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Photochemistry of *cis*-3-Diazo-5,6-dimethyl-1,4-oxathian-2-one *S*-Oxide in Argon Matrices

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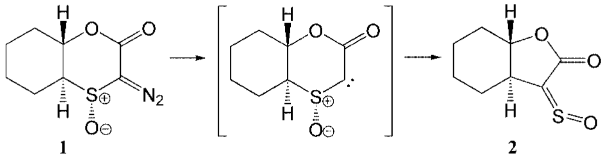
The photochemistry of the α-diazo sulfoxide **7** has been investigated in solid argon at 10 K by IR spectroscopy. The sulfinyl carbene was not detected directly but instead underwent photochemically induced hetero-Wolff rearrangement to the sulfine **8** which could be detected and characterized following irradiation at 248 nm. Further photochemical reaction of this intermediate led to the oxathiirane **9** which was most readily detected on irradiation of **7** at 308 nm. The matrix-isolated species were identified by comparison of experimental and calculated IR spectra.

Introduction

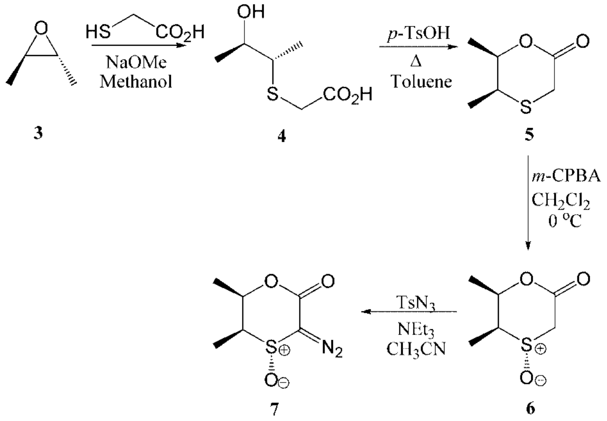
Rhodium-catalysed transformations of α-diazo sulfoxides have displayed very interesting reaction pathways via α-oxo sulfine intermediates.[1,2] Investigation of this reaction pathway for the bicyclic derivative **1** has been undertaken using photolysis in an argon matrix allowing direct spectroscopic detection of the α-oxo sulfine intermediate **2** as illustrated in Scheme 1.[3]



Scheme 1.

In this paper we wish to report an extension of this earlier work to include a detailed investigation of the photolysis of *cis*-3-diazo-5,6-dimethyl-1,4-oxathian-2-one *S*-oxide (**7**) in an argon matrix at both 248 nm and 308 nm. The synthesis of diazo sulfoxide **7** is outlined in Scheme 2 according to the procedures described earlier for related compounds.[1]

The diazo sulfoxide **7** was irradiated in argon matrices at 10 K at different wavelengths using excimer lasers. Depending on the wavelength, different photoproducts could be generated in the argon matrix and spectroscopically characterised. Due to the flexibility of the ring, various stereoisomers and conformers for the intermediates were calculated at the DFT level of theory. The comparison of experimental and theoretical IR spectra shows that, in each case, only one of the conformers is present in the matrix.



Scheme 2. Synthesis of α-diazo sulfoxide **7**.

Results and Discussion

Irradiation of 7 at 308 nm

Irradiation of **7** with an excimer laser at 308 nm results in decomposition of the starting material and its conversion into a new compound. Figure 1 shows a difference spectrum of the IR spectrum after 120 pulses irradiation relative to the initial spectrum of the starting material. The bands from the starting material disappear while some new bands simultaneously appear in the spectrum. These bands can be assigned to an oxathiirane intermediate **9d**.

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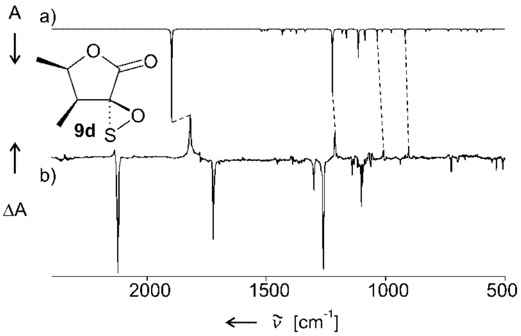


Figure 1. a) Calculated IR spectrum of **9d** [B3LYP/6-31G(d,p), unscaled]. b) Difference spectrum after irradiation of **7** at 308 nm (120 pulses, 120 mJ, 1 Hz).

The diazo sulfoxide **7** is almost completely converted into the oxathiirane **9d** upon irradiation at 308 nm. On further irradiation at 308 nm, the bands from **9d** disappear while new bands appear at 2344 cm^{-1} (CO_2), 2055 cm^{-1} (COS), 1751 cm^{-1} and 1729 cm^{-1} (**10**), as well as several weak absorptions assigned to *cis*-2-butene (Figure 2).

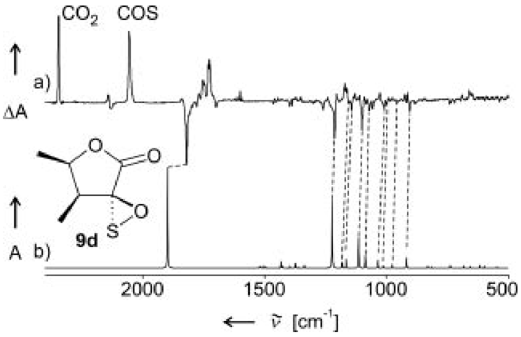


Figure 2. a) Difference spectrum after further irradiation of **7** at 308 nm (6600 pulses – 3000 pulses, 120 mJ, 1 Hz). b) Calculated spectrum of **9d** [B3LYP6-31G(d,p), unscaled].

For the oxathiirane intermediate **9d** different stereoisomers and conformers are possible, depending on the position of the methyl groups (pseudo-equatorial or pseudo-axial) and the position of the oxygen and sulfur atoms relative to the ring system. Figure 3 shows the calculated geometries of these molecules and the calculated relative energies.[4] The calculated spectra for these different stereoisomers and conformers show a strong absorption in the carbonyl region between 1897 cm^{-1} and 1895 cm^{-1} and a slightly different pattern of bands in the region between 1200 cm^{-1} and 700 cm^{-1}. The comparison of the relative intensities and band positions of the spectra calculated for the four conformers and isomers, **9a**–**9d** (Figure 4), with the experimental spectrum suggests that the lowest energy isomer **9d** is formed on photolysis of **7** in the argon matrix at 10 K.

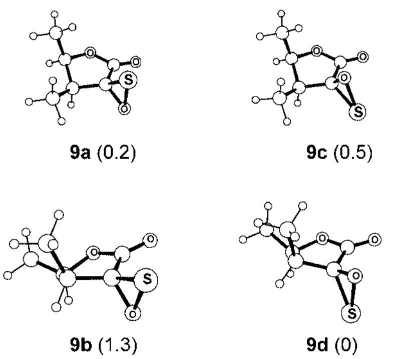


Figure 3. Calculated geometries and relative energies (after zero-point energy correction) in kcal mol^{-1} (in parentheses) of the different stereoisomers and conformers of the oxathiirane derivatives [B3LYP/6-31G(d,p)].

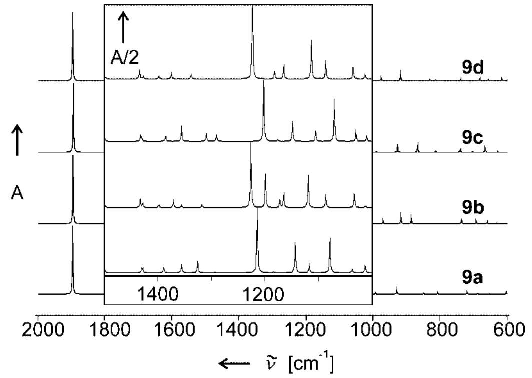


Figure 4. Comparison of the calculated spectra of the different stereoisomers and conformers of the oxathiirane derivatives **9a**–**9d** [B3LYP6-31G(d,p), unscaled].

Irradiation of 7 at 248 nm

On irradiation with an excimer laser at 248 nm, the bands of the starting material disappear and several new bands appear. These bands are different to those which could be observed on irradiation at 308 nm. The new compound has a strong absorption in the carbonyl region at 1778 cm^{-1}. Comparison of the experimental bands with those of calculated spectra shows that this new compound is one of four possible sulfine intermediates, *E*-**8a**, *E*-**8b**, *Z*-**8a**, and *Z*-**8b**. Figure 5 compares the experimental difference spectrum with the calculated spectrum of the possible sulfine intermediate *E*-**8b**.

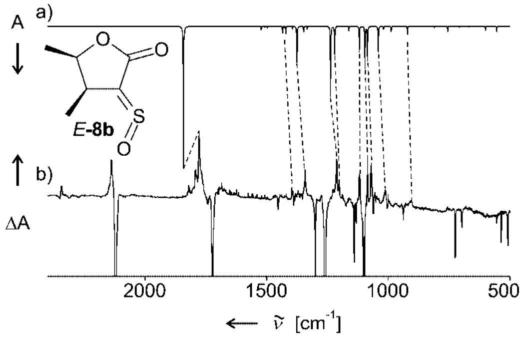


Figure 5. a) Calculated IR spectrum of *E*-**8b** [B3LYP/6-31G(d,p), unscaled]. b) Difference spectrum after irradiation of **7** with 248 nm (320 pulses, 120 mJ, 1 Hz).

For the sulfine **8**, four different stereoisomers and conformers can be considered depending on the position of the methyl groups (pseudo-axial or pseudo-equatorial) and whether the SO group is orientated towards the carbonyl group (*Z*) or away from the carbonyl group (*E*). The calculated geometries and relative energies of these different conformers are shown in Figure 6.[4] The calculations show that the (*E*)-sulfines are about 5 kcal mol^{-1} lower in energy than the corresponding (*Z*)-sulfines.

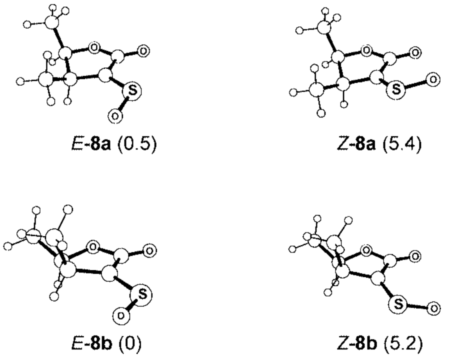

E-**8a** (0.5)
Z-**8a** (5.4)
E-**8b** (0)
Z-**8b** (5.2)

Figure 6. Calculated geometries and relative energies (after zero-point energy correction) in kcal mol^{-1} (in parentheses) of the different conformers of the sulfine derivatives [B3LYP/6-31G(d,p)].

The calculated spectra of the different stereoisomers and conformers are shown in Figure 7; these show a strong absorption in the carbonyl region between 1857 cm^{-1} and 1856 cm^{-1} for the (*Z*)-sulfines and between 1842 cm^{-1} and 1841 cm^{-1} for the (*E*)-sulfines. The relatively large energy difference between the (*E*)- and (*Z*)-sulfines would suggest that it is the former that is isolated in the argon matrix. There are striking differences between the calculated spectra of *E*-**8a** and *E*-**8b** in the region between 1400 cm^{-1} and 1000 cm^{-1}, the most notable of which are two bands at 1220 cm^{-1} and 1237 cm^{-1} in the calculated spectrum of *E*-**8b** which are comparable with bands at 1202 cm^{-1} and 1213 cm^{-1} in the experimental spectrum (Figure 5). The calculated spectrum of *E*-**8a** contains only one peak at 1227 cm^{-1} and the absence of a second peak is a strong indication that this species is not present. In addition, vibrations at 1069 cm^{-1}, 1085 cm^{-1} and 1120 cm^{-1} in the experimental spectrum are in good agreement with peaks at 1085 cm^{-1}, 1095 cm^{-1} and 1119 cm^{-1} in the calculated spectrum of *E*-**8b** as opposed to bands at 1064 cm^{-1}, 1100 cm^{-1} and 1114 cm^{-1} in the calculated spectrum of *E*-**8a**. From these different patterns one can assign the experimental IR bands to the sulfine conformer *E*-**8b**.

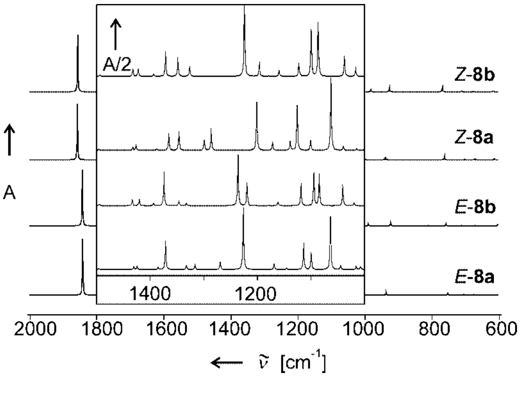


Figure 7. Calculated spectra of the different conformers of the sulfine derivatives *E*-**8a**–*Z*-**8b** [B3LYP6-31G(d,p), unscaled].

Irradiation of 7 at 308 and 248 nm

The starting material was irradiated at 308 nm until the bands of the starting material had nearly completely disappeared and the diazo sulfoxide **7** was converted into the oxathiirane intermediate **9d** (Figure 8).

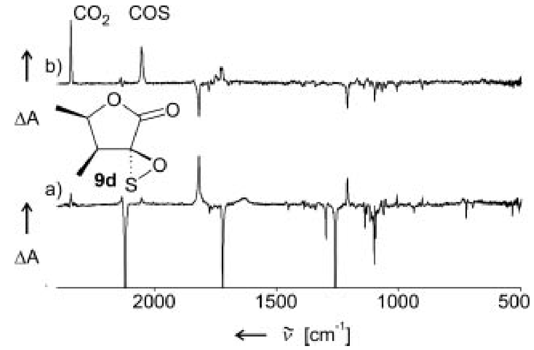


Figure 8. a) Difference spectrum of **7** after irradiation at 308 nm (2040 pulses, 100 mJ, 1 Hz). b) Difference spectrum of the formed **9d** after irradiation at 248 nm (360 pulses, 120 mJ, 1 Hz).

The oxathiirane intermediate was then irradiated at 248 nm, and it shows the same photochemistry as is observed with continuous irradiation at 308 nm. The bands of the oxathiirane disappear to form CO_2, COS, butene and two bands in the carbonyl region (Figure 8).

Irradiation of 7 at 248 and 308 nm

Compound **7** was irradiated at 248 nm to convert the starting material into the sulfine intermediate *E*-**8b** (Figure 9). The band at 1820 cm^{-1} indicates that the oxathiirane intermediate **9d** is also formed in small amounts. The sulfine intermediate *E*-**8b** was then irradiated at 308 nm and the difference spectrum shows that the bands of the sulfine compound disappear on irradiation at this wavelength while new bands of the already observed oxathiirane intermediate **9d** are growing simultaneously (Figure 10). After the sulfine derivative had been mostly converted into the oxathiirane intermediate, the bands of the oxathiirane disappear again on further irradiation at 308 nm to form the known photoproducts CO_2 (2344 cm^{-1}) and COS (2055 cm^{-1}). In addition to these assigned bands, the two bands in the carbonyl region at 1751 cm^{-1} and 1729 cm^{-1} are observed to grow on sustained irradiation at 308 nm (Figure 11). On integrating the experimental spectra, one can see that CO_2 and COS are always formed in the same ratio and in almost the same intensity. The experimental ratio of band integrals for CO_2 and COS is 1:1.16 (CO_2/COS) which is in good agreement with the calculated ratio [B3LYP/6-31G(d,p)] of 1:1.19. This suggests that CO_2 and COS are formed simultaneously and to the same extent from the oxathiirane. Loss of CO_2 and COS from the oxathiirane should result in the formation of *cis*-but-2-ene in the matrix; however, because of the low intensities of the butene bands, this is difficult to verify. By careful comparison of the matrix IR spectrum (argon, 10 K) of *cis*-but-2-ene with the spectra obtained after photolysis, *cis*-but-2-ene could be identified, although its IR bands at 1459 cm^{-1}, 1445 cm^{-1}, 1410 cm^{-1}, 1383 cm^{-1}, 980 cm^{-1} and 690 cm^{-1} are of very low intensity only.

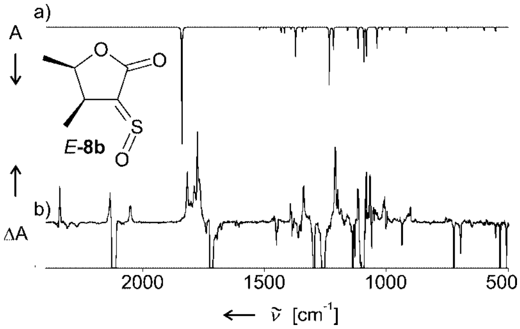


Figure 9. a) Calculated IR spectrum of *E*-**8b** [B3LYP/6-31G(d,p), unscaled]. b) Difference spectrum after irradiation of **7** at 248 nm (180 pulses, 170 mJ, 1 Hz).

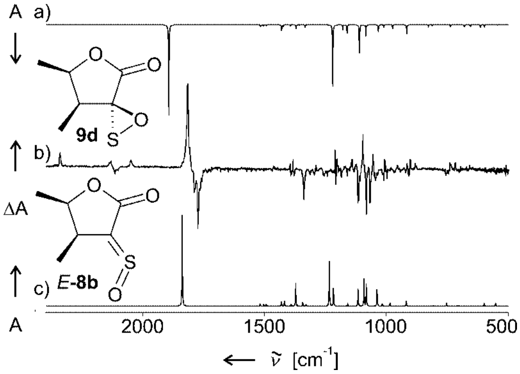


Figure 10. a) Calculated IR spectrum of **9d** [B3LYP/6-31G(d,p), unscaled]. b) Difference spectrum after irradiation of *E*-**8b** at 248 nm (240 pulses, 160 mJ, 1 Hz). c) Calculated IR spectrum of *E*-**8b** [B3LYP/6-31(d,p), unscaled].

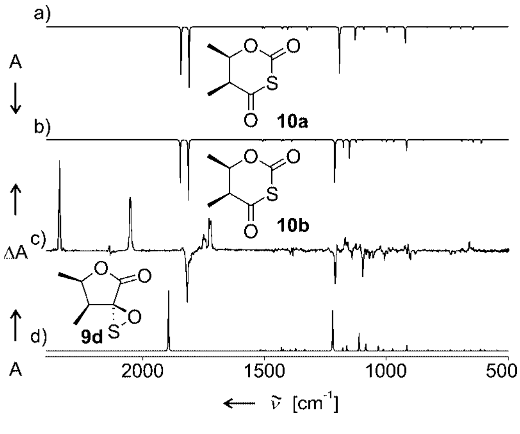


Figure 11. a) Calculated IR spectrum of **10a** [B3LYP/6-31G(d,p), unscaled]. b) Calculated IR spectrum of **10b** [B3LYP/6-31G(d,p), unscaled]. c) Difference spectrum after irradiation of **9d** at 308 nm (6000 pulses, 160 mJ, 10 Hz). d) Calculated IR spectrum of **9d** [B3LYP/6-31(d,p), unscaled].

Integration of the bands which are formed upon sustained irradiation at 308 nm also shows that the bands in the carbonyl region (1751 and 1729 cm^{-1}) under all experimental conditions are formed in the same ratio. These bands do not disappear on further irradiation at 308 nm, which indicates that they do not belong to a molecule in the photolysis pathway involving formation of CO_2, COS and *cis*-but-2-ene. As the two bands consistently appear at the same relative intensity, this indicates that the two carbonyl groups are likely to belong to the same molecule. This might be formed by rearrangement of the oxathiirane to form a thiolactone derivative. Depending on the rearrangement process two different isomers **10** and **11**, each with two different conformers **10a**, **10b**, **11a**, **11b**, are possible. Spectra were calculated for each of these possibilities and the calculated spectra were compared with the experimental ones. Figure 12 shows the calculated geometries and relative energies of these molecules and one can see that the DFT calculations predict the isomer **10** to be about 9 kcalmol^{-1} lower in energy.

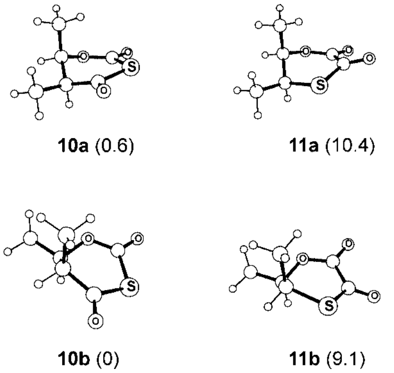


Figure 12. Calculated geometries and relative energies (after zero-point energy correction) in kcal/mol (in parentheses) of the different conformers of the possible rearrangement products **10a**–**11b** [B3LYP/6-31G(d,p)].

Figure 13 gives a comparison of the calculated spectra for the different conformers of **10** and **11**. Examination of the carbonyl region indicates which molecule, **10** or **11**, was generated. The intensities and the wavenumber differences of the two carbonyl absorptions in molecules **10** and **11** vary. The experimental difference in wavenumbers between both carbonyl bands is 22 cm^{-1}, the theoretical difference for **10** is calculated to be 32 cm^{-1} (**10a**) or 33 cm^{-1} (**10b**), whereas for molecule **11** it is calculated to be 52 cm^{-1} (**11a**) or 57 cm^{-1} (**11b**).

The experimental relative intensities of the carbonyl bands at 1751 cm^{-1} and 1729 cm^{-1} are 51:100. The calculated relative intensities for the two conformers of **10** are 79:100 (**10a**) and 71:100 (**10b**) and for the calculated species **11**, the relative intensities are 100:98 (**11a**) and 97:100 (**11b**).

From this data, one can surmise that molecule **10** is the photochemical rearrangement product formed by irradiation of the oxathiirane **9d**. Due to the fact that the calculated spectra of the two conformers of **10** differ only slightly, one cannot positively assign the experimental bands to one particular conformer. The bands in the car-

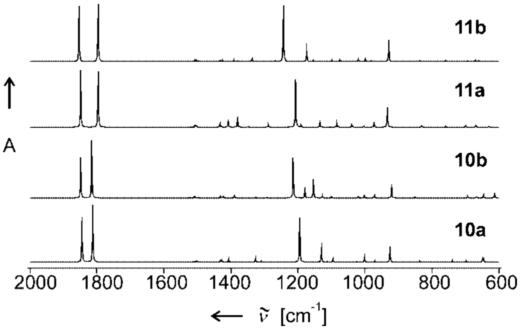


Figure 13. Calculated spectra of the different conformers and isomers from the thiolactone derivatives **10a**–**11b** [B3LYP6-31G(d,p), unscaled].

bonyl stretching region are split which makes a mixture of both conformers also possible.

Figure 14 shows the calculated geometries and relative energies (DFT level) of the lowest lying singlet and triplet states of carbene **12**. The singlet carbene conformer *S*-**12b** is calculated to have the lowest energy with conformer *S*-**12a** being only 0.2 kcal mol^{-1} higher in energy. The triplet carbene conformers *T*-**12a** and *T*-**12b** are 6.8 and 5.3 kcal mol^{-1}, respectively, higher in energy.

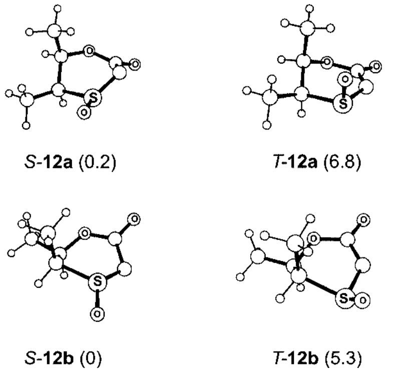

S-**12a** (0.2)
T-**12a** (6.8)
S-**12b** (0)
T-**12b** (5.3)

Figure 14. Calculated geometries and relative energies (after zero-point energy correction) in kcal/mol (in parentheses) of the different conformers from the singlet and triplet carbenes [B3LYP/6-31G(d,p)].

Table 1. B3LYP/6-31G(d,p) energies in hartrees; zero point energies (*ZPE*) and relative energies (E_{rel}) in kcal mol^{-1} (including *ZPE* corrections) of different $C_6H_8O_3S$ species.

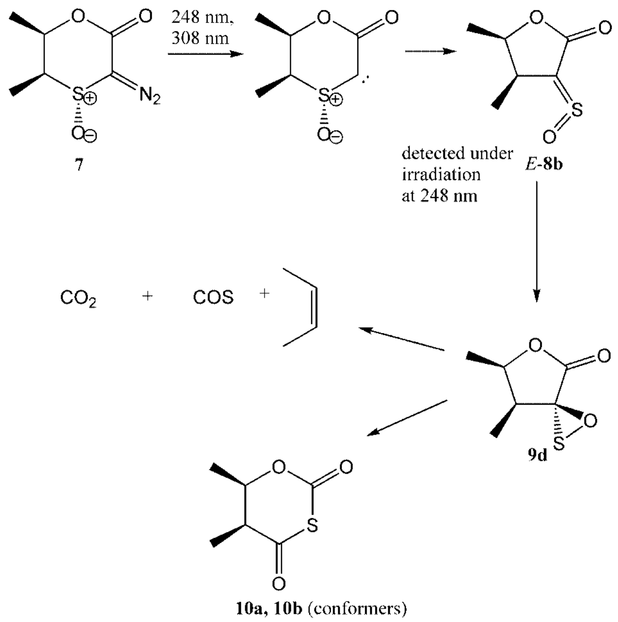
Molecule	$E_{\mathrm{calcd.}}$[a]	*ZPE*[b]	$E_{\mathrm{rel,calcd.}}$[b]
E-**8a**	–857.2824392	86.1	49.3
E-**8b**	–857.2832851	86.1	48.8
Z-**8a**	–857.2745304	85.9	54.2
Z-**8b**	–857.2748762	86.0	54.0
9a	–857.2712673	86.1	56.4
9b	–857.2691946	86.1	57.5
9c	–857.2707361	86.1	56.7
9d	–857.2716978	86.2	56.2
10a	–857.3377888	86.1	14.7
10b	–857.3385819	86.1	14.1
11a	–857.3220461	86.1	24.5
11b	–857.3240584	86.0	23.2
S-**12a**	–857.1561344	84.5	127.0
S-**12b**	–857.1567702	84.7	126.8
T-**12a**	–857.1451779	84.2	133.6
T-**12b**	–857.1475529	84.2	132.1
CO_2, COS, *cis*-2-butene	–857.3528866	80.9	0

[a] hartrees. [b] kcal mol^{-1}.

Singlet carbene *S*-**12b** is calculated to be 126.8 kcal mol^{-1} higher in energy than the lowest energy products, 70.6 kcal mol^{-1} higher than oxathiirane **9d**, and 78.0 kcal mol^{-1} higher than (*E*)-sulfine *E*-**8b** (Table 1). In contrast to calculations by Sander and Maguire[3] for an analogous bicyclic system, (*E*)-sulfine *E*-**8b** is 7.4 kcal mol^{-1} lower in energy than the oxathiirane **9d**.

Mechanistic Interpretation of the Results

Scheme 3 outlines the photochemistry observed for the diazo sulfoxide **7** when the compound is irradiated by excimer lasers at 308 nm and 248 nm while isolated in argon matrices at 10 K. The first step on irradiation may be loss of nitrogen to form a carbene intermediate; however, this species could not be isolated. The carbene undergoes hetero-Wolff rearrangement to form the (*E*)-sulfine *E*-**8b**. Alternatively the sulfine may also be produced in a concerted reaction involving loss of nitrogen and rearrangement.[3,5]



Scheme 3. Photochemistry of **7** in argon matrices at 10 K.

The (*E*)-sulfine *E*-**8b** undergoes photochemical rearrangement to form the oxathiirane **9d**. This was also postulated in a related system based on experiments carried out by Sander and Maguire, but the oxathiirane was not detected in the matrix.[3] The oxathiirane reacts photochemically in two different ways. It either decomposes to form CO_2, COS and *cis*-butene or it rearranges to form an oxathiane-dione. This oxathiane-dione may be formed as either conformer **10a** or **10b** exclusively or possibly a combination of both. On irradiation at 248 nm, decomposition products predominate, whereas rearrangement products predominate on irradiation at 308 nm.

In photolysis experiments at 308 nm the sulfine intermediate could not be detected. The reason for this seems to be that there is fast rearrangement of the sulfine to the oxathiirane intermediate **9d** on irradiation at 308 nm and this precludes the isolation of the sulfine.

On irradiation at 248 nm (*E*)-sulfine *E*-**8b** is produced in good yield. Subsequent irradiation produces the oxathiirane **9**, which rapidly decomposes to CO_2, COS and *cis*-but-2-ene, or rearranges to **10**. Therefore, the stationary concentrations of **9** are low, which makes it difficult to be observed experimentally.

Combination of both laser wavelengths shows that the (*E*)-sulfine *E*-**8b** can be produced from the starting material by irradiation at 248 nm, and this sulfine rearranges in good yield to the oxathiirane **9d** by irradiation at 308 nm. With both laser wavelengths the oxathiirane **9d** decomposes (to a greater extent in the case of 248 nm irradiation) to form CO_2, COS and *cis*-but-2-ene or it rearranges (to a greater extent upon irradiation at 308 nm) to form either **10a** or **10b** or a combination of both.

Our earlier report[3,5] of the transformation of *trans*-hexahydro-3-diazobenz[1,4]oxathiin-2-one *S*-oxide (**1**) to the sulfine **2** indicated that the (*Z*)-sulfine **2** was formed on photolysis as indicated in Scheme 1; however, the assignment of the stereochemistry in this instance relied on the comparison of relative intensities of bands in the calculated spectra and in the light of these results warrants reinvestigation.

Conclusions

Irradiation of *cis*-3-diazo-5,6-dimethyl-1,4-oxathian-2-one *S*-oxide (**7**) results in loss of nitrogen and rearrangement to form an α-oxo sulfine **8** followed by subsequent transformation to an oxathiirane **9**, which undergoes either rearrangement to **10** or decomposition on fragmentation to CO_2, COS and butene. These results support the reaction pathways observed in synthetic transformations of diazo sulfoxides in solution and in particular provide firm evidence for the formation of α-oxo sulfines as key intermediates.

Experimental Section

***cis*-5,6-Dimethyl-1,4-oxathian-2-one (5):** Thioglycolic acid (6.35 g, 4.79 mL, 0.069 mol, 1 equiv.), dissolved in methanol (5 mL), was added slowly to a freshly prepared solution of sodium methoxide (3.19 g sodium, 0.145 mol, 80 mL methanol, 2 equiv.) at 0 °C under N_2. The solution was stirred for 5 min, after which *trans*-2,3-epoxybutane (**3**) (5 g ampule from Aldrich, 0.069 mol, 1 equiv.), dissolved in methanol (5 mL), was added dropwise. The temperature was maintained at 0 °C until the addition of epoxide was complete. The reaction mixture was heated under reflux for 1.5 h. The entire reaction was carried out under nitrogen. The solvent was evaporated to leave a white solid which was dissolved in water (120 mL) and acidified to pH = 1 with concentrated hydrochloric acid (14 mL). The aqueous solution was extracted with diethyl ether (3 × 20 mL). The organic layer was then dried with $MgSO_4$ and concentrated under reduced pressure to form the hydroxy acid **4** as a colourless oil which was carried through to the next step directly without further purification. The hydroxy acid **4** was dissolved in toluene (250 mL) and a catalytic amount of *p*-toluenesulfonic (tosic) acid (15 mg, 0.087 mmol) was added. The reaction mixture was heated in a Dean–Stark trap overnight. The solution was washed with water (15 mL), dried with $MgSO_4$ and concentrated under reduced pressure to give a colourless oil (4.84 g, 48 %) which was carried forward directly. An analytical sample was obtained by flash chromatography (ethyl acetate/hexane, 20:80). IR (film): $\tilde{\nu}_{max}$ = 1731 (C=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.29 (d, $^{3}J_{H,H}$ = 6.9 Hz, 3 H, $C\mathit{H}_3$), 1.43 (d, $^{3}J_{H,H}$ = 6.5 Hz, 3 H, $C\mathit{H}_3$), 3.21 (A of ABq, $^{3}J_{H,H}$ = 14.7 Hz, 1 H one of $SC\mathit{H}_2$), 3.28 (qd, $^{3}J_{H,H}$ = 6.9 Hz, 2.7 Hz, 1 H, C*H*S), 3.58 (B of ABq, $^{3}J_{H,H}$ = 14.7 Hz, 1 H, one of $SC\mathit{H}_2$), 4.66 (qd, $^{3}J_{H,H}$ = 6.5 Hz, 2.6 Hz, 1 H, C*H*O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 16.1, 17.8 (2 $\mathit{C}H_3$), 26.0 (CH_2, $S\mathit{C}H_2$), 37.3 (CH, *C*HS), 77.1 (CH, *C*HO), 168.3 (*C*=O) ppm. HRMS (EI): calcd. for $C_6H_{10}O_2S$ [M^+] 146.04015, found 146.03951; *m*/*z* (%) = 146 (48) [M^+], 120 (5), 104 (12), 87 (8), 74 (45), 60 (100), 56 (52), 45 (31), 41 (40).

***cis*-5,6-Dimethyl-1,4-oxathian-2-one *S*-Oxide (6):** *m*CPBA (1.533 g, 77 %, 6.84 mmol) in CH_2Cl_2 (50 mL) was added dropwise to a stirred solution of **5** (1.00 g, 6.84 mmol) in dichloromethane (20 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 25 min. The solution was then filtered and diluted with CH_2Cl_2 (20 mL). It was washed with saturated sodium hydrogencarbonate (2 × 20 mL), water (20 mL) and brine (20 mL). The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure to give the sulfoxide as a colourless oil (469 mg, 42.3 %) which was carried forward directly. An analytical sample was prepared by flash chromatography (ethyl acetate/hexane, 60:40). M.p. 107–109 °C. IR (KBr): $\tilde{\nu}_{max}$ = 1731 (C=O lactone), 1052 (S=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.22 (d, $^{3}J_{H,H}$ = 7.5 Hz, 3 H, $C\mathit{H}_3$), 1.36 (d, $^{3}J_{H,H}$ = 6.6 Hz, 3 H, $C\mathit{H}_3$), 2.94 (qdd, $^{3}J_{H,H}$ = 7.4 Hz, 1.5 Hz, $^{4}J_{H,H}$ = 0.6 Hz, 1 H, C*H*S), 3.42 [finely split A of ABq, $^{3}J_{H,H}$ = 16.6 Hz, $^{4}J_{H,H}$ = 0.6 Hz, 1 H, one of $S(O)C\mathit{H}_2$], 4.05 [B of ABq, $^{3}J_{H,H}$ = 16.6 Hz, 1 H, one of $S(O)C\mathit{H}_2$], 5.43 (qd, $^{3}J_{H,H}$ 6.6 Hz, 1.5 Hz, 1 H, C*H*O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 6.4, 18.1 (2 × $\mathit{C}H_3$), 49.0 [CH_2, $S(O)\mathit{C}H_2$], 55.4 (CH, *C*HS), 70.5 (CH, *C*HO), 167.2 (*C*=O) ppm. $C_6H_{10}O_3S\cdot H_2O$ (180.2): calcd. C 39.99, H 6.71; found C 40.09, H 6.61. HRMS (EI): calcd. $C_6H_{10}O_3S$ [M^+] 162.03507, found 162.03658; *m*/*z* (%) = 162 (15) [M^+], 149 (5), 129 (2), 119 (7), 101 (5), 90 (100), 73 (92), 62 (83), 55 (82), 43 (95), 31 (9).

***cis*-3-Diazo-5,6-dimethyl-1,4-oxathian-2-one *S*-Oxide (7):** The sulfoxide **6** (469 mg, 2.89 mmol) was dissolved in acetonitrile (70 mL), and triethylamine (292 mg, 0.402 mL, 2.89 mmol), dissolved in acetonitrile (5 mL), and *p*-toluenesulfonyl azide (570 mg, 2.89 mmol), dissolved in acetonitrile (5 mL), were added to the solution while stirring at 0 °C under nitrogen. The solution was allowed to return slowly to room temperature and was stirred under nitrogen overnight. The solvent was then evaporated to yield the crude product as a red oil (1.051 g). Purification by flash chromatography (hexane/ethyl acetate, 1:1) gave the pure diazo sulfoxide as a pale yellow solid (278 mg, 50.5 %). M.p. 105–107 °C. IR (KBr): $\tilde{\nu}_{max}$ = 2126 ($C=N_2$), 1688 (C=O), 1068 (S=O) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.23 (d, $^{3}J_{H,H}$ = 7.2 Hz, 3 H, $C\mathit{H}_3$), 1.53 (d, $^{3}J_{H,H}$ = 6.6 Hz, 3 H, $C\mathit{H}_3$), 2.95 (qd, $^{3}J_{H,H}$ = 7.1 Hz, 1.1 Hz, 1 H, C*H*S), 5.40 (qd, $^{3}J_{H,H}$ = 6.6 Hz, 1.1 Hz, 1 H, C*H*O) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 5.7, 18.4 (2 $\mathit{C}H_3$), 56.2 (CH, *C*HS), 69.1 (CH, *C*HO), 159.5 (*C*=O) ppm; $C=N_2$ signal was not detected. $C_6H_8N_2O_3S$ (188.2): calcd. C 38.29, H 4.28, N 14.88, S 17.04; found C 38.21, H 4.29, N 14.83, S 17.23. MS: *m*/*z* (%) = 188

(7) [M^+], 171 (2), 160 (5), 142 (2), 129 (1), 116 (8), 97 (56), 84 (86), 72 (15), 56 (13), 49 (100), 43 (24), 35 (4).

Matrix Isolation: Matrix-isolation experiments were performed by standard techniques with an APD Cryogenics HC-2 closed-cycle helium cryostat. Matrices were produced by the deposition of argon onto a cold CsI (IR) window using the slow-spray-on technique.[6] In order to obtain optically clear matrices, the cold window was maintained at 30 K during deposition, and the matrix was subsequently cooled to 10 K. The diazo sulfoxide **7** was sublimed onto the cold window independently of the argon. The argon/**7** ratio was $>$ 1000:1. IR spectra were recorded with a Bruker IFS/66 FT-IR spectrometer with a nitrogen-cooled MCT detector. Measurements were made with a standard resolution of 0.5 cm^{-1} in the range 400–4000 cm^{-1}. Irradiations were carried out with a 248-nm Lambda Physik Laser Technik Compex 100 excimer laser and a 308-nm Lambda Physik Laser Technik Lextra 200 excimer laser.

Calculations: Calculations were performed using the Gaussian 03 program package.[7] Geometries and vibrations were calculated at the B3LYP/6-31G(d,p) level of theory.

Supporting Information (see footnote on the first page of this article): Tables S1–S4 include a comparison of the experimental and calculated spectra.

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[1] A. R. Maguire, P. G. Kelleher, G. Ferguson, J. F. Gallagher, *Tetrahedron Lett.* **1998**, *39*, 2819–2822.
[2] P. G. Kelleher, G. Ferguson, *Tetrahedron Lett.* **1998**, *39*, 3849–3852.
[3] W. Sander, A. Strehl, A. R. Maguire, S. Collins, P. G. Kelleher, *Eur. J. Org. Chem.* **2000**, 3329–3335.
[4] Calculated by DFT calculation methods using the B3LYP level of theory and 6-31G(d,p) basis set.
[5] Anja Strehl, Ph. D. Thesis, Ruhr-Universität, Bochum, **2000**.
[6] B. Meyer, *Lower Temperature Spectroscopy*, American Elsevier Publishing Company, New York, **1971**.
[7] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03*, Gaussian, Inc., Pittsburgh PA, **2003**.

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