Dye-Sensitized Photooxygenation of 2,3-Dihydrofurans: Competing [2 + 2] Cycloadditions and Ene Reactions of Singlet Oxygen with a Rigid Cyclic Enol Ether System

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Singlet oxygen reacts with 2,3-dihydrofuran (1), 5-methyl- (7), 4,5-dimethyl- (13), and 4-carbomethoxy-5-methyl-2,3-dihydrofuran (20), 5,6-dimethyl-3,4-dihydro-2*H*-pyran (26), and 3-methoxy-2-methyl-2-butene (32) in nonpolar and polar aprotic solvents to yield dioxetanes and allylic hydroperoxides, except 32, which gives only allylic hydroperoxides. The dioxetanes were isolated, but decompose slowly with weak chemiluminescence at room temperature to yield the corresponding dicarbonyl compounds. The allylic hydroperoxides produced by the cyclic enol ethers could not be isolated or separated by high vacuum distillation or by chromatography; the endocyclic allylic hydroperoxides arising from the dihydrofurans eliminate H_2O_2 to yield the corresponding furans while the exocyclic allylic hydroperoxides give unknown products. Allylic hydroperoxides 28 and 29 and the dioxetane 27 obtained from 26 yield the same dicarbonyl compound 31. The proportion of dioxetanes to allylic hydroperoxides depends on ring size and substitution of the enol ethers and on solvent polarity. Smaller ring size, greater electron-donor substitution, and solvent polarity favor the formation of dioxetanes at the expense of allylic hydroperoxides. It is noteworthy that enol ether 20, an α,β-unsaturated ester, forms appreciable amounts of a dioxetane in polar solvents (44% in acetonitrile). Kinetic results show that the rate and product distribution of the ene reaction are independent of solvent polarity, whereas the rate of dioxetane formation increases with solvent polarity. It is suggested that [2 + 2] cycloadditions and ene reactions occur via different transition states and intermediates, zwitterions and perepoxides, respectively. Furthermore, the remarkable propensity to dioxetane formation of dihydrofurans compared to that of dihydropyrans and the other enol ethers seems to be due to the rigidity of the five-membered ring in the transition state and intermediate zwitterion.

Introduction

With monoolefins, singlet oxygen ($^1O_2$, $^1\Delta_g$) can undergo ene reactions and [2 + 2] cycloadditions to give allylic hydroperoxides and 1,2-dioxetanes, respectively.[1] Structural details such as endocyclic, exocyclic, and acyclic double bonds and their substitution by alkyl and aryl groups and hetero atoms (enol ethers, enol esters, vinyl sulfides, and enamines), the capability and accessibility of allylic hydrogen atoms for the ene reactions, the strain of the double-bond system, steric hindrance to $^1O_2$ attack on the C=C system and on the allylic H atom by remote substituents, etc., as well as the nature of the solvent (aprotic/protic solvents; polarity) and the reaction temperature determine the extent to which the two reaction modes compete with each other for singlet oxygen on the one hand, and the product distributions among the ene products on the other.[1,2] Concerted ene reactions proceeding via a six-membered transition state[2e] and dioxetane formation occurring as a $[2_s + 2_s]$ cycloaddition[3] have been discussed as well as stepwise sequences leading to ene products and dioxetanes involving either diradicals,[4]

Chart I

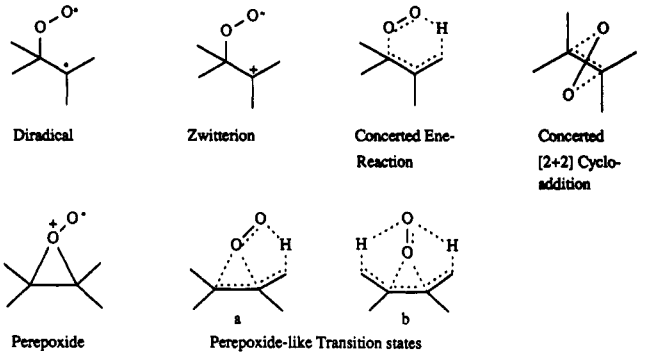
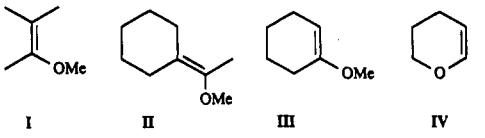


Chart II



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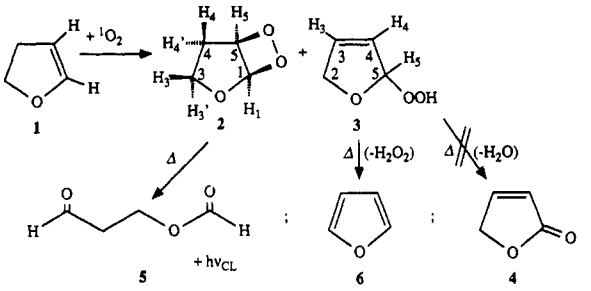
zwitterions,[2d,5,6] or perepoxides[2g] as common intermediates (Chart I). Perepoxide-like transition states (a, Chart I) yielding directly ene products were also discussed.[2c,7] Interaction of the terminal perepoxide oxygen atom with two allylic hydrogens (b, Chart I) are assumed to lower the free enthalpy of activation for transition state b[8] as compared to transition state a,[9] thus providing an explanation for the observation that trisubstituted olefins react with $^1O_2$ predominantly on the more crowded side, a phenomenon known as the "cis effect".[10,11] Houk, Yamaguchi, and co-workers[2m,n] interpreted the cis effect as being due to lowering the rotational barriers of the allylic CH_3 groups to a somewhat higher extent on the more congested cis side than on the less congested trans side of trialkyl-substituted olefins. However, this view was criticized as being oversimplified since ene reactions, at least with simple alkyl-substituted olefins, and $^1O_2$ reactions with enol ethers are controlled by entropy rather than enthalpy.[12,13] Recently, Gorman et al.[12b] suggested that the reversible formation of an exciplex is the rate-determining step in $^1O_2$ reactions with enol ethers; competitive reaction of the exciplex through "ene"- and $[2_s + 2_a]$-like transition states is supposed to lead to allylic hydroperoxides and dioxetanes directly, i.e., without the formation of intermediates.

Theoretical calculations have not clarified the situation. Kearns,[2g] Inagaki and Fukui,[14] Dewar and Thiel,[15] and Hotokka et al.,[16] using orbital correlation diagrams and CNDO/2 CI, MINDO/3, and CASSCF-CCI calculations, respectively, favor perepoxide intermediates. However, Harding and Goddard,[4a,b,17] applying GVB-CI calculations, conclude that diradicals rather than perepoxides are formed in the reaction sequence, whereas Yamaguchi et al.[18] favor a concerted mechanism involving a perepoxide-like transition state on the basis of STO-3G and unrestricted MINDO/3 (UM3) calculations.

For enol ethers, the formation of dioxetane appears to be favored at the expense of allylic hydroperoxide on passing from the acyclic enol ethers I to enol ethers II and III, having exocyclic alkoxy groups and either an exocyclic or an endocyclic double bond, respectively, to cyclic enol ethers such as IV of Chart II (vide infra). In addition, polar solvents and low temperatures favor [2 + 2] cycloaddition products over ene products.

Scheme I. Singlet Oxygen Reaction with 2,3-Dihydrofuran (1)



The propensity to dioxetane formation by cyclic enol ethers to that of acyclic enol ethers prompted us to study the influence of ring size on the competition between the two modes of $^1O_2$ reactions. 2,3-Dihydrofuran (1) and its 5-methyl (7), 4,5-dimethyl (13), and 4-carbomethoxy-5-methyl derivatives (20) were taken as examples of five-membered cyclic enol ethers and the results are compared with those obtained with six-membered enol ethers such as 5,6-dimethyl-3,4-dihydro-2*H*-pyran (26) and dihydropyrans reported in the literature as well as with that obtained from the acyclic enol ether 3-methoxy-2-methyl-2-butene (32). Moreover, in order to avoid ambiguities arising by determining the relative yields of [2 + 2] cycloaddition products and ene products from secondary products, we tried to isolate the primary products and to determine the product distributions from the original product mixtures by ^1H and ^{13}C NMR spectroscopic means. Secondary products as, e.g., dicarbonyl compounds may arise by cleavage of 1,2-dioxetanes as well as by Hock cleavage of allylic hydroperoxides; in such a case (see, for example, the thermal transformations of dioxetane 27 and allylic hydroperoxides 28 and 29), determination of secondary products could lead to wrong conclusions.

Results

Preparative Photooxygenation of 2,3-Dihydrofurans, 5,6-Dimethyl-3,4-dihydro-2*H*-pyran, and 3-Methoxy-2-methyl-2-butene in Aprotic Solvents. General Results. When irradiated in oxygen-saturated aprotic solvents in the presence of typical singlet oxygen photosensitizers such as tetraphenylporphin (TPP) (in CCl_4, $CHCl_3$, CH_2Cl_2, $CDCl_3/CFCl_3$, and benzene) and rose bengal (RB) (in acetone and acetonitrile) at temperatures between −78 and +13 °C, 2,3-dihydrofuran (1), 5-methyl-2,3-dihydrofuran (7), 4,5-dimethyl-2,3-dihydrofuran (13), 4-carbomethoxy-5-methyl-2,3-dihydrofuran (20), 5,6-dimethyl-3,4-dihydro-2*H*-pyran (26), and 3-methoxy-2-methyl-2-butene (32) each consumed 1 molar equiv of oxygen.

Immediately after the oxygen consumption had ceased, solvents were removed at −20 °C/10^{-4} Torr; subsequent distillation of the residues at −5 °C/10^{-4} Torr yielded the dioxetanes 2, 8, 14, 21, and 27, respectively (yellow oils, except 21, which was isolated as a yellow solid). Allylic hydroperoxides, the other primary products, could not be isolated by vacuum distillation or chomatographic procedures. Under these conditions, allylic hydroperoxides 3, 9, 15, and 22, having endocyclic double bonds, eliminated H_2O_2 to give the corresponding furans 6, 12, 19, and 25. Elimination of water from 3, yielding butenolide (4) was not observed. Allylic hydroperoxides 16 and 23, having exocyclic double bonds, gave rise to some unknown decomposition products.

^1H and ^{13}C NMR spectra in $CDCl_3$ at low temperatures were obtained for the isolated 1,2-dioxetanes as well as for the original product mixtures. From the latter, the NMR

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Table I. Product Yields and Kinetic Parameters of Singlet Oxygen Reactions with 2,3-Dihydrofuran (1) at 13 °C

solvent	pol[a]	τ_Δ[b] (μs)	2 (%)	3 (%)	$10^3\beta$ (M)	$10^{-6}k_r$ (M^{-1} s^{-1})	$10^{-6}k_{[2+2]}$ (M^{-1} s^{-1})	$10^{-6}k_{ene}$ (M^{-1} s^{-1})
CCl_4	0.222	700	24	76	0.92	1.55	3.72	11.8
C_6H_6	0.232	24	32	68	19.93	2.09	6.69	14.2
$CHCl_3$	0.356	250[c]	73	27	3.93	1.02	7.43	2.6
CH_2Cl_2	0.420	105	74	26	3.02	3.15	23.34	8.2
Me_2CO	0.465	26	71	29	13.99	2.75	19.52	7.8
MeCN	0.480	30	70	30	7.11	4.69	32.82	14.1
MeOH	0.477	7	*d*	*d*	58.23	2.45	*d*	*d*

[a] Polarity $(\epsilon - 1)/(2\epsilon + 1)$. [b] After Merkel, P. B.; Kearns, D. R. *J. Am. Chem. Soc.* **1972**, *94*, 7244. [c] After (a) Byteva, I. M.; Gurinovich, G. P. *J. Luminesc.* **1979**, *21*, 17; (b) Hurst, J. R.; McDonald, J. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1982**, *104*, 2065. [d] Not determined (see text).

Table II. Product Yields and Kinetic Parameters of Singlet Oxygen Reactions with 5-Methyl-2,3-dihydrofuran (7) at 13 °C

solvent[a]	8 (%)	9 (%)	$10^3\beta$ (M)	$10^{-7}k_r$ (M^{-1} s^{-1})	$10^{-6}k_{[2+2]}$ (M^{-1} s^{-1})	$10^{-6}k_{ene}$ (M^{-1} s^{-1})
CCl_4	53	47	*b*			
C_6H_6	52	48	2.85	1.46	7.60	7.02
$CHCl_3$	72	28	*b*			
CH_2Cl_2	79	21	*b*			
Me_2CO	78	22	1.36	2.83	22.06	6.22
MeCN	85	15	0.97	3.44	29.21	5.16
MeOH	*c*	*c*	10.41	1.38	*c*	*c*

[a] Polarity and τ_Δ: see Table I. [b] Not determined. [c] Not determined (see text).

spectra of the allylic hydroperoxides were extracted.

Detailed Results. 2,3-Dihydrofuran (1). From the partially decoupled ^{13}C NMR spectrum of dioxetane **2**, 2,6,7-trioxabicyclo[3.2.0]heptane, the doublets at δ 88.6 and 107.3 are attributed to C-5 and C-1, respectively, whereas the triplets at 31.5 and 68.2 are due to carbon atoms C-4 and C-3, respectively (Scheme I).

^1H NMR chemical shifts at δ 6.33 (d) (J = 3 Hz) and 5.93 (m) (J = 3 Hz) are due to H-1 and H-5, respectively. From spread ^1H NMR spectra (5 Hz/cm, 80 MHz), the multiplets at 1.84 (H-4′), 2.41 (H-4), 4.50 (H-3′), and 4.72 (H-3), are partially resolved and some coupling constants of the AA′XX′ system could be determined: $^2J_{4,4'}$ = 14.5 Hz, $^3J_{3,4}$ = 5.0 Hz, and $^3J_{3',4}$ = 0. Coupling constants $^2J_{3,3'}$ = 15.0 Hz, $^3J_{3,4'}$ = 12.0 Hz, and $^3J_{3',4'}$ = 8.0 Hz were estimated in analogy to those obtained for dioxetane **14** from proton-decoupled NMR spectra at 200 and 400 MHz (see below).

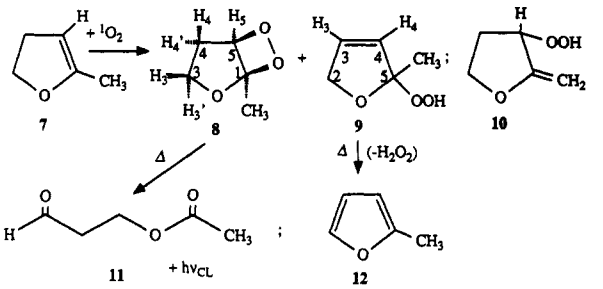
Product mixtures obtained from irradiations of **1** in CCl_4 were used to extract NMR data for allylic hydroperoxide **3**, 5-hydroperoxy-2,5-dihydrofuran, produced as the main component in this solvent (Table I). The ^{13}C NMR spectrum showed only four more signals at δ 74.9 (t), 112.1 (d), 121.9 (d), and 134.6 (d) in addition to those of **2**. The new chemical shifts are easily attributed to carbon atoms C-2, C-5, C-3, and C-4, respectively, of **3**. Likewise, the ^1H NMR spectrum exhibited, in addition to signals due to dioxetane **2**, only four multiplets at δ 4.72 (H-2), 5.58 (H-3), 6.13 (H-4), and 6.37 (H-5) and a broad singlet at 9.66 (OOH) in a ratio of 2:1:1:1:1 attributed unambiguously to hydrogens H-2 through H-5 and OOH of **3** as indicated in brackets.

Relative amounts of **2** and **3**, obtained from ^1H NMR spectra by using the integrals of hydrogens H-4 and H-4′ of **2** and OOH of **3**, are shown in Table I.

At room temperature, dioxetane **2** slowly transforms into 3-(formyloxy)propanal (**5**), whereas the mixture of **2** and **3** gives rise to **5** and furan (**6**). At elevated temperatures, rearrangement of **2** is fast and accompanied by a weak chemiluminescence that may be enhanced strongly by addition of 9,10-dibromoanthracene.

5-Methyl-2,3-dihydrofuran (7). Dioxetane **8**, 1-methyl-2,6,7-trioxabicyclo[3.2.0]heptane, rearranges slowly at room temperature to 3-acetoxypropanal (**11**). Again,

Scheme II. Singlet Oxygen Reaction with 5-Methyl-2,3-dihydrofuran (7)



rearrangement of **8** is accompanied by a weak chemiluminescence (Scheme II).

The ^{13}C NMR spectrum of **8** shows a singlet at δ 114.3, a doublet at 90.4, two triplets at 32.4 and 68.4, and a quartet at 20.1, attributed unambiguously to carbon atoms C-1, C-5, C-4, C-3, and that of the CH_3 group at C-1, respectively. In its ^1H NMR spectrum, **8** exhibits a singlet at δ 1.74 due to the CH_3 group and a doublet at 5.60 (J = 4 Hz), which belongs to H-5. From spread ^1H NMR spectra (5 Hz/cm, 80 MHz), the multiplets at 2.00 (H-4′), 2.38 (H-4), 4.38 (H-3′), and 4.64 (H-3) are attributed to the AA′XX′ system of the hydrogen atoms at C-3 and C-4 with coupling constants $^2J_{4,4'}$ = 14.0 Hz, $^3J_{3,4}$ = 5.0 Hz, and $^3J_{3',4}$ = 0. Coupling constants $^2J_{3,3'}$ = 17.0 Hz, $^3J_{3,4'}$ = 3.0 Hz, and $^3J_{3',4'}$ = 8.0 Hz were estimated in analogy to those obtained for dioxetane **14**.

Analysis of the ^{13}C and ^1H NMR spectra of the product mixtures revealed that, besides dioxetane **8**, only allylic hydroperoxide **9** (5-hydroperoxy-5-methyl-2,5-dihydrofuran) is formed. Allylic hydroperoxide **10**, the other possible ene product, is not observed in either of the solvents applied. A singlet at δ 105.4 (C-5), two doublets at 140.6 (C-4) and 128.9 (C-3), a triplet at 75.7 (C-2), and a quartet at 13.5 (CH_3 at C-5) in the ^{13}C NMR spectrum shows unequivocally the structure of the allylic hydroperoxide to be that of **9**. Similarly, the ^1H NMR spectrum with multiplets at δ 4.64 (H-2), 5.65 (H-3), and 6.18 (H-4), a singlet at 1.48 (CH_3), and a broad singlet at 9.00 (OOH) in a ratio of 2:1:1:3:1 is only compatible with structure **9** for the allylic hydroperoxide.

Relative amounts of **8** and **9** (Table II) were obtained

Table III. Product Yields and Kinetic Parameters of Singlet Oxygen Reactions with 4-Carbomethoxy-5-methyl-2,3-dihydrofuran (20) at 13 °C

solvent[a]	21 (%)	22 (%)	23 (%)	$10^2\beta$ (M)	$10^{-5}k_r$ (M^{-1} s^{-1})	$10^{-5}k_{[2+2]}$ (M^{-1} s^{-1})	$10^{-5}k_{ene}$ (M^{-1} s^{-1})
CCl_4	3	83	14	0.72	1.98	0.06	1.93
C_6H_6	4	82	14	21.11	1.98	0.08	1.90
$CHCl_3$	35	56	9	5.70	0.70	0.25	0.46
CH_2Cl_2	32	59	9	4.05	2.35	0.75	1.60
Me_2CO	39	52	9	6.34	6.07	2.37	3.70
MeCN	44	50	6	3.77	8.84	3.89	4.95
MeOH	29	60	11	19.46	7.34	2.13	5.21

[a] Polarity and τ_Δ: see Table I.

Table IV. Product Yields of Singlet Oxygen Reactions with 4,5-Dimethyl-2,3-dihydrofuran (13), 5,6-Dimethyl-3,4-dihydro-2*H*-pyran (26), and 3-Methoxy-2-methyl-2-butene (32) at 13 °C

solvent	14 (%)	15 (%)	16 (%)	27 (%)	28 (%)	29 (%)	33 (%)	34 (%)
CCl_4	80	13	7	28	20	52	70	30
C_6H_6	82	13	5	21	18	61	*a*	*a*
$CHCl_3$	86	9	5	30	17	53	65	35
CH_2Cl_2	87	8	5	30	16	54	68	32
Me_2CO	84	10	6	26	16	58	56	44
MeCN	87	7	6	35	10	55	65	35
MeOH	82	12	6	23	17	60	67	33
av	84 ± 3[b]	10 ● 2	6 ± 1	28 ● 5	16 ● 3	56 ± 4	65 ● 5	35 ● 5

[a] Not determined. [b] Standard deviation.

by using the ^1H NMR signals of H-3 and H-3′ of **8** and of H-3 and H-4 of **9**.

Mixtures of **8** and **9** gave rise to the formation of aldehyde **11** and 2-methylfuran (**12**) at elevated temperatures.

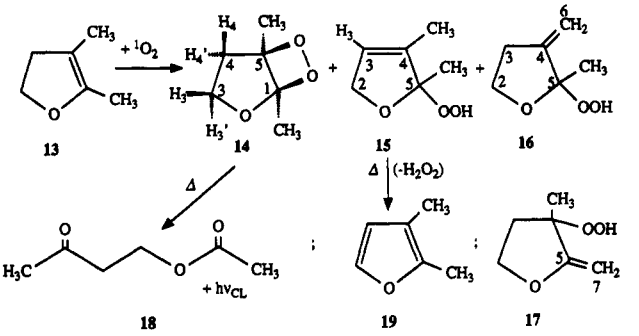
4,5-Dimethyl-2,3-dihydrofuran (13). At room temperature, dioxetane **14**, 1,5-dimethyl-2,6,7-trioxabicyclo-[3.2.0]heptane, yields slowly 4-acetoxy-2-butanone (**18**) accompanied by a weak chemiluminescence (Scheme III).

The ^{13}C NMR spectrum of **14** contains two singlets at δ 115.6 (C-1) and 96.5 (C-5), two triplets at 37.4 (C-4) and 67.1 (C-3), and two quartets at 19.4 (CH_3 at C-1) and 18.1 (CH_3 at C-5). The ^1H NMR spectrum of **14** shows two singlets at δ 1.56 and 1.60 due to the CH_3 groups at C-5 and C-1, respectively, as well as four multiplets at 1.79 (H-4′), 2.28 (H-4), 4.23 (H-3′), and 4.57 (H-3). From spread (5 Hz/cm, 80 MHz) ^1H NMR spectra as well as from ^1H NMR spectra at 200 and 400 MHz, the chemical shifts of hydrogens H-3, H-3′, H-4, and H-4′,forming an AA′XX′ system, as well as the six coupling constants $^2J_{4,4'}$ = 13.6 Hz, $^2J_{3,3'}$ = 8.4 Hz, $^3J_{3,4}$ = 5.2 Hz, $^3J_{3',4}$ = 0, $^3J_{3,4'}$ = 12.0, and $^3J_{3',4'}$ = 8.0 Hz were determined.

Analysis of the ^{13}C and ^1H NMR spectra of the product mixture showed that, in addition to dioxetane **14**, two rather than three allylic hydroperoxides were formed in a ratio of about 1:1 during the photooxygenation of **13**. In the ^{13}C NMR spectra, the doublets at δ 135.5 and 124.4 and the triplet at 73.7 are undoubtedly due to carbon atoms C-4, C-3, and C-2, respectively, of 4,5-dimethyl-5-hydroperoxy-2,5-dihydrofuran (**15**), whereas the singlet at 141.6 and the triplet at 134.3 are expected for carbon atoms C-4 and C-6, respectively, of allylic hydroperoxide **16** (4-methylene-5-methyl-5-hydroperoxytetrahydrofuran) rather than **17**. The latter compound should exhibit a singlet at about δ 150 for C-5 and a triplet at about 90 for C-7 (compare with data of compound **29**, below). The triplets at δ 31.4 and 66.4 are thus due to C-3 and C-2 of **16**, respectively. The singlets at δ 111.9 and 110.7 belong to the C-5 atoms of **15** and **16**, respectively. The three quartets at δ 19.1, 11.5, and 20.4 are attributed to the methyl groups at C-5 and C-4 of **15** and at C-5 of **16**, respectively.

Hydroperoxide **17** is obviously formed in negligible amounts, if at all. This result is in accord with the observation that hydroperoxide **10** is absent in the product mixture obtained from 5-methyl-2,3-dihydrofuran (**7**).

Scheme III. Singlet Oxygen Reaction with 4,5-Dimethyl-2,3-dihydrofuran (13)



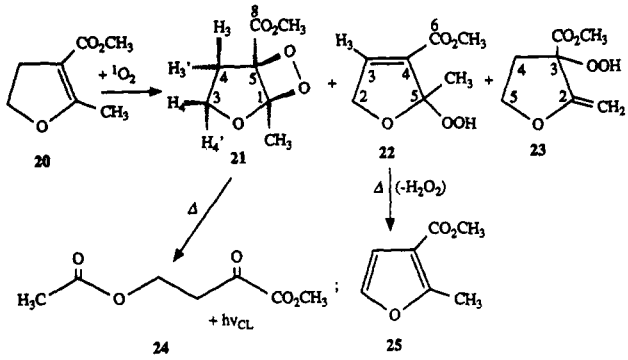
From the ^1H NMR spectra of the product mixtures, signals at δ 1.48 (s, CH_3 at C-5), 1.75 (d, CH_3 at C-4, J = 2 Hz), 5.75 (m, H at C-3), 4.28 (m, 2 H at C-2), and 8.66 (s, br, OOH) are easily attributed to hydroperoxide **15**. Signals at δ 1.41 (s, CH_3 at C-5), 5.18 (m, 2 H at C-6), 2.04 (m, 2 H at C-3), 4.28 (m, 2 H at C-2), and 8.79 (s, br, OOH) are compatible with structures **16** as well as **17**; they are attributed to hydroperoxide **16** because of the results obtained by ^{13}C NMR analysis.

Relative amounts of products **14**, **15**, and **16** (Table IV) were determined by using the ^1H NMR signals of H-3 and H-3′ of **14**, of the olefinic H at C-3 of **15**, and of the two methylene protons at C-6 of **16**.

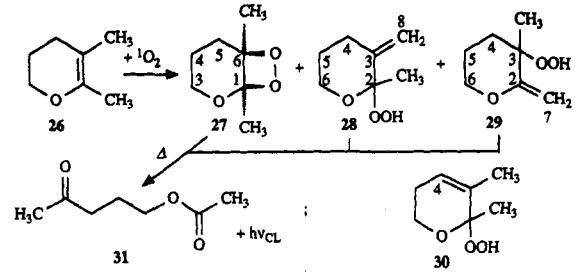
At elevated temperatures, the product mixture yielded 1-acetoxy-3-butanone (**18**), 2,3-dimethylfuran (**19**), and some unknown product. In accord with the observed transformations of hydroperoxides **3** and **9**, furan **19** should originate from hydroperoxide **15**, whereas the unknown decomposition product is assumed to be formed from hydroperoxide **16**.

4-Carbomethoxy-5-methyl-2,3-dihydrofuran (20). Dioxetane **21** (5-carbomethoxy-1-methyl-2,6,7-trioxabicyclo[3.2.0]heptane) starts to rearrange at about 10 °C, yielding the α-keto ester **24**, methyl 4-acetoxy-2-oxobutanoate, accompanied by a weak chemiluminescence (Scheme IV).

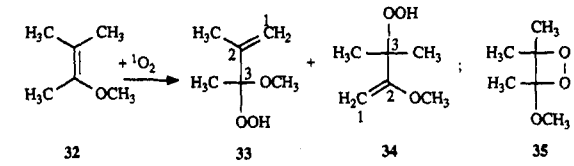
Scheme IV. Singlet Oxygen Reaction with 4-Carbomethoxy-5-methyl-2,3-dihydrofuran (20)



Scheme V. Singlet Oxygen Reaction with 5,6-Dimethyl-3,4-dihydro-2*H*-pyran (26)



Scheme VI. Singlet Oxygen Reaction with 3-Methoxy-2-methyl-2-butene (32)



The ^{13}C NMR spectrum of **21** exhibits three singlets at δ 115.5, 96.0, and 168.2 due to carbon atoms C-1, C-5, and C-8, respectively. Furthermore, it contains two triplets at 35.4 and 68.5 due to C-4 and C-3, as well as two quartets at 18.9 and 53.3 due to the methyl groups at C-1 and of the ester group, respectively.

The ^1H NMR spectrum of **21** shows two singlets at δ 1.63 and 3.89 for the CH_3 groups at C-1 and of the ester group, respectively. The AA'XX' system of hydrogens at C-3 and C-4 occur at 2.42 (m, H-4, H-4') and 4.60 (m, H-3, H-3'), exhibiting a similar pattern to the corresponding hydrogens of dioxetanes **2**, **8**, and **14**. However, the shift differences between H-3 and H-3' as well as between H-4 and H-4' are too small as to allow the determination of the individual chemical shifts and coupling constants.

Analysis of the ^{13}C NMR spectrum of the product mixture showed the presence of hydroperoxide **22** (4-carbomethoxy-5-hydroperoxy-5-methyl-2,5-dihydrofuran) besides dioxetane **21**. Thus, the three singlets at δ 115.2, 130.1, and 162.2 are attributed to carbon atoms C-5, C-4, and C-6, respectively, whereas the doublet at 144.0, the triplet at 73.5, and the two quartets at 21.4 and 52.1 are due to C-3, C-2, the CH_3 group at C-5, and the CH_3 group of the ester group, respectively.

The ^1H NMR spectra revealed, however, that two hydroperoxides (in a ratio of about 6:1) rather than one are present in the product mixtures. The main component is hydroperoxide **22** with singlets at δ 1.65 (CH_3 at C-5), 3.79 (CH_3 of the ester group), 9.64 (br, OOH), a multiplet at 7.19 (1 H at C-3), and two doublets at 4.68 and 4.75 (2 H at C-2, $J_{2,3}$ = 2 Hz). The remaining ^1H NMR signals, compatible with structure **23** (3-carbomethoxy-3-hydroperoxy-2-methylenetetrahydrofuran) occur as singlets at δ 3.78 (CH_3 of the ester group) and 9.64 (br, OOH), as doublets at 4.49 (J = 2 Hz) and 4.96 (J = 2 Hz) due to the two methylene protons, and as multiplets at 2.35 (2 H at C-4) and 4.29 (2 H at C-5).

Relative amounts of products **21**, **22**, and **23** (Table III) were determined by using the ^1H NMR signals of H-3 and H-3' of **21**, of the olefinic H at C-3 of **22**, and of the methylene protons of **23**.

At room temperature, the product mixture yielded slowly the α-keto ester **24** and 3-carbomethoxy-2-methylfuran (**25**).

5,6-Dimethyl-3,4-dihydro-2*H*-pyran (26). Dioxetane **27** (1,6-dimethyl-2,7,8-trioxabicyclo[4.2.0]octane) rearranges slowly at room temperature to yield 5-acetoxy-2-pentanone (**31**) and a weak chemiluminescence (Scheme V).

The ^{13}C NMR spectrum of **27** shows two singlets at δ 107.6 (C-1) and 88.3 (C-6), three triplets at 29.6 (C-4), 61.7 (C-3), and 17.9 (C-5), and two quartets at 22.4 (CH_3 at C-1) and 21.4 (CH_3 at C-6).

The ^1H NMR spectrum of **27** exhibits two singlets at δ 1.60 (CH_3 at C-1) and 1.51 (CH_3 at C-6), a broad multiplet in the range from 1.7 to 2.1 due to four protons at C-4 and C-5, and a multiplet between 4.24 and 4.53 due to two protons at C-3.

Analysis of the ^{13}C NMR spectrum of the product mixture revealed the presence of hydroperoxides **28** (2-hydroperoxy-2-methyl-3-methylenetetrahydropyran) and **29** (3-hydroperoxy-3-methyl-2-methylenetetrahydropyran) in addition to dioxetane **27**. The absence of a doublet in the range of δ 130 to 140, expected for carbon atom C-4 of hydroperoxide **30**, indicates that this hydroperoxide is formed with yields below about 5% of the total product mixture, if at all. The two singlets at δ 159.0 (C-2) and 79.4 (C-3), the four triplets at 22.2 (C-4), 33.0 (C-5), 70.0 (C-6), and 96.6 (C-7), and the quartet at 22.4 (CH_3 at C-3) are attributed to the major hydroperoxide **29**, whereas the two singlets at 113.2 (C-2) and 124.6 (C-3), the four triplets at 20.5 (C-4), 27.0 (C-5), 61.5 (C-6), and 104.1 (C-8), and the quartet at 29.6 (CH_3 at C-2) belong to the minor component, hydroperoxide **28**.

Similar results are obtained from the analysis of the ^1H NMR spectra of the product mixture. Thus, the major component **29** exhibits chemical shifts at δ 1.43 (s, CH_3 at C-3), 2.09 (m, 4 H at C-4 and C-5), 3.83 (m, 2 H at C-6), 4.53 (s, br) and 4.64 (s, br) (2 H at C-7), and 8.45 (s, br, OOH). The minor component **28** shows signals at δ 1.59 (s, CH_3 at C-2), 2.09 (m, 4 H at C-4 and C-5), 3.83 (m, 2 H at C-6), 4.95 (s, br) and 5.10 (s, br) (2 H at C-8), and 8.50 (s, br, OOH).

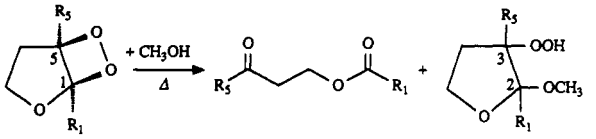
Relative amounts of products **27**, **28**, and **29** (Table IV) were determined by using the ^1H NMR signals of the two protons at C-3 of **27** and those of the methylene protons of **28** and **29**.

At elevated tempertures, product mixtures containing about 30% of dioxetane **27** and about 70% of hydroperoxides **28** and **29** were transformed quantitatively into 5-acetoxy-2-pentanone (**31**), indicating that hydroperoxides **28** and **29** and dioxetane **27** rearrange to the same product.

3-Methoxy-2-methyl-2-butene (32). According to the ^{13}C and ^1H NMR spectra of the product mixtures, there is no evidence for the formation of a dioxetane (**35**) from the acyclic enol ether **32** (Scheme VI).

The ^1H NMR spectrum of the product mixture exhibits only signals that are easily attributed to hydroperoxides **33** (3-hydroperoxy-3-methoxy-2-methyl-1-butene) and **34** 3-hydroperoxy-2-methoxy-3-methyl-1-butene). Chemical

Scheme VII. Reactions of 1,2-Dioxetanes in $CDCl_3/CH_3OH$



2	(R_1=R_5=H)	5	36
8	(R_1=CH_3; R_5=H)	11	37
14	(R_1=R_5=CH_3)	18	38

shifts at δ 1.44 (s, CH_3 at C-3), 1.81 (s, CH_3 at C-2), 3.30 (s, OCH_3), 5.03 (m) and 5.20 (m) (2 H at C-1), and 7.66 (s, br, OOH) belong to the major component **33**, whereas those at 1.40 (s, 2 CH_3 at C-3), 3.60 (s, OCH_3), 4.09 (d) and 4.28 (d) (J = 2.8 Hz, 2 H at C-1), and 7.71 (s, br, OOH) are due to the minor component **34**.

Relative amounts of **33** and **34** (Table IV) were determined by using the ^1H NMR signals of the methylene protons of these compounds.

Reactions of Dioxetanes with Methanol. As shown above, dioxetanes **2**, **8**, **14**, **21**, and **27** are relatively stable at low temperatures. They start to rearrange to the corresponding carbonyl compounds **5**, **11**, **18**, **24**, and **31**, respectively, when the temperature is raised. In order to study their reactions with nucleophiles such as methanol, we dissolved the dioxetanes in precooled $CDCl_3$ and added one or two drops of precooled methanol. When the mixtures were slowly warmed up to room temperature, dioxetanes **2**, **8**, and **14** underwent rearrangements to **5**, **11**, and **18**, respectively, as well as methanol additions yielding methoxy hydroperoxides **36–38**, respectively. Dioxetanes **21** and **27**, however, did not add methanol; they only rearranged to **24** and **31**, respectively (Scheme VII).

Methoxy hydroperoxides **36–38** were not isolated. Their formation is inferred from the appearance of new singlets at δ 3.68, 3.60, and 3.61 due to the OCH_3 groups and from the displacement of the R_5 proton NMR signals of **2**, **8**, and **14** to those appearing at δ 5.29 (t, J = 6 Hz) for R_5 = H in 3-hydroperoxy-2-methoxytetrahydrofuran (**36**), at 5.58 (t, J = 5 Hz) for R_5 = H in 3-hydroperoxy-2-methoxy-2-methyltetrahydrofuran (**37**), and at 1.38 (s) for R_5 = CH_3 in 2,3-dimethyl-3-hydroperoxy-2-methoxytetrahydrofuran (**38**). The protons of the OOH groups display broad weak signals in the range of 8 to 9 ppm.

The structure of the methanol addition products as 3-hydroperoxy-2-methoxytetrahydrofurans **36–38** rather than 2-hydroperoxy-3-methoxytetrahydrofurans is inferred from the assumption that methanol addition occurs regiospecifically via heterolytic ring opening to the more effectively stabilized electron-deficient site at C-2. Similar arguments have been applied to account for the regioselectivity of methanol addition to unsymmetrically substituted furan endoperoxides.[19]

Photooxygenation of 2,3-Dihydrofurans and 5,6-Dimethyl-3,4-dihydro-2*H*-pyran in Methanol. As expected from the results discussed in the preceding paragraph, RB-sensitized photooxygenations of **20** and **26** at 13 °C yield the same products in methanol as in aprotic solvents, i.e., addition products of methanol to the primary oxygenation products were not observed.

On the other hand, RB-sensitized photooxygenations of dihydrofurans **1** and **7** at 13 °C in methanol afforded allylic hydroperoxides **3** and **9** as well as transformation products **5** + **36** and **11** + **37**, respectively, rather than dioxetanes **2** and **8**. These results show that, at room temperature, rearrangements of dioxetanes **2** and **8** and methanol additions to these dioxetanes occur with comparable rates.

Compared with the reactions of **2** and **8**, rearrangement of and methanol addition to dioxetane **14** both proceed much more slowly. Thus, RB-sensitized photooxygenation of **13** in methanol at 13 °C leads to dioxetane **14** and allylic hydroperoxides **15** and **16**. Only after keeping the reaction mixture for some hours at 25 °C is **14** quantitatively transformed into **18** + **38**.

Kinetic Results. Kinetic studies were carried out to determine the influence of solvent polarity on the rates of the two competing $^1O_2$ reactions.

In photosensitized singlet oxygen reactions, the rate of oxygen consumption is given by eq 1, with v_A = number

$$v_A = I_a \times \Phi_\Delta \times \eta_A \quad (1)$$

of oxygen molecules consumed by substrate A per unit time, I_a = number of photons absorbed by the photosensitizer per unit time, Φ_Δ = quantum yield of singlet oxygen formation by interaction of $^3O_2$ with the electronically excited sensitizer, and η_A = efficiency of $^1O_2$ reactions with substrate A to give oxygenated products.[2h]

With 2,5-dimethylfuran (DMF) as substrate A, the efficiency η_{DMF} equals unity in *all* solvents for DMF concentrations larger than 5×10^{-4} M.[2k,19,20] The rate of oxygen uptake by DMF for [DMF] $\gg 5 \times 10^{-4}$ M is thus given by eq 2.

$$v_{DMF} = I_a \times \Phi_\Delta \quad (2)$$

With use of DMF at initial concentrations of 10^{-2} M and sensitizer concentrations between 2×10^{-4} and 10^{-3} M, v_{DMF} was independent of the sensitizer concentration and constant in all solvents until DMF was consumed to better than 95%.

With substrates less reactive than DMF, the O_2 consumption rate generally decreases continuously during a run until it becomes zero when 1 molar equivalent of oxygen has been absorbed. Due to the following reaction steps: (a) spontaneous deactivation of $^1O_2$, (b) "chemical" quenching of $^1O_2$ = product forming step, (c) "physical" quenching of $^1O_2$ by substrate A, and (d) "physical" quenching of $^1O_2$ by the sensitizer (a–d), τ_Δ = lifetime of

$$^1O_2 \rightarrow {}^3O_2 \qquad k_d = 1/\tau_\Delta \quad (a)$$

$$^1O_2 + A \rightarrow AO_2 \qquad k_r \quad (b)$$

$$^1O_2 + A \rightarrow {}^3O_2 + A \qquad k_Q^A \quad (c)$$

$$^1O_2 + \text{sens} \rightarrow {}^3O_2 + \text{sens} \qquad k_Q^S \quad (d)$$

singlet oxygen in solution, A = substrate, AO_2 = product(s), and sens = sensitizer, the efficiency η_A depends on the substrate concentration according to eq (3).

$$\eta_A = k_r[A]/[(k_r + k_Q^A)[A] + k_d + k_Q^S[\text{sens}]] \quad (3)$$

If substrate A does not quench the excited (singlet and/or triplet) state of the sensitizer, the ratio of the constant oxygen uptake rate by DMF to the substrate concentration-dependent oxygen uptake rate of A is given by eq 4. A plot of v_{DMF}/v_A vs $[A]^{-1}$ should be linear,

$$v_{DMF}/v_A = (1 + k_Q^A/k_r) + (k_d/k_r + k_Q^S[\text{sens}]/k_r)[A]^{-1} \quad (4)$$

permitting us to determine $(1 + k_Q^A/k_r)$ as the intercept and $(k_d/k_r + k_Q^S[\text{sens}]/k_r)$ as the slope (= α).

We applied A (= **1**, **7**, **13**, **20**, and **26**) at initial concentrations between 4×10^{-2} and 8×10^{-3} M and DMF at an

(19) Gollnick, K.; Griesbeck, A., in ref 1j, p 2057.

(20) Gollnick, K.; Griesbeck, A., *Tetrahedron Lett.* **1984**, *25*, 725.

Table V. Kinetic Parameters of Singlet Oxygen Reactions with 2,5-Dimethylfuran (DMF), 4,5-Dimethyl-2,3-dihydrofuran (13), and 5,6-Dimethyl-3,4-dihydro-2*H*-pyran (26) in Methanol at 13 °C

compd	solvent	k_r (M^{-1} s^{-1})	$k_{[2+2]}$ (M^{-1} s^{-1})	k_{ene} (M^{-1} s^{-1})	$\Delta S^{\ddagger}_r$ (eu)	$\Delta S^{\ddagger}_{[2+2]}$ (eu)	$\Delta S^{\ddagger}_{ene}$ (eu)
DMF	MeOH	1.83×10^8			−20.8[a]		
13	MeOH	1.09×10^8	0.89×10^8	0.20×10^8	−21.8[b]	−22.2	−25.2
26	MeOH	0.72×10^8	0.17×10^8	0.56×10^8	−22.3[b]	−25.2	−22.8

[a] DMF yields a [4 + 2] cycloaddition product; $\Delta H^{\ddagger} = 0$ according to Schenck, G. O.; Koch, E. *Z. Elektrochem.* **1960**, *64*, 170. Koch, E. *Tetrahedron* **1968**, *24*, 6295. [b] Assuming $\Delta H^{\ddagger}_r = 0$ kcal/mol).

initial concentration of 2×10^{-2} M in a series of solvents. For each sensitizer concentration, at least three runs were executed with A. Furthermore, two runs with DMF were made before the photooxygenation was done with A, and two runs were made thereafter. The values of v_{DMF} were found to be within the limits of ±2%, indicating the stability of the whole irradiation arrangement, especially that of a constant output of photons from the irradiation source.

The photooxygenations were carried out at 13 °C. With A = 13 and 26 in MeOH and with A = 1, 7, and 20 in all the solvents used, the oxygen consumption rates decreased continuously during a run and became zero after A had taken up 1 mol of oxygen per mole of A.[21] From the automatically recorded O_2 uptake vs time curves, v_A was determined as a function of [A].

For all the enol ethers studied, linear plots of v_{DMF}/v_A vs 1/[A] were obtained for each solvent.

Furthermore, the intercept, $(1 + k_Q^A/k_r)$, was found to be always within the limits of (1 ± 0.1), indicating that "physical" quenching of singlet oxygen by these substrates is negligible (if it occurs at all).

For non-chlorinated solvents, v_A turned out to be independent of the sensitizer concentration, showing that (k_Q^S/k_r)[sens] $\ll k_d/k_r$. In this case, the β values, defined as k_d/k_r,[2h,22] are equal to the slope of the plots of v_{DMF}/v_A vs 1/[A] according to eq 5 or, since $k_Q^A/k_r \ll 1$ (see above), according to eq 6.

$$v_{DMF}/v_A = (1 + k_Q^A/k_r) + (k_d/k_r)/[A] \quad (5)$$

$$v_{DMF}/v_A = 1 + (k_d/k_r)/[A] \quad (6)$$

For the chlorinated solvents, however, the v_A values were found to depend on the sensitizer concentration. Linear plots of the slope values of eq 4 (= α) vs the sensitizer concentration according to eq 7 yielded the k_d/k_r values from the intercepts and the k_Q^S/k_r values from the slopes.

$$\alpha = k_d/k_r + (k_Q^S/k_r)[\text{sens}] \quad (7)$$

With 2,3-dihydrofuran (1), the (k_Q^S/k_r) values were determined to be 6.0, 20.1, and 4.5 for CCl_4, $CHCl_3$, and CH_2Cl_2 solutions, respectively. With the k_r values shown in Table I for these solvents, singlet oxygen quenching by TPP occurs with rate constants $k_Q^S = 0.9 \times 10^7$, 2.1×10^7, and 1.4×10^7 $M^{-1} \cdot s^{-1}$, respectively, in good agreement with recently obtained results.[2k,20]

Tables I, II, and III show the product yields and β values of dihydrofurans 1, 7, and 20, as well as the rate constants k_r, $k_{[2+2]}$, and k_{ene} derived from these experimental values. Rate constant k_r either represents that with which $^1O_2$ reacts with A in a rate-determining step to a common intermediate or it equals the sum of $k_{[2+2]}$ and k_{ene}, the rate constants of $^1O_2$ with A to yield dioxetanes and allylic hydroperoxides via different transition states and possibly intermediates. For dihydrofuran 13, dihydropyran 26, and the acyclic enol ether 32, the product distributions are listed in Table IV. Table V shows the rate constants for 13 and 26 obtained for methanolic solutions. For aprotic solutions, in which $^1O_2$ is longer lived than in MeOH, v_A equaled v_{DMF} until 90% of these substrates had been consumed. This result means that η_A equals unity for the respective concentration range, indicating that singlet oxygen is almost completely trapped by these substrates in the product formation step (b) (see above). No rate constants were determined for 32 because the enol ether was contaminated with its isomer, 3-methoxy-2-methyl-1-butene.

Discussion

2,3-Dihydrofurans 1, 7, 13, and 20 and 5,6-dimethyl-3,4-dihydro-2*H*-pyran (26) react with singlet oxygen, yielding [2 + 2] cycloaddition products (1,2-dioxetanes) and ene products (allylic hydroperoxides).

At room temperature, dioxetanes 2, 8, 14, 21, and 27 undergo ring cleavage to give the corresponding carbonyl compounds 5, 11, 18, 21, and 31, respectively. Chemiluminescence is generally observed to accompany the decomposition of 1,2-dioxetanes.[23] For the relatively stable dioxetane 14, the chemiluminescence was used to determine the free energy of activation, $\Delta G^{\ddagger}$, and the activation enthalpy, $\Delta H^{\ddagger}$, which were found to be 28.1 ± 1.0 kcal/mol at 343 K and 28.2 ± 1.1 kcal/mol, respectively.[24] In comparison to a series of other 1,2-dioxetanes, dioxetane 14 appears to be more stable by about 2 to 3 kcal/mol, probably due to the rigidity of this molecule.[24]

On heating, the allylic hydroperoxides 3, 9, 15, and 22, containing endocyclic double bonds, yield the corresponding furans 6, 12, 19, and 25 by H_2O_2 elimination. Allylic hydroperoxides having exocyclic double bonds (16 and 23) decompose to some unknown products.

Allylic hydroperoxides 28 and 29, derived from dihydropyran 26, undergo transformation to keto ester 31, the ring-cleavage product obtained from dioxetane 27. It is tempting to assume that 28 and 29 yield 31 via the intermediate formation of dioxetane 27, according to the "Farmer mechanism".[25] Chan and co-workers[26] reported that a corresponding reaction sequence occurred with the allylic hydroperoxide derived from 5-carbethoxy-6-methyl-3,4-dihydro-2*H*-pyran. However, ring closure of allylic hydroperoxides 28 and 29 to yield dioxetane 27 followed by a *slower* cleavage of 27 to keto ester 31 may be excluded. Kept at room temperature, the ^1H NMR

(21) With A = 13 and 26 in all the other solvents used (Table IV), the oxygen consumption remained constant until the substrate was nearly used up (≥95%). 13 and 26 behave in these solvents as does DMF: because $k_r[A] \gg 1/\tau_\Delta$ for [A] ≥ 2×10^{-3} M, $v_A = I_a \times \Phi_\Delta$. The oxygen consumption rates of DMF, 13, and 26 were found to be identical in nonpolar solvents such as CCl_4 as well as in polar solvents such as MeCN when these substrates were applied at initial concentrations of 4×10^{-2} M.

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Table VI. Kinetic Parameters of Singlet Oxygen Reactions with 2,3-Dihydrofurans 1, 7, and 20 in Benzene and Acetonitrile at 13 °C

compd	solvent	$\Delta G^{\ddagger}_{r}$ (kcal/mol)	$\Delta G_{[2+2]}$ (kcal/mol)	$\Delta G_{ene}^{\ddagger}$ (kcal/mol)
7	C_6H_6	7.3 (−25)[b]	7.7 (−27)	7.9 (−28)
	MeCN	6.9 (−24)	7.0 (−24)	7.8 (−27)
	$\Delta\Delta G^{\ddagger}$[a]	0.4 (−1)[c]	0.7 (−3)	0.1 (−1)
1	C_6H_6	8.5 (−30)	9.1 (−32)	8.7 (−30)
	MeCN	8.0 (−28)	8.2 (−29)	8.7 (−30)
	$\Delta\Delta G^{\ddagger}$	0.5 (−2)	0.9 (−3)	0.0 (±0)
20	C_6H_6	9.8 (−34)	11.6 (−41)	9.8 (−34)
	MeCN	8.9 (−31)	9.4 (−33)	9.3 (−33)
	$\Delta\Delta G^{\ddagger}$	0.9 (−3)	2.2 (−8)	0.5 (−1)

[a] $\Delta\Delta G^{\ddagger} = \Delta G^{\ddagger}(C_6H_6) - \Delta G^{\ddagger}(MeCN)$. [b] $\Delta S^{\ddagger}$ (eu), assuming $\Delta H^{\ddagger} = 0$ kcal/mol. [c] $\Delta\Delta S^{\ddagger}$ (eu) = $\Delta S^{\ddagger}(C_6H_6) - \Delta S^{\ddagger}(MeCN)$.

spectrum of the mixture shows no increase of the signals attributed to **27** at the expense of those attributed to **28** and **29**. Only if the ring cleavage of **27** is *faster* than the ring closure of **28** and **29** to **27** may the Farmer mechanism prevail. However, a Hock cleavage[27,28] appears to be the most likely mechanism.[2a]

Formation of dioxetane **14** as a primary product in methanol, followed by solvent addition at elevated temperatures to methoxy hydroperoxide **38**, shows that methanol does not intercept an intermediate zwitterion Zw (Chart I). But this result does not exclude such an intermediate; it merely indicates that, if there is a Zw intermediate, its ring closure to dioxetane is *faster* than its reaction with a protic solvent such as methanol.

In nonpolar as well as in polar solvents, the reactivity toward $^1O_2$ (k_r) increases in the following order, **20** < **1** < **7** < **13**. Substitution of an olefinic hydrogen by an (electron-donating) methyl group enhances the reactivity by about 1 order of magnitude, whereas substitution by an (electron-withdrawing) carbomethoxy group decreases the reactivity by about 2 orders of magnitude.

Competition between [2 + 2] cycloaddition and ene reaction depends on the solvent polarity: whereas the ene reaction is little affected by the solvent, the [2 + 2] cycloaddition increases appreciably with increasing solvent polarity (see Table VI, $\Delta\Delta G^{\ddagger}_{[2+2]}$ and $\Delta\Delta G^{\ddagger}_{ene}$ values). Consequently, the influence of the solvent on the competing singlet oxygen reaction modes decreases with increasing reactivity of the dihydrofuran derivative toward $^1O_2$.

With the most reactive dihydrofuran (**13**), the influence of the solvent on the two pathways is almost absent, yielding 84 ± 3% dioxetane **14** and 16 ± 2% ene products **15** + **16**. In methanol, these products are formed with a rate constant k_r of about 1.1×10^8 M^{-1} s^{-1}. These results are compatible with the assumption that $\Delta H^{\ddagger} \approx 0$ kcal/mol for the [2 + 2] cycloaddition as well as for the ene reaction. In this case, the competition between the two modes of $^1O_2$ reactions with **13** is entropy-controlled, yielding $\Delta S^{\ddagger}_{[2+2]} \approx -22$ eu and $\Delta S^{\ddagger}_{ene} \approx -25$ eu (Table V). These $\Delta S^{\ddagger}$ values agree well with those obtained for other enol ethers and olefins such as 1-ethoxy-2-methylpropene,[12b] 1-methoxycyclopentene,[12b] and 2,3-dimethyl-2-butene[2e,13] for which activation enthalpies $\Delta H_r^{\ddagger}$ of almost zero and activation entropies $\Delta S_r^{\ddagger}$ of about −23, −27, and −24 eu, respectively, were determined.[29]

Comparison of the results obtained with dihydrofurans **1**, **13**, and **20** with their higher homologues, 3,4-dihydro-2*H*-pyran, dihydropyran **26**, and 5-carbethoxy-6-methyl-3,4-dihydro-2*H*-pyran, respectively, exhibits some correspondences but also some interesting differences of the behavior of five- and six-membered cyclic enol ethers toward singlet oxygen.

Thus, the ratios of dioxetane to ene product from **1** in benzene (32:68) and MeCN (70:30) show similar dependencies on the solvents as those from 3,4-dihydro-2*H*-pyran (9:91 in benzene, 85:15 in MeCN)[30] and 4-methyl-3,4-dihydro-2*H*-pyran (17:83 in benzene, 84:16 in MeCN).[9]

The reactivities of dihydrofuran **13** and dihydropyran **26** toward $^1O_2$ are almost the same, and, as with **13**, the product distribution from **26** is nearly independent of the solvent. As with **13**, these results indicate that $\Delta H^{\ddagger} \approx 0$ kcal/mol for both reaction modes, thus yielding $\Delta S^{\ddagger}_{[2+2]} \approx -25$ eu and $\Delta S^{\ddagger}_{ene} \approx -23$ eu (Table V).

However, formation of ene products is favored over dioxetane formation from **26** in contrast to the results obtained with **13**. Furthermore, remarkable differences between dihydrofuran **13** and dihydropyran **26** are observed with respect to their ene reactions with singlet oxygen.

Firstly, of the two allylic hydroperoxides **16** and **17** containing exocyclic double bonds, **17** was formed to less than about 5%, if at all,[31] i.e., the ratio of the two exocyclic allylic hydroperoxides **16** and **17** equals 6:(<5), whereas the ratio of the corresponding allylic hydroperoxides **28** and **29** equals 2:7.

Secondly, attack of singlet oxygen on **13** occurs preferentially on that side of the double bond where the ether functional group is located, whereas attack of $^1O_2$ on **26** occurs almost exclusively on the opposite side of the double bond. Thus, **13** forms appreciable amounts of allylic hydroperoxide **15** containing an endocyclic double bond, whereas the corresponding product **30** was not detected (showing that less than about 5% of **30** was formed from dihydropyran **26**, if at all). It is interesting to note that similar differences are found for the ene product distribution of the corresponding cyclopentenes and cyclohexenes. For the dimethyl-substituted enol ethers **13** and **26**, the ratios of endocyclic allylic hydroperoxides to exocyclic allylic hydroperoxides are **15**:**16** ≥ 1.7 and **30**:(**28** + **29**) < 0.04, respectively. For 1,2-dimethylcyclopentene and 1,2-dimethylcyclohexene, the corresponding ratios are about 0.7 and 0.1.[8b] Thus, apart from dioxetane formation, the distributions of ene products from correspondingly substituted 2,3-dihydrofurans and 3,4-dihydro-2*H*-pyrans seem to parallel remarkably well those obtained from their carbocyclic counterparts.

Obviously, the more rigid systems, **13** and 1,2-dimethylcyclopentene, tend to produce appreciably higher

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(29) Our irradiation device is well-suited for kinetic studies at temperatures between about 5 to 25 °C and for preparative studies between about dry ice temperature and room temperature. It is, unfortunately, not well-suited for kinetic studies below about 5 °C. Therefore, we carried out the kinetics only at 13 °C. In view of the results obtained by Gorman[12] and Schuster,[13] we may assume that $\Delta H_r^{\ddagger}$ for $^1O_2$ reactions with enol ethers **1** and **7** is ≤2 kcal/mol. In Table VI, $\Delta S^{\ddagger}$ and $\Delta\Delta S^{\ddagger}$ values are estimated by assuming $\Delta H^{\ddagger} = 0$ resulting in $\Delta S^{\ddagger}$ values for dioxetane and allylic hydroperoxide formation in the range of −24 to −30 eu. However, for enol ether **20**, bearing an electron-withdrawing carbomethoxy group, this assumption may not be warranted. If $\Delta S^{\ddagger}$ for $^1O_2$ reactions with **20** falls also in the range between −24 to −30 eu, these reactions are associated with activation enthalpies $\Delta H^{\ddagger}$ of about 3 to 1 kcal/mol in benzene and about 2 to 0.3 kcal/mol in MeCN.
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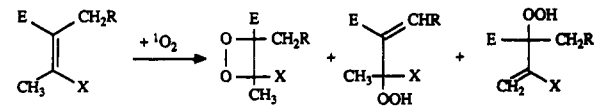
(31) This result agrees with that obtained with dihydrofuran **7**, where allylic hydroperoxide **10**, corresponding to allylic hydroperoxide **17** from **13**, was not detected in the product mixture.

Scheme VIII. Singlet Oxygen Reactions with Compounds 20 and 39



	21	22	23
20: R-X = CH_2-O, E = CO_2CH_3			
in C_6H_6 :	4%	82%	14%
in Me_2CO:	39%	52%	9%
39: R = X = H, E = CO_2CH_3	--	40	41
in Me_2CO:	--	86%	14%

yields of allylic hydroperoxides with endocyclic double bonds than do the more flexible systems **26** and 1,2-dimethylcyclohexene. This ring-size effect on the ene reaction with singlet oxygen is apparently due to the accessibility of the endocyclic allylic hydrogens, which is enhanced in five-membered rings compared to that in six-membered ring systems. We suppose that the rigidity of the ring system is also the crucial factor for the enhanced dioxetane formation from **13** compared with that from **26** (Table IV).

The latter assumption seems to account also for the different results obtained with 4-carbomethoxy-5-methyl-2,3-dihydrofuran (**20**) and 5-carbethoxy-6-methyl-3,4-dihydro-2*H*-pyran. Whereas dihydrofuran **20** gives appreciable amounts of dioxetane **21** (from 4% in benzene to 44% in MeCN, see Table III), the dihydropyran derivative is reported to yield no dioxetane as a primary singlet oxygen product in any solvent.[26]

With respect to ene product formation from **20**, the ratio of allylic hydroperoxides **22** and **23** equals about 6 for polar and nonpolar solvents (Table III). This ratio agrees well with that of **40** and **41** (Scheme VIII) obtained from the methyl ester of angelic acid (**39**) in acetone.[32]

It is interesting to note that enol ether **20**, an α,β-unsaturated carbonyl compound, yields a dioxetane on reaction with $^1O_2$, because reactions of $^1O_2$ with α,β-unsaturated esters,[26,32] acids,[33] aldehydes[34] and ketones,[32,35] even if they bear a β-alkoxy group, are reported to give rise to allylic hydroperoxides exclusively.

In accord with the supposition that rigidity of the enol ether framework favors dioxetane formation, the acyclic enol ether **32** forms no detectable amounts of a dioxetane.

The latter result, in turn, fits well into observations that have been made with various types of enol ethers (Chart II, types I through IV). Thus, as mentioned in the Introduction, cyclic enol ethers, such as 3,4-dihydro-2*H*-pyran[30] and 4-methyl-3,4-dihydro-2*H*-pyran,[9] tend to form higher amounts of dioxetanes than do cycloalkenyl alkyl ethers and cycloalkylidene alkyl ethers, such as 1-methoxycyclohexene[36] and cyclohexylidene methyl ether,[37] whereas acyclic 1-alkoxyethylenes yield only small amounts of dioxetanes or none at all as, e.g., *cis*- and *trans*-2-cyclopropyl-1-methoxypropene.[38,39]

Conclusion

In view of the results discussed above, it seems to be most reasonable and economical to assume that ene reactions of $^1O_2$ with enol ethers occur in the same manner as they do with the correspondingly substituted olefins. Of the various pathways discussed, the one involving a perepoxide-like transition state, and perhaps a perepoxide intermediate, appears to us to be the most likely one.[2k,8b]

If dioxetane formation shall compete with the ene reaction, the C–C double bond should apparently be substituted by groups that are capable of accommodating a cationic site. Enol ethers, enol esters,[2j] enamines[6] and *transoid*[40] 1,3-dienes,[2k,l,p] for example, may (but not necessarily must) therefore give rise to 1,2-dioxetanes.

Furthermore, increasing rigidity of the double-bond system seems to favor dioxetane formation. Such a trend, which is, in addition, favored by increasing solvent polarity, may be expected if a zwitterionic intermediate is involved. Provided that the rigidity of the double-bond system is maintained in the zwitterion Zw (Chart I) (and Dreiding models of dihydrofurans and their corresponding zwitterions indicate that this is the case), the newly formed C–O bond and the empty p orbital of the sp^2 carbon atom, carrying the positive charge and the OR, NR_2, or $CH{=}CR_2$ group, will line up almost perfectly for bonding of the second C–O bond. If increasing flexibility of the enol ether is reflected in the zwitterion Zw (and, again, inspection of Dreiding models of dihydropyrans and enol ethers of types II and III of Chart II and their corresponding zwitterions supports this assertion), dioxetane formation should become less favorable, until in acyclic enol ethers this mode of reaction has little or even no chance to occur in comparison with the ene reaction. In the latter reaction, interaction or even bonding of one of the oxygen atoms of $^1O_2$ should occur simultaneously with the two sp^2 carbon atoms of the C–C double bond. Thus, we feel that our results are most reasonably interpreted by assuming that ene products and dioxetanes are formed via different transition states and intermediates, perepoxides, and 1,4-zwitterions, respectively, rather than via a common intermediate. Our results do not allow us to either invoke or reject the involvement of reversible exciplexes that may precede the product-determining transition states and intermediates.

Experimental Section

Caution! Preparations and reactions of 1,2-dioxetanes and hydroperpoxides were carried out behind safety shields. Neat samples of dioxetanes can be very hazardous and should be handled only in amounts less than about 100 mg.

Solvents and commercially available compounds were purchased from standard suppliers and purified to match reported physical constants and spectral data. Special care was taken to remove traces of metal ions to avoid catalytic degradation of the 1,2-dioxetanes. Disodium ethylenediaminetetraacetate (EDTA) (10–15 g) was added to 100 mL of solvent; after being refluxed for several hours, EDTA was filtered off and the solvent was subsequently filtered through a basic alumina column. Acetone and methanol were distilled from EDTA by using a 15-cm Vigreux column. Acetonitrile was distilled over P_2O_5 and K_2CO_3 in sequence to obtain pure and dry MeCN. Melting points are uncorrected.

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(41) (a) Wasserman, H. H.; Lipshutz, B. H., in ref 1a, p 429. (b) Saito, I.; Matsuura, T., in ref 1a, p 511. (c) Gollnick, K.; Schenk, G. O. In *1,4-Cycloaddition Reactions; the Diels Alder Reaction in Heterocyclic Syntheses*; Hamer, J., Ed.; Academic Press: New York, 1967; p 255.

^{1}H NMR spectra were recorded with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. ^{13}C NMR spectra were recorded at 22.3 MHz with $CDCl_3$ as solvent and TMS as internal standard. IR spectra were taken as thin films.

The purity of 1,2-dioxetanes **2**, **8**, **14**, **21**, and **27** was judged to be ≥90% by ^{1}H and/or ^{13}C NMR spectral determinations. The spectra are published as supplementary material.

Preparation of Oxygen Acceptors. 2,3-Dihydrofuran (**1**) (Fluka) and 5-methyl-2,3-dihydrofuran (**7**) (Fluka) were distilled (10-cm Vigreux column) before use. **1**: ^{1}H NMR δ 2.53 (m, 2 H), 4.18 (m, 2 H), 4.80 (m, 1 H), 6.18 (m, 1 H); ^{13}C NMR δ 29.2 (t), 69.5 (t), 99.5 (d), 145.9 (d). **7**: ^{1}H NMR δ 1.75 (d, 3 H, J = 2 Hz), 2.55 (m, 2 H), 4.25 (t, 2 H, J = 9 Hz), 4.49 (m, 1 H); ^{13}C NMR δ 13.4 (q), 30.4 (t), 69.9 (t), 94.4 (d), 154.9 (s).

4,5-Dimethyl-2,3-dihydrofuran (13). To a sample of 20.9 g (0.18 mol) of 3-methyl-5-hydroxypentan-2-one,[42] obtained from α-acetyl-α-methyl-γ-butyrolactone[43] by hydrolysis under concomitant decarboxylation, were added three drops of concentrated phosphoric acid, and the mixture was distilled at 155 °C through a 10-cm Vigreux column. After removal of water, distillation of the residue on a 100-cm spinning band column gave 8.84 g (50%) of a colorless liquid, bp 106 °C at 760 Torr (lit.[42] bp 108–110 °C): ^{1}H NMR δ 1.60 (s, br, 3 H), 1.69 (s, br, 3 H), 2.49 (m, 2 H), 4.15 (t, 2 H, J = 9 Hz); ^{13}C NMR δ 11.0 (q), 11.6 (q), 35.7 (t), 67.5 (t), 102.1 (s), 147.0 (s).

4-Carbomethoxy-5-methyl-2,3-dihydrofuran (20). A sample of 125 g of α-acetyl-γ-butyrolactone (EGA) in 900 mL of a 0.5 M methanolic HCl solution was refluxed for 12 h and kept at room temperature for 3 d. The solution was neutralized with aqueous saturated $KHCO_3$ (2.5 L) and extracted eight times with 300 mL of ether each time. The organic layer was dried over $MgSO_4$ and the solvent removed by distillation at normal pressure. Subsequent distillation of the residue at 12 Torr gave a liquid, bp 40–70 °C, which, after addition of three drops of concentrated sulfuric acid, was redistilled at 12 Torr, affording a solid product. After recrystallization from petroleum ether, 27.9 g (20%) of **20** was obtained: colorless crystals, mp 32 °C (lit.[44] mp 31.5–32.5 °C); ^{1}H NMR δ 2.15 (s, 3 H), 2.83 (m, 2 H), 3.66 (s, 3 H), 4.33 (t, 2 H, J = 9 Hz); ^{13}C NMR δ 13.9 (q), 29.8 (t), 50.7 (q), 70.4 (t), 102.0 (s), 166.5 (s), 168.9 (s).

5,6-Dimethyl-3,4-dihydro-2*H*-pyran (26). A sample of 25 g of γ-acetylvaleronitrile[45] was refluxed with 55 mL of a concentrated HCl solution for 4 h. The mixture was cooled to room temperature, diluted with water until the precipitate of NH_4Cl was dissolved, neutralized with NaOH, and subsequently acidified with HCl to a pH value of 3 to 4. The aqueous solution was saturated with sodium chloride and extracted ten times with 25 mL of ether each time. The organic layer was dried over $MgSO_4$. After removal of the solvent, the residue was distilled in vacuo, yielding 39.1 g (85%) of γ-acetylvaleric acid: bp 105 °C at 2 Torr (lit.[45] bp 160–162 °C at 16 Torr). Refluxing 39.1 g (0.27 mol) of γ-acetylvaleric acid with 27.6 g (0.27 mol) of acetic anhydride and 1 mL of acetyl chloride for 3 h yielded 28.8 g (76%) of 5,6-dimethyl-3,4-dihydro-2-pyrone as a liquid, bp 68 °C at 5 Torr, which was treated with 4.7 g (0.12 mol) of $LiAlH_4$ in 500 mL of dry ether. After 24 h, 40 mL of methanol and 100 mL of water were added. The organic layer was separated, the aqueous layer was extracted with ether, and the combined organic layers were dried over K_2CO_3. After removal of the ether, the residue was distilled at normal pressure in the presence of iodine, affording a mixture of water and an organic liquid. The latter was separated and distilled through a 10-cm Vigreux column, yielding 8.5 g (33%) of **26** as a colorless liquid: bp 132 °C (lit.[46] bp 108 °C at 762 Torr); ^{1}H NMR δ 1.55 (s, br, 3 H), 1.71 (s, br, 3 H), 1.85 (m, 4 H), 3.80 (m, 2 H); ^{13}C NMR δ 16.3 (q), 18.1 (q), 23.5 (t), 26.7 (t), 65.6 (t), 101.6 (s), 144.5 (s).

3-Methoxy-2-methyl-2-butene (32). A sample of 51.8 g (0.4 mol) of 2,2-dimethoxy-3-methylbutane[47] was treated with 0.2 g of *p*-toluenesulfonic acid and subsequently distilled through a 10-cm Vigreux column at normal pressure. The fraction of bp 93–95 °C was redistilled on a 100-cm spinning band column, yielding a liquid of bp 96 °C (lit.[47] bp 97 °C). In spite of repeated distillation on a spinning band column, the product contained always about 70% of **32** and about 30% of the isomeric 3-methoxy-2-methyl-1-butene. In the ^{1}H NMR spectrum of the mixture, the signals appearing t δ 1.60 (s, br, 3 H), 1.64 (s, br, 3 H), 1.78 (s, 3 H), and 3.45 (s, 3 H) are attributed to compound **32**. (Since the 1-butene derivative is photooxygenated much slower than the isomeric 2-butene derivative **32**, the products observed undoubtedly originate from the latter olefin. Kinetic experiments were, however, not executed with this mixture).

General Procedure for Photooxygenations. A 25-mL irradiation unit with an automatic O_2 consumption recording system[48] was used for product distribution studies and kinetic measurements. A 150-W halogen lamp (Philips) and a band filter transparent between 500 and 595 nm (Hoya) were employed for electronic excitation of rose bengal (RB) and tetraphenylporphin (TPP). RB and TPP were applied in concentrations between 2 and 10 × 10^{-4} M in kinetic runs; for product distribution studies and preparative oxygenations (see below), RB was applied in 5 × 10^{-4} M and TPP in 8 × 10^{-4} M concentrations. The solutions were saturated with oxygen before irradiation. The irradiation unit, the oxygen buret, and the tubings connecting the unit with the buret were kept at 13 ± 0.1 °C by cooling with water, using a Julabo-P thermostat. A similar 25-mL irradiation unit was used for low-temperature kinetic and product studies. This unit was fitted with an evacuated window[49] and cooled by an ultracryostat, providing temperatures between −60 and +20 °C. Preparative oxygenations were conducted in 50-mL, two-necked flasks, supplied with gas inlet and outlet tubes. The solutions were cooled in a dry ice–acetone bath and irradiated with a 500-W halogen lamp (Argaphoto, Philips). The progression of oxygenation was followed by drawing samples, which were analyzed by their ^{1}H NMR spectra.

1,2-Dioxetanes. Samples of 3 to 7 mmol of 2,3-dihydrofurans (**1**, **7**, **13**, and **20**) and 5,6-dimethyl-3,4-dihydro-2*H*-pyran (**26**) were dissolved in a 1:1 mixture of $CDCl_3$ and $CFCl_3$, containing 8 × 10^{-4} M of TPP, and cooled to −78 °C while being purged with a gentle stream of oxygen gas. The solution was irradiated with a constant oxygen flow for 3 to 6 h. The solvent was removed at −50 to −30 °C at 10^{-4} Torr, and the 1,2-dioxetane was distilled at −20 to 0 °C at 10^{-4} Torr in a cold trap kept at liquid nitrogen temperature. The dioxetanes are yellow oils, which can be stored in solution on dry ice for several months. The NMR spectroscopic data of the 1,2-dioxetanes are reported in the Results as are those of the allylic hydroperoxides produced along with the dioxetanes.

The NMR signals of the allylic hydroperoxides were extracted from the NMR spectra of the original product mixtures, published as supplementary material.

Cleavage Products of the 1,2-Dioxetanes. The cleavage products were synthesized independently, following literature procedures.

3-(Formyloxy)propanal (5):[50] bp 71 °C at 12 Torr; ^{1}H NMR δ 2.78 (t, 2 H, J = 6 Hz), 4.43 (t, 2 H, J = 6 Hz), 8.00 (s, br, 1 H), 9.70 (s, br, 1 H).

3-Acetoxypropanal (11):[51] bp 70–71 °C at 12 Torr; ^{1}H NMR δ 2.01 (s, 3 H), 2.76 (t, 2 H, J = 6 Hz), 4.36 (t, 2 H, J = 6 Hz), 9.68 (d, 1 H, J = 2 Hz).

4-Acetoxy-2-butanone (18):[52] 76 °C at 12 Torr; ^{1}H NMR δ 2.00 (s, 3 H), 2.16 (s, 3 H), 2.73 (t, 2 H, J = 6 Hz), 4.25 (t, 2 H, J = 6 Hz).

5-Acetoxy-2-pentanone (31):[53] bp 103–104 °C at 12 Torr; ^{1}H NMR δ 1.90 (t, 2 H, J = 7 Hz), 2.03 (s, 3 H), 2.15 (s, 3 H), 2.53

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(t, 2 H, J = 7 Hz), 4.05 (t, 2 H, J = 7 Hz).

Comparison of these authentic materials with the cleavage products of the dioxetane decomposition reaction showed identical spectra and physical data.

Addition of Methanol to 1,2-Dioxetanes. Samples of 1,2-dioxetanes **2**, **8**, **14**, **21**, and **27** were dissolved in $CDCl_3$, precooled to about −20 °C, and an equimolar amount of methanol, precooled to this temperature, was added. The mixture was slowly warmed up to room temperature; after several hours, the dioxetanes had disappeared (^1H NMR spectra).

With **2**, **8**, and **14** as starting dioxetanes, the ^1H NMR spectra of the product mixtures exhibited signals of dioxetane cleavage products **5**, **11**, and **18**, respectively, in addition to those attributed to methanol addition products **36**, **37**, and **38**, respectively, obtained by RB-photosensitized oxygenation of 2,3-dihydrofurans **1**, **7**, and **13** in methanol (for numerical values, see Results). Attempts to isolate methanol addition products by distillation at reduced pressure or by chromatography failed.

From dioxetanes **21** and **27**, only cleavage products **24** and **31**, respectively, were observed.

H_2O_2 Elimination Products from Allylic Hydroperoxides. The furans were identified by their ^1H NMR spectra.

Furan (6):[54] δ 6.30 (m, 2 H), 7.38 (m, 2, H).

2-Methylfuran (12):[55] δ 2.24 (s, br, 3 H), 5.88 (m, 1 H), 6.18 (m, 1 H), 7.18 (m, 1 H).

2,3-Dimethylfuran (19):[56] δ 1.90 (s, 3 H), 2.15 (s, 3 H), 6.08 (d, 1 H, J = 2 Hz), 7.10 (d, 1 H, J = 2 Hz).

3-Carbomethoxy-2-methylfuran (25):[56] δ 2.53 (s, 3 H), 3.78 (s, 3 H), 6.54 (d, 1 H, J = 2 Hz), 7.14 (d, 1 H, J = 2 Hz).

Supplementary Material Available: ^1H NMR spectra of **2**, **3**, **8**, **9**, **14**, **16**, **21**, **22** + **23**, **27**, **28**, and **33** + **34** and ^{13}C NMR spectra of **2**, **8**, **14**, **16**, **21**, **22** + **23**, **27**, and **28** (16 pages). Ordering information is given on any current masthead page.

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Dye-Sensitized Photooxygenation of 2,3-Dihydrothiophenes: Formation of Stable 1,2-Dioxetanes from 4,5-Dialkyl-Substituted Derivatives

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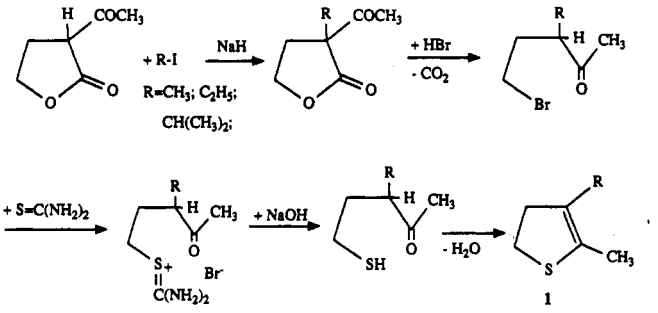
Singlet oxygen reacts with 4,5-dimethyl- (**1a**), 4-ethyl-5-methyl- (**1b**), and 4-isopropyl-5-methyl-2,3-dihydrothiophene (**1c**) to give 1,2-dioxetanes **2a–c** in high yields (>90%). **2a–c** represent the first examples of sulfur-substituted dioxetanes that could be isolated. Less than 5% of allylic hydroperoxides **3a**, **4a**, and **3b**, identified by their ^1H NMR spectra, and less than 5% of *S*-oxides **5a–c** were formed in competing ene reactions and sulfoxide-producing steps, respectively. Due to its decreased rigidity, dioxetane **2a** is less stable than its oxygen counterpart. Increased flexibility of dioxetanes derived from dihydrothiophenes and dihydrothiopyrans, as compared to those derived from dihydrofurans and dihydropyrans, causes dioxetanes **9** and **16**, obtained from 4-carbomethoxy-5-methyl-2,3-dihydrothiophene (**8**) and 5,6-dimethyl-3,4-dihydro-2*H*-thiopyran (**14**), to cleave into dicarbonyl compounds readily at low temperatures. Sulfur-substituted allylic hydroperoxides are also less stable than their oxygen counterparts. Formation of the expected endocyclic allylic hydroperoxides **3a**, **3b**, and **10** is inferred from the appearance of their H_2O_2 elimination products, thiophenes **7a**, **7b** and **13**, respectively.

Introduction

A considerable number of alkyl- and/or aryl-substituted 1,2-dioxetanes and 1,2-dioxetanes derived from enol ethers have been prepared, isolated, and characterized.[1,2a] Although many thioenol ethers were subjected to dye-sensitized photooxygenation, only a few sulfur-substituted 1,2-dioxetanes have been obtained and characterized by spectroscopic means at low temperatures in solution.[2b-4] Due to the rather labile nature of sulfur-substituted 1,2-dioxetanes, none of these compounds was isolated in substance, and, in fact, formation of most hetero (O, S, and N) substituted 1,2-dioxetanes was postulated on the basis of the observed characteristic cleavage products.[5-8]

Scheme I. Synthesis of 4-Alkyl-5-methyl-2,3-dihydrothiophenes



In the preceding paper,[9] we showed that singlet oxygen ($^1O_2$) reacts with 2,3-dihydrofurans to form 1,2-dioxetanes in high yields. Alkyl substitution at the C–C double bond of 2,3-dihydrofuran increases the reaction rate and stabilizes the resulting bicyclic dioxetane. Compared with a series of other dioxetanes,[2a] that derived from 4,5-dimethyl-2,3-dihydrofuran is more stable by 2 to 3 kcal/mol,

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