General Procedure for Table II (Table II, entry 1). To a stirred solution of **7a** (0.869 g, 3.62 mmol) in DMF (10 mL) under Ar at rt were sequentially added Et_3N (0.731 g, 0.6 mL, 4.34 mmol), I (1.81, 2.3 mL, 18.1 mmol), DPPP (0.044 g, 0.1 mmol), and $Pd(OAc)_2$ (0.0203 g, 0.090 mmol). The reaction temperature was raised to 80 °C. After 3 h the conversion was complete (GLC), and the reaction mixture was cooled to rt. HCl (5%, 15 mL) was added and after another 0.5 h of stirring the mixture was poured into CH_2Cl_2 (40 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL), and the combined organic layers were washed with water until neutrality, dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography[27] (hexane/ethyl acetate 9/1 by volume), affording **7e** (0.436 g, 90%).

2-Acetylbenzonitrile (16e): pale yellow solid; mp 46–48 °C (CH_3OH) (lit.[28] mp 48 °C); IR (Nujol) 2215, 1695 cm^{-1}; ^1H NMR δ 7.94 (dd, J = 6.9, 1.7 Hz, 1 H), 7.80–7.51 (m, 3 H), 2.64 (s, 3 H). Anal. Calcd for C_9H_7NO: C, 74.47; H, 4.86. Found: C, 74.43; H, 4.90.

The reaction described in eq 1 was carried out as described above with 5 equiv of **(E/Z)-1-ethoxy-1-propene (26)**. A sample of the crude product was analyzed before acidic treatment. **(E/Z)-1-Ethoxy-1-(1'-naphthyl)propene (27)**: colorless oil; H^1 NMR δ 8.10–7.31 (m, 7 H), 5.18–4.95 (m, 2 H), 3.90 (q, J = 7.0 Hz, 1.6 H, E isomer), 3.50 (q, J = 7.0 Hz, 0.4 H, Z isomer), 1.33 (t, J = 7.0 Hz, 2.4 H, E isomer), 1.17 (t, J = 7.0 Hz, 0.6 H, Z isomer); GLC-MS (Z)-**27** m/e 212 (M^+), 183, 155 (100). (E)-**27** m/e 212 (M^+), 183, 155 (100).

General Procedure for Table III and Table IV (Table III, entry 4). To a stirred solution of **2b** (0.3 g, 1.46 mmol) in DMF (3.5 mL) under Ar at rt were sequentially added TlOAc (0.420 g, 1.6 mmol), I (0.726 g, 0.938 mL, 7.26 mmol), DPPP (0.0166 g, 0.040 mmol), and $Pd(OAc)_2$ (0.008 g, 0.036 mmol). The reaction temperature was raised to 100 °C. After 0.8 h the conversion was complete (GLC) and the reaction mixture was cooled to rt, filtered, and treated with HCl (5%, 15 mL). After another 0.5 h of stirring the mixture was diluted with CH_2Cl_2 (35 mL). The aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL), and the combined organic layers were washed with water until neutrality, dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/ethyl acetate 9/1 by volume), affording **5** (0.214 g, 86%).

2-Acetyl-6-methoxynaphthalene (25e): white solid; mp 106–108 °C (CH_3OH) (lit.[29] mp 108 °C (CH_3OH)); IR (Nujol) 1685, 1620 cm^{-1}; ^1H NMR δ 8.37 (bs, 1 H), 8.02–7.75 (m, 3 H), 7.28–7.02 (m, 2 H), 3.93 (s, 3 H), 2.68 (s, 3 H). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.96; H, 6.07.

Registry No. 1, 111-34-2; **2a**, 99747-74-7; **2b**, 90-11-9; **2c**, 90-14-2; **2d**, 879-18-5; **3**, 134576-01-5; **Z-4**, 127087-65-4; **E-4**, 127087-64-3; **5**, 941-98-0; **6a**, 17763-67-6; **6b**, 108-86-1; **6c**, 591-50-4; **6d**, 98-88-4; **6e**, 98-86-2; **7a**, 66107-34-4; **7e**, 577-16-2; **8a**, 32578-31-7; **8e**, 585-74-0; **9a**, 29540-83-8; **9b**, 106-38-7; **9c**, 624-31-7; **9e**, 122-00-9; **10a**, 59099-58-0; **10e**, 579-74-8; **11a**, 66107-33-3; **11e**, 586-37-8; **12a**, 66107-29-7; **12b**, 104-92-7; **12c**, 696-62-8; **12e**, 100-06-1; **13a**, 129849-05-4; **13e**, 704-00-7; **14a**, 138313-22-1; **14b**, 2142-63-4; **14e**, 6781-42-6; **15a**, 109613-00-5; **15e**, 1009-61-6; **16a**, 138313-23-2; **16e**, 91054-33-0; **17a**, 66152-74-7; **17b**, 6952-59-6; **17e**, 6136-68-1; **18a**, 66107-32-2; **18e**, 1443-80-7; **19a**, 132993-22-7; **19e**, 577-59-3; **20a**, 32578-25-9; **20e**, 121-89-1; **21a**, 17763-80-3; **21b**, 586-78-7; **21c**, 636-98-6; **21e**, 100-19-6; **22a**, 17763-70-1; **22c**, 610-97-9; **22e**, 1077-79-8; **23a**, 29540-84-9; **23d**, 122-01-0; **23e**, 99-91-2; **24a**, 3857-83-8; **24b**, 580-13-2; **24e**, 93-08-3; **25a**, 129731-74-4; **25b**, 5111-65-9; **25e**, 3900-45-6; **26**, 928-55-2; **27**, 138313-24-3; **28**, 2876-63-3; DPPM, 2071-20-7; DPPE, 1663-45-2; DpTE, 138313-25-4; DPPP, 6737-42-4; DPPB, 7688-25-7; DPPF, 12150-46-8; c-DPPET, 983-80-2; PPh_3, 603-35-0; P(p-tolyl)$_3$, 1038-95-5; P(o-tolyl)$_3$, 6163-58-2; PCH_3Ph_2, 1486-28-8; $P(CH_3)_2Ph$, 672-66-2; $Pd(OAc)_2$, 3375-31-3; HOC_6H_4-o-Me, 95-48-7.

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Selective Solid-State Photorearrangement through the Less Stable of Two Possible Biradical Intermediates

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Received November 28, 1990

The photochemistry of methyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate is completely medium-dependent. In solution, two primary di-π-methane-type photoproducts are formed. Neither of these products is produced when the photolysis is carried out in the solid state; instead, three new photoproducts are formed. The results are interpreted as being due to reaction through 1,3-biradical intermediates, the more stable of which are preferred in solution whereas the less stable ones are formed in the solid state as a result of topochemical restrictions of molecular motion. X-ray crystallographic evidence in support of these ideas is presented and discussed.

Most organic reactions are carried out in solution. It is becoming increasingly apparent, however, that chemical studies in organic solids and other "organized media" offer several advantages over studies in liquid media.[1] Key among these is the interesting situation that arises when liquid- and solid-phase reactions give entirely different products. New reactions are discovered that offer new possibilities for organic synthesis, and fresh insights are provided into reaction mechanisms. Solid/liquid reactivity differences can arise, for example, when the reaction in solution occurs through a conformational isomer that is not present in the solid state.[2] Another source of sol-

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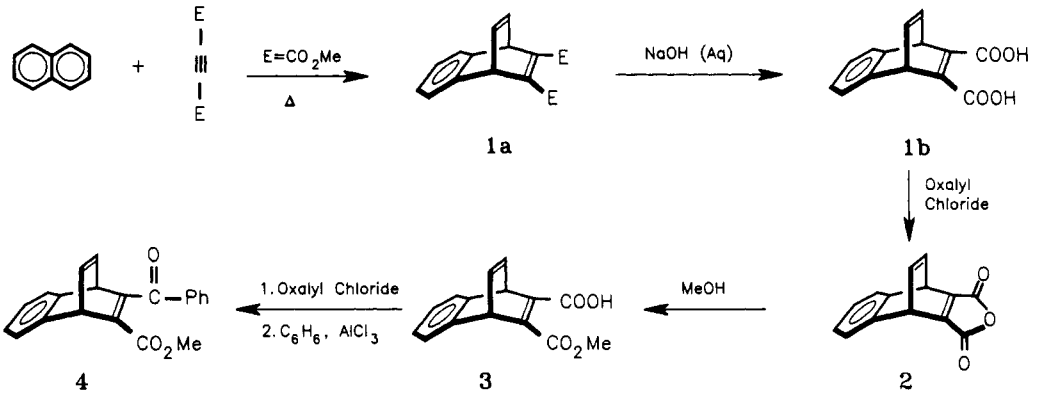
Scheme I



id/liquid reactivity differences is the close contact between neighboring molecules that is characteristic of the crystalline phase; this may favor a bimolecular reaction in the solid state as opposed to unimolecular processes that may predominate in dilute solution.[1a]

More subtle is the situation in which the liquid- and solid-phase reactions are both unimolecular, both occur from the same conformer, and are different because of crystal lattice restraints on the molecular motions associated with the solution process. Our approach to understanding such medium-dependent reactivity differences has been to identify the substituent or portion of the reactant that moves most during the solution reaction and then to search the X-ray crystal structure derived packing diagrams for *specific* H···H, H···C, or H···O contacts with neighboring molecules that might prevent (through atom–atom, nonbonded repulsion) such motions while at the same time allowing the motions associated with the solid-state reaction.[3] In the present paper we report the use of these ideas to explain the crystalline-phase photoreactivity of a molecule that, while rearranging normally in solution through the more stable of two possible biradical intermediates, reacts selectively in the solid state via the less stable biradical.

Results and Discussion

Choice and Preparation of the Starting Material. As a logical extension of previous work from our laboratory on the solid-state di-π-methane photoreactivity of substituted dibenzobarrelenes,[4] we embarked on a similar investigation of the corresponding *mono*benzobarrelenes. The compound chosen for study, methyl 2-benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (**4**, Scheme I) was selected for three main reasons: (1) crystallinity and ease of synthesis, (2) triplet photoreactivity as the result of facile intersystem crossing, and (3) a rich variety of possible di-π-methane photorearrangement pathways. The key step in the preparation of the starting material was the known[5] Diels–Alder reaction between dimethyl acetylenedicarboxylate and naphthalene (Scheme I). Following this, a series of straightforward functional-group transformations afforded the desired keto ester **4** as colorless prisms, mp 127–128 °C. The structure of compound **4** is supported by a direct-method X-ray crystal structure analysis: space group $P\bar{1}$; a = 9.772 (8) Å, b = 11.034 (2) Å, c = 8.174 (8) Å; α = 92.58°, β = 111.50°, γ = 97.96°; Z = 2; R = 0.042 for 2887 reflections with $I > 3\sigma(I)$.[6]

Photochemical Studies in Solution. Previous studies of the di-π-methane photorearrangement of vinyl-substituted benzobarrelenes and related compounds in solution have established a reasonably clear picture of the reaction mechanism.[7] The initial interaction, which can be either vinyl–vinyl or vinyl–benzo in nature, is thought to produce the cyclopropyldicarbinyl diradical species A (Scheme II). Whether this species represents a true intermediate, or is simply a nonminimum energy point on the reaction hypersurface, is still unclear;[8] we include it for ease in visualizing the mechanistic possibilities. The next step in the process is thought to involve cleavage of one of the cyclopropane ring bonds of A to form the 1,3-biradical intermediate B (overall 1,2-benzo or 1,2-vinyl shift of 4), and the rearrangement is completed by closure of this species with formation of the so-called benzosemibullvalene ring system.

Owing to the lack of symmetry in the starting keto ester **4**, there are eight possible 1,3-biradical intermediates that may be formed (B1–B8, Scheme II). Because intermediates B2 and B5 both lead to photoproduct **6** and biradicals B4 and B6 give **8**, the total number of possible di-π-methane rearrangement products is reduced to six. When it is considered that non-di-π-methane photoproducts may be formed and that there is also the possibility of secondary photoreactions, an investigation of the photochemistry of compound **4** presents a challenging prospect. Fortunately, as we shall see, the secondary photoreactions proved to be a help rather than a hindrance in that their internal consistency lent confidence to the structural assignments.

Direct photolysis ($\lambda > 330$ nm) of compound **4** to low conversions in a variety of solvents (benzene, acetonitrile, methanol, hexane) gave two major products in equal proportions with only small amounts of any other compounds being formed. These photoproducts were subsequently identified as the benzosemibullvalene derivatives **5** and **7**, and the quantum yields for their formation in benzene at 313 nm (extrapolated to 0% conversion) were 0.147 ± 0.029 and 0.142 ± 0.030, respectively.

Photoproducts **5** and **7** are the result of vinyl–vinyl bridging to form biradicals A1 and A2 (Scheme II) followed by cleavage so as to produce the 1,3-biradicals B1 and B3. These latter two species, having one benzylic and one

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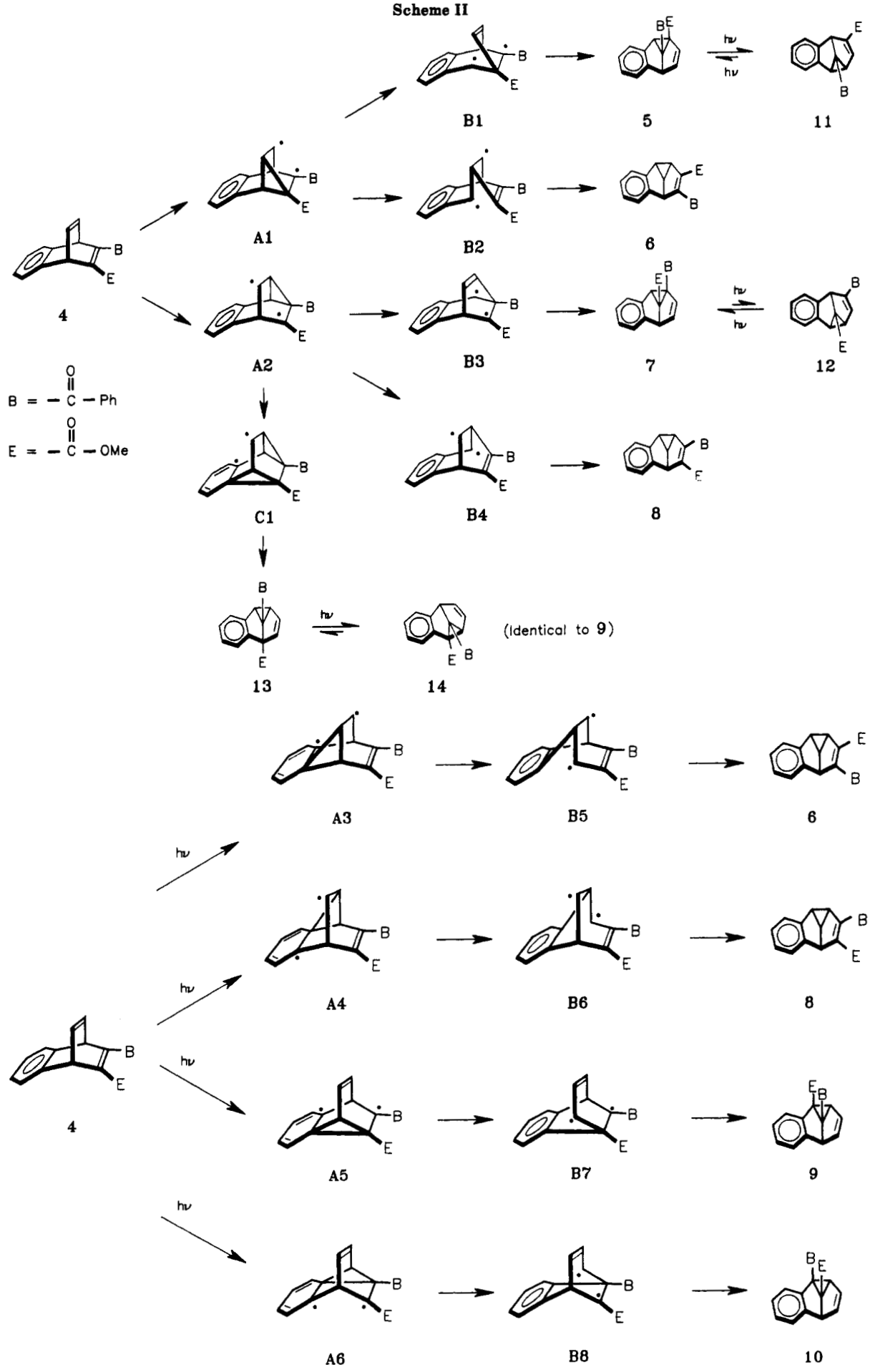
(8) For a recent discussion of this controversy, see: Hemetsberger, H.; Nispel, F. *Tetrahedron* **1990**, *46*, 3823.

Scheme II


B1
5
11
A1
B2
6
4
A2
B3
7
12
B = —C(=O)—Ph
E = —C(=O)—OMe
C1
B4
8
13
14
(Identical to 9)
A3
B5
6
hν
A4
B6
8
A5
B7
9
A6
B8
10

carbonyl-stabilized radical center, are presumably more stable than their counterparts B2 and B4 in which the nonbenzylic radical centers lack resonance stabilization. It is for this reason, we believe, that compounds 6 and 8 are produced in only trace amounts in solution.

Preparative-scale photolyses in benzene carried out until no starting material 4 remained gave somewhat different results. Under these conditions, the major photoproducts were compounds 7 and 11, and these could be isolated in 36 and 22% yields, respectively, following column chromatography on silica gel. Gas chromatography and NMR analysis of the crude photolysis mixture prior to column chromatography indicated the presence of small amounts of several other compounds as well (including significant levels of 5), but overlapping peaks prevented an accurate assessment of their relative amounts. Similar results from photolyses conducted in benzene in the presence and absence of a 10-fold (mol/mol) excess of benzophenone indicated the triplet nature of the primary photoreaction.

Compound 11 is formed by a photochemically initiated 1,3-shift of photoproduct 5. This is indicated by the fact that, during the photolysis of compound 4, the 5:11 product ratio decreases with increasing irradiation time. In addition, independent photolysis of 11 (either direct or sensitized) leads to a photostationary-state mixture consisting of 20% of 5 and 80% of 11, and a similar mixture is produced by irradiation of pure 5. Independent studies showed that photoproduct 7 also undergoes a secondary 1,3-shift process upon irradiation. The product of this reaction is benzosemibullvalene derivative 12 (Scheme II), which in this case is the minor (20%) component of the photostationary state mixture. This is in accord with the fact that only traces of compound 12 can be detected in the compound 4 photolysate. Analogous photochemically initiated 1,3-shift reactions of benzosemibullvalene derivatives have been observed by us (and others) previously.[9]

Photochemical Studies in the Crystalline State and in Polymer Matrices. Samples of keto ester 4 were irradiated in the solid state at room temperature through Pyrex ($\lambda > 290$ nm) in the form of carefully grown single crystals or as polycrystalline powders; both methods gave identical results. At conversions between 2 and 20%, none of the solution-phase products was detectable; instead, three new photoproducts (6, 8, and 13, Scheme II) were formed in a 5:3:2 ratio. At higher conversions, however, the crystals became noticeably tacky, and small amounts of photoproduct 7 began to appear in GC traces of the photolysis mixture. No secondary photoproducts were produced in the solid state. After workup and product isolation, however, the solution-phase photochemical behavior of compounds 6, 8, and 13 was briefly investigated. Extended irradiation of photoproducts 6 and 8 in a variety of solvents led to a >95% recovery of starting material. This may be interpreted either as a lack of reactivity of these compounds or as the establishment of a 1,3-shift photostationary state that greatly favors 6 and 8. Finally, we found that compound 13 reacts photochemically in solution to afford its 1,3-shift isomer 14 (Scheme II), a reaction that aided substantially in establishing the structure of the unusual, non-di-π-methane photoproduct 13. In this instance, the photostationary state favors compound 14 (80%).

As outlined in Scheme II, there are two distinct di-π-methane mechanisms by which photoproduct 6 can be formed (via biradical intermediates B2 or B5), and the same is true for photoproduct 8 (via biradicals B4 or B6). These mechanistic possibilities can be differentiated by appropriate labeling studies, and the results of experiments of this type will be presented later in the paper. As noted above, photoproduct 13 cannot be formed by a standard di-π-methane mechanism. Labeling studies (vide infra) are consistent with the mechanism shown in Scheme II, namely 4 → A2 → C1 → 13.

As materials having properties intermediate between those of liquids and crystalline solids, polymer matrices have been found to be useful and interesting "solvent" media for carrying out photochemical studies.[10] For this reason, the photochemistry of keto ester 4 was briefly investigated in poly(methyl methacrylate) films. The films were prepared by dissolving compound 4 plus 10 times its weight of PMMA (Aldrich) in methylene chloride, coating a glass surface with the resulting solution, and then removing the solvent in vacuo. Irradiation of such films through Pyrex afforded a mixture of five compounds. These were identified as solution photoproducts 5, 7, and 11 plus solid-state photoproducts 6 and 8. After irradiation to 100% conversion, the photoproduct ratios according to GC were 5:7:11:6:8 = 30:34:12:12:12. Interestingly, solid-state photoproduct 13 was not observed. The polymer matrix photolyses could also be carried out conveniently on a preparative scale, and it was experiments of this type that allowed us to isolate and characterize primary solution photoproduct 5. In solution, 5 cannot be isolated owing to its facile isomerization to 11. For reasons that are not clear, the rate of this process is much slower in PMMA matrices.

Photoproduct Characterization. Altogether, eight disubstituted benzosemibullvalene derivatives were isolated and characterized in the present work. This includes the primary solution-phase photoproducts 5 and 7 and their 1,3-shift isomers 11 and 12 as well as solid-state photoproducts 6, 8, and 13 plus 14, the (solution-phase) 1,3-shift isomer of 13. The structures of these compounds were assigned primarily on the basis of their proton NMR spectra (see below). Our confidence in the correctness of the structural assignments was increased a great deal by the internal consistency between the spectra of a given compound and its 1,3-shift isomer. As a final confidence builder, some months after our initial assignment based on NMR, the structure of compound 13 was corroborated by an X-ray crystal structure, space group *Pbca*, $a = 33.023$ (2) Å, $b = 11.210$ (1) Å, $c = 8.637$ (2) Å, $Z = 8$, $R = 0.042$ for 3730 reflections with $I > 3\sigma(I)$.[6]

Table I summarizes the ^{1}H NMR data for all eight compounds. The signals due to the aromatic protons and the methyl group protons are omitted, as they were not helpful in the structural assignments. Of the six possible sites 1–6 (refer to structure in Table I), one position will be occupied by a benzoyl group and another by a carbomethoxy group. Depending on the location of these substituents, the protons attached to the four remaining sites will display various unique combinations of chemical shifts and coupling patterns that are quite straightforward to unravel, even for binary photoproduct mixtures. For compounds 6, 8, 13, and 14, spin decoupling experiments verified the NMR assignments. For compounds 6 and 8, H_1 and H_2 were assigned as shown in Table I on the basis of shift reagent studies that are reported in the Experimental Section. While it is clear that the benzoyl and carbomethoxy groups of photoproducts 6 and 8 occupy the vinyl positions, some doubt still remains as to which vinyl

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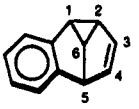
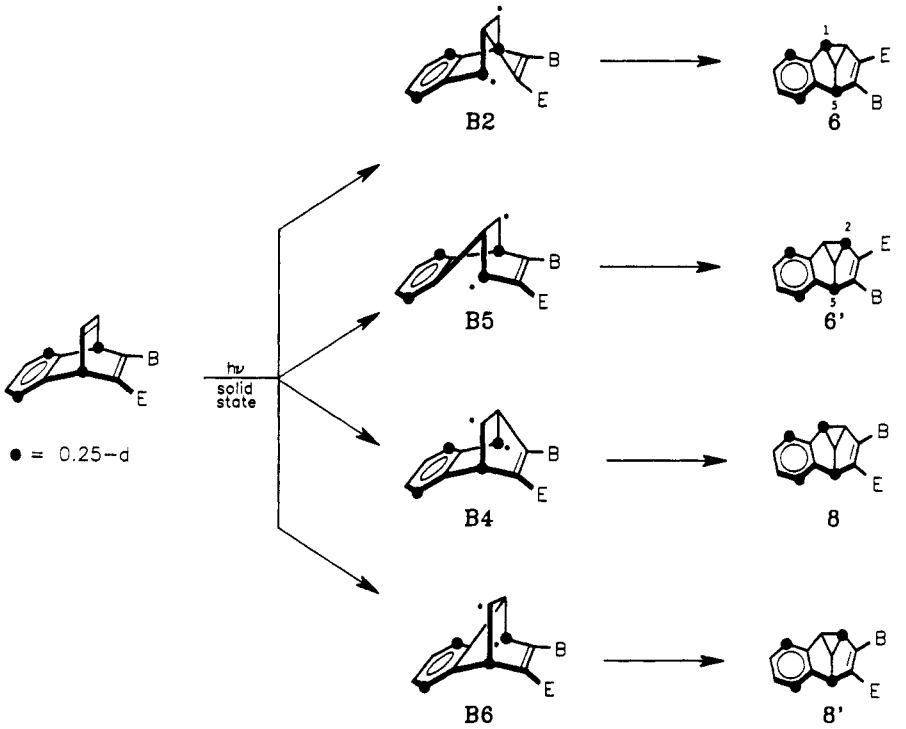
Table I. Chemical Shifts and Coupling Patterns for Nonaromatic Protons of Benzosemibullvalene Photoproducts



compd	chemical shift[a] (coupling pattern)[b]					
	H_1	H_2	H_3	H_4	H_5	H_6
5	4.55 (s)		5.64 (d)	5.91 (dd)	4.30 (d)	
7	4.57 (s)		5.27 (d)	5.93 (dd)	4.69 (d)	
11	4.07 (d)	3.66 (dd)	6.29 (d)		4.62 (s)	
12	3.97 (d)	3.54 (dd)	5.95 (d)		4.96 (s)	
6	3.40 (t)[c]	3.00 (t)[c]			4.40 (d)	3.62 (q)[c]
8	3.33 (t)[c]	3.18 (t)[c]			4.35 (d)	3.58 (q)[c]
13	4.07 (d)	3.44 (dd)	5.40 (dd)	6.06 (d)		
14 (9)		4.24 (d)	5.42 (dd)	5.87 (dd)	4.27 (d)	

[a] Chemical shifts are expressed in ppm downfield from TMS. [b] Singlet = s, doublet = d, doublet of doublets = dd, triplet = t and quartet = q; see Experimental Section for coupling constant values. [c] Simplified pattern owing to $J_{1,2} = J_{1,6} = J_{2,6} = J_{5,6}$.

Scheme III



carbon bears which substituent. Our assignments are based on the idea, for which there is some evidence in the literature,[11] that a benzoyl group exerts a greater deshielding effect on an adjacent proton than a carbomethoxy group. Thus, the lower field H_2 is assigned to 8 and the lower field H_5 is assigned to 6.

Deuterium-Labeling Studies. In order to distinguish among the mechanistic possibilities leading to solid-state photoproducts 6 and 8, compound 4 was specifically deuterated at C(1), C(4), C(5), and C(8). This was accomplished by substituting 1-detuerionaphthalene[12] for naphthalene in the synthetic sequence outlined in Scheme I. Assuming no significant deuterium isotope effect on the Diels–Alder reaction or on the opening of the anhydride 2 with methanol, this synthesis would generate compound 4 with 0.25-*d* at the positions indicated in Scheme III. These expectations were confirmed by the ^1H NMR spectrum of the deuterated material.

As outlined in Scheme III, initial vinyl–vinyl bridging and formation of biradical B2 leads to photoproduct 6 with depletion of the protium content at positions C(1) and C(5); the alternative mechanism, which proceeds through vinyl–benzo bridging and intermediate B5, produces the same compound with depletion at C(2) and C(5). Thus, by integrating the signals due to H_1 (δ 3.40) and H_2 (δ 3.00), the preference for vinyl–vinyl versus vinyl–benzo bridging may be assessed. As can be seen from Scheme III, exactly the same reasoning applies in the case of photoproduct 8. Experimentally, it was found that the NMR spectra of compounds 6 and 8 prepared by solid-state photolysis of deuterated 4 both showed a clear diminution in the integration of H_1, a result consistent with a preference for initial vinyl–vinyl bridging. Owing to the relatively low deuterium levels present, however, as well as to the rather imprecise nature of NMR integration techniques, we cannot completely rule out some small contribution from vinyl–benzo bridging in the solid state. It is worth mentioning at this point that previous studies of the di-π-methane photorearrangement of benzobarrelene derivatives in solution were also found to be consistent with a

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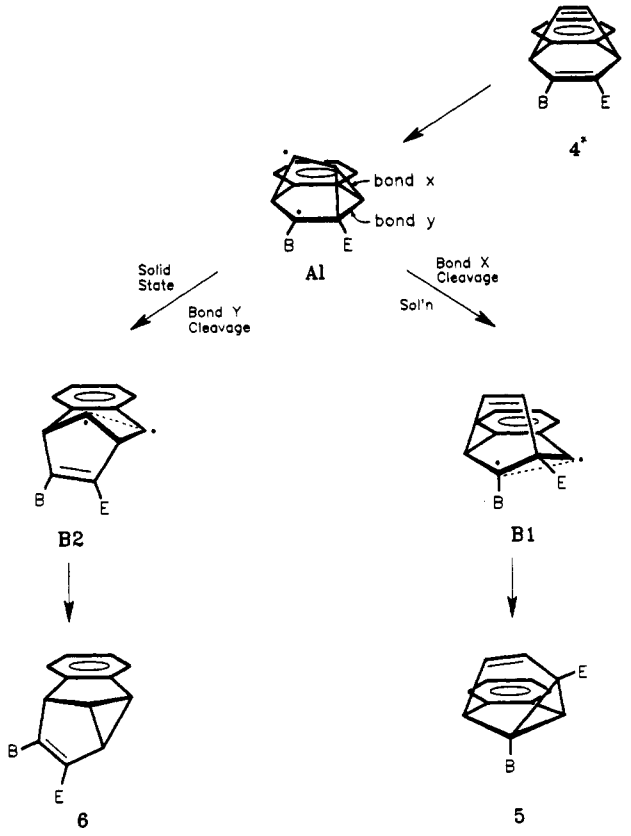
(12) Goubeau, J.; Luther, H.; Feldmann, K.; Brandes, G. *Chem. Ber.* **1953**, *86*, 214.

Scheme IV



mechanism involving initial vinyl–vinyl bridging.[9b,13] For this reason, we favor a vinyl–vinyl bridging mechanism proceeding through species A2 (Scheme II) for the formation of photoproduct **13** in the solid state. Photoproduct **13** can also be formed by a vinyl–benzo bridging process involving initial formation of A5, which then goes on to form C1 and eventually **13**. Since biradical C1 is common to both mechanisms, deuterium labeling is incapable of distinguishing between them.[14] One might argue that intermediate C1 could be formed from **4** by a concerted process, but molecular orbital calculations by Zimmerman indicate that such a mechanism has a higher barrier than the stepwise process, at least in the case of barrelene itself.[15]

Solid-State Structure–Reactivity Correlations. Having established that the solid-state reaction occurs via biradicals B2 and B4 and that the solution-phase reaction proceeds through biradicals B1 and B3, it is now apparent that the key solid/liquid differentiation process is the partitioning of the excited state of keto ester **4** (via A1 and A2) to B1–B4 (Scheme II). Strikingly, the crystalline medium directs the reaction through the *less* stable biradical in each case. In this section, we discuss possible reasons for the novel solid-state selectivity.

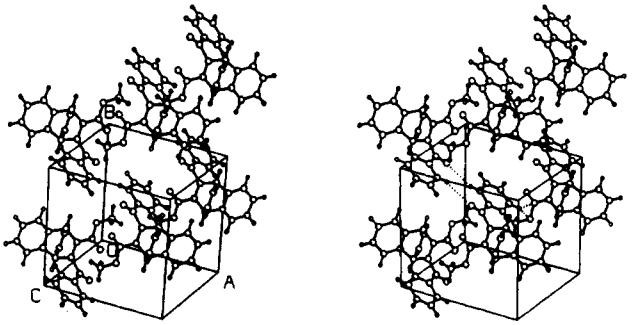


Figure 1. Packing diagram for keto ester **4** showing contacts (dotted lines) thought to be responsible for controlling photoreactivity.

If the above analysis is correct, then there must be some feature or combination of features associated with the crystalline medium that slows the processes 4* → B1 and 4* → B3 to the point that they can no longer compete with reactions 4* → B2 and 4* → B4. What features could these be? The idea that underlies most interpretations of organic solid-state reactivity is that nonbonded steric interactions between the reacting molecule and its lattice neighbors are product-determining.[1] Our approach has been to suggest that the portion of the reactant that is most likely to suffer an unfavorable steric interaction with the crystal lattice during reaction is the part that is required to move most under the assumed mechanism. In the case of **4**, the carbomethoxy and benzoyl substituents undoubtedly sweep out the greatest volume of space as the carbons to which they are attached become involved in bond formation and bond breaking. Scheme IV depicts the structures of the relevant species as deduced from molecular models. From this it is apparent that the ester substituent E moves much more in the 4* → B1 (solution) transformation than in the 4* → B2 (solid-state) reaction.[16] During the 4* → B1 process, the ester group moves upward and to the right from a point well below the mean plane of the aromatic ring to an essentially coplanar position. In contrast, the ester substituent moves only slightly to the left during the conversion of 4* to B2. Although not shown, exactly the same situation applies in the formation of solution biradical B3. This process involves much greater motion of the benzoyl group than formation of solid-state biradical B4 (to visualize this, simply exchange the benzoyl and ester substituents in Scheme IV). Our working hypothesis to explain the solid-state reactivity is thus that solution pathways 4* → B1 and 4* → B3 are topochemically forbidden in the crystal resulting in a preference for the sterically less demanding processes 4* → B2 and 4* → B4.[17] The next step is to see whether this hypothesis is consistent with the crystal-packing arrangement of keto ester **4**.

From the table of intermolecular atom–atom contacts below 3.5 Å, we find that there are several nonbonded interactions involving atoms in the carbomethoxy and

(13) (a) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 6096. (b) Zimmerman, H. E.; Amick, D. R.; Hemetsberger, H. *J. Am. Chem. Soc.* **1973**, *95*, 4606. (c) Bender, C. O.; King-Brown, E. H. *J. Chem. Soc., Chem. Commun.* **1976**, 878. (d) Bender, C. O.; Brooks, D. W.; Cheng, W.; Dolman, D.; O'Shea, S. F.; Shugarman, S. S. *Can. J. Chem.* **1978**, *56*, 3027. (e) Bender, C. O.; Bengston, D. L.; Dolman, D.; Herle, C. E. L.; O'Shea, S. F. *Can. J. Chem.* **1982**, *60*, 1942.

(14) The ^{1}H NMR spectrum of photoproduct **13** obtained from solid-state photolysis of deuterated **4** shows depletion of protium at positions 1 and 4, a result that is consistent with the mechanism postulated for its formation (Scheme II).

(15) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932.

(16) The assumption implicit in this discussion is that the ground and triplet excited states of keto ester **4** have similar geometries. Apart from small changes in bond lengths associated with the unsaturated keto ester portion of the molecule, this assumption is probably justified, particularly in view of the rigidity of the benzobarrelene ring system, which would make twisting about the substituted double bond difficult. For a discussion of excited-state ene–dione geometry, see: Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 2163.

(17) Because portions of the reactant other than the ester and benzoyl groups undoubtedly move during these transformations, a complete understanding of the medium effects will come only after a full analysis of all contacts developed along the reaction coordinate between the reacting molecule and its lattice neighbors. This is clearly a formidable task, and the present approach can be considered as a first step in this direction.

benzoyl groups. Of these, there are four that would clearly inhibit the motion of the ester or ketone moieties required for the 4* → B1 and 4* → B3 (solution) processes. Figure 1 shows the packing diagram for keto ester 4 with the relevant contacts indicated by dotted lines. Columns of molecules along the direction of the c-axis are related to molecules in adjacent columns by a center of symmetry. About this center, the benzoyl group oxygen atoms are involved in C-H···O hydrogen bonding (2.70 Å)[18] with the ortho hydrogen atoms of the neighboring phenyl groups, an interaction that would prevent the benzoyl groups from moving toward each other as required for the 4* → B3 transformation. The carbomethoxy group is required to move along c during the 4* → B1 process, and in a direction that is hindered in the solid state by intracolumn contacts between an aromatic hydrogen atom and the carbonyl carbon and ether oxygen atoms of the ester group (2.82 and 2.78 Å, respectively).

Significantly, the contacts discussed above are very close to the sum of the van der Waals radii of the atoms involved (2.72 Å for H···O and 2.90 Å for H···C).[19] This lends credence to the arguments presented, as it is reasonable to expect that closer contacts correlate with greater control of reactivity. As an alternative approach, we very briefly investigated the use of volume calculations to rationalize the solid-state results. This is based on the recent, elegant work of Zimmerman and Zuraw,[20] who successfully correlated overall changes in molecular volume (ΔV), nonhydrogen atom displacements (ΔM) and lattice interference (ΔS) with solid-state/solution-phase photoreactivity differences. The structures of biradicals B1 and B2 were estimated from molecular mechanics methods and their volumes calculated using a locally written program. The calculations showed that these biradicals differ only slightly in volume (less than 2 Å^3 out of a total volume of approximately 287 Å^3). In general it would appear that such calculations, which do not contain any information on the *directionality* of the crystal lattice steric effects, may be rather insensitive indicators of solid-state reactivity.

Experimental Section

General Procedures. Melting points are uncorrected. ^{1}H NMR spectra were recorded in $CDCl_3$ unless otherwise stated. ^{13}C NMR spectra were recorded at 75 MHz for proton-decoupled experiments. Mass spectra were recorded at 70 eV. GC was carried out with a flame ionization detector and either 15-m DB-1 or 15-m DB-17 capillary columns. Reagent solvents were purified according to known procedures.[21] Spectral-grade solvents for photochemical and UV studies were used directly as obtained. Photolyses were carried out with a 450-W Hanovia medium-pressure mercury lamp, and the desired wavelengths were achieved by using Corex ($\lambda > 260$ nm), Pyrex ($\lambda > 290$ nm), or uranium glass ($\lambda > 330$ nm) filter sleeves. Analytical photolyses were conducted in 0.02-mL Pyrex tubes, and preparative photolyses were performed in 10-mL Pyrex tubes, both sealed with ground-glass caps. Samples were degassed by repeating the freeze–pump–thaw cycle twice and sealing under N_2.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid (1b). To a solution of 21.8 g (80.7 mmol) of diester **1a**[5] in 150 mL of ethanol was added 650 mL of 9.61 M NaOH(aq). The resulting solution was refluxed for 2 h, cooled to rt, and washed with 200 mL of diethyl ether to remove unreacted starting material. The basic aqueous layer was then neutralized with concentrated HCl to give a white precipitate. This was extracted twice with 500 mL of diethyl ether, and the combined extracts were washed twice with 200 mL of water, dried over $MgSO_4$, and evaporated under reduced pressure to give the diacid **1b** as a white solid (17.0 g, 87%). Recrystallization from acetonitrile gave colorless prisms, mp 204–205 °C; IR (KBr) 2300–3100 (OH), 1450–1700 (C=O) and 1279 (CO) cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.00 (br s, 2 H), 6.9–7.4 (m, 6 H), 5.26 (m, 2 H); ^{13}C NMR (DMSO-d_6) δ 167.14, 147.27, 145.68, 139.51, 124.34, 123.20, 50.16; MS *m/e* (rel intensity) 242 (M$^+$, 30), 224 (32), 198 (16), 180 (37), 152 (100), 128 (38); HRMS calcd for $C_{14}H_{10}O_4$ 242.0579, found 242.0576. Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.40; H, 4.26.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Anhydride (2). To a solution of 13.0 g (53.7 mmol) of **1b** dissolved in 500 mL of freshly distilled CH_2Cl_2 was added 17.4 mL (0.200 mol) of oxalyl chloride. The solution was refluxed for 15 h under N_2. The solvent and excess oxalyl chloride were evaporated, and the remaining solid was recrystallized from a 1:4 mixture of benzene–hexanes to give 10.0 g (83%) of needles: mp 129–130 °C; IR (KBr) 1838 (C=O) and 1767 (C=O) cm^{-1}; ^{1}H NMR (400 MHz) δ 7.0–7.4 (m, 6 H), 5.29 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 160.30, 159.92, 143.67, 139.58, 125.17, 124.40, 45.39; MS *m/e* (rel intensity) 224 (M$^+$, 40), 180 (38), 152 (100), 128 (4), 76 (45); HRMS calcd for $C_{14}H_8O_3$ 224.0473, found 224.0472. Anal. Calcd for $C_{14}H_8O_3$: C, 75.00; H, 3.60. Found: C, 75.13, H, 3.60.

1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylic Acid Monomethyl Ester (3). A solution of 9.1 g (40.6 mmol) of anhydride **2** in 300 mL of dry methanol was refluxed under N_2 for 2 h. The methanol was evaporated and the resulting yellow oil dissolved in 100 mL of CH_2Cl_2 and washed twice with 75 mL of water. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to afford 10.8 g (100%) of a viscous, light yellow oil. The structure was assigned according to the following data: IR (neat) 2500–3400 (OH), 1719 (C=O), 1637 (C=O), 1278 (CO) cm^{-1}; ^{1}H NMR (300 MHz) δ 6.9–7.3 (m, 6 H), 5.89 (d, J = 5 Hz, 1 H), 5.60 (d, J = 5 Hz, 1 H), 4.00 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 166.50, 166.05, 148.25, 146.19, 145.38, 145.26, 139.47, 139.25, 124.29, 124.25, 123.15, 123.11, 52.20, 49.94, 49.79; MS *m/e* (rel intensity) 256 (M$^+$, 25), 212 (31), 196 (20), 179 (18), 152 (100), 128 (30); HRMS calcd for $C_{15}H_{12}O_4$ 256.0736, found 256.0728.

Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (4). To a solution of 5.5 g (22 mmol) of acid ester **3** in 180 mL of anhydrous CH_2Cl_2 was added dropwise 5.6 mL (64 mmol) of oxalyl chloride, and the reaction was refluxed. After 1 h, the solvent was evaporated under reduced pressure and the crude acyl chloride, a yellow oil, was dissolved in 2.4 L of dry thiophene-free benzene. Then, approximately 4.4 g (33 mmol) of anhydrous $AlCl_3$ was added to the solution. The reaction mixture was stirred at rt for 1 h 45 min under N_2 and the deep red solution then quenched with 300 mL of water. The benzene solution was reduced in volume to 1 L, washed with water (3 × 200 mL), dried over $MgSO_4$, and evaporated. The resulting oil was flash chromatographed on silica gel and eluted with hexanes–diethyl ether (9:1, v/v). This gave 1.4 g (21%) of a white solid. Recrystallization from hexanes gave prisms: mp 127–128 °C; IR (KBr) 1713 (ester C=O), 1667 (benzoyl C=O), 1244 (CO) cm^{-1}; ^{1}H NMR (400 MHz) δ 6.9–7.6 (m, 11 H), 5.55 (d, J = 6 Hz, 1 H), 5.04 (d, J = 6 Hz, 1 H), 3.40 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 195.60, 164.14, 159.27, 145.41, 144.12, 141.97, 140.27, 138.03, 135.69, 133.39, 128.57, 128.52, 124.55, 124.34, 123.25, 123.07, 52.29, 51.61, 48.89; MS *m/e* (rel intensity) 316 (M$^+$, 11), 284 (11) 256 (12), 211 (12), 152 (20), 128 (90), 105 (100), 77 (39); HRMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1103; UV (hexane) 247 (ϵ 16 890), 290 sh (ϵ 3220) nm. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.75; H, 5.13. The structural assignment is supported by an X-ray crystal structure determination.[6]

Analytical Photolyses of Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (4). Crystals of 4 were dissolved in four analytical phototubes using benzene, acetonitrile, hexane, and methanol (ca. 0.05 M). The degassed solutions were photolyzed through a uranium glass filter ($\lambda > 330$ nm) and followed by GC to complete conversion. Two major products subsequently shown to have structures 7 and 11 were seen along

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(21) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd Ed.; Pergamon Press: Oxford, England, 1980.

with some minor products. The GC ratios show the reaction is independent of solvent. A solution of 25 mg of 4 in 1 mL of $CDCl_3$ was degassed and transferred under N_2 to an NMR tube. The solution was photolyzed by using the above conditions to complete conversion, and the integrated NMR spectrum of the resulting mixture showed six products (7, 11, 5, 12, 6, and 8) in a ratio of 50:25:17:trace:8:trace, respectively. Benzophenone sensitization was also studied. A benzene solution 0.02 M in 4 and 0.2 M in benzophenone was photolyzed through uranium glass ($\lambda > 330$ nm). GC showed results similar to the direct photolysis of 4 above.

For solid-state photolyses, crystals of 4 were placed in phototubes and irradiated through a Pyrex filter ($\lambda > 290$ nm). GC showed the formation of three new products: 6, 8, and 13. NMR analysis of the reaction mixture at 17% conversion indicated a 6:8:13 ratio of 5:3:2. No 7, 11, or 5 were detected at low conversions, but at conversions above ca. 20% the crystals began to melt and stick to the tube surface, and detectable amounts of compound 7 began to form.

For polymer matrix studies, 3 mg of 4 was dissolved with 30 mg of medium molecular weight poly(methyl methacrylate) (Aldrich) in 2 mL of CH_2Cl_2 and spread evenly over three microscope slides. The solvent was evaporated under vacuum for 24 h. The resulting clear films were photolyzed at 20 °C through Pyrex ($\lambda > 290$ nm). In monitoring the reaction, portions of film were dissolved in CH_2Cl_2 and methanol was added to precipitate the PMMA before GC analysis. Irradiation to complete conversion gave 5 products, 7, 11, 5, 6, and 8, in a GC ratio of 34:12:30:12:12, respectively. Low-temperature photolysis (−50 °C) gave similar results, but the rate was much slower.

Preparative Photolysis of Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (4) in Benzene. A solution of 4 (130 mg, 0.411 mmol) in 40 mL of benzene was placed in four 10-mL phototubes. The tubes were degassed and photolyzed through uranium glass ($\lambda > 330$ nm) until no starting material remained. The benzene was evaporated, and the resulting oil was flash chromatographed on silica gel with hexanes–diethyl ether (95:5, v/v) as the eluting solvent. The first band contained 47 mg (36 %) of 7. Recrystallization from hexanes gave two crystal morphologies, colorless prisms (mp 113–114 °C), and needles (mp 106–107 °C): IR (KBr, prisms) 1723 (ester C=O), 1677 (benzoyl C=O), 1225 (CO) cm^{-1}; IR (KBr, needles) 1733 (ester C=O), 1674 (benzoyl C=O), 1224 (CO) cm^{-1}; ^1H NMR (400 MHz) δ 7.2–8.0 (m, 9 H), 5.93 (dd, J = 3, 5 Hz, 1 H), 5.27 (d, J = 5 Hz, 1 H), 4.69 (d, J = 3 Hz, 1 H), 4.57 (s, 1 H), 3.45 (s, 3 H); MS m/e (rel intensity) 316 (M^+, 28), 256 (31), 228 (40), 152 (30), 105 (100), 77 (80); HRMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1103; UV (CH_3CN) 244 (ϵ 14 000), 277 sh (ϵ 3100) nm. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.48; H, 5.15. The second band contained 29 mg (22%) of 11. Recrystallization from pentane gave prisms: mp 100–101 °C; IR (KBr) 1703 (ester C=O), 1663 (benzoyl C=O), 1253 (CO) cm^{-1}; ^1H NMR (300 MHz) δ 7.2–7.7 (m, 9 H), 6.29 (d, J = 3 H, 1 H), 4.62 (s, 1 H), 4.07 (d, J = 8 Hz, 1 H), 3.72 (s, 3 H), 3.66 (dd, J = 3, 8 Hz, 1 H); MS m/e (rel intensity) 316 (M^+, 7), 284 (8), 180 (23), 152 (50), 105 (100), 77 (72); HRMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1106; UV (CH_3CN) 244 (ϵ 16 500), 280 sh (ϵ 4900) nm. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.80; H, 5.10.

Quantum Yield Determinations. Solution-phase quantum yields were determined on a merry-go-round apparatus.[22] The desired wavelength of 313 nm was achieved by combining a solution filter of K_2CrO_3 (0.2 g/L) with a Corning glass filter no. 7-54. A Hanovia medium-pressure mercury lamp was the light source, and valerophenone was the actinometer; tetracosane was used as the internal standard for both photoproducts 7 and 5. Quantum yields were plotted as a function of conversion and the graphs were extrapolated to 0% conversion to determine the true quantum yields.

Preparative Photolysis of Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (4) in the Solid State. Crystals of 4 (291 mg, 0.921 mmol) were placed inside three vials and photolyzed through a Pyrex filter ($\lambda > 290$ nm) until the crystals were yellow but showed no sign of melting (18% conversion by GC). The crystals were dissolved in benzene and flash chromatographed on silica gel by using a solvent system of hexanes–diethyl ether (92:8, v/v) to give three overlapping bands. The first band was rechromatographed as above to give 13 mg (4.5%) of 13. Recrystallization from hexanes gave colorless needles: mp 162–163 °C; IR (KBr) 1742 (ester C=O), 1668 (benzoyl C=O), 1285 (CO) cm^{-1}; ^1H NMR (300 MHz) δ 7.1–7.7 (m, 9 H), 6.06 (d, J = 5 Hz, 1 H), 5.40 (dd, J = 3, 5 Hz, 1 H), 4.07 (d, J = 8 Hz, 1 H), 3.44 (dd, J = 3, 8 Hz, 1 H), 3.12 (s, 3 H); spin decoupling experiments, irradiation of H_4 collapsed H_3 to a doublet (J = 3 Hz), irradiation of H_3 collapsed H_4 to a singlet and collapsed H_2 to a doublet (J = 8 Hz), irradiation of H_2 collapsed H_3 to doublet (J = 5 Hz) and H_1 to a singlet, irradiation of H_1 collapsed H_2 to a doublet (J = 3 Hz); MS m/e (rel intensity) 316 (M^+, 12), 284 (13), 256 (20), 152 (20), 105 (100), 77 (35); HRMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1098; UV (CH_3CN) 240 (ϵ 9500), 280 sh (ϵ 1760) nm. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.73; H, 5.16. The assigned structure was also supported by an X-ray crystal structure determination.[6] The second band was starting material 4, 190 mg (65%). The third band was rechromatographed using similar conditions as above to give 26 mg (9%) of an inseparable oily mixture of 6 and 8 (75:25). Therefore, these compounds were characterized together (IR (film, 1:1 mixture) 1714 (ester C=O), 1673 (benzoyl C=O), 1267 (CO) cm^{-1}). In the NMR, the peaks of 6 can be distinguished from those of 8 by analyzing several spectra with different compositions of 6 and 8, varying from 1:1 to 4:1. For 6: ^1H NMR (300 MHz) δ 6.8–7.6 (m, 9 H), 4.40 (d, J = 6 Hz, 1 H), 3.62 (q, J = 6 Hz, 1 H), 3.45 (s, 3 H), 3.40 (t, J = 6 Hz, 1 H), 3.00 (t, J = 6 Hz, 1 H); spin decoupling experiments, irradiation of H_1 modifies H_6 and H_2, irradiation of H_2 modifies H_1 and H_6, irradiation of H_5 modifies H_6, and irradiation of H_6 collapses H_5 to a singlet and H_2 to a doublet (J = 6 Hz). The assignment of the two triplets corresponding to H_1 and H_2 was made on the basis of a lanthanide shift reagent study. It was reasoned that H_2, being closer to the site of shift reagent complexation (the ester and benzoyl substituents), should be more strongly deshielded than H_1. Successive addition of 4, 10, 20, and 30 mol % of Eu(hfc)$_3$ (Aldrich) to an NMR sample of 6 showed a greater shift of the signal at δ 3.00 compared to that at δ 3.40. Accordingly, the former was assigned to H_2 and the latter to H_1: GCMS m/e (rel intensity) 316 (M^+, 10), 284 (40), 179 (10), 152 (15), 105 (100), 77 (69); HR-GCMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1097.

The data for 8 are as follows: ^1H NMR (300 MHz) δ 6.8–7.6 (m, 9 H), 4.35 (d, J = 6 Hz, 1 H), 3.58 (q, J = 6 Hz, 1 H), 3.33 (t, J = 6 Hz, 1 H), 3.18 (t, J = 6 Hz, 1 H), 3.17 (s, 3 H); shift reagent studies similar to those described above allowed assignment of the triplet at δ 3.33 to H_1 and that at δ 3.18 to H_2; spin decoupling experiments, irradiation of H_1 modifies H_2 and H_6, irradiation of H_2 modifies H_1 and H_6, irradiation of H_5 modifies H_6, irradiation of H_6 collapses H_5 to a singlet and modifies H_1 and H_2; GCMS m/e (rel intensity) 316 (M^+, 5), 284 (7), 152 (8), 105 (100), 77 (38); HR-GCMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1103.

Preparative Photolysis of Methyl 2-Benzoyl-1,4-dihydro-1,4-ethenonaphthalene-3-carboxylate (4) in Poly(methyl methacrylate). A solution of 4 (200 mg, 0.63 mmol) and 2.0 g of medium molecular weight PMMA (Aldrich) in 30 mL of CH_2Cl_2 was poured into a 24 × 5 cm Pyrex vacuum tube and spread evenly over the inner surface. The solvent was removed by flushing with N_2 for 30 min followed by pumping on the vacuum line for 50 h. The tube was sealed under nitrogen and photolyzed at 20 °C through a Pyrex filter sleeve ($\lambda > 290$ nm). The tube was rotated every 15 min and the reaction was monitored by GC to a maximum conversion of 93%. The polymer was dissolved in 100 mL of CH_2Cl_2, and 75 mL of methanol was added. The solvent was evaporated until approximately 75 mL remained, by which time most of the polymer had precipitated. The mixture was stirred for another 30 min to precipitate the rest of the polymer and the solution was then filtered and evaporated to a yellow oil. Flash chromatography on silica gel by using hexanes–diethyl ether (9:1, v/v), as the eluent gave three major bands. The first band consisted of 61 mg (31%) of photoproduct 7 (spectral data reported above). The second band contained 27 mg (14%) of compound 5. Recrystallization of this material from hexanes gave colorless prisms, mp 129–130 °C; IR (KBr) 1718 (ester C=O), 1676 (benzoyl C=O), and 1287 (CO) cm^{-1}; ^1H NMR

(22) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; Chapter 14.

(300 MHz) δ 7.1–7.9 (m, 9 H), 5.91 (dd, J = 2, 5 Hz, 1 H), 5.64 (d, J = 5 Hz, 1 H), 4.55 (s, 1 H), 4.30 (d, J = 2 Hz, 1 H), 3.70 (s, 3 H); MS m/e (rel intensity) 316 (M^+, 25), 284 (49), 256 (25), 152 (15), 105 (100), 77 (30); HRMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1105; UV (CH_3CN) 245 (ε 25 800), 278 sh (ε 3900) nm. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.82; H, 5.14. The third band consisted of 39 mg (20%) of a 3:1 mixture of **6** and **8** as shown by GC.

Photolysis of Compound 7. Crystals of **7** were dissolved in three analytical phototubes by using benzene, acetonitrile, and acetone to make up approximately 0.01 M solutions. The samples were degassed, photolyzed (λ > 290 nm), and monitored by GC to show the formation of one compound, subsequently characterized as **12**. The reaction was independent of solvent except that the rate of reaction in acetone was noticeably slower. In all three cases, the **7**:**12** ratio after prolonged photolysis (corrected for detector response) was 8:2. That this represents a true photostationary state ratio was shown by subsequent independent photolysis of compound **12**. On a preparative scale, a solution of 50 mg (0.16 mmol) of **7** in 40 mL of benzene was degassed and photolyzed in four 10-mL phototubes through Pyrex to a **7**:**12** ratio of 83:10. The solvent was evaporated and the resulting yellow oil chromatographed on silica gel by using diethyl ether–hexanes (1:9, v/v) as the solvent. Two overlapping bands were eluted, compound **7** first, followed by **12**. A partial separation of **7** from **12** was achieved, and the pure **7** isolated (32 mg) was rephotolyzed under the same conditions. Chromatography as above gave partial separation of **12** again. The fractions of **12** were collected and rechromatographed to give complete separation resulting in 12 mg (24%) of a white solid. Recrystallization from hexane gave colorless needles: mp 100–101 °C; IR (KBr) 1726 (ester C=O), 1639 (benzoyl C=O), 1329, 1267, 1213 cm^{-1}; ^1H NMR (300 MHz) δ 7.1–7.6 (m, 9 H), 5.95 (d, J = 3 Hz, 1 H), 4.96 (s, 1 H), 3.97 (d, J = 8 Hz, 1 H), 3.74 (s, 3 H), 3.54 (dd, J = 3, 8 Hz, 1 H); MS m/e (rel intensity) 316 (M^+, 20), 284 (4), 256 (10), 152 (13), 105 (100), 77 (45); HRMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1100. Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.63; H, 5.21.

Photolysis of Compound 13. Crystals of **13** were dissolved in three analytical phototubes by using benzene, acetonitrile, and acetone to make up approximately 0.01 M solutions. The sample were degrassed and photolyzed through Pyrex. GC indicated the formation of one volatile product, subsequently shown to have the structure **14**, at a photostationary state ratio of **13**:**14** = 2:8; prolonged photolysis led to decomposition of the sample. The results were the same in all three solvents, except that the rate of the reaction was slower in acetone. Following its isolation (see below), independent photolysis of compound **14** under the same conditions led to an identical photoproduct mixture. Photoproduct **14** was isolated by photolysis of a solution of 7.5 mg (0.025 mmol) of **13** in 1 mL of $CDCl_3$. The photolysis was halted at a **13**:**14** ratio of 57:43 in order to avoid photodecomposition. The reaction mixture was flash chromatographed on silica gel by using hexanes–diethyl ether (9:1, v/v) as the solvent system; compound **13** eluted first followed closely by **14**. Pure **13** isolated was rephotolyzed and chromatographed as above. The two pure portions of **14** were combined to give 3 mg (40%) of this material as a colorless oil: IR (liquid film) 1728 (ester C=O), 1675 (benzoyl C=O), 1264 (CO) cm^{-1}; ^1H NMR (300 MHz) δ 7.1–7.9 (m, 9 H), 5.87 (dd, J = 2, 5 Hz, 1 H), 5.42 (dd, J = 3, 5 Hz, 1 H), 4.27 (d, J = 2 Hz, 1 H), 4.24 (d, J = 3 Hz, 1 H), 3.73 (s, 3 H); spin decoupling experiments, irradiation of H_4 collapses H_3 to a doublet (J = 3 Hz) and collapses H_5 to a singlet, irradiation of H_3 collapses H_4 to a doublet (J = 2 Hz) and collapses H_2 to a singlet; MS m/e (rel intensity) 316 (M^+, 13), 300 (8), 152 (12), 105 (100), 77 (39); HRMS calcd for $C_{21}H_{16}O_3$ 316.1100, found 316.1096. The positions of the benzoyl and ester groups were assigned from our understanding of the 1,3-shift reaction and the knowledge of the structure of the precursor **13**.

Photolysis of Compound 5. Crystals of **5** were dissolved in two analytical phototubes by using benzene and acetonitrile to make up approximately 0.01 M solutions. The samples were degassed and photolyzed through Pyrex. GC indicated a photostationary state composition of **5**:**11** = 2:8, and this was verified by an independent photolysis of compound **11** under identical conditions. It was also noticed that **5** rearranges thermally to **11** in the GC above 200 °C.

Photolysis of Compounds 6 and 8. A 1:1 mixture of photoproducts **6** and **8** was dissolved in three analytical Pyrex phototubes by using benzene, acetone, and acetonitrile to make up approximately 0.02 M solutions. The samples were degassed and photolyzed through Pyrex. GC showed the formation of a new peak with an area ratio of 4% relative to the starting materials. It is very likely that the unidentified product is a 1,3-shift isomer of one or the other of the starting materials, but insufficient material prevented its isolation or identification.

Deuterium-Labeling Studies. By substituting 1-deuterionaphthalene[12] for naphthalene in the preparation of Diels–Alder adduct **1**,[5] keto ester **4** was prepared with 0.25-d at positions 1, 4, 5, and 8 as indicated by ^1H NMR (($CDCl_3$, 400 MHz) δ 6.9–7.6 (m, 10.5 H), 5.55 (d, J = 6 Hz, 0.75 H), 5.03 (d, J = 6 Hz, 0.75 Hz), 3.40 (s, 3 H)). Crystals of **4**-d_1, mp 127–128 °C (54 mg, 0.17 mmol), were crushed between two pairs of microscope slides and photolyzed through Pyrex for 1 h on each side. The resulting mixture was flash chromatographed on silica gel by using hexanes–diethyl ether (9:1, v/v) as the eluting solvent. This gave three overlapping bands, the first of which contained mainly photoproduct **13**, the second consisting primarily of starting material **4**-d_1, and the third being 10 mg of a 57:43 mixture of photoproducts **6** and **8**. The mixture of **6** and **8** was rechromatographed as above and analyzed by ^1H NMR at 300 MHz ($CDCl_3$). Photoproduct **6** exhibited a clear diminution (0.8 H) in the integrated area of the signal due to H_1 at δ 3.40 but no diminution of the signal for H_2 at δ 3.00. The $CDCl_3$ was evaporated and the mixture redissolved in benzene-d_6 in order to better differentiate H_1 of photoproduct **8** from H_2. At 400 MHz, H_1 appeared at δ 2.86 integrating for 0.7 H, whereas H_2 appeared at δ 2.80 and showed no diminution of its integrated value.

Acknowledgment. We acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully ackowledged.

Registry No. **1a**, 19981-73-8; **1b**, 135107-72-1; **2**, 4365-08-6; **3**, 135107-65-2; **4**, 135107-66-3; **5**, 135107-67-4; **6**, 135107-68-5; **7**, 135144-14-8; **8**, 135144-15-9; **11**, 135107-69-6; **12**, 135107-70-9; **13**, 135107-71-0; **14**, 135144-16-0; oxalyl chloride, 79-37-8.