J. Org. Chem. 1987, 52, 434-438

$C_{21}H_{15}SO_2Br$: 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); ^{1}H 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′-thioxanthenylidene *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); ^{1}H 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^{-5} M **9** dissolved in parrafin 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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Registry No. **2**, 61574-06-9; **9**, 3166-17-4; **10**, 66688-14-0; **11**, 100-42-5; **12**, 637-69-4; **13**, 622-97-9; **14**, 1073-67-2; **15**, 2039-86-3; **16**, 873-66-5; **18**, 101220-45-5; **19**, 101220-43-3; **20**, 101220-44-4; **21**, 101220-46-6; **22**, 101220-47-7; **26**, 106006-88-6; **28**, 26430-92-2.

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

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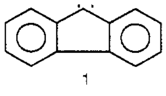
A Hammett study of the reactions of carbenadibenzocycloheptane with para-substituted styrenes indicates that this carbene adds to the styrenes as a weak ambiphile. Evidence is obtained that reaction from both singlet and triplet states of this carbene can be observed.

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]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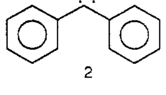
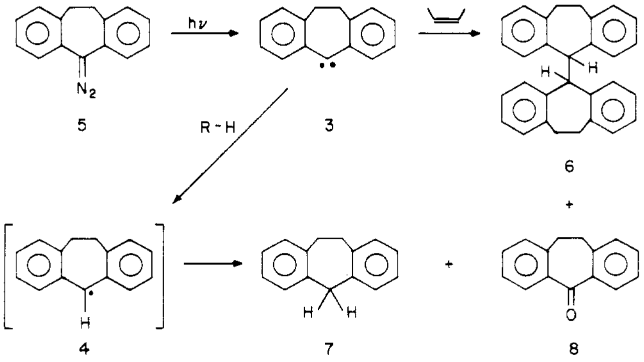

2

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[4b] and at room temperature in liquid paraffin using conventional flash photolysis.[4c] It was observed that at room temperature

Scheme I



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[§] Present address: Eastman Kodak Company, Rochester, New York.

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

(2) Grasse, P. B.; Braur, B.-E.; Zupancic, J. J.; Kaufman, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

(3) (a) Eisenthal, K. B.; Turro, N. J.; Sitzman, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543. (b) Closs, G. L.; Rabinow B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190.

0022-3263/87/1952-0434$01.50/0

Scheme II

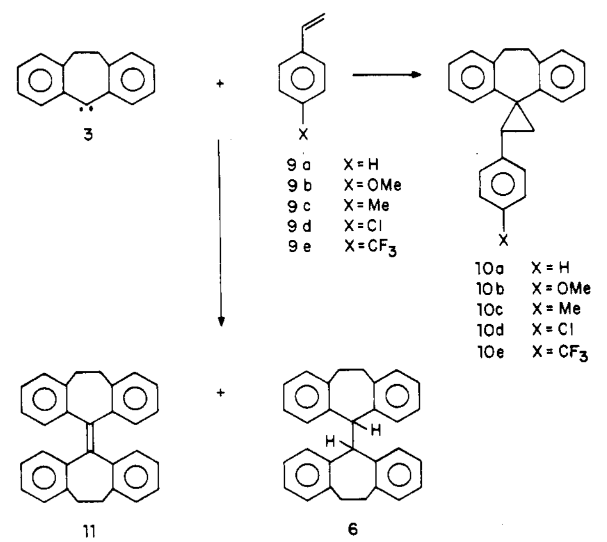
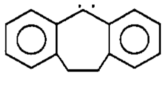


Table I. Products from the Photolysis of 5-Diazo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptane (5) in the Styrenes 9a–d

	product yield, %		
	10	6	11
styrene (**9a**)	71	17	
p-methoxystyrene (**9b**)	82	11	
p-methylstyrene (**9c**)	63	11	
p-chlorostyrene (**9d**)	53	7.5	7

in liquid paraffin the carbene abstracts a hydrogen to form the radical **4** (Scheme I), although no kinetic data were reported.[4c] The same workers also reported that steady-state photolysis of the diazo precursor **5** in the presence of *cis*-2-butene results in the formation of three products **6** (81%), **7** (6%), and **8** (6%) (Scheme I). These products are consistent with the triplet character of carbene **3**, but it is surprising that no cyclopropane is formed, a product typical of the reactions of **2**.[5]

Recently a laser flash photolysis study of carbene **3** was reported.[6] The absolute kinetics of the rates of hydrogen abstraction of **3** from various solvents were reported. In addition a new transient species, formed upon reaction of **3** with pyridine and tentatively assigned to an ylide, was observed. The similarity of the reactions of **3** with those of carbene **2** were noted.



3

In this work we report that the reaction of carbene **3** with styrenes yields cyclopropane adducts and that the addition reaction with *trans*-β-methylstyrene is stereospecific. Additionally we provide evidence concerning the philicity and the mechanism of this cycloaddiiton reaction of **3**.

Results

Steady-State Photolysis. Irradiation of diazobenzosuberone **5** in the presence of the styrenes **9a–d** yields the cyclopropane addition products **10a–d**, in addition to the dimer (**6**) of radical **4** (Scheme II). For reaction of **3** with styrene **9d** (X = Cl) the dimer of the carbene (**11**) was also detected (Table I). The products were characterized by means of their UV, NMR, and IR spectra. Photolysis of **5** in the presence of *trans*-β-methylstyrene (**12**) gave **6** (70%) together with the *trans*-cyclopropane **13** (19%) as the only detectable cycloadduct (eq 1). This experiment was repeated in the presence of hexafluorobenzene as an inert diluent.[7] In these experiments diazo compound **5** was photolyzed in mixtures of *trans*-β-methylstyrene and hexafluorobenzene containing 0, 36, 53, 69, 85, and 93 mol % hexafluorobenzene. In each case the only products which were isolated were the dimeric compound **6** and the *trans*-cyclopropane **13**. This result indicates that the addition reaction of **3** with *trans*-β-methylstyrene occurs with retention of configuration. This behavior is usually taken as evidence that the reactive spin state of the carbene in the cycloaddition reaction is the singlet state.[5] The product **6** is characteristic of a hydrogen abstraction followed by recombination which is indicative of a triplet species. Thus, with this styrene at least, the reactions of **3** may be characterized as hydrogen abstraction from the triplet state, and cyclopropanation, possibly from the singlet state.

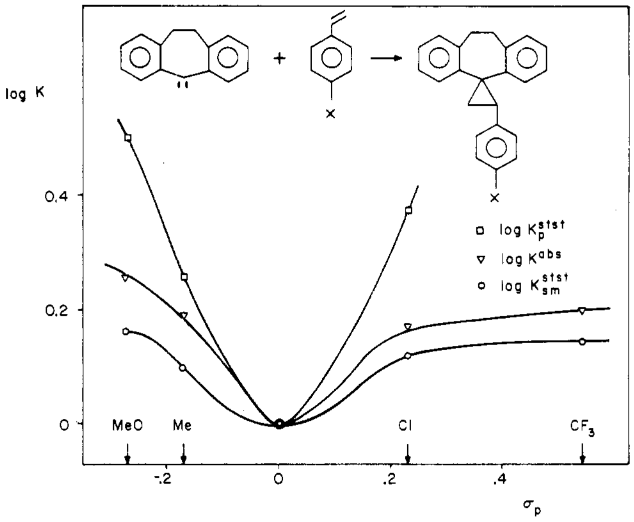
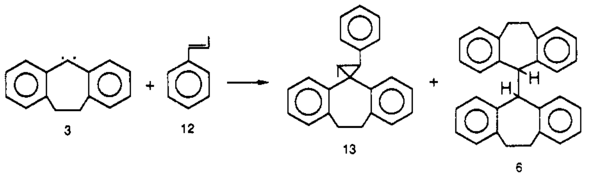


Figure 1. Plots showing the relative rates of reaction of carbene **3** with the styrenes **9**, as determined from time-resolved (K^{abs}) and steady-state (K_p^{stst}, K_{sm}^{stst}) measurements.



(1)

Relative rate constants for the reaction of **3** with the styrenes **9** were determined by using two methods. In the first **5** was irradiated in equimolar mixtures of **9a** with **9b–d**. Analysis of the cyclopropane product ratio (**9b–d**/**9a**) gave the relative rate constants K_p^{stst} for the addition of **3** to **9** (Table II).[8] In another method of analysis (after Sadler[9]), equimolar mixtures of **9a** and **9b–e** were irradi-

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(4) (a) Moritani, I.; Murahashi, S.-I.; Yoshinaga, K.; Ashitaka, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1507. (b) Moritani, I.; Murahashi, S.-I.; Nishino, M.; Kimura, K.; Tsubomura, H. *Tetrahedron Lett.* **1966**, 373. (c) Moritani, I.; Murahashi, S.-I.; Ashitaka, H.; Kumura, K.; Tsubomura, H. *J. Am. Chem. Soc.* **1968**, *90*, 5918.

(5) Jones, M., Jr.; Moss, R. A. *Carbenes*; Wiley: New York; Volume 1 (1973); Volume 2 (1975).

(6) Hadel, L. M.; Platz, M. S.; Wright, B. B.; Scaiano, J. C. *Chem. Phys. Lett.* **1984**, *105*, 539.

(7) These experiments are analogous to those reported by Jones in 1965 in which hexafluorobenzene was used as an inert diluent for the reaction between fluorenylidine and *cis*-2-butene. At low concentrations of alkene less stereospecific addition or more triplet reaction was observed. Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, *87*, 4013.

(8) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58.

(9) Sadler, I. H. *J. Chem. Soc. B* **1969**, 1024.

Table II. Absolute and Relative Rate Constants for the Reaction of Carbenadibenzocycloheptane (3) with the Styrenes 9

styrene	k_t(app)[a]	K^{abs}[b]	K_p^{stst}[c]	K_{sm}^{stst}[d]	σ[e]	HOMO[f,g]	LUMO[f,g]
9a	6.4×10^4	1.00	1.00	1.00	0.00	−8.43	0.25
9b	11.5×10^4	1.80	3.16	1.08	−0.27	−7.74	0.48
9c	9.9×10^4	1.55	1.80	1.28	−0.17	−8.20	0.34
9d	9.4×10^4	1.47	2.37	1.31	0.23	−8.78	−0.33
9e	10.0×10^4	1.56		1.37	0.54	−8.79	−0.27

[a] Errors are ±10% for each rate constant. [b] Relative rates from absolute rate studies. [c] Relative rates of cyclopropane formation. [d] Relative rates of styrene consumption. [e] Reference 10. [f] References 11 and 17. [g] In units of eV.

ated in benzene until the diazo percursor **5** was consumed. After reaction the relative amounts of the remaining styrenes were determined by GLC, and hence the relative rates of styrene consumption (K_{sm}^{stst}) determined[9] (Table II). Plots of log K_p^{stst} and log K_{sm}^{stst} vs. Hammett σ values[10] gave the curves shown in Figure 1.

Time-Resolved Studies. Laser flash photolysis of **5** in argon-saturated cyclohexane at room temperature results in strong transient absorption signals in the region 300–360 nm. At wavelengths less than 340 nm a decay of absorption as a function of time is observed, and in the 345–355-nm region, an initial growth followed by a decay is observed. In accord with previous literature reports,[4,6] we assign the species which decays at wavelengths less than 340 nm to the lowest triplet state of **3** and the species which initially grows in to the radical **4**, which is formed via a hydrogen abstraction reaction of the triplet of **3** from the solvent. The lifetime of the carbene under these conditions is difficult to determine, since the carbene and radical absorptions overlap extensively. The rate of radical growth can be determined, but this is affected by the second-order decay of this species which decreases the apparent growth time. At low laser powers the radical growth is first order and occurs with a lifetime of ca. 20 μs. This growth lifetime has previously been reported to be 2 μs.[6] In argon-purged benzene, decay of the carbene at 331 nm is observed as before, but no corresponding growth can be detected at wavelengths greater than 340 nm. The decay of the carbene follows mixed-order kinetics, but in the presence of a sufficient concentration of styrene **9** (ca. 1.0 M), the decay monitored at 331 nm is cleanly first order. Under these conditions, the slopes of plots of the pseudo-first-order rate constant for carbene decay vs. styrene concentration yield the apparent quenching constants for the triplet state (k_t(app)) (Figure 2) (Table II). From the values of k_t(app) we can determine relative rates K^{abs} for reaction of the triplet state as determined from the absolute rate constants. We observe that a plot of log K^{abs} vs. the Hammett σ constants is curved in a manner similar to that of the plots of K^{stst} (Figure 1), although the relative rate constants determined using all three methods are slightly different.

Discussion

The three sets of relative rate constants are not the same (Table II, Figure 1). This is not surprising considering the complexity of the chemical system. The relative rates of cyclopropane formation show a stronger Hammett dependance than the relative rates of triplet quenching and total styrene consumption. In part this must be because cyclopropanes are not the only products of reaction of carbene **3** with the styrenes. The relative rates of triplet quenching and styrene consumption are in better agreement, which might be expected since both are closer to measures of the total reactivity of the carbene.

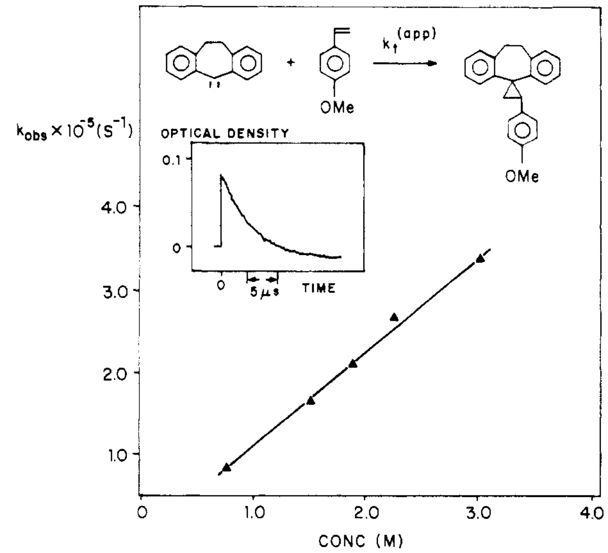

Figure 2. Typical plot of the carbene decay rate (monitored at 331 nm) vs. styrene concentration for the determination of k_t(app) (insert shows typical decay of transient absorption monitored at this wavelength).

Although the stereospecific addition of carbene **3** to *trans*-β-methylstyrene is inconsistent with the observation of an ESR spectrum assignable to **3** at 77 K, the products **6** and **7** almost certainly arise as a result of hydrogen abstraction/recombination reactions and are thus consistent with a ground triplet state for this species. The differing reactivities of **3** toward the para-substituted styrenes is perhaps unexpected and deserves some discussion. The curved Hammett plots may be taken as evidence that in its additions to the styrenes **9**, carbene **3** exhibits weakly "ambiphilic" character.[8] This type of behavior is normally discussed in the context of the reactivity of carbene singlet states.[8] It is certainly reasonable that the more zwitterionic singlet state would be more sensitive to the extent of charge distribution within the reaction transition state than the radical-like triplet state. Indeed, apparant ambiphilic behavior of singlet carbenes is not without precedent. Hammett studies of the reactions of the singlet carbenes methoxychlorocarbene[11a] and phenoxychlorocarbene[11b] have revealed ambiphilic behavior for these species. A curved Hammett plot similar to those in Figure 2 was reported for the reaction of xanthylidene,[12] which has recently been shown to have a singlet ground state.[12b] Similar results have also been reported for the reactions of the ground-state triplet diphenylcarbene with styrenes,[13] although in this case the results were interpreted in terms of stabilization of a presumed biradical intermediate

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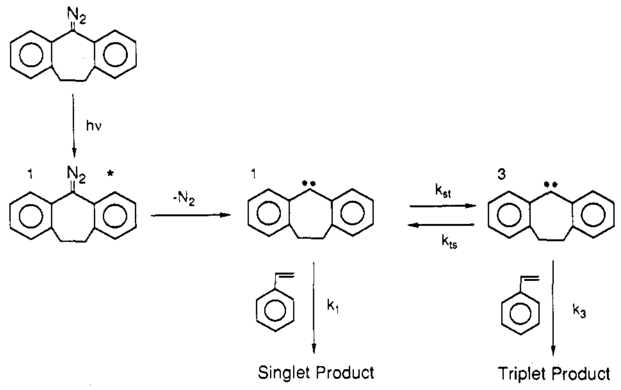
(10) Cary, F. A.; Sundberg, R. J. *Advanced Organic Chemistry*; Plenum Press: New York, 1977.

(11) (a) Moss, R. A.; Guo, W.; Krogh-Jesperson, K. *Tetrahedron Lett.* **1982**, *23*, 15. (b) Moss, R. A.; Perez, L. A. *Tetrahedron Lett.* **1983**, *24*, 2719.

(12) (a) Jones, G. W.; Chong, K. T.; Munjal, R.; Schecter, H. *J. Am. Chem. Soc.* **1978**, *100*, 2922. (b) Lapin, S. C.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 4243.

(13) Tomioka, H.; Ohno, K.; Izawa, Y.; Moss, R. A.; Munjal, R. C. *Tetrahedron Lett.* **1984**, *25*, 5415.

Scheme III

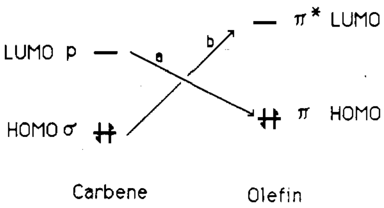


formed upon reaction of the triplet state of diphenylcarbene. However, it has also been shown that the triplet and singlet states of this carbene exist as an equilibrium mixture at room temperature.[3] For example, the ground triplet state of diphenylcarbene apparantly reacts with methanol (via the thermally accessible singlet state) with a rate constant of 2.4×10^7 M^{-1} s^{-1}.[3a] It has been shown that the triplet state of **3** is quenched by methanol with a rate of 2.5×10^6 M^{-1} s^{-1}.[6] Additionally, it was suggested that the triplet state of **3** could form an ylide in the presence of pyridine, which would be expected to be a reaction from the singlet state.[6] Thus we believe that the participation of the singlet state should not be ruled out at this stage for the reaction of **3**. A possible interpretation of the results is that the singlet state of **3** is the precursor to at least a part of the total amount of the cyclopropane adduct and that the triplet state of **3** leads to the other products of the reaction.

Although this interpretation requires reactivity from two spin states of **3**, this can easily be explained by reference to the proposed reaction (Scheme III). Irradiation of the diazo compound **5** leads to the first excited singlet state of **5**, which rapidly loses nitrogen to form the singlet state of **3**. Intersystem crossing from singlet **3** to triplet **3** then occurs (k_{st}) followed by reaction from this spin state (k_3). At sufficiently high concentrations of a styrene quencher, some of the singlet state of **3** can be intercepted (k_1), before intersystem crossing takes place, to form a cyclopropane adduct. This is especially reasonable under the normal conditions for relative rate studies, i.e., high concentrations of quenchers or even neat quenchers.[8] Thus the relative rates of cyclopropane formation might be expected to show a stronger Hammett dependance than the relative rates of styrene comsumption, which will also include cyclopropanation and other reactions of the triplet state. Indeed this is the behavior which is observed (Figure 1).

Whereas reaction from the singlet state of **3** by interception of this species before intersystem crossing occurs may be thought of as a "trivial" mechanism for singlet involvement, a more subtle question is whether the singlet state of **3** can be accessed from the ground triplet state at room temperature (k_{ts} in Scheme III). The current data do not allow us to decide whether such a process occurs in the case of reaction of **3** with the styrenes, as probably occurs for the reaction of **3** with methanol.[3,6] The data which is available from the reactions of the related diphenylcarbene suggest that this is unlikely since it has been shown that reaction of this carbene with isoprene and probably also styrene occurs from the triplet state.[3,14] However, the similarity in the Hammett plots obtained from the steady-state experiments, which are probably biased toward reaction from the singlet state for reasons explained previously, and the time-resolved experiments which must reflect reaction from the triplet state only, is obvious. Thus although we can come to no definite conclusion concerning the multiplicity of the reactive state from the current data alone, we feel that the possibility of reaction from a thermally accessible singlet state cannot be dismissed and that this carbene could be another example of a ground-state triplet diarylcarbene with an accessible reactive singlet state.[2,3,15]

Scheme IV



The possibility that the singlet state of **3** could be ambiphilic in its addition reactions with styrenes **9a–e** deserves further comment. Singlet carbenes are normally electrophilic, although nucleophilic behavior is observed when electron-donating substituents interact directly with the carbene center.[8] Only electrophilic reactivity is expected for the singlet state of **3**. However, as previously indicated, apparent ambiphilic behavior of singlet carbenes is not without precedent, and an explanation for the shape of the Hammett plots of Figure 2 is possible based upon these previous studies.[11]

Moss has suggested that the reactivity of singlet carbenes in their cycloadditions to olefins may be explained in terms of Frontier Molecular Orbital (FMO) theory.[8,11] The relevant orbital description is shown in Scheme IV. For electrophilic carbenes the interaction given by (a) is the most important, for nucleophilic carbenes that given by (b) is more important. FMO theory states that the rate of a reaction is controlled by the energy difference between the relevant orbitals and the extent of orbital overlap at the transition state.[16] If there is no significant change in the orbital overlap integral for the electrophilic reaction of the singlet state of **3** with each of the styrenes **9a–e**, we need only consider the differences in the carbene LUMO/olefin HOMO energy gap for each styrene.[8,16] The energies of the HOMOs and LUMOs for each of the styrenes have been calculated,[11,17] and these values are summarized in Table II. As expected the HOMO energies decrease in the order **9b** > **9a** > **9e** and thus if the reaction rates are controlled by the electrophilic step given by (a) in Scheme IV, then **9d** and **9e** should react more slowly than **9a**. It is certainly the case that styrenes **9d** and **9e** both react at similar rates and have similar HOMO energies, however each is faster than **9a**. Of course as the HOMO energies decrease in the series **9b** > **9a** > **9e** then so do the LUMO energies. Thus the nucleophilic interaction (b) becomes more favorable for the less electron-rich styrenes. A large drop in LUMO energy occurs for the styrenes with the electron-withdrawing groups (**9d** and **9e**) which suggests that nucleophilic attack may become important for these two styrenes. Additionally the LUMO

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[14] Baron, W. J.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6286.

[15] Abdel-Wahab, A. A.; Doss, S. H.; Dürr, H.; Turro, N. J.; Gould, I. R. *J. Org. Chem.*, previous paper in this issue.

[16] Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley Interscience: New York, 1976.

[17] Krogh-Jesperson, K. Rutgers University, unpublished results. We thank Professor Krogh-Jesperson for communicating these results prior to publication.

energies for these two are similar (as are their HOMO energies), which is consistent with their similar rate constants for reaction with **3**. It is important to note that the above discussion is necessarily only qualitative without an estimate of the HOMO and LUMO energies of the carbene. Additionally, we may not expect an explanation of all of the kinetic data based upon the orbital energies alone. For example, the orbital overlap requirements for electrophilic and nucleophilic attack are entirely different.[8] Also the products are not exclusively cyclopropanes (Table I), although the cyclopropanation reaction would be expected to show the largest Hammett dependence. If the cycloaddition process is controlled by frontier molecular orbital interactions, then we would expect an early transition state for the reaction. This is entirely consistent with the observation that the ground-state singlet phenylchlorocarbene exhibits very low activation energies for reaction with other olefinic species.[18]

Conclusion

The reaction of the title carbene gives rise to cycloaddition products as well as products which can be ascribed to hydrogen abstraction and recombination reactions. The reaction with *trans*-β-methylstyrene occurs with no loss in stereospecificity. These results are consistent with reaction from both singlet and triplet states of the carbene. Reaction from the singlet state of the carbene which is thermally accessible from the ground triplet state is also postulated, although this proposal is not required to explain the results.

Experimental Section

All melting points are uncorrected and were determined on a Büchi SMP 20 apparatus. UV spectra were recorded on a Beckman D8 spectrophotometer. IR spectra were recorded on a Leitz Unicam SP 200 spectrophotometer. ^{1}H NMR were acquired on Varian EM-360 (60 MHz) and Bruker HX-90 (90 MHz) machines using Me_4Si as an internal standard. ^{13}C NMR and off-resonance ^{13}C NMR spectra were recorded on the Bruker HX-90.

Elemental analyses were performed at the microanalysis laboratory of the Institute of Organic Chemistry, 66 Saarbrücken, West Germany. Analytical TLC chromatography was carried out on foil slides coated with polygram silica gel G/UV 254 (0.25 mm) (Machery, Nagel + Co.).

Photolyses were carried out on degassed solutions in closed Vycor tubes (25 mm) equipped with side arms and internal cooling. The light source was a 450-W Hanovia lamp and the whole system was placed in an aluminium container which served as a light reflector. The photolysates were separated by using column chromatography with silica gel (0.02–0.5 mm, Merck), and the chromatographic solvents (benzene, petroleum ether (40–80), methylene chloride, and methanol) were purified by distillation.

Diazobenzosuberone was prepared as previously described.[4] The styrenes were obtained from the Aldrich Chemical Company and were distilled immediately prior to use, except for *p*-(trifluoromethyl)styrene which was prepared in low yield (12%) by Wittig addition to *p*-(trifluoromethyl)benzaldehyde and in higher yield (25%) following the method of Broos and Anteunis.[19]

Product Analyses. Reaction with Styrene. Diazobenzosuberone (**5**) (1 g) was dissolved in 20 mL of styrene (**9a**) and irradiated for ca. 1.5 h at 25 °C until **5** was completely removed, whereupon the excess styrene was removed under vacuum and the products were purified by column chromatography. 1-Phenylspiro[cyclopropane-2,5′-10′,11′-dihydro-5′*H*-dibenzo[*a*,*d*]cycloheptene] (**10a**) (0.95 g, 70.6%) was eluted with benzene/methylene chloride (1:1): mp 88–89 °C; [M$^+$] at *m/z* 296; ^{1}H NMR δ 7.7–6.8 (m, 13 H, Ar), 3.82–3.32 (m, 2 H, methylene), 3.1–2.7 (m, 2 H, methylene), 2.5–2.2 (m, 2 H, methylene on cyclopropane), 2.17–1.80 (t, 1 H, methyne on cyclopropane); ^{13}C NMR δ 17.99 (t, C3), 31.70 (t, C10), 32.03 (t, C11), 34.00 (d, C1), 38.39 (s, C2), 125.5–143.62 (m, aromatic carbons). Anal. Calcd $C_{23}H_{20}$: C, 93.24; H, 6.75. Found: C, 93.35; H, 6.72. In addition 5,5′-bi(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptyl) (**6**) (17.1%) was eluted with benzene/methylene chloride (1:3), mp 266 °C, lit.[20] mp 264–265 °C.

Reaction with *p*-Methoxystyrene. Irradiation of 1 g of **5** as before in 20 mL of *p*-methoxystyrene (**9b**) gave 1-(*p*-methoxyphenyl)spiro[cyclopropane-2,5′-10′,11′-dihydro-5′*H*-dibenzo-[*a*,*d*]cycloheptene] (**10b**) (1.2 g, 81%) which was eluted with benzene/methylene chloride (1:1): mp 110 °C; [M$^+$] at *m/z* 326; ^{1}H NMR δ 7.8–6.7 (m, 12 H, Ar), 3.8 (s, 3 H, methoxy), 3.68–3.3 (m, 2 H, methylene), 2.92–2.68 (m, 2 H, methylene), 2.5–2.2 (m, 2 H, methylene on cyclopropane), 2.19–1.76 (m, 1 H methyne on cyclopropane). Anal. Calcd $C_{24}H_{22}O$: C, 88.34; H, 6.74. Found: C, 87.89; H, 6.71. The dimer **6** was also formed in 11% yield.

Reaction with *p*-Methylstyrene. Irradiation as before gave 1-(*p*-methylphenyl)spiro[cyclopropane-2,5′-10′,11′-dihydro-5′*H*-dibenzo[*a*,*d*]cycloheptene] (**10c**) (0.88 g, 63%) which was eluted with benzene/methylene chloride (1:1): mp 89–90 °C; [M$^+$] at *m/z* 310; ^{1}H NMR δ 7.7–6.78 (m, 12 H, Ar), 4.0–3.69 (m, 2 H, methylene), 3.6–3.2 (m, 2 H, methylene), 3.13–2.8 (m, 2 H, methylene on cyclopropane), 2.27 (s, 3 H, methyl), 2.1–1.78 (m, 1 H, methyne on cyclopropane). Anal. Calcd $C_{24}H_{22}$: C, 92.90; H, 7.09. Found: C, 92.85; H, 7.08. The dimer was also formed in 11.4% yield.

Reaction with *p*-Chlorostyrene. Irradiation as before gave 1-(*p*-chlorophenyl)spiro[cyclopropane-2,5′-10′,11′-dihydro-5′*H*-dibenzo[*a*,*d*]cycloheptene] (**10d**) (0.8 g, 53%) which was eluted with benzene/methylene chloride (1:1): mp 120 °C; [M$^+$] at *m/z* 330.5; ^{1}H NMR δ 7.8–6.68 (m, 12 H, Ar), 3.97–3.60 (m, 2 H, methylene), 3.35–2.95 (m, 2 H, methylene), 2.5–2.2 (m, 2 H, methylene on cyclopropane), 2.0–1.57 (m, 1 H, methyne on cyclopropane). Anal. Calcd $C_{23}H_{19}Cl$: C, 83.50; H, 5.70; Cl, 10.74. Found: C, 83.03; H, 5.91. The dimer (**6**) was also formed in 7.4% yield. Additionally 5,5′-bi(10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptenylidene) (**11**) (7.2%) was eluted with benzene/methylene chloride (1:4), mp 291–293 °C, lit.[20] mp 266 °C.

Relative Rate Studies. The relative rates of cyclopropane formation (K_p^{stst}) were determined by irradiating diazo compound **5** in degassed equimolar mixtures of the styrenes **9** in sealed Vycor tubes according to ref 8. Quantitative product analysis was performed by using HPLC. In each case control experiments in the dark showed that no products could be detected due to thermal reaction of **5** with **9** during the time period of the irradiations. The relative rates of styrene consumption (K_{sm}^{stst}) were determined by irradiating 5×10^{-3} M styrene and 5×10^{-3} M substituted styrene in 20 mL of benzene to which 1 g of **5** had been added. The solution was irradiated as before. After irradiation the remaining solution was analyzed by GLC to quantitatively determine the relative amounts of the remaining styrenes.

Laser Flash Photolysis Studies. These experiments were carried out by using a Lambda Physik EMG-101 excimer laser (308 nm, ca. 15 ns, ca. 30 mJ) which used a pulsed 450-W xenon lamp (Osram XBO-450) as the analyzing light. The transmitted light intensities were monitored on an RCA 4840 PMT. The output of the PMT was terminated into 50 Ω and digitized using a Tektronix 7912AD under the control of a PDP11/23 minicomputer.[3a]

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