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, 1510 (s, CF₃), 1110 and 1155 (s, CF₃), 815 and 855 (m, 1,2,4-trisubstituted-benzene) cm⁻¹; mass spectrum, exact mass m/e calcd for C₉H₁₃F₃O 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 0.25 g of SnCl₄ in 150 mL of anhydrous CH₂Cl₂. Generally, 12.5 mL of this solution was added under N₂ to a dry, preweighed reaction vial equipped with a septum, and 12.5 mL of dry CH₂Cl₂ was added to adjust solution concentrations to the desired values. A known quantity of o-dichlorobenzene was added as an internal standard. 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 SnCl₄), %, and the vial was shaken rapidly and then vibrated gently throughout the reaction. Aliquots of the solution were removed by syringe and quenched in aqueous NaHCO₃. A portion of the organic layer was injected into a Hewlett-Packard 5712 GC equipped with a 4 ft × 1/8 in. 5% OV 101 column (temperature programming was used) and an integrator/recorder, and the extent of reaction was determined by integrator areas and the area/weight ratios of the alcohol and o-dichlorobenzene. The reactions were followed to >90% completion. Data reduction and determination of pseudo-first-order rate constants were done by methods described by DeHaan. (1R*,4R,4aR,8aR)-Decahydr0-4-phenyl-1-naphthol. In dried apparatus under N₂, a 0.31-g sample of trans-5,6-epoxy-cyclohexene (2) (2 mmol) in 10 mL of dry CH₂Cl₂ was added over 15 min to a solution of dry benzene (23 g), 0.003 g of SnCl₄ (.01 mmol), and 20 mL of CH₂Cl₂ held at 0 °C. After 1 h, the solution was stirred at room temperature for 1 h and quenched with 5% NaHCO₃ and worked up as usual. After solvent evaporation, the crystals formed (0.31 g, 71% pur) were recrystallized from toluene/hexane: mp 119–120 °C (0.217 g, 70%); NMR (CDCl₃) δ 7.2 (s, 5 ArH), 3.9 (t, 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 C₉H₈O: C, 83.43; H, 9.63. Found: C, 83.13; H, 10.00.

**Acknowledgment** is made to the donors of the Petroleum Research Fund (administered by the American Chemical Society), to Research Corporation (C1108), and to the National Science Foundation (CHE8405642) for partial support of this work. John Grutzner (Purdue University) helped interpret some NMR spectra. Frank L. Schadt, III, and Dee Brooks provided stimulating discussions. We particularly thank Franklin DeHaan and Donald Deardorff for their hospitality at Occidental College, where much of the kinetic work was done.

**Mechanistic Investigations of the Cycloaddition Reactions of Thioxanthylene 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 bis-9,9'-thioxanthenyldiene 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 anlyle (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-2,3-dimethylycyclohexane.

**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. Of special interest are the results of Durr and Patrick concerning thioxanthylidene (1) and thioxanthylidene S,S-dioxide (2). Durr found that photolysis of 9-diazothioxanthene (3), the precursor of 1, in the presence of tri- and tetra-

methylcyclohexane gives no addition or insertion products. Dithioxanthene (4) and thioxanthene (5) were the main

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1 Present address: University of Assiut (Egypt).
2 Present address: National Research Center (Egypt).
3 Present address: Eastman Kodak Company, Rochester, NY.
4 Chosen because of its inertness to the reaction conditions and its GC retention time.
5 Present address: University of Assiut (Egypt).
6 Present address: National Research Center (Egypt).
7 Present address: Eastman Kodak Company, Rochester, NY.
8 Partial support of this work. John Grutzner (Purdue University) helped interpret some NMR spectra. Frank L. Schadt, III, and Dee Brooks provided stimulating discussions. We particularly thank Franklin DeHaan and Donald Deardorff for their hospitality at Occidental College, where much of the kinetic work was done.

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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 Dürre and showed that the reaction of 3 with neat dimethyl fumarate produced as an adduct trans-1,2-dicarboxymethoxyspiro[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 thioxanthenyldiene S,S-dioxide (2) from 9-diazothioxanthene S,S-dioxide (9) afforded only the dimer bi-9,9'-thioxanthenyldiene S,S,S',S'-tetroxide (10).

In the present work we report on the generation of thioxanthenyldiene S,S-dioxide (2) via photolysis of 9-diazothioxanthene S,S-dioxide (9) 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 (67–96%), in addition to small amounts of bi-9,9'-thioxanthenyldiene 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 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 phenylchlorocarbene8 than that of 1,6,7,12,17-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 spectrometry, 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 (t, CH), 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

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>82</td>
<td>5.8</td>
</tr>
<tr>
<td>19</td>
<td>19</td>
<td>4.5</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>11.5</td>
</tr>
<tr>
<td>21</td>
<td>21</td>
<td>6.9</td>
</tr>
<tr>
<td>22</td>
<td>22</td>
<td>6.9</td>
</tr>
<tr>
<td>26</td>
<td>26</td>
<td>20</td>
</tr>
<tr>
<td>27</td>
<td>27</td>
<td>20</td>
</tr>
</tbody>
</table>

8 Bi-9,9'-dithioxanthyldiene S,S,S',S'-tetroxide. 9 9,9'-Di- hydrobi-9,9'-thioxanthyldene S,S,S',S'-tetroxide. * In method A the diazo compound 9 was irradiated directly, in method B 3- methoxyacetophenone was irradiated as a triplet sensitizer.

Cycloaddition Reactions of Thioxanthenylidene S,S-Dioxide

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

<table>
<thead>
<tr>
<th>Styrene</th>
<th>( k_r (M^{-1} s^{-1})^a )</th>
<th>( k_{rel}^b )</th>
<th>( k_{rat} (rel)^c )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methoxystyrene</td>
<td>2.07</td>
<td>-0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-methylstyrene</td>
<td>1.35</td>
<td>1.26</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>styrene</td>
<td>1.00</td>
<td>1.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>p-chlorostyrene</td>
<td>0.89</td>
<td>0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-bromostyrene</td>
<td>0.66</td>
<td>0.39</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*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%.

**Relative rates of quenching derived from the absolute rate constants.**

**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 bleeding 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 bleeding of 9 is more pronounced at the shorter wavelengths. The 324-nm band decays with a lifetime of ca. 5 µs, whereas the band at 356 nm has a lifetime of ca. 50 µs. 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 µs) 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 diarylcyanobenzes;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...
agree with the relative rates of cyclopropane formation obtained from steady-state experiments (vide infra) \( (k_{\text{rel}}) \) (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 \(^{15,16,18,21} \) 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 carbones 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.

\[
\begin{align*}
\text{triplet} & \xrightarrow{k_{t}} \text{singlet} \\
& \text{ROH} \rightarrow \text{product}
\end{align*}
\]

\[
\begin{align*}
{k_{t}} = k_{s}/K_{eq} \\
K_{eq} = k_{ss}/k_{ts}
\end{align*}
\]

with alcohols occur with rates that are close to the diffusion limit.\(^{18} \) Since \( k_{t} \) cannot be greater than \( k_{diff} \), then \( K_{eq} \leq k_{diff}/9.3 \times 10^{6} \), therefore \( K_{eq} \leq 2.2 \times 10^{5} \). Thus, according to this analysis, the energy gap between the lowest triplet and singlet state of 2 is probably similar to diphenylcarbene \( (3 \text{ kcal M}^{-1}) \)\(^{16} \) and larger than that of fluorenylidene \( (1 \text{ kcal M}^{-1}) \).\(^{15} \)

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 \( \text{2a} \) 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 carbencic center with respect to dip phenylcarbene, 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.\(^{24} \) Fluorenylidene\(^{15} \) and 1-naphthylcarbene\(^{14} \) 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 \( (k_{t}) \) is required.

**Stereochemistry of the Cycloadditon.** Photoysis of 9 in pure \( (>99.5%) \) trans-\( \beta \)-methylstyrene \( (16) \) gave in addition to trans-1-methyl-2-phenyls [cyclopropane-3,9'-thioxanthene] \( \text{SSO}_{2} \) dioxide \( (26) \), 9,9'-dihydro-bi-9',9'-thioxanthylidene \( \text{SS,S',S'-tetroxide} \) \( (28) \) \( (11.5%) \), 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.\(^{3,18} \) Photolysis of 16 under the same conditions did not result in isomerization of cis-\( \beta \)-methylstyrene \( (17) \), as confirmed by UV and GLC analysis. Irradiation of 9 in 16 at 355 nm using a monochrometer, 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 nuclophilicity,\(^{10} \) 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 \( \sigma \) 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 carbones 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


Photolyses were carried out according to the following methods. 

**Method A.** A solution of 1 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 (7.5 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 

**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 SO₂ 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) spectrophotometers. ¹H NMR spectra were recorded on A60 (EM 360, Varian) and WH90 (HX 90, Bruker) instruments with Me₄Si (δ 0.0) as an internal standard. ¹³C 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 aluminia N/UV 254 (0.2 mm) (Macherey, 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 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-phenylisopropycyclopropane-2,9'-thioxanthene S,S-dioxide (18, 1.06 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 (C₉H₇), 1302, 1290, and 1160 (SO₂); ¹H NMR δ 2.21–2.46 (m, 3 H, methylene and methyne), 6.46–8.15 (m, 3 H, Ar); ¹³C NMR δ 121.2 (t, CH₃), 32.17 (s, C), 389.60 (d, CH₃), 123.81–141.81 (m, Ar). Anal. Calcd for C₁₇H₁₅S₀₂Cl: C, 68.75; H, 4.09; S, 8.73; Cl, 9.66. Found: C, 68.52; H, 4.10. Also obtained was 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).

Photolyses 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)isopropycyclopropane-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) 2920 cm⁻¹ (OCH₃), 1585 (aryl), 1302, 1285, and 1160 (SO₂); ¹H NMR δ 2.21–2.45 (m, 3 H, methylene and methyne), 2.81 (s, 3 H, CH₃), 6.25–8.13 (m, 12 H, Ar). Anal. Calcd for C₁₇H₁₅O₁S₀₂C: C, 72.5; H, 4.97; S, 8.8. Found: C, 72.76; H, 4.96. Also 10 was obtained (0.04 g, 4.5%).

Photolyses of 9 in p-Methylstyrene (13). As before, 1-(p-methy1phenyl)isopropycyclopropane-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 (CH₃), 1580 (aryl), 1300, 1285, and 1160 (SO₂); ¹H NMR δ 2.19–2.39 (m, 3 H, methylene and methyne), 6.39–8.09 (m, 12 H, Ar). Anal. Calcd for C₁₉H₁₅O₁S₀₂C: C, 76.3; H, 5.20; S, 9.24. Found: C, 76.16; H, 5.34. The dimer 11 was also found (0.05 g, 5.8%).

Photolyses of 9 in p-Chlorostyrene (14). As before, 1-(p-chlorophenyl)isopropycyclopropane-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; IR (KBr) 1685 cm⁻¹ (aryl), 1280 and 1160 (SO₂); ¹H NMR δ 2.20–2.42 (m, 3 H, methylene and methyne), 6.42–8.13 (m, 12 H, Ar). Anal. Calcd for C₁₉H₁₄Cl₁S₀₂C: 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, 6.5%).

Photolyses of 9 in p-Bromostyrene (15). As before, 1-(p-bromophenyl)isopropycyclopropane-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 385; IR (KBr) 1580 cm⁻¹ (aryl), 1280 and 1144 cm⁻¹ (SO₂); ¹H NMR δ 2.19–2.46 (m, 3 H, methylene and methyne), 6.39–8.15 (m, 12 H, Ar). Anal. Calcd for
Carbenadibenzocycloheptane: Steady-State and Time-Resolved Spectroscopic Laser Studies

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Received June 3, 1986

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. In particular these studies have revealed the differences in the absolute reactivities of the ground-state triplet species fluorenylidene (1) and diphenylcarbene (2) and have allowed (together with steady-state measurements) estimates of the free energy differences between the lowest triplet and singlet states of these carbens.\(^1\)\(^2\)

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\(^b\)\(^6\) and at room temperature in liquid paraffin using conventional flash photolysis.\(^4\) It was observed that at room temperature

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