10-5; *dl*-**11**, 92817-27-1; *dl*-**12**, 92817-28-2; DL-**13b**, 92998-31-7; DL-**13c**, 92935-41-6; DL-**13d**, 92935-42-7; *dl*-**13e**, 92817-29-3; DL-**14b**, 92998-32-8; DL-**14c**, 92935-43-8; DL-**14d**, 92935-44-9; *dl*-**14e**, 92817-30-6; *dl*-**14e** (mesylate), 92817-97-5; *dl*-**15**, 92817-31-7; *dl*-**16**, 92817-32-8; *dl*-**17**, 92935-45-0; *dl*-**18**, 41921-90-8; *dl*-**19**, 92935-46-1; DL-**20b**, 92935-47-2; DL-**20c**, 92935-48-3; DL-**20d**, 92935-49-4; *dl*-**20e**, 92817-33-9; DL-**21b**, 92935-50-7; *dl*-**21e**, 92817-34-0; DL-**22b**, 92998-33-9; DL-**22c**, 92935-51-8; DL-**22d**, 92935-52-9; *dl*-**22e**, 92844-11-6; DL-**23b**, 92936-87-3; DL-**23c**, 92935-53-0; DL-**23d**, 92935-54-1; *dl*-**23e**, 92817-35-1; DL-**24b**, 92935-55-2; DL-**24b** (β-acetate), 92817-99-7; DL-**24b** (α-hydroxy, β-acetate), 92818-01-4; DL-**24c**, 92935-56-3; DL-**24c** (β-acetate), 92817-98-6; DL-**24c** (α-hydroxy, β-acetate), 92818-00-3; DL-**24d**, 92935-57-4; *dl*-**24e**, 92817-36-2; DL-**25b**, 92935-58-5; DL-**25c**, 92935-59-6; DL-**25d**, 92935-60-9; *dl*-**25e**, 92817-37-3; DL-**26c**, 92817-59-9; *dl*-**26e**, 92817-60-2; DL-**27c**, 92817-64-6; *dl*-**27e**, 92844-12-7; **28**, 92817-38-4; (*E*)-**28**, 92818-02-5; *dl*-**29**, 34713-70-7; *dl*-**30**, 64869-28-9; *dl*-**31**, 92935-61-0; *dl*-**32**, 92935-62-1; DL-**33**, 78957-60-5; DL-**33** (7-monoacid), 92818-03-6; DL-**34**, 79026-94-1; DL-**34** (7-monoacid), 92818-04-7; DL-**35**, 92817-39-5; DL-**36**, 92817-40-8; *dl*-**37**, 92817-41-9; *dl*-**38**, 92817-42-0; *dl*-**39**, 92817-43-1; DL-**40a**, 92817-44-2; DL-**40b**, 92817-45-3; DL-**40c**, 92817-46-4; *dl*-**40e**, 92817-47-5; DL-**41a**, 92817-48-6; DL-**41b**, 92817-49-7; DL-**41c**, 92817-50-0; DL-**41d**, 92817-51-1; *dl*-**41e**, 92817-52-2; DL-**42c**, 92817-53-3; *dl*-**42e**, 92817-54-4; DL-**43c**, 92817-55-5; *dl*-**43e**, 92817-56-6; DL-**44a**, 92935-63-2; DL-**44b**, 92935-64-3; DL-**45a**, 92935-65-4; DL-**45b**, 92935-66-5; DL-**45c**, 92935-67-6; *dl*-**45e**, 92817-57-7; DL-**46**, 92817-58-8; DL-**47**, 56709-62-7; DL-**48**, 92817-61-3; DL-**49**, 92817-62-4; DL-**50**, 92817-63-5; *dl*-**51**, 92817-65-7; **52a**, 92817-66-8; **52b**, 92817-67-9; **53a**, 92817-68-0; *dl*-**54**, 92817-69-1; *dl*-**55**, 92817-70-4; **56**, 92817-71-5; **57**, 92817-72-6; **58**, 92817-73-7; **59**, 92817-74-8; DL-**60c**, 92817-75-9; *dl*-**60e**, 92817-76-0; DL-**61c**, 92817-77-1; *dl*-**61e**, 92817-78-2; DL-**62c**, 92817-79-3; DL-**63c**, 92817-80-6; *dl*-**63e**, 92817-81-7; *dl*-**64**, 92817-82-8; DL-**65**, 92817-83-9; *dl*-**66**, 92817-84-0; *dl*-**67**, 92817-85-1; *dl*-**68**, 92817-86-2; DL-**69**, 92817-87-3; **70a**, 79027-28-4; **70b**, 92817-88-4; **71a**, 92817-89-5; **71b**, 92817-90-8; **72a**, 92817-91-9; **72b**, 92817-92-0; *dl*-**73**, 92817-93-1; *dl*-**74**, 92817-94-2; *dl*-**74** ((*E*)-Δ^4 isomer), 92818-06-9; *dl*-**74** ((*Z*)-Δ^4 isomer), 92818-07-0; *dl*-**75**, 92935-68-7; **76**, 92817-95-3; **77**, 92817-96-4; MEMCl, 3970-21-6; DMP, 576-26-1; DIPP, 2078-54-8; BHT, 128-37-0; *i*-PrI, 75-30-9; $MeSO_2Cl$, 124-63-0; *dl*-$CH_3CH(OH)CO_2Et$, 2676-33-7; Ac_2O, 108-24-7; Me_3SiCl, 75-77-4; *dl*-$CH_3CH(OCH_2Ph)COCl$, 74406-96-5; CH_2=$CHCHO$, 107-02-8; *dl*-$CH_3CHBrCO_2H$, 10327-08-9; *dl*-$CH_3CHBrCO_2Na$, 56985-74-1; PhOH, 108-95-2; *dl*-$CH_3CH(OPh)CO_2H$, 1912-21-6; *dl*-$CH_3CH(OMe)COCl$, 23943-97-7; *dl*-$CH_3CH(OPh)COCl$, 84771-76-6; 4-$MeOC_6H_4OH$, 150-76-5; *dl*-$CH_3CH(OC_6H_4$-4-$OMe)CO_2H$, 4276-73-7; *dl*-$CH_3CH(OC_6H_4$-4-$OMe)COCl$, 92818-05-8; 2,2,5-trimethyloxazolidin-4-one, 92935-69-8.

Supplementary Material Available: Experimental details containing stereoscopic ORTEP plots, positional thermal parameters of non-hydrogen atoms, bond lengths, bond angles, and torsion angles for compounds **11**, **45c**, **45e**, **65**, and **66** (36 pages). Ordering information is given on any current masthead page.

Stereochemical Studies of Dioxetane Formation with Hindered Olefins

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Abstract: Two stereoisomeric di-*tert*-butylbis(bicyclo[3.3.1]non-9-ylidenes) (*anti*-**2** and *syn*-**2**) and related hindered olefins were synthesized, and their reactivities and stereochemistries in various dioxetane formations were evaluated. Whereas the singlet oxygenation of a series of three closely related olefins, **1**, **3**, and **4**, gave the corresponding dioxetanes in almost the same reactivity, in the electrode-catalyzed oxygenation the relative reactivities of the three olefins decreased in a ratio 1:0.74:0.06. The singlet oxygenation and 9,10-dicyanoanthracene-sensitized photooxygenation of **2** occurred stereospecifically to yield three stereoisomeric dioxetanes (*cis,trans*-**12**, *cis,cis*-**12**, and *trans,trans*-**12**), while the electrode-catalyzed oxygenation was nonstereospecific. Conclusions dealing with the mechanistic aspects of these reactions are presented and references are made to their possible usefulness in the elucidation of transition-state geometries.

In recent years it has become apparent that several oxygenation reactions do not involve singlet oxygen ($^1O_2$). Dioxetane and endoperoxide, once thought to be products characteristic of a singlet oxygen reaction, were also produced by electron-transfer photooxygenation. Foote[1a-e] first suggested that 9,10-dicyanoanthracene(DCA) sensitizes oxygenation of polyaryl olefins through the intervention of a superoxide anion and the radical cation of substrates to form dioxetanes which finally decompose to carbonyl compounds reminiscent of the singlet oxygen reaction. Subsequently, Barton,[2a-c] Tang,[2e] and Landis[2f] proposed a new route to nonsinglet oxygenation, in which the cation radical of dienes reacts with triplet oxygen and propagates a chain oxidation to form endoperoxide. Examples are trityl cation-photosensitized or Barton's reagent-catalyzed oxygenation of dienes such as ergosteryl acetate and the photosensitized oxygenation of azines. More recently, Nelsen[2g] and Clennan[2h] have reported that the cation radical of adamantylideneadamantane (**1**) could react with triplet oxygen to afford dioxetane.

These observations suggest a number of experiments, especially using sterically hindered olefins such as **1**, in order to elucidate

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(1) DCA-sensitized photooxygenation of aromatic olefins, vinyl ether, and vinyl sulfide: (a) Eriksen, J.; Foote, C. S.; Parker, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6455. (b) Spada, L. T.; Foote, C. S. *Ibid.* **1980**, *102*, 391. (c) Eriksen, J.; Foote, C. S. *Ibid.* **1980**, *102*, 6083. (d) Steichen, D. S.; Foote, C. S. *Ibid.* **1981**, *103*, 1855. (e) Jiang, Z. Q.; Foote, C. S. *Tetrahedron Lett.* **1983**, *24*, *461*. (f) Schapp, A. P.; Zaklika, K. A.; Kasker, B.; Fung, L. W.-M. *J. Am. Chem. Soc.* **1980**, *102*, 389. (g) Ando, W.; Nagashima, T.; Saito, K.; Kohmoto, S. *J. Chem. Soc., Chem. Commun.* **1979**, 154. DCA-sensitized photooxygenation of aromatics: (h) Saito, I.; Tamoto, K.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2889. (i) Santamaria, J. *Ibid.* **1981**, *22*, 4511. (j) Liang, J. J.; Foote, C. S. *Ibid.* **1982**, *23*, 3039. DCA-sensitized photooxygenation of acetylenes: (k) Berenjian, N.; de Mayo, P.; Phoenix, F. H.; Weeden, A. C. *Ibid.* **1979**, 4179. (l) Mattes, S. L.; Farid, S. *J. Chem. Soc., Chem. Commun.* **1980**, 457. DCA-sensitized photooxygenation of epoxides and cyclopropanes: (m) Futamura, S.; Kusunose, S.; Ohta, H.; Kamiya, Y. *Ibid.* **1982**, 1223. (n) Schaap, A. P.; Lopez, L.; Anderson, S. D.; Gagnon, S. D. *Tetrahedron Lett.* **1982**, *23*, 5493. (o) Mizuno, K.; Kamiya, N.; Ohtsuji, Y. *Chem. Lett.* **1983**, 477. (p) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663. (q) Schaap, A. P.; Siddiqui, S.; Gagnon, S. D.; Lopez, L. *Ibid.* **1983**, *105*, 5149. (r) Kirschen-heuter, G. P.; Griffin, G. W. *J. Chem. Soc., Chem. Commun.* **1983**, 596.

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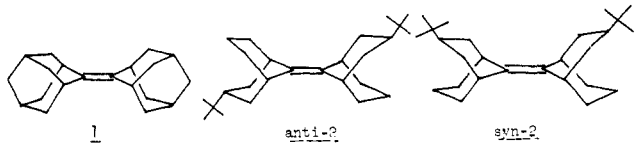
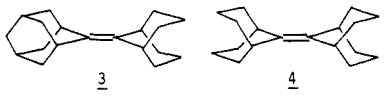
Table I. Dye- and DCA-Sensitized Photooxygenation and Electrode-Catalyzed Oxygenation

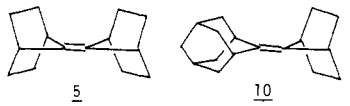
olefins	E_p vs. SCE,[a] V	yields of dioxetanes,[b] %			Coulombic data[f]		
		$^1O_2$[c]	DCA[d]	-e, $^3O_2$[e]	time, min	charge, C	av chain length[g]
1	1.52	98	66	87	15	0.46	78
3	1.53	92	59	72	20	0.68	58
4	1.54	100	21	80	200	7.60	5
5	1.86	15	NR[h]	NR			
10	1.65			69	260	7.50	4

[a] At a Pt electrode; solvent MeCN containing 0.1 M TBAP; scan rate 200 mV/s; full-scale deflection +0.20 V. [b] Isolated yields. [c] Olefin (0.20 mmol) in 20 mL of CH_2Cl_2 containing TPP was photolyzed for 3 h. [d] Olefin (0.20 mmol) in 20 mL of MeCN-CH_2Cl_2 (2:1) containing DCA was photolyzed for 4 h. [e] Exhaustive electrolysis was conducted by using 0.40 mmol olefin in 30 mL of 0.1 M TBAP CH_2Cl_2 solution with C electrode. [f] Coulometer was simultaneously operated. [g] Average chain length = (theoretical Coulombs for 1-e$^-$ process/Coulombs passed) - 1. [h] No reaction.

the mechanistic feature of dioxetane formation via nonsinglet oxygen routes, because the oxygenation of such hindered olefins gives the remarkably stable dioxetanes. Furthermore, we have also incorporated stereochemical probes into the oxygenation of hindered olefins that might be diagnostic for the nonsinglet oxygenation. For this reason, we have synthesized two stereoisomeric-hindered olefins, *anti*- and *syn*-di-*tert*-butylbis(bicyclo[3.3.1]non-9-ylidenes) (**2**),[3] and related hindered olefins (**1**, **3**–**10**).







In this report we describe a series of oxygenations of these olefins, which provides further mechanistic understanding of nonsinglet oxygenation.

Results and Discussion

1. Photosensitized and Electrode-Catalyzed Oxygenations of Several Hindered Olefins. The dye- and DCA-sensitized photooxygenations were carried out with **1** and **5**, together with **4** and the structurally mixed analogue **3**. A solution of the olefin in dichloromethane containing tetraphenylporphine (TPP) was irradiated under bubbling oxygen in a water-cooled Pyrex tube with a 300-W halogen lamp. The DCA-sensitized photooxygenations were conducted similarly with DCA as a sensitizer in acetonitrile–dichloromethane (2:1). The results are shown in Table I. These olefins showed similar reactivities except for **5**, which was inert to DCA-sensitizied oxygenation.

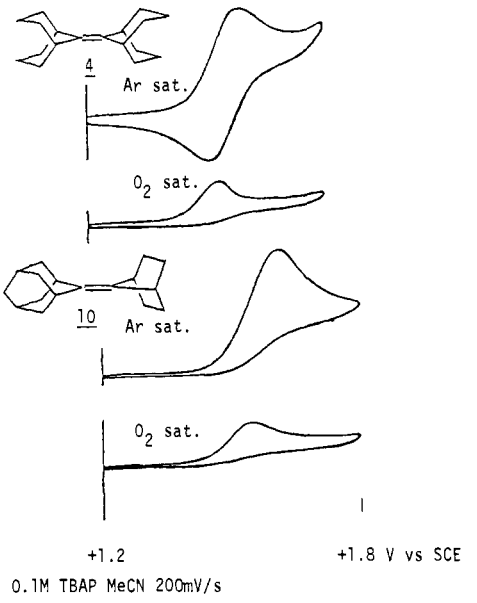
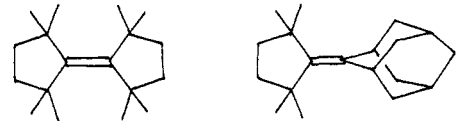
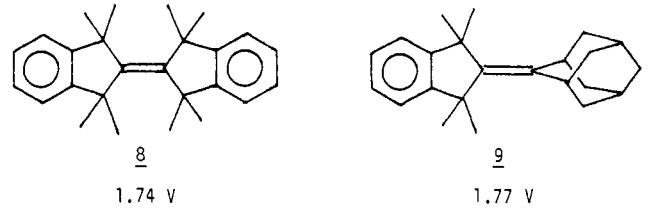


Figure 1. Cyclic voltammogram in argon- and oxygen-saturated solution.

Before the electrode-catalyzed oxygenation was carried out, the oxidation potentials of all the olefins were measured (**6**–**9** and Table I). Gerson and Krebs[2i] timely reported that sterically





crowded bicycloalkylidenes such as octamethylalkylidene **6** form stable cation radicals. Hence, **6** and several analogous sterically crowded alkenes, **7**–**9** were prepared and their electrochemical behaviors were analyzed by cyclic voltammetry.

The cyclic voltammograms of **6**–**9** in acetonitrile showed electrochemical behavior characteristic of reversible one-electron oxidation, indicating that the cation radicals have long lifetimes as suggested.[2i] The E_p values of **6**–**9** were surprisingly low in comparison with the E_p value range of usual olefins (2.27–3.20 V). The cation radicals of these olefins were not air sensitive.

(2) Barton-type oxygenation of ergosteryl acetate: (a) Barton, D. H. R.; Lechlerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Chem. Commun.* **1972**, 447. (b) Barton, D. H. R.; Haynes, R. K.; Magnus, P. D.; Menzies, I. D. *Ibid.* **1974**, 511. (c) Barton, D. H. R.; Haynes, R. K.; Lechlerc, G.; Magnus, P. D.; Menzies, I. D. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2055. (d) Haynes, R. K. *Aust. J. Chem.* **1978**, *31*, 121, 131. (e) Tang, R.; Yue, H. J.; Wolf, J. F.; Mares, F. *J. Am. Chem. Soc.* **1978**, *100*, 5248. Barton-type oxygenation of azine: (f) Landis, M. E.; Madoux, D. C. *Ibid.* **1979**, *101*, 5106. Barton-type oxygenation of adamantylideneadamantane: (g) Nelsen, S. F.; Akaba, R. *Ibid.* **1981**, *103*, 2096. (h) Clennan, E. L.; Simmons, W.; Almgren, C. W. Ibid. **1981**, *103*, 2098. Stable monoolefin cation radicals: (i) Gerson, F.; Lopez, J.; Krebs, A.; Rugner, W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 95. (j) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503. (k) Gerson, F.; Lopez, J.; Akaba, R.; Nelsen, S. F. *Ibid.* **1981**, *103*, 6716.

(3) (a) Ando, W.; Kabe, Y.; Takata, T. *J. Am. Chem. Soc.* **1982**, *104*, 7314. (b) Ando, W.; Kabe, Y.; Takata, T.; Ueno, K. *J. Photochem.* **1984**, *25*, 161.

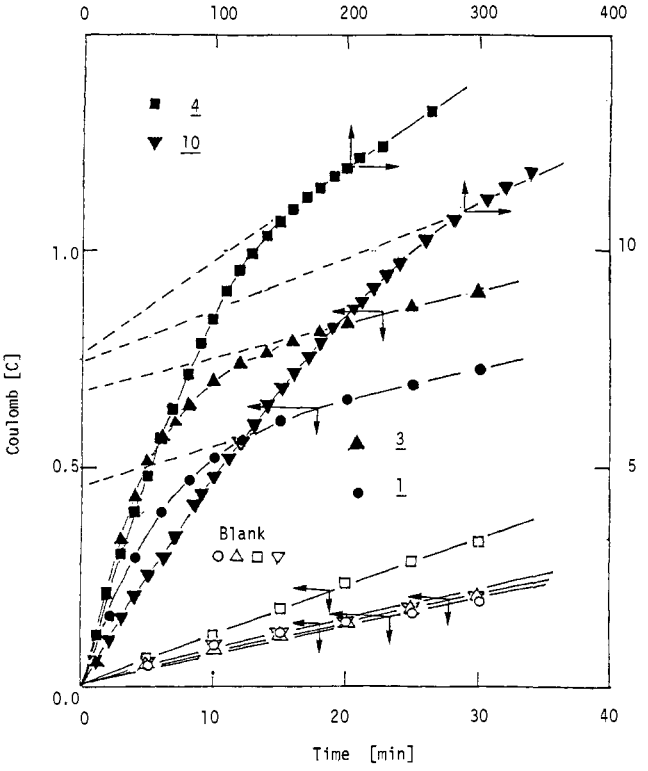
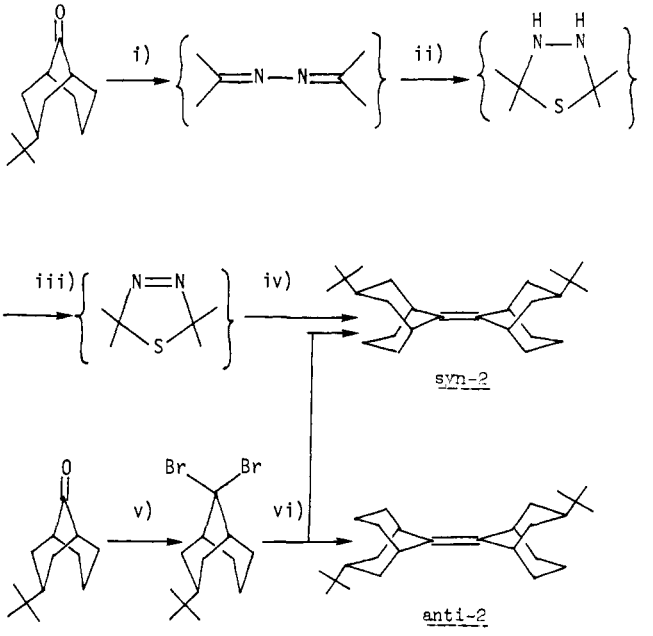


Figure 2. Coulomb vs. time curves in the electrode-catalyzed oxygenation.

Scheme I



i) NH_2NH_2, ^tBuOH, NH_2NH_3, HSO_4, 100%
ii) H_2S, TsOH, C_6H_6-Me_2CO, 72%
iii) $Pb(OAc)_4$-$CaCO_3$, C_6H_6, 20%
iv) $^nBu_3P$, 150 °C, 82%
v) PBr_5, 91%
vi) Zn-Cu, 61%

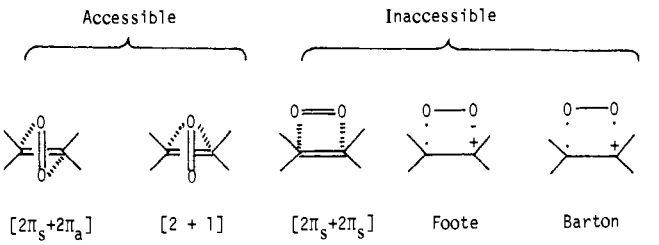
However, the allylically bridgehead olefins **1**, **3**, **4**, and **10** gave the corresponding cation radicals which were air sensitive, although **5** was not. As reported by Nelsen[2g] and Clennan,[2h] cyclic voltammetric behavior of air-sensitive cation radicals in oxygen-saturated solution was significantly different from that in argon-saturated solution, where the current for the reduction wave disappears and the cation radical once produced near the electrode is depleted by chain reaction with oxygen. Figure 1 (top) shows an example with compound **4**. In the case of **10**, no reduction peak could be observed even in the argon-saturated solution. However, when oxygen was introduced, the oxidation peak was cleanly reduced as shown in Figure 1 (bottom). This phenomenon is not inconsistent with the formation of dioxetane (Table I).

The cation radicals of the allylically methylated or the bridgehead olefins presumably have lifetimes at least of seconds. The reason for the stability is clearly explained by Bredt's rule, as suggested by Nelsen.[2j,k] That is, the main reason for instability of the cation radicals in the absence of acids is due to rapid deprotonation at the allylic position. Therefore, when such C–H bonds are forced by bicyclic systems to be perpendicular to π-bond cation radical, or when the allylic proton is structurally absent, the cation radicals become considerably more stable.

What factor, then, controls whether cation radicals react with oxygen or not? We have already examined other cation radicals stabilized by heteroatoms or π conjugation and found that they did not react with oxygen in spite of having fairly low oxidation potentials. Therefore, one of the important factors is the presence of an independent π system in which odd-electron density is not delocalized. Failure of the reaction in allylically methylated olefins (**5**–**9**) would represent the second and third factors, i.e., insufficient steric hindrance to block the attack of oxygen on the olefin face and comparably low oxidation potential ($E_{ox} < 1.7$ V).

The electrode-catalyzed oxygenations of **1**, **3**, **4**, and **10** were carried out by the method reported by Clennan.[2h] The average chain lengths were calculated by using a coulometer (Figure 2, Table I).

In comparison with the electrode-catalyzed oxygenations of a series of the three closely related olefins (**1**, **3**, and **4**), it is demonstrated that the more flexible the trimethylene bridge becomes to cover the face of the olefin the slower the reaction rate and the smaller the chain lengths are (Table I). In contrast, the reactivity of **1**, **3** and **4** in the dye-sensitized photooxygenation was nearly equal. It is attractive to consider that perpendicular $[2\pi_s + 2\pi_a]$ or [2 + 1] approach of singlet oxygen is most open and accessible, whereas radical coupling of oxygen and the cation radical may be blocked by a trimethylene bridge lying flexibly on the required approach path. Although DCA-sensitized



photooxygenation showed similar reactivity to electrode-catalyzed oxygenation, the data obtained in this study could not definitively distinguish the three types of oxygenations.

2. Photosensitized and Electrode-Catalyzed Oxygenations of Stereoisomeric Di-*tert*-butylbis(bicyclo[3.3.1]non-9-ylidenes). The syntheses of two stereoisomers of **2** were attempted by three procedures. It was found that the McMurry procedure,[4] reductive dimerization of two ketones using reduced titanium reagent, was not suitable, because of concomitant formation of large amounts of polymeric byproducts. The synthesis of **2** was accomplished by a double-extrusion method[5] and carbenoid dimerization pro-

(4) (a) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708. *J. Org. Chem.* **1976**, *41*, 896. (b) McMurry, E. J.; Silverstri, M. *Ibid.* **1975**, *40*, 2687. (c) McMurry, J. E.; Krepski, L. R. *Ibid.* **1976**, *41*, 3929. (d) McMurry, J. E.; Kees, K. L. *Ibid.* **1977**, *42*, 2655. (e) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *Ibid.* **1978**, *43*, 3255. (f) Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *Ibid.* **1976**, *41*, 260. (g) Baumstark, A. L.; Bechara, E. J. H.; Semigram, M. J. *Tetrahedron Lett.* **1976**, 3265. (h) Wynberg, H.; Lammertsma, K.; Hulshof, L. A. *Ibid.* **1975**, 3794. (i) Langler, R. F.; Tidwill, T. T. *Ibid.* **1975**, 777. (j) Bose, D. S.; Morton, T. H. *Ibid.* **1975**, 781. (k) Lenoir, D.; Frank, R. *Ibid.* **1978**, 53. (l) Olah, G. A.; Prakash, G. K. S. *J. Org. Chem.* **1977**, *42*, 580.

Table II. Dye- and DCA-Sensitized Photooxygenation and Electrode-Catalyzed Oxygenation of *anti*-2 and *syn*-2

system	olefins	time, min	yields of dioxetanes,[a] % *cis,trans*-12	*cis,cis*-12	*trans,trans*-12	recovered, %
TPP, $h\nu$, O_2 [b]	*anti*-2	120	94			
	syn-2	120		66	34	
DCA, $h\nu$, O_2 [c]	*anti*-2	420	49			25
	syn-2	300		27	22	15
$-e^-$, O_2 [d]	*anti*-2	300	34	24	21	11
	syn-2	80	23	51	11	9

[a] Isolated yields. [b] CH_2Cl_2 solution (20 mL) containing olefin (ca. 0.20 mmol) and TPP was irradiated. [c] MeCN-CH_2Cl_2 (2:1) containing olefin (ca. 0.20 mmol) and DCA was irradiated. [d] Exhaustive electrolysis was conducted by using ca. 0.20 mmol of olefin in 30 mL of 0.1 M TBAP CH_2Cl_2 solution with C electrode.

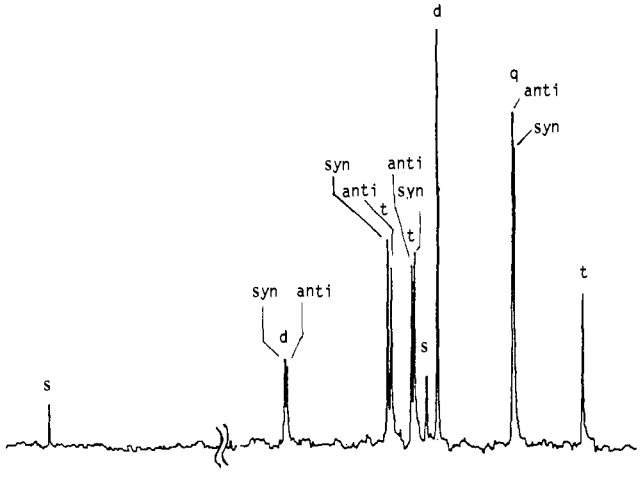


Figure 3. ^{13}C NMR spectrum of a mixture of *anti*-2 and *syn*-2.

cedure[6] in 82% and 61% yields, respectively (Scheme I). A modification of an approach of the literature[7] was also adopted to the synthesis of the precursor ketone, 3-*tert*-butylbicyclo-[3.3.1]non-9-one. The purity of each isomer was easily determined by ^{13}C NMR spectrum in which several absorptions could be separately observed (Figure 3). Assignment of the stereochemistry followed from the X-ray crystal analysis of the *anti*-2 isomer. The molecular structure is given in Figure 4. Several sterically hindered olefins have been shown to be twisted about the central double bond.[8] However, in this olefin, *anti*-2 the crystallographically imposed center of symmetry precludes any such twist and the central olefinic unit is essentially planar, as reported for 1.[8f]

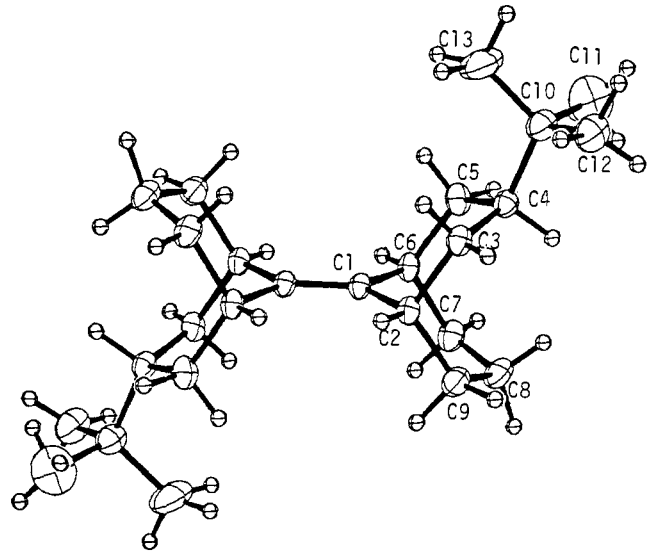


Figure 4. Perspective drawing of *anti*-2.

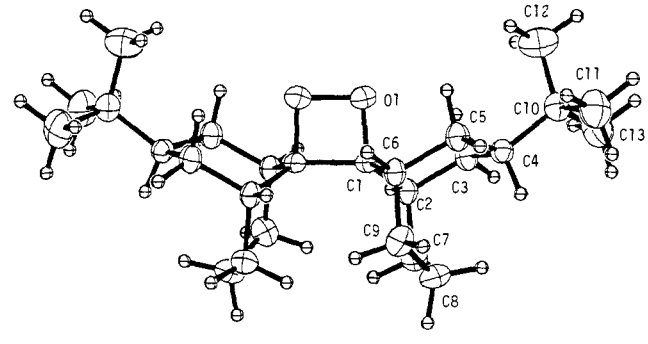


Figure 5. Perspective drawing of *cis,cis*-12.

The TPP- and DCA-sensitized photooxygenations and electrode-catalyzed oxygenation were carried out as described previously. Both photooxygenations of *anti*-2 gave a single dioxetane, *cis,trans*-12. The observation of two *tert*-butyl absorptions in equal intensity in the ^1H NMR spectrum (at 0.85 and 0.90 ppm) and

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Table III. Bond Distances (Å) and Angles (deg) for *cis,cis*-**12**

C1–C1	1.575 (6)	C4–C10	1.562 (5)
C1–O1	1.482 (4)	C5–C6	1.542 (5)
C1–C2	1.519 (4)	C6–C9	1.530 (5)
C1–C6	1.534 (4)	C7–C8	1.532 (5)
O1–O1	1.507 (5)	C8–C9	1.530 (6)
C2–C3	1.533 (4)	C10–C11	1.537 (5)
C2–C7	1.551 (5)	C10–C12	1.524 (6)
C3–C4	1.544 (5)	C10–C13	1.529 (5)
C4–C5	1.552 (5)		
O1–O1–C1	89.2 (3)	C4–C5–C6	115.7 (3)
O1–C1–C1	86.5 (3)	C1–C6–C5	109.5 (3)
O1–C1–C2	109.3 (3)	C1–C6–C9	111.3 (3)
O1–C1–C6	107.2 (3)	C5–C6–C9	113.4 (3)
C1–C1–C2	123.9 (3)	C2–C7–C8	115.0 (3)
C1–C1–C6	118.1 (3)	C7–C8–C9	112.1 (3)
C2–C1–C6	107.8 (3)	C6–C9–C8	114.1 (3)
C1–C2–C3	108.7 (3)	C4–C10–C11	108.9 (3)
C1–C2–C7	110.6 (3)	C4–C10–C12	113.1 (3)
C3–C2–C7	114.0 (3)	C4–C10–C13	109.4 (3)
C2–C3–C4	115.9 (3)	C11–C10–C12	108.4 (4)
C3–C4–C5	110.7 (3)	C11–C10–C13	108.7 (4)
C3–C4–C10	113.6 (3)	C12–C10–C13	108.2 (4)
C5–C4–C10	113.4 (3)		

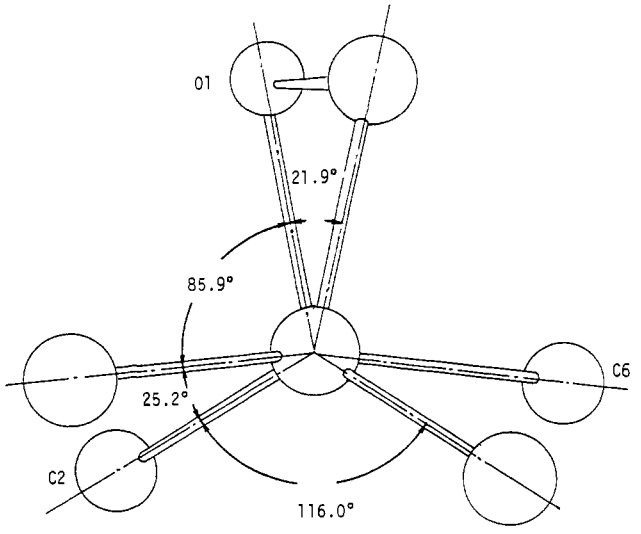

Figure 6. Perspective drawing of *cis,cis*-**12** seen along with Cl–Cl′, with torsion angles.

the absorptions of two dioxetane ring carbons in the ^{13}C NMR spectrum (at 95.5 and 95.3 ppm) established the cis,trans structure. Photooxygenation of *syn*-**2** sensitized by either TPP or DCA gave two dioxetanes, *cis,cis*-**12** and *trans,trans*-**12** (Table II). For each dioxetane a single *tert*-butyl absorption in ^1H NMR (0.85 and 0.90 ppm, respectively) and a single dioxetane ring carbon resonance in ^{13}C NMR (95.3 and 95.9 ppm, respectively) confirmed the *cis,cis*-**12** and *trans,trans*-**12** structures. Structures of these two dioxetanes were assigned by X-ray crystal analysis of *cis,cis*-**12**. The molecular structure is given in Figure 5 and its bond distances and angles are shown in Table III. The oxygen-containing four-membered ring is nonplanar (Figure 6), which has been already reported in the case of dioxetane **1**.[9]

In contrast to the photooxygenations mentioned above, electrode-catalyzed oxygenation of either isomeric olefins gave mixtures of all three dioxetanes as shown in Table II.

Clearly the dye-sensitized photooxygenations of **2** are stereospecific, as expected by considering the results of Bartlett and Schaap.[10] However, the electrode-catalyzed oxygenation was not stereospecific, and this behavior is consistent with the Barton-type mechanism involving the reaction of a cation radical with $^3O_2$, as suggested by Nelsen[2g] and Clennan.[2h] In the dye-sensitized photooxygenation it is excluded that the reaction proceeds through a singlet oxygen-initiated Barton-type oxidation like the result by Landis.[2f] The ^{13}C NMR spectrum of recovered olefin in the electrode-catalyzed oxygenation indicated that extensive isomerization of **2** occurred under the same conditions. The same isomerization of the olefins was observed in the exhaustive electrolyses of both isomers under argon atmosphere. As anticipated, the isomerization indeed took place in the cation radical species. Surprisingly, the DCA-sensitized photooxygenation once presumed to proceed by way of cation radical and superoxide anion ($O_2^{-}\cdot$) reaction (Foote mechanism)[1a-e] occurred stereospecifically (Table II). In this case, the recovered olefins retained their configurations. In contrast to this result, Foote[1c] has reported the isomerization of starting olefins in the DCA-sensitized photooxygenation of stilbene. We concluded that dye- and DCA-sensitized photooxygenations show closely similar features for the reactivity and stereochemistry but the electrode-catalyzed oxygenation, which is considered to proceed through a Barton-type mechanism, is completely different from the other two types of oxygenations especially on the viewpoint of stereochemistry.

Foote[1d,11] and Santamaria[1i] recently reported that singlet oxygen is very efficiently formed in DCA-sensitized photooxygenation by intersystem crossing and energy transfer from singlet and triplet excited DCA on the basis of emission spectra and solvent isotope effects as well as the reaction products. Furthermore, Schaap[1f] postulated that singlet oxygen could be generated as a result of the back-electron transfer from $O_2^{-}\cdot$ to the cation radical from stereoselective formation of *cis*-ozonide from *cis*- and *trans*-oxiranes. On the other hand, Foote and Schaap reported that DCA-sensitized photooxygenation was quenched by methoxybenzenes[1c] and accelerated by stilbene[1d] or biphenyl.[1p,q] Actually, DCA-sensitized photooxygenations of **1** and **2** in acetonitrile–dichloromethane (2:1, [C] = 0.01 M) are strongly quenched by 0.1 equiv of 1,4-diazabicyclo[2.2.2]octane (DABCO). An attempt to quench the photooxygenation by dimethoxybenzene was also successful with 1 equiv ([C] = 0.01 M), but 0.1 equiv ([C] = 0.001 M) did not completely quench. Dimethoxybenzene is a singlet oxygen quencher as well as an electron-transfer quencher. Addition of excess *trans*-stilbene or biphenyl could not change the result of DCA-sensitized photooxygenation of *anti*-**2**. These experiments interpret that singlet oxygen is efficiently produced in DCA-sensitized reactions and is the reactive species which oxygenates the hindered olefins.

As described above, seriously modified olefins **1**, **3**, and **4** and stereoisomeric olefins *anti*-**2** and *syn*-**2** may have general usefulness in addition to other devices for sorting out concerted (singlet oxygen) and stepwise (Barton-type) oxygenations of the attack on the double bond.

Experimental Section

All melting points are uncorrected. ^1H NMR spectra were recorded at 60 MHz on a Varian EM360A spectrometer and at 100 MHz on a JEOL FX-100 spectrometer while ^{13}C NMR spectra were also recorded at 90 MHz on a JEOL FX-90Q, using tetramethylsilane as an internal standard. Mass analyses were carried out with a Hitachi RMU-6M spectrometer. Preparative gas chromatographic separations were operated on an Ohkura gas chromatograph with 3$^{\phi}$ × 2 m glass column containing 10% SF-96 on Celite 545. Preparative high-pressure liquid chromatographic separations were carried out on a Nippon Bunseki Kōgyō liquid chromatograph LC-08 with a JAIGEL-1H column (20$^{\phi}$ × 600 mm × 2). A Beckmann Model 39273 Pt inlay electrode was utilized for cyclic voltammetry along with a Hokuto Model HA-104 potentiostat galvanostat and a Hokuto Model HB-107A function generator. A Hitachi 057 X-Y recorder was used for a scan rate of 200 mV/s with full-scale deflection of less than +2.0 V. A Hokuto HF-201 coulometer was used for monitoring constant potential electrolyses along with the potentiostat.

The olefins **1–5**, and **10** were synthesized by the double-extrusion method via azine (iv, Scheme I),[5i] starting from corresponding bicyclo ketones. Olefins **2** and **4** were synthesized by the carbenoid route (vi,

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Scheme I).[6] Adamantanone was obtained commercially. Bicyclo[2.2.1]heptan-7-one was prepared by the method of Gassman.[12] Bicyclo[3.3.1]non-9-one and 3-*tert*-butylbicyclo[3.3.1]non-9-one were synthesized by the method of Stork and Foote.[7] $\alpha,\alpha,\alpha',\alpha'$-Tetramethylcyclopentanone derivatives were obtained by repeated alkylations of the corresponding ketones with sodium amide and methyl iodide.[13] The separation of stereoisomers of *anti*-**2** and *syn*-**2** was accomplished by preparative high-pressure liquid chromatography to which is attached by a recycling system with 30 recycles. While the former fraction was *anti*-**2** the latter was *syn*-**2** (carrier solvent: chloroform). The crossed olefins **3** and **10** could not easily be separated as sole products. Although adamantanone hydrazine reacted with bicyclo[2.2.1]heptan-7-one and bicyclo[3.3.1]non-9-one, a mixture of three possible azines was formed and led to mixtures of three olefins (two homo- and one hetero-coupled bicycloalkylidenes) in both cases. Therefore, the mixtures of these olefins were separated by preparative gas chromatography.

The tetramethylated olefins **6**, **7**, **8**, and **9** were synthesized by the double-extrusion method.[5l-p] Adamantanethione was prepared according to the method of Gredianus[14] and was offered to syntheses of **7** and **9**.

Preparation of Bridgehead Olefins (Scheme I). The following procedure for **2** was adopted for all the bridgehead olefins (**1**–**5** and **10**).

(a) Double-Extrusion Method via Azine (Paths i, ii, iii, and iv). (i) A solution of hydrazine hydrate (1.7 g, 0.034 mol), hydrazine hydrogen sulfate (2.2 g, 0.017 mol) and 6.5 g (0.034 mol) of 3-*tert*-butyl[3.3.1]-non-9-one in 40 mL of *tert*-butyl alcohol was refluxed for 5 h. The solvent was removed by a rotary evaporator. Water was added and then the mixture was extracted with dichloromethane. The combined extract was dried with anhydrous magnesium sulfate and concentrated to give azine as white solid, 6.5 g (yield 100%). This material was used in the subsequent step without further purification.

(ii) Hydrogen sulfide was bubbled into a solution of the crude azine (6.5 g) and a catalytic amount of *p*-toluenesulfonic acid in 160 mL of acetone–benzene (1:3) at ambient temperature. Thin-layer chromatography (silica gel/acetone) indicated complete consumption of azine after 19 h. The solvent was removed by a rotary evaporator to afford thiadiazolidine as white powder (5.1 g, 72%). This material was used in the subsequent step without further purification. Similar treatment gave 4.5 g (81%) of crude thiadiazolidine.

(iii) To a suspension of $CaCO_3$ (13.4 g, 0.13 mol) in 200 mL of benzene at 0 °C was added in several portions lead tetraacetate (19.2 g, 0.043 mol); the mixture was stirred for 20 min. A solution of thiadiazolidine (9.6 g, 0.023 mol) and 200 mL of benzene was added to the mixture with stirring over a period of 45 min. After the addition was complete, the mixture was stirred at ambient temperature for 4 h. Thin-layer chromatography (silica gel/carbon tetrachloride) indicated the formation of thiadiazene (R_f 0.6). Upon addition of 400 mL of water, brown precipitates were formed. The organic layer was separated. The aqueous layer was saturated with NaCl and extracted with ether. The combined organic layer was dried with anhydrous magnesium sulfate and concentrated to give a white solid, 1.9 g (20%).

(iv) An intimate mixture of thiadiazene (0.29 g, 0.69 mmol) and tri-*n*-butylphosphine (ca. 2.2 mL) was heated at 165 °C in a Pyrex tube. Vigorous nitrogen evolution was observed. After evolution ceased, the mixture was quenched with methyl iodide, cooling and an ice bath. The purification was accomplished by elution through a silica gel column with pentane: white solid, 0.20 g (82%).

(b) Carbenoid Method (Paths v and vi). (v) Mixing 3-*tert*-butylbicyclo[3.3.1]non-9-one (3.3 g, 0.017 mol) and phosphorus pentabromide (10.9 g, 0.025 mol) immediately gave a hot liquid. After the solution was stirred further at 70 °C for 1 h, the reaction mixture was poured into hot water and extracted with dichloromethane. The extract was washed with aqueous NaOH solution and dried with anhydrous magnesium sulfate. Removal of the solvent gave geminal dibromide as yellow crystals, 5.5 g (91%).

(vi) To a solution of 0.29 g of cuprous acetate in 6 mL of glacial acetic acid was added 4.4 g of zinc powder. The suspension was heated until brown copper coated all over the surface of the zinc. The resulting solution was decanted, and the metallic residue was washed once with 10 mL of glacial acetic acid, 4 times with 10 mL of ether, and last with 10 mL of tetrahydrofuran. To the fresh reagent thus obtained was added 3.0 g (8.4 mmol) of *gem*-dibromide dissolved in 10 mL of tetrahydrofuran, and the mixture was vigorously shaken for 30 min. After a gently exothermic reaction took place, the mixture was refluxed for 10 min. Adding ether, washing with water, drying with anhydrous magnesium sulfate, and removing the solvent gave white solid. Repeating the same procedure 4 times gave the total 1.84 g (61%) of the desired olefins (**2**) as an isomeric mixture.

Table IV. Bond Distances (Å) and Angles (deg) for *anti*-**2**

C1–C1	1.341 (4)	C5–C6	1.540 (3)
C1–C2	1.511 (3)	C6–C7	1.551 (3)
C1–C6	1.508 (3)	C9–C8	1.517 (4)
C2–C3	1.542 (3)	C8–C7	1.521 (4)
C2–C9	1.538 (3)	C10–C11	1.532 (4)
C3–C4	1.539 (3)	C10–C12	1.535 (4)
C4–C5	1.533 (3)	C10–C13	1.527 (4)
C4–C10	1.556 (3)		
C1–C1–C2	125.1 (2)	C1–C6–C7	109.5 (2)
C1–C1–C6	125.4 (2)	C5–C6–C7	114.4 (2)
C2–C1–C6	109.5 (2)	C2–C9–C8	114.7 (2)
C1–C2–C3	109.1 (2)	C9–C8–C7	112.3 (2)
C1–C2–C9	108.6 (2)	C6–C7–C8	114.6 (2)
C3–C2–C9	115.5 (2)	C4–C10–C11	109.5 (2)
C2–C3–C4	116.2 (2)	C4–C10–C12	108.9 (2)
C3–C4–C5	110.0 (2)	C4–C10–C13	112.9 (2)
C3–C4–C10	112.3 (2)	C11–C10–C12	109.1 (3)
C5–C4–C10	112.3 (2)	C11–C10–C13	107.5 (3)
C4–C5–C6	116.1 (2)	C12–C10–C13	108.7 (3)
C1–C6–C5	109.0 (2)		

Adamantylideneadamantane (1): mp 181–182 °C (lit.[6] 184–185 °C); ^{1}H NMR δ ($CDCl_3$) 1.70–2.20 (bs, 24 h), 2.95 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 133.1 (s), 39.7 (t), 37.4 (t), 32.0 (d), 28.6 (d); mass spectrum *m/e* 268 (M^+).

Di-*tert*-butylbis(bicyclo[3.3.1]non-9-ylidene) (2). *anti*-**2**: mp 214–216 °C; ^{1}H NMR δ ($CDCl_3$) 0.85 (s, 18 H), 1.75 (m, 22 H), 2.90 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 131.7 (s), 42.1 (d), 35.2 (t), 33.9 (t), 32.9 (s), 32.2 (d), 27.2 (q), 22.6 (t); mass spectrum *m/e* 356 (M^+). *syn*-**2**: mp 143–146 °C; ^{1}H NMR δ ($CDCl_3$) 0.85 (s, 18 H), 1.75 (m, 22 H), 2.90 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 131.7 (s), 42.2 (d), 35.4 (t), 33.7 (t), 32.9 (s), 32.2 (d), 27.1 (q), 22.6 (t); mass spectrum *m/e* 356 (M^+). Anal. Calcd for $C_{26}H_{44}$: C, 87.56; H, 12.43. Found for *anti*-**2**: C, 87.77; H, 12.28. Found for *syn*-**2**: C, 87.70; H, 12.66.

X-ray Crystal Analysis of *anti*-2. Intensity data were collected on a Nicolet P_3/F four-circle diffractometer with graphite monochromated Cu Kα radiation. Of 2247 reflections obtained within $2\theta < 150°$, 1268 had intensities greater than $3\sigma|F_o|$ and were used for structure analysis. The structure was refined to a value of $R = 0.084$. The molecular structure is shown in Figure 4 and the bond distances and angles are listed in Table IV. Crystal data of *anti*-**2**: $C_{26}H_{44}$, monoclinic space group $P2_1/n$, a = 9.243 (1) Å, b = 10.760 (1) Å, c = 12.465 (2) Å, β = 111.43 (1)°, z = 2.

Bicyclo[3.3.1]non-9-ylideneadamantane (3): mp 133–134 °C; ^{1}H NMR δ (CCl_4) 1.50–2.20 (bs, 24 H), 2.95 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 133.7 (s), 131.7 (s), 39.7 (t), 37.4 (t), 33.9 (t), 32.0 (d), 31.9 (d), 28.7 (d), 22.3 (t); mass spectrum *m/e* 256 (M^+).

Bis(bicyclo[3.3.1]non-9-ylidene) (4): mp 140–141 °C (lit.[2k,6b] 142–143 °C); ^{1}H NMR δ (CCl_4) 1.60–1.90 (bs, 24 H), 2.90 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 132.3 (s), 34.0 (t), 32.0 (d), 22.4 (t); mass spectrum *m/e* 244 (M^+).

Bis(bicyclo[2.2.1]heptan-7-ylidene) (5): mp 140.5–141 °C (lit.[6c] 137–138 °C); ^{1}H NMR δ (CCl_4) 1.10–1.70 (m, 16 H), 2.45 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 130.9 (s), 37.0 (d), 29.5 (t); mass spectrum *m/e* 188 (M^+).

Bicyclo[2.2.1]heptan-7-ylideneadamantane (10): mp 66–68 °C; ^{1}H NMR δ ($CDCl_3$) 1.20–1.70 (m, 8 H), 1.70–2.10 (bs, 12 H), 2.70 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 135.3 (s), 129.3 (s), 39.6 (t), 37.4 (t), 35.0 (d), 34.6 (d), 29.4 (t), 28.7 (d); mass spectrum *m/e* 228 (M^+).

Preparation of Octamethylated Olefins by the Double-Extrusion Methods via Diazo Compounds and Thioketones. A typical procedure for bi(2,2,5,5-tetramethylcyclopentanylidene) (**6**) is described. Diazo compounds and thioketones were prepared from the pyrolyses of phosphoranylidenehydrazones.[5n,5p,15]

The mixture of $\alpha,\alpha,\alpha',\alpha'$-tetramethylcyclopentanone (50 g, 0.35 mol), hydrazine hydrate (72 g, 1.44 mol), and hydrazine hydrogen sulfate (46 g, 0.36 mol) in ethylene glycol (200 mL) was heated to reflux overnight. The cooled mixture was poured into water, extracted with ether, and dried with anhydrous magnesium sulfate. Removal of solvent gave a colorless oily solid. This material was used in the subsequent step without further purification.

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Bromine (28 g, 0.13 mol) was added over a period of 1 h to a stirred and cooled solution of triphenylphosphine (47 g, 0.18 mol) in dry benzene (200 mL). After yellow triphenylphosphine dibromide was completely precipitated, triethylamine (36 g, 0.36 mol) was added and the temperature was allowed to rise to room temperature. Hydrazone prepared above and dissolved in dry benzene was introduced slowly to the dibromide solution. The mixture was stirred overnight. The salt of triethylamine hydrogen bromide was filtered off, and the filtrate was concentrated to give yellow solid. Purification by column chromatography (silica gel/benzene) and recrystallization from isopropyl alcohol gave phosphoranylidenehydrazone (14.5 g, 10% yield from the ketone).

The phosphoranylidenehydrazone (7.5 g, 0.018 mol) was heated for 2 h at ca. 180 °C under reduced pressure (5 mmHg), volatile material being collected into a dry ice–acetone trap and giving crude diazo compound as a red orange liquid.

The phosphoranylidenehydrazone (7 g, 0.017 mol) and sulfur (16 g, 0.50 mol) were heated for 2 h at ca. 180 °C under reduced pressure (5 mmHg) with vigorous stirring, and volatile material was collected in a dry ice–acetone trap. The red orange solid was obtained (thioketone).

To a solution of the diazo compound in *n*-hexane (ca. 1 mL) was added dropwise a solution of the thioketone in *n*-hexane (ca. 1 mL) with stirring at room temperature until the red color disappeared. Removal of solvent under reduced pressure gave colorless crystals (2.4 g, 20% yield from phosphoranylidenehydrazone).

A mixture of thiadiazene (2.0 g, 6 mmol) and tri-*n*-butylphosphine (ca. 6 mL) was heated at 150 °C in a Pyrex tube. Vigorous nitrogen evolution was observed. After evolution of nitrogen ceased, the residue was dissolved into small amounts of chloroform and quenched with methyl iodide, cooling with an ice bath. The chromatographic purification (silica gel/pentane) gave colorless olefin (**6**, 0.72 g, 45%).

Bis(2,2,5,5-tetramethylcyclopentanylidene) (6): mp 126–126.5 °C (lit.[5l] 104–105 °C); ^{1}H NMR δ (CCl_4) 1.32 (s, 24 H), 1.50 (s, 8 H); ^{13}C NMR δ ($CDCl_3$) 150.3 (s), 46.5 (s), 44.5 (t), 31.7 (q); mass spectrum *m/e* 248 (M^+).

2,2,5,5-Tetramethylcyclopentanylideneadamantane (7): mp 62–63 °C; ^{1}H NMR δ (CCl_4) 1.15 (s, 12 H), 1.50 (s, 4 H), 1.85 (bs, 10 H), 3.00 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 144.4 (s), 139.9 (s), 44.0 (s), 42.2 (t), 39.0 (t), 37.3 (t), 33.5 (d), 29.0 (q), 28.0 (d); mass spectrum *m/e* 258 (M^+).

Bis(1,1,3,3-tetramethylindan-2-ylidene) (8): mp 260–261 °C (lit.[5m,o] 263–265 °C); ^{1}H NMR δ (CCl_4) 1.80 (s, 24 H), 7.20 (bs, 8 H); ^{13}C NMR δ ($CDCl_3$) 154.4 (s), 150.9 (s), 126.5 (d), 121.9 (d), 50.2 (s), 33.0 (q); mass spectrum *m/e* 344 (M^+).

1,1,3,3-Tetramethylindan-2-ylideneadamantane (9): mp 153–154 °C; ^{1}H NMR δ (CCl_4) 1.54 (s, 12 H), 1.90 (bs, 10 H), 3.25 (bs, 4 H), 7.15 (s, 4 H); ^{13}C NMR δ ($CDCl_3$) 151.1 (s), 144.6 (s), 142.4 (s), 126.6 (d), 122.2 (d), 47.0 (s), 39.0 (t), 37.1 (t), 33.8 (d), 30.3 (q), 27.8 (d); mass spectrum *m/e* 306 (M^+).

Photooxygenation and Electrode-Catalyzed Oxygenations of Hindered Olefins. Detailed procedures were already mentioned in the text and footnotes of Tables I and II.

The dioxetanes except for the stereoisomeric dioxetanes from **2** were easily purified by eluting with carbon tetrachloride in silica gel column chromatography. In the case of stereospecific oxygenations, *anti*-**2** only gave *cis,trans*-**12** eluted with 200–350 mL of solvent, whereas *syn*-**2** gave *cis,cis*-**12** and *trans,trans*-**12** with elutions of 160–280 mL and 320–400 mL, respectively, into 25$^\phi$ × 220 mm silica gel column. On the other hand, in the case of nonstereospecific oxygenations, *cis,cis*-**12** and the mixture of *cis,trans*-**12** and *trans,trans*-**12** were separated by chromatography with elution of 100–150 mL and 300–400 mL, respectively, using 25$^\phi$ × 220 mm silica gel column. The ratio of the dioxetanes in the latter mixture was determined by ^{1}H NMR integration of *tert*-butyl groups. Isolated yields are shown in Table II.

Physical data for the dioxetanes are shown below. All dioxetanes showed beautiful chemiluminescences on heating above ca. 150 °C.

Adamantylideneadamantane Dioxetane: mp 160–163 °C (lit.[16] 164–165 °C); ^{1}H NMR δ ($CDCl_3$) 1.60–2.20 (m, 24 H), 2.65 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 95.8 (s), 47.0 (d), 39.3 (t), 37.3 (t), 36.3 (t), 34.6 (t), 32.8 (t), 31.9 (d), 27.5 (d), 26.8 (d), 26.6 (t).

Bicyclo[3.3.1]non-9-ylideneadamantane Dioxetane: mp 132–135 °C; ^{1}H NMR δ ($CDCl_3$) 1.30–2.30 (m, 24 H), 2.60 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 96.0 (ns), 95.1 (s), 47.0 (d), 46.6 (d), 39.2 (t), 37.3 (t), 36.3 (t), 34.6 (t), 34.4 (t), 32.9 (t), 32.0 (d), 29.3 (t), 27.4 (nd), 27.3 (t), 26.8 (t), 26.6 (t), 20.6 (t).

Bis(bicyclo[3.3.1]non-9-ylidene) Dioxetane: mp 130–132 °C; ^{1}H NMR δ ($CDCl_3$) 1.20–2.30 (m, 24 H), 2.60 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 95.5 (s), 46.5 (d), 34.3 (t), 32.0 (d), 29.2 (d), 27.5 (t), 20.5 (t).

Bis(bicyclo[2.2.1]heptan-7-ylidene) Dioxetane: ^{1}H NMR δ ($CDCl_3$) 1.10–2.00 (m, 16 H), 2.45 (m, 4 H).

Bicyclo[2.2.1]heptan-7-ylideneadamantane Dioxetane: mp 80–84 °C; ^{1}H NMR δ ($CDCl_3$) 1.10–2.30 (m, 20 H), 2.60 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 105.4 (s), 94.0 (s), 47.0 (d), 45.0 (d), 39.3 (t), 37.4 (d), 37.1 (t), 36.3 (t), 34.7 (t), 34.0 (d), 33.6 (t), 32.2 (t), 30.9 (d), 27.4 (t), 26.9 (t), 26.5 (t), 24.6 (t), 24.2 (t), 23.6 (t), 20.6 (t).

Di-*tert*-butylbis(bicyclo[3.3.1]non-9-ylidene) Dioxetane (12). *cis,trans*-**12**: mp 127–130 °C; ^{1}H NMR δ ($CDCl_3$) 0.85 (s, 9 H), 0.90 (s, 9 H), 1.10–2.30 (m, 22 H), 2.70 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 95.5 (s), 95.3 (s), 41.2 (d), 40.7 (d), 33.5 (s), 32.6 (d), 32.4 (d), 31.0 (t), 28.8 (t), 27.5 (q), 27.1 (t), 27.0 (d), 20.4 (t) (A Singlet peak is hidden at the range from 27.1–27.5 ppm). *cis,cis*-**12** mp 167.5–169 °C; ^{1}H NMR δ ($CDCl_3$) 0.85 (s, 18 H), 1.30–2.20 (m, 22 H), 2.70 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 95.3 (s), 40.6 (d), 33.4 (s), 32.5 (d), 29.4 (t), 28.8 (t), 26.9 (q), 20.4 (t). *trans,trans*-**12**: ^{1}H NMR δ ($CDCl_3$) 0.90 (s, 18 H), 1.20–2.30 (m, 22 H), 2.70 (bs, 4 H); ^{13}C NMR δ ($CDCl_3$) 95.9 (s), 41.2 (d), 32.3 (d), 31.4 (t), 27.8 (q), 27.4 (s), 26.8 (t), 20.0 (t). Anal. Calcd for $C_{26}H_{44}O_2$: C, 80.35; H, 11.41. Found for *cis,trans*-**12**: C, 80.32; H, 11.68. Found for *cis,cis*-**12**: C, 80.13; H, 11.59. Found for *trans,trans*-**12**: C, 80.43; H, 11.65.

X-ray Crystal Analysis of *cis,cis*-12. Intensity data were collected under the same conditions as those of *anti*-**2**. Of 2587 reflections obtained with $2\theta < 53°$, 1752 had intensities greater than $3\sigma|F_o|$ and were used for structure analysis. The structure was refined to a value of $R = 0.088$. This compound was slightly unstable under the X-ray analysis conditions, and measurements could not be made for a long time. The molecular structure is given in Figure 5, and its bond distances and angles are shown in Table III. Crystal data of *cis,cis*-**12** $C_{26}H_{44}O_2$, monoclinic space group P_{ccn}, $a = 21.840$ (8) Å, $b = 8.428$ (3) Å, $c = 13.064$ (5) Å, $z = 4$.

Registry No. 1, 30541-56-1; *syn*-**2**, 83709-00-6; *anti*-**2**, 83665-47-8; **3**, 83665-49-0; **4**, 55993-21-0; **5**, 51689-29-3; **6**, 71691-01-5; **7**, 92957-71-6; **8**, 78305-14-3; **9**, 92957-72-7; **10**, 92957-73-8; *cis,cis*-**12**, 83665-48-9; *cis,trans*-**12**, 83709-01-7; *trans,trans*-**12**, 83709-02-8; TPP, 917-23-7; DCA, 1217-45-4; O_2, 7782-44-7; H_2NNH_2, 302-01-2; $H_2NNH_2 \cdot H_2SO_4$, 10034-93-2; H_2S, 7783-06-4; Ph_3PBr_2, 1034-39-5; S, 7704-34-9; superoxide, 11062-77-4; 3-*tert*-butylbicyclo[3.3.1]nonan-9-one, 92957-74-9; bis(3-*tert*-butylbicyclo[3.3.1]non-9-ylidene)hydrazine, 92957-75-0; 3′,3″-di-*tert*-butyldispiro[[1,3,4]thiadiazolidine-2,9′:5,9″-bisbicyclo[3.3.1]nonane], 92957-76-1; 3′,3″-di-*tert*-butyl-2,5-dihydrodispiro[[1,3,4]thiadiazole-2,9′:5,9″-bisbicyclo[3.3.1]nonane], 92957-77-2; 3-*tert*-butyl-9,9-dibromobicyclo[3.3.1]nonane, 92957-78-3; 2,2,5,5-tetramethylcyclopentanone, 4541-35-9; 2,2,5,5-tetramethylcyclopentanone hydrazone, 70302-22-6; 2,2,5,5-tetramethylcyclopentanone (triphenylphosphoranylidene)hydrazone, 70302-23-7; 2-diazo-1,1,3,3-tetramethylcyclopentane, 71690-98-7; 2,2,5,5-tetramethylcyclopentanethione, 43090-71-7; 2′,2′,2″,2″,5′,5′,5″,5″-octamethyl-2,5-dihydrodispiro[[1,3,4]thiadiazole-2,1′:5,1″-biscyclopentane], 71690-99-8; adamantylideneadamantanedioxetane, 35544-39-9; bicyclo[3.3.1]non-9-ylideneadamantanedioxetane, 92984-14-0; bis(bicyclo[3.3.1]non-9-ylidene)dioxetane, 55993-24-3; bis(bicyclo[2.2.1]hept-7-ylidene)dioxetane, 51689-32-8; bicyclo[2.2.1]hept-7-ylideneadamantanedioxetane, 92957-79-4.

Supplementary Material Available: Tables of coordinates of atoms and an FOFC map for dioxetane and olefin (19 pages). Ordering information is given on any current masthead page.

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