Photochemical Pathways to Benzosemibullvalene Derivatives from Dimethyl 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate

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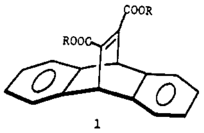
The direct and triplet-sensitized solution-phase photochemistry of dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (**2**) has been reinvestigated and shown to lead to three distinct and isomeric benzosemibullvalene derivatives. The reaction in the presence of triplet-energy sensitizers consists of initial formation of benzosemibullvalene **4** through a di-π-methane rearrangement involving vinyl–vinyl bridging. Once formed, **4** undergoes a reversible vinylcyclopropane to vinylcyclopropane interconversion to afford the isomeric benzosemibullvalene derivative **5**. On direct photolysis, the title compound **2** forms the benzocyclooctatetraene derivative **3**. Irradiation of this latter material leads, via electrocyclic ring closure to valence isomer **6** followed by di-π-methane photorearrangement, to a third benzosemibullvalene derivative **7**. The structure of **7** is such that its vinylcyclopropane to vinylcyclopropane transformation is degenerate.

Introduction

As a logical extension of our work on the di-π-methane photorearrangement of diesters of dibenzobarrelene-11,12-dicarboxylic acid (**1**) in solution and the solid state,[1-4] we decided to investigate the photochemistry of the corresponding monobenzobarrelene diesters. The title compound, dimethyl 1,4-dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (**2**), is readily available through Diels–Alder addition of dimethylacetylene dicarboxylate to naphthalene,[5] and a preliminary account of the solution-phase photobehavior of **2** was published nearly 20 years ago by Grovenstein, Campbell, and Shibata.[5] This report was incomplete in several respects, and therefore before embarking on an extensive study of related diesters, we felt it necessary to establish the photoreactivity of **2** on a firm basis. The present paper does just that and in addition reports some novel secondary reactions of the primary photoproducts.



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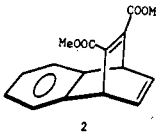

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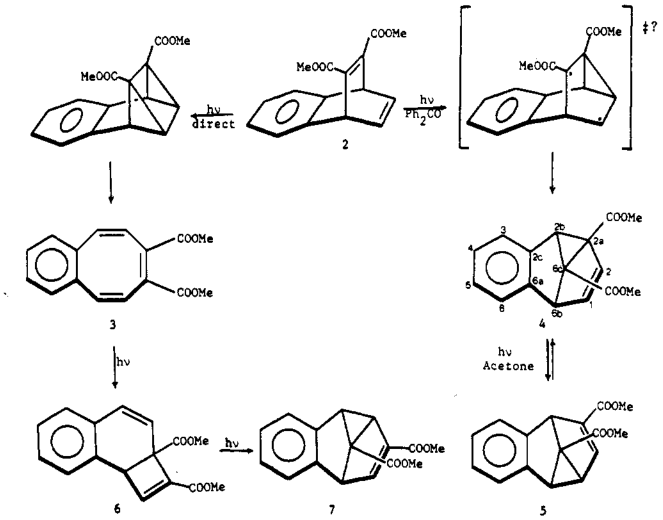
Results and Discussion

In agreement with the initial report,[5] as well as a more recent study by Bender and Brooks,[6] we find that direct irradiation of dimethyl 1,4-dihydro-1,4-ethenonaphthalene (**2**) in benzene or acetonitrile leads to essentially quantitative chemical yields of dimethyl benzocyclooctatetraene-7,8-dicarboxylate (**3**). The mechanism of the reaction (singlet-mediated [2 + 2] photocycloaddition between the two vinyl groups followed by electrocyclic ring opening) was established by deuterium labeling studies and thoroughly discussed by Bender and Brooks[6] (Scheme I).

Our interest lay primarily in the triplet-sensitized photochemistry of **2**. Grovenstein, Campbell, and Shibata[5] had briefly investigated this, and they reported that irradiation of compound **2** in acetone gave a mixture of three photoproducts (GC ratio 5:3:2), none of which was isolated or conclusively identified. We also detected three products in acetone and found that their ratio depends on the initial concentration of **2** and on the length of irradiation. These observations suggested a possible concentration-dependent competition between direct and acetone-sensitized excitation of **2** as well as the possibility of secondary photolysis of the primary photoproduct(s). Direct photolysis of **2** in acetone is certainly feasible in light of its reported[6] long-wavelength absorption band (λ_{max} = 335 nm in cyclohexane, $\epsilon = 40$). These suspicions were verified by the observation that benzophenone-sensitized photolysis of **2** under conditions where the sensitizer absorbs essentially 100% of the incident irradiation (12-fold molar excess of benzophenone, uranium glass filter, $\lambda > 340$ nm) afforded a single photoproduct, which was subsequently shown to have the benzosemibullvalene structure **4**.

Scheme I



The structure of **4** follows from its spectra, the most informative of which was the 300-MHz ^{1}H NMR spectrum. The methyl resonances from the nonequivalent ester substituents appear as singlets at 3.85 and 3.70 ppm. We tentatively assign the latter resonance to the ester at position C(6c) on the basis of our extensive experience with the NMR spectra of similar dibenzosemibullvalene diesters.[1-4] The vinyl hydrogens appear at δ 5.82 (dd, J = 5 and 3 Hz) and 5.36 (d, J = 5 Hz) and were assigned to the hydrogens attached to C(1) and C(2), respectively. The remaining hydrogen resonances appear at δ 4.49 (d, J = 3 Hz, C(6b) methine), 4.48 (s, C(2b) methine), and 7.1–7.5

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[1] Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648.

[2] Garcia-Garibay, M.; Scheffer, J. R.; Trotter, J.; Wireko, F. *Tetrahedron Lett.* **1987**, *28*, 4789.

[3] Garcia-Garibay, M.; Scheffer, J. R.; Trotter, J.; Wireko, F. *Tetrahedron Lett.* **1988**, *29*, 2041.

[4] Scheffer, J. R.; Trotter, J.; Garcia-Garibay, M.; Wireko, F. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *156*, 63.

[5] Grovenstein, E., Jr.; Campbell, T. C.; Shibata, T. *J. Org. Chem.* **1969**, *34*, 2418.

[6] Bender, C. O.; Brooks, D. W. *Can. J. Chem.* **1975**, *53*, 1684.

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(m, 4 H, aromatics). Mechanistically, photoproduct **4** is the result of a triplet state di-π-methane photorearrangement of **1** in which the initial bonding mode is necessarily vinyl–vinyl in nature.[7] Other vinyl-substituted benzobarrelenes have been observed to photorearrange in a similar fashion.[8]

Working on the assumption that the other two products observed in acetone[5] come from secondary photochemical processes, we irradiated benzosemibullvalene **4** in this solvent (Pyrex filter). This led to a single new photoproduct subsequently shown to have the isomeric benzosemibullvalene structure **5**. Benzophenone was ineffective as a photosensitizer, thus accounting for the absence of **5** in the benzophenone-sensitized irradiation of **2**. Direct irradiation of **4** in acetonitrile slowly led to **5** with the formation of numerous (unidentified) byproducts. The key to the structure assignment for **5** was once again the 300-MHz ^{1}H NMR spectrum, which showed nonequivalent methyl ester resonances at 3.72 and 3.71 ppm, a vinyl hydrogen signal at δ 6.15 (d, J = 2.5 Hz), a singlet due to the hydrogen at C(6b) at δ 4.69, and cyclopropyl hydrogen resonances at δ 3.89 (d, J = 7.5 Hz, C(2b) methine) and 3.43 (dd, J = 7.5 and 2.5 Hz, C(2a) methine); the aromatic hydrogens appeared as a multiplet from 7.1 to 7.4 ppm.

By following the conversion of **4** to **5** by gas chromatography, it was noted that the reaction was initially rapid but slowed with continued irradiation and finally stopped at a **4**:**5** ratio of approximately 4:1. This suggested that **4** and **5** were involved in a photostationary state equilibrium through the common intermediacy of the triplet biradical formed by homolysis of the C(2a)–C(6c) bond. This was verified by photolyzing pure **5** under identical conditions and observing the same **4**:**5** = 4:1 mixture. A similar photostationary state mixture could also be obtained by irradiating either **4** or **5** in benzene with a Corex filter. Direct analogy for the conversion of **4** into **5** is found in the work of Bender and Wilson.[8a] These workers showed that direct irradiation of 4,5-dimethoxy-**4** afforded an approximately 1:1 mixture of starting material and 4,5-dimethoxy-**5**; no mention was made of the reverse transformation.[9]

Having now identified two of the three products formed by irradiation of benzobarrelene **2** in acetone, we turned our attention to the third and discovered that it is formed through an acetone-sensitized transformation of the cyclooctatetraene derivative **3**. Compound **3** is presumably formed in acetone as a result of the direct absorption of light by **2** and then rapidly photolyzed further. Thus independent irradiation of **3** in acetone through a Pyrex filter leads to high yields of a single product whose spectra are in accord with a benzosemibullvalene derivative of structure **7**. The 300-MHz NMR was most informative: δ 7.1–7.4 (m, 4 H, aromatics), 6.58 (d, 1 H, J = 3 Hz, vinyl), 4.51 (d, 1 H, J = 3 Hz, C(6b) methine), 3.84 (d, 1 H, J = 6 Hz, C(2a) methine), 3.74 (d, 1 H, J = 6 Hz, C(2b) methine), 3.70 (s, 3 H, OMe), 3.65 (s, 3 H, OMe). The structure assigned to photoproduct **7** predicts (unlike the case of photoproducts **4** and **5**) a degenerate, triplet-sensitized 1,3-shift. Consistent with this, acetone-sensitized irradiation of **7** led to no observable reaction.

The conversion of the benzocyclooctatetraene derivative **3** into the benzosemibullvalene derivative **7** has precedent in the elegant work of Bender et al.,[10] who showed that such transformations proceed via electrocyclic ring closure to benzobicyclo[4.2.0]octatrienes such as **6** followed by di-π-methane photorearrangement of the latter. Unequivocal proof for the involvement of benzobicyclo[4.2.0]octatrienes was obtained by their isolation and independent photolysis, and the di-π-methane mechanism of their conversion to benzosemibullvalenes was established by deuterium labeling. In our case, compound **6** proved to be undetectable by GC owing to its facile thermal reversion to **3**; it also proved to have the same R_f as **3** on thin-layer chromatography. It was, however, readily detectable by NMR. Direct irradiation of **3** in $CDCl_3$ at wavelengths where **6** was not expected to absorb (≥340 nm, uranium glass filter) gave an approximately 1:1 ratio of **3** and **6** as inferred from the 400-MHz NMR spectrum of the mixture. Signals attributable to **6** were methyl ester singlets at δ 3.75 and 3.78, a one proton singlet at δ 4.24 assigned to the benzylic methine, a pair of mutually coupled 10-Hz doublets at δ 6.21 and 6.47 due to the cyclohexene vinyl hydrogens, a one proton singlet at δ 6.72 assigned to the cyclobutene vinyl hydrogen, and four aromatic hydrogen resonances at 7.0–7.3 ppm. This spectrum compares very favorably with the spectra reported by Bender et al.[10] for close analogues of **6**. Compound **6** (along with **7**) could also be detected by NMR in the acetone-sensitized photolysis of **3**; the presence of both compounds in the same mixture is strong evidence that **6** is truly involved in the formation of **7**.

We are currently investigating the crystalline-phase photochemistry of **2** and related diesters. The results of these experiments will be reported in due course.

Experimental Section

General Procedures. Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected. IR spectra were measured on a Perkin-Elmer 1710 FTIR instrument by using KBr disks or liquid films on NaCl plates and are reported as ν_{max} in cm^{-1}. Proton NMR spectra were recorded on a Varian XL-300 and Bruker WH-400 instruments by using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard. Mass spectra were recorded with a Kratos MS-50 instrument operating at 70 eV, and gas chromatography was carried out on a Hewlett-Packard 5890 instrument with a 15-m DB-1 capillary column and a flame ionization detector; the carrier gas was helium. Spectral grade solvents were used directly as obtained. Photolyses were carried out with a 450-W Hanovia medium-pressure mercury lamp, and the desired wavelength was achieved by using either Corex (λ > 260 nm), Pyrex (λ > 290 nm) or uranium glass (λ > 340 nm) filter sleeves. Analytical photolyses were conducted in Pyrex or quartz tubes sealed with ground-glass caps. Samples were degassed by repeating the freeze–pump–thaw cycle twice and sealing under nitrogen. Preparative photolyses were conducted with the immersion well setup. Solutions were degassed by a 1-h nitrogen purge prior to photolysis.

Photolysis of Dimethyl 1,4-Dihydro-1,4-ethenonaphthalene-2,3-dicarboxylate (2) in Acetone. A solution of

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[7] The terms vinyl–vinyl and vinyl–benzo refer to the location of the initial bond formation in the Zimmerman mechanism for the di-π-methane photorearrangement. We note that a question still remains as to the transition state versus intermediate nature of 1,4-biradical intermediates such as that shown (‡?) leading to photoproduct **4**. See, for example: Zimmerman, H. E.; Kamath, A. P. *J. Am. Chem. Soc.* **1988**, *110*, 900. Adam, W.; Dorr, M.; Kron, J.; Rosenthal, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 7074. Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4597. For a review of the di-π-methane reaction, see: Zimmerman, H. E. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 3, Essay 16.

[8] (a) Bender, C. O.; Wilson, J. *Helv. Chim. Acta* **1976**, *59*, 1469. (b) Bender, C. O.; Brooks, D. W.; Cheng, W.; Dolman, D.; O'Shea, S. F.; Shugarman, S. S. *Can. J. Chem.* **1978**, *56*, 3027.

[9] In a footnote to unpublished work, Bender et al. (Bender, C. O.; Bengston, D. L.; Dolman, D.; Herle, C. E. L.; O'Shea, S. F. *Can. J. Chem.* **1982**, *60*, 1942) reported the phototransformation of compound **4** into **5**. Here again no mention was made of the reverse reaction and no experimental details were given.

[10] (a) Bender, C. O.; Cassis, I. M.; Dolman, D.; Heerze, L. D.; Schultz, F. L. *Can. J. Chem.* **1984**, *62*, 2769. (b) Bender, C. O.; Bengston, D. L.; Dolman, D.; O'Shea, S. F. *Can. J. Chem.* **1986**, *64*, 237. (c) Bender, C. O.; Dolman, D.; Murphy, G. K. *Can. J. Chem.* **1988**, *66*, 1656.

compound 2[5] (1.50 g, 5.6 mmol) in 425 mL of acetone was photolyzed through Pyrex until GC indicated that no starting material remained (18 h). GC showed the formation of three new photoproducts (ratio 65:25:9), which were subsequently identified as the isomeric benzosemibullvalenes **4**, **5**, and **7**, respectively. While compounds **5** and **7** were invariably eluted from the column together, the major product **4** could be isolated in pure form by flash column chromatography on 250 g of silica gel 60 (230–400 mesh) with petroleum ether (30–60 °C)–diethyl ether, 93:7 (v/v), as the eluting solvent. This afforded 0.96 g (64%) of a colorless oil, which was assigned the structure dimethyl 2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2a,6c-dicarboxylate (**4**) on the basis of the following spectral data: ^{1}H NMR (see text); IR (liquid film) 1730 (C=O) cm^{-1}; MS *m*/*e* (relative intensity) 270 (M$^+$, 37), 238 (14), 210 (94), 183 (90), 152 (100); HRMS calcd for $C_{16}H_{14}O_4$ (M$^+$) 270.0892, found 270.0892; UV (CH_3CN) 278 nm, ϵ 1100.

Benzophenone-Sensitized Photolysis of Compound 2. A solution consisting of 50 mg (0.18 mmol) of **2** and 0.40 g (2.2 mmol) of benzophenone in 10 mL of acetone was photolyzed through a uranium glass filter sleeve for 3 h, at which time GC indicated no remaining starting material and the formation of a single volatile photoproduct corresponding in retention time to **4**. The photoproduct was isolated in 78% yield by flash chromatography on silica gel; its spectra proved to be identical in every respect with those described above.

Photochemical Interconversion of Compounds 4 and 5. These photolyses could be conducted in either benzene (Corex filter) or acetone (Pyrex filter). The former method gives slightly better yields of **5** and was therefore used in a preparative run. A solution of 0.64 g (2.4 mmol) of compound **4** in 200 mL of benzene was irradiated for 13 h, at which time GC indicated the **4**:**5** ratio to be invariant at ca. 66:34. After removal of solvent the mixture was subjected to flash chromatography on silica gel with low-boiling petroleum ether–ethyl acetate 95:5 (v/v) as the eluting solvent. Compound **5** (59 mg, 9%) was eluted as a colorless oil followed closely by the starting material **4**. Compound **5** was identified as dimethyl 2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-1,6c(2a*H*)-dicarboxylate on the basis of the following spectral data: ^{1}H NMR (see text); IR (liquid film) 1719 (C=O) cm^{-1}; MS *m*/*e* (relative intensity) 270 (M$^+$, 55), 210 (62), 183 (47), 152 (100), 84 (42); HRMS calcd for $C_{16}H_{14}O_4$ (M$^+$) 270.0892, found 270.0885. The NMR spectrum of this material was identical with the spectrum of a sample of **5** (mixed with **7**) isolated from photolysis of **2** in acetone.

The photostationary state nature of the reaction was established by a series of analytical-scale photolyses of mixtures of **4** and **5** of widely varying composition in both benzene (Corex) and acetone (Pyrex). The **4**:**5** GC ratios were (7 ± 1):(3 ± 1) in the former solvent and (8 ± 1):(2 [illegible] 1) in the latter.

Acetone-Sensitized Photolysis of Compound 3. A solution of 100 mg (0.37 mmol) of benzocyclooctatetraene derivative **3** in 200 mL of acetone was irradiated through a Pyrex filter, and the course of the reaction was followed by GC. After 2 h, GC showed the complete disappearance of starting material and the formation of a single new photoproduct. The solution was evaporated to dryness, and the residue was subjected to flash chromatography with low-boiling petroleum ether–diethyl ether, 3:1 (v/v), as the eluting solvent. This afforded 71 mg (71%) of a colorless oil that was identified as dimethyl 2b,6b-dihydrobenzo[*a*]cyclopropa[*cd*]pentalene-2,6c(2a*H*)-dicarboxylate (**7**) on the basis of the following spectral data: ^{1}H NMR (see text); IR (liquid film) 1718 (C=O) cm^{-1}; MS *m*/*e* (relative intensity) 270 (M$^+$, 34), 238 (19), 210 (92), 183 (58), 152 (78), 43 (100); HRMS calcd for $C_{16}H_{14}O_4$ 270.0892, found 270.0889. The NMR spectrum of this material was identical with the spectrum of a sample of **7** (mixed with **5**) isolated from photolysis of **2** in acetone.

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Syntheses and Electrochemical Properties of Tetracyano-*p*-quinodimethane Derivatives Containing Fused Aromatic Rings

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Several fused aromatic tetracyano-*p*-quinodimethane (TCNQ) derivatives (**11a–c**, **5**, and **12**) have been synthesized by the reaction of the corresponding quinones and malononitrile. Syntheses of these derivatives by Diels–Alder reactions of *o*-quinodimethane and TCNQ have been attempted. In comparison with TCNQ, cyclic voltammetric data of these new compounds reveal a more negative value for the first and the second reduction potential.

Introduction

Many substituted TCNQ (tetracyano-*p*-quinodimethane) derivatives have been synthesized in order to obtain charge-transfer (CT) complexes.[1] In general, it has been found that substitution on the basic TCNQ skeleton results in CT complexes that are less conducting than those of TCNQ itself.[2] This behavior could be explained with the lower acceptor properties in some cases or to the complete charge transfer of stronger electron acceptors in other cases. Thus, TCNQ and tetrafluorotetracyano-*p*-quinodimethane ($TCNQF_4$) react with hexamethylenetetraselenafulvalene (HMTSF) to form the corresponding organic salts. However, the complex HMTSF–TCNQ is one of the most highly conducting organic salts ever known. The reason for this behavior is due to the stronger electron-acceptor character in $TCNQF_4$ leading to a complete charge transfer in this complex. The result is a fully ionic Mott–Hubbard insulator.[2]

TCNQ analogues fused with aromatic rings have received less attention.[3] From theoretical studies it was

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(1) Wheland, R. C.; Gillson, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 3916.
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(3) Gerson, F.; Heckendorn, R.; Cowan, D. O.; Kini, A. M.; Maxfield, M. *J. Am. Chem. Soc.* **1983**, *105*, 7017.

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