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NOVEL PHOTOCHEMISTRY OF A STERICALLY CROWDED MONOBENZOBARRELENE DERIVATIVE

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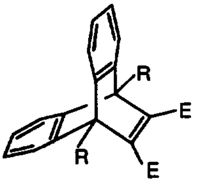
Abstract. The solution phase photochemistry of the sterically congested tetramethylated benzobarrelene derivative **2b** differs completely from that of its non-methylated counterpart, **2a**. Based on molecular mechanics calculations, the factor that is suggested to be responsible for this difference is relief of the unfavorable methyl-methyl interactions present in **2b**.

Previous work from our laboratory has established that, owing to radical stability and steric effects, bridgehead-methylated dibenzobarrelene derivatives (e.g. **1b**) undergo highly unusual photorearrangements compared to their non-methylated counterparts (e.g. **1a**).[1-3] In order to determine whether such reactivity differences apply to related systems, we undertook an investigation of the corresponding monobenzobarrelene derivatives. In this communication we report the photochemistry of the tetramethylated compound **2b** and compare it with that of its non-methylated counterpart **2a**. The results confirm that increased methyl substitution brings about a profound change in the photochemical reactivity of the monobenzobarrelene system as well.



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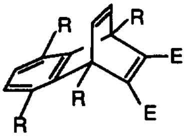

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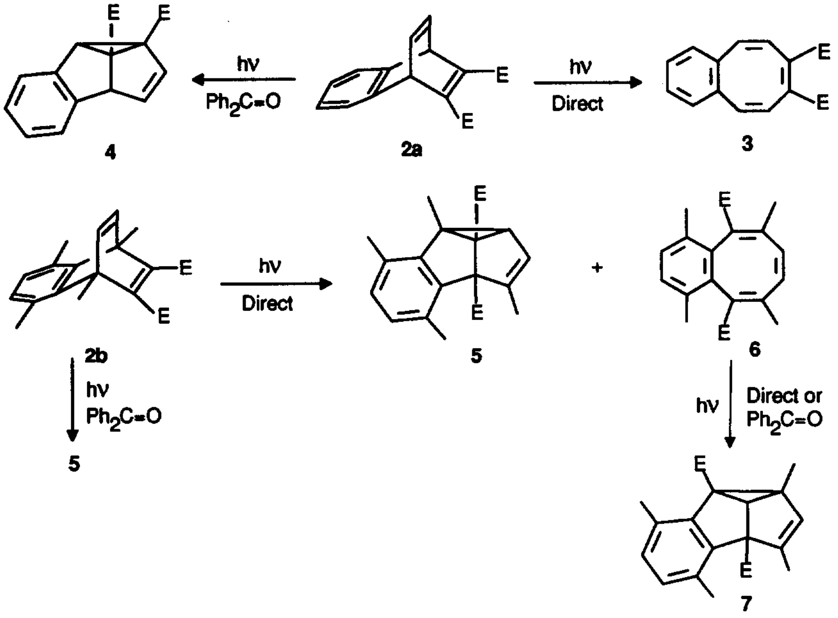
(a) R = H, E = COOMe
(b) R = Me, E = COOMe

The preparation of diester **2a** and its unsensitized solution phase irradiation to give benzocyclooctatetraene derivative **3** was originally reported by Grovenstein, Campbell and Shibata in 1969;[4a] a subsequent paper by Bender and Brooks[4b] corroborated these results and established the mechanism of the reaction through deuterium labeling. Later work from our laboratory[5] established that benzophenone-sensitized irradiation of **2a** affords the di-π-methane rearrangement product **4** exclusively.[6]

With these results in hand, we prepared dimethyl 1,4-dihydro-1,4,5,8-tetramethyl-1,4-ethenonaphthalene-2,3-dicarboxylate (**2b**) via Diels-Alder addition of dimethyl acetylenedicarboxylate to 1,4,5,8-tetramethylnaphthalene.[7] The structure of this adduct was confirmed by an X-ray crystal structure determination.[8] Unsensitized photolysis of compound **2b** in benzene or acetonitrile gave complete conversion to an approximately 1:1 mixture of two products (Φ_{total} = 0.24) whose structures were established by X-ray crystallography as the benzosemibullvalene derivative **5** and the benzocyclooctatetraene derivative **6**.[8] Note that the location of the ester substituents in each of these photoproducts is very different from that in photoproducts **3** and **4**. Benzophenone-sensitized irradiation of compound **2b** led to diester **5** as the sole isolable photoproduct.[9] Control experiments established that benzosemibullvalene **5** is not formed through direct or sensitized photolysis of benzocyclooctatetraene **6**. A new photoproduct is formed under these conditions whose spectra are consistent with the benzosemibullvalene derivative **7**. The occurrence and mechanism of transformations similar to that of **6** → **7** have been established thoroughly by Bender and co-workers[10] and will not be discussed further in this communication.

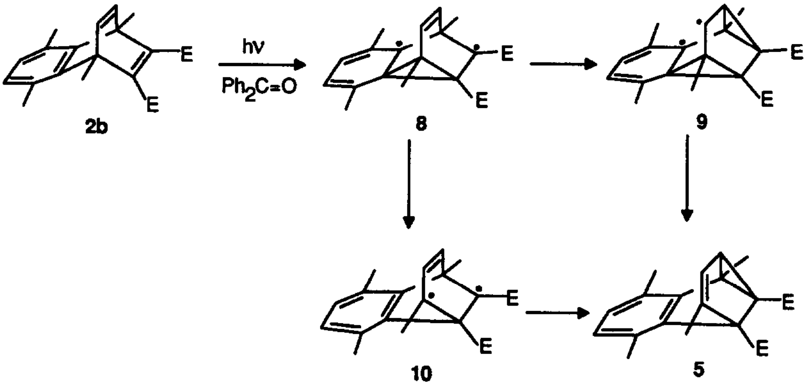


We suggest that relief of methyl-methyl steric crowding in benzobarrelene **2b** is the factor that causes it to react differently from compound **2a**. The crystallographically-derived methyl carbon to methyl carbon distances in compound **2b** are 2.96 and 3.01 Å, much shorter than the commonly accepted value of 4.0 Å for the sum of the van der Waals radii of two methyl groups.[11] Bender and Brooks have shown through deuterium labeling studies that the mechanism by which photoproduct **3** is formed from **2a** involves initial intramolecular [2+2] photocycloaddition between the two vinyl groups followed by electrocyclic ring opening.[4b] Molecular modeling calculations indicate that, were benzobarrelene derivative **2b** to follow the same pathway, the clashing methyl groups would be driven even more closely together, ultimately reaching an interatomic separation of 2.86 Å in the intermediate [2+2] cycloadduct.[12] While conclusions based on such calculations must be drawn with care, our faith in them in this instance is bolstered by the fact that they reproduce the crystallographic methyl-methyl distances for **2b** quite well (2.96 and 2.97 Å).

The formation of the experimentally observed singlet state photoproduct **6** can be rationalized as occurring through intramolecular [2+2] photocycloaddition in **2b** between the ester-substituted double bond and the double bond of the benzene ring followed by electrocyclic reorganization. This mechanism relieves the steric crowding between the methyl groups as indicated by the results of molecular modeling, which predict methyl-methyl contacts of 3.10 and 3.14 Å in the intermediate cycloadduct. In this case, therefore, the sterically favored pathway is followed despite the fact that it involves disruption of aromaticity.

The formation of photoproduct **5** from benzobarrelene derivative **2b** can be analyzed in a similar manner. Sterically assisted benzo-vinyl bridging followed by involvement of the second vinyl group in cyclopropane ring formation affords intermediate **9**, and this species can undergo 1,4-biradical cleavage to regenerate aromaticity and form **5**. As Zimmerman, Binkley, Givens and Sherwin[13] showed in the case of barrelene itself, however, such bis-cyclopropylcarbinyl biradical intermediates are unlikely on energetic grounds, and it is therefore more probable that photoproduct **5** is formed through the intermediacy of biradical **10**. The **8** → **10** conversion is favored by relief of ring strain, regeneration of aromaticity and the formation of a tertiary allylic radical. Closure of biradical **10** to give **5** is presumably favored over the alternative mode of closure on steric grounds.

We are continuing to explore the fascinating and dramatic effects that substituents exert on the photochemical reactions of mono- and dibenzobarrelene derivatives.



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References and Footnotes

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3. C.V. Asokan, S.A. Kumar, S. Das, N.P. Rath and M.V. George, J. Org. Chem., **56**, 5890 (1991).
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5. J.R. Scheffer and M. Yap, J. Org. Chem., **54**, 2561 (1989).
6. For a recent review of the di-π-methane or Zimmerman photorearrangement, see H.E. Zimmerman in "Organic Photochemistry," A. Padwa, Ed., Marcel Dekker, New York, 1991, Vol. 11, p. 1.
7. 1,4,5,8-Tetramethylnaphthalene was prepared by the method of W.L. Mosby, J. Am. Chem. Soc., **74**, 2564 (1952).
8. Compound **2b**: $P2_1/c$; $a = 12.643(1)$, $b = 9.288(1)$, $c = 15.153(1)$ Å; $\beta = 105.70(1)°$; $Z = 4$; $R = 0.037$. Compound **5**: $Pca2_1$; $a = 7.325(1)$, $b = 14.781(1)$, $c = 15.535(1)$ Å; $Z = 4$, $R = 0.045$. Compound **6**: Pbca; $a = 17.716(2)$, $b = 15.298(2)$, $c = 13.210(3)$ Å; $Z = 8$; $R = 0.046$. Full crystallographic details will be published separately.
9. Substantial amounts of a second photoproduct were detectable by thin layer chromatography, but this material could not be isolated owing to its extreme thermal lability.
10. (a) C.O. Bender, D. Dolman and G.K. Murphy, Can J. Chem., **66**, 1656 (1988); (b) C.O. Bender, D. Dolman and N. Tu, J. Org. Chem., **56**, 5015 (1991).
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12. The methyl-methyl distances were calculated using the MMX minimization program present in PC Model, Serena Software, Bloomington, Indiana, 1988.
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