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Communications to the Editor

1,3-Dipolar Cycloaddition of Fluorenethione *S*-Oxide and *trans*-Cyclooctene: Isolation of a Sultene and Its Novel Acid-Catalyzed Diastereoselective Sulfur-Atom Transfer to Cyclic Olefins

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In our work on the direct episulfidation[1,2] of alkenes, we recently reported the photochemically induced sulfur-atom transfer from thiocarbonyl *S*-oxides (sulfines) to cyclic alkenes.[2] Oxathiiranes,[3] which are known to be generated photochemically from sulfines,[4] were postulated as the active sulfur-transferring species.[2] Since the cyclization of sulfines to oxathiiranes is not only a photochemically but also a thermally allowed process,[5] we have investigated herein the thermolysis of the sulfine fluorenethione *S*-oxide (**1**) in the presence of *trans*-cyclooctene (***trans*-5a**), and discovered a highly efficient sulfur-atom transfer (Scheme 1). Surprisingly, the sulfine **1** was not transformed to fluorenone, which should have been formed if an oxathiirane were the intermediate.[2,4] Instead, the oxetane **3** and the aldehyde **4** were formed. Thus, different mechanisms operate in the photochemically and thermally induced sulfur transfer from sulfine **1**. Indeed, presently we demonstrate that the initial step is a 1,3-dipolar cycloaddition of sulfine **1** to *trans*-cyclooctene (***trans*-5a**), the first example of a sulfine that reacts as a 1,3-dipole with a CC multiple bond.[6] Moreover, this cycloaddition affords the heterocycle **2**, an isolable sultene[7,8] with sulfur-transferring propensity.

The thermolysis (50 °C, 50 h) of a $CDCl_3$ solution of sulfine **1** in the presence of excess *trans*-cyclooctene (***trans*-5a**) led to thiirane ***trans*-6a** (85%),[2] oxetane **3** (14%), and the aldehyde **4** (68%).[9] The conversion of sulfine **1** depended on the ***trans*-5a** concentration, which indicates that *trans*-cyclooctene (***trans*-5a**) is involved in the rate-determining step. When the reaction was performed in the presence of potassium carbonate, sulfur-atom transfer did not take place. Instead, sultene **2** was observed as the sole product (Scheme 1).

The reaction was also run on the preparative scale (500 mg of sulfine **1**) and sultene **2** was isolated in 80−90% yield by silica gel chromatography and subsequent sublimation (90 °C/0.03 mbar). Recrystallization from petroleum ether afforded an analytically pure sample for elemental analysis. The characteristic chemical shifts of the sultene hydrogen [δ_H 2.99 (ddd), 4.60 (ddd)] and carbon atoms [δ_C 59.0 (d), 73.8 (s), 90.9 (d)] substantiate its structure.[7] The *trans* configuration of ***trans*-5a** is preserved in the sultene **2**, which was assigned by NOE effects (cf. the Supporting Information). This clearly speaks for a concerted 1,3-dipolar cycloaddition, since ***trans*-5a** is a highly strained molecule and open dipolar or diradical intermediates would imply bond rotation and, thus, *trans*/*cis* isomerization.[10,11]

Scheme 1

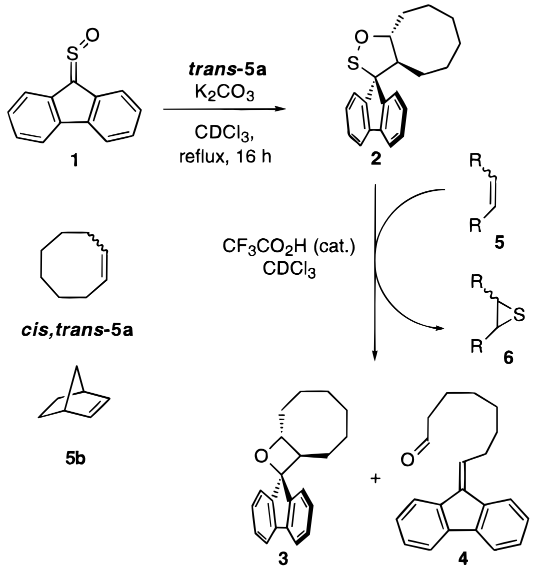

Table 1. Acid-Catalyzed Diastereoselective Sulfur-Atom Transfer from Sultene **2** to the Olefins **5**

				products [%][b,c]		
olefin[a]	*T* [°C]	*t* [h]	convn **2**[b] [%]	**3**	**4**	**6**
***trans*-5a**	20	0.5	>95	68	32	>95
		24		37	63	
		72		28	72	
***cis*-5a**	20	24	11	50	50	>95
	80	144	>95	<5	>95	90
5b	20	0.5	85	61	39	>95

[a] Five equivalents of olefin. [b] Determined from the ^{1}H NMR spectra of the crude reaction mixture by comparison of characteristic signals with dimethyl isophthalate as internal standard, mass balance >90%. [c] Based on converted **2**.

Sultene **2** persisted in the presence of *trans*-cyclooctene (***trans*-5a**) when $CDCl_3$ was used, which was filtered over basic alumina before use. The addition of catalytic amounts of trifluoroacetic acid induced complete sulfur transfer to form thiirane ***trans*-6a** and the desulfurized products **3** and **4** (Table 1). The sulfur-transfer reaction is completely stereoselective, and the thermodynamically favored ***cis*-6a** diastereomer was not observed.[2] *cis*-Cyclooctene (***cis*-5a**) and norbornene (**5b**) also functioned as efficient sulfur-atom acceptors (Table 1).[1,2]

The rate of sultene **2** disappearance depends strongly on the olefin **5** structure, i.e., ***trans*-5a** > **5b** > ***cis*-5a**. When a less

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(9) Analyzed by quantitative ^{1}H NMR spectroscopy. In a preparative-scale reaction [442 mg (2.08 mmol) of sulfine **1**, $CDCl_3$, reflux, 16 h], the products were isolated by silica gel chromatography (85% thiirane ***trans*-6a**, 34% oxetane **3**, and 42% aldehyde **4**). The unknown products **3** and **4** were fully characterized (cf. the Supporting Information).

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

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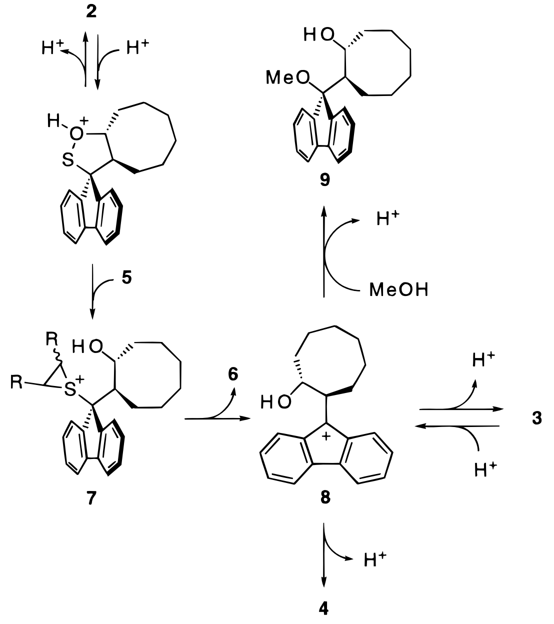
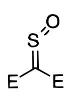
Scheme 2

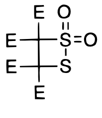


reactive olefin was used, e.g. cyclohexene, sultene **2** persisted. A reasonable mechanism consistent with the above experimental results, is shown in Scheme 2. After protonation of the sultene oxygen atom, the nucleophilic olefin **5** attacks the activated sulfur atom to form the episulfonium ion **7**. A related episulfonium intermediate was postulated by Block to intervene in the reaction of a bicyclic sultene with alcohols.[7] On release of the thiirane **6** with retained configuration, the intermediary episulfonium ion **7** is transformed to the cation **8**, which may either cleave to the aldehyde **4** or cyclize to the oxetane **3**. The oxetane formation is a reversible reaction, since the **3**:**4** ratio changed after complete conversion of the sultene **2** from 68:32 (0.5 h) to 28:72 (72 h), cf. Table 1. Such an acid-catalyzed ring opening is known for various oxetanes[12,13] and was confirmed in the present case by acidification of a CDCl$_3$ solution of the authentic sample of oxetane **3**. When the sulfur-transfer reaction from sultene **2** to olefin ***trans*-5a** was performed in the presence of MeOH, the cation **8** was trapped to form the methoxy alcohol **9** (81% yield), which was completely characterized (cf. the Supporting Information).

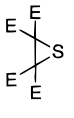
The strained *trans*-cyclooctene (***trans*-5a**) reacted readily with sulfine **1**, but with *cis*-cyclooctene (***cis*-5a**) or norbornene (**5b**) no 1,3-dipolar cycloaddition products were observed.[14] Instead, bifluorenylidene (**10**) was formed, accompanied by sulfur-atom transfer to the olefins ***cis*-5a** or **5b**. The thermal dimerization of sulfine **1** to produce bifluorenylidene (**10**) is known[14] and a similar reaction was observed for the *in-situ*-generated sulfine **11**.[15] By analogy with Block's work on the dimerization of thiopropionaldehyde *S*-oxide,[16] it was postulated that first the dimer **12** is formed, which after elimination of sulfur dioxide should result in the thiirane **13**. Subsequent extrusion of elemental sulfur would lead to the corresponding olefin.[15]



11 E = CO$_2$Et



12



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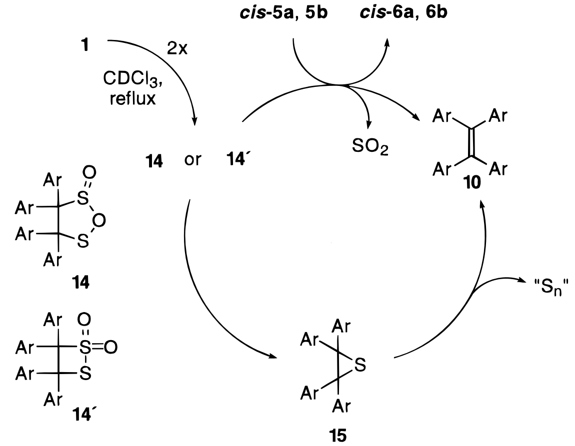
Scheme 3



Application of this thermal chemistry to sulfine **1** allows us to rationalize the formation of olefin **10**. Thus, first the [3 + 2] cycloadduct **14** is produced, which subsequently may rearrange to the dithietane 1,1-dioxide **14′** (Scheme 3). Elimination of sulfur dioxide from **14** or **14′** generates the thiirane **15**, which is finally transformed into bifluorenylidene (**10**) either by stepwise extrusion of elemental sulfur[17,18] or by sulfur-atom transfer to the olefins ***cis*-5a** or **5b**. To check this, thiirane **15** was synthesized independently.[19] Indeed, it was possible to transform **15** thermally to bifluorenylidene (**10**), but all attempts to transfer a sulfur atom to the olefins ***cis*-5a** or **5b** failed. Therefore, the dimer **14** or its rearrangement product **14′** are presumably the sulfur-transferring species; consequently, a mechanism operates, which is analogous to the sulfur-atom transfer from sultene **2** (Scheme 2). Further studies will be necessary to assess whether our novel sulfur-transfer concept may be extended to other sultenes or sulfenates and optimized for preparative purposes.

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Supporting Information Available: Experimental section (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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