Laser Flash Photolysis of Disulfonyldiazomethanes: Partitioning between Hetero-Wolff Rearrangement and Intramolecular Carbene Oxidation by a Sulfonyl Group

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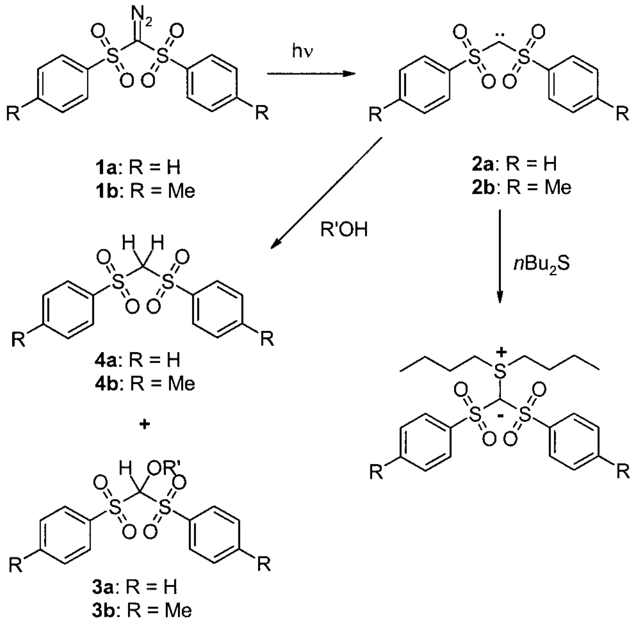
Laser flash photolysis of bis(phenylsulfonyl)diazomethane (**1a**) and ditosyldiazomethane (**1b**) leads to the formation of sulfonylsulfenes **8a/8b** (λ_{max} = 310 nm). Non-first-order kinetics and non-linear Stern–Volmer behavior suggest the formation of another transient species also absorbing at λ = 310 nm. Based on the results of DFT calculations, these species are tentatively identified as dithiocarbonate *S,S,S′*-trioxides **12a/b**, which are formed from the oxathiirene *S*-oxides **9a/b**. The latter compounds bear the characteristics of masked carbenes (τ estimated as 700 ps) and are quenched by methanol and cyclooctene. Singlet disulfonylcarbenes **2a/b** are not predicted to be minima, since all attempts at optimizing the geometry of **2a** led to **9a** instead.

Introduction

Advances in photoresist technology have been essential for the rapid pace of progress in information technology. The need to create ever-more-delicate patterns has led to a situation in which the maximum resolution attainable is limited by the wavelength of the excitation light used. Therefore, the classical photoresist formulations based on novolac and naphthoquinone diazides, which can be used in combination with visible or near-UV (but not deep-UV) light, have reached their physical limits. For the development of photoresists for use with deep-UV light, research has focused on the optimization of compounds designed to yield acids through photochemistry. Among others, 1,2-dibromoalkanes,[1] trichloromethyltriazines,[2,3] onium salts,[4] and 2,6-dinitrobenzylsulfonate[5] derivatives have been suggested or used for that purpose. α,α′-Disulfonyldiazomethanes **1** represent another promising class of photoacid generators.[7] The photochemistry of **1** has been investigated in a number of studies.[6−11] Diekmann examined the photochemistry of bis(phenylsulfonyl)diazomethane (**1a**) using a variety of solvents and trapping reagents.[6] In ethanol, photolysis of **1a** yields the corresponding ether **3a** (R′ = Et, 66%) and the bis(phenylsulfonyl)methane (**4a**, 34%), formed by hydrogen abstraction. The product ratio varies depending upon the alcohol used; formation of ether **3a** predominates with methanol and *tert*-butyl alcohol, while photolysis of **1a** in 2-propanol yields mostly **4a**. Photolysis of **1a** in diethyl ether gives exclusively **3a** (R′ = Et) and no **4a**; this reaction presumably runs via an oxonium ylide as an intermediate.[6] Ylides derived from carbene **2a** have been isolated upon photolysis of **1a** in di-*n*-butyl sulfide or DMSO (Scheme 1).



Scheme 1

Pawlowski et al. conducted the photolysis of **1c** in an acetonitrile/water mixture.[7] Under these conditions, sulfone **4c** was formed only as a side product, while the main

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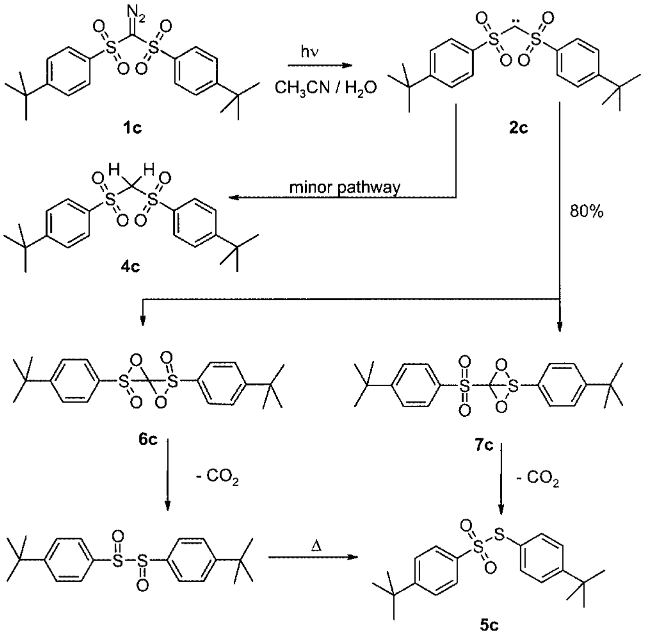
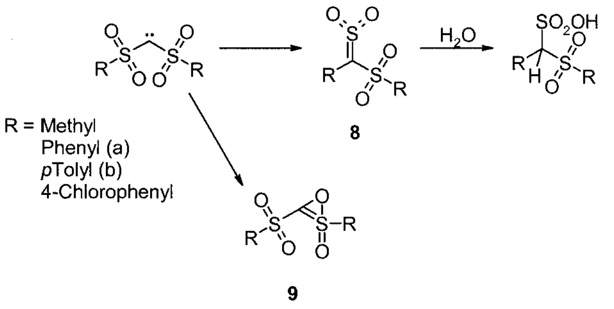
product was the sulfonic acid thioester **5c**, which was formed in 80% yield. Thermolysis of compounds of this type during "baking" of the polymer matrix then yielded sulfonic and sulfinic acids.[7,8] With regard to the mechanism for the formation of thioester **5c**, Pawlowski et al.[7a] suggested a rearrangement of carbenes **2c** via a strained oxathiiran *S*-oxide **6c** or a bicyclic oxathiirane **7c** (Scheme 2). Similar suggestions had been made before by Varvoglis and co-workers.[7b]



Scheme 2

Another reactive intermediate that has been suggested to play a role in the photochemistry of **1** is sulfene **8**, which could form from **2** by a hetero-Wolff rearrangement.[7a] Reaction of **8** with water would then yield sulfonic acids.[7a] This hetero-Wolff rearrangement was confirmed recently by means of matrix-isolation spectroscopy.[10] In addition, evidence for the formation of oxathiirene *S*-oxides **9** was also obtained (Scheme 3).



Scheme 3

Further evidence for the formation of sulfene **8a** was recently presented by Scaiano and co-workers,[11] who were able to characterize **8a** by using the pyridine-ylide probe technique. The product from the reaction of sulfene **8a** with pyridine exhibited a λ_{max} = 440 nm and was formed with a rate constant of $k_q = 3.9 \cdot 10^6\ \mathrm{M}^{-1}\mathrm{s}^{-1}$. Sulfene **8a** was found to react rapidly with anionic nucleophiles [k_q (N_3^-) = $2.4 \cdot 10^7\ \mathrm{M}^{-1}\mathrm{s}^{-1}$], while the rate of quenching with water or methanol was not measurable.

Despite the recent advances,[10,11] the overall scenario still is a rather complex one, and the mechanistic suggestions presented so far are not conclusive and are partially contradictive. To shed light on the reactions occurring after photolysis of **1**, we undertook the present study using the tools of laser flash photolysis (LFP) and density functional theory. Specifically, we investigated the photochemistry of bis(phenylsulfonyl)diazomethane (**1a**) and bis[(4-methylphenyl)sulfonyl]diazomethane (**1b**).

Results and Discussion

We performed LFP studies on diazo compounds **1a** and **1b**, using the highly inert solvent 1,1,2-trichlorotrifluoroethane (freon-113). The precursors were excited with the fourth harmonic (λ = 266 nm) of an Nd-YAG laser.

LFP of a solution of **1a** in freon-113, which had been purged with argon, gives a transient spectrum with an intense absorption (λ_{max} = 310 nm) and a broad, weak band extending to ca. 500 nm (Figure 1). The transient decay is non-first-order (inset Figure 1), with an approximate half-life of $t_{1/2}$ = 10 μs.[13a] Purging the solution with oxygen had no influence on the transient behavior.

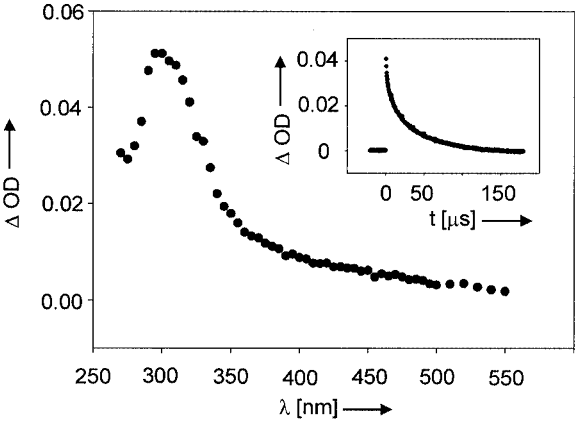


Figure 1. Transient spectrum, monitored 2 μs after LFP (λ_{exc} = 266 nm) of **1a** in argon-purged freon-113. Inset: Transient trace, λ_{mon} = 310 nm

LFP of a solution of **1b** in freon-113 under otherwise identical conditions led to very similar observations. Again, a transient species was observed showing non-first-order kinetics with λ_{max} = 310 nm and a weak band tailing out to ca. 500 nm. A plot of transient intensity vs. laser power is linear, with an intercept very close to zero (see Figure S1, Supporting Information; see also footnote on the first page of this article). Thus, the transient data clearly reveal that the mode of decay for excited compounds **1a** and **1b** must be similar and that the transient observed is formed in a monophotonic process.

Upon addition of typical carbene quenchers, such as methanol or cyclooctene, to the stock solution containing **1b**, no direct quenching of the transient was observed. Instead, Stern−Volmer quenching occurred, indicating the trapping of a precursor transient. Figure 2 shows a plot of the inverse transient intensity at 310 nm vs. methanol concentration. It shows clearly that the slope of the Stern−Volmer plot levels off at high MeOH concentration. The corresponding plot for cyclooctene is available in the Supporting Information as Figure S2.

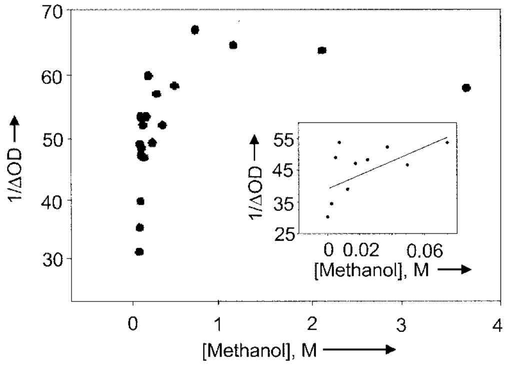
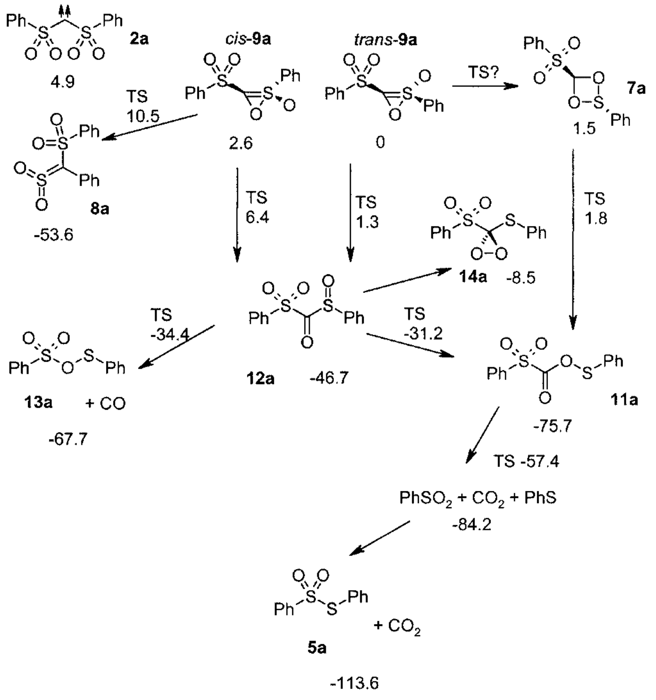


Figure 2. Plot of the inverse optical density at λ = 310 nm, monitored after LFP (λ_{exc} = 266 nm) of **1b** in freon-113, vs. the concentration of methanol. Inset: "Linear" regime at low MeOH concentration

Reaching a plateau in Stern−Volmer plots usually indicates a branching in the photochemistry of a substrate prior to the formation of the transient monitored.[12] Only one of the transients initially formed is quenched by the added trapping agent, which results in a residual absorption. A linear fit of the initial part (low MeOH concentration) of the Stern−Volmer plot obtained for methanol quenching gives $k_q\tau$ = 7.0. Given a diffusion-controlled rate (k_q = $1\cdot10^{10}$ $\mathrm{M^{-1}s^{-1}}$) for the reaction of the precursor transient with methanol, the lifetime of this species thus can be estimated to be of the order $\tau \approx$ 700 ps. Evaluation of the Stern−Volmer plot obtained for cyclooctene quenching gives an identical value for $k_q\tau$ within the rather-large error margins. Here, the slope of the linear fit gives $k_q\tau$ = 8.0. Because of the nonlinearity of the Stern−Volmer plots, $\Delta(k_q\tau)$ is estimated to be of the order ±50%. The precursor transient being quenched appears to be an extremely reactive species that is unlikely to be monitored using an LFP set-up having ns time-resolution.

What is the nature of the transient signals monitored at λ = 310 nm upon LFP of **1a** or **1b**? Given the similarity between the transient spectra presented here and the spectra published by Scaiano and co-workers,[11] it appears very likely that the transient absorption is partially due to sulfenes **8a**,**b**. The observation of curved Stern−Volmer plots indicates the presence of at least one more transient species absorbing at λ = 310 nm. This feature again is in agreement with Scaiano's results, where the observation of a second, as-yet-unidentified, species with τ = 50 μs was reported.[11,13b]

At this point, it is helpful to consider the product distribution reported for the photolysis of diazo compounds **1**.[6−11] If diazo compounds **1** are photolyzed in solvents generally considered "inert", such as freon-113 or acetonitrile, moderate-to-good yields of thioesters **5** are formed.[7,10] Assignment of any transient must account for the formation of **5**. To identify the very-short-lived precursor transient, and the long-lived "second" transient observed by us as well as by Scaiano and co-workers,[11] we calculated the potential-energy surface for decay of singlet carbene **^{1}2a** (R = Ph), using standard density functional theory [DFT, (U)B3LYP/6-31G(d)].[14] Scheme 4 shows the results.



Scheme 4. Energies (in kcal/mol) of stationary points relevant to the decay of *trans*-**9a**, relative to the energy of *trans*-**9a**, as calculated by (U)B3LYP/6-31G(d)

Attempts to optimize the geometry of the singlet disulfonylcarbene **^{1}2a** using restricted DFT [B3LYP/6-31G(d)] led to the geometry of the oxathiirene *S*-oxide **9a**. This result was also obtained when we attempted to optimize **^{1}2a** as an open-shell singlet.[15] Therefore, our calculations focused on elucidating the possible fate of these exotic species. We were not able to find transition states (TS) for the conversion of *cis*/*trans*-**9a** to dioxathietane **7a**. The TS for the shift of the oxygen atom to the carbene carbon atom, however, could be localized and the barriers were found to be small (1.3 or 3.8 kcal/mol). The product of this reaction is the dithiocarbonate *S*,*S*,*S*′-trioxide **12a**, which itself is expected to undergo follow-up reactions. Among those reactions, the TS for the rearrangement leading to ester **11a** could be localized (E_a = 15.5 kcal/mol). Sulfoxide **12a** may also decay by intramolecular attack of the nucleophilic sulfoxide oxygen atom at the sulfonyl moiety, leading to sulfonic acid sulfenyl ester **13a** plus carbon monoxide (E_a = 12.3 kcal/mol). No transition state could be localized for a reaction leading directly from **12a** to the final product **5a** plus carbon dioxide. If this reaction were to proceed intramolecularly in a stepwise fashion, dioxirane **14a** would be one possible closed-shell intermediate. Not unexpectedly, the formation of **14a** from **12a** is calculated to be strongly endothermic by 38.2 kcal/mol.[16] Thus, **5a** is likely to be formed from ester **11a**. We searched for a reaction pathway connecting **11a** to **5a** plus carbon dioxide. While no TS directly linking **11a** to **5a**/CO_2 could be located, we found a TS for the cleavage of **11a** into the benzenesulfonyl radical $PhSO_2^{\cdot}$, the thiophenoxyl radical $PhS^{\cdot}$, and CO_2.[17] The barrier for this exothermic reaction is calculated to be 18.3 kcal/mol. Sulfonic thioester **5a** would eventually result from collapse of the radical pair thus formed. Figure 3 shows the geometries of oxathiirene-*S*-oxide *trans*-**9a**, the geometry of the TS for rearrangement of *trans*-**9a** to **12a**, the geometry of **12a**, the TS linking **12a** to **13a**, and the TS linking **12a** to **11a**, as well as the TS linking **11a** to $PhSO_2^{\cdot}$/$PhS^{\cdot}$ plus carbon dioxide. The relevant bond parameters are given in Table 1.

Activation energies are expected to be underestimated by B3LYP calculations.[18] Nevertheless, the calculations should allow for some mechanistic conclusions:

– Excitation of diazo compounds **1** gives rise to oxathiirene *S*-oxides **9**. Singlet carbenes **2** are not minima.

– The hetero-Wolff rearrangement leading to sulfenes **8** is predicted to have a significant activation energy (e.g., **8a**: 10.5 kcal/mol, relative to *trans*-**9a**). This feature suggests that sulfenes **8** are not formed by the "carbene" route, but by rearrangement of the excited state of the diazo compound. There is ample precedence for this kind of behavior in diazirine and diazo photochemistry.[19]

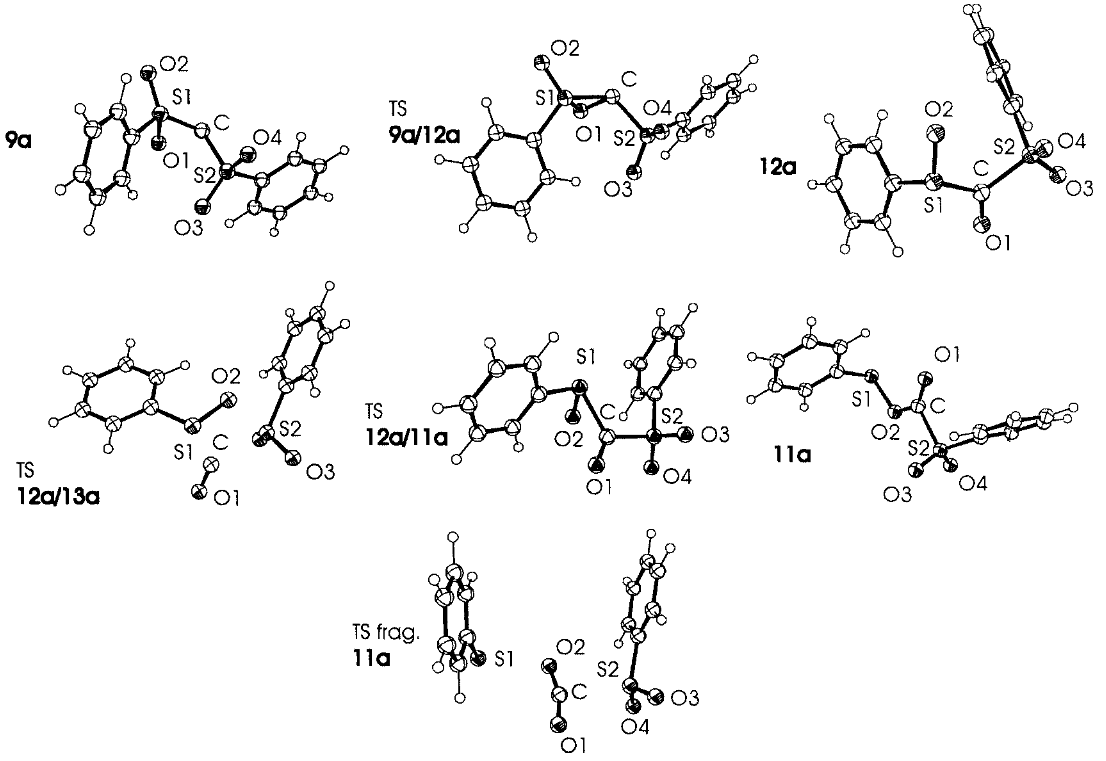


Figure 3. Calculated geometries [B3LYP/6-31G(d)] of **9a**, the transition state linking **9a** to **12a**, **12a**, the TS linking **12a** to **13a**, the TS linking **12a** to **11a**, **11a**, and the TS for fragmentation of **11a** into $PhSO_2$, PhS, and CO_2

Table 1. Structural parameters for the rearrangement of *trans*-**9a** to **12a**, the rearrangements of **12a** to **13a** and **11a**, and the fragmentation of **11a** into $PhSO_2$, PhS, and CO_2, as calculated by B3LYP/6-31G(d). Bond lengths in pm, bond angles in °

Stationary point	R_{S1-O1}	R_{S1-O2}	R_{S1-C}	R_{O1-C}	R_{C-S2}	R_{S2-O3}	$A_{S1-O1-C}$
trans-**9a**	159	146	173	164	183	147	64.6
TS *trans*-**9a**/**12a**	171	147	187	143	189	148	72.5
12a	274	151	193	118	193	146	39.7
TS **12a**/**13a**	314	152	223	115	230	147	30.2
TS **12a**/**11a**	277	162	192	118	189	146	75.0
11a	301	177	266	119	190	147	62.0
TS **11a** fragment	372	247	320	117	250	148	50.6

− Oxathiirene *S*-oxides **9** can be regarded as masked carbenes or intramolecular sulfonyl ylides. They decay either by typical carbene reactions (C−H insertion or hydrogen abstraction, either directly or via an equilibrium with triplet carbenes ^{3}**2**), or they undergo a rearrangement to dithiocarbonate *S,S,S*′-trioxides **12**.

− The low barriers predicted for the rearrangement of **9** correspond to a lifetime of these species in the sub-nanosecond range. For example, a barrier of 5 kcal/mol for the decay of **9a/b** in combination with log$A$ = 13 results in an estimated decay rate constant of $k = 2.4 \cdot 10^{9}$ s^{-1} ($\tau \approx 420$ ps), which compares well with the $\tau \approx 700$ ps estimated from the Stern−Volmer studies. Hence, oxathiirene *S*-oxides *cis*/*trans*-**9a/b** are assigned to the invisible precursor transients quenched by methanol or cyclooctene.

− The long-lived transients, which are observed in addition to sulfenes **8a/b**, are tentatively assigned to dithiocarbonate *S,S,S*′-trioxides **12a/b**.[20] For **12a**, a time-dependent DFT calculation[21] [TD-B3LYP/6-31G(d)] predicts absorption maxima $\lambda_{\max}$ = 410.8 nm (f = 0.0032), 301.6 nm (f = 0.0009), and 289.8 nm (f = 0.1513) that are in qualitative agreement with the experimental observations (Figure 1). Both *S*-acyl bond lengths in **12a** are calculated to be long ($r_{(\mathrm{PhSO2-CO})}$ = 193 pm, $r_{(\mathrm{PhSO-CO})}$ = 194 pm), which indicates that **12a** will be a rather labile molecule (Figure 3). Calculated barriers of the order of 12−15 kcal/mol for intramolecular decay modes of **12a** require high Arrhenius pre-exponential factors of $\log(A/\mathrm{s}^{-1}) \geq 13$ to be consistent with decay lifetimes of the order of $t_{1/2} \approx 10$ μs (our results) or 50 μs (Scaiano's results).[11] This condition may be fulfilled at least for the reaction yielding **13a** (favorable activation entropy because of liberation of carbon monoxide). Additionally, we cannot rule out intermolecular self-quenching of **12a/b**.

− The mechanistic scenario outlined here is consistent with the observation of curved Stern−Volmer plots, as the formation of sulfenes **8a/b** on the excited diazo surface amounts to a branching of the photochemical reaction sequence prior to the formation of the SV-quenchable precursor transient **9a/b**.

− The final products **5a/b** can be formed in secondary photoreactions from **13a/b**, or are generated by thermal fragmentation of **11a/b**.

Experimental Section

Laser Flash Photolysis: A standard LFP set-up was used, consisting of a Spectra-Physics Quanta-Ray LAB 130 Nd-YAG laser, operated at 1 Hz and 266 nm (50 mJ/pulse, 8 ns pulse duration), a pulsed Xe arc lamp (Müller, Germany), a SPEX Minimate monochromator coupled to a photoelectron multiplier tube, and a LeCroy 9361 digital oscilloscope. The entire set-up was controlled from a PC by using LabView software. Data evaluation was performed by using SigmaPlot software. A flow cell was used to avoid depletion of the precursor and product build-up. Solutions of **1a** or **1b** were $1.4 \cdot 10^{-6}$ M (**1a**) or $1.1 \cdot 10^{-6}$ M (**1b**) in freon-113. The stock solutions were purged with argon for 30 minutes prior to starting the experiment. Attenuation of the laser dose was achieved by placing suitable filters (cut-off filters by Schott; e.g., WG 280 or UG 5) in the laser beam. Calculations were performed by using the Gaussian 98 suite of programs.[22]

Supporting Information (see also footnote on the first page of this article)**:** Calculated geometries [B3LYP/6-31G(d)] for the stationary points shown in Scheme 4. Figure S1: Plot of the transient intensity, monitored at λ = 310 nm, upon LFP (266 nm) of **1b** in freon-113 (1 atm. argon, ambient temperature), vs. laser power. Figure S2: Plot of the inverse optical density at λ = 310 nm, monitored after LFP (λ_{exc} = 266 nm) of **1b** in freon-113, vs. the concentration of cyclooctene.

Acknowledgments

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[13] [13a] There was no pronounced effect of the laser intensity on the measured decay kinetics. The non-first-order kinetics probably result from a multi-exponential decay resulting from different transient species absorbing at λ = 310 nm. [13b] The transient lifetimes measured by us are somewhat shorter than those reported by Scaiano and co-workers. This result is likely to be related to the different solvents used (this study: freon-113; Scaiano's work: acetonitrile).

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