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New Insight into the Reaction of Singlet Oxygen with Sulfur-Containing Cyclic Alkenes: Dye-Sensitized Photooxygenation of 5,6-Dihydro-1,4-dithiins

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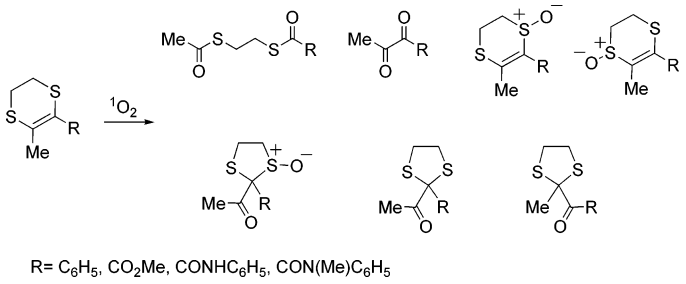

R= C_6H_5, CO_2Me, $CONHC_6H_5$, $CON(Me)C_6H_5$

The reaction of 3-methyl-5,6-dihydro-1,4-dithiins with singlet oxygen affords dicarbonyl compounds and/or ring-contracted ketosulfoxides, the latter regio- and stereoselectively, depending on the nature of the substituent at C-2 and on the reaction conditions. In competition with normal fragmentation, the intermediate dioxetanes, derived from [2 + 2] cycloaddition of singlet oxygen to the double bond, undergo an intramolecular oxygen transfer to the sulfur-1 atom, leading to labile epoxide intermediates. The latter convert to *cis*- and *trans*-ketosulfoxides through a non-concerted S-4 migration. This pathway is promoted by the electron-withdrawing group at C-2 and, for monosubstituted amide, by the solvent basicity. S-Oxidation of dithiins is insignificant, except for the monosubstituted amide derivative or in the presence of protic species, and occurs selectively at the S-1 atom.

Introduction

The reaction of sulfides with singlet oxygen has received great attention due to the many important roles of sulfur-containing substances in key positions of proteins, enzymes, etc. or as antioxidants in polymers or rubbers.[1] Studies have been particularly devoted to the question of the identities of the reactive intermediates.[2] Persulfoxide (R_2S^+-$OO^- \leftrightarrow R_2S^\bullet$-$OO^\bullet$) is accepted as the first formed intermediate.[3] It is well-known that it is subject to decomposition to sulfide and ground-state oxygen (physical quenching)[4] and to chemical processes. Although sulfoxide formation is its main reaction, persulfoxide undergoes a myriad of inter- and intramolecular reactions strongly depending on the substituents or on the reaction conditions (nature of solvent, presence of acid traces, temperature, etc.).[5] Among the others, recently it has been reported that the presence of α-hydrogens may favor the oxidation capability of a sulfide and induce the breakage of the sulfur−α-carbon bond.[6]

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(1) For some reviews: (a) Clennan, E. L. *Sulfur Rep.* **1996**, *19*, 171. (b) Jensen, F. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 4, pp 1−48. (c) Ando, W.; Takata, T. In *Singlet Oxygen*; Frimer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. III, part 2.

(2) For some recent reports: Clennan, E. L.; Hightower, S. E.; Greer, A. *J. Am. Chem. Soc.* **2005**, *127*, 11819.

(3) Nahm, K.; Foote, C. S. *J. Am. Chem. Soc.* **1989**, *111*, 1909.

(4) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717.

(5) (a) Akasaka, T.; Ando, W. In *Organic Peroxides*; Ando, W., Ed.; J. Wiley and Sons: New York, 1992; p 599. (b) Clennan, E. L.; Pace, A. *Tetrahedron* **2005**, *61*, 6665. (c) Iesce, M. R.; Cermola, F.; Rubino, M. *Curr. Org. Chem.* **2007**, *11*, 1053.

(6) (a) Takata, T.; Tamura, Y.; Ando, W. *Tetrahedron* **1985**, *41*, 2133. (b) Bonesi, S. M.; Torriani, R.; Mella, M.; Albini, A. *Eur. J. Org. Chem.* **1999**, 1723.

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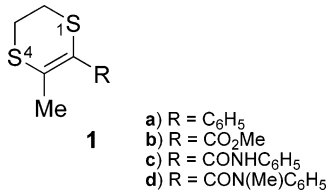


FIGURE 1. 2,3-Disubstituted dithiins.

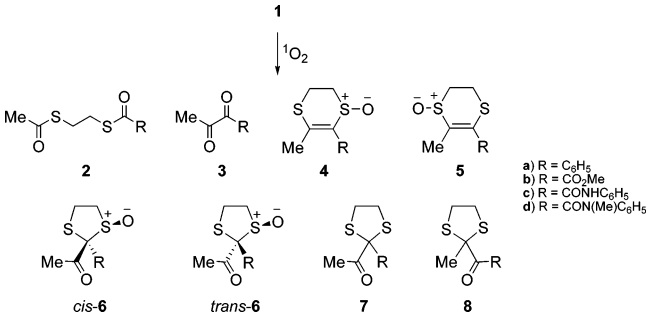
Sulfur oxidation goes to a lesser extent in the singlet oxygen reaction of cyclic and acyclic vinyl sulfides so that the [2 + 2] cycloaddition of singlet oxygen to the double bond, or the ene-mode reaction in the presence of allylic hydrogens, becomes the preferential pathway.[1] In this context, we recently found that the reaction of 5,6-dihydro-1,4-oxathiins with singlet oxygen led to the corresponding dioxetanes almost exclusively.[7] The presence of a sulfur atom influences the behavior of the bicyclic peroxides, which bear an electron-withdrawing group, promoting the formation of unusual ring-contracted ketosulfoxides instead of the usual O−O and C−C bond breakage products.[7] To gain further information on the role of sulfur in the singlet oxygen reaction of sulfur-substituted cycloalkenes, we have devoted our attention to the 5,6-dihydro-1,4-dithiin system. In particular, we have examined the dye-sensitized photooxygenation[8] of derivatives **1a**−**d** with a substituent pattern suitable to study the substituent effect (Figure 1).[9] The reactions were carried out in CH_2Cl_2 but also in protic media, known to favor the oxidation of sulfides (e.g., trifluroethanol (TFE)[10a] or methanol,[4,10b] the latter also capable of trapping ionic intermediates in the oxygenation of electron-rich alkenes[10c]). Further experiments were also carried out in CH_3CN and acetone, which could have a role, as hydrogen bond acceptors, in the presence of an amidic hydrogen (e.g., **1c**).

Results and Discussion

Photooxygenation of **1a**−**d** (0.02 M solution) was carried out at −20 °C using tetraphenylporphine (in CH_2Cl_2) or methylene blue (in MeOH, CH_3CN, and acetone) as sensitizers. The reaction products that were generally isolated by TLC are shown in Scheme 1. Table 1 reports the relative amounts of the products that were spectroscopically deduced by ^{1}H NMR of the crude reaction mixtures, as well as the yields of pure isolated compounds. Isolated yields were lower than those estimated by ^{1}H NMR spectra of the crude mixtures since all products underwent partial chromatographic alteration.

As shown in Table 1, product distribution depends on the nature of the substituents at the double bond and on the solvent used. In CH_2Cl_2, methyl aryl dithiin **1a** gives dicarbonyl compound **2a** and diketone **3a** (Table 1, entry 1). Dicarbonyl compound **2c** was a minor product in the reaction of amide **1c**, which led mainly to sulfoxide **4c** (Table 1, entry 8). Ester **1b** and *N*-methyl amide **1d** gave ketoesters *cis*-**6b**,**d** besides small amounts of their trans-isomers (Table 1, entries 4 and 13, respectively).

SCHEME 1. Oxygenation Products



Concentration or solvent change (from CH_2Cl_2 to acetone or to more polar CH_3CN) showed no significant effects except for **1c**. In this case, a serious change of the **2c**/**4c** ratio was found by using a more diluted solution [8:2 in 10^{-2} M (Table 1, entry 8) and 4:6 in 10^{-3} M (Table 1, entry 9)]. The basic nature of the solvent was also significant. Indeed, the ^{1}H NMR spectrum of the reaction mixture in CH_3CN showed, in addition to **2c** and **4c** and *trans*-**6c**, the presence of *cis*-**6c** as a labile compound that converted to *trans*-**6c** (Table 1, entry 11). A similar result, but with a higher amount of the labile compound, was obtained using acetone as the solvent (Table 1, entry 12). TLC gave only *trans*-**6c** (35% in CH_3CN and 61% in acetone). Ketothioketal **7c** was also found in both solvents.

For all series, a drastic change in product distribution was observed in MeOH or by adding 10−100 equiv of trifluoroethanol (TFE)[10a] in CH_2Cl_2. Under these conditions, *S*-oxides **4b**−**d** were selectively formed (Table 1, entries 5, 6, 10, 14, and 15). Methyl phenyl dithiin **1a** led to both sulfoxides **4a** and **5a**. Moreover, ketosulfoxide **6a** was found besides a small amount of ketothioketals **7a** and **8a** (Table 1, entries 2 and 3).

Identification of Products. All compounds were characterized on the basis of analytical and/or spectroscopic data. The stereochemistry of *cis*- and *trans*-**6b**,**d** and *trans*-**6c** was assigned by X-ray analysis. The crystallographic determination also accounted for the upfield value of Me−CO protons (δ 1.54) in the ^{1}H NMR of *cis*-**6d**. It shows that the methyl group is above the ring current of phenyl and is, hence, affected by its strong diamagnetic effect, as previously reported for similar compounds.[7] NMR data for the labile *cis*-**6c** were deduced from the reaction mixture in acetone, by performing the spectra in acetone-d_6, in which the conversion to *trans*-**6c** occurred slowly. The close similarity of the data with those of *trans*-**6c** allowed us to tentatively assign the structure *cis*-**6c**. In particular, the ^{13}C spectrum exhibited two signals as triplets at δ 35.8 and 58.3, which were correlated to a complex proton pattern in the δ range of 3.80−4.46 due to the SCH_2CH_2SO system. In addition to the amide carbon signal (δ 166.3), two quaternary carbons at δ 95.2 and 199.8 due to the quaternary carbon linked to two heteroatoms and to the carbonyl carbon, respectively, were observed.

Compounds **4** and **5** showed typical sulfoxide bands at 1020−1010 cm^{-1} in the IR spectra as well as the downfield shift of one triplet signal in the δ range of 42−43 due to the CH_2SO carbon in the ^{13}C spectra. Structures **4** were assigned on the

(7) (a) Cermola, F.; Iesce, M. R. *J. Org. Chem.* **2002**, *67*, 4937. (b) Cermola, F.; De Lorenzo, F.; Giordano, F.; Graziano, M. L.; Iesce, M. R.; Palumbo, G. *Org. Lett.* **2000**, *2*, 1205.

(8) The use of a dye, visible light, and molecular oxygen is one of the most common and efficient procedures to produce singlet oxygen. Foote, C. S.; Clennan, E. L. In *Active Oxygen in Chemistry*; Foote, C. S., Valentine, J. S., Greenberg, A., Liebman, J. F., Eds.; Chapman and Hall: London, 1995; p 105.

(9) A symmetrically substituted dithiin (2,3-diphenyl derivative) was previously photooxygenated giving the corresponding dicarbonyl compound and benzyl: Handley, R. S.; Stern, A. J.; Schaap, A. P. *Tetrahedron Lett.* **1985**, *26*, 3183.

(10) (a) Bonesi, S. M.; Mella, M.; d'Alessandro, N.; Aloisi, G. G.; Vanissi, M.; Albini, A. *J. Org. Chem.* **1998**, *63*, 9945. (b) Clennan, E. L.; Greer, A. *J. Org. Chem.* **1996**, *61*, 4793. (c) Gorman, A. A.; Gould, I. R.; Hamblett, I. *J. Am. Chem. Soc.* **1982**, *104*, 7098.

TABLE 1. Dye-Sensitized Photooxygenation of 1a−d[a]

			product distribution[b]						
entry	dithiin	solvent	**2**	**3**	**4** [**5**]	*cis*-**6**	*trans*-**6**	**7**	**8**
1	**1**a	CH_2Cl_2[c]	50(35)	50(55)	(trace)				
2		CH_2Cl_2[c]/TFE[d,e]	19(15)	34(24)	21(13)[10(6)]		12(7)[f]	4(2)	(trace)
3		MeOH[g]	25(20)	38(29)	15(8)[9(4)]		8(4)[f]	2(<2)	3(2)
4	**1**b	CH_2Cl_2[c]			(<2)	90(62)	10(8)		
5		CH_2Cl_2[c]/TFE[d,e]			70(39)	30(20)	(trace)		
6		MeOH[g]			26(19)	67(51)	7(3)		
7		MeOH[g]/−50 °C			34(23)	63(48)	3(<2)		
8	**1**c	CH_2Cl_2[c]	20(15)	(trace)	80(58)		(trace)		
9		CH_2Cl_2[c,h]	50(34)	15(10)	35(28)		(trace)		
10		MeOH[g]	20(16)	9(6)	68(50)		3(<2)		
11		CH_3CN[g]	11(9)		41(38)	28[i]	17[j](35)	3(<2)	
12		acetone[g]	3(<2)		15(7)	47[i]	25[j](61)	10(4)	
13	**1**d	CH_2Cl_2[c]			(trace)	95(58)	5(2)		
14		CH_2Cl_2[c]/TFE[d,e]			89(31)	11(3)			
15		MeOH[g]			56(25)	44(25)			

[a] 0.02 M solution at −20 °C except otherwise stated. [b] Product ratios that have been determined by ^{1}H NMR spectra of crude reaction mixtures are an average of two or three determinations. In parentheses, yields of pure products that have been isolated by preparative TLC are reported. They are lower than those deduced spectroscopically due to the partial decomposition during chromatographic separation. [c] Tetraphenylporphine (TPP) as the sensitizer. [d] **1**: trifluoroethanol (TFE) = 1:100. [e] Under these conditions, the low chromatographic yield is due to the presence of unidentified material. [f] Stereochemistry not assigned. [g] Methylene blue as the sensitizer. [h] 10^{-3} M solution. [i] This value diminishes in time since the product converted to *trans*-**6c**. [j] This value increases in time at the expense of that of *cis*-**6c**.

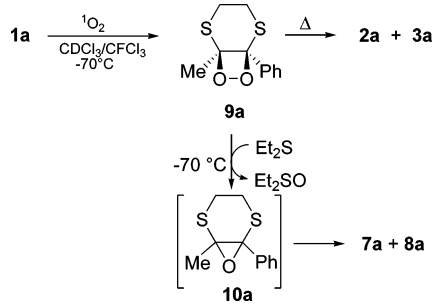
basis of the 2-D spectra (HMBC), which showed a correlation between the Me protons and the CH_2S carbon (δ range of 23−24) through J_4 coupling.

Intermediates. Attempts to detect labile intermediates at low temperatures failed except for **1a**. In this case, when the reaction was carried out at −70 °C in $CDCl_3/CFCl_3$, NMR analysis at this temperature showed the presence of the dioxetane **9a**.[11] This compound exhibited a Me singlet at δ 1.40, as linked to a saturated carbon in the proton spectrum and, in the ^{13}C spectrum, two characteristic dioxetane carbons at δ 98.2 and 102.5. On raising the temperature, dioxetane **9a** converted mainly to dicarbonyl compounds **2a** and **3a**.

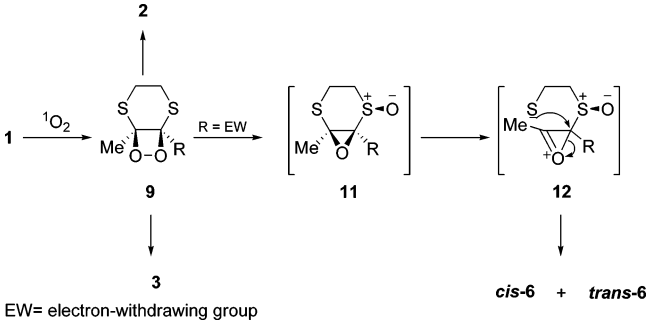
The peroxidic nature of dioxetane **9a** was proven by treatment at low temperature with pre-cooled Et_2S. The sulfoxide Et_2SO was rapidly formed in addition to ketothioketals **7a** and **8a**. As reported,[1c] dioxetane reduction by phosphorus or sulfide compounds involves the intermediacy of an epoxide. It is therefore possible that epoxide **10a** is formed but, as it is thermodynamically unstable as observed for similar condensed compounds,[7,12] quickly rearranges by 1,2-migration of the sulfur atom.

Mechanistic Interpretation. On the basis of these results and previous data,[7] it can be assumed that the reaction of dithiins with singlet oxygen[13] occurs mainly via [2 + 2] cycloaddition leading to dioxetanes **9**. The usual fragmentation of these peroxides gives dicarbonyl compounds **2**, while α,α′-diketones **3** should derive from **9** via cleavage of both C−S bonds, as reported for 2,3-diphenyl-1,4-dithiin[9] and thioethylene derivatives[14] (Scheme 3). These pathways compete with the formation of ketosulfoxides **6** in the presence of an electron-withdrawing group. As reported for oxathiins,[7] the increased electron demand by the peroxide O−O bond induces an intramolecular nucleophilic attack, by one of the neighboring sulfurs to the peroxidic oxygen, leading to ketosulfoxides **6** likely via the undetected labile epoxides **11**. Structures **6b−d** clearly indicate that the attack occurs by S-1 rather than S-4. The latter is, instead, involved in the migration step (Scheme 3). As suggested by the mixture of stereoisomers, migration should occur in a non-

SCHEME 2



SCHEME 3



(11) The lower stability of electron-withdrawing substituted dioxetanes than that of alkyl- or aryl-substituted analogues has already been observed in the oxathiin systems.[7a]

(12) Rearrangements of labile epoxides to carbonyl compounds are well-documented. See, for example: (a) Adam, W.; Hadjiarapoglou, L.; Wang, X. *Tetrahedron Lett.* **1991**, *32*, 1295. (b) Baylon, C.; Hanna, I. *Tetrahedron Lett.* **1995**, *36*, 6475. (c) Katritzky, A. R.; Xie, L.; Serdyuk, L. *J. Org. Chem.* **1996**, *61*, 7564.

(13) We confirmed the occurrence of singlet oxygen by carrying out the photooxygenation of dithiins **1** either in the absence of the dye or in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), a well known quencher of singlet oxygen.[8] In both cases, dithiins were recovered unchanged even after prolonged irradiation times.

(14) See, for example: (a) Adam, W.; Liu, J.-C. *J. Am. Chem. Soc.* **1972**, *94*, 1206. (b) Ando, W.; Watanabe, K.; Migita, T. *Tetrahedron Lett.* **1975**, *47*, 4130.

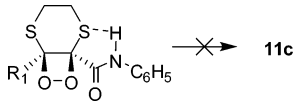


FIGURE 2.

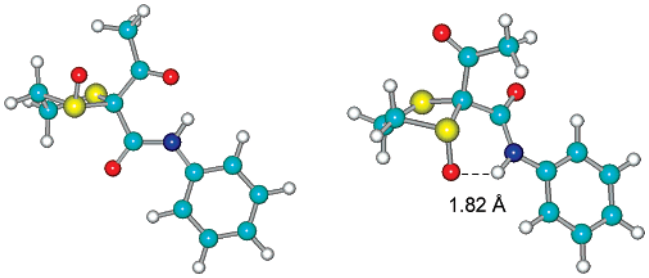


FIGURE 3. Theoretical calculations.

SCHEME 4

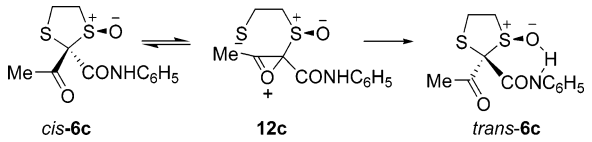


TABLE 2. HOMO Energy Values[a] of 1a−d versus Tetrasubstituted Olefin

	1a	1b	1c	1d	
HOMO (eV)	−7.83	−8.11	−8.29	−8.12	−9.0

[a] Calculated by Hyperchem 6.0 with AM1 force field.

concerted manner (e.g., via the charged species **12** that may decay to both *cis*-**6** and, to a lesser extent, *trans*-**6**).

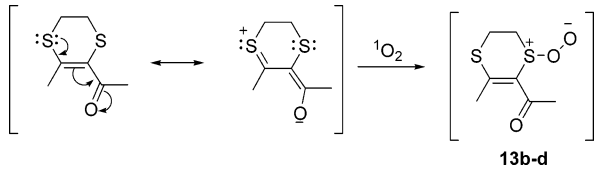
The anomalous results in the oxygenation of amide **1c** where ketosulfoxides **6c** are not found (Table 1, entries 8−10), except in CH_3CN (Table 1, entry 11) and acetone (Table 1, entry 12), can be explained assuming that the sulfur attack to peroxide oxygen may be difficult due to the H-bonding between NH and S, as shown in Figure 2. In basic solvents, instead NH bonding occurs with the solvent, and ketosulfoxides **6c** can be formed.

The conversion of *cis*-**6c** to the more thermodynamically stable *trans*-**6c** could be ascribed to the kinetic−thermodynamic control through the species **12c** (Scheme 4). Indeed, a MM^+ conformational analysis assigned a lower energy to the trans-isomer of ca. 4 kcal/mol than to the *cis*-isomer **6c** (Figure 3), likely due to intramolecular hydrogen bonding.

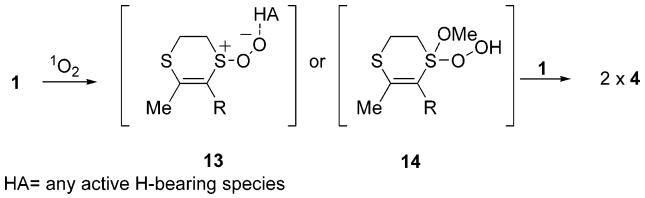
In all cases examined, no ene products were ever found despite the presence of allylic hydrogens. This should be due to the high nucleophilicity of the double bond as shown by HOMO values, which are higher than that of tetramethylethylene, a well-known singlet oxygen reactant[15] (Table 2). Hence, the electrophilic singlet oxygen attacks preferentially the electron-rich double bond.

The high HOMO values and the reversibility of sulfur oxidation account for the low, if any, amount of sulfoxides **4**

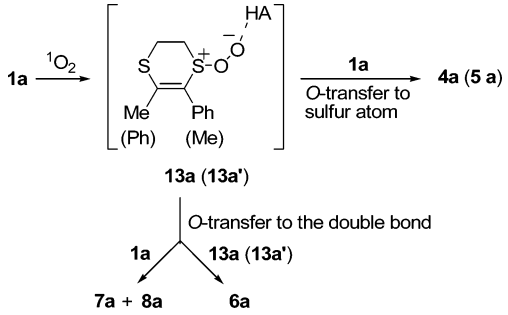
SCHEME 5



SCHEME 6



SCHEME 7



(or **5**). These compounds are significant only in the presence of a protic species (TFE) or in MeOH as the solvent. According to the accepted mechanism, the initial persulfoxide **13**, when stabilized by hydrogen bonding (or via an intermediate **14**), does not quench but transfers oxygen to a second molecule of dithiin to give two molecules of sulfoxides **4** (Scheme 5). The formation of sulfoxide **4c**, even in CH_2Cl_2 (Table 1, entry 8), should be due to the stabilization of the persulfoxide intermediate through intermolecular NH hydrogen bonding. This hypothesis is supported by the significant decrease of sulfoxide **4c** in more diluted solutions (10^{-3} M, Table 1, entry 9) and in acetone (Table 1, entry 12), where NH bonding is preferentially formed with the basic solvent.

Oxidation occurs selectively at the S-1 atom, with the formation of sulfoxides **4b**−**d**, due to the presence of the electron-withdrawing group that decreases the nucleophilicity of the S-4 atom (Scheme 6).[16] For series **a**, both S-1 and S-4 oxidation can occur. Moreover, intermediates **13a** and **13a′** can give inter- or intramolecular O-transfer to the electron-rich double bond with the formation of ketothioketals **7a** and **8a** and of ketosulfoxide **6a**, likely by means of a labile epoxide intermediate (Scheme 7).[17]

Conclusion

As found for the oxathiin system,[7] the presence of two heteroatoms in the dithiin system makes the double bond highly reactive toward singlet oxygen, promoting the dioxetane mode.

(15) Schaap, A. P.; Zaklika, K. A. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979; p 234.

(16) It is interesting to note that the oxidation of **1b** with MCPBA showed the same chemoselectivity affording sulfoxide **4b**: unpublished results from G. Palumbo and A. Guaragna.

(17) Trapping of persulfoxides by alkenes with formation of epoxides is reported: Akasaka, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, *113*, 2696.

Once more, the electron-poor substituent makes the geminal peroxidic oxygen an electrophile that can easily react with the sulfur-1 atom. However, according to the migratory aptitude S $\gg$ S^+-O^- > O, the undetected epoxide intermediate undergoes exclusively a S-migration,[18] and this occurs through a charged intermediate that should be favored by the easy cleavage of the C−S bond.[19]

In both systems (oxathiins and dithiins), the oxidation of ring sulfur is a secondary reaction. It takes place only under certain conditions (low temperature and protic media) and gives sulfoxides. Despite the presence of α-hydrogens, no sulfones nor C−S bond breaking products are found likely due to the low acidity of these hydrogens[20] or to geometrical factors that make the intramolecular abstraction of the α-proton difficult to form the hydroperoxy sulfonium ylide.[21]

Experimental Section

Compounds **1a**,[22] **1b**,[23] and **1c** [mp 100−101 °C (lit.[24] 100−102 °C)] were prepared by *N*-bromosuccinimide-promoted ring expansion of the related 1,3-dithiolanes; the latter were synthetized in good yields by refluxing the corresponding carbonyl compounds and 1,2-ethanedithiol in the presence of PPh_3/I_2.[25]

General Procedure of Photooxygenation. Each 0.02 M solution of **1a**−**d** (0.5 mmol) in dry solvent (for Table 1, entry 9: 0.001 M) in the presence of the sensitizer (2×10^{-3} mmol) (tetraphenylporphine in CH_2Cl_2; methylene blue in the other solvents) was irradiated at −20 °C with a halogen lamp (650 W). During irradiation, dry oxygen was bubbled through the solution. When the reaction was complete (2−3 h, ^{1}H NMR), removal of the solvent gave a residue that was carefully analyzed by ^{1}H NMR. Then, the residue was chromatographed on TLC. Table 1 reports the various conditions used as well as the product distribution.

From **1a**: oxygenation in CH_2Cl_2 led to a mixture composed of **2a**, **3a**, and an unidentified polymeric material. TLC chromatography [light petroleum/Et_2O (1:3)] gave, with decreasing R_f values: **2a** (35%): IR 1691, 1662 cm^{-1}; MS *m*/*z* 240 (M^+), 165, 105 (base peak), 77, 43; ^{1}H NMR ($CDCl_3$) δ 2.36 (s, 3H), 3.16 (t, J = 6.3 Hz, 2H), 3.26 (t, J = 6.3 Hz, 2H), 7.40−7.60 (m, 3H), 7.96 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 28.8 (t), 29.1 (t), 30.6 (q), 127.3 (d), 128.6 (d), 133.6 (d), 136.1 (s), 191.2 (s), 195.2 (s); Anal. calcd for $C_{11}H_{12}O_2S_2$: C, 54.97; H, 5.03; S, 26.68. Found: C, 54.76; H, 5.01; S, 26.78. **3a** (55%): identified by comparison with the commercially available product. **4a** (trace): identified by comparison with an authentic sample. Photooxygenation in methanol and successive TLCs of the residue carried out as stated previously led to **2a** (20%), **3a** (29%), **7a** (<2% with a purity of 86%), **8a** (2% with a purity of 85%), **6a** (4%), **4a** (8%), and **5a** (4%). **4a**: oil; IR ($CHCl_3$) 1673, 1025 cm^{-1}; MS *m*/*z* 224 (M^+), 180, 59; ^{1}H NMR δ 1.98 (s, 3H, Me), 2.78 (t, J = 13.8 Hz, 1H), 2.95 (dd, J = 12.2 Hz, 1H), 3.58 (d, J = 12.2 Hz, 1H), 3.72 (t, J = 13.8 Hz, 1H), 7.20−7.45 (m, 5H); ^{13}C NMR δ 16.8 (q), 22.0 (t), 44.4 (t), 128.6 (d), 128.7 (d), 129.0 (d), 133.1 (s), 137.2 (s), 138.8 (s). Anal. calcd for $C_{11}H_{12}OS_2$: C, 58.89; H, 5.39; S, 28.58. Found: C, 59.10; H, 5.37; S, 28.69. **5a**: oil; IR ($CHCl_3$) 1020 cm^{-1}; MS *m*/*z* 224 (M^+), 195, 178, 163, 121; ^{1}H NMR δ 2.13 (s, 3H), 2.80−3.05 (m, 2H), 3.45−3.60 (m, 2H), 7.20−7.45 (m, 5H); ^{13}C NMR δ 18.1 (t), 19.3 (q), 45.3 (t), 126.8 (s), 128.6 (d), 128.7 (d), 129.0 (d), 131.1 (s), 137.4 (s). Anal. calcd for $C_{11}H_{12}OS_2$: C, 58.89; H, 5.39; S, 28.58. Found: C, 59.12; H, 5.41; S, 28.70. **6a** (stereochemistry not assigned): oil; IR ($CHCl_3$) 1711, 1062 cm^{-1}; MS *m*/*z* 240 (M^+), 197, 163, 121; ^{1}H NMR δ 2.24 (s, 3H), 2.70 (ddd, J= 13.6, 9.6, 8.3 Hz, 1H), 3.14 (ddd, J= 13.6, 6.8, 2.4 Hz, 1H), 3.41 (ddd, J= 13.6, 8.3, 2.4 Hz, 1H), 3.92 (ddd, J= 13.6, 9.6, 6.8 Hz, 1H), 7.40−7.80 (m, 5H); ^{13}C NMR δ 29.7 (q), 32.0 (t), 50.8 (t), 96.8 (s), 127.5 (d), 129.5 (d), 129.8 (d), 132.0 (s), 198.3 (s). Anal. calcd for $C_{11}H_{12}O_2S_2$: C, 54.97; H, 5.03; S, 26.68. Found: C, 54.75; H, 5.01; S, 26.57. **7a** (with a purity of 86%): GC-MS *m*/*z* 181 ($M - 43)^+$, 121, 77; ^{1}H NMR δ 2.14 (s, 3H), 3.30−3.45 (m, 4H), 7.30−7.60 (m, 5H); ^{13}C NMR δ 21.9 (q), 39.8 (two overlapping t), 80.5 (s), 127.1 (d), 128.9 (d), 128.8 (d), 137.8 (s), 198.0 (s). **8a** (with a purity of 75%): GC-MS *m*/*z* 224, 119 (base peak), 105, 77, 59; ^{1}H NMR δ 2.06 (s, 3H), 3.38 (m, 2H), 3.44 (m, 2H), 7.35−7.45 (m, 3H), 7.95 (d, J = 7.1 Hz, 2H); ^{13}C NMR δ 28.9 (q), 40.3 (two overlapping t), 72.0 (s), 127.9 (d), 129.4 (d), 131.7 (d), 133.5 (s), 195.2 (s).

From **1b**: oxygenation in CH_2Cl_2 and TLC chromatography (Et_2O) led, with decreasing R_f values: *cis*-**6b** (62%): mp 79−80 °C; IR ($CHCl_3$) 1734, 1065 cm^{-1}; MS *m*/*z* 163 ($M^+ - 59$), 59, 43 (base peak); ^{1}H NMR δ 2.49 (s, 3H), 3.40 (ddd, J= 12.5, 4.5, 2.0 Hz, 1H), 3.55−3.65 (m, 2H), 3.78 (s, 3H), 4.10 (dt, J = 4.5, 11.3 Hz, 1H); ^{13}C NMR δ 30.3 (q), 35.4 (t), 53.7 (q), 57.4 (t), 90.1 (s), 167.6 (s), 197.1 (s). Anal. calcd for $C_7H_{10}O_4S_2$: C, 37.82; H, 4.53; S, 28.85. Found: C, 37.95; H, 4.51; S, 28.96. *trans*-**6b** (8%): mp 74−75 °C; IR ($CHCl_3$) 1736, 1053 cm^{-1}; MS *m*/*z* 179 ($M^+ - 43$) 163 ($M^+ - 59$), 59 (CO_2Me), 43 (base peak); ^{1}H NMR δ 2.28 (s, 3H), 3.25−3.35 (m, 2H), 3.55 (m, 1H), 3.87 (m, 1H), 3.94 (s, 3H); ^{13}C NMR δ 26.1 (q), 34.4 (t), 54.6 (q), 58.6 (t), 93.5 (s), 163.5 (s), 197.1 (s); Anal. calcd for $C_7H_{10}O_4S_2$: C, 37.82; H, 4.53; S, 28.85. Found: C, 37.97; H, 4.55; S, 28.74. **4b** (trace): identified by comparison with authentic sample. Oxygenation in methanol and TLC chromatography of the residue carried out as stated previously led, with decreasing R_f values, to *cis*-**6b** (51%), *trans*-**6b** (3%), and **4b** (19%). **4b**: viscous; IR ($CHCl_3$) 1716, 1029 cm^{-1}; MS *m*/*z* 206 (M^+), 190, 175, 162, 59 (base peak); ^{1}H NMR δ 2.48 [overlapping s and dt (J = 13.9, 2.3 Hz), 4H], 2.87 (ddd, J = 13.9, 5.0, 2.3 Hz, 1H), 3.44 (ddd, J = 13.9, 5.0, 2.2 Hz, 1H), 3.67 (dt, J = 13.9, 2.2 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR δ 16.9 (q), 25.5 (t), 41.5 (t), 52.2 (q), 123.0 (s), 160.5 (s) 163.1 (s); Anal. calcd for $C_7H_{10}O_3S_2$: C, 40.76; H, 4.89; S, 31.09. Found: C, 40.61; H, 4.87; S, 31.20.

Low Temperature Photooxygenation of 1a−d. A solution of **1a** (0.15 mmol) in $CDCl_3$/$CFCl_3$ (2:1, 5 mL) was photooxygenated as stated previously at −70 °C. After 3 h, NMR analysis of a sample recorded at this temperature showed the presence, in addition to small amounts of **2a** and **3a**, of 6-methyl-1-phenyl-7,8-dioxa-2,5-dithiabicyclo[4.2.0]octane (**9a**) [selected signals ^{1}H NMR (500 MHz, $CDCl_3$/$CFCl_3$) δ 1.43 (s, 3H), 3.20 (m, 2H), 3.75 (m, 2H), 7.20−7.60 (m, 5H); ^{13}C NMR δ 24.4 (t), 25.2 (q), 26.0 (t), 98.2 (s), 102.5 (s), 128.6 (d), 128.8 (d), 129.3 (d), 133.1 (s)]. On raising the temperature, the signals of this transient disappeared, and the final spectrum was similar to that obtained by oxygenation at −20 °C. A precooled solution of Et_2S (0.3 mmol) in $CDCl_3$ (1 mL) was added to the remainder of the mixture, which then was examined by NMR at −70 °C. In addition to the signals of **2a** and **3a**, the signals of Et_2SO, **7a** and **8a**, were also detected.

(18) In the oxygenation of oxathiins, the related epoxide rearranges via both O-migration and SO-migration, and the latter is the relevant mode.[7] In the dithiin series, sulphur migration overcomes completely the sulfoxide-migration.

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When dithiins **1b**−**d** were photooxygenated in $CDCl_3/CFCl_3$ at −70 °C as **1a**, after completion of the reactions, NMR analysis of each solution at −70 °C showed no transient, and the spectrum was similar to that obtained from the reaction at −20 °C.

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Supporting Information Available: Detailed experimental procedures, analytical data, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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