**, 62926-81-2; **2e**, 62926-82-3; **2f**, 62926-83-4; **4a**, 128-37-0; **4b**, 4130-42-1; **4c**, 5427-03-2; **4d**, 732-26-3; **6a**, 107-71-1; **6b**, 14206-05-4; **6c**, 18072-84-9; **6d**, 3377-89-7; **6e**, 109-13-7; **7a**, 13211-32-0; **7b**, 87100-50-3; **7b** methyl ester, 87100-51-4; **7c**, 87100-52-5; **7c** methyl ester, 87100-53-6; **7d**, 66667-02-5; **7d** methyl ester, 87100-54-7; acetyl chloride, 75-36-5; propanoyl chloride, 79-03-8; benzeneacetyl chloride, 103-80-0; 2-methylpropanoyl chloride, 79-30-1; benzoyl chloride, 98-88-4; 2,2-dimethylpropanoyl chloride, 3282-30-2; 4-methyl-2,3-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienone, 6485-57-0; 4-ethyl-2,6-di-*tert*-butyl-4-(hydroxperoxy)-2,5-cylcohexadienone, 87013-27-2; 4-isopropyl-2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienone, 87013-28-3; 2,4,6-tri-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienone, 33919-05-0; *tert*-butyl hydroperoxide, 75-91-2; butanoyl chloride, 141-75-3; methyl (*o*-*tert*-butyoxyphenyl)acetate, 87100-55-8; methyl (*p*-*tert*-butoxyphenyl)acetate, 87100-56-9.

Peroxy Esters. 9. Base- and Radical-Induced Decomposition of 1-Alkyl-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl 3,5-Di-*tert*-butyl-4-hydroxyperbenzoates[1]

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Received January 24, 1983

The title peroxy esters **1**, when deprotonated with *t*-BuOK in DMF to the corresponding phenolate anions, decompose even at −78 °C to give compounds **2–10**. These compounds result undoubtedly from homolysis of the peroxy bond in **1**, indicating that the generation of a carbanion at the α-position of the acyl group in peroxy esters (via resonance in the present case) induces ready homolysis of the peroxy bond. The oxidation of **1** with one-electron oxidizing agents gives rise to the corresponding phenoxy radicals, which also induce homolysis of the peroxy bond.

In the preceding paper,[1] we reported that 1-alkyl-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl and *tert*-butyl peroxy acetates underwent base-catalyzed rearrangement at −60 °C or below to give the corresponding alkoxyacetic acid derivatives resulting from cleavage of the peroxy bond. The proposed mechanism involves homolysis of the peroxy bond, which is accelerated when a carbanion is generated in the α-position of the acyl group of the peroxy esters. On the other hand, Leffler et al.[2] have argued a heterolytic cleavage of the peroxy bond for the base-catalyzed decomposition of *tert*-butyl 3,5-di-*tert*-butyl-4-hydroxyperbenzoate. However, an insufficient search for the fate of the *tert*-butoxy moiety of the ester has made their argument uncertain. We have therefore investigated the base-catalyzed reaction as well as the oxidation of 1-al-

(1) Preliminary communication: Nishinaga, A.; Nakamura, K.; Matsuura, T. *Tetrahedron Lett.* **1978**, 3557. Part 7: Nishinaga, A.; Nakamura, K.; Matsuura, T. *J. Org. Chem.*, preceding paper in this issue.

(2) Hucek, A. M.; Barbas, J. T.; Leffler, J. E. *J. Am .Chem. Soc.* **1973**, *95*, 4698.

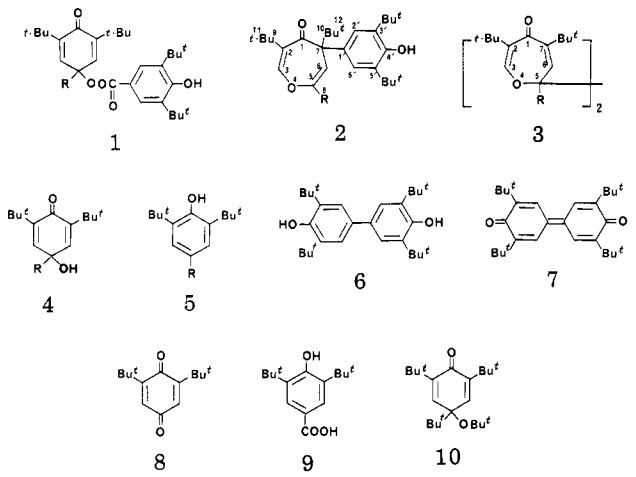
0022-3263/83/1948-3700$01.50/0

Table I. Base-Catalyzed Decomposition of Peroxy Esters 1 with *t*-BuOK in DMF[a]

substrate 1	yield of product, %[b]								
	2	3	4	5	6	7	8	9	10
1a	46	22	3	0	5	7	4	24	
1b	38[c]	20[c]	12	0	10	3	8	29	
1c	0	0	10	9	16	3	80	52	
1d	0	0	13	21	11	0	45	58	21

[a] Reaction time, 1 h; reaction temperature −78 °C; conversion, 100%. [b] Determined by ^{1}H NMR. [c] Not isolated in pure form.

Chart I

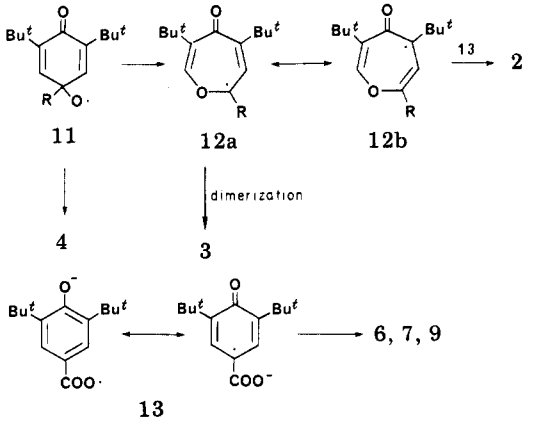


kyl-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl 3,5-di-*tert*-4-hydroxyperbenzoates, which were expected to be suitable for investigating the fate of the alkoxy moiety and in turn finding out easily the nature of the peroxy bond cleavage.

Results and Discussion

Base-Catalyzed Reaction of 1-Alkyl-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl 3,5-Di-*tert*-butyl-4-hydroxyperbenzoates (1). The peroxy esters 1 were synthesized in good yield by the Schotten–Baumann reaction with 3,5-di-*tert*-butyl-4-hydroxybenzoyl chloride and 4-alkyl-3,5-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadienones readily available from the base-catalyzed oxygenation of the corresponding 4-alkyl-2,6-di-*tert*-butylphenols (5)[3,4] (see Chart I). The peroxy esters 1 were obtained as crystals, which are stable at ambient temperature for a long time in the dark (more than several months). When a solution of 1 in a mixture of petroleum ether and benzene was added to a solution of *t*-BuOK in *N,N*-dimethylformamide (DMF) even at −78 °C under N_2, however, 1 was quite unstable and underwent base-catalyzed decomposition. Silica gel chromatographic separation of the reaction mixture gave 5-alkyl-2,7-di-*tert*-butyl-4-oxa-7-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,5-cycloheptadienone (2), 5,5′-bi(5-alkyl-2,7-di-*tert*-butyl-4-oxa-2,6-cycloheptadienone) (3), 4-alkyl-2,6-di-*tert*-butyl-4-hydroxy-2,5-cyclohexadienone (*p*-quinol) (4), 4-alkyl-2,6-di-*tert*-butylphenol (5), 3,3′,5,5′-tetra-*tert*-butylbiphenyl-4,4′-diol (6), 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (7), 2,6-di-*tert*-butyl-*p*-benzoquinone (8), 3,5-di-*tert*-butyl-4-hydroxybenzoic acid (9), and 2,4,6-tri-*tert*-butyl-4-*t*-butoxy-2,5-cyclohexadienone (10). The results are summarized in Table I.

Analytical and spectral data of 2 and 3 are in good agreement with the structures. All the other products, 4–10, are known compounds. Undoubtedly, compound 3 is the dimerization product of the ring-expanded isomer **12a** of quinoxyl radical 11. Similarly, the formation of 2 is reasonably interpreted in terms of coupling between the other ring expanded radical **12b** and 3,5-di-*tert*-butyl-4-hydroxybenzoyloxyl radical 13 followed by decarboxyla-



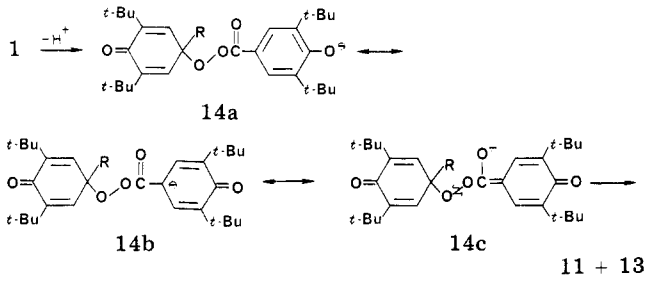
tion. No product resulting from the coupling of **12a** with 13 or of **12b** at C_7 with another **12b** was obtained. Compounds 6 and 7 were formed undoubtedly by the dimerization of the radical 13 followed by decarboxylation.[3] However, the higher yield of phenolcarboxylic acid 9 compared to the biphenol 6 indicates that the carboxyl radical 13 has an appreciable lifetime and underwent more easily reduction than the coupling with each other. The migration of 11 to 12 followed by the radical coupling reactions becomes difficult as the size of R in 11 increases, and the reduction and the β-cleavage of 11 predominates. Thus, with **1c** and **1d**, no such radical coupling products as 2 and 3 were detected in the reaction mixture, where compounds 8 and 9 became the main products. The formation of 10 from **1d** resulted from the coupling between 11 and *tert*-butyl radical generated by the β-cleavage of 11 (R = *t*-Bu).[4] Phenol 5 could also be formed by the coupling of 13 with the R radical generated by the β-cleavage of 11 followed by decarboxylation, because 5 was formed only when 11 was susceptible to the β-cleavage. It is, however, possible that the phenol 5 may also be formed by the nucleophilic attack by the *tert*-butoxy anion on the carbonyl carbon of the acyl group in 1, because the corresponding peroxyquinolate anion thus formed can liberate molecular oxygen, giving rise to the phenol.[5]

Thus, the results obtained in the present base-catalyzed reation of 1 are rationalized by homolytic cleavage of the peroxy bond, which readily occurs only by deprotonation even at −78 °C. It is noted that the peroxycarbonylphenolate anion 14 is analogous to the anions of *p*-quinol peroxyacetates described in the preceding paper.

(3) Compound 7 could be formed by electron transfer from an anion of 6 probably to the radical 12 or 13. A reviewer comments on another possibility that 7 could also be formed from diradical 18 produced by disproportionation of 13.

(4) Nishinaga, A.; Nakamura, K.; Matsuura, T. *Chem. Lett.* **1977**, 303.

(5) Nishinaga, A.; Itahara, T.; Shimizu, T.; Matsuura, T. *J. Am. Chem. Soc.* **1978**, *100*, 1820.



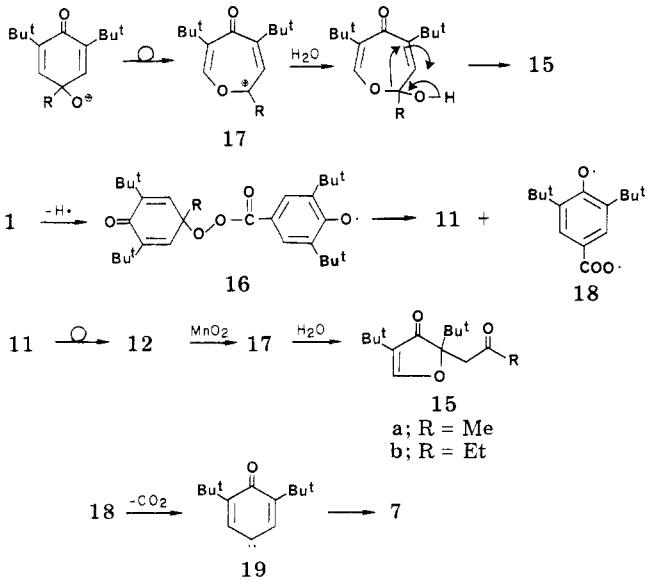
14a 14b 14c 11 + 13

Radical-Induced Decomposition of 1. The oxidation of **1a** and **1b** with $K_3Fe(CN)_6$, a one-electron oxidizing reagent, gave **3**, **7**, and **8** as main products, whereas with MnO_2 2,5-di-*tert*-butyl-4-oxa-2-cyclopentenone derivatives (**15**), **7**, and **8** were obtained. The oxidation of **1c** and **1d**, on the other hand, with the either oxidant gave mainly **7** and **8** (Table II).

The formation of **3** verifies the generation of *p*-quinoxyl radical **11** that undergoes a ring expansion, leading to the isomeric oxepinone radical **12**. The predominant formation of **8** in the oxidation of **1c** and **1d** is similar to the case described in the base-catalyzed decomposition of these substrates.

The results in the one-electron oxidation of **1** clearly show that the generation of phenoxy radical **16** induces readily the homolysis of the peroxy bond in **1** as expected.[2] Compound **15** has been shown to be formed by hydration of oxepinonium cation **17** resulting from the ring expansion of the corresponding *p*-quinoxy cation.[6] The formation of **15** in the oxidation with MnO_2, therefore, indicates that the oxepinone radical intermediate **12** was further oxidized with MnO_2 to oxepinonium cation **17** under the reaction conditions.

The yield of diphenoquinone **7** did not change much in all the cases examined, indicating that biradical **18** undergoes predominantly decarboxylation, probably to give carbene intermediate **19**, and has no influence on the fate of quinoxyl radical **11**, as no coupling between **11** and **18** was observed.

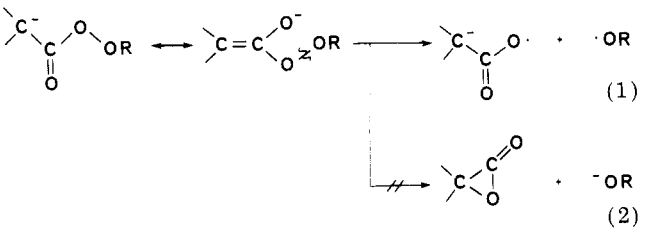


17 16 18 15 a; R = Me b; R = Et 19

The difference between the results obtained in both the oxidation reactions is due to the different oxidation conditions; that is, the results with MnO_2 should be understood in terms of absorption of the substrate on the surface of the solid oxidant.

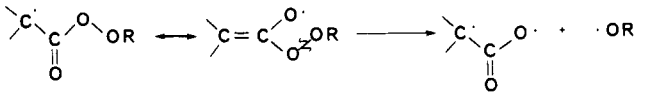
Conclusion

All the findings in the present work also lead us to the conclusion that the generation of a carbon anion at the α-position of peroxy esters induces readily the homolysis of the peroxy bond but not the heterolysis (eq 1, 2). The



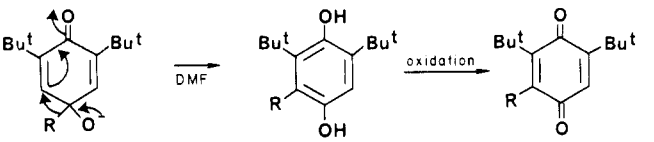
(1)

(2)



(3)

generation of a carbon radical at the α-position of peroxy esters also induces the homolysis of the peroxy bond as expected.[2] If the reaction illustrated in eq 2 takes place as proposed by Hucek et al.,[2] the base-catalyzed reaction of **1** should give hydroquinone derivatives (**21**) or their oxidation products since quinolate anion (**20**) has been shown to undergo readily the migration of R in DMF, giving rise to **21** quantitatively.[7] Neither hydroquinone



20 21

21 nor its oxidation product was detected in the base-catalyzed reaction of **1**.

Eventually, the results obtained in the present work also reveal that *p*-quinoxyl radicals of type **11** easily undergo a ring expansion as seen in quinoxy cations,[6] establishing reactions of all three types for the *p*-quinoxy moiety, i.e., anion, radical, and cation.

Experimental Section

All melting points were uncorrected. Elemental analyses were performed by the Analytical Center of Pharmaceutical Department, Kyoto University. Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer. Ultraviolet spectra were determined with a Shimazu UV-200 spectrophotometer. Proton magnetic resonance spectra were determined with a Varian T-60 spectrometer. Carbon-13 magnetic resonance spectra were obtained with a Bruker HFX-90 multi-nucleus spectrometer.

1-Alkyl-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadienyl 3,5-Di-*tert*-butyl-4-hydroxyperbenzoates (1). A solution of pyridine (0.59 g, 7.5 mmol) in dry petroleum ether (15 mL) was added dropwise to a solution of 3,5-di-*tert*-butyl-4-hydroxybenzoyl chloride[8] (2 g, 7.5 mmol) and the corresponding peroxy-*p*-quinol[5] (7.5 mmol) in dry petroleum ether (30 mL) in 30 min with stirring at −20 °C. The mixture was stirred for 1 h at the same temperature and allowed to stand at −5 °C overnight. Pyridine hydrochloride precipitated and was then filtered (a Celite layer; 4 g, 1.5 cm) and washed with the same solvent. The filtrate was

(6) Nishinaga, A.; Nakamura, K.; Matsuura, T.; Rieker, A.; Koch, D.; Griesshammer, R. *Tetrahedron* **1979**, *35*, 2493; *Tetrahedron Lett.* **1978**, 3597.

(7) Nishinaga, A.; Itahara, T.; Matsuura, T.; Berger, S.; Henes, G.; Rieker, A. *Chem. Ber.* **1976**, *109*, 1530.

(8) Müller, E.; Rieker, A.; Mayer, R.; Scheffler, K. *Liebigs Ann. Chem.* **1961**, *645*, 36.

Table II. Oxidation of Peroxy Esters 1 with One-Electron Oxidant

oxidant	ester 1	yield of product, %[a] 3	15	7	8	9	10	others[b]
$K_3Fe(CN)_6$	1a	48		38				20
	1b	25		48	47			7
	1c			37	99	10		10
	1d			48	84		13	6
MnO_2	1a		75	37	10	26		8
	1b		50	49	48			3
	1c			23	89	32		7
	1d			32	89	16	8	20

[a] Determined by ^1H NMR. [b] Not identified.

evaporated to give a yellow, viscous oily residue, which was triturated with petroleum ether to give the peroxy ester 1 as crystals. The yields of 1 were based on the isolation.

1a: colorless needles (petroleum ether) (74% yield); mp 126–128 °C dec; ^1H NMR ($CDCl_3$) δ 1.19 (s, 18 H), 1.40 (s, 18 H), 1.51 (s, 3 H), 5.67 (s, 1 H, OH), 6.65 (s, 2 H), 7.62 (s, 2 H); IR (Nujol) 3620, 1755, 1675, 1650 cm^{-1}. Anal. Calcd for $C_{30}H_{44}O_5$: C, 74.34; H, 9.15. Found: C, 74.09; H, 9.38.

1b: colorless needles (petroleum ether) (85% yield); mp 118–120 °C dec; ^1H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 7.5 Hz), 1.21 (s, 18 H), 1.40 (s, 18 H), 1.86 (q, 2 H, J = 7. 5 Hz), 5.68 (s, 1 H, OH), 6.60 (s, 2 H), 7.62 (s, 2 H); IR (Nujol) 3620, 1755, 1675, 1650 cm^{-1}. Anal. Calcd for $C_{31}H_{46}O_5$: C, 74.66; H, 9.30. Found: C, 74.48; H, 9.28.

1c: colorless needles (petroleum ether) (75% yield); mp 101–103 °C dec; ^1H NMR ($CDCl_3$) δ 0.99 (d, 6 H, J = 7.5 Hz), 1.20 (s, 18 H), 1.41 (s, 18 H), 2.20 (sep, 1 H, J = 7.5 Hz), 5.71 (s, 1 H, OH), 6.68 (s, 2 H), 7.63 (s, 2 H); IR (Nujol) 3620, 1750 1670, 1650 cm^{-1}. Anal. Calcd for $C_{32}H_{48}O_5$: C, 74.96; H, 9.44; Found: C, 74.80; H, 9.52.

1d: colorless needles (petroleum ether) (73% yield); mp 101–103 °C dec; ^1H NMR ($CDCl_3$) δ 1.10 (s, 9 H), 1.17 (s, 18 H), 1.38 (s, 18 H), 5.66 (s, 1 H, OH), 6.83 (s, 2 H), 7.58 (s, 2 H); IR (Nujol) 3620, 1750, 1670, 1645, cm^{-1}. Anal. Calcd for $C_{33}H_{50}O_5$: C, 75.24; H, 9.57. Found: C, 75.18; H, 9.83.

t-BuOK-Catalyzed Decomposition of 1 in DMF. A solution of 1 (2.06 mmol) in dry petroleum ether (12 mL) containing benzene (3 mL) was added dropwise to a solution of *t*-BuOK (0.924 g, 8.25 mmol) in dry DMF (20 mL) containing dry petroleum ether (10 mL) in 30 min with vigorous stirring at −78 °C under a nitrogen atmosphere. The resulting green mixture was stirred for 1 h at −60 to −78 °C, acidified with ice-cooled aqueous HCl, and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. Repeated chromatographic separation of the resulting products (silica gel plates developing with a mixed eluent (petroleum ether/CH_2Cl_2 2:1) followed by elution with ether) gave the known compounds **4–10** and new compounds **2** and **3**. Compounds **2a** and **3a** were purified by recrystallization from petroleum ether, but the purification of **2b** and **3b** was unsuccessful, although their spectral data were in good agreement with the structures.

2a: colorless needles (petroleum ether); mp 141–143 °C; ^1H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 1.20 (s, 9 H), 1.44 (s, 18 H), 2.16 (d, 3 H, J = 0.67 Hz), 5.17 (s, 1 H, OH), 5.68 (q, 1 H, J = 0.67 Hz), 7.17 (s, 2 H), 7.94 (s, 1 H); IR (Nujol) 3600, 1690 cm^{-1}; UV (CH_2Cl_2) λ_{max} 262 nm (log ϵ 4.20); ^{13}C NMR ($CDCl_3$) δ 204.4 (C-1), 135.7 (C-2), 170.2 (C-3), 127.5 (C-5), 121.9 (C-6), 95.8 (C-7), 18.3 (C-8), 34.3 (C-9), 40.1 (C-10), 28.3 (C-11), 24.5 (C-12), 29.6 (C-13), 30.2 (C-14), 127.6 (C-1′), 122.9 (C-2′, C-6′), 135.4 (C-3′, C-5′), 153.3 (C-4′). Anal. Calcd for $C_{29}H_4O_3$: C, 79.04; H, 10.07. Found: C, 78.75; H, 10.15.

2b: not purified; ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H, J = 7.0 Hz), 1.04 (s, 9 H), 1.21 (s, 9 H), 1.43 (s, 18 H), 2.58 (q, 2 H, J. = 7.0 Hz), 5.15 (s, 1 H, OH), 5.58 (broad unresolved, 1 H), 7.11 (s, 2 H), 7.95 (s, 1 H); IR (Nujol) 3600, 1690 cm^{-1}.

3a: colorless needles (petroleum ether); mp 230–232 °C dec; *m/e* (M^+) 470; ^1H NMR ($CDCl_3$) δ 1.20 (s, 18 H), 1.24 (s, 18 H), 1.54 (s, 6 H), 5.93 (s, 2 H), 6.79 (s, 2 H); IR (Nujol) 1655, 1640 cm^{-1}; UV (CH_2Cl_2) λ_{max} 248, 292 nm (log ϵ 3.90, 3.75). Anal. Calcd for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85. Found: C, 76.38; H, 10.15.

3b: not purified; ^1H NMR ($CDCl_3$) δ 1.21 (s, 18 H), 1.24 (s, 18 H), 0.88 (br t, 3 H, J = 7 Hz), 5.93 (s, 2 H), 6.70 (s, 2 H); IR (Nujol) 1655, 1640 cm^{-1}.

Compound **10** was identical with an authentic sample (^1H NMR, IR, TLC).[9]

Oxidation of 1 with $K_3Fe(CN)_6$. A solution of 1 (0.4 mmol) in benzene (5 mL) was added dropwise to a solution of $K_3Fe(CN)_6$ (0.53 g, 1.6 mmol) and KOH (0.28 g, 5.7 mmol) in H_2O (2.5 mL) in 1.5 min with vigorous stirring at 0 °C under N_2. The mixture was stirred for 1 h, acidified with ice-cooled aqueous HCl, and extracted with ether. The extract was dried (Na_2SO_4) and evaporated. The ^1H NMR of the resulting residue showed the formation of compounds **3** and **7–10**, which were separated by TLC and identified with authentic samples.

Oxidation of 1 with MnO_2. A solution of 1 (0.4 mmol) in benzene (5 mL) was added dropwise to a suspension of MnO_2 (1.74 g, 20 mmol) in benzene (5 mL) with vigorous stirring at 0–10 °C under N_2. The mixture was stirred for 2.5 h. The inorganic solid was filtered off (a Celite layer, 2 g, 1.5 cm) and washed with benzene. The benzene solution was evaporated at 50 °C. The ^1H NMR and TLC of the resulting residue showed the formation of compounds **7–10** and **15**, which were separated by TLC and identified with authentic samples.

Acknowledgment. We thank Prof. A. Rieker and Dr. K. Albert at Tübingen University for measurement of the ^{13}C NMR and for their helpful discussions.

Registry No. **1a**, 69901-39-9; **1b**, 69901-40-2; **1c**, 69901-41-3; **1d**, 69901-42-4; **2a**, 69901-43-5; **2b**, 69901-45-7; **3a**, 87013-29-4; **3b**, 87013-30-7; **5** (R = COCl), 40056-43-7; 4-methyl-2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadiene, 6485-57-0; 4-ethyl-2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadiene, 87013-27-2; 4-isopropyl-2,6-di-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadiene, 87013-28-3; 2,4,6-tri-*tert*-butyl-4-hydroperoxy-2,5-cyclohexadiene, 33919-05-0; $K_3Fe(CN)_6$, 13746-66-2; MnO_2, 1313-13-9.

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