Photorearrangements of Bridgehead-Aryl-Substituted Dibenzobarrelenes. Steady-State and Laser Flash Photolysis Studies[1]

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Examples of a novel di-π-methane rearrangement of 9-aryl-substituted dibenzobarrelenes containing 1,2-dibenzoylalkene moieties (1a–f) are presented. Steady-state irradiation of the dibenzobarrelenes 1a–f in benzene gives the regioselectively formed dibenzopentalenofurans, 5a–f, in excellent yields (74–90%). The structure of the bromo derivative 5f was confirmed through X-ray crystallographic analysis. Controlled irradiation of 1b, a representative example, at low temperatures suggests that the dibenzopentalenofurans (5a–f) are formed through the thermal isomerization of the corresponding dibenzosemibullvalenes 6a–f, which, in turn, arise through a di-π-methane type of rearrangement. Laser flash photolysis (337.1 nm) of 1a–f in benzene gives rise to transient phenomena, attributable to dibenzobarrelene triplets (ϕ^T = 0.2–0.5). These transients are characterized by broad and diffuse absorption spectra and possess short lifetimes (0.13–0.19 μs). They are readily quenched by oxygen, HTEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy), ferrocene, and β-carotene, with rate constants in the limit of diffusion control (10^8–10^{10} M^{-1} s^{-1}).

Introduction

In earlier studies,[3] we have shown that dibenzobarrelenes containing 1,2-dibenzoylalkene moieties undergo the di-π-methane rearrangement (Zimmerman rearrangement)[4,5] to give dibenzosemibullvalenes or dibenzocyclooctatetraenes and not the 1,2-dibenzoylalkene rearrangement, leading to ketene-derived products.[6] Further, it has been observed that the nature of the bridgehead substituent plays a major role on the observed regioselectivity of these rearrangements and that both electronic and steric factors are involved in deciding the regioselectivity. Thus, it has been observed that dibenzobarrelenes bearing methyl, methoxy, formyl, and acetoxy 9-bridgehead substituents gave, on irradiation, predominantly the 4b-substituted dibenzosemibullvalenes, whereas, 9-hydroxy- and 9-cyano-substituted dibenzobarrelenes gave the 8b-substituted dibenzosemibullvalenes or products derived from them.[3a,b] Similarly, the irradiation of 9-(hydroxymethyl)-,

9-ethyl-, and 9-benzyl-substituted dibenzobarrelenes gave 4b- or 8b-substituted dibenzosemibullvalenes or products derived thereof, whereas 9-cyclopentyl-substituted dibenzobarrelene upon irradiation gave the corresponding 4b-substituted dibenzosemibullvalene and dibenzocyclooctatetraene. On the other hand, the irradiation of 9-isopropyl- and 9-cyclohexyl-substituted dibenzobarrelenes gave exclusively the corresponding dibenzocyclooctatetraenes. In the present investigation we have examined the phototransformations of some 9-aryl-substituted dibenzobarrelenes, containing 1,2-dibenzoylalkene moieties, and studied the role of these substituents in deciding the regioselectivity of these rearrangements. We reasoned that if 9-aryl-substituted dibenzobarrelenes undergo the di-π-methane rearrangement, leading to the corresponding dibenzosemibullvalenes, both the 4b- and 8b-aryl-substituted products would be rather unstable due to steric considerations, and hence some interesting rearrangement could occur in these cases.

The substrates that we have examined in the present studies include: 11,12-dibenzoyl-9,10-dihydro-9-phenyl-9,10-ethenoanthracene (1a), 11,12-dibenzoyl-9,10-dihydro-9-p-tolyl-9,10-ethenoanthracene (1b), 9-p-anisyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1c), 9-(p-cyanophenyl)-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1d), 9-(p-chlorophenyl)-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1e), and 9-(p-bromophenyl)-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1f).

Results

1. Preparative Photochemistry and Product Identification.

The starting dibenzobarrelenes 1a–f were obtained in 78–88% yield through the reaction of the appropriate anthracenes with dibenzoylacetylene (DBA) in the presence of anhydrous aluminum chloride. They have been fully characterized by analytical results and spectral data.

Irradiation of 1a in benzene gave a 84% yield of a product, identified as the dibenzopentalenofuran 5a. Similarly, the irradiation of 1b–f in benzene gave the corresponding dibenzopentalenofurans, 5b–f (74–90%). The structures of 5a–f were arrived at on the basis of analytical results and spectral data. The ¹H NMR spectra

(1) Document No. NDRL-3123 from the Notre Dame Radiation Laboratory and No. RRLT-PRU-1 from the Regional Research Laboratory Trivandrum.

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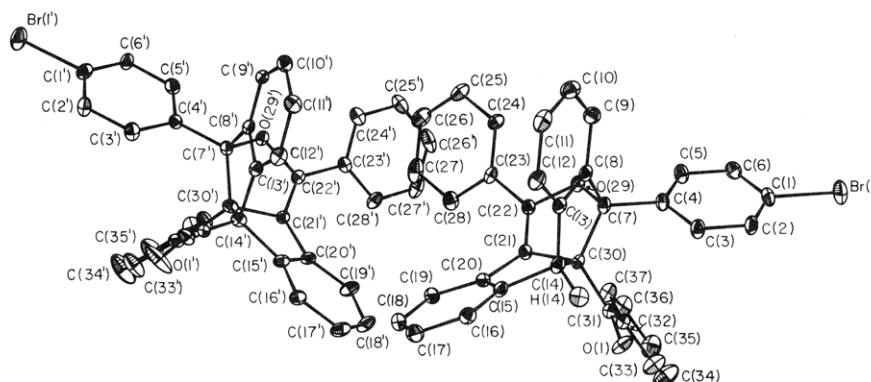
Figure 1. The ORTEP drawing of the structure of **5f**. The thermal ellipsoids are drawn at 50% probability.

Table I. Summary of Crystal Data and Intensity Collection Parameters for 5f ($BrO_2C_{36}H_{23}$)

formula	$BrO_2C_{36}H_{23}$
fw, amu	567.48
crystal dimensions, mm	$0.35 \times 0.35 \times 0.45$
space group	$P1$ bar
temperature, K	298
a, Å	9.253 (4)
b, Å	17.647 (6)
c, Å	18.540 (7)
α, deg	113.59 (3)
β, deg	102.10 (3)
γ, deg	90.43 (3)
V, Å^3	2698.6
Z	4
d_{calc}, g/cm^3 (298 K)	1.402
d_{obs}, g/cm^3 (298 K)	1.40
radiation	graphite monochromated Mo Kα (0.710 73 Å)
scan technique	$\theta - 2\theta$
maximum 2θ, deg	54.9
criterion for observed	$F_o > 3\sigma(F_o)$
data measured	13668
unique obsd data	4775
background	profile analysis
merging R value (I)	2.3%
final number of variables	712
μ(Mo Kα), mm^{-1}	1.536
R_1	0.064
R_2	0.065
goodness of fit	1.76

of these compounds, for example, showed a singlet due to one proton at δ 5.63–5.70, in each case, assigned to the 6b-proton. Similarly, the ^{13}C NMR spectra of these compounds showed characteristic signals at δ 55.61–55.78,

85.12–85.68, and 99.38–110.11, assigned to the sp^3 carbons at the 6b-, 10c-, and 10b-positions, respectively. In addition, they showed a single peak at δ 199.01–200.01 due to the carbonyl carbon, in each case.

2. X-ray Crystallographic Analysis of 5f. In view of the unusual structural features of the photoproducts **5a–f**, derived from **1a–f**, the structure of a representative example, namely, **5f**, was determined by a single-crystal X-ray diffraction study. The results are summarized in the ORTEP diagram shown in Figure 1. As is evident from Figure 1, two independent molecules are present in the asymmetric unit and the chemically equivalent atoms of these molecules are indicated by atom and atom′. A summary of crystal data and collection parameters for **5f** is given in Table I, whereas selected bond distances and bond angles are given in Table II.

3. Steady-State Photolysis of 1b at Subambient Temperature. In order to sort out whether the pentalenofurans **5a–f** arise through the thermal isomerization of the corresponding semibullvalenes **6a–f**, formed initially from the dibenzobarrelenes **1a–f**, we carried out the photolysis of **1b**, a representative example, at subambient temperatures. Irradiation of **1b** in benzene-d_6 for 10 min at ~15 °C gave a mixture of **6b** (71%) and **5b** (17%), along with some unchanged **1b** (12%). The product mixture was analyzed by ^{1}H NMR, following the bridgehead proton signals. The bridgehead protons in **1b** and **5b** in benzene-d_6 were observed at δ 5.47 and 6.01, respectively, whereas the signal of **5b** in CDCl$_3$ appeared at δ 5.62. The signal at δ 5.11 has been assigned to the bridgehead proton in **6b**, on the basis of literature precedences.[3,5c,7] On

Table II. Selected Bond Distances (Å) and Angles (deg) of 5f

	mol 1	mol 2		mol 1	mol 2
			Distances		
Br(1)–C(1)	1.895 (7)	1.906 (7)	O(1)–C(31)	1.217 (8)	1.187 (9)
O(29)–C(7)	1.475 (8)	1.455 (8)	O(29)–C(22)	1.398 (8)	1.388 (8)
C(7)–C(8)	1.51 (1)	1.55 (1)	C(7)–C(30)	1.55 (1)	1.538 (9)
C(13)–C(14)	1.49 (1)	1.50 (1)	C(14)–C(30)	1.58 (1)	1.539 (9)
C(15)–C(20)	1.41 (1)	1.43 (1)	C(20)–C(21)	1.47 (1)	1.478 (9)
C(21)–C(22)	1.32 (1)	1.332 (9)	C(21)–C(30)	1.538 (8)	1.52 (1)
C(30)–C(31)	1.50 (1)	1.56 (1)	C(31)–C(32)	1.50 (1)	1.52 (1)
			Angles		
C(7)–O(29)–C(22)	104.2 (5)	105.4 (4)	C(4)–C(7)–O(29)	106.7 (6)	108.3 (5)
C(4)–C(7)–C(30)	119.7 (6)	120.6 (6)	O(29)–C(7)–C(30)	104.9 (5)	106.1 (6)
O(29)–C(7)–C(8)	108.8 (5)	108.2 (5)	C(7)–C(8)–C(13)	112.2 (7)	109.3 (6)
C(13)–C(14)–C(15)	115.3 (6)	113.8 (6)	C(13)–C(14)–C(30)	102.7 (6)	101.8 (6)
C(15)–C(14)–C(30)	103.2 (6)	103.3 (6)	C(14)–C(15)–C(20)	109.7 (6)	110.0 (6)
C(15)–C(20)–C(21)	108.4 (6)	106.3 (6)	C(20)–C(21)–C(22)	135.3 (6)	135.6 (7)
C(20)–C(21)–C(30)	107.3 (6)	107.4 (6)	C(22)–C(21)–C(30)	108.6 (6)	109.7 (6)
C(21)–C(22)–O(29)	114.4 (6)	112.9 (6)	C(7)–C(30)–C(14)	106.9 (6)	110.4 (6)
C(7)–C(30)–C(31)	118.6 (6)	116.8 (6)	C(14)–C(30)–C(21)	100.0 (5)	102.1 (6)
C(30)–C(31)–C(32)	123.1 (6)	123.6 (7)	C(31)–C(32)–C(37)	126.5 (7)	125.5 (7)

Table III. Photophysical Properties of Dibenzobarrelene Triplets in Benzene at 295 K

substrate (9-C_6H_4X-p)	$\lambda_{mon}^{T,a}$ nm	$\epsilon_{max}^{T,b}$ 10^3 M^{-1} cm^{-1}	$\phi^{T\,b}$	$\tau^{T,c}$ μs	$k_q^{T,c}$ 10^9 M^{-1} s^{-1}			
					O_2	HTEMPO^d	ferrocene	β-carotene
1a (X = H)	460	5.8	0.3	0.19	0.29	0.19	2.4	5.2
1b (X = CH$_3$)	440	3.9	0.4	0.18	1.0	0.11	3.1	3.8
1c (X = OCH$_3$)	440	4.8	0.2	0.13	0.91	0.14	4.1	8.5
1d (X = CN)	460	4.1	0.5	0.23	0.68	0.17	3.2	5.8
1e (X = Cl)	460	4.2	0.4	0.18	0.96	0.16	3.3	6.0
1f (X = Br)	460	5.4	0.3	0.19	0.39	0.14	3.8	8.3

^{a}These are the wavelengths where the triplets were monitored. $^b\pm30\%$; the monitoring wavelengths are in column 2. $^c\pm15\%$. ^{d}HTEMPO: 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy.

keeping the irradiated mixture at ~4 °C in the dark for 30 h, there was an increase in the yield of **5b** (38%) at the expense of **6b** (52%), while there was very little change in the composition of **1b** (10%). On the other hand, when the irradiation of **1b** in benzene-d_6 was carried out for 1 h at ~15 °C, the product mixture consisted entirely of **5b** (15%) and **6b** (85%). However, when this mixture was kept in the dark at ~25 °C for 4 h, none of the semibullvalene **6b** was observed; the product consisted exclusively of **5b**. These experiments clearly illustrate that the semibullvalene **6b** is the primary photoproduct of **1b**, which undergoes thermal isomerization at room temperature to give the pentalenofuran **5b**.

4. Laser Flash Photolysis Studies. The barrelene–semibullvalene rearrangement is recognized to be a process occurring from the triplet state.[4] In order to characterize the triplets of the substrates under study, these were subjected to laser flash photolysis studies based on 337.1-nm excitation. Upon laser pulse excitation (337.1 nm), benzene solutions of **1a–f** produce short-lived transients characterized by broad and diffuse absorption spectra. Representative spectra and decay kinetics in three cases are presented in Figure 2. For none of the substrates **1a–f** could well-defined absorption maxima be discerned at the spectral region monitored (360–700 nm). Following the decay of the transients by clean first-order kinetics, no significant residual absorptions could be observed (see spectra A', B', and C' in Figure 2). The decay lifetimes of the short-lived transients were found to be in the submicrosecond domain and were essentially independent of monitoring wavelengths.

From their quenching behaviors toward oxygen, 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO, stable free radical) and ferrocene as well as the fact that the formation of β-carotene triplet was sensitized when **1a–f** were flash photolyzed in the presence of millimolar β-carotene, the observed transients were assigned as triplets. The triplet lifetimes (τ^T), triplet yields (ϕ^T) and bimolecular quenching rate constants (k_q^T), measured by methods described in earlier papers,[3] are compiled in Table III.

When considered in the light of the mechanism in Scheme I and in the context of the data we previously reported on other dibenzobarrelenes,[3] the following three points deserve special mention. First, the triplet yields (ϕ^T) for the present series are relatively low (0.2–0.5). The presence of the heavy atom, bromine, in **1f** has no effect on the intersystem crossing efficiency. Second, the triplet lifetimes (τ^T) are relatively short (0.13–0.23 μs), suggesting the reactive nature of the triplets. Third, the lack of long-lived residual absorptions in the case of the present systems signifies that the biradical entities proposed in Scheme I are short-lived and/or weakly absorbing in the
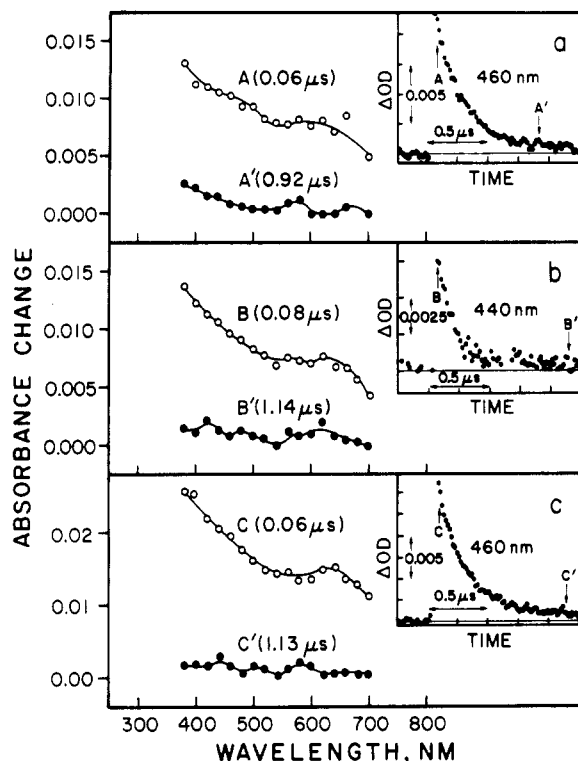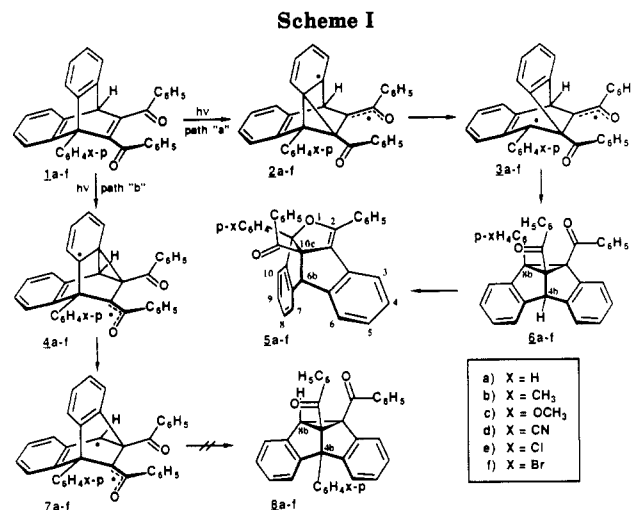
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Figure 2. Transient absorption spectra at the indicated times following 337.1-nm laser excitation of (A, A') **1a**, (B, B') **1c**, and (C, C') **1d** in deaerated benzene (absorbances of solutions $\simeq$ 0.4 in 2-mm cells at 337.1 nm). Insets: kinetic traces for transient absorption decay at the indicated wavelengths, as observed for (a) **1a**, (b) **1c**, and (c) **1d**.

Scheme I

spectral region of our observation.

Discussion

The formation of the photoproducts **5a–f** from the di-

benzobarrelenes **1a–f** can be understood in terms of the pathways shown in Scheme I. In tune with the earlier reported mechanism for the barrelene rearrangement,[8] it is assumed that the initial step involves a benzo-vinyl bridging of the excited state, leading to the diradical species **2a–f** and **4a–f**, arising through paths "a" and "b", respectively. These diradicals could undergo subsequent transformation to give two new sets of diradical species **3a–f** and **7a–f**, which would be the precursors of the expected 8b-aryl-substituted dibenzosemibullvalenes **6a–f** and the 4b-aryl-substituted dibenzosemibullvalenes **8a–f**, respectively. The fact that the dibenzopentalenofurans **5a–f** are formed exclusively (74–90%) from **1a–f** would suggest that path "a" involving the diradical species **3a–f** is the preferred mode of transformation. This would be expected in terms of the relative stabilities of **3a–f**, having the radical center on the carbon, bearing the aryl substituent, as compared to the other diradical species **7a–f**. It appears that the 8b-aryl-substituents in the dibenzosemibullvalenes **6a–f** would greatly destabilize the cyclopropane ring due to steric crowding, and hence they facilitate the ring opening reaction to give the observed dibenzopentalenofurans **5a–f**.

In conclusion, it may be pointed out that the photorearrangements of **1a–f**, leading to the formation of **5a–f**, appears to be a novel variation of the di-π-methane rearrangement. These examples vividly illustrate the role of steric effects in deciding the regioselectivity in di-π-methane rearrangements.

Experimental Section

The equipment and procedures for melting point determination and spectral recording are described in earlier papers.[3] The ^{13}C NMR spectra were recorded on a Nicolet/Oxford NT-300 NMR spectrometer and the mass spectra were recorded on a Hitachi RMU-6E single-focusing mass spectrometer or a Finnigan MAT Model 8430 mass spectrometer. All steady-state irradiations were carried out in a Srinivasan-Griffin-Rayonet Photochemical Reactor (RPR 3000Å). Low-temperature irradiations were carried out in a Merry-go-Round apparatus by using a Hanovia 450-W medium-pressure mercury lamp in a Pyrex-jacketed immersion well. Solvents for steady-state photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies.

Starting Materials. Dibenzoylacetylene (DBA),[9] mp 110–111 °C, 9-phenylanthracene,[10] mp 151–153 °C, 9-*p*-tolylanthracene,[11] mp 144–145 °C, 9-anisylanthracene,[11] mp 166–167 °C, 9-(*p*-cyanophenyl)anthracene,[12] mp 178–179 °C, 9-(*p*-chlorophenyl)-anthracene,[11] mp 179–180 °C, and 9-(*p*-bromophenyl)anthracene,[12] mp 176–178 °C were prepared by known procedures. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of 9-Aryl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes (1a–f). The dibenzobarrelenes **1a–f** were prepared by treating an equimolar mixture of the appropriate anthracene and anhydrous aluminum chloride with DBA in chloroform at 0–5 °C. After stirring for 1 h, the mixture was poured over crushed ice, acidified with dilute hydrochloride acid, and extracted with chloroform. The chloroform layer was washed with water and dried over anhydrous magnesium sulfate. The solvent was then removed under vacuum to give the crude **1a–f**, which were purified by recrystallization from a mixture (1:1) of chloroform and methanol.

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1a (88%): mp 259–260 °C; IR ν_{max} (KBr) 3030, 3020 (CH), 1650 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 255 nm (ϵ 22150); ^{1}H NMR (CDCl$_3$) δ 5.48 (1 H, s, bridgehead), 7.40 (23 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 54.30 (>C-H), 64.00 (>C<), 123.67–155.61 (aromatic), 194.65 (C=O), 195.59 (C=O). Anal. Calcd for C$_{36}$H$_{24}$O$_2$: C, 88.52; H, 4.91. Found: C, 88.34; H, 4.67.

1b (83%): mp 249–250 °C; IR ν_{max} (KBr) 3040, 3010 (CH), 1640 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 255 nm (ϵ 17150); ^{1}H NMR (CDCl$_3$) δ 2.40 (3 H, s, CH$_3$), 5.4 (1 H, s, bridgehead), 7.20 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 20.98 (CH$_3$), 54.24 (>C-H), 63.76 (>C<), 123.61–155.40 (aromatic), 194.62 (C=O), 195.68 (C=O). Anal. Calcd for C$_{37}$H$_{26}$O$_2$: C, 88.44; H, 5.18. Found: C, 88.06; H, 5.43.

1c (83%): mp 223–224 °C; IR ν_{max} (KBr) 3060, 3030 (CH), 1640 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 226 (ϵ 24290, sh), 255 nm (19280); ^{1}H NMR (CDCl$_3$) δ 3.82 (3 H, s, OCH$_3$), 5.45 (1 H, s, bridgehead), 7.25 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 54.22 (>C-H), 55.20 (OCH$_3$), 63.38 (>C<), 113.58 (C ortho to OCH$_3$), 123.65–158.30 (aromatic), 194.61 (C=O), 195.83 (C=O). Anal. Calcd for C$_{37}$H$_{26}$O$_3$: C, 85.71; H, 5.01. Found: C, 85.98; H, 5.44.

1d (78%): mp 259–260 °C; IR ν_{max} (KBr) 3060, 3040 (CH), 2230 (C≡N), 1650 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 223 (ϵ 30090), 254 nm (21280); ^{1}H NMR (CDCl$_3$) δ 5.48 (1 H, s, bridgehead), 7.45 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 54.34 (>C-H), 63.68 (>C<), 111.20 (C ortho to CN), 118.47 (C≡N), 124.03–156.37 (aromatic), 194.38 (C=O), 194.97 (C=O). Anal. Calcd for C$_{37}$H$_{23}$O$_2$: C, 86.55; H, 4.48; N, 2.73. Found: C, 86.09; H, 4.22; N, 2.38.

1e (79%): mp 241–242 °C; IR ν_{max} (KBr) 3050, 3020 (CH), 1640 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 255 nm (ϵ 19260); ^{1}H NMR (CDCl$_3$) δ 5.35 (1 H, s, bridgehead), 7.38 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 54.27 (>C-H), 63.39 (>C<), 123.80–155.78 (aromatic), 194.48 (C=O), 195.42 (C=O). Anal. Calcd for C$_{36}$H$_{23}$O$_2$Cl: C, 82.76; H, 4.41. Found: C, 82.31; H, 4.07.

1f (84%): mp 234–235 °C; IR ν_{max} (KBr) 3050, 3020 (CH), 1645 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 228 (ϵ 24520, sh), 255 mm (20870); ^{1}H NMR (CDCl$_3$) δ 5.58 (1 H, s, bridgehead), 7.57 (22 H, m, aromatic). Anal. Calcd for C$_{36}$H$_{23}$O$_2$Br: C, 76.19; H, 4.06. Found: C, 76.56; H, 4.42.

Irradiation of the Dibenzobarrelenes 1a–f. A general procedure was to irradiate a solution of the appropriate dibenzobarrelene (1 mmol) in benzene (175 mL) for 2 h and remove the solvent under vacuum. The residual solid, in each case, was recrystallized from a mixture (1:1) of chloroform and methanol to give the photoproducts **5a–f**.

Irradiation of 1a. Compound **5a** was obtained in a 84% yield: mp 240–241 °C; IR ν_{max} (KBr) 3050, 3020 (CH), 1650 (C=O), and 1630 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 236 (ϵ 17960, sh), 300 (6870, sh), 318 (7790), 352 mm (3430); ^{1}H NMR (CDCl$_3$) δ 5.64 (1 H, s, >C-H), 7.40 (23 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 55.65 (>C-H), 85.39 (>C<), 110.11 (>C-O), 121.22–152.33 aromatic), 199.58 (C=O); mass spectrum, *m/e* (rel intensity) 488 (M$^+$, 10), 383 (M$^+$ – COC$_6$H$_5$, 4), 382 (M$^+$ – COC$_6$H$_5$, – H, 100), 365 (17), 354 (39), 277 (43), 275 (36) and 105 (COC$_6$H$_5$$^+$, 84) and other peaks. Anal. Calcd for C$_{36}$H$_{24}$O$_2$: C, 88.52; H, 4.92. Found: C, 88.96; H, 5.32.

In repeat runs, **1a** was irradiated in methanol and acetone to give **5a** in 84% and 78% yields, respectively.

Irradiation of 1b. Compound **5b** was obtained in a 90% yield: mp 204–205 °C; IR ν_{max} (KBr) 3040, 3010, 2920, and 2910 (CH), 1650 (C=O), 1625 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 220 (ϵ 38740, sh), 300 (8590, sh), 320 (10050), 350 nm (4610); ^{1}H NMR (CDCl$_3$) δ 2.21 (3 H, s, CH$_3$), 5.63 (1 H, s, CH), 7.52 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 21.00 (CH$_3$), 55.78 (>C-H), 85.36 (>C<), 100.36 (>C-O), 121.16–152.44 (aromatic), 200.01 (C=O); mass spectrum, *m/e* (rel intensity) 502 (M$^+$, 7), 487 (M$^+$ – CH$_3$, 3), 397 (M$^+$ – COC$_6$H$_5$, 12), 385 (21), 384 (99), 383 (100), 355 (94), 277 (94), 275 (84), 105 (C$_6$H$_5$CO$^+$, 97), and other peaks. Anal. Calcd for C$_{37}$H$_{26}$O$_2$: C, 88.45; H, 5.18. Found: C, 88.14; H, 4.83.

Low-Temperature Irradiation of 1b. A solution of **1b** in degassed benzene-d_6 (~10 mg in 1 mL; ~0.02 M) was divided into equal halves, which were transferred to two NMR tubes. One of these was irradiated at ~15 °C for 10 min and its ^{1}H NMR spectrum was recorded. Integration of the bridgehead methine peak positions revealed that the product mixture consisted of 71% of °**6b** and 17% of **5b**, along with 12% of unchanged **1b**. This

mixture was kept in the dark at ~4 °C for 30 h to give 52% of **6b** and 38% of **5b**, along with 10% of **1b**.

The second tube containing **1b** in benzene-d_6 was irradiated at ~15 °C for 1 h to give a mixture of 85% of **6b** and 15% of **5b**. Keeping the irradiated solution at ~25 °C for 4 h resulted in the complete conversion of **6b** to **5b**.

Irradiation of 1c. Compound **5c** was obtained in a 89% yield: mp 168–169 °C; IR ν_{max} (KBr) 3050, 3030, 2920, and 2820 (CH), 1650 (C=O), 1630 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 230 (ϵ 38 010), 300 (9110, sh), 320 (10 490), 352 nm (4450); ^{1}H NMR (CDCl$_3$) δ 3.70 (3 H, s, OCH$_3$), 5.63 (1 H, s, CH), 7.60 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 54.91 (OCH$_3$), 55.61 (>C-H), 85.12 (>C<), 100.13 (>C-O), 113.20 (C ortho to OCH$_3$), 121.18–158.77 (aromatic), 199.87 (C=O). Anal. Calcd for C$_{37}$H$_{26}$O$_3$: C, 85.71; H, 5.02. Found: C, 85.36; H, 4.68.

Irradiation of 1d. Compound **5d** was obtained in a 84% yield: mp 223–224 °C; IR ν_{max} (KBr) 3040 (CH), 2220 (C≡N), 1650 (C=C), 1630 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 237 (ϵ 44 570), 300 (9020, sh), 329 (10 220), 350 nm (4430); ^{1}H NMR (CDCl$_3$) δ 5.65 (1 H, s, CH), 7.56 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 55.74 (CH), 85.68 (>C<), 99.38 (>C-O), 111.51 (C ortho to CN), 118.51 (C≡N), 121.44–152.28 (aromatic), 199.01 (C=O); mass spectrum, m/e (rel intensity) 513 (M$^+$, 9) 408 (M$^+$ – COC$_6$H$_5$, 20), 380 (10), 303 (8), 301 (8), 105 (C$_6$H$_5$CO$^+$, 100) and other peaks. Anal. Calcd for C$_{37}$H$_{23}$O$_2$N: C, 86.55; H, 4.48; N, 2.73. Found: C, 86.87; H, 4.02; N, 3.13.

Irradiation of 1e. Compound **5e** was obtained in a 74% yield: mp 207–208 °C; IR ν_{max} (KBr) 3020 and 3008 (CH), 1655 (C=O), 1635 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 222 (ϵ 39 050), 299 (8540, sh), 320 (9940), 350 nm (4250); ^{1}H NMR (CDCl$_3$) δ 5.67 (1 H, s, CH), 7.54 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 55.78 (>C-H), 121.37, 123.32–149.48 (aromatic), 199.59 (C=O); mass spectrum, m/e (rel intensity) 522 (M$^+$, 14), 419 (20), 418 (19), 417 (M$^+$ – COC$_6$H$_5$, 50), 389 (16), 352 (4), 314 (7), 312 (18), 105 (C$_6$H$_5$CO$^+$, 100), and other peaks. Anal. Calcd for C$_{36}$H$_{23}$O$_2$Cl: C, 82.76; H, 4.41. Found: C, 82.98; H, 4.44.

Irradiation of 1f. Compound **5f** was obtained in a 86% yield: mp 216–217 °C; IR ν_{max} (KBr) 3040 and 3020 (CH), 1640 (C=O) cm^{-1}; UV λ_{max} (CH$_3$OH) 226 (ϵ 38 390), 300 (8800, sh), 320 (10 210), 349 nm (4420); ^{1}H NMR (CDCl$_3$) δ 5.70 (1 H, s, CH), 7.55 (22 H, m, aromatic); ^{13}C NMR (CDCl$_3$) δ 55.73 (CH), 85.40 (>C<), 99.75 (>C-O), 115.23, 121.34–152.31 (aromatic), 199.57 (C=O); mass spectrum, m/e (rel intensity) 461 (M$^+$ – COC$_6$H$_5$, 72), 435 (16), 433 (18), 362 (18), 277 (50), 105 (C$_6$H$_5$CO$^+$, 100), and other peaks. Anal. Calcd for C$_{36}$H$_{23}$O$_2$Br: C, 76.19; H, 4.06. Found: C, 75.74; H, 4.41.

X-ray Structure Determination of 5f. A colorless rectangular crystal of **5f** having approximate dimensions 0.35 × 0.35 × 0.45 mm was mounted on a glass fiber in random orientation. Preliminary examination was carried out with Mo Kα radiation (λ = 0.710 73 Å) on a Kappa geometry automated Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal incident beam monochromator. Final cell constants were obtained by least-squares refinement of 25 reflections (24° < 2θ < 30°) measured by the computer-controlled diagonal slit method of centering. Final cell parameters are given in Table I. Experimental density was measured by flotation method using a mixture of solvents (CCl$_4$/hexane). Observed density was found to be 1.40 g/cm^3. The data were collected at 298 K using $\theta/2\theta$ scan technique at a variable scan rate to a 2θ maximum of 54.9°. The scan range was determined as a function of θ. The scan width was calculated as: ω scan width = 0.8 × 0.350 × (tan θ). Moving-crystal moving-counter background counts were made by scanning an additional 25% above and below this range.

A total of 13668 reflections ($+h,\pm k,\pm l$) were measured of which 4775 were unique observed reflections (F_o > 3σF_o). As a check on the crystal stability, four representative reflections were measured every 60 min of X-ray exposure. As the intensity of these standards remained constant within experimental error, no decay correction was applied. Orientation of three reflections were monitored every 250 reflections, and a new orientation matrix was calculated by centering the 25 reflections if the angular variation was > 0.10°.

Data reduction was carried out by the profile analysis software of R. H. Blessing.[13] No absorption correction was applied to the data.

The structure was solved by Patterson methods using SHELXS[14] in space group P1 bar. A complete structure of two independent molecules containing 78 non-hydrogen atoms were located from the SHELXS solution. After several cycles of least-squares refinement, all the hydrogen atom positions were revealed from the difference Fourier map. However, due to lack of sufficient data and as the hydrogen atoms other than the hydrogens bonded to C(14) were of no particular interest, only H(14) and H(14') were refined isotropically. All the other hydrogen atom positions were included in their idealized positions (calculated) in the final refinement and were held fixed. The non-hydrogen atoms were refined anisotropically, whereas, only two hydrogen atom positional parameters and isotropic thermal parameters were refined to convergence. The final difference Fourier was featureless and the highest peak had height of 0.60 e/Å^3.

Atomic form factors used were taken from Cromer and Mann.[15] Anomalous dispersion effects were included in F_c for Br. The values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[16] The final refinement included 712 variables. The converged model had unweighted (R_1) and weighted (R_2) agreement factor of 0.064 and 0.065,[17] respectively.

Laser Flash Photolysis. The laser pulse excitation was carried out in a front-face geometry with 337.1-nm laser pulses (8 ns, 2–3 mJ) from a Molectron UV-400 nitrogen laser source. The kinetic spectrophotometer and the data collection system are described elsewhere.[18,19] For transient spectra, a flow cell was used. Deoxygenation of solutions was effected by saturation with argon.

Registry No. **1a**, 124562-59-0; **1b**, 124562-60-3; **1c**, 124562-61-4; **1d**, 124562-62-5; **1e**, 124562-63-6; **1f**, 124562-64-7; **5a**, 124562-65-8; **5b**, 124562-66-9; **5c**, 124562-67-0; **5d**, 124562-68-1; **5e**, 124562-69-2; **5f**, 124562-70-5; **6b**, 124562-71-6; DBA, 1087-09-8; HTEMPO, 2226-96-2; O$_2$, 7782-44-7; 9-phenylanthracene, 602-55-1; 9-*p*-tolylanthracene, 23674-14-8; 9-(*p*-methoxyphenyl)anthracene, 23674-15-9; 9-(*p*-cyanophenyl)anthracene, 56164-85-3; 9-(*p*-chlorophenyl)anthracene, 23674-16-0; 9-(*p*-bromophenyl)-anthracene, 24672-71-7; ferrocene, 102-54-5; β-carotene, 7235-40-7.

Supplementary Material Available: A complete list of bond distances and bond angles, tables of positional parameters and anisotropic thermal parameters of the refined atoms, and a table of fractional coordinates and isotropic thermal parameters of fixed atoms (H's) (13 pages); list of structure factors (F_{obs} and F_{cal}) (22 pages). Ordering information is given on any current masthead page.

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