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CARBONYL SULFIDES AS POSSIBLE INTERMEDIATES IN THE PHOTOLYSIS OF OXATHIIRANES[1]

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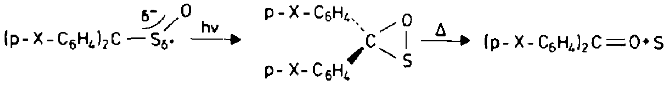
Abstract—Diphenyl oxathiirane, formed by irradiation of thiobenzophenone S-oxide at 77 K, is photochemically converted into a blue, thermally unstable compound which decomposes at *ca* 100–110 K (λ_{max} 550 nm, (ϵ *ca* 11,000). Lack of change in magnetic susceptibility during the light induced conversion of sulfine to ketone via the oxathiirane and the subsequent blue intermediate implies the absence of triplet and biradical singlet transients. The unknown carbonyl sulfide functionality, $R_2C{=}O{=}S$, thereby emerges as a strong candidate for producing the visible absorption.

Comparison of the wave functions for $CH_2{=}S{=}O$ and $CH_2{=}O{=}S$ arising from MNDO limited CI geometry optimizations leads to the conclusion that the carbonyl sulfide structure is best described as a zwitterion rather than as a singlet biradical. The failure to observe cycloaddition products between the blue species and several dipolarophiles is rationlized in terms of a labile carbonyl sulfide intermediate capable of facile sulfur extrusion from a long, weak O–S bond. Finally, the electronic absorption spectra of a series of *para*-substituted benzaldehyde O-sulfide model system have been calculated with CNDO/S–CI and correlated with the λ_{max}'s of the corresponding series of diaryl blue substrates.

The sum of the available experimental and theoretical data is consistent with the existence of closed shell carbonyl sulfides as observable, though labile, intermediates from the photolysis of oxathinanes.

Recently, evidence was presented for the intermediacy of diphenyl oxathiirane (2, X = H) in the photolytic transformation of thiobenzophenone S-oxide (diphenyl sulfine) (1, X = H) into benzophenone (3, X = H). Diphenyl oxathiirane (2, X = H) was characterized at 85 K by its electronic absorption spectrum (λ_{max} 390 nm, ϵ *ca* 200 l/mol cm) and by its thermal and photochemical properties.[1a]

It was further observed that continuous irradiation into the long wavelength absorption at 390 nm caused formation of a thermally unstable blue compound (λ_{max} 550 nm, ϵ *ca* 11000 l/mol cm), which decomposes on heating to *ca* 100–110 K. *A priori* several structures are possible for this substance. Allotropes of sulfur and compounds formed by fragmentation of the oxathiirane ring, SO and diphenyl carbene, could be excluded. Furthermore, the color phenomenon is confined to a monomeric species as indicated by the product distribution of its transformations. Therefore only two formal structures 4 and 5, formed by S–O and C–S bond cleavage, respectively, apparently remain to be discussed. Conceivable candidates for the blue intermediate, 4 and 5, are singlet, triplet or zwitterionic states. However, no ESR signals were detected from the blue intermediate at the X-band frequency in the magnetic field range from 20 to 7200 Gauss.[1a] Tentatively, this is not in favour of a triplet state biradical. Large spin–spin interactions may, however, give rise to a large zero-field splitting (D > 1 cm^{-1}) shifting the triplet transition out of the available magnetic field. Furthermore, relaxation effects can cause the signals to broaden and thus escape detection.



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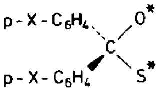

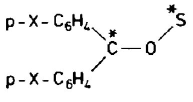

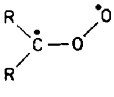

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a: * = +/−; b: * = •/•

Magnetic susceptibility measurements

In order to monitor the possible formation of a ground state triplet biradical, the photochemical conversion of sulfine 1 was followed by magnetic susceptibility measurements. The compound (10^{-2} M) in EPA glass at 77 K was converted into the oxathiirane 2 by photolysis (λ_{ex} 330 nm) for 2 hr. The blue intermediate (10%) was formed together with benzophenone (75%) and thiobenzoic acid S-phenyl (14%) and O-phenyl (1%) ester on irradiation (λ_{ex} 390 nm) into the absorption max of 2 for 1 hr as previously described.[1a] Finally, irradiation (λ_{ex} 550 nm) into the absorption max of the blue intermediate for approximately 2 min eradicated to the color completely. No changes in the magnetic susceptibility were observed during these processes. On this basis it is possible to conclude (Experimental) that less than 0.4% of a ground state triplet derived from sulfine 1 has accumulated during these transformations. It is highly unlikely that any changes in diamagnetism could be so large as to cancel the triplet paramagnetism exactly. The constant diamagnetism observed is in agreement with Pascal's rule[2] assuming the constitutive correction to be small.

An additional open shell possibility represented by structures **4** and **5** is the formation of a ground state biradical singlet possessing a low-lying triplet excited state. The energy of the former would then be described in terms of the usual Heisenberg–Dirac–Van Vleck hamiltonian $\mathcal{H} = J \cdot S_1 \cdot S_2$, where J corresponds to the singlet-triplet energy gap.[3] Assuming 100% conversion to an intermediate with these properties, it can be concluded that under the present experimental conditions J must exceed 400 cm^{-1} (1.1 kcal/mol). The singlet-triplet splitting of the vast majority of open-shell biradicals is much smaller than this lower limit,[4] thereby reducing the likelihood of the intervention of a biradical singlet.

Structures **4b** or **5b** might conceivably be involved in a facile ring closure equilibrium reaction were they to represent the blue intermediate. Scrutiny of the electronic absorption spectrum during thermal transformation of the latter around 110 K, a temperature at which the oxathiirane 2 is thermally stable,[1a] does not, however, indicate a reversal to 2 as the absorption band at 390 nm, characteristic for oxathiirane, was not observed to be reformed.

Biradical vs zwitterionic character

A well studied first row member of the $R_2C{=}X{=}Y$ series is the methylene peroxide **6**, the reactive intermediate in the ozonolysis of alkenes. Recent generalized valence bond (GVB) and configuration interaction (CI) calculations have been interpreted to mean that methylene peroxide is best described as a singlet biradical rather than as a zwitterion.[5] A similar treatment of ozone,[6] the isoelectronic all-oxygen counterpart of methylene peroxide, has likewise shown that the ground state is basically a singlet biradical rather than a zwitterion. In this connection, it should be noted that the calculations mimic the isolated molecule in the gas phase in agreement with experiments in this medium suggesting radical character for **6**.[7]

Substitution of sulfur for the terminal or the central O atom in **6** leads to a carbonyl sulfide (**5**) or to a thioketone S-oxide (**7/8**) respectively. Theoretical evaluation of biradical content for the S-containing substrates relative to peroxide **6** requires a configuration interaction treatment at a comparable level. To a first approximation, however, the effects of CI can be appreciated qualitatively by focusing on the frontier orbitals and by delimiting the two conditions which most effectively mix the $LUMO^2$ configuration into the $HOMO^2$ configuration. We recall that a "true" biradical would arise were the ground states of the systems under consideration to be described be a 50:50 blend of the latter configurations.[8] At the other extreme a closed shell ground state involves an admixture of a minimum of $LUMO^2$; the region between can be classified as biradicaloid. Configurational mixing is favored first by a reduced HOMO–LUMO energy gap, and secondly when these two MO's are most evenly distributed over the same regions of space. The latter is quantified by the CI exchange integral (K_{ij}) coupling the $HOMO^2$ and $LUMO^2$ configurations.

In order to gain some insight pertaining to the S species, MNDO [9] geometry optimizations employing 2 × 2 HOMO/LUMO CI were carried out for the parent structures, $CH_2{=}S{=}O$ and $CH_2{=}O{=}S$ (Experimental). The frontier orbital gaps are nearly identical, 7.9 and 7.7 eV respectively. The shapes of the corresponding MO's are shown in Fig. 1. It should be noted that the MO's in question are isomorphic with the non-bonding and antibonding π_2 (HOMO) and π_3 (LUMO) orbitals for the isoelectronic, but molecular symmetric, allyl anion. As expected for a strongly perturbed analog of $(CH_2{-}CH{-}CH_2)^-$, the nodal surface in π_2 moves in the direction of the terminal electronegative atom in the S-oxide structure.[10] The result is a considerable contribution from the central sulfur to π_2 ($C_s = 0.32$, Fig. 1). It should be clear from Fig. 1 that HOMO and the LUMO interpenetrate quite strongly and thereby favor configurational mixing. The MNDO CI exchange integral is calculated to be 2.0 eV. By comparison, the π orbitals for the relatively symmetrical carbonyl sulfide would appear to interpenetrate considerably less. Indeed the corresponding MNDO exchange integral is found to be diminished by 45% to 1.1 eV.

Within the MNDO framework, then, the similar frontier orbital gap but quite different CI exchange integrals for the thioketone S-oxide and carbonyl sulfide isomers suggests the latter to possess less of a disposition for biradical character than the former. Sulfines (**7/8**) are shelf-stable, crystalline substances, show no tendency to

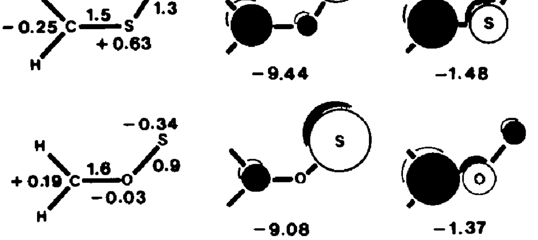


Fig. 1. MNDO quantities for thioformaldehyde S-oxide and formaldehyde O-sulfide. The frontier orbitals (HOMO and LUMO) correspond to π_2 and π_3 respectively. Orbital shapes are given by the circle diameters which are proportional to the eigenfunction coefficients. The associated eigenvalues (eV) are listed beneath each. To the left are tabulated bond orders and charge densities in accord with the Armstrong–Perkins–Stewart prescription.[27]

dimerize and are transparent to ESR measurements. They have been attributed dipolar character by analogy to SO_2, thionylimides, sulfoxides and related compounds[11] and as a consequence of their cycloaddition reactions[12] and X-ray crystallographic structures.[13] The above analysis, by comparison, implies that the carbonyl sulfide formulation like the isomeric sulfine is probably best represented as a closed shell species stabilized but not dominated by a small contribution from the biradical electron distribution as depicted by **5b**. This result is likewise in accord with the above deductions based on the magnetic susceptibility measurements.

Chemical behaviour of the blue intermediate CONTRA a carbonyl sulfide model

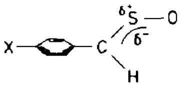
The constitution of **4** and **5** may be compared with that of thiocarbonyl ylides,[14] azomethine ylides[15] and carbonyl ylides,[16] the latter recently being assigned to the coloured intermediates formed on irradiation of certain heterocyclic compounds, e.g. aryloxiranes.[16] In many cases the colour is apparent only in matrices at 77 K. Several such photogenerated carbonyl 1,3 dipoles have been intercepted with common dipolarophiles including 2,3-dimethyl-2-butene,[17] methyl acrylate,[18] and maleic anhydride.[18] In the present case unsuccessful attempts were made to trap compound **4** or **5** with methyl acrylate, 2,3-dimethyl-2-butene and the very potent dipolarophile ethyl trifluoroacetate.[19] These negative results are undoubtedly related to the pronounced thermal liability of the blue intermediate as demonstrated by the disappearance of its colour (*ca* 110 K) even before melting of the EPA glass (*ca* 140 K).

The MNDO calculations permit reflection both on the instability of the proposed carbonyl sulfide and its lack of reactivity. As indicated by the bond orders given in the Figure, the S-oxide possesses a normal S–O bond (1.47 Å) participating in delocalized π-bonding within the allylic heavy atom fragment. The COS moiety, on the other hand, is characterized by a relatively long[11] O–S bond (1.58 Å) with slightly less than full single bond character. Geometry optimization of $CH_2{=}O{=}S$ with the minimum basis set *ab initio* STO–3G sheme[20] provides a similar result: rC–O = 1.320 Å; rO–S = 1.606 Å; < COS = 117.6°. The tendency of the blue substance to exist only as a fugitive intermediate is in accord with cleavage of a weak carbonyl sulfide O–S bond[21] and establishment of a full carbonyl double bond, presumably accompanied by the concatenation of sulfur. The failure to trap the blue species via cycloaddition is likewise consistent with diminished reactivity relative to sulfines as a consequence of reduced charge development in the 1,3-dipole and a considerable imbalance of orbital coefficients at the terminal atoms in the HOMO (see Fig. 1).[22] If the blue intermediate is indeed carbonyl sulfide, even utilizing dipolarophile as solvent at 77°K (Experimental) is insufficient to make cycloaddition competitive with unimolecular fragmentation.

UV spectra

As a supplement to the above mentioned investigations, we examined trends of the electronic absorption spectra of a series of para-substituted benzaldehyde O-sulfides by a CNDO/S–CI procedure.[23] Once again the question to be addressed concerns the identity of the species responsible for the 550 absorption when oxathiiranes **2** are irradiated in the cold matrix. For reasons outlined above, a viable candidate is the charge separated carbonyl sulfide **5a**. Since our evaluation of the electronic absorption spectra will rely heavily on the use of CNDO/S–CI, it is necessary to ascertain the ability of the computational method to properly describe similar compounds. The starting sulfines **1** would seem to be reasonable working model substances in this regard. In the sequel, we compare the UV-VIS spectra of the S–O isomers **7/8** and **9/10**; as a function of conformation.

Two rotamers for the mono-phenyl derivatives have been considered, the orthogonal and the planar isomers **7** and **8**, respectively. The local geometry around the C(H) SO moiety was taken from recent X-ray measurements: rSO = 1.47Å, rCS = 1.62Å, <CSO = 115°.[13a]



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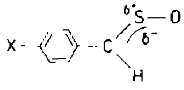

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The first absorption band observed for the diarylsulfines is intense (ϵ 10–15,000 l/mol cm) and found between 347 and 329 nm. In Table 1 the experimental and theoretical λ_{max}'s are compared. These absorptions are assigned as $\pi \rightarrow \pi^*$ transitions as a consequence of the ϵ values and the calculated MO compositions. Qualitatively, the same trends are shown by the calculated λ_{max}'s of **7** and **8** as for the experimentally obtained values.

Although the $\pi \rightarrow \pi^*$ shifts as a function of X are accurately mimicked by CNDO/S–CI, the experimental values fall almost halfway between those computed for the rotamers **7** and **8**. A recent X-ray study[13a] reports the twisting of the phenyl rings in thiobenzophenone *S*-oxide to be 48° and 27° for the *trans* and *cis* rings (relative to oxygen), respectively. Given the excellent qualitative λ_{max} correlation of the derivatives in Table 1 with the sulfines, we suggest that the average of the calculated values for **7** and **8** reflects an intermediary twist angle and therefore best describes the experimental situation. The maximum disagreement between the experimental and theoretical sulfine spectra then amounts to only 6 nm (Table 1). It should be noted that our final comparison involves a mono-phenyl model and a bi-phenyl substrate. Experimental justification for the analogy lies to some extent in the observation that addition of a second phenyl ring in the corresponding ketone and thioketone series causes only diminutive λ_{max} shifts (see Table 2).

Higher energy absorption for sulfines **1** is intense (ϵ 9000–15,000). Band maxima are centered between 240 and 270 nm with the exception of **1** (X = OMe) which shows an additional max at 228 nm (ϵ 14,000). For example, for **1** (X=H) two λ_{max}'s at 255 and 242 nm (ϵ 10,500 and 9100 respectively) capping a broad absorption

Table 1. The experimentally observed first absorption band for diaryl sulfines **1** and calculated $\pi \rightarrow \pi^*$ values for the orthogonal (**7**) and planar (**8**) monoaryl conformations

X	1	7	8	average 7/8
OCH_3	347 nm	310 nm	376 nm	343 nm
CH_3	339 nm	306 nm	369 nm	338 nm
H	329 nm	305 nm	364 nm	335 nm
Cl	333 nm	306 nm	365 nm	336 nm

Table 2. Electronic absorption spectra of some compounds of the common structure $R^IR^{II}C = Y$

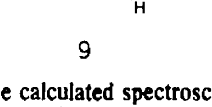
R^I	R^{II}	Y	λ_{max} (nm)	Solvent
Ph	H	O	241, 283, 290	hexane [a]
Ph	Ph	O	252, 333, 342	ethanol[b]
4-MeC_6H_4	4-MeC_6H_4	O	260, 335, 344, 359	cyclohexane[b]
4-ClC_6H_4	4-ClC_6H_4	O	261, 336, 346	cyclohexane[b]
4-$MeOC_6H_4$	4-$MeOC_6H_4$	O	221, 280, 328, 339	cyclohexane[b]
Ph	H	S	228, 320, 575	-[c]
Ph	Ph	S	235, 315, 607	cyclohexane[b,d]
4-MeC_6H_4	4-MeC_6H_4	S	237, 325, 605	cyclohexane[d]
4-ClC_6H_4	4-ClC_6H_4	S	328, 601	methylene chloride[e]
4-$MeOC_6H_4$	4-$MeOC_6H_4$	S	350, 570	ethanol[f]

[a] "Atlas of Spectral Data and Physical Constants for Organic Compounds", CRC-press, Cleveland, 1973, Vol. 2. [b] "DMS UV Atlas of Organic Compounds", Butterworths/Verlag Chemie, Weinheim/London, 1966, Vol. II. [c] H.G. Giles, R.A. Marty, and P. de Mayo, J.C.S. Chem. Comm. 409 (1974). The solvent was not reported. [d] O. Korver, J.U. Veenland, and Th.J. de Boer, Rec. Trav. Chim. 84, 289 (1965). [e] L. Carlsen, unpublished observation. [f] G. Oster, L. Citarcl, and M. Goodman, J. Amer. Chem. Soc. 84, 703 (1962).

base (225–277 nm) are evident. CNDO/S–CI yields a rich series of transitions from 226 to 271 nm corresponding to excitation into and out of the unsubstituted phenyl ring. The situation is analogous for the *para*-substituted derivatives.

In summary, the above results suggest that CNDO/S–CI is capable of qualitatively reproducing the short wavelength transitions as well as trends for the π-π^* absorption of $(p\text{-}X\text{-}C_6H_4)_2\text{–}C{=}A{=}B$ systems when monophenyl models are employed in calculations. Furthermore, by considering rotational isomerism, a close quantitative correspondance with experiment appears to be achievable for the long wavelength species. The quantitative aspect of the computations may be fortuitous or related to the fact that we have employed experimental geometries for the well-characterized sulfine substrates. We now turn to the unknown carbonyl sulfide isomer. In this case the absence of structural information coupled with possible limitations in the original parameterization of CNDO/S for sulfur causes us to expect at best only a qualitative prediction of trends as a function of substituent.

The geometry of the carbonyl sulfide moiety derived from the STO–3G calculations mentioned above was employed unchanged in the CNDO/S–CI electronic absorption spectra evaluation for rotamers **9** and **10**.



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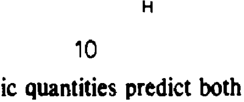

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The calculated spectroscopic quantities predict both **9** and **10** to show two long wavelength bands. The first is a weak $n \rightarrow \pi^*$ type excitation (**9**/**10** average: 625–655 nm) the second a strons $n_{s,\pi} \rightarrow \pi^*$ transition (**9**/**10** average: 455–470 nm) if the 550 nm intermediate is a carbonyl sulfide, the assignment of the first observed band to the second calculated one follows from our estimation of the molar absorption coefficient of the 550 nm peak to be *ca* ϵ 11,000 l/mol cm. The dependence of the 550 nm band on substitution is illustrated in Table 3.

Table 3. The first observed absorption band for the 550 nm intermediate and the calculated values for the carbonyl sulfide rotamers **9** and **10**

X	"550"	9	10
OCH_3	542 nm	488 nm	420 nm
CH_3	549 nm	487 nm	429 nm
H	550 nm	488 nm	438 nm
Cl	567 nm	492 nm	448 nm

In contrast to sulfine behaviour, a small redshift occurs from $X{=}OCH_3$ to H followed by a much larger shift in the same direction for X=Cl.

The λ_{max} trends for both **9** and **10** approximately parallel the observed values. However, in the bisected **9** the bunching of λ_{max} for $X{=}OMe_3$–H and the calculated gap from H to Cl provides a closer match. That conformer **9** best mirrors the experimental spectra is supported by an additional point. The $n_{s,\pi} \rightarrow \pi^*$ line falls at considerably longer wavelength than the same band for planar **10** giving a closer correspondance to the observed λ_{max}'s. This is a consequence of the finding that the relative positioning of $\pi \rightarrow \pi^*$ calculated for planar and bisected pairs **7**/**8** and **9**/**10** is reversed (Tables 1 and 3).

Summary. While the evidence presented here is decidedly circumstantial, it is entirely consistent with the formation of carbonyl sulfides as observable, but very labile intermediates in the photolysis of oxathiiranes 2. The lack of triplet absorption as monitored by both ESR and magnetic susceptibility suggests a closed shell singlet ground state with the capability to the absorp in the visible and to fragment even thermally as low as 100°K. In a previous investigation[10] it was shown that a low energy pathway for thermal conversion of oxathiirane to carbonyl sulfide is abailable in agreement with the thermal instability of the *bis*-hetero 3-membered ring. While the thermal intervention of the O-sulfide has not yet been demonstrated experimentally, the photochemically generated blue species and its subsequent thermal decomposition implicates it in the heat-induced oxathiirane transformation as well. Accordingly, the present MNDO calculations for the carbonyl sulfide model imply it to be no more a biradical singlet than the isomeric closed shell S-oxide, but much more susceptible to sulfur extrusion as a result of a remarkably weak O–S bond. The same calculations predict the carbonyl O-sulfide to show less willingness to participate in cycloaddition reactions relative to the S-oxide, again in concert with observation. Finally, the UV-visible spectra of a series of *p*-phenyl substituted "blue" intermediates were calculated on the basis of a closed shell carbonyl sulfide model. The trends are reproduced qualitatively for the latter and quantitatively for the isomeric S-oxides.We take these results as sufficient to tentatively assign the 550 nm absorption to benzophenone O-sulfide and its *para* substituted congeners.

EXPERIMENTAL

Thiocarbonyl S-oxides. These were prepared from the corresponding thioketones by peracid oxidation.[24] Two of the compounds, 4,4′-dimethylthiobenzophenone S-oxide and 4,4′-dichlorothiobenzophenone S-oxide, have not been reported previously. 4,4′-Dimethylthiobenzophenone S-oxide: Found: C, 74.50; H, 5.97; S, 13.08. Calc. for $C_{15}H_{14}SO$: C, 74.38; H, 5.79; S, 13.22%, m.p. 97–98°. 4,4′-Dichlorothiobenzophenone S-oxide: Found: D, 55.00; H, 3.08; S, 11.19; Cl, 24.83. Calc. for $C_{13}H_8SOCl_2$; C, 55.12; H, 2.83; S, 11.31; Cl, 25.09%. m.p. 87.5–88°. Details of the irradiation procedure as well as product yield determination following the different steps in the photolytical transformations of thiocarbonyl S-oxides have been described previously.[1a]

Magnetic susceptibility measurements. These were measured on a modification of an instrument described previously[25] by application of the Faraday method. The 4 in. magnet operating at 9500 Gauss at the sample position gave a constant value of $B\delta B/\delta x = 9.5 \cdot 10^6$ Gauss$^2 \cdot$ cm$^{-1} \pm 0.1\%$) over a volume of $1 \cdot 1 \cdot 2$ cm^3. The field was controlled via a servo with a Hall probe giving constant values of the field better than $1:10^5$. The sample container was made from the lower 1.5 cm of a 0.5 cm high quality NMR sample tube equipped with a teflon cap and was suspended in a 0.05 mm copper wire from the Cahn electrobalance with a pyrex tube.

The pyrex tube was internally silvered but equipped with a hole in the silver layer to permit irradiation of the sample. The silver coat and suspension wire were grounded together in order to avoid static electricity problems during irradiation. A pressure of 10 torr of helium was maintained in pyrex tube during the irradiations and measurements. The silvered tube was immersed in a pyrex dewar flask with liquid nitrogen. Samples of 200 μl 10^{-2} M solutions (at room temperature) of diphenylsulfine (obtained as previously described[1a]) in EPA (dithyl ether–isopentane–alcohol (5:5:2)) were used. Irradiations were preformed with a Bausch and Lomb SP-200 mercury point source equipped with monochromater (typical bandwidth 20 nm). During a continuous digital recording of the susceptibility with a period of 1 min the samples were irradiated for 2 hr at 330 nm, followed by 1 hr at 390 nm, and finally 30 min at 550 nm. The change in susceptibility observed during these periods corresponds to a change in force of less than 10^{-3} dyn. The total force on the sample including the container was *ca* 1.3 dyn. Assuming a value of $\mu_{eff} = 2.83$ for a triplet ground state of a possible radical formed during the irradiation at 390 nm and again disintegrating rapidly at 550 nm (the colour disappeared within 2 min), this would correspond to a change in force of 0.26 dyn for 100% conversion to triplet states. We therefore conclude that less than 0.4% of the converted diphenylsulfine had accumulated as a compound with a triplet ground state. The photolyzed samples were analyzed by electronic absorption spectroscopy for their content of sulfine; 100% conversion was observed. Blank experiments with the solvent with irradiation and recording of magnetic susceptibilities showed no changes in susceptibility.

Attempt to trap **4** *or* **5** *by cycloaddition reactions.* Solns of **1** (X=H) (5×10^{-3} M) in 2,3-dimethyl-2-butene, methyl methyacrylate, or ethyl trifluoroacetate were photolyzed at 77 K 30 min (λ_{ex} 330 nm) followed by 15 min irradiation into the oxathiirane band ($\lambda_{ex} = 390$ nm). The solns which were now marked purple, corresponding to the formation of **4** and/or **5**, were slowly heated to room temp and analyzed by tlc. Only the well known product composition, i.e. benzophenone and phenyl thiobenzoates) were observed. No cycloaddition products could be detected.

MNDO[9] calculations. Thioformaldehyde S-oxide was geometry optimized by inclusion of 2 × 2 HOMO–LUMO double excitation CI with the assumption of a planar molecule skeleton. In the following tabulation the experimental values[26] are given in parentheses (bond lengths, Å; bond angles, deg): rC–S 1.629 (1.610), rS–O 1.478 (1.469), rC–H 1.081/1.083 (1.085/1.077), ∠ CSO 109.4 (114.7), ∠ HCS (*cis*-O) 124.7 (122.5), ∠ HCS (*trans*-O) 117.4 (115.6). Coefficients for the lowest CI root: 0.952 (HOMO^2), −0.306 (LUMO^2); $K_{ij} = 2.012$ eV. The CI energy lowering is 14 kcal/mol. Formaldehyde O–sulfide was evaluated similarly: rC–O 1.278, rO–S 1.584, rC–H 1.094/1.096, ∠ COS 124.2, ∠ HCO (*cis*-S) 124.0, ∠ HCO (*trans*-S) 117.0. Coefficients for the lowest CI root: 0.992 (HOMO^2), −0.124 (LUMO^2); $K_{ij} = 1.073$ eV; CI energy lowering, 3 kcal/mol.

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