Phototransformations of Bridgehead-Disubstituted Dibenzobarrelenes. Interesting Rearrangements of Dibenzosemibullvalene Intermediates Derived from 9-(Hydroxyalkyl)-10-methoxy-Substituted Dibenzobarrelenes[1]

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Received November 20, 1995[⊗]

The photochemistry of 11,12-dibenzoyl-9,10-dihydro-9-(hydroxymethyl)-10-methoxy-9,10-ethenoanthracene (**7a**) and 11,12-dibenzoyl-9,10-dihydro-9-(1-hydroxyethyl)-10-methoxy-9,10-ethenoanthracene (**7b**) has been studied through steady-state photolysis, product analysis, and laser flash photolysis. Irradiation of **7a** in benzene, methanol, or acetone gave 69−72% yields of a dibenzopentalene ketone **11a**, arising through a dibenzosemibullvalene precursor. Irradiation of **7b**, which exists in equilibrium with its cyclic form **7b′**, gave a mixture of the dibenzopentalene ketone **11b** (41%) and the dibenzopentalenopyran derivative, **16b′** (26%). The photochemistry of 11,12-dibenzoyl-9,10-dihydro-9,10-dimethoxy-9,10-ethenoanthracene (**17**) has been reinvestigated. Irradiation of **17** in benzene and methanol gives a 90% yield of an isomeric pentacyclic product **24**, formed through the rearrangement of a dibenzosemibullvalene precursor. Irradiation of **17** in aqueous methanol gives a mixture of the dibenzopentalene ketone **22** (40%) and a pentacyclic methanol adduct **21** (34%). The structures of **7b′**, **11a,b, 16b′**, **21**, and **24** were confirmed through X-ray crystallographic analysis. The 308 nm laser flash photolysis of **7a,b** in benzene results in the formation of their triplets ($\phi^{T} = 0.55-0.76$). These triplets possess short lifetimes (0.45−0.75 μs) and are quenched by oxygen, 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO), 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (HTEMPO), ferrocene, and β-carotene at rates in the range $(0.26-4.7) \times 10^{9}\ M^{-1}\ s^{-1}$.

Introduction

Several aspects of the phototransformations of dibenzobarrelenes are reported in the literature.[3] In general, they undergo photorearrangement, leading primarily to dibenzocyclooctatetraenes and dibenzosemibullvalenes. It has been suggested that the dibenzocyclooctatetraenes are formed through a singlet state pathway, involving a [2 + 2] cycloaddition (phenyl−vinyl bridging), followed by further rearrangements, whereas the dibenzosemibullvalenes arise through triplet state mediated pathways.[4] In an earlier publication,[5] we had reported that a bridgehead disubstituted dibenzobarrelene such as 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (**1**) on photolysis gives a mixture of products consisting of a dibenzocyclooctatetraene **2** and a dibenzopentalene derivative **3**, in addition to an oxygenated hexacyclic peroxy carbinol **4**, formed through the oxygen trapping of diradical intermediates (Scheme 1). The formation of the dibenzocyclooctatetraene **2** with C_2 symmetry and the dibenzopentalene derivative **3** has been rationalized on the basis of a tri-π-methane pathway[6] and involving 1,4-diradical intermediates. In contrast, the phototransformations of an analogous bridgehead disubstituted dibenzobarrelene, namely 11,12-dibenzoyl-9,10-dihydro-9-(hydroxymethyl)-10-methyl-9,10-ethenoanthracene (**5**), resulted in the formation of an oxadibenzopropallane carbinol **6** exclusively, arising through a dibenzosemibullvalene precursor[7] (Scheme 2). The objective of the present investigation has been to study the photochemistry of two dibenzobarrelenes with unsymmetrical bridgehead substituents such as hydroxyalkyl and methoxy groups with a view to examining the nature of the products formed in these cases. Further, we wanted to examine whether the dibenzosemibullvalenes, formed in these reactions as primary prod-

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[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

[1] Contribution No. NDRL-3616 from the Notre Dame Radiation Laboratory and No. RRLT-PRU-32 from the Regional Research Laboratory (CSIR), Trivandrum.

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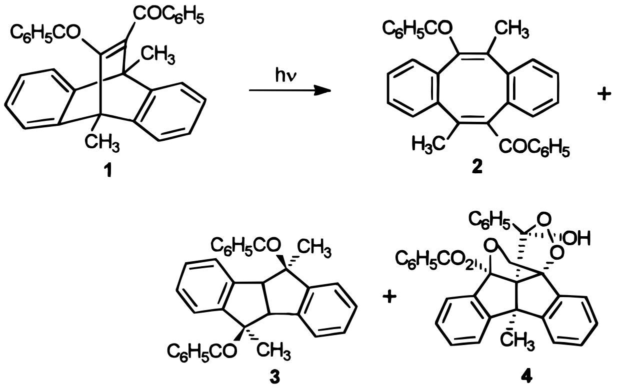
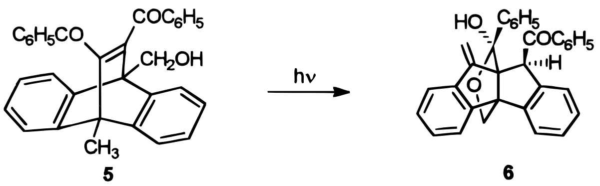
S0022-3263(95)02046-9 CCC: $12.00

Scheme 1



Scheme 2



ucts, having trisubstituted cyclopropyl ketone functionalities, would undergo subsequent rearrnagements, leading to different secondary products. Also, it was of interest to examine the nature of the transients involved in these cases through nanosecond laser flash photolysis studies.

The substrates that we have examined are 11,12-dibenzoyl-9,10-dihydro-9-(hydroxymethyl)-10-methoxy-9,10-ethenoanthracene (**7a**) and 11,12-dibenzoyl-9,10-dihydro-9-(1-hydroxyethyl)-10-methoxy-9,10-ethenoanthracene (**7b**). In addition, the photochemistry of 11,12-dibenzoyl-9,10-dihydro-9,10-dimethoxy-9,10-ethenoanthracene (**17**) has been reexamined.

Results

1. Steady-State Photolysis and Product Identification. The starting dibenzobarrelenes **7a,b** were obtained in 70−80% yields by the reaction of the appropriate anthracenes with DBA in refluxing xylene, whereas **17** was prepared as per a reported procedure.[8] In the case of **7b**, the ^{1}H NMR spectrum showed the presence of an isomeric cyclic carbinol **7b′**, formed through the interaction of the hydroxyethyl substituent at the C-9 position with the benzoyl group at the C-12 position. Both **7b** and **7b′** exist in equilibrium in solution. The IR spectrum of **7b** in KBr showed a single absorption for hydroxyl group at 3448 cm^{-1}, whereas in chloroform solution it showed two peaks at 3560 and 3448 cm^{-1} due to **7b′** and **7b**, respectively. Further, the equilibrium between **7b** and **7b′** has been found to be solvent dependent, which has been confirmed by ^{1}H NMR analysis. The methyl protons of **7b** and **7b′** in $CDCl_3$, for example, appear as two distinct doublets, centered at δ 1.65 (J = 7 Hz) and 2.35 (J = 7.5 Hz), respectively. The methoxy protons appeared as two distinct singlets at δ 3.60 and 3.68, and the hydroxyl protons appeared as singlets at 3.30 and 3.71, which are exchangeable with D_2O. The methine protons appeared as quartets at δ 5.50 and 5.85. Similarly, the ^{13}C NMR spectrum revealed that the methyl carbons of **7b** and **7b′** in $CDCl_3$ appear at 16.76 and 22.10 and the methoxy carbons at δ 56.47 and 57.10, respectively.

On the basis of ^{1}H NMR analysis in various deuterated solvents, it was found that the ratio of **7b** and **7b′** is 2:1 in C_6D_6, 1:1 in $CDCl_3$ and CD_3CN, and 1:2 in C_5D_5N, CD_3OD, and DMSO-d_6, thereby indicating that in less polar solvents it exists predominantly in the open form (**7b**), whereas in more polar solvents the cyclic carbinol (**7b′**) is preferred. The structure of the cyclic carbinol **7b′** was unambiguously proved through X-ray crystallographic analysis.[9]

Irradiation of **7a** in benzene, methanol, or acetone gave 69−72% yields of **11a** (Scheme 3). Irradiation of **7b** in benzene, on the other hand, gave a mixture of products consisting of **11b** (41%) and **16b′** (26%). In order to examine the effect of the equilibrium ratio between **7b** and **7b′** on product formation, we have carried out the photolysis at ambient temperature in both $CDCl_3$ and C_6D_6 and monitored the progress of the reaction in each case by ^{1}H NMR. Irradiation of **7b** in $CDCl_3$, where it exists in equilibrium with **7b′** in a 1:1 ratio, for 1 h resulted in a mixture of **11b** (50%) and **16b′** (28%), along with 22% of the unreacted starting mixture as analyzed by ^{1}H NMR, following the methyl and methoxy protons. Thus, for example, the methyl protons of **11b** in $CDCl_3$ appeared as a doublet at δ 1.25 (J = 7 Hz), whereas in **16b′** they appeared as a singlet at δ 2.45. In addition, the methanol formed in the reaction could be detected through the presence of a singlet at δ 3.45, roughly equal to the yield of **11b**. Similarly, when the irradiation of **7b** was carried out in C_6D_6, where it exists in equilibrium with **7b′** in the ratio of 2:1, for 1 h and the reaction mixture analyzed by ^{1}H NMR the presence of **11b** and **16b′** in nearly a 2:1 ratio was revealed. The structures of the photoproducts **11a,b** and **16b′** were confirmed through X-ray crystal structure determination.[9]

In view of the formation of the demethylated dibenzopentalene ketones **11a,b** from the methoxy-substituted dibenzobarrelenes **7a,b,** respectively, we have reexamined the phototransformation of the 9,10-dimethoxydibenzobarrelene **17**. We had reported earlier[8] that the irradiation of **17** in methanol, benzene, or acetone gave good yields of the dibenzosemibullvalene **20** (Scheme 4). A careful reexamination of the structure of the photoproduct (90%) formed in a mixture (4:1) of methanol and benzene from **17** through X-ray crystallographic analysis[9] reveals that it is correctly represented as the dibenzopentalenofuran derivative **24**. When the photolysis of **17**, however, was carried out in a mixture of benzene and aqueous methanol, a mixture of products consisting of the pentacyclic methanol adduct **21** (34%) and the dibenzopentalene ketone **22** (40%) was formed. The structures of **21** and **22** were based on analytical results and spectral data. Further confirmation of the structure of **21** was derived through X-ray crystallographic analysis.[9]

To examine whether **21** is formed through the addition of methanol to **24**, we have irradiated a solution of **24** in methanol and have observed that none of **21** is formed under analogous reaction conditions. When the irradiation of **24** was carried out in methanol containing a small amount of hydrochloric acid, none of **21** could be observed; instead, a complex mixture of products resulted, as revealed by ^{1}H NMR.

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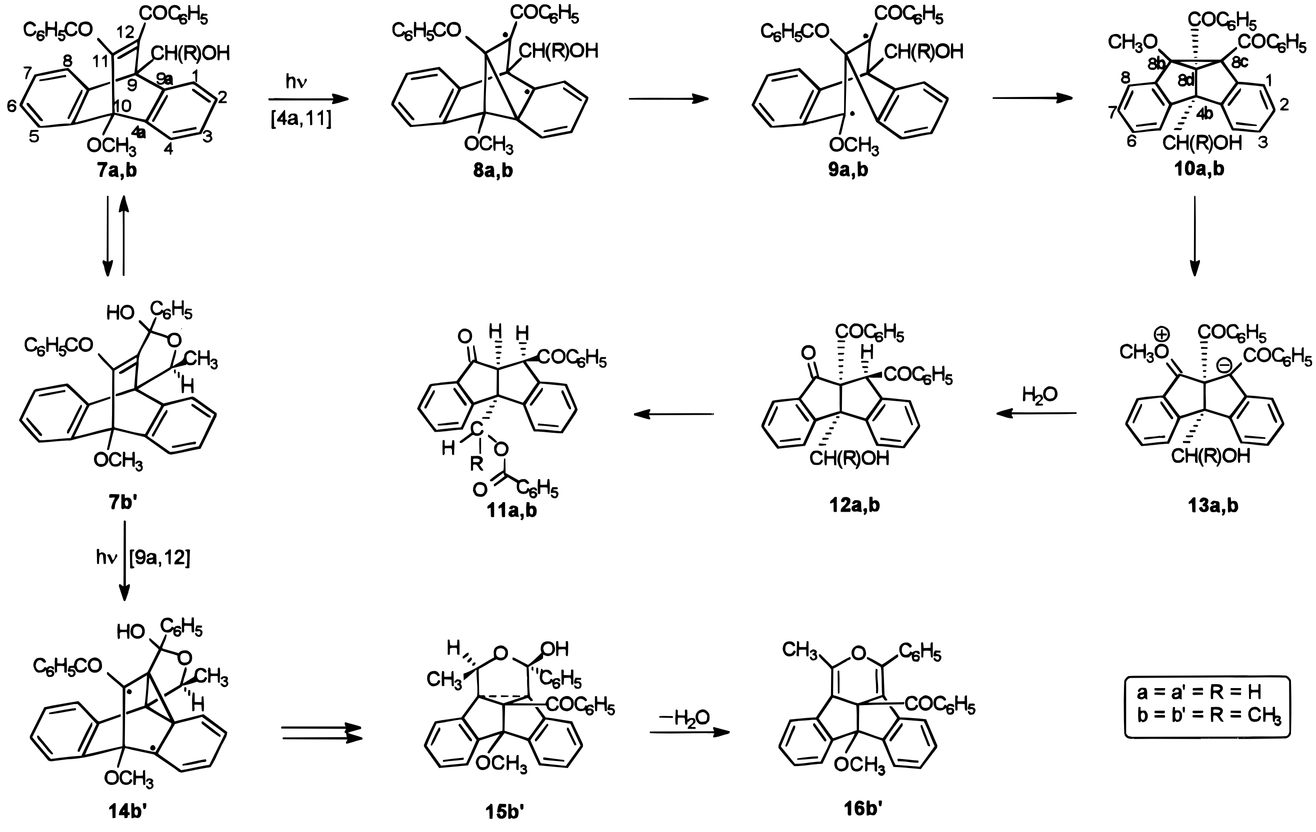
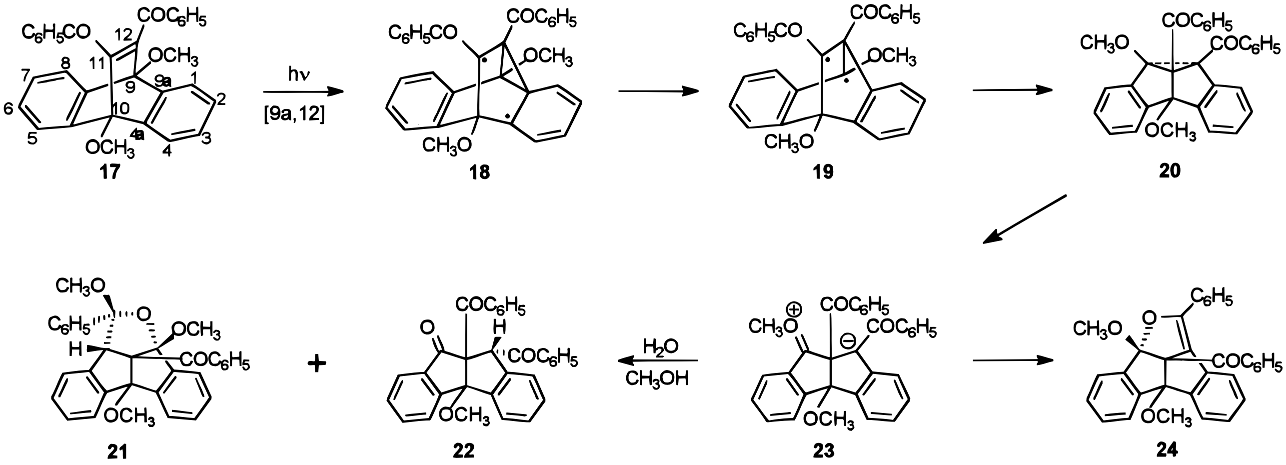
[9] Full details on the crystal and molecular structures will be published separately.

Scheme 3



Scheme 4



2. Laser Flash Photolysis Studies. In order to obtain information on the nature of the transients involved in the phototransformations of **7a,b**, they were subjected to laser flash photolysis studies, employing either 308 or 337.1 nm laser pulse excitation. The transients observed over 0.1−100 μs, following 308 nm laser excitation of **7a,b**, were characterized by broad and diffuse absorption spectra extending beyond 700 nm. The transient spectra are presented in Figure 1. The transients which are produced within the laser pulse, as a result of laser excitation, decay predominantly by first-order kinetics with lifetimes varying in the range of 0.45−0.75 μs (see the insets a and b in Figure 1). These transients are quenched efficiently by typical triplet quenchers, such as oxygen, TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy), HTEMPO (4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy), ferrocene, and β-carotene. With β-carotene as the triplet quencher, the growth of intense transient absoprtions due to β-carotene triplet was observed at 510−550 nm on the same time scale as the decay of the transients of **7a,b**. The quenching characteristics of these transients strongly suggest a triplet assignment for them. The triplet yields (ϕ^{T}) and $\epsilon_{max}{}^{T}$ of **7a,b** were determined in benzene solutions by comparative techniques using benzophenone triplet ($\phi^{T} = 1$, $\epsilon_{max}{}^{T} = 7.6 \times 10^{3}$ M^{-1} cm^{-1} at 532 nm) formation in benzene for actinometry and β-carotene as a triplet quencher by methods described in earlier publications.[10,11] The bimolecular rate constants (k_q) for the quenching were obtained from the slopes of the linear plots of observed, pseudo-first-order rate constants (k_{obsd}) for transient decay against quencher concentration. The triplet photo-

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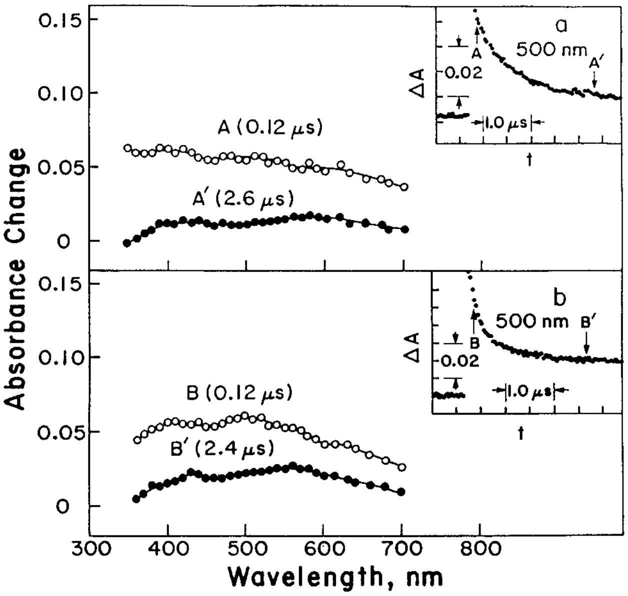

Figure 1. Transient absorption spectra, following 308 nm laser excitation of **7a** (A, A′) and **7b** (B, B′) in deaerated benzene at the indicated times. Insets: kinetic traces for decay of transient absorption at the indicated wavelengths, as observed for **7a** (a) and **7b** (b) in benzene.

physical properties such as ϕ^T, ϵ_{max}^T, τ^T and the quenching rate constants (k_q^T) are summarized in Table 1.

The broad and diffuse nature of the triplet−triplet absorption spectra of **7a,b** suggests that the triplet excitation is not localized on the dibenzoylalkene moiety, but involves the dibenzobarrelene chromophore as a whole. The fact that the triplets of **7a** and **7b** are efficiently quenched by ferrocene (E_T = 38−41 kcal mol^{-1})[12] and other low-energy triplet quenchers (Table 1) suggests that the E_T values for these compounds are near 40 kcal mol^{-1}. The triplet yields (ϕ^T) of **7a** (0.76) and **7b** (0.55) are close to the ϕ^T of several substituted dibenzobarrelenes (0.6−0.7) reported earlier.[8,13] The high ϕ^T values for **7a** and **7b** support the experimental observation that mainly the triplet-state-mediated di-π-methane rearrangement products are observed in each case.

Discussion

Phototransformations of bridgehead-unsymmetrically disubstituted barrelenes such as **7a** and **7b** would be expected to proceed through multichannel pathways, leading to isomeric dibenzosemibullvalenes. Thus, the irradiation of **7a,** for example, could proceed through a phenyl−vinyl bridging (di-π-methane pathway), involving a [4a,11] bonding, to give the diradical intermediate **8a,** which could then lead to the 4b-(hydroxymethyl)-8b-methoxydibenzosemibullvalene (**10a**) (Scheme 3). In contrast, a [9a,12] bonding would lead to the isomeric 4b-methoxy-8b-(hydroxymethyl)dibenzosemibullvalene. The formation of the dibenzopentalene ketone **11a** could be rationalized in terms of an ionic opening of the cyclopropyl ketone functionality in **10a** to give the zwitterionic intermediate **13a**, which could then lead to the demethylated dibenzopentalene ketone **12a** through hydrolysis with adventitious water present in the solvent. It may be pointed out that a similar demethylated dibenzopentalene ketone has been isolated as a minor product in the photolysis of dimethyl 9,10-dihydro-9-methoxy-9,10-ethenoanthracene-11,12-dicarboxylate.[14] The bridgehead hydroxymethyl and benzoyl groups in **12a** are close to each other, and the formation of the rearranged product **11a** could proceed through an aldol intermediate, involving the interaction of these two groups. Such an aldol intermediate has actually been isolated, in an analogous case, where the subsequent migration of the benzoyl group is not feasible.[7]

It is interesting to note that **7b** with a hydroxyethyl group at 9-position, instead of hydroxymethyl group as in **7a**, exists in equilibrium with the cyclic carbinol **7b′** in solution. This may be due to steric interactions exerted by the methyl group in **7b**, favoring the interaction between the hydroxyethyl substituent at the 9-position with the benzoyl group at the 12-positon leading to the cyclic carbinol **7b′**. Similar cases favoring carbinol formation in related systems have been reported in the literature.[15]

The formation of **11b** from **7b** could be rationalized through the dibenzosemibullvalene intermediate **10b**, formed by involving a [4a,11] bonding as in the case of **7a**, whereas **16b′** could be formed through the hexacyclic dibenzosemibullvalene intermediate **15b′**, formed through a [9a,12] bonding in **7b′** (Scheme 3). The observed regioselectivity arising through a [4a,11] bonding in the case of **7a,b** and [9a,12] bonding in **7b′** could be due to the relative stabilities of the diradical intermediates **8a,b** and **14b′** involved in these transformations. Similar observations were made earlier by Zimmerman[3b] and Scheffer[16] in the phototransformations of several substituted 9,10-ethenoanthracene derivatives, where the radical-stabilizing ability of the substituents is important in determining the regioselectivity. The fact that the formation of photoproducts **11b** and **16b′** in the ratio of 2:1 in benzene as well as in chloroform, where the equilibrium ratio between **7b** and **7b′** is 2:1 and 1:1, respectively, indicates that **7b** may have a greater photoreactivity as compared to **7b′**.

The involvement of ionic intermediates such as **13a,b** in the transformation of the dibenzosemibullvalenes **10a,b** has been inferred through the isolation of the pentacyclic, ring-enlarged product **24** in the photolysis of the symmetrically substituted 9,10-dimethoxydibenzobarrelene **17** in benzene−methanol mixture. The formation of **24** is assumed to be through the zwitterionic intermediate **23**, derived from the dibenzosemibullvalene **20**, which in turn is formed through a [9a,12] bridging of **17**, as shown in Scheme 4. Similar ring-enlarged, pentacylic products have been isolated in the photolysis of 9-aryldibenzobarrelenes.[13b] The isolation of the demethylated, dibenzopentalene ketone **22** and the methanol adduct **21**, when the photolysis of **17** is carried out in a mixture of benzene and aqueous methanol, would clearly support the involvement of the ionic intermediate **23** (Scheme 4). The fact that none of **21** is formed, on

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[14] Paddick, R. G.; Richards, K. E.; Wright, G. J. *Aust. J. Chem.* **1976**, *29*, 1005−1015.

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Table 1. Photophysical Properties of Dibenzobarrelene Triplets in Benzene at 298 K

					$k_q^{T,c}$ 10^9 M^{-1} s^{-1}				
substrate	$\lambda_{mon}^{T,a}$ nm	$\epsilon_{max}^{T,b}$ 10^3 M^{-1} cm^{-1}	$\phi^{T,b}$	$\tau^{T,c}$	O$_2$	TEMPO^d	HTEMPO^e	ferrocene	β-carotene
7a	500	6.15	0.76	0.75	0.57	0.24	0.40	5.1	4.2
7b	500	2.82	0.55	0.45	0.51	0.26	0.43	4.6	4.7

[a] These are the wavelengths where the triplets were monitored. [b] ±30%; the monitoring wavelegnths are indicated in column 2. [c] ±15%. [d] TEMPO: 2,2,6,6-tetramethylpiperidinyl-1-oxy. [e] HTEMPO: 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy.

irradiation of **24** in methanol, both in the absence and in the presence of a small amount of acid, would indicate that **21** is formed most likely through the addition of methanol to the zwitterionic intermediate **23** under our reaction conditions.

Experimental Section

The equipment and procedures for melting point determination and spectral recordings are described in earlier papers.[7,8,11,13] All steady-state irradiation experiments were carried out in a Srinivasan-Griffin-Rayonet Photochemical Reactor (RPR 3000 Å) or by using Pyrex-filtered light from a Hanovia 450 W medium-pressure mercury lamp. Solvents for photolysis experiments were purified and distilled before use. Aldrich Gold-Label solvents were used for laser studies. TEMPO and HTEMPO, from Aldrich, were used as received, whereas ferrocene and β-carotene were recrystallized from suitable solvents before use.

Starting Materials. Dibenzoylacetylene (DBA)[17,18] mp 110−111 °C, 9-(hydroxymethyl)-10-methoxyanthracene,[19] mp 149−151 °C, and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethoxy-9,10-ethenoanthracene (**17**),[8] mp 221 °C, were prepared by reported procedures.

Preparation of 9-(1-Hydroxyethyl)-10-methoxyanthracene. Treatment of methylmagnesium bromide (Grignard reagent prepared from 423 mg (3 mmol) of methyl iodide and 75 mg (3 mmol) of magnesium in 20 mL of diethyl ether) with 9-methoxyanthracene-10-carboxaldehyde (715 mg, 3 mmol) in dry benzene (20 mL) for 2 h and workup in the usual manner by treatment with a mixture of crushed ice and ammonium chloride and extraction with ether gave 212 mg (84%) of 9-(1-hydroxyethyl)-10-methoxyanthracene, mp 129−130 °C, after recrystallization from diethyl ether: IR ν_{max} (KBr) 3424, 3381, 2979, 2935, 1620, 1603 cm^{-1}; UV λ_{max} (CH$_3$OH) 251 nm (ϵ 65 800), 258 (115 300), 340 (2420), 356 (4690), 375 (6860), 396 (5950); ^{1}H NMR (CDCl$_3$) δ 1.81 (3H, d, J = 6 Hz), 4.20 (3H, s), 5.25 (1H, s, D$_2$O-exchangeable), 6.32 (1H, q, J = 6 Hz), 7.1−8.8 (8H, m); ^{13}C NMR (CDCl$_3$) δ 23.41, 62.95, 66.80, 122.68, 124.11, 124.53, 124.98, 125.36, 129.36, 131.90; mass spectrum *m/e* (relative intensity) 252 (M$^+$, 87), 237 (100), 220 (47), 193 (29), 178 (33), 165 (52), 152 (18); mol wt calcd for C$_{17}$H$_{16}$O$_2$ 252.1150, found 252.1156 (high-resolution mass spectrometry).

Preparation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes 7a,b. The dihydrobarrelenes **7a** and **7b** were prepared by refluxing mixtures of the appropriate anthracenes and DBA in xylene. The solvent, from the reaction mixture, in each case, was removed under vacuum, and the residual solid was subjected to flash chromatography over silica gel using chloroform and later recrystallized from cyclohexane.

7a. Reaction of 476 mg (2 mmol) of 9-hydroxymethyl-10-methoxy-anthracene with DBA (468 mg, 2 mmol) for 10 h gave 755 mg (80%) of **7a**, mp 216−217 °C: IR ν_{max} (KBr) 3430, 1652 cm^{-1}; UV λ_{max} (CH$_3$OH) 224 nm (ϵ 24 300), 258 (24 800); ^{1}H NMR (CDCl$_3$) δ 2.43 (1H, t, J = 5 Hz, D$_2$O-exchangeable), 3.72 (3H, s), 5.02 (2H, d, J = 5 Hz), 6.80−7.85 (18H, m); ^{13}C NMR (CDCl$_3$) δ 56.80, 57.10, 59.15, 89.09, 121.27, 121.87, 125.12, 125.31, 127.95, 128.13, 129.37, 133.13, 133.46, 136.92, 137.22, 143.36, 146.27, 151.33, 153.09, 153.23, 193.46, 196.43; mass spectrum *m/e* (relative intensity) 472 (M$^+$, 25), 442 (52), 367 (40), 337 (46), 245 (96), 238 (96), 105 (100), 77 (33); mol wt calcd for C$_{32}$H$_{24}$O$_4$ 472.1674, found 472.1670 (high-resolution mass spectrometry).

7b + 7b′. Reaction of 2.52 g (10 mmol) of 9-(1-hydroxyethyl)-10-methoxyanthracene with DBA (468 mg, 2 mmol) for 3 h gave 680 mg (70%) of **7b**, mp 163−164 °C (single crystal of **7b′**, mp 147−148 °C): IR ν_{max} (KBr) 3448, 1655 cm^{-1}; IR ν_{max} (CHCl$_3$) 3560, 3448, 1655 cm^{-1}; UV λ_{max} (CH$_3$OH) 207 nm (ϵ 41 300), 253 (19 100); ^{1}H NMR (CDCl$_3$) δ 1.65 (3H, d, J = 7 Hz), 2.35 (3H, d, J = 7.5 Hz), 3.30 (1H, s, D$_2$O-exchangeable) 3.60 (3H, s), 3.68 (3H, s) 3.71 (1H, s, D$_2$O-exchangeable), 5.50 (1H, q, J = 7 Hz), 5.85 (1H, q, J = 7.5 Hz), 6.73−8.45 (36H, m); ^{1}H NMR (C$_6$D$_6$) δ 1.61 (3H, d, J = 7 Hz), 2.05 (3H, d, J = 7.4 Hz), 3.25 (1H, s, D$_2$O-exchangeable), 3.43 (3H, s), 3.55 (3H, s), 3.57 (1H, s, D$_2$O-exchangeable), 5.35 (1H, q, J = 7 Hz), 5.85 (1H, q, J = 7.4 Hz), 6.55−8.15 (36H, m); ^{13}C NMR (CDCl$_3$) δ 16.76, 22.10, 56.47, 57.10, 60.94, 62.29, 88.78, 89.56, 101.52, 120.97, 121.42, 122.49, 122.91, 124.64, 125.15, 125.45, 126.25, 127.15, 127.54, 127.89, 128.10, 129.15, 129.21, 132.58, 133.23, 136.13, 136.81, 137.17, 139.53, 143.41, 144.27, 144.87, 145.50, 148.21, 162.89, 193.41, 194.46; mass spectrum *m/e* (relative intensity) 486 (M$^+$, 10), 442 (16), 337 (33), 259 (43), 252 (13), 105 (100), 77 (30); mol wt calcd for C$_{33}$H$_{26}$O$_4$ 486.1831, found 486.1820 (high-resolution mass spectrometry).

Irradiation of 7a. A benzene solution of **7a** (472 mg, 1 mmol in 350 mL) was irradiated (Hanovia 450 W) for 30 min. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:1) of petroleum ether (bp 60−80 °C) and chloroform gave 340 mg (72%) of **11a**, mp 176−177 °C, after recrystallization from acetonitrile: IR ν_{max} (KBr) 3063, 2952, 1713, 1682 cm^{-1}; UV λ_{max} (CH$_3$OH) 250 nm (ϵ 28900); ^{1}H NMR (CDCl$_3$) δ 4.10 (1H, d, J = 3 Hz), 5.05 (2H, dd, J = 11 Hz), 5.52 (1H, d, J = 3 Hz), 6.85−8.35 (18H, m); ^{13}C NMR (CDCl$_3$) δ 52.60, 58.92, 60.07, 68.52, 123.69, 123.84, 124.04, 126.41, 128.17, 128.32, 128.53, 128.60, 129.02, 129.24, 129.41, 132.96, 135.64, 138.08, 140.86, 143.03, 154.76, 166.05, 198.66, 203.35; mass spectrum *m/e* (relative intensity) 458 (M$^+$, 21), 336 (15), 231 (24), 189 (20), 105 (100), 76 (56); mol wt calcd for C$_{31}$H$_{22}$O$_4$ 458.1518, found 458.1509 (high-resolution mass spectrometry).

In repeat runs, irradiations of methanol (30 min) and acetone (2 h) solutions of **7a** gave **11a** in 69% and 71% yields, respectively.

Irradiation of 7b. A solution of **7b** (486 mg, 1 mmol) in benzene (250 mL) was irradiated (Hanovia 450 W) for 15 min. Removal of the solvent under vacuum gave a residual solid, which was subsequently chromatographed over alumina. Elution with a mixture (1:1) of petroleum ether (bp 60−80 °C) and chloroform gave 122 mg (26%) of **16b′**, mp 232−233 °C, after recrystallization from acetonitrile: IR ν_{max} (KBr) 3064, 2938, 2840, 1679, 1598 cm^{-1}; UV λ_{max} (CH$_3$OH) 270 nm (ϵ 22 000), 326 (10 200); ^{1}H NMR (CDCl$_3$) δ 2.45 (3H, s), 3.10 (3H, s), 7.08−7.95 (18H, m); ^{13}C NMR (CDCl$_3$) δ 17.18, 53.69, 69.72, 97.00, 119.44, 119.93, 120.73, 122.36, 125.52, 127.34, 127.76, 128.37, 128.64, 129.49, 129.74, 129.94, 131.71, 133.12, 138.10, 138.22, 138.54, 142.35, 143.27, 149.00, 152.78, 157.03, 200.38; mass spectrum *m/e* (relative intensity) 468 (M$^+$, 14), 363 (78), 332 (100), 303 (16), 105(5); mol wt calcd for C$_{33}$H$_{24}$O$_3$ 468.1725, found 468.1725 (high-resolution mass spectrometry).

Further elution with chloroform gave 195 mg (41%) of **11b**, mp 173−174 °C, after recrystallization from acetonitrile: IR ν_{max} (KBr) 3060, 2930, 1702, 1680 cm^{-1}, UV λ_{max} (CH$_3$OH) 205 nm (ϵ 36 200), 251 (17 500); ^{1}H NMR (CDCl$_3$) δ 1.25 (3H, d, J = 7 Hz), 4.15 (1H, d, J = 11 Hz), 5.61 (1H, d, J = 11 Hz), 6.05 (1H, q, J = 7 Hz), 6.95−8.25 (18H, m); ^{13}C NMR (CDCl$_3$) δ

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16.45, 26.84, 53.52, 56.63, 64.43, 123.81, 124.22, 125.76, 128.30, 128.42, 128.48, 128.74, 129.15, 130.04, 133.00, 133.17, 135.55, 136.68, 138.13, 140.99, 143.83, 155.42, 165.62, 198.98, 204.18; mass spectrum *m/e* (relative intensity) 473 (MH^+, 60), 351 (29), 307 (20), 245 (15), 229 (22), 154 (87), 136 (56), 105 (100), 77 (19); mol wt calcd for $C_{32}H_{24}O_4$ 472.1675, found 472.1666 (high-resolution mass spectrometry).

^{1}H NMR Monitoring of the Photoreaction of 7b. A solution of **7b** in $CDCl_3$ (20 mg in 1 mL) in an NMR tube was irradiated with an RPR (3000 Å) light source for 1 h, and its ^{1}H NMR spectrum was recorded. The ^{1}H NMR spectrum revealed that the product mixture consisted of 50% of **11b**, 28% of **16b′**, and methanol (equal to the yield of **11b**), along with 22% of the unreacted starting material. When the irradiation was carried out for 2 h, the product mixture consisted of **11b** (64%), **16b′** (36%), and methanol.

In a separate experiment, when the irradiation of **7b** in C_6D_6 (20 mg in 1 mL) in an NMR tube was carried out for 1 h, under analogous conditions, the product mixture consisted of **11b** (62%), **16b′** (38%), and methanol (equal to that of **11b**) as analyzed by ^{1}H NMR.

Irradiation of 17. A solution of **17** (188 mg, 0.25 mmol) in a mixture (4:1, 50 mL) of methanol and benzene was irradiated (RPR 3000 Å light source) for 8 h (after bubbling with nitrogen) and worked up by removal of the solvent under vacuum and chromatographing the residue on Chromatotron. Elution with a mixture (19:1) of petroleum ether (bp 60−80 °C) and ethyl acetate gave 106 mg (90%) of **24**, mp 158−159 °C, after recrystallization from a mixture (1:1) of methylene chloride and methanol: IR ν_{max} (KBr) 3060, 2970, 2920, 2850, 1690, 1610 cm^{-1}; UV λ_{max} (CH_3OH) 223 nm (ϵ 24 100), 240 (17 100), 320 (9150); ^{1}H NMR ($CDCl_3$) δ 3.26 (3H, s), 3.72 (3H, s), 7.00−7.90 (18H, m); ^{13}C NMR ($CDCl_3$) δ 54.08. 55.04, 57.04, 80.72, 97.22, 118.8, 121.00, 121.50, 121.82, 124.05, 124.85, 125.51, 127.30, 127.63, 127.86, 127.98, 128.34, 128.49, 128.88, 129.51, 129.95. 130.49, 133.59, 133.95, 136.84, 141.05, 141.50, 142.04, 143.95, 149.55, 200.48; mass spectrum *m/e* (relative intensity) 472 (M^+, 40), 441 (16), 367 (94), 336 (100), 293 (69), 105 (23), 77 (14); mol wt calcd for $C_{32}H_{24}O_4$ 472.1675, found 472.1662 (high-resolution mass spectrometry).

In repeat runs, when the irradiation of **17** was carried out in benzene (1.5 h) and acetone (5 h), **24** was formed in 30% and 82% yields, respectively.

Irradiation of 17 in a Mixture of Benzene and Aqueous Methanol. A solution of **17** (472 mg, 1 mmol) in a mixture of methanol (150 mL), benzene (40 mL), and water (10 mL) was irradiated (RPR, 3000 Å light source) for 8 h under bubbling nitrogen. Removal of the solvent under vacuum gave a residual solid, which was chromatographed on a Chromatotron. Elution with a mixture (19:1) of petroleum ether (bp 60−80 °C) and ethyl acetate gave 160 mg (34%) of **21**, mp 249−250 °C, after recrystallization from a mixture (4: 1) of methylene chloride and methanol: IR ν_{max} (KBr) 3080, 2980, 2950, 2850, 1680, 1605, 1585 cm^{-1}; UV λ_{max} (CH_3OH) 232 nm (ϵ 13 400), 2500 (11 800), 275 (3360); ^{1}H NMR ($CDCl_3$) δ 2.60 (3H, s), 3.29 (3H, s), 3.65 (3H, s), 5.45 (1H, s), 5.80 (1H, d, J = 8 Hz), 6.65−7.95 (17H, m); ^{13}C NMR ($CDCl_3$) δ 50.61, 52.55, 52.80, 63.60, 83.52, 97.85, 116.90, 118.15, 123.51, 124.00, 124.25, 127.89, 128.00, 128.22, 128.58, 128.96, 129.05, 129.23, 129.55, 130.52, 131.68, 131.92, 137.60, 138.57, 139.43, 141.68, 147.45, 195.65; mass spectrum *m/e* (relative intensity) 472 ($M^+ - CH_3OH$, 14), 368 (47), 263 (100), 232 (67), 217 (28), 105 (27); mol wt calcd for $C_{32}H_{24}O_4$ ($M - CH_3OH$) 472.1674, found 472.1678 (high-resolution mass spectrometry).

Further elution with a mixture (9:1) of petroleum ether and ethyl acetate gave 190 mg (40%) of **22**, mp 210 °C, after recrystallization from a mixture (1:1) of methylene chloride and methanol: IR ν_{max} (KBr) 3080, 2950, 2870, 1710, 1690, 1600, 1585 cm^{-1}; UV λ_{max} (CH_3OH) 225 nm (ϵ 28 600), 252 (30 000), 308 (2040); ^{1}H NMR ($CDCl_3$) δ 3.30 (3H, s), 5.82 (1H, s), 6.85−8.45 (18H, m); ^{13}C NMR ($CDCl_3$) δ 53.05, 55.51, 83.50, 94.59, 122.51, 122.60, 124.50, 124.95, 126.65, 127.01, 127.42, 127.95, 128.05, 128.21, 129.52, 131.45, 132.67, 134.75, 136.78, 137.56, 138.95, 139.98, 156.53, 193.95, 196.53, 198.63; mass spectrum *m/e* (relative intensity) 458 ($M^{+,}$ 30), 353 (12), 322 (27), 294 (9), 217 (13), 105 (100), 77 (23); mol wt calcd for $C_{31}H_{22}O_4$ 458.1518, found 458.1536 (high-resolution mass spectrometry).

Irradiation of 24 in a Mixture of Benzene and Aqueous Methanol. A solution of **24** (47mg, 0.1 mmol) in a mixture of methanol (75 mL), benzene (20 mL), and water (5 mL) was irradiated (RPR, 3000 Å light source) for 4 h under bubbling nitrogen. Removal of the solvent under vacuum gave 47 mg (100%) of the unreacted starting material **24**, mp 158−159 °C (mixture mp).

In a separate experiment, when the irradiation of **24** (47 mg, 0.1 mmol) in a mixture of methanol (75 mL), benzene (20 mL), and water (5 mL containing 0.25 N hydrochloric acid) was carried out under analogous conditions for 4 h, a complex mixture of products was formed. No **21** could be detected in the mixture on the basis of ^{1}H NMR comparision.

X-ray Structure Determination of 7b′, 11a,b, 16b′, 21, and 24. Colorless crystals of **7b′, 11a,b, 16b′, 21**, and **24** were subjected to X-ray crystallographic analysis, employing a Siemens R3 automated four-circle diffractometer. The results of these studies will be published elsewhere.[9] **7b′**: space group *Pbca*, $a = 16.722(5)$ Å, $b = 16.680(5)$ Å, $c = 17.561(7)$ Å, $Z = 8$, $R = 0.0856$ ($wR = 0.200$) for 4464 reflections ($F > 2.0\sigma(F)$). **11a**: space group $P2_1/c$, $a = 10.960(3)$ Å, $b = 9.246(2)$ Å, $c = 23.0976(5)$ Å; $\beta = 99.15\ (2)°$, $Z = 4$, $R = 0.046$ ($wR = 0.042$) for 2512 reflections ($F > 4.0\sigma(F)$). **11b**: space group $P1$, $a = 10.634(3)$ Å, $b = 11.278(3)$ Å, $c = 12.470(3)$ Å, $\alpha = 69.00(2)°$, $\beta = 79.72\ (2)°$, $\gamma = 77.37\ (2)°$, $Z = 2$, $R = 0.081$ ($wR = 0.079$) for 3262 reflections ($F > 4.0\sigma(F)$). **16b′**: space group $P1$, $a = 9.503(7)$ Å, $b = 12.158(3)$ Å, $c = 12.549(6)$ Å, $\alpha = 83.41(3)°$, $\beta = 76.49(5)°$, $\gamma = 71.52(4)°$, $Z = 2$, $R = 0.055$ ($wR = 0.038$) for 3220 reflections ($F > 1.5\sigma(F)$). **21**: space group *Pbca*, $a = 17.513(5)$ Å, $b = 14.897(6)$ Å, $c = 19.587(8)$ Å, $Z = 8$, $R = 0.042$ ($wR = 0.055$) for 2500 reflections ($F > 3.0\sigma(F)$). **24**: space group $P2_1/n$, $a = 11.664(4)$ Å, $b = 17.476(6)$ Å, $c = 12.408(4)$ Å, $\beta = 94.81(3)°$, $Z = 4$, $R = 0.064$ ($wR = 0.068$) for 2145 reflections ($F > 3.0\sigma(F)$).

Laser Flash Photolysis. Pulse excitation was carried out mainly at 308 nm using a Lambda Physic EMG 101 MCS excimer laser (50 mJ, 10 ns, XeCl) and 337.1 nm (8 ns, 2−3 mJ) from a Molectron UV-400 nitrogen laser source. The output from the excimer laser was suitably attenuated to 20 mJ pulse^{-1} or less and defocused to minimize multiphoton processes. The transient phenomena were observed in 3 × 7 mm quartz cells by using a kinetic spectrometer, described elsewhere.[20,21] For transient absorption spectra, a flow cell was used. Unless oxygen effects were to be studied, the solutions were deoxygenated by purging with pure argon.

Acknowledgment. This work was supported by the Council of Scientific and Industrial Research, Government of India (D.R., S.A.K., C.V.A., T.M., S.D.), and the Office of Basic Energy Sciences of the U.S. Department of Energy (M.V.G. (in part)).

Supporting Information Available: Copies of ^{1}H NMR spectra of compounds **7a**, **7b** + **7b′**, **11a**,**b**, **16b′**, **21**, **22**, and **24**, ^{13}C NMR spectra of compounds **7a**, **7b** + **7b′**, **11b**, **16b′**, **21**, **22**, and **24**, and X-ray ORTEP diagrams of **7b′**, **11a,b**, **16b′, 21,** and **24** (22 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO952046U

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