

Chemical and Physical Properties of 2,3-Benzofluorenylidene. Closing the Gap between Singlet and Triplet Carbenes

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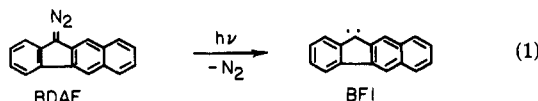
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Irradiation of 2,3-benzo-11-diazofluorene generates the carbene 2,3-benzo-11-fluorenylidene. This carbene was detected in frozen media by EPR and optical spectroscopy and shown to have a triplet ground state. The carbene was detected in fluid solution at room temperature by nanosecond and picosecond laser spectroscopy. The reactions of the carbene with methyl alcohol, cyclohexane, and α -methylstyrene were examined. Direct photolysis, triplet sensitization, and analysis of the reaction kinetics all show that the singlet state of the carbene is present in equilibrium with the triplet in significant concentration. The energy gap between the ground-state triplet and the first singlet state (ΔG_{ST}) is estimated to be less than or equal to 1.0 kcal/mol. The properties of this carbene are compared with those of fluorenylidene, and a correlation of carbene structure and reactivity is suggested.

The investigation of the chemical and physical properties of aromatic carbenes ($Ar_2C:$) has focused recently on the influence of structure on the energy difference (ΔG_{ST}) between the lowest electronic states of these intermediates.¹⁻⁶ The ground state of methylene (the prototypical carbene) has been shown to be a bent triplet (3B_1).^{7,8} The lowest energy excited state of this species is a singlet (1A_1) that is believed to be ca. 10 kcal/mol above the triplet.^{7,8} All of the aromatic carbenes which have been investigated to date are thought to have triplet ground states. The triplet state of diphenylmethylene (the prototypical aromatic carbene) has been estimated to be ca. 4 kcal/mol below the singlet.⁹ Recently we^{2,10} reported that for fluorenylidene (FL) this energy difference is decreased to less than 1.9 kcal/mol and that for 9-mesityl-9,10-dihydro-9-boraanthrylidene (BA) the difference increases to more than 5.2 kcal/mol.¹

The seemingly small changes in the energy separating the triplet state of a carbene from its singlet state in fact has a remarkable influence on the chemical properties of these intermediates. This conclusion can be traced to a competition between the bimolecular reactions of the ground-state carbene and the equilibration with and reaction from its upper state. Thus it is of some interest to identify those structural features that play important roles in controlling the relative energies of the singlet and triplet states of these carbenes.

To this end we have continued the investigation of the chemical and physical properties of aromatic carbenes. In this report we describe the analysis of 2,3-benzofluorenylidene (BFL) by a combination of picosecond and nanosecond laser spectroscopy with conventional chemical probes. In related papers¹¹ we present the results of similar investigations of 3,6-dimethoxyfluorenylidene and of 9-xanthylidene. The findings from these studies combined with those previously reported permit the clear identification of several major factors controlling the properties of aromatic carbenes.



Results

(1) **Photolysis of BDAF in Frozen Media.** Irradiation of BDAF in a 2-methyltetrahydrofuran (MTHF) glass

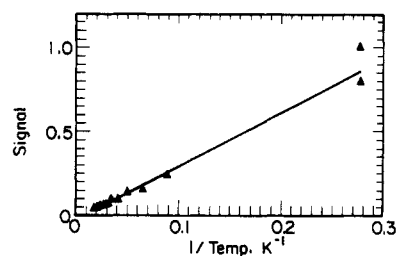


Figure 1. Curie law plot for 3BFL .

at low temperature gives a paramagnetic species readily identified as triplet benzofluorenylidene (3BFL). The

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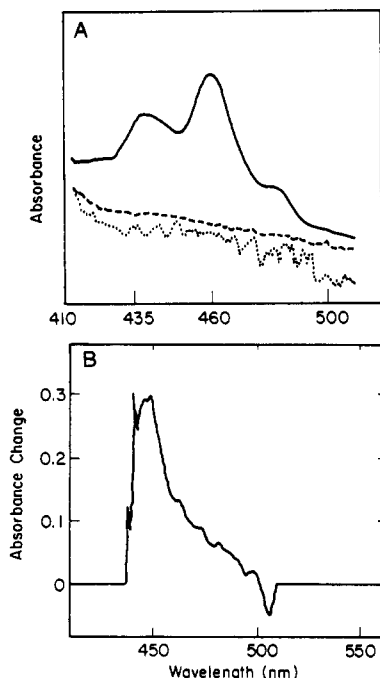


Figure 2. (A) Absorption spectrum recorded at 77 K from irradiation of BDAF (solid line), before irradiation (dotted line), and after warming the irradiated sample to room temperature and recoiling to 77 K (dashed line). (B) Absorption spectrum recorded 50 ps after irradiation of BDAF in cyclohexane. Note the difference in wavelength scales between A and B. There is no probe light below ca. 440 nm and no detectable absorption above 550 nm in the picosecond experiment.

zero-field parameters obtained from fitting the usual spin Hamiltonian¹² are $|D| = 0.39 \text{ cm}^{-1}$ and $|E| = 0.030 \text{ cm}^{-1}$. These values are quite similar to those observed for fluorenylidene¹³ and are thus indicative of the nearly identical geometry at the carbene carbon for these two triplet species.¹⁴

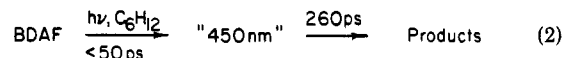
The ground state of BFL is identified as the triplet by analysis of the Curie law plot (Figure 1). The EPR signal observed at 770 G increases linearly with the reciprocal of temperature from 3.8 to 58 K. Nonlinear behavior might be expected if the singlet were below a nearby triplet state of the carbene.¹⁵

Irradiation of BDAF in MTHF at 77 K generates a meta-stable species with apparent absorption maxima at 485, 459, and 434 nm (Figure 2A). Warming the frozen glass to room temperature and then recoiling to 77 K destroy the species responsible for these absorptions.

Comparison of the results from the electron resonance spectroscopy with those from optical measurements points to assignment of one or more of the absorption bands between 485 and 434 nm to BFL. This assignment cannot be made with certainty from the available data, but it is strongly supported by the results of some picosecond and nanosecond experiments described below.

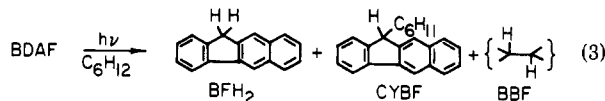
(2) Transient Absorption Spectroscopic Analysis of BDAF. Irradiation of a $2 \times 10^{-4} \text{ M}$ solution of BDAF in cyclohexane at room temperature with the frequency

tripled output of a mode-locked Nd-YAG laser (ca. 30 ps, 355 nm, 4 mJ) generates a transient product detected by its optical absorption spectrum. This spectrum exhibits a maximum at ca. 450 nm which is fully present in less than 50 ps (Figure 2B). On a longer time scale, the transient product decays following first-order kinetics ($t_{1/2} = 260 \text{ ps}$). Weakly absorbing products from the reaction of the 450-nm transient are detected between 480 and 600 nm in this experiment and in a related nanosecond (15 ns, 337 nm, 7 mJ) time scale photolysis. These findings are summarized in eq 2. Similar results are obtained when the photolysis of BDAF is carried out in perdeuteriocyclohexane (C_6D_{12}).



Irradiation of BDAF in acetonitrile solution also leads to the generation of transient intermediates. In this solvent the transient absorbs at ca. 460 nm and is formed in less than 100 ps. The lifetime of the transient in this case is greater than it is in cyclohexane. Its decay obeys first-order kinetics and a second absorption appears in the spectrum as the first disappears. This second species has an absorption maximum at ca. 520 nm and is stable indefinitely. The final spectrum in this experiment is quite similar to that of the carbene dimer (bis(2,3-benzofluorenylidene)) reported previously.¹⁶ The lifetime of the first transient and the yield of presumed carbene dimer depend on the BDAF concentration ($t_{1/2} = 62 \text{ ns}$, $7 \times 10^{-4} \text{ M}$). The lifetime of the transient product absorbing at 460 nm is independent of the laser power, and the changes in absorbance both at 460 and 520 nm vary linearly with the power. Also, the species absorbing at 520 nm does not react with dimethyl fumurate, a reagent known to combine rapidly with the nitrile ylide formed from FL and acetonitrile.² Comparable results are obtained when the irradiation of BDAF in benzene solution is monitored spectroscopically.

(3) Chemical and Kinetic Behavior of Benzofluorenylidene. The irradiation of BDAF in cyclohexane at room temperature gives benzofluorene (BFH_2), 11-cyclohexylbenzofluorene (CYBF), and dihydrobis(benzofluorenylidene) (BBF) in a ratio of ca. 1:11:4 (eq 3). When



the irradiation of BDAF is carried out in a 1:1 mixture of C_6H_{12} and C_6D_{12} , the mass spectrum of the 11-cyclohexylbenzofluorene shows no measurable formation of a singly deuterated component. In contrast, the BBF formed in this reaction is a mixture of d_0 , d_1 compounds (74:26). These findings, together with the picosecond absorption spectroscopy, indicate that BFL reacts with cyclohexane to form CYBF primarily by direct insertion into a carbon-hydrogen bond rather than by a two-step abstraction recombination sequence proceeding through free radicals. Direct insertion reactions of this type are usually associated with the chemistry of singlet carbenes.¹⁷ The formation of BBF, on the other hand, must involve combination of free 11-benzofluorenyl radicals (BFLH \cdot) to account for the isotope distribution.

(10) This finding is consistent with related results from other laboratories; see ref 3 and 6.

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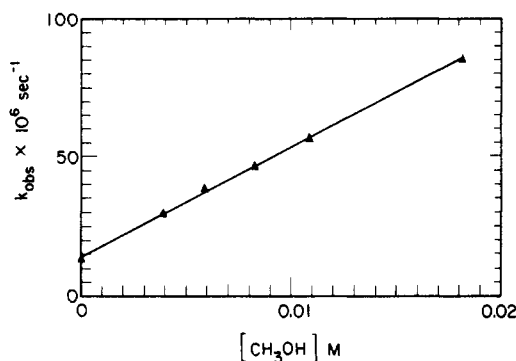
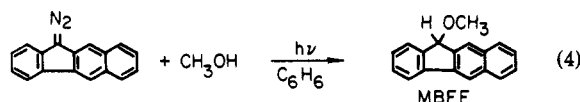


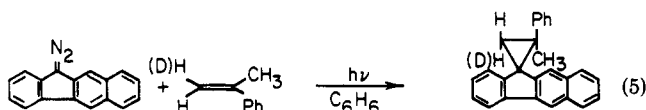
Figure 3. Effect of methyl alcohol concentration the observed rate constant (k_{obs}) for reaction of the transient intermediate.

Irradiation of BDAF in benzene containing 2.5 M methyl alcohol gives methyl 11-benzofluorenyl ether (MBFE) in 80% yield¹⁸ (eq 4). Analysis of this reaction by nanose-



cond transient absorption spectroscopy shows that the lifetime of the intermediate absorbing at 460 nm decreases as the concentration of methyl alcohol in the solution increases (Figure 3). Least-squares analysis of these data reveals that the transient product appears to react with methanol with a bimolecular rate constant ($k_{\text{MeOH}}^{\text{C}_6\text{H}_6}$) equal to $6.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Exactly analogous results are obtained when the rate of this reaction is measured in acetonitrile solvent ($k_{\text{MeOH}}^{\text{CH}_3\text{CN}} = 3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Formation of an ether from reaction of a carbene with an alcohol has generally been a process associated with the singlet state of the carbene.¹⁹

Photolysis of BDAF in benzene containing 0.7 M α -methylstyrene gives the appropriate cyclopropanes (a mixture of regioisomers) in ca. 90% yield (eq 5). The laser



spectroscopy shows that the transient product absorbing at 460 nm reacts with the styrene with a bimolecular rate constant ($k_{\text{sty}}^{\text{C}_6\text{H}_6}$) equal to $5.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. When (*E*)- β -deuterio- α -methylstyrene is used, the NMR spectrum of the isolated cyclopropanes shows that they are formed with retention of 80% of the stereochemistry of the starting olefin.

We conducted a classical competition experiment to confirm that the rate constants measured for the reactions of the transient product with methanol and with α -methylstyrene correspond to the actual formation of the observed major products. Irradiation of an acetonitrile solution of BDAF containing 0.049 M methyl alcohol and 0.69 M α -methylstyrene is anticipated to give the ether and the cyclopropane in a ratio of 1.0:2.0. The ratio observed by analysis of the ¹H NMR spectrum of the mixture is within experimental error of the expected value.

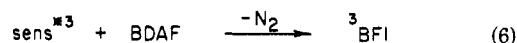
The direct photolysis of BDAF presumably generates singlet benzofluorenylidene, which in turn intersystem

Table I. A Comparison of Fluorenylidene and Benzofluorenylidene

	FL	BFL
$k_{\text{MeOH}}^{\text{CH}_3\text{CN}}$	$8.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	$3.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$k_{\text{PhCH}=\text{CH}_2}^{\text{CH}_3\text{CN}}$	$9.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$	$2.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$
k_{ST}^{a}	$2.5 \times 10^9 \text{ s}^{-1}$	$>2 \times 10^{10} \text{ s}^{-1}$
ΔG_{ST}	$\leq 1.9 \text{ kcal/mol}$	$\leq 1.0 \text{ kcal/mol}$

^a Rate of formation of transient identified as the carbene.

crosses to its triplet ground state.²⁰ Triplet sensitization, on the other hand, is expected to give triplet benzofluorenylidene without first forming the singlet carbene (eq 6). We examined the triplet benzil sensitized reactions



of BDAF with methyl alcohol, (*E*)- β -deuterio- α -methylstyrene, and a 1:1 mixture of C_6H_{12} and C_6D_{12} .

BDAF quenches the phosphorescence of benzil. Irradiation (424 nm) of benzil ($3.5 \times 10^{-2} \text{ M}$) in the presence of BDAF leads to the consumption of the diazo compound. This reaction is appropriately slowed when anthracene, a specific quencher of benzil triplet, is included in the reaction solution. This observation confirms the triplet sensitization.

Triplet benzil sensitized decomposition of BDAF in benzene containing 2.5 M methyl alcohol gives the ether (MBFE) in 92% yield. This result indicates that the carbene spin state required for ether formation can be formed either by direct irradiation, which presumably generates ¹BFL initially, or by triplet sensitization, which is expected to give ³BFL first. Similarly, the stereochemical outcome of the cyclopropanation of α -methylstyrene is the same for the triplet sensitization as it is in the direct irradiation. Finally, the deuterium incorporation in CYBF is the same for triplet sensitization of BDAF in a mixture of C_6H_{12} and C_6D_{12} as it is for the direct irradiation.

Discussion

The chemical and physical properties of BFL are closely related to those of FL. There are some notable differences however (see Table I), and these highlight the features that relate structure to reactivity for these aromatic carbenes.

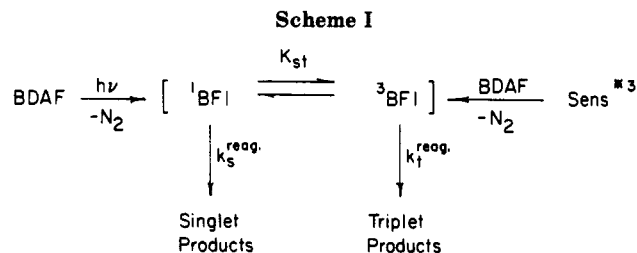
The laser spectroscopy reveals that the transient detected at 450 nm is consumed very rapidly in cyclohexane solution. The products in this case indicate that the dominant mechanism of this transformation is direct insertion into a carbon-hydrogen bond of the solvent accompanied by a smaller contribution from an abstraction-recombination sequence that goes through free benzofluorenyl radicals. This conclusion is supported also by the absence of strong transient absorptions due to BFLH following irradiation of BDAF in cyclohexane. Direct insertion is generally thought to be a singlet carbene reaction. However, the low-temperature EPR spectroscopy indicates that the ground state of BFL is the triplet carbene.

The formation of an ether from reaction of a carbene with an alcohol has generally been attributed exclusively to reaction of the singlet spin state.¹⁹ This spin-selective reactivity is directly supported by the observation that triplet boraanthrylidene (³BA), formed by sensitization, does not give ethers from alcohols.¹ It has recently been suggested that triplet diphenylmethylene can react in one step with methyl alcohol to give the appropriate ether.²¹

(18) This represents a minimum yield since the ether is unstable to secondary photolysis: Tomioka, H. *J. Chem. Soc.; Chem. Commun.* 1983, 1070.

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However, studies with fluorenylidene seem to support the classical, spin-selective reaction sequence.²² In this report the findings on the reaction of BFL with methyl alcohol are interpreted within the classical, spin-selective reaction model.

The rate of reaction of the transient product detected in benzene, or acetonitrile, increases when methyl alcohol is present in solution. The formation of the ether MBFE in high yield is taken to indicate that this is a reaction of the singlet carbene. Thus, in this reaction it appears also that a ground-state triplet carbene gives a typical singlet carbene product. Related dilemmas have been resolved previously by proposing an equilibration between the singlet and triplet states of the carbene.^{2,9,19} The triplet sensitization reactions reported above strongly support such a process for BFL.

The Curie plot shows clearly that the ground state of BFL is the triplet. The sensitization by triplet benzil is presumed to generate this triplet carbene directly. If the singlet carbene were not formed from the triplet, then one might anticipate a different chemical outcome from sensitization than from direct irradiation. In fact, both the direct irradiation and the triplet-sensitized reactions give identical products, and moreover, these products are predominantly those believed to originate with ¹BFL. These facts are most comfortably rationalized by rapid (relative to reaction) equilibration of ¹BFL and ³BFL (Scheme I).

Our investigation of 3,6-dimethoxyfluorenylidene and of 9-xanthylidene¹¹ shows that these singlet carbenes react with alcohols with rates very close to the diffusion limit. If we assume that ¹BFL reacts with methyl alcohol (k_s^{MeOH}) at a rate no faster than the diffusion limit, then, from the measured rate constant for reaction ($k_{\text{MeOH}}^{\text{CH}_3\text{CN}}$), we can estimate K_{ST} , and thereby ΔG_{ST} , according to eq 7, which

$$(K_{\text{ST}}+1) = k_s^{\text{MeOH}}/k_{\text{MeOH}}^{\text{CH}_3\text{CN}} \quad (7)$$

corresponds to ΔG_{ST} less than or equal to 1.0 kcal/mol. These findings indicate that there is a substantial concentration of ¹BFL present in the carbene equilibrium mixture. Although there are several assumptions, explicitly stated, in this estimate of K_{ST} , the final conclusion is substantiated by examination of the stereochemistry of the α -methylstyrene cyclopropanation²³ reaction and the reaction of the carbene with cyclohexane.

In summary, all of the available evidence points to the reaction mechanism outlined in Scheme I. The key feature in this scheme is that equilibration of the carbene spin states is more rapid than reaction of either the ground-state triplet or excited singlet with trapping reagents. In this circumstance it is not possible to assign with certainty the optical absorption of BFL to a specific spin state of the carbene.

It is instructive to compare our estimates of ΔG_{ST} for FL and BFL with the theory developed by Gleiter and Hoffmann.²⁴ The similar geometry at the carbene carbon, indicated by the EPR spectra, eliminates one variable (the carbene-carbon bond angle) they identify as controlling ΔG_{ST} for methylene. The other important variables are the availability, occupancy, and energy of an orbital of proper symmetry for mixing with the *p*-type nonbonding carbene orbital.²⁴ For FL and BFL the aromatic π -system contains orbitals of proper symmetry for this mixing. One clear difference between FL and BFL is the relative energies of the occupied and unoccupied aromatic orbitals that mix with the carbene *p* orbital. The energy of singlet BFL is predicted to be lowered relative to the triplet by this mixing more than for FL. Just this effect is observed. The results show that the singlet-triplet gap of BFL is about one half of what it is for FL. These simple considerations can be used to understand the factors controlling the chemical and physical properties of all of the aromatic carbenes that have been studied.²⁵ This analysis is discussed in more detail in the related papers on bis(methoxy)fluorenylidene and xanthylidene.¹¹

Experimental Section

General Procedures. Proton magnetic resonance (¹H NMR) spectra were recorded on Varian Associates XL-200 (200 MHz) or HR220 (220 MHz) spectrometers operated in FT mode in deuteriochloroform (unless otherwise noted) with tetramethylsilane as an internal standard. Mass spectra were obtained with Finnegan-MAT 731 and CH5-DF mass spectrometers. Steady-state ultraviolet-visible (UV-vis) absorption spectra were recorded with a Perkin-Elmer Model 552 or Model Lambda 3 or Cary 14 spectrophotometer. Electron paramagnetic resonance (EPR) were recorded on a Varian Associates E-4 or Bruker X-band spectrometer equipped with an Oxford helium flow cryostat. Signal intensity is reported in arbitrary units. Elemental analyses were performed by the Analysis Laboratory, University of Illinois. The nanosecond and picosecond laser equipment has been described previously.^{1,26}

Materials. Acetonitrile (Aldrich Gold Label) was refluxed for 4–6 h over CaH₂ and distilled under nitrogen. 2-Methyltetrahydrofuran (Aldrich) was passed through a column of freshly activated neutral alumina (Wolem, activity grade I). All other solvents are commercially available and were used as received.

BDAF was prepared by oxidation of the corresponding hydrazone with use of either mercuric or silver oxide. The resulting solid was recrystallized from hexane or petroleum ether, giving red crystals, mp 138 °C. Anal. Calcd for C₁₇H₁₀N₂: C, 84.28; H, 4.16; N, 11.56. Found: C, 84.39; H, 4.26; N, 11.58.

Irradiation of BDAF in Cyclohexane. A solution of BDAF (2.4 × 10⁻³ M) in cyclohexane (20 mL) was purged with N₂ and irradiated in a Rayonet photoreactor with 350-nm lamps. After irradiation the solvent was evaporated under vacuum and the residue analyzed by ¹H NMR and GC/MS spectroscopy. The GC trace (3 ft, 5% OV-101 on Chromosorb W, column temperature 180–290 °C, 10 °C/min) shows four components with areas in the ratio of 1:4:11:4. Analysis of the mass spectrum of the minor component (retention time 2.89 min) reveals it to be 2,3-benzofluorene. The second component (retention time 4.27 min) is 11-benzofluorenone. The major component (retention time 7.36 min) is 11-cyclohexylbenzofluorene (CYBFL); MS (70 eV), *m/e* (relative abundance) 298 (23), 216 (62), 215 (100); molecular ion calcd for C₂₃H₂₂ *m/e* 298.1722, found 298.1723. The fourth component (retention time 16.25 min) is the dimer BBF; MS (70 eV), *m/e* (relative abundance) 430 (24), 215 (100); molecular ion calcd for C₃₄H₂₂ *m/e* 430.1722, found 430.1717. The ¹H NMR spectrum of the reaction mixture shows a doublet at δ 4.1 characteristic of CYBF and a singlet at δ 5.1 characteristic of BBF.

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The singlet at δ 4.09 characteristic of BFLH₂ cannot be detected.

In a similar experiment, BDAF was irradiated in a 1:1 (V:V) mixture of C₆H₁₂ and C₆D₁₂. The reaction mixture was analyzed by FI mass spectroscopy for incorporation of deuterium. The 2,3-benzofluorene was 9% monodeuterated, the CYBF derived from C₆H₁₂ showed no significant deuterium incorporation and the dimer BBF was 26% monodeuterated.

Irradiation of BDAF in Benzene Containing Methanol.

A solution of BDAF (1.3 mg, 5.3×10^{-3} mmol) in benzene (5 mL) containing methyl alcohol (2.5 M) was purged with N₂ and irradiated at 424 nm through an interference filter. When the reaction was complete (UV), the solvent and unreacted alcohol were removed under vacuum, and the residue was analyzed by mass and ¹H NMR spectroscopy. The NMR spectrum shows MBFE (90% by integration against hexamethylbenzene internal standard): (CDCl₃) δ 3.1 (s, 3 H), 5.8 (s, 1 H), 7.3-8.1 (m, 10 H); MS (70 eV), *m/e* (relative abundance) 246 (42), 231 (22), 215 (100); molecular ion calcd for C₁₈H₁₄O *m/e* 246.1045, found 246.1044.

Triplet-Sensitized Reaction of BDAF with Methanol.

Three samples of BDAF (all 1.0×10^{-3} M, 5 mL) in benzene were prepared, N₂ purged, and irradiated at 424 nm through an interference filter. Sample A contained only BDAF and methyl alcohol (2.5 M). Sample B contained BDAF, methyl alcohol, and benzil (3.6×10^{-2} M). Sample C contained BDAF, methyl alcohol, benzil, and anthracene (1.7×10^{-2} M). After 5 h of irradiation the solvent and unreacted alcohol were removed from the samples under vacuum and the residues analyzed by ¹H NMR spectroscopy with hexamethylbenzene as a standard for integration. The yield of MBFE in sample A was 80%, in sample B 92%, and in sample C 19%. Control experiments showed that there is no ether formation in the absence of light.

Direct Irradiation of BDAF in CH₃CN Containing α -Methylstyrene. An acetonitrile solution (5 mL) of α -methylstyrene (0.81 M) and BDAF (1.9×10^{-3} M) was purged with N₂ and irradiated in a Rayonet photoreactor with 350 nm lamps until the diazo compound was consumed (UV). The solvent and excess α -methylstyrene were removed under vacuum. The ¹H NMR

spectrum of the residue showed it to be a mixture of isomeric cyclopropanes formed in essentially quantitative yield as indicated by integration against *p*-dioxane as a standard; ¹H NMR (C₅D₅N) δ 2.45 (t, 1 H), 2.1 (q, 1 H), 1.75 (d, 3 H), 7.2-8.6 (m, 15 H);²⁷ MS (70 eV), *m/e* (relative abundance) 332 (83), 255 (6), 215 (51); molecular ion calcd for C₂₆H₂₀ *m/e* 332.1565, found 332.1570.

In an analogous experiment, (*E*)- β -deuterio- α -methylstyrene (1.76 M) was used and the stereochemistry of the cyclopropanation reaction was determined by ¹H NMR spectroscopy to be $77 \pm 13\%$ retention.

Triplet-Sensitized Photolysis of BDAF in CH₃CN Containing α -Methylstyrene. An acetonitrile solution (10 mL) of BDAF (2.0×10^{-3} M), α -methylstyrene (0.73 M) and benzil (6.6×10^{-2} M) was purged with N₂ and irradiated through a 424-nm interference filter. The solvent and unreacted styrene were removed under vacuum. The ¹H NMR spectrum of the residue revealed formation of the expected cyclopropane in greater than 80% yield.

In an analogous experiment, (*E*)- β -deuterio- α -methylstyrene (0.70 M) was used. The stereochemistry of the cyclopropanation reaction was found to be the same as in the direct irradiation.

Control experiments showed that benzil is not quenched significantly by the styrene at the concentrations used and that the styrene is not significantly isomerized under these conditions.

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(27) Residual α -methylstyrene and residual hydrogen in the deuterated solvents complicate integration of the aromatic region for this compound. Subtraction of the solvent contribution gives an aromatic proton count of 13 H.

Total Synthesis of (+)-Pipoxide and (+)- β -Senepoxide and Their Diene Precursors

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(2*R*)-*trans*-2,3-Diacetoxy-1-[(benzoyloxy)methyl]cyclohexa-4,6-diene (6), a diene precursor in the biosynthesis of highly oxygenated cyclohexane epoxides, has first been totally synthesized from the bromo lactone 16 derived from (1*S*)-*endo*-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (15), adapting the procedure formerly used for the preparation of racemic 6. Chemical conversions of 6 into the other dienes (10 and 13) and epoxides, (+)-pipoxide (4) and (+)- β -senepoxide (5), have also been achieved. The present syntheses constitute formal total synthesis of (-)-senepoxide (2), (-)-tingtanoxide (3), and (-)-zeylenol (14).

The plant metabolites (+)-crotepoxide (1),¹ (-)-senepoxide (2),² and (+)-pipoxide (4)³ belong to a family of highly oxygenated cyclohexane epoxides exhibiting interesting biological activity. Recent extensive work on plants

in the *Uvaria* genus^{4,5} has led to the discovery of intermediate, the "missing link", dienes 6, 10, and 13, which are key substances for elucidation of the biogenesis of the compounds of this class, and further added two new epoxides, (-)-tingtanoxide (3) and (+)- β -senepoxide (5), to

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(5) Kodopinid, M.; Sadavongvivad, C.; Thebtaranonth, C.; Thebtaranonth, Y. *Tetrahedron Lett.* 1983, 24, 2019. (-)-Senepoxide (2) was obtained, although in a small yield, by epoxidation of the diene 6. (-)-Tingtanoxide (3) was obtained by epoxidation of the diene 10.