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Experimental and Theoretical Exploration of the Detailed Mechanism of the Rearrangement of Barrelenes to Semibullvalenes: Diradical Intermediates and Transition States[1]

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Abstract: The question of which stage of the triplet di-π-methane rearrangement controls the regiochemistry and excited-state rate was resolved in the present investigation. In this study, using *m*-cyanodibenzobarrelene, the *m*-cyano substituent was located in a strategic location such that bridging between the vinyl and substituted benzo moiety would lead to stabilized diradical I but nonstabilized diradical II. Conversely, the substitution was such that with bridging between the vinyl and unsubstituted benzo ring, diradical II would be stabilized but diradical I would not. The study of the di-π-methane rearrangement of this system thus weighed the relative importance of stabilization of diradical I versus stabilization of diradical II along the excited triplet hypersurface. Although in *m*-cyanodibenzobarrelene the two alternative pathways lead to the same *m*-cyanodibenzosemibullvalene, *m*-cyanodibenzobarrelene labeled with deuterium on the vinyl bridge affords different products via the two pathways. Experimentally, it was found that the di-π-methane rearrangement of dideuterio-*m*-cyanodibenzobarrelene was completely regioselective. The reaction proceeded selectively to afford the regioisomer resulting from formation of the more delocalized diradical I. Stabilization of diradical II proved not to be competitive. In the same study, a theoretical approach was applied to the rearrangement of barrelene itself. Ab initio computations were carried out with geometry optimization of each point on the triplet surface. Additionally, energies were obtained for points on the ground-state surface with triplet geometries. Also, for strategic points, geometry-optimized ground-state energies were obtained. These computations provided insight into the observed photochemistry. The most striking feature of the theoretical results was the appearance of a real energy minimum for diradical I with the appearance of a triplet reaction transition state corresponding to formation of diradical I from triplet barrelene.

Introduction

The di-π-methane rearrangement and its mechanism have been known for nearly three decades.[2] During this period, aspects of the reaction have been elaborated including stereochemistry,[3] regioselectivity,[4] the role of reaction multiplicity,[5] control of excited-state rates by structure,[6] and reaction reversibility[7] as well as an assortment of more subtle aspects.

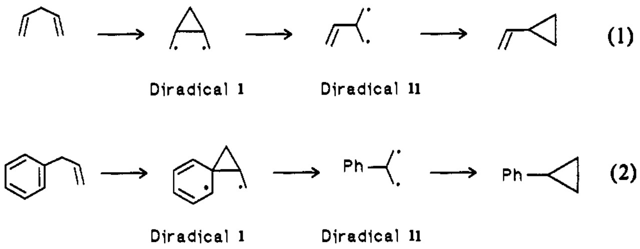

Figure 1. Basic di-π-methane rearrangement mechanism.

In a variety of our publications, we have noted that the general mechanism we provided permits the writing of four structures: (a) the di-π-methane reactant and its excited state, (b) a cyclopropyldicarbinyl 1,4-diradical formed by π–π bridging and termed "diradical I", (c) a 1,3-diradical resulting from cyclopropyldicarbinyl ring opening and termed "diradical II", and then (d) the final π-substituted cyclopropane photoproduct.

The basic reaction mechanism as outlined in eqs 1 and 2 of Figure 1 seems to have withstood the test of experiment and time. Yet there are features of the reaction which have received discussion as well as question. One question is whether there is an alternative mechanism not involving diradical I and whether the product-determining stage of the excited-state reaction is formation of this diradical or, instead, formation of diradical II. These and related matters constitute the subject of the present publication. Here we concentrate on our barrelene- to semibullvalene-type of di-π-methane system.

One approach to judging the portion of the hypersurface which controls the reaction rate utilizes the reaction regioselectivity. In this study, we made use of a dibenzobarrelene substituted with a single cyano group.

Results

Synthesis of Photochemical Reactants. The synthesis of the requisite cyanodibenzobarrelene 1 is outlined in Scheme I. This

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(1) (a) This is publication 165 of our photochemical series and 227 of our general sequence.

(2) (a) For the original publications recognizing the di-π-methane rearrangement, see refs 2b and 2c. (b) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183–184. (c) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933.

(3) (a) Zimmerman, H. E.; Robbins, J. D.; McKelvey, R. D.; Samuel, C. J.; Sousa, L. R. *J. Am. Chem. Soc.* **1974**, *96*, 4630–4643. (b) Zimmerman, H. E.; Keck, G. E.; Gannett, T. P. *J. Org. Chem.* **1979**, *44*, 1982–1989. (c) Zimmerman, H. E.; Baeckstrom, P.; Johnson, T.; Kurtz, D. W. *J. Am. Chem. Soc.* **1974**, *96*, 1459–1465. (d) Zimmerman, H. E.; Pratt, A. C. *J. Am. Chem. Soc.* **1970**, *92*, 6267–6271.

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(5) Zimmerman, H. E.; Givens, R. S.; Pagni, R. M. *J. Am. Chem. Soc.* **1968**, *90*, 4191–4193.

(6) (a) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1974**, *96*, 439–449. (b) Zimmerman, H. E.; Gruenbaum, W. T.; Klun, R. T.; Steinmetz, M. G.; Welter, T. R. *J. Chem. Soc., Chem. Commun.* **1978**, 228–230. (c) Zimmerman, H. E.; Steinmetz, M. G.; Kreil, C. L. *J. Am. Chem. Soc.* **1978**, *100*, 4146–4162.

(7) (a) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383. (b) Zimmerman, H. E.; Factor, R. E. *Tetrahedron* **1981**, *37*, Supplement 1, 125–141. (c) Zimmerman, H. E.; Oaks, F. L.; Campos, P. *J. Am. Chem. Soc.* **1989**, *111*, 1007–1018.

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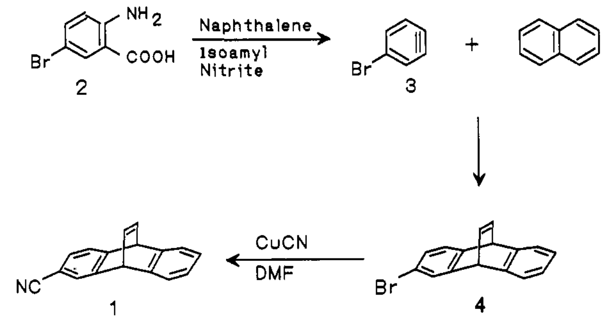
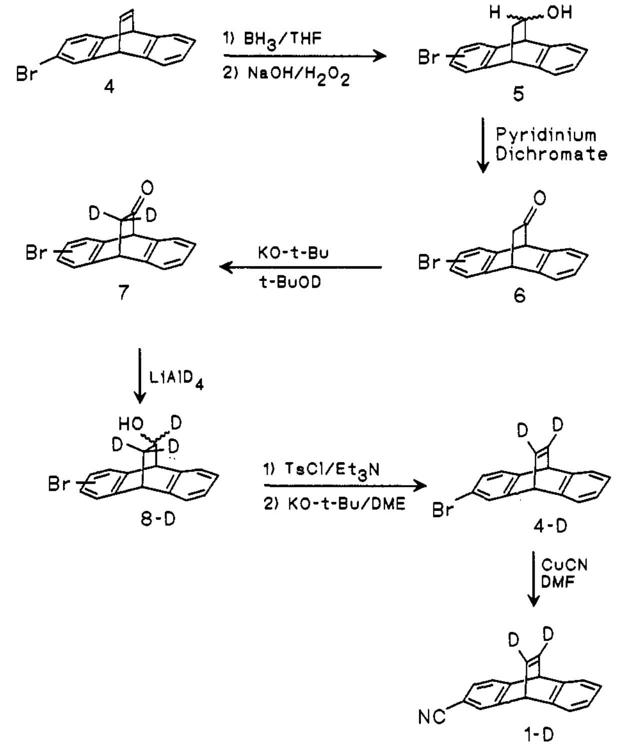
Scheme I. Synthesis of Cyanodibenzobarrelene 1



Scheme II. Deuteration of *m*-Bromodibenzobarrelene and Conversion to *m*-Cyanodibenzobarrelene



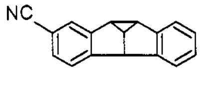
began with the reaction of 4-bromobenzyne (**3**) with naphthalene to afford *m*-bromodibenzobarrelene (**4**). The first step was accomplished by generating the bromobenzyne by diazotization of the known[8] 5-bromoanthranilic acid (**2**) in molten naphthalene at 95 °C. Although the yields were relatively low (35–60%), the simplicity of the procedure made this approach practical. Reaction of the *m*-bromodibenzobarrelene (**4**) with cuprous cyanide in DMF afforded the desired *m*-cyanodibenzobarrelene (**1**).

Our plans for study of the di-π-methane reaction mechanism required this molecule with the vinyl bridge deuterated. Scheme II outlines our approach which involved deuterium introduction at one carbon by base-catalyzed enolate exchange of ketone **6** and at the second carbon by lithium aluminum deuteride reduction. All attempts to introduce deuterium by use of the deuterium counterpart of Streitwieser's base,[9] a method so useful in our earlier efforts,[10] led to not unexpected complications when either *m*-bromodibenzobarrelene (**4**) or *m*-cyanodibenzobarrelene (**1**) was reacted with the base.

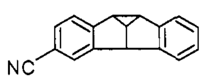
Exploratory Photochemistry of *m*-Cyanodibenzobarrelene (1). Irradiation of *m*-cyanodibenzobarrelene with acetophenone as a sensitizer in benzene afforded a photoproduct, mp 155–156 °C. Comparison of the NMR spectrum of this photoproduct with the NMR spectrum of unpurified material indicated that no additional isomers formed. Similarly, in photolyses of dideuterio-*m*-cyanodibenzobarrelene (**1-D**) where the dideuterio photoproduct NMR spectrum was simpler, no peaks assignable to a regioisomeric photoproduct could be detected. The photoproduct had an NMR spectrum characteristic of all of the aromatic-substituted semibullvalenes we have studied.[5,10]

Analysis of the NMR spectrum of the photoproduct of **1** showed, in addition to seven aromatic hydrogens, a low-field doublet (δ 4.50) assignable to the doubly benzylic methine of semibullvalenes. Additionally, at somewhat higher field (δ 3.77), there was a methine which appeared as a quartet, and thus was approximately equally coupled to the three benzylic methines. At still higher field, a pair of triplets (δ 3.19, 3.11), each with the same coupling constant as that of the quartet methine, could be ascribed to the two benzylic methines.

This evidence led us, without the use of mechanistic reasoning, to two regioisomeric semibullvalenes **9** and **10** as possibilities. However, further NMR evidence permits the structural assignment of **10** as the photoproduct. This regiochemical assignment utilized the spectra of both deuterated and undeuterated photoproduct. This analysis is discussed as follows.

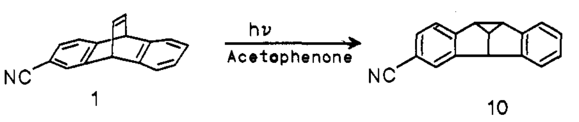


9



10

First, the NMR spectrum with Eu(FOD)$_3$ showed the presence of a low-field AB quartet assignable to a pair of vicinal aromatic hydrogens, one ortho to cyano and the other meta to cyano. Additionally, there was a low-field aromatic singlet assignable to a second hydrogen ortho to cyano. In an NOE investigation (note Experimental Section), it was found that irradiation of the benzylic methine at higher field led to greater enhancement of the aromatic hydrogen meta to cyano compared to that of the aromatic singlet ortho to the cyano group. This permitted us to assign structure **10** to the photoproduct rather than **9**, since for **10** the AB quartet would be most enhanced as observed, while for **9** the ortho singlet would be most increased. Thus, the photolysis of cyanodibenzobarrelene **1** may be depicted as in eq 3.



(3)

The next question concerns the assignment of the two singly benzlyic NMR peaks. Naively, one might assume that the methine nearest the cyanobenzene group would be at lower field; however, this was not the case. There are two pieces of evidence to support the contention that the upfield triplet at δ 3.11 derives from the methine benzylic to the cyanobenzo ring. We note that the Eu(FOD)$_3$ experiments showed that it was the higher field triplet at δ 3.11 which was shifted downfield more than the lower field, δ 3.19 triplet. This alone is subject to ambiguity (vide infra). However, in agreement with this, the praseodymium shift reagent Pr(FOD)$_3$ shifted the upfield triplet (δ 3.11) more rapidly upfield than the low-field, δ 3.19 triplet. The shift experiments are depicted in Figure 2.

The NMR situation results from two independent effects. First, one can anticipate that the three-ring banana bonds are conjugated

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[8] (a) Misra, R. S.; Dwivedi, C.; Parmar, S. S. *J. Heterocycl. Chem.* **1980**, *17*, 1337–1338. (b) Wheeler, A. S.; Oats, W. M. *J. Am. Chem. Soc.* **1910**, *32*, 770.

[9] Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1963**, *85*, 1757–1761.

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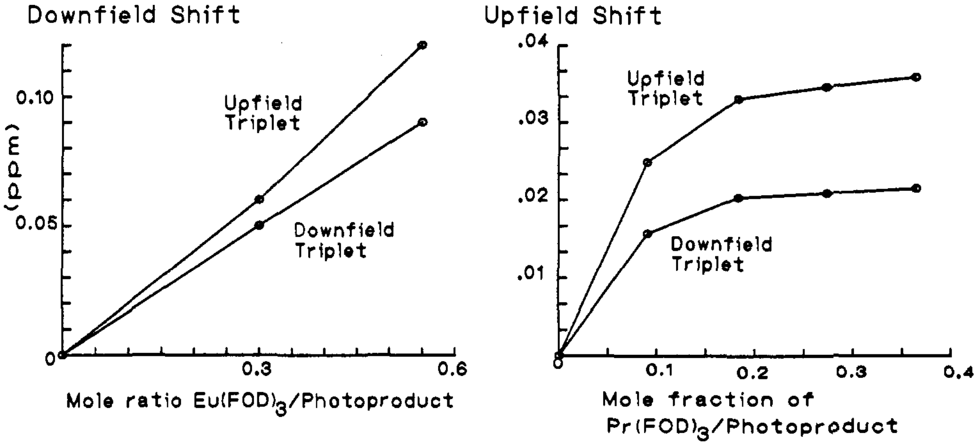
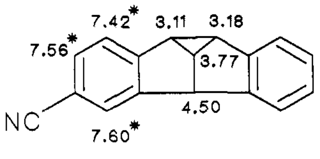


Figure 2. NMR shift reagent results.



* Sites Measured
With 0.30 *M* Ratio Europium

Figure 3. NMR assignments to cyanodibenzosemibullvalene.

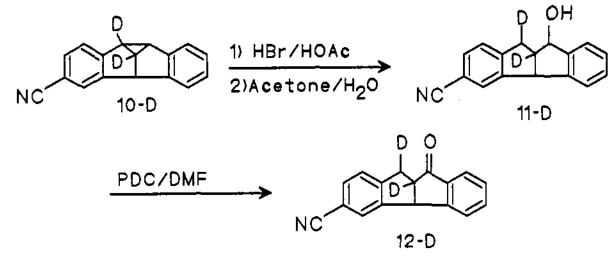
with the benzo rings, and therefore, the effect of the cyano group is to shift the β-methine hydrogen to a greater extent downfield. This is analogous to the hydrogens on the β-carbon of an enone which are shifted downfield to a greater extent than the α-hydrogen. Any coordination of the shift reagents with the cyano lone pair will tend to enhance this effect. A second effect is the magnetic field of the shift reagents which will tend to shift the more proximate, α-benzylic methine to a greater extent than the more remote β-methine. Thus, in the case of the europium shift reagent, the conjugative and magnetic effects will operate differently on the two different benzylic methines. Since coordination of europium with the cyano group should enhance the conjugative effect by increased polarization of the CN π bond, the downfield shift by europium might conceivably be rationalized as a β-methine being shifted more due to an increase in the conjugative effect. Alternatively, the magnetic field effect might dominate with the more proximate α-methine being shifted downfield more. Thus, taken alone, the europium shift results are ambiguous.

However, the two effects operate in concert in the case of the praseodymium reagent, since both methines are observed to be shifted upfield and the high-field methine is shifted to a greater extent. This establishes the high-field benzylic methine as the α one and the low-field methine as the β one. Hence, in the absence of shift reagents, the conjugative effect was, indeed, operative in analogy to the enone example. In the europium shift runs, we now can recognize that the magnetic field effect was overriding any conjugative effects, since it was the α-hydrogen which was shifted most.

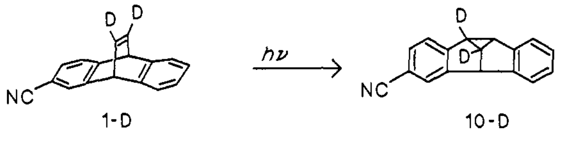
Further evidence was obtained from the nuclear Overhauser effect. With $Eu(FOD)_3$ present to spread the aromatic peaks, irradiation of the upfield (δ 3.11) methine and the low-field (δ 3.18) methine revealed that the aromatic AB quartet hydrogen β to cyano was enhanced (ca. 15%) by the high-field irradiation relative to the low-field one. The NMR assignments from the shift reagent and NOE results are given in Figure 3.

We now turn to consideration of the regioselectivity of the di-π-methane rearrangement of **1**. As will be seen in the Discussion section, there are four a priori modes of aryl–vinyl bridging, that is, each end of the vinyl group has an opportunity to bridge to either the cyano-substituted ring or the unsubstituted ring. The experimentally observed course of the reaction, as shown in eq 3, limits the actual mechanism to two of these possibilities, each involving bridging of the distal vinyl carbon (i.e., the one most remote from cyano) to the benzo ring (vide infra). However, to determine which ring is involved in the bridging process, photolysis of deuterium-labeled cyanodibenzobarrelene **1-D** was required. Photolysis of **1-D** led to a dideuteriocyanodibenzosemibullvalene. This revealed only two aliphatic methine peaks—these being at δ 4.50 (doubly benzylic) and δ 3.19 (β-benzylic methine). The deuterium NMR showed methine peaks at δ 3.78 (nonbenzylic) and δ 3.11 (α-benzylic). Thus, of the two benzylic methine peaks, α and β, present in the undeuterated semibullvalene, only the downfield one remains in the deuterated photoproduct. This downfield benzylic methine has been assigned as the one remote from the cyanobenzo ring (i.e., β).

Scheme III. Regioselective Removal of the Benzylic Hydrogen in the Deuterated Cyanodibenzosemibullvalene Photoproduct



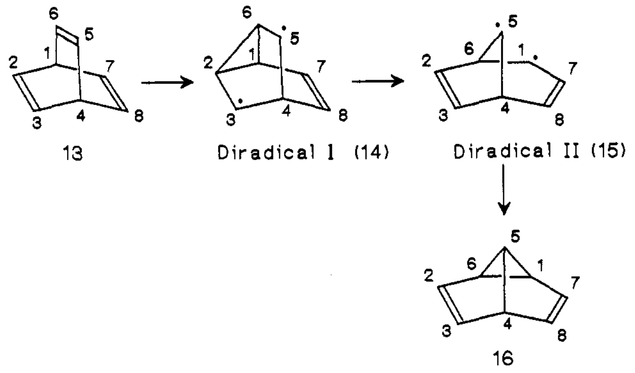
With the NMR assignments established, we can write the photolysis as in eq 4. However, despite the multiple NMR



(4)

approaches to the assignment of the α- and β-methylene triplet peaks, it was thought worthwhile to add a chemical proof. The basic approach was designed to remove that hydrogen or deuterium substituted on the carbon remote from the cyanodibenzo group and to leave untouched the hydrogen or deuterium on the cyanobenzylic position. The procedure involved regioselective addition of hydrogen bromide in acetic acid to the strained benzylic–benzylic three-membered ring bond, solvolysis of the resulting ring-opened bromide in aqueous acetone, and then oxidation of benzylic carbinol **11** to afford ketone **12**. The sequence was developed using undeuterated material, as outlined in the Experimental Section, and then applied to the deuterated photoproduct, as shown in Scheme III. It was determined by NMR analysis that the deuterium label originally present in the cyanodibenzosemibullvalene photoproduct (i.e., **10-D**) was still present and that the benzylic atom lost in the ring opening and

Scheme IV. Bonding Changes in the Barrelene to Semibullvalene Rearrangement



oxidation was hydrogen. With Markovnikov control of the hydrogen bromide three-ring opening, this provides further evidence that the deuterium in the photoproduct is, indeed, located as depicted for **10-D**.

Theoretical Efforts. Since it is the excited-state hypersurface which controls photochemical reactivity,[11] it seemed of interest to explore the triplet surface for the di-π-methane rearrangement of bicyclic systems. For computational simplicity, the rearrangement of the parent molecule, barrelene (**13**), was selected. Quite some time ago, we had carried out three dimensional computations at the Hückel level on this process.[5a,12] This led to the conclusion that there were two reaction intermediates in the barrelene to semibullvalene rearrangement. The first was the cyclopropyldicarbinyldiradical (diradical I) resulting from vinyl–vinyl bridging of the barrelene triplet. The second intermediate was diradical II of the di-π-methane rearrangement mechanism. More recently, higher level computations on the basic di-π-methane system, as exemplified by 1,4-pentadiene itself, have been carried out by Borden, Davidson, et al.[13] who concluded that the triplet does give both diradical I and diradical II as energy minima, in agreement with our earlier computations.

However, it did seem necessary to proceed with computations on an example which is known to occur experimentally in solution.[14] Also, a case closely related to the system presently under study was desired. Thus, the case of the barrelene to semibullvalene rearrangement was investigated using semiempirical and ab initio computations.

This rearrangement involves three discrete changes in bonding, as shown in Scheme IV: (a) vinyl–vinyl bonding between carbons 2 and 6 with formation of diradical I (**14**), (b) loss of bond 1–2 to afford diradical II (**15**), and (c) bond formation between carbons 1 and 5 to form semibullvalene. This is true independent of whether diradicals I and/or II are reaction intermediates or transition states. In any case, it can be seen that there are three regions along the reaction coordinate which are of interest; these we term "region 1", "region 2", and "region 3". In region 1, the computations were done with complete geometry optimization except for bond 2–6 which was systematically shortened until diradical I was reached. In region 2, all bond distances and angles were optimized except for bond 1–2 which was increased from computation to computation until diradical II was formed. Finally, in region 3, bond distance 1–5 was decreased until semibullvalene geometry was formed.

Since some common parameter was required for placement along the reaction coordinate, for each region, the reaction coordinate abscissa was defined as in eq 5. In this equation, the

$$\text{reac\_coord}(\text{pt\_}X) = \text{abs val}\,[\text{dist}(\text{pt\_}X)/\{\text{dist(final)} - \text{dist(init)}\}] + \text{region} - 1 \quad (5)$$

term "region" will be 1, 2, or 3 with the consequence that the reaction coordinate, reac_coord, will range from 0 to 1 in region 1, from 1 to 2 in region 2, and from 2 to 3 in region 3 of the reaction mechanism. While this choice of the reaction coordinate is arbitrary, it does permit a plot of two-dimensional energy versus extent of reaction.

The triplet surface was obtained using the GAMESS,[15a,b] GAUSSIAN90,[15c] and GAUSSIAN92[15c] implementations of ROHF and RHF 6-31G* computations with geometry optimization. For points of interest, triplet-optimized geometries were used for single-point computation of the vertical singlet ground-state energies. Additionally, reactant and product 6-31G* geometry-optimized ground-state energies were obtained. In some instances, initial geometries were obtained using MNDO[17a,b] with minimal configuration interaction but with geometry optimization. Also, for comparison, ab initio computations using the MNDO-optimized geometry were carried out using a 3-21G basis set. Geometries and energies are given in the Experimental and supplemental sections, and Figure 5 in the Discussion section gives plots of energies versus reaction coordinates with the reaction coordinates being defined as in eq 5. In Figure 5, the oval points correspond to 6-31G* geometry-optimized T_1 energies. The diamond-shaped symbols give corresponding singlet points of species using CASSCF/6-31G* with the triplet-optimized geometries. The triangular points are ground-state (S_0) CASSCF/6-31G* points with geometry optimization.

Interpretative Discussion

The first point to be noted is that the rearrangement of *m*-cyanodibenzobarrelene (**1**) to 4-cyanodibenzosemibullvalene (**10**) is completely regioselective within experimental limits. This regioselectivity is 2-fold. First, benzo–vinyl bridging occurs to the cyanobenzo ring rather than to benzo. Second, the bridging is distal to the cyano substituent. Mechanisms I and II, in which vinyl–aryl bridging is distal to the cyano substituent, are illustrated in Scheme V, part a, while the remaining two alternatives (mechanisms III and IV), in which bridging is proximate to the cyano substituent, are outlined in Scheme V, part b. It is seen that mechanisms III and IV afford no odd-electron stabilization by cyano at either stage of the mechanism. In accord with this mechanistic reasoning, the NMR spectral results rule out either rearrangement product derived from mechanisms III and IV.

Of the two mechanisms in Scheme V, part a, mechanism I is in accord with the deuterium labeling observed and described above in the Results section, while mechanism II is not. Mechanism I has cyano stabilization in forming diradical I while mechanism II has cyano stabilization in forming diradical II.

However, we need to discuss our results in the present study in context with the literature. For this, there are several items

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(14) (a) The rearrangement of 1,4-pentadiene itself has been observed in the gas phase.[14b,c] This may not proceed via a di-π-methane mechanism since an alternative process involving 1,2-hydrogen migration from the central methylene also might lead to the observed product. (b) Meinwald, J.; Smith, G. W. *J. Am. Chem. Soc.* **1967**, *89*, 4923–4932. (c) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932–4936.

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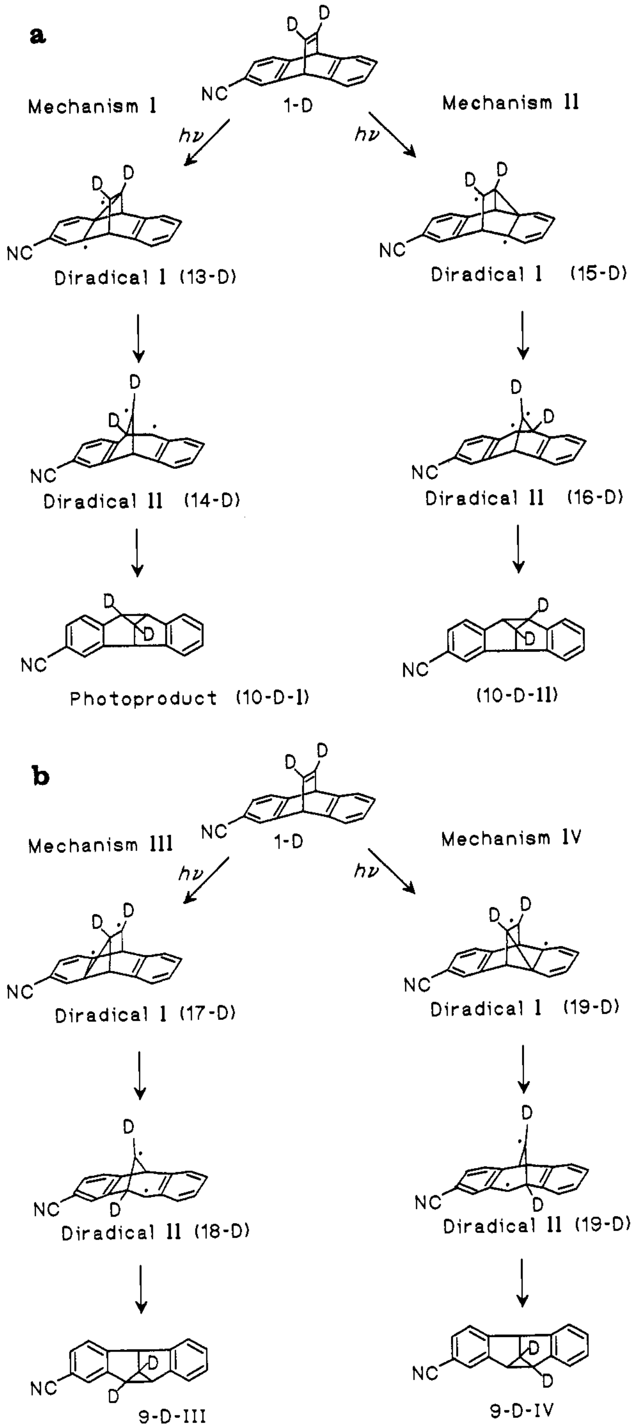
Scheme V. Regioselective Mechanism of *m*-Cyanodibenzobarrelene Rearrangement: (a) Application to Distal Vinyl–Aryl Bridging and (b) Application to Proximal Vinyl–Aryl Bridging



to consider. (a) Whether diradicals I and II are really involved in the di-π-methane rearrangement. (b) Whether there exists a second mechanism not involving diradical I. (c) Whether these species are reaction intermediates and energy minima or just points of interest on the reaction hypersurface. (d) If such diradicals were merely points on the reaction hypersurface for which the organic chemist can draw discrete structures, is it invalid to do so. (e) Lastly, which portion of the hypersurface and formation of which diradical species control regioselectivity and are product-determining.

In context of the first question, the reality of diradical II is easiest to discuss, since clear evidence was obtained in one of our early studies[2c] bearing on this point. Thus, it was shown by using hexadeuteriobarrelene, deuterium labeled on the vinyl bridges with hydrogen only at the bridgehead positions, that although diradical II was formed in an unsymmetrical process (i.e., **14** → **15**, note Scheme IV), this species had time to conformationally equilibrate, with the result that carbon 5 bonded with carbons 1 and 8 with equal probability. This establishes that carbons 1 and 8 have equivalent odd-electron and geometrical characteristics and that diradical II has a finite lifetime and is a true intermediate. A discordant view dealt with some elegant research by Sheridan[18] and Askani.[19] The view was put forth by Paquette,[20c] based on the thermal decomposition of azo compounds with an azo bridge between the radical centers of diradicals similar to di-π-methane type diradicals II. However, it is well-known[21a] that S_0, S_1, and T_1 diradicals behave differently; S_0 diradicals are potentially produced by thermolysis, while the di-π-methane rearrangement proceeds by excited-state species (i.e., S_1 or T_1 in general and T_1 in the case of barrelenes and norbornadienes).

Diradical I is more elusive and controversial. Its discussion is closely related to question b, above, about whether there exists a second mechanism not involving this diradical. In our early efforts,[2c,21] we noted that, in general, in the di-π-methane rearrangement, both diradicals might be either intermediates or just points on the reaction hypersurface depending on structure and multiplicity. In either case, we have generally written this species explicitly in delineating the di-π-methane reaction mechanism.

A different view has been presented by Paquette,[20a] who has suggested that there is an alternative reaction mechanism not involving diradical I. The suggested mechanism was termed "direct 1,2-aryl migration" to generate diradical II directly without proceeding via diradical I. The idea is that diradical I is "bypassed in favor of a direct 1,2-aryl shift" to generate diradical II directly.[20b] A case was presented "against aryl–vinyl bridging".[20b] Similarly, some criticism has been directed at users of the di-π-methane reaction mechanism, as we originally formulated it for writing a structure corresponding to diradical I.[20c] In another critique,[20d] although it was conceded that we did not consider diradicals I necessarily to be reaction intermediates, it was said, "Despite this disclaimer, however, bridged diradicals have been repeatedly invoked as central intermediates in the di-π-methane process".

In the same publication, Paquette notes that a referee emphasized[20d] that the aromatic π-systems must utilize their aromatic electrons even if a bridged species is not an intermediate, a point made by the present author in the present publication and often in the past.[21]

The occurrence of diradical I as a species in the di-π-methane rearrangement is virtually a truism. This is seen by reference to Figure 4. Here, carbon 2 is bonded to "methane carbon" 3, while carbon 1 is the adjacent carbon of a vinyl or aryl π-system. As carbon 2 migrates from carbon 3 to carbon 4 to generate diradical II, at some point, it must be equidistant from carbons 3 and 4. At this point, it is diradical I. One can envisage the σ-bond from initial c–d orbital overlap being broken with eventual formation

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(18) (a) Sheridan, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5140. (b) Reedich, D. E.; Sheridan, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 3360–3361. (c) Reedich, D. E.; Sheridan, R. S. *J. Am. Chem. Soc.* **1988**, *110*, 3697–3698.

(19) Askani, R.; Hornykiewytsch, T.; Müller, K. M. *Tetrahedron Lett.* **1983**, 5513–5514.

(20) (a) Paquette, L. A.; Bay, E. *J. Org. Chem.* **1982**, *47*, 4597–4599. (b) Paquette, L. A.; Varadarajan, A.; Bay, E. *J. Am. Chem. Soc.* **1984**, *106*, 6702–6708. (c) Paquette, L. A.; Varadarajan, A.; Burke, L. D. *J. Am. Chem. Soc.* **1986**, *108*, 8032–8039. (d) Paquette, L. A.; Bay, E. *J. Am. Chem. Soc.* **1984**, *106*, 6693–6701. (e) Paquette, L. A.; Cottrell, D. M.; Snow, R. A.; Gifkens, K. N.; Clardy, L. *J. Am. Chem. Soc.* **1975**, *97*, 3275–3276. However, note that the very pretty HOMO–LUMO interpretation by Houk[20f] operates because of, rather than in spite of, vinyl–benzo delocalization and supports the structure of diradical I: (f) Santiago, C.; Houk, K. N. *J. Am. Chem. Soc.* **1976**, *98*, 3380–3381. (g) Paquette, L. A.; Burke, L. D.; Irie, T.; Tanida, H. *J. Org. Chem.* **1987**, *52*, 3246–3250.

(21) (a) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N. E.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680–7689. (b) Zimmerman, H. E.; Little, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 4623–4630. (c) Hixson, S. S.; Mariano, P. S.; Zimmerman, H. E. *Chem. Rev.* **1973**, *73*, 531–551.

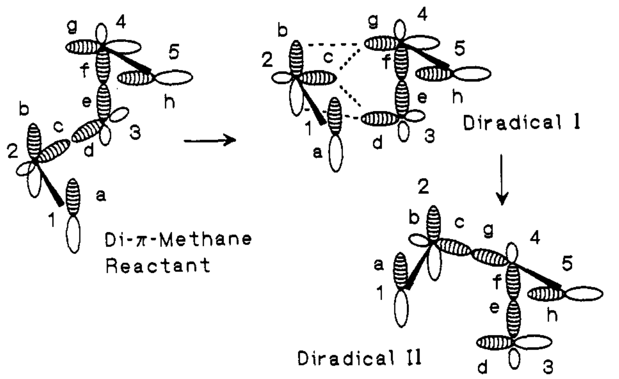

Figure 4. Truncated set of orbitals utilized in the di-π-methane rearrangement.

of a σ-bond between orbitals c and g to afford diradical II. Nevertheless, at the midpoint of the migration, there is overlap between the two π-systems as well (i.e., overlap b–g). This overlap can be inhibited neither physically nor intellectually. The existence of diradical I, then, is independent of whether it is an energy minimum or not. Throughout organic chemical history, it has been helpful in writing potential mechanisms for the organic chemist to write each discrete structure en route to product. Thus, criticism[20c] of the followers of the Zimmerman mechanism is really unjustified.

It also signifies that there is no second mechanism. The "direct" mechanism is just the same mechanism written with omission of diradical I which is physically present by virtue of its geometric positioning between the excited state of the reactant and diradical II.

More generally, when a vinyl or aryl group migrates 1,2 in organic chemistry, unless the π-system is positioned orthogonally to the valence deficient centers, energy is lowered by interaction of such centers with the π-system. Hence, "σ-migrations", if these are considered as possible and separate mechanisms, would be of higher, not lower, energy. Thus, concern about disruption of aromaticity is unwarranted when the reference point is no π interaction.

The presently observed regioselectivity provides evidence for the role of the π-system where, for just one of the four mechanisms, odd-electron delocalization is possible. If the rearrangement was just a "σ-migration" in which only the σ-bond holding the cyanodibenzo moiety to the methane carbon was broken and involved, no effect of the cyano-substituted π-system would be observed. Curiously, the present selectivity has precedent in the observation of Paquette[20e] and earlier studies by Hahn and Johnson.[22] While this selectivity was properly interpreted by Hahn and Johnson, it was interpreted by Paquette with a different conclusion.[20e]

Finally, regarding the question of whether diradical I or diradical II is the "product determining intermediate",[20g] it is clear in the present study that, at least in the cases studied, formation of diradical I and not diradical II is controlling.

Discussion of the Quantum Mechanical Results. We are now left with the question of whether diradical I is a reaction intermediate, an energy maximum, or just a point on the triplet-reaction hypersurface. This was approached quantum mechanically. The triplet hypersurface (the oval points) for the barrelene to semibullvalene conversion is shown in Figure 5. It is seen that there are four triplet minima. These correspond to T_1 of barrelene, diradical I, diradical II, and semibullvalene. With the 6-31G* basis set, a barrier of 0.0247 hartrees, or 15 kcal/mol, was observed separating diradical I from diradical II. The diamond points correspond to singlet species forced to have the triplet geometry. Finally, the triangular points are ground-state singlets with geometry optimization. The conclusion here that diradical I is an energy minimum on the triplet-reaction hypersurface applies

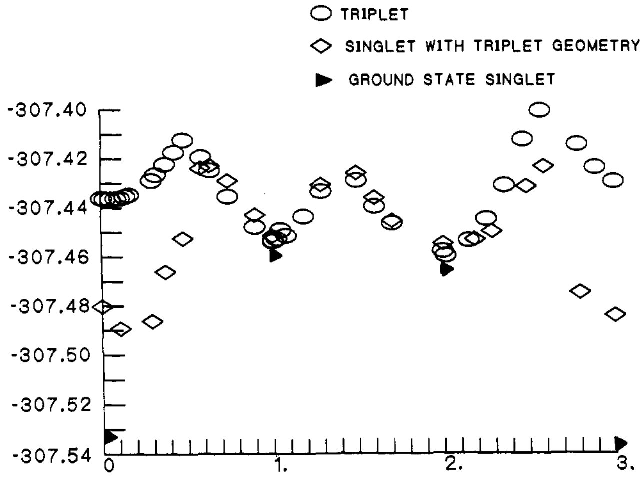

Figure 5. Triplet hypersurface for conversion of barrelene to semibullvalene, including selected singlet points. The ordinate is in hartrees. The abscissa is 0 for barrelene, 1 for diradical I, 2 for diradical II, and 3 for semibullvalene.

to this example and seems likely to be characteristic of triplet surfaces. To the extent that aromatic rings are involved in the bridging process, it seems likely that the energetic barrier will be lowered due to restoration of the aromatic π-system. However, the barrelene surface is consistent with the cyanodibenzobarrelene photochemistry presently studied experimentally.

Another approach to treatment of diradical I makes use of the elegant Weinhold NBO Analysis[16] which is able to convert an arbitrary eigenfunction basis into one composed of bond orbitals and/or hybrid orbitals. Additionally, the method is able to arrive at that resonance structure most completely accounting for the total electron density. When applied to diradical I, a structure resulted which is semiquantitatively that which we have been drawing in our mechanisms. With 98.9% of the electron density accounted for, the three-ring bonds are comprised of ca. $sp^{3.8}$ hybrids. The π-bond 7–8 appears nicely. Finally, the odd-electron centers at carbons 3 and 5 appear as 90% pure p orbitals. These results are summarized in Table I.

A relevant point in interpreting the triplet hypersurface is that the S_0 surface for species constrained to the optimized triplet geometry is remote from the triplet until well along the reaction coordinate, at which point intersystem crossing may occur, followed by relaxation to the undistorted ground state of semibullvalene.

For singlet di-π-methane rearrangements, often observed in acyclic systems, the probability of a concerted reaction mechanism without energy intermediates is greater than what we have noted in our previous studies.[2c,21b] In any case, depiction of the reaction mechanism using diradicals I and II in similar "electron-pushing" fashion does account for much of the stereochemistry, regiochemistry, and reactivity results we have encountered and described. Thus, even without minima, the organic chemist is aided with this mechanistic description.

Conclusion. In addition to the inferences specific to this study, we note that the conclusions are in accord with a view expressed throughout many of our publications. This view suggested[23] that in photochemical reactions of any complexity, the reaction course is determined on the hypersurface of the excited state with the reacting molecule selecting a low-energy route. While the necessity for conversion to ground state is a truism, radiationless decay most often occurs only after the reaction course is determined in the excited state. Decay to ground state tends to

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[22] Hahn, R. C.; Johnson, R. P. *J. Am. Chem. Soc.* **1977**, *99*, 1508–1513.

[23] (a) Note, for example: Zimmerman, H. E. *Science* **1966**, *153*, 837–844. (b) Bernardi, F.; Olivucci, M.; Rgagazo, I. N.; Robb, M. A. *J. Am. Chem. Soc.* **1992**, *114*, 8211–8220. Recently, Bernardi et al. have discussed the photochemistry of ergosterol with essentially the same reasoning but apparently overlooked earlier studies[24,25] including the role of bifunnels or funnels.

Table I. NBO Analysis Giving the Composition of Bonds of Diradical I[a]

bond	occupancy	orbital	hybrdztn	orbital	hybrdztn	bond	occupancy	orbital	hybridztn	orbital	hybrdztn
α-Spins											
C1–C2	0.97297	1(to 2)	1:3.82	2(to 1)	1:3.91	C4–C5	0.98734	4(to 5)	1:3.12	5(to 4)	1:2.38
C1–C6	0.97297	1(to 6)	1:3.82	6(to 1)	1:3.91	C4–C8	0.99213	4(to 8)	1:3.03	8(to 4)	1:2.23
C1–C7	0.99135	1(to 7)	1:2.32	7(to 1)	1:2.20	C4–H12	0.99344	4(to 12)	1:2.78	12(to 4)	1:0
C1–H9	0.99366	1(to 9)	1:2.54	9(to 1)	1:0	C5–H13	0.99444	5(to 13)	1:2.32	13(to 5)	1:0
C2–C6	0.97817	2(to 6)	1:3.85	6(to 2)	1:3.85	C7–C8	0.99161	7(to 8)	1:1.63	8(to 7)	1:1.65
C2–C3	0.99268	2(to 3)	1:2.45	3(to 2)	1:2.28	π C7–C8	0.98501	p 7(to 8)	0:1	p 8(to 7)	0:1
C2–H10	0.99389	2(to 10)	1:2.35	10(to 2)	1:0	C7–H15	0.99172	7(to 15)	1:2.26	15(to 7)	1:0
C6–C5	0.99268	6(to 5)	1:2.45	5(to 6)	1:2.28	C8–H16	0.99273	8(to 16)	1:2.19	16(to 8)	1:0
C6–H14	0.99390	6(to 14)	1:2.35	14(to 6)	1:0	LP C3	0.95484	3	1:9.22		
C3–C4	0.98734	3(to 4)	1:2.38	4(to 3)	1:3.12	LP C5	0.95484	5	1:9.25		
C3–H11	0.99443	3(to 11)	1:2.32	11(to 3)	1:0						
β-Spins											
C1–C2	0.95913	1(to 2)	1:3.86	2(to 1)	1:3.79	C4–C5	0.98707	4(to 5)	1:3.14	5(to 4)	1:2.16
C1–C6	0.95915	1(to 6)	1:3.86	6(to 1)	1:3.79	C4–C8	0.97335	4(to 8)	1:2.92	8(to 4)	1:2.29
C1–C7	0.99126	1(to 7)	1:2.33	7(to 1)	1:2.20	C4–H12	0.99037	4(to 12)	1:2.84	12(to 4)	1:0
C1–H9	0.99197	1(to 9)	1:2.49	9(to 1)	1:0	C5–H13	0.99518	5(to 13)	1:1.95	13(to 5)	1:0
C2–C6	0.96184	2(to 6)	1:3.97	6(to 2)	1:3.97	C7–C8	0.99155	7(to 8)	1:1.63	8(to 7)	1:1.64
C2–C3	0.99261	2(to 3)	1:2.45	3(to 2)	1:2.12	π C7–C8	0.97959	p 7(to 8)	0:1	p 8(to 7)	0:1
C2–H10	0.99337	2(to 10)	1:2.36	10(to 2)	1:0	C7–H15	0.99068	7(to 15)	1:2.26	15(to 7)	1:0
C5–C6	0.99261	5(to 6)	1:2.45	6(to 5)	1:2.12	C8–H16	0.99187	8(to 16)	1:2.15	16(to 8)	1:0
C6–H14	0.99337	6(to 14)	1:2.36	14(to 6)	1:0	LP* C3	0.04231	3	1:43		
C3–C4	0.98707	3(to 4)	1:2.16	4(to 3)	1:3.14	LP* C5	0.04230	5	1:43		
C3–H11	0.99518	3(to 11)	1:1.95	11(to 3)	1:0						

[a] LP refers to lone pairs, π orbitals are marked as such, vacant orbitals bear an asterisk, and hybridization is given as a ratio of s:p.

be a major controlling feature mainly in reactions involving relatively little skeletal modification, such as cis–trans isomerization. However, many variations are possible. The present reaction is of the type controlled by hypersurface barriers, since decay to ground state occurs only after extensive geometric reorganization.

Experimental Section

General Procedures. Melting points were obtained on a Mel-Temp heating block and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Deuterium NMR spectra were obtained at 500 MHz, and ^{1}H NMR spectra were at 200 MHz except where noted. Column chromatography was performed using silica gel (J. T. Baker, 60–200 mesh) mixed with Sylvania 2282 phosphor and slurry-packed into a quartz column which was monitored using a handheld UV lamp.

Photolysis Apparatus and Equipment. A quartz Hanovia 450-W water-cooled medium-pressure immersion lamp was used along with a Pyrex glass filter and a 0.07 M sodium metavanadate in 5% NaOH filter solution. The irradiation flask was fitted with a nitrogen inlet, stirring bar, and capillary outlet. The photograde benzene was purified by extracting the benzene four times with 100 mL of potassium permanganate and 10 mL of concentrated sulfuric acid, once with 100 mL of water, with 50 mL of concentrated sulfuric acid until two successive portions did not turn brown, once with 100 mL of sarurated sodium bicarbonate solution, and twice with 100 mL of saturated sodium chloride solution. The benzene was dried over magnesium sulfate and filtered. The benzene was refluxed over calcium hydride overnight and then distilled to yield photograde benzene.

***m*-Bromodibenzobarrelene (4).** To 100 g of molten naphthalene at 115 °C were added 7.0 g of 5-bromoanthranilic[8] acid and 14 mL of freshly distilled isoamyl nitrite in small portions. It was observed that if the addition was too slow, the isoamyl nitrite tended to decompose, while if addition was too rapid, other byproducts formed. Heating was continued for an additional 20 min after addition was completed. Then, 50 mL of water was added. The molten reaction mixture was sublimed for 4 days at 70 °C (30 mmHg). The remaining residue was placed on a 2.5- × 100-cm silica column and eluted with hexane to give the crude product containing some naphthalene. The remaining naphthalene was removed via sublimation. Recrystallization in acetone and methanol yielded 5.34 g (58%) of light yellow crystals, mp 118 °C.

The spectral data are as follows: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.42 (d, J = 2 Hz, 1 H, ortho to bromo), 7.27 (m, 2 H, ortho hydrogens on benzo ring), 7.13–7.05 (m, 2 H, ortho and meta to bromo), 7.02–6.94 (m, 4 H, meta on benzo ring and vinyls), 5.12–5.07 (m, 2 H, bridgeheads); IR (CCl$_4$, cm^{-1}) 3072 m, 2972 m, 1602 w, 1591 w, 1469 w, 1455 s, 1406 w, 1317 w, 1150 w, 1059 w, 957 w, 883 w, 687 s; MS (70 eV, EI) *m/e* 282.0015 (calcd for $C_{16}H_{11}Br$ 282.0044). Anal. Calcd for $C_{16}H_{11}Br$: C, 67.86; H, 3.92. Found: C, 67.34; H, 4.14.

Cyanodibenzobarrelene 1. A stirred solution of 5.30 g (18.7 mmol) of *m*-bromodibenzobarrelene (**4**) in 25 mL of dimethylformamide with added, suspended 4.25 g (47.5 mmol) of copper(I) cyanide under nitrogen was refluxed for 16 h. The reaction mixture was quenched with 50 mL of 10% sodium cyanide solution and extracted with toluene. The extracts were washed with 10% sodium cyanide solution, 6% ammonium hydroxide solution, water, and saturated sodium chloride solution and dried over MgSO$_4$; the solvent was removed in vacuo to give 3.12 g of crude *m*-cyanodibenzobarrelene (**1**). Recrystallization from diethyl ether yielded 2.06 g (48%) of product as fine, white crystals, mp 172.5–173.0 °C.

The spectral data are as follows: ^{1}H NMR (C$_6$D$_6$, 200 MHz) δ 7.51 (m, 1 H, ortho to cyano and to bridgehead), 7.36–7.25 (m, 4 H), 7.02–6.97 (m, 4 H), 5.22–5.17 (m, 2 H, bridgeheads); IR (CCl$_4$, cm^{-1}) 3070 m, 3024 m, 2974 m, 2229 s, 1462 s, 1317 m, 843 m, 694 s; MS (70 eV, EI) *m/e* 229.0897 (calcd for $C_{17}H_{11}N$ 229.0891). Anal. Calcd for $C_{17}H_{11}N$: C, 89.03; H, 4.83; N, 6.13. Found: C, 88.68; H, 4.82; N, 5.88.

Sensitized Photolysis of *m*-Cyanodibenzobarrelene (1). A solution of 91.1 mg (0.40 mol) of *m*-cyanodibenzobarrelene and 10 mL of acetophenone in 200 mL of benzene was degassed for 1 h and then photolyzed for 2 h using a Pyrex filter and 0.07 M NaVO$_3$ in 5% NaOH filter solution. The benzene was removed in vacuo, and the acetophenone was removed under vacuum at room temperature. NMR analysis showed only 4-cyanodibenzosemibullvalene. This material was recrystallized in diethyl ether to yield 45.1 mg (50%) of 4-cyanodibenzosemibullvalene (**10**) as white crystals, mp 164–164.5 °C.

The spectral data are as follows: ^{1}H NMR (CDCl$_3$, 270 MHz) δ 7.33–7.24 (m, 4 H), 7.12–7.04 (m, 3 H), 4.50 (d, 1 H, J = 6 Hz, α-benzylic and α-cyanobenzylic), 3.77 (q, 1 H, J = 6 Hz, β both aryl rings), 3.19 (t, 1 H, J = 6 Hz), 3.11 (t, 1 H, J = 6 Hz); IR (NaCl, cm^{-1}) 3059 m, 3051 m, 3039 m, 2926 m, 2851 w, 2222 s, 1608 w, 1478 s, 1474 s, 1270 w, 1062 w, 1018 w, 852 w, 835 w, 825 w, 762 s, 746 s; MS (70 eV, EI) *m/e* 229.0893 (calcd for $C_{17}H_{11}N$ 229.0891). Anal. Calcd for $C_{17}H_{11}N$: C, 89.03; H, 4.84; N, 6.13. Found: C, 88.93; H, 4.65; N, 6.13.

In a second run, a solution of 90 mg (0.39 mmol) of **1** and 10 mL (86 mmol) of acetophenone in 175 mL of benzene was photolyzed for 2 h. The solvent was removed in vacuo. Acetophenone was removed via low-pressure distillation. The NMR of the residue revealed only photoproduct. This was chromatographed on a silica thick-layer plate and eluted with 40% ether/hexane. After extraction and concentration in vacuo, 58 mg (64%) of 4-cyanodibenzosemibullvalene (**10**) was obtained.

Lanthanide Shift Reagent Study of Photoproduct 10. To a solution of 11.2 mg of photoproduct **10** in 500 μL of CDCl$_3$ were added 100-μL portions of a solution of 45.3 mg of Pr(FOD)$_3$ in 1 mL of CDCl$_3$. Five additions were performed. The NMR spectral data (270 MHz) for the two triplets are as follows: 0.000 mol fraction of Pr(FOD)$_3$/photoproduct, 860.97 and 839.65 Hz; 0.091 mol fraction, 856.26 and 832.18 Hz; 0.184 mol fraction, 854.86 and 829.71 Hz; 0.274 mol fraction, 854.69 and 829.24 Hz; 0.365 mol fraction, 854.52 and 828.78 Hz; and 0.456 mol fraction, 853.65 and 827.16 Hz. Thus, the upfield triplet was shifted more upon increasing concentrations of $Pr(FOD)_3$, indicating that this triplet is located α to the cyanobenzene ring.

Two samples with molar ratios of $Eu(FOD)_3$ to photoproduct of 0.30 and 0.55 afforded chemical shifts of the upfield triplets of δ 3.17 and 3.23, respectively, and of the downfield triplets of δ 3.24 and 3.28, respectively. Without any shift reagent present, the shifts were observed at δ 3.19 and 3.11. Once again, the shift was greatest in the upfield triplet, as above, which implies that the upfield triplet is α to the cyanobenzo ring.

NOE Study of Cyanodibenzosemibullvalene Photoproduct 10. Using a solution of 7.2 mg of photoproduct and 8.6 mg of $Eu(FOD)_3$ in 500 μL of $CDCl_3$, we irradiated the upfield and downfield triplets at 35L power. When the downfield triplet was irradiated the β-cyano aromatic hydrogen was integrated as 0.95 H, using the α-cyano aromatic hydrogens as a reference of 2 H. When the upfield triplet was irradiated, the β-cyano peak was measured as 1.05 H. When the upfield triplet was irradiated at 30L, the β-cyano integrated to 1.07 H, but when the downfield triplet was irradiated, it was integrated to 0.93 H. Due to the nuclear Overhauser effect, irradiation of the triplet of the α-methine hydrogen closer to the β-cyano aromatic hydrogen should enhance this β-cyano aromatic peak more than irradiation of the more remote β-methine. Therefore, it was concluded that the upfield triplet was the triplet α to the cyanobenzyl ring, while the downfield triplet derived from the β-benzylic hydrogen.

***m*-Bromodibenzobicyclo[2.2.2]octadien-2-ol and *m*-Bromodibenzobicyclo[2.2.2]octadien-3-ol (5).** To a stirred and cooled (0 °C) solution of 7.90 g (27.9 mmol) of *m*-bromodibenzobarrelene (4) in 160 mL of dry tetrahydrofuran was passed a stream of 83.7 mmol of diborane under nitrogen. The diborane was generated by the addition of 2.14 g (56.6 mmol) of sodium borohydride dissolved in 54 mL of diglyme to 10.3 mL (83.7 mmol) of boron trifluoride etherate in 21 mL of diglyme. The exit gases were passed through a bottle containing acetone to catch and destroy excess diborane. The solution was then stirred at room temperature for 2 h. Then, 20.0 mL of methanol was carefully added at 0 °C to quench any unreacted diborane. Hydrogen peroxide (30%, 30 mL) containing 3.0 g of sodium hydroxide was added and the reaction mixture refluxed for 30 min. It was added to 300 mL of water and, after tetrahydrofuran and methanol had been removed in vacuo, ether extracted and the solution dried over sodium sulfate. Concentration in vacuo yielded 7.15 g of crude product which was chromatographed on a 4- × 35-cm silica gel column slurry-packed in hexane. After all impurities had been washed out with hexane, 4.82 g (16.0 mmol, 57.4%) of *m*-bromodibenzobicyclo[2.2.2]octadien-2-ol and *m*-bromodibenzobicyclo[2.2.2]octadien-3-ol (5) were obtained upon elution with ether to yield an oil consisting of the four possible isomers in a 1:1:1:1 ratio.

The spectral data are the following: ^1H NMR (C_6D_6, 200 MHz) δ 7.35–6.50 (m, 7 H, arom), 3.95–3.58 (m, 3 H, bridgeheads and C*H*OH), 1.95–1.75 (m, 1 H, CH_2), 1.13–0.75 (m, 1 H, CH_2); IR (CCl_4, cm^{-1}) 3615 w, 3583 m, 3073 w, 3025 w, 2956 s, 2936 m, 2863 w, 1598 w, 1462 s, 1411 w, 1394 m, 1277 w, 1166 m, 1145 w, 1066 m, 1050 s, 1033 s, 967 w, 950 w, 914 w.

***m*-Bromodibenzobicyclo[2.2.2]octadien-2-one and *m*-Bromodibenzobicyclo[2.2.2]octadien-3-one (6).** To a stirred solution of 4.45 g (14.8 mmol) of alcohols **5** in 30 mL of dimethylformamide under nitrogen was added 23.2 g (61.6 mmol) of pyridinium dichromate in 30 mL of dimethylformamide[26] at room temperature. Stirring was continued for 3 h, and the mixture was poured into 600 mL of water and ether extracted. The extracts were washed with water, dried over sodium sulfate, and concentrated in vacuo to give 4.48 g of a pale yellow oil which contained the crude ketone mixture. Crystallization from ether yielded 1.29 g of the ketones as white crystals. The mother liquor was subsequently chromatographed on a 2- × 80-cm silica gel column slurry-packed in hexane. Elution with 2% ether/hexane gave another 2.01 g of the ketones as a colorless oil. Together, 3.30 g (11.03 mmol, 74.5%) of *m*-bromodibenzobicyclo[2.2.2]octadien-2-one and *m*-bromodibenzobicyclo[2.2.2]octadien-3-one (**6**) was obtained.

The spectral data are the following: ^1H NMR (C_6D_6, 200 MHz) δ 7.35–6.95 (m, 7 H, arom), 4.59 (s, 0.5 H, bridgehead α to carbonyl of isomer A), 4.52 (s, 0.5 H, bridgehead α to carbonyl of isomer **B**), 3.70–3.67 (t, $J = 2$ Hz, 0.5 H, bridgehead β to carbonyl of isomer B), 3.62–3.60 (t, $J = 2$ Hz, 0.5 H, bridgehead β to carbonyl of isomer A), 1.85–1.76 (m, 2 H, CH_2) (note: the assignment of A and B is only relative); IR (CCl_4, cm^{-1}) 3074 w, 3026 w, 2960 w, 2922 w, 1737 s, 1597 w, 1460 s, 1412 w, 1406 w, 1094 m, 1064 m, 972 w. Anal. Calcd for $C_{16}H_{11}BrO$: C, 64.24; H, 3.71. Found: C, 63.91; H, 3.90.

One-Pot Conversion of Bromodibenzobarrelene to Ketone 6. To an ice-cooled solution of 5.90 g (20.7 mmol) of bromodibenzobarrelene in 120 mL of THF was added 42.3 mmol of diborane. The diborane was generated by the addition of 7.7 mL (62.6 mmol) of boron trifluoride etherate in 16 mL of dimethoxyethane to 1.60 g (42.3 mmol) of sodium borohydride in 40 mL of DME. The exit gases were passed through acetone to destroy any remaining diborane. The reaction mixture was stirred for 2 h at room temperature after diborane addition and then the reaction cautiously quenched at 0 °C with 20 mL of methanol. To the reaction mixture was added a solution of 23 mL of 30% hydrogen peroxide and 2.25 g of sodium hydroxide. The resulting solution was refluxed for 0.5 h. The reaction mixture was diluted with water and ether extracted. The extracts were concentrated in vacuo. The remaining aqueous layer was ether extracted, the extracts were dried over $MgSO_4$, and the ether was removed in vacuo to yield 4.87 g of a yellow, foamy solid containing four isomers of the alcohol. This was used without further purification.

To a solution of 4.87 g (16 mmol) of the alcohol mixture in 32 mL of DMF was added 25 g of pyridinium dichromate under a nitrogen atmosphere. This solution was stirred for 3 h at room temperature. The reaction mixture was poured into water and ether extracted. The extract was washed with water and saturated sodium chloride solution and dried over $MgSO_4$, and the solvent was removed in vacuo to yield 4.20 g (72%) of a mixture of 2-bromo-9,10-dihydro-11-oxo-9,10-ethenoanthracene and 2-bromo-9,10-dihydro-12-oxo-9,10-ethenoanthracene, mp 140–144 °C, the two isomers of ketone **6**.

The spectral data are as follows: ^1H NMR (C_6D_6, 200 MHz) δ 7.35–6.95 (m, 7 H, arom), 4.59 (s, 0.5 H, bridgehead α to carbonyl of isomer A), 4.52 (s, 0.5 H, bridgehead α to carbonyl of isomer B), 3.68 (t, $J = 2$ Hz, 0.5 H, bridgehead β to carbonyl of isomer B), 3.61 (t, $J = 2$ Hz, 0.5 H, bridgehead β to carbonyl of isomer A), 1.85–1.76 (m, 2 H, CH_2); IR (CCl_4, cm^{-1}) 3074 w, 3026 w, 2960 w, 2922 w, 1737 s, 1597 w, 1460 s, 1412 w, 1406 w, 1064 m, 972 w; MS (70 eV, EI) *m/e* 297.9970 (calcd for $C_{16}H_{11}BrO$ 297.9993). Anal. Calcd for $C_{16}H_{11}BrO$: C, 64.24; H, 3.71. Found: C, 63.97; H, 3.85.

Preparation of *tert*-Butyl Alcohol-*O-d*. To a stirred slurry of 100 g (0.891 mol) of potassium *tert*-butoxide in 60 mL of diethyl ether was added slowly 30 mL (1.498 mol) of deuterium oxide under a nitrogen atmosphere. After deuterium oxide addition, the slurry was stirred for an additional 2 h. The *tert*-butyl alcohol-*O-d* was purified by distillation to yield 55.7 g (83%) with >98% deuteration.

***m*-Bromo-3,3-dideuteriodibenzobicyclo[2.2.2]octadien-2-one and *m*-Bromo-2,2-dideuteriodibenzobicyclo[2.2.2]octadien-3-one (7a,b).** To a stirred solution of 3.84 g (12.8 mmol) of ketones **6** and 56 mL (586 mmol) of *tert*-butyl alcohol-*O-d* in 50 mL of toluene was added 382 mg (3.4 mmol) of potassium *tert*-butoxide at –15 °C. After the solution had stirred for 10 min, 154 mL of toluene cooled to 0 °C and 23 mL of deuterium oxide were added. The solution was extracted with toluene, the toluene extract was washed with water and saturated sodium chloride solution and dried over $MgSO_4$, and the solvent was concentrated in vacuo to yield 3.34 g (87%) of ketones **7** with 86% deuteration. This process was repeated once more to increase the percent deuteration to yield 2.84 g (74%) of ketones **7** with 91% deuteration.

The spectral data are as follows: ^1H NMR (C_6D_6, 200 MHz) δ 7.16–6.52 (m, 7 H, arom), 4.60 (s, 0.5 H, bridgehead α to carbonyl of isomer A), 4.52 (s, 0.5 H, bridgehead α to carbonyl of isomer B), 3.68 (s, 0.5 H, bridgehead β to carbonyl of isomer B), 3.61 (s, 0.5 H, bridgehead β to carbonyl of isomer A), 1.80 (m, 0.18 H, CH_2); IR (CCl_4, cm^{-1}) 3073 w, 3045 w, 3026 w, 2980 w, 2960 w, 2932 w, 2282 w, 1737 s, 1596 m, 1478 m, 1460 s, 1410 m, 1260 m, 1098 m, 1095 m, 1079 m, 1064 m, 930 w, 840 w, 800 s.

***m*-Bromo-2,3,3-trideuteriodibenzobicyclo[2.2.2]octadien-2-ol and *m*-Bromo-2,2,3-trideuteriodibenzobicyclo[2.2.2]octadien-3-ol (8-D).** To a stirred solution of 212 mg (5 mmol) of lithium aluminum deuteride in 7.0 mL of diethyl ether was added 2.60 g (8.6 mmol) of deuterated ketones **7** in 4.5 mL of ether and 9.0 mL of toluene at 0 °C. The reaction mixture was stirred for an additional hour. To the reaction mixture were added

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(24) (a) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1566–1567. (b) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564–1565. (c) In refs 24a,b, there is a discussion of degeneracies along the excited-state surface and their role in enhancing the rate of radiationless conversion to the ground state. (d) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393–401. (e) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538–3548. (f) Zimmerman, H. E. *Top. Curr. Chem.* **1982**, *100*, 45–73. (g) Zimmerman, H. E.; Werthemann, D. P.; Kamm, K. S. *J. Am. Chem. Soc.* **1973**, *95*, 5094–5095. (h) Zimmerman, H. E. *Acc. Chem. Res.* **1982**, *10*, 312–317.

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6.6 mL of water and then cautiously 6.6 mL of 10% HCl. The resulting mixture was extracted three times with ether. The combined organics were washed with saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed in vacuo to yield 1.61 g (61%) of *m*-bromo-2,3,3-trideuteriodibenzobicyclo[2.2.2]octadien-2-ol and *m*-bromo-2,2,3-trideuteriodibenzobicyclo[2.2.2]octadien-3-ol (**8-D**) as a mixture of the two isomers.

The spectra data are the following: ^{1}H NMR (C_6D_6, 200 MHz) δ 7.35–6.50 (m, 7 H, arom), 3.93 (s, 0.5 H, bridgehead α to hydroxyl in isomer A), 3.85 (s, 0.5 H, bridgehead α to hydroxyl in isomer B), 3.70 (s, 0.5 H, bridgehead β to hydroxyl in isomer B), 3.62 (s, 0.5 H, bridgehead β to hydroxyl in isomer A), 1.90–1.75 (m, 0.09 H, CH_2), 1.10–0.90 (m, 0.09 H, CH_2); IR (CCl_4, cm^{-1}) 3583 m, 3443 br s, 3072 w, 3046 w, 3025 w, 2953 m, 2281 m, 1598 w, 1479 w, 1462 s, 1411 m, 1286 m, 1168 m, 1109 m, 1097 m, 1061 s, 940 s, 927 w, 814 w, 805 w; MS (70 eV, EI) *m/e* 301.0175 (calcd for $C_{16}H_{10}D_3BrO$ 301.0197).

***m*-Bromo-2,3-dideuteriodibenzobarrelene (4-D).** To a solution of 402 mg (1.32 mmol) of the deuterated alcohols and 42 mg of 4-(dimethoxyamino)pyridine in 225 μL (1.6 mmol) of triethylamine and 1.4 mL of dichloromethane was added 0.33 g of *p*-tosyl chloride at 0 °C. After being stirred for 5 min, the reaction mixture was allowed to stand for 80 h at -10 °C. Water was added, and the mixture was ether extracted. The combined organics were washed with water, saturated copper(II) sulfate solution, and saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed in vacuo at room temperature yielding 499 mg of alcohol tosylates.

To a stirred solution of 499 mg (1.09 mmol) of the tosylates in 21 mL of dimethoxyethane was added 2.1 g of potassium *tert*-butoxide. The reaction mixture was refluxed for 20 min, diluted with ether and water, and ether extracted. The ether extracts were washed with water and brine and dried over magnesium sulfate, and the solvent was removed in vacuo to yield 245 mg of the crude deuterated barrelene. The brown oil was chromatographed on a 2- × 50-cm silica gel column eluted with hexane to yield 192 mg (62%) of 2-bromo-11,12-dideuterio-9,10-dihydro-9,10-ethenoanthracene (**4-D**), mp 115 °C.

The spectral data are as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.47–6.92 (m, 7 H, arom), 5.07 (m, 2 H, bridgeheads); IR (CCl_4, cm^{-1}) 3068 m, 3058 m, 3043 m, 3022 m, 2971 m, 2927 m, 2856 w, 1721 s, 1455 s, 1159 m, 1150 s, 1141 s; MS (70 eV, EI) *m/e* 284.0180 (calcd for $C_{16}H_9D_2Br$ 284.0170).

***m*-Cyano-2,3-dideuteriodibenzobarrelene (1-D).** To a solution of 438 mg (1.54 mmol) of *m*-bromo-2,3-dideuteriodibenzobarrelene (**4-D**) in 3.5 mL of dimethylformamide was added 438 mg (4.90 mmol) of copper(I) cyanide under a nitrogen atmosphere. The reaction mixture was refluxed for 22 h. To the reaction mixture was added 10 mL of 10% sodium cyanide solution and ether, and then the mixture was ether extracted. The extracts were washed with 150 mL of 10% sodium cyanide solution, 6% ammonium hydroxide solution, water, and saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed in vacuo to yield 340 mg of a yellow solid. The solid was chromatographed on a 2- × 50-cm silica gel column and eluted first with hexane and then with diethyl ether to yield 209 mg (59%) of *m*-cyano-2,3-dideuteriodibenzobarrelene (**1-D**), mp 169–170 °C.

The spectral data are as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.27–6.62 (m, 7 H, arom), 4.60 (s, 1 H, bridgehead), 4.52 (s, 1 H, bridgehead); IR (CCl_4, cm^{-1}) 2930 s, 2853 s, 2282 m, 1687 s, 1609 m, 1447 m, 1374 m, 1357 m, 1267 s, 1183 w, 1066 w, 1027 w; MS (70 eV, EI) *m/e* 231.1026 (calcd for $C_{17}H_9D_2N$ 231.1017).

The extent of deuteration was determined directly by preparing a solution of 11 mg (47.5 μmol) and 48.5 μmol of an internal deuterium standard in carbon tetrachloride. Deuteration was determined to be greater than 90%. The ^{2}H NMR is as follows: (500 MHz) δ 9.11 (s, 1 D, std), 7.04 (s, 1.88 D, vinyl).

Photolysis of *m*-Cyano-2,3-dideuteriodibenzobarrelene (1-D). A solution of 83 mg (0.359 mmol) of *m*-cyanodideuteriodibenzobarrelene (**1-D**) and 5.0 mL of acetophenone in 175 mL of benzene was degassed with nitrogen for 1 h. The reaction mixture was photolyzed for 1 h through a Pyrex filter and 0.07 M sodium metavanadate in 5% NaOH solution. Benzene was removed in vacuo, and acetophenone was removed via low-pressure distillation. NMR analysis of the crude material showed only the single photoproduct to be present. Recrystallization from ether afforded 40 mg (48%) of *m*-cyanodibenzosemibullvalene (**10**), mp 154–156 °C.

The spectral data are as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.40–6.95 (m, 7 H, arom), 4.50 (s, 1 H, α to benzo ring and α to cyanobenzo ring), 3.17 (s, 1 H, α to benzo ring and β to cyanobenzo ring); IR ($CHCl_3$, cm^{-1}) 3027 m, 3009 w, 2964 w, 2855 w, 1605 s, 1472 s, 1460 m, 1228 m, 851 m, 612 m; MS (70 eV, EI) *m/e* 231.1017 (calcd for $C_{17}H_9D_2N$ 231.1017); ^{2}H NMR ($CHCl_3$, 500 MHz) δ 3.78 (s, 1 D, β to cyanobenzo ring and benzo ring), 3.11 (s, 1 D, α to cyanobenzo ring and β to benzo ring).

HBr Ring Opening of Cyanodibenzosemibullvalene To Afford 10-Cyanodibenzobicyclo[3.3.0]octadien-4-ol (11). To a stirred solution of 60 mg (0.262 mmol) of *m*-cyanodibenzosemibullvalene (**10**) in 9.0 mL of acetic acid was added 0.90 mL (16.6 mmol) of 48% hydrobromic acid. The reaction mixture was stirred for 24 h at 40 °C, diluted with water, ether extracted, washed with sodium bicarbonate, water, and saturated sodium chloride, dried over magnesium sulfate, and concentrated in vacuo.

To the residue in 15 mL of acetone were added 4.0 mL of water and 185 μL of pyridine. The reaction mixture was refluxed for 2 h, then diluted with ether, washed with 10% hydrochloric acid, water, and saturated sodium chloride solution, and dried over magnesium sulfate; the solvent was removed in vacuo to yield 43 mg (66%) of 10-cyanodibenzobicyclo[3.3.0]octadien-4-ol (**11**).

The spectral data are as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.50–7.17 (m, 7 H, arom), 5.02 (m, 1 H, C*H*OH), 4.83 (m, 1 H, H α to both rings), 3.33 (m, 2 H, CH_2 α to cyanobenzo), 3.00 (m, 1 H, CH); IR ($CHCl_3$, cm^{-1}) 3419 br m, 3025 m, 3011 m, 2955 s, 2926 s, 2855 s, 1716 m, 1261 m, 1229 m, 1089 m, 1022 m, 1010 m, 670 m; MS (70 eV, EI) *m/e* 247.0997 (calcd for $C_{17}H_{13}NO$ 247.0997).

10-Cyanodibenzobicyclo[3.3.0]octadien-4-one (12). To a stirred solution of 43 mg (0.174 mmol) of 10-cyanodibenzobicyclo[3.3.0]octadien-4-ol (**11**) in 4.5 mL of DMF was added 282 mg (0.750 mmol) of pyridinium dichromate. The reaction mixture was stirred at room temperature for 3 h. Water was added, and the mixture was ether extracted. The combined organics were washed with water and saturated sodium chloride solution and dried over magnesium sulfate, and the solvent was removed in vacuo to yield 33 mg (77%) of 10-cyanodibenzobicyclo[3.3.0]octadien-4-one (**12**), mp 179–180 °C.

The spectral data are as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.75–7.27 (m, 7 H, arom), 5.00 (d, J = 6 Hz, 1 H), 3.66–3.42 (m, 3 H, H α- and β-cyanophenyl); IR ($CHCl_3$, cm^{-1}) 3026 m, 3010 m, 2928 m, 2854 w, 1713 s, 1602 s, 1486 m, 1291 m, 1250 m, 1230 m, 825 m; MS (70 eV, EI) *m/e* 245.0886 (calcd for $C_{17}H_{11}NO$ 245.0841).

10-Cyano-5,6-dideuteriodibenzobicyclo[3.3.0]octadien-4-one (11-D). To a solution of 53 mg (0.229 mmol) of dideuteriocyanodibenzosemibullvalene (**10-D**) in 9.0 mL of glacial acetic acid was added 0.90 mL (16.6 mmol) of hydrobromic acid. The reaction mixture was stirred for 24 h at 40 °C. Diethyl ether extraction, washing the extracts with saturated sodium bicarbonate solution, water, and saturated sodium chloride solution, drying over magnesium sulfate, and solvent removal in vacuo left an oil.

To this oil were added 15 mL of acetone, 4.0 mL of water, and 185 μL of pyridine. The reaction mixture was stirred at reflux for 2 h. Diethyl ether was added. The mixture was washed with 10% hydrochloric acid solution, water, and saturated sodium chloride solution and dried over magnesium sulfate and solvent removed in vacuo to yield 38 mg (67%) of 10-cyano-5,6-dideuteriodibenzobicyclo[3.3.0]octadien-4-ol (**11-D**). This was used without further purification.

The spectral data are as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.70–7.15 (m, 7 H, arom), 4.99 (s, 1 H, on hydroxyl carbon), 4.82 (s, 1 H, α to benzo ring and to cyanobenzo ring), 2.95 (s, 1 H, α to cyanobenzo ring and β to hydroxy group).

10-Cyano-5,6-dideuteriodibenzobicyclo[3.3.0]octadien-4-one (12-D). To a solution of 38 mg (0.152 mmol) of 10-cyano-5,6-dideuteriodibenzobicyclo[3.3.0]octadien-4-ol in 4.0 mL of DMF was added 249 mg (0.663 mmol) of pyridinium dichromate. The reaction mixture was stirred at room temperature for 3 h. Addition of water, ether extraction, washing with water and saturated sodium chloride solution, drying over magnesium sulfate, and concentration in vacuo afforded 33 mg (87%) of 10-cyano-5,6-dideuteriodibenzobicyclo[3.3.0]octadien-4-one (**12-D**).

The spectral data are as follows: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76–7.18 (m, 7 H, arom), 4.99 (s, 1 H, α to cyanobenzo ring and to benzo ring), 3.36 (s, 1 H, α to cyanobenzo ring and β to carbonyl); IR ($CHCl_3$, cm^{-1}) 3023 s, 2929 w, 2230 m, 1715 s, 1602 m, 1485 m, 1292 m, 1229 m; MS (70 eV, EI) *m/e* 247.0969 (calcd for $C_{17}H_9D_2NO$ 247.0966); ^{2}D NMR ($CHCl_3$, 500 MHz) δ 3.64 (m, 1 D, α to carbonyl), 3.49 (m, 1 D, α to cyanobenzene ring and β to carbonyl).

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