References and Notes

(1) (a) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); (b) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," Interscience, New York, N.Y., 1964, p 908; (c) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); **6**, 16 (1967); (d) A. Wassermann, "The Diels–Alder Reaction," Elsevier, Amsterdam, 1965, p 24.

(2) (a) V. Mark and E. D. Weil, *J. Org. Chem.*, **36**, 676 (1971); (b) E. T. McBee, W. L. Dilling, and H. P. Braendlin, *ibid.*, **28**, 2255 (1963).

(3) (a) V. Mark, 156th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1968, Abstract ORGN-92; (b) V. Mark, Chlorocarbon Conference, Wayland, Mass., May 1968; (c) D. I. Davies and M. J. Parrott, *J. Chem. Soc. C*, 659 (1970).

(4) Since **2** contained 0.7% of **5**, 19.9% of it underwent isomerization.

(5) Although the reaction of **1** and **2** at 190–210° for 48 hr was claimed to give **4**,[6a] repetition of the experiment yielded aromatic breakdown products only.[3c] The products of another experiment at 200° were not identified.[6b] A 37.7% yield of **3** was secured when **1** was heated at 200° with a 9:1 mixture of **5** and **2**.[3c]

(6) (a) B. A. Arbuzov and A. N. Vereshchagin, *Bull. Acad. Sci. USSR*, 586 (1965); (b) E. T. McBee, H. Rakoff, and R. K. Meyers, *J. Amer. Chem. Soc.*, **77**, 4427 (1955).

(7) The neat thermal isomerization of **2** was shown to be not unimolecular but significantly accelerated by high temperature (275 to 391°): (a) B. S. Rabinovich and M. J. Hulatt, *J. Chem. Phys.*, **27**, 592 (1957); (b) C. Steel, *J. Phys. Chem.*, **64**, 1588 (1960).

(8) (a) R. E. Wood and R. G. Dickinson, *J. Amer. Chem. Soc.*, **61**, 3259 (1939); (b) K. S. Pitzer and J. L. Hollenberg, *ibid.*, **76**, 1493 (1954); (c) A. H. Ewald, S. D. Hamann, and J. E. Stutchbury, *Trans. Faraday Soc.*, **53**, 991 (1957).

(9) Although on heating at higher temperature (240–250°) **1** yields chlorine, chlorinated **1**, and various C_9, C_{15}, and C_{20} chlorocarbons presumably *via* a dissociative process involving $C_5Cl_5\cdot$ and $Cl\cdot$,[2] no products of these radicals were detected in the reaction mixtures of **1** with **2** or **5** at 165°, suggesting that these radicals are not involved in the isomerization of **2**. Furthermore, both **7** and **8**, which are less likely sources of radicals than **1**, also yielded significant amounts of cis adducts. Also, the presence of oxygen (air) had no apparent effect on the rate of isomerization, as did neither that of anhydrous potassium carbonate (to intercept HCl). Attempts to use conventional radical inhibitors, such as phenols and anilines, were frustrated by their high reactivity with **1**.

(10) Significantly, these reactions yielded no 2 + 2 adducts, which, based on the analogy of 1,2,3,4,4,5,6,7,7-nonachlorobicyclo[3.2.0]-2-nonene,[11] are thermally stable under the reaction conditions. The reason for their absence may well be due to the dominance of competing epimerization, β scission, and radical coupling processes of lower energy requirements,[12] resulting in **5**, and **3** as end products.

(11) A. Roedig and L. Hornig, *Justus Liebigs Ann. Chem.*, **598**, 208 (1956).

(12) The activation energy of biradical ring closure to a four-membered ring is considerably higher than that to a six-membered ring: (a) H. E. O'Neil and S. W. Benson, *Int. J. Chem. Kinet.*, **2**, 423 (1970); (b) R. G. Bergman in "Free Radicals," Vol. I, J. Kochi, Ed., Wiley, New York, N.Y., 1973, p 191.

(13) For a critical, in-depth review of 2 + 2 and 2 + 4 cycloadditions to conjugated dienes, see (a) P. D. Bartlett, *Science*, **159**, 833 (1968); (b) P. D. Bartlett, *Quart. Rev., Chem. Soc.*, **24**, 473 (1970).

(14) A monitoring of the products from the beginning indicates that in the reaction of **1** with **2** the rate of adduct formation (**3**) increases as the concentration of **5** increases. Since the rate of disappearance of **5** is higher than that of **2** in their reactions with **1**, the appearance of a sigmoid segment in the rate of formation of **3** in the latter reaction can readily be rationalized.[15]

(15) I thank a referee for his helpful comments, which elicited this and several other footnotes and references.

(16) These considerations do not apply, of course, when the olefins (*e.g.*, 1,2-dibromoethylene, *trans*-1,4-dichloro-2-butene) can undergo isomerization *per se* under the reaction conditions.

(17) The fact that, contrary to the conclusion of an earlier study,[6b] 1,1-dichloroethylene does yield a 2 + 4 adduct with **1**,[18] indicates that, if the reaction evolves stepwise, a biradical analogous to **6** can undergo ring closure to the octachloronorbornene, presumably because in the absence of competing isomerization steps ring closure to the 2 + 4 adduct remains its only forward option. Significantly, tetrachloroethylene does not yield an adduct with **1** under the above conditions, even though perchloronorbornene is a stable chlorocarbon, readily accessible by another route.[19] These olefins thus parallel the behavior of the sterically hindered systems described by Newman, for which he proposed that the Diels–Alder reaction can proceed by a stepwise mechanism.[20]

(18) V. Mark, *J. Org. Chem.*, **39**, 3181 (1974).

(19) V. Mark, unpublished results; *cf.* G. E. Hawkes, R. A. Smith, and J. D. Roberts, *J. Org. Chem.*, **39**, 1276 (1974).

(20) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961).[15]

(21) J. B. Lambert and J. D. Roberts, *Tetrahedron Lett.*, 1457 (1965).

(22) Address correspondence to Engineering Polymer Products Department, General Electric Co., Mt. Vernon, Ind. 47620.

Hooker Research Center
Niagara Falls, New York 14302
Victor Mark[22]

Received June 3, 1974

Nonstereospecific Diels–Alder Reaction. II. Reaction of Hexachlorocyclopentadiene with 1,1-Disubstituted and Monosubstituted Ethylenes

Summary: The major epimers in the adducts of hexachlorocyclopentadiene, and related dienes, with unsymmetrical 1,1-disubstituted ethylenes are those in which the bulkier substituents are endo, irrespective of secondary orbital interaction considerations; similar results obtain with monosubstituted ethylenes as well, where the cyano and aldehydo substituents yield significant proportions of the novel exo adducts.

Sir: In the preceding communication we described the Diels–Alder reaction of hexachlorocyclopentadiene (**1**) with a variety of 1,2-disubstituted ethylenes, which takes place with a *de facto* violation of the cis principle, and suggested that steric hindrance may be the main underlying cause for the anomalous behavior.[1] To gain a better insight into the role of various substituents in these reactions, we examined the behavior of 1,1-disubstituted olefins as well.

The experiments were carried out by heating **1** with the olefin in a stirred and sealed, all glass system at the lowest temperature at which the reaction proceeded at a convenient rate and quantitatively analyzing the crude product by proton nmr before any subsequent separation, purification, and identification steps. To facilitate structure assignment, adducts of **1** with symmetrically 1,1-disubstituted ethylenes have also been prepared as model compounds; the pertinent 1,2,3,4,7,7-hexachloronorbornenes yielded the following nmr parameters: 5,5-dimethyl- (**2**) δ, H_{exo} 2.499, H_{endo} 1.963 ($J_{gem} = -13.0$ Hz), $CH_{3,exo}$ 1.50, $CH_{3,endo}$ 1.02; 5,5-diphenyl- (**3**), H_{exo} 3.633, H_{endo} 3.158 ($J_{gem} = -13.6$ Hz); 5,5-dichloro- (**4**), H_{exo} 3.497, H_{endo} 3.114, ($J = -14.7$ Hz), $CDCl_3$ solution. Isomer distribution data in adducts of representative, 1,1-dissimilarly substituted ethylenes are shown in Table I.

The results of these kinetically controlled[2] experiments indicate the following competitive relationships for the less hindered endo position.

$$(CH_3)_2CH > CH_3CH_2 > H_3C$$

$$CH_3OOC \sim Cl \sim Ph \gg H_3C \sim ClCH_2 \sim CHO > CN$$

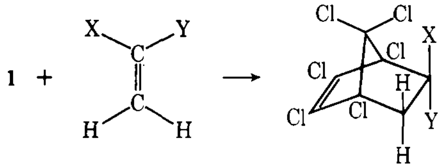
$$Cl \gg CH_3OCH_2 > H_3C$$

While the alkyl series underlines the role of size in the competition, and it apparently can be extended to include the aldehydo and cyano substituents, several of the cases reflect the results of opposing forces. Thus, while secondary orbital interaction[3] between the π system of **1** and the dienophile can be invoked with phenyl, methoxycarbonyl, and perhaps even chlorine,[4] to rationalize their endo selectivity, it cannot account for the preferentially exo pattern of the aldehydo and cyano substituents.[5] However, size and secondary attractive forces, when considered jointly, seem to accommodate the results. When in competition, size appears to dominate over secondary interactions (methyl *vs.* the planar aldehydo and the linear nitrile substituents) and, expectedly, the two effects reinforce each other when not in opposition (phenyl *vs.* methyl).[6]

The results of the reaction of **1** with α-methylstyrene (**5**) differ from literature data in two respects.

(a) The structure assigned[7] to the crystalline adduct[8] (**6A**) of **1** and **5** had the phenyl group exo and was derived from the nmr spectrum of its deuterium-labeled analog based on the assumption that the exo proton resonates downfield from the endo proton. Exact repetition of the reaction conditions[7] yielded in our hands a crystalline ad-

Table I
Distribution of Isomers in Adducts of 1 with Unsymmetrically 1,1,-Disubstituted Ethylenes[a]



X	Y	%	Y_{endo}/Y_{exo}
CH_3	CH_3CH_2	64	1.8
CH_3	$(CH_3)_2CH$	85	5.7
CH_3	$ClCH_2$	45	0.8
CH_3	CH_3OCH_2	70	2.3
CH_3	C_6H_5	89	8.1
CH_3	OHC	48	0.9
CH_3	NC	24[b]	0.3
CH_3	CH_3OOC	92	11.5
CH_3	Cl	90[c]	9.0
C_6H_5	$ClCH_2$	10	0.1
C_6H_5	Cl	55[d]	1.2
CH_3OCH_2	Cl	81	4.3
NC	Cl	97	32.3
CH_3OOC	Cl	60	1.5
$BrCH_2$	Br	86	6.1

[a] The numerical values are the extent of the given isomers present in the adduct; hence they are not necessarily yield data. The other epimers are present in complementary percentages. [b-d] In the corresponding adducts of 7 the analogous epimer is present in 30, 89, and 56%, respectively.

duct as the major product, mp 67-69°, **6A**, whose nmr analysis, in $CDCl_3$, showed the methylene doublets (δ 2.67 and 3.15, $J = -13.9$ Hz), the methyl singlet (δ 1.88), and the closely bunched aromatic protons (δ 7.24). A comparison of these parameters with those of model compounds **2** and **3** indicates that the downfield doublet of **6A** coincides well with the upfield (endo) doublet of **3**, and the upfield doublet of **6A** matches closely the downfield (exo) doublet of **2**. The converse matching for the epimeric adduct **6B** (δ H_{exo} 3.495, H_{endo} 2.125, $J = -13.2$ Hz, CH_3 1.375, Ph 7.1-7.4 and 7.5-7.66, multiplets) plus the fact that the methyl peak of **6A** is more deshielded than that of **6B**, indicate that in the major adduct, **6A**, the methyl group is exo[9] (Figure 1).

(b) The reaction of **5** with **1** yields not one, but two epimeric adducts. As such, it is not exo/endo stereospecific, as is neither its reaction with 5,5-dimethoxytetrachlorocyclopentadiene (**7**) and tetrachlorofuran (**8**), which yield 88 and 80%, respectively, of the analogs of **6A**. In fact, none of the reactions of Table I are completely stereospecific.[10]

The data of Table I suggest that the sterically least demanding aldehydo and cyano substituents are forced in the sterically unfavored exo position when they are in competition with bulkier substituents. To evaluate them against the smallest of substituents, several monosubstituted ethylenes were allowed to react with **1** and the adducts analyzed for isomeric composition.

As anticipated, the halogens and bulky carbon substituents, such as *tert*-butyl, phenyl, and methoxycarbonyl yielded endo adducts only, but propylene, acrolein, and acrylonitrile produced 5, 14, and 14%, respectively, of the exo products as well. With **1**, **7**, and **8**, acrylonitrile yielded increasingly more exo adducts, 14, 17 and 38%, respectively, providing thus additional support for the steric argument and suggesting again the relatively subordinated role of secondary orbital interaction in these reactions.

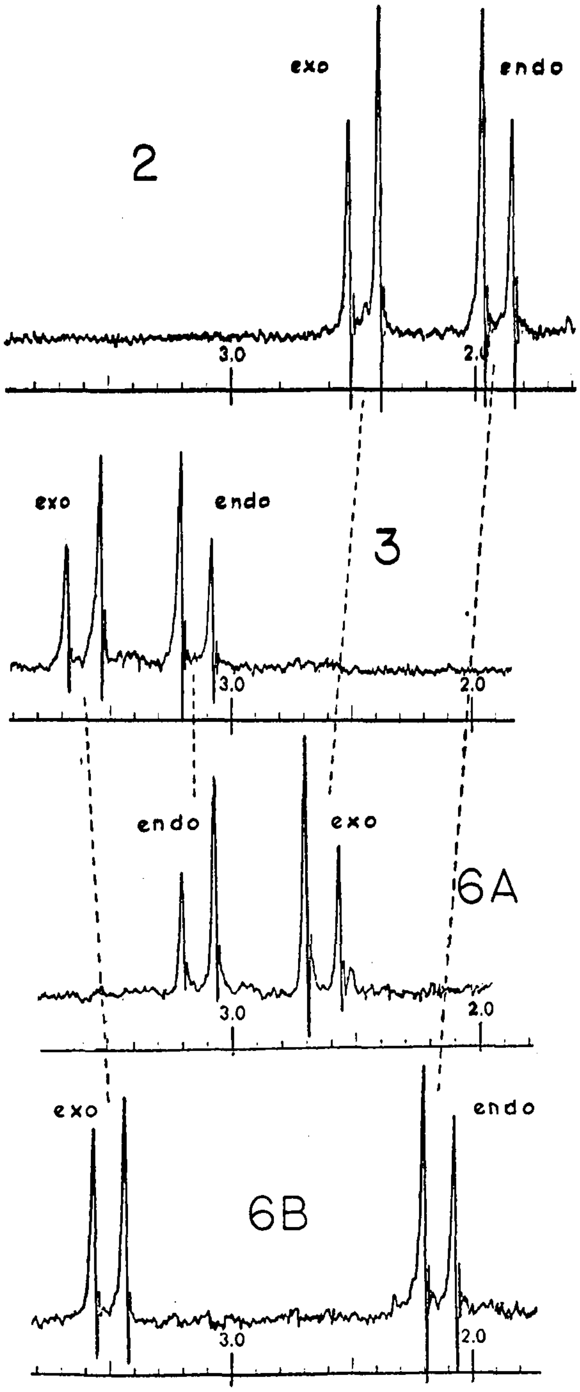


Figure 1. Pmr spectrum of the methylene protons in **2**, **3**, **6A**, and **6B**.

References and Notes

(1) V. Mark, *J. Org. Chem.*, **39**, 3179 (1974).
(2) As indicated by the theral stability of the isomerically pure adducts under reaction conditions.
(3) Which is the expression in quantum chemical terms of Alder's rule of maximum accumulation of unsaturation (endo rule): R. Hoffmann, and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 4388 (1965).
(4) (a) K. L. Williamson, Y. L. Hsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, **91**, 6129 (1969); (b) K. L. Williamson and Y. L. Hsu, *ibid.*, **92**, 7385 (1970).
(5) It is becoming increasingly more apparent from thoroughly investigated systems that, when not in competition with hydrogen, unsaturated substituents tend to violate the rule of endo addition in kinetically controlled Diels-Alder reactions: (a) J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Amer. Chem. Soc.*, **84**, 297 (1962); (b) ref 4; (c) Y. Kobuke, T. Fueno, and J. Furukawa, *J. Amer. Chem. Soc.*, **92**, 6548 (1970); Y. Kobuke, T. Sugimoto, J. Furukawa, and T. Fueno, *ibid.*, **94**, 3633 (1972); (d) K. N. Houk and L. J. Luskus, *ibid.*, **93**, 4606 (1971); (e) E. T. McBee, M. J. Keogh, R. B. Levek, and E. P. Wesseler, *J. Org. Chem.*, **38**, 632 (1973); (f) B. M. Jacobson, *J. Amer. Chem. Soc.*, **95**, 2579 (1973); (g) J. M.

Mellor and C. F. Webb, *J. Chem. Soc., Perkin Trans. 2,* 17, 26 (1974); B. C. C. Cantello, J. M. Mellor, and C. J. Webb, *ibid.,* 22 (1974).

(6) While a detailed analysis of the data is deferred to the full paper, several correlations emerge even from a cursory comparison with analogous nonchlorinated dienes. Thus, in both systems (a) increased size of the alkyl group enhances their endo selectivity;[5g] (b) increased steric bulk destabilizes both the endo and exo transition states;[1,5g] (c) repulsive nonbonding interactions between the diene and a bulky substituent seem to be the major cause for their endo selectivity;[1,5d,g] size and its unfavorable geometry for secondary overlap are probably responsible for the low endo selectivity of the nitrile group.[5g]

(7) J. B. Lambert and J. D. Roberts, *Tetrahedron Lett.,* 1457 (1965).

(8) J. Sauer, Habilitationsschrift, University of Munich, 1963, p 113.

(9) The assignment of the downfield doublet to the endo proton in **6A** is supported also by its line widths, which are somewhat broader than those upfield, thus suggesting a ^4J W-coupling with the methyl protons and, hence, a trans relationship. In epimer **6B** it is again the downfield doublet, assigned now to the exo proton that is broader in accordance with the proposed structure.

(10) The reaction of **1** and **5**-*d* is often quoted[11] in support of the concerted nature of the Diels–Alder reaction, which, although heavily weighted in favor of a biradical pathway, still yielded, reportedly, one cis/trans stereospecific adduct.[7] Although our finding that **6A** has the stereochemistry opposite to that proposed[12] does not invalidate the conclusion that the stereochemical integrity of the deuterium-labeled olefin was maintained in the adduct, the formation in significant proportion of **6B** weakens the validity of the argument in support of the mechanism of the Diels–Alder reaction until the cis–trans stereospecificity of **6B** is determined. Should, however, subsequent experiments establish, *e.g., via* similar deuterium labeling, the conservation of the steric integrity of the olefin in **6B** as well, the finding would reinforce the argument in favor of the one-step mechanism, since it would clearly underline the relevance of molecular alignment in the preadduction state.

(11) *Cf., inter alia,* (a) T. L. Gilchrist and R. C. Storr, "Organic Reactions and Orbital Symmetry," Cambridge University Press, London, 1972, p 97; (b) S. Seltzer in "Advances in Alicyclic Chemistry," H. Hart and G. J. Karabatsos, Ed., Academic Press, New York, N.Y., 1968, p 43; (c) J. Sauer, *Angew. Chem. Int. Ed. Engl.,* **6,** 16 (1967); (d) B. Capon, M. J. Perkins and C. W. Rees, "Organic Reaction Mechanisms," Interscience, New York, N.Y., 1965, p 123.

(12) The reversal of assignment in the stereochemistry of **6A** was not unanticipated.[7] While recognizing that it violated the endo rule, and done only reluctantly, the placement of the phenyl group in the exo position was necessary based on the then available chemical shift data, which indicated that, without exception, the endo methylene protons in adducts of **1** resonate at higher field.[7,13]

(13) Other examples where the endo methylene proton is not upfield from the exo include the adduct of **1** with 2-chloropropene (in the *exo*-methyl epimer), with *ar*-pentachloro- and *ar*-pentabromostyrene, and with α-methylacrylonitrile (where they are adventitiously equivalent in the exo methyl epimer in $CDCl_3$, but not in C_6D_6 solution).

(14) Address correspondence to Engineering Polymer Products Department, General Electric Co., Mt. Vernon, Ind. 47620.

Hooker Research Center
Niagara Falls, New York 14302
Victor Mark[14]

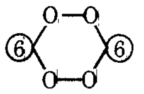
Received June 3, 1974

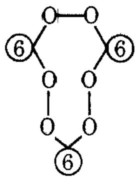
Singlet Oxygen Scavenger Method for the Determination of Ketone Peroxide Kinetics

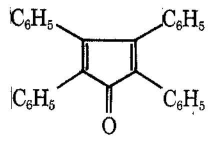
Summary: The rate of decomposition of dicyclohexylidene diperoxide (I) has been monitored spectrophotometrically by use of the colored singlet oxygen scavenger "tetracyclone" (III) (tetraphenylcyclopentadienone). The rate constants determined for I are in good agreement with those determined iodometrically.

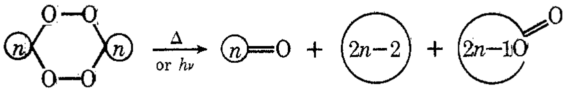
Sir: In 1967 Story and coworkers[1] found that the thermal and photochemical decomposition of cyclic ketone peroxides such as I and II produced macrocyclic hydrocarbons and lactones (eq 1 and 2). About 5–10% ketone was also produced. Story suggested that the ketone was produced with the evolution of singlet oxygen.

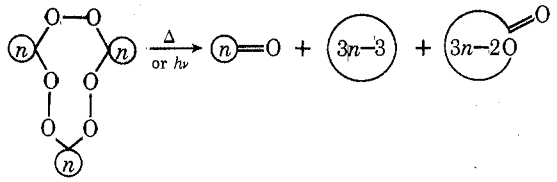
The detection of singlet oxygen in liquid phases is restricted almost entirely to chemical methods which might be misleading (but several methods are available).[2-4] In order to determine the singlet oxygen in a liquid phase, one may decompose the precursor in the presence of an appropriate singlet oxygen acceptor.[5]


I

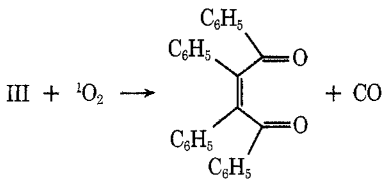

II


III


(1)


(2)

For example, Murray and coworkers used tetracyclone to measure the per cent of singlet oxygen evolved from ozone adducts of isopropyl alcohol and isopropyl ether (eq 3).[6] In our laboratory Brennan used tetracyclone to scavenge singlet oxygen from phosphorus ozone adducts.[7]


IV

(3)

It occurred to us that this highly colored compound might be used (if thermally stable) to measure the singlet oxygen evolved from peroxide precursors. The extinction coefficient of this compound is high [$\epsilon \simeq 1250$ l./(mol cm)], thus allowing the singlet oxygen yields to be determined on dilute peroxide solutions with the aid of a spectrophotometer.

The stable free radical technique for the determination of free radical initiator kinetics had been so successful for the determination of the kinetics and free radical efficiencies of diacyl peroxides that we decided to apply the same technique to peroxides which might give singlet oxygen on decomposition.[8]

The advantages are (a) the solution of peroxide is dilute enough so that induced decomposition is negligible; (b) the rate constant and the efficiency of singlet oxygen production (the fraction of singlet oxygen per mole of peroxide which reacts with the scavenger) may be determined in a single experiment.

The rate data for the decomposition of cyclohexanone diperoxide obtained by monitoring the disappearance of the colored band at 510 mμ in tetracyclone were calculated from eq 4 and are presented in Table I (see ref 8 for derivation of a similar equation). The rate data are in good agreement with that obtained by following the rate iodometrically in all solvents except cyclohexane.[9] The reason for this discrepancy has not been completely resolved.

$$\ln (A - A_\infty) = -kt + \ln \varepsilon P_0 e_s$$ (4)[10]

The values of e_s for I range from 0.05 to 0.02 in the solvents studied, and it appears that the peroxide is not an efficient source of singlet oxygen. The yield of cyclohexanone varies from 0.10 to 0.20 mol/mol of peroxide; so the maximum available singlet oxygen is 5 to 10% (0.05 to 0.10 for e_s). Furthermore, it is likely that the values of e_s recorded in Table I are too high since it is possible for the fading of