

Table IV. Deviation in Torsional Angles of 1,1-Dimethylcyclotridecanes Relative To Those Found in the Parent Cyclotridecane Having the Same Conformation

compd	conformation	methyls	Σ ldev in ϕ	largest ldev in ϕ
1a	[33331]	C1	5°	2°
1b	[33331]	C11	18°	4°
1c	[33331]	C8	36°	7°
1d	[33331]	C5	22°	7°
1e	[33331]	C4	28°	6°
2a	[43312]	C1	15°	4°
2b	[43311]	C4	14°	3°
2c	[43312]	C8	30°	7°
3a	[643]	C5	18°	4°
3b	[643]	C1	11°	2°
3c	[643]	C11	38°	6°

the methyl group carbon atoms is present. This additional strain varies according to the methyl group placement.

In Table III, E_{Δ_3} represents the additional strain energy in adding a *gem*-dimethyl group to cyclotridecane relative to the lowest energy case; the difference in strain energy due merely to the ring skeleton conformation has been corrected for by subtracting E_{Δ_2} from E_{Δ_3} . Table IV suggests that this additional strain energy is higher in cases where the methyl groups force larger changes in the torsional angles than those found in the respective parent cyclotridecane.

As reflected by E_{Δ_3} (in Table III) the dimethylcyclotridecane having the *gem*-dimethyl group at C₁ of the [33331] conformation (Figure 1) has the lowest strain energy (13.30 kcal/mol) with the strain energies of the other dimethyl compounds increasing largely according to the respective increase in nonbonded interaction strain (E_{nb}). This lowest energy conformation compares with that found crystallographically for the 13-membered ring compound reported here and one of the two molecules reported by Samuel and Weiss⁸ (Figure 7). The second molecule in the cyclotridecane hydroxyl phosphonate appears to have a geometry corresponding to compound 1b and thus to have a calculated strain energy approximately 0.84 kcal/mol greater than that of the other molecule in the asymmetric unit and the structure reported here.

Conformational Interconversions in 1,1-Dimethylcyclotridecanes. Since the X-ray data indicate disorder, which could involve a facile conformational interconversion, molecular mechanics calculations were carried out on the energy required to distort the [33331] conformation, particularly in the vicinity of C₅ to C₈. Major changes in the two torsional angles, C₆-C₇-C₈-C₉ and C₄-C₅-

C₆-C₇ in fact result in and interchange of the [33331] and the [643] conformations, with a calculated barrier of 6.9 kcal/mol (from the more stable [33331] conformation). This barrier, which is quite high compared to thermal energies at room temperature, implies two distinct conformations. Interconversion between them, however, would be rapid on the laboratory or NMR time scales.

While the torsional angles for the ordered structure (Figure 7a) and for conformation A (Figure 7c) agree to approximately 10° with those calculated for the [33331] conformation, one torsional angle of conformation B, C₇-C₈-C₉-C₁₀, deviates by 36° from that calculated for the respective [643] conformation (Figure 8). To see what this deviation does to the strain energy, torsional angle C₇-C₈-C₉-C₁₀ of the [643] conformation was driven from the initial -80° value to -112° by 8° increments. An energy maximum of 15.21 kcal/mol is found at a torsional angle of -97°, and this represents a conformational energy barrier of only 0.25 kcal/mol.

The further driving of the same torsional angle gives the previously calculated [33124] conformation, whose strain energy is very slightly lower than that of the [643] conformation (Table III). Thus these two conformations are close in energy and are separated by a very small barrier. Such a situation should lead to a favorable entropy for this group of conformations when considered as a unit. In fact, this system should be considered as a single conformation that is undergoing a rapid librational motion.

A proper calculation of the entropy requires a knowledge of the potential energy surface, followed by vibrational analysis. However, an approximate treatment can be used in which the librating system is replaced by several distinct species. Thus, if, for simplicity, three equally energetic species are considered (e.g., the [643], [33124], and an intermediate "conformation") and if the energy difference with the [33331] conformation is 1.6 kcal/mol (approximately the mean difference), then the combined population of the three species is 17% at room temperature, in excellent agreement with the 20% minor conformation required by the X-ray data.

Acknowledgment. We are grateful to the National Science Foundation and the National Institutes of Health for support of this work.

Supplementary Material Available: Tables I-IX of atomic coordinates, temperature factors, hydrogen coordinates, and structure factors for disordered anisotropic and ordered model refinement and crystallographic data (30 pages). Ordering information is given on any current masthead page.

9-Mesityl-9,10-dihydro-9-boraanthrylidene: A Probe of Structure and Reactivity for Aromatic Carbenes

Stephen C. Lapin, Beth-Ellen Brauer, and Gary B. Schuster*

Contribution from the Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801. Received August 18, 1983

Abstract: Photolysis of 10-diazo-9-mesityl-9,10-dihydro-9-boraanthracene (1) causes loss of nitrogen and formation of 9-mesityl-9,10-dihydro-9-boraanthrylidene (BA). Direct irradiation leads first to the singlet carbene, which intersystem crosses to the triplet. Photosensitization with triplet 2-acetonaphthone gives the triplet carbene directly. The singlet carbene reacts with isopropyl alcohol to give the appropriate ether. The triplet carbene forms cyclopropanes nonstereospecifically from terminal olefins and abstracts hydrogen atoms from hydrocarbons and alcohols. Kinetic and product analysis shows that, in contrast to fluorenylidene, the rate of equilibrium between ¹BA and ³BA is slow compared with most of the bimolecular reactions of the triplet. This is believed to be a consequence of the larger energy gap between ground-state ³BA and ¹BA compared with that of fluorenylidene. The effect of carbene structure on the magnitude of this energy gap is discussed.

The chemical and physical properties of carbenes have intrigued a generation of chemists.¹ Intensive experimental and compu-

tational research has focused on the difference in structure, in energy, and in reactivity between the two lowest electronic states

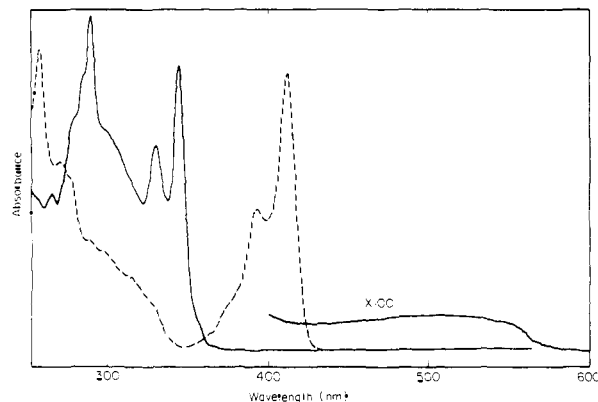
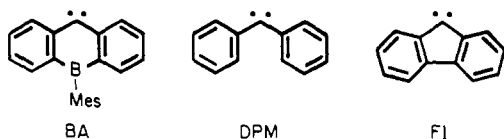


Figure 1. Absorption spectrum of 9-diazo fluorene in pentane (solid line) and of diazoboraanthracene **1** in pentane.

of these intermediates. One objective of these studies is to establish a useful link connecting the structure of a carbene with its chemical properties. To this end we have conducted an extensive analysis of 9-mesityl-9,10-dihydro-9-boraanthrylidene (BA). The prop-



erties of this carbene, particularly when they are compared with those of methylene,² diphenylmethylene (DPM),³ and fluorenylidene (FI),⁴ provide a guide to the influence of structure on the magnitude of the energy gap separating the ground-state triplet from the singlet state of aromatic carbenes. This gap depends on structural features of the carbene that affect differently the singlet and triplet states. In this regard, introduction of the boron atom that converts fluorenylidene to boraanthrylidene provides a test of the influence of both the carbene carbon bond angle and the energy level of the π -electron system on the magnitude of the triplet-singlet gap. Moreover, the findings show that it is the size of this gap that in large part controls the chemical behavior of these reactive intermediates.

Results

(1) Preparation of Diazodihydroboranthracene 1. The preparation of 9-mesityl-9,10-dihydro-9-boraanthracene (**2**) has been described by Van Veen and Bickelhaupt.⁵ Conversion of **2** to diazoboraanthracene **1** is accomplished in good yield by reaction with tosyl azide in diethylamine according to the procedure of

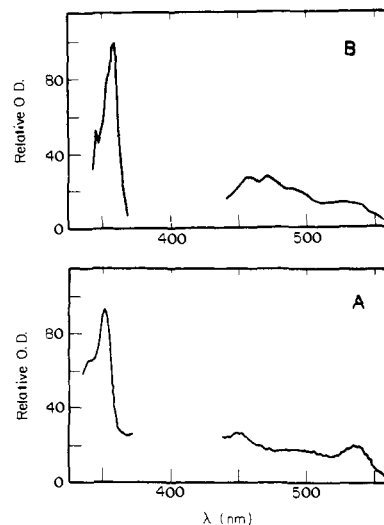
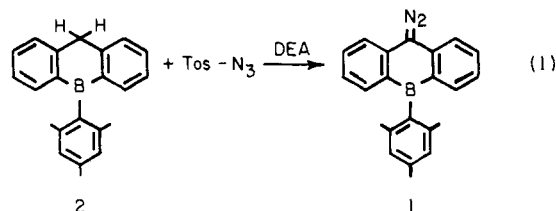


Figure 2. (A) Absorption spectrum obtained by photolysis of diazoboraanthracene **1** in MTHF at ca. 10 K. (B) Absorption spectrum of transient product recorded 150 ns after pulsed irradiation of diazoboraanthracene **1** in benzene solution at room temperature.

Weil and Cais⁶ (eq 1). Details for these reactions are given in the Experimental Section.



Diazoboraanthracene **1** is a stable, intensely red substance. The mesityl group, which we presume lies in a plane approximately perpendicular to that of the boraanthracene, apparently protects the boron atom from nucleophilic attack without being directly conjugated with it.

The UV-vis absorption spectrum of **1** is shown in Figure 1 along with that of 9-diazo fluorene (DAF) for comparison. It is apparent that there is an intense band in the spectrum of **1** that is not present in DAF. We associate this with a charge-transfer transition (diazo to boron) of **1**.⁷ This band obscures part of the spectral region probed during analysis of **1** by laser flash photolysis (vide infra) but does not appear to otherwise influence the photochemical properties of this diazo compound.

(2) Photolysis of 1 in Frozen Media. Irradiation of diazoboraanthracene **1** in a 2-methyltetrahydrofuran (MTHF) glass at 4.6 K gives a paramagnetic species readily characterized from its EPR spectrum as triplet 9-mesityl-9,10-dihydro-9-boraanthrylidene (³BA). The EPR signals from ³BA are stable for at least several hours at either 4.6 or 77 K. These observations establish the triplet as the ground state of this carbene. Fitting the observed spectrum to the usual spin Hamiltonian⁸ gives the zero-field parameters $|D| = 0.360 \text{ cm}^{-1}$ and $|E| = 0.0156 \text{ cm}^{-1}$. In the past there have been attempts to deduce fine details of structure from the magnitude of D and E and in particular from the ratio $|E|/|D|$.⁹ This approach has been criticized,¹⁰ and it sometimes is necessary to invoke special effects to rationalize these parameters within a particular model.¹¹ Nevertheless, the

(1) (a) Kirmse, W. "Carbenes", 2nd ed.; Academic Press: New York, 1971. (b) Moss, R. A.; Jones, M., Jr. "Carbene Chemistry"; Wiley: New York, 1973; Vol. 1; (c) "Carbene Chemistry"; Wiley: New York, 1975; Vol. 2; (d) "Reactive Intermediates"; Wiley: New York, 1978, 1981; Vol. 1, 2. (e) Abramovitch, R. A. "Reactive Intermediates"; Plenum: New York, 1980, 1982; Vol. 1, 2. (f) Closs, G. L. *Top. Stereochem.* **1968**, *3*, 193.
(2) (a) Feller, D.; McMurchie, L. E.; Borden, W. T.; Davidson, E. R. *J. Chem. Phys.* **1982**, *77*, 6141. (b) Hayden, C. C.; Neumark, D. M.; Shoatke, K.; Sparks, R. K.; Lee, Y. T. *Ibid.* **1982**, *76*, 3607.
(3) (a) Closs, G. L.; Rabinow, B. E. *J. Am. Chem. Soc.* **1976**, *98*, 8190. (b) Eisenthal, K. B.; Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr.; Dupuy, C.; Hefferon, G.; Hetherington, W.; Korenowski, G. M.; McAuliffe, M. J. *Ibid.* **1980**, *102*, 6563. (c) Dupuy, C.; Korenowski, G. M.; McAuliffe, M.; Hetherington, W. M., III; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *77*, 272. (d) Baron, W. J.; Hendrick, M. E.; Jones, M., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6286.
(4) (a) Moss, R. A.; Joyce, M. A. *J. Am. Chem. Soc.* **1978**, *100*, 4475. (b) Zupancic, J. J.; Schuster, G. B. *Ibid.* **1980**, *102*, 5958; (c) *Ibid.* **1981**, *103*, 2423. (d) Brauer, B.-E.; Grasse, P. B.; Kaufmann, K. J.; Schuster, G. B. *Ibid.*, **1982**, *104*, 6814. (e) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *Ibid.* **1983**, *105*, 6833. (f) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *Ibid.* **1982**, *104*, 6813. (g) Wong, P. C.; Griller, D.; Scaiano, J. C. *Ibid.* **1981**, *103*, 5934.
(5) Van Veen, R.; Bickelhaupt, F. *J. Organomet. Chem.* **1974**, *74*, 393.

(6) Weil, T.; Cais, M. *J. Org. Chem.* **1963**, *28*, 2472.
(7) Birks, J. B. "Photophysics of Aromatic Molecules"; Wiley: New York, 1970; p 405.
(8) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.
(9) Higuchi, J. *J. Chem. Phys.* **1963**, *39*, 1339.
(10) Hoffmann, R.; Zeiss, G. D.; Van Dine, G. W. *J. Am. Chem. Soc.* **1968**, *90*, 1485.
(11) Wasserman, E.; Trozzolo, A. M.; Yager, W. A.; Murray, R. W. *J. Chem. Phys.* **1964**, *40*, 2408. Wasserman, E.; Barash, L.; Trozzolo, A. M.; Murray, R. W.; Yager, W. A. *J. Am. Chem. Soc.* **1964**, *86*, 2304.

zero-field parameters for ^3BA do show clearly, if predictably, that the carbene is nonlinear with a large one-center (presumably the carbene carbon) interaction.

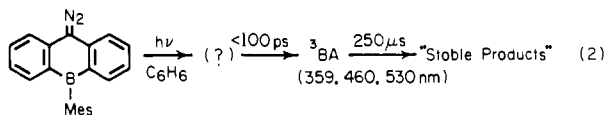
Optical spectroscopy in the frozen medium leads to analogous results. Figure 2a shows the absorption spectrum obtained after irradiation of **1** in a MTHF glass at ca. 10 K. The spectrum consists of three identifiable features. There is a sharp, relatively intense UV band with a maximum at 359 nm, and the visible portion of the spectrum shows two broad overlapping bands with apparent maxima at 460 and 530 nm. The region from 370 to 430 nm is obscured by the strong absorption of the residual starting diazoboraanthracene **1**. The absorptions at 359, 460, and 530 nm are stable for hours at 10 or 77 K. However, warming the sample to room temperature leads to their disappearance.

The optical absorption spectra of several triplet aromatic carbenes have been assigned.^{14,e,12} Typically, they consist of an intense UV band and a weaker visible transition. These features are present in the spectrum obtained from photolysis of **1**. Moreover, the paired observation of the EPR and an optical spectrum, particularly at very low temperature, supports the assignment of the three observed absorption bands to ^3BA . It is not possible to be absolutely unequivocal in this assignment. However, it is strongly supported by the results of laser flash photolysis and chemical analysis described below.

(3) Nanosecond and Picosecond Laser Flash Photolysis. Irradiation of a benzene solution of diazoboraanthracene **1** at room temperature with the output of a nitrogen laser¹³ gives the transient absorption spectrum shown in Figure 2b. It is apparent that the three features observed in the low-temperature spectrum and assigned to ^3BA are present in the transient spectrum. The three bands all appear to rise within the ca. 13-ns pulse width of the laser, and they all disappear with similar complex kinetic behavior over a period of ca. 250 μs . The eventual stable products formed from irradiation of **1** under these conditions are complex (vide infra) but consist mainly of dimeric structures.

Irradiation of **1** on a picosecond time scale with a frequently-tripled Nd-YAG laser¹⁴ also generates the transient product. We cannot probe the UV transition with this apparatus, and the low intensity and breadth of the visible transitions lead to noisy spectra. Nevertheless, these data show that the visible light absorbing transient is formed from diazoboraanthracene in less than 100 ps.

On the basis of the low-temperature and pulsed laser spectroscopy, and the chemical analysis to be described below, we assign the transient product obtained from photolysis of **1** in benzene to ^3BA . These results are summarized in eq 2.



Photolysis of diazoboraanthracene **1** in cyclohexane solution with the nanosecond laser leads to spectroscopic changes apparently similar to those observed in benzene. A transient product is formed with absorption maxima at ca. 360, 460, 530 nm. However, it is readily shown that the transient product observed on a nanosecond time scale from irradiation of **1** in cyclohexane is not the same as that formed by its irradiation in benzene.

Many carbenes react with styrene to give cyclopropanes in high yield.¹ This is true of this boraanthrylidene (vide infra). Addition of 0.35 M styrene to a benzene solution of **1** results in a decrease in the lifetime of the transient product by a factor of over 1000 from ca. 250 μs to 220 ns. The measured rate of reaction obtained

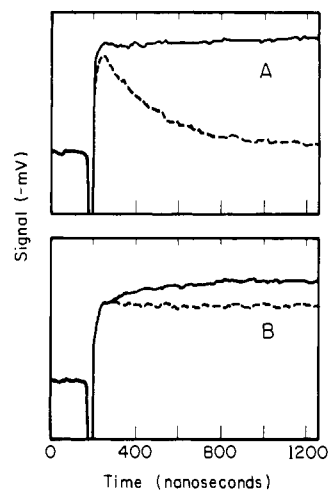
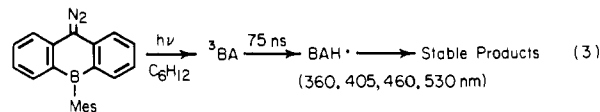


Figure 3. (A) Transient signal obtained at 460 nm by pulse irradiation of diazoboraanthracene **1** in benzene (solid curve) and in the presence of 0.35 M styrene (dashed curve). (B) Transient signal obtained at 460 nm by pulse irradiation of **1** in cyclohexane solution (solid curve) and in the presence of 0.35 M styrene (dashed curve).

is the same when it is monitored at each of the three observed absorption bands. In contrast, addition of 0.35 M styrene to a cyclohexane solution of **1** does not cause any decrease in the lifetime of the transient product. Instead, the amount of the transient obtained, as indicated by the absorbance change shortly after the laser pulse, is decreased (Figure 3).

These findings indicate that there are two transient products with similar absorption spectra. The first, formed in benzene, reacts with styrene to become a cyclopropane. The second, formed in cyclohexane, does not react rapidly with styrene, and it eventually goes on to form radical combination and disproportionation products (vide infra). These results led us to suspect that hydrogen atom abstraction by ^3BA gives rise to the 9-mesityl-9,10-dihydro-9-boraanthryl radical ($\text{BAH}\cdot$) rapidly in cyclohexane solution. This is substantiated by the independent generation of this radical.

The *tert*-butoxy radical readily abstracts a hydrogen atom from benzylic positions. This reaction has been used to generate and confirm the identity of the 9-fluorenyl radical in laser flash photolysis experiments.⁴⁸ In a similar way we have formed $\text{BAH}\cdot$ by 2-acetonaphthone-sensitized photolysis of a benzene solution containing *tert*-butyl peroxide and dihydroboraanthracene **2**. The spectrum of the radical thus obtained is quite similar to that obtained from photolysis of **1** in cyclohexane, except that an additional band is observed at 405 nm, a region obscured in the other spectra by the absorption of **1**. These findings are summarized in eq 3.



The similarity of the spectra of ^3BA and $\text{BAH}\cdot$ is not unexpected.¹⁵ However, it precludes simple spectroscopic analysis of ^3BA . Nevertheless, by taking advantage of the quite different chemical properties of these two species, the kinetic behavior of ^3BA can be revealed.

(4) Chemical and Kinetic Behavior of Boraanthrylidene. The varied chemical properties of carbenes have often been associated with reactions originating from either the electrophilic singlet or the radical-like triplet state. Thus, hydrogen atom abstraction and nonstereospecific cyclopropanation of olefins have usually been attributed to reaction of the triplet,¹⁶ while ether formation from

(12) Closs, G.; Hutchison, C. A., Jr.; Kohler, B. E. *J. Chem. Phys.* **1966**, *44*, 413.

(13) Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 239. Moritani, I.; Murahashi, S.-I.; Yoshinaga, K.; Ashitaka, H. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 1506. Moritani, I.; Murahashi, S. I.; Nishino, M.; Kimura, K.; Tsudomura, H. *Tetrahedron Lett.* **1966**, 373. Murahashi, S. I.; Moritani, I.; Nishino, M. *Tetrahedron* **1971**, *27*, 5131.

(14) This laser apparatus has been described previously: Horn, K. A.; Schuster, G. B. *Tetrahedron* **1982**, *38*, 1095.

(15) This apparatus is described in detail in ref 4e.

(16) Trozzolo, A. M. *Acc. Chem. Res.* **1968**, *1*, 329.

(17) (a) Closs, G. L.; Trifunac, A. D. *J. Am. Chem. Soc.* **1970**, *92*, 2186. (b) Roth, H. D. *Acc. Chem. Res.* **1977**, *10*, 85. (c) Baldwin, J. E.; Andrist, A. H. *J. Chem. Soc., Chem. Commun.* **1971**, 1512. (d) Moss, R. A.; Dolling, U.-H. *J. Am. Chem. Soc.* **1971**, *93*, 954.

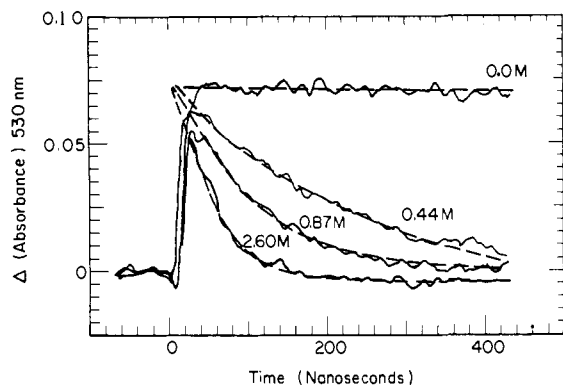
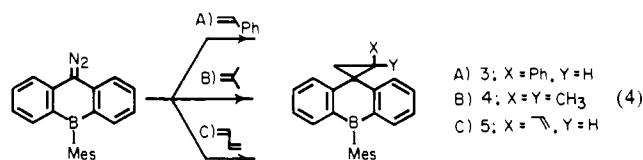


Figure 4. Effect of increasing styrene concentration on the rate of decay of ^3BA following pulse irradiation in benzene solution at room temperature, monitored at 530 nm. The dashed lines are least-squares extrapolation to time equals zero.

alcohols and stereospecific cyclopropanation are thought to be specific reactions of the singlet state.^{17,18} We have examined the reaction of boraanthrylidene with the panoply of typical carbene reagents. Analysis of the products and kinetics of these reactions permits the clear assignment of spin-selective properties and illuminates the relationship between the singlet and triplet states of this carbene.

(A) Reaction of Boraanthrylidene with Olefins. The formation of cyclopropanes from the reaction of carbenes with olefins is both the most important and most thoroughly studied of their reactions.¹ Among the aromatic carbenes two classes of behavior have been observed.¹⁹ The first is illustrated by diphenylmethylene. This carbene reacts with terminal olefins to give cyclopropanes in high yield, but when more hindered olefins are used, hydrogen abstraction becomes the dominant path. For both sets of olefins the cyclopropanation reaction appears to be nonstereospecific. The second class is illustrated by fluorenylidene. With this carbene both terminal and internal olefins give good yields of cyclopropanes, and the reaction with cis olefins appears to be nonstereospecific. We have investigated the reaction of boraanthrylidene with a range of olefins.

Irradiation of diazoboraanthracene **1** in neat isobutylene, or in a benzene solution containing styrene or 1,3-butadiene, leads to the appropriate cyclopropane in high yield (eq 4). The details



of the isolation and characterization of these products are given in the Experimental Section. In contrast, irradiation of **1** in a benzene solution containing β -methylstyrene gives products characteristic of hydrogen atom abstraction (vide infra) and very little, if any, of the expected cyclopropane. Thus, the reactivity pattern of boraanthrylidene appears to be more like that of diphenylmethylene than that of fluorenylidene.

The rate of reaction of boraanthrylidene with styrene can be obtained readily from analysis of the rate of decay of its absorption spectrum following pulsed laser excitation in benzene solution.

(17) (a) Bethell, D.; Howard, R. D. *J. Chem. Soc. B* **1969**, 745. (b) Kirmse, W. *Liebigs Ann. Chem.* **1963**, 666, 9. (c) Bethell, D.; Stevens, G.; Tickle, P. *J. Chem. Soc. D* **1970**, 792. (d) Bethell, D.; Newall, A. R.; Whittaker, D. *J. Chem. Soc. B* **1971**, 23. (e) Tomioka, H.; Miwa, T.; Suzuki, S.; Izawa, Y. *Bull. Chem. Soc. Jpn.* **1980**, 53, 753. (f) Moritani, I.; Nagai, T. *Nippon Kagaku Zasshi* **1965**, 86, 157.

(18) Skell, P. S.; Garner, A. Y. *J. Am. Chem. Soc.* **1956**, 78, 3409. Skell, P. S.; Woodworth, R. C. *Ibid.* **1956**, 78, 4496. Moss, R. A.; Pyzybyla, R. J. *J. Org. Chem.* **1968**, 33, 3816. Jones, M., Jr.; Rettig, K. R. *J. Am. Chem. Soc.* **1965**, 87, 4013.

(19) Jones, M., Jr.; Baron, W. J.; Shen, Y. H. *J. Am. Chem. Soc.* **1970**, 92, 7475.

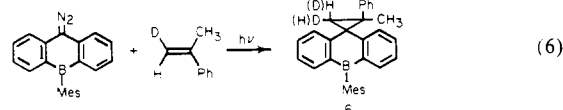
When styrene is present in the reaction solution, the decay of ^3BA no longer show complex kinetic behavior but can easily be fit to a simple first-order decay (Figure 4). The observed pseudo first-order rate constants (k_{obsd}) increase appropriately with the styrene concentration and, when plotted according to eq 5, give

$$k_{\text{obsd}} = k_0 + k_{\text{sty}}[\text{styrene}] \quad (5)$$

a second-order rate constant for reaction of boraanthrylidene with styrene (k_{sty}) equal to $1.2 \pm 0.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The same rate constant for reaction, within experimental error, is obtained when the reaction is monitored at 530 nm (as shown in Figure 4) or at 360 or 460 nm.

The data displayed in Figure 4 also reveal that the short-lived precursor to ^3BA , the question mark in eq 2, does not react rapidly with styrene. The absorbance of the carbene at extrapolated time equals zero is not diminished significantly by the addition of up to 2.6 M styrene. This indicates that approximately as much ^3BA is formed in the presence of styrene as in its absence and suggests a triplet carbene origin for this cyclopropanation reaction. Further support for this suggestion comes from an analysis of the stereochemistry of the cyclopropanation reaction.

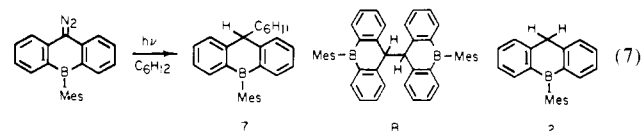
The clearest test of stereochemical outcome of cyclopropanation comes from specifically deuterated olefins. The use of these olefins is critical with boraanthrylidene because nonterminal olefins do not give much cyclopropane. We examined the reaction of BA with (*E*)- β -deutero- α -methylstyrene²⁰ (eq 6).



The proton NMR spectrum of **6** (undeuterated) shows an AB pattern for the two cyclopropyl hydrogens. We presume that the farther upfield resonance (δ 2.54, 2.75 in C_6F_6) is due to the hydrogen opposite the phenyl group, but the specific assignment is not required for analysis of the stereochemistry of the cyclopropanation reaction.

Irradiation of diazoboraanthracene **1** in benzene solutions containing variable concentrations of the deuterated olefin gives the expected cyclopropane in high yield. Integration of the NMR absorptions of the cyclopropyl hydrogens shows that the two isomeric cyclopropanes are formed in nearly equal amounts regardless of the initial olefin concentration. This finding suggests that only one spin state of the carbene is responsible for cyclopropanation of the styrene, and the total loss of stereochemistry implies that this state is the triplet.

(B) Reaction of Boraanthrylidene with Cyclohexane. Irradiation of diazoboraanthracene **1** in cyclohexane leads to its rapid consumption and the formation of the products shown in eq 7 with



an overall yield of ca. 60%. The details of the isolation and characterization of these products are given in the Experimental Section. The products of this reaction are characteristic of the combination and disproportionation of the cyclohexyl radical with $\text{BAH}\cdot$. This is consistent with our spectroscopic observation of $\text{BAH}\cdot$ and with the properties of other triplet carbenes. The relatively low mass balance is probably a consequence of the reaction of ^3BA or $\text{BAH}\cdot$ with diazoboraanthracene **1** to give complex or dimeric products.

The rate of reaction of ^3BA with cyclohexane cannot be obtained directly from the pulsed laser spectroscopy because of the overlap of its spectrum with that of $\text{BAH}\cdot$. However, analysis of the

(20) Accidental equivalence of the two cyclopropyl hydrogen atoms and their overlap with a mesityl methyl group precluded the use of deuteriostyrene.

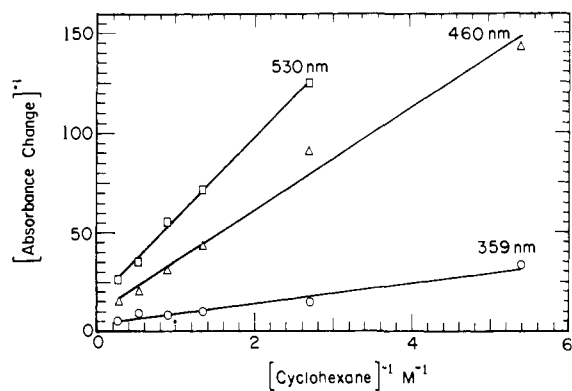


Figure 5. Double-reciprocal plot of the relative yield of BAH 3 μ s after pulse irradiation of diazoboranthracene **1** in benzene solution containing 0.26 M styrene and various concentrations of cyclohexane.

competition between hydrogen atom abstraction from cyclohexane and the cyclopropanation of styrene permits calculation of the rate constant for the former reaction.

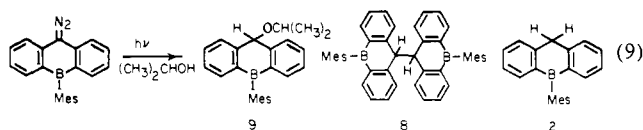
When a solution of **1** is irradiated in benzene containing 0.26 M styrene, the absorption due to ^3BA decays to zero in about 1.3 μ s (four half-lives). Thus, 3 μ s after the laser pulse there is no detectable absorption at any of the wavelengths characteristic of ^3BA . When cyclohexane is also present in the reaction solution there are observable absorptions 3 μ s (and longer) after the pulse. These are due to the generation of $\text{BAH}\cdot$ (which does not react rapidly with styrene) in competition with cyclopropanation of styrene by ^3BA . The intensity of the absorption due to $\text{BAH}\cdot$ increase as the amount of cyclohexane in the solution increases. These data can be analyzed according to eq 8 where $\Delta(\text{OD})$ is

$$\frac{1}{\Delta(\text{OD})} = \frac{1}{A} \left(1 + \frac{k_{\text{sty}}[\text{styrene}]}{k_{\text{chex}}[\text{C}_6\text{H}_{12}]} \right) \quad (8)$$

the absorbance change due to formation of $\text{BAH}\cdot$ 3 μ s after the laser flash, A is a constant containing the extinction coefficient of the radical, and k_{chex} is the second-order rate constant for reaction of ^3BA with cyclohexane. The data are plotted according to eq 8 as a function of cyclohexane concentration on Figure 5 for the UV and the two visible maxima of the $\text{BAH}\cdot$ spectrum. A similar family of linear plots is obtained when the cyclohexane concentration is held constant and the reciprocal of the optical density is plotted against styrene concentration. The ratio of the slopes to intercepts of these plots, in combination with the independently determined value of k_{sty} (vide supra), gives $8.1 + 2.1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for k_{chex} . Substitution of C_6D_{12} for the cyclohexane shows that its reaction with ^3BA leads eventually to the same yield of $\text{BAH}\cdot$ obtained from C_6H_{12} but that the rate constant for reaction with C_6D_{12} is smaller indicating a primary kinetic isotope effect of ca. 7. In comparison, we have recently shown^{4d,e} that fluorenylidene reacts with cyclohexane with a rate constant of $7.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, i.e., more than 90 times faster than does boraanthrylidene, and shows a kinetic isotope effect of only ca. 2.

(C) **Reaction of Boraanthrylidene with Isopropyl Alcohol.** The reaction of carbenes with alcohols to form ethers is a process widely regarded as originating exclusively from the singlet state of carbenes.¹⁷ We have examined the reaction of boraanthrylidene with isopropyl alcohol under a variety of conditions.

In contrast to diphenylmethylene^{17c} and fluorenylidene,^{4d,e} BA does not give high yields of ethers when photolyzed in solutions containing alcohols. Irradiation of diazoboranthrylidene **1** in isopropyl alcohol gives the mixture of products shown in eq 9. The



details of isolation and characterization of these products are

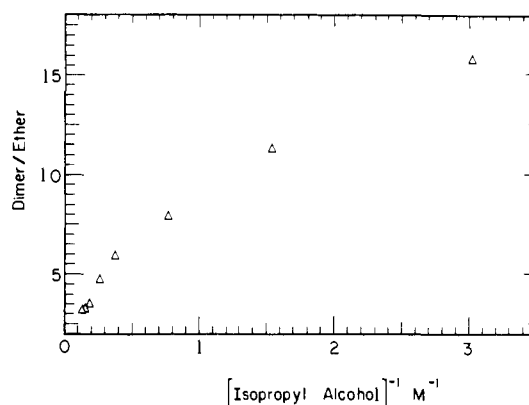


Figure 6. Effect of isopropyl alcohol concentration on the ratio of the dimer **8** to ether **9** yields from irradiation of diazoboranthracene in benzene at room temperature.

reported in the Experimental Section. It is clear from the nature of the products that both hydrogen atom abstraction (products **2** and **8**) and addition to form ether **9** are occurring. The yield of ether **9** under these conditions is ca. 17%. This is to be compared with the yield of the corresponding ether from the reaction of fluorenylidene and isopropyl alcohol of 90% and with diphenylmethylene 77%.^{17c}

The apparent rate of reaction of ^3BA with isopropyl alcohol can be measured by using the competition technique described above for its reaction with cyclohexane. Appropriate adaptation of eq 8 gives $k_{\text{IPA}} = 3.4 \pm 0.9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and the use of $(\text{CH}_2)_2\text{CDOH}$ reveals an isotope effect of ca. 5. The corresponding rate constant for reaction of fluorenylidene with isopropyl alcohol is $5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (measured in acetonitrile solution). Again, the data reveal that BA is much less reactive than Fl.

A series of experiments has demonstrated that one of the important reactions of triplet diphenylmethylene and of triplet fluorenylidene is intersystem crossing to form their more energetic singlet states. We have investigated the involvement of this process in the transformations of boraanthrylidene.

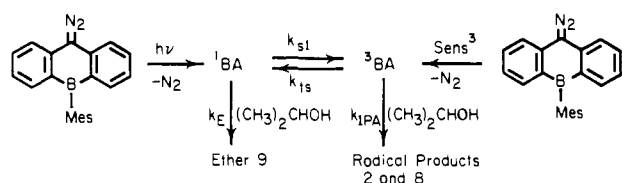
One of the first experiments to demonstrate the rapid equilibration of aromatic carbene spin states showed that for diphenylmethylene the ratio of hydrogen abstraction to ether products formed with isopropyl alcohol is relatively insensitive to dilution with acetonitrile.^{17c} In contrast, we find that with boraanthrylidene this ratio is strongly dependent on dilution of the alcohol with benzene (Figure 6). As the concentration of the alcohol in the benzene solution decreases, the relative amount of ether formed decreases concomitantly. This behavior is not consistent with maintenance of a rapid equilibrium between ^1BA and ^3BA .

One of the most convincing demonstrations that a triplet aromatic carbene can eventually give ether products with alcohols is the triplet sensitized photolysis of DAF.^{4d,e} In this case, a high yield of ether is obtained despite the clear initial formation of triplet reactive intermediates. In contrast, sensitization of diazoboranthracene **1** with 2-acetonaphthone in isopropyl alcohol does not give a significant yield (less than 5% of that formed by direct irradiation) of ether **9**. Instead, the products (**2** and **8**) correspond to those expected from hydrogen atom abstraction. Control experiments show that **1** quenches triplet 2-acetonaphthone at approximately the diffusion limited rate, that *trans*-1,3-pentadiene quenches the sensitization, and that ether **9** is stable to the conditions of reaction and workup.

The results of these experiments show that formation of ^1BA from ^3BA does not compete successfully with the reaction of the latter with isopropyl alcohol. Instead, the relatively low yield of ether obtained by photolysis of **1** in neat alcohol likely arises from the reaction of ^1BA formed directly from the loss of nitrogen from singlet excited diazo compound **1**^{3c,16b,21} before the singlet carbene

(21) Dietrich, H.; Griffin, G. W.; Petterson, R. C. *Tetrahedron Lett.* **1968**, 153.

Scheme I



crosses to the lower energy ^3BA . These results are summarized in Scheme I.

Further support for the reaction mechanism outlined in Scheme I comes from comparison of the yield of $\text{BAH}\cdot$ formed from photolysis of **1** in cyclohexane with that obtained by its irradiation in isopropyl alcohol. The results of the direct and sensitized irradiation experiments indicate that the nearly exclusive reaction of ^3BA in these solvents is hydrogen abstraction to form $\text{BAH}\cdot$. Irradiation of equally absorbing solutions of **1** in cyclohexane or in isopropyl alcohol with the nitrogen laser gives $\text{BAH}\cdot$ detected by its characteristic absorptions 2 μs after pulsed photolysis. At this time, the reaction of ^3BA with both cyclohexane and isopropyl alcohol is complete, but there has been no significant reaction of the radical. Under these conditions, the absorbance of the radical is directly proportional to its yield. Comparison of the absorbance in cyclohexane with that in the alcohol shows that ca. 30% less $\text{BAH}\cdot$ is formed in the latter solvent. With the assumption that the quantum yield of carbene formation is the same in the two solvents and that the extinction coefficient of $\text{BAH}\cdot$ does not depend on solvent, the rate constant for reaction of ^1BA with isopropyl alcohol (k_E , Scheme I) can be estimated to be $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ or greater. The diffusion limit in isopropyl alcohol is estimated to be ca. $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Thus, as has been suggested for both fluorenylidene⁴ and for diphenylmethylene³ singlets, ^1BA appears to react with alcohols at a nearly diffusion-limited rate.

Discussion

(1) Properties of 9-Mesityl-9,10-dihydro-9-boraanthrylidene.

To a large extent the chemical properties of boraanthrylidene are consistent with those that have come to be associated with "classical" singlet and triplet carbenes. The chemical and spectroscopic results presented above show that irradiation of **1** leads to loss of nitrogen and generation of ^1BA . The singlet carbene can react with alcohol to form ether, or it can intersystem cross to generate ^3BA . The triplet carbene reacts with terminal olefins to give cyclopropanes apparently by a step-wise process and with hydrogen atom donors to give radical pairs that eventually couple or disproportionate. An important question surrounding ^3BA is the rate of its reaction to form ^1BA (k_{TS}) and whether this process can compete with bimolecular reactions originating from ^3BA .

The spin-selective reactivity of boraanthrylidene, coupled with the spectroscopically determined reaction rates, can be used to estimate a lower limit for the equilibrium constant connecting ^1BA and ^3BA ($K_{\text{eq}} = ^3\text{BA}/^1\text{BA} = k_{\text{ST}}/k_{\text{TS}}$). This value, in turn, provides a measure of the minimum free energy difference between these carbene spin states (ΔG_{ST}) and an estimate of k_{TS} .

The mechanism outlined in Scheme I suggests that ^1BA is the sole source of ether **9**. The triplet-sensitized reaction of diazoboraanthracene **1** is presumed to generate directly ^3BA . Thus, in order to form **9** by sensitization, ^3BA must intersystem cross to ^1BA before it reacts with isopropyl alcohol to become $\text{BAH}\cdot$. As noted above, in contrast to DAF, the triplet sensitization of **1** does not give a detectable yield of ether. Consequently, it appears that hydrogen atom abstraction by ^3BA from isopropyl alcohol is faster than its conversion to ^1BA . The relationship between the observed product yields in the sensitization experiment and the reaction rate parameters is given in eq 10.

$$\text{singlet product/triplet products} = k_E/(k_{\text{IPA}}K_{\text{eq}}) \quad (10)$$

Using the estimates of k_E and k_{IPA} reported above and taking the conservative limit that we could detect 3% of ether **9** in the sensitization experiment, we calculate K_{eq} to be greater than 6

Table I. Comparison of Carbenes

	ΔG_{ST} , kcal/mol	k_{ST} , s^{-1}	k_{TS} , s^{-1}
DPM ^a	4.6	9.1×10^9	1.7×10^6
Fl ^b	<1.9	2.5×10^9	$>1.1 \times 10^5$
BA	>5.2	$>1 \times 10^{10}$	$<8 \times 10^5$
CH_2	10, ^c 19.5 ^d		

^a Reference 3. ^b Reference 4e. ^c References 2b, 22, and 29. ^d Reference 30.

$\times 10^3$. This corresponds to ΔG_{ST} greater than 5.2 kcal/mol and k_{TS} less than $8 \times 10^5 \text{ s}^{-1}$.

The values for ΔG_{ST} and k_{TS} obtained for boraanthrylidene can be compared with similarly obtained values for fluorenylidene and diphenylmethylene. These data are collected in Table I. It is clear that the chemical properties of these carbenes are directly related to ΔG_{ST} . The rate constants for intersystem crossing from the singlet carbene to the triplet carbene (k_{ST}) appear to be only slightly affected by the changes in structure. In contrast, the magnitude of ΔG_{ST} , and thereby the value of k_{TS} , is strongly dependent on the specific structure of the carbene. In particular, this energy difference is increased by more than 3.0 kcal/mol on going from fluorenylidene to boraanthrylidene. An interpretation of this finding is presented in more detail below. Here we focus on the chemical consequences of this energy difference.

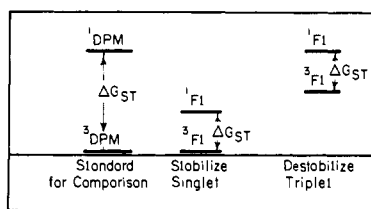
The most important consequence of the change in ΔG_{ST} is the much smaller value of k_{TS} for ^3BA than for ^3Fl . This has special significance when compared with the rates of bimolecular reactions originating from these triplet carbenes. For BA, in general, the rates of the bimolecular reactions of the triplet are faster than its conversion to the singlet. Thus, except for a small amount of reaction from initially formed ^1BA , the chemistry of boraanthrylidene is dominated by the ground-state triplet. On the other hand, for fluorenylidene the rate of forming ^1Fl from ^3Fl is comparable to that of the bimolecular reactions of the triplet. Thus, the observed chemical properties of fluorenylidene depend on the reagent available to the carbene. A "singlet reagent", such as an alcohol, will drain the equilibrium mixture of ^1Fl and ^3Fl from the singlet side and give ether as a product. Whereas a "triplet reagent", such as a hydrocarbon, will drain the same equilibrium mixture from the triplet side and give radical products. A similar relationship between k_{TS} and bimolecular reaction rates also explains the often noted different properties of Fl and DPM.¹⁹ In the case of diphenylmethylene, reformation of the singlet competes with some reactions of the triplet, and the net chemistry observed therefore depends on the concentration and specific nature of the trapping reagent used.

These considerations also explain the reaction rate differences between boraanthrylidene and fluorenylidene noted above. For example, the slower rate of reaction of ^3BA with isopropyl alcohol compared with the corresponding reaction of Fl results, in part, because there is no (or very little) electrophilic singlet in equilibrium with ^3BA . On the other hand, the 90-fold decrease in rate of reaction of ^3BA with cyclohexane compared with that of ^3Fl may reflect the lower inherent reactivity of the boraanthrylidene. An analysis of the structural cause of this decreased reactivity is presented below.

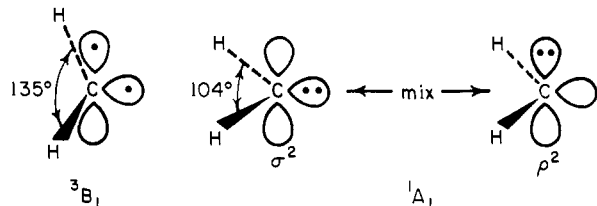
(2) The Effect of Structure on the Properties of Aromatic Carbenes. The simplest carbene is methylene (H_2C). Despite its simplicity, significant uncertainty still surrounds some of its properties.² Our attempt to understand the properties of boraanthrylidene, and thereby aromatic carbenes in general, begins with an analysis of methylene and proceeds to examine how various structural changes will affect this species.

There are two low-lying electronic states of methylene. The first is the ground-state triplet with one electron in an in-plane σ orbital and one in an orthogonal p orbital. This state is designated $^3\text{B}_1$. The second state is a somewhat higher energy singlet state designated $^1\text{A}_1$. This state is a hybrid formed from the configuration interaction mixing of the in-plane σ^2 and the perpendicular p^2 configurations.^{10,22}

Scheme II



Early spectroscopic experiments on the structure of methylene were interpreted to show that the 3B_1 state was linear or nearly linear.²³ A series of increasingly sophisticated calculations²² and eventual measurement of the EPR spectrum of triplet methylene,²⁴ encouraged reinterpretation of the earlier experiments.²⁵ Now there is universal agreement that the 3B_1 state is bent with a bond angle of about 135° .



The structure of 1A_1 methylene is bent more sharply than that of the triplet. In this case, both experiment,^{24,25} and theory²² have been in consistent agreement and place the carbene-carbon bond angle at about 104° . It is important to note that theory predicts that forcing methylene to adopt a smaller bond angle raises the energy of the triplet faster than that of the singlet.²² Thus, these two states are expected to cross somewhere before a bond angle of about 90° .^{22,26} Attempts to obtain experimental verification of this point have been inconclusive.²⁷

A value for ΔG_{ST} of methylene is still not universally accepted. Early experiments indicated a very small gap, on the order of 1–2 kcal/mol.²⁸ High-level theoretical analysis consistently predicts a gap of ca. 10 kcal/mol,²² a value consistent with a number of quite recent experimental determinations.^{2b,29} However, the “most direct” experimental determination places ΔG_{ST} of methylene at ca. 20 kcal/mol.³⁰ Thus, it is clear that the singlet-triplet gap of the aromatic carbenes is considerably smaller than that of methylene, but exactly how much so remains a bit uncertain. Nevertheless, the factors believed to control the energy gap of methylene can be applied to the analysis of aromatic carbenes.

(22) (a) Harrison, J. F. *J. Am. Chem. Soc.* **1971**, *93*, 4112. (b) O’Neil, S. V.; Schaefer, H. F., III; Bender, C. F. *J. Chem. Phys.* **1971**, *55*, 162. (c) Hay, P. J.; Hunt, W. J.; Goddard, W. A., III *Chem. Phys. Lett.* **1972**, *13*, 30. (d) Meadows, J. H.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 4383. (e) Bauschlicher, C. W., Jr.; Schaffer, H. F., III; Bagus, P. S. *Ibid.* **1977**, *99*, 7106. (f) Harding, L. B.; Goddard, W. A., III *J. Chem. Phys.* **1977**, *67*, 1777. (g) Lucchese, R. R.; Schaefer, H. F., III *J. Am. Chem. Soc.*, **1977**, *99*, 6765. (h) Roos, B. O.; Sieghahn, P. M. *Ibid.* **1977**, *99*, 7716. (i) Bauschlicher, W. S., Jr.; Shavitt, I. *Ibid.* **1978**, *100*, 739.

(23) Herzberg, G. *Proc. Roy. Soc. London, Ser. A* **1961**, *262*, 291.

(24) Bernheim, R. A.; Bernard, H. W.; Wang, P. S.; Woop, L. S.; Skell, P. S. *J. Chem. Phys.* **1970**, *53*, 1280. Wasserman, E.; Yager, W. A.; Kuck, V. *J. Chem. Phys. Lett.* **1970**, *7*, 409.

(25) Herzberg, G.; Johns, J. W. C. *J. Chem. Phys.* **1971**, *54*, 2276.

(26) Bodor, N.; Dewar, M. J. S.; Wasson, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9095. Staemmler, V. *Theor. Chim. Acta* **1974**, *35*, 309. Metcalfe, J.; Halevi, E. A. *J. Chem. Soc., Perkin Trans. 2* **1977**, 634. Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333.

(27) Dürr, H.; Nickels, H.; Pacala, L. A.; Jones, Jr., M. *J. Org. Chem.* **1980**, *45*, 973.

(28) Halberstadt, M. L.; McNesby, J. R. *J. Am. Chem. Soc.* **1967**, *89*, 3417. Carr Jr., R. W.; Eder, T. W.; Topor, M. G. *J. Chem. Phys.* **1970**, *53*, 4716.

(29) Frey, H. M.; Gordon, J. K. *J. Chem. Soc., Chem. Commun.* **1975**, 233. Simons, J. W.; Curry, R. *J. Chem. Phys. Lett.* **1976**, *38*, 171. Feldmann, D.; Meier, K.; Zacharias, H.; Welge, K. H. *Ibid.* **1978**, *59*, 171. Lengel, R. K. Zare, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 7495.

(30) Zittle, P. F.; Ellison, G. B.; O’Neil, S. V.; Herbst, E.; Lineberger, W. C.; Reinhardt, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 3731. Engelking, P. C.; Corderman, R. R.; Wendoloski, J. J.; Ellison, G. B.; O’Neil, S. V.; Lineberger, W. C. *J. Chem. Phys.* **1981**, *74*, 5460.

First we compare diphenylmethylene to fluorenylidene. The singlet-triplet gap of FI is ca. 3 kcal/mol less than that of DPM. This smaller gap can arise in principle either from forces that stabilize the singlet of FI more than the triplet or by forces that destabilize the triplet of FI more than the singlet. These possibilities are illustrated in Scheme II.

There are valid expectations that either, or both, of these factors are important. The lowest singlets of these aryl carbenes can be expected to arise from configuration interaction mixing of σ^2 and p^2 states.^{22,26} The relative energies of the p^2 states may be estimated from the pK_a of the corresponding hydrocarbons. Fluorene, of course, forms a p^2 anion that is a textbook example of $4n + 2$ π -electron resonance stabilization. The mixing of this lower energy (relative to DPM) configuration into fluorenylidene may decrease the energy of the singlet more than the triplet and thereby account for the smaller energy gap of this carbene.

On the other hand, the carbene-carbon bond angle of 3FI is about 110° ,³¹ while the corresponding angle in 3DPM is 140° .³² As noted above for methylene, contraction of this angle raises the energy of the triplet faster than that of the singlet. Thus, consideration of this structural feature indicates that destabilization of the triplet may be the more important factor causing the difference between FI and DPM.

The properties of boraanthrylidene permit a relatively clean separation of these two forces potentially influencing ΔG_{ST} . Not surprisingly, dihydroboraanthracene **2** is even a stronger acid than fluorene. Measurement of the pK_a of **2** indicates that inclusion of the boron atom lowers the energy of its anion ca. 8 kcal/mol more than the fluorenyl anion.⁵ Thus, if stabilization of the p^2 configuration is the critical factor, then the energy gap in BA should be smaller than in FI. This is opposite to the experimental results.

Alternatively, the change in the carbene-carbon bond angle may be the dominant factor affecting the relative energy gap between the triplet and singlet states of these carbenes. If we assume that the central ring of BA is planar, or nearly so, then this carbene will have a bond angle of ca. 120° . The theoretical investigation of the properties of methylene suggests that the opening of this angle from ca. 110° (FI) to ca. 120° (BA) should lead to an increase in ΔG_{ST} by lowering the energy of the triplet more than the singlet. This prediction is consistent with our experimental results. Also, the greater rate of reaction of 3FI with cyclohexane compared with 3BA suggests that the former is higher energy than the latter. Thus, these experiments indicate that the carbene-carbon bond angle plays a critical role in determining ΔG_{ST} and hence the chemical properties of these carbenes. Of course, other factors contribute to the properties of these reactive intermediates. Indeed, the energy gap for BA is estimated to be greater than for DPM. This may reflect the additional stabilization of 3BA obtained by elimination of the “ortho-hydrogen” interactions in DPM permitting 3BA to adopt a more stable planar structure. We are continuing the investigation of carbenes to illuminate these parameters.

Experimental Section

General. Proton magnetic resonance (1H NMR) spectra were recorded on Varian Associates EM-390 (90 MHz) or HR 220 (220 MHz), operated in FT mode) spectrometers or using the NSF Midwest Regional NMR center’s Nicolet NT 360 (360 MHz, operated in FT mode with deuterium lock) spectrometer in deuteriochloroform (unless otherwise noted) with tetramethylsilane as an internal standard. Mass spectra (MS) were obtained with a Varian MAT CH-5 and 731 mass spectrometers. Steady-state ultraviolet-visible (UV-vis) absorption spectra were recorded on a Perkin-Elmer Model 552 spectrometer. Electron spin resonance (ESR) spectra at 4.0 K were obtained with the help of M. Hendrich and Dr. P. DeBrunner of the University of Illinois Physics Department on a Bruker instrument. Elemental analyses were performed by the Analysis Laboratory, University of Illinois. Melting points were determined in sealed capillary tubes employing a Büchi Schmelzpunktbestimmungsapparat and are uncorrected. High-performance liquid chromatography (HPLC) was performed on a Perkin-Elmer

(31) Hutchison, C. A., Jr.; Pearson, G. A. *J. Chem. Phys.* **1967**, *47*, 520.

(32) Anderson, R. J. M.; Kohler, B. E. *J. Chem. Phys.* **1976**, *65*, 2451.

Series 2-Liquid chromatograph equipped with variable-wavelength detector using a 5 × 25 cm, 10- μ m silica column or a Whatman Partisil M9 column (1 × 45 cm). Chloroform (1% in hexane or isopropyl alcohol (0.5%) in hexane) was used as eluant.

9-Mesityl-9,10-dihydro-9-boraanthracene (2). The general procedure described by Bickelhaupt and Van Veen⁵ was used with some modification. (*o,o'*-Dichlorodiphenyl)methane^{33,34} was used in place of the corresponding dibromide. The double Grignard reagent was formed from the dichloride using specially activated magnesium.³⁵ A suspension of anhydrous magnesium chloride (4.0 g, 43.2 mmol) and potassium iodide (3.56 g, 21.4 mmol) in 100 mL of THF (distilled from benzophenone ketyl) was prepared in a 250-mL round-bottom flask equipped with a reflux condenser and a rubber septum. The suspension was kept under Ar atmosphere as freshly cut potassium (3 g, 76.8 mmol) was added. Next the suspension was heated at reflux with vigorous stirring for 2 h, and then the (*o,o'*-dichlorodiphenyl)methane (2.54 g, 10.7 mmol) was slowly added to the activated magnesium. After an additional 0.5 h of reflux, a solution of diphenylaminoboron dichloride³⁶ (2.57 g, 10.7 mmol) in 35 mL of anhydrous benzene was added to the double Grignard reagent. After 15 min the reaction was quenched by the cautious addition of 20 mL of water and then 20 mL of 5% aqueous HCl. The resulting clear solution was extracted 3 times with 20-mL portions of ether. The combined extracts were dried with Na₂SO₄, and then the solvents were removed under reduced pressure leaving a viscous oil. Ethanolamine (2 mL, 33 mmol) was added to the oil, and after 5 min the reaction solution was poured into a mixture of ether and water (30 mL of each). The resulting (9-(2-aminomethoxy)-9,10-dihydro-9-boraanthracene) was collected by suction filtration and recrystallization from ethanol giving 1.53 g (61%), 172–175 °C (lit.⁵ 170–176 °C).

Bis(9,10-dihydro-9-boraanthryl) oxide prepared from the ethanolamine (2 g, 8.4 mmol) as previously described⁵ was dissolved in 25 mL of THF contained in a 100-mL round-bottom flask equipped with a septum inlet, reflux condenser, and magnetic stirring bar. Mesityl magnesium bromide in THF (25 mL, 1 M, Aldrich) was added through the septum. The reaction mixture was heated at reflux for 3 h, cooled, and then quenched with 15 mL of water followed by 15 mL of dilute HCl. The resulting solution was extracted 3 times with 20-mL portions of ether, and the combined extracts were dried with Na₂SO₄ and concentrated. The crude product was purified by chromatography on neutral alumina eluting with hexane to give 1.67 g (67%) of 9-mesityl-9,10-dihydro-9-boraanthracene, mp 130–132 °C (lit.⁵ 131–134 °C).

10-Diazo-9-mesityl-9,10-dihydro-9-boraanthracene (1). The synthesis of **1** was modeled after similar reactions described by Weil and Cais.⁶ A solution of *p*-toluenesulfonyl azide (132 mg, 0.673 mmol) and **2** (200 mg, 0.673 mmol) in 10 mL of diethylamine was stirred at room temperature for 12 h. The resulting red reaction mixture was added to a mixture of pentane (25 mL) and water (25 mL). The water layer was extracted with two 10-mL portions of pentane, and the combined pentane solutions were washed with water until the washes were neutral. The pentane solution was dried with Na₂SO₄ and concentrated under vacuum until crystals just began to form. The solution was then stored at –20 °C for 12 h to complete the crystallization, which yielded 56 mg (26%) of **1**: mp 165–167 °C dec; ¹H NMR (CDCl₃) δ 1.90 (s, 6 H), 2.35 (s, 3 H), 6.75 (s, 2 H), 7.50 (m, 8 H); IR (CCl₄) 3025, 2090, 1245, 900, 850 cm⁻¹.

Anal. Calcd for C₂₂H₁₉N₂B: C, 82.01; H, 5.94; N, 8.69. Found: C, 81.85; H, 6.02; N, 8.85.

Low-Temperature ESR. A 6.4 × 10⁻³ M solution of diazoboraanthracene **1** in 2-methyltetrahydrofuran in a quartz ESR tube was placed in a liquid helium cooled variable-temperature probe within the ESR cavity. The sample was photolyzed for 15 min through the grid in the front of the cavity using a 450-W medium-pressure Hanovia lamp which was contained in a Pyrex water cooling jacket. The ESR spectrum was recorded at 4.0 K.

Low-Temperature UV-vis Spectra. A 3.1 × 10⁻³ M solution of diazoboraanthracene **1** in 2-methyltetrahydrofuran was placed in a liquid helium cooled Oxford cryostat Dewar equipped with quartz outer windows and sapphire inner windows. After cooling to 10 K the sample was irradiated for ca. 5 min with a 450-W medium-pressure Hanovia lamp through a Pyrex filter. Subtraction of the base line that was obtained before irradiation provided the spectrum shown on Figure 2A.

Nanosecond Laser Flash Photolysis. The laser flash photolysis apparatus has been described previously.¹³ A nitrogen laser was used for excitation (337 nm). Concentrations were adjusted so that the sample absorbed a significant portion of the laser light (ca. 1.5 × 10⁻³ M for **1**). Solutions were placed in a 1.0-cm quartz fluorescence cell equipped with a stir bar and Teflon-brand stopcock. Oxygen was removed by purging the solution with dry nitrogen for 5 min.

Photolysis of Diazoboraanthracene in Isopropyl Alcohol. A nitrogen-purged solution of **1** (2.2 × 10⁻³ M) in isopropyl alcohol was photolyzed (Rayonet 350 lamps) until >95% of the absorption of the diazo compound at 412 nm had disappeared. The following products were separated by preparative HPLC.

9-Mesityl-9,10-dihydro-9-boraanthracene (**2**), which has been previously characterized.⁵

Isopropyl ether **9**: ¹H NMR (CDCl₃) δ 0.90 (d, *J* = 6.0 Hz, 6 H, isopropyl methyls), 1.92 (s, 6 H, mesityl methyls), 2.31 (s, 3 H, mesityl methyl), 3.63 (m, 1 H, isopropyl), 5.66 (s, 1 H, 10-boraanthryl), 6.72 (s, 2 H, aromatic), 7.45 (m, 8 H, aromatic); MS (10 eV), *m/e* (relative abundance) 354 (58), 311 (100), 295 (79). Molecular ion calcd for C₂₅H₂₇BO, *m/e* 354.2155; found, 354.2163.

Dimer **8**: ¹H NMR (CDCl₃) δ 1.51 (s, 3 H, mesityl methyl), 1.76 (s, 3 H, mesityl methyl), 2.33 (s, 3 H, mesityl methyl), 4.94 (s, 1 H, 10-boraanthryl), 7.20 (m, 10 H, aromatic); MS (field desorption), *m/e* (relative abundance) 590 (30), 295 (100). Anal. Calcd for C₄₄H₄₀B₂: C, 89.51; H, 6.83. Found: C, 88.87; H, 6.81.

These three products, formed in the mole ratio of 47:16:37, account for 65% of the photolyzed **1** as determined from integration of the ¹H NMR spectrum with diphenylmethane as internal standard.

Photolysis of Diazoboraanthracene 1 in Cyclohexane. A nitrogen-purged solution of **1** (4.7 × 10⁻³ M) in cyclohexane (40 mL) was irradiated (Rayonet 350-nm lamps) until >95% of the absorption of the diazo compound at 412 nm had disappeared. The following products are formed in 58% overall yield in the ratio 5:70:25 and were isolated by preparative HPLC: 9-mesityl-9,10-dihydro-9-boraanthracene (**2**), dimer **8**, and the cyclohexyl coupling product **7**. The cross coupling product is a white solid; ¹H NMR (CDCl₃) δ 1.40 (m 11 H, cyclohexyl), 1.78 (s, 3 H, mesityl methyl), 2.02 (s, 3 H, mesityl methyl), 2.25 (s, 3 H, mesityl methyl), 4.17 (d, *J* = 4.0 Hz, 1 H, 10-boraanthryl) 7.20 (m, 10 H, aromatic); MS (10 eV), *m/e* (relative abundance) 378 (59), 596 (100). Molecular ion calcd for C₂₈H₃₁B, *m/e* 378.255; found, 378.252.

Photolysis of Diazoboraanthracene 1 in Isobutylene Solution. A solution of **1** (15 mg) in ca. 10 mL of isobutylene was prepared by condensing the gas at –78 °C in a Pyrex test tube fitted with a Teflon-brand stopcock. The cold solution was placed in a Rayonet RPR 100 photochemical reactor (350-nm lamps), and the sample was irradiated for 20 min at –78 °C. After photolysis the isobutylene was removed by evaporation at room temperature. Analysis of the crude product by ¹H NMR spectroscopy showed only cyclopropane **4**, which was then purified by preparative HPLC: ¹H NMR (CDCl₃) δ 0.76 (s, 6 H, cyclopropyl methyls), 1.92 (s, 2 H, cyclopropyl), 1.98 (s, 3 H, mesityl methyl), 2.07 (s, 3 H, mesityl methyl), 2.33 (s, 3 H, mesityl methyl) 6.8 (d, 2 H, aromatic), 7.3 (m, 8 H, aromatic); MS (10 eV), *m/e* (relative abundance), 350 (35), 230 (100). Molecular ion calcd for C₂₆H₂₇B, *m/e* 350.2206; found, 350.2203.

Irradiation of 1 in Benzene Solution with Styrene. Diazoboraanthracene **1** (50 mg, 0.15 mmol) was dissolved in benzene (40 mL) containing freshly distilled styrene (3.6 × 10⁻² M). The solution was purged with nitrogen for 15 min and irradiated (Rayonet 350-nm lamps) for 90 min. The solvent was removed under vacuum, and ¹H NMR of the residue showed that cyclopropane **3** is the only significant product (88%). This cyclopropane was isolated and purified by preparative HPLC: ¹H NMR (CDCl₃) δ 2.02 (s, 3 H, mesityl methyl), 2.05 (s, 3 H mesityl methyl), 2.40 (s, 3 H, mesityl methyl), 2.69 (d, 2 H, cyclopropyl), 3.14 (t, 1 H, cyclopropyl), 6.64 (d, 2 H, aromatic), 7.25 (m, 13 H, aromatic); MS (10 eV), *m/e* (relative abundance), 398 (100), 278 (94); mp 168–170 °C. Molecular ion calcd for C₃₀H₂₇B, *m/e* 398.225; found, 398.220.

Irradiation of Diazoboraanthracene 1 in Benzene with *cis*- β -Methylstyrene. Diazoboraanthracene **1** (30 mg, 0.093 mmol) was dissolved in benzene (50 mL) containing freshly distilled *cis*- β -methylstyrene (5.0 × 10⁻² M). The solution was purged with nitrogen and photolyzed (Rayonet 350-nm lamps) for 45 min. After removal of the solvent under vacuum, the crude products were analyzed by ¹H NMR. The only identifiable product in the spectrum was dimer **8**. Resonances that could be assigned to the predicted cyclopropane were not observed.

Photolysis of Diazoboraanthracene (1) in a Benzene Solution of 1,3-Butadiene. Diazoboraanthracene (**1**) (30 mg, 0.093 mmol) was dissolved in 40 mL of benzene in a 65-mL round-bottom flask equipped with a magnetic stirring bar and rubber septum. The solution was purged with nitrogen then cooled in an ice water bath. Butadiene (ca. 1.0 g, 18.5 mmol) was condensed in the flask. The solution was irradiated for 20

(33) Haller, H. L.; Bartlett, P. D.; Darke, N. L.; Newman, M. S.; Crisol, S. J.; Eaker, C. M.; Hayes, R. A.; Kilmer, G. W.; Magerlein, B.; Mueller, G. P.; Schneider, A.; Wheatley, W. *J. Am. Chem. Soc.* **1945**, *67*, 1591.

(34) Gribble, G. W.; Kelly, W. J.; Emery, S. E. *Synthesis* **1978**, 763.

(35) Ricke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775.

(36) Becher, H. J. *Z. Anorg. Allg. Chem.* **1957**, *289*, 277.

(37) The ¹H NMR in CDCl₃ has the cyclopropyl resonances overlapped with one of the mesityl methyl groups.

Table II. 2-Acetonaphthone-Sensitized Photolysis of Diazoboranthracene in Isopropyl Alcohol

sample	relative product mole ratios, % ^a		
	ether 9	dimer 8	dihydroboraanthracene 2
1	31	47	21
2	34	45	21
3	2 ^b	70	30
4	ND ^d	ND	ND
5 ^c	ND	ND	ND

^a Due to generation of colored side products the conversion of diazoboranthracene may be different in the various samples. However, the product ratios remain constant throughout the photolysis. ^b This small amount of ether could be due to the light absorbed directly by 1 in the presence of sensitizer. ^c ¹H NMR analysis shows that >90% of the diazoboranthracene 1 remains at the end of the photolysis. ^d None detected by ¹H NMR spectroscopy.

min with a 250-W tungsten halogen lamp which was filtered through a water cooling cell and a Corning CS-400 nm cutoff filter. The solvent was removed at reduced pressure. The ¹H NMR showed the cyclopropane 5 to be the only major product, which was then purified by preparative HPLC. ¹H NMR (CDCl₃) δ 1.91 (s, 3 H, mesityl methyl), 2.04 (s, 3 H, mesityl methyl), 2.34 (s, 3 H, mesityl methyl), 2.47 (m, 2 H, cyclopropyl), 2.55 (m, 1 H, cyclopropyl), 5.03 (d of d, 2 H, vinyl), 5.57 (m, 1 H, vinyl); MS (10 eV), *m/e* (relative abundance) 348 (22), 228 (100). Molecular ion calcd for C₂₆H₂₃B, *m/e* 348.2049; found 348.2044.

Irradiation of Diazoboranthracene 1 in Benzene with α -Methylstyrene. Diazoboranthracene 1 (60 mg, 0.19 mmol) was dissolved in benzene (60 mL) containing freshly distilled α -methylstyrene (4.0×10^{-2} M). The solution was purged with nitrogen and photolyzed for 15 min with a 250-W tungsten-halogen lamp. The light was filtered through a water cooling cell and a Corning CS-400 nm cutoff filter. Evaporation of the solvent under vacuum gave cyclopropane 6, which was further purified by preparative HPLC: ¹H NMR (C₆F₆)³⁷ δ 1.31 (s, 3 H, methyl), 2.06 (s, 3 H, mesityl methyl), 2.20 (s, 3 H, mesityl methyl), 2.37 (s, 3 H, mesityl methyl), 2.63 (d of d, 2 H, cyclopropyl), 7.15 (m, 15 H, aromatic); MS (10 eV), *m/e* (relative abundance) 412 (5), 334 (12), 292 (100). Molecular ion calcd for C₃₁H₂₉B, *m/e* 412.236; found, 412.237.

The procedure was repeated using (*E*)- α -methyl- β -deuteriostyrene^{38,39} (79% isomeric purity, >95% isotopic purity by ¹H NMR). Photolysis was carried out by using 0.45 and 2.40 M solutions of the deuterated

olefin. The ¹H NMR spectrum is the same as that of the nondeuterated cyclopropane except that the cyclopropyl protons are two singlets of equal integrated area. ¹H NMR (C₆F₆) δ 2.75 (s, 0.5 H), 2.54 (s, 0.5 H). The ¹H NMR resonances of unreacted (*E*)- α -methyl- β -deuteriostyrene shows that no isomerization of the olefin occurred under the experimental conditions.

Triplet-Sensitized Irradiation of 1 in Isopropyl Alcohol. Five samples were prepared. Samples 1 and 2 contained only 1 in isopropyl alcohol (2.5×10^{-3} M, OD₃₃₇ = 2.27). Samples 3 and 4 contained both 1 (2.5×10^{-3} M) and 2-acetonaphthone (1.9×10^{-2} M, OD₃₃₇ = 27.0). Sample 5 contained in addition to 1 and 2-acetonaphthone, *trans*-piperylene (0.21 M). Each sample was placed in a cylindrical cell equipped with Pyrex windows, a Teflon-brand stopcock, and a magnetic stirring bar. Samples 1, 2, 3, and 5 were irradiated for 45 min with a nitrogen laser (337 nm, 10 Hz). Sample 4 is a dark control. After the initial irradiation of sample 2, 2-acetonaphthone (1.9×10^{-2} M) was added. The solution was purged again with nitrogen and then was irradiated for an additional 45 min. The isopropyl alcohol was removed from each sample by evaporation at reduced pressure, and the products were analyzed by ¹H NMR spectroscopy. The results are summarized in Table II.

Photolysis of Diazoboranthracene 1 in Benzene with Isopropyl Alcohol. Eight samples were prepared containing 1 (3.5×10^{-3} M) in benzene and various concentrations of isopropyl alcohol ranging from 0.33 to 7.84 M. The samples were placed in quartz test tubes fitted with Teflon-brand stopcocks and purged with nitrogen. The tubes were placed in a merry-go-round apparatus and irradiated with a 250-W tungsten-halogen lamp filtered through a water cooling cell and a Corning CS-400 nm cutoff filter for 70 min. The solvents were evaporated under reduced pressure and the products were dissolved in CDCl₃. The ratio of dimer 8 to isopropyl ether 9 was then determined by integration of the ¹H NMR spectrum. The data are presented on Figure 6.

Generation of the Boraanthryl Radical (BAH \cdot) from the Reaction of *tert*-Butoxy Radical with Dihydroboraanthracene 2. A deaerated solution containing 2 (8.6×10^{-4} M), *tert*-butyl peroxide (0.54 M), and 2-acetonaphthone (2.3×10^{-3} M, OD₃₃₇ = 3.4) as sensitizer in benzene was irradiated at 337 nm by using the nitrogen laser apparatus. The absorption spectrum of the transient products observed ca. 50 μ s after the pulse was recorded and shown to correspond to that obtained from photolysis of 1 in cyclohexane under similar conditions. Control experiments showed that formation of this transient required all three components to be present and that the peroxide quenched the triplet of 2-acetonaphthone with a rate constant of ca. 5×10^5 M⁻¹ s⁻¹.⁴⁰

Acknowledgment. We thank Cynthia Teeters for her help with the low-temperature absorption spectroscopy. This work was supported in part by the National Science Foundation and in part by The National Institutes of Health.

(38) Davis, D. R.; Roberts, J. D. *J. Am. Chem. Soc.* **1962**, *84*, 2252.

(39) McKinny, M. A.; Nagarajan, S. C. *J. Org. Chem.* **1979**, *44*, 2233.

(40) Scaiano, J. C.; Wubbels, G. G. *J. Am. Chem. Soc.* **1981**, *103*, 640.