and the upper part was washed out with ether. The ether washings were extracted with deoxygenated aqueous KOH (1 N) and dried. Removal of solvent from the ether phase by evaporation under reduced pressure left a residue of 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**; 50.1 mg, 0.338 mmol, 63.8%), which was identical by IR and NMR with an authentic sample.[12b] Solvent was removed from the basic aqueous extracts by evaporation in vacuo, and the residue was redissolved in water (0.1 mL). The solution was then acidified, saturated with NaCl, and extracted with ether. Careful removal of solvent from the dried ether extracts by evaporation under reduced pressure left a residue of pure phenol (39.1 mg, 0.415 mmol, 78.3%), which was identified by its ^{1}H NMR spectrum.

The conditions of the pyrolysis were modified slightly to simplify isolation of the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium. 2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (**3**; 93.7 mg, 0.390 mmol) was heated at 165 °C for 5 h in vacuo (0.01 Torr) in an open tube. Under these conditions, phenol and 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**) distilled from the tube. Sublimation of the residue at 150 °C (0.015 Torr) removed a small amount of unreacted starting material. Further sublimation at 150–190 °C (0.007 Torr) then yielded the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium (28.9 mg, 0.121 mmol, 62.1%), which was identified by its IR and ^{1}H NMR spectra.

Control Reaction of 2,3-Dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (3) with 1,3-Dimethylbenzimidazolium Phenoxide. A mixture of 2,3-dihydro-2-(2-hydroxyphenyl)-1,3-dimethyl-1*H*-benzimidazole (**3**; 9.4 mg, 0.039 mmol), 1,3-dimethylbenzimidazolium iodide[14] (11 mg, 0.040 mmol), and lithium phenoxide (3.7 mg, 0.037 mmol) was treated with CD_3CN (1.5 ml), and lithium iodide was removed by filtration. After 28 h at 25 °C, the inner salt **4** of 2-(2-hydroxyphenyl)-1,3-dimethylbenzimidazolium and 2,3-dihydro-1,3-dimethyl-1*H*-benzimidazole (**7**) could be detected in the filtrate by ^{1}H NMR spectroscopy.

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1,2-Dioxetanes Derived from 4,5-Dimethyl-2,3-dihydrofuran and 4,5-Dimethyl-2,3-dihydrothiophene: Synthesis via Photooxygenation, Activation Parameters, and Excitation Properties

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Photooxygenation of 4,5-dimethyl-2,3-dihydrofuran (**1a**) and 4,5-dimethyl-2,3-dihydrothiophene (**1b**) in a variety of solvents gave the respective 1,2-dioxetanes **2a,b** ([2 + 2] cycloaddition) as major products (82–90%) and the allylic hydroperoxides **3a,b** and **4a,b** (ene reaction) as minor products (10–18%). The 2,3-dihydrofuran-derived dioxetane **2a** shows higher thermal stability ($\Delta G^{\ddagger}$ = 28.1 ± 1.0 kcal/mol at 343 K) compared to other known alkoxy-substituted dioxetanes; but more remarkable is the 2,3-dihydrothiophene derivative **2b** ($\Delta G^{\ddagger}$ = 22.7 ± 1.2 kcal/mol at 343 K), the most stable sulfur-substituted dioxetane to date, isolable by molecular distillation. Concerning their excitation properties, both dioxetanes afford preferentially triplet excited state products during thermal decomposition, e.g. Φ^T = 3.2 ± 0.5% for **2a** and $\Phi^T \sim$ 0.002% for **2b**, the latter being the first triplet excitation yield (Φ^T) for a sulfur-substituted dioxetane. Mechanistic rationales for the 1000-fold lower efficiency of generating excited states for the 2,3-dihydrothiophene dioxetane **2b** are presented.

Introduction

Numerous examples of 1,2-dioxetanes bearing heteroatom substituents directly at the four-membered ring have been isolated and characterized.[1] Whereas oxygen-substituted dioxetanes are moderately stable and can be handled at ambient temperatures,[2] only a few sulfur-substituted examples have been described.[3] The synthesis of these labile derivatives utilized photooxygenation of the corresponding thio enol ethers, instead of the Kòpecky route[4] (cyclization of β-bromo hydroperoxides). Since these substrates do not possess allylic hydrogens, competing ene reaction[5] with singlet oxygen presented no problems. Normally, for substrates with allylic hydrogens the ene reaction becomes a serious side reaction and in many cases the dominant pathway. For example, for simple enol ethers such as (*E*)- and (*Z*)-2-methoxy-2-butene, ene reaction takes place exclusively.[6] Increasing solvent polarity

(1) Adam, W.; Cilento, G., Eds. In *Chemical and Biological Generation of Electronically Excited States*; Academic Press: New York, 1982.
(2) Adam, W. In *Small Ring Heterocycles*, Part 3; Hassner, A., Ed.; John Wiley and Sons: New York, 1985, and reviews cited therein.
(3) (a) Geller, G. G.; Foote, C. S.; Pechman, D. B. *Tetrahedron Lett.* **1983**, *24*, 673. (b) Adam, W.; Arias, L. A.; Scheutzow, D. *Tetrahedron Lett.* **1982**, *23*, 2835. (c) Handley, R. S.; Stern, A. J.; Schaap, A. P. *Tetrahedron Lett.* **1985**, *26*, 3183.
(4) Kopecky, K. R.; Mumford, C. *Can. J. Chem.* **1969**, *47*, 709.
(5) Gollnick, K.; Kuhn, H. J. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 287.
(6) Hammond, W. B. *Tetrahedron Lett.* **1979**, 2309.

0022-3263/88/1953-1492$01.50/0

Table I. Rate Constants[a] and Activation Parameters of the Thermal Decomposition of Dioxetanes 2a,b in Toluene

dioxetane[b]	temp,[c] °C	$10^5 k$,[d] s^{-1}	activation parameters[e] $\Delta H^{\ddagger}$ kcal/mol	$\Delta S^{\ddagger}$, e.u.	$\Delta G^{\ddagger}$,[f] kcal/mol
2a	76.9	1.9 ± 0.05			
	79.2	2.6 ± 0.3			
	82.3	4.1 ± 0.4	28.2 ± 1.1	0.3 ± 3.0	28.1 ± 1.0
	86.2	5.7 ± 0.4	(28.3 ± 0.6)	(−0.1 ± 1.2)	(28.1 ± 1.0)
	90.5	9.6 ± 0.3			
	94.3	14.0 ± 0.5			
2b	35.8	115 ± 5			
	41.2	198 ± 3			
	43.2	238 ± 8	19.4 ± 0.8	−9.2 ± 2.5	22.7 ± 1.2
	49.7	460 ± 20	(22.1 ± 2.1)[g]	(−1.2 ± 2)[g]	(22.4 ± 2.3)[g]
	53.7	660 ± 38			

[a] Four independent measurements. [b] Concentration ca. 5×10^{-4} M. [c] Controlled within ca. 0.1 °C. [d] Data processed by means of a first-order kinetic program with statistical analysis using a NCR personal computer. [e] Determined by isothermal kinetics, except the values in parentheses, which were determined by "temperature jump" kinetics. [f] At 343 K. [g] High error limits due to lability of dioxetane **2b**.

and decreasing temperature are known to favor [2 + 2] cycloaddition over ene reaction, as documented for acyclic[7,8] as well as for cyclic[9] enol ether systems.

An additional problem is the labile nature of the 1,2-dioxetanes leading to cleavage products due to their thermal decomposition. In fact, the formation of most heterosubstituted 1,2-dioxetanes was postulated on the basis of the observed cleavage products.[2] Specific examples to be mentioned, in view of our interest here in cyclic substrates, are benzofurans[10] and 2,3-dihydropyrans.[11] In this work we report on the synthesis and characterization of the 1,2-dioxetanes derived from 4,5-dimethyl-2,3-dihydrofuran (**1a**) and 4,5-dimethyl-2,3-dihydrothiophene (**1b**).[12] Furthermore, their activation parameters and excitation properties are described.

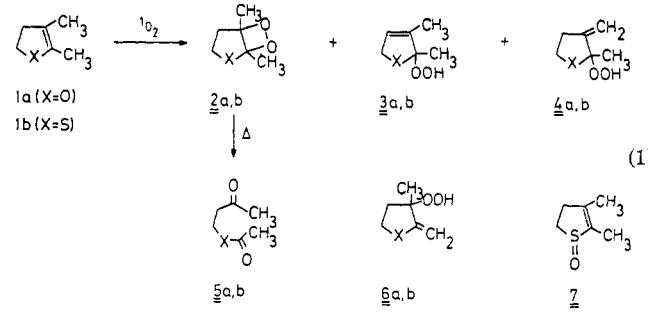
Results

Starting Materials. 4,5-Dimethyl-2,3-dihydrofuran (**1a**) was prepared in a modified three-step synthesis starting with α-acetyl-γ-butyrolactone.[13] The 4,5-dimethyl-2,3-dihydrothiophene (**1b**) was synthesized from 5-bromo-3-methyl-2-pentanone by reaction with thiourea.

Photooxygenation. Photooxygenations of the heterocycles **1a,b** were carried out in a variety of solvents by using tetraphenylporphine (TPP) or Rose Bengal (RB) as sensitizers at temperatures between −20 °C and −78 °C. The reaction progress was monitored either by oxygen consumption or by TLC. In the case of the dihydrothiophene **1b**, free radical type autoxidation could be suppressed by running the photooxygenation in the presence of catalytic quantities of 2,4-di-*tert*-butylphenol as inhibitor. Both the rates as well as the product ratios were identical in the presence and absence of the inhibitor. The product composition was determined by means of quantitative ^1H NMR spectroscopy directly on the reaction mixtures prior to workup or chemical transformations. The dioxetanes **2a,b** were isolated by means of molecular distillation at ca. 10^{-4} Torr and immediately dissolved in toluene or deuteriochloroform for subsequent experimentation. The concentrations of these stock solutions were assessed by iodometric titrations with 0.01 N sodium thiosulfate. Due to the propensity of these dioxetanes toward catalytic decomposition by acids and transition-metal ions, all glassware was washed with aqueous sodium hydroxide prior to use, followed by doubly distilled (from EDTA) water. For the characterization the pure dioxetanes **2** were obtained by silica gel flash chromatography at −20 °C using methylene chloride as eluant.

With a variety of solvents, e.g., nonpolar ones such as C_6H_6, CCl_4, $CHCl_3$, and CH_2Cl_2, aprotic polar ones such as $(CH_3)_2CO$ and CH_3CN, or protic polar ones such as CH_3OH, and TPP or RB as sensitizers, the dihydrofuran **1a** gave 80–88% of dioxetane **2a** and 6–13% and 4–7% of the hydroperoxides **3a** and **4a**, respectively. Similarly, the dihydrothiophene **1b** gave 82–90% of dioxetane **2b** and 5–6% and 5–12% of the hydroperoxides **3b** and **4b**, respectively.

The dioxetanes **2a,b** and the allylic hydroperoxides **3a,b** and **4a,b** (eq 1) were fully characterized on the basis of their spectral data (cf. Experimental Section). In addition, on thermolysis the dioxetanes **2** gave the expected keto esters **5a,b** as cleavage products (eq 1). For dioxetane **2a**



(1)

the latter was formed quantitatively, but for **2b** also ca. 10–15% of unidentified, thermally labile side products were detected by ^1H NMR. The keto esters **5a,b** were characterized by spectral comparison with authentic materials, prepared according to known procedures.[14] The allylic hydroperoxides **6a,b**, products of the ene reaction with singlet oxygen via hydrogen abstraction from the 5-methyl group in **1**, were not detected. Furthermore, in the case of the dihydrothiophene **1b** ca. 5% sulfoxide **7** was formed (eq 1), resulting from sulfur oxidation by $^1O_2$.[15] Sulfoxide **7** was characterized by spectral comparison with

(7) Ando, W.; Watanabe, K.; Suzuki, J.; Migata, T. *J. Am. Chem. Soc.* **1974**, *96*, 6766.
(8) Mirbach, M. J.; Henne, A.; Schaffner, K. *J. Am. Chem. Soc.* **1978**, *100*, 7127.
(9) Asveld, E. W. H.; Kellogg, R. M. *J. Am. Chem. Soc.* **1980**, *102*, 3644.
(10) Rio, G.; Berthelot, J. *Bull. Soc. Chim. Fr.* **1971**, 1705.
(11) (a) Bartlett, P. D.; Mendenhall, G. D.; Schaap, A. P. *Ann. N.Y. Acad. Sci.* **1970**, *171*, 79. (b) Frimer, A. A.; Bartlett, P. D.; Boschung, A. F.; Jewett, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 7977.
(12) For the photooxygenation of further 2,3-dihydrofurans and 2,3-dihydrothiophenes, cf.: Knutzen-Mies, K., Dissertation, University of Munich, 1987.
(13) McGreer, D. E.; Chiu, N. W. F.; Vinje, M. G. *Can. J. Chem.* **1965**, *43*, 1398.
(14) (a) Daeniker, H. U.; Druey, J. *Helv. Chim. Acta* **1960**, *43*, 983. (b) Arbuzov, A. *J. Gen. Chem. USSR* **1959**, *29*, 3244.
(15) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

material synthesized from **1b** by treatment with H_2O_2 at 0 °C.

Activation Parameters. Isothermal kinetics[1] by monitoring the chemienergized 9,10-dibromoanthracene (DBA) chemiluminescence served well for both dioxetanes. The direct chemiluminescence[1] could only be used for **2a** because for the dihydrothiophene derivative **2b** the direct emission was too weak to be detected by our photometric apparatus (cf. Experimental Section). For the dihydrofuran system **2a** also the "initial rates" method[16] was used. The results are summarized in Table I.

The kinetic data clearly reveal the much lower thermal stability of the sulfur-substituted dioxetane **2b** compared to the oxygen-substituted dioxetane **2a**, about 6 kcal/mol in the activation free energies ($\Delta G^{\ddagger}$). Nevertheless, **2b** is to date the most stable sulfur-substituted dioxetane, isolable by molecular distillation!

The appreciably more negative activation entropies ($\Delta S^{\ddagger}$) of **2b** compared to **2a** (Table I) suggest dark catalysis for the sulfur system. The activation parameters from the "initial rates" method support this assumption; while the activation energy stays constant in the error limits, the activation entropy increases. Comparison of the data of the isothermal and "initial rates" kinetics of the oxygen-substituted dioxetane **2a** (Table I) shows that dark catalysis is unimportant for this case. In fact, the near zero $\Delta S^{\ddagger}$ value substantiates this finding. That the sulfur-substituted dioxetane **2b** should be prone to dark catalytic decomposition is hinted at by the fact that ca. 15% of presumably sulfur-oxidized transient products were detected by ^{1}H NMR in the thermal decomposition of **2b**. Indeed, sulfur-substituted dioxetanes are known[17] to undergo C–S bond cleavage and the resulting sulfides and/or disulfides can catalyze the decomposition of dioxetanes via dark processes.[18]

Excitation Yields. The singlet (Φ^S) and triplet (Φ^T) excitation yields of the dioxetanes **2a,b** were determined by the well-established[1] chemiluminescence methods, using 9,10-diphenylanthracene (DPA) for singlet and 9,10-dibromoanthracene (DBA) for triplet counting. In the latter case, the cited[19] value for the fluorescence quantum yield (Φ^f_{DBA}) is in error; instead of 0.10 it should be 0.20, as reported originally.[20] With this value, the excitation yields for the dihydrofuran dioxetane **2a** were determined to be $\Phi^T = 3.2 \pm 0.5\%$ and $\Phi^S = 0.39 \pm 0.06\%$, resulting in $\Phi^T/\Phi^S = 10$. For the dihydrothiophene dioxetane **2b** only the triplet excitation yield could be estimated, affording $\Phi^T \sim 0.002\%$. The DPA-enhanced emission of **2b** was too weak to obtain reliable data on Φ^S. However, comparison of the triplet excitation yields of these two dioxetanes clearly emphasizes the much lower ability of the sulfur-substituted dioxetane **2b** to produce electronically excited products.

Discussion

From the product distributions (**2**:**3**:**4** ratios), e.g., for **1a** 82:13:5 (in CCl_4) and 87:6:7 (in CH_3CN) or for **1b** 90:5:5 (in CCl_4) and 90:5:5 (in CH_3CN), clearly in all cases the dioxetanes are the major products. No ene product with abstraction of allylic hydrogens from the 5-methyl group could be detected, indicating that they are formed to an extent of less than 3% (if at all). If one assumes an open zwitterionic intermediate, one should expect at least some hydrogen abstraction from the 5-methyl group. Therefore, we postulate attack of singlet oxygen on the double bond along a perepoxide-like coordinate with preferential orientation of the terminal oxygen above the ring plane. For a detailed discussion of this complex mechanistic course cf. ref 12.

An obvious and very pronounced effect lies in the difference between the activation and excitation parameters of the oxygen-substituted dioxetane **2a** and the sulfur analogue **2b**. The ^{1}H NMR data (see Experimental Section) of these dioxetanes provide interesting information on the geometry of the bicyclo[3.2.0] system. The vicinal coupling constant $^3J_{b,c} = 0$ for the dihydrofuran dioxetane **2a** indicates a dihedral angle H_b–C_4–C_3–H_c nearly 90°, while for the sulfur-substituted dioxetane **2b** it is $^3J_{b,c} = 6.0$ Hz. As Dreiding models suggest, the oxygen-substituted dioxetane is much more rigid than the corresponding sulfur analogue. This rigidity of dioxetane **2a** should lead to higher thermal stability, whereas the more flexible sulfur derivative **2b** needs less activation for puckering of the dioxetane ring and should, therefore, be less stable. In addition, the intramolecular electron exchange mechanism[21] may be responsible for the labile nature of **2b**. This was argued recently[3] for a related series of dioxetanes with heteroatom substitutents, since the stability of these dioxetanes correlated well with the oxidation potentials of the heteroatom substituents.

Nevertheless, the activation energy (Table I) for cleavage of the sulfur dioxetane **2b** is appreciably higher compared to other known examples.[3] Similarly, also the oxygen-substituted case **2a** is clearly more stable than monocyclic tetraalkyl-substituted 1,2-dioxetanes. For example, tetramethyl-1,2-dioxetane has an activation free energy ranging between 25 and 26 kcal/mol[2] at 343 K compared to 28 kcal/mol for the dihydrofuran dioxetane **2a**. This stabilization must again be due to the rigidity of the bicyclic ring system of **2a**. For example, it is known that six-membered annelation lowers the activation energy for the decomposition of dioxetanes, whereas five-membered ring annelation increases it compared to their monocyclic analogues.[22] For the puckered, six-membered ring-annelated 1,2-dioxetanes the twisting motion necessary for ring cleavage is already predestined (one axial and one equatorial C–O bond), whereas in the essentially planar, five-membered ring-annelated 1,2-dioxetanes the twisting motion needs to be vibrationally induced, thus requiring higher activation energy.[2]

The triplet and singlet quantum yields (Table I) for the oxygen-substituted dioxetane **2a** lie in the expected range for simple dioxetanes, whereas for the sulfur-substituted case **2b** they are dramatically decreased, especially the triplet quantum yield. Presumably, the decreased propensity of the sulfur derivative **2b** to form excited states like its decreased thermal stability can be explained in terms of the intramolecular electron exchange mechanism.[21] Thus, the dramatically lower (1000-fold) triplet quantum yield of the sulfur-substituted dioxetane compared to the oxygen-substituted analogue should not be surprising.

(16) Wilson, T.; Schaap, A. P. *J. Am. Chem. Soc.* **1971**, *93*, 4126.
(17) (a) Adam, W.; Liu, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 1206. (b) Ando, W.; Watanabe, K.; Migata, T. *Tetrahedron Lett.* **1975**, 4127.
(18) Campbell, B. S.; Denney, D. B.; Denney, D. Z.; Shih, L. S. *J. Am. Chem. Soc.* **1975**, *97*, 3850.
(19) Engel, P. S.; Monroe, B. M. *Adv. Photochem.* **1971**, *8*, 245.
(20) (a) Melhuish, R. *J. Phys. Chem.* **1961**, *65*, 229.
(21) (a) Schuster, G. B. *Acc. Chem. Res.* **1979**, *12*, 366. (b) McCapra, F.; Beheshti, I.; Burford, A.; Hann, R. A.; Zaklika, K. A. *J. Chem. Soc., Chem. Commun.* **1977**, 944. (c) Zaklika, K. A.; Kissel, T.; Thayer, A. L.; Burns, P. A.; Schaap, A. P *Photochem. Photobiol.* **1979**, *30*, 35. (d) Schaap, A. P.; Gagnon, S. D.; Zaklika, K. A. *Tetrahedron Lett.* **1982**, *23*, 2943.
(22) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1986**, *51*, 5213. (b) Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* **1981**, *22*, 4263. (c) Lechtken, P.; Reissenweber, G.; Grubmüller, P. *Tetrahedron Lett.* **1977**, 2881.
(23) Janda, M.; Srogl, J.; Nemec, M.; Vopatrna, P. *Synthesis* **1972**, 54.

Other reasons could be the enhanced dark catalytic decomposition due to carbon–sulfur bond cleavage that accompanies peroxide bond fragmentation[17] and possibly the heavy-atom effect exerted by the sulfur substitutent. There are no precedents to substantiate this hypothesis, since the triplet excitation yield of **2b** is the first ever reported for a sulfur-substituted dioxetane.

Experimental Section

Caution! All preparations and reactions of the dioxetanes and hydroperoxides were carried out behind safety shields. Neat samples of dioxetanes can be extremely hazardous and should be handled only in amounts less than 100 mg.

Solvents and commercially available compounds were purchased from standard suppliers and purified to match reported physical constants and spectral data. Other known compounds were prepared according to literature procedures and purified appropriately.

^{1}H NMR were recorded on Bruker WP-80 and WM-400 as well as Varian FX-100, EM-390, and A-60 spectrometers with tetramethylsilane (TMS) as internal standard. ^{13}C NMR were recorded at 22.3 and 100 MHz on Bruker WP-80 and WM-400 spectrometers, with TMS as internal standard. Solvents for NMR measurements were $CDCl_3$ or mixtures of $CDCl_3$ and $CFCl_3$. IR spectra were taken on a Perkin-Elmer 125 spectrometer as thin films. The dioxetane kinetics were carried out on a Mitchell-Hastings photometer[24] equipped with a RCA PF 1006 photomultiplier tube and Lauda thermostats NB-D8/17 or K4RD for temperature control of the cell compartment. The cell temperature was measured by means of a Ni–Cr–Ni thermocouple and a Mawi-Therm 4003 detector. Temperature control was within ±0.1 °C during the measurements. Packard scintillation vials were used as reaction vessels. A Servogar 210 recorder registrated the output signal of the kinetic run. The data were processed on a NCR personal computer. The chemiluminescence measurements were carried out as described.[25]

4,5-Dimethyl-2,3-dihydrofuran. To a sample of 20.9 g (180 mmol) of 3-methyl-5-hydroxypentan-2-one[13] was 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, redistillation on a 100-cm spinning band column gave 8.84 g (50%) colorless product, bp 106 °C at 760 Torr (lit. 13 bp 108–110 °C).

4,5-Dimethyl-2,3-dihydrothiophene. To a solution of 33.8 g (190 mmol) of 1-bromo-3-methylpentan-4-one[26] in 20 mL of water was added 14.5 g (190 mmol) of thiourea, and the mixture was refluxed for 15 h. The solution was hydrolyzed with 15 mL of 5% sodium hydroxide under nitrogen and refluxed for another 15 h. After cooling under nitrogen, the solution was neutralized with 2 N HCl and extracted three times with ether. The organic layer was dried over $MgSO_4$ and the solvent removed by distillation up to 200 Torr. Subsequent distillation at 12 Torr into a dry ice cooled trap gave a mixture of product and water. For further purification the product was distilled twice through a 15-cm Vigreux column, yielding 4.49 g (21%) a colorless liquid, bp 42 °C at 12 Torr (purity: 99% GC). The product was stored under nitrogen in a refrigerator. ^{1}H NMR: δ 1.63 (br s, CH_3), 1.79 (br s, CH_3), 2.70 (m, CH_2), 3.06 (m, CH_2).

General Procedure for Photooxygenations. A 25-mL irradiation unit with automatic O_2 consumption recording system[27] was used for product distribution studies. 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 tetraphenylporphine (TPP). RB was applied in 5×10^{-4} M and TPP in 8×10^{-4} M concentrations, respectively. The solutions were saturated with oxygen before irradiation. The irradiation unit, the oxygen burette, and the tubing connecting the unit with the burette were kept at 13.5 ± 0.1 °C by cooling with water, using a Julabo-P thermostat. A similar 25-mL irradiation unit[28] was used for the low-temperature product studies. This was fitted with an evacuated window and cooled by a Lauda Ultracryostat UK 60 SDW, providing temperatures between −60 °C 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.

1,2-Dioxetanes. Samples of 500 to 700 mg (3–7 mmol) of **1a,b** were dissolved in a 1:1 mixture of $CDCl_3$ and $CFCl_3$ (8×10^{-4} M solutions of TPP) and cooled to −78 °C while purging with a gentle stream of oxygen gas. The solution was irradiated with a constant oxygen flow for 4–5 h. The solvent was removed at −50 °C to −30 °C at 10^{-4} Torr and the 1,2-dioxetane **2a** was distilled at 5 °C and 10^{-4} Torr in a cold trap kept at liquid nitrogen temperature. Dioxetane **2b** was distilled at 0 °C and 10^{-4} torr. The dioxetanes **2a,b** are yellow oils which can be stored in solution on dry ice for several months.

1,5-Dimethyl-2,6,7-trioxabicyclo[3.2.0]heptane (2a): yellow oil (48%); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.56 (s, 3 H), 1.60 (s, 3 H), 1.79 (ddd, J = 13.6, 12.0, 8.0 Hz, 1 H, 4-H_{exo}), 2.28 (dd, J = 13.6, 5.2 Hz, 1 H, 4-H_{endo}), 4.23 (dd, J = 8.0, 8.0, 1 H, 3-H_{exo}), 4.57 (ddd, J = 12.0, 8.4, 5.2 Hz, 1 H, 3-H_{endo}); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.1 (q), 19.4 (q), 37.4 (t), 67.1 (t), 96.5 (s), 115.6 (s).

1,5-Dimethyl-2-thia-6,7-dioxabicyclo[3.2.0]heptane (2b): yellow oil (31%); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.61 (s, 3 H), 1.79 (s, 3 H), 1.98 (ddd, J = 14.5, 11.5, 6.5 Hz, 1 H, 4-H_{exo}), 2.45 (ddd, J = 14.5, 6.0, 5.0 Hz, 1 H, 4-H_{endo}), 2.98 (ddd, J = 12.0, 6.5, 6.0 Hz, 1 H, 3-H_{exo}), 3.71 (ddd, J = 12.0, 11.5, 5.0 Hz, 1 H, 3-H_{endo}); ^{13}C NMR ($CDCl_3$, 22 MHz) δ 19.8 (q), 21.2 (q), 30.4 (t), 43.1 (t), 98.8 (s), 106.8 (s).

The physical and spectral data of the allylic hydroperoxides **3a,b** and **4a,b** are given in ref 12b.

Cleavage Products of the 1,2-Dioxetanes 5a,b. 4-Acetoxybutan-2-one (**5a**)[15a] and 4-acetylmercaptobutan-2-one (**5b**)[15b] were synthesized independently, following literature procedures. Comparison of these authentic materials with the cleavage products of the dioxetane decomposition reaction showed identical spectral and physical data.

4,5-Dimethyl-2,3-dihydrothiophene *S*-Oxide (7).[14] A sample of 50 mg (5.0 mmol) of 4,5-dimethyl-2,3-dihydrothiophene in 10 mL of acetone was added to 0.4 mL of 30% hydrogen peroxide at 0 °C. The solution was stirred for 50 h at this temperature. After evaporation of the acetone, the residue was dissolved in chloroform, dried over $MgSO_4$, and distilled. **7**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.86 (s, 3 H), 2.03 (s, 3 H), 2.73 (m, 2 H), 3.36 (m, 2 H); IR (film) 1650, 1030 cm^{-1}; UV (CH_3CN) λ_{max} 260 nm.

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(24) Mitchell, G. W.; Hastings, J. W. *Anal. Biochem.* **1971**, *39*, 243.
(25) Adam, W.; Baader, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 410.
(26) 1-Bromo-3-methylpentan-4-one was prepared in analogy to 1-bromo-3-ethylpentan-4-one described by Schow, S. R.; McMorris, T. C. *J. Org. Chem.* **1979**, *44*, 3763.
(27) (a) Paur, H. Dissertation, University of Munich, 1982. (b) Griesbeck, A. G. Dissertation, University of Munich, 1984.
(28) Koegler, S. Dissertation, University of Munich, 1987.