2.72-3.42 (m, 1 H), 6.51 (d, 1 H, *J* = 10 Hz), 7.24-7.66 (m, 5 H). Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65. Found: C, 88.26; H, 7.80.

Base-Catalyzed Reaction of *n*-Butyraldehyde and Chloroform. To a solution of *n*-butyraldehyde (100 mmol) and chloroform (100 mmol) in DMF (50 mL) was added a suspension of base (10 mmol) in DMF (10 mL) at 0 °C for 1 h. After the mixture was stirred at 0 °C for 4 h, it was poured into 300 mL of a saturated solution of sodium chloride and extracted with ether. After evaporation of ether, 1a was isolated by distillation.

Registry No. 1a, 6111-12-2; 1b, 32766-45-3; 1c, 78409-34-4; 1d, 2000-43-3; 1e, 14337-31-6; 1f, 70033-16-8; 1g, 815-00-9; 1h, 96349-56-3; 1i, 4776-43-6; 1j, 82772-36-9; 1k, 82772-38-1; 1l, 82772-37-0; 1m, 85363-86-6; 1n, 96349-57-4; 1o, 96349-58-5; 1p, 96349-59-6; 1q, 6111-14-4; 1r, 58369-59-8; 1s, 59424-91-8; 1t, 75820-73-4; 1u, 7228-30-0; 1v, 5333-82-4; 1w, 19126-05-7; 1x, 96349-60-9; 1y, 62798-94-1; 1z, 67916-20-5; 2a, 3508-84-7; 2b, 10292-51-0; 2c, 96349-61-0; 2d, 90347-44-7; 2e, 6111-25-7; 3, 19376-15-9; 4a, 96349-62-1; 4b, 38158-81-5; 5a, 96349-63-2; 5b, 29804-78-2; 5c, 96349-64-3; 5d, 96349-65-4; 5e, 96349-66-5; 5f, 16715-03-0; 5g, 96349-67-6; 5h, 96349-68-7; *threo*-7a, 96349-70-1; *erythro*-7a, 82584-40-5; *threo*-7b, 17226-94-7; *erythro*-7b, 17226-93-6; 8, 6519-09-1; 9, 96349-69-8; 10, 6519-10-4; 11, 2510-95-4; CCl_4, 56-23-5; $CHCl_3$, 67-66-3; *n*-C_3H_7CHO, 123-72-8; *i*-C_3H_7CHO, 78-84-2; $CH_3CH_2CH(CH_3)CHO$, 96-17-3; C_6H_5CHO, 100-52-7; *p*-$CH_3OC_6H_4CHO$, 123-11-5; CH_2=CHCHO, 107-02-8; (*E*)-CH_3CH=CHCHO, 123-73-9; $CH_3(CH_2)_6CHO$, 124-13-0; $CH_3(CH_2)_3CH(CH_2CH_3)CHO$, 123-05-7; $C_6H_5(CH_2)_2CHO$, 104-53-0; $(CH_3)_2C$=CH($CH_2)_2CH(CH_3)CH_2CHO$, 106-23-0; $CH_3O(CH_2)_2$-CHO, 2606-84-0; $CH_3(CH_2)_2CH$=CHCHO, 505-57-7; (*E*)-C_6H_5CH=CHCHO, 14371-10-9; (*E*)-$(CH_3)_2C$=CH($CH_2)_2C$-(CH_3)=CHCHO, 141-27-5; $(CH_3)_2C$=CHCHO, 107-86-8; *o*-$CH_3OC_6H_4CHO$, 135-02-4; *m*-$CH_3OC_6H_4CHO$, 591-31-1; *p*-$C_6H_5CH_2OC_6H_4CHO$, 4397-53-9; *p*-ClC_6H_4CHO, 104-88-1; *p*-$CH_3O_2CC_6H_4CHO$, 1571-08-0; *o*-$O_2NC_6H_4CHO$, 552-89-6; CH_3C-$O(CH_2)_4CH_3$, 110-43-0; $C_6H_5COCH_3$, 98-86-2; $CH_3(CH_2)_2CO(C$-$H_2)_2CH_3$, 123-19-3; CBr_4, 558-13-4; $CHBr_3$, 75-25-2; $CCl_3CO_2CH_3$, 598-99-2; $CHCl_2CO_2CH_3$, 116-54-1; $C_6H_5CH_2CO_2CH_3$, 101-41-7; $C_6H_5CHBrCO_2CH_3$, 3042-81-7; $C_6H_5CH_2CN$, 140-29-4; C_6H_5CH-BrCN, 5798-79-8; CH_2=CHOAc, 108-05-4; $C_6H_5CH(OH)CH_2Cl$, 1674-30-2; $C_6H_5CHClCH_2OH$, 1004-99-5; $CH_3CH_2CH(OH)CH_2Cl$, 1873-25-2; furfural, 98-01-1; piperonal, 120-57-0; 1-naphthalene-carboxaldehyde, 66-77-3; nicotinaldehyde, 500-22-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; phenyloxirane, 96-09-3; ethyloxirane, 106-88-7.

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

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The photochemistry of bridgehead-substituted dibenzobarrelenes 1a–h (Scheme I) has been investigated by steady-state photolysis, product analysis, and time-resolved laser flash photolysis. 4b-Substituted dibenzo-semibullvalenes 8b,c,f,g are formed as major photoproducts from dibenzobarrelenes 1b,c,f,g, bearing acetoxy, formyl, ethyl, and methoxy 9-bridgehead substituents, whereas 8b-substituted dibenzosemibullvalenes (or products derived from them) (7 and 6e) are formed from 9-hydroxy- and 9-cyano-substituted dibenzobarrelenes 1a,e. Laser flash photolysis gives rise to transient phenomena attributable to the triplets of dibenzobarrelenes (ϕ_T = 0.2–0.7 in benzene). These are characterized by broad and diffuse absorption spectra, short lifetimes (0.07–11 μs), and varying degrees of quenchability by azulene, ferrocene, β-carotene, and *p*-methoxyphenol. The rate constants for triplet quenching by the latter quenchers as well as oxygen and di-*tert*-butylnitroxy radicals are presented.

Several reports have appeared on the phototransformations of barrelenes and different barrelene derivatives.[3] Barrelenes undergo facile photoisomerization to give the corresponding semibullvalenes, under triplet-sensitized irradiation, whereas on direct irradiation, cyclooctatetraene derivatives are formed. Vinylic and bridgehead substituents affect the stabilities of the diradical intermediates and thereby influence the regioselectivities of these rearrangements.[4-8] Electronegativities of the bridgehead substituents[8] and the presence of methoxycarbonyl and

similar groups on the vinyl moiety, which can stabilize adjacent radical sites through π-delocalization,[4] are factors that affect the stabilities of such diradical intermediates. In addition, the presence of proximal hydroxy and acetoxy groups also stabilizes radical sites by through-space interactions, in some cases.[5,6]

Earlier,[9] we have shown that dibenzobarrelenes containing 1,2-dibenzoylalkene moieties prefer to undergo the di-π-methane rearrangement (Zimmerman rearrangement)[3b] than the 1,2-dibenzoylalkene rearrangement.[10] In

(1) Document No. NDRL-2616 from the Notre Dame Radiation Laboratory.

(2) (a) Indian Institute of Technology. (b) University of Notre Dame.

(3) For some recent reviews containing references to the photorearrangement of barrelenes, see: (a) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551. (b) Zimmerman, H. E. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, pp 131–166.

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

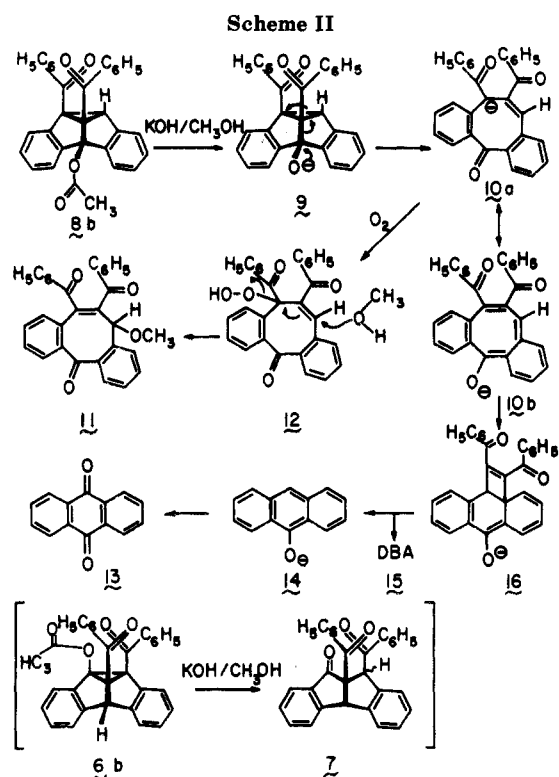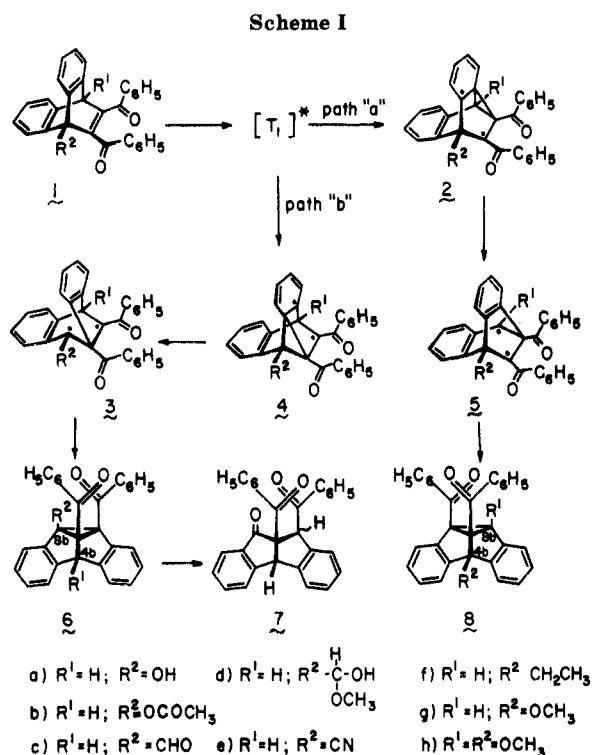(6) Hart, H.; Love, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4592–4599.

(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.

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(10) For some examples of the photorearrangement of 1,2-dibenzoyl-alkenes, see: (a) Griffin, G. W.; O'Connell, E. J. *J. Am. Chem. Soc.* **1962**, *84*, 4148–4149. (b) Zimmerman, H. E.; Dürr, H. G. 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.; Chackachery, E.; Kumar, C. V.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1980**, *45*, 3782–3790. (g) Lahiri, S. Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1977. (h) Kumar, C. V. Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1981. (i) Murty, B. A. R. C. Ph.D. Thesis, Indian Institute of Technology, Kanpur, 1982.

Scheme I

a) R^1 = H; R^2 = OH   d) R^1 = H; R^2 -$\overset{H}{\underset{OCH_3}{C}}$-OH   f) R^1 = H; R^2 CH$_2CH_3$

b) R^1 = H; R^2 OCOCH$_3$ g) R^1 = H; R^2 = OCH$_3$

c) R^1 = H; R^2 = CHO   e) R^1 = H; R^2 = CN   h) R^1 = R^2 = OCH$_3$

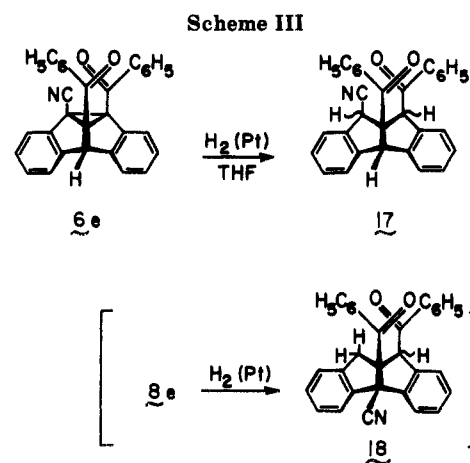**Scheme II**

Scheme III

the present investigation, several bridgehead-substituted dibenzobarrelenes have been examined through steady-state and laser flash photolysis to understand the mechanistic details. The substrates include 11,12-dibenzoyl-9,10-dihydro-9-hydroxy-9,10-ethenoanthracene (1a) (Scheme I), 9-acetoxy-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1b), 11,12-dibenzoyl-9,10-dihydro-9-formyl-9,10-ethenoanthracene (1c), 9-cyano-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (1e), 11,12-dibenzoyl-9,10-dihydro-9-ethyl-9,10-ethenoanthracene (1f), 11,12-dibenzoyl-9,10-dihydro-9-methoxy-9,10-ethenoanthracene (1g), and 11,12-dibenzoyl-9,10-dihydro-9,10-dimethoxy-9,10-ethenoanthracene (1h).

Results and Discussion

1. Preparation of 11,12-Dibenzoyl-9,10-dihydro-9,10-ethenoanthracenes 1a–c,e–h. A convenient method of preparation involves the reaction of anthracenes with dibenzoylacetylene (DBA), either by direct heating[11a] or in the presence of catalysts such as aluminum chloride.[11b] Thus 1a, 1f, 1g, and 1h could be prepared through the reaction of the appropriate anthracenes with DBA in the presence of aluminum chloride in dichloromethane. In the case of 1a, however, addition of a catalytic amount of pyridine gave better results. On the other hand, 1b, 1c, and 1e were prepared by refluxing, in each case, an equimolar mixture of the anthracene and DBA in dry xylene.

2. Preparative Photochemistry and Product Identification. Irradiation of 1a in benzene gave a 26% yield of 9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-9-oxo-cis-indeno[1,2-a]indene (7) (Scheme I), 4% of benzoic acid, and 50% of the starting material (1a), whereas in acetone, the corresponding yields of 7 and benzoic acid were 62% and 7%, respectively. Irradiation of 1b in methanol gave an 88% yield of 4b-acetoxy-8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[c,d]pentalene (8b),

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whereas the corresponding yields of 8b in benzene and acetone were 88% and 92%, respectively. Treatment of 8b with methanolic potassium hydroxide gave a mixture of 11 (39%) and anthraquinone (13, 26%). A probable pathway for the formation of 11 and 13 is shown in Scheme II. If the photoproduct from 1b were the 8b-acetoxy derivative 6b, then the base hydrolysis would have given the keto derivative 7 and not the observed product 11 (Scheme II).

Similarly, 1c, 1f, and 1g on irradiation gave the corresponding 4b-substituted semibullvalenes 8c, 8f, and 8g, respectively. In methanol 1c could exist as the hemiacetal 1d, and therefore the photoreaction of 1d was separately examined. Refluxing 1c in methanol for 30 min gave a nearly quantitative yield of 1d. Irradiation of 1d in methanol gave a 48% yield of 8c, and it is likely that 8d, which is initially formed in the photoreaction, is undergoing conversion to 8c during workup.

Irradiation of 1e gave the 8b-cyano-substituted semibullvalene 6e. Catalytic hydrogenation of 6e over platinum in THF gave a 82% yield of 9-cyano-9a,10-dibenzoyl-4b,9,9a,10-tetrahydro-cis-indeno[1,2-a]indene (17) (Scheme III). If 8e were the photoproduct from 1e, wherein the

CN group is at the C-4b position, then **18** would have resulted on hydrogenation (Scheme III). The ^{1}H NMR results clearly indicate that the hydrogenation product is **17** and not **18**.

The formation of the different dibenzosemibullvalenes in the phototransformations of **1a–g** could be rationalized by the pathway shown in Scheme I, which is in tune with the earlier reported mechanism for the barrelene rearrangement.[12] A benzo–vinyl bridging could lead to the diradical intermediates **2** or **4**, which are then transformed to the regioisomeric products **8** or **6**, respectively. The exclusive formation of the 4b-regioisomer **8b** in the case of **1b** could be due to the destabilization of the cyclopropane ring in **4** by the strongly electronegative acetoxy group, as compared to **2**. Thus, path a (Scheme I), involving **2** and leading to **8b**, is the preferred route in this case. In general, the presence of electronegative substituents at the bridgehead position of the dibenzobarrelenes favors the formation of the 4b-substituted semibullvalenes, if there are no overriding steric factors influencing the regioselectivity. In the case of **1a**, however, despite the high electronegativity of the hydroxy group, path b is followed, leading to the 8b-isomer **6a**, which ultimately leads to the keto derivative **7**. It is feasible that the hydroxy group is involved in hydrogen bonding with the adjacent benzoyl group. Since the electron density of the benzoyl group in **2** is reduced by resonance delocalization, structure **4** will be more stabilized through hydrogen bonding and hence path b will be preferred. The cyano derivative **1e**, unlike other barrelene derivatives containing electronegative groups, gives exclusively the 8b-isomer **6e**. The anomalous effect of the cyano group in such photoisomerizations has also been observed earlier. Thus, in the photoisomerization of benzobarrelene to benzocyclooctatetraene, a benzo–vinyl bridging is involved to the extent of 94%,[13a] whereas in the case of 2-cyanobenzobarrelene, a cyanovinyl–vinyl bridging is involved to the extent of 76%.[13b] The effect of the cyano substituent here cannot be rationalized in terms of simple electronegativity considerations alone.

The formation of small amounts of benzoic acid in these reactions may be through dioxetane intermediates, formed by the reaction of the starting dibenzobarrelenes with singlet oxygen. A possible source of singlet oxygen would be through the quenching of dibenzobarrelene triplets by oxygen, present in small amounts as a contaminant, under the reaction conditions. To verify this possibility, we have measured the efficiency (ϕ_Δ) of singlet oxygen ($^1O_2{}^*$) generation by laser flash photolysis (337.1 nm), using 1,3-diphenylisobenzofuran (DPBF) as a monitor for singlet oxygen.[14] The ϕ_Δ values for **1a–c,e,f** have been found to vary between 0.17 and 0.66, indicating that singlet oxygen will be generated easily under the reaction conditions, even if oxygen is present in small amounts.

Irradiation of the 9,10-dimethoxybarrelene **1h** in methanol for 1.5 h gave a 32% yield of **8h** (**6h**), whereas continued irradiation for 5 h gave an 86% yield of **8h** (**6h**) (Scheme I). Similar results were obtained when the irra-
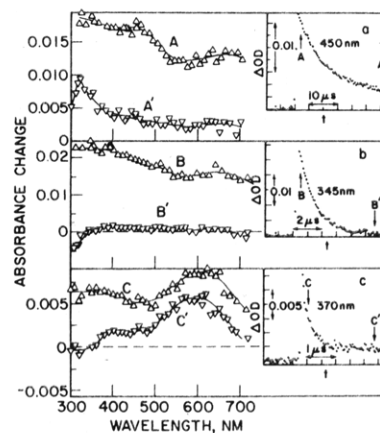
(12) (a) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. .. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933. (b) Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1969**, *91*, 1718–1727.

(13) (a) Rabideau, R. W.; Hamilton, J. B.; Friedman, L. *J. Am. Chem. Soc.* **1968**, *90*, 4465–4466. (b) Bender, C. O.; Shugarman, S. S. *J. Chem. Soc., Chem. Commun.* **1974**, 934–935.

(14) The efficiency (ϕ_Δ) of singlet oxygen generation by oxygen quenching of the dibenzobarrelenes **1a–c, e–h** was determined by a reported procedure (see: Chattopadhyay, S. K.; Kumar, C. V.; Das, P. K. *J. Photochem.* **1984**, *24*, 1–9). The observed ϕ_Δ values are indicated in parentheses: **1a** (0.66), **1b** (0.62), **1c** (0.41), **1e** (0.44), **1f** (0.57), **1g** (0.57), and **1h** (0.17).

Figure 1. Transient absorption spectra observed upon 337.1-nm laser flash photolysis of **1a** (A, A′), **1f** (B, B′), and **1h** (C, C′) in benzene. The times after laser flash at which the spectra were taken are marked by arrows in the representative kinetic traces in the insets a, b, and c, respectively.
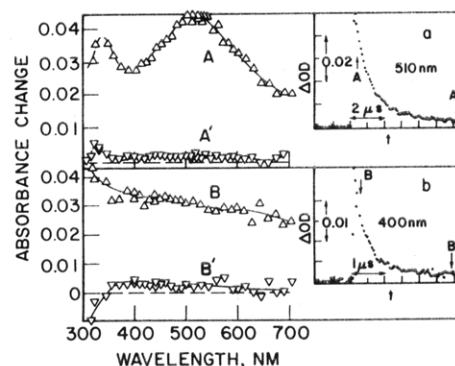

Figure 2. Transient absorption spectra observed upon laser flash photolysis of **1b** (A, A′), and **1e** (B, B′) in benzene. The times following laser flash at which the spectra were taken are indicated by arrows in the kinetic traces in the insets a and b, respectively.
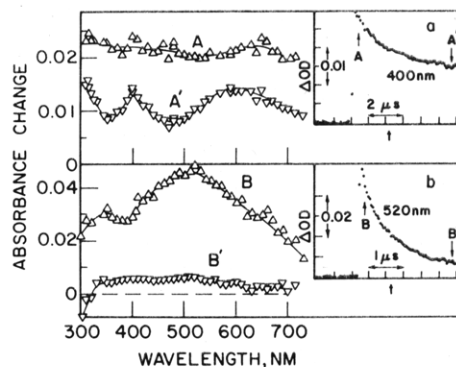

Figure 3. Transient absorption spectra observed upon laser flash photolysis of **1c** (A, A′) and **1g** (B, B′) in benzene. The times following laser flash at which the spectra were taken are indicated by arrows in the kinetic traces in the insets a and b, respectively.

diation was carried out in benzene or acetone.

3. Laser Flash Photolysis Studies. (a) General Features. The transients observed over 0.1–100 μs following 337.1-nm laser excitation of **1a–c,e–h** were characterized by broad and diffuse absorption spectra extending beyond 700 nm. These were assigned primarily to the triplets of the dibenzobarrelenes on the basis of quenching effects of oxygen, di-*tert*-butyl nitroxide (DTBN, stable free radical), azulene, ferrocene, and β-carotene. With β-carotene as the quencher, growths of intense transient absorption due to β-carotene triplet were observed at 510–550 nm at the same time scale as that of the decay of the dibenzobarrelene triplets (monitored at

Table I. Absorption Spectral and Kinetic Data of the Triplets of Dibenzobarrelenes

substrate (R^1, R^2)	solvent	λ_{max},[a] nm	$10^{-3}\epsilon T_{max}$,[b] M^{-1} cm^{-1}	τ_T,[c] μs	ϕ_T[b]
1a (H, OH)	benzene	430	3	11 (0.20)	0.7
	methanol	440		2.0	
1b (H, OCOCH$_3$)	benzene	510	7	0.85 (0.33)	0.7
	methanol	510		1.7	
1c (H, CHO)	benzene	~410	6	1.8 (0.18)	0.6
	methanol	~510		1.5	
1e (H, CN)	benzene	510	6	0.34 (0.15)	0.7
	methanol	510		0.50	
1f (H, C$_2$H$_5$)	benzene	510	5	1.0 (0.21)	0.6
	methanol	500		1.7	
1g (H, OCH$_3$)	benzene	~390	6	1.2 (0.17)	0.6
	methanol			1.6	
1h (OCH$_3$, OCH$_3$)	benzene	~370		0.28 (0.10)	0.2
	methanol			0.07	

[a] ±10 nm. [b] ±30%. [c] ±15%; the data in parentheses are triplet lifetimes in oxygen-saturated benzene.

Table II. Bimolecular Rate Constants for the Quenching of Dibenzobarrelene Triplets in Benzene

substrate (R^1, R^2)	10^{-9} k_q T,[a] M^{-1} s^{-1}					
	O$_2$	DTBN	p-methoxyphenol	azulene	ferrocene	β-carotene
1a (H, OH)	0.59	0.85	2.2	2.1	6.7	5
1b (H, OCOCH$_3$)	0.28	0.96	5.0	4.6	5.7	7
1c (H, CHO)	0.57	1.2	3.9	1.1	6.4	5
1e (H, CN)	0.60	1.7	6.1	3.7	6.3	7
1f (H, C$_2$H$_5$)	0.48	0.49	3.6	0.75	5.0	4
1g (H, OCH$_3$)	0.59	0.14	1.0	~0.4	2.1	5
1h (OCH$_3$, OCH$_3$)	0.71		0.5	<0.2	3.0	3

[a] ±15%.

600–700 nm). For **1a**, **1c**, and **1e**, the triplet assignment was corroborated by using pulse-radiolytically[15] produced biphenyl triplet (in benzene) as the sensitizer to generate the same transient species as seen in the course of laser flash photolysis. Interestingly, p-methoxyphenol was found to be an efficient quencher[16] of dibenzobarrelene triplets in benzene; that hydrogen abstraction occurred in the course of this quenching interaction was shown by the formation of p-methoxyphenoxy radical with a characteristic absorption spectrum[17] at 370–430 nm (λ_{max} = 405 nm).

In Figures 1–3, several absorption spectra and kinetic traces in benzene are presented to illustrate the transient processes. The spectral and kinetic data of the triplets and triplet yields (ϕ_T) are given in Table I. ϵ^T_{max} and ϕ_T data were obtained by comparative techniques using benzophenone triplet formation in benzene for actinometry and β-carotene as a triplet counter. Details of these methods are described in earlier papers.[9,18] The linear plots of pseudo-first-order rate constants for the decay of dibenzobarrelene triplets against quencher concentrations gave the bimolecular rate constants (k_q^T) for quenching. The data concerning k_q^T are presented in Table II. *trans*-Stilbene (E_T = 50 kcal mol^{-1})[19] at concentrations ≤4 mM had no appreciable effect on the decay of the dibenzobarrelene triplets.

(b) Dibenzobarrelenes 1a, 1g, and 1h. For **1a**, in addition to the relatively long-lived triplet (τ_T = 11 μs, λ_{max} = 325, 430, and 670 nm), the transient spectra (Figure 1A)

(15) For a description of pulse-radiolytic generation of triplets, see: Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904–1915.

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show a photoproduct (λ_{max} = 325 nm) persisting at the end of the triplet decay. In methanol, the triplet is shorter-lived (τ_T = 3 μs) and acts as a precursor for a long-lived transient product (τ ~ 150 μs, λ_{max} = 340 and 450 nm). We assign the latter as the product of hydrogen abstraction by the triplet of **1a** on the basis of the fact that upon quenching the triplet of **1a** by p-methoxyphenol in benzene, a species having spectral features similar to those of the photoproduct in methanol is formed (in addition to p-methoxyphenoxy radical). The triplet of **1g** is shorter lived (τ_T = 1.2 μs in benzene) and gives rise to practically no residual absorption (Figure 1B,B'), except a small depletion at 310–330 nm. The triplet decay is slightly slower in methanol (τ_T = 1.6 μs), and there is no indication of hydrogen abstraction by the triplet from methanol. The lower propensity for hydrogen abstraction by **1g** is also reflected in the smaller k_q^T for p-methoxyphenol (Table II); however, the absorption spectra of the photoproducts from triplet quenching by p-methoxyphenol bear resemblance to those from **1a**. Compared to **1a** and **1g**, τ_T for **1h** is very short (0.28 μs in benzene) and a long-lived triplet-mediated photoproducts (τ > 200 μs, λ_{max} = 600 nm, Figure 1C,C') becomes apparent after the completion of triplet decay. The transient absorption signals from **1h** are very poor, presumably due to smaller triplet yield (ϕ_T = 0.2 in benzene). The transient behavior in methanol is complex, as is evident from dual decay kinetics (τ ~ 0.07 and ~0.8 μs) at all wavelengths (350–700 nm).

(c) Dibenzobarrelenes 1b and 1e. The triplets of both **1b** and **1e** display broad absorption maxima at ~510 nm (Figure 2A,A',B,B') and have their lifetimes lengthened by a factor of ~2 on going from benzene to methanol (Table I). The residual absorption following the decay of triplet of **1b** shows a weak band system at 310–340 nm (Figure 2A'), while for **1e**, ground-state bleaching is observed (Figure 2B').

(d) Dibenzobarrelenes 1c and 1g. A prominent feature for **1c** in benzene is the formation of a long-lived photoproduct (triplet mediated) with λ_{max} at 320, 410, and

595 nm (Figure 3A'). Conceivably the photoproduct can be a radical from the photocleavage of the formyl group or a diradical produced by intramolecular formyl hydrogen abstraction, followed by the loss of CO. The photoproduct in question is not produced in methanol in which the triplet lives nearly as long as in benzene. There is no special reason for the C–C bond photofragmentation and the loss of ·CHO to be more facile in benzene than in methanol; it seems more plausible that the observed photoproduct in benzene is related to the intramolecular hydrogen abstraction, this process being less favorable in methanol, because of hydrogen bonding of the carbonyl chromophore with the solvent. For **1g** (Figure 3B,B'), although the triplet lifetimes are relatively short, there is no indication of the formation of a long-lived photoproduct (e.g., by intramolecular hydrogen abstraction in the triplet state).

(e) Summary and Conclusions. The diffuse nature of the triplet–triplet absorption spectra of the dibenzobarrelenes suggests that the triplet excitation involves the barrelene chromophore as a whole, rather than being localized on the dibenzoylakene moiety. It is also possible that specific triplet diradicals represented by structures **2–5** exist in variable concentrations in equilibrium with their precursor triplet and contribute to the observed absorption spectra. The complex decay behaviors noted for **1h** in methanol can possibly arise due to the transformation of the initially formed triplet to longer-lived diradical structures. The rate constants (Table II) for quenching by azulene (E_T = 39 kcal mol^{-1})[20] and ferrocene (E_T = 38–41 kcal mol^{-1})[20] indicate that the triplet energies (E_T) of the dibenzobarrelenes (**1a–c,e–h**) are close to 40 kcal mol^{-1}. The relatively small k_q^T values in the case of **1f** and **1h** are explainable either by the lowering of E_T because of greater contribution of diradical structures to the triplet or in terms of equilibrium mixtures of dibenzoylalkene triplets and diradical triplets, with the latter predominating.

Experimental Section

All steady-state irradiations were carried out in a Srinivasan-Griffin Rayonet photochemical reactor (RPR) or by using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketed immersion well. Solvents for photolysis were purified and distilled before use, whereas Aldrich Gold Label solvents were used for laser studies. All new compounds were fully characterized, on the basis of analytical results and spectral data. Due to limitations of space, only the bare minimum data are presented.

Preparation of Dibenzobarrelenes 1a–h. Dibenzobarrelenes **1a–c,e** were prepared by refluxing an equimolar mixture of the appropriate anthracene and DBA in xylene, in each case, and chromatographing the product over silica gel, followed by recrystallization from suitable solvents. **1d** was prepared by refluxing **1c** in dry methanol for 0.5 h and workup by removal of the solvent under vacuum. **1f–h** were prepared by treating an equimolar mixture of the appropriate anthracene and AlCl$_3$ with DBA in dichloromethane and workup, after treatment with water. Melting points, percentage yield, spectral data [IR ν_{max} (KBr) (cm^{-1}; UV λ_{max} (CH$_3$OH) (nm (ϵ)); ^{1}H NMR (CDCl$_3$) (δ); ^{13}C NMR (CDCl$_3$) (δ)], and analytical results are presented in that order for each compound.

1a: mp 212–213 °C (72%); IR ν_{max} 3450 (OH); UV λ_{max} 268 (5760), 300 (2000, sh); ^{1}H NMR δ 5.10 (1 H, s, D$_2$O exchangeable, OH), 5.60 (1 H, s, bridgehead), 6.90–7.90 (18 H, m, aromatic). Anal. Calcd for C$_{30}$H$_{20}$O$_3$: C, 84.11; H, 4.67. Found: C, 83.58; H, 4.25.

1b: mp 232–233 °C (50%); IR ν_{max} 1740 (C=O, ester), 1660 (C=O, keto); UV λ_{max} 230 (21 700), 236 (27 500), 242 (33 300), 246 (43 400), 253 (50 600); ^{1}H NMR δ 2.38 (3 H, s, CH$_3$), 5.47 (1, H, s, bridgehead), 6.78–7.69 (18 H, m, aromatic); ^{13}C NMR δ 21.30

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(CH$_3$), 52.33 (C-10), 86.27 (C-9), 121.16–150.31 (aromatic); 169.88 (C=O, ester), 192.10 (C=O, keto), 194.24 (C=O, keto). Anal. Calcd for C$_{32}$H$_{22}$O$_4$: C, 81.70; H, 4.68; M_r = 470. Found: C, 82.13; H, 4.37; M_r = 470 (mass spectrum).

1c: mp 191 °C (40%); IR ν_{max} 1730 (C=O, formyl), 1650 (C=O, keto); UV λ_{max} 230 (25 600), 236 (26 000), 242 (30 200), 247 (36 900), 253 (41 500), 259 (35 600); ^{1}H NMR δ 5.56 (1 H, s, bridgehead), 6.88–7.91 (18 H, m, aromatic), 10.88 (1 H, s, formyl). Anal. Calcd for C$_{31}$H$_{20}$O$_3$: C, 84.55; H, 4.55; M_r = 440. Found: C, 84.30; H, 4.72; M_r = 440 (mass spectrum).

1d: mp 170–172 °C (d); IR ν_{max} 3300 (OH), 1650 (C=O); UV λ_{max} 270 (8200), 300 (2300, sh); ^{1}H NMR δ 1.25 (1 H, s, D$_2$O exchangeable, OH), 3.5 (3 H, s, OCH$_3$), 5.5 (1 H, s, bridgehead), 5.9 (1 H, s, methine), 7.6 (18 H, m, aromatic). Anal. Calcd for C$_{32}$H$_{24}$O$_4$: C, 81.36; H, 5.09. Found: C, 81.10; H, 4.82.

1e: mp 198 °C (40%); IR ν_{max} 2240 (C≡N), 1650 (C=O); UV λ_{max} 237 (27 000), 242 (31 800), 246 (42 100), 253 (49 300), 260 (41 300); ^{1}H NMR δ 5.66 (1 H, s, bridgehead), 6.94–8.06 (18 H, m, aromatic); ^{13}C NMR δ 52.63 and 53.91 (C-9, C-10), 115.12 (CN), 122.61–151.50 (aromatic), 191.71 (C=O), 193.11 (C=O). Anal. Calcd for C$_{31}$H$_{19}$O$_2$N: C, 85.13; H, 4.35; N, 3.20; M_r = 437. Found: C, 84.92; H, 4.51; N, 3.09; M_r = 437 (mass spectrum).

1f: mp 217 °C (78%); IR ν_{max} 1650 (C=O); UV λ_{max} 232 (23 600), 237 (24 300), 242 (27 800), 247 (33 800), 253 (35 200), 259 (33 800); ^{1}H NMR δ 1.19 (3 H, t, CH$_3$), 2.91 (2 H, q, CH$_2$), 5.47 (1 H, m, aromatic); ^{13}C NMR δ 11.07 (CH$_3$), 19.28 (CH$_2$), 53.42 (C-10), 58.18 (C-9), 122.64–152.96 (aromatic), 194.40 (C=O), 195.69 (C=O). Anal. Calcd for C$_{32}$H$_{24}$O$_2$: C, 87.26; H, 5.45; M_r = 440. Found: C, 86.98; H, 5.53; M_r = 440 (mass spectrum).

1g: mp 146 °C (78%); IR λ_{max} 1645 (C=O); UV λ_{max} 231 (27 600), 236 (28 600), 242 (33 800), 247 (42 100), 253 (48 400), 259 (41 600); ^{1}H NMR δ 3.94 (3 H, s, OCH$_3$), 5.56 (1 H, s, bridgehead), 6.91–8.16 (18 H, m, aromatic); ^{13}C NMR δ 52.23 (OCH$_3$), 57.38 (C-10), 90.48 (C-9), 121.85–156.28 (aromatic), 193.73 (C=O), 194.23 (C=O). Anal. Calcd for C$_{31}$H$_{22}$O$_3$: 84.16; H, 4.77; M_r = 442. Found: C, 84.30; H, 4.77; M_r = 442 (mass spectrum).

1h: mp 221 °C (74%); IR ν_{max} 1645 (C=O); UV λ_{max} 231 (30 000), 238 (31 300), 242 (38 400), 246 (50 100), 252 (57 900), 260 (48 800); ^{1}H NMR δ 3.94 (6 H, s, OCH$_3$), 6.91–8.47 (18 H, m, aromatic); ^{13}C NMR δ 57.07 (OCH$_3$), 88.00 (bridgehead), 121.16–152.70 (aromatic), 193.96 (C=O). Anal. Calcd for C$_{32}$H$_{24}$O$_4$: C, 81.36; H, 5.08; M_r = 472. Found: C, 81.54; H, 4.79; M_r = 472 (mass spectrum).

Irradiation of 1a–h. General Procedure. A general procedure involved the irradiation of a dilute solution of the appropriate barrelene in a solvent (0.25–6.5 mmol in 50–1500 mL) for 1–10 h, followed by removal of the solvent under vacuum. The product was extracted with bicarbonate to give benzoic acid (acidification with dilute HCl), and the nonacid fraction was chromatographed over silica gel and finally purified by recrystallization from different solvents. The products formed, in each case, their melting points, percentage yield, spectral data (IR ν_{max} (KBr) (cm^{-1}); UV λ_{max} (CH$_3$OH) (nm (ϵ)); ^{1}H NMR (CDCl$_3$) (δ); ^{13}C NMR (CDCl$_3$) (δ)), and analytical results are presented in that order.

Irradiation of 1a. 1a in C$_6$H$_6$ (1 h, RPR, 3500 Å) gave 7, mp 209–210 °C (26%), and benzoic acid, mp 121–122 °C (4%); 1a in acetone (1 h) gave 7 (62%), benzoic acid (7%), and 1a (20%). 7: IR ν_{max} 1675 (C=O); UV λ_{max} 253 (45 800), 300 (4100); ^{1}H NMR δ 5.85 (1 H, s, H-4b), 6.33 (1 H, s, H-10), 6.9–8.4 (18 H, m, aromatic); ^{13}C NMR δ 56.42 (C-4b), 58.15 (C-10), 82.02 (C-9a), 125.40–157.65 (aromatic), 192.58 (C=O), 197.73 (C=O), 201.60 (C=O). Anal. Calcd for C$_{30}$H$_{20}$O$_3$: C, 84.11; H, 4.67. Found: C, 84.62; H, 4.40.

Irradiation of 1b. 1b in C$_6$H$_6$ (1.25 h, RPR, 3000 Å) gave 8b, mp 211 °C (88%); 1b in acetone (1.25 h) gave 8b (92%). 8b: IR ν_{max} 1740 (C=O, ester), 1675 and 1665 (C=O, keto); UV λ_{max} 237 (29 700), 242 (32 600), 248 (36 700), 253 (36 700), 260 (29 300); ^{1}H NMR δ 1.62 (3 H, s, CH$_3$), 4.88 (1 H, s, methine), 6.30–8.40 (18 H, m, aromatic); ^{13}C NMR δ 20.01 (CH$_3$), 48.46 (C-8b), 61.63 (C-8c), 79.64 (C-8d), 93.5 (C-4b), 118.94–148.43 (aromatic), 169.67 (C=O, ester), 193.23 (C=O, keto), 195.00 (C=O, keto). Anal. Calcd for C$_{32}$H$_{22}$O$_4$: C, 81.70; H, 4.68; M_r = 470. Found: C, 82.00; H, 4.60; M_r = 470 (mass spectrum).

Irradiation of 1c. 1c in CH$_3$OH (1 h, RPR, 3000 Å) gave 8c, mp 175 °C (60%); 1c in C$_6$H$_6$ (1.25 h) gave 8c (57%). 8c: IR

ν_{max} 1720 (C=O, formyl), 1680 and 1670 (C=O, keto); UV λ_{max} 231 (32 000), 237 (35 000), 242 (40 000), 248 (52 000), 253 (56 000), 259 (41 000); ^{1}H NMR δ 4.72 (1 H, s, methine), 6.80–7.90 (18 H, m, aromatic), 9.79 (1 H, s, formyl). Anal. Calcd for $C_{31}H_{20}O_3$: C, 84.55; H, 4.55; M_r = 440. Found: C, 83.98; H, 4.64; M_r = 440 (mass spectrum).

Irradiation of 1d. 1d in CH_3OH (3 h, RPR, 3000 Å) gave 8c, mp 175 °C (mixture melting point) (48%); 1d in benzene (3 h) gave 8c (46%); 1d in acetone (3 h) gave 8c (40%).

Irradiation of 1e. 1e in CH_3OH (4 h, RPR, 3000 Å) gave 6e, mp 204 °C (75%); 1e in C_6H_6 (5 h) gave 6e (85%); 1e in acetone gave 6e (80%) and 1e (10%). 6e: IR ν_{max} 2250 (C≡N), 1650 (C=O); UV λ_{max} 235 (31 900), 241 (35 700), 248 (43 300), 253 (47 100), 260 (38 000); ^{1}H NMR δ 5.0 (1 H, s, 4b-H), 6.90–8.30 (18 H, m, aromatic); ^{13}C NMR δ 58.61 (C-4b), 68.51 (C-8c), 73.25 (C-8d), 111.46 (C-8b), 121.99–149.81 (aromatic), 190.57 (C=O), 192.97 (C=O). Anal. Calcd for $C_{31}H_{19}O_2N$: C, 85.13; H, 4.35; N, 3.20; M_r = 437. Found: C, 84.84; H, 4.39; N, 3.01; M_r = 437 (mass spectrum).

Irradiation of 1f. 1f in CH_3OH (10 h, RPR, 2537 Å) gave 8f, mp 192 °C (21%), and 1f (7%); 1f in CH_3OH (2 h, RPR, 3000 Å) and in C_6H_6 (11 h) gave 8f in 60% and 46% yields, respectively. 8f: IR ν_{max} 1670 (C=O); UV λ_{max} 236 (36 500), 242 (42 100), 247 (51 500), 253 (55 900), 259 (41 500); ^{1}H NMR δ 0.87 (3 H, t, CH_3), 2.36 (2 H, m, CH_2), 4.62 (1 H, s, methine), 6.60–7.90 (18 H, m, aromatic). Anal. Calcd for $C_{32}H_{24}O_2$: C, 87.26; H, 5.45; M_r = 440. Found: C, 87.20; H, 5.39; M_r = 440 (mass spectrum).

Irradiation of 1g. 1g in CH_3OH (1.5 h, RPR, 3000 Å) gave 8g, mp 196.5–197.5 °C (76%); 1g in C_6H_6 (1.5 h) and acetone (1.5 h) gave 8g in 70% and 73% yields, respectively. 8g: IR ν_{max} 1670 and 1660 (C=O); UV λ_{max} 236 (38 000), 242 (42 400), 248 (49 500), 253 (53 000), 260 (41 600); ^{1}H NMR δ 3.34 (3 H, s, OCH_3), 4.69 (1 H, s, methine), 6.90–8.30 (18 H, m, aromatic); ^{13}C NMR δ 48.16 (C-8b), 54.28 (OCH_3), 61.48 (C-8c), 78.35 (C-8d), 99.08 (C-4b), 120.71–149.19 (aromatic), 194.53 (C=O), 194.70 (C=O). Anal. Calcd for $C_{31}H_{22}O_3$: C, 84.16; H, 4.98; M_r = 442. Found: C, 84.13; H, 5.12; M_r = 442 (mass spectrum).

Irradiation of 1h. 1h in CH_3OH (1.5 h, RPR, 3000 Å) gave 8h, mp 158.5–159.5 °C (32%); 1h in CH_3OH (5 h), C_6H_6 (1.5 h) and acetone (1.5 h) gave 8h in 86%, 30%, and 23% yields, respectively. 8h: IR ν_{max} 1635 (C=O); UV λ_{max} 236 (35 000), 242 (36 100), 248 (38 600), 253 (39 400), 260 (30 400); ^{1}H NMR δ 3.35 (3 H, s, OCH_3), 3.81 (3 H, s, OCH_3), 7.10–8.00 (18 H, m, aromatic); ^{13}C NMR δ 54.09 (OCH_3), 55.06 (OCH_3), 80.09 (C-8b), 99.08 (C-4b), 118.66–149.60 (aromatic), 197.68 (C=O), 200.50 (C=O). Anal. Calcd for $C_{32}H_{24}O_4$: C, 81.36; H, 5.08; M_r = 472. Found: C, 81.20; H, 4.82; M_r = 472 (mass spectrum).

Reaction of 8b with Methanolic Potassium Hydroxide. Stirring a mixture of 8b (3.2 mmol) and KOH (14 mmol) in methanol for 6 h at room temperature and workup by removal of the solvent under vacuum and recrystallization from a mixture (4:1) of cyclohexane and dichloromethane gave 11, mp 164–165 °C (39%), and 13, mp 282 °C (mixture melting point) (26%). 11: IR ν_{max} 1660 (C=O); UV λ_{max} 252 (40 000), 258 (38 500); ^{1}H NMR δ 3.40 (3 H, s, OCH_3), 5.40 (1 H, s, methine), 7.00–8.40 (18 H, m, aromatic). Anal. Calcd for $C_{31}H_{22}O_4$: C, 81.22; H, 4.80; M_r = 458. Found: C, 81.41; H, 4.53; M_r = 458 (mass spectrum).

Hydrogenation of 6e. A mixture of 6e (0.69 mmol) and platinum dixoide (30 mg) in THF (20 mL) was hydrogenated for 6 h and worked up by chromatographing over silica gel (3:2 mixture of benzene and petroleum ether), followed by recrystallization from a mixture (1:1) of methanol and dichloromethane, to give 17, mp 233–234 °C (82%). 17: IR ν_{max} 2245 (C≡N), 1680 and 1665 (C=O); ^{1}H NMR δ 4.5 (1 H, s, H-8b), 5.6 (1 H, s, H-4b), 5.9 (1 H, s, H-8d), 6.6–8.0 (18 H, m, aromatic). Anal. Calcd for $C_{31}H_{21}O_2N$: C, 84.74; H, 4.78; N, 3.19. Found: C, 84.20; H, 4.80; N, 2.74.

Laser Flash Photolysis. The laser flash photolysis experiments were carried out at 337.1 nm (2–3 mJ, ~8 ns) in a computer-controlled setup using a Molectron UV-400 nitrogen laser system. Details of the apparatus and the procedures are described elsewhere.[21,22]

Pulse Radiolysis. The computer-controlled pulse radiolysis apparatus, which allows determination of transient spectra at various times after the pulse and kinetic measurements of the spectral changes, has been described elsewhere.[23]

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