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

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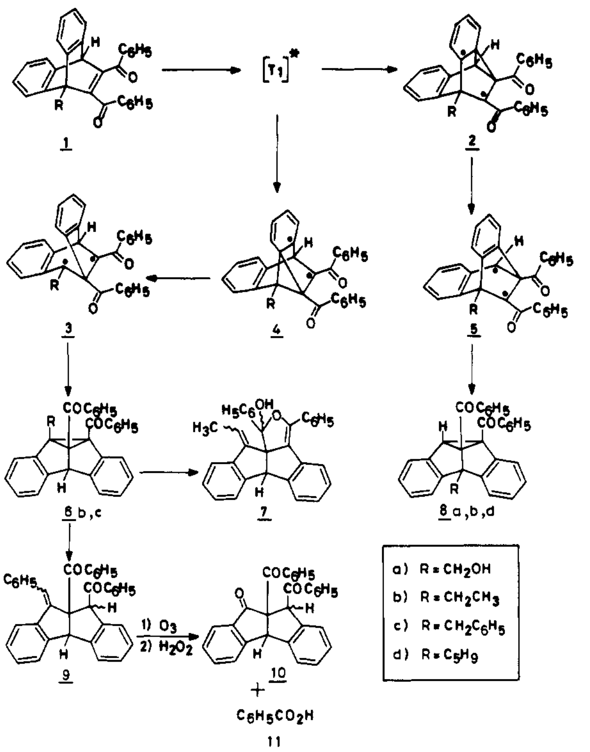
The photochemistry of bridgehead-substituted dibenzobarrelene derivatives **1a–f** has been investigated by steady-state photolysis, product analysis, and laser flash photolysis. 4b- or 8b-substituted dibenzosemibullvalenes or products derived thereof were formed in the course of irradiation of 9-(hydroxymethyl)-, 9-ethyl-, and 9-benzyl-substituted dibenzobarrelenes. 9-Cyclopentyl-substituted dibenzobarrelene upon irradiation gave the corresponding 4b-substituted dibenzosemibullvalene and dibenzocyclooctatetraene, whereas from the photolyzates of 9-isopropyl- and 9-cyclohexyl-substituted dibenzobarrelenes the corresponding dibenzocyclooctatetraenes were obtained as the only isolable products. The 337.1-nm laser flash photolysis of **1a–f** in benzene results in the formation of their triplets in high yields ($\phi_T = 0.7–1.0$). The triplets possess short lifetimes (0.03–2.2 μs) and are readily quenchable by oxygen, di-*tert*-butyl nitroxide, and ferrocene ($k_q^T = (0.2–8) \times 10^9$ M^{-1} s^{-1}). In spite of high ϕ_T's, some of the dibenzobarrelene substrates are reluctant to undergo the barrelene–semibullvalene rearrangement under steady-state irradiation; this appears to be related to the unusually short lifetimes of their triplets; that is, decay modes other than those eventually leading to dibenzosemibullvalenes are available to these triplets.

The photochemistry of barrelenes and their derivatives is well-studied.[3] Depending on the irradiation conditions, barrelenes can photoisomerize to the corresponding semibullvalenes or cyclooctatetraenes. It has been established that cyclooctatetraenes are formed under direct irradiation, whereas semibullvalenes are formed under triplet sensitization. Furthermore, diradical intermediates are proposed for the rearrangement to semibullvalenes. The stabilization of these intermediates largely decides the observed regioselectivity in these transformations.[4-8] The electronegativity of the bridgehead substituents[8] and the presence of an appropriate functionality on the vinyl moiety, which can stabilize adjacent radical sites through π-delocalization,[4] are some of the factors that affect the stabilities of the diradical intermediates leading to appropriate semibullvalenes.

Scheme I



In our earlier reports[9,10] we have shown that dibenzobarrelenes containing 1,2-dibenzoylalkene moieties undergo the di-π-methane rearrangement (Zimmerman rearrangement)[3b] in preference to the 1,2-dibenzoylalkene rearrangement[11] and that the nature of the bridgehead substituent plays a major role in deciding the regioselectivity of the observed transformations. Though the observed regioselectivity can, by and large, be correlated with the electronegativity of the bridgehead substituent, it appears that other factors may also be important. For example,

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[4] Ciganek, E. *J. Am. Chem. Soc.* 1966, *88*, 2882–2883.

[5] Hart, H.; Murray, R. K., Jr. *J. Am. Chem. Soc.* 1969, *91*, 2183–2184.

[6] Hart, H.; Love, G. M. *J. Am. Chem. Soc.* 1973, *95*, 4592–4599.

[7] Richards, K. E.; Tillman, R. W.; Wright, G. J. *Aust J. Chem.* 1975, *28*, 1289–1300.

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

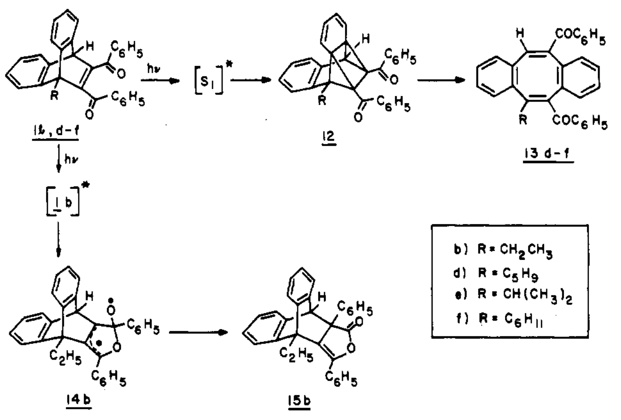
[9] Kumar, C. V.; Murty, B. A. R. C.; Lahiri, S.; Chakachery, E.; Scaiano, J. C.; george, M. V. *J. Org. Chem.* 1984, *49*, 4923–4929.

[10] Murty, B. A. R. C.; Pratapan, S.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem.* 1985, *50*, 2533–2538.

[11] For some examples of the photorearrangement of 1,2-dibenzoylalkenes, see: (a) Griffin, G. W.; O'Connell, E. J. *J. Am. chem. Soc.* 1962, *84*, 4148–4149. (b) Zimmerman, H. E.; Dürr, H. C. C.; Lewis, R. G.; Bram, S. *J. Am. Chem. Soc.* 1962, *84*, 4149–4150. (c) Padwa, A.; Crumrine, D.; Shubber, A. *J. Am. chem. Soc.* 1966, *88*, 3064–3069. (d) Sugiyama, N.; Kashima, C. *Bull. Chem. Soc. Jpn.* 1970, *43*, 1875–1877. (e) Zimmerman, H. E.; Dürr, H. G. C.; Givens, R. S.; Lewis, R. G. *J. Am. Chem. Soc.* 1967, *89*, 1863–1874. (f) Lahiri, S.; Dabral, V.; Chauhan, S. M. S.; Chakachery, E.; Kumar, C. V.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* 1980, *45*, 3782–3790.

0022-3263/87/1952-5512$01.50/0

Scheme II



the role of steric factors has hitherto not been systematically explored. In the present investigation, several dibenzobarrelenes containing bridgehead substituents of varying sizes, but of comparable electronegativities, have been examined by steady-state photolysis and laser flash photolysis. The primary aim has been to elucidate the role of these substituents in deciding the major reaction pathway. The substrates include 11,12-dibenzoyl-9,10-dihydro-9-(hydroxymethyl)-9,10-ethenoanthracene (**1a**), 11,12-dibenzoyl-9,10-dihydro-9-ethyl-9,10-ethenoanthracene (**1b**), 9-benzyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (**1c**), 9-cyclopentyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (**1d**), 11,12-dibenzoyl-9,10-dihydro-9-isopropyl-9,10-ethenoanthracene (**1e**), and 9-cyclohexyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (**1f**).

Results

1. Preparation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes (1a–f). Dibenzobarrelenes containing 1,2-dibenzoylalkene moieties were conveniently prepared through the reaction of appropriate anthracenes with dibenzoylacetylene (DBA) either by direct heating in suitable solvents[12a] or in the presence of a catalyst, e.g., aluminum chloride.[12b] We have prepared the 9-substituted 11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes, **1b–f** in high yields through the aluminum chloride catalyzed reaction of the appropriate anthracenes with DBA in chloroform. Compound **1a**, however, was prepared by refluxing an equimolar mixture of the corresponding anthracene and DBA in toluene for 36 h. All the dibenzobarrelenes **1a–f** have been characterized by analytical results and spectral evidence.

2. Preparative Photochemistry and Product Identification. Irradiation of **1a** in benzene, methanol, and acetone gave, in each case, 8c,8d-dibenzoyl-4b-(hydroxymethyl)-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene (**8a**) (64–82%) (Scheme I). The irradiation of **1b** in benzene and methanol resulted in a mixture of 8c,8d-dibenzoyl-4b-ethyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene (**8b**)[10] (62–68%), an isomeric hydroxy compound (**7**) (13–18%) derived from the **8b**-substituted semibullvalene **6b**, and unchanged **1b** (3%) in each case. However, the irradiation of **1b** in acetone gave, in addition to **8b** (63%) and **7** (19%), an isomeric lactone **15** (2%). The irradiation of **1c** in different solvents, on the other hand, gave 9a,10-dibenzoyl-9-benzylidene-4b,9,9a,10-tetrahydro-*cis*-indeno[1,2-*a*]indene (**9**), which on ozonolysis gave a mixture of 9a,10-dibenzoyl-9-oxo-4b,9,9a,10-tetrahydro-*cis*-indeno[1,2-*a*]indene (**10**) (57%) and benzoic acid (**11**) (50%) (Scheme I). The irradiation of **1d** gave a mixture of 4b-cyclopentyl-8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[*a,f*]cyclopropa[*cd*]pentalene (**8d**) (18–23%) and 5-cyclopentyl-1,4-dibenzoyl-2,6-dibenzocyclooctatetraene (**13d**) (21–24%). In contrast to the cases of **1a–d**, the irradiation of **1e** and **1f** in solvents like benzene, methanol, and acetone gave the corresponding dibenzocyclooctatetraenes **13e** (21–22%) and **13f** (46–55%), respectively (Scheme II).

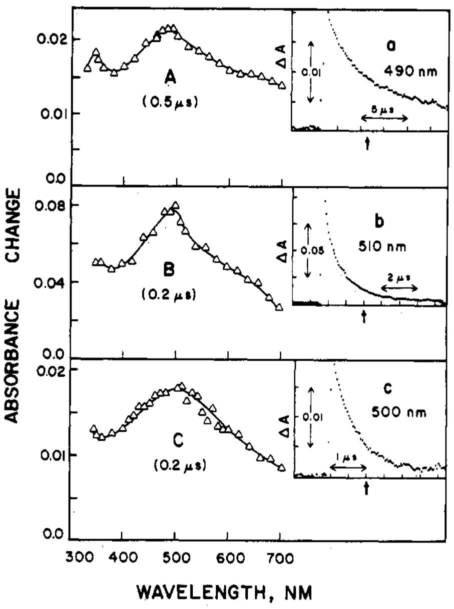


Figure 1. Transient absorption spectra at the indicated times following 337.1-nm laser excitation of (A) **1a**, (B) **1b**, and (C) **1c** in deaerated benzene (absorbances of solutions = 0.5–0.7 in 2-mm cell at 337.1 nm). Insets: representative kinetic traces for decay of transient absorption at the respective wavelength maximum as observed for (a) **1a**, (b) **1b** and, (c) **1c** in benzene.

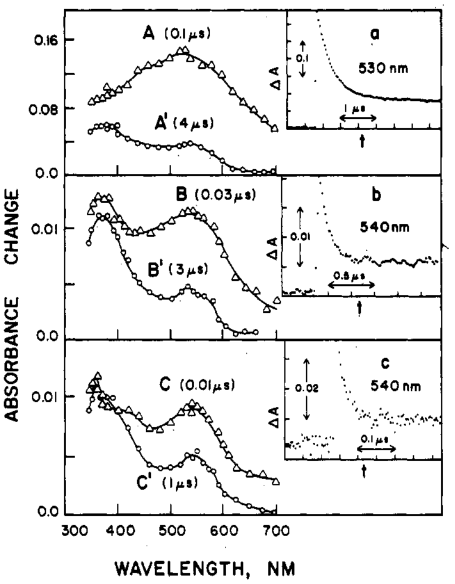


Figure 2. Transient absorption spectra at the indicated times following 337.1-nm laser excitation of (A, A′) **1d**, (B, B′) **1e**, and (C, C′) **1f** in deaerated benzene (absorbances of solutions = 0.5–0.7 in 2-mm cell at 337.1 nm). Insets: representative kinetic traces for decay of transient absorption at the respective wavelength maximum as observed for (a) **1d**, (b) **1e**, and (c) **1f** in benzene.

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(13) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–393. (b) Zimmeran, H. E.; Mariano, P. S. *J. Am. Chem Soc.* **1969**, *91*, 1718–1727.

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

						$k_q^{T,c}$ 10^9 M^{-1} s^{-1}		
substrate	9-substituent	$\lambda_{max}^{T,a}$ nm	$\epsilon_{max}^{T,b}$ 10^3 M^{-1} cm^{-1}	$\phi^{T\,b}$	$\tau^{T,c}$ μs	O_2	DTBN	ferrocene
1a	CH_2OH	490	4	1.0	2.2	0.54	0.84	7.9
1b	C_2H_5	510	5^d	0.7	1.0	0.48^c	0.49^d	5.0^d
1c	$CH_2C_6H_5$	500		0.7	0.65	0.60	0.16	5.7
1d	cyclopentyl	520		0.9	0.46	0.30	0.21	4.1
1e	$CH(CH_3)_2$	540		0.7	0.10	0.80	0.37	5.1
1f	cyclohexyl	540		0.7	0.03	*e*	*e*	*e*

[a] ±10 nm. [b] ±30%. [c] ±15%. [d] Data taken from ref 10. [e] Could not be reliably measured because of the unusually short triplet lifetime.

3. Laser Flash Photolysis Studies. In order to obtain information on the triplets of the dibenzobarrelenes **1a–f**, these substrates were examined by nanosecond laser flash photolysis. Upon 337.1-nm laser pulse excitation of benzene solutions (0.5–1 mM), substrates **1a–f** produce transients characterized by broad and diffuse absorption spectra (λ_{max} = 490–540 nm) extending beyond 700 nm. The transient spectra are presented in Figures 1 and 2. The transients, produced within the pulse as a result of the laser photoexcitation, decay predominantly by first-order kinetics with lifetimes varying in the range 0.03–2 μs (for representative kinetic traces, see the insets of Figures 1 and 2). In the case of **1d–f**, long-lived residual absorption (λ_{max} = 380 and 540 nm) are observed following the decay of the initial transients (see parts A′, B′, C′ in Figure 2); these do not show any sign of decay over our longest time scale (~100 μs). Practically no such residual absorption (long-lived) is noted in the case of substrates **1a–c**.

The initial transients (λ_{max} = 490–540 nm) are efficiently quenched by typical triplet quenchers, namely, oxygen, di-*tert*-butyl nitroxide (DTBN, stable free radical), and ferrocene. 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 concentrations. No effect of oxygen (≤9 mM), DTBN (≤30 mM), and ferrocene (≤5 mM) was observed on the decay kinetics of the residual absorptions (λ_{max} = 380 and 540 nm) in the case of **1d–f**, except for **1e** where the long-lived absorption at and near short-wavelength maximum (350 nm) was found to undergo partial decay in the presence of oxygen and DTBN.

The quenching characteristics of the relatively short-lived transients (λ_{max} = 490–540 nm) strongly suggest a triplet assignment for them. To obtain fruther support for this, triplet sensitization experiments were carried out. Attempts to generate the triplet of **1a** via energy transfer from di-*tert*-butyl thioketone (E_T = 45 kcal mol^{-1})[14] under 532-nm laser excitation and from camphorquinone (E_T = 52 kcal mol^{-1})[15] under 485-nm laser excitation in the presence of millimolar concentration of **1a** in benzene were not successful.[16] This is apparently due to the fact that the spectroscopic triplet energy of the dibenzobarrelene is higher than or close to E_T's of the two intended sensitizers.[17] We employed the pulse radiolysis technique[18] to generate biphenyl triplet in the presence of millimolar concentrations of **1a**,**b** in benzene. In this method, deaerated benzene solutions containing biphenyl at a high concentration (0.1 M) and a substrate at a relatively low concentration (≤5 mM) were irradiated with 5-ns electron pulses. Biphenyl triplet (λ_{max}^T = 360 nm) was produced as a result of energy transfer from the short-lived benzene triplet (pulse-radiolytic); this subsequently acted as an excitation donor to the substrates. The formation of the triplets of the latter was observed at long wavelengths (450–600 nm). The transient absorption spectra and decay behaviors following the enhanced decay of biphenyl triplet in the presence of **1a**,**b** agreed well with those observed under direct laser excitation (337.1 nm) of these substrates (vide supra). These results, along with quenching behaviors described earlier, strongly favor the assignment of the laser-flash-photolytic transients as triplets. In the case of **1a**, the comparison of absorbances due to biphenyl triplet (donor) and the triplet of **1a** (acceptor) allowed us to estimate[18,19] the maximum extinction coefficient (ϵ_{max}^T) of the latter at 4×10^3 M^{-1} cm^{-1} (at 490 nm).

The triplet yields (ϕ^T) of **1a–f** were determined in benzene solutions optically matched with one another at the laser excitation wavelength (337.1 nm). The formation of benzophenone triplet ($\phi^T = 1$, $\epsilon_{max}^T = 7.6 \times 10^3$ M^{-1} cm^{-1} at 532 nm)[20] in benzene was used for actinometry. To obtain ϕ^T, the end-of-pulse absorbance change due to a substrate triplet divided by its extinction coefficient was compared with that for benzophenone. For each of substrates **1c–f**, ϵ_{max}^T was assumed to be equal to that of **1b** (namely, 5×10^3 M^{-1} cm^{-1} estimated in an earlier study[10]). The triplet photophysical properties, λ_{max}^T, ϵ_{max}^T, ϕ^T, and τ^T, and quenching rate constants (k_q^T) are summarized in Table I.

The long-lived residual absorptions (λ_{max} = 350 and 540 nm) in the case of **1d–f** are due to triplet-mediated photoproducts. This is established by the fact that upon quenching the triplets by ferrocene, the decrease in the residual absorbances occurs in a manner proportionate to the shortening of the triplet lifetimes. Although we do not observe any tendency of decay in these absorptions on our longest time scale (~100 μs), these probably do not represent stable photoproducts because no long wavelength absorption band systems were found to develop in the solutions of **1d–f** that had been extensively photolyzed by repetitive laser pulses (337.1 nm). Furthermore, note that the products (dibenzosemibullvalenes and cyclooctatetraenes) isolated from the photolyzates of **1d–f** do not absorb at the long-wavelength spectral region (500–600 nm) where the laser-flash-photolytic products exhibit

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[14] Bhattacharyya, K.; Kumar, C. V.; Das, P. K.; Jayasree, B.; Ramamurthy, V. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1383–1393.

[15] Evans, T. R.; Leermakers, P. A. *J. Am. Chem. Soc.* **1967**, *89*, 4380–4382.

[16] In addition, one should reckon the inefficiency of exchange interaction in energy transfer involving the sterically crowded donor and acceptor.

[17] Steady-state photolysis of biacetyl (22 mM) in the presence of 2.2 mM of **1d**, **1e**, or **1f** in benzene using the output from a Hanovia 450-W medium-pressure Hg lamp (selectively filtered through a Pyrex glass sleeve and a 0.02% solution of 9,10-dibromoanthracene in toluene) did not effect any observable photochemistry in the dibenzobarrelene substrates.

[18] For a description of the pulse-radiolytic method of triplet production, see: Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904–1915.

[19] The comparative method could not be reliably used for the other substrates because of their short triplet lifetimes (≤1 μs).

[20] Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191.

well-defined band systems (parts A′–C′, Figure 2).

Discussion

The formation of the dibenzosemibullvalenes and products derived thereof in the phototransformations of **1a–d** can be rationalized in terms of the pathway shown in Scheme I involving triplet excited states.[13] A benzovinyl bridging of the excited-state species can lead to the diradical intermediates **4** or **2**, which can then be transformed to the regioisomeric products **6** or **8**, respectively. The exclusive formation of the 4b-substituted semibullvalene from **1a** may be due to the stabilization of the radical centers in **2** by through-space interaction with the hydroxy group. A similar role of the hydroxy group in deciding regioselectivity has been reported in the literature.[5,6]

In contrast to the exclusive formation of the 4b-substituted semibullvalene from 9-methyldibenzobarrelene,[9] both 9-ethyl- and 9-benzyl-substituted (**1b** and **1c**, respectively) dibenzobarrelenes on irradiation gave partially or exclusively the 8b-substituted dibenzosemibullvalenes. This preference may be attributed to the larger size of the substituents since electronic effects due to methyl, ethyl, and benzyl group on the diradical intermediates **4** or **2** are expected to be comparable. The 9-cyclopentyl substituent in **1d** also lowers the yield of 4b-substituted dibenzosemibullvalene. We, however, do not understand why the 8b-substituted dibenzosemibullvalene is not formed at all in this case. The formation of cyclooctatetraenes **13d–f** from **1d–f** is understood in terms of the pathway shown in Scheme II involving singlet excited states. The implication of the singlet state in this phototransformation is based on precedents in the literature.[3] The formation of a small amount of **15b** from **1b** is explained in terms of the rearrangement of the diradical intermediate **14b** shown in Scheme II. A similar rearrangement in a bicyclo[2.2.2]octane system containing the dibenzoylalkene component has been reported earlier.[11f]

The barrelene–semibullvalene rearrangement is known[3] to proceed through the triplet state. As evident from the ϕ^T data in Table I, all of the dibenzobarrelenes under examination are characterized by high intersystem crossing efficiencies (close to unity). This, combined with the fact that the triplets are short-lived, is taken to mean that the latter can constitute important intermediates in the photochemistry observed under direct irradiation. Interestingly, for **1e** and **1f**, the triplets are unusually short-lived (Table I). These are also the substrates for which, in spite of high ϕ^T's, the barrelene–semibullvalene rearrangement does not occur as shown by preparative photochemical studies. It appears that the triplets of these systems undergo fast decay to metastable intermediates, which eventually revert to the reactant ground states. On the basis of our results, however, we are unable to ascertain if these intermediates are diradicals **2** or **5** (Scheme I), which are reluctant to undergo transformation to the corresponding semibullvalenes. It should be noted that the triplets of the substrates under study may also undergo Norrish type II photoreaction (intramolecular γ-hydrogen abstraction) leading to biradicals, which may eventually reketonize to the original reactants.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on a Perkin-Elmer Model 377 infrared spectrometer, and the electronic spectra were recorded on a Cary 17D or Cary 219 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian EM-390 and a Bruker HFX-90 spectrometer, respectively. All steady state irradiation experiments were carried out in a Srinivasan-Griffin Rayonet photochemical reactor, with Pyrex vessels or with a Hanovia 450-W medium-pressure mercury lamp with Pyrex filters in a quartz-jacketted immersion well.

Starting Materials. Dibenzoylacetylene (DBA)[21,22] mp 110–111 °C, 9-(hydroxymethyl)anthracene,[23] mp 162–163 °C, and 11,12-dibenzoyl-9,10-dihydro-9-ethyl-9,10-ethenoanthracene (**1b**),[10] mp 217–219 °C, were prepared by reported procedures. 9-Benzylanthracene, mp 135 °C, 9-isopropylanthracene, mp 75–76 °C, 9-cyclopentylanthracene (semisolid), and 9-cyclohexylanthracene, mp 125–126 °C, were prepared by adaptations of known procedures.[24] Solvents for photolysis were purified and distilled before use. The petroleum ether used was the fraction with bp 60–80 °C. Aldrich Gold-Label solvents were used for laser studies.

Preparation of Dibenzobarrelenes 1a–f. Dibenzobarrelene **1a** was prepared by refluxing an equimolar mixture of 9-(hydroxymethyl)anthracene and DBA in dry toluene for 36 h. Removal of the solvent under reduced pressure gave a solid, which was washed with slightly chilled methanol and recrystallized from a 4:1 mixture of benzene and petroleum ether. Compounds **1c–f** were prepared by treating an equimolar mixture of the appropriate anthracene and aluminum chloride with DBA in chloroform at 0 °C. After 1 h, the mixture was poured over crushed ice, acidified, and then extracted with chloroform. After removal of chloroform, the residue was washed with methanol and then recrystallized from a 1:1 mixture of chloroform and methanol.

1a (88%): mp 223–224 °C; IR ν_{max} (KBr) 3600, 3570 (OH), 3060, 2920, 2880 (CH), 1640 (C=O), 1590 and 1575 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 255 nm (ϵ 19 800), 322 (1600); ^{1}H NMR (CDCl$_3$) δ 2.8 (1 H, t, D$_2$O exchangeable OH), 5.1 (2 H, d, CH$_2$), 5.6 (1 H, s, bridgehead), 7–7.8 (18 H, m, aromatic). Anal. Calcd for $C_{31}H_{22}O_3$: C, 84.16; H, 4.98. Found: C, 83.88; H, 4.78.

1c (83%): mp 163–164 °C; IR ν_{max} (KBr) 3050, 3020, 2980 (CH), 1645 (C=O), 1590 and 1570 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 256 nm (ϵ 19 400), 330 (1050); ^{1}H NMR (CDCl$_3$) δ 4.35 (2 H, s, CH$_2$), 5.6 (1 H, s, bridgehead), 6.9–7.6 (23 H, m, aromatic). Anal. Calcd for $C_{37}H_{26}O_2$: C, 88.45; H, 5.18. Found: C, 88.92; H, 4.80.

1d (81%): mp 211–212 °C; IR ν_{max} (KBr) 3050, 3020, 2920, 2850 (CH), 1640 (C=O), 1590 and 1560 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 256 nm (ϵ 19 800), 326 (1100); ^{1}H NMR (CDCl$_3$) δ 1.3–2.8 and 3.8 (9 H, m, cyclopentyl), 5.45 (1 H, s, bridgehead), 6.8–7.8 (18 H, m, aromatic). Anal. Calcd for $C_{35}H_{28}O_2$: C, 87.5; H, 5.83. Found: C, 87.45; H, 5.78.

1e (90%): mp 180–181 °C; IR ν_{max} 3050, 2980, 2890 (CH), 1650 (C=O), 1590 and 1570 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 256 nm (ϵ 20 800), 330 (1310); ^{1}H NMR (CDCl$_3$) δ 1.35 (3 H, d, CH$_3$), 1.65 (3 H, d, CH$_3$), 3.65 (1 H, m, CH), 5.35 (1 H, s, bridgehead), 6.9–7.85 (18 H, m, aromatic). Anal. Calcd for $C_{33}H_{26}O_2$: C, 87.22; H, 5.73. Found: C, 87.15; H, 5.58.

1f (92%): mp 219–220 °C; IR ν_{max} (KBr) 3060, 3020, 2930, 2850 (CH), 1635 (C=O), 1580 and 1560 (C=C) cm^{-1}; UV λ_{max} (CH$_3$OH) 256 nm (ϵ 20 000), 327 (1500); ^{1}H NMR (CDCl$_3$) δ 1–2.8 and 3.3 (11 H, m, cyclohexyl), 5.35 (1 H, m, bridgehead), 7–7.9 (18 H, m, aromatic). Anal. Calcd for $C_{36}H_{30}O_2$: C, 87.45; H, 6.07. Found: C, 87.20; H, 5.95.

Irradiation of Dibenzobarrelenes 1a–f. General Procedure. The general procedure was to irradiate a dilute, degassed solution of appropriate barrelenes in benzene, methanol, or acetone (1–2 mmol in 150–175 mL) for $^1/_4$–4 h and then remove the solvent under vacuum. The IR and ^{1}H NMR spectra of the residue were recorded to have an approximate idea about the product composition. The residual solid was chromatographed on silica gel and eluted with different solvents to separate the products, which were finally purified by recrystallization from suitable solvents.

Irradiation of 1a. A benzene solution of **1a** (442 mg, 1 mmol in 175 mL) was irradiated with a Hanovia 450-W medium-pressure mercury vapor lamp with Pyrex filter for $^1/_4$ h. Removal of the

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solvent gave a residue, which was triturated with carbon tetrachloride to separate 285 mg (64%) of **8a**, mp 190–191 °C, after recrystallization from a 4:1 mixture of benzene and petroleum ether.

8a: IR ν_{max} (KBr) 3470, 3320 (OH), 3060, 3025, 2960, 2920 (CH), 1650 (C=O), 1590 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 221 nm (ϵ 34 400 sh), 248 (24 800), 284 (5080); ^1H NMR ($CDCl_3$) δ 2.4 (1 H, br, D_2O exchangeable, OH), 4.6 (2 H, s, CH_2), 4.7 (1 H, s, H-8b), 6.8–7.9 (18 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 48.37 (C-8b), 59.53 (CH_2), 61.67 (C-4b), 119.9–150.11 (aromatic), 195.27 and 197.0 (C=O). Anal. Calcd for $C_{31}H_{22}O_3$: C, 84.16; H, 4.98; M_r = 442. Found C, 84.10; H, 5.25; M_r = 442 (mass spectrum).

In a repeat run, a methanol solution of **1a** was irradiated for $^1/_4$ h under analogous conditions to give 83% of **8a**. In another run, irradiation of an acetone solution of **1a** for $^1/_4$ h under analogous conditions gave 79% of **8a**.

Irradiation of 1b. A benzene solution of **1b** (880 mg, 2 mmol in 175 mL) was irradiated with a Hanovia 450-W medium-pressure mercury vapor lamp for 1 h and worked up to isolate 545 mg (62%) of **8b**, mmp 192–193 °C[10] (elution with a 2:3 mixture of benzene and petroleum ether), 25 mg (3%) of unchanged **1b**, mmp 216–217 °C (elution with a 1:1 mixture of benzene and petroleum ether) and 160 mg (18%) of **7**, mp 175 °C dec, after recrystallization from a 1:1 mixture of chloroform and methanol (elution with a 7:3 mixture of benzene and petroleum ether).

7: IR ν_{max} (KBr) 3500 (OH), 3050, 3020, 2960 (CH), and 1590 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 218 nm (ϵ 29 300 sh), 244 (28600), 272 (5790 sh), 293 (1710 sh); ^1H NMR (DMSO-d_6) δ 1.3 (3 H, d, CH_3), 3.2 (1 H, s, D_2O exchangeable, OH), 4.6 (1 H, s, bridgehead), 5.2 (1 H, q, CH), 7.2–8 (18 H, m, aromatic). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.26; H, 5.45. Found: C, 86.93; H, 5.65.

In a repeat run, a method solution **1b** was irradiated and worked up under analogous conditions to give 68% of **8b**, 3% of **1b** and 13% of **7**. In another run an acetone solution of **1b** (880 mg, 2 mmol in 175 mL) was irradiated under analogous conditions and worked up to separate 20 mg (2%) of **15**, mp 171–172 °C (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from methanol), 555 mg (63%) of **8b**, 25 mg (3%) of **1b**, and 165 mg (19%) of **7**.

15: IR ν_{max} (KBr) 3060, 2980, 2920 (CH), 1750 (C=C), 1645 and 1590 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 236 nm (ϵ 7740), 265 (2530 sh), 272 (2070 sh), 279 (1680 sh); ^1H NMR ($CDCl_3$) δ 1.5 (3 H, t, CH_3), 2.8 (2 H, q, CH_2) 5.1 (1 H, s, bridgehead), 6.8–7.7 (18 H, m, aromatic). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.26; H, 5.41; M_r = 440. Found: C, 87.20; H, 5.74; M_r = 440 (mass spectrum).

Irradiation of 1c. A benzene solution **1c** (502 mg, 1 mmol in 150 mL) was irradiated (RPR, 3500-Å light source) for 3 h and worked up in the usual manner to isolate 110 mg (22%) of **9**, mp 222 °C (elution with a 3:7 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of chloroform and methanol), and 210 mg (42%) of unchanged **1c**, mp 163–4 °C (elution with a 1:1 mixture of benzene and petroleum ether).

9: IR ν_{max} (KBr) 3050, 3020, 2960 (CH), 1665 (C=O), 1590 and 1570 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 244 nm (ϵ 32 700), 274 (12 900), 283 (11 300 sh), 292 (10 200 sh); ^1H NMR ($CDCl_3$) δ 5.65 (1 H, s, H-4b), 6.29 (1 H, s, H-10), 6.5–8.3 (24 H, m, benzylidenic and aromatic); ^{13}C NMR ($CDCl_3$) δ 56.22 (C-10), 61.32 (C-4b), 73.32 (C-9a), 123.76–148.8 (vinylic and aromatic), 198.88 and 199.14 (C=O). Anal. Calcd for $C_{37}H_{26}O_2$: C, 88.45; H, 5.18; M_r = 502. Found: C, 88.36; H, 5.22; M_r = 502 (mass spectrum).

In a repeat run, the irradiation of a methanol solution of **1c** under identical conditions yielded 21% of **9** and 56% of unchanged **1c**. In another run, an acetone solution of **1c** was irradiated (RPR, 2537-Å light source) for 2 h and worked up to separate 90 mg (18%) of **9** and 265 mg (53%) of **1c**.

Irradiation of 1d. A benzene solution of **1d** (480 mg, 1 mmol in 150 mL) was irradiated (RPR, 3500-Å light source) for 2 h. Workup in the usual manner gave 95 mg (20%) of **1d**, mmp 211–212 °C (elution with a 2:3 mixture of benzene and petroleum ether) and a mixture of **8d** and **13d** (elution with a 1:1 mixture of benzene and petroleum ether). **8d** and **13d** were separated by fractional crystallization from a 1:1 mixture of chloroform and methanol and further purified by recrystallization from a 1:1 mixture of benzene and petroleum ether.

8d: 85 mg (18%); mp 170–171 °C; IR ν_{max} (KBr) 3050, 3010, 2920, 2840 (CH), 1660 (C=O), 1590 and 1580 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 221 nm (ϵ 32 000 sh), 255 (23 100); ^1H NMR ($CDCl_3$) δ 0.9–2.2 and 3.3 (9 H, m, cyclopentyl), 4.7 (1 H, s, H-8b), 6.9–7.9 (18 H, m, aromatic). Anal. Calcd for $C_{35}H_{28}O_2$: C, 87.5; H, 5.83. Found: C, 87.15; H, 6.05.

13d: 115 mg (25%); mp 188–189 °C; IR ν_{max} (KBr) 3050, 3020, 2910, 2840 (CH), 1650 (C=O), 1590 and 1570 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 248 nm (ϵ 27 800), 286 (9330 sh); ^1H NMR ($CDCl_3$) δ 0.9–2.9 (9 H, m, cyclopentyl), 7–8.4 (19 H, m, vinylic and aromatic). Anal. Calcd for $C_{35}H_{28}O_2$: C, 87.5; H, 5.83. Found: C, 87.85; H, 5.91.

In a repeat run, a methanol solution of **1d**, irradiated under analogous conditions, gave a mixture of **1d** (20%), **8d** (21%), and **13d** (23%). In another run, an acetone solution of **1d** was irradiated (RPR, 2537-Å light source) for 2 h and worked up to yield **1d** (20%), **8d** (23%), and **13d** (21%).

Irradiation of 1e. A solution of **1e** in benzene (454 mg, 1 mmol in 150 mL) was irradiated (RPR, 3500-Å light source) for 3 h. Workup in the usual manner yielded 215 mg (45%) of unchanged **1d**, mp 180–181 °C (mixture melting point) (elution with a 2:3 mixture of benzene and petroleum ether), and 100 mg (22%) of **13e**, mp 149–150 °C (elution with a 1:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of chloroform and methanol).

13e: IR ν_{max} (KBr) 3060, 2960, 2020 (CH), 1660 (C=O), 1590 and 1575 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 248 nm (ϵ 28 800), 280 (10 900 sh); ^1H NMR ($CDCl_3$) δ 0.85 (3 H, d, CH_3), 0.95 (3 H, d, CH_3), 3.5 (1 H, m, CH), 5.8 (1 H, s, vinylic), 7–8 (18 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.75 (CH_3), 34.00 (CH), 126–148.14 (vinylic and aromatic), 195.80 and 197.68 (C=O). Anal. Calcd for $C_{33}H_{26}O_2$: C, 87.12; H, 5.73; M_r = 454. Found: C, 87.05; 4, 5.58; M_r = 454 (mass spectrum).

In a repeat run, the irradiation of a methanol solution of **1e** under analogous conditions gave, after workup, **1e** (48%) and **13e** (21%). In another run, an acetone solution of **1e** was irradiated (RPR, 2537-Å light source) and worked up in the usual manner to yield 51% of **1e** and 21% of **13e**.

Irradiation of 1f. A benzene solution of **1f** (494 mg, 1 mmol in 150 mL) was irradiated (RPR, 3000-Å light source) for 4 h. Workup in the usual manner yielded 105 mg (21%) of unchanged **1f**, mp 219–220 °C (mixture melting point) (elution with a 2:3 mixture of benzene and petroleum ether), and 270 mg (55%) of **13f**, mp 228–229 °C (elution with a 1:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of chloroform and methanol).

13f: IR ν_{max} (KBr) 3060, 3020, 2920, 2840 (CH), 1650 (C=O), 1590 and 1575 (C=C) cm^{-1}; UV λ_{max} (CH_3OH) 248 nm (ϵ 25 900), 275 (9410 sh); ^1H NMR ($CDCl_3$) δ 0.7–2.7 (11 H, m, cyclohexyl), 7–8.5 (18 H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 25.37, 26.1, 31.65, 31.87 and 45.06 (cyclohexyl), 126.35–148.39 (vinylic and aromatic), 195.79 and 197.77 (C=O). Anal. Calcd for $C_{36}H_{30}O_2$: C, 87.45; H, 6.07; M_r = 494. Found: C, 87.11; H, 6.41; M_r = 494 (mass spectrum).

In a similar run, a methanol solution of **1f** yielded 16% of unchanged **1f** and 46% of **13f**. In a repeat experiment, an acetone solution of **1f** was irradiated (RPR, 2537-Ålight source) for 3 h and worked up in the usual manner to separate **1f** (16%) and **13f** (46%).

Ozonolysis of 9. A solution of **9** (250 mg, 0.5 mmol in 50 mL of methanol) was ozonized at 0 °C. The reaction mixture was then treated with excess alkaline hydrogen peroxide, poured into water, and extracted with chloroform. Removal of the solvent gave a residue, which was triturated with methanol to yield 125 mg (57%) of **10**, mp 208–209 °C (mixture melting point).[10] The aqueous layer was acidified and worked up to separate 30 mg (50%) of benzoic acid (**11**), mp 121–122 °C (mixture melting point).

Laser Flash Photolysis. The laser flash photolysis experiments were performed mostly with 337.1-nm laser pulses (8 ns, 2–3 mJ) from a Molectron UV-400 nitrogen laser system. For some experiments, outputs at 485 and 532 nm (6 ns, 5–10 mJ) from a Quanta-Ray Nd-YAG DCR-1 source coupled with Quanta-Ray PDL-1 dye laser were also used. The details of the kinetic spectrophotometer and data collection system are given elsewhere.[25,26]

Pulse Radiolysis. The pulse radiolysis apparatus, which makes use of 5-ns electron pulses from Notre Dame ARCO linear accelerator (8 MeV, $\sim 10^{17}$ eV/g per pulse) and allows spectrophotometric observation of transients on microsecond-to-second time scales, is described elsewhere.[27,28]

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Registry No. **1a**, 110971-39-6; **1b**, 96555-76-9; **1c**, 110971-40-9; **1d**, 110971-41-0; **1e**, 110971-42-1; **1f**, 111004-89-8; **7**, 110971-45-4; **8a**, 110971-44-3; **8b**, 96555-83-8; **8d**, 110971-48-7; **9**, 111004-90-1; **10**, 96555-79-2; **13d**, 110971-47-6; **13e**, 110971-49-8; **13f**, 110971-50-1; **15b**, 110971-46-5; DTBN, 2406-25-9; DBA, 1087-09-8; O_2, 7782-44-7; ferrocene, 102-54-5; 9-(hydroxymethyl)anthracene, 1468-95-7; 9-(phenylmethyl)anthracene, 1498-71-1; 9-cyclopentylanthracene, 110971-43-2; 9-isopropylanthracene, 1498-80-2; 9-cyclohexylanthracene, 4368-48-3.

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Modification of Photochemical Reactivity by Cyclodextrin Complexation: A Remarkable Effect on the Photobehavior of α-Alkyldibenzyl Ketones

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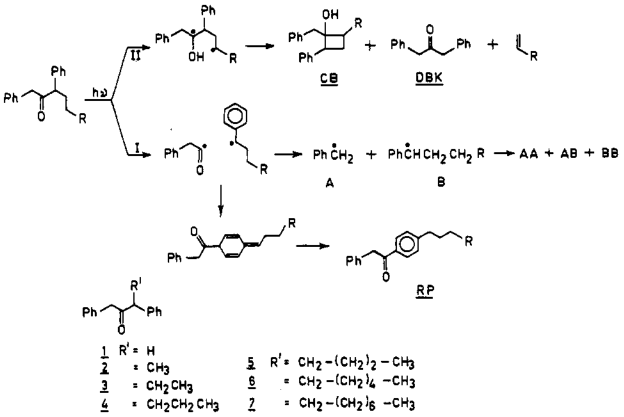
The Norrish type I and type II reactions of cyclodextrin-included α-alkyldibenzyl ketones have been investigated in the aqueous solution and in the solid state. The photolysis of solid cyclodextrin complexes led to a single product, diphenylethane (AB), and that of complexes in the aqueous solution resulted in a product arising from the rearrangement of α-alkyldibenzyl ketones. Conformational and super-cage effects are proposed to be responsible for the dramatic alteration observed in the above photobehavior. The difference in the product distribution between solid and solution complexes is attributed to the differences in the restriction imposed by the host on the translational motions of the geminate radical pairs.

During the last few years, our group has been investigating the influence of cyclodextrin cavity on the photochemical reactions in host–guest complexes.[1,2] The goal is to achieve selectivity in photochemical reactions using this unusual environment and to understand the features controlling such selectivity. During one such study a remarkable effect was observed on the photoreactivity of benzoin alkyl ethers and alklkyldeoxybenzoins upon cyclodextrin complexation.[3] This was attributed to a combination of the "cage effect" and "conformational control" afforded by the cyclodextrin.

In order to explore the general utility of the "conformational control" and the "cage effect" offered by cyclodextrin in modifying photoreactions, we have investigated the photobehavior of dibenzyl ketones 1–7 (Scheme I). The photolysis of dibenzyl ketones has been explored extensively in several anisotropic environments.[4] We envisioned that cyclodextrin encapsulation of 3–7 can impose a conformational control on these substrates and thus alter the type I and the type II product distributions with respect to an isotropic medium. Further, we noted that the cavity might have an impact on the diffusional separartion of the radical pairs resulting from the type I process and also on the choice of reactions that these radical pairs might undergo. The results of such a study are presented below.

Results

Scheme I



Photolysis of dibenzyl ketones 3–7 in nitrogen-saturated benzene and methanol gave products resulting from the Norrish type I and the type II reactions. A statistical mixture of the coupling products AA, AB, and BB (1:2:1) resulting from the photodecarbonylation were major and those from the γ-hydrogen abstraction minor (~15%). Expectedly, from 3–7, the products resulting from the

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