Sensitized Photooxygenation. 3. Mechanistic Studies on the Singlet Oxygenation of 5,6-Disubstituted 3,4-Dihydro-2*H*-pyrans[1]

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Studies on the photooxygenation of four 5,6-disubstituted 3,4-dihydro-2*H*-pyrans under singlet oxygen ($^1\Delta_g$) conditions are presented. For the 6-methyl-substituted substrates (**1a,c**), two hydroperoxides (**2, 3**) are formed as the primary products, the ratio of which is solvent dependent, with the polar solvent favoring the production of **2**. Hock cleavage of 5-hydroperoxide **2a** and **2c** is observed to occur via the possible intermediacy of dioxetane **4a** and **4c**. For the 6-phenyl analogue (**1b,d**), dioxetanes are observed to form directly, which decompose to ring-cleavage products (**5b,d**) readily. 6-Hydroperoxide **3a** and **3c** isomerize to 4-hydroperoxide **6a** and **6c** thermally, which further transform to 4-alcohol **7a** and epoxy alcohols **8a** and **8c**. The singlet oxygenation reaction shows very significant effects of substitution and solvent. Both 6-phenyl and 5-acetyl substituents and polar solvents favor the "dioxetane-mode" process. Kinetic studies by the competition method indicate that the overall reaction rate decreases with increasing temperature, giving rise to a very significant negative enthalpy of activation. The experimental data is interpreted in terms of a prior formation of a reversible exciplex, which collapses to perepoxides, and the possible involvement of a zwitterionic transition state or intermediate along the "dioxetane" path.

Singlet oxygenation ($^1\Delta_g$) of alkenes and enol ethers has been a subject of much interest.[2] Compounds that cannot form hydroperoxides furnish cleavage products derived from dioxetane only,[3] while those having accessible allylic hydrogens react with singlet oxygen to yield allylic hydroperoxides, together with dioxetane as primary products.[4-6,7a] The mechanism leading to the formation of the two primary products is an area still under intense investigation.

Experimentally, it has been demonstrated that the partition between the ene product and the dioxetane is very solvent dependent, as exemplified by the 3,4-dihydro-2*H*-pyran system.[8-10] However, the ene reaction is reported to be generally little affected by the polarity of the solvent, as expected should the ene reaction be concerted in nature.[11]

It has also been shown that in the ene-type addition of singlet oxygen to olefins, there is a preference for the syn-ene addition (PSEA).[12,13] Hydrogen abstraction occurs preferentially on the more substituted side of a trisubstituted double bond[6,12,14,15] and on the cis-disubstituted olefins over the trans-olefins,[16] lending support to a stepwise mechanism involving a perepoxide intermediate.

The deuterium isotope effect has been reported to be small, but significant,[6,9,10,17-21] and dependent on the relative placement of the competing groups.[22] This led to the suggestion that of an irreversible formation of a complex between singlet oxygen and olefin in which frontier orbital interactions between the oxygen and both the olefin π orbitals and CH bonds are important.[22] However, reactivity parameters established by time-resolved kinetic studies on enol ether raised the possibility of a reversible complex being formed instead.[7,23] Recent work on the inter- and intramolecular deuterium isotope effect arrived at a similar conclusion as well.[24]

The advent of theoretical calculations does not decrease the mechanistic controversy. For the ene reaction, orbital correlation diagrams,[25] CNDO/2,[26] CNDO/2-CI,[27] and MINDO/3[28] calculation favor initial perepoxide formation, while GVB-CI[29] calculation claimed to rule out this intermediate in favor of the 1,4-biradical. However recent works on STO-3G and unrestricted MINDO/3 (UM 3) exclude both perepoxide and biradical mechanisms and favor the concerted process.[30]

High sensitivity of the dioxetane path to solvent polarity

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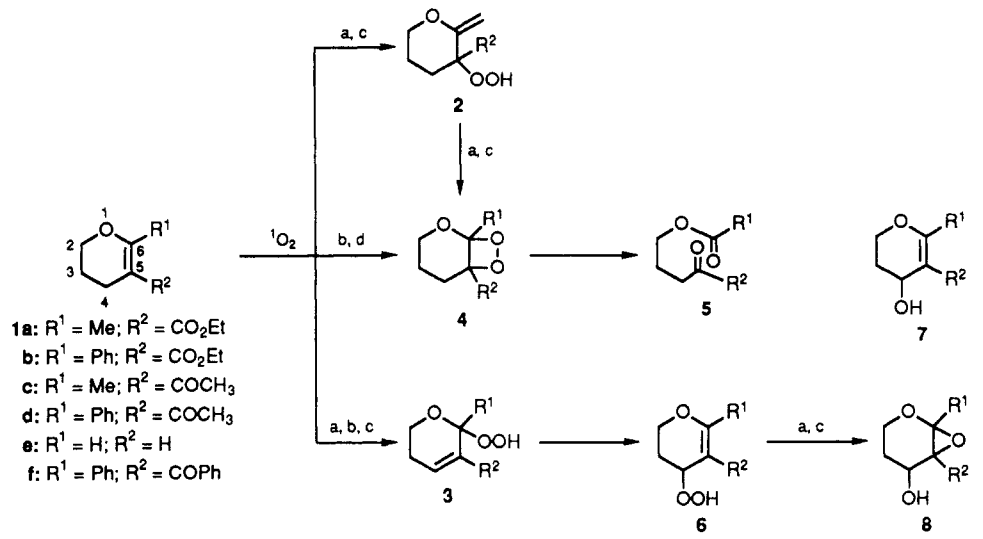
Scheme I



reveals the possibility of the existence of a polar intermediate along the reaction coordinate.[9,10,31,32] Both theoretical calculation[28,33] and trapping experiments[3,34] suggested the intermediate to be a zwitterionic species. A recent report[35] showed that the ene reaction is not entirely solvent-independent either. A quantitative treatment of which implied that the ene reaction proceeds via a transition state or intermediate with a dipole moment similar to that of perepoxide.

In this paper, we would like to report our investigation on the singlet oxygenation of a series of substituted cyclic enol ethers, 5,6-disubstituted 3,4-dihydro-2*H*-pyrans (**1a–d**) (Scheme I). Due to its special substituent effects, this versatile system allows us to isolate or observe spectroscopically some otherwise unstable intermediates, such as hydroperoxide or possibly, dioxetane. In some cases, we manage to follow even the interconversion among them. We find significant substituent and solvent effects of the singlet oxygenation of this system useful in probing the mechanism of the reaction.

Results and Discussion

Photooxygenation of **1a** using tetraphenylporphin (TPP) as the sensitizer at room temperature in benzene gives a mixture of two compounds which are unstable upon prolonged irradiation, thermal decomposition, or prolonged storage even at −5 °C. Chromatography of the mixture as soon as **1a** was totally consumed led to the isolation of two hydroperoxides, 5-hydroperoxide **2a** and 6-hydroperoxide **3a** in the ratio of 1:9 in 90% isolated yield (Scheme I). Pure hydroperoxides can be stored in benzene solution at −5 °C for more than 2 weeks.

Hydroperoxide **2a** was observed to decompose completely to ring-cleavage product **5a** on standing at 70 °C in carbon tetrachloride for an hour. No other intermediate was detected by ^{1}H NMR spectroscopy. But if the decomposition was followed at 28 °C in carbon tetrachloride, a new intermediate **4a** was clearly detected and isolated. It took 13 h for **2a** to rearrange completely to **4a**, at which time some **5a** was also detectable. Compound **4a** was also isolated from the reaction mixture after prolonged irradiation or from the reaction mixture being kept at −5 °C for a long time. At room temperature, **4a** decomposed slowly to **5a** in 24 h. If **4a** is kept at 70 °C, it converts to **5a** immediately. This is probably the reason why no **4a** was ever detected in the decomposition of **2a** at 70 °C. The decomposition can also be effected by treatment with triphenylphosphine[5] (over 90% isolated yield) or hydrochloric acid.[36] Ten minutes after the addition of one drop of hydrochloric acid (12 N) to a solution of pure **2a** in carbon tetrachloride, **4a** and ring-cleavage product **5a** were detected together with **2a** in the ratio of 1:1:1. The mixture transformed completely to **5a** in 30 min.

Thermal transformation of pure 6-hydroperoxide **3a** in carbon tetrachloride was followed by ^{1}H NMR spectroscopy at 70 °C. After 30 min, a new intermediate, 4-hydroperoxide **6a**, became evident. After 8 h, more than 70% of **3a** was converted to **6a**, which further transformed to allyl alcohol **7a** and epoxy alcohol **8a**. High-resolution (200-MHz) ^{1}H NMR and ^{13}C NMR spectroscopy confirmed the structure of **8a** also. The complete conversion of **6a** to **7a** and **8a** in the ratio of 1:3.5 took more than 60 h. In the presence of dibenzoyl peroxide, a radical initiator, the 1,3-allylic isomerization increases by a factor of 5.

In order to study the solvent effect of the reaction, we studied the photooxygenation of **1a** in five other solvents. All the products were isolated in good yields (over 90%) by column chromatography on silica gel immediately after the starting material was consumed as indicated by ^{1}H NMR spectroscopy. Percentage of the two hydroperoxides (**2a** and **3a**) or their derivatives isolated in five solvents, namely benzene, carbon tetrachloride, chloroform, methylene chloride, and acetonitrile are listed in Table I. In going from benzene, the most nonpolar solvent used, to acetonitrile, the most polar, the ratio of **2a**/**3a** increases by a factor of 17. The overall rate of the reaction as indicated by the total volume of oxygen consumed was observed to increase with the polarity of the solvent also

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Table I. Product Distribution of the Photooxygenation Reaction

substrate/solvent[a]/sens	time, h	convn, %	% 2[b]	% 3[b]	2:3
1a/benzene/TPP	9	100	10	90	0.11
1a/CCl_4/TPP	7	100	17	83	0.18
1a/$CHCl_3$/TPP	5	100	45	55	0.82[c]
1a/CH_2Cl_2/TPP	5	100	50	50	1.00
1a/CH_3CN/MB	$3^1/_2$	100	65	35	1.86[c]
1b/benzene/TPP	65	70	48	52	0.92
1b/CH_2Cl_2/TPP	18	90	60	40	1.50
1b/CH_3CN/MB	18	97	100		–
1c/benzene/TPP[d]	$3^1/_2$	100	33	67	0.49
1c/CH_2Cl_2/TPP[d]	5	100	67	33	2.03
1c/CH_3CN/MB[d]	4	100	90	10	9.00
1d/benzene/TPP[e]	–	–	100		
1d/CH_3CN/MB	14	90	100		

[a] Dielectric constant: benzene, 2.3; carbon tetrachloride, 2.2; chloroform, 4.8; dichloromethane, 9.1; acetonitrile, 37.5 (from *Handbook of Chemistry and Physics*: CRC Press: Boca Raton, FL, 1971; p E-43. [b] Including secondary products derived from **2** and **3**. [c] Similar ratio (by NMR) was obtained for reaction in deuteriated solvents. [d] Estimated from NMR and GC data. [e] Reaction done in an NMR tube with benzene-d_6 as solvent.

Table II. Solvent Effect on Rate of Photooxygenation of 1a[a]

sens/solv	O_2 absorbed, cm^3 (±0.06)	rel rate	$\tau(^1O_2)$,[37] μs
MB/CD_3CN	1.50	4.55	690
MB/CH_3CN	1.40	4.24	46.5
TPP/CH_2Cl_2[b]	0.76	2.30	100[57]
TPP/CCl_4	0.60	1.82	900[57]
TPP/C_6D_6	0.60	1.82	550
TPP/C_6H_6	0.33	1.00	26.7

[a] Conditions: **1a** = 0.3 M; [sens] = 3×10^{-4} M; reaction time 25 min. [b] MB/CH_2Cl_2 gave similar results.

(Table II). The rate of the reaction does not correlate with the lifetime of singlet oxygen in the appropriate solvent.[9,37] In going from benzene to acetonitrile, the total rate increases by a factor of 4. The partial rate[10] leading to the formation of hydroperoxide **2a** is estimated to increase by a factor of 27, while that of hydroperoxide **3a** is little affected as the solvent is changed from benzene to acetonitrile.

Photooxygenation of **1c** was carried out in three solvents. Hydroperoxide **2c**, **3c**, and dioxetane **4c** are no longer as stable as those of the 5-carboxylate analogue. However, their transient existence could still be detected by ^1H NMR spectroscopy and gas chromatography. Hydroperoxide **2c**: ^1H NMR δ 1.7–2.3 (m, 4 H, methylene), 2.34 (s, 3 H, CH_3CO), 4.5, 4.7 (2 d, each 1 H, vinyl), 9.2 (broad s, 1 H, OOH); GC decomposed to **5c**, 6.17 min. Hydroperoxide **3c**: ^1H NMR δ 1.60 (s, 3 H, CH_3), 2.46 (s, 3 H, CH_3CO), 7.06 (dd, 1 H, vinyl), 8.8 (s, 1 H, OOH); GC 5.1 min. The possible dioxetane **4c**: ^1H NMR δ 1.40 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3CO); GC decomposed to **5c**, 6.17 min. According to the ^1H NMR spectrum of the crude reaction mixture, the primary reaction seems to proceed neatly without complication. However, column chromatography of the reaction mixture upon total consumption of the starting material afforded only two compounds, ring-cleavage product **5c** and epoxy alcohol **8c** in poor to moderate yield (isolated yield: from benzene, **5c**, 5%, **8c**, 11%; from methylene chloride, **5c**, 45%, **8c**, 13%; from acetonitrile, **5c**, 49%). The solvent effect on partition between two paths is summarized in Table I. The product percentage was estimated by integration of the characteristic ^1H NMR signals (in carbon tetrachloride) of the crude reaction mixture and from GC data.

Solvent effects on the photooxygenation of enol ethers are normally attributed to the competition between the two modes of addition: polar solvents favor the dioxetane mode,[4,9,10] while the ene mode is little affected by the solvent polarity.[11] When the solvent is changed from benzene to acetonitrile, the ratio of dioxetane mode/ene mode varies over a 59-fold range for 3,4-dihydro-2*H*-pyran,[9] and 25-fold for 4-methyl-3,4-dihydro-2*H*-pyran.[10] A zwitterionic intermediate is believed to be involved along the dioxetane path.[9,10,31,32] In our case, only the ene-mode reaction occurs as the primary reaction for substrates **1a** and **1c**, irrespective of the polarity of the solvent. It is demonstrated that 5-hydroperoxide **2a** is the precursor of the possible dioxetane, **4a**, which further decomposes to ring-cleavage product **5a**. This serves as the first direct experimental evidence supporting Farmer's proposal[38] of the Hock cleavage[39] of hydroperoxide via the intermediacy of dioxetane. It occurs to us that the acetyl analogue (**1c**, **2c**, **4c**, and **5c**) behaves similarly, although, due to the instability of the compounds, **2c** and **4c** were not isolated and investigated as vigorously as their carboxylate-substituted counterparts.

The ene reaction of singlet oxygen with enol ethers is regioselective. The more crowded side of the double bond is more susceptible to attack (cis effect),[6,14,15] and oxygen tends to add on the same side as the alkoxy group, with a C–O bond forming preferentially at the carbon bearing the alkoxy group.[29,40] Special regioselectivity has been reported for the photooxygenation of α,β-unsaturated ketones,[41] ester,[42] and acids[43] also. In all cases, preferential abstraction of the allylic hydrogen forming the conjugated hydroperoxides were reported. The regioselectivity of the reaction of α,β-unsaturated ketones was independent of solvent polarity.[41] In the case of ethyl 2-methoxycyclopentene carboxylate,[44] a β-alkoxyenolate, only one ene product, the conjugated hydroperoxide, was formed, in accord with the geometrical effect[45] as well as the directing effects of both the alkoxy and the carboxylate groups. As

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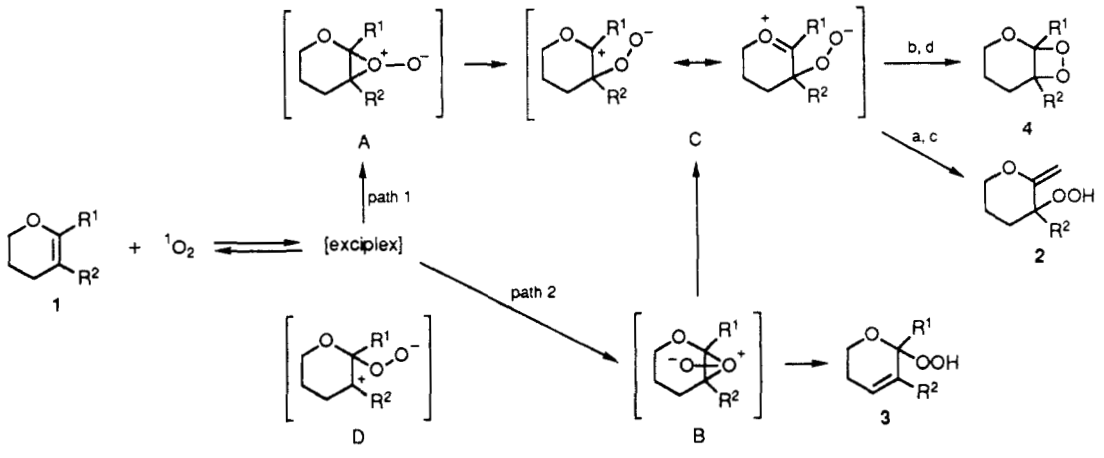
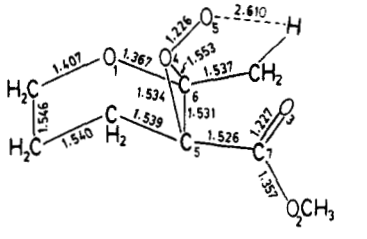
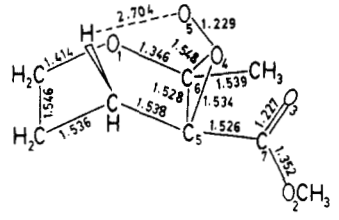
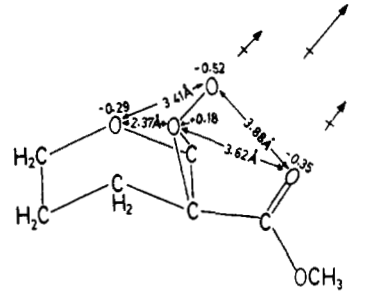
Scheme II

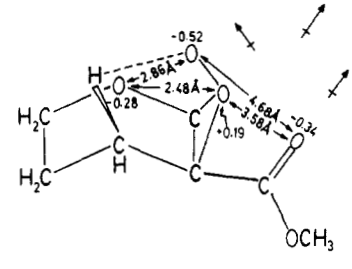








Perepoxide A



Perepoxide B

Figure 1. Perepoxide A. Bond distance in Å; bond angle between O(5), O(4), and the midpoint between C(6) and C(5), 126.5°; dihedral angle, O(5)–O(4)–C(5)–C(6) = 87.9°, O(4)–C(6)–C(5)–C(7) = 107.5°; total molecular energy, −269735.9 KJ/mol; dipole moment, 4.267 D; Wiberg indices, O(4)–C(6) = 0.727; O(4)–C(5) = 0.798; O(4)–O(5) = 1.107; C(6)–C(5) = 0.925.

Figure 2. Perepoxide B. Bond distance in Å; bond angle between O(5), O(4), and midpoint between C(6), C(5), 127.0°; dihedral angle, O(5)–O(4)–C(5)–C(6) = −92.5°, O(4)–C(6)–C(5)–C(7) = 68.9°; total molecular energy, −269743.1 KJ/mol; dipole moment, 3.291 D; Wiberg indices, O(4)–C(6) = 0.724; O(4)–C(5) = 0.796; O(4)–O(5) = 1.110; C(6)–C(5) = 0.920.

β-alkoxyenoates, substrate **1a** and **1c** are expected to show similar regioselectivity to that of ethyl 2-methoxycyclopentene carboxylate, with the conjugated hydroperoxide **3** as the preferred product. This is indeed the case in a nonpolar solvent. But as the solvent polarity increases, there is an increase in the formation of the unconjugated hydroperoxide **2**, contrary to the directing effects of both the alkoxy and the carboxylate group. This phenomenon cannot be explained by the geometrical effect[45] of the substrate. Taking into consideration that hydroperoxide **2** finally transforms to dioxetane **4**, we obtain a "dioxetane/ene" ratio change of 17-fold in going from benzene to acetonitrile for substrate **1a**. The significant solvent effect, with a polar solvent favoring the presumably unpreferred product, clearly suggests that the photooxygenation of **1a** follows a different mechanistic pathway from that of α,β-unsaturated ketones and esters.[41,42]

Perepoxide can be a possible primary intermediate of the singlet oxygenation reaction.[16] In our system, two perepoxides can be formed, namely the extended form A and the folded form B, which are respectively the precursor of hydroperoxide **2a** and **3a**. By optimization with the energy gradient method,[33] we established the full geometry, total molecular energy, dipole moment, and Wiberg indices of the two forms (Figures 1 and 2). The minor difference in dipole moment of the two forms (A, 4.267 D; B, 3.291 D) cannot account for the solvent effect observed on the partition of the reaction pathways leading to the two hydroperoxides.

Experimentally, it was demonstrated that the partial rate leading to the formation of **2a** increased by a factor of 27, while that of **3a** was little affected, when the solvent was changed from benzene to acetonitrile.[1] The data was treated with the Kirkwood–Laidler–Eyring equation[35,46]

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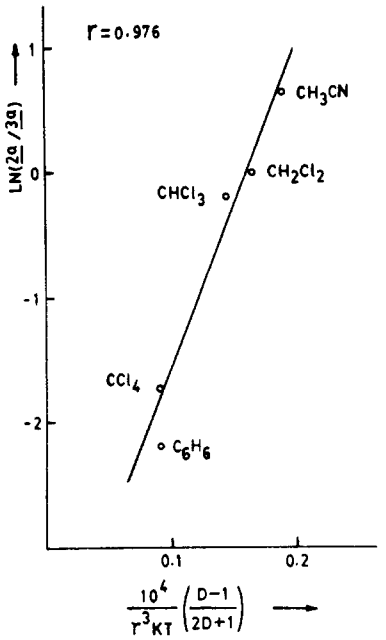

Figure 3. Dependence of ln (**2a**/**3a**) on solvent polarity.

modified for a pair of competitive reactions with a common precursor. Plotting ln **2a**/**3a** vs $(D-1)/(2D+1)$ (Figure 3), we obtained the dipole moment of the transition state leading to **2a** to be 6.06 D, assuming that the transition state leading to **3a** closely resembles perepoxide B.[35] (Figure 2). We would like to suggest that the transition state leading to **2a** has a significantly zwitterionic character (C in Scheme II).

Comparing the solvent effect on product distribution of the photooxygenation of **1a** and **1c**, we can see that the acetyl group in the 5-position favors the "dioxetane" path in all solvents (33% in benzene, 67% in methylene chloride, and 90% in acetonitrile for **1c** versus 10% in benzene, 50% in methylene, chloride and 65% in acetonitrile for **1a**) (Table I). In going from benzene to acetonitrile, the "dioxetane/ene" ratio in the photooxygenation of **1c** increases by 18-fold, similar to that of **1a**, suggesting that a similar mechanism is involved.

In order to look at the situation when the allylic hydrogens necessary for the formation of **2** are missing, we synthesized and studied the photooxygenation of substrates **1b** and **1d**. For substrate **1b**, the ^{1}H NMR signals of the ethoxy group appear at δ 0.96 and 3.78, shifted upfield significantly from that of **1a** (δ 1.29 and 4.03), indicating that the ethoxy group situates at the shielding zone of the phenyl ring at the 6-position. This phenomenon serves as a good indicator both for structure determination and the detection of new products in the photoreaction. Photooxygenation of **1b** in benzene afforded, after column chromatography of the reaction mixture, three products, the ring-cleavage product **5b**, 6-hydroperoxide **3b**, and 4-hydroperoxide **6b** in 48%, 31%, and 21% isolated yields, respectively (Scheme I, Table I). The reaction rate of **1b** is much slower than that of **1a** (Table I). 2,6-Di-*tert*-butyl-*p*-cresol, a radical scavenger, was found to have little effect on the rate of the reaction, while DABCO, a singlet oxygen quencher, was observed to suppress the reaction efficiently. In the presence of the radical scavenger, only **5b** and **3b** were isolated (35:55). The other hydroperoxide, **6b**, was not detected.

In TPP/methylene chloride, another new compound, identified possibly as dioxetane **4b**, was isolated in a small amount and decomposed to ring-cleavage product **5b** on standing in carbon tetrachloride solution in a NMR tube at room temperature. When photooxygenation was carried out in acetonitrile with methylene blue as the sensitizer, only ring-cleavage product **5b** was obtained in 97% yield. No hydroperoxide was detected.

Compared to that in benzene, the reaction rate in methylene chloride and acetonitrile is much enhanced, taking approximately 18 h for completion. The three intermediates were somewhat stable if isolated pure and stored in benzene at −5 °C. However, due to the slow rate of the photooxygenation reaction, isolation of dioxetane **4b** is difficult. The solvent effect on product distribution is summarized in Table I.

Photooxygenation of **1d** was carried out in three solvents: benzene, methylene chloride, and acetonitrile. For all three solvents, the only product isolated was the dioxetane-mode ring-cleavage product **5d** in over 85% yield. When the reaction was carried out in benzene-d_6 in a NMR tube, an intermediate was detected, having characteristic ^{1}H NMR signals consistent with the structure of dioxetane **4d**, δ 2.06 (s, 3 H), 4.20 (m, 2 H), 7.40 (s, 5 H). This compound is very unstable, transforming to the ring-cleavage product **5d** readily on storage or purification. Even under very careful scrutiny by ^{1}H NMR spectroscopy, no characteristic peak for hydroperoxide **3d** was ever detected, indicating that the ene reaction did not occur to any significant extent.

Similarly to 3,4-dihydro-2*H*-pyran (**1e**),[9] the 6-phenyl substrates **1b** and **1d**, being deprived of the allylic hydrogen necessary for the formation of the hydroperoxide analogous to **2a** and **2c**, react with singlet oxygen via a direct [2 + 2] addition to give dioxetanes **4b** and **4d** (Scheme I). For **1b**, the process is very solvent dependent. In going from benzene to acetonitrile, the percentage of dioxetane product increases from 48% to 100%, and the overall reaction rate increases accordingly. Compared with the 6-methyl analogue (**1a**, 10% in benzene, 50% in methylene chloride, and 65% in acetonitrile), the phenyl substituent causes an increase in the dioxetane-mode product in all three solvents (48% in benzene, 60% in methylene chloride, and 100% in acetonitrile) (Table I). This substituent effect is also demonstrated by 6-aryl-3,4-dihydro-2*H*-pyran,[47,48] where only the cleavage product of dioxetane is obtained. However, due to the directing effect of the 5-carboxylate substituent in **1b**, the ene-mode reaction still takes place to a certain extent (52% in benzene and 40% in methylene chloride) (Table I). The dioxetane/ene ratio is much more sensitive to solvent polarity than that of substrate **1a**, suggesting that a more polar transition state or may be even an intermediate[28,31-34] is involved along the dioxetane path.

The combined directing effect of the 5-acetyl group and the 6-phenyl group is demonstrated by the photooxygenation of **1d**, where only one product, the dioxetane cleavage product **5d** is obtained in high yield. This reaction is not sensitive to solvent polarity.

The kinetics of the singlet oxygenation reaction were studied by a competition method,[49,50] with rubrene or 2,5-diphenylbenzofuran (DPBF) as the standard. Rubrene is a good singlet oxygen sensitizer as well as a good acceptor of singlet oxygen.[49] So, in the experiments where rubrene was used, no other sensitizer was needed. DPBF is a good acceptor of singlet oxygen, but is not a singlet oxygen sensitizer.[51] The observed rate constant, k_{obs}, is a com-

(47) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1969**, 3609.
(48) Atkinson, R. S. *J. Chem. Soc., Chem. Commun.* **1970**, 177; *J. Chem. Soc. C* **1971**, 784.
(49) Monroe, B. M. *J. Phys. Chem.* **1977**, *81*, 1861.
(50) Monroe, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 7253.

Table III. The Reaction Rate Constant k_{obs}[a] of the Photooxygenation of Substrate 1c, 1e, 1a, 1b

solvent	temp, °C	1c	1e	1a	1b
CH_3CN[b]	10	6.83×10^5	1.77×10^5	1.54×10^5	1.11×10^5
CH_3Cl[c]	25	1.46×10^5	7.12×10^4	4.01×10^4	1.22×10^4
CCl_4[c]	10	1.21×10^5	7.86×10^4	4.68×10^4	2.80×10^4

[a] In L mol^{-1} s^{-1}. [b] DBPF (3.8×10^{-5} M)/MB (8.7×10^{-7} M). [c] Rubrene (5.3×10^{-5}).

Table IV. The Reaction Rate Constant k_{obs}[a] of the Singlet Oxygenation of Substrate 1a and 1c at Different Temperatures

substrate	solvent	0 °C	10 °C	25 °C	40 °C	50 °C
	CH_3CN[b]	2.11×10^5	1.54×10^5	1.02×10^5	7.54×10^4	4.87×10^4
1a	$CHCl_3$[c]		5.57×10^4	4.01×10^4	2.78×10^4	2.37×10^4
	CCl_4[c]	5.02×10^4	4.68×10^4	3.93×10^4	3.46×10^4	2.92×10^4
1c	$CHCl_3$	3.44×10^5	2.21×10^5	1.46×10^5	9.67×10^4	8.77×10^4

[a] In L mol^{-1} s^{-1}. [b] DPBF/MB. [c] Rubrene.

Table V. The Kinetic Parameters of the Singlet Oxygenation of 1a and 1c

substrate	solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/mol	$\tau(^1O_2)$,[a] μs
	CH_3CN	−5.44	−53.89	54
1a	$CHCl_3$	−4.56	−52.80	140
	CCl_4	−5.41	−45.77	900
1c	$CHCl_3$	−5.41	−52.97	140

[a] *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. I, p 183.

bination of the reaction rate constant, k_r, and the rate constant for physical quenching, k_q. The values of k_q for alkenes and enol ethers are normally very small.[23,41,45,52,53] In order to estimate the contribution of physical quenching in k_{obs}, we studied the kinetics of singlet oxygenation of substrate **1f**, which, in methylene blue/acetonitrile, remained unchanged chemically after irradiation with oxygen bubbling for 38 h. The k_{obs} obtained for this compound is 1.92×10^3 L mol^{-1} s^{-1}. Therefore, we assume physical quenching is not significant in our system and we approximate k_r to be k_{obs}. The results are summarized in Table III. For substrate **1a**, we have run the experiment in three solvents (carbon tetrachloride, chloroform, and acetonitrile) at five temperatures (0, 10, 25, 40, and 50 °C) and for substrate **1d** in chloroform for the same five temperatures (Table IV). In all cases, we observed that the rate of the reaction to increase with a decrease in reaction temperature. An Arrhenius' plot[54] yields the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values for each reaction, as shown in Table V. In Table III is shown the rate of the singlet oxygenation reaction of substrate **1a**, **1b**, **1c**, and unsubstituted dihydropyran **1e** in three solvents (acetonitrile, chloroform, carbon tetrachloride). In all solvents, the order of the rate of reaction observed is as follows: k(**1c**) > k(**1e**) > k(**1a**) > k(**1b**), in general accord with the preparative experiments.

It has been proposed that the singlet oxygenation of alkenes occurs via a prior formation of an exciplex.[10,22] Gorman[7] and Schuster[23] have studied the kinetics of the singlet oxygenation of enol ethers and obtained evidence for a reversible exciplex formation. Our result is similar to that of Gorman et al., only with an even more significant negative value for the enthalpy of activation, as shown in Table V. The rate of the reaction increases significantly with decreasing temperature, leading to a negative activation enthalpy in all cases. This strongly suggests the formation of an exciplex along the reaction coordinate. The observed rate constants ($k_{obs} = k_r$) are in the order of 10^4–10^5, much smaller than the rate constant for the formation of the exciplex, which should be approaching diffusion control. Therefore, we propose a reversible exciplex formation in our case:

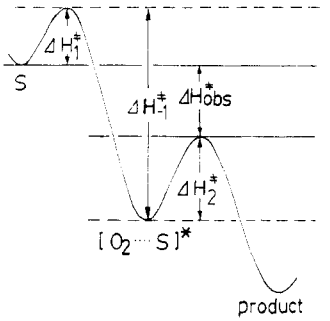

Figure 4. Possible enthalpy profile leading to a negative experimental activation enthalpy for the following reaction: $^1O_2 + S \rightleftharpoons [O_2 \cdots S] \rightarrow$ product.

$$^1O_2 + S \underset{-k_1}{\overset{k_1}{\rightleftharpoons}} [O_2 \cdots S] \xrightarrow{k_2} \text{product}$$

$$k_{obs} = (k_1/k_{-1})k_2 = Kk_2$$

where k_{obs} is the observed rate constant, K is the equilibrium constant of the formation of the exciplex, and k_2 is the rate constant for the collapsing of the exciplex to give products. The observed activation enthalpy of the above reaction is

$$H^{\ddagger}_{obs} = \Delta H^{\ddagger}_1 - \Delta H^{\ddagger}_{-1} + \Delta H^{\ddagger}_2$$

The enthalpy change of the reaction is given in Figure 4. Because of the exciplex formation, $\Delta H^{\ddagger}_{-1}$ is larger than the sum of $\Delta H^{\ddagger}_1$ and $\Delta H^{\ddagger}_2$, giving rise to a negative value of $\Delta H^{\ddagger}_{obs}$. An increase in the reaction temperature enhances the rate of the reverse reaction, which would mean a decrease of k_{obs} ($=k_r$).

From the forgoing we can draw the following conclusions: (1) The 5-carboxylate substituent exerts a stabilizing effect on the 3,4-dihydro-2*H*-pyran system, such that the primary products, allylic hydroperoxides and possibly, dioxetanes, can be isolated. (2) The 5-carboxylate substituent favors ene products. (3) In the presence of a 6-methyl substituent, the possible dioxetane is formed via the intermediacy of one of the ene products, allylic hydroperoxide **2**. (4) Polar solvents favor "dioxetane-mode" products. In one of the cases, **1a**, it has been demonstrated that the rate of the "dioxetane-mode" process increases with the polarity of the solvent, while that of the ene-mode

(51) Young, R. H.; Wehrly, K.; Martin, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 5774.
(52) Reference 11, Table in pp 291–295.
(53) Hollinden, G. A.; Timmons, R. B. *J. Am. Chem. Soc.* **1970**, *92*, 4181.
(54) Drenth, W.; Kwart, H. *Kinetics Applied to Organic Reactions*; Marcel Dekker, Inc.: New York, 1980; p 69.

reaction is little affected. (5) The 6-phenyl group favors the dioxetane-mode process. (6) The 5-acetyl group favors "dioxetane-mode" products. (7) The combined directing effect of 5-acetyl and 6-phenyl substituents leads to the dioxetane-mode exclusively even in nonpolar solvents. (8) Kinetic studies on the singlet oxygenation of substrate **1a** and **1d** indicate that the reaction goes through the intermediacy of a reversible exciplex.

For discussion purposes, we would like to propose a mechanistic pathway as shown in Scheme II. Singlet oxygen adds to the double bond to form a reversible exciplex,[7,23] which collapses to hydroperoxide **2** or dioxetane **4** and hydroperoxide **3** via a possible intermediacy of perepoxide A and B, respectively. A recent report suggests that the formation of perepoxide can be reversible also.[24] Heterolytic cleavage of C(6)–O bond of the perepoxide leads to zwitterion C, while cleavage of C(5)–O bond gives zwitterion D. It is interesting to note that for substrate **1a**, path 2 is rather independent of the polarity of the solvent, so a full cation may not develop at C(5), and we suggest that zwitterion D is not important along this path.[35] The effect of solvent polarity on path 1 is very significant. This can be explained by the fact that the positive charge is stabilized by the presence of the ether functionality, and thus a well-developed zwitterion (C) is formed along the reaction coordinate.[28] Therefore, path 1 is favored in polar solvents relative to path 2.

Compared to the 6-methyl group, the 6-phenyl substituent favors the formation of dioxetane and increases the sensitivity of the dioxetane-mode process to solvent polarity. This can be rationalized by the phenyl group stabilizing the zwitterion-like species involved even more.[48] The 5-acetyl group favors the "dioxetane-mode" process also. Compared to the carboxylate group, the acetyl group is more electronegative, implying that the C(5)–O bond in the perepoxide ring is stronger toward heterolytic cleavage, decreasing the amount of ene-mode product **3** formed.

6-Hydroperoxide **3a**, **3b**, and **3c** rearrange thermally to 4-hydroperoxide **6a**, **6b**, and **6c** via a possible radical mechanism.[55] **6a** and **6c** further transform to the corresponding epoxy alcohol **8a** and **8c**. Whether the epoxidation reaction occurs intermolecularly or intramolecularly remains to be investigated, but it is interesting to note that **6b** is very stable. The 6-phenyl group is playing a role in **6b** not undergoing the epoxidation reaction like its 6-methyl counterparts.

Experimental Section

The proton magnetic resonance spectra were determined with a Varian EM360L (60 MHz) instrument in carbon tetrachloride using methylene chloride as internal standard, or with a Varian XL200 (200 MHz) in chloroform-*d* with tetramethylsilane as internal standard. The chemical shifts were reported as δ values (ppm) with respect to tetramethylsilane. All OOH or OH signals were exchangeable with deuterated water. The FT-IR spectra were recorded on Nicolet 20 SX spectrophotometer, using a KBr disk (neat). Only strong and pertinent peaks are reported, in cm^{-1}. The low-resolution mass spectra were determined with a Finnigan 4021 Model, chemical ionization (CI) with methane gas, and electron impact (EI) at 25 or 70 eV. High-resolution mass spectra were recorded on an AEI MS-50 instrument with an EI source operated at 70 eV. Only strong and pertinent fragments are reported in m/z units. Gas chromatography was carried out on a Shimadzu GC-7A instrument, with a 3 m × 3 mm column, packed with 20% SE 30 on chromosorb W (column temperature at 190 °C) or 25% PEG 20M on Shimalite (AW) (201) (column temperature at 180 °C). Temperature of the injector and FID detector were at 210 °C, and the carrier gas used was nitrogen at 50 mL/min. Retention time is reported in minutes.

3,4-Dihydro-6-methyl-2*H*-pyran-5-carboxylic Acid Ethyl Ester (1a). To a suspension of potassium carbonate (40 g, 0.3 mol) in acetone (150 mL) in a round-bottom flask equipped with a water condenser was added ethyl acetoacetate (26 g, 0.2 mmol) and 1,3 dibromopropane (19.8 g, 0.1 mol). The mixture was refluxed for 70 h. The solvent was evaporated, and the residue was extracted with chloroform (150 mL × 2). The combined organic extracts, after being washed with 10% sodium carbonate solution (50 mL × 3), water (100 mL), and saturated brine (50 mL), were dried over anhydrous magnesium sulfate. Evaporation of the solvent yielded a light yellow oil, which was subjected to column chromatography on silica gel. Elution with petroleum ether (30–50 °C) afforded the title compound **1a**[56] (10.9 g, 38% yield): ^{1}H NMR 1.29 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.80 (quintet, 2 H, J = 5 Hz, $CH_2CH_2CH_2$), 2.10 (s, 3 H, CH_3), 2.20 (t, 2 H, J = 5 Hz, $CH_2C{=}C$), 3.93 (t, 2 H, J = 5 Hz, OCH_2CH_2), 4.03 (q, 2 H, J = 7 Hz, OCH_2CH_3); IR, 1705, 1625, 1260; MS (EI) 170 (M^+); GC 8.4 (SE 30), 5.01 (PEG).

3,4-Dihydro-6-phenyl-2*H*-pyran-5-carboxylic Acid Ethyl Ester (1b). The reaction conditions were similar to those reported in the previous section. From ethyl benzoylacetate (6.5 g, 0.034 mol), 1,3-dibromopropane (6 g, 0.03 mol), and potassium carbonate (12 g, 0.09 mol), title compound **1b** (2.7 g, 35%) was isolated after recrystallization from methanol: mp 55 °C: ^{1}H NMR 0.96 (t, 3 H, J = 7 Hz, OCH_2CH_3), 2.00 (m, 2 H, $CH_2CH_2CH_2$), 2.52 (t, 2 H, J = 6 Hz, $CH_2C{=}C$), 3.78 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.21 (t, 2 H, J = 5 Hz, OCH_2CH_2), 7.36 (broad s, 5 H, phenyl); IR 1675, 1610, 1280; MS (EI), 232 (M^+, 27), 203 ($M^+ - C_2H_5$, 25.5), 187 ($M^+ - OC_2H_5$, 19), 159 ($M^+ - CO_2C_2H_5$, 21.5). Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.40; H, 6.95. Found: C, 72.34; H, 6.94.

3,4-Dihydro-6-methyl-2*H*-pyran-5-yl Methyl Ketone (1c). The reaction conditions were similar to those reported in the previous section. From acetylacetone (12 mL, 0.12 mol), 1,3-dibromopropane (10 mL, 0.1 mol), and potassium carbonate (35 g, 0.3 mol), title compound **1c** (4.3 g, 31%) was obtained after column chromatography on silica gel, elution with chloroform–petroleum ether (1:5) mixture: ^{1}H NMR 1.66–2.00 (m, 1 H, $CH_2CH_2CH_2$), 1.99 (s, 6 H, 2 CH_3), 2.22 (2 H, J = 6 Hz, $CH_2C{=}C$), 3.90 (t, 2 H, J = 6 Hz, OCH_2CH_2); IR 1670, 1580, 1268; MS (EI) 140 (M^+, 17), 125 ($M^+ - CH_3$, 36), 97 ($M^+ - C_2H_3O$, 12); exact mass calcd for $C_8H_{12}O_2$ 140.0834, found 140.0808; GC 7.19 (SE 30).

3,4-Dihydro-6-phenyl-2*H*-pyran-5-yl Methyl Ketone (1d). The reaction conditions were similar to those reported in the previous section. From benzoylacetone (8.1 g, 0.05 mol), 1,3-dibromopropane (5 mL, 0.05 mol) and potassium carbonate (20.7 g, 0.15 mol), the title compound **1d** (1.2 g, 24%) was obtained after column chromatography on silica gel, elution with chloroform–petroleum ether (1:7) mixture: ^{1}H NMR 1.66 (s, 3 H, CH_3), 1.76–2.15 (m, 2 H, $CH_2CH_2CH_2$), 2.48 (t, 2 H, J = 6 Hz, $CH_2C{=}C$), 4.20 (t, J = 6 Hz, OCH_2CH_2), 7.36 (broad s, 5 H, phenyl); IR 1645, 1590, 1280; MS (CI) 203 (M + 1, 100); exact mass calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0980. Together with its isomer, 3,4-dihydro-5-benzoyl-6-methyl-2*H*-pyran: ^{1}H NMR 1.76 (s, 3 H, CH_3), 1.80–2.15 (m, 2 H, $CH_2CH_2CH_2$), 2.46 (t, 2 H, J = 6 Hz, $CH_2C{=}C$), 4.11 (t, 2 H, J = 6 Hz, OCH_2CH_2), 7.40–7.75 (m, 5 H, phenyl); IR 1660, 1600, 1280; MS (CI) 203 (M + 1, 100); exact mass calcd for $C_{13}H_{14}O_2$ 202.0993, found 202.0982.

Photooxygenation Reaction. A mixture of substrate **1** (0.2–0.4 M) and tetraphenylporphine (3×10^{-4} M) in the appropriate solvent was irradiated externally with a 500-W tungsten–halogen lamp, operated at 180 V, with oxygen bubbling through the solution continuously. The disappearance of the starting material was monitored by ^{1}H NMR spectroscopy or gas chromatography. Upon completion of the reaction, the solvent was evaporated, and the residue was subjected to column chromatography on silica gel. The products thus obtained were isolated and characterized. Product distribution ("dioxetane" product vs ene product) in different solvent studied is summarized in Table I.

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(56) Pioner, K. J.; Wamhoff, H.; Korte, F. *Chem. Ber.* **1967**, *100*, 1675.

(57) Hurst, J. R.; MacDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065.

Characterization of Photooxygenated Products. 5-Hydroperoxide 2a: ^{1}H NMR 1.42 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.80, 2.30 (2 m, each 2 H, methylene protons), 3.9–4.2 (m, 2 H, CH_2O), 4.15, 4.65 (2 d, each 1 H, J = 1.5 Hz, vinyl), 4.2 (q, 2 H, J = 7 Hz, OCH_2CH_3), 9.0 (s, 1 H, OOH); IR 3200–3550, 1730, 1635, 1280; GC, 8.8 (SE 30); MS (CI) 203 (M^+ + 1); MS (EI) 185 (M^+ - OH, 3.1), 169 (M^+ - OOH, 100); exact mass calcd for $C_9H_{13}O_4$ (M^+ - OH) 185.0813, found 185.0815.

6-Hydroperoxide 3a: ^{1}H NMR 1.40 (t, 3 H, J = 7 Hz, CH_2CH_3), 1.70 (s, 3 H, CH_3), 2.3 (m, 2 H, OCH_2CH_2), 3.75–4.10 (m, 2 H, CH_2CH_2O), 4.25 (q, 2 H, J = 7 Hz, CH_2CH_3), 7.23 (dd, 1 H, J = 3, 7 Hz, vinyl), 8.7 (s, 1 H, OOH); IR 3200–3500, 1710, 1635 (weak), 1280; GC 6.94 (SE 30); MS (CI) 203 (M + 1); MS (EI) 185 (M^+ - OH, 4), 169 (M^+ - OOH, 100); exact mass calcd for $C_9H_{13}O_3$ (M^+ - OOH) 169.0863, found 169.0864.

Dioxetane 4a: ^{1}H NMR 1.42 (t, 3 H, J = 7 Hz, CH_2CH_3), 1.57 (s, 3 H, CH_3), 1.9–2.3 (m, 4 H, $OCH_2CH_2CH_2$), 3.9–4.2 (m, 2 H, OCH_2CH_2), 4.30 (q, 2 H, CH_2CH_3); IR 1735, 1250; GC 11.85, decomposed to **5a**; MS (CI) 203 (M + 1); MS (EI) 143 (M^+ - $C_2H_3O_2$, 100).

Ring-cleavage product 5a: ^{1}H NMR 1.42 (t, 3 H, J = 7 Hz, CH_2CH_3), 2.05 (s, 3 H, CH_3), 1.8–2.3 (m, 2 H, $CH_2CH_2CH_2$), 2.9 (t, 2 H, J = 5 Hz, CH_2CH_2CO), 4.06 (t, 2 H, OCH_2CH_2), 4.30 (q, 2 H, CH_2CH_3); ^{1}H NMR (200 MHz, in $CDCl_3$) 1.36 (t, 3 H, J = 7 Hz, CH_2CH_3), 2.00 (m, 2 H, $CH_2CH_2CH_2$), 2.02 (s, 3 H, CH_3), 2.93 (t, 2 H, J = 7 Hz, CH_2CH_2CO), 4.06 (t, 2 H, J = 5 Hz, CH_2CH_2O), 4.29 (q, 2 H, J = 7 Hz, OCH_2CH_3); IR 1738, 1720, 1245; GC 11.85 (SE 30); MS (CI) 203 (M + 1); MS (EI) 143 (M^+ - CH_3CO_2, 73), 129 (M^+ - $C_3H_5O_2$, 29), 87 (M^+ - $C_5H_7O_3$, 100); exact mass calcd for $C_7H_{11}O_2$ 143.0705 found 143.0696.

4-Hydroperoxide 6a: ^{1}H NMR 1.47 (t, 3 H, J = 7 Hz, CH_2CH_3), 2.15–2.40 (m, 2 H, $CH_2CH_2CH_2$), 2.30 (s, 3 H, CH_3), 4.13 (t, 2 H, CH_2CH_2O), 4.2 (q, 2 H, J = 7 Hz, CH_2CH_3), 4.86 (broad s, 1 H, CHOOH), 9.10 (s, 1 H, OOH); IR 3200–3550, 1710, 1605, 1265; GC, 7.09 (SE 30); MS (CI) 203 (M + 1); MS (EI) 185 (M^+ - OH, 5), 169 (M^+ - OOH, 100).

Allyl alcohol 7a: ^{1}H NMR 1.42 (t, 3 H, J = 7 Hz, CH_2CH_3), 2.15–2.40 (m, 2 H, CH_2CH_2CHOH), 2.30 (s, 3 H, CH_3), 4.13 (t, 2 H, CH_2CH_2O), 4.20 (q, 2 H, J = 7 Hz, CH_2CH_3), 5.10 (broad s, CHOH); IR 1710, 1605, 1265; MS (EI) 186 (M^+, 2.8), 169 (M^+ - OH, 100); exact mass calcd for $C_9H_{14}O_4$ 186.0891, found 186.0841.

Epoxy alcohol 8a: ^{1}H NMR 1.40 (t, 3 H, J = 7 Hz, CH_2CH_3), 1.54 (s, 3 H, CH_3), 1.75–2.35 (m, 2 H, $CH_2CH_2CH_2$), 3.45–4.05 (m, 3 H, OCH_2CH_2, CHOH), 4.00 (s, 1 H, OH), 4.23 (q, 2 H, J = 7 Hz, OCH_2CH_3); ^{1}H NMR (200 MHz, in $CDCl_3$) 1.31 (t, 3 H, J = CH_2CH_3), 1.55 (s, 3 H, CH_3), 1.93, 2.16 (2 m, 1 H each, $CH_2CH_2CH_2$), 3.55 (dd, 1 H, J = 5, 12 Hz, one of the methylene protons to O), 3.96 (d, 1 H, J = 5 Hz, CHOH), 4.02 (dt, 1 H, J = 5, 10 Hz, the other methylene proton to O), 4.26 (q, 2 H, J = CH_2CH_3); ^{13}C NMR 14 (q, methyl of ethoxy), 22 (t, C-3), 25 (q, methyl), 55 (t + s, methylene of ethoxy and C-5), 57 (d, C-4), 62 (t, C-2), 93 (s, C-6), 170 (s, carbonyl); IR 3200–3500, 1740, 1280; MS (CI) 203 (M + 1); MS (EI) 185 (M^+ - OH, 74), 169 (M^+ - OH - O, 11.4), 142 (M^+ - C_2H_3O - OH, 100); exact mass calcd for $C_9H_{13}O_4$ 185.0813, found 185.0805.

6-Hydroperoxide 3b: ^{1}H NMR 1.21 (t, 3 H, J = 7 Hz, OCH_2CH_3), 2.46 (m, 2 H, CH_2CH_2CH), 3.76–4.36 (m, 4 H, methylene), 7.06–7.56 (m, 6 H, phenyl and vinyl), 8.96 (s, 1 H, OOH); IR 3450–3100, 1690, 1620, 1280; MS (CI) 265 (M + 1); MS (EI) 247 (M^+ - OH, 38), 231 (M^+ - OOH, 100).

Dioxetane 4b: ^{1}H NMR 0.91 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.91–2.61 (m, 4 H, methylene), 3.75 (q, 2 H, J = 7 Hz, OCH_2CH_3), 4.26 (m, 2 H, OCH_2CH_2), 7.26–7.71 (m, 5 H, phenyl).

Ring-cleavage product 5b: ^{1}H NMR 1.40 (t, 3 H, J = 7 Hz, OCH_2CH_3), 2.14 (m, 2 H, $CH_2CH_2CH_2$), 2.98 (t, 2 H, J = 7 Hz, CH_2CH_2CO), 4.06–4.44 (m, 4 H, CH_2CH_2O), 7.36, 1.96 (2 m, 3 H, 2 H, phenyl); IR 1720, 1600, 1280; MS (CI) 265 (M + 1).

4-Hydroperoxide 6b: ^{1}H NMR 0.94 (t, 3 H, J = 7 Hz, OCH_2CH_3), 1.8–2.3 (m, 2 H, CH_2CH_2CHOOH), 3.86 (q, 2 H, J = 7 Hz, OCH_2CH_3, 4.41 (m, 2 H, CH_2CH_2O), 5.04 (broad s, 1 H, CHOOH), 7.36 (s, 5 H, phenyl), 9.45 (s, 1 H, OOH); IR 3450–3150, 1700, 1600, 1290; MS (CI) 265 (M + 1); MS (EI) 247 (M^+ - OH, 15), 231 (M^+ - OOH, 100). Anal. Calcd for $C_{14}H_{16}O_5$: C, 63.63; H, 6.11. Found: C, 63.77; H, 6.12.

Ring-cleavage product 5c: ^{1}H NMR 1.86–2.26 (m, 2 H, $CH_2CH_2CH_2$), 2.01 (s, 3 H, CH_3), 2.35 (s, 3 H, CH_3), 2.81 (t, 2 H, J = 6 Hz, CH_2CH_2CO), 4.08 (t, 3 H, J = 6 Hz, CH_2CH_2O); IR 1750, 1730, 1715, 1250; MS (EI) 171 (M^+ - H, 0.2), 129 (M^+ - C_2H_3O, 65), 101 (M^+ - $C_3H_3O_2$, 36), 87 (M^+ - $C_4H_5O_2$, 10), 73 (M^+ - $C_5H_7O_2$, 12); exact mass calcd for $C_8H_{11}O_4$ 171.0654, found 171.0654; GC 6.17 (SE 30).

Epoxy alcohol 8c: ^{1}H NMR 1.38 (s, 3 H, CH_3), 2.11 (s, 3 H, CH_3CO), 2.26–2.86 (m, 2 H, CH_2CH_2CH), 3.50 (broad s, 1 H, CHOH), 3.7–4.1 (m, 2 H, CH_2CH_2O), 4.65 (s, 1 H, OH); IR 3600–3200, 1715, 1280; MS (CI) 173 (M + 1); MS (EI) 155 (M^+ - OH, 19), 154 (M^+ - H_2O, 20), 139 (M^+ - CH_3 - H_2O, 20), 112 (M^+ - OH - C_2H_3O, 26); exact mass calcd for $C_8H_{11}O_3$ (M^+ - OH) 155.0705, found 155.0658; calcd for $C_8H_{10}O_3$ (M^+ - H_2O) 154.0627, found 154.0608; GC 11.49 (SE 30).

Ring-cleavage product 5d: ^{1}H NMR 2.21 (m, 2 H, $CH_2CH_2CH_2$), 2.36 (s, 3 H, CH_3), 2.96 (t, 2 H, J = 6 Hz, CH_2CH_2CO), 4.35 (t, 2 H, J = 6 Hz, CH_2CH_2O), 7.36, 7.96 (2 m, 3 H, 2 H, phenyl); IR 1730, 1675, 1300; MS (CI) 235 (M + 1).

Kinetic Experiment. The kinetic experiments were performed by a competition method. The working equation developed by Monroe and coworkers is given as follows:[49,50]

$$k_{obs} = \frac{k_R([R]_f^s - [R]_f^o) + k_D \ln ([R]_f^s/[R]_f^o)}{[S] \ln ([R]/[R]_f^s)}$$

where k_{obs} is the overall observed quenching constant of singlet oxygen by substrate S; k_R is the reaction rate constant of standard R with singlet oxygen; K_D is the reciprocal of the lifetime of singlet oxygen in the appropriate solvent; [S] and [R] are the initial concentrations of substrate S and standard R; $[R]_f^s$ and $[R]_f^o$ are the concentrations of standard R with or without the addition of substrate S after irradiation.

The kinetic experiments were performed on a Hitachi-557 double wave length double beam spectrophotometer. Irradiation was carried out with a built-in tunable 500-W iodine-halogen lamp, through the appropriate filter (JB 420, total absorption <420 nm for the rubrene experiments and HB 630, total absorption <630 nm for the methylene blue–DPBF experiments) orthogonal to the detector beam. The absorption of the standard was monitored photometrically concurrently at 528 nm for rubrene and 410 nm for DPBF, respectively. k_{obs} in each experiment was obtained by the Monroe Equation.

In order to estimate the accuracy of the system, we determined the k_{obs} of substrate **1e** in rubrene (5×10^{-5} mol L^{-1})–chloroform seven times at 50 °C and obtained the following data for k_{obs} (in L mol^{-1} s^{-1}): mean = 6.11×10^4; range = 1.02×10^4; standard deviation = 0.37×10^4; average deviation = 0.12×10^4.

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Registry No. **1a**, 10226-28-5; **1b**, 29943-21-3; **1c**, 86302-11-6; **1d**, 29943-23-5; **1f**, 29943-24-6; **2a**, 97732-85-9; **2c**, 129000-59-5; **3a**, 97732-86-0; **3b**, 129000-60-8; **3c**, 129000-61-9; **4a**, 97732-87-1; **4b**, 129000-62-0; **4c**, 129000-63-1; **4d**, 129000-64-2; **5a**, 97732-88-2; **5b**, 129000-65-3; **5c**, 129000-66-4; **5d**, 129000-67-5; **6a**, 97732-89-3; **6b**, 129000-68-6; **7a**, 97732-90-6; **8a**, 97732-91-7; **8c**, 129000-69-7.