Matrix Isolation of Diphenylsulfene and Diphenyl-α-sultine

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Abstract: Diphenylsulfene (**5**) and diphenyl-α-sultine **6** were generated in cryogenic matrices by three independent routes: (i) the thermal reaction of diphenylcarbene (**8**) and SO_2, (ii) the photochemically induced hetero Wolff rearrangement of sulfonylcarbene **11**, and (iii) oxygen transfer from ozone to diphenylsulfine **16**. Isotopic labeling with ^{13}C and ^{18}O allows for the assignment of several characteristic IR vibrations of **5**. Irradiation with $\lambda > 375$ nm results in the rearrangement of **5** to **6**, which is the first α-sultine that has been characterized spectroscopically. The final product on UV irradiation of **6** is benzophenone (**9**) and sulfur monoxide.

Introduction

Sulfonyldiazomethanes **1** are important components of a class of photoresists which upon irradiation produce acids (photoacids).[1] The nature of the acids and the mechanism of their formation is largely unknown, and several short-lived and highly reactive intermediates have to be considered. As the primary product, a sulfonylcarbene (**2**) is expected, which, depending on its lifetime, could be either trapped by solvent, oxygen or water, or rearrange to sulfene **3**[2,3] (Scheme 1). The sulfenes **3** are kinetically labile[4,5] but can be stabilized by amino substituents (e.g., thiourea dioxide is completely stable and was characterized by X-ray crystallography).[6] The parent compound (R = R′ = H) was generated as transient species by gas phase elimination[5] or photo-cycloreversion processes[7] and could be trapped and spectroscopically characterized at low temperature. In contrast, the cyclic isomers **4** (α-sultines) have never been directly observed.

A completely different approach to sulfenes is the direct reaction of a diphenylcarbene (**8**) with SO_2. In an earlier report, Hiraoka investigated the reaction of methylene, generated from ketene or diazomethane, with SO_2.[8] On the basis of final products (H_2O, COS, and other products), the formation of both the sulfene and α-sultine was proposed. However, since diazo compounds also react with SO_2 (Staudinger–Pfenninger reaction),[9] alternative pathways not involving methylene have to be considered.

Recently, Skrypnik and Lyashchuk used this route to synthesize a crystalline sulfene by the reaction of the stable Arduengo carbene[10] and SO_2.[11] Sterically demanding groups

Scheme 1
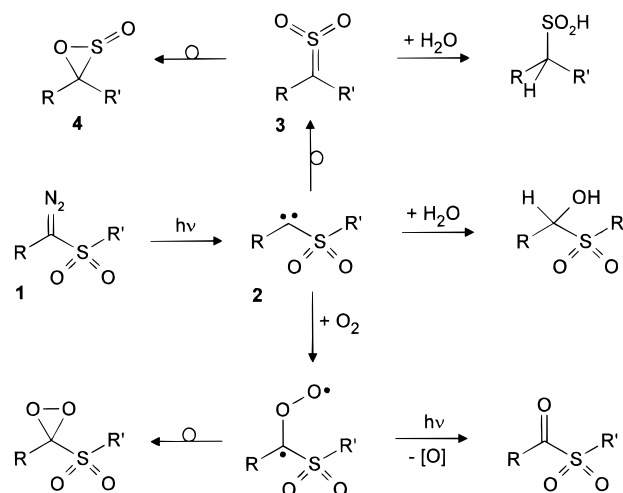
destabilize aminosulfenes,[12] and thus it is not unexpected that this sulfene is less stable than thiourea dioxide and rapidly decomposes at room temperature.
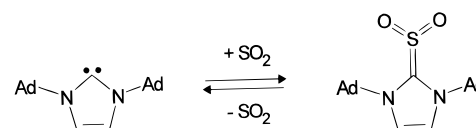
Here, we report on the matrix isolation and spectroscopic characterization of diphenylsulfene (**5**) and diphenyl-α-sultine **6** synthesized by the hetero Wolff rearrangement of the corresponding sulfonyldiazomethane **10** and by the reaction of diphenylcarbene (**8**) with SO_2. In addition, the oxidation of diphenylsulfine with ozone as source of **5** is described as the third independent route.

Results and Discussion

Diphenylcarbene (8) and SO_2. Carbene **8** is readily generated by irradiation of matrix-isolated diphenyldiazomethane (**7**).[13,14] If **7** is deposited in a 5% SO_2-doped argon matrix, an

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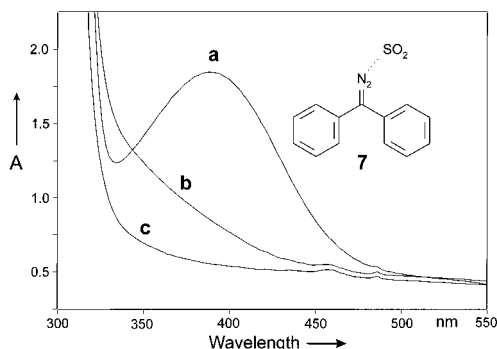
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Figure 1. UV-vis spectra showing the absorptions of **7**/SO$_2$, sulfene **5**, and sultine **6** in 5% SO$_2$-doped argon. The λ_{max} of SO$_2$ is at 282 nm, and the weak absorptions at 460 nm are caused by traces of carbene **8**. (a) Spectrum of **7**/SO$_2$ matrix isolated in argon/5% SO$_2$ at 10 K. (b) Spectrum after irradiation with $\lambda > 420$ nm, mainly **5**. (c) Spectrum after irradiation with $\lambda = 375-450$ nm, mainly **6**.

intense yellow-orange coloring of the matrix ($\lambda_{max} = 390$ nm) is observed (Figure 1), in contrast to the pale red color of **7** ($\lambda_{max} = 284$ and 511 nm), matrix-isolated in pure argon. In the IR spectrum, the regions at 525, 1151, 1347, and 2475 cm^{-1} are blocked due to the very strong SO$_2$ absorptions with half-widths around 10$-$25 cm^{-1}. The major difference of the spectrum of **7** in argon/SO$_2$ compared to pure argon is the broadening of the C=N=N stretching vibration at 2047 cm^{-1} (half-width 15$-$20 cm^{-1}). This reveals the formation of a charge-transfer (CT) complex with a strong interaction of the C=N=N group and SO$_2$ during the deposition of the matrix. No additional IR absorptions other than those belonging to SO$_2$/**7** could be detected. The thermal formation of cycloadducts from the SO$_2$/**7** complex, as expected in the Staudinger$-$Pfenninger reaction,[9] can therefore be excluded under these conditions.

Irradiation with $\lambda > 455$ nm results in the disappearance of the SO$_2$/**7** complex and formation of a new bright yellow product **5** (λ_{max} 238, ca. 316 nm with tailing into the visible region, Figure 1). The IR exhibits strong absorptions at 550, 984, 1163, and 1265 (br) cm^{-1} (Table 1). Isotopic labeling using [13]C-**7** and S[18]O$_2$, respectively, as starting materials allowed the generation of three isotopomers and the assignment of the new product the structure of diphenylsulfene (**5**, Scheme 2). In addition to the four modes mentioned above, a strong absorption of **5** at 1355 cm^{-1} is completely masked by the broad mode of SO$_2$ at 1347 cm^{-1}. This vibration can only be observed if **5** is synthesized by an independent route, avoiding excess SO$_2$ in the matrix (vide infra).

If the concentration of SO$_2$ is lowered to 1%, diphenylcarbene (**8**), the product of the direct photolysis of **7**, is also formed in addition to **5**. Subsequent annealing at 35 K for several minutes converts **7** partially to **5**. However, prolonged annealing does not result in the complete conversion of **8**.

The sulfene unit can be approximately described as a distorted SO$_3$ molecule, and thus, the comparison with SO$_3$ allows for the assignment of most of the characteristic absorptions of **5**. The absorption at 1355 cm^{-1} is close to the degenerate $\nu_3(e')$ mode of SO$_3$ at 1386 cm^{-1} (argon matrix)[15] and to ν_{asym} of SO$_2$ at 1347 cm^{-1} and, thus, is assigned to ν_{asym} O=S=O of **5**.

The vibration at 1266 cm^{-1} exhibits a large ^{13}C isotopic shift ($\nu_i/\nu = 0.985$), while the [18]O$_2$ isotopic shift could not be determined (overlap with broad satellite peaks of the very strong S[18]O absorption). This absorption could be assigned to the C=S stretching vibration or to the asymmetric C$-$C(1)$-$C stretching vibration. The latter mode involves the central carbon atom

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Table 1. IR Absorptions of Three Isotopomers of Sulfene **5** Compared to SO$_3$

5[a] ν(I$_{rel}$)	5[b] ν(I$_{rel}$)	[13]C-5[b] ν$_i$/ν	[18]O$_2$-5[b] ν$_i$/ν	5[c] ν	SO$_3$[d] ν(I$_{rel}$)
1355 (86)	-			1353	1386 (vs) ν_{asym}(O=S=O)
1266 (57)	1265 (62)	0.985	-	1262	ν_{asym} (C-C(1)-C) or ν (C=S)
1166 (81)	1163 (83)	0.998	0.987	1162	ν_{sym} (O=S=O)
1034 (9)	1035 (7)	0.999	1.001	-	phenyl
1004 (30)	1002 (28)	0.998	0.999	-	phenyl
989 (48)	984 (79)	0.983	0.981	983	1068 (inact.) ν_{sym}
617 (18)	616 (21)	0.997	0.998	-	phenyl
549 (100)	550 (100)	0.998	0.978	546	528 (m) δ_{sym} (O=S=O)
-	-	-	-	-	490 (w)

[a] Generated by irradiation ($\lambda > 475$ nm) of **10** in argon at 10 K. Wavenumbers in cm^{-1} (relative intensity based on the strongest absorption). [b] Generated by irradiation ($\lambda > 475$ nm) of **7** in SO$_2$-doped argon (5% SO$_2$) at 10 K. [c] Generated by irradiation ($\lambda > 455$ nm) of **16** in O$_3$-doped argon (1.5% O$_3$) at 10 K. [d] Reference 15.

C(1) and the two ipso carbon atoms of the phenyl groups and is frequently found in derivatives of diphenylmethane as an intense absorption around 1250$-$1300 cm^{-1} with a large ^{13}C isotopic shift (e.g., benzophenone 1280 cm^{-1}, $\nu_i/\nu = 0.990$; diphenyldiazomethane 1268 cm^{-1}, $\nu_i/\nu = 0.993$).[14] Our IR data do not allow to distinguish between these assignments.

The 1163 cm^{-1} absorption exhibits a large [18]O$_2$ shift but only a small ^{13}C isotopic shift and is assigned to the symmetrical O=S=O stretching vibration located mainly at the SO$_2$ moiety. The infrared inactive, totally symmetric 1068 cm^{-1} vibration (gas phase, very weak) of SO$_3$ corresponds to the strong absorption of **5** at 984 cm^{-1}. Both the ^{13}C and [18]O$_2$ isotopic shifts are large, confirming this assignment. The fourth vibration associated with the sulfene moiety in **5** at 550 cm^{-1} with a large [18]O$_2$ isotopic shift is close to the 528 cm^{-1} vibration in SO$_3$ and assigned to a O=S=O in plane deformation mode.

This assignment of IR vibrations is in qualitative agreement with the IR data of the parent sulfene reported by King et al.[5] The strong absorptions of **5** at 1355, 1163, and 984 cm^{-1} correspond to vibrations of CH$_2$SO$_2$ at 1330, 1230, and 950 cm^{-1}.

Scheme 2
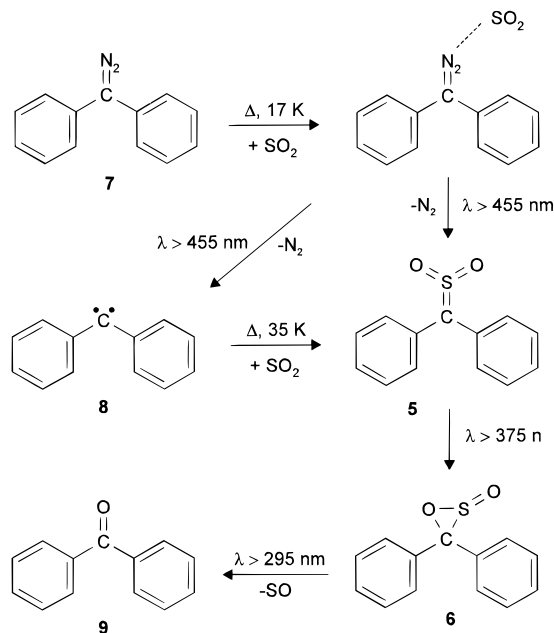
Table 2. IR Absorptions of Three Isotopomers of Sultine **6**, Matrix Isolated in Argon at 10 K

6^a $\nu(I_{rel})$	6^b $\nu(I_{rel})$	$^{13}\text{C-}6^b$ ν_i/ν	$^{18}\text{O}_2\text{-}6^b$ ν_i/ν	
1454 (18)	1454 (26)	0.999	1.0	phenyl
1221 (30)	1218 (22)	0.984	0.997	ν_{asym} C—C(1)—C
1196 (100)	1166 (100)			ν (S=O)
1020 (12)	1018 (26)	0.990	0.990	ν (C—O)
907 (7)	914 (17)	0.990	0.997	
743 (39)	740 (64)	0.999	0.997	
698 (57)	701 (90)	1.0	0.999	phenyl
679 (6)	678 (26)	0.994	0.994	
626 (22)	624 (61)	0.995	1.0	
590 (5)	595 (22)	0.993	0.978	ν (S—O)

^{a} Generated by irradiation ($\lambda > 360$ nm) of sulfene **5** (via rearrangement of carbene **11**) in argon at 10 K. Wavenumbers in cm^{-1} (relative intensity based on the strongest absorption). ^{b} Generated by irradiation ($\lambda > 375$ nm) of sulfene **5** (via SO$_2$/**7** CT complex) in SO$_2$-doped argon (5% SO$_2$) at 10 K.

When a 1:2:1 mixture of S^{16}O$_2$/S^{16}O^{18}O/S^{18}O$_2$ is used, the peaks at 984 and 1163 cm^{-1}, which both exhibit large ^{18}O isotopic shifts, are split into an overlapping triplet with the approximate ratio of 1:2:1 (984, 975, 967 cm^{-1} and 1163, 1154, 1149 cm^{-1}, respectively). This confirms that the two oxygen atoms are equivalent and only three ^{16}O/^{18}O isotopomers exist, in agreement with the postulated structure and in contrast to the expectation for the cyclic isomer **6** with four possible isotopomers.

Shorter wavelength irradiation ($\lambda > 375$ nm) of matrix-isolated **5** results in the rapid photolysis and formation of a colorless product (no UV-vis absorption above 300 nm, Figure 1), which was identified as diphenyl-α-sultine **6**. The strongest IR absorption at 701 cm^{-1} and several other bands of **6** exhibit only small or no isotopic shifts on ^{13}C or ^{18}O labeling (Table 2) and correspond to vibrations of the phenyl rings. The medium intensity absorption at 1218 cm^{-1} shows a large ^{13}C but no ^{18}O$_2$ isotopic shift and is assigned to ν_{asym} C—C(1)—C. The largest ^{18}O isotopic shift is found for the S—O (ring) stretching vibration at 595 cm^{-1}, which is considerably red-shifted compared to acyclic sulfinates.[16] This red shift might

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Table 3. Selected IR Modes Characteristic of a Sulfonyl Group

compd^a	ν_{asym}^b	ν_{sym}^b	δ^b
11	1325	1152	569
12	1362	1170	597
14	1352	1159	582
13	1329	1155	596
15	1329	1167	592

^{a} Matrix isolated in argon at 10 K. ^{b} Wavenumbers in cm^{-1}.

be attributed to the weakening of the S—O bond in the three-membered ring. The C—O stretching vibration of the ring with both large ^{13}C and ^{18}O shifts absorbs at 1018 cm^{-1}. (For a discussion of the S=O (exocyclic) stretching vibration see below.)

Using a 1:2:1 mixture of the three SO$_2$ isotopomers as described above results only in a broadening of several peaks. Due to the comparatively small isotopic shifts and the general line broadening in SO$_2$-doped matrices, the expected 1:1:1:1 ratio of the four ^{16}O/^{18}O isotopomers of **6** could not be clearly resolved. However, the line shape more easily fits a 1:1:1:1 ratio than a 1:2:1 ratio.

The final products obtained in the matrix on short-wavelength UV irradiation ($\lambda > 295$ nm) are benzophenone (**9**), with $\nu_{C=O}$ at 1638 cm^{-1} (br), and SO. In solid argon, $\nu_{C=O}$ of **9** is a sharp absorption at 1674 cm^{-1}, the red-shift and broadening is caused by the complexation of **9** with SO$_2$. This complex was independently obtained by deposition of **9** in SO$_2$-doped argon matrices, and a similar complex was observed by Dunkin and MacDonald in 10% SO$_2$-doped nitrogen matrices.[17] The IR absorption of matrix-isolated SO was described at 1137 cm^{-1},[18] which is close to ν_{sym} of SO$_2$ and thus difficult to observe in the presence of large excess of SO$_2$. In our experiments, an absorption at 1129 cm^{-1} not belonging to **9** is tentatively assigned to SO. The red-shift of 8 cm^{-1} might be due to the complexation of SO with **9** or SO$_2$.

Photochemistry of Phenyl(phenylsulfonyl)diazomethane (10). To avoid the problems associated with the strong SO$_2$ absorption in doped matrices, and to obtain an independent precursor of sulfene **5**, the photochemistry of the sulfonyldiazomethane **10** was investigated. Irradiation in solid argon at 10 K with $\lambda > 475$ slowly resulted in the photolysis of **10** and formation of small amounts of **5**. The main product was carbene **11** (Figure 2), identified by its subsequent photochemistry and by oxygen-trapping experiments.

Characteristic IR absorptions of **11** are at 1325, 1152, and 569 cm^{-1}, indicating a sulfonyl moiety. Thus, in contrast to keto carbenes, which can only be matrix isolated if the corresponding ketene is destabilized by ring strain,[19] the sulfonylcarbene **11** is easily trapped in solid argon.

A 400 nm irradiation induces the hetero Wolff rearrangement, and sulfene **5** is formed as the major product (Scheme 3). Irradiation with $\lambda > 360$ nm again converts **5** into **6** (Figure 2). Thus, the photochemistry of sulfene **5** is a unimolecular process independent of excess SO$_2$ in the matrix, which is in line with the proposed structure of α-sultine **6** and excludes cycloadducts of **5** and SO$_2$, the proposed intermediates in the Staudinger—Pfenninger reaction.[9]

A band at 1196 cm^{-1} with high intensity (which in the carbene/SO$_2$ route is red-shifted and partially overlapping with the 1163 cm^{-1} vibration of **5**) is assigned to the S=O stretching

(17) Dunkin, I. R.; MacDonald, J. G. *J. Chem. Soc., Perkin Trans.* **1984**, *2*, 2079—2084.
(18) Hopkins, A. G.; Brown, C. W. *J. Chem. Phys.* **1975**, *62*, 2511—2512.
(19) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.* **1985**, *107*, 7597—606.
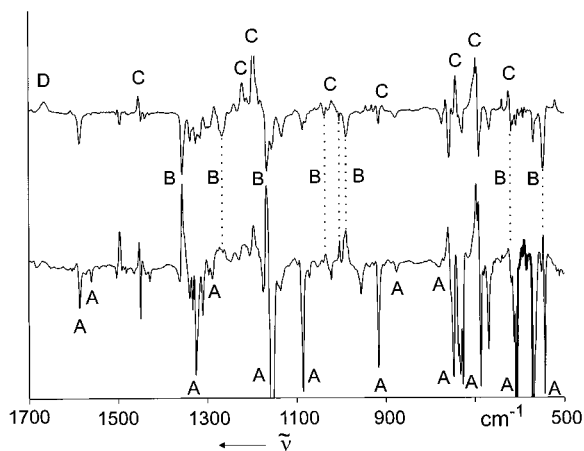
Figure 2. IR difference spectra showing the photochemistry of phenyl-(phenylsulfonyl)carbene (**11**) in argon at 10 K: (lower spectrum) bottom part, bands assigned to **11** (A) disappearing on irradiation with $\lambda >$ 400 nm; top part, bands assigned to diphenylsulfene **5** (B) appearing; (upper spectrum) bottom part, bands assigned to **5** (B) disappearing on irradiation with $\lambda > 360$ nm; top part, bands assigned to **6** (C) and benzophenone (D).

Scheme 3
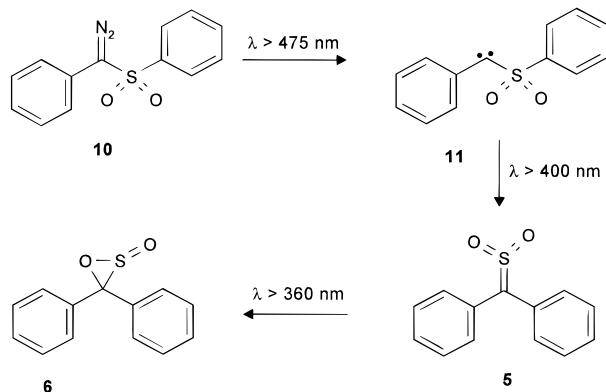
mode of **6**. The considerable blue-shift in relation to sulfinates of larger ring size $(1125-1140 \text{ cm}^{-1})^{16}$ is analogous to similar blue-shifts of C=X stretching vibrations of exocyclic double bonds in three-membered rings compared to those of the open chain systems.

The thermal reaction with $^3O_2$ in O_2-doped matrices at 25–40 K to give carbonyl O-oxides is highly characteristic and widely used for the identification of triplet carbenes.[20-23] If **10** is irradiated ($\lambda > 475$ nm) in an 0.5% O_2-doped argon matrix at 10 K, carbene **11** and several oxidation products are formed. Annealing the matrix for several minutes at 40 K results in the decrease of **11** and formation of a new, intensely yellow product with IR absorptions at 1362, 1170, and 597 cm^{-1}, characteristic of the sulfonyl moiety (Figure 3). Two strong absorptions at 951 and 931 cm^{-1} exhibit large $^{18}O_2$ red-shifts and are therefore assigned to the O–O stretching vibration of carbonyl O-oxide **12**. (Presumably syn and anti conformers are formed; however, in several cases, a splitting of the O–O stretching vibration was observed, although only one conformer was possible.)[22] The yellow color is caused by a broad UV-vis absorption with $\lambda_{\max} = 398$ nm, which is also highly characteristic of carbonyl oxides.[22]

(20) Bell, G. A.; Dunkin, I. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1213−1215.
(21) Bucher, G.; Sander, W. *Chem. Ber.* **1992**, *125*, 1851−1859.
(22) Sander, W. *Angew. Chem.* **1990**, *102*, 362−372; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344−354.
(23) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583−1621.
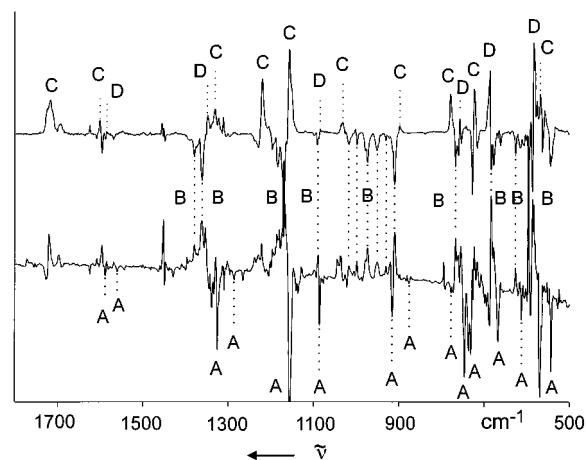
Figure 3. IR difference spectra showing the oxidation of phenyl-(phenylsulfonyl)carbene (**11**) in 5% O_2-doped argon: (lower spectrum) bottom part, bands disappearing; top part, bands appearing on annealing of **11** at 41 K; (upper spectrum) bottom part, bands disappearing; top part, bands appearing on subsequent irradiation with $\lambda > 590$ nm. (A) Bands assigned to **11**. (B) Bands assigned to **12**. (C) Bands assigned to **13**. (D) Band assigned to **14**.
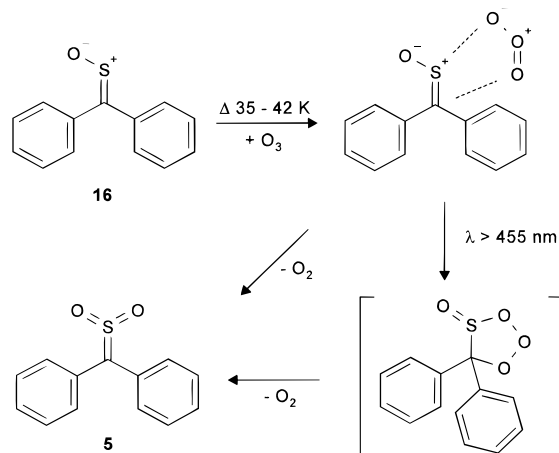
Scheme 4
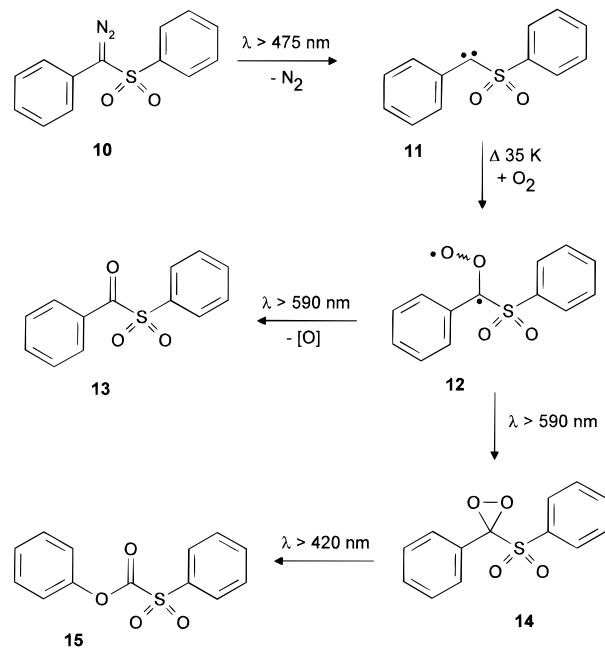
Carbonyl oxides are photochemically labile, and upon irradiation of the matrix with red light ($\lambda > 590$ nm), **12** rapidly disappears. Two new products are formed which are tentatively assigned to ketone **13** and dioxirane **14** (Figure 3, Scheme 4). Loss of oxygen atoms and rearrangement to dioxiranes are frequently observed photochemical reactions of carbonyl oxides.[22] Ketone **13** exhibits strong absorptions at 1329, 1155, and 596 cm^{-1} which are not shifted upon ^{18}O labeling, indicative of the sulfonyl moiety, and a carbonyl absorption at 1719 cm^{-1} with a large ^{18}O isotopic shift. The IR spectrum of the dioxirane **14** is, except for the missing carbonyl vibration, similar to that of the ketone **13**. When irradiated with blue light ($\lambda > 420$ nm), ketone **13** is stable while dioxirane **14** rearranges selectively to ester **15**. The IR spectroscopic data of **15** are in line with the expectation.

Oxidation of Diphenylsulfine. A third route to sulfene **5** is the oxidation of diphenylsulfine (**16**) with atomic oxygen. Sulfine **16** was matrix isolated in argon doped with 1−1.5% O_3 at 10 K. Annealing the matrix at 42 K results in a yellow

Scheme 5

coloring of the matrix, a shift of $\nu_{C=S}$ of **16** from 1129 to 1115 cm^{-1} and broadening of the strong O_3 absorption at 1040 cm^{-1}. These observations suggest that a complex of **16** and O_3 is formed (Scheme 5). Small amounts of benzophenone (**9**), CO_2, and new, unidentified IR absorptions (658, 774, 929, 1006, 1080, 1300, 1442, 1491, and 1590 cm^{-1}) indicate the partial oxidation of **16**. When irradiated with $\lambda > 455$ nm, the **16**/O_3 complex reacts to CO_2 and a complex of **9** and SO_2 with characteristic absorptions at 1649 and 1336 cm^{-1} (see above). Additional IR bands at 1353, 1262, 1162, 983, and 546 cm^{-1} correspond to the strong absorptions of **5**, which clearly shows that photolysis of the **16**/O_3 complex leads to the cleavage of the ozone molecule and transfer of an oxygen atom to sulfine **16**. Our experiments do not allow to distinguish between a one-step reaction **16**/$O_3 \rightarrow$ **5** and the formation of an intermediate adduct of **16** and ozone (Scheme 5). Compared to the other syntheses of **5** described above, the oxidation of sulfine **16** is less clean and leads to several byproducts of unknown constitution.

Conclusion

Three independent routes yield diphenylsulfene (**5**) as the primary product under the conditions of matrix isolation. The comparison of the IR spectra with that of the parent sulfene CH_2SO_2[5] and SO_3[15] in combination with isotopic labeling gives clear evidence for the structural assignment. The sulfene functional group is described best as a distorted SO_3 molecule.

The hetero-Wolff rearrangement of sulfonylcarbenes **2** is of importance since the sulfonyldiazomethanes **1** are major constituents of photoresists which are based on photoacids. In contrast to keto carbenes, which in most instances are short-lived even under the conditions of matrix isolation,[19,24,25] sulfonylcarbene **11** could be readily matrix isolated. This implies that intersystem crossing to the triplet ground state efficiently competes with the rearrangement to sulfene **5** and is in line with the chemistry of keto sulfonylcarbenes, which produce ketenes and not sulfenes as the primary photoproducts.[2,26]

The thermal rearrangement **11** $\rightarrow$ **5** was not observed under the conditions of matrix isolation (up to 40 K) which reveals that there is at least a small activation barrier. Time-resolved spectroscopy at higher temperatures is required to determine the activation barrier and to decide whether the formation of **5**

is a one- or two-photon process. Since the reaction of carbene **11** with oxygen is very rapid (at 35−40 K comparable to other triplet carbenes),[22] the question arises of whether sulfene **5** or a trapping product of carbene **11** is the precursor of the photoacid.

Sulfene **5** is stable toward visible light irradiation, but UV irradiation results in the irreversible rearrangement to **6**. The rearrangement is independent of the method for the synthesis of **6** and allows for the first time the spectroscopic characterization of an α-sultine. The final product of short-wavelength UV irradiation is benzophenone **9**. Two mechanisms have to be considered for the formation of **9**: (i) the photochemical extrusion of SO from **6** and (ii) the photochemical cleavage of sulfene **5** to diphenylcarbene (**8**) and SO_2 followed by the abstraction of an oxygen atom from SO_2 to give **9** and SO. Mechanism ii requires the photochemical ring-opening **6** $\rightarrow$ **5**, which was not observed in our experiments. However, the stationary concentration of **5** at short-wavelength irradiation might be too small for IR detection, and thus, mechanism ii can not be rigorously excluded, although i seems to be more reasonable. Further work including time-resolved spectroscopy is in progress in our laboratory to shed additional light on these technically important processes.

Experimental Section

Materials and General Methods. ^{1}H NMR spectra were taken at 80 MHz (Bruker WP-80) or 400.1 MHz (Bruker AM-400), ^{13}C NMR spectra were taken at 100.4 MHz (Bruker AM-400) with $(CH_3)_4Si$ as internal standard. Mass spectra (EI, 70 eV) were taken on a Varian MAT CH5.

[$^{18}O_2$]Sulfur dioxide was prepared according to a modified procedure by Schriver et al.[27] A 100 mL two-necked reaction flask with a valve and thermometer was connected via a transfer line to a 100 mL long-necked collection flask with a valve which was immersed in liquid nitrogen. The inner surface of the collection flask had been passivated by treatment with $SiMe_3Cl$ and then flame-dried under vacuum. The collection flask and transfer line were evacuated, and the reaction flask was filled with 0.5 g of sulfur (p.a.) under an atmosphere of 500 mbar $^{18}O_2$ (99.5% isotopic purity) and electrically heated. At 260 °C the reaction mixture was ignited with a Tesla coil. The electric discharge was maintained for ca. 30 s, and the gas mixture was transferred into the collection flask. Residual oxygen was quickly pumped off. The $S^{18}O_2$ (94% isotopic purity) could be stored at 77 K in vacuo without loss of isotopic purity, while at room temperature gradual oxygen exchange with the glass surface took place. A 1:2:1 mixture of $S^{16}O_2$, $S^{16}O^{18}O$, and $S^{18}O_2$ was obtained by using a 1:1 mixture of $^{16}O_2$ and $^{18}O_2$ in the procedure described above.

Diphenyldiazomethane (**7**) was freshly prepared from benzophenone tosylhydrazone sodium salt[14] by vacuum thermolysis at 60 °C/10^{-5} mbar. The synthesis of [1-^{13}C]-**7** is described in ref 14.

Diphenylsulfine (**16**) was synthesized via oxidation of thiobenzophenone, following a procedure by Zwanenburg et al.[28ab] and Tabuchi et al.[28c] IR (Ar, 10 K): 1452 (16), 1125 (100), 1009 (17), 767 (39), 756 (23), 699 (32), 689 (22) cm^{-1} (rel intensity).

Chloromethyl phenyl sulfone (**17**) was prepared by a procedure described by Vogt and Tavares.[29]

2-Phenyl-3-(phenylsulfonyl)oxirane (18). Oxirane **18** was prepared by modifying the method described by Zwanenburg et al.[30] A 50% aqueous solution of sodium hydroxide (21 mL) was added very slowly and with vigorous stirring to a solution of sulfone **17** (26 mmol, 5 g),

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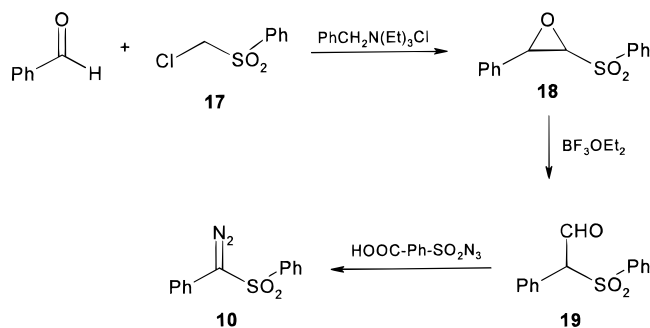
benzaldehyde (31 mmol, 3.3 g), and benzyltriethylammonium chloride (160 mg) in acetonitrile (8 mL) cooled in ice. After 1.5 h of stirring at 0 °C, the solid material was collected by filtration and washed with water until the filtrate was neutral. The product was dissolved in dichloromethane and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure to give 4.6 g (67%) of oxirane **18**, mp 102−103 °C (lit.[31] 102−104 °C). ^{1}H NMR (80 MHz, CDCl$_3$): δ = 4.18 (d, 1H), 4.55 (d, 1H), 7.15−8.05 (m, 10H, aromatic) ppm. MS: m/z (%) = 260 (1.3) [M$^+$], 141 (3.5) [M$^+$ − C$_6$H$_5$CH(O)CH], 119 (72) [M$^+$ − C$_6$H$_5$SO$_2$], 91 (100) [C$_6$H$_5$CH$_2^+$], 77 (36) [C$_6$H$_5^+$].

2-Phenyl-2-(phenylsulfonyl)acetaldehyde (19). A modification of a procedure by Zwanenburg et al.[30] was used to prepare aldehyde **19**. A solution of boron trifluoride−etherate (7.5 mmol, 1 g) in dichloromethane (7 ml) was added slowly to a solution of oxirane **18** (7 mmol, 1.8 g) in dichloromethane (52 mL) cooled in ice. After 10 min of stirring at 0 °C, water was added very carefully. The organic layer was separated and pentane was added to remove the main part of the contamination. The solution was filtered and evaporated under reduced pressure. The residue was chromatographed on silica in pentane/ether 1:1 to give 0.5 g (26%) of **19**. ^{1}H NMR (80 MHz, CDCl$_3$): δ = 4.9 (d, J = 2.5 Hz, 1H, C$_6$H$_5$C(CHO)HSO$_2$-), 7.15−7.7 (m, 10H, aromatic), 10.0 (d, J = 2.5 Hz, 1H, C$_6$H$_5$C(CHO)HSO$_2$-) ppm.

Phenyl(phenylsulfonyl)diazomethane (10). For the synthesis of **10** a modified method by van Leusen et al.[32] was used. To the stirred solution of 0.5 mg (1.8 mmol) of aldehyde **19** in 28 mL of dichloromethane were added 2.1 g (9.4 mmol) of *p*-carboxybenzenesulfonyl acid and 14 ml of 2 M aqueous ammonia. After 20 h of stirring at room temperature in the dark, the organic layer was slowly filtered over alumina (Merck, activity II-III) and concentrated. The resulting red oil was purified by chromatography on alumina with CCl$_4$ as eluent. The resulting red oil was crystallized from hexane to give 0.098 g (21%) of **10**, mp 45−46 °C (dec.). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.15− 7.62 (m, 8H, aromatic), 7.88 (d, ^3J = 8.3 Hz, 2H, aromatic) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ = 123.33, 124.61, 126.66, 127.19, 129.34, 133.48, 142.39 ppm. IR (KBr): ν = 2081 (s), 1594 (m), 1493 (m), 1329 (s), 1149 (s), 754 (m) cm^{-1}. UV (CH$_3$CN): λ_{max} (log ϵ) = 196 (4.42), 261 (4.03), 444 (2.06) nm. MS: m/z (%) = 258 (9) [M$^+$], 141 (7) [M$^+$ − C(C$_6$H$_5$)N$_2$], 77 (100) [C$_6$H$_5^+$], 28 (27) [N$_2^+$]. Anal. Calcd for C$_{13}$H$_{10}$N$_2$O$_2$S: C, 60.46; H, 3.90; N, 10.84; S, 12.41. Found: C, 60.52; H, 3.86; N, 10.76; S, 12.43.

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

(Messer-Griesheim, 99.9999%), mixtures of argon and oxygen (Messer Griesheim, 99.998%), or mixtures of argon and sulfur dioxide (99.97%) on top of a CsI (IR) or sapphire (UV-vis) window with a rate of approximately 0.15 mmol/min. In order to obtain optically clear matrices, the cold window was retained at 30 K (Ar), 25−30 K (Ar/ O$_2$), or 17 K (Ar/SO$_2$) during deposition and afterward cooled to 8−10 K. Ozone was generated with an Ozonizer (Demag), trapped at 77 K and purified according to ref 33.

Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer with a standard resolution of 1 cm^{-1} in the range of 400− 4000 cm^{-1}. Irradiations were carried out with use of Osram HBO 500 W/2 mercury high-pressure arc lamps in Oriel housings equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10 cm path of water. Schott cut off filters were used (50% transmission at the wavelength specified) in combination with dichroic mirrors.

The IR spectroscopic data of **5** and **6** are described in Tables 1 and 2.

Phenyl(phenylsulfonyl)carbene (11). Irradiation (λ > 475 nm, Ar, 10 K) of the matrix-isolated sulfonyldiazomethane **10** produced carbene **11** as the main product. IR (Ar, 10 K): 1587 (17), 1559 (5), 1325 (46), 1289 (10), 1154 (41), 1087 (37), 914 (37), 877 (3), 773 (3), 748 (27), 732 (44), 671 (32), 609 (5), 569 (100), 544 (54) cm^{-1} (rel intensity). UV (Ar, 10 K): 250, 274 nm.

Phenyl Phenylsulfonyl Ketone *O*-Oxide (12). Annealing carbene **11** in an 0.5% O$_2$-doped argon matrix at 41 K produced carbonyl oxide **12** as the main product. IR (Ar, 10 K): 1596 (43, 1.0), 1379 (43, 1.0), 1362 (57, 1.0), 1170 (89, 1.0), 1090 (36, 1.0), 1018 (29, 0.970), 999 (36, 0.965), 974 (43, 1.0), 951 (32, 0.928), 931 (18, 0.930), 909 (50, 1.0), 767 (46, 1.0), 728 (29, 1.0), 684 (71, 1.0), 627 (29, 0.976), 597 (100, 1.0), 587 (68, 1.0) cm^{-1} (rel intensity, ratio of ^{18}O/^{16}O isotopic frequencies ν_i/ν).

Phenyl Phenylsulfonyl Ketone (13). Irradiation (λ > 590 nm, Ar, 10 K) of matrix-isolated carbonyl oxide **12** produced ketone **13** and phenyl(phenylsulfonyl)dioxirane (**14**) as the main products. IR (Ar, 10 K): 1719 (38, 0.980), 1600 (15, 1.0), 1329 (31, 1.0), 1220 (69, 1.0), 1155 (100, 1.0), 1034 (15, 0.945), 898 (8, 1.0), 777 (46, 1.0), 724 (54, 1.0), 569 (46, 1.0) cm^{-1} (rel intensity, ratio of ^{18}O/^{16}O isotopic frequencies ν_i/ν).

Phenyl(phenylsulfonyl)dioxirane (14). IR (Ar, 10 K): 1582 (9, 1.0), 1352 (27, 1.0), 1159 (55, 1.0), 1091 (9, 1.0), 917 (5, 1.0), 755 (27, 1.0), 726 (36, 1.0), 687 (45, 1.0), 608 (55, 1.0), 582 (100, 1.0) cm^{-1} (rel intensity, ratio of ^{18}O/^{16}O isotopic frequencies ν_i/ν).

***O*,*S*-Diphenyl Thiocarbonate *S*,*S*-Dioxide (15).** Irradiation (λ > 420 nm, Ar, 10 K) of matrix-isolated dioxirane **14** produced **15** as the main product. IR (Ar, 10 K): 1775 (67, 0.982), 1411 (44, 1.0), 1329 (11, 1.0), 1238, (56, 1.0), 1223 (11, 0.995), 1205 (100, 1.0), 1167 (89, 1.0), 1111 (44, 1.0), 992 (56, 1.0), 827 (22, 0.947), 763 (78, 0.982), 653 (33, 1.0), 592 (78, 1.0) cm^{-1} (rel intensity, ratio of ^{18}O/^{16}O isotopic frequencies ν_i/ν).

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