

δ 1.4–2.1 (m, 4 H), 2.1 (s, OH), 2.4–3.1 (m, 3 H), 3.7 (d, $J = 7$ Hz, 2 H), 7.0–7.7 (overlapping singlet and AB pattern, 3 H); IR (AgCl disks) 3200–3600, 1310 (s, CF_3), 1110 and 1155 (s, CF_3), 815 and 855 (m, 1,2,4-trisubstituted-benzene) cm^{-1} ; mass spectrum, exact mass m/e calcd for $\text{C}_{12}\text{H}_{13}\text{F}_3\text{O}$ 230.0918, found 230.0907.

General Procedure for Kinetic Studies. A single stock solution of Lewis acid was prepared (for a series of kinetic studies) by dissolving 0.23 g of SnCl_4 in 150 mL of anhydrous CH_2Cl_2 .³⁴ Generally, 12.5 mL of this solution was added under N_2 to a dry, preweighed reaction vial equipped with a septum, and 12.5 mL of dry CH_2Cl_2 was added to adjust solution concentrations to the desired values. A known quantity of *o*-dichlorobenzene was added as an internal standard.^{35,36} The solution was cooled to -5°C in a constant temperature bath. After determining the amount needed for kinetic runs, the epoxide was added (twenty times the number of moles of SnCl_4),³⁶ and the vial was shaken rapidly and then vibrated gently throughout the reaction. Aliquots of the solution were removed by syringe³⁷ and quenched in aqueous saturated NaCl. A portion of the organic layer was injected into a Hewlett-Packard 5712 GC equipped with a 4 ft \times $1/8$ in. 5% OV 101 column (temperature programming was used) and an integrator/recorder, and the extent of reaction was determined

(34) This solution was kept under N_2 in a desiccator and was removed via a septum by syringe techniques.

(35) Chosen because of its inertness to the reaction conditions and its GC retention time. Generally, the weight ratio of *o*-dichlorobenzene to epoxide was 2:1.

(36) The weights of each substance added was determined by preweighing a filled syringe, adding the compounds, via syringe, and reweighing the emptied syringe. The volumes of compounds added, and their densities, were measured also to provide a check on the weights.

(37) The syringes were kept at -5°C by submerging them in dry CH_2Cl_2 in the kinetics constant temperature bath.

by integrator areas and the area/weight ratios of the alcohol and *o*-dichlorobenzene. The reactions were followed to $>90\%$ completion.²¹ Data reduction and determination of pseudo-first-order rate constants were done by methods described by DeHaan.³⁸

(1*R**,4*R*,4*aR*,8*aR*)-Decahydro-4-phenyl-1-naphthol. In dried apparatus under N_2 , a 0.31-g sample of *trans*-5,6-epoxy-*cis*-cyclododecene¹⁷ (2 mmol) in 10 mL of dry CH_2Cl_2 was added over 15 min to a solution of dry benzene (23 g), 0.003 g of SnCl_4 (.01 mmol), and 20 mL of CH_2Cl_2 held at 0°C . After 1 h, the solution was stirred at room temperature for 1 h and quenched with 5% NaHCO_3 and worked up as usual.¹ After solvent evaporation, the crystals formed (0.31 g, 71% pure by GC) were recrystallized from toluene/hexane: mp 119 – 120°C (0.217 g, 70%);³⁴ NMR (CDCl_3) δ 7.2 (s, 5 ArH), 3.9 (td, 1 H), 2.8 (dt, 1 H), 0.8–2.4 (m, 15 H); IR (KBr) 3200–3600 (s, OH), 1040 (s, OH), 735 and 690 (monosubstituted-benzene) cm^{-1} . Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}$: C, 83.43; H, 9.63. Found: C, 83.13; H, 10.00.

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Mechanistic Investigations of the Cycloaddition Reactions of Thioxanthenylidene *S,S*-Dioxide

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Photolysis of 9-diazothioxanthene *S,S*-dioxide (9) in the presence of the substituted styrenes 11–15 gave the corresponding spirocyclopropane adducts 18–22 in high yield (67–86%), in addition to minor amounts of 9,9'-thioxanthenylidene *S,S,S',S'*-tetroxide (10). Laser flash photolysis of 9 produced a transient absorption (λ_{max} 324 nm) which was efficiently quenched by oxygen and was assigned to the carbene 2. This species was quenched by alcohols in a fast reaction attributable to the singlet state of 2, and in acetonitrile an ylide (24) was obtained. Quenching of 2 with the styrenes allowed the determination of the absolute rate constants for these reactions. The reactive spin state of 2 was investigated by studying the stereochemistry of the (1 + 2) cycloaddition of the carbene with *trans*- β -methylstyrene.

Introduction

The reactions of sulfur-containing carbenes (Scheme I) with olefins have been the subject of several previous studies which have suggested that significant interactions occur between the carbene center and the sulfur atom.^{1–7} Of special interest are the results of Dürr⁵ and Patrick⁷ concerning thioxanthenylidene (1) and thioxanthenylidene *S,S*-dioxide (2).

Dürr found that photolysis of 9-diazothioxanthene (3), the precursor of 1, in the presence of tri- and tetra-

methylethylene gives no addition or insertion products.⁶



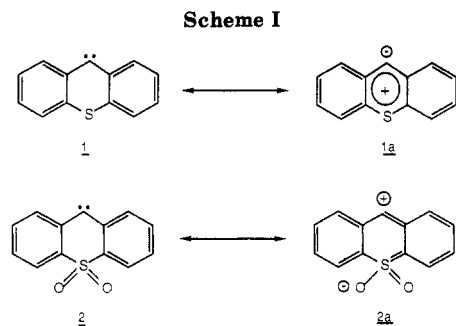
Dithioxanthene (4) and thioxanthone (5) were the main

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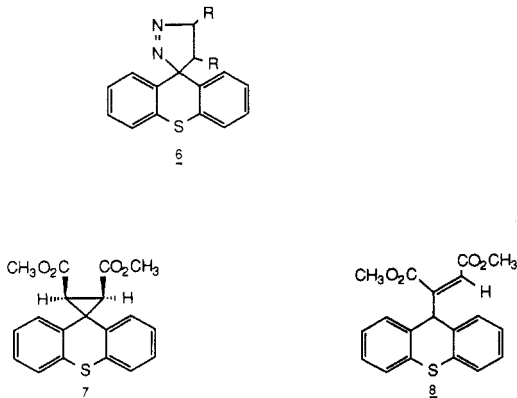
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products. With neat dimethyl maleate, the spiroheterocycle (6) was obtained as a result of a 1,3 dipolar addition reaction with 3. In 1978 Patrick et al. confirmed the results of Dürr and showed that the reaction of 3 with neat dimethyl fumarate produced as an adduct *trans*-1,2-dicarbomethoxyspiro[cyclopropane-3,9'-thioxanthene] (7), whereas with dimethyl maleate in tetrahydrofuran, dimethyl thioxanthylmaleate (8) was isolated.⁷ The same authors reported that attempts to generate thioxanthenyliene *S,S*-dioxide (2) from 9-diazothioxanthene *S,S*-dioxide (9) afforded only the dimer bi-9,9'-thioxanthenyliene *S,S,S',S'*-tetroxide (10).



In the present work we report on the generation of thioxanthenyliene *S,S*-dioxide (2) via photolysis of 9-diazothioxanthene *S,S*-dioxide (9)⁸ and the addition of 2 to the *para*-substituted styrenes (11–15). In addition we report the results of laser flash photolysis studies on the reactions of 2 with alcohols, acetonitrile, and the styrenes.

Results and Discussion

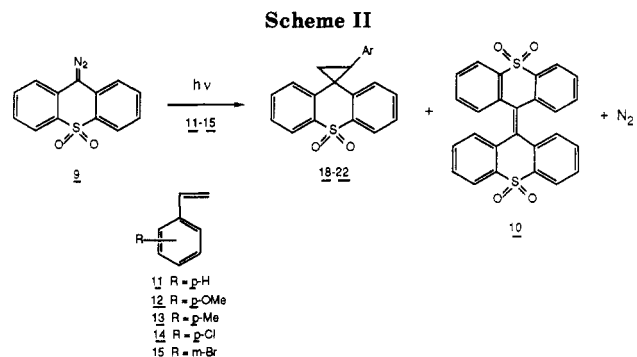
Product Analysis Studies. When photolysis of 9 in the styrenes 11–15 was carried out by using a Hanovia 450-W high pressure mercury lamp, 80% of the theoretical amount of nitrogen was collected during the first 30 min. After workup by chromatography on silica gel, the corresponding spirocyclopropane adducts (18–22) were obtained in high yield (67–86%), in addition to small amounts of bi-9,9'-thioxanthenyliene *S,S,S',S'*-tetroxide (10) in 4–7% yield (Scheme II, Table I).

In a control experiment 9 was allowed to stand in 11 in the absence of light. The solution was monitored by TLC and NMR spectroscopy at 2-h intervals. No reaction was detectable during the first 16 h, and the reaction was complete after only 4 days. The isolated product at the end of this time was found to be 18, in addition to a trace

Table I. Products from Photolysis of 9-Diazothioxanthene *S,S*-Dioxide (9) in the Styrenes 11–16

| styrene | spirocyclopropane | | yield (%) | | method ^c |
|---|-------------------|-----------|-----------------|-----------------|---------------------|
| | compound no. | yield (%) | 10 ^a | 28 ^b | |
| styrene (11) | 18 | 82 | 5.8 | | A |
| <i>p</i> -methoxystyrene (12) | 19 | 86 | 4.5 | | A |
| <i>p</i> -methylstyrene (13) | 20 | 81 | 5.8 | | A |
| <i>p</i> -chlorostyrene (14) | 21 | 80 | 6.9 | | A |
| <i>m</i> -bromostyrene (15) | 22 | 67 | 6.9 | | A |
| (<i>E</i>)- β -methylstyrene (16) | 26 | 70 | 12 | 11.5 | A |
| (<i>E</i>)- β -methylstyrene (16) | 26 | 60 | 20 | 13 | B |

^a Bi-9,9'-dithioxanthenyliene *S,S,S',S'*-tetroxide. ^b 9,9'-Dihydro-bi-9,9'-thioxanthenyliene *S,S,S',S'*-tetroxide. ^c In method A the diazo compound 9 was irradiated directly, in method B 3-methoxyacetophenone was irradiated as a triplet sensitizer.



amount of 10. However, no other products, such as the pyrazole derivative (6), could be detected during the course of the reaction. These results are consistent with the hypothesis that the spiropyrazolines (6) are not intermediates in the formation of the spirocyclopropanes (18–22) in the photolysis experiments. The chemistry of 2 is more like that of phenylchlorocarbene⁹ than that of 1,^{6,7} i.e., 1,2-cycloaddition is the major reaction pathway.

The spirocyclopropane structures of 18–22 were confirmed by detailed and extensive investigations of the reaction products by using elemental analysis, mass spectroscopy, ¹H NMR, ¹³C NMR, and off resonance NMR, the results of which are consistent with the proposed structures. The most revealing spectroscopic information is the ¹³C NMR spectrum of 18 which shows three aliphatic carbon atoms at 12.219 (t, CH₂), 13.172 (s, C), and 38.697 (d, CH) ppm. The structure of 10 was confirmed by using elemental analysis, mass spectrometry, and ¹H NMR in which no aliphatic protons could be observed. The ¹³C NMR and the off-resonance spectra of the cyclopropanes 18–22 will be described in detail elsewhere.

The spin state of 2 was studied at 77 K and at room temperature (vide infra). Irradiation of 9 in paraffin at 77 K in the cavity of an ESR spectrometer resulted in very weak signals at 4628 and 5590 G. This result can be taken as evidence for a ground triplet state of 2, although on its own it is not conclusive. The reasons for the weak signals are probably because of the limited solubility of 9 in the matrix and because of the known reactivity of triplet arylcarbenes even at 77 K.¹⁷

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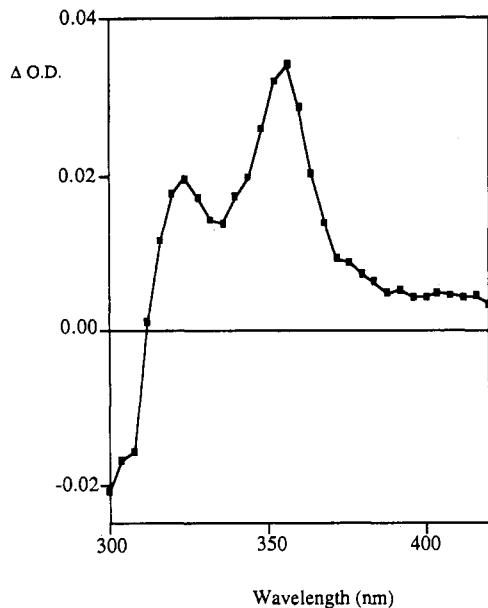


Figure 1. Transient absorption spectrum observed upon pulsed laser photolysis of **9** in argon-purged benzene.

Table II. Absolute and Relative Rate Constants for Quenching of Thioxanthenylidene *S,S*-Dioxide (**2**) by the Styrenes 11–16

| styrene | k_r ($M^{-1} s^{-1}$) ^a | k_r (rel) ^b | k_{stat} (rel) ^c | σ |
|--|--|--------------------------|-------------------------------|----------|
| <i>p</i> -methoxystyrene (12) | | | 2.07 | -0.27 |
| <i>p</i> -methylstyrene (13) | 2.43×10^7 | 1.35 | 1.26 | -0.17 |
| styrene (11) | 1.79×10^7 | 1.00 | 1.00 | 0.00 |
| <i>p</i> -chlorostyrene (14) | 1.68×10^7 | 0.93 | 0.89 | 0.23 |
| <i>m</i> -bromostyrene (15) | | | 0.66 | 0.39 |

^a Absolute rate constants determined from laser flash photolysis experiments. Typical errors derived from 2 standard deviations of the slopes of rate vs. styrene concentration plots were 10%. ^b Relative rates of quenching derived from the absolute rate constants. ^c Relative rates of cyclopropane formation from steady-state experiments.

Laser Flash Photolysis Studies. Laser flash photolysis of **9** in argon-purged benzene solution produced strong transient absorptions in the region 300–380 nm. Two main absorption bands (324 nm and 356 nm) were observed (Figure 1), which were superimposed upon an overall bleaching signal due to loss of **9**. Although the absorption band at the longer wavelength appears to be stronger, the band at 324 nm is actually more intense, since the bleaching of **9** is more pronounced at the shorter wavelengths. The 324-nm band decays with a lifetime of ca.

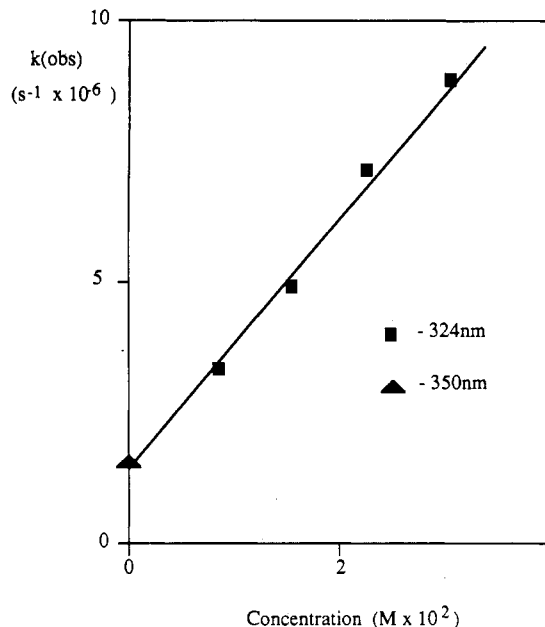
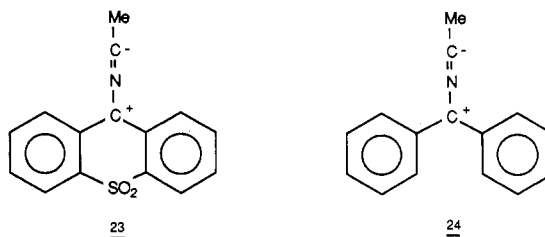


Figure 2. Plot showing the rate of carbene decay observed at 324 nm (squares) vs. *p*-methylstyrene concentration in argon-purged acetonitrile. Also shown is the rate of growth of the ylide observed at 350 nm (triangle) which is observed in argon-purged acetonitrile in the absence of quenchers.

5 μ s, whereas the band at 356 nm has a lifetime of ca. 50 μ s. Both absorption bands appear within the laser pulse, and both are quenched upon the addition of oxygen. In acetonitrile solvent, the short wavelength band is reduced in lifetime, and a new growth in transient absorption is observed at 350 nm. The growth lifetime is 650 ns in neat acetonitrile and depends upon the acetonitrile concentration. The bimolecular rate constant for the formation of the new species is $8 \times 10^4 M^{-1} s^{-1}$. The new band is extremely long-lived (>100 μ s) and is quenched upon addition of the electron-deficient olefins acrylonitrile and diethyl fumarate. The new band is assigned to the ylide **23** since (1) it is derived from a reaction of acetonitrile; (2)



these types of species have been observed previously in flash photolysis studies of other diarylcarbenes;^{13,14} (3) it has an absorption maximum at 350 nm which is very close to that of the known ylide **24** (356 nm);¹⁵ and (4) it is quenched by electron-deficient olefins. The 324-nm band is assigned to the carbene **2** on the basis of the following observations. The absorptions at this wavelength are quenched by the addition of the styrenes, and the time-resolved decays become cleanly first order in the presence of >5 mM styrene. Under these conditions plots of the absorption decay rate as a function of styrene concentration gave the rate constants for quenching (k_r) which are given in Table I (Figure 2). The rate constant for quenching by *p*-methoxystyrene could not be determined because of excessive absorption by this compound at the laser excitation wavelength (308 nm). Although the differences in the relative rate constants for quenching of the transient species by the different styrenes are small, they

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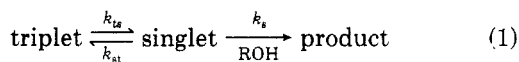
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agree with the relative rates of cyclopropane formation obtained from steady-state experiments (vide infra) ($k_{\text{stat}}(\text{rel})$, Table II). In neat acetonitrile a plot of the decay rate at 324 nm vs. styrene concentration has an intercept which is equal to the growth lifetime of the ylide monitored at 356 nm in the absence of styrene (Figure 2). This is strong evidence that the ylide precursor is the 324-nm band which is therefore the carbene. The observation of strong quenching of this species by oxygen is consistent with an assignment of the 324-nm band to a triplet species. In view of these results, and by analogy with literature results on related systems,^{13,14,16,21} the 324-nm species is assigned to the carbene **2** which is presumed to be a ground triplet state. The band with the absorption maximum at 356 nm which is observed in the absence of acetonitrile remains unassigned at this time.

The carbene **2** is also quenched by methanol and *tert*-butyl alcohol with rate constants of $9.3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $7.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. This behavior is similar to that observed for diphenylcarbene for which corresponding rate constants of $2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and $6.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ have been determined.^{16,21} These high reaction rates might not be expected since in each case it is the ground triplet state which is being quenched, and the reactions of carbenes with alcohols is usually considered to occur from the singlet state.^{16,21} An accepted explanation for these observations is that the ground triplet state reacts indirectly via the thermally accessible singlet state^{16,21} (eq 1). For this mechanism the rate constant for reaction of the triplet (k_t) is given by eq 2 and 3. The reactions of singlet carbenes

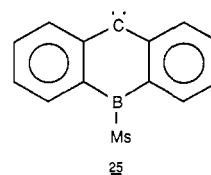


$$k_t = k_s / K_{\text{eq}} \quad (2)$$

$$K_{\text{eq}} = k_{\text{st}} / k_{\text{ts}} \quad (3)$$

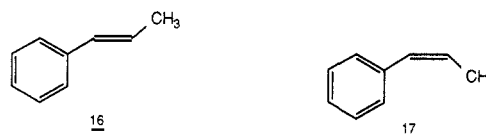
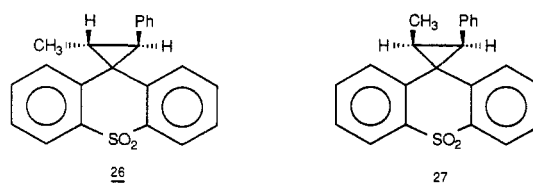
with alcohols occur with rates that are close to the diffusion limit.¹⁶ Since k_s cannot be greater than k_{diff} , then $K_{\text{eq}} \leq k_{\text{diff}} / 9.3 \times 10^6$; therefore $K_{\text{eq}} \leq 2.2 \times 10^3$. Thus, according to this analysis, the energy gap between the lowest triplet and singlet state of **2** is probably similar to diphenylcarbene (3 kcal M^{-1})¹⁶ and larger than that of fluorenylidene (1 kcal M^{-1}).¹³

The reaction of triplet arylcarbenes, which results in the formation of nitrile ylides, is also thought to occur via the lowest singlet states of these species.¹³⁻¹⁵ Diphenylcarbene does not form nitrile ylides in neat acetonitrile, whereas **2** is observed to do so. In this case, although **2** probably has a triplet/singlet energy gap similar to that of diphenylcarbene, the higher electrophilicity of **2** due to resonance structures such as **2a** presumably enhances the ylide-forming ability of this species. Furthermore, the sulfone bridge in **2** makes this carbene more planar than diphenylcarbene, which will allow for conjugation of an ionic center in **23** by both phenyl groups and thus stabilize **23** with respect to **24**. The planar nature of **2** should stabilize the singlet state of this carbene with respect to the triplet state, and thus the triplet/singlet gap for **2** might be expected to be less than that for diphenylcarbene. However, the sulfone linkage will also tend to increase the bond angle at the carbenic center with respect to diphenylcarbene, which will have the opposite effect on the relative stability of the two spin states. In this respect, **2** resembles carbene **25** which also has a ground triplet state.²⁴ Fluorenylidene¹³ and 1-naphthylcarbene¹⁴ form



ylides presumably because of smaller triplet/singlet energy gaps in these systems. Evidently, to observe singlet reactions from a ground-state triplet carbene either a small triplet/singlet free energy gap (i.e., small K_{eq}) and/or a large singlet reaction rate (k_s) is required.

Stereochemistry of the Cycloaddition. Photolysis of **9** in pure (>99.5%) *trans*- β -methylstyrene (**16**) gave in addition to *trans*-1-methyl-2-phenylspiro[cyclopropane-3,9'-thioxanthene] *S,S*-dioxide (**26**), 9,9'-dihydro-bi-9,9'-thioxanthenyliene *S,S,S',S'*-tetroxide (**28**) (11.5%), and **10** (12%). No evidence for the formation of the *cis* adduct **27** could be found. This stereospecificity is usually considered to be evidence that the reactive state in the cyclopropanation is the singlet state of the carbene.^{10,18} Photolysis of **16** under the same conditions did not result



in isomerization of *cis*- β -methylstyrene (**17**), as confirmed by UV and GLC analysis. Irradiation of **9** in **16** at 355 nm using a monochromator, or through a diazepine filter with 3-methoxyacetophenone as a triplet sensitizer, does not change the type of products, although the ratios of the products were altered (Table I). Carbene **2** does not add to simple olefins, therefore, the standard technique of studying the carbene spin multiplicity cannot be applied here.

Selectivity and Mechanism of the Reaction with Styrenes. To investigate the selectivity of **2**, i.e., the electrophilicity or nucleophilicity,¹⁰ competitive experiments were performed in which **9** was photolyzed in equimolar mixtures of unsubstituted styrene (**11**) and each of the other substituted styrenes (**12-15**).¹¹ The product mixture was analyzed in each case using HPLC. A Hammett correlation of the k_{rel} values with σ parameters indicated that **2** has electrophilic character ($\rho = -0.6 \pm 0.2$, Figure 3). Results for phenylhalocarbenes have suggested that the reactions between singlet carbenes and olefins may proceed via reversible formed intermediates.¹⁹ However, this mechanism, if valid in the present case, does not affect the interpretation of these results since in all of the cases investigated so far, the intermediates are sufficiently short-lived that time-resolved and steady-state experiments yield identical relative reaction rates.¹⁹

The addition reaction of **2** with the styrenes can occur either from the ground triplet state or via the singlet state

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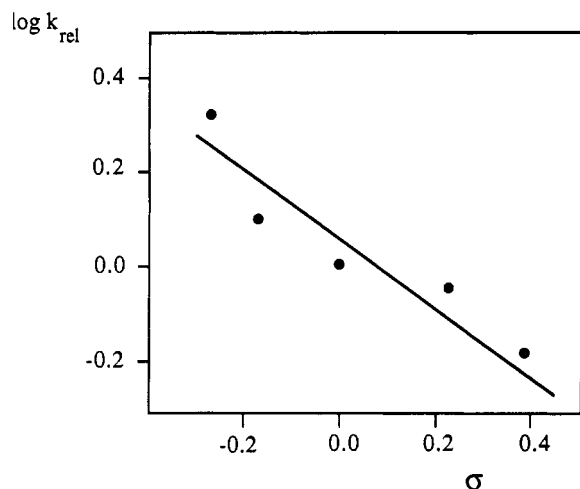


Figure 3. Plot of $\log(k_{\text{rel}})$ from the steady-state reaction of **2** with equimolar mixtures of substituted styrenes and styrene vs. Hammett σ parameters. The slope of the plot is -0.6 ± 0.2 (the error corresponds to 2 standard deviations).

which is thermally accessible at room temperature. The result with the β -methylstyrene suggests a reactive singlet state, and the electrophilic character of the carbene in the addition reactions is also consistent with a singlet state in which resonance contributions such as **2a** play a role.¹⁸⁻²⁴ Although the experimental data do not distinguish between the mechanisms for the cyclopropanation reaction, the latter is supported by both the steady-state results and the observations in the time-resolved experiments of the apparent quenching of the triplet state of **2** by alcohols and acetonitrile. Precedent for reaction from the singlet state of a ground-state triplet diarylcarbene is provided by the reactivity of diphenylcarbene.^{16,21}

Conclusion

In summary, the results of the time-resolved experiments confirm the triplet character of **2** because of the oxygen-quenching behavior and also suggest that a low-lying singlet state is accessible because of the quenching by alcohols and acetonitrile. These results are consistent with steady-state experiments which suggest that the reactive species in the cycloaddition reactions of **2** with styrenes is an electrophilic singlet state. Thus, **2** may be regarded as a diphenylcarbene in which the ortho positions are linked by SO_2 but which also has a contribution from delocalized structures such as **2a**.

Experimental Section

All melting points were uncorrected and were determined on a Buchi type SMP 20 apparatus. IR and UV spectra were recorded on SP 200 (Leitz Unicam) and DU 8 (Beckman) spectrometers. ^1H NMR spectra were recorded on A60 (EM 360, Varian) and WH90 (HX 90, Bruker) instruments with Me_4Si (δ 0.0) as an internal standard. ^{13}C NMR spectra were recorded on the Bruker WH 90 and HX 90 machines. Mass spectra were determined on a Varian MAT 311, and elemental analyses were performed by the Organische Chemie Laboratories, 6600 Saarbrücken.

Analytical TLC was performed on polygram silica gel G-UV 254 (0.25 mm) or polygram alumina N/UV 254 (0.2 mm) (Machery, Nagel & Co.) plates. Photolyses were carried out in all cases with degassed solutions contained in closed Vycor tubes (25 mL) fitted with a side arm and an internal cooling tube. The light source was a Hanovia high pressure mercury lamp (450 W), and the whole system was contained in an aluminum container which served as a light reflector. Reaction mixtures were separated by column chromatography on silica gel, and the chromatographic solvents (methylene chloride, petroleum ether, and methanol) were purified by distillation.

Photolyses were carried out according to the following methods.

Method A. A solution of 1.0 g (0.0039 mol) of 9-diazothioxanthene S,S-dioxide (**9**) in 20 mL of styrenes **11**–**15** was irradiated until the photolysis was complete (1–3 h) and the red color of the solution turned yellow. At the end of the irradiation, the styrene was distilled at diminished pressure (0.01 mm) and the residue was separated by using column chromatography. The separation and identification of the products will be described separately for each styrene.

Method B. As in method A, except a diazepine filter and 3-methoxyacetophenone as a triplet sensitizer were used.

Method C. A solution of **9** (0.1 g) in 4 mL of β -methylstyrene (**E**, 99.5%) was purged with nitrogen and irradiated at 335 nm by using a high intensity monochromator. After 36 h photolysis was complete and only **26**, **28**, and **10** were detected by TLC with authentic samples.

Method D. The competition experiments were carried out by dissolving 0.4 g (0.00136 mol) of **9** in an equimolar mixture of styrene **11** (7.8 g, 0.075 mol) and each of the styrenes **12**–**15** (0.075 mol). After photolysis and workup as described for method A (vide supra), the cyclopropane mixture was analyzed by quantitative HPLC using standard solutions of **18**–**22**.

Control Test. A solution of **9** (0.2 g) in 15 mL of styrene **11** was allowed to stand in the dark and was monitored by TLC and ^1H NMR at 2-h intervals. No evidence for any reaction could be observed during the first 16 h; after 24 h **18** could be detected by TLC. The red color of the solution had disappeared only after 4 days, when the reaction product was found to be a mixture of **18** (0.2 g, 80%) in addition to a trace of **10**.

The products of photolysis of **9** in the styrenes **11**–**15** are summarized in Table II.

Photolysis of 9 in Styrene (11). After photolysis for 25 min, 80% of the theoretical amount of nitrogen had been collected from 1.0 g of **9**, and the products were found to be 1-phenylspiro[cyclopropane-2,9'-thioxanthene] S,S-dioxide (**18**, 1.05 g, 82%), eluted with petroleum ether (60–80 °C):methylene chloride (20:80): mp 171–171.5 °C; MS, m^+ at m/e 332; IR (KBr) 1588 cm^{-1} (aryl), 1302, 1290, and 1160 (SO_2); ^1H NMR δ 2.21–2.46 (m, 3 H, methylene and methyne), 6.46–8.15 (m, 3 H, Ar); ^{13}C NMR δ 12.21 (t, CH_2), 32.17 (s, C), 389.60 (d, CH), 123.81–141.81 (m, Ar). Anal. Calcd for $\text{C}_{21}\text{H}_{16}\text{SO}_2$: C, 75.90; H, 4.8; S, 9.6. Found: C, 76.40; H, 4.9. The dimer **10** (0.05 g, 5.8%) was eluted with methylene chloride: MS, M^+ at m/e 456; ^1H NMR δ 7.64–8.36 (m, Ar).

Photolysis of 9 in p-Methoxystyrene (12). Photolysis of 1.0 g of **9** according to method A gave 1.2 g (86%) of 1-(p-methoxyphenyl)spiro[cyclopropane-2,9'-thioxanthene] S,S-dioxide (**19**), eluted with methylene chloride:n-pentane (1:2): mp 126 °C; MS, M^+ at m/e 362; IR (KBr) 2820 cm^{-1} (OCH_3), 1585 (aryl), 1302, 1285, and 1160 (SO_2); ^1H NMR δ 2.21–2.45 (m, 3 H, methylene and methyne), 2.81 (s, 3 H, CH_3), 6.25–8.13 (m, 12 H, Ar). Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{SO}_2$: C, 72.9; H, 4.97; S, 8.8. Found: C, 72.79; H, 4.96. Also **10** was obtained (0.04 g, 4.5%).

Photolysis of 9 in p-Methylstyrene (13). As before, 1-(p-methylphenyl)spiro[cyclopropane-2,9'-thioxanthene] S,S-dioxide (**20**, 1.1 g, 81%) was isolated from 1.0 g of **9** and eluted with methylene chloride:n-pentane (1:2): mp 190 °C; MS, M^+ at m/e 346; IR (KBr) 2905 cm^{-1} (CH_3), 1580 (aryl), 1300, 1285, and 1160 (SO_2); ^1H NMR δ 2.06 (s, 3 H, CH_3), 2.18–2.39 (m, 3 H, methylene methyne), 6.39–8.09 (m, 12 H, Ar). Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{SO}_2$: C, 76.3; H, 5.20; S, 9.24. Found: C, 76.16; H, 5.34. The dimer **10** was also found (0.05 g, 5.8%).

Photolysis of 9 in p-Chlorostyrene (14). As before, 1-(p-chlorophenyl)spiro[cyclopropane-2,9'-thioxanthene] S,S-dioxide (**21**, 1.15 g, 80%) was obtained from 1.0 g of **9** and eluted with methylene chloride:n-pentane (1:2): mp 157 °C; MS, m^+ at m/e 366.5; IR (KBr) 1585 cm^{-1} (aryl), 1290 and 1160 (SO_2); ^1H NMR δ 2.16–2.42 (m, 3 H, methylene and methyne), 6.42–8.13 (m, 12 H, Ar). Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{SO}_2\text{Cl}$: C, 68.75; H, 4.09; S, 8.73; Cl, 9.66. Found: C, 68.52; H, 4.10. Also **10** was isolated (0.06 g, 6.9%).

Photolysis of 9 in m-Bromostyrene (15). As before, 1-(m-bromophenyl)spiro[cyclopropane-2,9'-thioxanthene] S,S-dioxide (**22**, 1.08 g, 67%) was eluted using methylene chloride:n-pentane (1:2): mp 182 °C; MS, M^+ at m/e 411; IR (KBr) 1580 cm^{-1} (aryl), 1280 and 1144 cm^{-1} (SO_2); ^1H NMR δ 2.19–2.46 (m, 3 H, methylene and methyne), 6.39–8.15 (m, 12 H, Ar). Anal. Calcd for

$C_{21}H_{15}SO_2Br$: C, 61.31; H, 3.64; S, 7.78; Br, 19.48. Found: C, 61.15; H, 3.63. The dimer **10** was also isolated (0.07 g, 6.9%).

Photolysis of 9 in β -Methylstyrene. Three products were separated, (*E*)-1-methyl-2-phenylspiro[cyclopropane-3,9'-thioxanthene] *S,S*-dioxide (**26**, 0.95 g, 70%), which was eluted with petroleum ether (60–80 °C): mp 236 °C; IR (KBr) 2290 cm^{-1} (CH_3), 1575 (aryl), 1290, 1280, and 1157 (SO_2); 1H NMR δ 1.1 (d, 3 H, CH_3), 1.97–2.41 (m, 1 H, α to methyl), 3.26 (d, 1 H, α to phenyl), 6.42–8.16 (m, 13 H, Ar). Anal. Calcd for $C_{22}H_{18}SO_2$: C, 76.30; H, 5.2; S, 9.24. Found: C, 74.98; H, 5.25. 9,9'-Dihydrobi-9,9'-thioxanthenyldiene *S,S,S',S'*-tetroxide (**28**, 0.1 g, 11.5%) was the second fraction eluted with petroleum ether (60–80 °C): churrs above 280 °C, sparingly soluble in methylene chloride, chloroform, ether, and methanol; MS, M^+ at m/e 458; IR (KBr) 1575 cm^{-1} and 1565 (aryl), 1270, and 1145 (SO_2); 1H NMR δ 5.09 (s, 2 H, at C9 and C9'), 6.64–8.21 (m, 16 H, Ar). The last fraction contained **10** (0.11 g, 12%).

Photolysis of 9 in β -Methylstyrene with 3-Methoxyacetophenone. According to method B (vide supra), the product mixture was **26** (0.8 g, 60%), **28** (0.19 g, 13%), and **10** (0.18 g, 20%).

Pulsed Laser Experiments. These experiments were performed by using a Lambda Physik EMG-101 excimer laser (308 nm, ca. 50 mJ, ca. 15 ns) together with a 450-W Xenon arc lamp as the analyzing source. The analyzing lamp was operated in a pulsed mode using a PRA Model 305 pulser. Transient signals were detected by using 6 dynodes of an RCA 4840 photomultiplier tube which was terminated into 50 Ω . The signals were digitized

by using a Tektronix 7912 AD digitizer, and the data were analyzed on a PDP 11/23 minicomputer. Experiments were performed in MCB spectrograde solvents (used as supplied). The quenchers were from the Aldrich Chemical Company and were distilled immediately prior to use. All solutions were purged of dissolved oxygen by bubbling with argon.

ESR Spectroscopy. These experiments were performed with ca. 10^{-6} M **9** dissolved in paraffin which was degassed by purging with argon. The sample was immersed in a liquid nitrogen filled quartz Dewar which was positioned in the cavity of a Bruker ER 100D spectrometer. The sample was irradiated in the cavity by using a 1000-W xenon/mercury lamp at 313 nm.

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Carbenadibenzocycloheptane: Steady-State and Time-Resolved Spectroscopic Laser Studies

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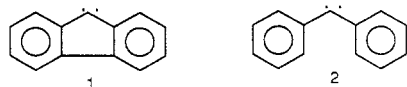
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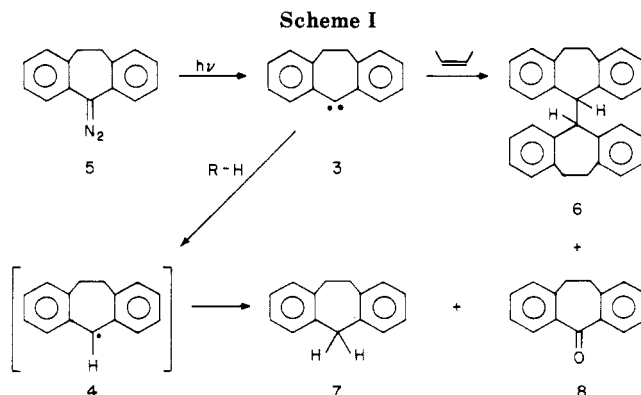
A Hammett study of the reactions of carbenadibenzocycloheptane with *para*-substituted styrenes indicates that this carbene adds to the styrenes as a weak ambiphile. Evidence is obtained that reaction from both singlet and triplet states of this carbene can be observed.

Introduction

Recent reports of the direct observation of several carbenes in homogeneous solution at room temperature using laser flash photolysis have stimulated renewed interest in the properties of these transient species.¹ In particular these studies have revealed the differences in the absolute reactivities of the ground-state triplet species fluorenylidene (**1**)² and diphenylcarbene (**2**)³ and have allowed (together with steady-state measurements) estimates of the free energy differences between the lowest triplet and singlet states of these carbenes.^{2,3}



The related carbene, carbenadibenzocycloheptane (**3**) has been reported to have a ground-state triplet by ESR at 77 K.⁴ Furthermore, the absorption spectrum of **3** has been reported both in a rigid glass at 77 K^{4b} and at room



temperature in liquid paraffin using conventional flash photolysis.^{4c} It was observed that at room temperature

(1) See, for example: "Recent Advances in Carbene Chemistry"; *Tetrahedron Symposium in Print*, 19, Platz, M. S., Ed. 1985.

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