Self-Initiated Autoxidation of a Sterically Crowded Cycloheptatriene Derivative via Norcaradienyloxyl Radicals

Toshikazu Kitagawa,* Atsushi Miyabo, Hideki Fujii, Takao Okazaki, Tetsuya Mori, Masaki Matsudou, Takeshi Sugie, and Ken'ichi Takeuchi*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan

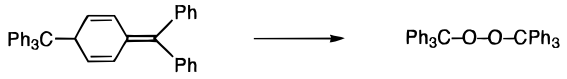
Received July 12, 1996[⊗]

An extremely crowded cycloheptatriene derivative, 1,3,5-tri-*tert*-butyl-7-(9-phenyl-9-fluorenyl)-1,3,5-cycloheptatriene (**1**), underwent autoxidation at 25 °C in cyclohexane to give 4-*tert*-butyl-2-pivaloylphenol (**3**) (33%), 5-*tert*-butyl-2-pivaloylphenol (**4**) (11%), 1,3,5-tri-*tert*-butylbenzene (**5**) (5%), *tert*-butyl 9-phenyl-9-fluorenyl peroxide (**6**) (44%), bis(9-phenyl-9-fluorenyl) peroxide (**7**) (7%), 1,1′,3,3′,5,5′-hexa-*tert*-butyl-7,7′-bicycloheptatriene (**8**) (2%), and carbon monoxide (4%). ESR studies showed that **1** dissociates into 1,3,5-tri-*tert*-butyltropyl radical (**11**) and 9-phenylfluorenyl radical (**12**) at 25−85 °C. The enthalpy and entropy of dissociation were determined to be 23.3 kcal/mol and 22.0 cal/mol·K, respectively. The formation of **3**−**5** can be explained by a mechanism involving attack of molecular oxygen to **11** and subsequent valence tautomerism of cycloheptatrienyloxyl radicals to norcaradienyloxyl radicals.

Introduction

The autoxidation of an unsaturated hydrocarbon is generally thought to be a radical chain reaction in which the substrate molecule undergoes hydrogen abstraction at the allylic position followed by an attack by molecular oxygen on the resulting delocalized radical. In the initiation step a hydrogen atom is abstracted by a radical that is generated from an added initiator.

The thermal cleavage of a weak C−C bond is another possible initiation step for the autoxidation of hydrocarbons. A typical example is the well-known formation of bis(triphenylmethyl) peroxide from the triphenylmethyl dimer.[1] This mechanism is of interest since the reaction does not require an added initiator and can proceed efficiently by nonchain mechanisms.

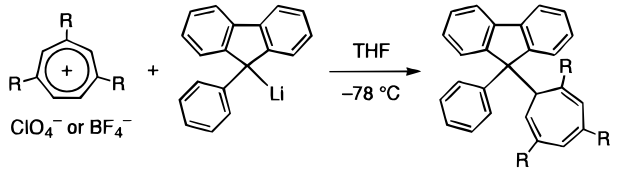


1,3,5-Cycloheptatriene derivatives having a bulky substituent at the C-7 position are also capable of producing a resonance-stabilized tropyl radical via cleavage of the C−C bond. Although reactions of cycloheptatrienes with singlet oxygen to form endoperoxides have been investigated intensively from both mechanistic and synthetic points of view,[2] there have been no systematic studies of the products and mechanism of their reaction with ground-state oxygen. Other oxidants, such as ceric ammonium nitrate,[3] chromic acid,[4] and selenium dioxide,[5] have been reported to oxidize cycloheptatriene to give various products, such as benzaldehyde, benzene and carbon monoxide, and tropone.

In this paper, we report the synthesis of a crowded cycloheptatriene derivative **1** and a study of its spontaneous autoxidation. The bulky phenylfluorenyl substituent at C-7 facilitates the homolytic cleavage of a carbon−carbon bond by extremely large intramolecular congestion and by resonance stabilization of the resulting radicals, initiating autoxidation at ambient temperature without an added initiator.

Results and Discussion

Sterically crowded cycloheptatrienes **1** and **2** were synthesized by the cation−anion combination reaction of 1,3,5-tri-*tert*-butyltropylium ion and unsubstituted tropylium ion, respectively, with 9-phenyl-9-fluorenyllithium in THF at −78 °C.



1 R = *t*-Bu 74%
2 R = H 49%

We have reported that cycloheptatriene (CHT)−norcaradiene (NCD) valence tautomerism is significantly shifted toward NCD by the presence of bulky substituents, especially *tert*-butyl groups on C-2 and C-5.[6] Compound **1** also showed NMR spectra that are characteristic of CHT−NCD equilibrium: the doublet for H-6 of the cycloheptatrienyl moiety at δ 3.83 at 25 °C disappeared when the CD_2Cl_2 solution of **1** was cooled to −60 °C and was split into two signals (δ 5.59, CHT; 2.27, NCD) at

* To whom correspondence should be addressed. Phone: +81-75-753-5713. Fax: +81-75-761-0056. E-mail: kitagawa@scl.kyoto-u.ac.jp.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

(1) Gomberg, M. *J. Am. Chem. Soc.* **1900**, *22*, 757; *Ber.* **1900**, *33*, 3150.

(2) (a) Adam, W.; Peters, E.-M.; Peters, K.; Rebollo, H.; Rosenthal, R. J.; Schnering, H. G. v. *Chem. Ber.* **1984**, *117*, 2393. (b) Adam, W.; Dürr, H.; Pauly, K.-H.; Peters, E.-M.; Peters, K.; Rebollo, H.; Schnering, H. G. v. *J. Org. Chem.* **1984**, *49*, 1333. (c) Adam, W.; Adamsky, F.; Klärner, F.-G.; Peters, E.-M.; Peters, K.; Rebollo, H.; Rüngeler, W.; Schnering, H. G. v. *Chem. Ber.* **1983**, *116*, 1848. (d) Adam, W.; Balci, M. *J. Am. Chem. Soc.* **1979**, *101*, 7537, 7542. (e) Adam, W.; Balci, M. *Angew. Chem.* **1978**, *90*, 1014. (f) Asao, T.; Yagihara, M.; Kitahara, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2131. (g) Mori A.; Takeshita, H. *Chem. Lett.* **1978**, 395.

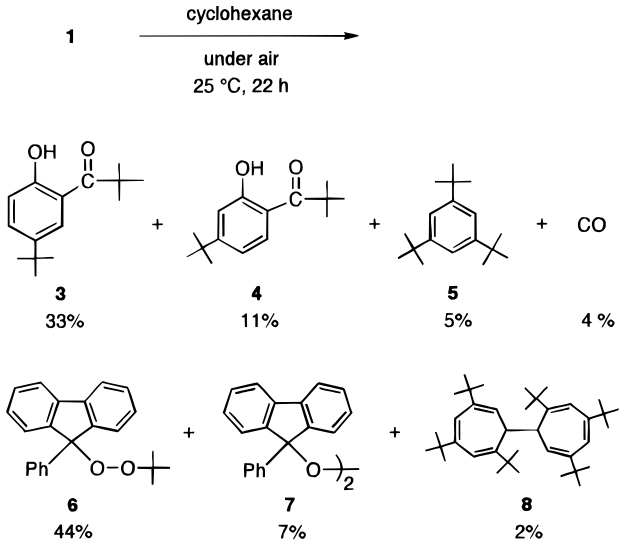
(3) (a) Trahanovsky, W. S.; Young, L. B.; Robbins, M. D. *J. Am. Chem. Soc.* **1969**, *91*, 7084. (b) Müller, P.; Katten, E.; Roček, J. *J. Am. Chem. Soc.* **1971**, *93*, 7116.

(4) Müller, P.; Roček, J. *J. Am. Chem. Soc.* **1974**, *96*, 2836.

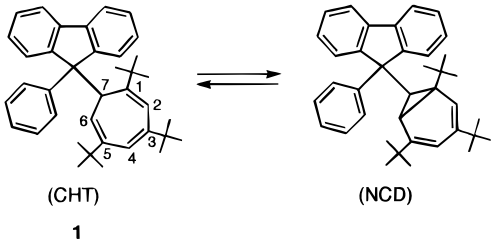
(5) Radrick, P. *J. Org. Chem.* **1964**, *29*, 960.

S0022-3263(96)01321-7 CCC: $14.00

Scheme 1



−100 °C. From the chemical shifts of H-6 at 25 and −100 °C the CHT:NCD ratio at 25 °C was calculated to be 47:53.



Although **1** was stable at room temperature in degassed solutions, it was oxidized rapidly in the presence of oxygen. When a cyclohexane solution of **1** was stirred in the presence of air at 25 °C for 22 h, a mixture consisting of substituted phenols **3** (33%) and **4** (11%), tri-*tert*-butylbenzene **5** (5%), peroxides **6** (44%) and **7** (7%), and bitropyl **8** (2%, mixture of *meso* and *dl* isomers) was obtained (Scheme 1). In addition, formation of carbon monoxide (4%) was detected by GC analysis. On the other hand, less crowded cycloheptatrienes **2** and **8** were inert to oxygen under the same conditions.

The products were identified by comparison of their NMR spectra with those of independently prepared authentic samples (Scheme 2). Phenols **3** and **4** were synthesized by Friedel−Crafts acylation of *p*- and *m*-*tert*-butylanisole, respectively, with pivaloyl chloride/$AlCl_3$ and subsequent demethylation with $AlCl_3$ in benzene. Peroxide **6** was synthesized by CuCl-catalyzed oxidation of 9-phenylfluorene with *tert*-butyl hydroperoxide.

The formation of products in Scheme 1 can be explained in terms of a mechanism involving the homolytic cleavage of a C−C bond in **1** into tri-*tert*-butyltropyl

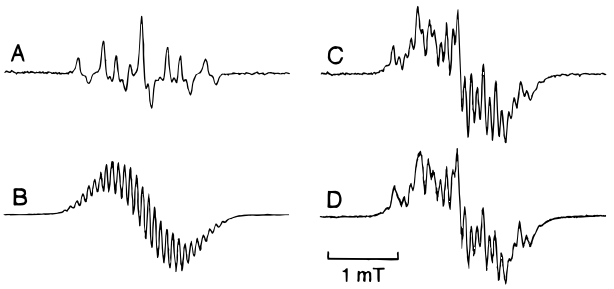
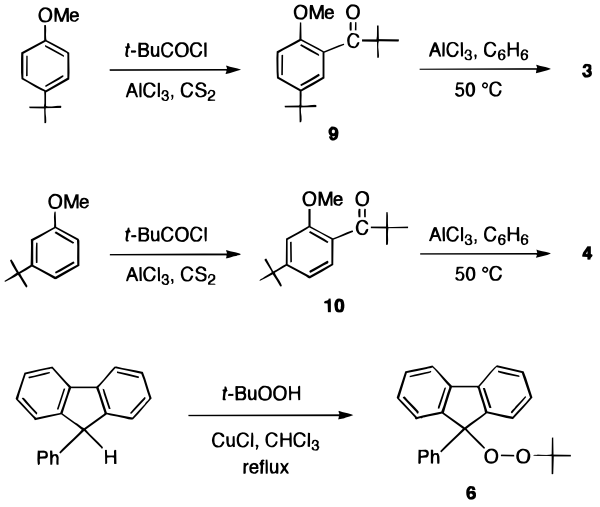
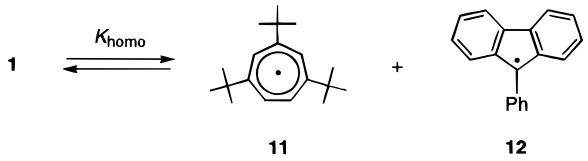


Figure 1. ESR spectra measured in degassed *m*-xylene at 85 °C. A: Radical **11** generated from **8**. B: Radical **12** generated from 9,9′-diphenyl-9,9′-bifluorene. C: The sum of the spectra A and B. D: Compound **1**.

Scheme 2



radical **11** and 9-phenylfluorenyl radical **12**.[7] The facile homolysis was demonstrated by ESR measurements for



degassed *m*-xylene or cyclohexane solutions (~10^{-2} M) of **1**. A weak signal was observed at 25 °C, which increased in intensity as the temperature was increased. The spectra agreed with the sum of the spectra of **11** and **12** generated by thermal dissociation of the corresponding dimers (Figure 1). By assuming that the homolysis of **1** had reached equilibrium, the enthalpy and entropy of dissociation were determined from the temperature dependence of the equilibrium constants, K_{homo}, observed for cyclohexane solution at 25−85 °C, to be 23.3 kcal/mol and 22.0 cal/mol·K, respectively (Figure 2).[8]

Scheme 3 shows plausible pathways for the formation of **3**−**5**. The radical **11** undergoes addition of oxygen to one of the carbons of the seven-membered ring. The resulting peroxyl radicals **13a**−**c** are transformed into cycloheptatrienyloxyl radicals **14a**−**c** by a well-known,

(6) (a) Takeuchi, K.; Arima, M.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 3081. (b) Takeuchi, K.; Fujimoto, H.; Okamoto, K. *Tetrahedron Lett.* **1981**, *22*, 4981. (c) Takeuchi, K.; Kitagawa, T.; Toyama, T.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1982**, 313. (d) Takeuchi, K.; Fujimoto, H.; Kitagawa, T.; Fujii, H.; Okamoto, K. *J. Chem. Soc., Perkin Trans. 2* **1984**, 461. (e) Takeuchi, K.; Senzaki, Y.; Okamoto, K. *J. Chem. Soc., Chem. Commun.* **1984**, 111. (f) Takeuchi, K.; Kitagawa, T.; Ueda, A.; Senzaki, Y.; Okamoto, K. *Tetrahedron* **1985**, *41*, 5455.

(7) It was shown, however, that **1** undergoes heterolytic fission of the same carbon−carbon bond to form an ion pair in polar solvents such as methanol. Controlling factors of the dissociation mode will be reported elsewhere.

(8) Attempts to detect cage recombination of **11** and **12** by ^{1}H CIDNP (at 100 °C in $CDCl_3$ under argon) were not successful, probably owing to low concentration of polarized molecule and/or small difference between the *g* values of these radicals.

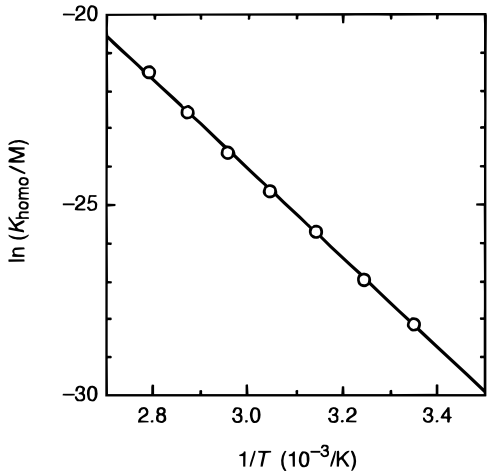


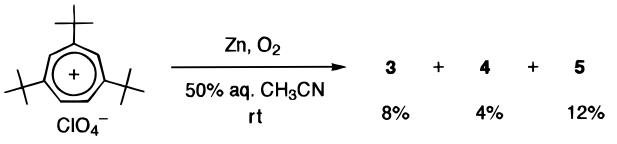
Figure 2. Temperature dependence of the equilibrium constant of the homolysis of **1** (1.45×10^{-2} M) in cyclohexane.

self-reaction mechanism through tetroxides.[9] Tautomerization of **14a**−**c** to the corresponding norcaradienyloxyl radicals **15a**−**c** and subsequent ring opening to form cyclohexadienyl radicals **16a**−**c** are based on analogy to the mechanism proposed for the oxidation of cycloheptatriene with ceric ammonium nitrate[3] or chromic acid.[4] In the present case, the valence isomerization of **14a**−**c** to **15a**−**c** is promoted by the steric effect of the *tert*-butyl groups on olefinic carbons.[6] The addition of a second oxygen molecule to the tertiary radical center of **16a** and **16b**, followed by elimination of a *tert*-butyl radical, yields *tert*-butylpivaloylphenols **3** and **4**. In path C, however, radical **16c** yields **5** by the loss of formyl radical, which, upon hydrogen abstraction by a radical in the reaction mixture, forms carbon monoxide.

The 9-phenylfluorenyl radical **12** is also attacked by oxygen molecule to form the (9-phenyl-9-fluorenyl)peroxyl radical **20** and when combined with the *tert*-butyl radical or another molecule of **12** yields peroxides **6** and **7**, respectively (Scheme 4).

The agreement of the yields of phenols (**3** + **4**) and peroxides (**6** + **7**) as well as those of **5** and carbon monoxide is consistent with mechanisms shown in Schemes 3 and 4.

Single-electron reduction of 1,3,5-tri-*tert*-butyltropylium ion under oxygen with zinc dust in 50% aqueous acetonitrile also gave **3**−**5**, consistent with the formation of the tri-*tert*-butyltropyl radical as the initiation step in the autoxidation of **1**. However, the yields of substituted phenols **3** and **4** were much lower (8 and 4%, respectively) than those observed for the autoxidation of **1**.[10] Possibly



a high [O_2]/[**11**] concentration ratio is important for the efficient conversion of radical **11** to **3** and **4** through pathways involving the consecutive addition of two oxygen molecules (Scheme 3, path A and B). Thermal homolysis of **1** generates radicals of very low concentrations,[11] thus providing conditions favorable for this conversion. If radical **11** is present in abundance, as would be expected for zinc reduction, significant amount of intermediate radicals **14**−**16** would escape these pathways, before the addition of the second oxygen, by coupling with other radicals. These results demonstrate the utility of the slow thermal dissociation of sterically congested molecules as systems for studies of the chemical behavior of free radicals.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 1600 spectrophotometer. ^{1}H NMR spectra were obtained with a JEOL EX400 (400 MHz), GSX270 (270 MHz), or FX90 (90 MHz) instrument. ^{13}C NMR spectra were measured with a JEOL EX400 (100 MHz), GSX270 (68 MHz), or FX90 (22.5 MHz) instrument. Elemental analyses were performed by the Microanalytical Center, Kyoto University. 9-Phenylfluorene,[12] 1,3,5-tri-*tert*-butyltropylium perchlorate,[13] tropylium tetrafluoroborate,[14] 9,9′-diphenyl-9,9′-bifluorene,[15] and 1,1′,3,3′,5,5′-hexa-*tert*-butyl-7,7′-bicycloheptatriene (**8**)[16] were prepared by literature methods.

1,3,5-Tri-*tert*-butyl-7-(9-phenyl-9-fluorenyl)-1,3,5-cycloheptatriene (1). A solution of (9-phenyl-9-fluorenyl)lithium was prepared from 1.24 g (5.13 mmol) of 9-phenylfluorene and butyllithium (1.58 M in hexane, 3.41 mL) in THF (60 mL) at −78 °C. This solution was added to a stirred suspension of 1,3,5-tri-*tert*-butyltropylium perchlorate (2.11 mg, 5.88 mmol) in 60 mL of THF at −78 °C. The mixture was stirred at 0 °C for 15 min, and the solvent was evaporated under reduced pressure. The residue was extracted with chloroform (60 mL). Evaporation of the chloroform afforded a faintly yellow semisolid, which was dissolved in 150 mL of methanol and kept at −20 °C overnight to yield colorless crystals of **1** (1.90 g, 74%): mp 145 °C dec; IR (KBr) 2960, 1477, 1450, 1361, 746 cm^{-1}; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.65−7.00 (m, 13H), 5.61 (s, 1H), 5.50 (s, 1H), 3.83 (d, J = 9.8 Hz, 1H, H-6), 3.35 (d, J = 9.8 Hz, 1H, H-7), 1.18 (s, 9H), 0.80 (s, 9H), 0.75 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 152.0, 149.1, 147.6, 145.2, 144.0, 141.2, 140.2, 88.8, 60.8, 36.2, 36.0, 34.9 (C); 128.5, 127.7, 127.4, 126.8, 126.7, 126.52, 126.48, 125.9, 125.2, 120.0, 119.4, 119.0, 117.0, 70.1, 31.0 (CH); 30.3, 30.0, 28.8 (CH_3). The ^{13}C signals at δ 88.8 and 70.1, which were assigned to C-1 and C-6, respectively, were extremely broadened due to CHT−NCD interconversion. The assignments of H-6 and H-7 are based on the H−C COSY spectrum, which indicated a strong coupling of the H-7 signal with the C-7 signal at δ 31.0. Anal. Calcd for $C_{38}H_{44}$: C, 91.14; H, 8.86. Found: C, 91.17; H, 8.86.

7-(9-Phenyl-9-fluorenyl)-1,3,5-cycloheptatriene (2). Compound **2** was synthesized as described above from 9-phenylfluorene (0.221 g, 0.913 mmol) and tropylium tetrafluoroborate (0.162 mg, 0.910 mmol). Recrystallization from ethanol gave **2** as white crystals (0.148 g, 49%): mp 193−194 °C; IR (KBr) 3021, 1447, 741, 706, 636 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 2H), 7.37 (t, J = 7.3 Hz, 2H), 7.33−7.12 (m, 7H), 7.10 (d, J = 8.3 Hz, 2H), 6.66 (s, 2H), 6.08 (d, J = 9.8 Hz, 2H), 5.00 (t, J = 7.5 Hz, 2H), 2.91 (br s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 150.7, 143.4, 141.1, 60.0 (C); 130.6, 128.5, 127.8, 127.7, 126.6, 125.1, 125.0, 124.8, 119.9, 45.6 (CH). Anal. Calcd for $C_{26}H_{20}$: C, 93.94; H, 6.06. Found: C, 93.71; H, 6.06.

(9) Ingold, K. U. *Free Radicals*; Kochi, J. K., Ed.; John Wiley and Sons: New York, 1973; Vol. 1, p 59.

(10) Dimer **8**, which is the major product of the reaction under inert atmosphere, was not detected.

(11) The ESR spectrum of a 1.45×10^{-2} M solution of **1** in cyclohexane indicated that the concentration of **11** was only 9.3×10^{-8} M at 25 °C.

(12) Rundel, W. *Chem. Ber.* **1966**, *99*, 2707.

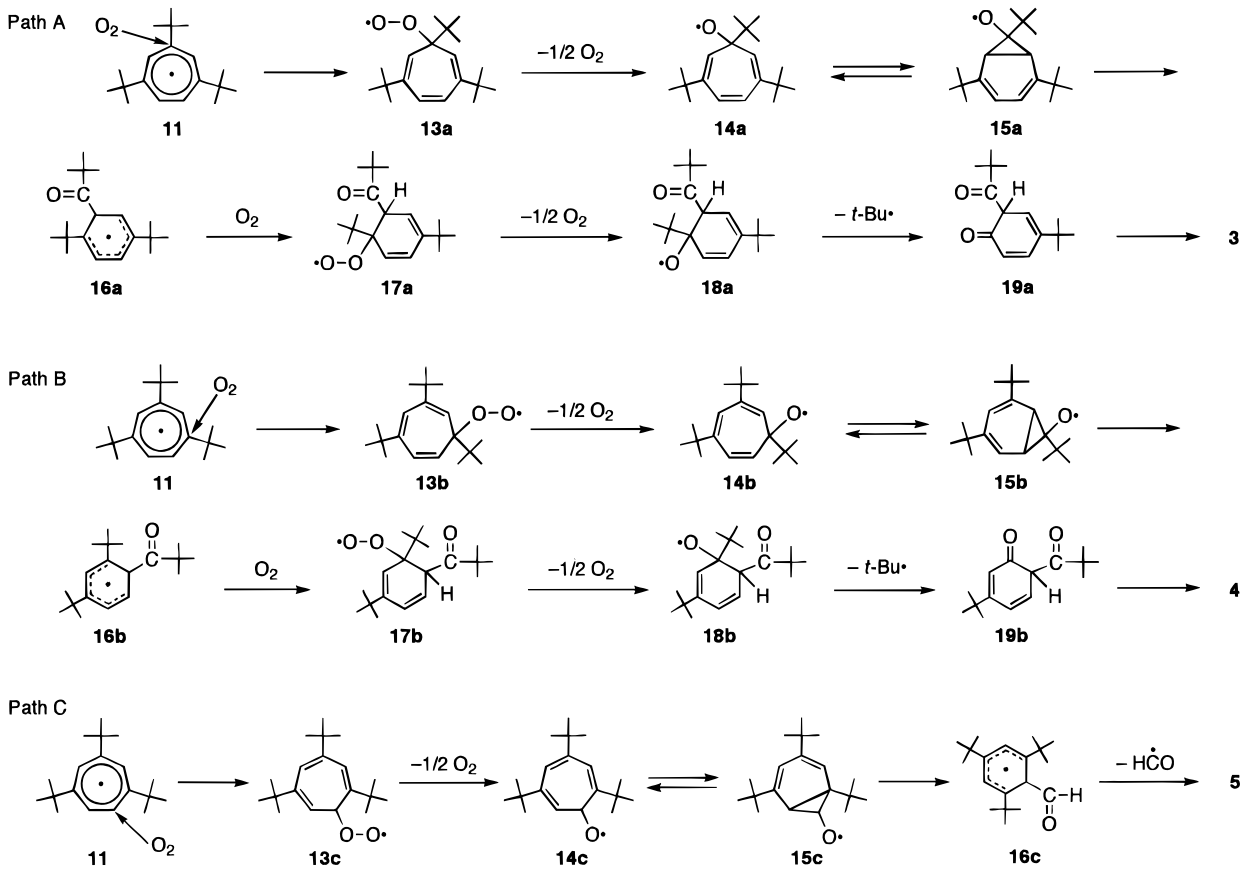
(13) Komatsu, K.; Takeuchi, K.; Arima, M.; Waki, Y.; Shirai, S; Okamoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3257.

(14) Conrow, K. *Organic Syntheses*; John Wiley and Sons: New York, 1973; Collect. Vol. 5, p 1138.

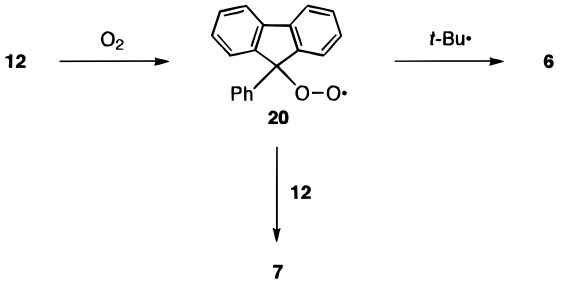
(15) Staab, H. A.; Rao, K. S.; Brunner, H. *Chem. Ber.* **1971**, *104*, 2634.

(16) Vincow, G.; Morrell, M. L.; Hunter, F. R.; Dauben, H. J., Jr. *J. Chem. Phys.* **1968**, *48*, 2876.

Scheme 3



Scheme 4



4-*tert*-Butyl-2-pivaloylanisole (9). To a solution of 4-*tert*-butylanisole (5.0 g, 30 mmol) and pivaloyl chloride (3.7 g, 31 mmol) in CS_2 (8 mL) was added $AlCl_3$ (4.1 g, 31 mmol). After initial exothermic reaction, the mixture was stirred at room temperature for 1 h. To the cooled mixture was cautiously added 100 mL of 0.6 M $NaHCO_3$. The mixture was extracted with ether, and the ether solution was dried ($MgSO_4$). Evaporation of the ether afforded a yellow liquid, which on MPLC (SiO_2, hexane−ether 97:3) gave **9** (1.9 g, 25%): white crystals; mp 30−31 °C (after recrystallization from hexane); IR (liquid film) 2964, 1697, 1499, 1250 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 7.32 (dd, J = 8.7, 2.5 Hz, 1H), 7.01 (d, J = 2.5 Hz, 1H), 6.82 (d, J = 8.7 Hz, 1H), 3.76 (s, 3H), 1.29 (s, 9H), 1.21 (s, 9H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 213.0, 152.6, 142.3, 130.2, 126.0, 122.8, 110.1, 54.8, 44.2, 33.6, 31.0, 26.4. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.09; H, 9.81.

4-*tert*-Butyl-2-pivaloylphenol (3). A mixture of **9** (0.55 g, 2.2 mmol) and $AlCl_3$ (0.31 g, 2.3 mmol) in benzene (10 mL) was stirred at 50 °C for 27 h. 5% $NaHCO_3$ (25 mL) was added, and the mixture was extracted with ether. The ether solution was washed with 5% $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the ether afforded a yellow oil, which on MPLC (SiO_2, hexane−ether 95:5) gave **3** (0.33 g, 63%): colorless oil; IR (film) 2963, 1635, 1482, 1299, 1167, 977 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 12.46 (s, 1H), 8.02 (d, 1H, J = 2.6 Hz), 7.48 (dd, 1H, J = 8.8, 2.6 Hz), 6.95 (d, 1H, J = 8.8 Hz), 1.47 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 212.1, 161.3, 140.2, 116.8, 44.4, 34.1 (C); 132.9, 127.1, 118.7 (CH); 31.4, 28.9 (CH_3). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.01; H, 9.75.

5-*tert*-Butyl-2-pivaloylanisole (10). 3-*tert*-Butylanisole was synthesized by adding dimethyl sulfate (8.4 g, 67 mmol) to a solution of 3-*tert*-butylphenol (10.0 g, 67 mmol) in 1.0 M NaOH (67 mL) and refluxing the mixture at 120 °C for 30 min. Extraction with ether and subsequent distillation gave a colorless liquid (bp 79.5−82 °C/5 mmHg, 8.8 g, 81%).

To a solution of 3-*tert*-butylanisole (2.03 g, 12.4 mmol) and pivaloyl chloride (1.49 g, 12.4 mmol) in CS_2 (5 mL) was added $AlCl_3$ (1.62 g, 12.1 mmol). After initial exothermic reaction, the mixture was stirred at room temperature for 1 h. To the cooled mixture was cautiously added 10 mL of 5% $NaHCO_3$. The mixture was extracted with ether, and the ether solution was washed with 5% $NaHCO_3$ and 10% NaCl and dried ($MgSO_4$). Evaporation of the ether afforded a yellow liquid, which on MPLC (SiO_2, hexane−ether 9:1) gave 3-*tert*-butylanisole (1.37 g) and **10** (orange crystals, 0.81 g). The orange crystals were recrystallized from hexane to give 0.53 g (17%) of **10** as white crystals: mp 45.5−46 °C; IR (KBr) 2967, 1690, 1610, 1234, 1030, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (s, 2H), 6.91 (s, 1H), 3.79 (s, 3H), 1.32 (s, 9H), 1.21 (s, 9H); ^{13}C NMR (100 MHz) δ 213.6, 155.0, 153.3, 128.3, 125.8, 117.0, 108.1, 55.1, 44.7, 34.8, 31.1, 26.6. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.27; H, 9.99.

5-*tert*-Butyl-2-pivaloylphenol (4). A mixture of **10** (0.43 g, 1.8 mmol) and $AlCl_3$ (0.23 g, 1.8 mmol) in benzene (10 mL) was stirred at 50 °C for 43 h. 5% $NaHCO_3$ (25 mL) was added, and the mixture was extracted with ether. The ether solution was washed with 5% $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the ether afforded a yellow oil, which on MPLC (SiO_2, hexane−ether 95:5) gave **4** (0.14 g, 34%) and **10** (0.26 g). **4**: colorless oil; IR (liquid film) 2967, 1627, 1187, 970 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.79 (s, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.01 (d, J = 2.0 Hz, 1H), 6.88 (dd, J = 8.8, 2.0 Hz, 1H), 1.44 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 211.4, 163.8, 159.6, 115.0, 44.4, 35.1 (C); 130.6, 115.8, 115.4 (CH);

30.7, 28.7 (CH_3). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.12; H, 9.66.

***tert*-Butyl 9-Phenyl-9-fluorenyl Peroxide (6).** To a solution of 9-phenylfluorene (1.00 g, 4.12 mmol) in chloroform (5 mL) were added 5.0 mg of CuCl and 1.40 g (15.5 mmol) of *tert*-butyl hydroperoxide. The mixture was refluxed for 6 h. The CuCl was filtered off, and the solution was washed with 10% NaCl and dried ($MgSO_4$). The solvent was evaporated, and the residue was subjected to MPLC (SiO_2, hexane−ether 98:2) to give **6** (1.17 g, 86%) as white crystals: mp 98.5−99.5 °C (after recrystallization from hexane); IR (KBr) 2979, 1452, 1360, 1194, 1011, 732 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.66 (d, $J = 7.3$ Hz, 2H), 8.42−8.17 (m, 11H), 1.07 (s, 9H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 146.7, 141.5, 140.7, 92.1, 79.8 (C); 129.0, 128.0, 127.4, 127.3, 126.7, 126.3, 119.7 (CH); 26.4 (CH_3). Anal. Calcd for $C_{23}H_{22}O_2$: C, 83.61; H, 6.71. Found: C, 83.90; H, 6.68.

Bis(9-phenyl-9-fluorenyl) Peroxide (7). A solution of 9,9′-diphenyl-9,9′-bifluorene (92 mg, 0.19 mmol) in cyclohexane (50 mL) was stirred at 60 °C for 2 h under O_2 atmosphere. Evaporation of the solvent gave reddish crystals. The crystals were dissolved in 2 mL of CH_2Cl_2, and the solution was diluted with 5 mL of hexane and allowed to stand for 30 min to form white crystals of **7** (45 mg, 46%): mp 189.5−191 °C (lit.[17] 194−195 °C); IR (KBr) 3063, 1449, 1169, 1019 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 7.58 (d, $J = 7.7$ Hz, 4H), 7.28 (td, $J = 7.4$, 1.4 Hz, 4H), 7.21−7.11 (m, 14H), 7.05 (td, $J = 7.4$, 1.1 Hz, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 146.0, 141.0, 140.6, 93.2 (C); 129.0, 128.0, 127.5, 127.3, 126.5, 126.1, 119.6 (CH).

ESR Spectra of 1. ESR spectra were recorded on a JEOL SR2EX spectrometer equipped with a standard variable-temperature controller using degassed solutions of **1** in cyclohexane or *m*-xylene. Total radical concentrations were determined from double integration of the first derivative ESR spectra. Signal intensities were calibrated with an 8.91×10^{-6} M 4-hydroxy-TEMPO solution in benzene.

Autoxidation of 1. Compound **1** (194 mg, 0.388 mmol) was placed in a 250-mL round-bottomed flask equipped with a two-way stopcock that was capped with a rubber septum. Cyclohexane (50 mL) was added, and the stopcock was closed under air. After the solution had been stirred at 25 °C for 22 h, the stopcock was opened, and the gas in the flask (0.5 mL) was taken with a syringe. GC analysis (molecular sieves 5A, 3 mm i.d. × 2 m, 80 °C) for the gas indicated the formation of carbon monoxide (4% based on **1**). The cyclohexane was evaporated under reduced pressure. NMR analysis of the residue showed the formation of **3**, **4**, and **6** in 33, 11, and 44% yields, respectively. The product mixture was dissolved in hexane (5 mL) and cooled to −20 °C. After 2 h, **7** (7.0 mg, 7.0%) was obtained as a white precipitate. The solvent was evaporated to give an oil. The oil was separated by MPLC (SiO_2, hexane−ether 99:1) to give a mixture of **5** and **8** (5 and 2% yields, respectively). Further elution gave a mixture of **3**, **4**, and **6**, which were separated by HPLC (Waters, μ-Porasil, hexane). The products were identified by comparison of their ^1H and ^{13}C NMR spectra with those of authentic samples.

Zinc Reduction of 1,3,5-Tri-*tert*-butyltropylium ion under O_2. In a two-necked flask equipped with a gas inlet tube was saturated a solution of 1,3,5-tri-*tert*-butyltropylium perchlorate (52.2 mg, 0.145 mmol) in 50% aqueous acetonitrile (100 mL) with O_2 by bubbling O_2 gas with stirring. Zinc dust (5.0 g, 16.0 mmol) was added in portions over 30 min, and bubbling and stirring were continued for 1.8 h. The zinc was filtered off, and the solution was extracted with CH_2Cl_2. The extract was dried ($MgSO_4$). Evaporation of the solvent gave a yellow solid, which was subjected to NMR analysis to determine the product yields: **3** (8%), **4** (4%), and **5** (12%).

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan.

Supporting Information Available: ^1H and ^{13}C NMR and H−C COSY spectra of **1** (including ^1H NMR spectrum at −100 °C) and a table of temperature dependence of equilibrium constant of the homolysis of **1** (5 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.

JO961321P

(17) Bassey, M.; Buncel, E.; Davies, A. G. *J. Chem. Soc.* **1955**, 2550.