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Stereochemical Evidence for the Formation of Intermediates in the Ene Reaction of Singlet Oxygen with Tetraalkyl-Substituted Alkenes

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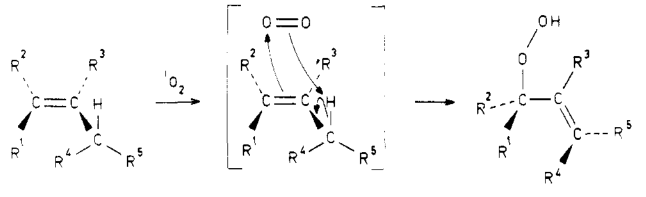
The tetrasubstituted alkenes *syn*- and *anti*-1-(4-*tert*-butylcyclohexylidene)-4-*tert*-butylcyclohexane (6 and 7, respectively), both of which have been shown to be conformationally fixed, undergo the ene reaction with singlet oxygen to afford the allylic hydroperoxides **8a** and **9a**, the stereochemistries of which have been assigned. The reactions are not stereospecific in the fashion anticipated for a concerted reaction of singlet oxygen with 6 and 7. Rather, the results are better explained by assuming the formation of an intermediate during photooxygenation; this intermediate must be long-lived relative to conformational changes. The distribution of allylic hydroperoxides from 6 and 7 is mildly temperature dependent; a possible explanation for this observation is given. The results of the photooxygenation of some other new tetrasubstituted conformationally fixed alkenes are also reported.

Singlet oxygen reacts readily with tetra- and trialkylalkenes having an allylic hydrogen atom to give allylic hydroperoxides (Scheme I).[1] The reaction is more sluggish with dialkyl-substituted alkenes. On the basis of extensive and elegant stereochemical studies with conformationally rigid alkenes, the well-known concerted "ene mechanism" was proposed.[2] Consistent with this mechanism as illustrated is the experimental observation that the allylic hydrogen to be abstracted must be coplanar, or nearly so, with the p lobes of the olefinic double bond.[3]

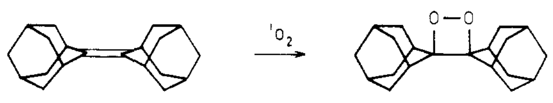
The different course followed in the reaction of adamantylideneadamantane 1 with singlet oxygen (Scheme II) to give the 1,2-dioxetane 2[4] is reasonable in the context of this mechanism because the allylic hydrogens in 1 are perpendicular, not parallel, to the π system, and, moreover, a shift of the double bond would lead to a strained olefin having the double bond at a bridgehead carbon atom. With no possibility present for an ene reaction, [2 + 2] cycloaddition to form the 1,2-dioxetane 2 can compete.

In recent years, however, considerable evidence has been accumulated for the reaction of singlet oxygen with a variety of olefinic substrates,[5] which casts doubt on the concertedness of the ene reaction.[2] Isotope effects,[6] product distributions,[7] computational evidence,[8] and examination of the mechanism of other "ene"-type reactions[9] indicate that an intermediate (or intermediates) may be formed during the molecular transpositions of the ene reaction. These intermediates are usually formulated as perepoxides (3), biradicals (4), or zwitterions (5). Unambiguous demonstration of the presence of intermediates, especially for the case of simple alkenes not bearing heteroatoms or other stabilizing substituents, has proven to be a demanding task, however.

Scheme I



Scheme II



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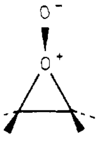

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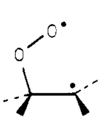

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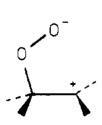

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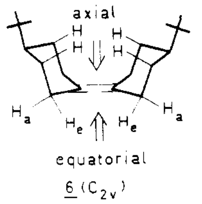
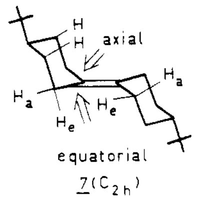
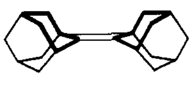
Some time ago we undertook an investigation of the tetrasubstituted olefins 6 and 7. These olefins, the synthesis of which has been previously described,[10] in the



6 (C_{2v})



7 (C_{2h})



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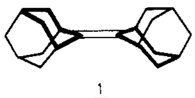

1

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[1] Schenck, G. O. German Patent 933 925, Dec 24, 1943. Schenck, G. O. *Naturwissenschaften* **1948**, *35*, 28.

[2] Reviews: (a) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133. (b) Gollnick, K.; Kahn, H. J. In "Singlet Oxygen-Organic Chemistry. A series of Monographs"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; Vol. 40, p 287. (c) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.

[3] (a) Nickon, A.; Bagli, J. F. *J. Am. Chem. Soc.* **1959**, *81*, 6330; **1961**, *83*, 1498. (b) Nickon, A.; Chuang, V. T.; Daniels, P. J. L.; Denny, R. W.; DiGiorgio, J. B. D.; Tsunetsugu, J.; Vilhuber, H. G.; Werstiuk, E. *Ibid.* **1972**, *94*, 5517.

[4] Wieringa, J. H.; Strating, J.; Wynberg, H.; Adam, W. *Tetrahedron Lett.* **1972**, 169.

[5] For a tabular survey of the ene reaction of singlet oxygen see ref 2a,b.

[6] See for examples: (a) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7977. (b) Grdina, M. B., Sr.; Orfanopoulos, M.; Stephenson, L. M. *Ibid.* **1979**, *101*, 3111.

[7] (a) Saito, I.; Imuta, M.; Takahashi, Y.; Matsugo, S.; Matsuura, T.; *J. Am. Chem. Soc.* **1977**, *99*, 2005. (b) Capdeville, P.; Manny, M. *Tetrahedron Lett.* **1980**, 2417.

[8] For examples from calculations: (a) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 439. (b) Dewar, M. J. S.; Thiel, W. *Ibid.* **1975**, *97*, 3978. (c) Inagaki, S.; Fukui, K. *Ibid.* **1975**, *97*, 7480.

[9] (a) Seymour, C. A.; Greene, F. D. *J. Am. Chem. Soc.* **1980**, *102*, 6384. These authors have examined the ene reaction of triazolinediones with olefins and have obtained evidence for an aziridinium imide intermediate, analogous to a perepoxide. (b) Meijer, E. W.; Kellogg, R. M.; Wynberg, H. *J. Org. Chem.*, in press. These authors have pointed out an analogy between the electrophilic halogenations of tetraalkylethylenes, including 6 and 7, and the singlet oxygen ene reaction. A bridged bromonium ion (also analogous to a perepoxide) is probably formed in these reactions.

[10] Kellogg, R. M.; Noteboom, M.; Kaiser, J. K. *Tetrahedron* **1976**, *32*, 1641.

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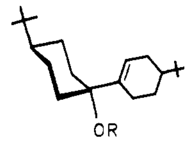
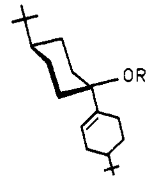
indicated chair conformations contain structural elements of adamantylideneadamantane **1** as emphasized in the structures shown. Compound **6** has C_{2v} symmetry, and the two sides of the double bond are diastereotopic. Approach from the side, which we denote as axial in the structures, presents a steric situation analogous to that encountered with **1**; approach from the equatorial side has, however, no analogy in **1**. Compound **7** has C_{2h} symmetry, and the two faces of the double bond are homotopic. However, the directions of attack at each carbon atom are *non*equivalent and are referred to as axial and equatorial as indicated in the drawing for **7**, the arrows referring to the alkylidene carbon at the left.

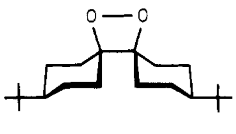
If **6** and **7** are locked virtually exclusively in the indicated chair conformations, then in view of the low (1–2 kcal/mol usually)[11] activation energies for reaction with singlet oxygen, one expects no violation of the Curtin–Hammett principle;[12] in other words, *concerted* reactions should proceed via the chair conformers. One predicts, therefore, for a concerted process that **6** will undergo the ene reaction only on attack from the equatorial side because only that side is a correctly oriented allylic hydrogen atom available. This would lead to the allylic hydroperoxide **8a**. To the extent that reaction occurs from the axial side of **6** in a concerted fashion, the 1,2-dioxetane **10** is anticipated analogously to the formation of **2**. For the alkene **7**, stereochemical analysis following the assumptions made above concerning concertedness and conformational rigidity leads to the prediction that the product of an ene reaction should be the allylic hydroperoxide **9a** with the hydroperoxy group oriented axially. Only for an attack from the axial side of a carbon atom of the double bond is an allylic hydrogen available with the proper stereochemistry for participation in the ene reaction. If cycloadduct formation should occur in the expected suprafacial–suprafacial manner the 1,2-dioxetane **11** is expected.



8a) R = OH
b) R = H



9a) R = OH
b) R = H



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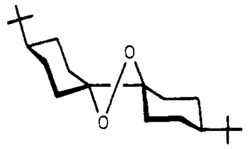

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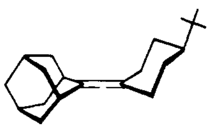
The above predictions are logical derivations from assumption of all suprafacial concerted mechanisms. It will be seen that these predictions in fact are incorrect. We will argue that the failure of the predictions is a consequence of nonconcertedness of the reaction; in other words, intermediates are formed.

Furthermore, in view of the fact that **1** gives with singlet oxygen a stable 1,2-dioxetane[4] and in a similar fashion the product of the photooxygenation of bis(bicyclo[3.3.1]-9-nonylidene) is a 1,2-dioxetane,[13] it became interesting, in conjunction with the results obtained in the photooxygenation of **6** and **7**, to look at the reactions of the crossed olefins **12** and **13** with singlet oxygen.



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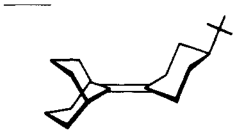

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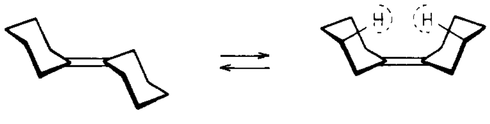
Results

A premise underlying the use of the alkenes **6** and **7** is that they are locked by the *tert*-butyl groups in the indicated chair conformations for the cyclohexyl rings. The ^{1}H NMR spectra of **6** and **7** are superposable, and both have at δ 2.67 ($CDCl_3$) a broadened doublet (J = 12.5 Hz). The spectra were temperature independent from ca −40 (**6** and **7** precipitate at lower temperatures) to 100 °C. This absorption is not found for cyclohexylidenecyclohexane (**14**), which has only an unresolved broad absorption. The δ 2.67 absorption is assigned to the equatorial allylic protons in **6** and **7**; these protons in chair cyclohexane rings have normal J_{gem} (12.5 Hz) coupling but a small J_{vic} coupling.[14] These observations are consistent with **6** and **7** being conformationally frozen whereas **14** converts rapidly from the C_{2v} to C_{2h} conformations; one observes time-averaged spectra for **14**, which consists of a mixture of C_{2v} and C_{2h} conformers.



14 (C_{2h}) 14 (C_{2v})

To establish the energy difference between **6** and **7**, we equilibrated these compounds in benzene solution at 30 °C using iodine and light. The equilibrium was approached from both sides. The equilibrium mixture consists of 83 ± 2% **7** and 17 ± 2% **6**, corresponding to a $\Delta\Delta G_{30 °C}$ = 0.95 kcal/mol. The difference in stability likely arises from a 1,6-interaction of the axial hydrogens on the axial face of **6** (one such interaction is illustrated for the C_{2v} conformers of **14** above). If this is the true cause of the differences in stability, this supports arguments that in adamantylideneadamantane, wherein similar interactions occur on both faces, any motion that forces the rings together will be opposed by a buttressing interaction.[15] In the crystalline state cyclohexylidenecyclohexane (**14**) is found exclusively as the C_{2h} conformer,[16] but the present results indicate that in solution a significant amount of the C_{2v} conformer will be present. This will have to be reckoned with in mechanistic and spectroscopic investigations on **14**.[17]

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[11] (a) Schenk, G. O.; Koch, E. *Z. Elecktrochem.* **1960**, *64*, 170. (b) Koch, E. *Tetrahedron* **1968**, *24*, 6295.

[12] (a) Curtin, D. Y.; *Rec. Chem. Prog.* **1954**, *15*, 111. (b) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; pp 151–156. (b) For applications of this argument in singlet oxygen chemistry, see: Gollnick, K. *Adv. Photochem.* **1968**, *6*, 1.

[13] (a) Keul, H. *Chem. Ber.* **1975**, *108*, 1207. (b) Lechtken, P. *Ibid.* **1976**, *109*, 2862.

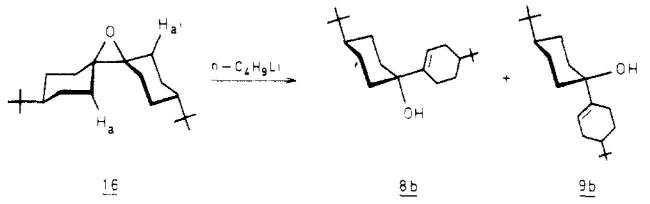
[14] For example: Jackman, L. M.; Sternhell, S. "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry"; Pergamon Press, Oxford, 1969.

[15] See for example: Olah, G. A.; Schilling, P.; Westerman, P. W.; Lin, H. C. *J. Am. Chem. Soc.* **1974**, *96*, 3581.

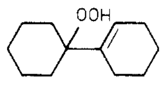
[16] Sasvari, K.; Löw, M. *Acta Crystallogr.* **1965**, *19*, 840.

[17] See for example: (a) McKillop, A.; Hunt, J. D.; Kienzle, F.; Bigham, E.; Taylor, E. C. *J. Am. Chem. Soc.* **1973**, *95*, 3635. (b) Webel, C. *J. Chem. Soc., Chem. Commun.* **1968**, 101. (c) Snyder, P. A.; Clark, L. B. *J. Chem. Phys.* **1970**, *52*, 998. (d) Yogev, A.; Sagiv, J.; Mazar, Y. *J. Am. Chem. Soc.* **1972**, *94*, 5122.

Scheme III



Photooxygenation of **14** in benzene is known to afford cleanly the allylic hydroperoxide **15**.[18] Photooxygenation of **6** in benzene with *meso*-tetraphenylporphine as sensitizer proceeded also very smoothly and gave *two* products as established by ^{1}H NMR.[19] In benzene solution with a 60- or 100-MHz apparatus the *tert*-butyl peaks are separated by several hertz and can be resolved by using slow sweep times; integrations are carried out at 100 MHz. In the case of the photooxygenation of **6**, two sets of two *tert*-butyl absorptions in the ratio 60:40 were observed. These absorptions accounted for at least 98% of the consumed **6**. Photooxygenation of **7** under the same conditions gave the same two products but now in the ratio 33:67.



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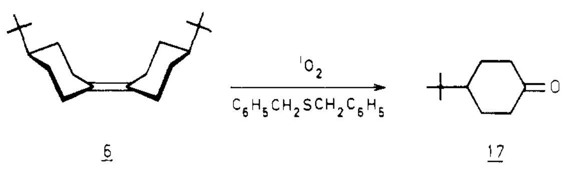
These two products were assumed to be the allylic hydroperoxides **8a** and **9a**. Attempts to separate and purify these materials were unsuccessful owing to fairly rapid decomposition. In the GLC chromatogram these materials gave a large peak for 4-*tert*-butylcyclohexanone. Reduction of the assumed hydroperoxides with $NaBH_4$ in CH_3OH afforded **8b** and **9b**. These materials, although sensitive, with care can be separated chromatographically and purified. The gross structures were established by ring opening of **16**, the epoxide derived from **7**. A single epoxide is obtained from **7** in contrast to **6**, which provides two isomeric epoxides. Treatment of **16** with *n*-butyllithium gave in a very sluggish reaction a mixture of **8b** and **9b** (Scheme III) identified chromatographically and spectroscopically. Abstraction of the diastereotopic H_a and $H_{a'}$ of **16** by base leads respectively to **8b** and **9b**.[20]

Assignment of configuration is based on the well-known observation[21] that axial alcohols elute more rapidly than equatorial alcohols on aluminum oxide. The isomer that elutes most rapidly is assigned the stereochemistry of **9b** and the slower one the stereochemistry of **8b**. The allylic hydroperoxides are assumed to have the same relative stereochemistries.

Clearly the reactions of **6** and **7** with singlet oxygen are not stereospecific. There is a mild (60:40) preference for the predicted allylic hydroperoxide **8a** from attack on the equatorial side of **6**, but there is also 40% of **9a** which arises from attack on the axial side. The latter is formed rather than 1,2-dioxetane **10**. The reaction of **7** does not exclusively afford **9a** as predicted (there is a 67:33 bias in this direction, however) but also gives **8a**. How then are these unpredicted products formed?

Scheme IV



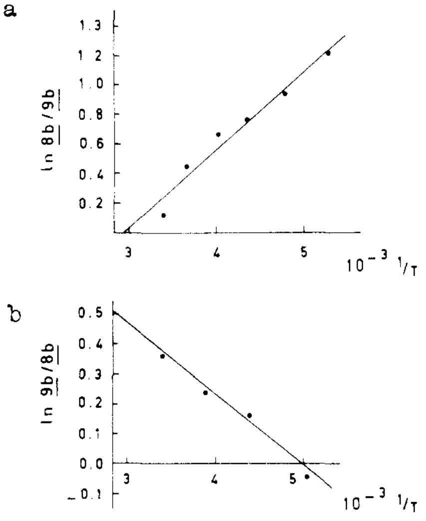


Figure 1.

First the possibility of isomerism of **6** and **7** was eliminated by following the photooxygenation of **6** and **7** with the aid of GLC. The rates of consumption of **6** and **7** are qualitatively equal; the two olefins can be separated, and in neither photooxygenation were detectable amounts of the other olefin formed during the course of the photooxygenation. Others[22] have also confirmed that cis/trans isomerizations do not occur during photooxygenation.

In an attempt to establish the presence of an intermediate, the photooxygenation of **6** was carried out in the presence of 1 equiv of dibenzylsulfide. The only product found is 4-*tert*-butylcyclohexanone (**17**, Scheme IV). By means of control experiments it was established that a reaction product of singlet oxygen with dibenzyl sulfide (the reaction of singlet oxygen with **6** is faster than with the sulfide) was responsible for decomposing the allylic hydroperoxides to the ketone. This is caused by an acidic product as shown by carrying out the photooxygenation of **6** in the presence of dibenzyl sulfide and dry, powdered K_2CO_3; the hydroperoxides **8a** and **9a** were formed in their normal ratio. From the literature it is known that benzenesulfenic acid can be present as an intermediate in the photooxygenation of dibenzylsulfide,[23] and, as is known, acids can decompose allylic hydroperoxides to ketone.[18] The same effect on the photooxygenation products, but to a lesser extent, is found with di-*n*-butyl sulfide, whereas with di-*tert*-butyl sulfide only the allylic hydroperoxides are found. This is in agreement with the scheme advanced by Corey and Ouannès[23] for the photooxygenation of sulfides, because in di-*tert*-butyl sulfide the carbon atom α to sulfur bears no hydrogen atom, and therefore a sulfenic acid cannot be formed.

The reactions of **6** and **7** with singlet oxygen in dichloromethane as solvent were carried out at low tem-

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(18) Schenck, G. O.; Schulte-Elte, K. H. *Justus Liebigs Ann. Chem.* **1958**, *618*, 185.

(19) Kellogg, R. M.; Kaiser, J. K. *J. Org. Chem.* **1975**, *40*, 2575. This is a preliminary communication of a portion of this work.

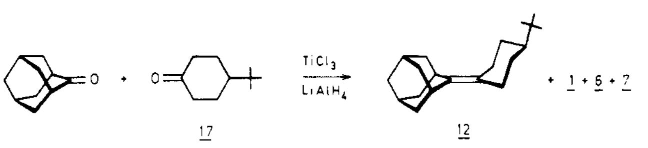
(20) Thummel, R. D.; Rickborn, B. *J. Am. Chem. Soc.* **1970**, *92*, 2064.

(21) (a) Savard, K. *J. Biol. Chem.* **1953**, *202*, 457. (b) Barton, D. H. R. *J. Chem. Soc.* **1953**, 1027. (c) Winstein, S.; Holness, N. S. *J. Am. Chem. Soc.* **1955**, *77*, 5562. (d) Garbisch, E. W., Jr.; Patterson, D. B. *Ibid.* **1963**, *85*, 3228.

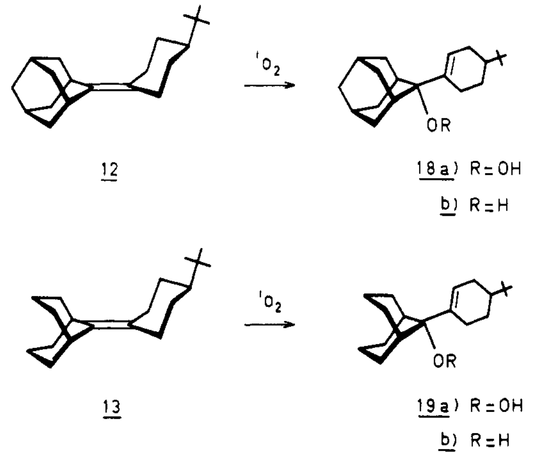
(22) Litt, F. A.; Nickon, A. In "Oxidation of Organic Compounds III", American Chemical Society: Washington, DC, 1981; Adv. Chem. Ser. No. 77, p 118.

(23) Corey, E. J.; Ouannès, C. *Tetrahedron Lett.* **1976**, 4263.

Scheme V



Scheme VI



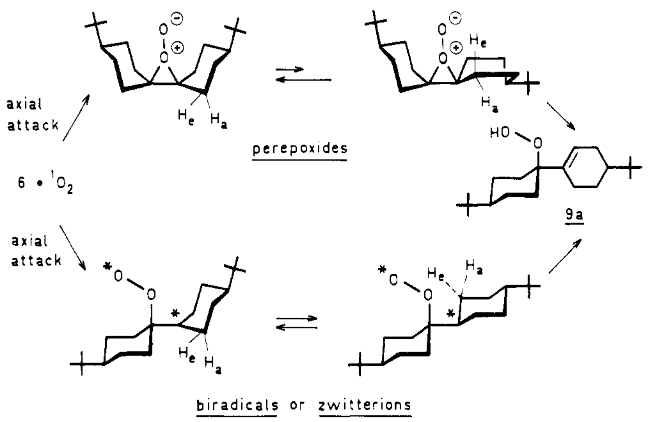
perature in the hope of influencing the course of the reaction. From the ^{1}H NMR spectrum of the reduced reaction products of the photooxygenation of **6** it appeared that at −85 °C more of the equatorial allylic alcohol **8b** and less of the axial allylic alchol **9b** (compared with the results at 20 °C) were formed.[24] From experiments carried out at intermediate temperatures, it is seen that there is a regular change in the ratio of **8b**/**9b**; the natural logarithms of the experimental ratio of **8b**/**9b** are plotted against T^{-1} in Figure 1a. From these data values of $\Delta\Delta H^{\ddagger}_{25^\circ\mathrm{C(8b/9b)}} = -1.0$ kcal/mol, $\Delta\Delta G^{\ddagger}_{25^\circ\mathrm{C(8b/9b)}} = -0.1$ kcal/mol, and $\Delta\Delta S^{\ddagger}_{25^\circ\mathrm{C(8b/9b)}} = -3.1$ eu can be calculated.

When **7** reacts with singlet oxygen in dichloromethane solvent at −75 °C and the products formed are reduced, it is seen that, compared with the results at 20 °C, again equatorial allylic alcohol **8b**, which is the unpredicted isomer, in this case is formed at the cost of **9b**. From the experiments at intermediate temperatures a regular change in the product ratio of **9b**/**8b** (see Figure 1b) was established although the temperature effect on this ratio is now smaller than the product ratio change found in the photooxygenation of **6**. At −75 °C the ratio of **8b**/**9b** is almost exactly 1.0. From Figure 1b one calculates $\Delta\Delta H^{\ddagger}_{25^\circ\mathrm{C(9b/8b)}} = 0.5$ kcal/mol, $\Delta\Delta G^{\ddagger}_{25^\circ\mathrm{C(9b/8b)}} = -0.2$ kcal/mol, and $\Delta\Delta\mathrm{o}S^{\ddagger}_{25^\circ\mathrm{C(9b/8b)}} = 2.4$ eu.

Olefin **12** was prepared by a McMurry reaction,[25] a crossed coupling of adamantanone and **17** with $TiCl_3$ and $LiAlH_4$ (Scheme V). From the GLC chromatogram it appeared that the reaction mixture consisted of about 80% **12** accompanied by the symmetrical olefins **1**, **6**, and **7**. By recrystallization the desired product could be obtained analytically pure. In a similar way **13** was prepared.

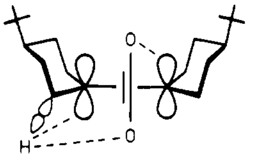
When **12** reacts with singlet oxygen in dichloromethane as the solvent, with *meso*-tetraphenylporphine as sensitizer, only one product is formed, namely, the allylic hydroperoxide **18a** [characteristic signals in the ^{13}C NMR spectrum: δ 133.9 (s), 128.0 (d), 87.7 (s)], which after reduction gives the corresponding alcohol **18b** (Scheme VI). Photooxygenation of **13** gives also exclusively the allylic hydroperoxide **19a** (Scheme VI). The allylic alcohol **19b** obtained on reduction has a tendency to rearrange by a shift of a double bond.

Scheme VII



Discussion

If the reactions of **6** and **7** with singlet oxygen are concerted, they must involve *in part* a pathway antarafacial on the alkenes in their most stable conformations. This is illustrated in the structure below for the formation of



"unexpected" product **9a** from **6**. This pathway would have to compete with a transition state leading to suprafacial products roughly in the manner shown in Scheme I. The possibility of an antarafacial pathway in singlet oxygen ene reactions has been considered by Frimer;[2c] it cannot be discounted entirely although the obvious steric difficulties in attaining this transition state argue weightily against it.

If neither **6**, which is beyond doubt attacked on both faces of the double bond even by reagents far larger than singlet oxygen,[10] nor **7** undergo competing concerted antarafacial and suprafacial ene reactions, then to explain the observed products one must postulate intermediates in the reactions of these materials with singlet oxygen. These intermediates must have lifetimes which are long relative to conformational changes that can deliver allylic hydrogen in a geometry suitable for abstraction. Two fundamentally different types of conformational changes that meet this requirement can be imagined. One possibility is that the double bond of the alkene becomes a freely rotating single bond in the intermediate; this condition could be met in the diradical (**4**) or zwitterionic (**5**) intermediates but not in the perepoxide (**3**). The second possibility is that chair to twist-boat conformational changes of the cyclohexyl rings occur (the *tert*-butyl group remaining equatorial) whereby an equatorial allylic hydrogen is moved into a quasi-axial position suitable for abstraction. This mechanism would be suitable for completion of the ene reaction from a perepoxide intermediate. An applied example is given in Scheme VII in which the intermediates and conformational changes that could occur on axial attack on **6** are analyzed. The open intermediates

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[24] Few cases of changes in product distributions at different temperatures are reported in the literature. For example see: (a) Reference 7a. (b) Ito, Y.; Kyono, K.; Matsuura, T. *Tetrahedron Lett.* **1979**, 2253. (c) Asveld, E. W. H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3644.

[25] (a) McMurry, J. E.; Fleming, M. P. *J. Am. Chem. Soc.* **1974**, *96*, 4708. (b) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255.

Table I

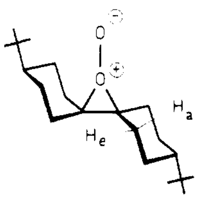
temp, °C	8b/9b ratio	temp, °C	8b/9b ratio
20	53:47	−45	68:32
0	61:39	−65	72:28
−25	66:34	−85	77:23

(**4** and **5**) are drawn identically without charge or unpaired electrons because on the basis of the present work we have no grounds for distinction. A similar analysis can be applied to the reactions of **7**.

Which of the explanations, biradical/zwitterionic vs. perepoxides, offered in Scheme VII is best in accord with the experimental results? (Note, of course, that the ring-flip mechanism reserved for the perepoxide could be used also in the biradical zwitterionic pathway although intuitively one suspects that this is a higher energy pathway than rotation about a single bond.) To attempt to answer this question, one finds it necessary to look more closely at the different possibilities.

Consider first the perepoxide intermediates. The perepoxide drawn in Scheme VII, arising from axial attack on **6**, would give compound **9a** as a product, whereas the perepoxide formed on equatorial attack on **6** would deliver **8a**. The fact that lowering the temperature causes an increased preference for formation of product **8a** can be explained with the assumption of a steric effect on the approach of singlet oxygen. The axial attack on **6** is hindered by four 1,3-diaxial interactions, whereas equatorial attack is not subject to such interactions.

An important point to realize is that in perepoxide intermediates arising from addition to **6**, the structure of the final product is *fixed* on addition of oxygen. The perepoxide drawn in Scheme VII *only* can give **9a** regardless of conformational changes; likewise, the perepoxide obtained on equatorial addition *only* can give **8a**. This means that the ratio of **8a** and **9a** would reflect directly the equatorial/axial attack ratio. In the single perepoxide that could be formed from **7** (see structure below) the structure of the final product is not necessarily fixed since oxygen is bonded equatorially and axially; passage to either **8a** or **9a** is in principle possible. The formation of both **9a** and **8a** (the latter by a conformational change of the ring) can be rationalized as for **6**. But the fact that on lowering the temperature the ratio **9a** to **8a** changes in favor of **8a** is not an observation readily interpreted in terms of a perepoxide; the two sides of the double bond are equivalent with equal 1,3-diaxial interactions. Why then the small but real increase in the **8a**/**9a** ratio at lower temperatures?



The other possible intermediates are the biradical/zwitterionic ones. The formation of **9a** from **6** by following this route[26] is shown in Scheme VII, and **6** can give **8a** by a similar open intermediate formed on equatorial attack of **6**.[27] The preference at low temperature for the formation of **8a** over **9a** can be explained by the fact that the axial attack of **6** by singlet oxygen is hindered by 1,3-diaxial interactions whereas the equatorial attack is not hindered by these interactions. In either of the two possible open intermediates the structure of the final product is already fixed at the instant of singlet oxygen addition. The results obtained with **7** can now be explained in a similar way. Two different open intermediates are possible, arising from axial or equatorial attack on **7**. Again in either intermediate the structure of the final product is fixed at the instant of oxygen addition. This was not true for a perepoxide intermediate from **7**. The formation of the open intermediate arising from axial attack is hindered by two 1,3-diaxial interactions whereas equatorial addition is not hindered by such interaction.

The results obtained with **12** and **13** support those found with **6** and **7**; namely, that if there is a possibility for the ene reaction to occur, this reaction will be preferred to 1,2-dioxetane formation (Scheme VI). However, there is no reason to believe for either **12** or **13** that there should be exclusive attack of singlet oxygen either on a particular face of the alkene or on a specific vinylidene carbon. Concerted mechanisms are inadequate to explain the exclusive formation of ene products on attack on both faces of the double bond of these olefins. In a biradical/zwitterionic mechanism the ene product only can arise when the vinylidene carbon allylic to an abstractable hydrogen is attacked, but from the results obtained with **6** and **7**, it is clear that both vinylidene carbons are attacked. If biradical/zwitterionic intermediates are involved, then they

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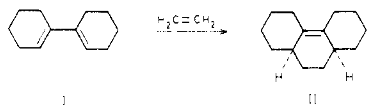
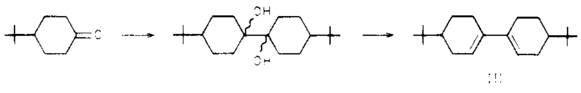
[26] Jefford, C. W. *Tetrahedron Lett.* **1979**, 985.

[27] If rotation about the single bond in open intermediates like **4** or **5** can be restricted so that an axial allylic hydrogen cannot be abstracted, one could expect 1,2-dioxetane formation. This possibility can be tested by bridging allylic carbons in olefin **6**. A way of accomplishing this was suggested by the results of Christol,[28] who observed (eq A) that Diels–

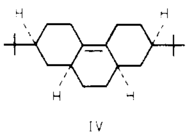


(A)

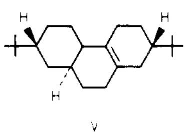


(B)

Alder reaction of I with ethylene at 70–80 atm of ethylene and 250 °C for 48 h provided II, in which, however, the cyclohexyl rings are not conformationally fixed. We prepared (Scheme II) the diene III as a mixture of meso and *dl* isomers, which could not be separated.[29] Reaction of this mixture of dienes with ethylene under these conditions led to isolation of a product, IV, which had the molecular formula expected for



IV



V

a Diels–Alder cycloadduct of III and ethylene. We anticipated on the basis of steric arguments that only the meso diene would react and that IV should be formed. However, both the ^{13}C NMR spectrum as well as the ^1H NMR spectrum, which showed two *tert*-butyl peaks, indicated that the cycloadduct had no symmetry element. The final structure was finally solved by X-ray crystallographic methods and was shown to be V.[30] The double bond has obviously shifted from the desired position. We were unable to suppress this reaction and therefore stopped investigation of the route outlined to a fully locked compound.

[28] (a) Levy, M. Thesis, Montpellier University, 1963. (b) Christol, H.; Pietrasanta, Y. *Tetrahedron Lett.* **1966**, 6471. (c) Christol, H.; Pietrasanta, Y.; Vernet, J. L. *Ann. Chim.* (*Paris*) **1968**, *3*, 145.

[29] This experiment was done at the High Pressure Laboratory of the Technical University Twente with assistance of the personnel of this laboratory and of Dr. H. J. den Hertog.

[30] This X-ray determination was done at the Department of Chemical Physics by Professor Dr. A. Vos and Mr. F. van Bolhius.

must be in equilibrium, a situation most conveniently achieved by means of a perepoxide. This, combined with the explantation given for **6** and **7**, indicates for singlet oxygen attack on tetraalkyl-substituted olefins a pathway in which oxygen may move from one vinylidene carbon to the other, a situation achievable if "open" biradical/zwitterionic intermediates are just slightly lower in energy than perepoxide intermediates, and the latter can form if necessary to allow transfer of oxygen from one vinylidene carbon to the other.

Conclusion

We have established that if there is a possibility for the ene reaction to take place in the photooxygenation of the tetraalkyl-substituted olefins, then this will occur at the cost of dioxetane formation. An essential observation is that the singlet oxygen ene reactions especially with **6** and **7** are explained most simply by the postulation of intermediates. These intermediates might be perepoxides or biradicals/zwitterions; there is likely not much difference in energy between the "closed" and "open" possibilities although the latter are likely somewhat more stable for the case at hand. These conclusions conflict with some aspects of the ab initio computational results of Houk and Yamaguchi,[31] who support, experimental indications to the contrary notwithstanding,[6-10] a concerted mechanism for the ene reaction of singlet oxygen with alkenes. We believe that the present work establishes the case for intermediates in the ene reaction of singlet oxygen with tetrasubstituted alkenes.

Experimental Section

Melting points were determined on a Mettler FP2 melting point apparatus equipped with a Mettler FP21 microscope. The elemental analyses were performed in the Microanalytical Department of this Laboratory. ^{1}H NMR spectra were taken on a Varian A-60, a JEOL C-60 HL, or a Varian XL-100 spectrometer with Me_4Si as the internal standard. ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer, and the chemical shifts have been measured relative to the solvent and converted to δ_{Me_4Si} values by using $\delta_{CDCl_3} = 76.9$ ppm and $\eta_{C_6D_6} = 128.0$ ppm. Mass spectra were recorded on an AEI MS-902 or a VG 3D8 mass spectrometer. IR spectra were taken on a Perkin-Elmer 117 infrared spectrophotometer. GLC analyses were done on a Varian Aerograph 1400 or a Perkin-Elmer F 17 gas chromatograph (both equipped with a flame-ionization detector and a 6 ft × $^1/_8$ in. column filled with 10% SE-30 on Chromsorb W-AW DMCS, 80–100 mesh). Preparative GLC separations were done on a Hewlett-Packard F&M 700 gas chromatograph (equipped with a thermal-conductivity detector and a 6 ft × $^1/_4$ in. column filled with 10% SE-30 Chromsorb W-AW DMCS, 60–80 mesh). HPLC separations were carried out on a Waters Associates HPLC, Model ALC/GPC 201, equipped with a Model 46 K injector, a Waters ri detector, and a Schoeffel SF 770 spectrophotometer.

The irradiations were carried out with a Hanau TQ 150 or a Hanau S81 high-pressure mercury lamp, with a filter solution of potassium dichromate in water as a coolant for the lamp. The temperature of the irradiated solutions was ca 18 °C. Low-temperature photooxygenations were done in a DEMA 13/100 low-temperature irradiation apparatus. The solutions were brought to the desired temperature by immersing the apparatus in a Dewar flask in which the temperature could be regulated. The reported temperatures are those measured in the solution and are accurate to ±2 °C.

General Procedure for the Photooxygenations and Reductions. The olefin and the sensitizer were dissolved in the appropriate solvent. The solution was brought, if necessary, to the indicated temperature. Oxygen was bubbled through the solution, which was stirred and irradiated until the olefin had been consumed. Thereafter the solvent was evaporated.

Table II

temp, °C	**9b**/**8b** ratio	temp, °C	**9b**/**8b** ratio
20	59:41	−45	54:46
−16	56:44	−75	49:51

The residue was dissolved in methanol, and the solution was filtered. $NaBH_4$ was added to the solution, which was stirred in an ice bath for about 20 min. The methanol solvent was removed on a rotary evaporator. Water and chloroform were added to the residue. The layers were separated, and the water layer was extracted three times with chloroform. The combined chloroform layers were washed with water and dried over Na_2SO_4, and thereafter the chloroform was evaporated to leave the alcohol product(s). In all cases ^{1}H NMR spectra were taken of the crude hydroperoxides prior to reduction, and the product ratio as determined by ^{1}H NMR was compared to that of the alcohols obtained after reduction. In all cases these ratios were equal within experimental error.

Preparative Photooxygenation of 6 or 7. A sample of **6** (150 mg, 0.545 mmol) was dissolved in CH_2Cl_2 (150 mL) to which Methylene Blue (15 mg) and pyridine (2 drops) were added. The solution was irradiated at room temperature for 55 min, after which time the starting material had disappeared as indicated by thin-layer chromatography on silica gel. The solvent was carefully removed on a rotary evaporator, taking care that the temperature in the flask did not rise about 15 °C. Fairly long evaporation is necessary to remove the trace of pyridine. The crude solid was taken up in *n*-hexane and filtered to remove Methylene Blue. A ^{1}H NMR spectrum of the crude product taken in C_6D_6 solution revealed four well-resolved absorptions at 0.830, 0.836, 0.908, and 0.997 ppm. The absorptions at 0.830 and 0.997 ppm were of equal intensity and larger than those at 0.836 and 0.908 ppm, which were of equal intensity. When a similar photooxygenation of **7** was carried out, the relative intensity ratios were found to be inverted. Quantitative measurements are described in subsequent sections of the Experimental Section.

The crude product from **6** was dissolved in 20 mL of CH_3OH, chilled in an ice bath, and treated with $NaBH_4$ (140 mg, 3.7 mmol). H_2O was added to the reaction mixture, and the solution was extracted twice with diethyl ether, the ether layer was back-extracted with H_2O, and the solution was dried over $MgSO_4$. Removal of the solvent left a white solid, which was subjected to thin-layer chromatography on silica gel. On elution with CH_2Cl_2/C_6H_{12} (33/67) there were observed two new spots with R_f values of 0.31 and 0.47. The entire reaction mixture was separated, and the separate spots were isolated. The material with an R_f value of 0.31 was recrystallized from CH_3OH: mp 154–155 °C; ^{1}H NMR (C_6D_6) δ 0.800 (s, 9 H, $(CH_3)_3C$), 0.857 (s, 9 H, $(CH_3)_3C$), 1.05–2.30 (br, 16 H, ring H), 5.80 (br s, 1 H, vinyl); IR (KBr) 3270 (OH), 2940 and 2860 (C–H), 1450, 1360, and 1050 cm^{-1} (all strong bands). Anal. Calcd for $C_{20}H_{36}O$: C, 82.11; H, 12.41. Found: C, 82.03; H, 12.71.

The component with R_f 0.47 was dissolved in *n*-hexane, and the mixture was cooled in liquid N_2, allowed to warm to −20 °C, and allowed to stand 5 days at this temperature. The fine white powder that separated was collected: mp 180.5–183 °C; ^{1}H NMR (C_6D_6) δ 0.920 (s, 9 H, $(CH_3)_3C$), 1.000 (s, 9 H, $(CH_3)_3C$), 1.05–2.30 (br, 16 H, ring H), 5.80 (br s, 1 H, vinyl); IR, similar to that of the other component; exact mass m/e 292.275, calcd for $C_{20}H_{36}O$ m/e 292.277. As discussed in the text the material with R_f 0.31 is assigned structure **9b** and that with R_f 0.47 structure **8b**.

Photooxygenation of 6 at Different Temperatures. Compound **6** (75 mg, 0.272 mmol) and *meso*-tetraphenylporphine (TPP, 15 mg) were dissolved in about 275 mL of CH_2Cl_2 and photooxygenated for 1.5 h at the indicated temperatures (Table I). The course of the reaction was followed by GLC, and the reaction was stopped when consumption of the olefin was complete. The crude product was reduced with $NaBH_4$ (800 mg, 21.1 mmol) in CH_3OH. After the workup the product was dissolved in C_6D_6, and the ^{1}H NMR was carefully measured and integrated

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(31) (a) Houk, K. N.; Williams, J. C., Jr.; Mitchell, P. A.; Yamaguchi, K. *J. Am. Chem. Soc.* **1981**, *103*, 949. (b) Yamaguchi, K.; Fueno, T.; Saito, I.; Matsuura, T.; Houk, K. N. *Tetrahedron Lett.* **1981**, 749. (c) Yamaguchi, K.; Yabushita, S.; Fueno, T.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5043.

in the *tert*-butyl region to give the **8b**/**9b** ratio. All experiments were done at least in duplicate. The ratios of products obtained are given in Table I.

Photooxygenation of 7 at Different Temperatures. Compound **7** (40 mg, 0.145 mmol) and TPP (10 mg) were dissolved in about 275 mL of CH_2Cl_2 and photooxygenated for 1.5 h (reaction at −75 °C, 2 h) at the indicated temperatures (Table II). The workup and treatment of the product were analogous to those for **6**. The ratios of products are given in Table II.

Photooxygenation of 6 in the Presence of Dibenzyl Sulfide. Compound **6** (82 mg, 0.297 mmol), dibenzyl sulfide (64 mg, 0.299 mmol), and TPP (15 mg) were dissolved in about 150 mL of CH_2Cl_2 and photooxygenated for 1.5 h. After removal of the solvent, a ^{1}H NMR spectrum (C_6D_6) was taken of the crude reaction product; the only product identifiable from **6** was 4-*tert*-butylcyclohexanone (**17**): ^{1}H NMR δ 0.71 (s, 9 H), 0.71–2.43 complex, 9 H); IR (neat) 1710 cm^{-1}; also identified by its GLC retention time. When dibenzyl sulfoxide or dibenzyl sulfone was substituted for dibenzyl sulfide, no **17** was formed, and the normal absorptions in the ^{1}H NMR for **8a**/**9a** were observed.

Photooxygenation of 8a/9a in the Presence of Dibenzyl Sulfide. Compound **6** (100 mg, 0.362 mmol) and TPP (15 mg) were dissolved in about 150 mL of CH_2Cl_2 and photooxygenated for 1.5 h to give a mixture of **8a**/**9a** as ascertained by ^{1}H NMR. To this mixture of allylic hydroperoxides was added dibenzyl sulfide (80 mg, 0.37 mmol) in 150 mL of CH_2Cl_2. The solution was photooxygenated for 1.5 h. Removal of the solvent left a crude reaction product that contained no **8a** or **9a** but only ketone **17**. When a similar experiment was carried out with nitrogen instead of oxygen during the 1.5-h irradiation period, no **17** was formed, and **8a** and **9a** were recovered unchanged.

Photooxygenation of 6 in the Presence of Dibenzyl Sulfide and K_2CO_3. Compound **6** (150 mg, 0.542 mmol), dibenzyl sulfide (116 mg, 0.542 mmol), and TPP (15 mg) were dissolved in about 150 mL of CH_2Cl_2. K_2CO_3 (5 g, 36.2 mmol) was added to this solution which was thereafter vigorously stirred and photooxygenated for 2 h. Thereafter, the solution was filtered, and the solvent was evaporated, yielding 268 mg of material which contained exclusively **8a** and **9a** with no detectable amount of ketone **17**.

Photooxygenation of 6 in the Presence of Different Sulfides. Compound **6** (150 mg, 0.542 mmol), di-*n*-butyl sulfide (79 mg, 0.541 mmol), and TPP (14 mg) were dissolved in about 150 mL of benzene and photooxygenated for 2 h. The crude material isolated consisted of roughly equal amounts of **17**, **8a**, and **9a**.

A mixture of **6** (159 mg, 0.576 mmol), diisopropyl sulfide (67 mg, 0.567 mmol), and TPP (15 mg) was dissolved in 150 mL of benzene. The solution was photooxygenated for 2 h. The crude reaction product (340 mg) contained **8a** **9a**, and a trace of ketone **17**.

Compound **6** (150 mg, 0.542 mmol), di-*tert*-butyl sulfide (79 mg, 0.541 mmol), and TPP (15 mg) were dissolved in about 160 mL of benzene and photooxygenated for 2 h. The crude product (290 mg) contained **8a** and **9a** but no detectable amount of ketone **17**.

The same result was obtained when instead of 1 equiv of di-*tert*-butyl sulfide 10 equiv were used.

Ring Opening of Epoxide 16. The olefin **7** (100 mg, 0.365 mmol) was dissolved in $CHCl_3$ and treated with *m*-chloroperbenzoic acid (74 mg, 0.37 mmol). After being allowed to stand overnight, the CH_2Cl_2 solution was shaken twice with $NaHCO_3$ solution and once with H_2O and then dried over $MgSO_4$. Removal of the solvent gave **16**: 80 mg (0.276 mmol, 76% yield); ^{1}H NMR (C_6D_6) δ 0.85 (s, 9 H, $(CH_3)_3C$), 0.87 (s, 9 H, $(CH_3)_3C$), 1.1–1.9 (br, 18 H, ring H).

This material was dissolved in ca. 10 mL of dry ether and put in a three-necked flask held under an N_2 atmosphere. By septum was added a solution of n-C_4H_9Li (2.5 mmol) in *n*-hexane. The solution was refluxed gently for 10 h after which time it was worked up. By careful sweeping of the *tert*-butyl area of the ^{1}H NMR spectrum (C_6D_6), one finds that the absorptions **8b** and **9b** could be resolved from those of remaining **16**, which had been about half-converted to alcohol. Analysis by thin-layer chromatography (silica gel; CH_2Cl_2/cyclohexane, 33:67) revealed the presence of **8b**, **9b** (ratio of roughly 5:1), and **16** as the only components of the reaction mixture. The identification was confirmed by coelution with authentic samples of **8b** and **9b**.

Equilibration of Alkenes 6 and 7. Solutions 1.8.10^{-2} M in pure **6** and **7** and 4.10^{-4} in I_2 in pure dry C_6H_6 were held in a thermostated bath at 30.4 ± 1.0 °C for 1 week after which time the samples were analyzed by GLC. Calibration curves were prepared for **6** and **7** and, on the basis of repeated determinations, the composition of the mixtures was established to be, starting from **6**, 80% **7** and 60% **6**. The ratio of 85% **7** and 15% **6** on starting from **7**.

Synthesis of 1-(4-*tert*-Butylcyclohexylidene)adamantane (12). To a stirred slurry of $TiCl_3$ (3.4 g, 22.0 mmol) in dry tetrahydrofuran was added $LiAlH_4$ (440 mg, 12.2 mmol) under a nitrogen atmosphere and at room temperature. The mixture was refluxed for 15 min; after the mixture cooled to room temperature, adamantanone (800 mg, 5.33 mmol) and 4-*tert*-butylcyclohexanone (820 mg, 532 mmol) dissolved *together* in THF were added dropwise, and then the mixture was refluxed for 4 h. After cooling to room temperature, the reaction mixture was poured into water, and this was extracted four times with $CHCl_3$. The combined $CHCl_3$ layers were washed with water and then dried over Na_2SO_4. The $CHCl_3$ was removed on a rotary evaporator, and the residue was passed over a silica gel column, eluting with *n*-hexane. GLC analysis showed the presence of four olefins (see text). The solid material obtained was recrystallized from *n*-hexane, yielding **12**: 0.398 g (1.46 mmol, 27.5%); mp 98.5–100.5 °C; ^{1}H NMR (C_6D_6) δ 0.82 (s, 9 H), 0.81–2.08 (br, 19 H), 2.55–3.02 (br, 4 H); ^{13}C NMR ($CDCl_3$) δ 136.2 (s), 125.8 (s), 48.8, 39.8, 38.9, 37.3, 32.3, 29.5, 29.4, 28.5, 28.2, 27.5; exact mass calcd *m*/*e* 272.250, found *m*/*e* 272.253. Anal. Calcd for $C_{20}H_{32}$: C, 88.24; H, 11.76. Found: C, 88.22; H, 11.92.

Synthesis of 1-(Bicyclo[3.3.3]non-9-ylidene)-4-*tert*-butylcyclohexane (13). To a stirred slurry of $TiCl_3$ (3.9 g, 19.4 mmol) in dry THF was added $LiAlH_4$ (380 mg, 10.5 mmol) under a nitrogen atmosphere and at room temperature. The mixture was refluxed for 20 min. After it cooled to room temperature, bicyclo[3.3.1]nona-9-one (690 mg, 4.99 mmol) and 4-*tert*-butylcyclohexanone (770 mg, 4.99 mmol) dissolved *together* in THF were added dropwise, and then the mixture was refluxed for 3.75 h. After cooling to room temperature, the reaction mixture was poured out into water, and this was extracted three times with $CHCl_3$. The combined $CHCl_3$ layers were washed with water and then dried over Na_2SO_4. The $CHCl_3$ was removed on the rotary evaporator, and the residue was passed over a silica gel column, eluting with *n*-hexane. The solid material obtained was crystallized from *n*-hexane. The solid material obtained was recrystallized from *n*-hexane, yielding **13**: 390 mg (1.5 mmol, 30%); mp 85.8–87.8 °C; ^{1}H NMR (C_6D_6) δ 0.86 (s, 9 H), 0.83–2.25 (br, 19 H), 2.54–3.04 (br, 4 H); ^{13}C NMR ($CDCl_3$) δ 134.9 (s), 126.2 (s), 48.9, 34.0, 33.2, 32.3, 29.6, 29.4, 27.6, 22.2, 22.0; exact mass calcd *m*/*e* 260.250, found *m*/*e* 260.250. Anal. Calcd for $C_{29}H_{32}$: C, 87.69; H, 12.31. Found: C, 87.39; H, 12.43.

Photooxygenation of 12. Compound **12** (88 mg, 0.324 mmol) and TPP (11 mg) were dissolved in about 150 mL of CH_2Cl_2 and photooxygenated for 3.5 h. The crude product had the following: ^{1}H NMR (C_6D_6) δ 0.84 (s, 9 H), 0.75–2.65 (br, 21 H), 5.67 (br, 1 H), 6.39 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 133.9 (s), 128.0 (d), 87.7 (s), 43.8, 37.4, 27.0, 26.8, 24.4. This material (**18a**) was reduced with $NaBH_4$ (500 mg, 13.16 mmol) in CH_3OH to give a sensitive alcohol (**18b**): ^{1}H NMR (C_6D_6) δ 0.84 (s, 9 H), 0.75–2.65 (br, 21 H), 5.67 (br, 1 H), 6.39 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 140.1 (s), 122.6 (d), 76.0 (s), 43.9, 37.8, 35.2, 34.7, 33.8, 33.1, 32.6, 32.1, 27.1, 24.6; IR (neat) 3580 (s), 3470 (w), 1440 (w) cm^{-1}; exact mass calcd for $C_{20}H_{32}O$ *m*/*e* 288.239, found *m*/*e* 288.245.

Photooxygenation of 13. Compound **13** (92 mg, 0.354 mmol) and TPP (20 mg) were dissolved in about 150 mL of CH_2Cl_2 and photooxygenated for 3.25 h. The crude product **19a** had the following: ^{1}H NMR (C_6D_6) δ 0.78 (s, 9 H), 0.62–2.51 (br, 21 H), 5.70 (br, 1 H), 6.47 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 133.7 (s), 128.2 (d), 86.6 (s), 43.8, 32.1, 32.0, 31.2, 29.9, 29.7, 29.5, 28.9, 27.5, 27.0, 26.2, 24.5, 21.1, 20.7.

The crude **19a** was dissolved in CH_3OH and reduced with $NaBH_4$ (0.5 g, 13.16 mmol). There was obtained 125 mg of material (containing some solvent), which contained sensitive allylic alcohol **19b**: ^{1}H NMR (C_6D_6) δ 0.85 (s, 9 H), 0.53–2.63 (br, 21 H), 5.54 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 140.0 (s), 122.6 (d), 130.8

(d), 128.7 (d), 75.1 (s), 65.7 (s), 43.8 and some smaller absorptions between 34.5 and 20.7 ppm; IR (KBr) 3570, 1440 cm^{-1}; exact mass calcd for $C_{19}H_{32}O$ *m/e* 276.248, found *m/e* 276.249. The alcohol apparently underwent a double bond shift on standing.

Synthesis of 4,4-Di-*tert*-butylbis[1-cyclohexen-1-yl] (III). To a stirred and refluxing solution of aluminum powder (8.75 g, 0.324 mol) and $HgCl_2$ (3.5 g, 0.0129 mol) in 50 mL of dry benzene, was added dropwise 17 (22.5 g, 0.146 mol) dissolved in 60 mL of dry benzene, and at the same time from another dropping funnel was added trimethylchlorosilane (50 mL, 43 g, 0.396 mol). The solution was stirred and refluxed for 2 h. Thereafter it was cooled and stirred in an ice bath, and 100 mL of wet benzene followed by 60 mL of ice water was added to the solution. The solid material was filtered with a Büchner filter. The layers from the filtrate were separated, and the water layer was extracted twice with benzene. After the benzene layers were dried over $MgSO_4$, the benzene was evaporated. The material obtained was dissolved in 150 mL of dry pyridine, and to this solution was added $POCl_3$ (15 mL, 0.163 mol). Thereafter the solution was refluxed for 8 h. After the mixture cooled, as much solvent as possible was removed with a rotary evaporator. The residue was cooled in an ice bath, and 100 mL of water was added carefully. Thereafter the mixture was shaken vigorously for 25 min followed by extraction with *n*-pentane. The pentane layers were shaken with 10% HCl solution and then with a saturated aqueous Na_2CO_3 solution and were dried over $MgSO_4$. After removal of the solvent, the solid material obtained was recrystallized from 1,4-dioxane followed by sublimation; yield 2.43 g (8.87 mmol, 12%). A second recrystallization from 1,4-dioxane gave material with the following: mp 152–153 °C; ^1H NMR (C_6D_6) δ 0.85 (s, 1 H), 0.78–2.41 (br, 14 H), 5.67 (br, 2 H); ^{13}C NMR ($CDCl_3/C_6D_6$) δ 136.7 (s), 136.5 (s), 121.9 (d), 121.5 (d), 44.4, 32.3, 27.7, 27.6, 27.4, 27.2, 24.7, 24.6. Anal. Calcd for $C_{20}H_{34}$: C, 87.59; H, 12.41. Found: C, 87.32; H, 12.34.

Despite the sharp melting point it is clear from the ^{13}C NMR spectrum, which shows two *tert*-butyl absorptions, that III is a mixture of *dl* and meso isomers.

Reaction of III with Ethylene. Compound III (4 g, 14.6 mmol) and hydroquinone (150 mg) were brought together under ethylene pressure in an autoclave (glass vessel in a metal bomb). This mixture was heated at 250 °C (pressure ±160 atm) and stirred under these conditions for 48 h.[29] Thereafter the mixture was cooled to room temperature and brought to atmospheric pressure. The material was taken up in CH_2Cl_2. The solvent was evaporated to leave 4.5 g of gummy material. After GLC separation there was obtained 0.899 g of [2*R*(*S*),4a*R*(*S*),7*S*(*R*),10a*S*(*R*)]-2,7-bis-(1,1-dimethylethyl)-Δ^{4b}(8a)-dodecahydrophenanthrene (V; 2.98 mmol, 20%). Recrystallization from 1,4-dioxane gave analytically pure material: mp 133.5–134.4 °C; ^1H NMR (C_6D_6) δ 0.86 (s, 18 H), 0.80–2.41 (br, 20 H). The ^1H NMR 100 MHz (C_6D_6) spectrum (sweep time 5000 s) showed that the *tert*-butyl peak consisted of two absorptions of almost identical chemical shifts: ^{13}C NMR ($CDCl_3$) δ 132.5, 126.9, 44.7, 42.6, 34.9, 33.2, 32.3, 32.1, 31.2, 28.4, 27.5, 27.4, 27.1, 24.5, 24.1; exact mass calcd for $C_{22}H_{38}$ *m/e* 302.299, found *m/e* 302.297. The ^{13}C NMR spectrum ($C_2H_2Cl_4$) recorded at 112 and 142 °C showed the same pattern. Anal. Calcd for $C_{22}H_{38}$: C, 87.42; H, 12.58. Found: C, 87.16; H, 12.56. During the GLC separation of the reaction mixture it was found that when the material was dissolved in as little CH_2Cl_2 as possible and this solution cooled, the solid material obtained was strongly enriched with the addition product.

Epoxidation of V. To *m*-chloroperbenzoic acid (70 mg, 85% MCPBA, 0.35 mmol) in $CHCl_3$, stirred in an ice bath, was added V (99 mg, 0.328 mmol) dissolved in $CHCl_3$. The mixture was stirred for one night. Thereafter the solution was washed with a 10% Na_2CO_3 in water solution. The chloroform layer was dried on Na_2SO_4 followed by evaporation of the solvent. The products were separated by HPLC [30-cm, Si 60 (5 μm column; eluting solvent CH_2Cl_2/n-hexane (26:74)]. Component A: ^1H NMR (C_6D_6) δ 0.79 (s), 0.84 (s), 0.63–2.07 (br); exact mass calcd for $C_{22}H_{38}O$ *m/e* 318.292, found *m/e* 318.295. Component B: ^1H NMR (C_6D_6) δ 0.78 (s), 0.82 (s), 0.67–2.13 (br); exact mass calcd for $C_{22}H_{38}O$ *m/e* 318.292, found *m/e* 318.296.

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Registry No. 6, 56577-76-5; **7**, 56577-77-6; **8a/9a**, 80540-44-9; **8b/9b**, 80559-49-5; **12**, 80540-45-0; **13**, 80540-46-1; **16**, 36614-63-8; **17**, 98-53-3; **18a**, 80540-47-2; **18b**, 80540-48-3; **19a**, 80540-49-4; **19b**, 80540-50-7; *dl*-III, 80540-51-8; *meso*-III, 80540-52-9; V, 80540-53-0; V (epoxide A), 80540-54-1; V (epoxide B), 80581-72-2; adamantanone, 700-58-3; bicyclo[3.3.1]nonan-9-one, 17931-55-4.