glacial acetic acid was added to 2.660 g (16.2 mmol) of bromine. After stirring for 8.0 min the reaction mixture turned from red-brown to a lemon yellow color and was immediately poured into 150 ml of water; this solution was extracted with 1:1 ether-pentane. The organic extracts were dried and concentrated *in vacuo* yielding 4.138 g of a pale yellow oil which was chromatographed on a 91 × 2.0 cm silica gel (Davison grade 950, 60–200 mesh) column slurry packed with 5% ether-hexane. Elution was with 2 l. of 4% ether–hexane, 5.75 l. of 6% ether–hexane, 1.25 l. of 8% ether–hexane, and 1.25 l. of 10% ether–hexane; 250-ml fractions were collected. Fractions 16–17 and 27–29 contained 0.032 and 0.048 g, respectively, of unidentifiable noncrystallizing oils. Fractions 7–15 contained 2.693 g of a white solid which, upon recrystallization from pentane, yielded 2.301 g (55.4%), mp 56.0–58.0°, of what was later shown (*vide infra*) to be 1-bromo-*cis*-1-acetyl-4-phenylcyclohexane. Physical data were as follows: infrared (CS_2) 5.83, 7.38, 9.00, and 12.35 μ; nmr (CCl_4) τ 2.82 singlet (5 H, aromatic), 7.62 singlet (3 H, methyl), and 7.10–8.80 multiplet (9 H, cyclohexyl).

Anal. Calcd for $C_{14}H_{17}BrO$: C, 59.80; H, 6.09; Br, 28.42. Found: C, 59.50; H, 6.10; Br, 28.84.

Fractions 18–26 contained 1.268 g of a white solid which, upon recrystallization from pentane, yielded 1.135 g (27.3%), mp 71.5–73.0°, of 1-bromo-*trans*-1-acetyl-4-phenylcyclohexane with the following physical data: infrared (CS_2) 5.83, 8.30, 9.12, and 12.11 μ; nmr (CCl_4) τ 2.81 singlet (5 H, aromatic), 7.59 singlet (3 H, methyl), and 7.20–8.50 multiplet (9 H, cyclohexyl).

Anal. Calcd for $C_{14}H_{17}BrO$: C, 59.80; H, 6.09; Br, 28.42. Found: C, 59.79; H, 6.53; Br, 28.33.

Zinc Debrominations. In a typical run 56 mg of either the *cis* or *trans* isomer of 1-acetyl-1-bromo-4-phenylcyclohexane was stirred in a given solvent with 300 mg of zinc dust and a proton source under a nitrogen atmosphere. After completion of the reaction the mixture was filtered, poured into water, and extracted with ether. The ether was dried and concentrated *in vacuo*. Quantitative ir analysis of the products gave the results summarized in Table I.

Hydriodic Acid Debromination of 1-Bromo-*cis*-1-acetyl-4-phenylcyclohexane. To 56 mg of 1-bromo-*cis*-1-acetyl-4-phenylcyclohexane in 2.0 ml of acetone was added 0.10 ml of 47% hydriodic acid. Iodine was liberated instantaneously, and after 0.5 hr the reaction mixture was poured into 15.0 ml of water containing 1.00 g of sodium sulfate and extracted with ether. The ether extract was dried and concentrated *in vacuo* leaving 42 mg of an oil which was shown by quantitative ir analysis to contain 41.3% of *cis*-1-acetyl-4-phenylcyclohexane.

Hydriodic Acid Debromination of 1-Bromo-*trans*-1-acetyl-4-phenylcyclohexane. To 56 mg of the *trans*-bromo ketone was added 0.1 ml of 47% hydriodic acid. Iodine was liberated more slowly than in the *cis*-bromo ketone case (*ca.* 10 sec before a red-brown color appeared). Quantitative infrared analysis of the product (41 mg) showed it to contain 40.0% of the *cis* ketone.

Acknowledgment. Support of this research by the Petroleum Research Fund of the American Chemical Society and by a predoctoral National Institutes of Health fellowship is gratefully acknowledged.

The Photochemistry of Benzobarrelene. Mechanistic and Exploratory Photochemistry. XXXV[1]

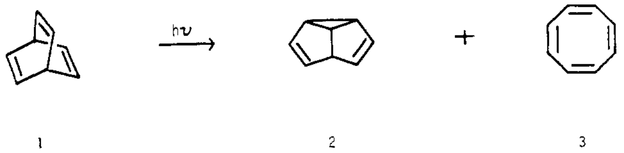
Howard E. Zimmerman, Richard S. Givens, and Richard M. Pagni

Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin. *Received May 6, 1968*

Abstract: The acetone-sensitized rearrangement of 1,4-dihydro-1,4-ethenonaphthalene (benzobarrelene) (**9**) afforded 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (benzosemibullvalene) (**16**) whose structure was established by spectral and degradative means. It was found that N-deuterated lithium cyclohexylamide in N,N-dideuteriocyclohexylamine selectively exchanged the aryl and vinyl protons of benzobarrelene. Photolysis of perdeuterated benzobarrelene with undeuterated bridgehead positions (**24**) afforded perdeuterated benzosemibullvalene with protons at carbons 2 and 5 (**25**). Of the various mechanisms possible for the benzobarrelene to benzosemibullvalene transformation, the labeling result uniquely identifies the process as utilizing the divinylmethane pathway reported earlier for barrelene (**1**). Furthermore, of two *a priori* possibilities, initial vinyl–vinyl and benzo–vinyl bonding, the former was shown to be preferred. Direct irradiation of benzobarrelene gave only benzocyclooctatetraene (**17**). Intersystem crossing of benzobarrelene is concluded to be slow. Direct irradiation of bridgehead hydrogen labeled benzobarrelene afforded benzocyclooctatetraene with the hydrogen label mainly at C-4 and C-7 (**27**) plus a small amount of the label at C-3 and C-8 (**28**). Irradiation of perdeuterated benzosemibullvalene with hydrogen label in the C-2 and C-5 positions gave benzocyclooctatetraene with the hydrogens at carbons 3 and 8 (**28**). This is in contrast with the results of the direct irradiation of perdeuterated benzobarrelene. It is concluded that there are two routes to benzocyclooctatetraene: (a) a triplet pathway from benzobarrelene to benzosemibullvalene followed by direct irradiation of the benzosemibullvalene involving cleavage of the 2–8 and 1–5 bonds; (b) a singlet route initiated predominantly by four-center cycloaddition of a vinyl group to the benzo group plus a small amount from vinyl–vinyl cycloaddition. The various transformations are considered from a mechanistic viewpoint.

Previously, we reported the rearrangement of barrelene (**1**) to semibullvalene (**2**) and cyclooctatetraene (**3**) on acetone photosensitization[2] as shown in Chart I. The mechanism of the barrelene to semibullvalene transformation was determined in our subsequent studies[3] using vinyl-deuterated barrelene (**4**). The reaction was noted[3] (Chart II) to be an

Chart I. Photorearrangement of Barrelene



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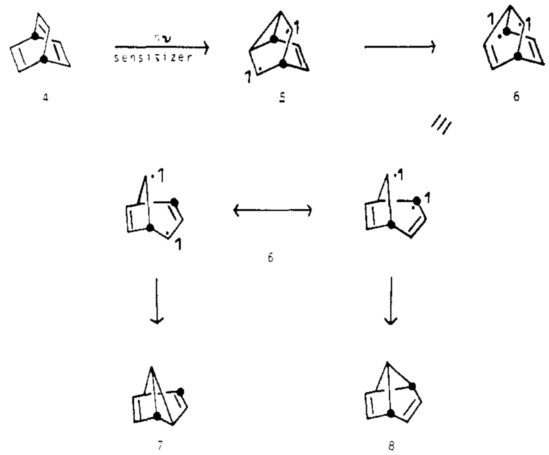
[1] (a) For our preliminary communication, note: *J. Am. Chem. Soc.*, 90, 4191 (1968); (b) paper XXXIII of the series: H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, 90, 4892 (1968).

[2] H. E. Zimmerman and G. L. Grunewald, *ibid.*, 88, 183 (1966).

Chart II. Mechanism of the Barrelene to Semibullvalene Rearrangement

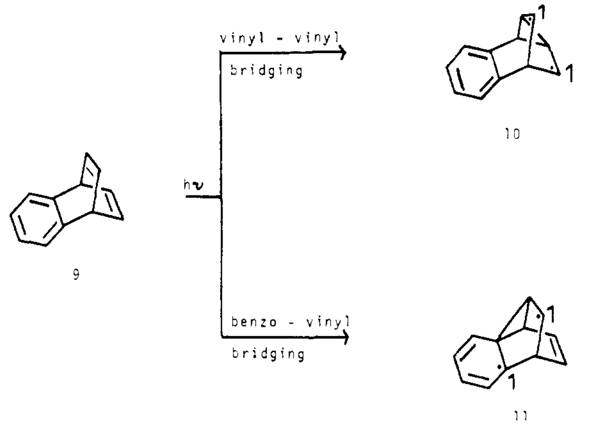


• represents hydrogen; deuterium elsewhere

example of a general excited-state divinylmethane or di-π-methane to vinylcyclopropane rearrangement, some examples of this being the rearrangement of 2,3-bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,8-triene to three isomeric bis(perfluoromethyl)tricyclo[3.3.0.0^{2,8}]-octa-3,6-dienes,[4a] the dibenzobarrelene to dibenzosemibullvalene photolysis,[4b] the benzonorbornadiene to tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-triene irradiation,[4c] the 1,3-diphenylpropene to 1,2-diphenylcyclopropane transformation,[4d] the 1,3,6-cyclooctatriene to bicyclo[5.1.0]-2,5-octadiene rearrangement,[4e,4f] and the 5,5-dimethyl-1,3,6-heptatriene to 1,2-divinyl-3,3-dimethylcyclopropane conversion.[4e,4g]

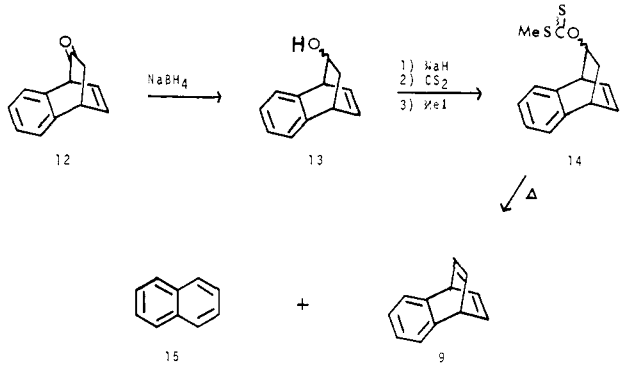
The present research began with four objectives: (a) to investigate the photochemistry of 1,4-dihydro-1,4-ethenonaphthalene (benzobarrelene) (**9**); (b) in the event that the same type of rearrangement occurred as in barrelene, to determine if the same general mechanism applied; (c) and if so, to see whether initial vinyl–vinyl or benzo–vinyl bridging is preferred (Chart III), since, unlike the barrelene case, two alternatives are possible; and (d) lastly, to look for a process paralleling the barrelene to cyclooctatetraene transformation.

Chart III. Benzobarrelene Bridging



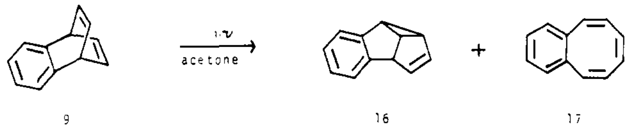
Synthesis of Benzobarrelene. Benzobarrelene was prepared from 1,4-dihydro-9-oxo-1,4-ethanonaphthalene (**12**)[5] as delineated in Chart IV. Reduction of **12** with sodium borohydride afforded a mixture of the epimeric 1,4-dihydro-9-hydroxy-1,4-ethanonaphthalenes (**13**) which was used directly in the next step. The xanthate ester **14**, in turn, was pyrolyzed neat at 225–230° to give naphthalene and benzobarrelene, mp 65.5–66°.

Chart IV. Synthesis of Benzobarrelene



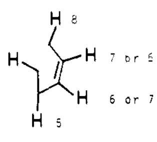
Photosensitized Rearrangement of Benzobarrelene. In a typical run 408.0 mg of benzobarrelene and 2.5 ml of acetone in 40 ml of isopentane were irradiated in a sealed Vycor tube for 135 min using a 450-W, medium-pressure mercury lamp. Under these conditions the acetone, the benzobarrelene, and the products all absorbed light. The products were separated, using aqueous silver nitrate–ether liquid–liquid partition chromatography, to give: 190.7 mg (47%) of unreacted starting material (**9**), 196.1 mg (48%) of 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (benzosemibullvalene) (**16**), and 21.8 mg (5%) of benzocyclooctatetraene (**17**). Note Chart V.

Chart V. Photosensitized Irradiation of Benzobarrelene

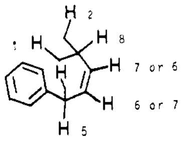


Characterization of Benzosemibullvalene. The benzosemibullvalene product was purified by gradient temperature molecular distillation. Elemental and mass spectral analysis indicated that the colorless oil was isomeric with starting material **9**. Structure elucidation was accomplished by nmr analysis and degradation.

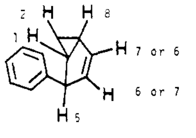
The nmr spectral and spin decoupling results are shown in Figure 1 and Table I. It can be seen that these results are nicely in accord with structure **16**.



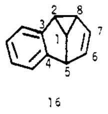
16i



16ii



16iii



16

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

(4) (a) R. S. H. Liu, *ibid.*, **90**, 215 (1968); (b) E. Ciganek, *ibid.*, **88**, 2882 (1966); (c) J. R. Edman, *ibid.*, **88**, 3454 (1966); (d) G. Griffin, J. Covell, R. C. Petterson, R. M. Dobson, and G. Klose, *ibid.*, **87**, 1410 (1965); (e) W. B. Roth and B. Peltzer, *Angew. Chem.*, **76**, 378 (1964); (f) J. Zirner and S. Winstein, *Proc. Chem. Soc.*, 235 (1964); (g) W. B. Roth and B. Peltzer, *Ann. Chem.*, **685**, 56 (1965).

(5) K. Kitahonoki and Y. Takano, *Tetrahedron Letters*, 1597 (1963).

Table I. 100-Mc Nmr and Spin Decoupling of Benzosemibullvalene[a]

Signal position, τ	Description and assignment	Coupling constant, cps	Proton irradiated[b]	Decoupling result[c]	Residual coupling constant,[c,d] cps
2.67–3.20	Multiplet, aromatic				
4.43–4.62	ABX quartet, vinyl next to benzyl, H-6	$J_{6,7} = 5.0$ $J_{5,6} = 2.0$	A, H-7[f] B, H-5[g]	Incomp[e] Doublet	 $J_{6,7} = 5.5$
4.83–5.00	ABX quartet, vinyl next to cyclopropyl, H-7	$J_{6,7} = 5.0$ $J_{7,8} = 2.0$	A, H-6[h] B, H-8[i]	Doublet Doublet	$J_{7,8} = 2.0$ $J_{6,7} = 5.0$
6.10–6.28	ABX quartet, benzylic and allylic, H-5	$J_{5,6} = 2.0$ $J_{1,5} = 6.0$	A, H-6[h] B, H-1[j]	Doublet Doublet	$J_{1,5} = 6.0$ $J_{5,6} = 2.0$
6.74–6.98	ABCD quartet, interior cyclopropyl, H-1	$J_{1,5}$, $J_{1,8}$, $J_{1,2} = 6.5$	A, H-5[g] B, H-2[k] C, H-8[i]	Triplet Incomp[e] Incomp[e]	$J_{1,2}$ and $J_{1,8} = 6.5$
7.02–7.25	ABC triplet, cyclopropyl and benzylic, H-2	$J_{1,2}$ and $J_{2,8} = 6.0$	A, H-1[j] B, H-8[i]	Hidden[l] Hidden[l]	
7.25–7.55	ABCX doublet of triplets, cyclopropyl, H-8	$J_{7,8} = 2.0$ $J_{1,8}$ and $J_{2,8} = 6.5$	A, H-7[f] B, H-1[j] C, H-2[k]	Triplet Incomp[e] Hidden[l]	 $J_{2,8}$ and $J_{1,8} = 6.5$

[a] Run in CCl_4 with TMS as internal standard. [b] Proton irradiated that affects proton in column 1. [c] Result of proton irradiation in spin decoupling. [d] Coupling constant of the residual peak originally described in columns 1, 2, and 3. [e] Incomplete decoupling. [f] Irradiation frequency and power, 509 cps, 100 mV. [g] Irradiation frequency and power, 380 cps, 400 mV. [h] Irradiation frequency and power, 547 cps, 200 mV. [i] Irradiation frequency and power, 264 cps, 200 mV. [j] Irradiation frequency and power, 323 cps, 200 mV. [k] Irradiation frequency and power, 292 cps, 100 mV. [l] The signal was buried in the side band of the irradiated proton.

Thus, hydrogens 6 and 7 (note the numbering of structure **16**) are coupled (J = 5.0 cps). Also, each is coupled to a single additional hydrogen—one to H-5 (J = 2.0 cps) and the other to H-8 (J = 2.0 cps). Similarly, H-5 is split by one additional proton (J = 6.0 cps) besides being split by H-6 or H-7. Thus far we have developed partial structure **16i**. Carbon 5 has only three bonds accounted for thus far, and hence is taken to be bonded additionally to the benzene ring. In an analogous manner, H-8 is found to be equally coupled to two other thus far unassigned hydrogens, H-1 and H-2, besides being coupled to H-6 or H-7. This generated its doublet of triplets patterns. Thus far we have partial structure **16ii**. The two unassigned hydrogens, H-1 and H-2, give rise to a quartet and a triplet, respectively. From the splitting, we know that one of these is coupled to both H-8 and H-5 and the other to H-8. The splitting patterns can be accommodated if H-1 and H-2 split each other. Specifically, H-1 is equally coupled to H-2, H-5, and H-8, and H-2 is equally coupled to H-1 and H-8 (**16iii**). And lastly, to complete the valency of C-2, this atom must be bonded to the benzene ring. This analysis now defines the structure of benzosemibullvalene as **16**, the only unclear point being the assignment of the two vinyl hydrogens, H-6 and H-7. Spin decoupling clarified this point and left some of the other assignments on firmer ground. Table I and Figure 1 show that irradiation of H-5 collapsed H-6 to a doublet and *vice versa*. Likewise, H-7 and H-8 are seen to split each other. Other spin decoupling merely confirmed that H-6 and H-7, and H-1 and H-5, were coupled. Information bearing on the coupling of protons 1, 2, and 8 was not obtainable either because of incomplete decoupling or due to the proton being in the oscillating side band.

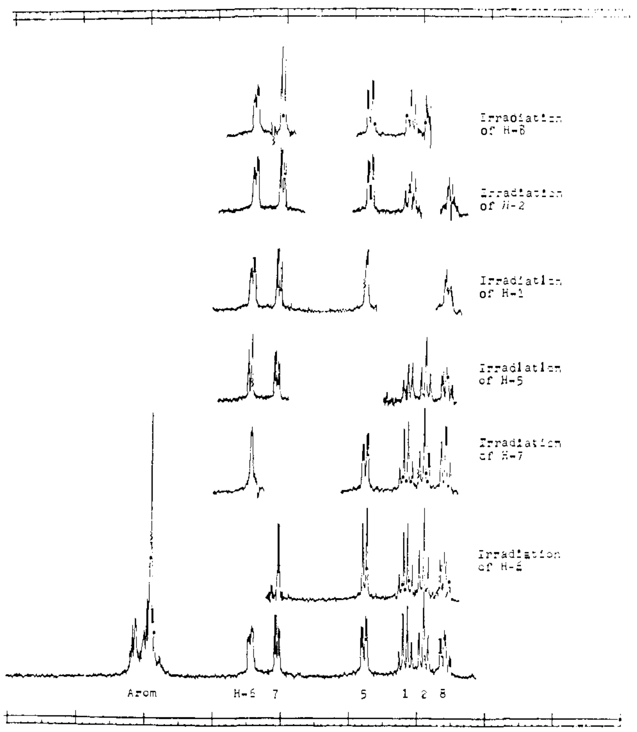
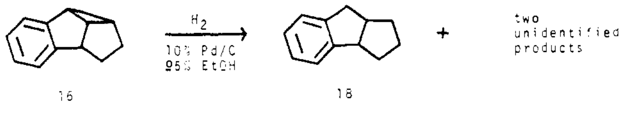


Figure 1. 100-Mc nmr and spin decoupling of benzosemibullvalene.

A final structure proof was obtained by chemical degradation as outlined in Chart VI. Atmospheric hy-

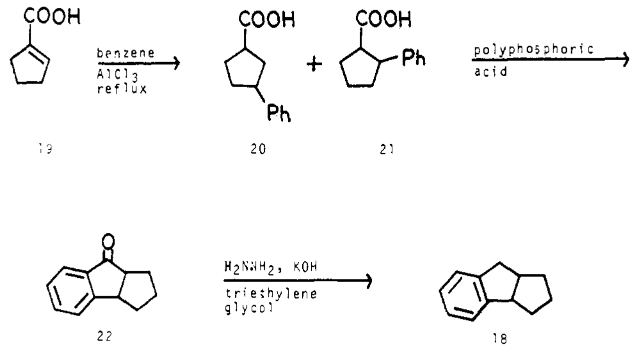
Chart VI. Reduction of Benzosemibullvalene



drogenation of **16** in 95% ethanol with 10% palladium on carbon resulted in the uptake of 1.86 molar equiv of hydrogen. Preparative gas chromatography and silica gel chromatography showed the presence of three products. The major product was a colorless oil identified as 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene (**18**) (Chart VI).

Although **18** had been prepared previously,[6] a different route was chosen for its preparation (note Chart VII). Baker and Leeds have reported the synthesis of 2- and 3-phenyl-1-cyclopentanecarboxylic acids, **21** and **20**, in one step.[7] Both of these were potential precursors to possible benzosemibullvalene hydrogenation products, and this route was selected. Refluxing 1-cyclopentenecarboxylic acid (**19**)[8] in benzene with aluminum chloride afforded a mixture of **19**, **20**, and **21**. Cyclization of the 2-phenyl acid (**21**), mp 86.5–88°, with polyphosphoric acid yielded [2,3]cyclopenta-1-indanone (**22**) which produced, under Wolff–Kishner conditions, the desired hydrocarbon (**18**). This compound (**18**) had an identical ir, nmr, and vpc retention time with the material obtained from the benzosemibullvalene reduction.

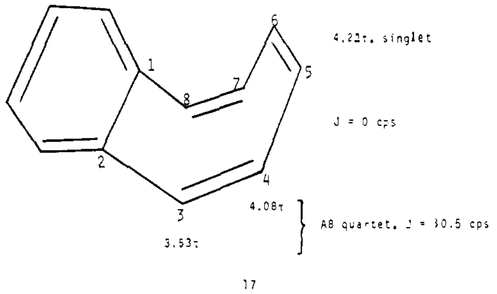
Chart VII. Preparation of 1,2,3,3a,8,8a-Hexahydrocyclopent[*a*]indene



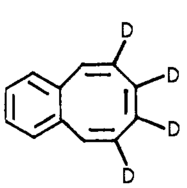
Characterization of Benzocyclooctatetraene. Benzocyclooctatetraene obtained from several sensitized irradiations of benzobarrelene was purified by silica gel chromatography and sublimation to give a colorless solid, mp 48–50°, that turned slightly yellow on standing. It had an infrared spectrum whose "fingerprint" region was identical with that of authentic benzocyclooctatetraene[9] and proved to be identical in all respects with independently synthesized benzocyclooctatetraene.[10]

The nmr of this compound was interesting and the assignment of the vinyl hydrogens proved to be relevant to some of the mechanistic work described later. In addition to the expected A_2B_2 multiplet for the aryl protons, the 100-Mc spectrum showed two sets of vinyl hydrogens at τ 3.53 and 4.08 as an AB quartet (J_{AB} = 10.5 cps) attributed to H-3, H-4, H-7, and H-8 and a two-hydrogen singlet at τ 4.23, which overlapped part of the high-field portion of the quartet. The two-hydrogen singlet was assigned to H-5 and H-6 (Chart VIII). This suggests that the molecule is tub-shaped with dihedral angles about bonds 4–5 and 6–7 not too far from 90°, and this has good analogy with cyclooctatetraene.[11,12]

Chart VIII. Assignment of the Benzocyclooctatetraene Vinyl Protons



The assignment of the peaks deriving from protons 3 and 8 *vs.* 4 and 7 was in doubt, for good models were not readily available. However, benzylic hydrogens tend to be at lower field than allylic ones.[13] Hence, we may tentatively conclude that protons 3 and 8 absorb at lower field than protons 4 and 7. This was born out when the nmr of 4,5,6,7-tetradeuteriobenzocyclooctatetraene (**23**) became available.[16,17]



23

The Preparation of Labeled Benzobarrelene. Since, as noted above, the barrelene to semibullvalene mechanism was elucidated using vinyl-deuterated barrelene by following the original bridgehead hydrogen labels to their locations in semibullvalene, a similar approach promised to reveal the benzobarrelene to benzosemibullvalene pathway. Deuterated benzobarrelene was required for this. As in the barrelene case, treatment of the hydrocarbon with N,N-dideuteriocyclohexylamine—lithium N-deuteriocyclohexylamide[18] exchanged the sp^2-bound hydrogens, leaving the bridgehead positions alone bearing hydrogens.

The deuterated benzobarrelene (**24**) was prepared by treating benzobarrelene with this base at 70–80° in three passes. Silica gel chromatography and sublimation afforded compound **24** as colorless needles, mp 65.5–66°, with undepressed mixture melting point with starting material (**9**). Nmr analysis revealed that there was 86.4 ± 1.2% deuteration in the aryl and vinyl positions, this quantity being derived by assuming no deuterated bridgehead carbon atoms (see Experimental

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(6) H. Pines, N. C. Sin, and E. Lewicki, *J. Org. Chem.*, **30**, 1457 (1965).

(7) W. Baker and W. G. Leeds, *J. Chem. Soc.*, 974 (1948).

(8) P. Maitte, *Bull. Soc. Chim. France*, **24**, 499 (1957).

(9) G. Wittig, H. Eggers, and P. Duffner, *Ann. Chem.*, **619**, 10 (1958).

(10) L. Friedman, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

(11) I. L. Karle, *J. Chem. Phys.*, 20, 65 (1952).

(12) F. A. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962).

(13) See T. Curphey, Ph.D. Thesis, Harvard University, Cambridge, Mass., 1961, for representative values. Additionally, the benzylic cyclopropyl hydrogen of benzosemibullvalene is at lower field than the allylic cyclopropyl proton. This is also true for benzonorcaradiene.[14,15]

(14) E. Vogel, D. Wendish, and W. R. Roth, *Angew. Chem. Intern. Ed. Engl.*, **3**, 442 (1964).

(15) M. Pomerantz and G. W. Gruber, *J. Am. Chem. Soc.*, **89**, 6798 (1967).

(16) W. Merk and R. Pettit, *ibid.*, **90**, 814 (1968).

(17) We thank Professor R. Pettit for a copy of the nmr spectrum of his deuterated benzocyclooctatetraene. Moreover, his unambiguous assignment of the vinyl hydrogens agrees with our interpretation.

(18) This is a modification of the procedure of A. Streitwieser, Jr., and W. C. Langworthy, *ibid.*, **85**, 1757 (1963), differing mainly in the utilization of deuterated base. For an earlier use of this technique see ref 3.

Section for details). Consideration of the number of nonexchanged hydrogens required to fit the mass spectrum confirmed the assumption that only eight positions were exchanging hydrogen for deuterium at an appreciable rate, and only 0.3 ± 0.1% contribution from d_9 and 0% from d_{10} species was found.

Finally, the extent of vinyl deuteration was needed for determining the mechanism of the benzobarrelene to benzosemibullvalene rearrangement. The distribution of hydrogen between aryl and vinyl positions obtained by nmr analysis (see Experimental Section) showed the vinyl positions to be more heavily exchanged; 9.0 ± 0.8% of the vinyl positions was found to bear hydrogen, and correction in all experiments was made for this residue.

The Benzobarrelene to Benzosemibullvalene Transformation. Determination of Skeletal Change by Photolysis of Bridgehead-Labeled Reactant. The acetone-sensitized irradiation of bridgehead-labeled benzobarrelene (**24**) containing the 9.0 ± 0.8% residual vinyl hydrogen (*vide supra*) was carried out as previously described. In each run, the same products were observed as in the photolysis of nondeuterated benzobarrelene (**9**).

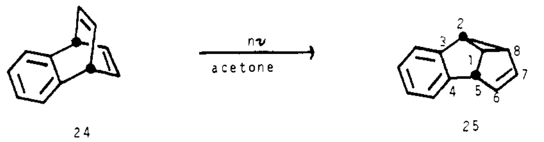
The nmr of deuterated benzosemibullvalene was much simpler than its nondeuterated counterpart (**16**), showing large singlets for H-2 and H-5 with smaller multiplets for the aromatic and remaining nonaromatic positions (note Table II). Qualitatively, the results shown in Table II revealed one proton at each of C-2 and C-5 with lesser but approximately equal amounts of hydrogen at the other positions, suggesting a benzylic–benzylic hydrogen-labeled benzosemibullvalene (**25**). Quantitative comparison of the experimental results with the predicted distribution for **25**, with only benzylic hydrogens and hydrogen resulting from residual vinyl hydrogen in benzobarrelene reactant, showed very good agreement within experimental error, except H-8, which was very slightly low. The rearrangement may therefore be formulated as in Chart IX.

Table II. Hydrogen Atom Distribution of Nonaromatic Positions in Deuterated Benzosemibullvalene Derived from Photolysis

Signal position, τ[a]	Description and assignment[b]	Hydrogen atom distribution[c]: Run 1[d] (est error)[e]	Run 2[d] (est error)[e]	Calcd for **25**[f]	Calcd for **26**[g]
4.43–4.57	Doublet, H-6	0.083 (±0.008)	0.100 (±0.012)	0.090 (±0.008)	0.545 (±0.004)
4.92	Singlet, H-7	0.087 (±0.010)	0.098 (±0.011)	0.090 (±0.008)	0.090 (±0.008)
6.22	Singlet, H-5	0.995 (±0.042)	0.974 (±0.052)	1.000 ...	0.545 (±0.004)
6.68–6.95	Triplet, H-1	0.103 (±0.013)	0.113 (±0.017)	0.090 (±0.008)	0.090 (±0.008)
7.12	Singlet, H-2	0.974 (±0.049)	0.949 (±0.050)	1.000 ...	0.545 (±0.004)
7.27–7.52	Doublet, H-8	0.118 (±0.010)	0.126 (±0.013)	0.090 (±0.008)	0.545 (±0.004)

[a] 60-Mc nmr in CCl_4 with TMS as internal standard. [b] Assignments based on nondeuterated benzosemibullvalene. [c] All distributions normalized to a total of 2.36 H as determined by mass spectral and nmr analysis. [d] Hydrogen distribution calculated from nmr integrations. [e] Errors estimated from the scatter of nmr integrations. [f] **25** is deuterated benzosemibullvalene labeled with hydrogen at C-2 and C-5 and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [g] **26** is a composite containing 50% of **26a** and 50% of **26b**; **26a** is deuterated benzosemibullvalene labeled with hydrogen at C-2 and C-6 and residual vinyl hydrogen from benzobarrelene reactant at the other positions; **26b** is deuterated benzosemibullvalene labeled with hydrogen at C-5 and C-8 and residual vinyl hydrogen from benzobarrelene reactant at the other positions.

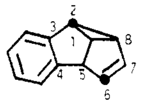
Chart IX. Location of Hydrogen Label in Deuterated Benzobarrelene and Benzosemibullvalene



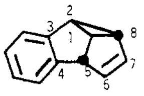
• represents hydrogen; deuterium elsewhere

Additionally, the splittings in the nmr of the rearranged material (**25**) were of interest. The multiplets observed were those which one would predict for **25**. With only 9% residual hydrogen at C-1, C-6, C-7, and C-8, complication of the H-2 and H-5 singlets by splitting proved to be very minor. The probability that there are adjacent hydrogens at two of C-1, C-8, C-7, and C-6 in a given molecule is less than 1%, and the H-7 proton was a singlet in the nmr as predicted. However, positions C-1, C-8, and C-6 are adjacent to C-2 and C-5, which always bear hydrogen, and residual H-1 protons were visibly split as a triplet because they are adjacent to both H-2 and H-5. Also residual H-6 and H-8 protons were split into doublets since they are adjacent to H-5 and H-2, respectively.

Other benzosemibullvalene structures do not seem to have been formed. If structure **26** (see Table II for hydrogen atom distribution), a composite of 50% **26a** and 50% **26b**, had been present to as much as 10% of the total deuterated benzosemibullvalene, the amount of hydrogen predicted for C-8 and C-6 would have been at the limit and above the limit, respectively, of the experimental values.[19] Similarly, other hypothetical deuterated benzosemibullvalenes occurred to no greater extent than 5–10%. Thus, **25** was formed in greater than 9:1 preference over any other benzosemibullvalene structure in the acetone-sensitized irradiation of bridgehead-labeled benzobarrelene. The significance of the formation of **25** will be discussed later in the paper.



26a



26b

• represents hydrogen; deuterium elsewhere

The small amount of deuterated benzocyclooctatetraene obtained from the two sensitized runs was combined and gave the results shown in Table III. The original hydrogen label appeared only in the two lower field signals and not in the high-field singlet, which had a hydrogen content exactly that due to residual vinyl hydrogen in one bridge of deuterated benzobarrelene. Comparison of three deuterated benzocyclooctatetraene structures of interest—**27**, **28**,

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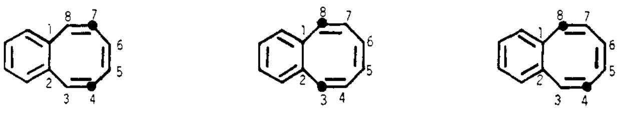
[19] The quantity of hydrogen at C-2 and C-5 could have been used to calculate this limit. However, these positions are less sensitive to changes in the hydrogen distribution because the relative magnitude of the experimental error is four to five times larger than for C-8 and C-6.

Table III. Hydrogen Atom Distribution of Nonaromatic Positions in Deuterated Benzocyclooctatetraene from Sensitized Irradiation of Deuterated Benzobarrelene

Signal position, τ^a	Description and assignment[b]	Hydrogen atom distribution[c] Exptl[d] (error)[e]	Calcd for **27**[f]	Calcd for **28**[g]	Calcd for **29**[h]
3.42–3.68	Multiplet,[i] H-3 and H-8	0.404 (±0.034)	0.180 (±0.016)	2.000 ...	1.090 (±0.008)
4.08	Singlet,[j] H-4 and H-7	1.759 (±0.106)	2.000 ...	0.180 (±0.016)	1.090 (±0.008)
4.22	Singlet,[j] H-5 and H-6	0.197 (±0.044)	0.180 (±0.016)	0.180 (±0.016)	0.180 (±0.016)

[a] 60-Mc nmr in CCl_4 with TMS as internal standard. [b] Assignments based on nondeuterated benzocyclooctatetraene. [c] All distributions normalized to a total of 2.36 H as determined by mass spectral and nmr analysis. [d] Hydrogen distribution calculated from nmr integrations. [e] Errors estimated from the scatter of nmr integrations. [f] **27** is deuterated benzocyclooctatetraene labeled with hydrogen at C-4 and C-7 and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [g] **28** is deuterated benzocyclooctatetraene labeled with hydrogen at C-3 and C-8 and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [h] **29** is deuterated benzocyclooctatetraene labeled with hydrogen at C-3 and C-4 or C-7 (formally the same) and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [i] Comprises a doublet, τ 3.46 and 3.67 (half an AB quartet), and an overlapping singlet, τ 3.57. [j] Slight overlap of τ 4.08 and 4.22 singlets.

and **29**—with the experimental results suggested the preponderant formation of **27** with lesser amounts of either **28** or **29** (87.5 ± 2.5% of **27** and 12.5 ± 2.5% of **28** or 75 ± 5% of **27** and 25 ± 5% of **29**). Structural considerations discussed below, however, favored the formation of **28** and not **29** as the minor process here.

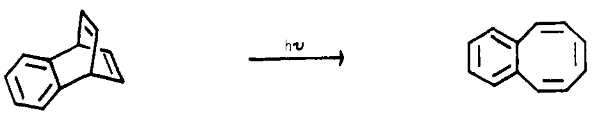


27 28 29

• represents hydrogen; deuterium elsewhere

The Direct Irradiation of Benzobarrelene and Labeled Benzobarrelene. It was of interest to look at the direct irradiation of benzobarrelene to determine the importance of added acetone sensitizer on the reaction. In unsensitized runs made to 22–78% reaction of benzobarrelene only benzocyclooctatetraene resulted, and no benzosemibullvalene could be detected (Chart X).

Chart X. Direct Irradiation of Benzobarrelene



9 17

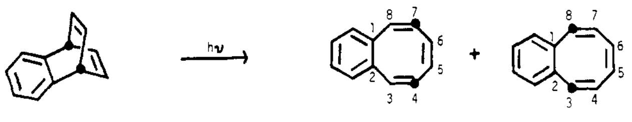
Table IV. Hydrogen Atom Distribution of Nonaromatic Positions in Deuterated Benzocyclooctatetraene from Direct Irradiation of Deuterated Benzobarrelene

Signal position, τ^a	Description and assignment[b]	Hydrogen atom distribution[c] Exptl[d] (error)[e]	Calcd for **27**[f]	Calcd for **28**[g]
3.42–3.67	Multiplet,[h] H-3 and H-8	0.288 (±0.035)	0.180 (±0.016)	2.000 ...
4.10	Singlet,[i] H-4 and H-7	1.883 (±0.121)	2.000 ...	0.180 (±0.016)
4.22	Singlet,[i] H-5 and H-6	0.189 (±0.039)	0.180 (±0.016)	0.180 (±0.016)

[a] 60-Mc nmr in CCl_4 with TMS as internal standard. [b] Assignments based on nondeuterated benzocyclooctatetraene. [c] All distributions normalized to a total of 2.36 H as determined by mass spectral and nmr analysis. [d] Hydrogen distribution calculated from nmr integrations. [e] Errors estimated from the scatter of nmr integrations. [f] **27** is deuterated benzocyclooctatetraene labeled with hydrogen at C-4 and C-7 and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [g] **28** is deuterated benzocyclooctatetraene labeled with hydrogen at C-3 and C-8 and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [h] Comprises a doublet at τ 3.45 and 3.65 (half of an AB quartet) and an overlapping singlet at τ 3.57. [i] Slight overlap of τ 4.10 and 4.22 singlets.

When the experiment was repeated on bridgehead-labeled benzobarrelene (**24**) containing 9.0 ± 0.8% residual vinyl hydrogen, the deuterated benzocyclooctatetraene which resulted had the nonaromatic hydrogen atom distribution shown in Table IV. Most of the hydrogen label was now at C-4 and C-7 of benzocyclooctatetraene with lesser amounts in the C-3 and C-8 positions and none at all in the other two. Comparison of the predicted distribution for structures **27** and **28** with experiment led to an estimation of 94 ± 3% of **27** and 6 ± 3% of **28** (Chart XI). Inspection of Table IV shows no third species in which the hydrogen label has enriched positions 5 and 6. One might worry, however, that the low percentage predicted for **28** was uncomfortably close to experimental error. But inspection of the pattern of the low-field multiplet for C-3 and C-8 hydrogens did reveal the presence of **28** in addition to **27**. Thus, the low-field signal for **27**, arising from residual hydrogen, was discernible as half an AB quartet with the same chemical shift as that of nondeuterated benzocyclooctatetraene (**17**). Similarly, the hydrogen label in the 6% of **28** was detected as a low-field singlet whose chemical shift was identical with that calculated for the low-field proton of the AB quartet of nondeuterated benzocyclooctatetraene (**17**).

Chart XI. Direct Irradiation of Labeled Benzobarrelene



24 27 28

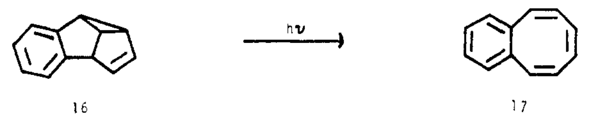
• represents hydrogen; deuterium elsewhere

One assumption that was made needs to be stated explicitly. Although there is no question that **27** is the major component of the benzocyclooctatetraene, the assignment of **28** as the minor component is not unambiguous. **29** has part of the hydrogen label in the benzylic positions and the remainder in a position whose chemical shift would be buried under the singlet due to the hydrogen label of **27**. Hence, **29** is indistinguishable from **28** by nmr. The choice of **28** is based on the simple presumption that the starting material **24** with hydrogen labels 1,4 related should not be converted to a product (*i.e.*, **29**) in which the hydrogens are 1,5 related (note Discussion sections to follow).

In conclusion, direct irradiation of bridgehead-labeled benzobarrelene (**24**) afforded mainly benzocyclooctatetraene labeled with hydrogen at carbons 4 and 7 (**27**) and a minor amount labeled at 3 and 8 (**28**).

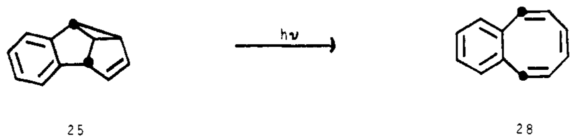
Photolysis of Benzosemibullvalene and Labeled Benzosemibullvalene. Still another aspect seemed of interest. Benzocyclooctatetraene was observed in addition to benzosemibullvalene in the sensitized runs. Although it is known (*vide supra*) that direct irradiation can give benzocyclooctatetraene, one might question whether any benzocyclooctatetraene arises from a secondary reaction of benzosemibullvalene. Indeed, the differing hydrogen distributions of deuterated benzocyclooctatetraene obtained from the direct and sensitized irradiation of bridgehead-labeled benzobarrelene (**24**) suggested that some benzocyclooctatetraene was coming from the irradiation of benzosemibullvalene. For this reason and for comparison with our previously reported acetone-sensitized semibullvalene to cyclooctatetraene rearrangement,[2] it was decided to look at the direct and sensitized irradiations of benzosemibullvalene. Interestingly, direct irradiation in isopentane afforded only benzocyclooctatetraene (Chart XII). In contrast, irradiation under identical conditions with acetone present led mainly to higher molecular weight material and a trace of benzocyclooctatetraene, probably arising from direct irradiation of benzosemibullvalene, which captured approximately 55% of the light as a minimum.

Chart XII. Direct Irradiation of Benzosemibullvalene



Repeating the direct irradiation on deuterated benzosemibullvalene (**25**) labeled with hydrogen at C-2 and C-5 and containing 9.0 ± 0.8% hydrogen at the other nonaromatic positions yielded (see Chart XIII) a small amount of deuterated benzocyclooctatetraene with the hydrogen label mainly at C-3 and C-8. The exact hydrogen atom distribution is shown in Table V, and can be seen to fit **28** rather than **27**. This is in contrast to the previously described direct irradiation of labeled benzobarrelene. One could not rule out, however, the possibility of a small percentage of other deuterated benzocyclooctatetraene structures because of a rather large error in the hydrogen atom distribution in this particular experiment.

Chart XIII. Direct Irradiation of Deuterated Benzosemibullvalene Labeled with Hydrogen at C-2 and C-5



• represents hydrogen; deuterium elsewhere

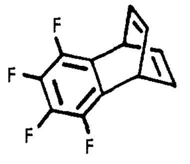
Table V. Hydrogen Atom Distribution of Nonaromatic Positions in Deuterated Benzocyclooctatetraene from Direct Irradiation of Deuterated Benzosemibullvalene Labeled with Hydrogen at C-2 and C-5

Signal position, τ^a	Description and assignment[b]	—Hydrogen atom distribution[c]— Exptl[d] (error)[e]	Calcd for **27**[f]	Calcd for **28**[g]
3.55	Singlet, H-3 and H-8	1.986 (±0.244)	0.180 (±0.016)	2.000 ...
4.05	Singlet,[h] H-4 and H-7	0.160 (±0.079)	2.000 ...	0.180 (±0.016)
4.23	Singlet, H-5 and H-6	0.214 (±0.073)	0.180 (±0.016)	0.180 (±0.016)

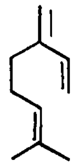
[a] 60-Mc nmr in CCl_4 with TMS as internal standard. [b] Assignments based on nondeuterated benzocyclooctatetraene. [c] All distributions normalized to a total of 2.36 H as determined by mass spectral and nmr analysis. [d] Hydrogen distribution calculated from nmr integrations. [e] Errors estimated from the scatter of nmr integrations. [f] **27** is deuterated benzocyclooctatetraene labeled with hydrogen at C-4 and C-7 and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [g] **28** is deuterated benzocyclooctatetraene labeled with hydrogen at C-3 and C-8 and residual vinyl hydrogen from benzobarrelene reactant at the other positions. [h] Lesser peak of this half of AB quartet predicted for the residual hydrogen of **28** is buried under the τ 4.23 singlet.

Discussion of Results

Multiplicities in the Benzobarrelene Photochemistry. Because acetone sensitization is necessary for the production of benzosemibullvalene, we can conclude that the reaction proceeds from the triplet excited state of benzobarrelene. Direct irradiation, on the other hand, affords only benzocyclooctatetraene, which means that the singlet excited state of benzobarrelene leads to this product. Also, the intersystem crossing from the excited singlet state of benzobarrelene to its triplet must be relatively inefficient since no benzosemibullvalene is formed on direct irradiation. Thus, this is one of the rare examples in photochemistry where the excited singlet and triplet states exhibited different intramolecular reactivity. Other examples of this phenomenon are the rearrangements of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (**30**)[20] and myrcene (**31**).[22]



30



31

Structural Aspects of the Benzobarrelene to Benzosemibullvalene Transformation. One of the most intriguing aspects of the whole problem is the pathway taken by the triplet excited state of benzobarrelene to form benzosemibullvalene. Two initial bonding processes seem possible, namely vinyl–vinyl bonding (mechanism I) and benzo–vinyl bridging (mechanism II) as seen in Chart XIV. It can be seen that the distribution of hydrogen in the deuterated benzosemibullvalene depends on which initial bonding process occurs. Mechanism I, beginning with vinyl–vinyl bridging, leads to a benzylic–benzylic hydrogen-labeled benzosemibullvalene (**25**), whereas mechanism II, involving

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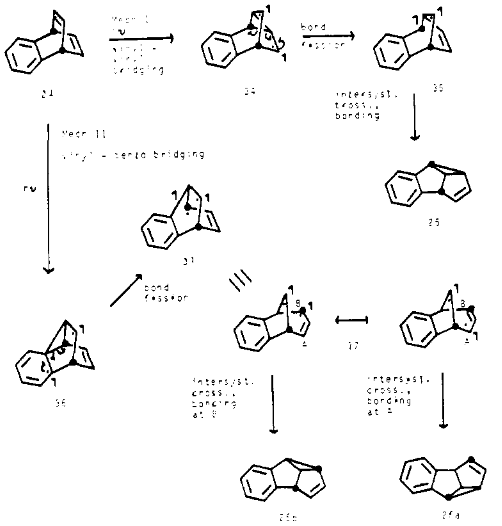
(20) After the structural features of the present study were complete, the related photochemical study of **30** appeared.[21] The photoproducts were assigned as tetrafluorobenzosemibullvalene (**32**) and tetrafluorobenzocyclooctatetraene (**33**) on the basis of nmr, mass spectral evidence, and analogy to the barrelene case.[2] Evidence was found for the same dependence on multiplicity as presently described but intersystem crossing did compete to some extent with singlet rearrangement, in contrast to the present study.

(21) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967).

(22) (a) K. J. Crowley, *Proc. Chem. Soc.*, 245 (1966); (b) K. J. Crowley, *ibid.*, 334 (1962); (c) K. J. Crowley, *Tetrahedron*, 21, 1001 (1965); (d) R. S. H. Liu and G. S. Hammond, *J. Am. Chem. Soc.*, 86, 1892 (1964); (e) R. S. H. Liu and G. S. Hammond, *ibid.*, 89, 4936 (1967); (f) W. G. Dauben, R. L. Cargill, R. M. Coates, and J. Saltiel, *ibid.*, 88, 2742 (1966).

Chart XIV. Benzobarrelene to Benzosemibullvalene Rearrangement; Initial Vinyl–Vinyl Bridging *vs.* Benzo–Vinyl Bridging

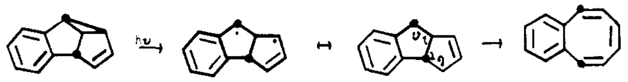


• signifies hydrogen; deuterium elsewhere

initial benzo–vinyl bridging, would afford deuterated benzosemibullvalene with equal amounts of the label at C-2, C-5, C-6, and C-8 (50% **26a** and 50% **26b**). The finding that the label is totally in the benzylic positions within experimental error can be construed to signify that mechanism I, with initial vinyl–vinyl bridging, is the pathway followed.[23] The rationale for this preference is discussed below.

The Conversion of Benzosemibullvalene to Benzocyclooctatetraene. Because semibullvalene is known to rearrange to cyclooctatetraene,[2] it is of special interest to consider the irradiation of benzosemibullvalene. The fact that direct irradiation of deuterated benzosemibullvalene (**25**) yielded deuterated benzocyclooctatetraene (**28**) with the hydrogen label in the benzylic positions strongly suggests that the excited state of benzosemibullvalene ruptures the 2–8 cyclopropyl bond to form a stabilized benzylic and allylic diradical, **38**, followed by 1–5-bond fission as shown in Chart XV.

Chart XV. Benzosemibullvalene to Benzocyclooctatetraene Rearrangement



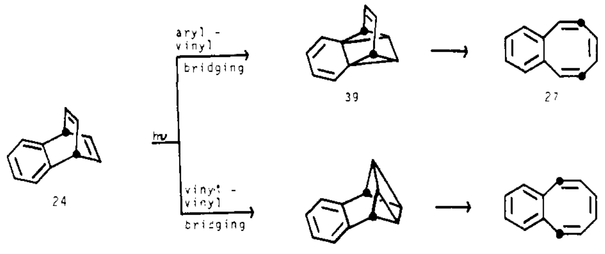
25 38 28

• signifies hydrogen; deuterium elsewhere

The multiplicity of the benzosemibullvalene to benzocyclooctatetraene rearrangement cannot be ascertained unequivocally from the data at hand. The interpretation of the acetone sensitization experiments is unclear because of an apparent reaction of acetone sensitizer with benzosemibullvalene[24] and unavoidable light absorption of the benzosemibullvalene. We conclude that benzocyclooctatetraene can be formed in a two-step process: triplet rearrangement of benzobarrelene to benzosemibullvalene followed by direct irradiation of benzosemibullvalene.

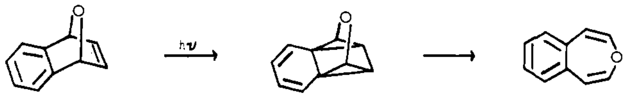
The Direct Formation of Benzocyclooctatetraene from Benzobarrelene. In addition, benzocyclooctatetraene must arise by a direct route not involving benzosemibullvalene as an intermediate. The fact that direct irradiation of benzobarrelene affords no benzosemibullvalene (*vide supra*) strongly suggests a direct route. When no sensitizer is employed benzobarrelene gives a composite of 94 ± 3% **27** and 6 ± 3% **28.** These facts imply that the direct irradiation proceeds by two routes, both different from that utilizing benzosemibullvalene as an intermediate. The predominant route is seen (Chart XVI) to involve initial benzo–vinyl cycloaddition and the minor one to proceed by initial vinyl–vinyl bridging. The formation of **27** is related to the recently reported 1,4-epoxy-1,4-dihydronaphthalene (**41**) to benz[*f*]oxepin (**43**) rearrangement (Chart XVII).[27]

Chart XVI. Benzobarrelene to Benzocyclooctatetraene Rearrangement



• represents hydrogen; deuterium elsewhere

Chart XVII. Rearrangement of 1,4-Epoxy-1,4-dihydronaphthalene



41 42 43

The formation of **43** was reported to proceed by an excited singlet because no **43** was formed on sensitization.

Of additional interest, the deuterated benzocyclooctatetraene obtained as a by-product in the acetone-sensitized rearrangement of deuterated benzobarrelene (**24**) had a hydrogen distribution which was intermediate between the benzocyclooctatetraene obtained from the direct irradiation of deuterated benzobarrelene and from deuterated benzosemibullvalene (**25**). This demonstrates that benzocyclooctatetraene does come from two routes in these runs. Approximately 5 to 10% of the benzocyclooctatetraene comes from the benzosemibullvalene rearrangement and the remainder from the direct irradiation of benzobarrelene.

Generalities of the Reaction and Different Types of Bonding of the Singlet *vs.* Triplet. The triplet reaction of benzobarrelene is another example of the divinylmethane or di-π-methane rearrangement we previously reported[3] as general. It is worthwhile surveying pertinent examples for comparison and contrast with benzobarrelene.

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(23) Other hypothetical reaction routes have been considered. None of them gives the correct distribution of hydrogen in deuterated benzosemibullvalene.

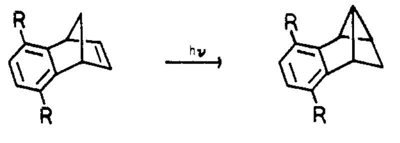
(24) When one observes a bimolecular reaction between a sensitizer and potential reactant rather than the desired unimolecular reaction, no conclusion may be drawn concerning the multiplicity of the desired reaction. Thus D. R. Arnold, R. L. Hinman, and A. H. Glick, *Tetrahedron Letters*, 1425 (1964), and H. D. Scharf and F. Korde, *ibid.*, 821 (1963), have observed, in ketone–olefin systems, energy transfer when E_T(ketone) > E_T(olefin) and oxetane formation when E_T(ketone) $\lesssim$ E_T(olefin). In the present case, the triplet energies of acetone sensitizer (E_T = *ca.* 80 kcal/mol[25]) and benzene (E_T = 84.2 kcal/mol[26]) are similar.

(25) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(26) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(27) G. R. Ziegler and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 513 (1968).

Edman has reported the rearrangement of two benzonorbornadienes, **44a** and **44b**, to the corresponding tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8,10-trienes, **45a** and **45b**, on acetophenone sensitization (eq 1).[4c] Unlike benzobarrelene, direct irradiation of **44b** afforded no **45b** while **44a** formed **45a** only very slowly.

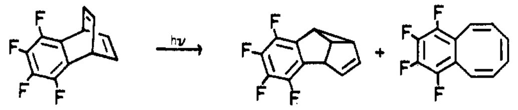


(1)

44 45

a) R = H
b) R = OAc

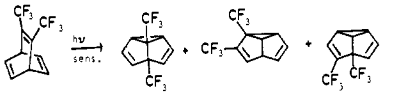
Rearrangement of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (**30**) on acetone sensitization has been shown to give mainly tetrafluorobenzosemibullvalene (**32**) plus a trace of tetrafluorobenzocyclooctatetraene (**33**) (eq 2).[21] **33** was the major product, however, on direct irradiation.



(2)

30 32 33

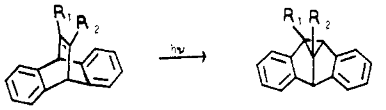
Sensitization of 2,3-bis(perfluoromethyl)bicyclo[2.2.2]octa-2,5,8-triene (**46**) led to three bis(perfluoromethyl)tricyclo[3.3.0.0^{2,8}]octa-3,6-dienes, **47**–**49** (eq 3),[4a] analogous to the parent compound, barrelene.[2] The divinylmethane rearrangement mechanism proposed for the barrelene to semibullvalene conversion nicely accounts for the formation of the three products, and these three isomers are the only ones predicted by our mechanism.



(3)

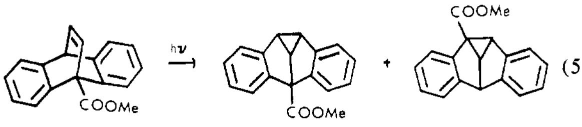
45 41 49 49

Ciganek has reported the rearrangement of a series of dibenzobarrelenes, **50a**–**e**, to **51a**–**e** on acetone sensitization (eq 4).[4b] Again the products are those expected from our di-π-methane mechanism. Direct irradiation of **50a**–**d** was reported to give **51a**–**d** again as the only photoproducts, although the reaction was slower in each one. In addition, the unsymmetrical dibenzobarrelene **50e** afforded **51e** in greater than 95% preference over other dibenzosemibullvalenes. The isomerization of **52** was also shown to lead to a mixture of **53** and **54** in a 2:1 ratio, respectively (eq 5). These are the two products anticipated by the general mechanism.



50 51 (4)

a) R_1, R_2 = H
b) R_1, R_2 = COOMe
c) R_1, R_2 = CN
d) R_1, R_2 = CF_3
e) R_1 = H, R_2 = COOMe

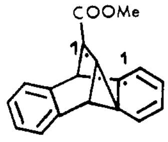


(5)

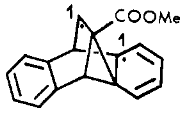
52 53 54

Each of these bicyclic dienes and trienes undergoes the divinylmethane rearrangement from its triplet state. It appears to be a general phenomenon for these types of compounds.

One example is of special interest, namely the rearrangement of **50e**, where the triplet showed selectivity in the choice of initial bonding. That **51e** was the major dibenzosemibullvalene formed (over 95%) from **50e** can be interpreted most simply to mean that initial bonding to give **55** is favored over **56** as a consequence of the odd-electron stabilization by the carbomethoxy group.



55



56

Hence, electronic effects are important in determining the course of initial bonding in the triplet divinylmethane rearrangement. The case of benzobarrelene is especially intriguing to consider, for as we have noted above, despite vinyl–vinyl and benzo–vinyl bridging both being *a priori* possibilities, only vinyl–vinyl bridging is observed. The electronic source of this preference is less obvious than in the case of the substituted dibenzobarrelene **50e**. Furthermore, there is the dramatically different singlet behavior where benzo–vinyl bridging is the preferred course, and any rationale must consider the difference between singlet and triplet behavior.

In the case of the triplet process, the preferred vinyl–vinyl bridging can be understood on the following basis. First, we note that as the vinyl groups begin to bond with endwise overlap, this part of the system is approximated electronically by cisoid butadiene. Alternatively, as a vinyl group begins to overlap endwise with the benzo group, an approximate styryl moiety is engendered. Thus, we should be able to compare the energies of the two types of bridging species qualitatively by comparing the energy of cyclohexadiene triplet (E_T = 53.5 kcal/mol[28]) with that of the styryl triplet (E_T(styrene) = 61.8 kcal/mol;[26] E_T(*trans*-β-methylstyrene) = 59.8 kcal/mol[29]).

It is of interest to note that in the initial triplet, prior to bridging, the excitation is probably more heavily weighted in the vinyl portions of the molecule since the triplet energy of ethylene (E_T = 82.1 kcal/mol[22]) is lower than that of benzene (E_T = 84.2 kcal/mol[26]). Thus, the preferred reaction is in the portion of the molecule in which initial excitation is most heavily distributed.

Turning finally to the singlet reaction, suitable models for the perturbed system are not available. However, we find that the singlet excited state of benzene is

[28] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[29] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 43, 2129 (1965).

much lower in energy (*i.e.*, long-wavelength absorption λ_{max} 260 mμ[30a]) than that of ethylene (long-wavelength absorption λ_{max} 160 mμ[30b,31]) and the preferential reaction of the benzo and vinyl groups parallels the preferred reaction of the most excited portions of the molecule in the triplet case. However, four-centered processes become preferred when paired electrons are present and the unsymmetrical cyclization is not enforced. It is of some interest to note that both of the major singlet processes, benzo–vinyl and vinyl–vinyl bridging, are symmetry allowed when correlation diagrams are considered.[33]

Experimental Section[36]

1,4-Dihydro-1,4-ethenonaphthalene (Benzobarrelene). This was prepared by a modification of the procedure described by Kitahonoki and Takano (*vide infra*).[5]

1,4-Dihydro-9-oxo-1,4-ethanonaphthalene.[37] A suspension of 250 g (0.961 mol) of 1,2,3,4-tetrahydro-9-oxo-1,4-ethanonaphthalene-2,3-*endo*-dicarboxylic acid,[38] 1 l. of dry benzene, and 170 ml of dry pyridine was heated at 55° for 2 hr under nitrogen. A vigorous reaction occurred when 440 g (0.992 mol) of lead tetraacetate and 0.290 g (1.45 mmol) of cupric acetate hydrate were added. The dark solution was stirred at 55° for 3 hr; dilute nitric acid (800 ml, 10%) was added and the two phases were stirred for 12 hr. The aqueous phase was separated and the benzene repeatedly extracted with 20% potassium hydroxide and water.

The reaction was repeated on 100, 224, 250, and 250 g of the diacid. The combined organic layer was dried and removed *in vacuo* leaving 220 g of dark viscous oil.

The oil was chromatographed on a 6.5 × 120 cm silica gel column (Davison, 60–200 mesh, grade 950) slurry packed in 1% ether–hexane. Elution was with 8 l. of 1%, 6 l. of 2%, 6 l. of 4%, 6 l. of 7%, and 21 l. of 10% ether–hexane, and 1-l. fractions were collected. Fractions 27–47 contained 86.84 g of a yellow oil that was crystallized from hexane–ether giving 78.66 g (0.462 mol, 11.2%) of white crystals of 1,4-dihydro-9-oxo-1,4-ethanonaphthalene, mp 55.5–56.6° (lit.[5] 56.5–58°).

Epimeric 1,4-Dihydro-9-hydroxy-1,4-ethanonaphthalenes. To a solution of 78.66 g (0.462 mol) of 1,4-dihydro-9-oxo-1,4-ethanonaphthalene and 900 ml of 95% ethanol, cooled to 0°, was added 11.2 g (0.296 mol) of sodium borohydride. The solution was stirred for 12 hr at room temperature; 400 ml of water was added and the solution stirred for 1 hr. The ethanol was removed *in vacuo* and the epimeric alcohols were ether extracted. The ether was dried and removed *in vacuo* giving 73.77 g (0.428 mol, 92.6%) of a mixture, mp 64–67°, of the epimeric 1,4-dihydro-9-hydroxy-1,4-ethanonaphthalenes.

The infrared spectrum (CS$_2$) showed bands at 2.75–3.20 (br), 3.25, 3.30, 3.37, 3.40 (sh), 3.49, 7.20, 7.43, 7.50–8.50 (several small bands), 8.72, 9.01, 9.45, 9.73, 10.01, 10.10 (sh), 10.39, 10.70, 12.05, 13.38, 14.23, 14.50, and 15.28 μ; nmr (CDCl$_3$) τ 2.67–3.08 multiplet (4 H, aromatic), 3.08–3.83 multiplet (2 H, vinyl), 5.67–6.33 multiplet (2 H, bridgehead; 1 H, methine), and 7.50–9.33 multiplet (2 H, CH$_2$; 1 H, OH).

Anal. Calcd for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.68; H, 7.12.

Benzobarrelene. After stirring a solution of 7.52 g (43.7 mmol) of the epimeric 1,4-dihydro-9-hydroxy-1,4-ethanonaphthalenes in 200 ml of dry benzene for 30 min under nitrogen, 1.69 g (0.070 mol, 2.84 g of a 59.5% suspension in mineral oil washed with benzene) of sodium hydride and 0.05 ml of 95% ethanol were added. After 3 hr, 15.0 ml (18.9 g, 0.284 mol) of carbon disulfide was added, followed by 15.0 ml (34.2 g, 0.241 mol) of methyl iodide after another 4.5 hr. The mixture was stirred for 19 hr, and the excess sodium hydride was destroyed by addition of water. The benzene phase was washed with water, dried, and concentrated *in vacuo* yielding 10.25 g of an orange oil.

The infrared spectrum (CS$_2$) showed strong bands at 8.20 and 9.40 μ characteristic for xanthate esters.[39] The nmr (CDCl$_3$) showed S-methyl singlets at τ 7.50 and 7.80. The xanthate ester was used without purification.

The 10.25 g of xanthate ester was heated neat at 225–230° for 35 min producing 8.90 g of a yellow oil. This was chromatographed on a 4.5 × 65 cm alumina (Fisher, 60–200 mesh) column slurry packed in hexane. All fractions were eluted with hexane, and the fraction size was 250 ml. Fractions 4–21 contained 4.75 g of a yellow solid that was chromatographed on a 4 × 95 cm column slurry packed in 1% ether–hexane with silica gel (Davison, 60–200 mesh, grade 950). Elution was with 15.75 l. of hexane and 3.75 l. of 4% ether–hexane, and the fraction size was 250 ml. Fractions 13–25 contained 1.34 g of a white solid, mp 79–80°, identified as naphthalene. Fractions 43–63 contained 75.1 mg of a yellow oil which was not investigated. Fractions 67–78 contained 1.99 g of essentially pure benzobarrelene as a faintly yellow solid, mp 63–66°.

The benzobarrelene was sublimed at 85° giving 1.76 g (11.4 mmol, 26.1% based on 43.7 mmol of the epimeric alcohols) of colorless needles, mp 65.5–66° (lit.[5,40] 65.5–66.5° and 65.0–65.5°). The melting point was unchanged on recrystallization from pentane.

The ir (CS$_2$) showed bands at 3.24, 3.30, 3.34, 6.20, 7.52, 8.18, 8.36, 8.76, 9.05, 9.81, 10.28, 10.83, 11.11, 12.63, 13.35, 14.41, and 15.19 μ; nmr (CCl$_4$) τ 2.80–3.38 multiplet (4 H, aromatic; 4 H, vinyl) and 5.10–5.38 multiplet (2 H, bridgehead); uv$_{max}$ (cyclohexane) 277 mμ (ϵ 710), 270 (670), 263 (470), and 233 sh (1100); mass spectrum (70 eV)[41] parent ion 154 and most intense ion 153.

Anal. Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.39; H, 6.42.

Acetone-Sensitized Photolysis of Benzobarrelene. A solution of 408.0 mg (2.65 mmol) of benzobarrelene, 2.50 ml (1.98 g, 0.034 mol) of reagent grade acetone, and 40 ml of isopentane was sealed under vacuum in a 2 × 18 cm, 50-ml Vycor tube. The tube was strapped to a water-cooled, quartz immersion well and photolyzed with a 450-W Hanovia medium-pressure mercury lamp for 135 min with external ice–water cooling. The seal was broken and concentration of the slightly cloudy solution *in vacuo* gave 405.0 mg of an orange oil.

This was subjected to liquid–liquid partition chromatography. A 4 × 150 cm water-jacketed column (28°) was dry packed, first, with a 5-cm layer of sand and, the remainder, with 700 g of Celite (Eagle Picher Co., Celatom FW-80) impregnated with a solution of 200 g (1.18 mol) of silver nitrate in 160 ml of distilled water. The column was eluted with water-saturated ether. The eluent absorbance was scanned at 255 mμ, and fractions of 40 ml were collected.

Four peaks were observed on the scan: fractions 34–39, 13.7 mg of an orange oil; 43–48, 196.1 mg of essentially pure 3,4-benzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (benzosemibullvalene) as a yellow oil; 62–70, 21.8 mg of benzocyclooctatetraene, mp 34–46°; and, 88–104°, 190.7 mg of benzobarrelene, mp 59–66°.

Characterization of Benzosemibullvalene. The 196.1 mg of benzosemibullvalene above was purified by gradient temperature (36 to 136°) molecular distillation in a 6 mm × 1 m tube *in vacuo* (2.0 mm). The tube was pretreated with 1% dichlorodimethylsilane–benzene. There was isolated 136.3 mg (0.88 mmol) of colorless oil. The infrared spectrum (CS$_2$) showed bands at 3.26 (sh), 3.28, 3.30 (sh), 3.38; weak bands 7.41 to 7.97, 8.21, 8.62 (br),

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(30) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules " John Wiley and Sons, Inc., New York, N. Y., 1963: (a) p 127; (b) p 51.

(31) The uv spectrum of *o*-xylene[32] and those of benzobarrelene (this work and ref 5), 1,4-etheno-1,2,3,4-tetrahydronaphthalene,[5] and 1,4-ethano-1,2,3,4-tetrahydronaphthalene[5] are very similar above 230 mμ. The excitation energy must be heavily localized in the benzene ring in these cases.

(32) M. J. Kamlet, Ed., "Organic Electronic Spectral Data," Vol. 1, Interscience Publishers, New York, N. Y., 1960, p 203.

(33) Vinyl–vinyl bridging is a 2 + 2 cycloaddition predicted to be photochemically allowed by the considerations of Hoffmann and Woodward[34] or from the circle device introduced by Zimmerman.[35] Similarly, benzo–vinyl bridging can be shown to involve crossing of one bonding and one antibonding MO of reactant proceeding to product, and is photochemically allowed. The device of Zimmerman would treat this as a perturbed cyclic eight-orbital system with no sign inversions in the basis set and thus allowed photochemically.

(34) R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, 87, 2046 (1965).

(35) (a) H. E. Zimmerman, *ibid.*, 88, 1564 (1966); (b) H. E. Zimmerman, *Science*, **153**, 837 (1966).

(36) All melting points were taken on a hot-stage apparatus calibrated with known samples.

(37) This preparation follows the scheme described without experimental detail by Kitahonoki and Takano.[5]

(38) R. C. Cookson and N. Waryar, *J. Chem. Soc.*, 2303 (1956).

(39) T. Taguchi and M. Nakao, *Tetrahedron*, 18, 245 (1962).

(40) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, 85, 1798 (1963).

(41) We thank Mr. R. McKelvey for running the mass spectrum.

9.82, 10.03, 10.12, 10.46, 10.65, 10.79, 11.10, 11.46, 11.65, 12.10, 12.52; intense bands at 12.85, 13.35, 13.58, and 13.75, 14.72, and 15.11 μ; uv$_{max}$ (95% ethanol) 281 mμ (ϵ 930), 274 (1100), and 268 sh (930); mass spectrum (70 eV)[41] parent ion 154 and most intense ion 153; nmr (CCl_4) τ 2.67–3.20 multiplet (4 H, aromatic), 4.43–4.62 ABX quartet (1 H, vinyl H-6 next to benzylic H-5, $J_{6.7}$ = 5.0 cps, $J_{5.6}$ = 2.0 cps), 4.83–5.00 ABX quartet (1 H, vinyl H-7 next to cyclopropyl H-8, $J_{6.7}$ = 5.0 cps, $J_{7.8}$ = 2.0 cps), 6.10–6.28 ABX quartet (1 H, benzylic and allylic H-5, $J_{5.6}$ = 2.0 cps, $J_{1.5}$ = 6.0 cps), 6.62–7.22 sextet (1 H, interior cyclopropyl H-1; 1 H, cyclopropyl and benzylic H-2), and 7.25–7.55 ABCX doublet of triplet (1 H, cyclopropyl and allylic H-8, $J_{7.8}$ = 2.0 cps, $J_{1.8}$ = 6.5 cps); 100-Mc nmr (CCl_4)[42] spectrum unchanged except for the sextet τ 6.62–7.22 splitting into τ 6.74–6.98 ABCD quartet (1 H, interior cyclopropyl H-1, $J_{1.5}$ = $J_{1.2}$ = $J_{1.8}$ = 6.5 cps), and 7.02–7.25 ABC triplet (1 H, cyclopropyl and benzylic H-2, $J_{1.2}$ = $J_{2.8}$ = 6.0 cps). Double resonance was performed on the 100-Mc nmr. Protons that were not affected or were in the oscillating side band are not included. Irradiation of H-6 (547 cps, 200 mV) collapsed H-7 to a doublet ($J_{2.8}$ = 2.0 cps), and H-5 to a doublet ($J_{1.5}$ = 6.0 cps); H-7 irradiated (509 cps, 100 mV), H-8 to a triplet ($J_{2.8}$ = $J_{1.8}$ = 6.5 cps); H-5 irradiated (380 cps, 400 mV), H-6 to a doublet ($J_{6.7}$ = 5.5 cps) and H-1 to a triplet ($J_{1.2}$ = $J_{1.8}$ = 6.5 cps); H-1 irradiated (323 cps, 200 mV), H-5 to a doublet ($J_{5.6}$ = 2.0 cps); and H-8 irradiated (264 cps, 200 mV), H-7 to a doublet ($J_{6.7}$ = 5.0 cps).

Anal. Calcd for $C_{12}H_{10}$: C, 93.46; H, 6.54. Found: C, 93.32; H, 6.63.

Characterization of Benzocyclooctatetraene. Combining 30.8, 21.8, and 35.3 mg of benzocyclooctatetraene from the acetone-sensitized photolyses of 401.9, 408.0, and 401.0 mg of benzobarrelene, respectively, gave 87.9 mg that was chromatographed on a 1.8 × 55 cm, 60–200 mesh silica gel (Davison, grade 950) column slurry packed in 1.5% ether–hexane. After eluting with 500 ml of hexane, the material was added and eluted with 750 ml of hexane and then 500 ml of 4% ether–hexane; 250-ml fractions were collected. Fractions 4–5 contained 64.8 mg of a yellow solid, mp 41–50°. Sublimation at 80° yielded 60.8 mg (0.394 mmol) of colorless crystals, mp 48–50°, which turned slightly yellow on standing. This proved identical (ir, nmr, undepressed mixture melting point) with benzocyclooctatetraene synthesized by the procedure of Friedman (*vide infra*).[10]

Hydrogenation of Benzosemibullvalene. A 795.3-mg (5.16 mmol) sample of benzosemibullvalene was hydrogenated at 1 atm in 15.0 ml of 95% ethanol with 476.0 mg of 10% Pd–C. After 220 min, 1.86 equiv (215.3 cc corrected to STP, 9.61 mmol) had reacted, and no further uptake was observed. The catalyst was filtered, the solution concentrated to 2.0 ml by distillation through a 2 × 25 cm helipack column, and the residue chromatographed on a 2.5 × 55 cm column slurry packed with 60–200 mesh silica gel (Davison, grade 950) in hexane. All fractions were eluted with hexane, and 250-ml fractions were collected. Fractions 3–11 contained 703.1 mg of a colorless oil: nmr (CCl_4) τ 2.97 singlet, 3.08 singlet, in the ratio 8:1, respectively, and a 6.17–9.27 multiplet. This material was subjected to preparative vpc on a 3.3 × 170 cm column packed with 15% Apiezon L on Chromosorb P (acid washed, 60–80 mesh) at 170° with a nitrogen flow of 200 cc/min. Two components with retention times of 27.0 and 36.1 min were obtained. The second component contained 386.0 mg of a yellow oil: nmr (CCl_4) τ 2.97 singlet, 3.08 singlet, in the ratio 7:1, respectively, and a 6.17–9.00 multiplet.

The second component was chromatographed on a 3 × 90 cm column slurry packed with 60–200 mesh silica gel (Davison, grade 950) in hexane. All fractions were eluted with hexane, and 40-ml fractions were collected, with uv scanning at 265 mμ. The trace consisted of a single broad peak, fractions 95–180. Fractions 123–180 contained two compounds (nmr τ 2.97 singlet and 3.08 singlet) whose ratio was changing on increasing elution. Fractions 95–119 afforded 196.6 mg of a yellow oil that was molecularly distilled at 90° and yielded 185.8 mg (1.17 mmol) of a colorless oil that had identical ir, nmr, and vpc retention time (15% Apiezon L on Chromosorb P, acid washed, mesh 60–80, at 170° with 75 cc of N_2/min) with independently synthesized 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene (*vide infra*).

Synthesis of Benzocyclooctatetraene. Benzocyclooctatetraene was prepared by the method of Friedman;[10] however, silver nitrate chromatography was utilized for the final separation. From a total of 9.00 g (0.066 mol) of anthranilic acid, there was isolated 311.4 mg of benzocyclooctatetraene, mp 49–50.5°; ir (CS_2) 3.25, 3.31, 8.25, 8.54, 9.02, 9.60, 10.38, 10.58, 10.90, 12.40, 13.03, 13.24, 13.65, 14.49, and 15.56 μ; 60-Mc nmr (CCl_4) τ 2.72–3.27 A_2B_2 multiplet (4 H, aromatic), 3.43 and 3.62 doublet of AB quartet (2 H, vinyl adjacent to benzo ring, H-3 and H-8), and 4.00 and 4.19 high-field doublet of AB quartet superimposed on a singlet at 4.19 (2 H, vinyl, protons H-4 and H-7; 2 H, vinyl, protons H-5 and H-6); 100-Mc nmr (CCl_4)[42] unchanged from 60-Mc nmr except for the singlet at τ 4.19 splitting into overlapping singlets at τ 4.17 (part of B proton of the AB quartet that now uniquely defines proton A, τ 3.53; proton B, τ 4.08; and $J_{3.4}$ = $J_{7.8}$ = 10.5 cps) and τ 4.23 (2 H, vinyl, protons H-5 and H-6, $J_{4.5}$ = $J_{6.7}$ = *ca.* 0 cps).

1-Cyclopentenecarboxylic Acid. This material was prepared by the method of Maitte,[8] and had mp 120–121° (soften 105°) (lit.[8] 123–123.5°).

2-Phenyl-1-cyclopentanecarboxylic Acid. This was prepared by a modified procedure of Baker and Leeds.[7]

To a solution of 30.1 g (0.268 mol) of 1-cyclopentenecarboxylic acid[8] in 1 l. of benzene, cooled in an ice–acetone bath, was added, under nitrogen, 147.3 g (1.11 mol) of aluminum chloride over 20 min. The mixture was refluxed with stirring for 110 min, cooled for 10 min, and poured onto a concentrated hydrochloric acid–ice slurry. The melted aqueous layer was ether extracted. The combined organic phase was concentrated *in vacuo* and the orange oil added to 300 ml of 20% potassium hydroxide, which was ether extracted, acidified with concentrated hydrochloric acid to litmus, and chloroform extracted. The ether and chloroform solutions, respectively, were dried and concentrated *in vacuo* yielding 21.8 g of an orange neutral oil and 22.3 g of acidic, oily orange solid. The reaction was repeated on 30.0 g (0.268 mol) of 1-cyclopentenecarboxylic acid, and there was obtained 18.0 g of neutral and 20.8 g of acidic material.

Three recrystallizations of the combined acidic fraction from ether afforded 14.6 g (0.130 mol) of 1-cyclopentenecarboxylic acid, mp 115.5–118.5°. The remaining 28.5 g was divided into six portions (*vide infra*) and each chromatographed on a 4 × 150 cm water-jacketed (28°) column, dry packed with 600 g of Celite (Eagle Picher Co., Celatom FW-80) impregnated with 600 ml of pH 6.6 buffer solution[43] of 163.5 ml of 0.100 *M* aqueous citric acid and 436.5 ml of 0.200 *M* aqueous disodium phosphate. Elution was with water-saturated ether. The eluent was scanned at 250 mμ, and 40-ml fractions were collected. Portions 1 through 5 weighed 4.76 g and 6 weighed 4.65 g. In each case, two peaks were observed on the scan, *e.g.*, portion 1 gave peaks for fractions 24–35 and 39–110. The ethereal fractions of the corresponding peaks were combined and concentrated *in vacuo*, and the residue was dissolved in 250 ml of chloroform, which was extracted with water, dried, and concentrated *in vacuo*. Peak 1 consisted of 22.1 g of an orange oil and peak 2 of 5.55 g (49.5 mmol) of 1-cyclopentenecarboxylic acid.

The material in peak 1 was chromatographed on a 7 × 85 cm column slurry packed with 60–200 mesh silica gel (Davison, grade 950) in 4% ether–hexane. The column was eluted with 6 l. of 4%, 6 l. of 7%, 6 l. of 12%, and 25 l. of 20% ether–hexane, and 1-l. fractions were collected. Fractions 21–43 consisted of a single peak containing 19.32 g of a colorless oil. From the 12.32 g in fractions 21–26, 7.13 g of an oily solid was crystallized from hexane. Three recrystallizations from hexane and three from ether–hexane afforded 2.50 g (13.1 mmol, 3.7% yield based on 0.356 mol of reacted 1-cyclopentenecarboxylic acid) of constant melting 2-phenyl-1-cyclopentanecarboxylic acid: mp 86.5–88° (lit.[7] mp 87–88°); ir (CS_2) 2.9–4.5, 5.90, 7.09, 7.85, 8.15, 8.71, 9.40, 9.71, 10.0–12.0, 13.25, and 14.36 μ; nmr ($CDCl_3$) τ −1.15 singlet (1 H, –COOH), 2.63 singlet (5 H, aromatic), 6.37–7.38 multiplet (2 H, methine), and 7.53–8.52 multiplet (6 H, methylene). The oil in the remaining fractions was not investigated, but was presumably 3-phenyl-1-cyclopentanecarboxylic acid.[7]

[2,3]Cyclopenta-1-indanone. This was also prepared by modifying the procedure of Baker and Leeds.[7]

A mixture of 758.2 mg (3.99 mmol) of 2-phenyl-1-cyclopentanecarboxylic acid and 25 ml of polyphosphoric acid (82–84% P_2O_5) was heated at 100° for 5 hr. The dark orange oil was diluted with 100 ml of water and extracted with 150 ml of ether. The ether was extracted successively with 10% potassium hydroxide and water, dried, and concentrated *in vacuo* yielding 709.6 mg of an orange

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[42] Appreciation is expressed to Mr. V. J. Hull for running the 100-Mc nmr spectra.

[43] "Handbook of Chemistry and Physics," 41st ed, Chemical Rubber Publishing Co., Cleveland, Ohio, p 1715.

oil. This was chromatographed on a 3 × 60 cm, 60–200 mesh silica gel (Davison, grade 950) column slurry packed in 2% ether–hexane and 250-ml fractions were collected. Elution was with 1 l. of 2%, 1 l. of 4%, 1 l. of 8%, and 1.5 l. of 16% ether–hexane. Fractions 15–18 contained 630.3 mg of a faintly yellowish oil that was molecularly distilled at 125° giving 591.9 mg (3.44 mmol, 86.2%) of [2,3]cyclopenta-1-indanone: ir (CCl_4) 3.23, 3.28, 3.38, 3.48, 5.85,[44] 6.12, 6.82, 6.90 (sh), 7.49, 7.58, 7.78, 7.99, 8.22, and a series of small bands at 8.39–11.70 μ; nmr (CCl_4) τ 2.28–2.92 multiplet (4 H, aromatic), 6.05–6.47 poorly resolved doublet of triplet (1 H, CH adjacent to C=O), 6.83–7.27 poorly resolved doublet of triplet (1 H, PhCH), and 7.58–9.33 multiplet (6 H, CH_2); melting point of 2,4-dinitrophenylhydrazone[45] 215–217° (lit.[7] 216–217°).

1,2,3,3a,8,8a-Hexahydrocylopent[*a*]indene. A solution of 591.9 mg (3.44 mmol) of [2,3]cyclopenta-1-indanone, 10 ml (10.3 g, 0.21 mol) of 99–100% hydrazine hydrate, 10 g (0.18 mol) of potassium hydroxide, and 50 ml of triethylene glycol was refluxed for 41 hr, cooled, and poured into 500 ml of 20% hydrochloric acid and ether extracted. The extracts were washed with water, dried, and concentrated *in vacuo* leaving 742.3 mg of an orange oil. The oil was chromatographed on a 3 × 60 cm column slurry packed with 60–200 mesh silica gel (Davison, grade 950) in hexane, and 250-ml fractions were collected with hexane elution. Fractions 5–10 comprised 398.1 mg (2.52 mmol, 73.3%) of 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene.

An analytically pure sample was obtained by gradient temperature (42–128°), molecular distillation (2.0 mm) in a 6 mm × 1 m tube, pretreated with 1% dichlorodimethylsilane–benzene, of a 180.0-mg (1.14 mmol) portion of the colorless oil. The 170.9 mg which was obtained had: ir (CS_2) 3.25, 3.28 (sh), 3.30, 3.40, 3.48, 3.50, very weak bands at 5.14–5.84, weak bands at 7.03–12.33, and strong bands at 13.15, 13.49, and 14.00 μ; uv$_{max}$ (95% ethanol) 273 mμ (ϵ 925), 266 (857), and 260 sh (699); mass spectrum (70 eV)[41] molecular ion 158; nmr (CCl_4) τ 2.97 singlet (4 H, aromatic), 6.17–6.62 poorly resolved doublet of triplet (1 H, PhCH), 6.67–7.57 multiplet (2 H, $PhCH_2$; 1 H, remaining methine), 7.73–9.00 multiplet (6 H, remaining methylenes).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.05; H, 8.95.

Direct Irradiation of Benzobarrelene. A solution of 80.6 mg (0.52 mmol) of benzobarrelene in 50 ml of isopentane was photolyzed for 15 min in a 2 × 18 cm, 50-ml Vycor tube as described previously (*vide supra*). Concentration of the slightly cloudy solution *in vacuo* afforded 86.9 mg of an oily yellow solid whose nmr (CCl_4) showed 22.0 ± 0.6% of benzocyclooctatetraene (18.7 ± 0.5 relative area of 6 vinyl H) and 78.0 ± 1.1% of benzobarrelene (22.2 ± 0.3 relative area of 2 bridgehead H). No other components were detected.

Other photolyses afforded the following results. Irradiation of 84.1 mg (0.55 mmol) of benzobarrelene for 30 min gave 32.0 ± 0.9% of benzocyclooctatetraene and 68.0 ± 1.1% of benzobarrelene; 75.7 mg (0.49 mmol) of benzobarrelene, 60 min, 57.8 ± 0.6% of benzocyclooctatetraene and 42.2 ± 1.1% of benzobarrelene; and 75.7 mg (0.49 mmol) of benzobarrelene, 120 min, 78.3 ± 0.5% of benzocyclooctatetraene and 21.7 ± 1.4% of benzobarrelene.

Direct Irradiation of Benzosemibullvalene. A solution of 82.7 mg (0.54 mmol) of benzosemibullvalene in 50 ml of isopentane was photolyzed for 280 min. The following results were obtained by nmr analysis (CCl_4) of the resulting 86.9 mg of orange oil: 12.0 ± 0.4% of benzocyclooctatetraene (14.7 ± 0.5 relative area of 6 vinyl H) and 88.0 ± 0.6% of benzosemibullvalene (36.0 ± 0.25 relative area of 2 vinyl H). No other constituents were seen. A second run on 79.6 mg (0.52 mmol) of benzosemibullvalene in 50 ml of isopentane, photolyzed for 120 min, gave 10.4 ± 0.3% of benzocyclooctatetraene and 89.6 ± 1.0% of benzosemibullvalene.

Acetone Photosensitization of Benzosemibullvalene. In a parallel experiment to the direct photolysis (*vide supra*), a solution of 87.4 mg (0.57 mmol) of benzosemibullvalene and 2.60 ml of reagent grade acetone in 50 ml of isopentane was irradiated for 280 min. The cloudy solution was concentrated *in vacuo* yielding 154.2 mg of a yellow oil that gave an nmr (CCl_4) analysis of 18.2 ± 4.6% of benzocyclooctatetraene (4.0 ± 1.0 relative area of the 2 low-field vinyl H) and 81.8 ± 4.5% of benzosemibullvalene (9.0 ± 0.5 relative area of high-field vinyl H), and, in addition, τ 7.82–8.12 triplet (18.0 relative area), 8.25–9.67 multiplet (230 relative area), and peaks buried under the cyclopropyl, benzylic, and low-field vinyl hydrogens of benzosemibullvalene and under the high-field vinyl hydrogens of benzocyclooctatetraene.

A second sensitized irradiation on a solution of 81.4 mg (0.53 mmol) of benzosemibullvalene and 2.60 ml of acetone in 50 ml of isopentane for 120 min yielded 147.3 mg of a yellow oil with the following nmr (CCl_4) analysis: 12.6 ± 2.0% of benzocyclooctatetraene (6.3 ± 1.0 relative area of 6 vinyl H) and 87.4 ± 3.0% of benzosemibullvalene (7.3 ± 0.25 relative area of the high-field vinyl H) plus τ 7.82–8.12 triplet (relative area 2.2), 8.25–9.67 multiplet (relative area 62.0), and peaks under the cyclopropyl and low-field vinyl hydrogens of benzosemibullvalene.

Direct Irradiation of Benzocyclooctatetraene. The photolysis was run on a solution of 144.3 mg (0.936 mmol) of benzocyclooctatetraene and 30 ml of isopentane in a vacuum-sealed, 2.5 × 12 cm Vycor tube strapped to a water-cooled immersion well. The tube and immersion well were covered with aluminum foil and photolyzed for 9.5 hr. Concentration of the photolysis solution *in vacuo* yielded 151.1 mg of a yellow oil whose nmr was unchanged from starting material.

Deuteration of Benzobarrelene. This was based on a procedure of Zimmerman, *et al.*,[3] for the deuteration of barrelene.

N,N-Dideuteriocyclohexylamine. To a solution of 120 ml (98.4 g, 0.991 mol) of cyclohexylamine and 40 ml of deuterium oxide that had been stirred under nitrogen for 12 hr was added 160 g of molecular sieve (Linde, Type 4A, activated at 400°). After the mixture had cooled to room temperature, 200 ml of pentane was added and the solution separated from the sieves. The sieves were washed with 300 ml of pentane and combined with the amine solution. The pentane was distilled from the solution and 110 ml of benzene added. Distillation of the benzene gave no azeotroped water. On repeating the deuteration three times, there was obtained 40 ml of N,N-dideuteriocyclohexylamine, bp 132–134°. Traces of benzene and nondeuterated amine (τ 8.88, $-NH_2$) were seen in the nmr (CCl_4).

Deuteration of Benzobarrelene.[18] To 50 ml of N,N-dideuteriocyclohexylamine was added under nitrogen 3.00 ml (6.6 mmol) of 2.2 *M* butyllithium in hexane. After 30 min, 1.30 g (8.43 mmol) of benzobarrelene dissolved in 10 ml of pentane was added and the resulting solution stirred at 70° for 48 hr; additional 3.00-ml (6.6 mmol) portions of 2.2 *M* butyllithium were added after 16 and 32 hr. The deep green solution was cooled and quenched with 5.0 ml of deuterium oxide. The yellow mixture was poured into 250 ml of 10% hydrochloric acid and extracted with hexane. The hexane was washed with 250 ml of 10% hydrochloric acid and twice with water, dried and concentrated *in vacuo* giving 1.40 g of a yellow solid which contained benzobarrelene that was 60.3 ± 1.1% deuterated in the aryl and vinyl positions (*vide infra*).

A solution of 3.50 mol (7.7 mmol) of 2.2 *M* butyllithium in hexane and 40 ml of N,N-dideuteriocyclohexylamine was stirred under nitrogen for 30 min when the partially deuterated benzobarrelene in 10 ml of pentane was added. The orange solution was stirred under nitrogen at 80° for 84 hr with additional 3.5-ml (7.7 mmol) samples of 2.2 *M* butyllithium being added after 12, 36, and 60 hr. The deep green solution was cooled and quenched with 10 ml of deuterium oxide. On work-up, there was obtained 1.55 g of yellowish solid benzobarrelene that was 82.9 ± 1.5% vinyl and aryl deuterated.

A third pass on the deuterated benzobarrelene in 40 ml of N,N-dideuteriocyclohexylamine containing 4.00 ml (8.8 mmol) of 2.2 *M* butyllithium in hexane for 43 hr at 70°, with additional 4.00-ml portions (8.8 mmol) of 2.2 *M* butyllithium being added after 12, 24, and 36 hr, afforded 1.64 g of 85.9 ± 1.6% deuterated benzobarrelene as an oily solid.

The material was chromatographed on a 3.5 × 80 cm silica gel column (Davison, grade 950) slurry packed in 1% ether–hexane. After eluting the column with 1 l. of hexane, the material was added, and 500-ml fractions were collected. The column was eluted with 9 l. of hexane and 2.5 l. of 4% ether–hexane. Fractions 7–12 contained 190.5 mg of partially deuterated naphthalene, and fractions 22–23 comprised 779.5 mg of deuterated benzobarrelene, mp 62–66°. Sublimation at 85° of fractions 22–23 afforded 703.6 mg of colorless needles, mp 65.5–66°; the mixture melting point was undepressed with nondeuterated benzobarrelene; ir (CS_2) 3.25, 3.33, weak bands at 7.25–15.96 μ. The benzobarrelene was 86.4 ± 1.2% deuterated in the aryl and vinyl positions.

Nmr and Mass Spectral Analysis of Deuterated Benzobarrelene. The nmr (CCl_4) of deuterated benzobarrelene consisted of τ 3.03

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[44] The parent compound, 1-indanone, has a C=O absorption at 5.80 μ: W. M. Schubert and W. A. Sweeney, *J. Am. Chem. Soc.*, 77, 4172 (1955).

[45] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1962, p 219.

and 3.30 broad singlet (aryl and vinyl) and 5.27 broad singlet (bridgehead). The ratio of aryl plus vinyl ($A + V$) to bridgehead (B) area is ($Q = [A + V]/B$). The per cent deuteration of nonbridgehead hydrogens is given by: $\% D = 100[8 - (A + V)]/8 = 100\{(8 - B[(A + V)/B]\}/8 = 100(8 - 2Q)/8 = 100(4 - Q)/4$; absence of bridgehead exchange is assumed and B is taken as 2, meaning that the areas will now give the number of hydrogens directly. The following results were obtained in the deuteration of benzobarrelene (*vide supra*): first pass, $A + V$ (relative area 56.0 ± 0.25) and B (relative area 35.3 ± 0.5) that yields $Q = 1.59 \pm 0.03$; second pass, $A + V$ (relative area 45.9 ± 0.5), B (relative area 67.0 ± 0.5), and $Q = 0.685 \pm 0.012$; third pass, $A + V$ (relative area 44.9 ± 0.5), B (relative area 79.4 ± 0.6), and $Q = 0.565 \pm 0.011$; and purified benzobarrelene, $A + V$ (relative area 52.9 ± 0.5), B (relative area 97.0 ± 0.5), and $Q = 0.545 \pm 0.007$.

That there was little or no bridgehead deuterium incorporation was confirmed by mass spectral analysis. By lowering the ionization voltage to 7.78 eV, the mass spectrum of benzobarrelene contained only the molecular ion and its M + 1 and M + 2 ^{13}C contributors; this ionization voltage was used for deuterated benzobarrelene.[41] The mass spectrum consisted of a series of peaks from mass 158 through 163 which contained contributions from protio and deuterio ^{12}C and ^{13}C molecules, but negligible lower mass peaks including those possibly due to three or less deuteriums. The corrected peak height P' for mass M can be obtained by subtracting the M + 1 and M + 2 ^{13}C contributions from previous mass units and then adding its own M + 1 and M + 2 ^{13}C contributions.[46] This gives the peak heights for the various masses as if all carbon atoms were ^{12}C and is a measure of the per cent deuterium content. Assuming no bridgehead deuterium incorporation (maximum of 8 D), mass 158 contributes 50% of its height to per cent deuterium, mass 159 contributes 62.5%, etc. This analysis gave 86.3 ± 1.4% deuteration in the aryl and vinyl positions with the following contributions from the various masses: mass 158, 1.1 ± 0.1%; mass 159, 4.1 ± 0.1%; mass 160, 15.8 ± 0.2%; mass 161, 35.5 ± 0.5%; mass 162, 29.5 ± 0.4%; and mass 163, 0.3 ± 0.1%. A second determination gave 86.1 ± 2.5% deuteration.

Acetone Photosensitization of Deuterated Benzobarrelene. A solution of 327.1 mg of deuterated benzobarrelene and 2.50 ml of reagent grade acetone in 40 ml of isopentane was photolyzed for 95 min as previously described (*vide supra*). Concentration of the slightly cloudy solution *in vacuo* afforded 341.1 mg of a yellow oil that was chromatographed on a 4.0 × 150 cm silver nitrate, liquid–liquid partition column (*vide supra*); 40-ml fractions were collected. Four peaks were observed: fractions 36–41, 20.6 mg of yellow oil; 42–49, 160.4 mg of deuterated benzosemibullvalene; 56–69, 19.5 mg of deuterated benzocyclooctatetraene, mp 33–44°; and 77–96, 126.2 mg of recovered starting material, mp 62–66°, that was 86.2 ± 1.6% deuterated by nmr and 86.3 ± 3.3% by mass spectrum. A second photolysis on 300.3 mg of deuterated benzobarrelene and 2.50 ml of acetone in 40 ml of isopentane for 90 min gave: fractions 32–38, 22.6 mg of yellow oil; 39–46, 137.2 mg of deuterated benzosemibullvalene; 58–68, 20.1 mg of deuterated benzocyclooctatetraene; and 140.0 mg of recovered benzobarrelene that was 86.5 ± 1.6% deuterated (nmr).

Nmr Analysis of Deuterated Benzosemibullvalene and Benzocyclooctatetraene. The vinyl deuterium incorporation of benzobarrelene could not be determined directly because of aryl and vinyl overlap in the nmr. With the assumption that the aryl and vinyl protons were not interconverted during the rearrangement, the nmr of the products were used to determine the two types, since these were separated. For each product, $Q' = A/(V + B)$ is defined, where V and B are the vinyl and bridgehead protons of deuterated benzobarrelene that had been converted to the nonaromatic protons of each product. Since $Q = (V + A)/B$ (deuterated benzobarrelene), one can eliminate A and write $V/B = (Q - Q')/(Q' + 1)$. Because there are four vinyl protons in benzobarrelene, the per cent vinyl deuterium content can be written as: $100(4 - V)/4 = 100[4 - B(V/B)]/4 = 100(2 - V/B)/2$, where again B is taken as 2.

The nmr (CCl_4) of deuterated benzosemibullvalene for the two runs had: τ 2.80 and 3.02 broad singlet (aromatic, run 1—relative area 40.0 ± 1.0, run 2—relative area 28.8 ± 0.3), 4.43–4.57 doublet (vinyl H-6, run 1—relative area 4.5 ± 0.3, run 2—relative area 4.0 ± 0.3), 4.92 singlet (vinyl H-7, run 1—relative area 4.7 ± 0.4, run 2—relative area 3.9 ± 0.3), 6.22 singlet (H-5, run 1—relative area 53.9 ± 0.4, run 2—38.8 ± 0.5), 6.68–6.95 triplet (H-1, run 1—relative area 5.6 ± 0.5, run 2—relative area 4.5 ± 0.5), 7.12 singlet (H-2, run 1—relative area 52.8 ± 0.8, run 2—relative area 37.8 ± 0.5), and 7.27–7.52 doublet (H-8, run 1—relative area 6.4 ± 0.3, run 2—relative area 5.0 ± 0.3). The nmr yielded the values for Q' of 0.313 ± 0.014 and 0.306 ± 0.011 for runs 1 and 2, respectively. An average value of 0.310 ± 0.013 was used in subsequent work and produced $V/B = 0.179 \pm 0.017$ that now defined the per cent vinyl deuteration as 91.0 ± 8.6% and the per cent residual vinyl hydrogen as 9.0 ± 0.8%.

The deuterated benzocyclooctatetraene from runs 1 and 2 was combined: nmr (CCl_4) τ 2.93 and 3.18 broad singlet (aromatic, relative area 15.9 ± 0.4), 3.42–3.68 multiplet (3.46 and 3.67 doublet of AB quartet overlapping a singlet at 3.57, H-3 and H-8, relative area 8.0 ± 0.3), and 4.08 and 4.22 slightly overlapping singlets (H-4 and H-7, relative area 34.8 ± 0.5; H-5 and H-6, relative area 3.9 ± 0.7).

Direct Irradiation of Deuterated Benzobarrelene. A solution of 128.1 g of deuterated benzobarrelene in 50 ml of isopentane was photolyzed for 235 min in a sealed Vycor tube as previously described. The clear solution was concentrated *in vacuo* giving 135.4 mg of an orange oil that afforded an nmr (CCl_4) with benzocyclooctatetraene protons at τ 3.42–3.67 multiplet (τ 3.45 and 3.65 doublet of AB quartet, overlapping a singlet at 3.57, H-3 and H-8, relative area 13.6 ± 1.0) and slightly overlapping singlets at 4.10 and 4.22 (H-4 and H-7, relative area 88.9 ± 1.4; H-5 and H-6, relative area 8.9 ± 1.4) and benzobarrelene protons at 5.25 singlet (bridgehead, relative area 20.3 ± 0.5).

Purification and Direct Irradiation of Deuterated Benzosemibullvalene. A 218.0-mg sample of deuterated benzosemibullvalene labeled with hydrogen at carbons 2 and 5 and residual vinyl hydrogen from benzobarrelene reactant at the other nonaromatic positions was obtained by gradient temperature molecular distillation (30–87° (1.0 mm)) in a 8 mm × 1 m tube of 297.6 mg of benzosemibullvalene from the acetone-sensitized photolyses of deuterated benzosemibullvalene (*vide supra*). The oil had an identical hydrogen distribution (nmr) as the material before distillation. A 153.5-mg portion in 50 ml of isopentane was photolyzed for 19 hr in a sealed Vycor tube as previously described. Concentration of the very cloudy, yellow solution afforded 161.0 mg of a yellow oil which gave the following nmr (CCl_4) results: in addition to unreacted starting material, there were benzocyclooctatetraene protons at τ 3.55 singlet (H-3 and H-8, relative area 18.6 ± 0.6), 4.05 singlet (H-4 and H-7, relative area 1.5 ± 0.6), and 4.23 singlet (H-5 and H-6, relative area 2.0 ± 0.5).

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(46) The corrections used in the calculation were: (a) probability that all 12 carbon atoms are $^{12}C = 0.8789$;[47] (b) P_{m+2}/P_m and P_{m+1}/P_m for 12 carbon atoms are 0.0077 and 0.1297, respectively.[48]

(47) J. H. Beynon, "Mass Spectrometry and its Applications to Organic Chemistry," Elsevier Publishing Co., Amsterdam, 1960, p 296.

(48) J. H. Beynon and A. E. Williams, "Mass and Abundance Tables for Use in Mass Spectrometry," Elsevier Publishing Co., Amsterdam, 1963, p 27.