Photochemistry of Bis(sulfonyl)diazomethanes

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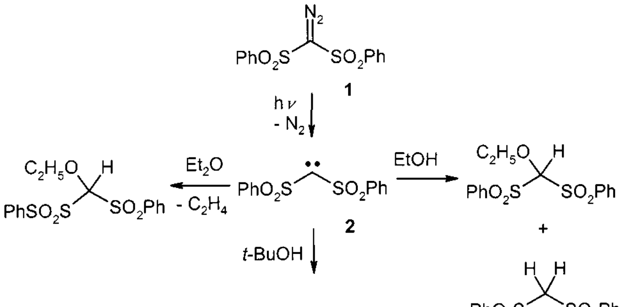
The photochemistry of a series of bis(sulfonyl)diazomethanes was investigated in solution and in low temperature matrices. These diazo compounds are of interest as photoacid generators in photoresists for deep UV lithography. Triplet carbenes could be trapped in solution, but attempts to isolate the carbenes in argon matrices at 10 K were unsuccessful, the corresponding sulfenes and other rearranged products being observed under these conditions instead. This is in line with DFT and ab initio calculations, which predict the singlet carbenes to be transition states on the pathway to oxathiirene oxides, which can be looked upon as intramolecularly stabilized carbenes. The triplet carbenes lie energetically above the singlet transition states and so are not expected to have a prolonged lifetime even in low-temperature matrices.

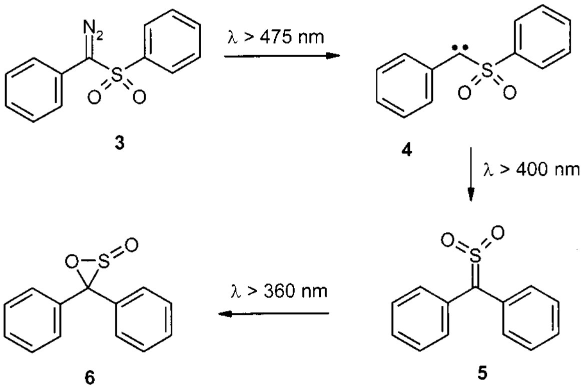
Introduction

The development of new photoresists suitable for deep UV lithography is a prerequisite for the development of electronic devices of ever higher density.[1−6] The resolution of the photolithographic process is limiting for the size of the circuit elements. Bis(sulfonyl)diazomethanes **1** have been proposed as constituents of photoresists for photolithographic applications using deep UV (248 nm) exposure.[7,8] The photolysis of **1** in solution produces typical carbene-trapping products, together with sulfonic acids (Scheme 1). The sulfonic acids are capable of crosslinking acid-sensitive compounds in negative tone materials. Despite the interest in technical applications of **1**, only a few mechanistic studies on the photochemistry of **1** and the role of carbene **2** in the formation of acids have been published.



Scheme 1

The photochemistry of phenyl(phenylsulfonyl)diazomethane (**3**) has been studied in our laboratory previously.[9] Use of the matrix isolation technique allowed us to characterize carbene **4** as the primary photochemical product on irradiation at λ > 475 nm. Further irradiation at shorter wavelengths results in rearrangement to diphenylsulfene **5** (hetero Wolff rearrangement), which subsequently yields diphenyl-α-sultine **6** (Scheme 2). The photochemistry of **3** is thus similar to that of α-diazo ketones. A major difference is the higher stability of carbene **4** (with respect to rearrangement) in comparison to that of keto carbenes under the matrix isolation conditions.



Scheme 2

Laser flash photolysis of bis(phenylsulfonyl)diazomethane (**1a**) in acetonitrile was investigated by Scaiano et al.[10] These authors postulate the formation of a sulfene by hetero Wolff rearrangement of carbene **2a** (which could not be detected directly) as the principal photochemistry of **1a**.

In solution, the photochemistry of **1** is fairly complex, resulting in the formation of trapping products of the carbenes **2** and also of rearranged products (Scheme 4). A study addressing the question of photoacid generation by UV photolysis of **1** in solution was published by Pawlowski et al.[8] It was shown that organic sulfonic acids were generated, and a complex sequence of reaction steps was postulated. Here we describe a matrix isolation investigation of the photochemistry of a series of bis(sulfonyl)diazomethanes **1a**−**1e** (Scheme 3).

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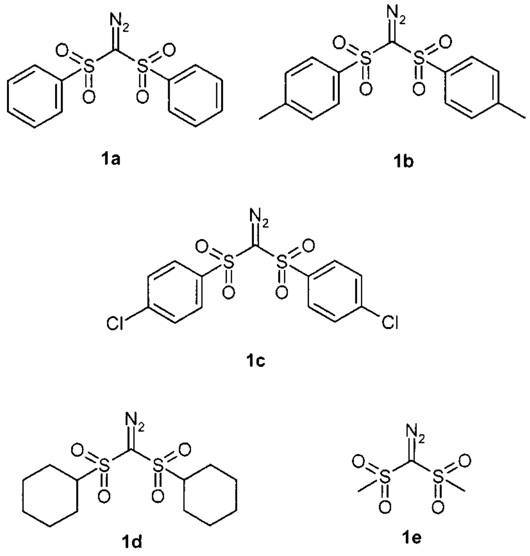


Scheme 3

Results and Discussion

Photochemistry of 1b in Solution

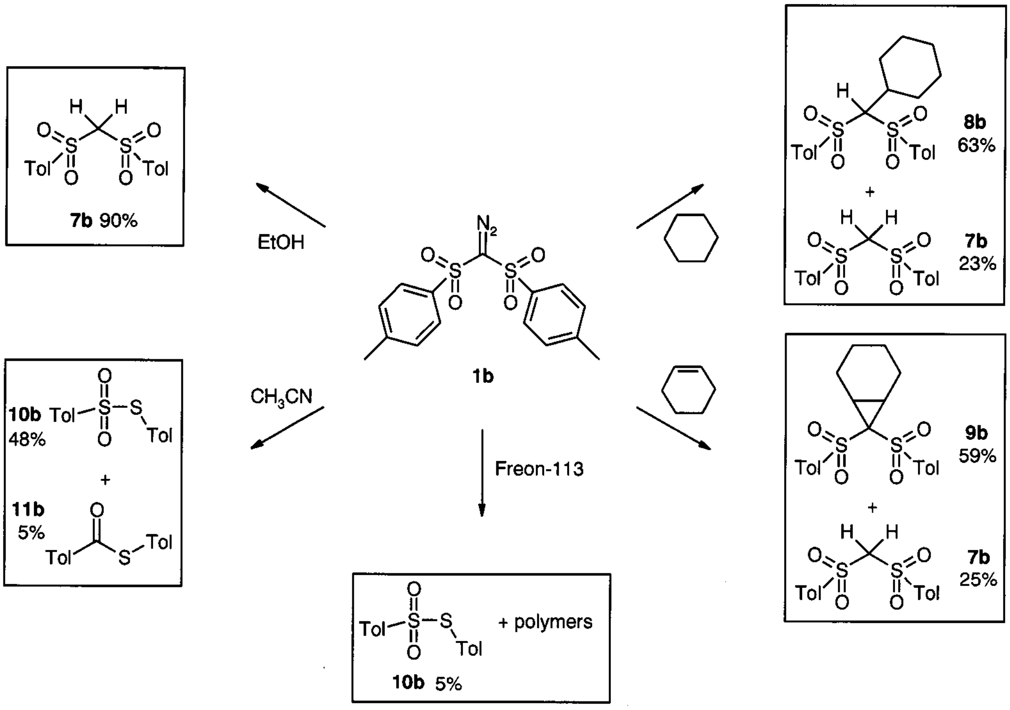
The photochemistry of bis(tolylsulfonyl)diazomethane (**1b**) as a prototypic derivative of **1** was investigated in a variety of solvents by irradiation with λ > 260 nm at room temperature. In ethanol or ethanol/water (3:2 mixture), bis(tolylsulfonyl)methane (**7b**) was formed in 90 and 85% yields, respectively (Scheme 4). Insertion products were not formed in this solvent.

The photolysis of **1b** in cyclohexane produces both the insertion product **8b** (in 63% yield) and **7b** (in 23% yield). Traces of bicyclohexyl clearly signify a radical mechanism. In cyclohexene **7b** is formed in 25% yield and the major product is the expected addition product **9b** (59% yield). In Freon-113, polymeric material was mainly formed, together with only 5% of *S*-*p*-tolyl toluene-4-thiosulfonate (**10b**). In acetonitrile, **10b** was formed in 48% yield, with *S*-*p*-tolyl 4-methylthiobenzoate (**11b**) as a minor product in 5% yield. These results clearly demonstrate that the triplet carbene **2b** is a primary product of the photolysis of **1b**, and that it can be trapped by hydrogen donors or olefins. In Freon and acetonitrile, thioester **10b** is formed by formal loss of CO_2. Obviously, this reaction requires a major rearrangement, with migration of two oxygen atoms from the sulfur atom to the carbene carbon atom.

Irradiation of **1b** in an EPA glass (isopentane/diethyl ether/ethanol, 4:4:2) at 77 K produces **10b** as the major nonpolymeric material, while **7b** – the main product in ethanol at room temperature – is not found. Thus, the mechanism and product distribution of the photodecomposition of **1b** not only depend on the solvent, but also change drastically on going from a solution at room temperature to a glass at 77 K. To gain insight into these complex processes, the photochemistry of the series **1a–e** was investigated under matrix isolation conditions.

Photochemistry of 1 in Argon Matrices

The IR spectra of the diazo compounds **1a–e**, matrix-isolated in argon at 10 K, exhibit strong IR absorptions in the 2100–2135 cm^{-1} range, attributable to the asym. CNN stretching vibration, and at 1350–1375 and 1150–1165 cm^{-1}, attributable to the asym. and the sym. SO_2 stretching vibrations, respectively. Irradiation with λ > 395 nm (**1a–d**) or λ > 350 nm (**1e**) results in the rapid disappearance of



Scheme 4

the IR absorptions attributable to **1** and formation of two major new products (Figure 1). These new products are photolabile, and irradiation at shorter wavelength ($\lambda >$ 305 nm) yields CO, CO_2, and COS as common products. The other products formed during the photolyses depend on the substituents R.

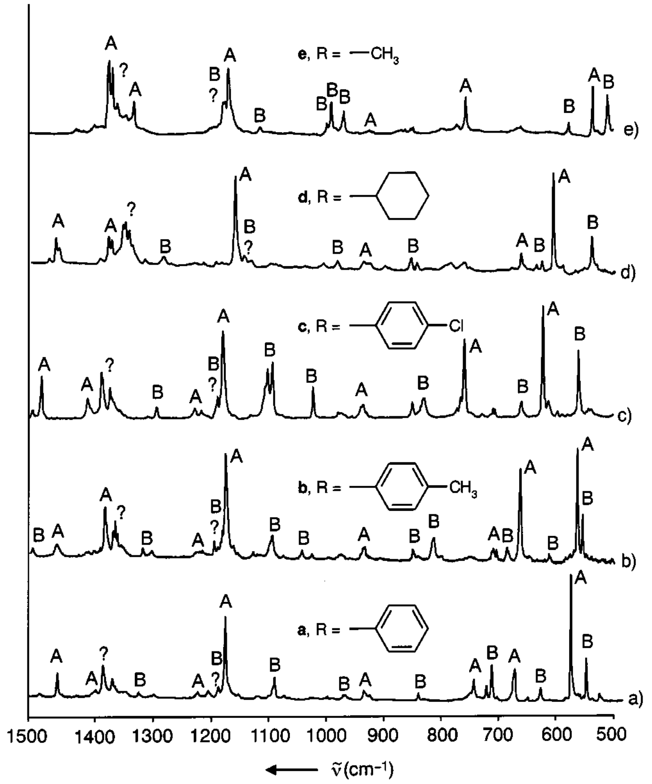
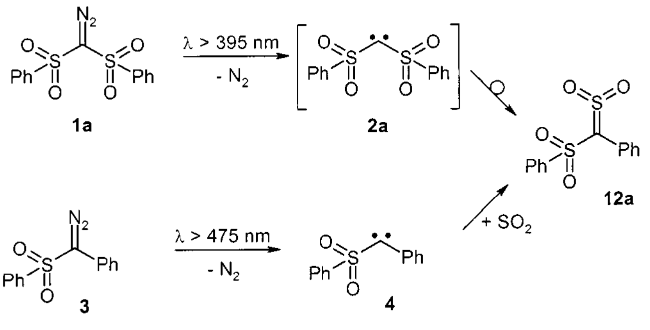


Figure 1. IR spectra of the photoproducts of diazo compounds **1a−e**

Irradiation of diazo compounds **1** is expected to result in the loss of N_2 and formation of carbenes **2**. Since carbenes are easily trapped by molecular oxygen,[11−18] the photolyses of **1** were repeated in 1% O_2-doped argon matrices. Subsequent annealing for several hours at 38 K did not result in any detectable new products, which suggests that carbenes **2** − at least as triplet ground state carbenes − are not trapped in the matrices. A similar negative result was found if CO was used as the carbene trapping reagent.[19,20] In this case, no formation of ketenes, which should be easily detectable in the IR spectra, was observed.

α-Sulfonylcarbenes are known to undergo photochemical rearrangements to sulfenes (hetero Wolff rearrangement).[9,21] Carbenes **2** might thus rearrange to sulfenes **12**. To provide evidence for the formation of sulfenes as one of the products of the photolysis of **1**, phenyl(phenylsulfonyl)sulfene (**12a**) was independently synthesized by SO_2 trapping of phenyl(phenylsulfonyl)carbene (**4**) (Scheme 5). This carbene is easily synthesized by irradiation of **3** in an argon matrix.[9] In an SO_2-doped argon matrix (1−5% SO_2 in argon), a new set of IR absorptions is observed. On annealing at 38 K this new set of signals slightly increases in intensity, and is identical within several wavenumbers to the IR spectrum of one of the photoproducts of **1a** (Table 1). The small differences in band positions are due to the different environments in argon and in argon/SO_2 matrices. Comparison of these IR data with those of diphenylsulfene (**5**) shows the similarities of the major IR bands attributed to the C=SO_2 moiety (Table 2). Thus, it is clear that sulfene **12a** is one of the primary photoproducts of **1a**.



Scheme 5

Table 1. IR spectroscopic data of matrix-isolated sulfene **12a**, generated by trapping of carbene **4** with SO_2 or photolysis of diazo compound **1a**

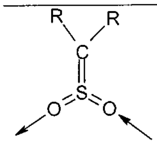
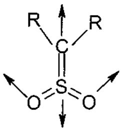
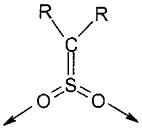
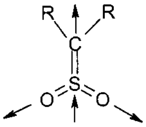
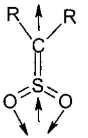
12a $\tilde{\nu}/cm^{-1}$ [a]	I_{rel}	**12a** $\tilde{\nu}/cm^{-1}$ [b]	I_{rel}	Assignment[c]
586	100	588	100	δ (SO_2)
693	64	692	81	phenyl
764	48	763	54	
934	9	934	15	ν_{sym} (CS)
1168	83	1170	78	ν_{sym} (SO_2)
1201	29	1204	26	ν_{asym} (CS)
1388	26	1385	21	ν_{asym} (SO_2)
1452	39	1451	46	phenyl

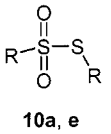
[a] Formed by the reaction between matrix-isolated carbene **4** and SO_2 (1% SO_2-doped argon matrix). − [b] Formed by irradiation ($\lambda >$ 395 nm) of diazo compound **1a** in argon at 10 K. − [c] Tentative assignment based on comparison with the IR data of diphenylsulfene.

The other diazo compounds exhibit a similar photochemical behavior, resulting in the formation of sulfenes **12** (Table 3). Most of the vibrations attributable to the C=SO_2 moiety are almost independent of the nature of the substituents R. An exception is **12e**, with several combination vibrations of the C=SO_2 with the CH_3 group. Since **12e** is the smallest molecule in this series, its vibrational spectrum was calculated at the MP2/6−31G(d,p) level of theory. The calculated band positions are in reasonable agreement with the experimental values.

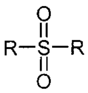
Several possible structures have to be considered for the second major photoproduct of **1**. By comparison with independently matrix-isolated compounds it was possible to rule out the structures **10**, **13**, **14**, and **15**. Diazirines exhibit characteristic absorptions around 1600 cm^{-1}, and these are not found in the IR spectra. Diphenylsulfene (**5**) rearranges

Table 2. Characteristic vibrations of diphenylsulfene (**5**) and phenyl(phenylsulfonyl)sulfene (**12a**) associated with the C=SO$_2$ moiety

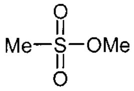
Vibration	Sulfene **5** $\tilde{\nu}$/cm^{-1}	Sulfene **12a** $\tilde{\nu}$/cm^{-1}
	1355	1385
	1265	1204
	1163	1170
	984	934
	550	588



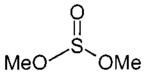
10a, e



13a, e



14e



15e

(Table 4). The *trans* isomer *trans*-**16e** is predicted to be 5 kcal/mol more stable than the *cis* isomer by both computational methods.

The IR spectrum of the photolysis products of **1e** shows several bands that nicely match the calculated absorptions for *cis*-**16e**, while in the case of *trans*-**16e** there is less agreement (Table 5). Because of overlapping absorptions (especially in the region characteristic of SO$_2$ vibrations), however, the assignment of absorptions to **16e** is difficult and only tentative. Photolysis of the other diazo compounds **1a−d** yields products that can be identified as **16a−d** by comparison with **16e**. We thus conclude that the two major primary photoproducts of compounds **1** are the sulfenes **12** and the oxathiirene oxides **16**.

Table 3. IR-spectroscopic data of the sulfenes **12** [$\tilde{\nu}$/cm^{-1} (rel. intensity)]

12a[a]	**12b**[a]	**12c**[a]	**12d**[a]	**12e**[a]	**12e**[b]	Assignment
588 (100)	566 (100)	623 (100)	608 (89)	537 (100)	499 (41)	δ (SO$_2$)
692 (81)	685 (89)	–	663 (14)	–	–	
763 (54)	–	762 (64)	759 (18)	756 (38)	793 (31)	
934 (15)	933 (12)	932 (11)	933 (14)	920 (6)	907 (31)	ν_{sym} (C=S) [+ν (CH$_3$)]
–	–	–	–	1106 (12)	1131 (54)	ν_{sym} (SO$_2$) + ν (CH$_3$)
1170 (78)	1168 (81)	1171 (78)	1152 (100)	1161[c]	1167 (27)	ν_{sym} (SO$_2$)
–	–	–	–	1166[c]	1187 (71)	combination
1204 (26)	1205 (5)	1208 (6)	1206 (8)	1321 (41)	1321 (48)	ν_{asym} (C=S) [+ν (CH$_3$)]
1345[c]	1339[c]	1349[c]	1361[c]	1352[c]	1375 (76)	ν_{asym} (SO$_2$)
1385 (19)	1372 (32)	1377 (26)	1367[c]	1368[c]	1395 (100)	ν_{asym} (SO$_2$) C=SO$_2$ group
1451 (46)	1453 (39)	1479 (49)	1468 (6)	–	–	

[a] Argon, 10 K. – [b] Calculated at the MP2/6−31G(d,p) level of theory. – [c] Overlapping vibrations, only tentatively assigned to **12**.

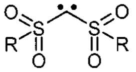
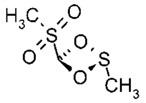
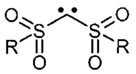
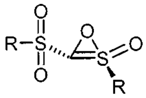
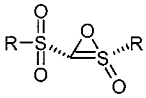
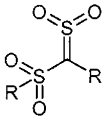
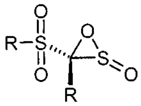
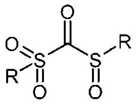
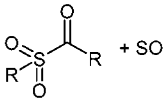
photochemically to α-sultine **6** (Scheme 2);[9] however, there is no evidence for the corresponding cyclization of sulfenes **12**.

A viable candidate for the second major photoproduct was found in the course of attempts to optimize the structure of the singlet carbene S-**2e** (R = CH$_3$) using ab initio [MP2/6−31G(d,p)] or DFT [B3LYP/6−31G(d,p)] methods. At both levels of theory, S-**2e** is a transition state rather than a minimum on the potential energy surface and the system converges to the structure of 3-methanesulfonyl-2-methyl-2λ^4-oxathiirene 2-oxide (**16e**). The *cis*-oxathiirene oxide *cis*-**16e** is calculated to be 6 and 1 kcal/mol more stable than S-**2e** at the MP2 and B3LYP levels, respectively

Mechanistic Considerations

The electron affinities (*EA*s) and the ionization potentials (*IP*s) of carbenes correlate with their nucleophilicities or electrophilicities.[22] A high electron affinity corresponds to a strongly electrophilic character, whilst nucleophilic carbenes are characterized by low ionization potentials. Only a few experimental data are available for carbenes; however, *EA* and *IP* are much less dependent than LUMO and HOMO energies on the computational method applied, and so can be calculated with some confidence (Table 6). For (HSO$_2$)$_2$C:, these calculations predict an unusually large *EA* and thus an extremely high electrophilicity both in its sing-

Table 4. Relative energies calculated at the MP2/6−31G(d,p) and B3LYP/6−31G(d,p) levels of theory, including zero point energy (ZPE) correction

		R = CH_3 MP2	R = CH_3 B3LYP	R = H MP2
T-2		0	0	0
17		−5		
S-**2**[a]		−2	−2	−2
cis-**16**		−8	−3	−10
trans-**16**		−13	−8	
12		−70	−59	−68
18		−95	−85	−87
19		−88	−79	−81
19		−168	−145	−159

[a] Transition state.

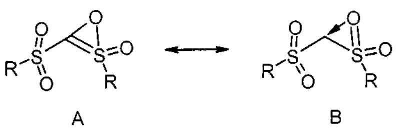
Table 5. IR-spectroscopic data of the oxathiirene oxides **16** [ṽ/cm^{-1} (rel. intensity)]

16a[a]	**16b**[a]	**16c**[a]	**16d**[a]	**16e**[a]	*cis*-**16e**[b]	*trans*-**16e**[b]	Assignment
563 (100)	557 (100)	562 (100)	541 (100)	511 (100)	432 (65)	501 (29)	δ (SO_2)
845 (8)	847 (3)	848 (24)	861 (32)	853[c]	910 (20)	803 (21)	δ (COS)
986 (28)	974 (13)	969 (15)	988 (18)	961 (32)	998 (20)	894 (21)	ν (CO)
1022 (15)	1038 (14)	1017 (55)	997 (14)	986 (24)	1013 (27)	1021 (17)	ν (SO)
1087 (36)	1074 (32)	1095[c]	1079 (4)	993 (36)	1017 (16)	1056 (12)	
1181[c]	1165[c]	1189[c]	1127[c]	1172[c]	1158 (63)	1149 (43)	ν_{sym} (SO_2)
–	–	–	1335[c]	1341[c]	1345 (87)	1338 (55)	ν_{asym} (SO_2)
1371[c]	1363[c]	1362[c]	1333[c]	1356[c]	1364 (100)	1351 (100)	ν_{asym} (SO_2)

[a] Argon, 10 K. – [b] Calculated at the MP2/6−31G(d,p) level of theory. – [c] Overlapping vibrations, only tentatively assigned to **16**.

let and in its triplet states. From this, a very high reactivity is expected for the carbenes **2**.

The oxathiirene oxides **16** are an interesting new class of highly strained heterocycles. The C−S bond lengths in *cis*- and *trans*-**16e** are calculated [MP2/6−31G(d,p)] as 1.706 and 1.700 Å, respectively, halfway between C−S single and double bonds (Figure 2). The S−O bond is shorter than typical S−O single bonds, indicating a partial double bond character. The C−O bond lengths of 1.728 and 1.655 Å for *cis* and *trans* are much longer than expected for typical C−O single bonds. The bonding situation in **16** can be explained by the two structures A and B, with A being a classical three-membered ring and B an intramolecular complex of carbene **2** with one of the oxygen lone pairs donating electron density to the vacant p-orbital at the carbene center. The higher stability of the *trans* isomer coincides with the shorter C−O bond length and a smaller dipole moment. Thus, **16** can be viewed as the intramolecularly stabilized singlet carbene **2**, which is in agreement with the extreme electrophilicity predicted for these carbenes.



The oxathiirene oxides **16** are only a few kcal/mol more stable than the much more reactive triplet carbenes T-**2**. At room temperature, T-**2** and **16** are in an equilibrium, and so typical triplet carbene reactivity (H abstraction from the solvent etc.) is observed in solution. If the temperature is lowered (organic glass at 77 K or argon matrix at 10 K), only products derived from **16** (mainly secondary photoproducts and products of the reaction with the solvent) are formed. The major photoproducts at low temperature are the sulfenes **12**. At the MP2 level, **12e** (R = CH_3) and **12f** (R = H) are predicted to be 70 kcal/mol and 68 kcal/mol more stable than the corresponding triplet carbenes T-**2e** and T-**2f**, respectively (Table 4).

The mechanism resulting in **10**, which is a major photoproduct of **1** in acetonitrile at room temperature, is less straightforward. The formation of **10** requires the migration of two oxygen atoms from one sulfur atom to the carbene carbon atom, followed by decarboxylation. Pawlowski et al. postulated that the 2,4-dioxa-1-thiabicyclo-[1.1.0]butane **17** might be an intermediate in this reaction sequence (Scheme 6).[8] MP2/6−31G(d,p) calculations found that a structure related to **17** is indeed a minimum on the potential energy surface (Figure 3, Table 4).

Table 6. Electron affinities *EA* and ionization potentials *IP* in eV for a series of carbenes

	Carbene	$EA_{(\text{calcd.,vert.})}$ [a]	$IP_{(\text{calcd.,vert.})}$ [a]	$EA_{(\text{exp})}$ [b]	$IP_{(\text{exp})}$ [b]
Singlet	H_2C:	1.2	10.5	0.63[30]	10.4[32]
Singlet	Cl_2C:	1.5	10.2	1.6[31]	9.3[33]
Singlet	$F_2C{=}C$:	2.2	11.4	–	–
Triplet	$(HSO_2)HC$:	2.1	11.2	–	–
Singlet (transition state)	$(HSO_2)HC$:	0.4	10.2	–	–
Triplet	$(HSO_2)_2C$:	4.5	9.7	–	–
Singlet	$(HSO_2)_2C$:	3.2	11.3	–	–

[a] Vertical EA and IP calculated at the B3LYP/6−311++G(d,p) level of theory. − [b] Adiabatic electron affinities.

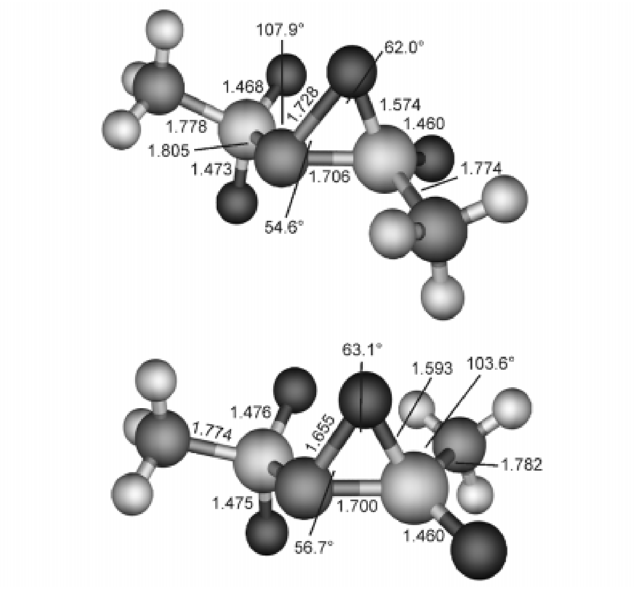


Figure 2. Some geometric data of *cis*- and *trans*-**16e** calculated at the MP2/6−31G(d,p) level of theory

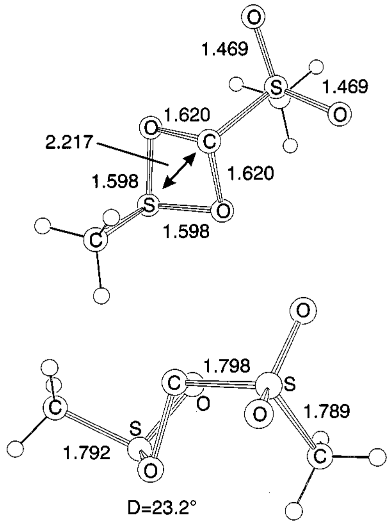
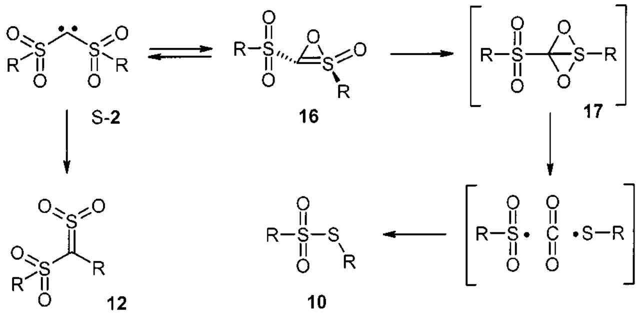
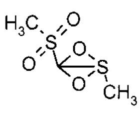


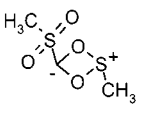
Figure 3. Some geometric data of **17e** calculated at the MP2/6−31G(d,p) level of theory



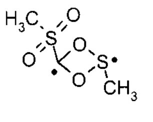
Scheme 6



17e I



17e II



17e III

At 1.620 Å, the ring system C−O bond is still quite long, but considerably shorter than those in *cis*- or *trans*-**16e** (1.728 and 1.655 Å, respectively). The S−O bond, on the other hand, is longer (Figure 3). A bicyclic structure I, a dipolar structure II, or a diradicaloid structure III can be formulated as representing the electronic structure of **17e**. The carbon atom in **17e** is highly pyramidalized, resulting in a folded, four-membered ring system with a dihedral angle of 23.2°, and a considerable amount of charge is transferred from the ring sulfur atom to the ring carbon atom (Figure 4). A topological analysis of the electron density distribution[26] reveals that no maximum electron density path connects the two nuclei, and therefore no (3,−1) bond critical point (BCP) exists between them; instead, a (3,+1) ring critical point is found. Since the existence of a BCP is usually taken as a necessary condition for the presence of a chemical bond, we reject description I for **17e**. No significant diradical character can be assigned to **17e**, since the RHF/6-31G(d,p) wavefunction is internally and externally stable[27] and the vertical singlet triplet energy gap is substantial [49.1 kcal/mol at B3LYP/cc-pVTZ//MP2/

6−31G(d,p)]. This indicates that structure II is the most satisfactory representation of **17e** (or at least dominates a resonance hybrid of several nonequivalent resonance structures).[28]

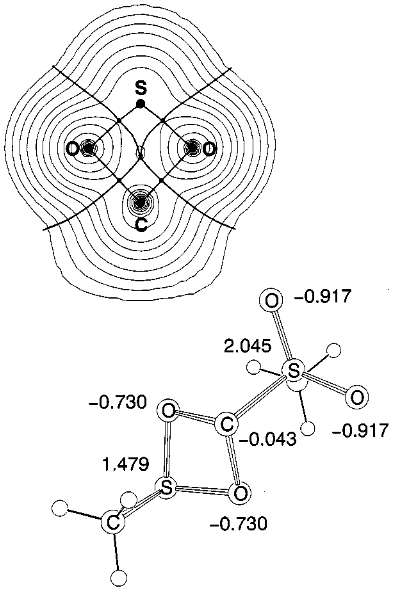


Figure 4. Important topological features of the electron density distribution within the OCO plane of the four-membered ring of **17e** and NPA charges for some atoms of this molecule from B3LYP/cc-pVTZ//MP2/6−31G(d,p) calculations

MP2 predicts that **17e** is about 3 kcal/mol below the transition state S-**2e** and 3 kcal/mol above *cis*-**16e**. Thus, **17** is readily thermally accessible from **16** at room temperature, providing a plausible route to **10**. However, since neither **17** nor other intermediates could be directly observed in our experiments, this pathway remains speculative.

Experimental Section

Matrix Spectroscopy: Matrix isolation experiments were performed by standard techniques with an APD CSW-202 Displex closed-cycle helium cryostat. Matrices were produced by deposition of argon (Linde, 99.9999%) at 30 K on top of a CsI (IR) or sapphire (UV/Vis) window at a rate of approximately 0.15 mmol/min. Irradiation was carried out using Osram HBO 500-W high-pressure mercury arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water and a Schott KG1 filter. For broadband irradiation, Schott cut-off filters were used (50% transmission at the wavelength specified), and for narrowband irradiation interference filters in combination with dichroic mirrors and cut-off filters were employed.

Bis(phenylsulfonyl)diazomethane (1a): IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 2339.5 (3), 2115.8 (4), 2111.9 (54), 1450.8 (7), 1374.1 (29), 1359.2 (18), 1225.8 (7), 1165.5 (46), 1087.6 (10), 1003.1 (5), 990.3 (11), 753.3 (5), 730.3 (4), 723.5 (17), 685.3 (10), 641.9 (11), 590.3 (100), 578.4 (3), 567.5 (18) cm^{-1}.

Bis(*p*-tolylsulfonyl)diazomethane (1b): IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 2951.4 (9), 2868.7 (6), 2116.2 (51), 1493.3 (2), 1454.8 (4), 1370.8 (9), 1355.1 (39), 1350.9 (17), 1221.6 (3), 1197.8 (2), 1163.0 (37), 1154.1 (28), 1088.0 (5), 994.2 (4), 811.9 (8), 586.4 (9), 572.1 (100) cm^{-1}.

Bis(*p*-chlorophenylsulfonyl)diazomethane (1c): IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 3776.1 (3), 3756.5 (4), 3711.0 (5), 2116.1 (59), 1612.2 (2), 1588.1 (13), 1479.2 (21), 1399.8 (7), 1375.5 (24), 1360.6 (11), 1282.3 (3), 1225.0 (11), 1208.2 (4), 1178.5 (4), 1171.8 (2), 1166.9 (39), 1094.3 (10), 1086.1 (25), 1018.0 (5), 993.8 (26), 828.1 (8), 763.1 (5), 758.0 (48), 708.6 (7), 660.3 (17), 622.4 (100), 603.6 (3), 589.4 (2), 566.8 (34), 484.2 (21) cm^{-1}.

Bis(cyclohexylsulfonyl)diazomethane (1d): IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 2944.887 (9), 2866.4 (3), 2121.9 (81), 2091.4 (15), 1600.1 (3), 1455.8 (7), 1365.4 (29), 1341.5 (43), 1327.6 (11), 1271.8 (3), 1232.3 (3), 1147.6 (61), 986.1 (9), 851.4 (3), 821.2 (2), 762.4 (4), 662.9 (7), 638.9 (2), 628.5 (3), 609.4 (100), 590.8 (3), 553.7 (18) cm^{-1}.

Bis(methylsulfonyl)diazomethane (1e): IR (Ar, 10 K): $\tilde{\nu}$ (rel. int.) = 3018.0 (1), 2935.9 (1), 2135.2 (15), 2131.7 (36), 1363.0 (26), 1361.2 (100), 1355.2 (17), 1348.3 (6), 1322.8 (21), 1242.6 (36), 1157.9 (89), 1008.1 (10), 1002.9 (31), 966.7 (27), 770.5(9), 758.7 (42), 587.4 (15), 548.3 (35), 534.5 (61), 508.2 (17) cm^{-1}.

Calculations: Calculations were performed with the Gaussian 98 program package.[23] Geometries and vibrations were calculated at the B3LYP/6−31G(d,p)[24] or MP2/6−31G(d,p)[25] levels of theory. Electron densities for analysis within the AIM framework[26] were calculated at the B3LYP/cc-pVTZ//MP2/6−31G(d,p) level of theory, using Cartesian d and f functions. The AIM 2000 program by Biegler−König et al. was used for topological analysis of the electron density distribution.[29]

Acknowledgments

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