Thermolysis and Photosensitized Oxygenation of Tetrasubstituted Cyclopropenes

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Bicyclic cyclopropenes **14a**, **14b**, and **26** were prepared by various synthetic routes. Polymer rose Bengal (p-RB) photosensitized oxygenation of bicyclooctenes **14a,b** in $CDCl_3$ proceeded sluggishly (variable O_2 uptake of ca. 0.35−0.75 equiv in 8 h) and was accompanied by sensitizer bleaching. Preparative gas chromatography of the complex product mixtures from **14a** and **14b** yielded both dienes (*Z*- and *E*-**29**, **30**, and **31**) and enones (*E*- and *Z*-**12**, **32, 34**). By contrast, p-RB photosensitized oxidation of bicyclononene **26** in $CDCl_3$ proceeded somewhat more rapidly (O_2 uptake of ca. 1 equiv in 2.5 h) yielding enones (**20, 42**−**45**) exclusively upon GC separation. The diene products, observed in the case of **14**, result from the thermolysis of the remaining unreacted cyclopropenes, while the enones are the oxygenation products. The oxygenation was slowed by radical inhibitors, but not by $^1O_2$ quenchers; nor were any oxidation products observed when these cyclopropenes were reacted with triphenylphosphine ozonide, a chemical $^1O_2$ source. The data indicates that a photosensitizer-initiated free radical autoxidative process is involved. Likely intermediates in this oxygenation are epoxide **27** or **37** and hydroperoxide **28** or **38**, for the bicyclooctene (**14**) and bicyclononene (**26**) systems, respectively. The absence of $^1O_2$ product in these cyclopropene systems, in contradistinction to their higher homologues, may be attributable to either the relatively long $C_\alpha-H_{allylic}$ distance in alkylcyclopropenes, which places the abstractable allylic hydrogen "out of reach", or their relatively high IP. Either, or both, of these factors may have slowed the rate of the singlet oxygenation of the cyclopropenes to a point where free radical processes compete favorably. In the course of this study, we also explored the singlet oxygenation (DABCO inhibited) of enones **12a**,**b** and **20**. These generated, respectively, a mixture of peroxides identified as α-keto hydroperoxides **51/54** and hemiperketals **52/55** (the cyclic form of *β*-keto hydroperoxides **53/56**). Phosphine reduction of these peroxides yields the corresponding alcohols **33/43** and **32/42**.

Introduction

Over the past two decades, we have been exploring the effect of strain on the rate, mode, and direction of singlet oxygen ($^1O_2$) reactions.[1] In particular, we have focused on various small ring olefin systems in which ring-strain decreases or develops as we proceed toward product. These studies have suggested that, in the transition state leading to product, $^1O_2$ is essentially insensitive to strain considerations.[1a−1c] This conclusion is consistent with prior evidence that singlet oxygen reactions have very small activation energies (0.5−8 kcal/mol)[2] and that the product-determining transition state is reactant-like and occurs quite early.[3]

Cyclopropene is a petite storehouse of ca. 50 kcal of strain energy,[4] which clearly suggests itself as an intriguing candidate for singlet oxygenation. Indeed, more than 20 years ago, Griffin and co-workers[5] carried out the first in a series of studies on the $^1O_2$ reaction of alkylated and arylated derivatives of 1,2-diarylcyclopropenes **1a**−**d** (eq 1). In each case, the oxidative cleavage products observed could be rationalized by invoking dioxetanes **2**[5] or endoperoxides **3**[1d,e,3] as the initial intermediates. Indeed, in the case of vinyl aromatics, dioxetanes and endoperoxides are generally observed as

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(1) (a) Frimer, A. A.; Roth, D.; Sprecher, M. *Tetrahedron Lett.* **1977**, 1927−1930. (b) Frimer, A. A.; Farkash, T.; Sprecher, M. *J. Org. Chem.* **1979**, *44*, 989−995. (c) Frimer, A. A.; Roth, D. *J. Org. Chem.* **1979**, *44*, 3882−3887. (d) Frimer, A. A.; Antebi, A. *J. Org. Chem.* **1980**, *45*, 2334−2340. (e) Frimer, A. A. *Isr. J. Chem.* **1981**, *21*, 194−202. (f) Frimer, A. A. *J. Photochem.* **1984**, *25*, 211−226. (g) Frimer, A. A. In *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1983; pp 201−234. (h) Frimer, A. A.; Stephenson, L. M. In *Singlet O_2 − Volume II: Reaction Modes and Products - Part I*; Frimer, A. A., Ed.; Chemical Rubber Company, Boca Raton, FL, 1985; pp 67−91. (i) Frimer, A. A.; Weiss, J. *J. Org. Chem.* **1993**, *58*, 3660−3667. (j) Frimer, A. A.; Weiss, J.; Gottlieb, H. E.; Wolk, J. L. *J. Org. Chem.* **1994**, *59*, 780−792.

(2) (a) Koch, E. *Tetrahedron* **1968**, *24*, 6295−6318. (b) Ashford, R. D.; Ogryzlo, E. A. *J. Am. Chem. Soc.* **1975**, *97*, 3604−3607.

(3) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359−387.

(4) Baird, N. C.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1967**, *89*, 3966−3970.

(5) (a) Politzer, I. R.; Griffin, G. W. *Tetrahedron Lett.* **1973**, 4775−4778. (b) Griffin, G. W.; Politzer, I. R.; Ishikawa, K.; Turro, N. J.; Chow, M.-F. *Tetrahedron Lett.* **1977**, 1287−1290. (c) Vaz, C.; Griffin, G.; Christensen, S.; Lankin, D. *Heterocycles* **1981**, *15*, 1643−1658. (d) See also the introduction to Griffin, G. W.; Kirschenheuter, G. P.; Vaz, C.; Umrigar, P. P.; Lankin, D.; Christensen, S. *Tetrahedron* **1985**, *41*, 2069−2080.

(6) (a) Denny, R. W.; Nickon, A. *Org. React.* **1973**, *20*, 133−336. (b) Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, A. A., Murray, R. W., Eds.; Academic Press: New York, 1979; pp 287−427; see especially pp 318−327.

(7) (a) Schenk, G. O.; Koch, E. *Z. Electrochemistry* **1960**, *64*, 170. (b) Rosental, I. In *Singlet O_2 − Volume I: Physical-Chemical Aspects*; Frimer, A. A., Ed.; Chemical Rubber Company: Boca Raton, FL, 1985; pp 13−38.

(8) Closs, G. L.; Closs, L. E.; Boll, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 3796−3800.

(9) Friedrich, L. E.; Leckonby, R. Y.; Stout, D. M.; Lam, Y.-S. P. *J. Org. Chem.* **1978**, *43*, 604−610.

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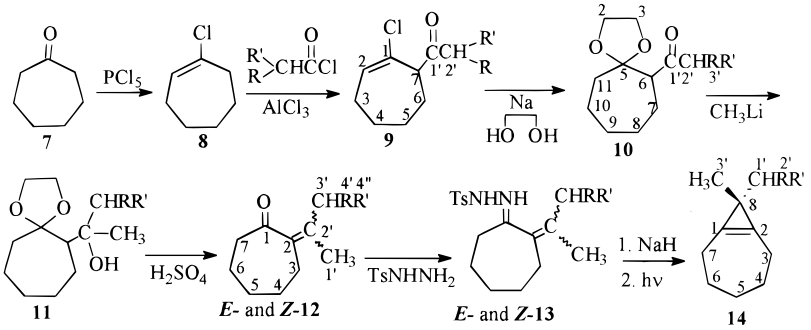
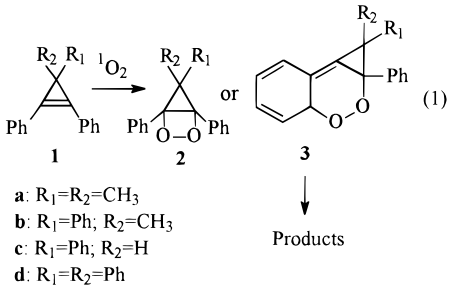
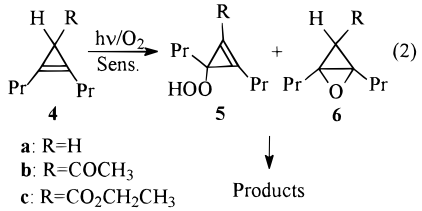
Scheme 1. Synthetic Scheme for the Preparation of Cyclopropenes 14a (R = R′ = CH_3) and 14b (R = CH_3; R = H)



the sole primary singlet oxygenation products, even if allylic hydrogens are available for a possible ene reaction mode.[1e,g,3,6]



In an attempt to focus in on the $^1O_2$ ene reaction in cyclopropenyl systems, Frimer and Antebi[1d] carried out the photosensitized oxygenation of cycloolefins **4a**−**c** (eq 2). A plethora of products were formed which were rationalized in terms of secondary rearrangements of initially formed allylic hydroperoxide **5** and cyclopropene epoxide **6**. Although the former is the expected ene product, the authors demonstrate that $^1O_2$ is *not* involved. The oxygenation is rather a free-radical ("type I")[7] autoxidative process, presumably photosensitizer-initiated via the abstraction of the labile C-3 ring hydrogen.

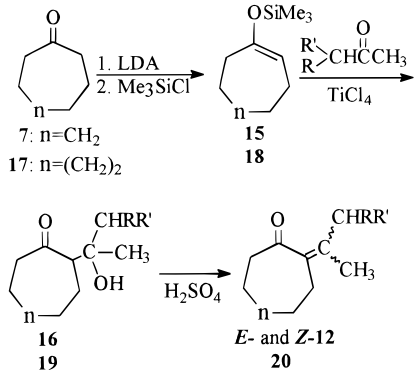


The above results lead us to the conclusion that our search for a singlet oxygen ene process should be directed toward tetraalkylated cyclopropenes, in which only exocyclic allylic hydrogens are available. The preparation and photosensitized oxygenation of several such systems is reported below. In brief, our results demonstrate that, while the expected oxygenation is indeed observed, the process is once again free-radical in nature and does *not* involve $^1O_2$.

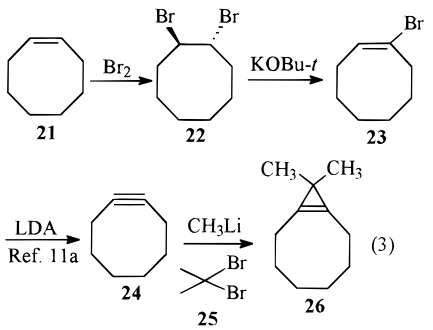
Results and Discussion

A. Synthesis and Photooxidation of Cyclopropenes 14a, 14b, and 26. In initial studies, we prepared the simplest tetrasubstituted cyclopropene, tetramethylcyclopropene.[8] Upon photosensitized oxidation, a sluggish oxygen uptake was indeed observed; however, we

Scheme 2. Synthetic Scheme for the Preparation of Alkylidenecycloheptanones 12a (R = R′ = CH_3) and 12b (R = CH_3; R′ = H), and Isopropylidenecyclooctanone 20 (R = R′ = H)



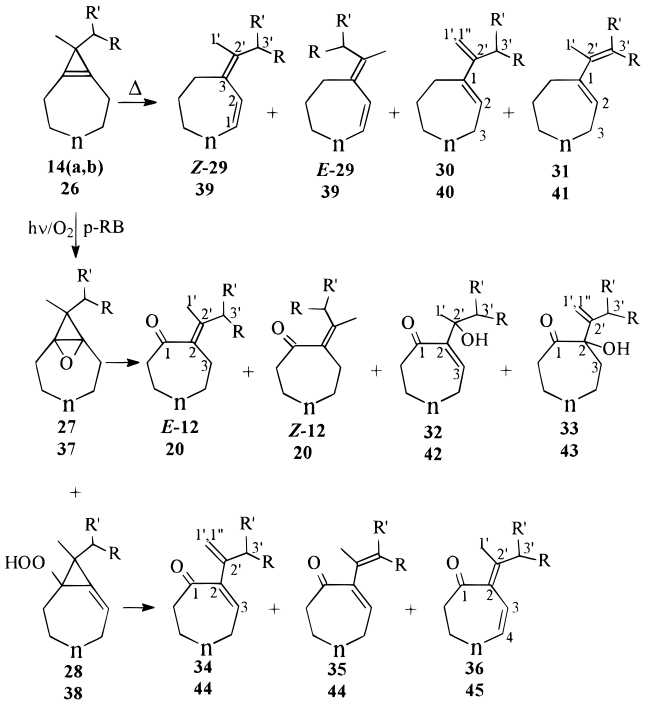
were unsuccessful in fishing out reaction products. We decided, therefore, to prepare bulkier systems, namely bicyclooctenes **14a** and **14b** and bicyclononene **26**. The former were initially prepared from cycloheptanone (**7**) by a modification of the Friedrich procedure (Scheme 1).[9] We found, however, that this approach to the crucial precursors, alkylidenecycloheptanones **12a** and **12b**, was both tedious and afforded low yields. Hence, we turned to the far more convenient silyl enol ether crossed aldol method,[10] outlined in Scheme 2. For the purpose of oxidation product identification in the corresponding bicyclononene system (vide infra), we also utilized Scheme 2 to synthesize isopropylidenecyclooctanone **20**. The preparation of bicyclononene **26** was effected via the cyclopropanation of cyclooctyne (eq 3).[11]



(10) (a) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736−738. (b) Mukaiyama, T.; Narasaki, K. *Org. Synth.* **1987**, *65*, 6−11.

(11) (a) Brandsma, L.; Verkruijsig, H. D. *Synthesis* **1978**, 290. (b) Wittig, G.; Hutchison, J. J. *Justus Leibigs Ann. Chem.* **1970**, *741*, 79−88.

Scheme 3. Product Formation in the Photosensitized Oxygenation of Tetrasubstituted Cyclopropenes 14a, 14b, and 26



Legend

12, 14, 27-36: n=(CH_2)	**20, 26, 37-45**: n=$(CH_2)_2$
a: R=R'=CH_3	R=R'=H
b: R=H; R'=CH_3	
c: R=CH_3; R'=H	

Polymer Rose Bengal (p-RB) photosensitized oxidation of bicyclooctenes **14a,b** in $CDCl_3$ proceeded sluggishly (variable O_2 uptake of ca. 0.35−0.75 equiv in 8 h) and was accompanied by sensitizer bleaching.[12] As summarized in Scheme 3, preparative gas chromatography of the complex product mixtures from **14a** and **14b** yielded both dienes (*Z*- and *E*-**29**, **30**, and **31**) and enones (*E*- and *Z*-**12**, **32, 34**). By contrast, p-RB photosensitized oxidation of bicyclononene **26** in $CDCl_3$ proceeded somewhat more rapidly (O_2 uptake of ca. 1 equiv in 2.5 h) yielding enones (**20, 42**−**45**) exclusively upon GC separation.

For the purpose of our later discussion, it should be noted that triphenylphosphine is commonly added at the end of $^1O_2$ reactions to reduce any hydroperoxides formed to the more stable alcohols. In addition, the Ph_3P reduction of hydroperoxides is typically quite exothermic. Indeed, instances where release of heat are not observed indicate either that hydroperoxides are either not formed at all, or are so labile that they rearrange to nonperoxidic products prior to Ph_3P treatment.[1b,d,f,g] In the present study, the addition of Ph_3P generated no heat and had little if any effect on the product distribution. Hence, workup of the present reaction mixtures proceeded without prior addition of Ph_3P.

(12) (a) Sensitizer bleaching is often the first indication of the involvement of free radical processes. See, for example, refs 1d and 1i. Indeed, we had chosen p-RB because it is generally not bleached photochemically[12b] and is compatible with nonpolar solvents.[12c] (b) Graf, G.; Braun, A. M.; Faure, J. *J. Org. Chimia* **1980**, *34*, 234. (c) Paczkowska, B.; Paczkowska, J.; Neckers, D. C. *Photochem. Photobiol.* **1985**, *42*, 603−604.

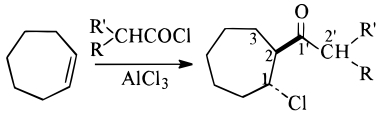
Table 1. Distribution of Diene Products in the Photosensitized Oxygenation of Cyclopropenes 14a and 14b

	diene product distribution[a] (%)			
substrate **14**	*Z*-**29**	*E*-**29**	**30**	**31**
a	36	28	36	–
b	25	25	25	25

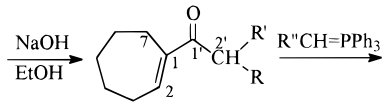
[a] The values are the average of at least three runs with a spread of ≤2%.

Our working hypothesis was that the diene products obtained result from GC-induced thermolysis of unreacted cyclopropene, while the enones are rearranged oxygenation products. For the purpose of clarity, we will deal separately with the identification and mechanism of formation of these two classes of compounds.

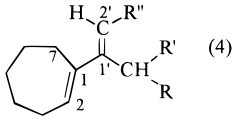
B. Formation of the Diene Products. The relative distribution of diene products obtained from the photooxidation of cyclopropenes **14a** and **14b** are given in Table 1. The products in each case were identified based on their spectral data, with NOE assisting in the *E* and *Z* assignments in the case of **29a** and **29b**, and **31b** (*E*-isomer exclusively). In addition, compounds **30a**, **30b**, and **31b** were independently synthesized in three steps: Friedel Crafts acylation of cycloheptene[9] generates *β*-chloroketones **46**;[13] base-catalyzed elimination of HCl from the latter yields enones **47**; a Wittig reaction produces the desired dienes (eq 4). (While **31b** isolated from the photooxidation of **14b** was exclusively the *E*-isomer, the NMR of **31b** prepared by the Wittig reaction revealed the presence of ca. 20% of the corresponding *Z*-isomer **31c**; see Experimental Section and eq 12 below).



46a: R=R'=CH_3
46b: R=H; R'=CH_3
46c: R=R'=H



47a: R=R'=CH_3
47b: R=H; R'=CH_3
47c: R=R'=H



(4)

30a: R=R'=CH_3; R"=H
30b: R=H; R'=CH_3; R"=H
31b: R=R'=H; R"=CH_3

As noted above, we assumed that the dienes result from GC-induced thermolysis/rearrangement of unreacted cyclopropene. Indeed, such rearrangements are well precedented.[14] An excellent case in point is the report of

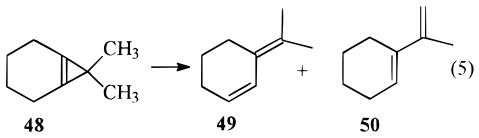
(13) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: Interscience: New York; 1985; p 536. The large $J_{1,2}$ = 9.8 Hz in **46a** indicates that H_1 and H_2 are quasi-*trans a,a* to each other (i.e., that the chlorine and acyl group are in a quasi *trans e,e* relationship); see Experimental Section.

Table 2. Oxidation Product Distribution in the Photosensitized Oxygenation of Cyclopropenes 14a, 14b, and 26 under Various Conditions

olefin	rxn cond	rxn rate[a] (mL/min/mmol)	oxygenation product distribution (%)[b]						
14	P-RB/$CDCl_3$		*E*-**12**	*Z*-**12**	**32**	**33**	**34**	**35**	**36**
a	RT	0.04[c]	5	5	8	–	61	21	–
b	RT	0.02[d]	–	–	69	–	31	–	–
26	P-RB/CH_3CN		**20**	**42**	**43**	**44**	**45**		
	RT	0.160[e]	17	27	38	5	13		
	RT; DABCO	0.270	10	38	36	1	15		
	−40 °C	0.015	13	38	31	–	18		
	RT; DTBP[f]	0.022	87	–	–	–	13		
	RT; dark	0.003	84	3	3	5	5		

[a] The reaction rate is based on the rate of oxygen uptake (mL/min) per mmol of substrate. [b] The values are the average of at least three runs with a spread of ≤2%. [c] Approximately 0.75 equiv of O_2 were absorbed in 8 h. [d] Approximately 0.35 equiv of O_2 were absorbed in 8 h. [e] Approximately 1 equiv of O_2 was absorbed in 2.5 h. [f] 2,6-Di-*tert*-butylphenol.

Closs and co-workers who note that 7,7-dimethylbicycloheptene **48** (a lower homologue of **26**) readily rearranges to **49** and **50** (eq 5; lower homologues of **39** and **40**).[15]



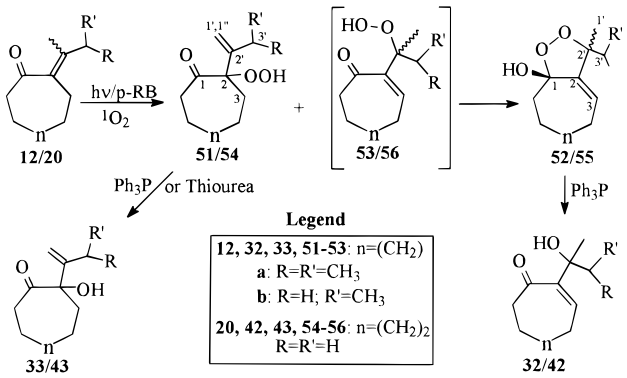
This hypothesis explains why the relative total amount of dienes isolated by GC from the photooxygenation of **14a** and **14b,** as compared to the total amount of enones observed, varied from photooxidation to photooxidation; it was simply proportional to the amount of unreacted substrate remaining (as approximated by the amount of oxygen uptake). Also consistent with this hypothesis is the fact that no dienes (e.g., **39, 40**, or **41**) are observed in the case of bicyclononene **26**, where the photooxidation proceeded essentially to completion.

To check the validity of this hypothesis, cyclopropenes **14a** and **14b** were injected into the GC. When the injector, detector, and column temperatures were maintained below 110 °C, the starting olefins were obtained essentially unchanged. However, above these conditions rearrangement is observed. In the case of **14a**, with the GC injector and detector set for 190 °C and the column at 120 °C, the products *E*- and *Z*-**29a** and **30a** were obtained essentially in the ratio of Table 1. Similarly, heating a neat sample of **14a** to 170 °C for 0.5 h gave the same results. Surprisingly, in the case of **14b**, GC thermolysis as above yielded *E*- and *Z*-**29b** exclusively, in a 1:1 ratio; heating a neat sample of **14b** to 170 °C for 0.5 h yielded equivalent amounts of **30b** and **31b**. The source of this discrepancy is not yet clear to us; we suspect the involvement of secondary rearrangements, but we have not pursued the question further.

We note in closing that molecular modeling studies[16] suggest that *Z*-**29a** is 0.3 kcal more stable than the *E*-analogue, while *Z*- and *E*-**29b** are essentially degenerate. These data are, of course, consistent with the results of Table 1.

C. Formation of the Enone Products. The product distribution in the photosensitized oxygenation of cyclopropenes **14a**, **14b**, and **26** is summarized in Table 2. For the purpose of elucidating the mechanism of these photooxidations (vide infra), the photosensitized oxygenation of **26** was repeated under various conditions, and these results are also given in Table 2. The products in each case were identified based on their spectral data, with NOE assisting in the *E* and *Z* assignments for **12a** and **12b**. In addition, most of these products could be independently synthesized as outlined in Scheme 4. Thus, singlet oxygenation (DABCO inhibited) of enones[17] **12a**, **12b**, and **20** generated, in each case, a mixture of peroxides identified as α-keto hydroperoxides **51/54** and hemiperketals **52/55** (the cyclic form of *β*-keto hydroperoxides **53/56**). Phosphine reduction of these peroxides yields the corresponding alcohols **33/43** and **32/42**.

Scheme 4. Product Formation in the Singlet Oxygenation of Enones 12 and 20



Several comments are appropriate at this juncture. Generally speaking, in the above-mentioned singlet oxygenation of enones **12**, we irradiated the *E*/*Z*-mixture. In one instance we did react pure (from GC) *E*-**12a** and pure *Z*-**12a** and obtained from each essentially the same product distribution of peroxides **51a** and **52a**. As shown in Scheme 5, since $^1O_2$ can attack the double bond from above or below, both *E*- and *Z*-isomers generate the same enantiomeric mixture of α-hydroperoxy ketones **51**/**51′** and *β*-hydroperoxy ketones **53**/**53′** as the primary products. As already noted above, the latter cyclize to hemiperketals **52**, a process which generates another chiral carbon and, hence, two diastereomers. Indeed, the NMR

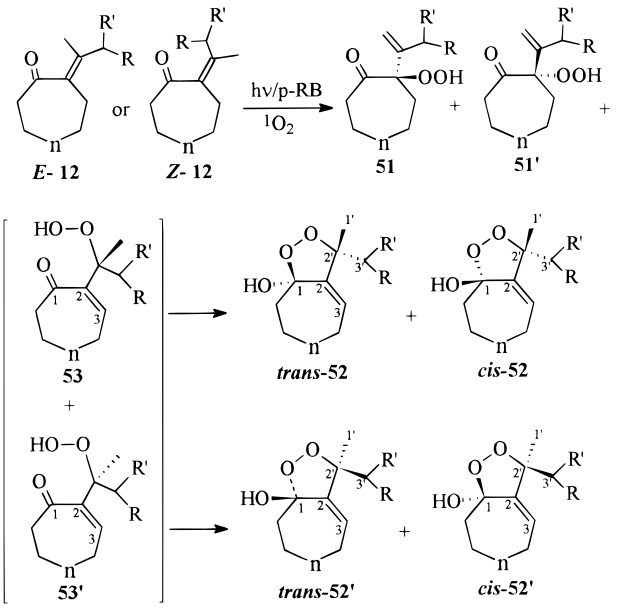
(14) (a) Closs, G. L. In *Advances in Alicyclic Chemistry*; Hart H., Karabtsos, G. J., Eds.; Academic Press: New York, 1966; Vol. I, pp 86−94. (b) Halton, B.; Banwell, M. G. In *Chemistry of the Cyclopropyl Group*; Patai, S., Rappaport, Z., Eds.; Wiley: 1980; pp 1272−1281.

(15) Closs, G. L.; Böll, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173−178, especially p 174.

(16) Autodesk HyperChem 3, AM1 semiempirical calculations.

(17) (a) Frimer, A. A. In *The Chemistry of Enones - Part 2*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; pp 781−921. (b) Ensley, H. In *Advances in Oxygenated Processes*; Baumstark, A., Ed.; JAI Press Inc.: Greenwich, CT, 1990; Volume 2, pp 181−201. (c) Elemis, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 6044−6050.

Scheme 5. Stereochemical Aspects of the Singlet Oxygenation of Enones 12



spectral data for hemiperketals **52** reveals the presence of two diastereomeric forms—in a ratio of 2:1 for **52a** and 1.2:1 for **52b**. NOE studies indicate that the major isomer in each case has the methyl and hydroxyl groups cis to each other (*cis*-**52**; see Scheme 5). Studying Scheme 5 makes it clear that while **53** cyclizes to *trans*-**52** and *cis*-**52**, its enantiomer **53′** cyclizes to *trans*-**52′** and *cis*-**52′**. While these are actually *four* different diastereomers, the "primed" set are merely mirror images of the unprimed analogues and hence indistinguishable by NMR in nonchiral solvents.

Second, we have suggested above that hemiperketals **52/55** result from the cyclization of the initial ene product *β*-keto hydroperoxides **53/56**. We should note, however, that in the case of **52a**, we have found no spectral evidence for the presence of the open form **53a** in the product mixture. Indeed, we see no carbonyl absorption in the FTIR of **52a**. Furthermore, while thiourea readily reduces the open hydroperoxide **51a**, it does not do so for cyclic peroxide **52a**. In the case of **52b**, however, we do see a moderate IR absorption at 1701 cm^{-1} (conjugated carbonyl) suggesting the presence of a low equilibrium concentration of **53b**.

Finally, we note that the hydrogens α to the carbonyl of several of the above enones (**20**, **34a**, **35a**, **42**, **44**, and **45**) appear in the ^1H NMR as an "inverted quintet" (abbreviated as inv quint) with peaks in a ratio of ca. 5:1:4:1:5. Such a pattern is typical of an AA′XX′ systems.[18]

Turning now to the question of mechanism, the reader is reminded that there are two major classes of photosensitized oxidative processes, appropriately called "type I" and "type II".[19] The former is a photoinitiated autoxidation in which only ground-state triplet molecular oxygen ($^3O_2$) is involved. A "type I" process is characterized by the direct reaction of the triplet sensitizer with a molecule of *substrate*, which generally results in hydrogen atom abstraction from the substrate, and initiates free radical autoxidative processes (equations 6 and 7). "Type II", on the other hand, is characterized by initial interaction between the sensitizer triplet and a molecule of *oxygen*. The traditional "type II"[20] involves transfer of the sensitizer's excitation energy to molecular oxygen generating singlet molecular oxygen ($^1O_2$), which is the oxygenation species (eqs 8 and 9).

Type I:

$$\mathrm{Sens}^3 + \mathrm{RH} \rightarrow {}^{\bullet}\mathrm{SensH} + \mathrm{R}^{\bullet} \quad (6)$$

$$\mathrm{R}^{\bullet} + {}^3\mathrm{O}_2 \rightarrow \mathrm{ROO}^{\bullet} \rightarrow \text{oxygenation products} \quad (7)$$

Type II:

$$\mathrm{Sens}^3 + {}^3\mathrm{O}_2 \rightarrow \mathrm{Sens}^1 + {}^1\mathrm{O}_2 \quad (8)$$

$$\mathrm{RH} + {}^1\mathrm{O}_2 \rightarrow \text{oxygenation} \quad (9)$$

There is ample evidence in this study to rule out a "type II" oxygenation and demonstrate that a nonsinglet oxygen/free radical mechanism predominates in the photosensitized oxidation of tetraalkylatedcyclopropenes: (1) The $^1O_2$-quencher DABCO[1g,21] did not slow the rate or course of the reaction. (2) On the other hand, addition of the free-radical inhibitor 2,6-di-*tert*-butylphenol[1g,22] had a dramatic damping effect on the rate, with a concomitant change in the product distribution. (3) When the reaction temperature was lowered from 25 °C to −40 °C, the rate of oxygen uptake dropped by a factor of 10. Such an effect is typical of free radical autoxidations. However, because of their low activation energies, the rate of singlet oxygenations are well-known to be *insensitive* to reaction temperature.[1g] (4) When **26** was exposed to $^1O_2$ chemically generated from triphenyl phosphite ozonide,[1d,23] no reaction products were observed.

Having determined that these cyclopropenes undergo photosensitized oxidation via a "type I" mechanism, we now turn to the details of product formation. The mechanism which we believe best fits the available data involves free radical autoxidative generation of two *initial* products (see Scheme 3): cyclopropyl epoxides **27/37**—via short chain polyperoxidation,[24] and alkylidenecyclopropyl hydroperoxides **28/38**—from a competing autoxidative hydroperoxidation process.[22] As we shall outline

(18) Gunther, H. *NMR Spectroscopy*; Wiley: Chichester: 1980; pp 181ff.

(19) (a) Schenk, G. O.; Koch, E. *Z. Electrochemistry* **1960**, *64*, 170. (b) Rosenthal, I. In *Singlet O_2 - Volume I: Physical-Chemical Aspects*; Frimer, A. A., Ed.; Chemical Rubber Company, Boca Raton, FL, 1985; pp 13−38. (c) For a more complete discussion, see ref 1i.

(20) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* **1977**, *60*, 2673−2685.

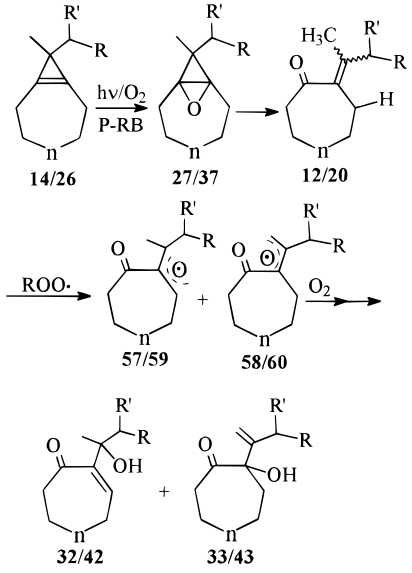
(21) (a) Ouannes, C.; Wilson, T. *J. Am. Chem. Soc.* **1968**, *90*, 6527−6528. (b) Davidson, R. S.; Trethewey, K. R. *J. Am. Chem. Soc.* **1976**, *98*, 4008−4009. (c) Davidson, R. S.; Trethewey, K. R. *J. Chem. Soc., Perkin Trans. 2* **1977**, 178−182. (d) Monroe, B. M. *J. Phys. Chem.* **1977**, *81*, 1861−1864. (e) Deneke, C. F.; Krinsky, N. I. *Photochem. Photobiol.* **1977**, *25*, 299−304.

(22) Cf. Foote, C. S. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. II, pp 85, 101.

(23) Cf. Murray, R. W.; Kaplan, M. L. *J. Am. Chem. Soc.* **1969**, *91*, 5358−5364.

(24) (a) Mayo, F. R. *J. Am. Chem. Soc.* **1958**, *80*, 2465−2480. (b) Mayo, F. R.; Miller, A. A.; Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 2500−2507. (c) Van Sickle, D. E.; Mayo, F. R.; Gould, E. S.; Arluck, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 977−984. (d) Mayo, F. R. *Acc. Chem. Res.* **1968**, *7*, 193−201. (e) Howard, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, pp 3−62; see especially p 25ff. (f) Filippova, T. V.; Blyumberg E. A. *Russian Chem. Rev.* **1982**, *51*, 582−591. (g) This short-chain polyperoxidation occurs only very slowly at room temperature to ultimately yield **20**; see the last entry in Table 2.

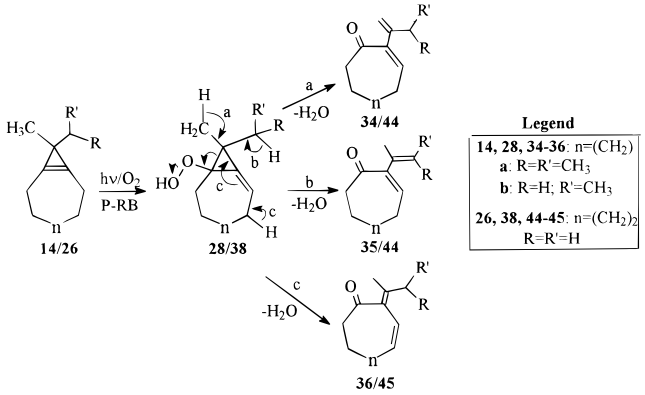
Scheme 6. Proposed Mechanism of Enone Formation in the Photosensitized Oxygenation of Tetrasubstituted Cyclopropenes 14a, 14b, and 26



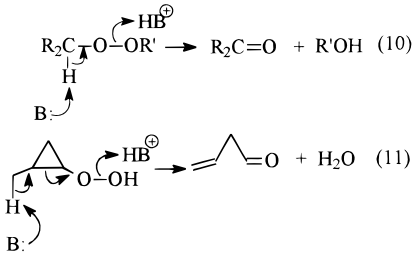
below, it is the well-precedented secondary transformations of each of these initial products which yields the plethora of final products observed.

Regarding epoxides **27/37**, the rearrangement of cyclopropyl epoxides to the corresponding enones is well documented.[25] Indeed, the MCPBA epoxidation of **14a** and **14b** is reported to yield *E*- and *Z*-**12a** and **12b**, respectively;[9] we verified that the same transformation occurs in the case of **26** as well. We suggest that, under the free radical reaction conditions prevailing in this system, enones **12** and **20** are further autoxidized,[17a] presumably via allylic hydrogen abstraction, ultimately yielding hydroxyenones **32/42** and **33/43** (Scheme 6). These hydroxyenones are clearly not generated via a singlet oxygen mechanism (*cf.* Scheme 4), since the data of Table 2 indicate that the addition of the $^1O_2$ quencher DABCO has only a small effect if any on the product distribution. Table 2 further reveals that, in the presence of the radical chain-breaker, 2,6-di-*tert*-butylphenol, the rate of oxygen uptake is strongly inhibited; nevertheless, of the small amount of reaction that does occur, the short chain epoxide-derived enone product **20** predominates and is not further oxidized. This is consistent with the mechanism of Scheme 6.

Scheme 7. Proposed Mechanism of Dienone Formation in the Photosensitized Oxygenation of Tetrasubstituted Cyclopropenes 14a, 14b, and 26



Turning now to hydroperoxides **28/38**, one common secondary reaction of peroxides in general, and hydroperoxides (R′ = H) in particular, is the Kornblum–DeLaMare reaction (eq 10).[1f,1h,3,17a] A homologous dehydration reaction would be expected for cyclopropyl hydroperoxides, yielding β,λ-enones (eq 11).



As shown in Scheme 7, similar transformations in the case of alkylidenecyclopropyl hydroperoxides **28/38** could easily lead to any of the remaining products, dienones **34**–**36**/**44**–**45**, depending on which hydrogens are lost.

D. Absence of $^1O_2$ Product. We have thus demonstrated that the photooxidation of tetrasubstituted cyclopropenes **14a**, **14b**, and **26** occurs via a "type I" free-radical process. The question remains, however, as to why no $^1O_2$ ene reaction is observed. Two possible approaches are available. We have previously suggested[1b,1e] that the interatomic distance between the α-olefinic carbon and the γ-allylic hydrogen, the distance which the attacking $^1O_2$ must span in the ene reaction irrespective of mechanism, may be a pivotal consideration in determining whether the hydrogen is abstractable. Too great a distance may well place legitimate candidates "out of reach".

Using bond lengths and angles from literature data, we have calculated the $C_\alpha-H_{allylic}$ distance for isobutylene,[1e] methylenecyclobutane,[1e] methylcyclobutene,[26] methylenecyclopropane,[1e] and methylcyclopropene.[27] It should be noted that in these calculations, the preferred $^1O_2$ ene reaction orientation[6] was used whenever possible, i.e., the

(25) See the following leading papers and the references therein: (a) Maynard, G. D.; Paquette, L. A. *J. Org. Chem.* **1991**, *56*, 5480–5482. (b) Friedrich, L. E.; Leckonby, R. A.; Stout, D. M. *J. Org. Chem.* **1980**, *45*, 3198–3202. (c) Crandall, J. K.; Conover, W. W., II. *J. Org. Chem.* **1978**, *43*, 1323–1327. (d) refs 1d and 9.

(26) Based on the electron diffraction data of Shand and coworkers,[26a] the $C_\alpha-H_{allylic}$ distance is calculated as 3.013 Å. MINDO 3 calculations by Dewar et al.[26b] give a substantially higher value of 3.164 Å. In Scheme 8, we have given the average value of 3.088 Å. (a) Shand, W., Jr.; Schomaker, V.; Fischer, J. F. *J. Am. Chem. Soc.* **1944**, *66*, 636–640. See also: Huang, Y. S.; Beaudet, R. A. *J. Chem. Phys.* **1970**, *52*, 935–940. (b) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294–1301.

(27) The microwave spectral data of Kemp and Flygare[27a] yields a $C_\alpha-H_{allylic}$ distance of 3.241 Å. MINDO 3 calculations by Dewar et al.[26b] give almost the same value of 3.238 Å. IMOA calculations of Eckert-Makasic and Makasi[27b] yield a substantially lower value of 3.229 Å. In Scheme 8, we have cited the experimental value of 3.241 Å. (a) Kemp, M. K.; Flygare, W. H. *J. Am. Chem. Soc.* **1969**, *91*, 3163–3167. See also: Allen, F. A. *Tetrahedron* **1982**, *38*, 645–655. (b) Eckert-Makasic, M.; Makasic, Z. B. *J. Mol. Struct., THEOCHEM* **1982**, *86*, 325–340.

Scheme 8. Calculated $C_\alpha-H_{allylic}$ Distances for Isobutylene and Various Cycloolefins

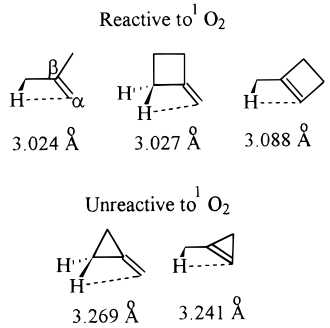


Table 3. Ionization Potential and Relative $^1O_2$ Reactivity of Small Ring Cycloalkenes

Cycloalkene	Relative $^1O_2$ Rate[31] (R=CH_3)	IP (eV)[30b] (R=H)
	No $^1O_2$ Reaction	9.82
	9.3	9.59
	17.4	9.20

abstracted allylic hydrogen was aligned in a plane perpendicular to the plane of the double bond. The necessary bond rotations were accomplished using Gaussian 76.[28] As shown in Scheme 8, the reactive cycloolefins all have a $C_\alpha-H_{allylic}$ distance below 3.09 Å, while for those which are unreactive this value is above 3.24 Å. As suggested above, it may be these crucial 0.15 Å which, in the latter case, place the abstractable allylic hydrogen "out of reach".

An additional, perhaps more convincing, rationale is available to explain the lack of $^1O_2$ reactivity in these cyclopropene systems. Several authors have found a good general correlation between olefin HOMO energies (or ionization potentials) and the relative rates of $^1O_2$ ene reaction,[6,29] i.e., the higher $E_{(olefin-HO)}$ (or the lower the IP) the greater the rate. As shown in Table 3, the ionization potential (IP) of cyclopropene is substantially higher than that of its homologues.[30] We suggest, therefore, that in the case of cyclopropene, the rate of the singlet oxygenation has slowed to a point where free radical processes compete favorably.[31] Future work will explore the effect of IP lowering substituents on the course of this reaction.

Experimental Section

NMR spectra were obtained on 600 (designated as NMR*), 300 and 200 Fourier transform spectrometers, using TMS as the internal standard. Assignments (see Supporting Information) were facilitated by correlating proton and carbon chemical shifts through analysis of residual couplings in off-resonance decoupled spectra. The carbon numbering of the various compounds used in the nomenclature and spectral assignments is shown in Schemes 1 and 3. EI and CI mass spectra were measured at 70 eV, unless otherwise indicated. Analytical thin-layer chromatography (TLC) was performed using Merck silica gel microcards. Preparative runs (PTLC) were carried out on Merck silica gel F_{254} precoated plates, and the products were extracted from the silica by stirring overnight in a solution of 10% CH_3OH in $CHCl_3$. The retention times given are for the analytical runs. Column chromatography was performed on Merck silica (230−400 mesh). For preparative gas chromatography (GC), a thermal conductivity detector was used, and peak areas were determined by triangulation.

Compounds **8**−**14**,[9] **22-26**,[11] **43**[32] and **47a**−**c**[33] are all known.

Preparation of *E*- and *Z*-2-(3′-Methyl-2′-butylidene)-cycloheptanone (12a), *E*- and *Z*-2-(2′-Butylidene)cycloheptanone (12b), and 2-Isopropylidenecyclooctanone (20). (a) Friedrich Procedure. The compounds **12a** and **12b** were prepared as previously described by Friedrich and coworkers[9] (Scheme 1), scaled up 5-fold. Two modifications are worth mentioning. The conversion of vinyl chloride **9** to ketal **10** was accomplished as follows: A three-necked round-bottom flask, fitted with a reflux condenser topped with a nitrogen inlet, was charged under with ethylene glycol (15 g; 242 mmol), *p*-dioxane (18 mL), and freshly cut sodium pieces (0.72 g; 36.3 mmol). The mixture was heated under reflux (oil bath temperature up to 165−170 °C) for 4 h, at which time vinyl chloride **9** (**a** or **b**; 20 mmol) was added dropwise to the refluxing solution. Heating and stirring under nitrogen were continued for another 40 h; workup and distillation, as described by Friedrich,[9] gave the desired product **10** (ca. 11−15 mmol; 55−75% yield). We also note that the dehydration−deprotection of β-hydroxyketals **11** generating enones **12** is accompanied by a 50% yield of cycloheptanone, presumably formed in a retroaldol process from the β-hydroxyketone intermediate **16** (see next paragraph). For enones **12**, the *Z* to *E* ratio is 1:2 in the case of **12a**, and 1:1 in the case of **12b**. We succeeded in purifying and separating the *Z*- and *E*-isomers of **12a** and **12b** from each other either by GC[34a] [at 145 °C, and with a flow rate of 75 mL/min (retention times: 27 and 30.5; 29.5 and 32 min. respectively)] or by silica column chromatography (TLC retention times given in data below). The previously published[9] NMR spectral data for compounds **8**−**12** were obtained on a 60 MHz instrument and the corresponding ^{13}C data are lacking. In addition, CW, 2D-COSY, and NOE experiments were performed to assist in atom and configuration assignments. Hence, the improved and missing data are recorded below.

(b) Silyl Enol Ether Crossed Aldol Method. As outlined in Scheme 2, the title compounds could be prepared from silyl enol ethers **15** and **18**, which were prepared in turn via the procedure of Fleming and Paterson.[10a] The $TiCl_4$-mediated condensation of the silyl ethers with the appropriate ketone in dichloromethane, according to the procedure of Mukaiyama and Narasaka,[10b] yielded the desired β-hydroxyketones **16a**,

(28) Binkley, J. S.; Whiteside, R. A.; Hariharan, B. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D., Gaussian Inc., Pittsburgh, PA, 1976.

(29) (a) Kearns, D. R. *J. Am. Chem. Soc.* **1969**, *91*, 6554−6563. (b) Paquette, L. A.; Liotta, D. C.; Baker A. D. *Tetrahedron Lett.* **1976**, 2681−2684. (c) Adam, W.; Carballiera, N.; Cheng, C.-C.; Sakanishi, K.; Gleiter, R. *J. Org. Chem.* **1979**, *44*, 851−853. (d) van den Heuvel, C. J. M.; Verhoeven, J. W.; de Boer, Th. *Recl. Trav. Chim. Pays-Bas* **1980**, 99, 280−284. (e) Hurst, J. R.; Schuster *J. Am. Chem. Soc.* **1982**, *104*, 6854−6856. (f) Reference 6b, Table 2, pp 291−295 and 298ff. (g) Monroe, B. M. In *Singlet O_2 − Volume I: Physical-Chemical Aspects*; Frimer, A. A., Ed.; Chemical Rubber Company: Boca Raton, FL, 1985; pp 177−224; see especially pp 201−206. (h) Reference 1h, p 71. (i) We note, however, that the IP/rate correlation is far from perfect,[29e−h] primarily because ionization potential is by no means the sole determinant of reaction rate.

(30) (a) Bischof, P.; Heilbronner, E. *Helv. Chim. Acta* **1970**, *53*, 1677−1682. (b) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J.; Brundle, C. R.; Kuebler, N. A. *J. Am. Chem. Soc.* **1976**, *98*, 7179−7182. (c) Turner, D. W. In *Molecular Photoelectron Microscopy*; Wiley-Interscience: New York, 1970. (d) Aue, D. H.; Mishishnek, M. J.; Shelhammer, D. F. *Tetrahedron Lett.* **1973**, 4799−4802.

(31) Cf. Jefford, C. W.; Rimbault, C. G. *Tetrahedron Lett.* **1981**, *22*, 91−94.

(32) Maignan, C.; Rouessac, F. *Bull. Chim. Soc. Fr.* **1974**, 2035−2039.

(33) Freerksen, R. W.; Selikson, S. J.; Wroble, R. R.; Kyler, K. S.; Watt, D. S. *J. Org. Chem.* **1983**, *48*, 4087−4096.

(34) (a) 13 ft × 1/4 in. copper column packed with 20% Carbowax 20M Chromosorb WAW. (b) 13 ft × 1/4 in. copper column packed with 7% SE−30 on Chromosorb WAW.

16b, and **19**. It should be noted that both **16a** and **16b** were obtained as a mixture of diastereomers and partially contaminated by cycloheptanone and enones **12a** or **12b** (presumably formed via retroaldol and dehydration, respectively; see below). Attempts to purify **16a** and **16b** by distillation merely increased the amount of contamination. As a result, ^{1}H NMR data could not be assigned, though ^{13}C NMR and HRMS data could be readily extracted. Acid (H_2SO_4)-catalyzed dehydration of the latter in methanol, following the method of Friedrich and co-workers,[9] yielded the corresponding enones **12a** (*Z*:*E* = 1:1), **12b** (*Z*:*E* = 1:1) and **20** in 50% yield. The residue was predominantly the corresponding cycloheptanone or cyclooctanone, presumably regenerated via a retroaldol process. Azeotropic dehydration of **19** in refluxing benzene (using *p*-TsOH and a Dean−Stark trap) generated **20** in 75% yield, again accompanied by cyclooctanone In the ^{1}H NMR below of **20**, $H_{1'}$ are the hydrogens on the isopropylidenyl methyl which is *cis* to the carbonyl, while $H_{3'}$ are those that are on the *trans* methyl.

(c) Cyclopropene Epoxidation Procedure. Enone **20** was also synthesized via the MCPBA epoxidation of cyclopropene **26** in CCl_4. GC of the product mixture gave the desired product along with an as yet unidentified isomer. The MCPBA epoxidation of **14a** and **14b** is reported in the literature to yield *E*- and *Z*-**12a** and **12b**, respectively.[9]

8: ^{1}H NMR ($CDCl_3$) δ 5.94 (t, $J_{2,3}$ = 6.5 Hz, 1H), 2.57−2.52 (m, 2H), 2.11 (m, 2H), 1.71−1.57 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 136.16, 128.77, 38.38, 30.72, 27.79, 26.71, 25.93.

9a: ^{1}H NMR ($CDCl_3$) δ 6.17 (dd, $J_{1,7a}$ = 6 Hz, $J_{1,7b}$ = 7 Hz, 1H), 3.77 (dd, $J_{3,4a}$ = 4 Hz, $J_{3,4b}$ = 6, 1H), 2.90 (sept, $J_{2',3'}$ = $J_{2',3''}$ = 7 Hz, 1H), 2.22−1.32 (m, 8H), 1.14 (d, $J_{2',3'}$ = 7, 3H), 1.10 (d, $J_{2',3''}$ = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 211.99, 132.29, 132.20, 59.34, 38.96, 27.90, 26.78, 26.11, 25.96, 18.83, 18.46.

9b:^{1}H NMR ($CDCl_3$) δ 6.16 (t, $J_{1,7}$ = 6.6 Hz, 1H), 3.54 (dd, $J_{3,4a}$ = 3.5 Hz, $J_{3,4b}$ = 6.5 Hz, 1H), 2.62 and 2.60 (ABq of q, J_{gem} = 18.5 Hz, $J_{2',3'}$ = 7 Hz, 2H), 1.85−1.42 (m, 8H), 1.08 (t, $J_{2',3'}$ = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 208.07, 132.44, 132.06, 60.93, 34.28, 27.98, 26.97, 26.08, 25.96, 7.83.

10a: ^{1}H NMR ($CDCl_3$) δ 3.87 (s, 4H), 3.18 (dd, $J_{6,7a}$ = 4 Hz, $J_{6,7b}$ = 10 Hz, 1H), 2.80 (sept, $J_{2',3'}$ = $J_{2',3''}$ = 7 Hz, 1H), 2.10−1.30 (m, 10H),1.04 (d, $J_{2',3'}$ = $J_{2',3''}$ = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 214.79, 112.76, 64.51, 63.94, 57.05, 41.96, 37.48, 28.27, 26.63, 26.51, 22.47, 18.36, 17.58.

10b: ^{1}H NMR ($CDCl_3$) δ 3.89−3.84 (m, 4H), 2.99 (dd, $J_{6,7a}$ = 10 Hz, $J_{6,7b}$ = 4 Hz, 1H), 2.62 and 2.40 (ABq of q, J_{gem} = 18 Hz, J_{vic} = 7 Hz, 2H), 1.88−1.50 (m, 10H), 1.02 (t, $J_{2',3'}$ = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 211.62, 112.65, 64.58, 63.86, 59.20, 37.43, 36.87, 26.88, 26.85, 26.12, 22.39, 7.82.

11a: ^{1}H NMR ($CDCl_3$) δ 4.10−3.72 (m, 4H), 2.80 (sept, $J_{2',3'}$ = $J_{2',3''}$ = 7 Hz, 1H), 2.50−1.30 (m, 11H), 1.1 (s, 3H), 0.93 (d, $J_{2',3'}$ = 7 Hz, 3H), 0.82 (d, $J_{2',3''}$ = 7 Hz, 3H).

11b: ^{1}H NMR ($CDCl_3$) δ 4.13−3.81 (m, 4H), 2.99 (dd, $J_{6,7a}$ = 10 Hz, $J_{6,7b}$ = 4 Hz, 1H), 2.45 (ABq of q, J_{gem} = 18 Hz, $J_{vic\ 2',3'}$ = 7 Hz, 2H), 1.89−1.26 (m, 10H), 1.16 (s, 3H), 0.89 (t, $J_{2'.3'}$ = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 112.66, 74.20, 63.70, 58.20, 44.86, 31.58, 28.86, 28.55, 25.94, 25.08, 24.01, 7.90.

Z-**12a**: R_f (5% ethyl acetate in hexane) 0.20; ^{1}H NMR ($CDCl_3$) δ 2.89 (sept, $J_{3',4'}$ = 7 Hz, 1H), 2.51−2.38 (m, 2H), 2.27−2.19 (m, 2H), 1.75−1.63 (m, H_4, 6H), 1.62 (s, 3H), 0.96 (d, $J_{3',4'}$ = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 210.84, 143.20, 136.63, 43.72, 31.42, 30.28, 28.79, 28.15, 24.35, 20.95, 11.63; HRMS calcd ($C_{12}H_{20}O$, M^+) 180.1514, obsd 180.1509.

E-**12a**: R_f (5% ethyl acetate in hexane) 0.27; ^{1}H NMR ($CDCl_3$) δ 2.85 (sept, $J_{3',4'}$ = 7 Hz, 1H), 2.55−2.41 (m, 2H), 2.37−2.19 (m, 2H), 1.73−1.60 (m, 6H), 1.59 (s, 3H), 1.01 (d, $J_{3',4'}$ = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 210.94, 144.01, 135.82, 43.74, 30.46, 29.81, 29.16, 27.99, 24.33, 20.41, 13.37; HRMS calcd ($C_{12}H_{20}O$, M^+) 180.1514, obsd 180.1511.

Z-**12b**: R_f (10% ethyl acetate in hexane) 0.27; ^{1}H NMR ($CDCl_3$) δ 2.57−2.44 (m, 2H), 2.38−2.28 (m, 2H), 2.12 (2q, $J_{3',4'}$ = 7 Hz, 2H), 1.85 (s, 3H), 1.77−1.58 (m, 6H), 1.05 (t, $J_{3',4'}$ = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 209.50, 142.36, 136.87, 43.81, 30.67, 28.97, 28.68, 28.51, 24.45, 18.03, 13.31; HRMS calcd ($C_{11}H_{18}O$, M^+) 166.1358, obsd 166.1355.

E-**12b**: R_f (10% ethyl acetate in hexane) 0.35; ^{1}H NMR ($CDCl_3$) δ 2.59−2.44 (m, 2H), 2.38−2.25 (m, 2H), 2.19 (2q, $J_{3',4'}$ = 7 Hz, 2H), 1.77 (s, 3H), 1.76−1.59 (m, 6H), 1.02 (t, $J_{3',4'}$ = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 209.50, 142.85, 136.31, 43.91, 30.67, 29.22, 28.38, 27.73, 24.56, 19.47, 12.20; HRMS calcd ($C_{11}H_{18}O$, M^+) 166.1358, obsd 166.1351.

15: ^{1}H NMR* ($CDCl_3$) δ 4.98 (t, $J_{2,3}$ = 6 Hz, 1H), 2.19 (m, 2H), 1.96 (m, 2H), 1.65 (m, 2H), 1.53 (m, 2H), 1.49 (m, 2H), 0.14 (s, 9H); ^{13}C NMR* ($CDCl_3$) δ 155.93, 108.55, 35.45, 31.51, 27.74, 25.29, 25.17, 0.16; MS (CI, 70 ev) *m*/*z* 185 (MH^+, 1.83%), 113 ($MH^+ - HSiMe_3$, 49.49%), 95 ($MH^+ - HOSiMe_3$, 14.58%); HRMS (CI) calcd ($C_{10}H_{21}OSi$, MH^+) 185.1361, obsd 185.1360.

16a: Mixture of diastereomers: MS (CI, 70 ev) *m*/*z* 199 (MH^+, 14%), 181 ($MH^+ - H_2O$, 100%), 113 ($MH^+ - C_5H_{10}O$, 89%); HRMS calcd ($C_{12}H_{23}O_2$, M^+) 199.1698, obsd 199.1670. Major diastereomer: ^{13}C NMR* ($CDCl_3$) δ 219.35, 75.77, 55.81, 44.27, 35.08, 28.25, 27.94, 23.87, 23.57, 19.87, 16.94, 15.81. Minor diastereomer: ^{13}C NMR* ($CDCl_3$) δ 218.86, 75.04, 55.66, 43.32, 33.07, 27.87, 27.72, 24.36, 23.63, 19.59, 17.57, 16.23.

16b: Mixture of diastereomers: MS (CI, 70 ev) *m*/*z* 185 (MH^+, 15%), 167 ($MH^+ - H_2O$, 100%), 113 ($MH^+ - C_4H_8O$, 38%); HRMS (CI) calcd ($C_{11}H_{21}O_2$, MH^+) 185.1541, obsd 185.1520. Major diastereomer: ^{13}C NMR* ($CDCl_3$) δ 218.79, 73.57, 57.99, 44.09, 32.95, 28.31, 28.20, 25.61, 23.81, 22.96, 7.55. Minor diastereomer: ^{13}C NMR* ($CDCl_3$) δ 218.20, 73.38, 57.42, 44.03, 31.34, 28.26, 28.11, 25.15 (C_3), 24.25 (C_6), 23.78 ($C_{1'}$), 7.40 ($C_{4'}$).

18: ^{1}H NMR* ($CDCl_3$) δ 4.70 (t, $J_{2,3}$ = 8 Hz, 1H), 2.14 (m, 2H), 1.97 (m, 2H), 1.55 (m, 2H), 1.49 (m, 2H), 1.46 (m, 4H), 0.16 (s, 9H); ^{13}C NMR* ($CDCl_3$) δ 153.05, 105.45, 31.05, 30.98, 27.83, 26.40, 26.36, 25.52, 0.45; MS (EI, 70 ev) *m*/*z* 198 (M^+, 26.19%), 183 ($M^+ - CH_3$, 36.00%), 115 ($M^+ - CHCOSiMe_3$, 29.16%); HRMS calcd ($C_{11}H_{22}OSi$, M^+) 198.1439, obsd 198.1400.

19: ^{1}H NMR* ($CDCl_3$) δ 3.52 (bs, 1H, OH), 2.55 (dd, $J_{2,3a}$ = 4 Hz, $J_{2,3b}$ = 11 Hz, 1H, H_2), 2.12 (m, 2H), 1.62−1.25 (m, 10H), 0.93 (s, 3H), 0.92 (s, 3H); ^{13}C NMR* ($CDCl_3$) δ 222.61, 71.13, 56.38, 45.39, 29.04, 28.36, 27.91, 26.73, 24.69, 24.64, 22.83; MS (CI, 70 ev) *m*/*z* 185 (MH^+, 100%), 167 ($MH^+ - H_2O$, 56%); HRMS (CI) calcd ($C_{11}H_{21}O_2$, MH^+) 185.1541, obsd 185.1560.

20: ^{1}H NMR ($CDCl_3$) δ 2.53 (inv quint, J = 3 Hz, 2H), 2.50−2.45 (m, 2H), 1.84 (s, 3H), 1.79 (s, 3H), 1.83−1.75 (m, 2H), 1.60−1.51 (m, 4H), 1.47−1.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 212.48, 136.66, 136.06, 49.51, 29.05, 27.61, 27.22, 26.65, 25.72, 22.70, 21.23; IR ($CDCl_3$) 1667 (s, C=O), 1600 (m, C=C) cm^{-1}; MS (EI, 70 eV) *m*/*z* 166 (M^+, 10.85%), 95 ($M^+ - CO-CH_3$-CCH_3-H, 16.48%), 82 ($COCC(CH_3)_2$, 34.96%), 67 ($COCCCH_3$, 42.92%); MS (CI, 70 ev) *m*/*z* 167 (MH^+, 100%), 151 ($MH^+ - CH_3$, 87.00%); HRMS (CI) calcd ($C_{11}H_{18}O$, MH^+) 167.1435, obsd 167.1430.

Preparation of $\Delta^{1,7}$-8-Isopropylbicyblo[5.1.0]octane (14a) and $\Delta^{1,7}$-8-Ethylbicyblo[5.1.0]octane (14b). The title compounds were prepared from alkylidenecycloheptanones **12a** and **12b**, respectively, as previously described by Friedrich and co-workers[9] (see Scheme 1), with the following minor modifications. After the preparation of tosylhydrazones **13** in methanol, the solvent was rotary evaporated at room temperature and the colored residue recrystallized from CH_2Cl_2/pentane. The white crystals were washed with methanol chilled to −70 °C. Cyclopropanes **14a** and **14b** (retention times: ca. 16 min) were separated by GC[34b] at 90 °C (injector and detector at 100 °C) with a flow rate of 200 mL/min. Compounds **13** and **14** are known;[9] the substantially improved and missing spectral data are recorded below.

13a, Major isomer: ^{1}H NMR ($CDCl_3$) δ 7.92−7.81 (m, 2H), 7.43−7.26 (m, 2H), 5.55 (s, 1H), 2.89 (sept, $J_{3',4'}$ = $J_{3',4''}$ = 7 Hz, 1H), 2.45 (s, 3H), 2.25−1.35 (m, 10H), 1.53 (s, 3H), 0.96 (d, $J_{3',4'}$ = $J_{3',4''}$ = 7 Hz, 6H); **Minor isomer**: ^{1}H NMR ($CDCl_3$) δ 7.92−7.81 (m, 2H), 7.43−7.26 (m, 2H), 5.55 (s, 1H), 2.89 (sept, $J_{3',4'}$ = $J_{3',4''}$ = 7 Hz, 1H), 2.45 (s, 3H), 2.25−1.35 (m, 10H), 1.13 (s, 3H), 0.69 (6H, d, $J_{3',4'}$ = $J_{3',4''}$ = 7 Hz); ***Z*−*E* mixture**: ^{13}C NMR ($CDCl_3$) δ 162.39, 143.73, 137.80, 137.48, 135.85, 128.09, 126.72, 36.22−25.83, 21.55, 18.43, 12.39.

13b, Major isomer: ^{1}H NMR ($CDCl_3$) δ 7.88−7.82 (m, 2H), 7.30−7.27 (m, 3H), 2.46 (s, 3H), 2.25−1.40 (m, 10H), 2.03 (q, $J_{3',4'}$ = 7 Hz, 1H), 1.63 (q, $J_{3',4'}$ = 7 Hz, 1H), 1.62 (s, 3H), 0.97

(t, $J_{3',4'}$ = 7 Hz, 3H); **Minor isomer**: ^{1}H NMR ($CDCl_3$) δ 7.88−7.82 (m, 2H), 7.30−7.27 (m, 3H), 2.46 (s, 3H), 2.25−1.40 (m, 10H), 2.03 (q, $J_{3',4'}$ = 7 Hz, 1H), 1.63 (q, $J_{3',4'}$ = 7 Hz, 1H), 1.23 (s, 3H), 0.65 (t, $J_{3',4'}$ = 7 Hz, 3H); ***Z*−*E* mixture**: ^{13}C NMR ($CDCl_3$) δ 162.39, 143.73, 137.80, 137.48, 135.85, 128.09, 126.72, 36.22−25.83, 21.55, 18.43, 12.39.

14a: ^{1}H NMR ($CDCl_3$) δ 2.50−2.18 (m, 4H), 1.93−1.43 (m, 7H), 1.10 (s, 3H), 0.75 (d, $J_{1',2'}$ = 6.7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 130.14, 36.40, 31.98, 29.71, 28.18, 26.69, 22.71, 21.09.

14b: ^{1}H NMR ($CDCl_3$) δ 2.41−2.22 (m, 4H), 1.87−1.77 (m, 4H), 1.61−1.43 (m, 2H), 1.56 (q, $J_{1',2'}$ = 7.5 Hz, 2H), 1.14 (s, 3H), 0.69 (t, $J_{1',2'}$ = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 131.41, 32.83, 31.99, 29.71, 28.26, 26.64, 24.42, 12.04.

General Photooxidation Procedure. The previously described[35] photooxidation apparatus was flushed with oxygen and charged with solvent (1−5 mL) containing substrate (0.2−8.0 mmol) as well as a spatula tipful of polymer-based Rose Bengal (p-RB, Dye Tel Inc., POB 23, Perrysburg, Ohio) to serve as photosensitizer. The photooxidation (λ > 360 nm) was allowed to proceed until an 1 equiv of O_2 had been absorbed or until oxygen uptake had essentially ceased. At times, it was necessary to stop the photooxidation and add new p-RB, because the intense red color of the sensitizer had faded to a pale pink. At the conclusion of the photooxidation, 1.1 equiv of triphenylphosphine was added to the reaction mixture to reduce any hydroperoxides present to the corresponding alcohols. The product solution was filtered through a cotton plug to remove the polymer-based sensitizer, and concentrated prior to gas or column chromatography. Where indicated, fractions proved to be a mixture of isomers; the ^{1}H and ^{13}C NMR data was extracted from this mixture. The products were identified by their spectral data and, where possible, by independent synthesis (vide infra). Once all the products had been identified, the product distribution was determined based on the spectrum of the crude reaction mixture. DABCO (10^{-5} to 10^{-3} M)[21b,c] and DTBP (0.4 M) were added to the photooxidation solution to determine, respectively, whether $^1O_2$ or free radical processes, respectively, were involved.

Photooxidation of Cyclopropenes 14a, 14b, and 26. The title cyclopropenes were dissolved in solvent ($CHCl_3$ for **14a** and **14b**, CH_3CN for **20**) and irradiated, according to the above general oxidation procedure. The addition of Ph_3P generated no heat and had little if any effect on the product distribution; hence, workup of the reaction mixtures proceeded without prior addition of Ph_3P. The products were separated by preparative GC[33a] (oven: 140 °C; injector and detector: 200 °C; flow: 75 mL/min.). In the case of bicyclooctenes **14a** and **14b**, both dienes and enones were obtained. The relative total amount of dienes isolated by GC**,** as compared to the total amount of enones observed, varied from photooxidation to photooxidation; it was simply proportional, however, to the amount of unreacted substrate remaining (as approximated by the amount of oxygen uptake). Product distribution within each group is shown in Tables 1 and 2. Dienes **30a**, **30b**, and **31b** were independently synthesized as described below. Compound **43** is known;[32] the substantially improved and missing spectral data are recorded below. Compound **43** was also independently synthesized via the Grignard addition of isopropenylmagnesium bromide[32] to cyloocta-1,2-dione.[36] Attempted dehydration of **43** with thionyl chloride and pyridine[37] yielded only a few percent of **44**. The carbon numbering in the data below is as shown in Scheme 3. *Z*/*E* assignments were based on NOE experiments. In **34a** and **34b**, no ^{13}C NMR carbonyl absorption was observed.

When **14a** was injected into the GC,[34b] with the injector and detector set for 190 °C and the column at 120 °C, the products *E*- and *Z*-**29a** and **30a** were obtained essentially in the ratio of Table 1. Similarly, heating a neat sample of **14a** to 170 °C for 0.5 h gave the same results. When **14b** was injected into the GC[34b] as above, the products *E*- and *Z*-**29b** were obtained exclusively, in a 1:1 ratio; heating a neat sample of **14b** to 170 °C for 0.5 h yielded equivalent amounts of **30b** and **31b**.

29a (*E*/*Z* mixture): MS (CI, methane, 70 eV) *m*/*z* 181 (MH^+ + CH_4, 72.6%), 165 (MH^+, 47.9%), 149 ($MH^+ - CH_4$, 36.3%), 109 ($MH^+ - C_4H_8$, 51.3%), 95 ($MH^+ - C_5H_{10}$, 100%); HRMS exact mass calcd for $C_{12}H_{20}$ (M^+) 164.1565, found 164.1644. *Z*-**29a**: ^{1}H NMR ($CDCl_3$) δ 6.39 (d, $J_{1,2}$ = 11 Hz, 1H), 5.61 (dt, $J_{1,2}$ = 11 Hz, $J_{1,7}$ = 5 Hz, 1H), 2.92 (sept, $J_{3',4''}$ = 7 Hz, 1H), 2.38 (t, $J_{4,5}$ = 6 Hz, 2H), 2.18 (m, 2H), 1.69−1.60 (m, 4H), 1.58 (s, 3H), 0.94 (d, $J_{3',4'}$ = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 137.22, 131.19, 129.79, 129.60, 30.90, 28.52, 28.46, 27.00, 26.08, 20.54, 11.30. *E*-**29a**: ^{1}H NMR ($CDCl_3$) δ 6.30 (d, $J_{1,2}$ = 11 Hz, 1H), 5.64 (dt, $J_{1,2}$ = 11 Hz, $J_{1,7}$ = 5 Hz, 1H), 2.94 (sept, $J_{3',4'}$ = 7 Hz, 1H), 2.42 (t, $J_{4,5}$ = 6 Hz, 2H), 2.18 (m, 2H), 1.69−1.60 (m, 4H), 1.58 (s, 3H), 0.96 (d, $J_{3',4'}$ = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 137.22, 132.35, 129.79, 129.60, 30.26, 29.90, 29.51, 27.96, 26.25, 21.05, 12.20.

29b (*E*/*Z* mixture): MS (CI, methane, 70 eV) *m*/*z* 151 (MH^+, 100%), 135 ($M^+ - CH_3$, 6.8%), 109 ($M^+ - C_3H_5$, 21.3%), 95 ($M^+ - C_4H_7$, 67.2%), 81 ($M^+ - C_5H_9$, 41.3%); HRMS exact mass calcd for $C_{11}H_{18}$ (M^+) 150.1216, found 150.1408. *E*-**29b**: ^{1}H NMR* ($CDCl_3$) δ 6.30 (d, $J_{1,2}$ = 11 Hz, 1H), 5.63 (dt, $J_{1,2}$ = 11 Hz, $J_{1,7}$ = 5.5 Hz, 1H), 2.39 (q, J = 5.5 Hz, 2H), 2.19 (m, 2H), 2.09 (m, 2H), 1.71 (s, 3H), 1.70−1.60 (m, 4H), 0.99 (t, $J_{3',4'}$ = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 133.97, 131.72, 130.55, 129.82, 30.01, 28.31, 27.83, 27.13, 26.50, 18.08, 13.26. *Z*-**29b**: ^{1}H NMR* ($CDCl_3$) δ 6.34 (d, $J_{1,2}$ = 11 Hz, 1H), 5.61 (dt, $J_{1,2}$ = 11 Hz, $J_{1,7}$ = 5.5 Hz, 1H), 2.38 (q, J = 5.5 Hz, 2H), 2.19 (m, 2H), 2.10 (q, $J_{3',4'}$ = 7.5 Hz, 2H), 1.71 (s, 3H), 1.70−1.60 (m, 4H), 0.96 (t, $J_{3',4'}$ = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 134.00, 131.01, 130.46, 129.72, 30.59, 28.31, 27.62, 26.90, 26.31, 17.42, 12.66.

30a: ^{1}H NMR ($CDCl_3$) δ 5.85 (t, $J_{2,3}$ = 7 Hz, 1H), 4.84 (d, $J_{1',1''}$ = 1.5 Hz, 1H), 4.70 (t, $J_{1'',3'}$ = $J_{1',1''}$ = 1.5 Hz, 1H), 2.51 (m, 1H), 2.26 (m, 2H), 2.16 (m, 2H), 1.76 (m, 2H), 1.51 (m, 4H), 1.04 (d, $J_{3',4'}$ = 7 Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 158.84, 146.10, 127.76, 105 0.86 ($C_{1'}$), 98.94, 32.70, 31.36, 30.32, 26.67, 26.90, 22.33; MS (EI, 70 eV) *m*/*z* 164 (M^+, 100%), 149 ($M^+ - CH_3$, 20.3%), 135 ($M^+ - C_2H_5$, 5.6%), 121 ($M^+ - C_3H_7$, 58.18%), 107 ($M^+ - C_4H_9$, 38.96%), 93 ($M^+ - C_5H_{11}$, 19.07%); HRMS (CI) calcd ($C_{12}H_{21}$, MH^+) 165.1600, obsd 165.1643.

30b: ^{1}H NMR* ($CDCl_3$) δ 5.95 (t, $J_{2,3}$ = 7 Hz, 1H), 4.92 (d, $J_{1',1''}$ = 1 Hz, 1H), 4.78 (dt, $J_{1',1''}$ = 1 Hz, 1H, $J_{1'',3'}$ = 0.5 Hz), 2.23 (m, 4H), 2.19 (m, 2H), 1.76 (m, 2H), 1.49 (m, 2H), 1.47 (m, 2H), 1.04 (t, $J_{3',4'}$ = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 152.10, 144.74, 128.14, 107.87, 32.62, 30.00, 28.42, 26.98, 26.78, 26.51, 13.42; MS (EI, 70 eV) *m*/*z* 151 (MH^+, 35.86%), 150 (M^+, 8.11%), 135 ($M^+ - CH_3$, 6.56%), 121 ($M^+ - C_2H_5$, 9.78%), 111 ($M^+ - C_3H_7$, 16.56%), 109 ($M^+ - C_3H_5$, 19.51%), 97 ($M^+ - C_4H_9$, 14.12%), 95 ($M^+ - C_4H_7$, 53.00%); HRMS (CI) calcd ($C_{11}H_{19}$, MH^+) 151.1430, obsd 151.1486.

31b: ^{1}H NMR* ($CDCl_3$) δ 5.84 (t, $J_{2,3}$ = 7 Hz, 1H), 5.54 (q, $J_{3',4'}$ = 6 Hz, 1H), 2.32 (m, 2H), 2.18 (m, 2H), 1.75 (m, 2H), 1.74 (s, 3H), 1.68 (d, $J_{3',4'}$ = 6 Hz, 3H), 1.47 (m, 2H) 1.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 147.26, 137.70, 126.36, 118.60, 32.77, 29.48, 28.45, 27.01, 26.71, 14.12, 14.09; **MS** (EI, 70 eV) *m*/*z* 151 (MH^+, 35.86%), 150 (M^+, 8.11%), 135 ($M^+ - CH_3$, 6.56%), 121 ($M^+ - C_2H_5$, 9.78%), 111 ($M^+ - C_3H_7$, 16.56%), 109 ($M^+ - C_3H_5$, 19.51%), 97 ($M^+ - C_4H_9$, 14.12%), 95 ($M^+ - C_4H_7$, 53.00%); HRMS (CI) calcd ($C_{11}H_{19}$, MH^+) 151.1450, obsd 151.1486.

32a: ^{1}H NMR ($CDCl_3$) δ 6.61 (t, $J_{3,4}$ = 6.5 Hz, 1H), 2.61 and 2.57 (m, J_{gem} = 14 Hz, 2H), 2.41 (m, 2H), 1.98 (sept, $J_{3',4'}$ = $J_{3',4''}$ = 7 Hz, 1H), 1.80 (m, 2H), 1.69 (m, 2H), 1.23 (s, 3H), 0.93 (d, $J_{3',4'}$ = 7 Hz, 3H), 0.79 (d, $J_{3',4''}$ = 7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 141.2, 139.34, 43.42, 35.97, 27.51, 24.64, 22.25, 21.90, 18.24, 17.02; MS (EI, 70 eV) *m*/*z* 196 (M^+, 1.1%), 178 ($M^+ - H_2O$, 4.08%), 163 ($M^+ - H_2O - CH_3$, 2.98%), 153 ($M^+ - C_3H_7$, 100%), 125 ($M^+ - C_4H_7O$, 8.15%), 111 ($M^+ - C_5H_9O$, 15.0%), 97 ($M^+ - C_6H_{11}O$, 25.23%), 83 ($M^+ - C_7H_{13}O$, 24.49%), 69 (M^+

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(36) (a) The dione was prepared according to Wittig, G.; Krebs, A. *Chem. Ber.* **1961**, *94*, 3260 and purified by column chromatography [R_f (50% acetone in petetroleum ether) 0.70]. See also: Hach, C. C.; Banks, C. V.; Diehl, H. *Organic Syntheses*; Wiley: New York, 1963; Coll. Vol. IV, pp 229−232. (b) Spectral data is reported in Amon, C. M.; Banwell, M. G.; Gravatt, G. L. *J. Org. Chem.* **1987**, *52*, 4851−4855. See also: Bauer, D. P.; Macomber, R. S. *J. Org. Chem.* **1975**, *40*, 1990−1992.

(37) Alexandre, C.; Rouessac, F. *Bull. Chim. Soc. Fr.* **1977**, 117−119.

$-C_8H_{15}O$, 37.75%); HRMS calcd ($C_{12}H_{20}O_2$, M^+, 1.1%) 196.1463, obsd 196.1081; HRMS calcd ($C_9H_{13}O_2$, $M^+ - C_3H_7$, 100%) 153.0915, obsd 153.0914.

32b: ^{1}H NMR ($CDCl_3$) δ 6.63 (t, $J_{3,4} = 6$ Hz, 1H), 4.10−4.00 (m, 1H), 2.60 (t, $J_{6,7} = 7.5$ Hz, 1H), 2.58 (t, $J_{6,7} = 7.5$ Hz, 1H), 2.45−2.38 (m, 2H), 1.88−1.80 (m, 2H), 1.79−1.71 (m, 2H), 1.69 (q, $J_{3',4'} = 7.5$ Hz, 2H), 1.33 (s, 3H), 0.81 (t, $J_{3',4'} = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 209.25, 147.16, 139.36, 75.65, 43.34, 34.42, 27.35, 26.29, 24.57, 22.03, 8.93; FTIR ($CDCl_3$) 3422 (bs, OH), 1710 (s, C=O), 1661 (s, C=C) cm^{-1}; MS (EI, 70 eV) *m/z* 182 (M^+, 7.7%), 167 ($M^+ - CH_3$, 16.2%), 153 ($M^+ - CH_2CH_3$, 100%); HRMS calcd ($C_{11}H_{18}O_2$, M^+) 182.1307, obsd 182.1281.

34a: ^{1}H NMR ($CDCl_3$) δ 6.47 (t, $J_{3,4} = 6.5$ Hz, 1H), 4.94 (t, $J_{1',1''} = J_{1',3'} = 1.5$ Hz, 1H), 4.87 (dd, $J_{1',1''} = 1.5$ Hz, $J_{1'',3'} = 1$ Hz, 1H), 2.62 (inv quint, $J = 3$ Hz, 2H), 2.44 (sept, $J_{3',4'} = 7$ Hz, 1H), 2.40 (q, $J_{3,4} = J_{4,5} = 6.5$ Hz, 2H), 1.84 (m, 2H), 1.74 (m, 2H), 1.01 (d, $J_{3',4'} = 7$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 139.91, 135.77, 129.20, 111.40, 42.89, 31.41, 24.86, 24.69, 22.32, 21.79; MS (CI, methane, 70 eV) *m/z* 179 (MH^+); MS (EI, 70 eV) *m/z* 178 (M^+, 12.3%), 135 ($M^+ - C_3H_7$, 12.86%), 107 ($M^+ - C_5H_{11}$, 11.11%), 91 (21.43%); HRMS calcd ($C_{12}H_{18}O$, M^+) 178.1358, obsd 178.1353.

34b: ^{1}H NMR ($CDCl_3$) δ 6.38 (t, $J_{3,4} = 7$ Hz, 1H), 4.88 (m, 1H), 4.85 (m, 1H), 2.40−2.10 and 1.90−1.10 (m, 8H), 2.06 (q, $J_{3',4'} = 7.5$ Hz, 2H), 0.97 (t, $J_{3',4'} = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 136.88, 134.20, 131.88, 112.73, 43.75, 30.73, 29.70−24.38, 12.25; HRMS (CI) calcd ($C_{11}H_{17}O_1$, MH^+) 165.1279, obsd 165.1334.

35a: ^{1}H NMR ($CDCl_3$) δ 6.38 (t, $J_{3,4} = 6.5$ Hz, 1H), 2.55 (inv quint, $J = 3$ Hz, 2H), 2.42 (m, 2H), 1.93 (m, 2H), 1.77 (m, 2H), 1.71 (s, 6H), 1.57 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 195.80, 142.18, 138.91, 130.10, 129.77, 42.90, 27.71, 29.71, 25.22, 21.81, 21.81, 20.03; MS (CI, 70 eV) *m/z* 179 (MH^+, 26.40%), 163 ($MH^+ - O$, 29.9%), 150 ($MH^+ - C_2H_5$, 10.96%), 135 ($MH^+ - C_3H_7$, 29.4%), 121 ($MH^+ - C_4H_9$, 15.8%), 107 ($MH^+ - C_5H_{11}$, 28.3%), 93 ($MH^+ - C_6H_{13}$, 40.8%), 71 (C_5H_{11}, 100%); HRMS calcd ($C_{12}H_{18}O$, M^+) 178.1358, obsd 178.1344.

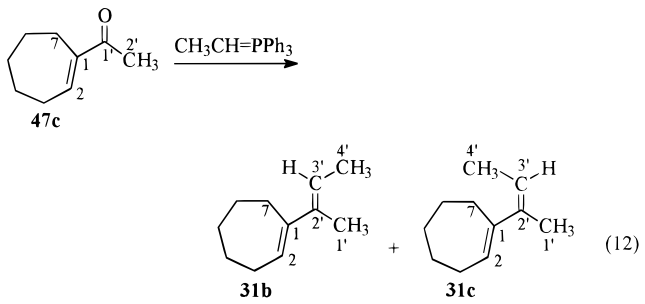
42: R_f (10% acetone in hexane) 0.23; ^{1}H NMR ($CDCl_3$) δ 6.06 (t, $J_{3,4} = 5.5$ Hz, 1H), 2.53 (inv quint, $J = 4$ Hz, 2H), 2.25 (m, 2H), 1.88 (m, 2H), 1.61 (m, 4H), 1.37 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 215.04, 143.91, 129.38, 71.29, 46.42, 29.41, 22.01, 22.54, 29.04, 29.27; HRMS calcd ($C_{11}H_{18}O_2$, M^+) 182.1306, obsd 182.1345.

43: R_f (20% acetone in hexane) 0.33; ^{1}H NMR* ($CDCl_3$) δ 5.15 (bs, 1H), 5.06 (bs, 1H), 4.20 (bs, 1H), 2.88 and 2.15 (m, 2H), 2.58 and 2.01 (m, 2H), 1.90 and 1.74 (m, 2H), 1.83 and 1.43 (m, 2H), 1.78 and 1.34 (m, 2H), 1.66 and 0.96 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 217.31, 145.91, 113.97, 82.32, 35.41, 30.15, 30.46, 25.36, 24.37, 22.72, 18.26; HRMS calcd ($C_{11}H_{19}O_2$, MH^+) 183.1385, obsd 183.1350.

44: ^{1}H NMR ($CDCl_3$) δ 5.88 (t, $J_{3,4} = 7$ Hz, 1H), 4.94 (bs, 1H), 4.69 (bs, 1H), 2.51 (inv quint., $J = 3.5$ Hz, 2H), 2.29−2.22 (m, 2H), 1.90 (t, $J_{3',1'} = J_{3',1''} = 0.75$ Hz, 3H), 1.88−1.82 (m, 2H), 1.69−1.62 (m, 4H); HRMS (CI) calcd ($C_{11}H_{27}O$, MH^+) 165.1279, obsd 165.1289.

45: R_f (10% acetone in hexane) 0.60; ^{1}H NMR ($CDCl_3$) δ 6.29 (d, $J_{3,4} = 12$ Hz, 1H), 5.61 (dt, $J_{3,4} = 12$ Hz, $J_{4,5} = 9$ Hz, 1H), 2.48 (inv quint., $J = 3$ Hz, 2H), 2.09−2.01 (m, 2H), 1.94−1.87 (m, 2H), 1.85 (bs, 6H), 1.58−1.50 (m, 2H); MS (EI, 70 eV) *m/z* 164 (M^+, 64.56%), 149 ($M - CH_3$, 32.71%), 135 ($M - HCO$, 30.19%); 121 ($M - CO - CH_3$, 46.30%); HRMS (CI) calcd ($C_{11}H_{27}O$, MH^+) 165.1279, obsd 165.1291.

Preparation of 1-(1-Isopropylvinyl)cycloheptene (30a), 1-(1-Ethylvinycycloheptene (30b), and 1-(1-Methylpropenyl)cycloheptene (31b). The title compounds were independently synthesized as outlined in eq 4. Friedel−Crafts acylation of cycloheptene (**7**)[9,13] yielded β-chloroketones **46a**, **46b**, and **46c**, which underwent elimination in hot ethanolic NaOH to the known corresponding enones **47**.[33] It should be pointed out that this elimination of HCl is a very facile process and often occurs spontaneously. Indeed, it is difficult to obtain pure samples of β-chloroketones **46** (which is contaminated with cycloheptene and other unidentified alkanes), since during silica column chromatography (eluting with ethyl acetate/hexane) variable amounts of enones **47** are generated and elute together with the β-chloroketones **46**. The stability of the latter increases as the alkyl group on the ketone becomes more bulky; thus **46a** is markedly more stable than **46c**, and only a small amount of **47a** is generated on chromatography. The β-chloroketones **46** were primarily characterized by their molecular weight (HRMS) and by the characteristic NMR data for H-2, i.e., the hydrogen α to the carbonyl and β to the chlorine, which consistently appears at 4.45 ppm as a ddd. The large $J_{1,2} = 9.8$ Hz in **46a** indicates that H_1 and H_2 are quasi-*trans a,a* to each other (i.e., that the chlorine and acyl group are in a quasi *trans e,e* relationship). Finally, reacting enones **47a**, **47b**, and **47c**, respectively, with methyl, ethyl, and *sec*-butyltriphenylphosphonium bromide and BuLi in THF generated the corresponding dienes **30a**, **30b**, and **31b**. The Wittig reagents were commercially available (Aldrich) or prepared by heating a 1:1 mixture of the bromides and Ph_3P in a sealed ampule overnight at 150 °C; the resulting salt was recrystallized from ethanol and vacuum-dried. Interestingly, in the case of the preparation of **31b**, NMR studies on the isolated product revealed it to be ca. 80% in the *E*-conformation (**31b**), and 20% in the corresponding *Z*-conformation (**31c**; see eq 12).



(12)

31c: ^{1}H NMR* ($CDCl_3$) δ 5.55 (t, $J_{2,3} =$ t Hz,1H), 5.13 (q, $J_{3',4'} = 6.5$ Hz, 1H), 2.32 (m, 2H), 2.18 (m, 2H), 1.75 (m, 2H), 1.73 (m, 3H), 1.59 (d, $J_{3',4'} = 6.5$ Hz, 3H), 1.48 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 144.51, 141.17, 128.87, 118.22, 32.88, 32.27, 28.62, 27.41, 27.09, 23.19, 14.71.

46a: ^{1}H NMR ($CDCl_3$) δ 4.45 (ddd, $J_{1,2} = 9.8$ Hz, $J_{2,3} = 7.5$ and 4.2 Hz, 1H), 3.07 ($J_{1,2} = 9.8$ Hz, $J_{1,7} = 9.0$ and 2.8 and 4.2 Hz, 1H), 2.74 (sept, $J_{2',3'} = 7$ Hz, 1H), 2.18 (dddd, $J_{gem} = 15$ Hz, $J_{3,4} = 8.8$ and 1.8 Hz, $J_{2,3} = 4.2$ Hz, 1H), 2.06 (dddd, $J_{gem} = 15$, $J_{3,4} = 10$ and 1.8 Hz, $J_{2,3} = 7.5$ Hz, 1H), 1.85−1.49 (m, 6H), 1.65 and 1.45 (m, 1H), 1.127 (d, $J_{2',3'} = 7$ Hz, 3H), 1.129 (d, $J_{2',3''} = 7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 62.22, 59.61, 40.65, 37.44, 28.34, 28.24, 26.84, 23.41, 18.14, 17.98; MS (CI, 70 ev) *m/z* 205 ($MH^+ + 2$, 35.62%), 203 (MH^+, 100%), 167 ($MH^+ -$ HCl, 53.75%); HRMS (CI) calcd ($C_{11}H_{20}OCl$, MH^+) 203.1203, obsd 203.1240.

46b: ^{1}H NMR ($CDCl_3$) δ 4.45 (ddd, 1H); ^{13}C NMR ($CDCl_3$) δ 62.35, 61.02, 37.38, 35.96, 28.09, 27.97, 26.61, 23.39, 7.62; MS (CI, 70 ev) *m/z* 191 ($MH^+ + 2$, 9.33%), 189 (MH^+, 26.94%); 153 ($MH^+ -$ HCl, 53.75%); HRMS (CI) calcd ($C_{10}H_{18}OCl$, MH^+) 189.1046, obsd 189.0990.

46c: ^{1}H NMR ($CDCl_3$) δ 4.45 (ddd, 1H); MS (CI, 70 ev) *m/z* 174 (MH^+, 39.03%); 139 ($MH^+ - Cl$, 73.75%); HRMS (CI) calcd ($C_9H_{15}OCl$, MH^+) 174.0811, obsd 174.0720; calcd ($C_9H_{15}O$, $MH^+ - Cl$) 139.1140, obsd 139.1138.

47a: ^{1}H NMR ($CDCl_3$) δ 7.06 (t, $J_{2,3} = 7$ Hz, 1H), 3.31 (sept, $J_{2',3'} = 4$ Hz, 1H), 2.50 (m, 2H), 2.35 (m, 2H), 1.79 (m, 2H), 1.55 (m, 2H), 1.46 (m, 2H), 1.08 (d, $J_{2',3'} = 4$ Hz, 6H); ^{13}C NMR ($CDCl_3$) δ 205.77, 145.12, 143.29, 33.64, 32.37, 29.08, 26.22, 26.05, 25.90, 19.73; MS (CI, 70 ev) *m/z* 167 (MH^+, 100%), 97 ($MH^+ - CH_3CO$, 13.05%); HRMS (CI) calcd ($C_{11}H_{19}O$, MH^+) 167.1435, obsd 167.1370.

47b: ^{1}H NMR ($CDCl_3$) δ 7.09 (t, $J_{2,3} = 6$ Hz, 1H), 2.67 (q, $J_{2',3'} = 7$ Hz, 2H), 2.49 (m, 2H), 2.34 (m, 2H), 1.78 (m, 2H), 1.55 (m, 2H), 1.47 (m, 2H), 1.09 (t, $J_{2',3'} = 7$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 201.85, 145.78, 143.74, 32.17, 30.05, 28.92, 26.04, 25.73, 25.51, 8.91; MS (CI, 70 ev) *m/z* 153 (MH^+, 100%); HRMS (CI) calcd ($C_{10}H_{17}O$, MH^+) 153.1279, obsd 153.1300.

47c: ^{1}H NMR ($CDCl_3$) δ 7.09 (t, $J_{2,3} = 7$ Hz, 1H), 2.49 (m, 2H), 2.35 (m, 2H), 2.30 (s, 3H), 1.77 (m, 2H), 1.55 (m, 2H),

1.46 (m, 2H); MS (CI, 70 ev) *m/z* 139 (MH^+, 2.81%), 123 ($MH^+ - CH_3$, 4.23%), 95 ($MH^+ - CH_3CO$, 100%); HRMS (CI) calcd ($C_9H_{15}O$, MH^+) 139.1122, obsd 139.1120.

Photooxidation of Enones 12a and 12b. The title compounds were dissolved in CH_3CN or $CHCl_3$ and irradiated, according to the above general oxidation procedure. After an uptake of an equivalent of O_2, concentration of the solvent and direct preparative TLC (eluting with 10% acetone in hexane for **12a**, or 10% ethyl acetate in hexane for **12b**) yielded the hydroperoxide products **51** and **52**. The latter can then be reduced to alcohols **33** and **32,** respectively, with 1.1 equiv of Ph_3P. Hydroperoxide **51**, but not cyclic peroxide **52**, can be reduced by 2 equiv of thiourea (in 1:1 $CHCl_3/CH_3OH$). Alternatively, upon conclusion of the irradiation, Ph_3P can be added prior to chromatography, in which case the corresponding alcohols **33** and **32** are isolated. In the singlet oxygenation of **12a**, peroxides **51a** and **52a** (or the corresponding alcohols **33a** and **32a**) are formed in a 1:3 ratio, respectively. In the case of **12b**, **51b** and **52b** (or **33b** and **32b**) are formed in a 1:2 ratio, respectively. The spectral data for **32a** [R_f (10% acetone in hexane) 0.33] and **32b** [R_f (5% ethyl acetate in hexane) 0.21] appear above. We found it difficult to purify compound **33b** by TLC since it has essentially the same R_f as enone **12b**. The NMR spectral data for **52** reveals the presence of two diastereomeric forms in a ratio of 2:1 for **52a** and 1.2:1 for **52b**. NOE studies reveal the major isomer in each case has the methyl and hydroxyl groups *cis* to each other. The numbering of the carbons of compounds **51**, **52**, **54**, and **55** are as shown in Scheme 4.

33a: R_f (10% acetone in hexane) 0.42; ^{1}H NMR ($CDCl_3$) δ 5.09 (bs, 1H), 5.07 (bs, 1H), 4.12 (bs, 1H), 2.81 (dt, $J_{gem} = 12$ Hz, $J_{6,7} = 3$ Hz, 1H), 2.44 (m, 1H), 2.43 (sept, $J_{3',4'} = 7.5$ Hz, 1H), 2.25−1.66 and 1.56−1.36 (8H, m), 1.08 (d, $J_{3',4'} = 7.5$ Hz, 3H), 0.97 (d, $J_{3',4''} = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 214.73, 157.65, 110.08, 80.00, 39.14, 34.85, 30.50, 28.30, 27.87, 24.60, 24.54, 23.28; MS (CI, 70 eV) *m/z* 195 (MH^+, 12.7%), 179 ($MH^+ - H_2O$, 100%); FTIR ($CDCl_3$) 3450 (br, s, OH), 1699 (s, C=O) cm^{-1}; HRMS calcd ($C_{12}H_{20}O_2$, M^+) 196.1463, obsd 196.1425.

33b: R_f (20% acetone in hexane) 0.33; ^{1}H NMR* ($CDCl_3$) δ 5.02 (bs, 1H), 4.98 (bs, 1H), 4.61 (bs, 1H), 2.79 (ddd, $J_{gem} = 13$ Hz, $J_{6,7} = 11$ and 3 Hz, 1H), 2.43 (m, 1H), 2.13 (m, 1H), 2.01 (m, 1H), 1.98 (m, 1H), 1.97 (m, 1H), 1.82 (m, 1H), 1.48−1.38 (m, 4H), 1.45 (m, 1H), 1.04 (t, $J_{3',4'} = 7.5$ Hz, 3H); MS (CI, 70 eV) *m/z* 165 (MH^+-H_2O, 70%); HRMS calcd ($C_{11}H_{18}O_2$, M^+) 182.1306, obsd 182.1372.

51a: R_f (10% acetone in hexane) 0.43; ^{1}H NMR ($CDCl_3$) δ 5.25 (bs, 1H), 4.85 (bs, 1H), 2.90 (m, 1H), 2.72 (td, $J_{gem} = 12$ Hz, $J_{6,7} = 3$ Hz, 1H), 2.48 (m, 3H), 2.25 (m, 1H), 2.00−1.75 (m, 5H), 1.15 (d, $J_{3',4'} = 6$ Hz, 3H), 1.10 (d, $J_{3',4''} = 6$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 217.48, 154.30, 113.92, 94.62, 42.35, 33.16, 30.11, 27.89, 27.43, 24.73, 24.61, 24.06; FTIR ($CDCl_3$) 3410 (br s, OH), 1712 (s, CO) cm^{-1}; MS (CI, 70 ev) *m/z* 213 (MH^+, 10%), 195 ($MH^+ - H_2O$, 100%), 179 ($MH^+ - H_2O_2$, 84%); HRMS (CI) calcd ($C_{12}H_{21}O_3$, MH^+) 213.1490, obsd 213.1510.

51b: R_f (10% acetone in hexane) 0.37; ^{1}H NMR ($CDCl_3$) δ 5.15 (bs, 1H), 4.80 (bs, 1H), 2.72 (td, $J_{gem} = 12$ Hz, $J_{6,7} = 3$ Hz, 1H), 2.48 (ddd, $J_{gem} = 12$ Hz, $J_{6,7} = 6$ and 3 Hz, 1H), 2.20 (m, 2H), 2.17−1.38 (m, 8H), 1.12 (t, $J_{3',4'} = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 212.29, 148.49, 113.75, 94.13, 42.43, 33.16, 30.28, 27.43, 24.21, 22.84, 11.78; MS (CI, 70 ev) *m/z* 199 (MH^+, 7.79%), 181 ($MH^+ - H_2O$, 61.51%), 165 ($MH^+ - H_2O_2$, 100%); HRMS (CI) calcd ($C_{11}H_{19}O_3$, MH^+) 199.1334, obsd 199.1370.

52a: Mixture of diastereomers: R_f (10% acetone in hexane) 0.29; FTIR ($CHCl_3$) 3419 (br, s, OH) cm^{-1}; MS (CI, 70 ev) *m/z* 213 (MH^+, 0.18%), 195 ($MH^+ - H_2O$, 10%), 179 ($MH^+ - H_2O_2$, 83%), 153 ($MH^+ - CH_3CO_2H$, 100%); HRMS (CI) calcd ($C_{12}H_{21}O_3$, MH^+) 213.1490, obsd 213.1450. *cis*-**52**: ^{1}H NMR ($CDCl_3$) δ 5.59 (m, 1H), 2.92 (bs, 1H), 2.27 (m, 1H), 2.10−1.80 (m, 8H), 1.21 (s, 3H), 0.98 (d, $J_{3',4'} = 6.6$ Hz, 3H), 0.92 (d, $J_{3',4''} = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 152.46, 123.82, 105.76, 90.35, 33.95, 32.52, 27.87, 26.81, 25.37, 17.76, 17.05; *trans*-**52**: ^{1}H NMR ($CDCl_3$) δ 5.54 (m, 1H, 3.00 (bs, 1H), 2.27 (m, 1H), 2.10−1.80 (m, 8H), 1.38 (s, 3H), 1.05 (d, $J_{3',4'} = 6.6$ Hz, 3H), 1.02 (d, $J_{3',4''} = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 151.71, 122.06, 105.76, 90.29, 34.32, 33.34, 27.35, 26.81, 24.79, 24.90, 17.60, 17.20.

52b: Mixture of diastereomers: R_f (10% acetone in hexane) 0.29; FTIR ($CHCl_3$) 3457 (br, s, OH), 1701.8 (m, conjugated CO) cm^{-1}; MS (CI, 70 ev) *m/z* 199 (MH^+, 4.40%), 181 ($MH^+ - H_2O$, 100%), 165 ($MH^+ - H_2O_2$, 68%); HRMS (CI) calcd ($C_{11}H_{19}O_3$, MH^+) 199.1334, obsd 199.1374. *cis*-**52b**: ^{1}H NMR* ($CDCl_3$) δ 5.565 (dd, $J_{3,4} = 8.5$ Hz and 4 Hz, 1H), 2.94 (bs, 1H), 2.32 (m, 1H), 2.18 (m, 1H), 2.04 (m, 1H), 1.90 (m, 2H), 1.58 (m, 1H), 1.40 (m, 2H), 1.75 and 1.51 (ABq, $J_{gem} = 14$ Hz, $J_{3',4'} = 7.5$ Hz, 2H), 1.31 (s, 3H), 0.93 (t, $J_{2',3'} = 7.5$ Hz, 3H);^{13}C NMR ($CDCl_3$) δ 155.04, 123.23, 105.47, 87.65, 32.92, 32.46, 27.79, 26.81, 25.24, 21.22, 8.33. *trans*-**52b**: ^{1}H NMR* ($CDCl_3$) δ 5.51 (dd, $J_{3,4a} = 8.5$ Hz, $J_{3,4b} = 4$ Hz, 1H), 2.88 (bs, 1H), 2.32 (m, 1H), 2.18 (m, 1H), 2.08 (m, 1H), 1.90 (m, 2H), 1.60 (m, 1H), 1.40 (m, 2H), 1.78 and 1.66 (ABq, $J_{gem} = 14$ Hz, $J_{3',4'} = 7.5$ Hz, 2H), 1.34 (s, 3H), 0.94 (t, $J_{3',4'} = 7.5$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 153.81, 122.84, 105.62, 87.41, 33.24, 29.93, 27.63, 26.81, 25.08, 26.62, 8.22.

Photooxidation of Enone 20. The title compounds were dissolved in CH_3CN and irradiated, according to the above general oxidation procedure. After an uptake of an equivalent of O_2, concentration of the solvent and direct preparative TLC (eluting with 20% acetone in hexane) yielded products **55**, **54**, and **43** in a ratio of 2:1:1. We were not able to obtain pure samples of hydroperoxide **54**, presumably because it decomposes on silica to alcohol **43**. It was tentatively identified in the photooxidation mixture by its vinyl absorptions at 5.18 (bs, 1H, $H_{1''}$) and 4.85 (bs, 1H, $H_{1'}$). These absorptions disappeared completely upon the addition of Ph_3P or thiourea, replaced by the corresponding vinyl absorptions of **43** at 5.15 (bs, 1H, $H_{1''}$), 5.06 (bs, 1H, $H_{1'}$).

55: R_f (20% acetone in hexane) 0.30; ^{1}H NMR* ($CDCl_3$) δ 5.47 (dd, $J_{3,4} = 10$ and 7.5 Hz, 1H), 2.92 (bs, 1H), 2.71 and 2.03 (m, 2H), 2.16 and 1.76 (m, 2H), 1.78 and 1.37 (m, 2H), 1.68 and 1.57 (m, 2H), 1.65 and 1.48 (m, 2H), 1.39 (s, 3H), 1.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 152.70, 122.46, 106.46, 85.46, 38.49, 27.05, 26.44, 26.28, 24.31, 23.13, 20.74; MS (CI, 70 ev) *m/z* 181 ($MH^+ - OH$, 85.07%), 165 ($MH^+ - H_2O_2$, 100%); HRMS calcd ($C_{11}H_{17}O_2$, $MH^+ - OH$) 181.1229, obsd 181.1246.

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Supporting Information Available: ^{1}H NMR spectra of *E*-**12a**, *Z*-**12a**, *E*-**12b**, *Z*-**12b**, **15**, **18**, **19**, **20**, *E*-**29a** and *Z*-**29a**, *E*-**29b** and *Z*-**29b**, **30a**, **30b**, **31b**, **32a**, **32b**, **33a**, **33b**, **34a**, **34b**, **35a**, **42**, **43**, **44**, **45**, **46a**, **46b**, **47a**, **47b**, **47c**, **51a**, **51b**, **52a**, **52b**, and **55**, and the complete ^{1}H and ^{13}C NMR peak assignments for the compounds described in the Experimental Section. This material is available free of charge via the Internet at http://pubs.acs.org.

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