Reaction of ¹O₂ with Strained Olefins. 3.[1] Photooxidation of Vinylcyclopropanes

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The reaction of ¹O₂ with 1,1-dicyclopropylpropene (13) and its 2-methyl analogue (12) yields two "ene" products corresponding to the abstraction of an allylic hydrogen from either the methyl or the cyclopropyl group. In the latter case an alkylidenecyclopropane is formed despite a resulting 11.4 kcal/mol increase in strain energy. This indicates that ¹O₂ is insensitive to any strain that might develop in the final product. In contradistinction, 2-cyclopropyl-3-methyl-2-butene (14) yields no alkylidenecyclopropane product, but this is explicable in terms of conformational analysis. 1,1-Dicyclopropylethylene (15) yields only the corresponding ketone and polymer by what is most probably a free-radical process. Kinetic data indicate that the unperturbed vinylcyclopropane double bond is not particularly electron rich. The question of mechanism for the ene mode of ¹O₂ attack is discussed in light of this study.

Introduction

The photooxidation of vinylcyclopropanes has been of interest for over a decade, particularly since this moiety is quite common in natural products. Until recently those studied—including[2] *cis*-Δ^2-carene (1),[3a,3b] (+)-Δ^4-carene (2),[3a,3b] (+)-α-thujene (3),[3c] sabinene (4),[4] thujopsene (5),[5] thujopsenol (6),[6] homosemibullvalene (7),[7] gurjunene (5),[8] tricyclo[3.2.1.0²,⁷]oct-3-ene (9),[9] illudin M (10),[10] and Diels–Adler adducts of spiro[2.4]hepta-4,6-diene (11)[11]— have all been conformationally rigid cycloolefins. Three modes of reaction were observed: (1) allylic hydroperoxide formation (1–10) via a singlet oxygen "ene" reaction; (2) oxidative cleavage of the double bond (4–9, 11) presumably via a dioxetane; (3) formation of a homo-Diels–Adler product (11). With the one notable exception of gurjunene (8), in all cases where the first mode obtained, no alkylidenecyclopropanes were formed. Strain considerations aside, the absence of such a product is indeed expected in all these cases since Dreiding stereomodels reveal that the cyclopropyl allylic C–H bond is far from being at a 90° dihedral angle with respect to the plane of the double bond as is preferred in ¹O₂ reactions.[12] In the instance of gurjunene (8), the cyclopropyl allylic hydrogen is *nearly parallel* with the plane of the double bond; hence, the abstraction of such a hydrogen in a ¹O₂ process is completely without precedent.[13]

We[14] and others[15] turned our attention to acyclic vinylcyclopropanes for the following reasons.

(1) Free rotation of the cyclopropyl ring ought to allow the allylic ring hydrogen to lie at times perpendicular to the plane of the double bond. This should in turn permit the formation of cyclopropylidene hydroperoxides which upon reduction would yield the corresponding carbinol. Cyclopropylidenecarbinols are difficult to obtain by classical synthetic methods.
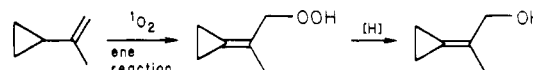
(2) The formation of an alkylidenecyclopropane would, however, require an investment of 11.4 kcal/mol of strain energy.[16] We were interested, therefore, in determining the effect this additional strain would have on the product distribution.

(3) Nishida and co-workers[17] have argued, on the basis of cycloaddition and ionization potential data, that cyclopropyl olefins are highly electron rich, of the same order as vinyl ethers. On the other hand, others have demonstrated that cyclopropyl groups are inductively similar to or only somewhat poorer electron donors than alkyl groups.[18] The mode and rate of singlet oxygen (¹O₂) attack

(1) For previous papers in this series, see ref 14 and 52.

(2) (a) Not included in this list is the photosensitized oxidation of the insecticide resmethrin.²ᵇ Although the vinylcyclopropyl moiety proved unreactive, this is undoubtedly due to the much greater reactivity of the furyl moiety. (b) K. Ueda, L. Gaughan and J. E. Casida, *J. Agric. Food Chem.*, 17, 208 (1969).

(3) (a) K. Gollnick and G. Schade, *Tetrahedron Lett.*, 2335 (1961); (b) H. Takeshita and I. Kuono, *Kyushu Daigaku Seisankagaku Kenkyusho Hokoku*, 65, 13 (1977). (c) E. Klein and W. Rojahn, *Chem. Ber.*, 98, 3045 (1965).

(4) (a) K. Gollnick, *Adv. Photochem.*, 6, 68 (1968); (b) S. Ito, personal communication.

(5) (a) S. Ito, H. Takeshita, T. Muroi, M. Ita, and K. Abe, *Tetrahedron Lett.*, 3091 (1969); (b) S. Ito, H. Takeshita and M. Hirama, *ibid.*, 1181 (1971); (c) H. Takeshita, T. Hatsui, and I. Shimoda, *ibid.*, 2889 (1978); (d) G. Ohloff, H. Strickler, B. Willhalm, C. Borer, and M. Hinder, *Helv. Chim. Acta*, 53, 624 (1970).

(6) H. Takeshita, T. Sato, T. Muroi, and S. Ito, *Tetrahedron Lett.*, 3095 (1969).

(7) M. Sakai, D. L. Harris, and S. Winstein, *J. Org. Chem.*, 37, 2631 (1972).

(8) (a) S. Ito, H. Takeshita, M. Hirama, and Y. Fukazawa, *Tetrahedron Lett.*, 9 (1972); (b) H. Takeshita, M. Hirama, and S. Ito, *ibid.*, 1775 (1972).

(9) H. Takeshita, T. Hatsui, and O. Jinnai, *Kyushu Diagaku Seisankagaku Kenkyusho Hokoku*, 65, 1 (1977).

(10) H. Takeshita, personal communication.

(11) (a) H. Takeshita, T. Hatsui, and H. Kanamori, *Tetrahedron Lett.*, 1697 (1973); (b) T. Hatsui and H. Takeshita, *Chem. Lett.*, 603 (1977); (c) H. Takeshita, T. Hatsui, R. Iwabuchi, and S. Itoh, *Bull. Chem. Soc. Jpn.*, 51, 1257 (1978); (d) H. Takeshita and T. Hatsui, *J. Org. Chem.*, 43, 3080 (1978).

(12) (a) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, 83, 1498 (1961); (b) A. Nickon and W. L. Mendelson, *Can. J. Chem.*, 43, 1419 (1965); (c) S. K. Chung and A. I. Scott, *J. Org. Chem.*, 40, 1652 (1975), footnote 6; (d) W. R. Adam and D. J. Trecker, *Tetrahedron*, 28, 2361 (1972); (e) R. W. Denny and A. Nickon, *Org. React.*, 20, 133 (1973); (f) C. S. Foote, *Acc. Chem. Res.*, 1, 104 (1968).

(13) (a) A Dabco¹³ᵇ quenching test has not yet been run on this system.¹⁰ (b) C. Quannès and T. Wilson, *J. Am. Chem. Soc.*, 90, 6527 (1968).

(14) For a preliminary communication, see A. A. Frimer, D. Rot, and M. Sprecher, *Tetrahedron Lett.*, 1927 (1977).

(15) (a) G. Rousseau, P. Le Perchec, and J. M. Conia, *Tetrahedron Lett.*, 45 (1977); (b) *ibid.*, 2517 (1977); (c) G. Rousseau, P. Le Perchec, and J. M. Conia, *Tetrahedron*, 34, 3475 (1978); (d) *ibid.*, 34, 3483 (1978), Table 3.

(16) (a) N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, 89, 3966 (1967). (b) The difference in heat of formation between di- and tetrasubstituted olefins is only on the order of 2–3 kcal. (c) R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry", Wiley-Interscience, New York, 1971, p 298.

(17) (a) S. Nishida, I. Moritani, and T. Teraji, *J. Org. Chem.*, 38, 1878 (1973); (b) S. Nishida, I. Moritani, and T. Teraji, *J. Chem. Soc., Chem. Commun.*, 1114 (1972).

(18) (a) R. G. Pews, *J. Am. Chem. Soc.*, 89, 5605 (1967); (b) Y. E. Rhodes and L. Vargas, *J. Org. Chem.*, 38, 4077 (1973); (c) B. R. Ree and J. C. Martin, *J. Am. Chem. Soc.*, 92, 1660 (1970).

upon olefins are quite sensitive to the electron density of the double bond.[12e-f,19] Indeed, the electron-rich vinyl ether dihydropyran not only reacts very rapidly to produce, via an "ene" mode, the corresponding allylic hydroperoxide but also cleaves as well, via the intermediacy of a dioxetane, to the corresponding dicarbonyl compound.[20] We were interested, therefore, in using this sensitivity of $^1O_2$ to test whether the double bond in vinylcyclopropanes is indeed particularly electron rich.

(4) Because of the impressive capability of cyclopropyl groups of stabilizing developing charge,[21] their placement α to the reacting double bond should serve as a sensitive probe as to whether a charged species such as a zwitterion or perepoxide is formed along the reaction pathway.

We now report in full[14] our results on the photooxidation of cyclopropylethylenes.

Results and Discussion

(A) Synthesis of the Starting Olefins. For this study we prepared olefins 12–16. The vinylcyclopropanes were
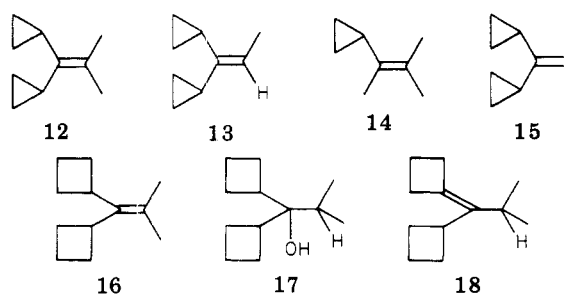
readily synthesized by condensing the appropriate phosphorane and cyclopropyl ketone in a Wittig reaction.[22] This procedure, however, proved unsuccessful for the synthesis of the corresponding vinylcyclobutane 16 which we prepared for the purpose of comparison. Dehydration of alcohol 17 (obtained from the reaction of dicyclobutyl ketone[23] and isopropylmagnesium bromide) using either POCl₃ in pyridine or P₂O₅ in benzene[24] yielded a mixture of isomeric olefins with a molecular weight of 164. The presence of tall doublets at chemical shifts less than 1.0 ppm, rather than at ~1.7 ± 0.1 ppm (allylic methyl absorptions), indicated that the reaction had not resulted in the desired olefin 16. The major product of these dehydrations was identified by its spectral data as olefin 18. Compound 16 was ultimately prepared by condensing dicyclobutyl ketone with acetone in the presence of Ti⁰ according to the procedure of McMurry.[25]

(B) Photooxidation and Product Isolation. Olefins 12–16 were photooxygenated as previously described[20b] in

Table I. Product Yields in the Photooxidation of Olefins 12–15[a]

[a] The reactions were carried out at 10 °C in acetonitrile containing 10^{-3} M methylene blue. A 10% excess of Ph₃P was added to the reaction mixture upon conclusion of the irradiation. The yields were determined by GLC.

Table II. Solvent Effect on the Product Yields in the Photooxidation of 12 and 13

olefin	solvent (sensitizer)[a]	dielectric constant[30]	% yield a form	% yield b form
12	C₆H₆ (TPP)	2.3	62	38
	acetone (RB)	20.7	66	34
	CH₃CN (MB)	38.8	72	28
13	C₆H₆ (TPP)	2.3	14	86
	acetone (RB)	20.7	19	81
	CH₃CN (MB)	38.8	45	55

[a] Sensitizer concentrations are ~10^{-3} M; TPP, tetraphenylporphyrin; RB, rose bengal; MB, methylene blue.

a variety of solvents, and the resulting mixtures were treated with a 10% excess of triphenylphosphine. When the phosphine was not added, thermolysis of the allylic hydroperoxides in the GC injector port led to cracking and/or substantial amounts of Hock-cleavage product.[12e]
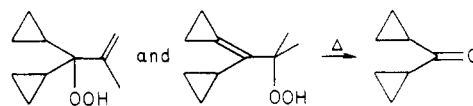
No reaction occurred in the absence of oxygen, sensitizer, or light, and, with the exception of 15, the uptake of oxygen essentially ceased upon the addition of the singlet oxygen quencher Dabco[13b] (10^{-3} M).[26]

The respective products were isolated by preparative GLC (see Table I) and identified by their spectral data. We should note that there is a remarkable solvent effect on the chemical shift and peak shape of the nonallylic cyclopropyl hydrogens of compound 12b. While these four hydrogens appear as the expected multiplet in C₆D₆, they take the shape of a doublet in CCl₄ or CDCl₃. A similar phenomenon occurs in compound 13b, though here the doublet observed in CDCl₃ is not clean but juts out of a broad multiplet. A related solvent effect has been reported by Hutton and Schaefer[27] for cyclopropylamine.

(19) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).

(20) (a) P. D. Bartlett and A. P. Schaap, *J. Am. Chem. Soc.*, **92**, 3223, (1970); (b) A. A. Frimer, P. D. Bartlett, A. F. Boschung, and J. G. Jewett, *ibid.*, **99**, 7977 (1977).

(21) (a) D. G. Garrat, A. Modio, K. Oyama, G. H. Schmid, T. T. Tidwell, and K. Yates, *J. Am. Chem. Soc.*, **96**, 5295 (1974), and references cited therein. (b) Rate enhancements of 10⁶ have been reported for the substitution of one cyclopropyl group for an isopropyl group; see E. N. Peters and H. C. Brown, *ibid.*, **95**, 2397 (1973), and references cited therein.

(22) (a) T. Teraji, I. Moritana, E. Tsuda, and S. Nishida, *J. Chem. Soc. C*, 3252 (1971). (b) A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 940 (1965). (c) For a review of the Wittig reaction, see A. Maercker *Org. React.*, **14**, 270 (1965).

(23) J. L. E. Erickson, F. E. Collins, and B. L. Owen, *J. Org. Chem.*, **31**, 480 (1966).

(24) Cf. P. C. Traas, H. Boelens, and H. J. Takken, *Recl. Trav. Chim. Pays-Bas*, **95**, 57 (1976).

(25) (a) J. E. McMurry and L. R. Krepski, *J. Org. Chem.*, **41**, 3930 (1976); (b) J. E. McMurry, M. P. Fleming, K. L. Kees, and L. R. Krepski, *ibid.*, **43**, 3255 (1978); (c) J. E. McMurry, personal communication.

(26) R. S. Davidson and K. R. Trethewey, *J. Am. Chem. Soc.*, **98**, 4008 (1976).

(27) H. M. Hutton and T. Schaefer, *Can. J. Chem.*, **41**, 2774 (1963).

Table III. Relative Rates^a of Reaction with $^1O_2$

olefin	serial no.	k_{rel}	IP,[17b] eV	olefin	serial no.	k_{rel}	IP,[17b] eV
	12	0.33	7.82		13	0.041	
	16	0.40				0.024[12f]	8.67
	14	1.05					
	19	0.88			15	0.000 035	8.08
		(1.00)[12f]	8.30			0.000 082[29]	9.23^b

^{a} $k_{rel} = k_{olefin}/k_{TME}$, where k_{TME} is set at 1.00;[12f] values are ±10%. ^{b} Value cited is actually for isobutene.

Product yields (see Table I) were determined by integration of the GLC peak areas and corroborated by ^1H NMR. The effect of solvent polarity on these yields was small, as shown by Table II. Relative rates for the reaction of these olefins with $^1O_2$ as compared to tetramethylethylene (TME; k_{rel} = 1.0[12f]) were determined in competition studies[28] with 1,2-dimethylcyclohexene (k_{rel} = 0.53[29] for olefins 12, 14, 16, and 19[12f,31]), 1-methylcyclohexene (k_{rel} = 0.0041[12f] for 13), or cyclohexene (k_{rel} = 0.000 048[12f] for 15). These rates and those of previously reported methyl analogues are listed in Table III along with selected ionization potential (IP) values.

(C) Product Analysis. The data in Table I are at once exciting and puzzling. Indeed, substantial amounts of alkylidenecyclopropane product are formed in the photooxidation of the 1,1-dicyclopropylethylenes 12 and 13 despite the resulting 11.4 kcal/mol of additional strain energy. Yet no such product is obtained in the case of 14, a monocyclopropylethylene. This discrepancy is readily resolved on the basis of conformational analysis. It has been well documented[4a,12,31] that the allylic hydrogens preferentially abstracted in the $^1O_2$ ene reaction are those which are aligned parallel to the plane of the p orbital of the double bond in the low-energy conformation(s) of the olefin. For the parent vinylcyclopropane, theoretical calculations and experimental studies[32-34] argue for a "bisected"[35] arrangement of the ring and the double bond as the most stable conformation. In such an arrangement the allylic cyclopropyl hydrogen lies perpendicular to the plane of the p orbitals and is thus unavailable for abstraction. Several authors[32,34] have argued in favor of a low-energy "gauche" conformation. In such a conformation, however, cyclopropyl hydrogen abstraction would be strongly disfavored, as the hydrogen would lie at a dihedral angle of 30-50° from the plane of the p orbitals.[32,34,36] Similar results were obtained for *trans*-1,2-dicyclopropylethylenes.[34,37] For 2-cyclopropylpropenes

both bisected and gauche forms are present. Here again the allylic ring hydrogen is misaligned and in the case of the latter conformation lies at a 17° dihedral angle from the plane of the p orbitals.[34,38] It is not surprising, therefore, that the monocyclopropyl olefin 14 yields no alkylidenecyclopropane photooxygenation product.

For 1,1-dicyclopropylethylenes the situation is quite different. Trovato and Favini[39] found that the allylic cyclopropyl hydrogens of compound 12 were essentially locked-in parallel to the plane of the p orbitals, perfectly aligned for a $^1O_2$ ene reaction. We would expect a similar situation in the case of olefin 13 as well.

On the basis of the above considerations, the report of Rousseau[15c] that 20[40] and 21 yield 20a and 21a, respectively, as the sole photooxygenation products is by no means surprising.
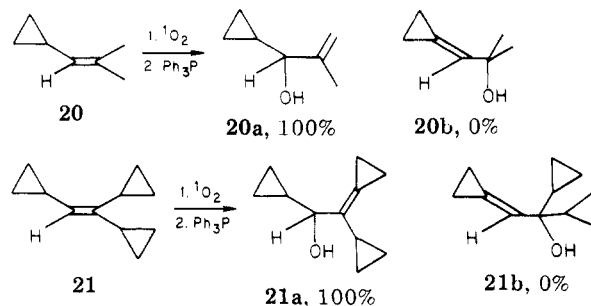
It may thus be concluded that in the product-determining transition state, singlet oxygen, though sensitive to conformational considerations in the starting material, is insensitive to the strain developing in the final product. We shall return to this point later.

We close this section by commenting on the photosensitized oxidation of olefin 15. The reaction, as followed by disappearance of starting material and concomitant uptake of oxygen, proceeded quite slowly, as would be expected for a disubstituted olefin. When approximately 80% of the starting material had been converted to product, the reaction mixture was analyzed by NMR and GLC. Both techniques corroborated the observation that

(28) R. Higgins, C. S. Foote, and H. Cheng, *Adv. Chem. Ser.*, **No. 77**, 102, (1968).
(29) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965).
(30) For an excellent collection of selected properties of assorted solvents, see G. P. Nilles and R. D. Schentz, *J. Chem. Educ.*, **50**, 267 (1973).
(31) C. S. Foote, and R. W. Denny, *J. Am. Chem. Soc.*, **93**, 5162 (1971).
(32) W. J. Hehre, *J. Am. Chem. Soc.*, **94**, 6592 (1972), and references cited therein.
(33) L. D. Kispert, C. Engelman, C. Dyas, and C. U. Pittman Jr., *J. Am. Chem. Soc.*, **93**, 6948 (1971).
(34) G. Favini and S. Trovato, *Gazz. Chim. Ital.*, **97**, 1152 (1967), and references cited therein.
(35) (a) C. U. Pittman and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5123 (1965); (b) H. G. Richey, Jr., *Carbonium Ions*, **3**, 1201 (1972).
(36) H. Gunther and D. Wendisch, *Angew. Chem., Int. Ed. Engl.*, **5**, 251 (1966).

(37) W. Luttke and A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **5**, 512 (1966).
(38) S. Sarel, Y. Yovell, and M. Sarel-Imber, *Angew. Chem., Int. Ed. Engl.*, **7**, 577, 584 (1968).
(39) S. Trovato and G. Favini, *Gazz. Chim. Ital.*, **99**, 960 (1969).
(40) (a) Similar results have been obtained by Sasaki et al.[40b] in the photosensitized oxygenation of *cis*- and *trans*-chrysanthemic acids and by Frimer[41] in the case of the corresponding ethyl esters. (b) T. Sasaki, S. Eguchi, and M. Ohno, *Synth. Commun.*, **1**, 75 (1971).
(41) A. A. Frimer, unpublished results.

the main volatile product was dicyclopropyl ketone and that it was formed in only a 25% yield. The remaining 75% was undoubtedly the white insoluble polymer which formed a thin film on the inside walls of the reaction vessel. The origin of the ketone is not likely to be dioxetane **22** or allylic hydroperoxide **23a** (via Hock cleavage[12e]) since

22   23a, R = OH   24
            b, R = H
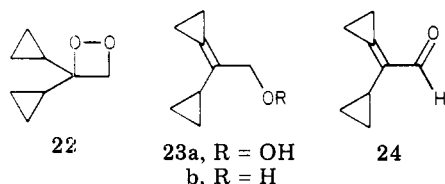
the addition of a large excess of either the dioxetane trap diphenyl sulfide[42] or the hydroperoxide reducing agent triphenyl phosphite[43] at the beginning of the reaction in no way affected the product yield. No traces of alcohol **23b** or aldehyde **24** were isolated.

Despite the observation that 2,6-di-*tert*-butylphenol[46] did not inhibit the oxidation of **15**, we nevertheless believe that the photooxidation of 1,1-dicyclopropylethylene proceeds via a free-radical mechanism.[47]   Indeed, in contradistinction to the other olefins described in this study, the uptake of oxygen in this case did not slow upon the addition of Dabco.[13b]   Furthermore, unlike singlet oxygen processes which generally have small activation energies and whose rates are negligibly temperature dependent,[48] the photooxidation rate of **15** was reduced almost to zero at −78 °C. Initiation of free-radical oxidation is well-known to be slowed or inhibited at low temperatures.[49c]   A free-radical process would well explain the formation of polymeric material; what is more, any polyperoxide formed could "unzip"[49] to yield dicyclopropyl ketone. In support of our suggestion we note that **15** autoxidizes slowly at 10 °C, producing the above ketone. Likewise, the methyl counterpart of **15**, isobutylene, is reported to autoxidize primarily via an addition mode, yielding polyperoxide as the major product and little allylic hydroperoxide.[49b]

(D) Kinetic Analysis. The relative rate data (Table III) is also quite interesting, for it indicates that the substitution of one or more of the methyl groups in TME with a cyclopropyl group does not dramatically affect the rate. We may conclude that the unperturbed vinylcyclopropane double bond is not particularly electron rich. The rate data of Table III demonstrate that the electronic effect of a cyclopropyl group in $^1O_2$ reactions[50] does not differ much from that of other alkyl groups such as cyclobutyl, isopropyl, or methyl. It would seem, then, that the well-known electron-donating capabilities of the cyclopropyl group only come into play when an electron-

deficient center is created, as may be found in many 2 + 2 cycloadditions or in the loss of an electron from the double bond via ionization.

Also of note is the absence of any substantial retardation of the rate of $^1O_2$ attack as a result of steric blocking[4a,12e] by the gem cyclopropyl or cyclobutyl groups. Indeed, the rates of **12** and **16** are both only approximately one-third that of TME.[51]   These observations are, however, consistent with the conclusion of Nishida and Kataoka[53] that the size of the cyclopropyl group is significantly smaller than that of the isopropyl group.

Comment is required regarding a table of relative rates of photooxygenation for a variety of vinylcyclopropanes recently reported by Rousseau et al.[15d] These values differ from ours because the former are based upon a half-time of reaction, not on competition studies[12e,f,28,33] (see Experimental Section). Thus the k_{rel} and β values they cite are not consistent with related values reported in the literature.[12e,f,33] For example, it has been generally observed that tetraalkylylated olefins are about 20 times more reactive than trialkylated olefins.[12e]   Nevertheless, Rousseau et al.[15d] report that the trisubstituted olefin 2-cyclopropyl-2-butene has approximately the same k_{rel} and β values as the tetrasubstituted 2-cyclopropyl-3-methyl-2-butene. The same is true for their values for olefins **12** and **13**. The data presented in Table II indicate that our k_{rel} values for cyclopropylethylenes **12–15** compare favorably with those previously reported for several analogous methylethylenes.

(E) Mechanistic Discussion. For the $^1O_2$ ene reaction there are three mechanisms currently in vogue:[62] (1) a concerted $[_\pi 2_s + _\sigma 2_s + _\pi 2_s]$ process analogous to the Alder ene reaction;[12e] (2) a nonconcerted process involving a perepoxide;[12e,19] (3) a process involving initial electron or charge transfer.[54,55] The kinetic data in Table III argue against electron or charge transfer as the rate-determining process. If this were so, then the cyclopropylethylenes as a class should react several orders of magnitude faster than the corresponding methylethylenes which have substantially higher ionization potentials than the former. This is indeed not the case as Table III shows. While it is true that the rates of $^1O_2$ attack can by and large be correlated with their ionization potentials,[56–58] this may simply stem from the mild electrophilicity of $^1O_2$. It certainly does not require a charge- or electron-transfer process as the initial step.

Let us now turn to the remaining two possibilities, the concerted ene and the perepoxide mechanisms. Two groups of data seem to argue against the latter. We noted above the absence of any increase in k_{rel} as a result of replacing a vinyl methyl with a cyclopropyl group. This observation, in addition to indicating that vinylcyclopropanes are not particularly electron rich, also demonstrates that little, if any, charge development occurs in the rate-determining transition state. Were this not the case,

(42) Diphenyl sulfide reacts rapidly with dioxetanes; see H. H. Wasserman and I. Saito, *J. Am. Chem. Soc.*, **97**, 905 (1975).

(43) This phosphite reduces hydroperoxides[44] in situ but reacts only sluggishly with singlet[41] and triplet[45] oxygen.

(44) R. Hiatt, *Org. Peroxides*, **2**, 50, 77 ff (1971).

(45) J. B. Plumb and C. E. Griffen, *J. Org. Chem.*, **28**, 290 (1963).

(46) See C. S. Foote in "Free Radicals in Biology", Vol. II, W. A. Pryor, Ed., Academic Press, New York, 1977, pp 85, 101.

(47) Phenol chain-breaking antioxidants are known not to be universally effective in suppressing autoxidations. For example, they are ineffective in inhibiting autoxidations with high initiation rates. See J. Betts, *Q. Rev., Chem. Soc.*, **25**, 265 (1971).

(48) (a) E. Koch, *Tetrahedron*, **24**, 6295 (1968); (b) R. D. Ashford and E. A. Ogryzlo, *J. Am. Chem. Soc.*, **97**, 3604 (1975).

(49) For reviews see: (a) G. A. Russel, *J. Chem. Educ.*, **36**, 111 (1959); (b) F. R. Mayo, *Acc. Chem. Res.*, 1, 193 (1968); (c) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

(50) Cf. E. V. Dehmlow and A. Eulenberger, *Angew. Chem., Int. Ed. Engl.*, **17**, 674 (1978).

(51) A similar rate-lowering factor has been observed for the $^1O_2$ reaction of isopropylidenecyclopropane (k_{rel} = 0.0056) as compared to that of cyclopropylidenedicyclopropylmethane (k_{rel} = 0.0021).[52]

(52) A. A. Frimer, T. Farkash, and M. Sprecher, *J. Org. Chem.*, **44**, 989 (1979).

(53) S. Nishida and F. Kataoka, *J. Org. Chem.*, **43**, 1612 (1978).

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the strong electron-releasing effect of the cyclopropyl group ought to lower the energy barrier leading to the activated complex. The product-distribution data (Table I) also argue against a perepoxide, for the latter would be expected to show a substituent effect on the direction of opening. In particular, stabilization of an incipient positive charge α to the ring(s) should promote cyclopropyl hydrogen abstraction.[15a] Yet the results gainsay any such preference. On the other hand, these observations are not problematic for a concerted process in which there is no development of charge and in which the rate- and product-determining transition states are one and the same.

Perepoxide proponents,[59] however, have argued in similar cases that both the rate- and product-determining transition states occur very early in $^1O_2$ reactions and are reactant-like; hence, substituents ought to have little effect on their energies. Indeed, many concerted ene proponents[60] agree to the suggestion of an early transition state, and our observation that $^1O_2$ is insensitive to strain developing in the product is consistent with this position. Thus, unfortunately, no clear conclusions can be drawn from the present data to ultimately resolve the question of mechanism in the singlet oxygen ene reaction.

Experimental Section

^{1}H NMR spectra were obtained on a Varian HA-100 spectrometer. IR spectra were taken with a Perkin-Elmer Model 257 spectrometer. Mass spectra were run on a single-focusing Hitachi Perkin-Elmer RMU-6 spectrometer. A Perkin-Elmer Model 402 ultraviolet–visible spectrophotometer was used for recording the UV spectra. When gas chromatograms were obtained by using a Varian Aerograph Model 920 preparative gas–liquid chromatograph, peak areas were determined by triangulation. For analytical work, however, the Packard Model 824 analytical gas–liquid chromatograph was used, and areas were determined by digital integration. 1,2-Dimethylcyclohexene (Chemical Samples Co.), 1-methylcyclohexene (Fluka), cyclohexene (Fluka), and 2,3,4-trimethyl-2-pentene (19; Chemical Samples Co.) are commercially available.

Preparation of Vinylcyclopropanes 12–15. Olefin 15 was obtained commercially (Aldrich) or prepared according to the instructions of Ketley and McClanahan.[22b] Traces of dicyclopropyl ketone[61] were removed by preparative GLC. Compounds 12–14 were synthesized in a fashion similar to that recently described by Rousseau et al.[15c] In our hands, the products following distillation were contaminated with Me_2SO. The impurity was precipitated out at -10 °C (freezer), and the supernatant liquid proved to be pure olefin. All olefins were further purified by preparative GLC prior to photooxidation.

1,1-Dicyclobutyl-2-methylpropene (16). This olefin was prepared in a 30% yield by condensing dicyclobutyl ketone (27)[23] and acetone in the presence of $TiCl_3$ and lithium according to the general procedure of McMurry for mixed carbonyl coupling.[25] The crude olefin was purified by preparative GLC using a 4 ft $\times$ $^1/_4$ in. aluminum column packed with 20% Carbowax on Chromosorb P. With the oven at 145 °C and a flow rate of 80 mL/min, the retention time of 16 was 23 min. Ozonolysis of 16 yielded ketone 27, thereby verifying the identity of the former.

^{1}H NMR (CDCl$_3$) δ 3.3 (2 H, m, cyclobutyl allylic), 2.1 (12 H, m, cyclobutyl), 1.6 (6 H, t, $J = 1.5$ Hz, methyl); MS (70 eV) m/e 164 (M$^+$), 149, 136, 121, 108, 94, 93, 91, 79, 77.

1,1-Dicyclobutyl-2-methylpropan-1-ol (17). Alcohol 17 was prepared according to the general procedure of Traas et al.[24] from dicyclobutyl ketone (27)[23] and isopropylmagnesium bromide.

Distillation [70 °C (8 mmHg)] gave the desired product in 80% yield. The alcohol, contaminated with ketone 27, was purified by preparative GLC (20% Carbowax 20M on Chromosorb P).

^{1}H NMR (CDCl$_3$) δ 2.5 (2 H, m), 2.3–1.3 (13 H, m), 0.85 (6 H, d, $J = 7.0$ Hz); MS (70 eV) 164 (M$^+$ – H$_2$O), 139, 127, 121, 109, 95, 93, 83, 79, 67, 55, 43.

Dehydration of Alcohol 17 and Isolation of Olefin 18. Alcohol 17 was dehydrated by using either POCl$_3$ in pyridine or P$_2$O$_5$ in benzene as described by Traas et al.[24] ^{1}H NMR spectra of the reaction mixture showed sharp absorptions below 1.0 ppm and overlapping multiplets from 1.5 to 3.0 ppm. Though the POCl$_3$ reaction seemed to be the cleaner of the two, the major product in both cases, isolated by preparative GLC, was olefin 18. No sharp absorptions at $\sim 1.7 \pm 0.1$ ppm were observed in the ^{1}H NMR of the reaction mixture, indicating the absence of product containing allylic methyl groups as would be expected for olefin 16.

18: ^{1}H NMR (CDCl$_3$) δ 2.78 (4 H, m, cyclobutyl allylic), 2.6–1.5 (9 H, m, cyclobutyl), 0.96 (6 H, d, $J = 8$ Hz, methyl); MS (70 eV) m/e 164, 136, 121, 107, 94, 93, 80, 75, 67, 55, 41.

General Photooxidation Procedure. The photooxidation apparatus[20b] was charged with 500 mg of olefin dissolved in 2 mL of solvent containing 10^{-3} M sensitizer (see Table II) and irradiated until the gas buret indicated that approximately 80% of the theoretical amount of oxygen had been taken up by the system. Triphenylphosphine (10% excess) was added cautiously since the reduction of hydroperoxides by Ph$_3$P is quite exothermic. The reaction mixture was then analyzed directly by GLC and the products collected by using a 3-m copper column packed with 20% Carbowax 20M on Chromosorb P (carrier-gas flow rate 70 mL/min).

Isolation of 12a and 12b. Olefin 12 was photooxidized as above, and the resulting reaction mixture was analyzed by GLC (oven temperature 130 °C). In addition to unreacted substrate (retention time (R_f) 6 min), two additional peaks were observed with retention times of 24 and 30 min. The two were identified as 12a and 12b, respectively, on the basis of their spectral data. When the reaction mixture was not reduced with Ph$_3$P prior to injection on the GC column, the two aforementioned peaks became substantially smaller, and a large new peak (R_f 10 min) appeared which was identified by its spectral data as dicyclopropyl ketone.[61]

12a: ^{1}H NMR (CCl$_4$) δ 4.96 (1 H, br s, vinyl), 4.68 (1 H, br s, vinyl), 3.6 (1 H, m, hydroxyl), 1.83 (3 H, s, methyl), 0.9 (2 H, m, methine cyclopropyl), 0.55 (8 H, m, cyclopropyl); IR (neat) 3600, 3500, 3045, 3007, 2930, 1644, 1500, 1460, 1375, 1310, 1255, 1180, 1134, 1025, 987, 910, 880, 830 cm^{-1}; MS (70 eV) 152 (M$^+$, barely perceptible), 137, 124, 111, 109, 95, 94, 91, 83, 81, 79, 77, 69, 55, 53, 51, 43, 41, 39.

12b: ^{1}H NMR (CDCl$_3$) δ 2.2 (1 H, br s, hydroxyl), 1.70 (1 H, m, methine cyclopropyl), 1.44 (6 H, s, methyl), 1.00 (4 H, s, allylic cyclopropyl), 0.68 (2 H, s, cyclopropyl), 0.61 (2 H, s, cyclopropyl); ^{1}H NMR (CCl$_4$) δ 1.9–1.4 (3 H, m), 1.35 (6 H, s), 0.95 (4 H, m), 0.62 (2 H, s), 0.56 (2 H, s); ^{1}H NMR (C$_6$D$_6$) δ 1.85 (1 H, br s), 1.52 (2 H, m), 1.45 (6 H, s), 0.75 (4 H, s), 0.60 (4 H, m); IR (CCl$_4$) 3590, 3450, 3045, 3010, 2960, 1750, 1150, 1020, 960, 890 cm^{-1}; MS (70 eV) 152 (M$^+$), 137, 123, 119, 109, 95, 93, 91, 81, 79, 77, 69, 67, 65, 59, 57, 55, 53, 50, 43, 41.

Isolation of 13a and 13b. Olefin 13 was photooxidized as above and the resulting mixture analyzed by GLC. The GC trace
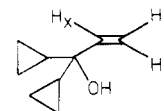
13a

(oven temperature 130 °C) showed two major peaks with retention times of 15 and 33 min which were identified as corresponding to compounds 13a and 13b, respectively.

13a: ^{1}H NMR (CDCl$_3$) δ 5.76 (H$_X$, dd, $J_{AX} = 18$ Hz, $J_{BX} = 10$ Hz), 5.29 (H$_A$, dd, $J_{AX} = 18$ Hz, $J_{AB} = 2$ Hz), 5.07 (H$_B$, dd, $J_{BX} = 10$ Hz, $J_{AB} = 2$ Hz), 2.6 (1 H, br s, hydroxyl), 1.2–0.7 (2 H, m, methine cyclopropyl), 0.4 (8 H, m, cyclopropyl); IR (CCl$_4$) 3600, 3500, 3070, 3000, 1630, 1400, 1100, 1010, 920 cm^{-1}; MS (70 eV) m/e 138 (M$^+$, barely perceptible), 123, 110, 109, 97, 95, 69, 55, 41.

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13b: ¹H NMR (CDCl₃) δ 4.52 (1 H, q, *J* = 6.5 Hz, α to hydroxyl), 2.23 (1 H, br s, hydroxyl), 1.50 (1 H, m, methine cyclopropyl), 1.39 (3 H, d, *J* = 6.5 Hz, methyl), 0.99 (4 H, s, allylic cyclopropyl), 0.65 (4 H, m, cyclopropyl; the pattern at δ 0.65 appears as two singlets at δ 0.69 and 0.61 jutting out of a multiplet centered at δ 0.65); IR (neat) 3450, 3090, 3020, 2980, 1770, 1720, 1450, 1380, 1260, 1060 cm⁻¹; MS (70 eV) *m/e* 138 (M⁺), 123, 109, 107, 105, 95, 91, 79, 77, 67, 55, 53, 51, 45, 43.

Isolation of 14a and 14b. Olefin 14 was photooxidized as above and analyzed by GLC (oven temperature 85 °C). Three major peaks were observed with retention times 3, 29, and 35 min and corresponded to starting olefin 14 and oxidation products 14a and 14b, respectively.

14a: ¹H NMR (CDCl₃) δ 5.05 (1 H, s, vinyl), 4.8 (1 H, s, vinyl), 2.6 (1 H, s, hydroxyl), 1.85 (3 H, s, allylic methyl), 1.40–0.9 (1 H, m, methine cyclopropyl), 1.22 (3 H, s, methyl α to hydroxyl), 0.4 (4 H, m, cyclopropyl); IR (neat) 3480, 3090, 3010, 2980, 2930, 1640, 1450, 1375, 1180, 1125, 1045, 1020, 950, 900 cm⁻¹; MS (70 eV) *m/e* 126 (barely perceptible), 111, 109, 98, 93, 91, 85, 83, 69, 55, 43.

14b: ¹H NMR (CDCl₃) δ 4.95 (1 H, m, vinyl), 4.54 (1 H, s, vinyl), 1.95 (1 H, m, hydroxyl), 1.41 (6 H, s, methyl), 1.50–1.25 (1 H, m, methine cyclopropyl), 0.85–0.35 (4 H, m, cyclopropyl); IR (neat) 3450, 3090, 2980, 2930, 2880, 1640, 1460, 1360, 1150, 1050, 1020, 970, 940, 885, 830 cm⁻¹; MS (70 eV) *m/e* 126, 111, 93, 91, 85, 81, 77, 69, 67, 63, 59, 55, 53, 43.

Photooxidation of Olefin 15. This olefin was photooxidized as above, but the addition of triphenylphosphine was not accompanied by the evolution of heat. During the course of the reaction a white translucent polymer coated the inside of the reaction vessel. Analysis of the reaction mixture via GLC (108 °C) revealed, in addition to the starting material (*R*ƒ 5 min), two product peaks in a ratio of 5:1 (*R*ƒ 23 and 29 min, respectively). The spectral data of the first peak corresponded to that of dicyclopropyl ketone. However, not enough material from the second peak could be collected to permit its identification. Use of an internal standard allowed us to determine that the ketone represented approximately 25% of the expected product yield based on starting material conversion. Neither the GLC trace nor the oxygen uptake was appreciably affected by the addition of 4 equiv of 2,6-di-*tert*-butylphenol, (PhO)₃P, or Ph₂S at the beginning of the reaction. The same was true for 10⁻³ M Dabco. The reaction did not occur in the absence of light, oxygen, or sensitizer or at −78 °C. Olefin 15 did, however, autoxidize appreciably after standing in the refrigerator (10 °C) for several months, yielding dicyclopropyl ketone.

Photooxidation of Olefin 16. Olefin 16 was photooxidized in the usual manner in acetonitrile, and the reaction mixture was analyzed on a 4-m column packed with 20% Carbowax on Chromosorb P (oven temperature 145 °C). The GLC trace indicated the presence of negligible amounts of unreacted starting material (*R*ƒ 24 min) and only one major product (*R*ƒ 72 min). The latter was collected and identified as 1,1-dicyclobutyl-2-methylprop-2-en-1-ol (28).
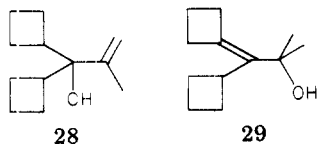
28: ¹H NMR (CDCl₃) δ 4.96 (1 H, br s, vinyl), 4.78 (1 H, m, vinyl), 2.5 (2 H, m, methine cyclobutyl), 2.3–1.3 (16 H, m with sharp singlet jutting out at δ 1.6); IR (neat) 3500, 2940, 2860, 1630, 1440, 1370, 1250, 1235, 1155, 980, 890, 820, 725 cm⁻¹; MS (70 eV) *m/e* 180, 152, 139, 126, 125, 109, 107, 97, 95, 93, 91, 83, 82, 81, 79, 77, 69, 67, 55, 53, 43, 41.

However, reinspection of the ¹H NMR of the reaction mixture revealed a large singlet at 1.4 ppm. Analysis of the reaction solution on an 8-m copper column packed with 10% SE-30 on Chromosorb WAW DMCS (oven temperature 125 °C) revealed the presence of two product peaks with peak areas in a ratio of 2:1. The former (*R*ƒ 40 min) was identified as compound 28. The latter (*R*ƒ 60 min) had a complex ¹H NMR spectrum (CDCl₃) with a broad singlet at δ 5.7 (3 integration units), overlapping multiplets extending from δ 3.2 to 1.1 centered at δ 2.9, 2.4, and 1.9 (7.5 integration units), and a large singlet at δ 1.4 (3 integration units). This last absorption indicates *gem*-dimethyl groups α to a hydroxyl group. The mass spectral (70 eV) data shows peaks at *m/e* 178 (small), 163 (small), 145, 135, 131, 125, 121, 119, 117, 115, 109, 107, 105, 93, 91, 88, 86, 84, 49, 47, and 43. This compound has been tentatively identified as impure olefin 29.

Competitive Photooxidation: Relative Rates. The relative rates of reaction of ¹O₂ with olefins 12–16 and 19 were determined by a series of competitive photooxidations[28] with acceptors, i.e., olefins whose relative rates of reaction vs. TME have been previously determined. Acetonitrile solutions (2 mL) containing GLC-purified olefin, acceptor, and benzene as internal standard (200 μL of each component) were irradiated, and samples were removed during the course of the reaction. The relative rates of disappearance of the olefin and acceptor could be calculated from their relative GLC peak areas. The relative rates (k_{rel}) were determined by using the equation[28]

$$k_{rel} = \frac{k_A}{k_B} = \frac{\log A_0/A_t}{\log B_0/B_t}$$

where A_0, A_t, B_0, and B_t are the peak areas of olefins A and B (normalized by the peak area of the inert internal standard) prior to irradiation ($t = 0$) and at time t. The only requirement for this equation to obtain is that the reaction of each competitor with ¹O₂ be pseudo first order. If it is a valid competition experiment, the relative rate will not be a function of the extent of reaction. Within experimental error (<10%) this was indeed found to be the case in these competition studies. The results are tabulated in Table III.