

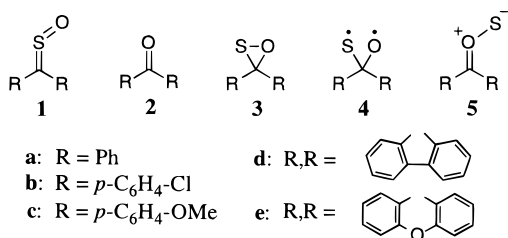
Direct Thioepoxidation of Strained Cyclic Alkenes by the Photolytic Sulfur-Atom Transfer from Thiocarbonyl *S*-Oxides (Sulfines)

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The syntheses and reactions of thiocarbonyl *S*-oxides **1** (sulfines) have been extensively studied and reviewed in the last 25 years.^{1–4} A characteristic behavior of these reactive heterocumulenes is the extrusion of elemental sulfur under thermal or photolytic conditions to produce the corresponding carbonyl compounds **2**.^{1,3} The cyclization to oxathiiranes **3** is postulated as initiating step,



which theory predicts to be a thermally and photochemically allowed process.⁵ Although there are literature reports in which oxathiiranes **3** have been invoked as reactive intermediates,^{1,3,6–8} no persistent derivatives have been isolated, contrary to dithiiranes⁹ and dioxiranes.^{6,10}

Experimental evidence for the existence of oxathiiranes **3** was provided by Carlsen *et al.*^{11,12} during the photolysis of diphenyl sulfine (**1a**) in an organic glass matrix at 85 K. The resulting diphenyl oxathiirane (**3a**) was characterized by low-temperature electronic absorption spectroscopy. This labile intermediate decomposed quantitatively to benzophenone (**2a**) and elemental sulfur when the glass matrix was heated to its melting point. Attempts to trap the oxathiirane **3a** (or its isomers **4a**, **5a**) with 2,3-dimethyl-2-butene, methyl methacrylate, or ethyl trifluoroacetate were unsuccessful.

Whereas the epoxidation of olefins by dioxiranes is a well established and synthetically valuable oxidation mode,^{6,10} the ability of oxathiiranes **3** (or their isomers

4, **5**) to transfer sulfur atoms to olefins was postulated in the thermolysis of thiophene endoperoxides,^{8,13} but has not been studied systematically. Therefore, we have investigated the photolysis of the series of diaryl sulfines **1a–e** in the presence of strained cyclic olefins as sulfur-atom acceptors, in the interest of developing a useful method for the direct thioepoxidation.¹⁴

As expected, all sulfines **1a–e** were converted quantitatively to the ketones **2a–e** by irradiation. In the absence of olefin, all available sulfur was extruded as elemental sulfur. In the presence of excess norbornene (**6a**), 12% of the sulfur was trapped in the form of thiirane **7a** (Table 1, entry 1). Additionally, traces of trithiolane **8a** and pentathiepane **9a** were detected, which are known to be products of the reaction of **6a** with sulfur allotropes.¹⁵ The sulfur balance (>90%) was determined by converting the extruded elemental sulfur to phosphine sulfides with triarylphosphines.

When an equimolar amount of *trans*-cyclooctene (*trans*-**6b**) was used, a more efficient, highly diastereoselective sulfur transfer (57%, entry 3) was observed to afford the thiirane *trans*-**7b**. The structural evidence for *trans*-**7b** rests on its elemental analysis, the chemical shifts of the thiirane hydrogen (δ_{H} 2.66) and carbon atoms [δ_{C} 43.4 (d)],⁸ and the symmetry of the molecule implied by only four ¹³C NMR resonances. The change of the temperature to –30 °C had no significant effect on the reaction time and thiirane yield (entries 2 and 4). On photolysis of the sulfine **1a** with visible light, sulfur-atom transfer also took place, but with the advantage that under such milder conditions less of *trans*-**6b** was isomerized to *cis*-**6b** (entries 5 and 6).

The results of the irradiations of the *para*-substituted benzothiophenone *S*-oxides **1b,c** (entries 7–10) do not differ significantly from those of the parent sulfine **1a**. The competition between sulfur transfer and extrusion is, thus, not sensitive to electronic effects.

cis-Cyclooctene (*cis*-**6b**) could not be thioepoxidized by the sulfines **1a–c**. It is known for the analogous epoxidation that *cis*-**6b** reacts slower than *trans*-**6b** by a factor of 112 (mCPBA)¹⁶ or 100 (dimethyldioxirane).¹⁷ While the less reactive *cis*-**6b** is quantitatively epoxidized, for its thioepoxidation by sulfines **1** competitive extrusion of elemental sulfur prevails. Nevertheless, for the sulfines **1d,e** some thiirane *cis*-**7b** was observed (entries 12 and 17) and the sulfur-transfer efficiency to norbornene (**6a**) was slightly increased (entries 11 and 16).

As already addressed above in connection with the wavelength dependence, besides sulfur transfer and extrusion, as additional reaction mode, the isomerization (6–39%) to *cis*-**6b** was observed for olefin *trans*-**6b** with all sulfines **1a–e** (entries 3, 8, 10, 13, 18). The ratio of isomerization and thiirane formation decreased with increasing starting concentration of *trans*-**6b**, as displayed by sulfine **1d** (entries 13–15). This trend indicates that the isomerization of *trans*-**6b** is not connected

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(1) Zwanenburg, B. *Phosphorus Sulfur* **1989**, *43*, 1–24.
(2) Still, I. W. J. *Phosphorus Sulfur* **1991**, *58*, 129–149.
(3) Metzner, P. *Phosphorus Sulfur* **1991**, *59*, 1–16.
(4) Block, E. *Angew. Chem.* **1992**, *104*, 1158–1203.
(5) Snyder, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5005–5007.
(6) Murray, R. W.; Singh, M. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 1A, pp 429–456.
(7) Huisgen, R.; Mloston, G.; Polborn, K.; Palacios-Gambra, F. *Liebigs Ann./Recueil* **1997**, 187–192.
(8) Adam, W.; Weinkötz, S. *J. Chem. Soc., Chem. Commun.* **1996**, 177–178.
(9) Ishii, A.; Hoshino, M.; Nakayama, J. *Pure Appl. Chem.* **1996**, *68*, 869–874.
(10) (a) Adam, W.; Smerz, A. K. *Bull. Soc. Chim. Belg.* **1996**, *105*, 581–599. (b) Kirschfeld, A.; Mthusamy, S.; Sander, W. *Angew. Chem.* **1994**, *106*, 2261–2263.
(11) Sander, W.; Kirschfeld, A. In *Advances in Strain in Organic Chemistry*; JAI Press Inc.: Greenwich, CT, 1995; Vol. 4, pp 1–80.
(12) Karlström, G.; Roos, B. O.; Carlsen, L. *J. Am. Chem. Soc.* **1984**, *106*, 1557–1561.

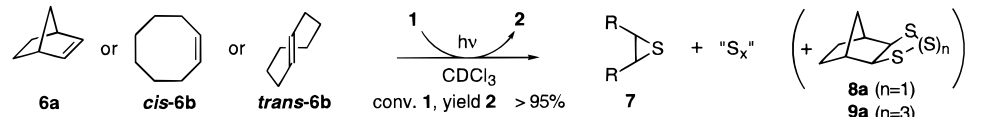
(13) Matturo, M. G.; Reynolds, R. P.; Kastrup, R. V.; Pictroski, C. *F. J. Am. Chem. Soc.* **1986**, *108*, 2775–2776.

(14) For other methods of thiirane syntheses see: Dittmer, D. C. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Rees, C. W., Eds.; Pergamon: Oxford, 1984; Vol. 7, pp 131–184. Nakayama, J.; Ito, Y.; Mizumura, A. *Sulfur Lett.* **1992**, *14*, 247–250. Abu-Yousef, I. A.; Harpp, D. N. *Tetrahedron Lett.* **1995**, *36*, 301–204.

(15) Bartlett, P. D.; Ghosh, T. *J. Org. Chem.* **1987**, *52*, 4937–4943.

(16) Shea, K. J.; Kim, J.-S. *J. Am. Chem. Soc.* **1992**, *114*, 3044–3051.

(17) Adam, W.; Curci, R.; D'Accolti, L.; Dinoi, A.; Fusco, C.; Gasparini, F.; Kluge, R.; Paredes, R.; Schulz, M.; Smerz, A. K.; Vellozo, L. A.; Weinkötz, S.; Winde, R. *Chem. Eur. J.* **1997**, *3*, 105–109.

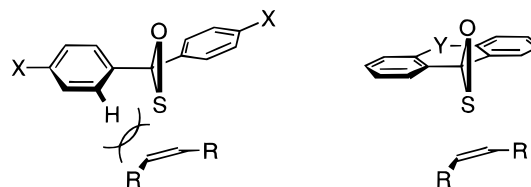
Table 1. Product Studies of the Photolytic Sulfur-Atom Transfer from Sulfines **1 to Cycloalkenes **7****


| entry | sulfine 1 ^a | olefin | equiv of olefin | T (°C) | λ (nm) | t (h) | products (%) ^b | |
|-------|-------------------------------|--------------------------|-----------------|--------|--------|-------|----------------------------------|-------------------------------------|
| | | | | | | | thiirane 7 ^{c,d} | <i>cis</i> - 6b ^e |
| 1 | 1a | 6a | 6.3 | 5 | 350 | 1.3 | 12 ^f | |
| 2 | 1a | 6a | 5.3 | -30 | 350 | 1.3 | 9 ^f | |
| 3 | 1a | <i>trans</i> - 6b | 1.0 | 5 | 350 | 1.3 | 57 | 32 |
| 4 | 1a | <i>trans</i> - 6b | 1.0 | -30 | 350 | 1.3 | 54 | 31 |
| 5 | 1a | <i>trans</i> - 6b | 3.3 | 5 | 350 | 1.3 | 94 | 16 |
| 6 | 1a | <i>trans</i> - 6b | 2.0 | 5 | >400 | 6.5 | 92 | 3 |
| 7 | 1b | 6a | 6.2 | 5 | 350 | 1.3 | 12 ^f | |
| 8 | 1b | <i>trans</i> - 6b | 2.2 | 5 | >400 | 4.0 | 91 | 20 |
| 9 | 1c | 6a | 5.8 | 5 | 350 | 3.0 | 13 ^f | |
| 10 | 1c | <i>trans</i> - 6b | 2.2 | 5 | >400 | 6.5 | 89 | 6 |
| 11 | 1d | 6a | 4.1 | 5 | 350 | 4.5 | 18 ^f | |
| 12 | 1d | <i>cis</i> - 6b | 4.9 | 5 | 350 | 3.5 | 13 | |
| 13 | 1d | <i>trans</i> - 6b | 1.1 | 5 | 350 | 3.5 | 51 | 39 |
| 14 | 1d | <i>trans</i> - 6b | 1.7 | 5 | 350 | 3.5 | 88 | 22 |
| 15 | 1d | <i>trans</i> - 6b | 2.7 | 5 | 350 | 4.8 | 94 | 7 |
| 16 | 1e | 6a | 4.2 | 5 | 350 | 1.5 | 17 ^f | |
| 17 | 1e | <i>cis</i> - 6b | 5.1 | 5 | >400 | 3.0 | 11 | |
| 18 | 1e | <i>trans</i> - 6b | 1.0 | 5 | >400 | 3.0 | 64 | 33 |

^a Concentration 0.15 M. ^b Yields were determined by ¹H NMR analysis of the crude reaction mixture (error ±5%), olefin mass balances were >90%. ^c Based on sulfine **1**. ^d By converting the extruded elemental sulfur with triarylphosphine to the phosphine sulfide, the sulfur mass balance was determined to be >90%. ^e Based on olefin *trans*-**6b**. ^f Traces of trithiolane **8a** and pentathiepane **9a** (ref 21b) were detected.

with the sulfur-transfer step. Although it is known that the olefin isomerization may be photosensitized by aromatic ketones¹⁸ or catalyzed by traces of acid, these isomerization modes are independent of starting olefin concentration and, therefore, should not be responsible. The suspicion that isomerization is mainly induced by the extruded elemental sulfur, since the extent of isomerization is lowest when most of the sulfur is trapped by *trans*-**6b** (entry 15), was confirmed when *trans*-**6b** was irradiated in the presence of elemental sulfur. Indeed, isomerization to *cis*-**6b** occurred, but under these conditions thirane *trans*-**7b** was also formed.^{15,19} The ratio *trans*-**7b**:*cis*-**6b** (17:83, 19:81, and 14:86) was within the error limits regardless of the amount (0.3, 1.0, and 3.1 equiv) of olefin *trans*-**6b** used. In contrast, in the photolytic sulfur transfer from sulfine **1d**, the *trans*-**7b**:*cis*-**6b** ratio (55:45, 70:30, and 84:16) increases with increasing number of equivalents of *trans*-**6b** (1.1, 1.7, and 2.7 equiv, entries 13–15). Consequently, different sulfur-transferring species operate in the photolysis of sulfines *versus* that of elemental sulfur.

The high diastereoselectivity of the sulfur transfer implies a concerted mechanism. If a stepwise diradical or dipolar mechanism had operated, the formation of the less strained, thermodynamically more stable thiirane *cis*-**7b** should have been observed in the sulfur transfer from sulfines **1** to *trans*-**6b**, but not even traces were detected.¹⁷ Such high diastereoselectivities are known for oxygen-atom (dioxiranes^{6,10,17} or N-substituted oxaziridines²⁰) or NH-group (oxaziridines²¹) transfer reactions of three-membered heterocycles. In analogy, the

**Figure 1.** Steric interaction between oxathiiranes **3a–c** and the attacking olefin.

oxathiiranes **3**, which are initially generated as labile intermediates in the sulfine photolysis,^{11,12} qualify as highly stereoselective sulfur-transferring species. Consequently, the enhanced sulfur-transfer efficiency in the photolysis of the planar fluorene- and xanthene-derived sulfines **1d,e** may be rationalized in terms of decreased steric interactions between the sulfur-transferring intermediate and the olefin (Figure 1).²² These novel results on the direct diastereoselective thioepoxidation of olefins allow hope that still more effective sulfines may be developed for preparative purposes.

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Supporting Information Available: Experimental section (3 pages).

JO971133E

(18) Wayne, R. P. *Principles and applications of photochemistry*; Oxford University Press: Oxford, 1988.

(19) Inoue, S.; Tezuka, T.; Oae, S. *Phosphorus Sulfur* **1978**, *4*, 219–221.

(20) Davis, F. A.; Reddy, R. T. In *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., Eds.; Pergamon: Oxford, 1996; Vol. 1A, pp 365–413.

(21) Andrae, S.; Schmitz, E. *Synthesis* **1991**, 327–341.

(22) These steric effects provide circumstantial evidence against the carbonyl *O*-sulfides **5** (formed thermally or photochemically from the oxathiiranes **3**) as sulfur-transfer intermediates.