J. Org. Chem. **1999,** *64,* 6347−6352

Photoisomerization of Bridgehead Monosubstituted Dibenzobarrelenes and Interesting Thermal Isomerization of Their Photoproducts[1]

Meledathu C. Sajimon,[†] Danaboyina Ramaiah,*[,†] Mohammed Muneer,[||] E. S. Ajithkumar,[†]
Nigam P. Rath,[‡] and Manapurathu V. George*[,†,§]

Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India, Department of Chemistry, University of Missouri, St. Louis, Missouri 63121, and Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560 064, India

Received March 25, 1999

Phototransformations of a few bridgehead monosubstituted dibenzobarrelenes, **4a**−**d**, and thermal isomerizations of their primary photoproducts, **7a** and **11a**−**c**, are described. Irradiation of **4a** in benzene gave a mixture of regioisomeric products, **7a** (*8b*-isomer) and **11a** (*4b*-isomer), in 20 and 70% yields, respectively. In contrast, irradiation of **4b**, under identical conditions, yielded only the corresponding *4b*-substituted dibenzosemibullvalene, **11b**, in 95% yield. Similarly, irradiation of the nitro- (**4c**) and chloro- (**4d**) substituted dibenzobarrelenes gave exclusively the corresponding dibenzosemibullvalenes, **11c** (81%) and **11d** (81%), respectively. The formation of regioselective products in these systems has been attributed to the relative stabilities of the diradical intermediates involved in these transformations. Interestingly, the dibenzosemibullvalene **7a**, on refluxing in xylene, gave the corresponding dibenzopentalenofuran **9a** (94%). Thermolysis of **11a** and **11c** in *o*-dichlorobenzene and, likewise, of **11b** in xylene, yielded 94−97% of the corresponding dibenzopentalenofurans **12a**, **12c**, and **12b**, respectively. Activation energies for the thermal isomerizations of **7a** to **9a**, **11a** to **12a**, and **11b** to **12b** have been found to be 21.57, 25.97, and 17.93 kcal/mol, respectively. The structures of **11a**, **11c**, **11b**, and **12b** were established unambiguously through X-ray crystallographic analysis, whereas the structures of the different photoproducts, **7a**, **11a**−**d**, **12a**−**c** and **9a**, have been arrived at on the basis of spectral data and analytical results.

Introduction

Several aspects of the phototransformations of dibenzobarrelenes are reported in the literature.[2] Depending on the reaction conditions, dibenzobarrelenes undergo photorearrangement, leading primarily to the corresponding dibenzosemibullvalenes or dibenzocyclooctatetraenes. It has been established that the cyclooctatetraenes are formed under direct irradiation, involving a singlet state mediated pathway, whereas the semibullvalenes arise through triplet state mediated di-π methane pathway.[3,4] Both electronic and steric effects of the bridgehead substituents play a major role in the observed regioselectivity of these rearrangements.[2−5]

In an earlier publication,[6] we had reported that the irradiation of aryl-substituted dibenzobarralenes **1a**−**f**, gives exclusively the dibenzopentalenofurans **3a**−**f**, derived from the corresponding *8b*-substituted semibullvalenes **2a**−**f** (Scheme 1). The formation of the regioselective semibullvalene derivatives **2a**−**f** in these systems has been rationalized on the basis of a di-π-methane pathway, in which the aryl group stabilizes the secondary diradical intermediates through π conjugation, irrespective of the nature of the substituents present at the para position of the aryl group. Further, the formation of the dibenzopentalenofurans **3a**−**f**, as exclusive products, was attributed to the ease of ring opening of the corresponding semibullvalene precursors **2a**−**f**.

The objective of the present investigation has been to study the photochemical transformations of some selected

---

* Corresponding author. Tel.: 91-471-490-392. Fax: 91-471-490-186. E-mail: mvg@csrrltrd.ren.nic.in.

[†] Regional Research Laboratory, Trivandrum.

[‡] University of Missouri.

[§] Jawaharalal Nehru Center for Advanced Scientific Research, Bangalore.

[||] Present address: Department of Chemistry, Aligarh Muslim University, Aligarh, India.

(1) Contribution no. RRLT-PRU-108 from the Regional Research Laboratory (CSIR), Trivandrum, India.

(2) For some recent reviews on the photochemistry of dibenzobarrelenes and the general di-π-methane rearrangement see: (a) Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 16, pp 131−166. (b) Zimmerman, H. E. In *Organic Photochemistry*; Padwa, A, Ed.; Marcel Dekker: New York, 1991; Vol. 11, pp 1−36. (c) Scheffer, J. R.; Pokkuluri, P. R. In *Photochemistry in Organized and Constrained Media*; Ramamurthy, V., Ed.; VCH: New York, 1991; pp 185−246. (d) de Lucchi, O.; Adam, W. In *Comprehensive Organic Synthesis*; Trost, B. M., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 193−214. (e) Chen, J.; Scheffer, J. R.; Trotter, J. *Tetrahedron* **1992**, *48*, 3251−3274. (f) Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. *J. Am. Chem. Soc.* **1993**, *115*, 6548−6556. (g) Scheffer, J. R.; Yang, J. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P. S., Eds.; CRC Press: Boca Raton, FL, 1995; Chapter 16, pp 204−221.

(3) (a) Ciganek, E. *J. Am. Chem. Soc.* **1966**, *88*, 2882−2883. (b) Rabideau, P. W.; Hamilton, J. B.; Friedmann, L. *J. Am. Chem. Soc.* **1968**, *90*, 4465−4466.

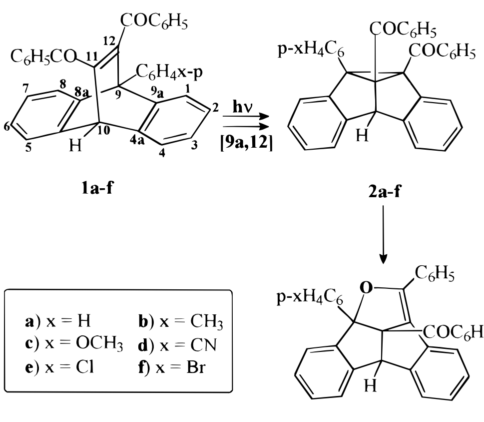
(4) (a) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183−184. (b) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932−3933. (c) Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1990**, *112*, 3675−3676. (d) Chen, J.; Pokkuluri, P. R.; Scheffer, J. R.; Trotter, J. *J. Photochem. Photobiol., A* **1991**, *7*, 21−26. (e) For some of the similarly substituted dicarbomethoxy esters, see; Iwamura, M.; Tukada, H.; Iwamra, H. *Tetrahedron Lett.* **1980**, *21*, 4865−4868.

(5) (a) Kumar, C. V.; Murthy, B. A. R. C.; Lahiri, S.; Chackachery, E.; Scaiano, J. C.; George, M. V. *J. Org. Chem.* **1984**, *49*, 4923−4929 (b) Kumar, S. A.; Ashokan, C. V.; Das, S.; Wilbur, J. A.; Rath, N. P.; George, M. V. *J. Photochem. Photobiol., A* **1993**, *71*, 27−31. (c) Ramaiah, D.; Kumar, S. A.; Ashokan, C. V.; Mathew, T.; Das, S.; Rath, N. P.; George, M. V. *J. Org. Chem.* **1996**, *61*, 5468−5473.

(6) Pratapan, S.; Ashok, K.; Gopidas, K. R.; Rath, N. P.; Das, P. K.; George, M. V. *J. Org. Chem.* **1990**, *55*, 1304−1308.

10.1021/jo9905322 CCC: $18.00

Scheme 1



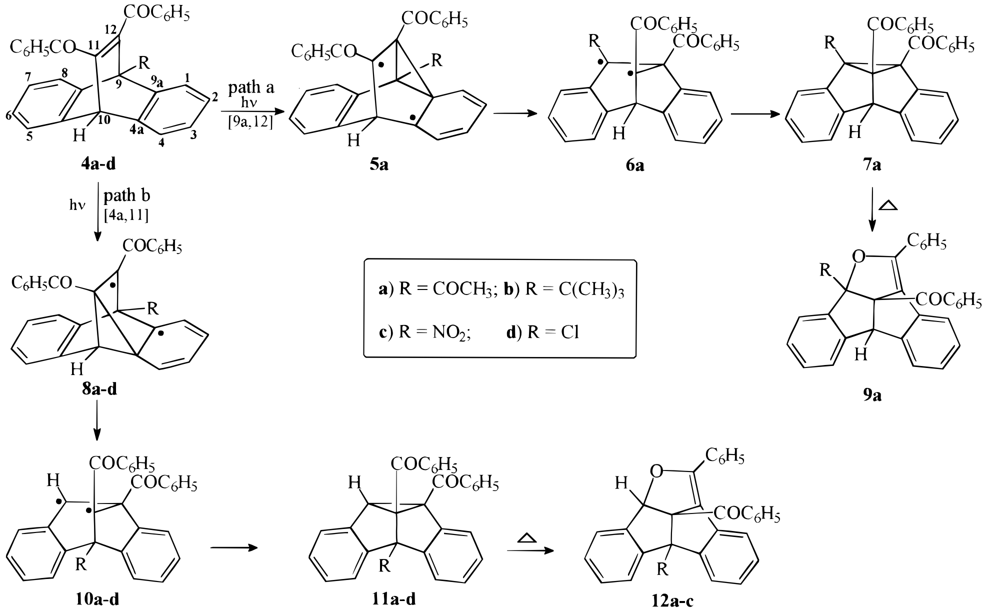
examples with a view to examining the role of both steric and electronic effects of the bridgehead substituents on the regioselectivity of these photorearrangements. Further, it was of interest to investigate the thermal isomerization of the primary photoproducts **7a** and **11a**−**c**, formed in these reactions. The substrates that we have examined in the present study include 9-acetyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (**4a**), 9-*tert*-butyl-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (**4b**), 11,12-dibenzoyl-9,10-dihydro-9-nitro-9,10-ethenoanthracene (**4c**), and 9-chloro-11,12-dibenzoyl-9,10-dihydro-9,10-ethenoanthracene (**4d**). The photoproducts that we have subjected to thermal isomerization include 8b-acetyl-8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[c,d]pentalene (**7a**), 4b-acetyl-8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[c,d]pentalene (**11a**), 4b-*tert*-butyl-8c,8d-dibenzoyl-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[c,d]pentalene (**11b**), and 8c,8d-dibenzoyl-4b-nitro-4b,8b,8c,8d-tetrahydrodibenzo[a,f]cyclopropa[c,d]pentalene (**11c**).

Results

1. Steady-State Photolysis and Product Identification. The starting dibenzobarrelenes containing 1,2-dibenzoylalkene moieties were prepared through the reaction of the appropriate anthracenes with dibenzoylacetylene (DBA) by neat heating or under refluxing conditions using a suitable solvent or in the presence of a Lewis acid catalyst such as aluminum chloride. All the dibenzobarrelenes **4a**−**d** have been fully characterized by analytical results and spectral data. For example, the ^1H NMR spectrum of **4a** showed a singlet at δ 5.34 that is due to the bridgehead proton, and the ^{13}C NMR spectrum showed characteristic signals at δ 54.17 and 70.04, assigned to the bridgehead sp^3 carbons. In addition, the latter showed two peaks at δ 194.32 and 194.41 which are due to the benzoyl carbonyl groups and a peak at δ 203.71 which was assigned to the carbonyl of the acetyl group.

Photolysis of **4a** in benzene afforded a mixture of the regioisomeric products **7a** and **11a** in 20 and 70% yields, respectively (Scheme 2). Yields reported herein are the isolated yields of products, after purification through recrystallization. In contrast, irradiation of **4b** in benzene, gave **11b** (95%) as the exclusive product. Similarly, irradiation of **4c** and **4d**, under identical conditions, yielded 81% of **11c** and 81% of **11d**, respectively, as the only isolable products in each case. To ascertain the exact composition of the various regioisomeric mixtures formed in these photoreactions, 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 ^1H NMR. Irradiation of **4a** in $CDCl_3$ for 1.6 h resulted in a mixture of **7a** (21%) and **11a** (72%), along with 7% of the unchanged starting material **4a**, as analyzed by ^1H NMR, following the bridgehead and acetyl protons. Thus, the ^1H NMR spectrum of the irradiated (45 min) solution of **4a** in $CDCl_3$ showed the acetyl and bridgehead protons of **7a** as singlets at δ 2.55 and 4.94, whereas, in **11a**, they appeared as singlets at δ 1.92 and 4.64. When the irradiation of **4a** was continued for another 30 min, the product mixture consisted of only **7a** and **11a** in the ratio of 1:3.5, as analyzed by the integration of their bridgehead and acetyl protons. In contrast, irradiation of **4b** in C_6D_6 for 45 min showed the formation of only **9c** (75%), along with the unchanged starting material **4b** (25%),

Scheme 2



as analyzed by ^{1}H NMR, following the bridgehead protons. Similarly, the irradiation of **4c** and **4d** resulted in the formation of the corresponding regioselective products, **11c** and **11d**, respectively, as evidenced by ^{1}H NMR.

The structures of the dibenzosemibullvalenes **7a** and **11a**−**d** were arrived at on the basis of analytical data and spectral evidence. The ^{1}H NMR spectrum of **7a** showed a singlet at δ 4.94, which is characteristic of the bridgehead *4b* proton. The bridgehead *8b* protons of the regioisomers **11a**−**d** were observed as singlets in the range of δ 4.64−4.78. The ^{13}C NMR spectra of **7a** and **11a**−**d**, showed the characteristic 4 peaks, in each case in the region of δ 47.46−103.67, assigned to the sp^3 carbons of the pentalene moiety. In addition, two peaks corresponding to benzoyl carbonyl groups appeared, in each case in the region of δ 191.33−196.85. The structures of the photoproducts **11a, 11c**, and **11d** were further confirmed through X-ray crystal structure determination.[7]

2. Thermal Isomerization of Dibenzosemibullvalenes to Dibenzo-pentalenofurans. The primary photoproducts, dibensemibullvalenes **7a** and **11a**−**c** were found to be thermally unstable and to undergo interesting isomerization to the corresponding dibenzopentalenofuran derivatives. For example, refluxing of a solution of **7a** in xylene for 30 min resulted in the formation of **9a** in a 92% yield, whereas **11a** when refluxed in *o*-dichlorobenzene for 20 min, gave of **12a** in 94%. Similarly, the thermolysis of **11b** in xylene and **11c** in *o*-dichlorobenzene, resulted in the formation of **12b** (97%) and **12c** (94%), respectively. The structures of the products **12a**−**c** and **9a** were arrived at on the basis of analytical results and spectral evidence. The ^{1}H NMR spectra of **12a**, **12b**, and **12c** showed the bridgehead protons at δ 6.40, 6.57, and 6.53, respectively. In addition, they showed only one peak, in each case, in the region of δ 199.05−197.20, assigned to the benzoyl carbonyl group, clearly demonstrating the participation of one of the benzoyl carbonyls in the furan ring formation. The structure of **12b** was further confirmed unambiguously through X-ray crystallographic analysis.[7] The ^{1}H NMR spectrum of **9a**, on the other hand, showed the acetyl and bridgehead *4b* protons as singlets at δ 2.14 and 5.39, respectively. The ^{13}C NMR spectrum showed two peaks at δ 198.03 and 203.83, assigned to the carbonyls of benzoyl and acetyl groups, respectively.

3. Kinetics of Thermal Isomerization of 7a to 9a, 11a to 12a, and 11b to 12b. The kinetic studies were carried out in either *n*-decane or *n*-tridecane by following the change in absorbance as a function of time at wavelengths characteristic of the appropriate end products. In the case of **7a** for example, the isomerization was carried out in *n*-decane at 110 °C by following the increase in absorbance at 325 nm (characteristic of **9a**). The Arrhenius parameters were evaluated by measuring the rates at 110, 120, and 130 °C.

Similarly, the thermal isomerization of **11a** to **12a** was carried out in *n*-tridecane by following the increase in absorbance at 320 nm (characteristic of **12a**), whereas the isomerization of **11b** to **12b** was carried out by monitoring the absorbance change at 335 nm (characteristic of **12b**). Figure 1 shows the kinetic plot for the thermal isomerization of **11b** to **12b** at 120 °C, and the inset shows the increase in absorbance of **12b** at 335 nm as a function of time. The kinetic parameters for the isomerization of **7a** to **9a**, **11a** to **12a**, and **11b** to **12b** are presented in Table 1.

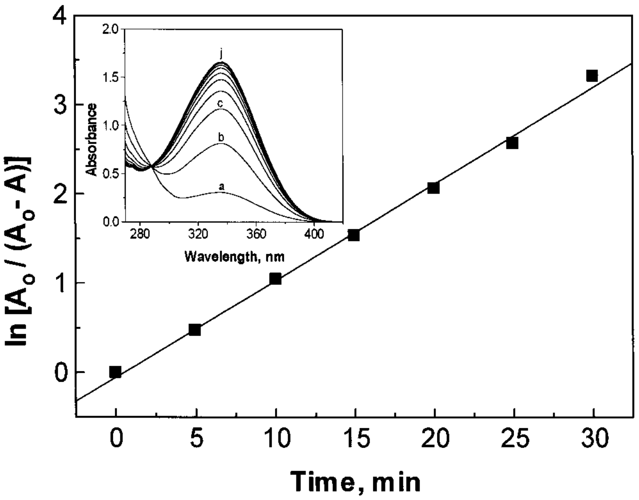


Figure 1. Kinetic plot for the thermal isomerization of **11b** to **12b** at 120 °C. Inset shows the increase in absorbance of **12b** at 335 nm as a function of time: (a) 0; (b) 5; (c) 10; (j) 45 min.

Table 1. Kinetic and Thermodynamic Data for the Thermal Isomerization of 7a, 11a, and 11b[a]

thermal isomerization[b]	temp (K)	rate constant k (10^{-3} s)	E_a (kcal mol^{-1})	$\Delta S^\ddagger$ (eu)
7a to **9a**	383	1.10	21.57 ± 0.7	−18.50
	393	2.21		
	403	4.49		
11a to **12a**	428	1.27	25.97 ± 0.6	−13.86
	438	2.51		
	448	4.46		
11b to **12b**	393	1.80	17.93 ± 0.1	−27.93
	398	2.40		
	403	3.19		

[a] Average of more than two experiments. [b] The thermal isomerization monitoring wavelengths (λ_{max}) are 325 nm for **7a** to **9a**, 320 nm for **11a** to **12a**, and 335 nm for **11b** to **12b**.

Discussion

The formation of the dibenzosemibullvalenes **7a** and **11a**−**d** in the phototransformations of **4a**−**d** can be rationalized in terms of the pathways shown in Scheme 2. Path a involves a [9a,12] benzo-vinyl bridging leading to the diradical intermediates **5a** and **6a**, which can subsequently be transformed to the regioisomeric *8b*-substituted product **7a**. Path b involves a [4a,11] benzo-vinyl bridging leading to the diradical intermediates **8a**−**d** which can undergo further transformations to give rise to the *4b*-substituted products **11a**−**d**. It is interesting to note that the acetyl-substituted dibenzobarrelene **4a** gives rise to both *4b*-isomer **7a** and *8b*-isomer **11a**, in the ratio of 1:3.5, whereas the other dibenzobarrelenes **4b**−**d** gave exclusively the *4b*-isomers **11b**−**d**.

The observed regioselectivity in these reactions could be directly correlated to the relative stabilization of the 1,3-diradical intermediates **5a** and **8a**−**d**, formed initially, and also the subsequently formed diradical intermediates **6a** and **10a**−**d**. It has been observed earlier[8] that strongly electron-withdrawing substituents with

---

[7] Full details of the crystal and molecular structures will be published separately.

minimal steric crowding favor Path a, leading to diradical intermediates analogous to **5a** and **6a** and ultimately to the *8b*-substituted product. Similarly, aryl substituents at the bridgehead position of the starting dibenzobarrelenes favor the formation of the *8b*-aryl-substituted dibenzosemibullvalenes.[8] In contrast, alkyl and methoxy substituents at the bridgehead position favor Path b, leading to *4b*-substituted dibenzosemibullvalenes.[9]

The fact that **11a** is formed as the major product in the reaction of **4a** and that both **11b** and **11d** are formed as exclusive products from **4b** and **4d**, respectively, would suggest that the directing effect of these substituents is similar to those of alkyl and methoxy substituents. The case of the nitro-substituted derivative **4c** deserves special mention. In this case, the reaction also proceeds through Path b, leading to the product **11c**. This could be due to the effective hyperconjugative stabilization[10−12] of the radical intermediate **6c** by the nitro group, thereby decreasing the probability of this radical undergoing further transformations. The net effect of this could result in a reaction that originates only from the isomeric radical intermediate **10c,** leading to the formation of **11c** as observed.

The thermal isomerizations of the dibenzosemibullvalenes **7a** and **11a**−**c** to the corresponding dibenzopentalenofurans are analogues to the rearrangement of vinylcyclopropanes to cyclopentenes, reported in the literature.[13] These isomerizations could proceed through a concerted pathway, involving a [1,3] sigmatropic shift or through 1,3-diradical intermediates.[14] The activation energy[13b] for the rearrangement of vinylcyclopropane to cyclopentene is 45 kcal mol^{-1}. It is known that increased carbon substitution, extended conjugation, and the presence of heteroatoms all lower the activation energy for the reorganization toward cyclopentene.[13−15] Our kinetic studies reveal that the isomerizations of **7a** and **11a,b** follow first-order kinetics, as expected. The activation energy for the thermal isomerization of **7a** to **9a,** for example, was found to be 21.57 kcal mol^{-1}, whereas the change in entropy was −18 eu, which is typical of sigmatropic rearrangements involving cyclic transition states.[16]

It is interesting to compare the energetics of the thermal isomerization of the *8b*-isomer **7a** and the *4b*-isomer **11a** (Table 1). The activation energy for the isomerization of **7a** is lower than that of **11a**. This could be due to steric and electronic effects of the acetyl group on the cyclopropane ring. It is equally important to note that a very low activation barrier was observed for the isomerization of **11b** to **12b**, when compared with those of **7a** and **11a**. Although the *tert*-butyl substituent in **11b** is away from the cyclopropane ring, the observed low activation barrier could be due to the steric interactions of the *tert*-butyl group with the adjacent benzoyl group of the cyclopropane ring. Both molecular modeling studies and strain energy calculations[12b] of these systems are in support of this explanation.

Experimental Section

The equipment and procedure for melting point determination and spectral recordings are described in earlier publications.[5c,17] All steady-state irradiation experiments were carried out in a Srinivasan-Griffin-Rayonet Photochemical Reactor (RPR 300 nm) or by using a Pyrex filtered light from a Hanovia 450 W medium-pressure mercury lamp. Solvents for photolysis experiments were purified and distilled before use. The petroleum ether used was the fraction with a bp of 60−80 °C.

Starting Materials. Dibenzoylacetylene (DBA),[18] mp 110−111 °C; 9-acetylanthracene,[19] mp 75−76 °C 9-*tert*-butylanthracene,[20] mp 104−105 °C; and 9-nitroanthracene,[21] mp 145−146 °C were prepared by reported procedures. 9-Chloroanthracene, mp 100−101 °C, from Aldrich was used as received.

Preparation of 4a. To a mixture of 9-acetylanthracene (2.20 g, 10 mmol) and aluminum chloride (1.35 g, 10 mmol) in dichloromethane (40 mL, dry) was added DBA (2.34 g, 10 mmol) in small amounts at 0 °C. The reaction mixture was stirred for 1 h and poured over crushed ice, acidified with hydrochloric acid (6.5 N, 500 mL), and extracted with dichloromethane. Removal of the solvent gave a solid residue, which was chromatographed over silica gel. Elution of the column with a mixture (1:9) of ethyl acetate and hexane gave 900 mg (45%) of the unchanged anthracene derivative, mp 75−76 °C (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 1.80 g (40%) of **4a,** mp 231−232 °C, after recrystallization from a mixture (1:1) of dichloromethane and methanol: IR $\upsilon_{\max}$ (KBr) 1727, 1664 cm^{-1}; UV $\lambda_{\max}$ (CH$_3$CN) 211 nm (ϵ 35 900); ^{1}H NMR (CDCl$_3$) δ 2.41 (3H, s), 5.34 (1H, s), 6.99−7.68 (18H, m); ^{13}C NMR (CDCl$_3$) δ 32.00, 54.17, 70.04, 123.78, 123.97, 125.57, 125.91, 128.27, 128.34, 128.68, 128.79, 133.11, 133.28, 136.66, 137.19, 142.91, 144.64, 151.24, 154.64, 194.32, 194.41, 203.71; mass spectrum *m/e* (relative intensity) 454 (M$^+$, 1), 105 (100). Anal. Calcd for $C_{32}H_{22}O_3$: C, 84.56; H, 4.88. Found: C, 84.90; H, 4.89.

Preparation of 4b. A mixture of 9-*tert*-butylanthracene (468 mg, 2 mmol) and DBA (468 mg, 2 mmol) in toluene (60 mL, dry) was refluxed for 6 h. The solvent was removed under reduced pressure to give a solid residue, which was chromatographed over silica gel. Elution of the column with a mixture

---

(8) (a) Murthy, B. A. R. C.; Pratapan, S.; Kumar, C. V.; Das, P. K.; George, M. V. *J. Org. Chem*. **1985**, *50*, 2533−2538. (b) Kumar, S. A.; Ramaiah, D.; Eldho, N. V.; Das, S.; Rath, N. P.; George, M. V. *J. Photochem. Photobiol., A* **1997**, *103*, 69−73.

(9) (a) Pratapn, S.; Ashok, K.; Cyr, D. R.; Das, P. K.; George, M. V. *J. Org. Chem*. **1987**, *52*, 5512−5517. (b) Ashokan, C. V.; Kumar, S. A.; Das, S.; Rath, N. P.; George, M. V. *J. Org. Chem*. **1991**, *56*, 5890−5893.

(10) For a review on steric effects in free radical chemistry, see Rüchardt, C. *Top. Curr. Chem*. **1980**, *88*, 1−32.

(11) Paquette, L. A.; Bay, E. *J. Am. Chem. Soc*. **1984**, *106*, 6693−6701.

(12) (a) We thank one of the reviewers for suggesting the hyperconjugative effect of the nitro group. (b) Our calculations using AM1 semiempirical molecular orbital method employing simplified model systems analogous to 1,3-diradical intermediate **6a** revealed the localization of electron potential on the nitro group.

(13) (a) Wenkert, E. *Acc. Chem. Res*. **1980**, *13*, 27−31. (b) Hudlicky, T.; Reed, J. W. In *Comprehensive Organic Synthesis*; Trost, B. M.; Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 899−970. (c) Carpenter, B. K. In *The Chemistry of the Cyclopropyl Group, Part 2*; Rappoport, Z., Ed.; Wiley: New York, 1987; p 1027.

(14) (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res*. **1980**, *13*, 317−323. (b) Gajewski, J. J.; Olson, L. P.; Willcott, M. R. *J. Am. Chem. Soc*. **1996**, *118*, 299−306. (c) Baldwin, J. E.; Villarica, K. A.; Freedberg, D. I.; Anet, F. A. L. *J. Am. Chem. Soc*. **1994**, *116*, 10845−10846.

(15) (a) Marino, J. P.; Laborde, E. *J. Org. Chem*. **1987**, *52*, 1−10. (b) Reissig, H.-U. *Topp. Curr Chem*. **1988**, *144*, 73.

(16) (a) Szwarc, M.; Murawski, J. *Trans. Faraday Soc*. **1951**, *47*, 269−274. (b) Schuler, F. W.; Murphy, G. W. *J. Am. Chem. Soc*. **1950**, *72*, 3155−3159. (c) Haszeldine, R. N.; Robinson, P. J.; Walsh, J. A. *J. Chem. Soc. B* **1970**, 578.

(17) (a) Ramaiah, D.; Muneer, M.; Gopidas, K. R.; Das, P. K.; Rath, N. P.; George, M. V. *J. Org. Chem*. **1996**, *61*, 4240−4246. (b) Ramaiah, D.; Ashok, K.; Barik, R.; Venugopal, D.; Rath, N. P.; Bhattacharyya, K.; Das, P. K.; George, M. V. *J. Org. Chem*. **1992**, *57*, 6032−6037.

(18) (a) Lutz, R. E. In *Organic Synthesis*; Horning, E. C., Ed.; Collect. Vol. 3; Wiley: New York, 1995; pp 248−250. (b) Lutz, R. E.; Smithy, W. R., Jr. *J. Org. Chem*. **1951**, *16*, 648−654.

(19) Merritt, C., Jr.; Braun, C. E. In *Organic Synthesis*; Rabjohn, N. Ed.; Collect. Vol. 4; Wiley: New York, 1967; pp 8−10.

(20) Meek, J. S.; Monroe, P. A.; Bouboulis, C. J. *J. Org. Chem*. **1963**, *28*, 2572−2577.

(21) Braun, C. E.; Cook, C. D.; Merrit, C., Jr.; Rousseau, J. E. In *Organic Synthesis*; Rabjohn, N., Ed.; Collect. Vol. 4; Wiley: New York; pp 711−713.

(1:9) of ethyl acetate and hexane gave 170 mg (35%) of the unchanged anthracene derivative, mp 104−105 °C (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane yielded 540 mg (57%) of **4b**, mp 238−239 ^{o}C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1681 cm^{-1}; UV λ_{max} (CH$_3$CN) 248 nm (ϵ 28 700); ^{1}H NMR (CDCl$_3$) δ 1.71 (6H, s), 1.96 (3H, s), 5.32 (1H, s), 7.07−8.89 (18H, m); ^{13}C NMR (CDCl$_3$) δ 32.54, 34.19, 54.19, 70.63, 124.05, 124.06, 124.82, 125.49, 127.12, 127.93, 128.10, 128.54, 129.38, 132.94, 136.80, 138.41, 144.45, 147.48, 152.88, 156.88, 194.94, 196.73; mass spectrum *m*/*e* (relative intensity) 468 (M$^+$, 3), 105 (100). Anal. Calcd for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 87.18; H, 5.99.

Preparation of 4c. An equimolar mixture of 9-nitroanthracene (2.23 g, 10 mmol) and DBA (2.34 g, 10 mmol) under neat heating at 140−150 ^{o}C for 5 h gave a product mixture, which was chromatographed over silica gel. Elution of the column with a mixture (1:9) of ethyl acetate and hexane gave 970 mg (44%) of the unchanged anthracene derivative, mp 145−146 °C (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 1.83 g (40%) of **4c**, mp 180−181 ^{o}C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1678 cm^{-1}; UV λ_{max} (CH$_3$CN) 288 nm (ϵ 22 000); ^{1}H NMR (CDCl$_3$) δ 5.48 (1H, s), 7.08−7.74 (18H, m); ^{13}C NMR (CDCl$_3$) δ 53.23, 98.48, 121.97, 126.23, 128.29, 128.45, 128.82, 133.41, 140.07, 142.11, 148.34, 151.35, 191.91, 193.16; mass spectrum *m*/*e* (relative intensity) 457 (M$^+$, 20), 105 (100). Anal. Calcd for $C_{30}H_{19}NO_4$: C, 78.76; H, 4.19; N, 3.06. Found: C, 78.99; H, 4.19; N, 2.70.

Preparation of 4d. A mixture of 9-chloroanthracene (1.20 g, 5.6 mmol) and DBA (1.30 g, 5.6 mmol) in toluene (50 mL, dry) was refluxed for 13 h. The solvent was removed under reduced pressure, and the solid thus obtained was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and hexane gave 310 mg (26%) of the unchanged anthracene derivative, mp 100−101 °C (mixture mp). Further elution with a mixture (1:4) of ethyl acetate and hexane gave 1.7 g (68%) of **4d**, mp 179−180 ^{o}C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1661 cm^{-1}; UV λ_{max} (CH$_3$CN) 255 nm (ϵ 33 000); ^{1}H NMR (CDCl$_3$) δ 5.52 (1H, s), 7.10−7.69 (18H, m); ^{13}C NMR (CDCl$_3$) δ 52.07, 73.29, 122.25, 123.44, 128.22, 128.41, 129.14, 133.14, 142.69, 143.28, 149.06, 156.02, 192.88, 193.01; mass spectrum *m*/*e* (relative intensity) 446 (M+, 3), 212 (100), 105 (88). Anal. Calcd for $C_{34}H_{28}O_2$: C, 80.62; H, 4.29. Found: C, 80.78; H, 4.29.

Photolysis of 4a. A solution of **4a** (400 mg, 0.88 mmol) in benzene (300 mL) was irradiated (Hanovia 450 W) for 40 min. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution of the column with a mixture (1:4) of ethyl acetate and petroleum ether gave (280 mg, 70%) **11a**, mp 213−214 ^{o}C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1657 cm^{-1}; UV λ_{max} (CH$_3$CN) 202 nm (ϵ 31 700); ^{1}H NMR (CDCl$_3$) δ 1.92 (3H, s), 4.64 (1H, s), 6.75−7.85 (18H, m); ^{13}C NMR (CDCl$_3$) δ 28.67, 47.82, 61.80, 75.87, 77.77, 121.89, 128.51, 128.57, 128.91, 130.02, 134.86, 148.04, 149.28, 194.21, 195.11, 202.34; mass spectrum *m*/*e* (relative intensity) 454 (M$^+$, 3), 105 (100). Anal. Calcd for $C_{32}H_{22}O_3$: C, 84.56; H, 4.88. Found: C, 84.34; H, 4.87.

Further elution of the column gave 80 mg (20%) of **7a**, mp 154−155 °C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1721, 1654 cm^{-1}; UV λ_{max} (CH$_3$CN) 209 nm (ϵ 32 000); ^{1}H NMR (CDCl$_3$) δ 2.55 (3H, s), 4.94 (1H, s), 6.82−8.05 (18H, m); ^{13}C NMR (CDCl$_3$) δ 30.92, 53.41, 59.29, 67.62, 67.87, 121.95, 128.48, 128.68, 129.11, 129.71, 136.27, 150.49, 151, 70, 192.99, 195.20, 202.51. Anal. Calcd for $C_{32}H_{22}O_3$: C, 84.56; H, 4.88. Found: C, 84.37; H, 4.91.

Photolysis of 4b. A solution of **4b** (468 mg, 1 mmol) in benzene (400 mL) was irradiated (RPR, 300 nm) for 50 min. The solvent was removed under vacuum, and the residual solid obtained was chromatographed over silica gel. Elution of the column with a mixture (1:4) of ethyl acetate and petroleum ether gave 445 mg (95%) of **11b**, mp 182−183 °C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1628 cm^{-1}; UV λ_{max} (CH$_3$CN) 281 nm (ϵ 27 980); ^{1}H NMR (CDCl$_3$) δ 1.52 (9H, s), 4.65 (1H, s), 6.53−7.77 (18H, m); ^{13}C NMR (C$_6$D$_6$) δ 30.75, 37.17, 47.94, 61.51, 77.13, 81.19, 123.17, 127.70, 128.34, 130.22, 136.69, 138.42, 151.53, 152.24, 196.19, 196.85; mass spectrum *m*/*e* (relative intensity): 468 (M$^+$, 1), 105 (100). Anal. Calcd for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 86.98; H, 6.08.

Photolysis of 4c. A solution of **4c** (457 mg, 1 mmol) in benzene (400 mL) was irradiated (RPR, 300 nm) for 2 h. The solvent was removed under vacuum, and the residual solid thus obtained was chromatographed over silica gel. Elution with a mixture (1:4) of ethyl acetate and petroleum ether gave 370 mg (81%) of **11c**, mp 211−212 °C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1664 cm^{-1}; UV λ_{max} (CH$_3$CN) 274 nm (ϵ 20 800); ^{1}H NMR (CDCl$_3$) δ 4.78 (1H, s), 6.85−7.92 (18H, m); ^{13}C NMR (CDCl$_3$) δ 47.46, 60.82, 76.61, 103.67, 121.00, 121.15, 126.37, 126.82, 128.07, 128.40, 128.58, 128.67, 129.27, 129.68, 130.10, 133.00, 133.29, 133.38, 136.34, 136.43, 145.05, 146.03, 191.23, 193.71; mass spectrum *m*/*e* (relative intensity) 457 (M$^+$, 3), 105 (100). Anal. Calcd for $C_{30}H_{19}NO_4$: C, 78.76; H, 4.19; N, 3.06. Found: C, 78.97; H, 4.27; N, 2.87.

Photolysis of 4d. A solution of **4d** (580 mg, 1.3 mmol) in benzene (300 mL) was irradiated (Hanovia 450 W) for 1 h. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (1:9) of ethyl acetate and petroleum ether gave 470 mg (81%) of **11d**, mp 181−182 °C, after recrystallization from a mixture (1:4) of dichloromethane and methanol: IR υ_{max} (KBr) 1681 cm^{-1}; UV λ_{max} (CH$_3$CN) 253 nm (ϵ 28 800); ^{1}H NMR (CDCl$_3$) δ 4.70 (1H, s), 6.75−7.89 (18H, m); ^{13}C NMR (CDCl$_3$) δ 48.78, 61.04, 78.39, 79.36, 120.91, 128.26, 128.32, 129.46, 130.08, 136.98, 137.26, 149.64, 150.58, 191.93, 195.06; mass spectrum *m*/*e* (relative intensity) 446 (M$^+$, 1), 105 (100). Anal. Calcd for $C_{30}H_{19}ClO_2$: C, 80.62; H, 4.29. Found: C, 80.62; H, 4.36.

^{1}H NMR Monitoring of the Photoreactions of 4a−d. A solution of **4a** in CDCl$_3$ (10 mg in 0.5 mL) in an NMR tube was irradiated with an RPR 300-nm light source for 1 h and 40 min, and its ^{1}H NMR spectrum was recorded. The ^{1}H NMR spectrum revealed that the product mixture consisted of 21% of **7a** and 72% of **11a**, along with 7% of the unchanged starting material **4a**. When the irradiation was continued for another further 30 min, the ratio of the products **7a** and **11a** was found to be 1:3.5.

In a separate experiment, the irradiation of the dibenzobarrelene **4b** in C$_6$D$_6$, for 45 min, under identical conditions, resulted in the formation of **11b** (75%), along with the unchanged starting material **4b** (25%), as analyzed by the ^{1}H NMR. Similarly, the irradiation of **4c** in C$_6$D$_6$ for 8 h gave 50% of **9c**, along with 50% of the unchanged starting material, whereas the irradiation of **4d** in CDCl$_3$ for 75 min, under identical conditions, resulted in the formation of **11d** (63%), along with some unchanged starting material **4d** (37%).

Thermal Isomerization of 7a. A solution of **7a** (100 mg, 0.22 mmol) in dry toluene (30 mL) was refluxed for 30 min. The solvent was removed under vacuum, and the residual solid was recrystallized from a mixture (1:4) of dichloromethane and methanol to give 94 mg (94%) of **9a**, mp 237−238 °C: IR υ_{max} (KBr) 1724, 1661 cm^{-1}; UV λ_{max} (CH$_3$CN) 328 nm (ϵ 34 500); ^{1}H NMR (CDCl$_3$) δ 2.14 (3H, s), 5.39 (1H, s), 7.04−7.92 (18H, m); ^{13}C NMR (CDCl$_3$) δ 27.78, 55.52, 83.26, 102.75, 121.36, 124.02, 124.79, 125.84, 127.85, 128.14, 128.21, 128.27, 128.38, 128.51, 128.70, 128.81, 129.84, 130.22, 130.74, 132.45, 137.88, 141.08, 142.37, 149.41, 152.23, 198.03, 203.83. Anal. Calcd for $C_{32}H_{22}O_3$: C, 84.56; H, 4.88. Found: C, 84.82; H, 4.92.

Thermal Isomerization of 11a. A solution of **11a** (150 mg, 0.33 mmol) in dry *o*-dichlorobenzene (40 mL) was refluxed under an argon atmosphere for 20 min. The solvent was removed under vacuum, and the residual solid thus obtained was recrystallized from a mixture (1:4) of dichloromethane and methanol to give 140 mg (94%) of **12a**, mp 185−186 °C: IR υ_{max} (KBr) 1721, 1665 cm^{-1}; UV λ_{max} (CH$_3$CN) 325 nm (ϵ 34 200); ^{1}H NMR (CDCl$_3$) δ 1.83 (3H, s), 6.40 (1H, s), 7.07−

8.02 (18H, m); ^{13}C NMR (CDCl$_3$) δ 27.85, 52.85, 85.95, 87.80, 120.83, 124.94, 126.42, 126.52, 127.89, 128.07, 128.22, 128.43, 128.53, 128.58, 129.24, 129.85, 130.27, 130.52, 132.95, 134.46, 136.75, 141.48, 141.91, 147.76, 152.25, 199.05, 203.93. Anal. Calcd for $C_{32}H_{22}O_3$: C, 84.56; H, 4.88. Found: C, 84.30; H, 4.90.

Thermal Isomerization of 11b. A solution of **11b** (100 mg, 0.21 mmol) in dry xylene (30 mL) was refluxed under an argon atmosphere for 20 min. The solvent was removed under vacuum, and the residual solid was recrystallized from a mixture (1:4) of dichloromethane and methanol to give 97 mg (97%) of **12b**, mp 212−213 °C: IR υ_{max} (KBr) 1627 cm^{-1}; UV λ_{max} (CH$_3$CN) 335 nm (ϵ 28,400); ^{1}H NMR (CDCl$_3$) δ 1.22 (9H, s), 6.57 (1H, s), 7.04−7.92 (18H, m); ^{13}C NMR (CDCl$_3$) δ 28.79, 36.76, 84.10, 90.67, 121.67, 127.35, 127.98, 128.19, 128.69, 139.98, 140.84, 146.25, 150.47, 152.31, 203.15. Anal. Calcd for $C_{34}H_{28}O_2$: C, 87.15; H, 6.02. Found: C, 87.11; H, 5.77.

Thermal Isomerization of 11c. The thermal isomerization of **11c** was achieved by refluxing a solution of **11c** (100 mg, 0.23 mmol) in *o*-dichlorobenzene (30 mL) for 20 min. The solvent was removed under vacuum to give a residual solid, which was recrystallized from a mixture (1:1) of chloroform and hexane to give 94 mg (94%) of **12c**, mp 285−286 °C: IR υ_{max} (KBr) 1664 cm^{-1}; UV λ_{max} (CH$_3$CN) 315 nm (22 300); ^{1}H NMR (CDCl$_3$) δ 6.53 (1H, s), 7.26−8.34 (18H, m); ^{13}C NMR (CDCl$_3$) δ 64.83, 85.14, 104.77, 121.72, 124.14, 125.46, 126.55, 126.97, 127.19, 127.95, 128.16, 128.44, 128.67, 128.81, 129.88, 128.79, 130.65, 131.27, 132.79, 136.99, 138.87, 142.92, 152.46, 160.07, 197.20. Anal. Calcd for $C_{30}H_{19}NO_4$: C, 78.76; H, 4.19; N, 3.06. Found: C, 78.87; H, 4.27; N, 2.68.

Kinetic Measurements. The kinetics of thermal isomerization of **7a** to **9a**, **11a** to **12a**, and **11b** to **12b** was studied by UV spectroscopy, using *n*-decane or *n*-tridecane as solvent. The required temperature was maintained using an oil bath, and aliquots of the reaction mixture were removed at desired time intervals. The reaction, in each case, was quenched by dipping it in ice−salt mixture. In all cases, $\ln[A_0/(A_0 - A)]$ was plotted against time to give a straight line, and the rate constant, *k*, was determined from the slope. The experiment was repeated for at least three different temperatures to determine the corresponding rate constants. The values of ln *k* were plotted against $1/T$ (K) to give a straight line, and the activation parameters Ea and $\Delta S^{\ddagger}$ were evaluated using standard equations (Table 1).

A degassed solution of **7a** in *n*-decane (2×10^{-5} M) was heated with stirring at 110 °C, and aliquots were removed after each 5-min time interval to record the UV spectrum. The formation of the product was observed by monitoring the absorption change at 325 nm, which is characteristic of the dihydropentalenofuran derivative **9a**. Similarly, the experiment was repeated at 120 and 130 °C, to calculate the corresponding rate constants. The thermal isomerization of **11a** (5×10^{-5} M) in *n*-tridecane was followed by a monitoring of the absorption change at 320 nm (characteristic absorption of **12a**) and a repetition of the experiment at three different temperatures, namely, 155, 165, and 175 °C. The thermal isomerization of **11b** (5.3×10^{-5} M) in *n*-decane was similarly carried out at three different temperatures (120, 125, and 130 °C), and the progress of the reaction was monitored at 335 nm (characteristic absorption of **12b**). The activation parameters for these thermal isomerizations are summarized in Table 1.

X-ray Structure Determination of 11a, 11c, 11d, and 12b. Good-quality crystals of **11a, 11c, 11d,** and **12b** were mounted on glass fibers in random orientations and subjected to X-ray crystallographic analysis, employing a Siemens R3 automated four circle diffractometer. Data reduction and structure solution were achieved by SHELXTL-PLUS (VMS) structure solution package.[22] Full details on the crystal and molecular structures will be published elsewhere.[7]

Acknowledgment. We (M.C.S., D.R., M.M., A.K., and M.V.G.) thank the Council of Scientific and Industrial Research, Department of Science and Technology, Government of India; the Regional Research Laboratory, Trivandrum; the Volkswagen Foundation, Germany (D.R.); the University of Missouri-St. Louis (N.P.R.); and Jawarharlal Nehru Centre for Advanced Scientific Research, Bangalore (M.V.G.) for financial support of this work.

Supporting Information Available: X-ray ORTEP diagrams of **11a**, **11c**, and **12b** copies of ^{1}H and ^{13}C NMR spectra of **7a, 9a, 11a−d**, and **12a−c**; kinetic plots of thermal isomerzations of **7a**, **11a**, and **11b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9905322

---

[22] Sheldrick, G. M. Siemens Analytical X-ray Division, Madison, WI, 1991.