Photooxygenation of 1-Vinylcycloalkenes. The Competition between "Ene" Reaction and Cycloaddition of Singlet Oxygen[1]

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The competition between the "ene" reaction and 1,4-cycloaddition reaction of $^1O_2$ in a series of 1-vinylcycloalkenes ($n = 5$–10, 12) and 1-isopropenylcycloalkenes ($n = 6$–8) was studied. Ring size had a profound effect. When $n = 5$ or 7, products of the "ene" reaction predominated, but as ring size increased cycloaddition competed closely with the "ene" process, the crossover being at ring size 10. 1-Vinylhexenes constituted an exception with 1,4-cycloaddition greatly predominant. "Ene" products were almost exclusively conjugated diene hydroperoxides or secondary products derived from them; small amounts of unconjugated diene hydroperoxides were formed only when $n = 9$, 10, or 12. The influence of ring size of the "ene" to cycloaddition product ratio is compared with the rates of photooxygenation and the degree of syn-regiospecificity exhibited by (Z)-1-methylcycloalkenes and attributed to the same mainly conformational factors, as is the geometry of the "ene" products. The 1,4-cycloaddition products were converted to furans by means of ferrous sulfate.

Fe(II)-induced rearrangement of epidioxides (3,6-dihydro 1,2-dioxides) (step b of Scheme I), available from dienes by reaction with singlet oxygen, is a simple method for making certain substituted furans[2] which, we have suggested, may mimic the path by which terpenoid furans are formed in nature.[3-5] Moreover, the rapidly increasing number of naturally occurring hydroperoxides and epidioxides formally derivable from other secondary metabolites found in the same or related organisms lends credence to the hypothesis that biological processes akin to step a of Scheme I also operate.[11]

From the preparative point of view, if R ≠ H, the utility of Scheme I is limited by competition between the "ene" reaction[13,14] and 1,4-addition of singlet oxygen.[13,15-17] As

Scheme I
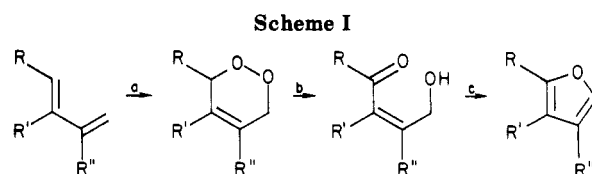
a number of naturally occurring terpenoid furans are compounds of type A, we decided to study this competition for a series of semicyclic dienes **1a–g** and **2a–c**. Earlier reports on the reactions of **2a**,[18] (*R*)-mentha-3,8(9)-diene (**3**),[18] and (+)-β-nopadiene (**4**)[19] with singlet oxygen are not very informative on this point, although all three compounds appear to undergo 1,4-addition preferentially. On the other hand, photooxygenation of 3β-acetoxy-24-nor-cholesta-5,16,20(22)-triene gives mainly a mixture of "ene" products.[20]

Preparation of Dienes. Semicyclic dienes **1a–g** and **2a–c** were prepared by dehydration of the corresponding 1-vinyl- and 1-isopropenylcycloalkanols with POCl₃–pyridine. GLC and NMR analysis indicated that the products from 1-vinylcyclononanol, 1-vinylcyclodecanol, and 1-vinylcyclododecanol were mixtures of *E*- and *Z*-dienes in the ratio of 99:1, 93:7 and 9:1, respectively, which could not be separated by TLC on plates impregnated with silver nitrate.[21,22] That the major isomer in the case of

(1) Supported in part by a grant from the U.S. Public Health Service (CA-13121) through the National Cancer Institute.

(2) Turner, J. A.; Herz, W. *J. Org. Chem.* 1977, *42*, 1900.

(3) Step b of Scheme I has been interpreted[2] as utilizing the FE-(II)–Fe(III) redox system. The biological equivalent might be catalysis by an electron-transfer shuttle mechanism.

(4) In the laboratory, using Fe(II), conversion of the intermediate hydroxy aldehydes or hydroxy ketones to product (step c) is spontaneous. Other methods for converting epidioxides to hydroxy aldehydes or hydroxy ketones and thence to furans are cited in ref 2.

(5) Support for the further suggestion[6] that Fe(II)-induced reactions of saturated epidioxides (3,4,5,6-tetrahydro-1,2-dioxins) may provide models for the biosynthesis of the prostaglandins, the thromboxanes and PGI₂ from the prostaglandin *endo*-peroxides has been provided recently.[7] Use of other transition metal catalysts for isomerizations of epidioxides and their dihydro derivatives has been reported.[8-10]

(6) Turner, J. A.; Herz, W. *Experientia* 1977, *33*, 1133.

(7) Porter, N. A.; Mebane, R. C. *Tetrahedron Lett.* 1982, *23*, 2289.

(8) Boyd, J. D.; Foote, C. S.; Imagawa, D. K. *J. Am. Chem. Soc.* 1980, *102*, 3641. See also: Bulci, M.; Sütbeyaz, Y. *Tetrahedron Lett.* 1983, *24*, 311, 4135.

(9) (a) Hagenbuch, J.-P.; Vogel, P. *Tetrahedron Lett.* 1979, *561*. (b) Hagenbuch, J.-P.; Vogel, P. *J. Chem. Soc., Chem. Commun.* 1980, 1062. (c) Hagenbuch, J.-P.; Birbaum, J.-L.; Metral, J.-L.; Vogel, P. *Helv. Chim. Acta* 1982, *65*, 887.

(10) (a) Suzuki, M.; Noyori, R.; Hamanaka, N. *J. Am. Chem. Soc.* 1981, *103*, 5606; *Ibid.* 1982, *104*, 2024. (b) Suzuki, M.; Oda, Y.; Noyori; R. *Tetrahedron Lett.* 1981, *22*, 4413.

(11) The possible involvement of singlet oxygen in biological reactions has been discussed: Krinsky, N. I. In "Singlet Oxygen"; Wassermann, H. H., Murray, R. W. Eds.; Academic Press: New York, San Francisco, London, 1979; p 597. Recently singlet oxygen has been detected in the chloroperoxidase- and lactoperoxidase-catalyzed decomposition of H₂O₂.[12]

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(14) Gollnick, K.; Kuhn, H. J. In "Singlet Oxygen"; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 287.

(15) Gollnick, K.; Schenck, G. D. In "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1967; p 225.

(16) For examples when R ≠ H other than those cited in ref 2, see: (a) Wahlberg, I.; Karlsson, K.; Curvall, M.; Nishida, T.; Enzell, C. R. *Acta. Chem. Scand., Ser. B* 1978, *B32*, 203. (b) Wahlberg, I.; Nordfors, K., Curvall, M.; Nishida, T.; Enzell, C. R. *Ibid.* 1979, *B33*, 437. (c) Mohanraj, S.; Herz, W. *J. Org. Chem.* 1981, *46*, 1362. (d) Yamada, S.; Nakayama, H.; Takayama, H.; Itai, A.; Iitaka, Y. *Ibid.* 1983, *48*, 3477.
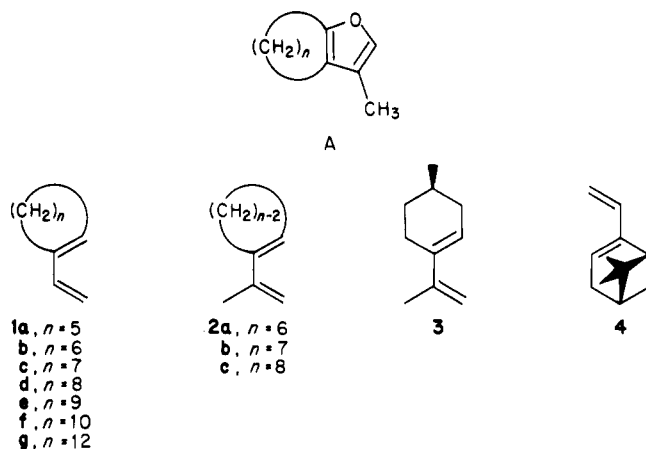
(17) For use of Scheme I in recent syntheses of terpenoid furans where R = H, see: (a) de Miranda, D. S.; Brendolan, G.; Imamura, P. M.; Sierra, M. G.; Marsaioli, A. J.; Ruveda, E. A. *J. Org. Chem.* 1981, *46*, 4851. (b) Nakano, T.; Agnero, M. E. *J. Chem. Soc., Perkin Trans. 1* 1982, 1163. (c) Herz, W.; Prasad, J. S. *J. Org. Chem.* 1982, *47*, 4171.

(18) Harirchian, B.; Magnus, P. D. *Synth. Commun.* 1977, *7*, 119. Only 1,4-addition products are reported.
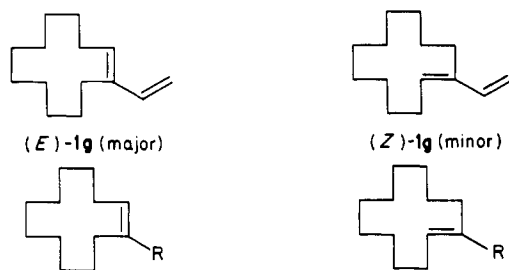
(19) Cited only in review articles.[13-15] The yield of 1,4-addition product is given as 35%, the yield of i, presumably resulting from decomposition of the "ene" product, is given as 23%.[14]
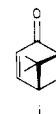
(20) Kocar, M.; Wojciewska, W. *Bull. Acad. Po. Sci., Ser. Sci. Chim.* 1973, *21*, 809.

A

1a, *n* = 5
b, *n* = 6
c, *n* = 7
d, *n* = 8
e, *n* = 9
f, *n* = 10
g, *n* = 12

2a, *n* = 6
b, *n* = 7
c, *n* = 8

3

4

1g was the *E*-isomer was shown as follows. Selective hydrogenation of the exocyclic double bond in the presence of tris(triphenylphosphine)rhodium chloride gave a 9:1 mixture of 1-ethylcyclododecene isomers **5b**. Comparison of the NMR spectrum in CCl_4 of the mixture with the NMR data, also in CCl_4, reported for (*Z*)- and (*E*)-1-methylcyclododecene (**5a**) (see below)[25] showed that the main component of the **5a** mixture was the *Z*-olefin; consequently, the main component of the **1g** mixture was the *E*-diene.[26]

(*E*)-1g (major)   (*Z*)-1g (minor)

R = Me (*Z*)-**5a**   H-2 δ 5.03 (t, 8 H$_2$)[25]   (*E*)-**5a**   H-2 δ 5.20 (t, 8 H$_2$)[25]
R = Et (*Z*)-**5b** (major) δ 5.05 (t, 8.5 H$_2$)   (*E*)-**5b** (minor) δ 5.28 (t, 8 H$_2$)

Assignment of *E*- and *Z*-stereochemistry to the major and minor components of the vinylcyclononene (**1e**) and vinylcyclodecene (**1f**) mixture is also based on NMR spectrometry. Olefinic proton signals of the vinylcycloalkenes **1a–g** are listed in Table I. It can be seen that the H_A, H_B and H_C resonances of the *E*-series remain reasonably constant, aside from those of 1-vinylcyclopentene, as do those of the *Z*-series, and that the H_A and H_B resonances of the *Z*-isomers are somewhat downfield from those of the *E*-isomers. More pronounced is the difference in the chemical shift of H_C which remains constant or nearly so for $n \geq 6$, with the H_C signal of the *E*-isomers appearing 0.40 ppm upfield from the H_C resonance of the *Z*-isomers.[27]

Table I. NMR Spectra of 1-Vinylcloalkenes (CDCl₃, 270 MHz)

geometry		*n*	chemical shift			
			H_A	H_B	H_C	H-2
E	a	5	5.04	5.05	6.58	5.72
	b	6	4.89	5.06	6.35	5.75
	c	7	4.88	5.09	6.32	5.89
	d	8	4.90	5.10	6.29	5.70
	e	9	4.92	5.09	6.30	5.60
	f	10	4.92	5.13	6.29	5.51
	g	12	4.92	5.11	6.28	5.48
Z	e	9	5.08	5.23	6.69	5.89
	f	10	5.09	5.27	6.70	5.64
	g	12	5.09	5.24	6.69	5.52

Thus, $POCl_3$–pyridine dehydration of the 1-vinylcycloalkanols (*n* = 9, 10, 12) produces predominantly the cis isomers, a result at variance with $POCl_3$–pyridine induced dehydration of cyclodecanol (see Experimental Section) which gave a 5:4 mixture of *trans*- and *cis*-cyclododecene. The predominance, though slight, of *trans*-cyclododecene is consistent with literature reports on bimolecular elimination reactions of medium ring compounds which produce predominantly trans isomers due to what is assumed to be competition between syn- and anti-elimination pathways.[28]

Photooxygenation of the Dienes 1a–g. Each diene was dissolved in 5% $MeOH$–CH_2Cl_2 which contained ca. 10^{-4} M rose bengal as sensitizer. The solution was irradiated with two tungsten–halogen lamps for 90 min while oxygen was passed through it continuously. Variations in oxygen flow rate and solvents which govern the $^1O_2$ lifetime in solution would be expected to affect only the concentration of $^1O_2$. Thus, while the rate of reaction might be affected by such changes, the product composition should not.

Allylic hydroperoxides, the initial products of "ene" reaction with the substrates, may undergo 1,3-allylic isomerization,[29] dehydration,[29] and fragmentation (thermal Hock cleavage)[30] subsequent to formation. To avoid such products which would have unnecessarily complicated product analysis, the photooxygenation mixture was kept below 10 °C and monitored by TLC. Allylic hydroperoxides were reduced to the corresponding allylic alcohols with triethyl phosphite[31] immediately after completion of the reaction. This reagent accomplishes the reduction homogeneously and quantitatively and does not cleave the O–O bond of the epidioxides.

(21) GLC retention times of the isomers were so close that separation on a preparative scale was not attempted.

(22) The literature contains a reference to the dehydration of 1-vinylcyclododecanol with $KHSO_4$, but the properties of the product were not recorded.[23] Repetition of this work gave a 1:1 mixture of 1g isomers. Dehydration of 1-vinylcyclododecanol with Burgess' reagent[24] also gave a 1:1 mixture of 1g isomers (see Experimental Section).

(23) (a) Tamaru, Y.; Yamada, Y.; Kagotani, M.; Ochiai, H.; Nakajo, E.; Suzuki, R.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 4669. (b) Bonnans-Plaisance, C. *Eur. Polym. J.* **1979**, *15*, 581.

(24) Burgess, E. M.; Penton, H. R., Jr.; Taylor, E. A. *J. Org. Chem.* **1973**, *38*, 26.

(25) Marshall, J. A.; Karas, L. J.; Royce, R. D., Jr. *J. Org. Chem.* **1979**, *44*, 1994.

(26) As the priorities change in going from 1g to 5a, the geometry of (*E*)-1-vinylcyclododecadiene corresponds to that of (*Z*)-1-ethylcyclododecene.

(27) The H_c resonance of acyclic (*E*)-1,2-disubstituted butadienes also appears 0.34–0.47 ppm upfield from that of *Z*-isomers although a priori it was not obvious that this generalization could be extended to semicyclic dienes. Examples are (CDCl₃) (*E*)- and (*Z*)-biformene, H δ 6.34 and 6.81 (from ref 16a), (*E*)- and (*Z*)-β-ocimene, H δ 6.37 and 6.81 (present work), (*E*)- and (*Z*)-ocimen-ol, H δ 6.36 and 6.72 (present work), and (*E*)- and (*Z*)-ocimene (in CCl_4) H δ 6.31 and 6.65 (from Ohloff, G.; Seibl, J.; Kovats, E. *Liebigs Ann. Chem.* **1964**, *675*, 83).

(28) Sicher, J. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 200.

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(30) (a) Hock, H.; Lang, S. *Chem. Ber.* **1942**, *75*, 300; *Ibid.* **1944**, *77*, 257. (b) Schenck, G. O.; Schulte-Elt, K. H. *Liebigs Ann. Chem.* **1958**, *618*, 185.

(31) (a) Walling, C.; Rabinowitz, R. *J. Am. Chem. Soc.* **1959**, *81* 1243. (b) Magelli, O. L.; Sheppard, C. S. In "Organic Peroxides"; Swern, D., Ed.; John Wiley and Sons, Inc.: New York, 1970; Vol. 1, p 19.

Table II. Photooxygenation Products of 1-Vinylcycloalkanes[a]

entry	n	6	(Z)-7	(E)-7	(Z)-8	(E)-8	9	10	ratio "ene" vs. cycloaddn.
a	5	13 (16.3)	46.1 (57.9)				8.2 (10.3)	12.3 (15.5)	5.1
b	6	66 (76.7)	8.9 (10.3)				5.8 (6.7)	5.4 (6.3)	0.3
c	7	14.8 (22.1)	44.7 (66.7)				5.7 (8.5)	1.8 (2.7)	3.5
d	8	34.3 (50.4)	8.7 (12.8)				28.9 (42.5)	2.2 (3.2)	1.2
e	9[b]	31.4 (47.1)	6.9 (10.3)		1.4 (2.1)		24.9 (37.3)	2.1 (3.1)	1.1
f	10[c]	43.7 (67.1)	4.1 (6.3)	4.1 (6.3)		0.4 (0.6)	12.4 (19.0)	0.4 (0.6)	0.5
g	12[d]	43.8 (61.5)		15.1 (21.2)		2.4 (3.4)	9.7 (13.6)	0.2 (0.3)	0.6

[a] Yields are isolated yields except for 9a–d and 10a–d which were determined by integration of peaks in NMR spectra of mixtures. Yields in parentheses are percentatges of total product. [b] Starting material contains 1% of Z-diene. [c] Starting material 93:7 mixture of E- and Z-diene. [d] Starting material 9:1 mixture of E- and Z-diene.

Results of ñe photooxygenations of vinylcycloalkenes 1a–g are listed in Table II. Product analysis is exemplified by the reaction of singlet oxygen with 1-vinylcyclohexene (1b) which was monitored by TLC (30% Et_2O–hexane) and showed three spots in addition to starting material. As the middle spot (R_f 0.31) emitted fluorescence on irradiation with short wave length UV light before spraying with 30% H_2SO_4, it could be associated with a dienic product. Upon reduction with $P(OEt)_3$ the fluorescent spot shifted to a lower position on the TLC plate. Disappearance of the fluorescence from the original position indicated completion of the reduction. Flash chromatography[32] of the reduced mixture gave three fractions in 66%, 9%, and 16% yield, in order of polarity.

The structure of the major product, $C_8H_{12}O_2$, was established as 6b by the NMR spectrum which exhibited the

6a, n = 5
 b, n = 6
 c, n = 7
 d, n = 8
 e, n = 9
 f, n = 10
 g, n = 12

7

8

9

10
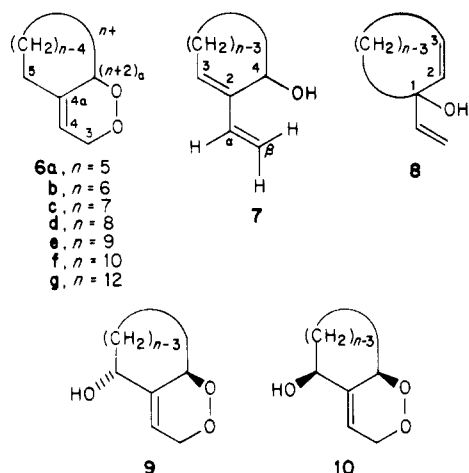
resonance of H-4 as a sextet (J = 2 Hz) at δ 5.60, the signals of H-3 as two mutually coupled doublets with fine splitting at δ 4.77 (ddd, J = 16.5, 4.5, 2.5 Hz) and δ 4.31 (dddd, J = 16.5, 4, 3, 2 Hz), and the signal of H-8a as a broad doublet at δ 4.59 (J = 10.5 Hz). Double irradiation experiments proved that H-4 was coupled to H-3 and H-3′, that H-5, H-5′, and H-8a were responsible for further splitting of H-4, that H-3 was long range coupled to H-5, and that the fine splitting of the H-3′ resonance was due to long range coupling to H-5 and H-8a.

The second product, diene alcohol 7b, $C_8H_{12}O$, fluoresced under UV irradiation due to the presence of the conjugated double bond and had significant IR bands at 3330 and 1603 cm⁻¹. The NMR spectrum exhibited the characteristic resonances of the vinyl group, i.e., a dd at δ 6.27 (J = 17.5, 11 Hz, α-H), a doublet at δ 5.37 (J = 17.5 Hz, trans-β-H), and a doublet at δ 5.03 (J = 11 Hz, cis-β-H), as well as another dd at δ 5.87 (J = 4.5, Hz, H-3) and a triplet at δ 4.48 (J = 2.5 Hz, H-1).

Table III. NMR Spectra of 9b and 10b (CDCl₃, 270 MHz)[a]

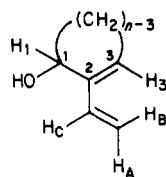|	9b	10b
H-3	4.71 dt (16.5, 2.5)	4.79 dq (16, 2)
H-3′	4.39 ddd (16.5, 4, 2)	4.44 dquint (16, 2)
H-4	5.86 quint (2)	5.94 sext (2)
H-5	4.45 t (2.8)[b]	4.10 m[b]
H-8a	4.94 dbr (11.5)	4.57 dbr (10.5)
OH	1.56 br	1.67 br

[a] Coupling constants in parentheses. [b] After addition of D_2O.

Although the most polar fraction gave a single spot on TLC, its NMR spectrum showed that it was a 1:1 mixture of stereomers contaminated by triethyl phosphate[33] which showed hydroxyl absorption in the IR. As the downfield region of the NMR spectrum resembled that of 7b, the conclusion could be drawn that the mixture consisted of two diastereomers 9b and 10b formed by cycloaddition of $^1O_2$ to 7b. This was confirmed by further reaction of 7b with $^1O_2$. After 5 h, the reaction was 50% complete and gave a 1:1 mixture of the diastereomers free of triethyl phosphate. Chromatography over a long silica gel column, the eluates being monitored by NMR spectrometry, permitted isolation from some of the fractions of two pure alcohols $C_8H_{12}O_3$, whose mass spectra showed the loss of O_2 characteristic of 1,2-dioxins and whose NMR spectra (Table III) showed that they were the trans and cis alcohols 9b and 10b. The assignment of stereochemistry is based on examination of Dreiding models: (1) In the trans isomer,[34] H-5 is situated in the deshielding cone of the double bond,[35] and in the cis isomer it is not. As the H-5 resonance of 9b is δ 0.35 downfield from that of 10b, 9b must be the trans isomer. (2) In the trans isomer H-8a is axial, close to and coplanar with axial OH, a circumstance which should result in deshielding of the H-8a resonance relative to that of the cis isomer. In fact, H-8a of 9b is δ 0.37 downfield from that of 10b. (3) In the trans isomer, H-5 is equatorial and should exhibit relatively small vicinal coupling constants. In fact, H-5 of 9b is a triplet, J = 2.5 Hz, whereas axial H-5 of 10b is a very broad multiplet. The axial orientation of H-5 in 10b is also responsible for the fine splitting of the H-4, H-8, and H-3′ signals by long

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(32) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1979**, *43*, 2923.

(33) Attempts to remove this impurity by vacuum distillation or chromatography failed nor was it possible to obtain the fraction in pure form by substituting Na_2SO_3 as a reducing agent. Although Na_2SO_3 is frequently used as a reducing agent for hydroperoxides,[30b] it appears to interfere with clean workup of the products resulting from photooxygenation of the vinylcycloalkenes.
(34) Trans designates that diastereomer in which hydroxyl and endoperoxide groups are in a trans relationship. The trans racemate has the 5S*,8aS* configuration, the cis racemate the 5R*,8aS* configuration.
(35) Günther, H.; Jekeli, G. *Chem. Rev.* **1977**, *77*, 599.

Table IV. NMR Spectra of 2-Vinyl-2-cycloalken-1-ols 7a–g (270 MHz, CDCl$_3$)

geometry		n	H_A	H_B	H_C	H_1	H_3
	a	5	5.15	5.42	6.46	5.00	5.89
	b	6	5.03	5.37	6.27	4.48	5.87
Z	c	7	4.94	5.23	6.28	4.69	5.92
	d	8	5.01	5.48	6.26	4.92	5.84
	e	9	5.02	5.49	6.27	4.96	5.82
	f	10	5.05	5.53	6.31	4.86	5.65
	g	12	5.04	5.48	6.30	4.85	5.60
	f	10	5.18	5.40	6.63	4.57	5.95
E	g	12	5.20	5.40	6.59	4.46	5.77

range coupling. This was proved by double irradiation experiments.

Reaction of the other semicyclic dienes with singlet oxygen gave analogous products (Table II) whose structures were established in the manner outlined in the previous paragraphs. Slight departures from the norm were noted for $n > 8$. Thus, a small amount (1%) of an additional photooxygenation product, (Z)-1-vinyl-2-cyclononen-1-ol ((Z)-8e), was isolated in the case of 1e as the result of an "ene" reaction which competes with the formation of 7e. Structure assignment was based on the empirical formula $C_{11}H_{18}O$, the IR spectrum which exhibited hydroxyl absorption but no diene band, and the NMR spectrum which exhibited a sharp hydroxyl singlet, the typical signals of the vinyl group, and (in C_6D_6) two mutually coupled signals at δ 5.47 and 5.25 ($J = 11.5$ Hz), characteristic of a cis olefin.[35]

Photooxygenation of 1f gave in addition to the major 1,4-adduct 6f a small amount (0.4%) of (E)-1-vinyl-2-cyclodecen-1-ol ((E)-8f) and 8% of a 1:1 mixture of E- and Z-alcohols 7f. The NMR spectrum of (E)-8f exhibited the resonances of the two endocyclic olefinic protons as a ddd at δ 5.71 ($J = 16, 8, 5.5$ Hz) and as a doublet at δ 5.54 ($J = 16$ Hz). Because of the large vicinal coupling constant which is characteristic of trans olefins,[35] the E-configuration was assigned to this alcohol. The NMR spectrum of the "ene" product 7f indicated that it was a mixture of E- and Z-isomers. Assignment of stereochemistry was made possible by double irradiation experiments and by comparison of the downfield signals with those of other secondary diene alcohols of the Z- and E-series which are listed in Table IV. The previously noted downfield shift of the H_C resonance in compounds with trans geometry in the ring is also evident here.

Minor products from the photooxygenation of 1-vinylcyclododecene (1g) were (E)-1-vinyl-2-cyclododecen-1-ol (E)-8g, 2%) and (E)-2-vinylcyclododecen-1-ol ((E)-7g, 15%). The ^{1}H NMR spectrum (in C_6D_6) of (E)-8g exhibited the endocyclic vinyl proton signals at δ 5.50 (ddd, $J = 15.5, 9, 5$ Hz) and 5.36 (dd, $J = 15.5, 1$ Hz). The small additional coupling constant of H-2 was due to allylic coupling. The assignment of E-configuration to the major "ene" product (E)-7g was again based on NMR criteria. Only a trace of (Z)-7g was detected in the NMR spectrum; the relevant peaks are included in Table IV.

In summary, reaction of the 1-vinylcycloalkenes 1a–g with singlet oxygen produces 1,2-dioxins 6a–g via 1,4-cycloaddition, the secondary alcohols 7a–g and the tertiary alcohols 8e–g by the "ene" reaction, and *trans-* and *cis-*1,2-dioxin alcohols 9a–g and 10a–g by further cyclo-

addition to 7a–g. Table II shows that "ene" reaction of $^1O_2$ with these substances leads predominantly to the secondary alcohols 7a–g, rather than the tertiary alcohols 8a–g. This is consistent with results in other 1,3-diene systems (vide infra).

As 6a–g were stable under the photooxygenation conditions, the diene hydroperoxide precursors of 7a–g are primary photooxygenation products rather than products resulting from rearrangement of unstable dioxin intermediates as has been suggested[36] in the case of the 1-phenylcycloalkenes.[37]

The ratio of "ene" vs. cycloaddition reaction in the last column of Table II was calculated by comparing the yields of products 7, 8, 9, and 10 with the yields of 6. Thus, 1a and 1c undergo the "ene" reaction predominantly. As ring size increases, cycloaddition competes closely with the "ene" process, the crossover being at ring size 10. 1-Vinylcyclohexene (1b) is an exception, 1,4-addition for this substrate surpassing the "ene" reaction. Possible explanations for these observations will be presented subsequently.

Photooxygenation of Dienes 2a–c. Magnitude and direction of diene s-cis/s-trans conformational equilibria are considered to play an important role in accounting for reactivity differences in Diels–Alder reactions.[38] The s-cis form, present in low concentration at conformational equilibrium, is the conformation required for 1,4-cycloaddition, but when substituents are situated at the 2- and/or 3-position of 1,3-butadiene, the double bonds of the s-cis conformers are twisted out of coplanarity.[39] The resultant increase in the distance between C-1 and C-4 of the diene is thought to be responsible for the reduced reactivity of such dienes toward Diels–Alder reactions.[40] Similar factors may govern the cycloaddition of singlet oxygen. This made it intriguing to study the behavior of 1-isopropenylcycloalkenes 2a–c toward $^1O_2$.

While the reaction of $^1O_2$ with 2a has been reported in a short communication,[18] the conditions differed somewhat from those employed in the present study and only the major product, the 1,2-dioxin 11a, was mentioned. When this photooxygenation was repeated under our standard conditions, not only 11a, but also the secondary diene alcohol 12a and a mixture of polar substances were ob-

(36) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359.
(37) Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1976**, 2479.
(38) (a) Rüker, C.; Lang, D.; Sauer, J.; Friege, H.; Sustmann, R., *Chem. Ber.* **1980**, *113*, 1663. (b) Sauer, J.; Sustmann, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 779.
(39) Tai, J. C.; Allinger, N. L. *J. Am. Chem. Soc.* **1976**, *98*, 7928.
(40) Sustmann, R.; Bohm, M.; Sauer, J. *Chem. Ber.* **1979**, *112*, 883.

Table V. Photooxygenation Products from 2a-c

| entry	n	11	12	13	14	15	16	17
a	6	44	14	0.9	2	2	5	6
b	7	11	65					
c	8	24	30			10 20–30		

tained in 44%, 14% and 17% yield, respectively. By further reaction of **11a** and **12a** separately with $^1O_2$, the five components of the polar mixture were identified as **13a** and **14a** (from **12a**) and **15–17** (from **11a**). Yields of the various products from **2a** are given in Table V; ratios of **13a** and **14a** from **12a** and **15–17** from **11a** were unchanged when pure **11a** and **12a** were photooxygenated.
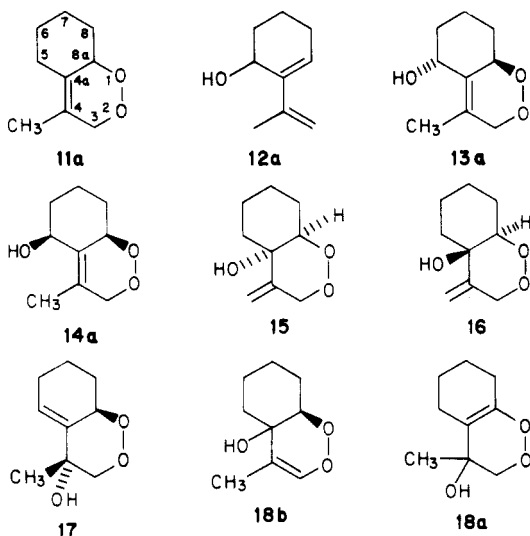
NMR spectra of **11a** and **12a** corresponded in an expected manner to those of **6b** and **7b**. Assignment of stereochemistry to the diastereomeric 1,2-dioxin alcohols **13a** and **14a** resulting from 1,4-cycloaddition of $^1O_2$ to **12a** was based on the criteria discussed previously for **9c** and **10c**. The downfield shifts of H-5 in the trans isomer **9c**, caused by the anisotropy of the 4,4a double bond, and of H-8a, caused by the deshielding effect of axial 5-OH, were paralleled in the NMR spectrum of the minor dioxin alcohol relative to that of major alcohol. Hence, the diene alcohol formed in 0.9% yield was **14a**.

Further "ene" reaction of $^1O_2$ with **11a** which underwent photooxygenation quite slowly[41] could theoretically take four paths as allylic hydrogen atoms on C-3, C-5, C-8a, and in the vinyl methyl group are aligned approximately perpendicularly to the 4,4a double bond: (1) Attack of $^1O_2$ at C-4 with abstraction of axial H-5 would give **17**. (2) Attack at C-4 with abstraction of H-8a would give **18a**. (3) Attack at C-4a with abstraction of quasi-axial H-3 would give **18b**. (4) Attack at C-4a with abstraction of hydrogen form the methyl group would give **15** and/or **16**. In fact, the absence of olefinic resonances in the NMR spectra of all products derived from **11a** excluded participation of processes 2 and 3, whereas the NMR spectrum of the substance formed in 5.9% yield revealed that it was formed by process 1 and therefore possessed stereochemistry **17**. In the NMR spectra of the two remaining compounds, the presence of signals characteristic of $CH_2=$ indicated that they were stereoisomers **15** and **16** whose configuration

depends on the direction of $^1O_2$ attack on the double bond of **11a**. Examination of Dreiding models led to the conclusion that the major tertiary alcohol was **16** ($\equiv$D) on the following grounds: (a) in D axial H-8a should give rise to a dd with one large and one small coupling constant, whereas in C equatorial H-8a should exhibit relatively small values of J. (b) In D one of the H-3's is close to and coplanar with C-4-OH and should be deshielded in relation to H-3 of C. The properties of the tertiary alcohol formed in larger amount corresponded to those expected for D.[42]
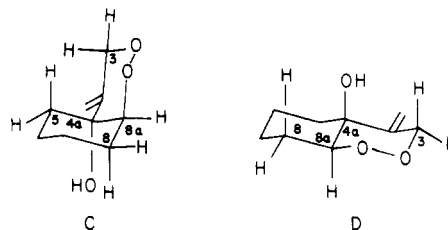
The yields of **11a**, **12a**, and **13–17** from **2a** provide a value of 0.29 for the ratio of "ene" reaction to cycloaddition, a ratio which does not differ significantly from that previously found for **1c** (Table II); likewise, the behavior of **2b** and **2c** resembled that of **1c** and **1d**. Thus, photooxygenation of **2b** gave the 1,2-dioxin **11b**, the diene alcohol **12b**, and a mixture of polar compounds in 11%, 65%, and 10% yield. Although due to separation problems, the components of the polar mixture could not be identified statisfactorily, the results clearly show that the "ene" reaction remained the preferred process for $n = 7$ regardless of the extra methyl on the exocyclic vinyl group. Similarly, photooxygenation of **2c** gave 1,2-dioxin **11c**, diene alcohol **12c**, and a complex mixture of polar substances in 24%, 30%, and 20–30% yield, respectively. Because of difficulties with the analysis of the polar mixture and the very similar yields of **11c** and **12c**, the "ene" reaction vs. cycloaddition ratio could not be calculated accurately, but should not differ significantly from the ratio found for **1d**.

In summary, therefore, the insertion of a methyl group into the α-position of 1-vinylcycloalkenes does not seem to exert a pronounced influence on the ratio of "ene" product to 1,4-cycloaddition. The main factor influencing the ratio of "ene" to cycloaddition product from compounds **1a–g** and **2a–c** appears to be the size of the cycloalkene ring. This is also shown by comparing the ratio of **21** to **20** (ca. 3.6) from the photooxygenation of 3β-acetoxy-24-norcholesta-5,16,20(22)-triene (**19**)[20] with the ratio for 1-vinylcyclopentene in Table II.

"Ene" Reaction vs. Cycloaddition of Singlet Oxygen. Despite extensive investigation during the past two decades, the mechanism of the "ene" reaction of $^1O_2$ with alkenes is still in dispute.[43–49] Most of the debate has

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(41) 1,2-Dioxins of type **6** failed to react further with $^1O_2$. Apparently the negative inductive effect on the dioxin group drastically reduces the electron density of the double bond and its propensity to react with $^1O_2$. In 1,2-dioxins of type **11** the extra alkyl group on the double bond partially compensates for the loss of reactivity so as to allow formation of small amounts of **15–17**.

(42) In the NMR spectrum of **15** the third small coupling constant of H-8a (1.2 Hz) is attributed to "W" type long range coupling with equatorial H-5.

(43) For reviews through 1978 see ref 14 and 36.

(44) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1979**, *99*, 7977.

(45) (a) Stephenson, L. M. *Tetrahedron Lett.* **1980**, *21*, 1005. (b) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* **1980**, *13*, 419. (c) Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1980**, *102*, 1417.

19

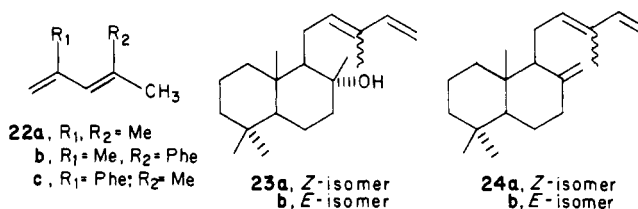$\xrightarrow[(2)\ Zn]{(1)\ ^1O_2}$

20 (17.4%)

+

21 (62%)
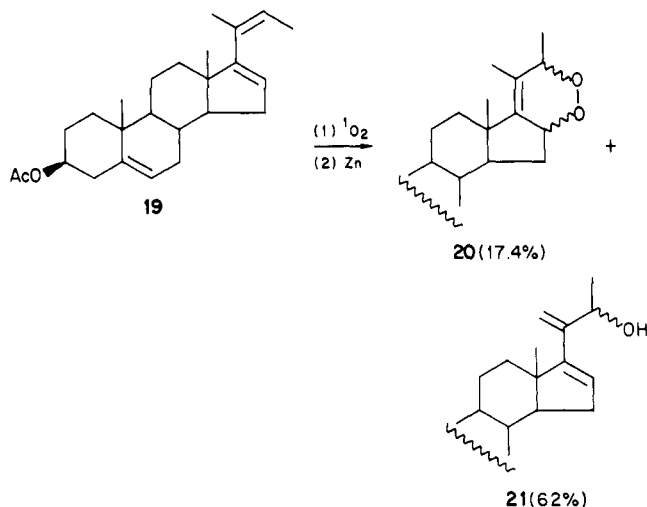
centered on two mechanisms: a one-step mechanism involving a six-center transition state and a two-step mechanism involving a perepoxide (or possibly a zwitterionic) intermediate. More recent proposals include a "perepoxide-like" transition state with unequal interaction between O-1 of $^1O_2$ and the two carbon atoms of the double bond,[14] irreversible formation of a complex,[44,45a] or reversible formation of an exciplex[49] which collapses to products. While less attention has been paid to the cycloaddition reaction,[13-15,37,50-53] again a concerted Diels–Alder-like mechanism and two-step mechanisms involving an intermediate which rearranges to the *endo*-peroxide have been advanced. Analyses of the competition between the two processes within the same 1,3-diene system are relatively sparse.[14,52,54]

1,3-Dienes in which one of the double bonds is trisubstituted may undergo both allylic hydroperoxidation and 1,4-cycloaddition with singlet oxygen. In the case of cyclic and acyclic 1,3-dienes whose double bonds are locked in the s-cis conformation 1,4-addition of $^1O_2$ generally predominates even if allylic hydrogens are available for the "ene" reaction.[13-15,16d] This has been rationalized as follows:[14] The activation energies for both cycloaddition and "ene" reaction are nearly zero, but $\Delta S^{\ddagger}$ for cycloaddition to a system held rigidly in the s-cis conformation is reduced from a large negative to a small negative value while $\Delta S^{\ddagger}$ for the "ene" reaction is not affected. As $S^{\ddagger}$ for a concerted cycloaddition depends on the distance between the reaction termini, the rate of cycloaddition to s-cis system forced out of the plane should be reduced as is found for cycloaddition of $^1O_2$ to 1,3-cycloheptadiene and 1,3-cyclooctadiene as compared with cycloaddition to cyclopentadiene and 1,3-cyclohexadiene.[52] Steric effects due to substituents at positions near the diene system may alter the reaction pathway.[55]

In acyclic 1,3-dienes with a trisubstituted double bond, the s-trans conformer predominates and, as has already been pointed out, the two double bonds of the s-cis conformer are twisted out of coplanarity. Nevertheless 22a–c appear to undergo 1,4-cycloaddition exclusively,[56] whereas the 12(*Z*)- and 12(*E*)-abienols 23a,b and the cis- and *trans*-biformenes 24a,b undergo predominantly the "ene" reaction, with preponderant formation of conjugated dienes, and give only small amounts of 1,4-cycloaddition products.[16a-c] Although conformational factors might conceivably be responsible for this striking difference, it should also be noted that "ene" reaction of $^1O_2$ with 22c cannot produce a conjugated diene and that the terminal double bond of 22a,b, attack on which would be required for formation of a conjugated diene, is less nucleophilic than the trisubstituted central double bond of 23a,b, 24a,b, and other conjugated dienes among whose "ene" products conjugated dienes predominate (vide infra).

22a, R_1, R_2 = Me
b, R_1 = Me, R_2 = Phe
c, R_1 = Phe; R_2 = Me

23a, *Z*-isomer
b, *E*-isomer

24a, *Z*-isomer
b, *E*-isomer

In the case of the 1-vinylcycloalkenes 1a–g which contain an endocyclic trisubstituted double bond,[57] inspection of Dreiding models constructed so as to reflect the most stable conformation of the cycloalkene part[35,58-61] indicates that ring size should have little effect on the position of the s-cis, s-trans conformational equilibrium or on the distance between the termini of the diene system. Nevertheless, there is a pronounced difference in the behavior of these substances which exhibits interesting parallels to the allylic hydroperoxidation of 1-alkylcycloalkenes.

Reactions with singlet oxygen of the 1-methylalkenes 25a–e,[62,63] the (*Z*)- and *E*)-1-methylcyclododecenes (25f and 29),[64] and the (*Z*)- and (*E*)-caryophyllenes (30 and 31), the only 1-methylcyclononenes studied,[65] have been described (eq 1).[66] The results of Foote[14,62] reinforced by the later work of Jefford and Rimbault[63] show that the partial rate constant (*k*p) for formation of the exocyclic hydroperoxides 28b–e (methyl attack) from 25b–e is essentially independent of ring size and that the overall rate constant (*k*r) for the "ene" reaction of 1-methylcyclohexene and 1-methylcyclooctene is considerably smaller than that for 5- and 7-membered ring olefins.[67] Although rates for the

(46) (a) Houk, K. N.; Williams, J. C.; Mitchell, P. A.; Yamaguchi, K. *J. Am. Chem. Soc.* **1980**, *102*, 439. (b) Yamaguchi, K.; Yabushita, S.; Fueno, T.; Houk, K. N. *Ibid.* **1981**, *103*, 5043. (c) Yamaguchi, K. Fueno T.; Saito, I.; Matsuura, T.; Houk, K. N. *Tetrahedron Lett.* **1981**, *22*, 749.

(47) Jefford, C. W. *Helv. Chem. Acta* **1981**, *64*, 2534.

(48) Hurst, J. R.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 6854.

(49) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1982**, *104*, 7098.

(50) Ashford, R. D.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1975**, *97*, 3604.

(51) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 2338.

(52) Monroe, B. M. *J. Am. Chem. Soc* **1981**, *103*, 7253.

(53) Clennan, E. L.; Mehrsheikh-Mohammed *J. Am. Chem. Soc.* **1983**, *105*, 5932.

(54) The site specificity of singlet oxygen reactions with substrates containing isolated double bonds as well as 1,3-diene systems has been analyzed in terms of the ionization potentials of the two potential reactive centers: Paquette, L. A.; Liotta, D. C.; Baker, A. D. *Tetrahedron Lett.* **1976**, 2681.

(55) Sasson, I.; Labovitz, J. *J. Org. Chem.* **1975**, *40*, 3670.

(56) Kondo, K. Matsumoto, M. *J. Chem. Soc., Synth. Commun.* **1972**, 1332.

(57) The competitive reactions reported for β-ionone, β-carotene, etc.[13-15] are not comparable as the endocyclic double bond is tetrasubstituted.

(58) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121.

(59) Allinger, N. L.; Sprague, I. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734.

(60) Dunitz, J. D. *Perspect. Struct. Chem.* **1968**, *2*, 57.

(61) Anet, F. A. L.; Rawdah, T. N. *Tetrahedron Lett.* **1979**, 1943.

(62) Foote, C. S. *Pure Appl. Chem.* **1971**, *27*, 635.

(63) Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1981**, *22*, 91.

(64) Schulte-Elte, K. H.; Rautenstrauch, V. *J. Am. Chem. Soc.* **1980**, *102*, 1738.

(65) (a) Schulte-Elte, K. H.; Ohloff, G. *Helv. Chim. Acta* **1968**, *51*, 494. (b) Gollnick, K.; Schade, G. *Tetrahedron Lett.* **1968**, 689.

(66) The relative rates and yields listed for 2b–e in ref 63 and the partial rate factors calculated from the yields given therein follow the same trends as *K*r and *K*p of ref 63 which are summarized in ref 14. Rates for 25f, 2a, 30, and 31 have not been determined; yields are as follows: From 25f,[65] 48% 26f, 22% 27f, and 30% 28f; from 29,[65] 33% 26f, ≤ 2% 27f, and 30% 28f; from 30,[66] 43% 26 analogues, 17% 27 analogue, and 40% 28 analogue; from 31,[66] 15% 26 analogue, 0% 27 analogue, and 85% 28 analogue. Thus (*Z*)-1-methylcyclononene and (*Z*)-1-methylcyclododecene exhibit very similar behavior, as do the *E*-isomers.

"ene" reaction of 25f and 30 are not available, it seems unlikely that k_p for formation of exocyclic hydroperoxides from 25f and 30 could be significantly different, so that, as for 25c and 25e, the larger proportion of exocyclic hydroperoxides in the total product from 25f and 30 could be ascribed to a reduction in k_p for the formation of endocyclic hydroperoxides.

25a, $n = 4$
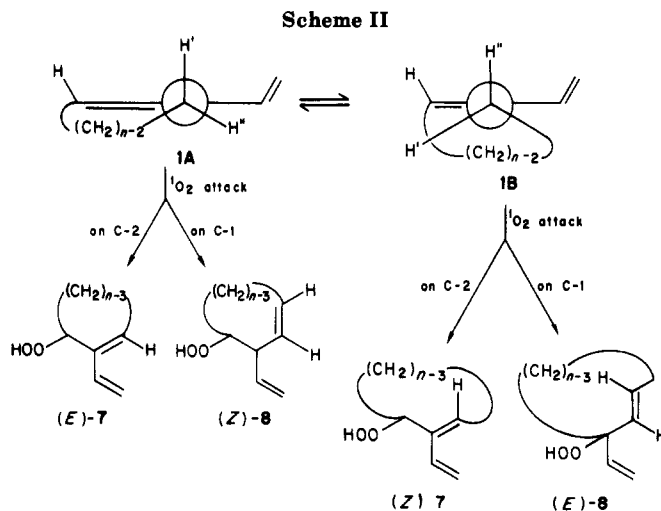b, $n = 5$
c, $n = 6$
d, $n = 7$
e, $n = 8$
f, $n = 12$
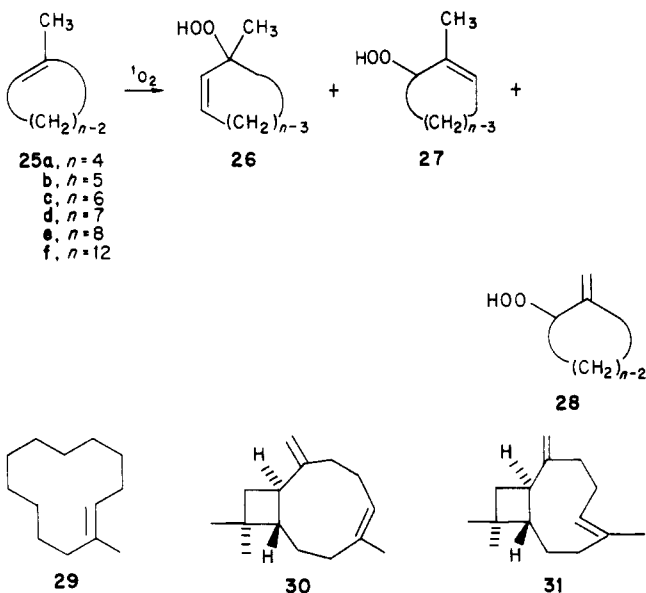
The situation is clearly analogous in the case of the 1-vinylcycloalkenes. If the rate of cycloaddition (k_{DA}) to 1a–g were relatively independent of ring size as seems likely, the difference in the "ene" to cycloaddition ratios listed in Table II would be due primarily to differences in the rate of the "ene" reaction (k_{ene}) which in the case of the 1-vinylcycloalkenes can lead only to endocyclic olefinic hydroperoxides. Hence, for 1a–g the effect of ring size on the "ene" to cycloaddition ratio is similar to the effect of ring size on the proportion of endo- and exocyclic products in the "ene" reaction of 1-methylcycloalkenes and can be attributed to the same factors. 1-Vinylcyclohexene exhibits the lowest "ene" to cycloaddition ratio; 1-methylcyclohexenes also furnish the lowest proportion of endocyclic olefinic hydroperoxides.

Possible reasons for the influence of ring size on the rates of formation of endocyclic allylic hydroperoxides from 1-alkylcycloalkenes for $n = 5$–7 have been discussed and appear to be related to the availability of allylic hydrogens capable of approaching a position orthogonal to the olefinic plane in the ground-state conformation of the cycloalkene moiety as well as to steric effects experienced by approaching $^1O_2$.[14,68] If the argument is extended to 1-alkylcycloalkylenes (or 1-vinylcycloalkenes) of ring size $n = 8$–12, inspection of models suggests that the availability of such hydrogens in the ground-state conformations[58–61] is no higher than in 1-alkylcyclohexenes, but that in contrast with the rather rigid cyclohexene system, the flexibility of the medium-sized rings permits the "ene" reaction to operate through transition states[19] of somewhat higher energy than when $n = 5$ and 7 but of lower energy than

Scheme II

(E)-7   (Z)-8   (Z) 7   (E)-8

when $n = 6$. With k_{DA} resonably constant, the "ene" to cycloaddition ratios of Table II for $n = 8$–12 would be a reflection of this energy difference.[70]

The proportion of geometric isomers in the secondary allylic hydroperoxides 7a–g can also be rationalized in terms of the conformations 1A and 1B (Scheme II) of the precursor 1-vinylcycloalkenes if these are related to transition-state geometry.[73] For rings where $n < 10$, the presence of angular strain excludes or strongly disfavors conformation 1B. When $n = 10$, the transannular strain in conformer 1A or the transition state corresponding to it is partially relieved in conformer 1B, thus leading to approximately equal amounts of (E)-7f and (Z)-7f. When $n = 12$, the exclusive formation of (E)-7g is in accord with conformation 1B which corresponds to a slightly distorted double bond segment of the cyclododecane conformations deduced by NMR spectrometry.[61] The preferred stereochemistry of the minor tertiary allylic hydroperoxides formed from 1e–g could be rationalized in the same manner.

Lastly, we return to the observation that the "ene" reaction of $^1O_2$ with 1a–g (and with 2a–c and 19) leads almost exclusively to conjugated diene hydroperoxides or to secondary products derived from them. Small amounts of unconjugated diene peroxides were formed only from 1e–g. Conjugated diene hydroperoxides are also the predominant, if not exclusive, "ene" products in the photooxygenation of other 1,3-dienes. Various explanations have been offered to account for this behavior in the case of styrene analogues;[37] however, the "ene" regiospecificity exhibited in this respect by non-styrene-like dienes is

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(67) The relative rate of photooxygenation of 25a is 4.0, compared with 7.6 for 25b, 1 for 25c, 7.6 for 25d, and 2.0 for 25e (data of ref 63 normalized for 25c). Yields of 26a, 27a, and 28a from 25a are 14.5%, 86.5% (sic!), and 0%; the absence of 28a has been ascribed to an interatomic distance unsuitable for hydrogen abstraction from the methyl group in a zwitterionic perepoxide.

(68) Gollnick, K.; Schade, G. *Liebigs Ann. Chem.* 1982, 1434.

(69) Cf. partial conformations 1A and 1B of Scheme II if these are related to transition-state geometry.

(70) The problem of competing "ene" reactions is dealt with in ref 64 where properties of ground-state conformations of 1-alkycycloalkenes are correlated with "ene" regiospecificity although the possibility that nondominant conformers might conceivably be involved in "ene" reactions is also considered. Parenthetically we note that contrary to a statement in ref 64 the relative proportions of endocyclic and exocyclic allylic hydroperoxides produced in the photooxygenation of 1-alkylcycloalkenes indicate syn regiospecificity (preference for syn "ene" addition or PSEA) regardless of ring size. PSEA, also characteristic of acyclic trisubstituted alkenes,[71,72] has been defined as preferential abstraction of allylic hydrogens from the more substituted (cis) side of the double bond, no distinction being made between formation of secondary and tertiary hydroperoxides. Although the proportion of exocyclic hydroperoxides is high for $n = 6$ (and becomes again very significant when $n = 8$, 9 and for (Z)-12), 1-alkylcyclohexenes constitute no exception to the rule.[14,63,65,68]

(71) (a) Schulte-Elte, K. H.; Muller, B. L.; Rautenstrauch, V. *Helv. Chim. Acta* 1978, 2777. (b) Schulte-Elte, K. H.; Muller, B. L.; Pamingle, H. *Ibid.* 1979, 62, 816.

(72) Orfanopoulos, M.; Grdina, M. B.; Stephenson; L. M. *J. Am. Chem. Soc.* 1979, 101, 275.

(73) The small amounts of Z-dienes admixed with (E)-1e,f would have little effect on product distribution.

**Table VI. Conversion of 3,6-Dihydro-1,2-dioxins into Furans 34a-t[a,b]**

substituent	ring size	react	product	yield, %
(a) R[1] = H, R[2] = H	5	6a	34a	0
	6	6b	34b	71
	7	6c	34c	78
	8	6d	34d	88
	9	6e	34e	80
	10	6f	34f	82
	12	6g	34g	86
(b) R[1] = H, R[2] = OH	5	9a + 10a	34h	0
	6	9b + 10b	34i	78
	7	9c + 10c	34j	76
	8	9d + 10d	34k	85
	9	9e + 10e	34l	96
	10	9f + 10f	34m	92
	12	9g + 10g	34n	96
(c) R[1] = CH₃, R[2] = H	6	11a	34o	80
	7	11b	34p	86
	8	11c	34q	82
(d) R[1] = CH₃, R[2] = OH	6	13a + 14a	34r	90
	7	13b + 14b	34s	88
	8	13c + 14c	34t	84

[a] In series b and d mixtures of *cis*- and *trans*-1,2-dioxin alcohols were used as reactant. [b] Yields based on material isolated after silica gel chromatography.

difficult to explain except in terms of a "perepoxide-like" transition state involving weaker bonding of O-1 of the $^1O_2$ reagent to the carbon carrying the vinyl group of intermediates such as zwitterionic peroxides or possibly biradicals. A particularly striking example of the effect of conjugation is offered by the contrasting behavior of 32[74] and 3[75] in the "ene" reaction with $^1O_2$.
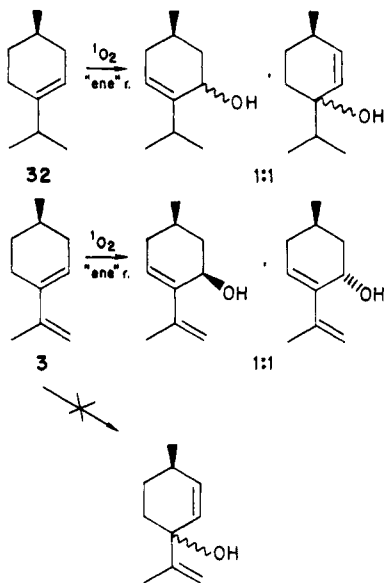

Preparation of Furans from the Dioxins. As expected, the cycloaddition products of type 33 were conveniently converted to furans 34 in very good to excellent yield by brief treatment with $FeSO_4$ in aqueous THF. A
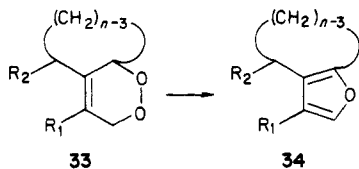
possible mechanism for the reaction has been discussed.[2]

(74) Ohloff, G.; Uhde, G. *Helv. Chim. Acta* **1965**, *48*, 1058.
(75) See accompanying article.

Products and yields are listed in Table VI. The only failures involved $FeSO_4$ treatment of the five-membered ring dioxins 6a, 9a, and 10a which, it was hoped, would give 2,3-trimethylenefurans.[76] A successful synthesis of 34a by pyrolysis of the 1,3-dioxolane 35 has been reported whereas acid-catalyzed cyclization of the diketones 36a,b was not successful.[78] Failure to obtain 34a by the $FeSO_4$ method can probably be attributed to the large activation energies involved in formation of the highly strained hemiacetals 37 and 38.

35

36a. R₁, R₂ = H
 b. R₁ = THP; R₂ = Me

37, R = H, OH   38, R = H, OH
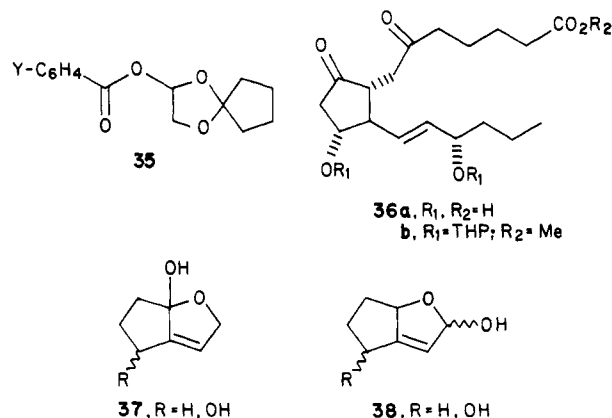
Experimental Section

Melting points were determined with a Mel-Temp apparatus by using open capillaries and are uncorrected as are boiling points. IR spectra were recorded on a Perkin-Elmer Model 257 instrument by using KBr pellets or thin films on NaCl plates, and ^1H NMR spectra on Varian A-60, JEOL 60, or Bruker HX-270 MHz spectrometers in CDCl₃ solution with Me₄Si as internal standard, unless specified otherwise, ^{13}C NMR spectra were run at 67.89 MHz on the Bruker instrument. Signals are characterized in the usual way: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; br, broadened signal; m, multiplet. High- and low-resolution mass spectra were obtained on an AEI MS-902 instrument at 70 eV. HPLC separations were performed on a Waters Prep LC/System 500 liquid chromatograph with two Prep PAK-500/silica cartridges (5.7 × 30 cm.). Precoated silica gel sheets (60F-254, 0.2 mm thick, EM Reagents) were used for analytical TLC. Silica gel 60 (250–460 mesh, EM Reagents) was used for flash column chromatography. Preparative TLC was carried out with silica gel plates (60 PF 254-366, EM Reagents); silica gel (70–230 mesh, particle size 0.063–0200 mm, EM Reagents) was used for column chromatography. Gas chromatographic analyses were performed on a Varian-Aerograph Model 2700 instrument equipped with a column oven linear temperature programmer, a dual-differential electrometer, and two flame-ionization detectors with a 50-m glass SE-30 capillary column. Elemental analyses were carried out by Galbraith Laboratories.

Preparation of 1-Vinylcycloalkenes. A solution of the freshly distilled cycloalkanone dissolved in a equal volume of dry THF was added with stirring over 20 min to a solution of 1.2–1.4 mol equiv of vinylmagnesium bromide (1.42 M in THF, Alfa Products) at 0 °C under nitrogen. The mixture was stirred at 60 °C for an additional 90 min, cooled, quenched with saturated NH_4Cl solution, and extracted thoroughly with ether. The combined ether fractions were washed, dried, and concentrated at reduced pressure. To the crude residue dissolved in four times its volume of pyridine was added slowly 10% excess of $POCl_3$ at 0–5 °C under nitrogen with stirring. After 24 h of stirring at room temperature the mixture was poured into ice water. The diene was extracted with *n*-pentane, washed, dried, concentrated at reduced pressure, filtered through a silica gel column, and distilled, precautions being taken at all times to prevent loss of volatile

(76) TLC and NMR analysis of the reaction mixtures indicated that more than three polar nonfuranoid products were formed.
(77) Scharf, H. D.; Wolters, E. *Chem. Ber.* **1978**, *111*, 639.
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diene. The freshly prepared dienes were sealed under nitrogen and stored in the refrigerator to prevent polymerization prior to use.

1-Vinylcyclopentene (**1a**),[79] 1-vinylcyclohexene (**1b**),[33] 1-vinylcycloheptene (**1c**),[80] and 1-vinylcyclooctene (**1d**)[23] had properties (bp, IR, ^{1}H NMR) identical with those reported in the literature. Dehydration of 1-vinylcyclononanol gave a 99:1 mixture of oily (*E*)- and (*Z*)-1-vinylcyclononene (**1e**) (GLC and NMR analysis): IR 3090, 3030, 300T, 1638, 1609, 1002, and 905 cm^{-1}; NMR signals of *E*-isomer, δ 6.30 (dd, *J* = 17.5, 11 Hz, α-vinyl H), 5.60 (t, *J* = 8.5 Hz, H-2), 5.09 (d, *J* = 17.5 Hz, *trans*-β-vinyl H), 4.92 (d, *J* = 11 Hz, *cis*-β-vinyl H), 2.37 (m, 2 H) and 2.2 (m, 2 H, allylic protons), 1.40–1.59 (m, 10 H); low-field signals of *Z*-isomer, 6.66 (dd, *J* = 17.5, 11 Hz, α-vinyl H), 5.89 (t, *J* = 8.5 Hz, H-2), 5.23 (d, *J* = 17.5 Hz, *trans*-β-vinyl H), signal of *cis*-β-vinyl H superimposed on that of *E*-isomer; MS/*m*/*z* (relative intensity) 150 (M$^+$, 39), 135 (15), 121 (18), 107 (20), 93 (41), 79 (85), 68 (100).

POCl$_3$ dehydration of 1-vinylcyclodecanol gave a 93:7 mixture of (*E*)- and (*Z*)-1-vinylcyclodecene (**1f**) as an oil: IR 3090, 1635, 1610, 1000, 908, and 870 cm^{-1}; NMR signals of *E*-isomer, δ 6.29 (dd, *J* = 17.5, 11 Hz, α-vinyl H), 5.51 (t, *J* = 8.5 Hz, H-2), 5.13 (d, *J* = 17.5 Hz, *trans*-β-vinyl H), 4.92 (d, *J* = 11 Hz, *cis*-β-vinyl H), 2.43 (t, *J* = 6.5 Hz) and 2.34 (m, 2 H, allylic protons), 1.59 (m, 4 H), 1.41 (m, 6 H), and 1.25 (m, 2 H); down-field signals of *Z*-isomer 6.70 (dd, *J* = 17.5, 11 Hz, α-vinyl H), 5.64 (t, *J* = 8.5, H-2), 5.27 (d, *J* = 17.5 Hz, *trans*-β-vinyl H), 5.09 (d, *J* = 11 Hz, *cis*-β-vinyl H); MS, *m*/*z* (relative intensity) 164 (M$^+$, 31), 149 (8), 135 (17), 121 (23), 107 (20), 93 (35), 79 (70), 68 (100).

Dehydration of 1-vinylcyclodecanol with POCl$_3$–pyridine furnished a 9:1 mixture of (*E*)- and (*Z*)-1-vinylcyclododecene (**1g**), 63% overall yield from cyclododecanone) as an oil: IR 3084, 1635, 1606, 1000, 902, 882 cm^{-1}; NMR signals of *E*-isomer, δ 6.25 (dd, *J* = 17, 11.5 Hz, α-vinyl H), 5.48 (t, *J* = 8 Hz, H-2), 5.11 (d, *J* = 17 Hz, *trans*-β-vinyl H), 4.92 (d, *J* = 11.5 Hz, *cis*-β-vinyl H). The corresponding signals of the *Z*-isomer were at δ 6.69 (dd, *J* = 17, 115 Hz), 5.52 (t, *J* = 7.5 Hz), 5.24 (d, *J* = 17 Hz), and 5.09 (d, *J* = 11.5 Hz); MS *m*/*z* (relative intensity) 192 (M$^+$, 28), 177 (2), 163 (7), 149 (9), 135 (15), 121 (47), 107 (18), 95 (33), 79 (63), 68 (100). Dropwise addition of 4 g of 1-vinylcyclododecanol in 10 mL of benzene to 4 g of Burgess' reagent[24] in 20 mL of benzene at ambient temperature, continued stirring at 50 °C for 30 min, cooling, quenching with H$_2$O, extraction with benzene, and the usual workup gave a 1:1 mixture of *E*- and *Z*-isomer in 84% yield. KHSO$_4$ dehydration of 1-vinylcyclododecanol also gave a 1:1 mixture (54%).

(***E***)- **and** (***Z***)-**1-Ethylcyclododecene** (**5b**). Hydrogen gas was passed through a solution of 0.500 g of 1-vinylcyclododecene (*E*/*Z* ratio 9:1) and 0.200 g of tris(triphenylphosphonium)rhodium chloride in 40 mL of benzene for 7 h. Filtration through a 5-g Florosil column and evaporation at reduced pressure gave 0.443 g (88%) of 1-ethylcyclododecene (*Z*/*E* ratio 9:1), low field signals (CCl$_4$) δ 5.03 (t, *J* = 8 Hz, H-2 of *Z*-isomer) and 5.20 (t, *J* = 8 Hz, H-2 of *E*-isomer). Reduction of the 1:1 mixture of (*E*)- and (*Z*)-1-vinylcyclododecene in a similar fashion gave a 1:1 mixture of (*Z*)- and (*E*)-**5b**.

Dehydration of Cyclodecanol. Dehydration of 0.80 g of cyclodecanol with POCl$_3$–pyridine by the procedure described above, followed by column chromatography over silica gel and Kugelrohr distillation, yielded 0.45 g (62%) of a 4:5 *cis*- and *trans*-cyclodecene mixture, based on the relative intensities of the allylic carbon signals at δ 26.95 (*cis*) and 32.12 (*trans*).[81]

Preparation of 1-Isopropenylcycloalkenes. The general procedure is illustrated by the preparation of **2a**. To isopropenylmagnesium bromide, prepared by slow addition (30 min) of 17 mL of 2-bromopropene in 20 mL of dry THF to a suspension of 5.65 g of Mg powder in 300 mL of THF, stirring for 30 min at 46–48 °C, and cooling, was added 14.86 g of freshly distilled cyclohexanone in 30 mL of THF dropwise. The solution was heated at gentle reflux for 2 h, cooled, poured into saturated or NH$_4$Cl solution, and worked up as usual. The crude alcohol (18.81

g) was dehydrated with 17.51 mL of POCl$_3$ in 108 mL of pyridine as described previously to give 9.92 g (60%) of **2a**.[82] bp 54–55 °C (9 mm); NMR δ 5.88 (t, *J* = 4.5 Hz, H-2), 4.94 and 4.82 (both br, =CH$_2$), 2.15 (m, 4 H, allylic protons), 1.87 (vinyl methyl), 1.55 (c, 4 H, CH$_2$). 1-Isopropenylcycloheptene (**2b**),[23b] 38% yield from cycloheptanone: bp 51–53 °C (4.5 mm); NMR δ 6.00 (t, *J* = 7 Hz, H-2), 4.97 and 4.83 (both br, =CH$_2$), 2.83 (m, 2 H) and 2.21 (m, 2 H, allylic protous), 1.88 (vinyl methyl), 1.76 (m, 2 H) and 1.49 (m, 4 H). 1-Isopropenylcyclooctene (**2c**), 28% from cyclo-octanone: bp 56–58 °C (1.8 mm); IR (neat) 3095, 3018, 1630, 1608, 910, 892, 858 cm^{-1}; NMR δ 5.84 (t, *J* = 8 Hz, H-2), 5.02 and 4.87 (both br, =CH$_2$), 2.46 (m, 2 H) and 2.21 (m, 2 H, allylic protons), 1.89 (vinyl methyl), 1.42–1.61 (c, 8 H); MS, *m*/*z* (relative intensity) 150 (M$^+$, 82), 135 (59), 122 (38), 107 (66), 93 (72), 79 (100) 67 (85) 55 (37); M_r calcd for C$_{11}$H$_{18}$, 150.1408, found (MS), 150.1390.

The freshly prepared dienes were sealed under nitrogen and stored in the refrigerator to prevent polymerization prior to use.

Photooxygenation of 1-Vinylcycloalkenes. (a) General Procedure. A solution of the diene and sensitizer (rose bengal) in CH$_2$Cl$_2$–MeOH (19:1) was irradiated in a cylindrical Pyrex Hanovia reactor with two Sylvania DVY-tungsten–halogen projection lamps as an internal light source. The lamps were operated at 60–70 V and were cooled with a stream of air. A constant stream of oxygen was passed through the mixture which was cooled by immersing the reaction vessel in a water–alcohol bath cooled to below 10 °C. The reaction was monitored by TLC (development with 30% Et$_2$O–hexane). Diene hydroperoxides fluoresced on irradiation with short wave UV before spraying with 30% sulfuric acid solution. Irradiation was stopped after 90 min at which time the mixture was transferred to a round-bottom flask and reduced immediately with P(OEt)$_3$. Completion of the reduction was indicated by disappearance of the fluorescence associated with hydroperoxide from the original spot and its shift to a lower position on the TLC plate. After removal of solvent at reduced pressure, the product mixture was separated by flash chromatography over silica gel. Because the 1,2-dioxins **6a–c** were quite volatile, photooxygenations of substrates **1a–c** were repeated until the values for the ratio of "ene" product to cycloaddition product remained reasonably constant. Due to the low boiling points of **1a–c**, the amounts of recovered **1a–c** was not determined.

(b) Photooxygenation of 1a. Reaction of 1.52 g of **1a** in 150 mL of CH$_2$Cl$_2$–MeOH (19:1) containing 20 mg of rose bengal for 90 min, addition of 2.7 g of P(OEt)$_3$, and flash chromatography over 60 g of silica gel gave 265 mg (13%) of **6a**, 822 mg (46.1%) of **7a**, whose special properties corresponded to those in the literature,[83] and a mixture of **9a** and **10a** contaminated with triethyl phosphate. Kugelrohr distillation removed most of the phosphate. The composition of the mixture, 188 mg of **9a** (8.2% based on starting material) and 283 mg of **10a** (12.3% based on starting material), was determined by NMR analysis. Pure samples of **9a** and **10a** were obtained by photooxygenation of 0.47 g of **7a** for 5 h; column chromatography of the crude product over 20 g of silica gel gave 0.140 g of recovered **7a**, 226 mg (38%) of **10a**, and 144 mg (24%) of **9a**. The ratio of **9a** to **10a** from **7a** is thus the same as from **1a**. Properties of **9a** and **10a** are supplied as Supplementary Material.

(c) Photooxygenation of 1b. Reaction of of 1.6 g of **1b** in 200 mL of CH$_2$Cl$_2$–MeOH (19:1) and 20 mg of rose bengal with singlet oxygen, addition of 1.8 g of P(OEt)$_3$, and flash chromatography gave 1.386 g (66%) of **6b**, 166 mg (8.9%) of **7b**, and a mixture of 135 mg (5.8%) of **9a** and 126 mg (5.9% of **10a** contaminated by triethyl phosphate. Pure **9b** and **10b** were obtained by reaction of **7b** with singlet oxygen and chromatography as described for **9a** and **10a**. Properties of **6b**, **7b**, **9b**, and **10b** are provided as Supplementary Material.

(d) Photooxygenation of 1c. Reaction of 1.83 g of **1c** with singlet oxygen as described above but for only 70 min when the dye was bleached, addition of 3 g of P(OEt)$_3$, and flash chromatography gave 342 mg (14.8%) of **6c**, 924 mg (44.7%) of **7c**,

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and a mixture of **9c** (146 mg, 5.7%) and **10c** (45 mg, 1.8%), and pure **9c** and **10c** (114 mg, 20%) were obtained by photooxygenation of 454 mg of **7c** for 5 h and subsequent column chromatography. Properties of **6c, 7c, 9c,** and **10c** are provided as Supplementary Material.

(e) Photooxygenation of 1d. Reaction of 2.00 g of **1d** with singlet oxygen in the usual manner, but for only 60 min when the dye was bleached, addition of 2 g of P(OEt)$_3$, and flash chromatography gave 260 mg of **1d**, 848 mg (34.3%) of **6d**, 195 mg (8.7%) of **7d**, and a mixture of 782 mg (28.9%) of **9d** and 60 mg (2,2%) of **10d**. Compounds **9d** and **10d** were separated by HPLC (solvent 25% ETDAc–hexane, flow rate 0.25 L/min). Properties of **6d, 7d, 9d,** and **10d** are provided as Supplementary Material.

(f) Photooxygenation of 1e. Reaction of 1.496 g of **1e** (99:1 mixture of *E*- and *Z*-isomers) with singlet oxygen and 25 mg of sensitizer in the usual manner, addition of 2.5 g of P(OEt)$_3$, and flash chromatography resulted in recovery of 176 mg (12%) of **1e**, as well as 571 mg (31.4%) of **6e**, 24 mg (1.4%) of (*Z*)-**8e**, 114 mg (6.9%) of (*Z*)-**7e**, 491 mg (24.9%) of **9e**, and 4.2 mg (2.1%) of **10e**. Properties of **6e,** (*Z*)-**7e,** (*Z*)-**8, 9e,** and **10e** are provided as Supplementary Material.

(g) Photooxygenation of 1f. Reaction of 1.034 g of **1f** (93:7 mixture of *E*- and *Z*-isomers) and 25 mg of sensitizer with singlet oxygen in the usual manner, addition of 1.5 g of P(OEt)$_3$, and flash chromatography gave 254 mg of starting material, 540 mg (43.7%) of **6f**, 5 mg (0.4%) of (*E*)-**8f**, 97 mg (8.2%) of a 1:1 mixture of (*E*)- and (*Z*)-**7f**, 165 mg (12.1%) of **9f**, and 6 mg (0.4%) of **10f**. Properties of these compounds are provided as Supplementary Material.

(h) Photooxygenation of 1g. Reaction of 2.314 g of **1g** (9:1 mixture of *E*- and *Z*-isomers) with singlet oxygen and 25 mg of sensitizer in the usual manner, addition of 3 g of P(Oet)$_3$, and flash chromatography afforded 392 mg of starting material, 1.182 g (43.8%) of **6g**, 60 mg (2.4%) of (*E*)-**8g**, 380 mg (14.1%) of (*E*)-**7g**, 280 mg (9.7%) of **9g**, and 57 mg (0.2%) of **10g**. Properties of these compounds are provided as Supplementary Material.

Photooxygenation of Isopropenylcycloalkenes. (a) Reaction of 3.00 g of **2a** and 25 mg of rose bengal with singlet oxygen in the usual manner, addition of 4.5 g of P(OEt)$_3$, and flash chromatography of the crude product gave 493 mg of starting material, 1.65 g (43.8%) of **11a**,[18] 483 mg (14.2%) of **12a** and a polar fraction contaminated with triethyl phosphate which contained 79 mg (19%) of **14a**, 38 mg (0.9%) of **13a**, 87 mg (2%) of **15**, 192 mg (4.6%) of **16**, and 247 mg (5.9%) of **17**. The structures of the components of the polar fractions and their proportions were clarified by further photooxygenation of **11a** and **12a** as follows: Reaction of 0.940 g of **11a** in 75 mL of CH$_2$Cl$_2$–MeOH (19:1) containing 10 mg of rose bengal with singlet oxygen for 5 h, addition of 1 g of P(OEt)$_3$, and column chromatography of the crude product gave 0.66 g of recovered **11a**, 28 mg (2.6%) of **15**, 64 mg (6.2%) of **16**, and 86 mg (8.3%) of **17**. Reaction of 236 mg of **12a** in 15 mL of CH$_2$Cl$_2$–MeOH (19:1) containing 2 × 10^{-4} mol of rose bengal with singlet oxygen for 5 h, addition of P(OEt)$_3$, and column chromatography of the crude product gave 57 mg of recovered **12a**, 90 mg (31%) of **14a**, and 42 mg (14.5%) of **13a**. Properties of the new compounds are listed as Supplementary Material.

(b) Photooxygenation of 2.50 g of **2b** in the usual manner, addition of 3.4 g of P(OEt)$_3$, and flash chromatography of the crude product gave 200 mg of starting material, 337 mg (10.9%) of **11b**, 1.79 g (64%) of **12b**, and a polar fraction (less than 10%)

contaminated with triethyl phosphate which was not investigated further due to difficulties in separating the components. Properties of **11b** and **12b** are given as Supplementary Materials.

(c) Reaction of 2.25 g of **2c** with singlet oxygen, addition of 2.6 g of P(OEt)$_3$, and flash chromatography of the crude product gave 0.398 g of starting material, 0.658 g (24.1%) of **11c**, 0.752 g (30.2%) of **12c**, and a complex mixture of polar products which were not examined further due to separation problems. Properties of **11c** and **12c** are listed as Supplementary Material.

Conversion of 3,6-Dihydro-1,2-dioxins to Furans. The furans listed in Table VI were prepared from the precursor 3,6-dihydro-1,2-dioxins with FeSO$_4$·7H$_2$O by using the method of Herz and Turner.[2] All new products were fully characterized by IR and NMR spectroscopy; elemental compositions of new compounds were determined by high-resolution MS and/or combustion analysis. Properties of the products are supplied as Supplementary Material. Furans **34b,c,g,h,o,p** have been prepared previously by other methods.[77,85]

Registry No. **1a,** 28638-58-6; **1b,** 2622-21-1; **1c,** 65811-18-9; **1d,** 80304-18-3; (*E*)-**1e,** 94325-29-8; (*Z*)-**1e,** 94325-25-4; (*E*)-**1f,** 94325-30-1; (*Z*)-**1f,** 94325-26-5; (*E*)-**1g,** 94325-31-2; (*Z*)-**1g,** 94325-27-6; **2a,** 6252-18-2; **2b,** 64425-47-4; **2c,** 94325-28-7; (*E*)-**5b,** 73775-25-4; (*Z*)-**5b,** 73775-24-3; **6a,** 94325-32-3; **6b,** 94325-33-4; **6c,** 94325-34-5; **6d,** 94325-35-6; **6e,** 94325-36-7; **6f,** 94325-37-8; **6g,** 94325-38-9; **7a,** 68332-31-0; **7b,** 70254-37-4; **7c,** 94325-39-0; **7d,** 94325-40-3; (*Z*)-**7e,** 94325-41-4; (*E*)-**7f,** 94325-42-5; (*Z*)-**7f,** 94325-43-6; (*E*)-**7g,** 94325-44-7; (*Z*)-**8e,** 94325-45-8; (*E*)-**8f,** 94325-46-9; (*E*)-**8g,** 94325-47-0; **9a,** 94325-48-1; **9b,** 94325-49-2; **9c,** 94325-50-5; **9d,** 94325-51-6; **9e,** 94325-52-7; **9f,** 94325-53-8; **9g,** 94325-54-9; **10a,** 94325-55-0; **10b,** 94325-56-1; **10c,** 94325-57-2; **10d,** 94325-58-3; **10e,** 94424-60-9; **10f,** 94424-61-0; **10g,** 94425-36-2; **11a,** 63159-76-2; **11b,** 94325-59-4; **11c,** 94325-60-7; **12a,** 94325-61-8; **12b,** 94325-62-9; **12c,** 94325-63-0; **13a,** 94325-64-1; **13b,** 94347-95-2; **13c,** 94325-65-2; **14a,** 94325-66-3; **14b,** 94325-67-4; **14c,** 94325-68-5; **15,** 94325-69-6; **16,** 94325-70-9; **17,** 94325-71-0; **34b,** 42768-88-7; **34c,** 4441-03-6; **34d,** 4744-79-0; **34e,** 94325-72-1; **34f,** 94325-73-2; **34g,** 66090-12-8; **34i,** 84099-58-1; **34j,** 94325-74-3; **34k,** 94325-75-4; **34l,** 94325-76-5; **34m,** 94325-77-6; **34n,** 94325-78-7; **34o,** 1919-00-2; **34p,** 66090-17-3; **34q,** 94325-79-8; **34r,** 94325-80-1; **34s,** 94325-81-2; **34t,** 94325-82-3; vinylmagnesium bromide, 1826-67-1; cyclodecanol, 1502-05-2; *cis*-cyclodecene, 935-31-9; *trans*-cyclodecene, 2198-20-1; isopropenylmagnesium bromide, 13291-18-4; 2-bromopropene, 557-93-7; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; cycloheptanone, 502-42-1; cyclooctanone, 502-49-8; cyclononanone, 3350-30-9; cyclodecanone, 1502-06-3; cyclododecanone, 830-13-7; 1-vinylcyclopentanol, 3859-35-6; 1-vinylcyclohexanol, 1940-19-8; 1-vinylcycloheptanol, 6244-47-9; 1-vinylcyclooctanol, 6244-48-0; 1-vinylcyclononanol, 64870-94-6; 1-vinylcyclodecanol, 94325-83-4; 1-vinylcyclododecanol, 6244-49-1; 1-isopropenylcyclohexanol, 3908-31-4; 1-isopropenylcycloheptanol, 3859-31-2; 1-isopropenylcyclooctanol, 94325-84-5; oxygen, 7782-44-7.

Supplementary Material Available: Lising of physical properties (mp or bp, IR, NMR and MS) and analytical data for compounds **6a–g, 7b–f,** (*E*)-**7g,** (*Z*)- and (*E*)-**8f,** (*E*)-**8g, 9a–g, 10a–g, 11a–c, 12a–c, 13a,b, 15, 17,** and **34b–t** (16 pages). Ordering information is given on any current masthead page.

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