Matrix Isolation and Photochemistry of α-Diazo Sulfoxides: Formation of α-Oxo Sulfine as an Intermediate

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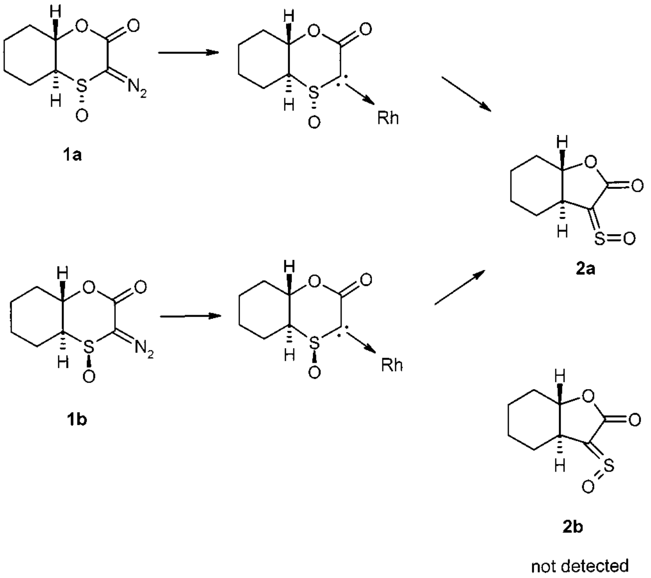
The photochemistry of the α-diazo sulfoxides **1a** and **1b** has been investigated in solid argon at 10 K by IR and UV/Vis spectroscopy. Both diazo compounds react to form sulfine **2a** by photochemically induced hetero Wolff rearrangement of sulfinyl carbene **3**, which itself cannot be detected in solid argon. Irradiation at $\lambda > 320$ nm results in decomposition of the sulfine **2a** to give 2-oxa-4-thiabicyclo[4.4.0]decane-3.5-dione (**5**) and 7-oxabicyclo[4.2.0]octan-8-one (**6**) under abstraction of COS. The matrix-isolated species have been identified by comparison of experimental and calculated IR spectra.

Introduction

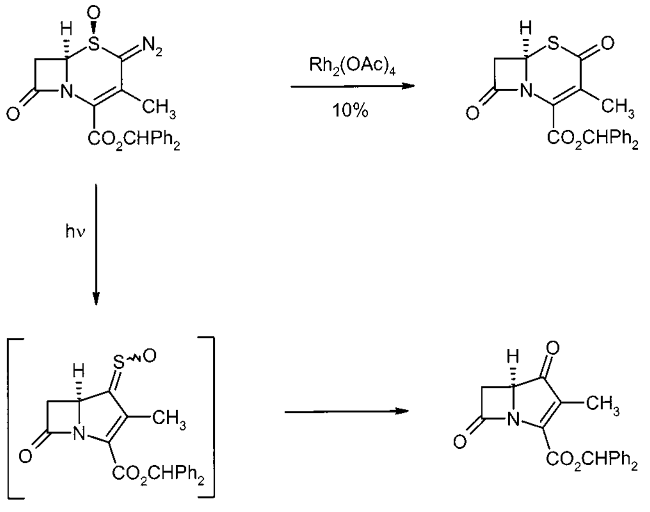
During investigations of the rhodium(II) carboxylate and carboxamide catalysed decomposition of diazo sulfoxide derivatives **1a** and **1b**, formation of the sulfine **2a** as an intermediate was confirmed by trapping it in crystalline cycloadducts with dienes such as 2,3-dimethylbutadiene and cyclopentadiene.[1,2] A variety of rhodium catalysts were explored, including rhodium acetate, rhodium trifluoroacetamide, rhodium trifluoroacetate, and rhodium heptafluorobutyrate. Under these conditions, the sulfinyl carbenoid undergoes a hetero Wolff rearrangement to the α-oxo sulfine, as illustrated in Scheme 1.[1] The *s-cis*-sulfine **2a** was formed from each of the two diastereomeric diazo sulfoxides. Although the isomeric sulfine **2b** was not detected, the fact that only moderate yields of cycloadducts were isolated from these reactions does not exclude its formation. In the absence of a diene trap, the sulfine **2a** reacts further in the presence of the rhodium(II) catalyst to form a dimeric lactone.[1]

Interestingly, the formation of the sulfine **2a** through Wolff contraction in the presence of a rhodium catalyst is in direct contrast to the results of Rosati and co-workers with 2-diazoceph-3-em oxides (Scheme 2). These authors observed that the sulfinyl carbene generated photochemically underwent Wolff rearrangement,[3,4] while oxygen transfer from the sulfoxide was observed in the presence of rhodium acetate.[5,6]

Although sulfinyl carbenes are rather unusual reactive intermediates, a few examples of both pathways, namely re-



Scheme 1. Rhodium-catalysed decomposition of α-diazosulfoxides **1**



Scheme 2

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arrangement to form sulfines and 1,2-oxygen transfer to form thiol ester derivatives, have been reported.[7−11] It appears that the choice of which pathway is followed, i.e. Wolff rearrangement or oxygen transfer, is very sensitive to the structure of the sulfinyl carbene as well as to the conditions employed to generate this intermediate. Since matrix-isolation spectroscopy[12,13] is an ideal tool for investigation of reaction intermediates, the photochemical decomposition of diazo sulfoxides **1a** and **1b** in an argon matrix has been investigated to establish the reaction pathway(s) of the sulfinyl carbenes generated under these conditions. Significantly, on irradiation at λ > 375 nm at 10 K in argon, both diazo sulfoxides **1a** and **1b** rearranged to form the same α-oxo sulfine intermediate **2a** as formed upon rhodium-catalysed decomposition. This suggests that the behaviour of the sulfinyl carbene is very similar to that of the analogous rhodium sulfinyl carbenoid.

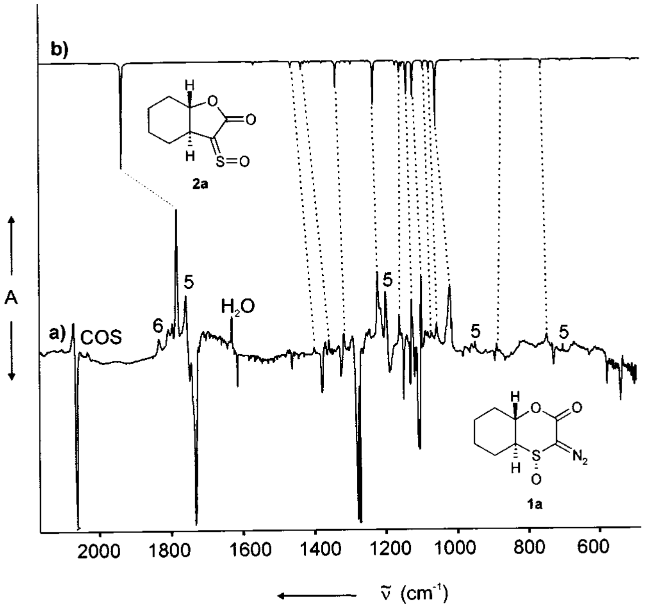


Figure 1. (a) IR difference spectrum showing the decomposition of **1a** upon irradiation at λ > 375 nm in argon at 10 K; bottom part: disappearance of bands due to **1a**; top part: appearance of bands due mainly to **2a** as well as to **5** and **6** on irradiation; (b) calculated IR spectrum of **2a** at the B3LYP/6-31/G(d,p) level of theory; the assignment of experimental and calculated IR bands is based on band positions and is only tentative

Results and Discussion

The two stereoisomeric α-diazo sulfoxides (1*R**,5*S**,6*R**)-4-diazo-2-oxa-5-thiabicyclo[4.4.0]decane-3,5-dione (**1a**) and (1*R**,5*R**,6*R**)-4-diazo-2-oxa-5-thiabicyclo[4.4.0]decane-3,5-dione (**1b**) were synthesized according to a literature procedure[1] and matrix-isolated in argon at 10 K. The diazo sulfoxides **1** exhibit characteristic IR absorptions at 2113 and 1725 cm^{-1} (**1a**) and 2118 and 1722 cm^{-1} (**1b**), attributable to the C=N=N and C=O stretching vibrations, respectively. Irradiation at λ > 375 nm led to a rapid decrease in all the absorptions associated with **1** with the concomitant formation of new products showing strong IR absorptions at 1004, 1084, 1111, 1145, 1206, and 1776 cm^{-1} (Figure 1). The same product IR spectrum was obtained irrespective of which isomer of **1** was irradiated. By comparison with IR spectra calculated at the B3LYP/6-31G(d,p) level of theory,[14] the main constituent of the product mixture was identified as *s-cis*-9-thiocarbonyl-7-oxabicyclo[4.3.0]nonan-8-one *S*-oxide (**2a**) (Table 1).

The most reasonable precursor of **2** is the α-oxo sulfinyl carbene **3**, which can be expected to readily undergo a Wolff rearrangement to **2** (Scheme 3). Alternatively, the loss of nitrogen and rearrangement to give **2** could be a concerted reaction. Since the carbene **3** could not be detected, even under the conditions of matrix isolation, these mechanistic alternatives cannot be distinguished on the basis of these experiments. Although the *s-trans* isomer **2b** is calculated to be more stable than **2a** by 4.3 kcal/mol, it was not observed in the matrix. It would seem that **2a** is probably formed in two consecutive photochemical steps from **1b**, the first step being dediazotization and subsequent rearrangement to **2b**, and the second step being **2b** → **2a** isomerization.

Similar rearrangements of α-sulfonyl carbenes have been described in the literature.[15,16] Photolyses of a number of α-diazo sulfones in methanol have been reported to lead not only to typical trapping products of carbenes, but also to sulfone acid esters.[15] The formation of the latter has been attributed to intermediately formed sulfenes, the products of a Wolff rearrangement of α-sulfonyl carbenes. The photolysis of phenyl(phenylsulfonyl)diazomethane in cryogenic matrices provided direct evidence for the formation of a sulfene from a matrix-isolated α-sulfonyl carbene.[16]

The energy difference between sulfine **2a** and carbene **3** was calculated at the B3LYP/6-31G(d,p) level of theory to be 63.9 kcal/mol. The singlet-triplet separation of **3** was calculated using B3LYP/6-31G(d,p) and BLYP/6-31G(d,p) theory as 6.0 and 10 kcal/mol, respectively, with the singlet predicted to be more stable than the triplet at both levels of theory. This is expected since sulfur atoms with lone pairs act as π-donors, which stabilize the singlet ground states of carbenes.[17,18] The calculated (B3LYP) bond angle at the carbene center amounts to 112° for S-**3** and 133° for T-**3** (Figure 2), and is thus in the typical range for acyclic carbenes.[19−21]

The characteristic asymmetric C=S=O stretching mode of **2a** is assigned to a strong vibration at 1289 cm^{-1} (B3LYP calculated: 1302 cm^{-1}). The corresponding symmetrical mode is seen at 1084 cm^{-1} (B3LYP calculated: 1101 cm^{-1}). These vibrations are red-shifted compared to those of difluorosulfine (ν_{as} = 1373 cm^{-1}, ν_s = 1118 cm^{-1}).[22]

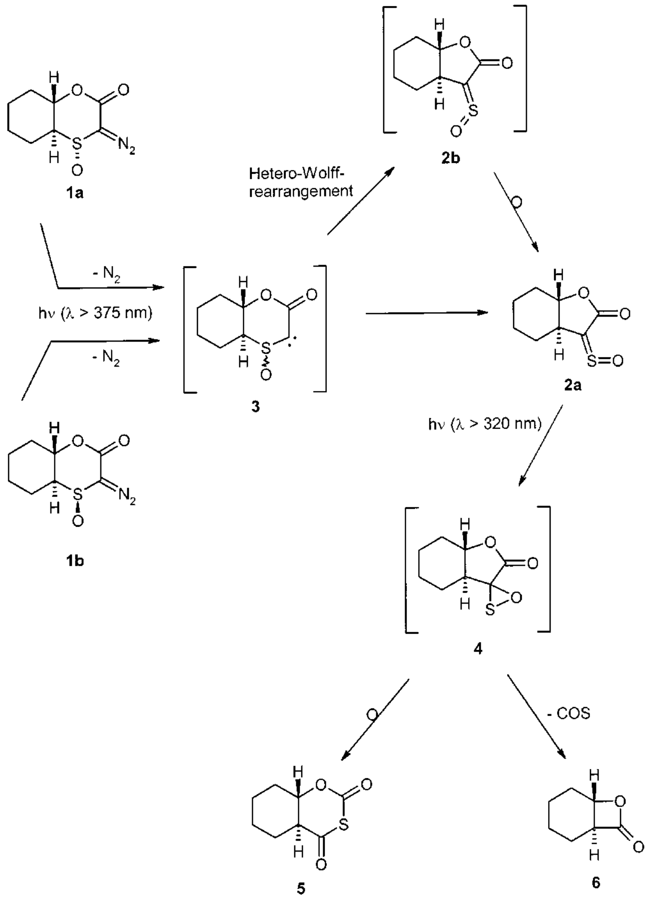
Compared to the parent sulfine CH_2CSO (ν_{as} = 1161 cm^{-1}, ν_s: 972 cm^{-1}),[23] dichlorosulfine (ν_{as} = 1169 cm^{-1}, ν_s = 1058 cm^{-1}),[22] and diphenylsulfine[24] (ν_{as} = 1121 cm^{-1}, ν_s = 1009 cm^{-1}), the bands of **2a** are blue-shifted (Table 1 and 2).

One reason why the experimental spectrum recorded upon photolysis of **1** can be assigned to **2a** rather than to **2b** is an intense band at 1111 cm^{-1}, attributable to a CH deformation vibration in the cyclohexyl ring. This band is calculated [B3LYP/6-31G(d,p)] to appear at 1118 cm^{-1} in

Table 1. IR-spectroscopic data of sulfine **2a**

Mode[a]	**2a**, generated in argon, 10 K $\tilde{\nu}$ [cm^{-1}]	I_{rel}[b]	**2a**, B3LYP/6-31G(d,p) $\tilde{\nu}$ [cm^{-1}]	I_{rel}[b]	Assignment[c]
18	732	9	764	5	
25	1004	71	1042	62	ν_{sym} (COC)
26	1040	26	1058	9	
27	1072	15	1074	6	
28	1084	84	1101	34	ν_{sym} (CSO)
29	1111	72	1118	32	δ (CH)
31	1145	42	1136	10	δ (SO)
33	1206	65	1204	41	ν_{asym} (COC)
38	1289	23	1302	24	ν_{asym} (CSO)
44	1350	9	1393	7	
45	1392	9	1420	5	
50	1776	100	1862	100	ν (CO)
52	–	–	3029	6	
53	–	–	3043	6	
54	–	–	3050	8	
55	–	–	3056	9	
56	–	–	3063	7	
58	–	–	3094	6	
59	–	–	3104	12	
60	2944	3	3114	17	

[a] Mode number from the calculation. IR bands with relative intensities lower than 5 are not tabulated. – [b] Relative intensity based on the strongest absorption (100%). – [c] The assignment is based on a comparison of the calculated and experimental spectra and is only tentative.



Scheme 3. Mechanism of the photochemical decay of α-diazo sulfoxides **1a** and **1b**

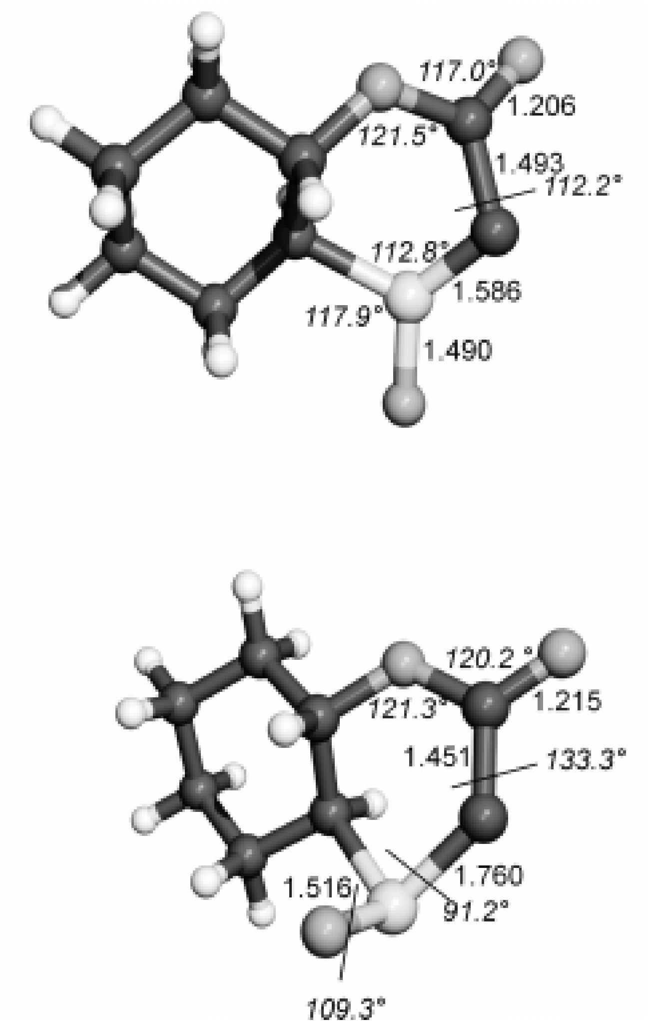


Figure 2. Structures of α-oxo sulfinyl carbenes S-**3** and T-**3** calculated at the B3LYP/6-31/G(d,p) level of theory

the case of **2a**, with a relative intensity of 32, whereas the corresponding absorption of **2b** (B3LYP calculated: 1116 cm^{-1}) is only of low intensity (rel. int.: 9). Further-

Table 2. CSO vibrations of some sulfines[22–24]

2a argon, 10 K $\tilde{\nu}$ [cm^{-1}]	**2a** B3LYP/6-31G(d,p) $\tilde{\nu}$ [cm^{-1}]	**2b** B3LYP/6-31G(d,p) $\tilde{\nu}$ [cm^{-1}]	CH_2SO argon, 10 K $\tilde{\nu}$ [cm^{-1}]	CH_2SO B3LYP/6-31G(d,p) $\tilde{\nu}$ [cm^{-1}]	CF_2SO argon, 10 K $\tilde{\nu}$ [cm^{-1}]	CCl_2SO argon, 10 K $\tilde{\nu}$ [cm^{-1}]	Ph_2CSO argon, 10 K $\tilde{\nu}$ [cm^{-1}]	Assignment
1289	1302	1316	1161	1164	1373	1196	1121	ν_{asym} (CSO)
1084	1101	1095	972	1001	1118	1058	1009	ν_{sym} (CSO)

more, two other bands are seen at 1040 and 1072 cm^{-1} with relative intensities of 26 and 15 in the experimental spectrum (Table 1). The intensity ratio of the calculated bands at 1058 (rel. int.: 9) and 1073 cm^{-1} (rel. int.: 6) for **2a** compares well with the experimental data. In contrast, calculations on **2b** predict two bands at 1054 and 1072 cm^{-1} with relative intensities of 14 and 2, which does not compare so well with the experimental spectrum. Apart from these vibrations, the calculated spectra of the two sulfines are very similar.

The UV/Vis spectrum of **2a** shows a new absorption at 280 nm (Figure 3 and Figure 4), which is in good agreement with the spectra of other cyclic sulfines. A few examples of cyclic sulfines exhibiting absorption maxima in the region of 270 nm have been reported.[25,26]

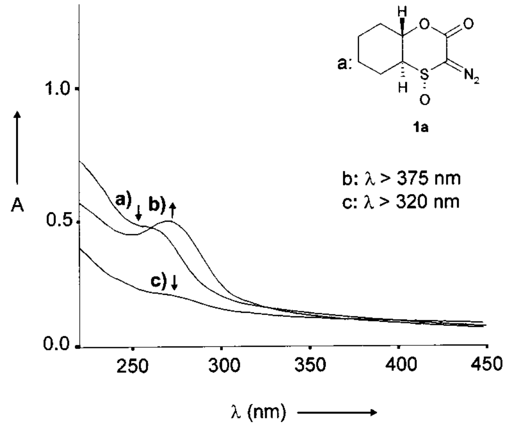


Figure 3. (a) UV/Vis spectrum of α-diazo sulfoxide **1a** matrix-isolated in argon at 13 K; (b) spectrum after irradiation at λ > 375 nm (mainly **2a**); (c) spectrum after irradiation at λ > 375 nm (mainly **5** and **6**)

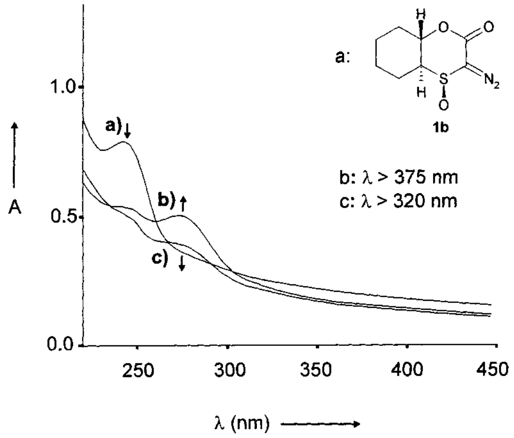


Figure 4. (a) UV/Vis spectrum of α-diazo sulfoxide **1b** matrix-isolated in argon at 13 K; (b) spectrum after irradiation at λ > 375 nm (mainly **2a**); (c) spectrum after irradiation at λ > 375 nm (mainly **5** and **6**)

The IR as well as the UV/Vis absorptions assigned to **2a** decrease on further irradiation at λ > 320 nm, while other bands seen in the initial photolysis mixture increase in intensity (Figure 5). By comparison with spectra calculated at the B3LYP/6-31G(d,p) level of theory, the latter absorptions are assigned to the compounds 2-oxa-4-thiabicyclo[4.4.0]decane-3,5-dione (**5**) (Figure 6) and 7-oxabicyclo[4.2.0]octan-8-one (**6**).

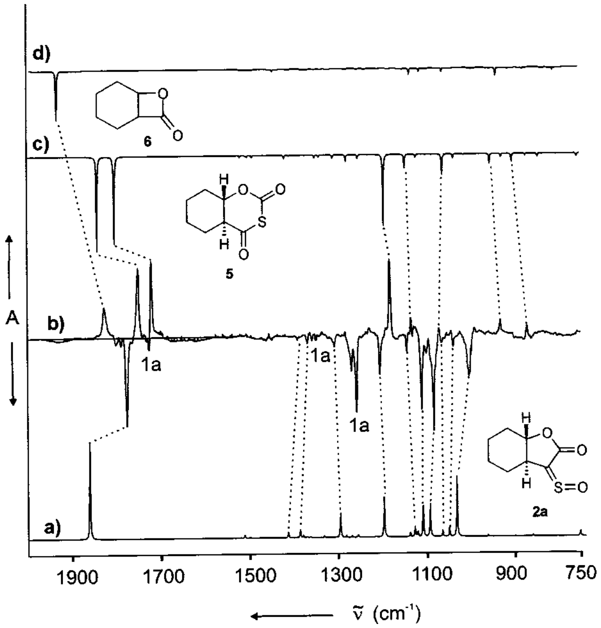


Figure 5. (a) Calculated IR spectrum of **2a**; (b) IR difference spectrum showing the decomposition of **2a**, itself formed by photolytic decomposition of **1a**, upon irradiation at λ > 320 nm in argon at 10 K; bottom part: disappearance of bands due to **2a** and **1a**; top part: appearance of bands due to **5** and **6** on irradiation; (c) calculated IR spectrum of **5**; (d) calculated IR spectrum of **6**; the assignment of experimental and calculated IR bands is based on band positions and is only tentative

The most characteristic IR absorptions of **5** are intense bands at 1183, 1721, and 1751 cm^{-1} (Table 3). The absorption at 1751 cm^{-1} is assigned to the CO stretching vibration of the carboxyl group, and that at 1721 cm^{-1} to the CO stretching vibration of the second carbonyl group. The band at 1183 cm^{-1} can be largely attributed to deformation vibrations of the heterocyclic ring. A plausible mechanism for the formation of **5** is cyclization of sulfine **2a** to oxathiirane **4**, which subsequently undergoes ring opening to give **5** (Scheme 3).

The IR band at 1827 cm^{-1} in the product spectrum is assigned to 7-oxabicyclo[4.2.0]octan-8-one (**6**), formed by elimination of COS from **4**. According to calculations at the B3LYP/6-31G(d,p) level of theory, the CO stretching

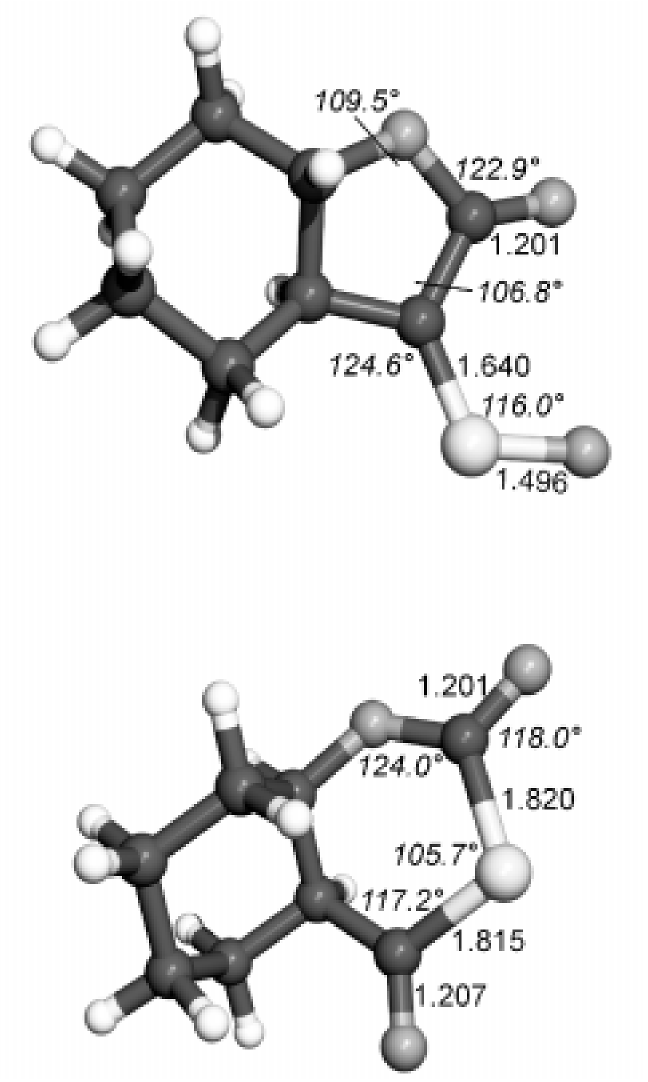
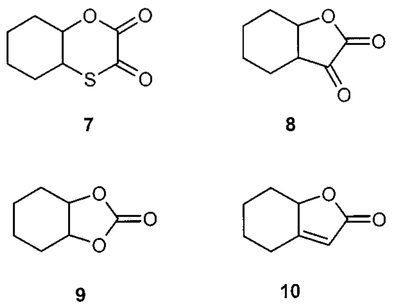


Figure 6. Structures of α-oxo sulfine **2a** and 2-oxa-4-thiabicyclo-[4.4.0]decane-3,5-dione (**5**) calculated at the B3LYP/6-31/G(d,p) level of theory

vibration, calculated to appear at 1936 cm^{-1}, should be the only strong absorption in the spectrum. An absorption at 2049 cm^{-1} is assigned to COS by comparison with literature data.[27] Prolonged irradiation leads to the decomposition of **5** and **6** with formation of CO (2138 cm^{-1}) and CO_2 (2345 cm^{-1}).

Other compounds that had been considered as potential products of the photolysis of **2a**, namely 2-oxa-5-thiabicyclo[4.4.0]decane-3,4-dione (**7**), 7-oxabicyclo[4.3.0]nonane-8,9-dione (**8**), 7,9-dioxabicyclo[4.3.0]nonan-8-one (**9**), and 7-oxabicyclo[4.3.0]non-9-en-8-one (**10**), can now be excluded (Scheme 4).



Scheme 4

Thus, **9** and **10** were readily excluded by matrix isolation of independently synthesized samples and comparison of the IR spectra.[28,29] The CO stretching vibrations of these compounds are seen at 1836 and 1799 cm^{-1}, respectively.

The product of oxygen transfer (**7**) and that of sulfur abstraction (**8**) can both be excluded by comparing the experimental data with spectra calculated at the B3LYP/6-31G(d,p) level of theory; in contrast to **5**, compound **7** is predicted to show two strong bands at 1225 and 1250 cm^{-1}. However, in the experimental spectrum only one intense IR absorption in the range 1150−1250 cm^{-1}, i.e. at 1183 cm^{-1}, can be detected. Furthermore, **5** is calculated to be 7.3 kcal/

Table 3. IR-spectroscopic data of 2-oxa-4-thiabicyclo[4.4.0]decane-3,5-dione (**5**

Mode[a]	**5**, generated by irradiation of **2a** in argon, 10 K $\tilde{\nu}$ [cm^{-1}]	I_{rel}[b]	**5**, B3LYP/6-31G(d,p) $\tilde{\nu}$ [cm^{-1}]	I_{rel} [b]	Assignment[c]
18	–	–	744	5	
23	872	11	906	8	
25	933	14	955	10	
28	1073	18	1064	21	ν_{sym} (COC)
32	1136	25	1148	14	
33	1183	91	1197	75	
49	1721	100	1804	91	ν (CO)
50	1751	89	1844	100	ν (CO)
51	–	–	3027	6	
53	–	–	3046	5	
55	–	–	3051	5	
57	–	–	3087	8	
58	–	–	3094	9	
59	–	–	3105	9	

[a] Mode number from the calculation. IR bands with relative intensities lower than 5 are not tabulated. – [b] Relative intensity based on the strongest absorption (100%). – [c] The assignment is based on a comparison of the calculated and experimental spectra and is only tentative.

mol more stable than **7**. Compound **8** is predicted to give rise to relatively intense bands at 1029 and 1423 cm^{-1}, which are not seen in the experimental spectrum.

Conclusion

Irradiation of both diastereomeric diazo sulfoxides **1a** and **1b** at $\lambda > 375$ nm in an argon matrix at 10 K has been found to result in formation of the α-oxo sulfine **2a** through a hetero Wolff rearrangement. Significantly, the same product was formed from each of the two precursors, indicating that the sulfine formed was independent of the relative stereochemistry of the precursor. In earlier work, in which these diazo sulfoxides were exposed to rhodium catalysts in solution,[1] formation of the same α-oxo sulfine **2a** as a key intermediate was proposed. While cycloadducts of this sulfine were isolated, it was not possible to isolate and identify the labile α-oxo sulfine in these solution experiments, as this intermediate underwent further reactions such as dimerization. Significantly, the matrix-isolation experiments described herein support the proposed reaction pathway for the decomposition of the diazo sulfoxides **1a** and **1b**, and have also allowed the detection and spectroscopic characterization of the α-oxo sulfine **2a**. Interestingly, the sulfinyl carbenes generated photochemically from the diazo sulfoxides **1a** and **1b** follow the same reaction pathway (hetero Wolff rearrangement) as the rhodium-generated sulfinyl carbenoids. Photochemical and transition metal catalyzed reactions of diazo carbonyl compounds often follow different reaction pathways, but not in this case.

When the α-oxo sulfine **2a** was further irradiated at $\lambda > 320$ nm, two rearrangement products **5** and **6** were identified. At this point, the behaviour of the α-oxo sulfine **2a** diverged from that observed in the earlier solution studies. This can be readily rationalized: in solution, in the presence of a rhodium catalyst, dimerization of the α-oxo sulfine **2a** occurred. Alternatively, **2a** could be trapped with dienes. In the matrix-isolation experiments, neither of these pathways are possible and consequently the α-oxo sulfine **2a** undergoes photochemically induced rearrangement instead.

Evidently, the matrix-isolation experiments provide excellent insight into the nature of the intermediates in the decomposition of the diazo sulfoxides.

Experimental Section

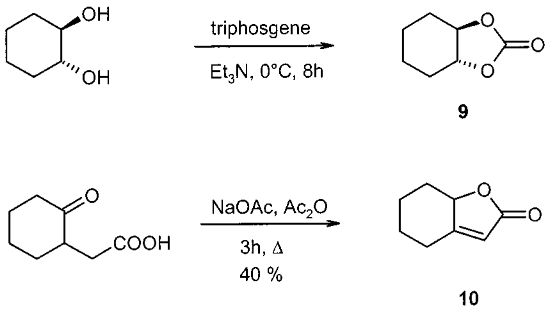
Matrix Isolation: Matrix-isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by the deposition of argon (Messer-Griesheim, 99.9999%) onto a cold CsI (IR) or quartz (UV/Vis) window using the slow-spray-on technique.[11] 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 sulfoxides **1** were sublimed onto the cold window independently of the argon. The argon/**1** ratio was > 1000:1. − Infrared spectra were recorded with a Bruker IFS66 FT-IR spectrometer with a standard resolution of 0.5 cm^{-1} in the range 400−4000 cm^{-1}. Irradiations were carried out using Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with a 10-cm. Schott cut-off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

Synthesis of α-Diazo Sulfoxides 1: The diazo compounds **1** were prepared according to a previously published procedure.[2]

(1*R,5*S**,6*R**)-4-diazo-2-oxa-5-thiabicyclo[4.4.0]decane-3,5-dione (1a):** IR (Ar, 10 K): ṽ (rel. int.) = 2113 (100), 1740 (10), 1724 (48), 1454 (6), 1369 (12), 1317 (8), 1269 (46), 1259 (81), 1172 (9), 1133 (10), 1113 (12), 1103 (5), 1082 (38), 1081 (41), 712 (6), 512 (11) cm^{-1}.

(1*R,5*R**,6*R**)-4-diazo-2-oxa-5-thiabicyclo[4.4.0]decane-3,5-dione (1b):** IR (Ar, 10 K): ṽ (rel. int.) = 2118 (100), 1722 (53), 1600 (12), 1593 (35), 1372 (19), 1271 (61), 1260 (95), 1113 (59), 514 (12) cm^{-1}.

Two possible photolysis products identified were 7,9-dioxabicyclo[4.3.0]nonan-8-one (**9**) and 7-oxabicyclo[4.3.0]non-9-en-8-one (**10**). The carbonate **9**[30−32] was prepared by treatment of *trans*-1,2-cyclohexanediol with triphosgene and triethylamine in CH_2Cl_2 at 0 °C. The butenolide **10**[28] was prepared by refluxing 2-oxocyclohexaneacetic acid with sodium acetate in acetic anhydride for 3 h according to a procedure described for the synthesis of a related unsaturated γ-lactone[29] (see Scheme 5).

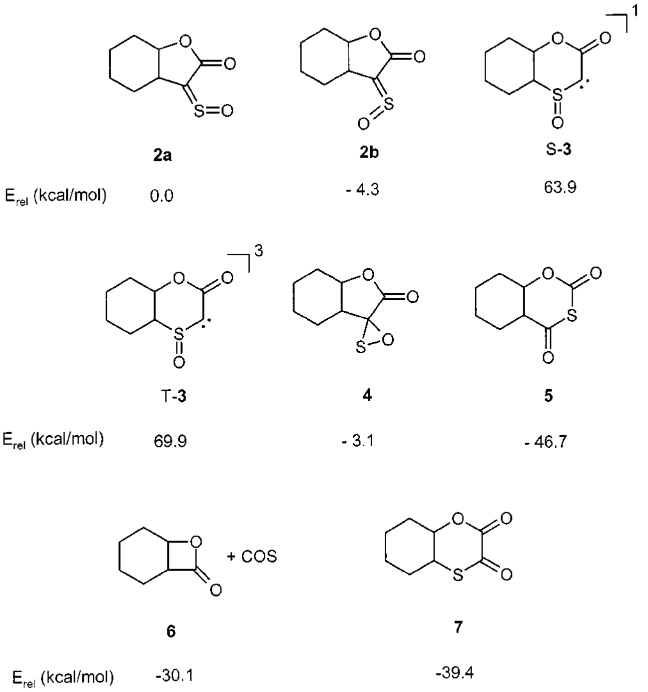


Scheme 5

***trans*-7,9-Dioxabicyclo[4.3.0]nonan-8-one (9):**[30−32] Triethylamine (0.3 mL, 2.15 mmol, 1 equiv.) was added to a stirred solution of *trans*-1,2-cyclohexanediol (0.25 g, 2.15 mmol) in dichloromethane (10 mL) at 0 °C. Stirring was continued for 15 min and then a solution of triphosgene (0.213 g, 0.71 mmol) in dichloromethane (15 mL) was added dropwise over a period of 10 min. The solution was stirred at 0 °C for 8 h and then at room temperature overnight. It was subsequently washed with 10% aq. sodium bicarbonate solution (2 × 5 mL), water (2 × 10 mL), and brine. The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give a colourless oil. Recrystallization from CH_2Cl_2/hexane gave a low-melting white solid (0.13 g, 50%). − IR (film): ṽ = 1790 (C=O carbonate), 1171, 1103, 1055 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 1.01−2.41 (m, 8 H, cyclohexyl ring), 3.91−4.03 (m, 2 H, bridgehead protons).

7-Oxabicyclo[4.3.0]non-9-en-8-one (10):[28,29] A stirred mixture of 2-oxocyclohexaneacetic acid (0.124 g, 0.8 mmol) and sodium acetate (0.031 g, 0.33 mmol) in acetic anhydride (7 mL) was refluxed for 3 h under N_2. The solution was then diluted with water (10 mL) and extracted with diethyl ether (30 mL). The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give an orange-red viscous oil. Purification by column chromatography on silica gel (ethyl acetate/hexane, 80:20) gave the butenolide as a colourless oil (0.045 g, 40%). − IR (film): $\tilde{\nu}$ = 1754, 1648 cm^{-1}. − ^{1}H NMR (CDCl$_3$): δ = 1.10−3.15 (m, 8 H, cyclohexyl ring), 4.72−4.73 (m, 1 H, CHO), 5.72 (s, 1 H, C=C−H).

Calculations: Calculations were performed using the Gaussian 98 program package. Geometries and vibrations were calculated at the B3LYP/6-31G(d,p) or BLYP/6-31G(d,p) levels of theory (Scheme 6).[33] The calculated geometries and IR-spectroscopic data of **2a**, **2b**, **3a**, **3b**, **4**, **5**, **6**, **7**, and **8** are included in the Supporting Information.



Scheme 6. Calculated relative energies [B3LYP/6-31G(d,p) + ZPE] of some isomeric $C_8H_{10}O_3S$ compounds

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