Competitive Naphtho *vs.* Benzo Bridging in the Di-π-methane Rearrangement of Benzo-2,3-naphthobarrelene. Exploratory and Mechanistic Organic Photochemistry. LXXIV[1]

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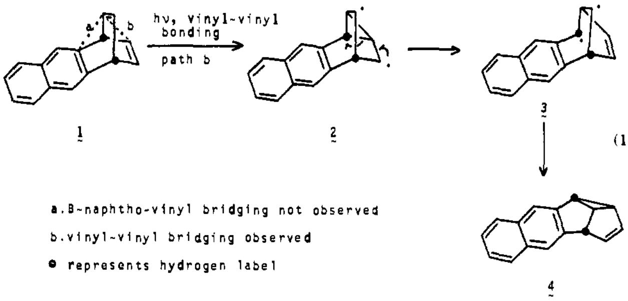
Abstract: The photochemistry of benzo-2,3-naphthobarrelene was investigated and found to give benzo-2,3-naphthosemibullvalene. The reaction mechanism was studied by labeling all but the bridgehead positions with deuterium. *A priori*, benzo-2,3-naphthosemibullvalene could be formed by pathways involving benzo–vinyl or naphtho–vinyl bridging; a combined degradative–nmr assay determination of the distribution of the label revealed that the reaction proceeded 50% by benzo–vinyl and 50% by naphtho–vinyl bridging. This example thus was the first proceeding by bridging between vinyl and β-naphthyl groups. The equal amounts of benzo and β-naphtho bridging indicate that the portion of the excited state molecule in which the excitation energy is most heavily concentrated is not necessarily constrained to be the portion reacting. The present evidence, along with the previous results, indicate an equal disinclination of excited benzo and excited β-naphtho groups to bridge to vinyl. This is further evidenced by a quantum efficiency of 0.077 which is lower than that found previously for 2,3-naphthobarrelene where vinyl–vinyl bridging was possible. The reaction seems to be controlled by a requirement for minimum electron localization in the excited state. Finally, on photolysis of benzonaphthosemibullvalene in aqueous dioxane the three-membered ring was found to open to give a mixture of alcohols. In the reaction, the benzylic–naphthylic bond was selectively opened with a preference for the hydroxyl group becoming β-naphthylic.

In our previous studies we have investigated the photochemistry of barrelene,[2] benzobarrelene,[3] 2,3-naphthobarrelene,[4] and 1,2-naphthobarrelene[4] as part of our effort to elucidate the generality and mechanism of the di-π-methane rearrangement.[5]

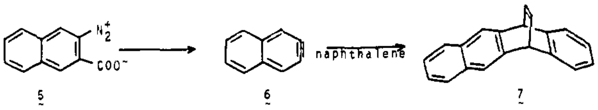
One particularly interesting facet was found in the photochemistry of the naphthobarrelenes and benzobarrelene where a disinclination for aryl–vinyl bridging in the reaction mechanism was found. The one exception to this generalization was a preference for α-naphtho bonding where possible. Thus, for example, in 2,3-naphthobarrelene (**1**) which was deuterated at all positions except for two bridgehead hydrogens, the reaction mechanism involved vinyl–vinyl bridging exclusively (note eq 1).



(1)

It was of considerable interest to investigate an example where the only two choices available to the excited state molecule would involve vinyl bridging with an aromatic ring and where the options would be bridging to benzo *vs.* bridging to naphtho at the β position. Thus, the photochemistry of benzo-2,3-naphthobarrelene was chosen for study.

Synthesis and Exploratory Photochemistry of Benzo-2,3-naphthobarrelene. Benzo-2,3-naphthobarrelene was a known compound, having been synthesized by the reaction of benzyne with anthracene.[6] However, the 1.5% yield necessitated a more practical approach. Previously we had successfully employed the reaction of β-naphthyne with benzene in our synthesis of 2,3-naphthobarrelene.[4] The same approach was presently employed except that β-naphthyne, generated from 3-diazoniumnaphthalene-2-carboxylate, was allowed to react with molten naphthalene at 81°. The product obtained agreed in melting point as well as in ultraviolet and nmr spectra with the known[6] material.[7] The method proved quite practical and gave an 11% yield (note eq 2).



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Irradiation of benzo-2,3-naphthobarrelene (**7**) gave a single product, mp 154–156°. That this product, indeed, was benzo-2,3-naphthosemibullvalene (**8**) was evidenced in particular by the nmr spectrum which was characteristic of the semibullvalenes previously encountered;[3,4] note the Experimental Section for delineation of the nmr interpretation and results. In a typical preparative run, photolysis of 1.13 g afforded, besides 530 mg of starting material, 488 mg of benzonaphthosemibullvalene (**8**) along with 134 mg of a mixture of reactant and product (*cf.* eq 3).

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[1] For paper LXXIII of the series note H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **94**, 8749 (1972).

[2] (a) H. E. Zimmerman and G. L. Grunewald, *ibid.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

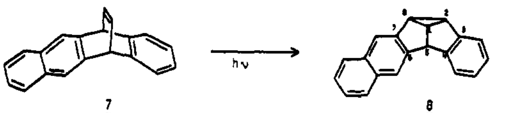
[3] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).

[4] (a) H. E. Zimmerman and C. O. Bender, *ibid.*, **91**, 7516 (1969); (b) *ibid.*, **92**, 4366 (1970).

[5] For a general discussion of the rearrangement note H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969).

[6] B. H. Klanderman, *ibid.*, **87**, 4649 (1965).

[7] We acknowledge the assistance of Mr. John Keller in exploratory efforts in the beginning of this research, namely in developing the benzo-2,3-naphthobarrelene synthesis, in running some preliminary photolyses leading to benzo-2,3-naphthosemibullvalene, and in running characterization spectra.



7 8 (3)

Labeling of Benzo-2,3-naphthobarrelene. In order to follow the skeletal change on photolysis, labeled benzonaphthobarrelene was required. Using the approach which proved useful previously, benzonaphthobarrelene was labeled in the vinyl and aryl positions with deuterium using lithium *N*-deuteriocyclohexylamide in *N*,*N*-dideuteriocyclohexylamine.[2b,3,4] The method readily afforded material which was 60–69% vinyl and aryl deuterated; and it proved convenient to use this material rather than subjecting benzonaphthobarrelene to further deuteration. That the exchange was solely at the vinyl and aryl positions and did not involve the bridgehead hydrogen atoms was also established (note the Experimental Section).

Photolysis of Deuterated Benzo-2,3-naphthobarrelene and Assay of the Deuterium Label. Photolysis of the deuterated benzonaphthobarrelene (**7D**) gave deuterated benzonaphthosemibullvalene, as expected from the irradiations of the nondeuterated material. Disappointingly, inspection of the nmr of the product revealed hydrogens 2 and 8 as overlapping triplets. Since the relative number of hydrogens at these two positions was needed to determine the relative extents of benzo-vinyl *vs.* naphtho-vinyl bridging (see below), direct nmr determination was not possible. Nevertheless, the nmr of the photolysis product did allow determination of the extent of vinyl deuteration compared with deuteration of the aryl positions; in benzonaphthobarrelene itself aryl-vinyl peak overlap precluded this measurement.

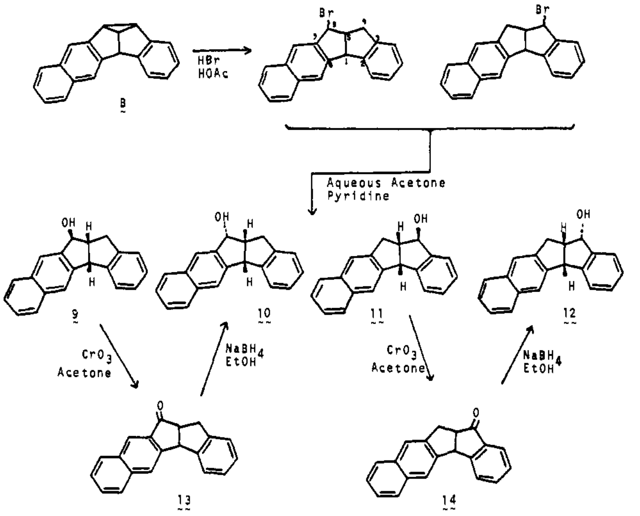
Thus, the mechanism for the reaction, whether it involves benzo-vinyl or naphtho-vinyl bridging, results in the hydrogen at C-1 of benzonaphthosemibullvalene product deriving from an original vinyl hydrogen and also in the hydrogen at C-5 deriving from an original bridgehead hydrogen atom. This point is discussed below in connection with the mechanism (note Chart II). The ratio of the H-1 to H-5 peak areas gave the amount of residual vinyl hydrogen left after deuteration. It can be seen from Table I that in the 60% overall deuteration the vinyl was 72% exchanged and in the 69% overall deuteration the vinyl was 82% exchanged. The observation of more rapid vinyl exchange than aryl deuteration has precedent in the naphthobarrelene studies.[4]

Table I. Observed Peak Areas in Deuterated Semibullvalenes Obtained from Photolysis

Run	% deuteration	H-1	H-5	H-2 + H-8	H-1/H-5	% vinyl deuteration
1	60	15	54	62	0.28	72
2	69	6.5	37	42	0.18	82

In order to resolve the problem of overlap of the nmr triplets of H-2 and H-8, the benzonaphthosemibullvalene product, deuterated and undeuterated, was treated with hydrobromic acid in acetic acid to give HBr adducts.[8] These were solvolyzed directly in aqueous acetone containing pyridine to afford four ring-opened alcoholic products (**9**, **10**, **11**, and **12**); note Chart I. These products were subjected to preparative thin layer separation. While two of these products, isomers **10** and **12**, could not be separated, they could be obtained from the sodium borohydride reduction of ketones **13** and **14** which were obtained by oxidation of alcohols **9** and **11** (note Chart I).

Chart I. Reactions of Benzonaphthosemibullvalene and Derivatives



Structural assignments to the ketones and the alcohols were made on the basis of the extent of downfield shift of the *o*-aryl hydrogens in the nmr on increasing concentration of europium dipivaloylmethide.[9] The *o*-naphthyl hydrogen could be identified by its occurrence as a singlet and the *o*-benzo hydrogen by its occurrence as a slightly split doublet. The assumption was made that the ortho hydrogen which was shifted most with increasing europium concentrations was the closer to the oxygen in each of the ketones and alcohols. The details of these shift experiments are given in the Experimental Section. The endo-exo assignments were made on the basis that the exo isomers of the alcohols would have the smaller J_{45} or J_{56} coupling constant as a result of the larger dihedral angle between hydrogens. Thus the 4-5 and 5-6 cis coupling constants were in the range of 7 cps while the trans constants were 2 to 3 cps (note the Experimental Section for details).

The first information available was derived from the determination of the amount of hydrogen present at C-6 relative to C-1 in the exo alcohol **9**. This approach was possible since in this compound H-6 was nicely separated in the nmr as was H-1; the H-5 and the H-4 hydrogens appeared as one group. Integration of the H-6 peak gave 0.63 hydrogen as the average of several nmr determinations (note Table II). Similarly, the sum of the H-5 and H-4 hydrogens totalled 1.98. Other areas observed experimentally are listed in Tables II and III.

Determination of the Relative Amounts of Benzo-Vinyl *vs.* Naphtho-Vinyl Bridging. Chart II describes

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[8] This was suggested by the work of S. J. Cristol, W. Y. Lim, and A. R. Dahl, *J. Amer. Chem. Soc.*, **92**, 4013 (1970), who found that two epimeric bromides resulted from the reaction of hydrogen bromide with dibenzosemibullvalene.

[9] J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

Table II. Observed and Theoretical Hydrogen Distributions in Run I

exo-6-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene (**9**)

	Label distribution				
Case	H-1	*endo*-H-6	H-5	*endo*- + *exo*-H-4	$\left(\frac{\text{H-5} + \text{H-4's}}{\text{H-1} + \text{H-6}}\right)$
Mech A, calcd	1.00	0.28 ± 0.02	0.28 ± 0.02	2.00	1.70 ± 0.04
Mech B, calcd	1.00	1.00	0.28 ± 0.02	1.28 ± 0.02	0.78 ± 0.04
50% Mech A + 50% mech B calcd	1.00	0.64 ± 0.02	0.28 ± 0.02	1.64 ± 0.02	1.17 ± 0.05
Experimental	1.00	0.63 ± 0.02	1.98 ± 0.04		1.21 ± 0.06

endo-4-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene (**11**)

	Label distribution				
Case	H-1	*endo*-H-4	H-5	*endo*- + *exo*-H-6	$\left(\frac{\text{H-5} + \text{H-6's}}{\text{H-1} + \text{H-4}}\right)$
Mech A, calcd	1.00	1.00	0.28 ± 0.02	1.28 ± 0.02	0.78 ± 0.04
Mech B, calcd	1.00	0.28 ± 0.02	0.28 ± 0.02	2.00	1.70 ± 0.04
50% Mech A + 50% mech B calcd	1.00	0.64 ± 0.02	0.28 ± 0.02	1.64 ± 0.02	1.17 ± 0.05
Experimental	1.58 ± 0.02		1.98 ± 0.02		1.25 ± 0.04

Benzo-2,3-naphthobicyclo[3.3.0]octadien-6-one (**13**)

	Label distribution			
Case	H-1	H-5	*endo*- + *exo*-H-4	$\left(\frac{\text{H-5} + \text{H-4's}}{\text{H-1}}\right)$
Mech A, calcd	1.00	0.28 ± 0.02	2.00	2.28 ± 0.02
Mech B, calcd	1.00	0.28 ± 0.02	1.28 ± 0.02	1.56 ± 0.02
50% Mech A + 50% mech B calcd	1.00	0.28 ± 0.02	1.64 ± 0.02	1.92 ± 0.04
Experimental	1.00	1.96 ± 0.04		1.96 ± 0.04

Benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one (**14**)

	Label distribution			
Case	H-1	H-5	*endo*- + *exo*-H-6	$\left(\frac{\text{H-5} + \text{H-6's}}{\text{H-1}}\right)$
Mech A, calcd	1.00	0.28 ± 0.02	1.28 ± 0.02	1.56 ± 0.02
Mech B, calcd	1.00	0.28 ± 0.02	2.00	2.28 ± 0.02
50% Mech A + 50% mech B calcd	1.00	0.28 ± 0.02	1.64 ± 0.02	1.92 ± 0.04
Experimental	1.00	2.02 ± 0.06		2.02 ± 0.06

Table III. Observed and Theoretical Hydrogen Distributions in Run 2

Benzo-2,3-naphthobicyclo[3.3.0]octadien-6-one (**13**)

	Label distribution			
Case	H-1	H-5	*endo*- + *exo*-H-4	$\left(\frac{\text{H-5} + \text{H-4's}}{\text{H-1}}\right)$
Mech A, calcd	1.00	0.18 ± 0.01	2.00	2.18 ± 0.01
Mech B, calcd	1.00	0.18 ± 0.01	1.18 ± 0.01	1.36 ± 0.02
50% Mech A + 50% mech B calcd	1.00	0.18 ± 0.01	1.59 ± 0.01	1.77 ± 0.03
Experimental	1.00	1.75 ± 0.09		1.75 ± 0.09

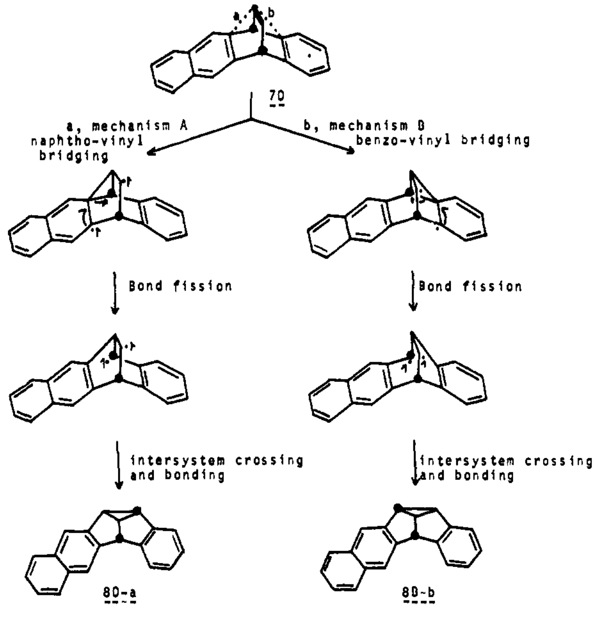
Benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one (**14**)

	Label distribution			
Case	H-1	H-5	*endo*- + *exo*-H-6	$\left(\frac{\text{H-5} + \text{H-6's}}{\text{H-1}}\right)$
Mech A, calcd	1.00	0.18 ± 0.01	1.18 ± 0.01	1.36 ± 0.02
Mech B, calcd	1.00	0.18 ± 0.01	2.00	2.18 ± 0.01
50% Mech A + 50% mech B calcd	1.00	0.18 ± 0.01	1.59 ± 0.01	1.77 ± 0.03
Experimental	1.00	1.78 ± 0.06		1.78 ± 0.06

the two alternative reaction mechanisms, one proceeding by benzo–vinyl bridging (path **B**) and the other going by naphtho–vinyl bridging (path **A**). It can be seen that these two differ in the final distribution of the bridgehead hydrogen label. Since in the present study, the original vinyl positions were not totally deuterated, it was necessary to correct expectation for each mechanism for the residual hydrogen. This is illustrated for the example of the distribution expected for exo alcohol **9** as derived from each of the two mechanisms, A and B; note Figure 1. This type of reasoning, giving the hydrogen distribution expected from each mechanism, is summarized in Tables II and III.

It is seen from comparison of the experimentally determined hydrogen distribution with the distributions expected for the two mechanisms that equal amounts of mechanisms A and B are utilized.

Chart II. Structural Consequences of the Benzo–Vinyl and Naphtho–Vinyl Bridging Mechanisms, B and A

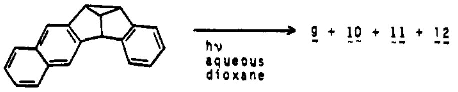


• represents hydrogen label

Quantum Yield Results. It was of some interest to compare the efficiency of the benzonaphthobarrelene rearrangement with that of 2,3-naphthobarrelene studied previously.[4] Determination of the efficiency using ferrioxalate actinometry[10] gave a value of 0.077 on direct irradiation. Because of experimental difficulties arising from a high reactivity of product, it was not possible to determine with certainty the sensitized efficiencies, even at low conversions. However, triplet reactivity was observed and is reported in the Experimental Section.

Photolysis of Benzonaphthosemibullvalene in Aqueous Dioxane. As an alternative approach to obtain the alcohols **9**, **10**, **11**, and **12**, the photolysis of benzonaphthosemibullvalene in aqueous dioxane was tried. The hydrolytic ring opening of similar semibullvalenes has been previously described by Hixson.[11] Presently it was observed that all four possible alcohols were obtained. However, there was a preference for the endo stereoisomers and also a preference for the structural isomer with the hydroxyl adjacent to the naphthyl group. The reaction is depicted in eq 4. The details are given in the Experimental Section.

Figure 1. Determination of the expected hydrogen distribution in exo alcohol 9: y represents hydrogen from HBr protonation, v represents original vinyl hydrogen, and b and ● represent hydrogens derived from original bridgehead locations. Thus, b = 1, v = r, y = 1, y + b = 2, and y + v = 1 + r, where r represents the amount of residual unexchanged vinyl hydrogen



(4)

Interpretative Discussion of Results

The most striking result was the equal preference for the benzo–vinyl and β-naphtho–vinyl bridging reaction mechanisms. This clearly was not what might have been anticipated if that portion of the molecule having a heavy concentration of the excitation energy were the portion to react preferentially. It is fair to conclude that in the benzonaphthobarrelene excited states, both singlet and triplet, the excitation energy is heavily localized in the naphtho portion. Thus the fluorescence spectrum of benzonaphthobarrelene proved essentially identical with that of naphthalene itself; this is described in the Experimental Section. Similarly, the phosphorescence emission spectrum in isopentane–methylcyclohexane at 77°K proved essentially identical with that of 2,3-naphthobarrelene as determined by us earlier;[4] the triplet energy obtained was again 62 kcal/mol. Finally in this regard, it is noted that what is meant by concentration of excitation is a situation where the excited state wave function differs from the ground state one primarily in the weighting of atomic orbital terms localized in one part of the molecule.

Actually, the present situation is part of a general pattern. Previously it had been observed that 2,3-naphthobarrelene rearranged by vinyl–vinyl bridging route rather than β-naphtho–vinyl bridging, although again one might have envisaged energy heavily concentrated in the naphtho portion of the molecule.[4] In the case of benzobarrelene, vinyl–vinyl bridging also was the preferred route;[3] here the triplet excitation would be expected to be more delocalized than in the other examples. In the one case of 1,2-naphthobarrelene,[4] vinyl–vinyl bridging was not the preferred process and α-naphtho–vinyl bridging proved dominant.

Thus, operationally there is a pattern of reactivity in the bridging process: α-naphtho–vinyl > vinyl–vinyl > β-naphtho–vinyl $\simeq$ benzo–vinyl. This pattern is understood on the basis proposed by us earlier.[3,4] Thus, rather than the nature of the unperturbed triplet state of the barrelene derivative, one finds that control is by the energy of a triplet species along the reaction coordinate where the bridging groups are brought into proximity and overlap weakly. By taking styryl triplet (E_T = 59.8[12]) as a model for the benzo–vinyl bridged species, β-vinylnaphthalene triplet (E_T = 59.5 kcal/mol[12]) for the β-naphtho–vinyl bridged species, α-vinylnaphthalene triplet (E_T = 56.3 kcal/mol[12]) for the α-naphtho–vinyl bridged molecule, and a butadiene-like

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[10] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

[11] S. S. Hixson and D. W. Garrett, *J. Amer. Chem. Soc.*, **93**, 5294 (1971).

[12] Note ref 3 and 4 for a discussion of the triplet energies of the moieties under discussion and for pertinent references.

triplet (E_T in the range of 53–61 kcal/mol[12]) for the vinyl–vinyl bridged case, one obtains the observed order of preference as long as the butadiene electrons are about 58 kcal/mol. Thus one can conclude that minimization of energy of the reacting triplet along the reaction coordinate at the stage of transannular bridging is the controlling factor.

Experimental Section[13]

Photolysis Equipment. Larger scale quantitative runs were made with the Black Box apparatus[14] previously described[15] using a 1000-W AH6 high-pressure mercury arc in a large parabolic reflector 14.0 cm in diameter and 750-ml quartz faced cells. Smaller scale runs were made on the organic chemists' optical bench described earlier;[14,15] this utilized a Bausch and Lomb high intensity monochrometer with a HBO 200-W high-pressure lamp and 40-ml, 10-cm cells. In both cases a beam splitter[15] and ferrioxalate actinometry[10] were used. Preparative runs were made in a 450-W Hanovia immersion apparatus.

Two filter combinations were used in the Black Box apparatus having three 2.4-cm path-length filter cells. Filter A: cell I, 526 g of nickel sulfate hexahydrate/l. of 5% sulfuric acid; cell II, 210 g of cobalt sulfate heptahydrate/l. of 5% sulfuric acid; cell III, 120 mg of bismuth trichloride/l. of 10% hydrochloric acid; transmission 250–305 nm, max at 283 nm.

Filter B: cell I, 36 g of nickel salt/l. of 10% sulfuric acid; cell II, 135 g of cobalt salt/l. of 10% sulfuric acid; cell III, 74 g of stannous chloride dihydrate/l. of 10% hydrochloric acid; transmission, 325–390 nm, max at 350 nm.

Benzo-2,3-naphthobarrelene. To a magnetically stirred, ice-cooled mixture of 6.0 g (0.032 mol) of 3-amino-2-naphthoic acid in 400 ml of absolute ethanol acidified with 20 ml of concentrated sulfuric acid, 10 ml (0.075 mol) of isoamyl nitrite was added over 5 min. The cooling was stopped and the stirring continued for an additional 2 hr. Dilution with 500 ml of ether precipitated 3-diazonium-2-naphthoic acid sulfate, which was washed with ether and used in the next step without further purification.

An ice-cooled solution of 2.50 g (0.045 mol) of potassium hydroxide in 20 ml of water was added during 10 min to an ice-cooled solution of the 3-diazonium-2-naphthoic acid sulfate in 30 ml of water. After stirring for an additional 60 min, the dark red mixture was filtered and the filtrate was added to 400 ml of ethanol and 1.5 l. of ether. The resulting yellow 3-diazoniumnaphthalene-2-carboxylate was filtered and washed with ether and tetrahydrofuran, and then with cyclohexane. The solid was not purified further. The diazonium carboxylate was added to 100 g (0.78 mol) of molten naphthalene, and the very dark red mixture was stirred at 81° for 3 hr. Naphthalene was sublimed from the mixture at 70° and 20-mm vacuum for 72 hr. The red residue in ether was washed with 10% sodium hydroxide and then water and concentrated *in vacuo*. This material was chromatographed on a 5 × 40 cm silica gel column slurry packed in hexane. The first light yellow fractions, eluted with 3% ether in hexane, were concentrated and chromatographed on a 2 × 30 cm column of silica gel impregnated with silver nitrate (10% by weight) slurry packed in hexane. Elution with 15% ether in hexane gave 800 mg of benzo-2,3-naphthobarrelene which was crystallized from hexane; mp 146–147° (lit.[6] 145–146°).

The spectral data were: ir ($CHCl_3$) 3.25, 3.32, 3.35, 6.25, 6.70, 6.82, 6.95, 7.12, 7.45, 7.60, 7.90, 8.40, 8.80, 9.12, 9.45, 9.80, 10.55, 11.40, 12.20, and 14.46 μ; uv max (cyclohexane) 224 sh (55,500), 233 (73,000), 240 (89,000), 255 (10,150), 266 (13,800), 274 (15,200), 284 (5550), 293 (825), 299 (665), 300 (1400), 311 (665), and 319 nm (1780); nmr (CCl_4) τ 2.35–3.25 (m, 12 H, aromatic and vinyl), 4.82–5.02 (m, 2 H, bridgehead).

Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.18; H, 5.58.

Benzo-2,3-naphthosemibullvalene from the Direct Photolysis of Benzo-2,3-naphthobarrelene. A solution of 1.134 g (4.47 mmol) of benzo-2,3-naphthobarrelene in 200 ml of cyclohexane was photolyzed for 1 hr in the preparative apparatus using a Vycor (1 mm) filter. The solvent was removed *in vacuo* and the residue was chromatographed on a 3 × 60 silica gel column impregnated with silver nitrate (10% wt), slurry packed in hexane. Elution in 200-ml fractions gave: 1–3, hexane, nil; 4–7, 7% ether in hexane, 488 mg of benzo-2,3-naphthosemibullvalene which was crystallized from hexane giving mp 154–156°; 8–10, 8% ether in hexane, 134 of a mixture of benzo-2,3-naphthosemibullvalene and starting material; 11–20, 10% ether in hexane, 530 mg of recovered benzo-2,3-naphthobarrelene.

The spectral data of benzo-2,3-naphthosemibullvalene were: ir ($CHCl_3$) strong 3.32, 6.80, 6.95, 7.90, 11.55; medium 3.38, 6.25, 9.85, 10.30 and 11.20 μ; uv (cyclohexane) max 240 (66,000), 264 (6850), 276 (7350), 284 (6850), 296 sh (3940), 313 (1265), 320 (735), and 328 nm (1710); nmr (CCl_4) τ 2.26–3.14 (m, 10 H, aromatic), 5.40–5.50 (AB d, 1 H, β-naphthylic and benzylic H-5, $J_{15} = 6$ Hz), 6.26–6.46 (ABCD q, 1 H, interior cyclopropyl H-1, $J_{15} = J_{12} = J_{18} = 6$ Hz), 6.84–7.12 (two ABC triplets, 2 H, cyclopropyl and β-naphthylic H-8, and cyclopropyl and benzylic H-2, $J_{12} = J_{18} = 6$ Hz, $J_{28} = 7$ Hz). Double resonance was performed at 100 MHz. Irradiation of H-5 (295 Hz, 500 mV) collapsed H-1 to a triplet ($J_{12} = J_{18} = 6$ Hz); H-1 irradiated (285 Hz, 600 mV) brought H-5 to a singlet and H-2 and H-8 to an AB quartet ($J_{28} = 7$ Hz); H-2 and H-8 irradiated (279 Hz, 400 mV) H-1 to a doublet ($J_{15} = 6$ Hz). The mass spectrum (70 ev) showed the molecular ion at *m/e* 254.

Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.32; H, 5.70.

Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadienes. An aqueous solution of 5.0 ml of 48% hydrogen bromide and 389 mg (1.58 mmol) of benzo-2,3-naphthosemibullvalene in 50 ml of acetic acid was allowed to stand for 24 hr at 25°. The mixture was diluted with ether, washed with saturated sodium bicarbonate and then water, dried ($MgSO_4$), and concentrated *in vacuo*.

The residue was refluxed in 80 ml of acetone, 20 ml of water, and 1.0 ml of pyridine for 2 hr and then diluted with ether, washed with 10% hydrochloric acid and then water, dried ($MgSO_4$), and concentrated *in vacuo*. The residue was chromatographed on a 4 × 40 cm silica gel column slurry packed in hexane. Elution in 150-ml fractions gave: 1–9, 15% ether in hexane, 87 mg, mixture of monoacetates (18%); 10–16, 30% ether in hexane, 330 mg, mixture of monoalcohols (80%). The mixture of monoalcohols was separated by preparative tlc on five 25 × 25 cm plates, each coated with 25 g of silica gel (Merck GF 254) activated at 100°. Mixtures were eluted with 30% ethyl acetate in cyclohexane and dried alternately until separation was observed under ultraviolet light. Each zone was ether extracted.

The first zone gave an inseparable mixture of *endo*-4-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene and *endo*-6-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene. The second zone gave *exo*-6-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene, mp 173–174° after crystallization from hexane–ether. The spectral data were: ir ($CHCl_3$) strong 2.78, 3.22, 3.42, 9.15, 9.80, 11.30; medium 2.93, 3.28, 6.25, 6.80, and 10.50 μ; nmr ($CDCl_3$) τ 2.05–2.90 (m, 10 H, aromatic), 4.88–5.05 (d, 1 H, β-naphthylic and geminal to OH, *endo*-H-6, $J_{65} = 3$ Hz), 5.07–5.25 (d, 1 H, β-naphthylic and benzylic, H-1, $J_{15} = 7$ Hz), 6.55–7.20 (m, 3 H, H-5, *endo*-H-4 and *exo*-H-4), 7.95 (s, 1 H, OH).

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.03; H, 6.03.

The third zone gave *exo*-4-hydroxybenzo-2,3-naphthobicyclo-[3.3.0]octadiene, mp 141–143° after crystallization from hexane–ether. The spectral data were: ir ($CHCl_3$) strong 2.78, 3.33, 3.42, 10.00, 11.50; medium 2.95, 3.25, 6.25, 6.80, 9.10, and 10.55 μ; nmr ($CDCl_3$) τ 2.06–2.86 (m, 10 H, aromatic), 4.95–5.22 (m, 2 H, benzylic and geminal to OH, *endo*-H-4; β-naphthylic and benzylic, H-1), 6.65–7.20 (m, 3 H, H-5, *endo*-H-6 and *exo*-H-6), 7.90 (s, 1 H, OH).

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.33; H, 6.01.

Benzo-2,3-naphthobicyclo[3.3.0]octadien-6-one. A 120-mg (0.44 mmol) sample of *exo*-6-hydroxybenzo-2,3-naphthobicyclo[3.3.0]-octadiene in 30 ml of acetone was treated with 1.0 ml of Jones reagent containing 114 mg (1.14 mmol) of chromium trioxide in 12% sulfuric acid. After 10 min, water dilution and ether extraction gave 110 mg of the benzo-2,3-naphthobicyclo[3.3.0]octadien-6-one, mp 195–196°, after recrystallization from hexane–ether. The spectral data were: ir ($CHCl_3$) strong 5.85, 6.15, medium 3.32, 3.43, 6.25, 6.95, 8.60, 8.80, 9.05, and 11.25 μ; uv (cyclohexane) max 250 (69,000), 282 sh (5850), 293 (9100), 305 (10,600), 322 (660), 336 (950), 353 nm (1000); nmr ($CDCl_3$) τ 1.76 (s, 1 H, aromatic, naphthyl ortho to C=O), 1.88 (s, 1 H, aromatic, naphthyl probably

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[13] All melting points were taken on a hot stage apparatus calibrated with known compounds.

[14] H. E. Zimmerman, *Mol. Photochem.*, 3, 281 (1971).

[15] H. E. Zimmerman, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, 93, 3662 (1971).

ortho to C_8), 2.06–2.88 (m, 8 H, aromatic), 4.84–5.00 (d, 1 H, β-naphthylic and benzylic, H-1, J_{15} = 7 Hz), 6.25–6.68 (m, 3 H, H-5, *endo*-H-4 and *exo*-H-4).

Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.51; H, 4.99.

Mass spectrum (70 eV) showed the molecular ion at *m/e* 270 (calcd for $C_{20}H_{14}O$, 270.31).

Benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one. Similar treatment as in the preceding preparation of 160 mg (0.59 mmol) of *exo*-4-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene in 40 ml of acetone with 1.0 ml of Jones reagent (*vide supra*) for 10 min and work-up gave a solid which was crystallized from hexane–ether to give 145 mg of benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one, mp 163–164°.

The spectral data were: ir ($CHCl_3$) strong 5.87; medium 3.35, 3.45, 5.25, 6.90, 7.80, and 11.60 μ; uv (cyclohexane) λ_{max} 229 (67,500), 275 (6100), 284 (6930), 293 sh (1850), 307 (1460), 314 sh (750), 321 nm (1660); nmr ($CDCl_3$) τ 2.12–2.70 (m, 10 H, aromatic), 4.90–5.00 (d, 1 H, β-naphthylic and benzylic, H-1), 6.20–6.74 (m, 3 H, H-5, *endo*-H-6 and *exo*-H-6).

Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.60; H, 5.15.

The mass spectrum (70 eV) showed the molecular ion at *m/e* 270 (calcd for $C_{20}H_{14}O$, 270.31).

***endo*-6-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene.** Sodium borohydride (200 mg, 5.2 mmol) was stirred with 148 mg (0.55 mmol) of benzo-2,3-naphthobicyclo[3.3.0]octadien-6-one in 50 ml of ethanol. The mixture was stirred at room temperature for 1 hr and poured onto ice; the mixture was ether extracted, and the extract was washed with water, dried, concentrated *in vacuo*, and crystallized from hexane–ether to give 126 mg of *endo*-6-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene, mp 182–183°.

The spectral data were: ir ($CHCl_3$) strong 2.75, 3.30, 3.40, 6.75, 9.30, 11.20; medium 2.90, 6.25 and 10.50 μ; nmr ($CDCl_3$) τ 2.15–2.90 (m, 10 H, aromatic), 4.50–4.68 (d, 1 H, β-naphthylic and geminal to OH, *exo*-H-6, J_{65} = 7 Hz), 5.20–5.42 (d, 1 H, β-naphthylic and benzylic, H-1, J_{15} = 7 Hz), 6.15–7.10 (m, 3 H, H-5, *endo*-H-4 and *exo*-H-4), 8.25 (s, 1 H, OH).

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 87.88; H, 6.13.

***endo*-4-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene.** Sodium borohydride (150 mg, 4.0 mmol) was stirred with 98 mg (0.36 mmol) of benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one in 50 ml of ethanol for 1 hr at room temperature and then poured onto ice. The organic product was ether extracted, washed with water, dried, concentrated *in vacuo*, and crystallized from hexane–ether to give 68 mg of *endo*-4-hydroxybenzo-2,3-naphthobicyclo[3.3.0]-octadiene, mp 182–184°.

The spectral data were: ir ($CHCl_3$) strong 2.75, 3.32, 9.60, 10.80, medium, 2.90, 3.38, 6.25, 6.80, and 10.30 μ; nmr ($CDCl_3$) τ 2.10–2.85 (m, 10 H, aromatic), 4.53–4.73 (d, 1 H, benzylic and geminal to OH, *exo*-H-4, J_{45} = 7 Hz), 5.20–5.30 (d, 1 H, β-naphthylic and benzylic, H-1, J_{15} = 7 Hz), 6.10–7.00 (m, 3 H, H-5, *endo*-H-6 and *exo*-H-6), 8.20 (s, 1 H, OH).

Anal. Calcd for $C_{20}H_{16}O$: C, 88.20; H, 5.92. Found: C, 88.72; H, 5.45.

Nmr Using Tri(dipivalomethanato)europium(III). All studies were carried out on a 100-MHz Varian apparatus, using TMS as an internal standard. The product (7.5×10^{-2} *M*) was dissolved in 1 ml of $CDCl_3$, with increasing amounts of $Eu(DPM)_3$. Data for individual runs are listed as follows: name of the compound, and different concentrations of $Eu(DPM)_3$ followed by the position (in τ) and the shape for the ortho aromatic proton.

exo-6-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene: 0 *M*, 2.12–2.81 (aromatic peak); 16×10^{-3} *M*, 1.68 (s); 26×10^{-3} *M*, 1.34 (s).

exo-4-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene: 0 *M*, 2.08–2.82 (aromatic peak); 14×10^{-3} *M*, 2.08–2.82 (aromatic peak); 60×10^{-3} *M*, 0.84 (d, J_{ortho} = 7 Hz).

endo-6-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene: 0 *M*, 2.15–2.90 (aromatic peak); 39×10^{-3} *M*, 0.95 (s).

endo-4-Hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene: 0 *M*, 2.10–2.85 (aromatic peak); 43×10^{-3} *M*, 0.48 (d, J_{ortho} = 7 Hz).

Benzo-2,3-naphthobicyclo[3.3.0]octadien-6-one: 0 *M*, 1.76 (s); 20×10^{-3} *M*, 1.50 (s); 60×10^{-3} *M*, 0.74 (s).

Benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one: 0 *M*, 2.10–2.80 (aromatic peak); 13×10^{-3} *M*, 2.10–2.80 (aromatic peak); 60×10^{-3} *M*, 1.58 (d, J_{ortho} = 7 Hz).

Direct Photolysis of Benzo-2,3-naphthosemibullvalene in Aqueous Dioxane. A solution of 110 mg (0.433 mmol) of benzo-2,3-naphthosemibullvalene in 100 ml of dioxane and water (8:2 v/v) was photolyzed with the 450-W Hanovia immersion apparatus, using a Vycor filter, for 1 hr. The solvent was removed *in vacuo;* the residue was ether extracted and chromatographed on a 3 × 60 cm silica gel column slurry packed in hexane. Elution with increasing amounts of ether in hexane gave 81 mg (68%) of a mixture of hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadienes (approximately 52 mg of the endo alcohols and 29 mg of the exo alcohols) in the 15% ether fractions. The product was identified by tlc and by Jones oxidation to the ketones and tlc of these, as well as by the nmr spectra of both alcohols and the ketones.

***N*,*N*-Dideuteriocyclohexylamine.** This was prepared by a very slight modification of the method used earlier.[3,4] Cyclohexylamine cycled four times with D_2O was used.

Deuteration of Benzo-2,3-naphthobarrelene. A 1.1-g (4.35 mmol) portion of benzo-2,3-naphthobarrelene was treated with lithium cyclohexylamide prepared from 20 ml of *N*,*N*-dideuteriocyclohexylamine and 3.0 ml (6.6 mmol) of 2.2 *M* butyllithium in hexane. The mixture was stirred under nitrogen at 70° for 70 hr. An additional 3.0-ml portion of 2.2 *M* butyllithium was added after 47 hr. The dark green mixture was quenched with 10 ml of deuterium oxide, diluted with 300 ml of hexane, and then washed with two 250-ml portions of 10% aqueous HCl and two 250-ml portions of water. The hexane solution was dried ($MgSO_4$) and concentrated *in vacuo* to give an orange-red material. Sublimation (140° at 18 mm), followed by silica gel chromatography, gave 240 mg (22%) of benzo-2,3-naphthobarrelene which was 60 ± 2% deuterated in the aromatic and vinyl positions.

In a subsequent run, a first pass gave 13% deuterated material, the second pass gave 49%, and the third pass brought the deuteration to 69%.

Nmr Analysis of Deuterated Benzo-2,3-naphthobarrelene. The nmr (CCl_4) of deuterated benzo-2,3-naphthobarrelene consisted of τ 2.33–3.30 (m, aromatic and vinyl), 4.96 (br s, bridgehead) absorption with the following areas, where A, V, and B are the aromatic, vinyl, and bridgehead areas, respectively. First run: A + V (rel area 90 ± 1), B (rel area 37 ± 1). This gives 60% deuteration assuming no bridgehead attack. Second run: (i) A + V (rel area 104 ± 2), B (rel area 20 ± 1); *i.e.*, 13% deuteration; (ii) A + V (rel area 70.5 ± 2), B (rel area 23 ± 1), *i.e.*, 49% deuteration; (iii) A + V (rel area 73 ± 2), B (rel area 40 ± 1), *i.e.*, 69% deuteration.

Direct Photolysis of Deuterated Benzo-2,3-naphthobarrelene and Deuterium Assay. A first photolysis was carried out on 230 mg (0.905 mmol) of 60% deuterated benzo-2,3-naphthobarrelene in 500 ml of cyclohexane using the 450-W immersion apparatus, for 1 hr. The solvent was removed *in vacuo* and the residue was chromatographed on a 3 × 60 cm silica gel column impregnated with silver nitrate (10% wt) and slurry packed in hexane. Elution in 150-ml fractions gave: 1–6, hexane, nil; 7–15, 7% ether in hexane, 205 mg of deuterated benzo-2,3-naphthosemibullvalene which was crystallized from hexane, mp 154–156°; 16–20, 10% ether in hexane, 20 mg of starting material.

The nmr (CCl_4) of the deuterated benzo-2,3-naphthosemibullvalene consisted of τ 2.40–3.20 (m, aromatic, rel area 199 ± 5), 5.50 (br s, H-5, rel area 54 ± 3), 6.40 (t, H-1, rel area 15 ± 1), 7.05 (2d, H-2 and H-8, rel area 62 ± 4). The ratio of the relative areas of H-5 and H-1 gives 72 ± 3% vinyl deuteration.

Addition of hydrogen bromide and solvolysis of the bromides in exactly the manner described for preparation of the undeuterated substances were carried out on 200 mg of 72% vinyl deuterated benzo-2,3-naphthosemibullvalene to give 167 mg of a mixture of deuterated alcohols.

Purification by preparative tlc gave 37 mg of *exo*-6-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene and 45 mg of *exo*-4-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene which were crystallized from hexane.

The nmr ($CDCl_3$) of the deuterated *exo*-6 alcohol consisted of τ 2.05–2.90 (m, aromatic, rel area 114 ± 2), 4.97 (br s, *endo*-H-6, rel area 19 ± 0.5), 5.19 (br s, H-1, rel area 30 ± 1), 6.50–7.35 (m, H-5, *endo*-H-4 and *exo*-H-4, rel area 59.5 ± 1.5), 7.75 (s, OH, rel area 27 ± 1).

The nmr ($CDCl_3$) of the deuterated *exo*-4-alcohol consisted of τ 2.20–2.90 (m, aromatic, rel area 95 ± 2), 5.00–5.30 (2 s, *endo*-H-4 and H-1, rel area 39.5 ± 1) 6.40–7.30 (m, H-5, *endo*-H-6 and *exo*-H-6, rel area 49.5 ± 1), 7.80 (s, OH, rel area 24 ± 1).

Jones oxidation (*vide supra* for method) of the two deuterated alcohols described above gave respectively the deuterated benzo-2,3-naphthobicyclo[3.3.0]octadienones.

The nmr ($CDCl_3$) of the deuterated benzo-2,3-naphthobicyclo-[3.3.0]octadien-6-one consisted of τ 1.75–3.00 (m, aromatic, rel area 117 ± 3), 4.90 (br s, H-1, rel area 28 ± 1), 6.20–6.80 (m, H-5, *endo*-H-4 and *exo*-H-4, rel area 55 ± 1).

The nmr ($CDCl_3$) of the deuterated benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one consisted of τ 2.10–2.80 (m, aromatic, rel area 113 ± 3), 4.95 (br s, H-1, rel area 29 ± 1), 6.25–6.75 (m, H-5, *endo*-H-6 and *exo*-H-6, rel area 59 ± 2).

A second photolysis was carried out on 237 mg (0.935 mmol) of 69% deuterated benzo-2,3-naphthobarrelene in 750 ml of cyclohexane using the Black Box apparatus with the filter combination A, for 3.5 hr. The solvent was removed *in vacuo* and the residue was chromatographed on a 3 × 50 cm silica gel column impregnated with silver nitrate (10% wt) and slurry packed in hexane. Elution in 150-ml fractions gave: 1–3, hexane, nil; 4–11, 7% ether in hexane, 115.0 mg of deuterated benzo-2,3-naphthosemibullvalene which was crystallized from hexane, mp 154–155°; 12–14, 10% ether in hexane, 33.9 mg of a mixture of benzo-2,3-naphthosemibullvalene and starting material; 15–20, 20% ether in hexane, 86.8 mg of starting material.

The nmr (CCl_4) of deuterated benzo-2,3-naphthosemibullvalene consisted of τ 2.40–3.20 (m, aromatic, rel area 126 ± 4), 5.50 (br s, H-5, rel area 37 ± 1), 6.40 (t, H-1, rel area 6.5 ± 0.5), 7.05 (2d, H-2 and H-8, rel area 42 ± 1), *i.e.*, 82 ± 1% vinyl deuteration.

A solution of 95 mg (0.374 mmol) of 82% vinyl deuterated benzo-2,3-naphthosemibullvalene in 100 ml of dioxane and water (8:2 v/v) was photolyzed with the 450-W Hanovia immersion apparatus, using a Vycor filter for 2 hr. The solvent was removed *in vacuo*; the residue was ether extracted and chromatographed on a 3 × 60 cm silica gel column slurry packed in hexane. Elution with 20% ether in hexane gave 44 mg of a mixture of hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadienes, which was directly converted to the ketones by Jones' oxidation. The ketones were separated by preparative tlc (*vide supra* for method). The first zone gave 13 mg of benzo-2,3-naphthobicyclo[3.3.0]octadien-6-one which was crystallized from hexane.

The nmr ($CDCl_3$) consisted of τ 4.90 (br s, H-1, rel area 62 ± 1), 6.20–6.80 (m, H-5, *endo-* and *exo*-H-4, rel area 108 ± 2).

The second zone gave 7 mg of benzo-2,3-naphthobicyclo[3.3.0]-octadien-4-one which was crystallized from hexane. The nmr ($CDCl_3$) consisted of τ 4.90 (br s, H-1, rel area 23 ± 0.5), 6.30–6.70 (m, H-5, *endo-* and *exo*-H-6, rel area 41 ± 1).

Evidence for Absence of Bridgehead Deuteration. Sodium borohydride reduction (*vide supra*) of 35 mg of deuterated benzo-2,3-naphthobicyclo[3.3.0]octadien-4-one, obtained in the first deuterium assay (72% vinyl deuterated benzo-2,3-naphthosemibullvalene), gave 30 mg of *endo*-4-hydroxybenzo-2,3-naphthobicyclo[3.3.0]octadiene, which was crystallized from hexane.

The nmr ($CDCl_3$) consisted of τ 4.60 (br s, H-4, rel area 22 ± 1), 5.25 (br s, H-1, rel area 22 ± 1). Since H-4 derives from the borohydride and H-1 derives from an original bridgehead position, the 1:1 ratio demonstrates lack of bridgehead exchange.

Quantum Yields. Semimicro Runs. Dilute solutions (0.001–0.004 *M*) of benzo-2,3-naphthobarrelene in cyclohexane were irradiated on the optical bench apparatus. Analysis was accomplished on a 2% SE 54 Chromosorb W vpc column using triphenylethylene as an internal standard. Data for individual quantum yield runs are listed as follows: mass of starting material, added reagent (if any), solvent, wavelength, light input, mass of benzo-2,3-naphthosemibullvalene, mass of unreacted starting material, conversion, quantum yield of formation of benzonaphthosemibullvalene, and where determined quantum yield of disappearance of benzonaphthobarrelene.

Run I-01: 13.7 mg (0.054 mmol); 39 ml of cyclohexane; 313 nm (band width 21 nm); 0.130 mEinstein; 2.50 mg (0.0099 mmol); 11.2 mg (0.041 mmol); 18.3%; $\Phi = 0.076$.

Run I-02: 22.1 mg (0.087 mmol); 39 ml of cyclohexane; 313 nm (band width 21 nm); 0.104 mEinstein; 2.07 mg (0.0082 mmol); 20.1 mg (0.079 mmol); 9.4%; $\Phi = 0.078$.

Run I-03: 23.4 mg (0.0921 mmol); benzophenone, 197.5 mg (1.08 mmol); 39 ml of cyclohexane; 370 nm (band width 21 nm); 0.248 mEinstein; 1.33 mg (0.00525 mmol); 17.8 mg (0.070 mmol); 24%; $\Phi = 0.021$; $\Phi_{dis} = 0.089$.

Run I-04: 24.0 mg (0.0945 mmol); acetophenone, 5.15 g (0.0429 mol); 39 ml of benzene; 335 nm (band width 21 nm); 0.072 mEinstein; 0.77 mg (0.00301 mmol); 22.9 mg (0.090 mmol); 4.8%; $\Phi = 0.042$; $\Phi_{dis} = 0.063$.

Run I-05: 38.2 mg (0.15 mmol); *m* methoxyacetophenone, 1 g (6.65 mmol); 39 ml of cyclohexane; 350 nm (band width 21 nm); 0.134 mEinstein; 0.335 mg (0.00132 mmol); 27.75 mg (0.109 mmol); 27%; $\Phi = 0.012$; $\Phi_{dis} = 0.30$.

Macro-Runs in the Black Box Apparatus. Dilute solutions (0.005–0.0015 *M*) of benzo-2,3-naphthobarrelene in cyclohexane were irradiated on the macro apparatus. Photolyzed solutions were concentrated *in vacuo*; the residues were chromatographed on silica gel impregnated with silver nitrate (10% wt). Quantum yields were determined gravimetrically by weighing appropriate fractions from the chromatogram.

Data for individual quantum yield runs are listed as follows: mass starting material, added reagent if any, solvent, filter solution, light input, mass of benzo-2,3-naphthosemibullvalene, mass of unreacted benzonaphthobarrelene, conversion, quantum yield of formation of benzo-2,3-naphthosemibullvalene, and where determined quantum yield of disappearance of benzo-2,3-naphthobarrelene.

Run II-01: 121.6 mg (0.478 mmol); 740 ml of cyclohexane; filter A; 3.08 mEinsteins; 43.5 mg; 82.0 mg; 35%; $\Phi = 0.055$.

Run II-02: 118.1 mg (0.465 mmol); 740 ml of cyclohexane; filter A; 0.695 mEinstein; 11.6 mg; 108 mg; 9%; $\Phi = 0.060$.

Run II-03: 303.0 mg (1.19 mmol); acetophenone, 118 ml (120 g, 1 *M*); 740 ml of cyclohexane; filter B; 3.00 mEinsteins; no 2,3-naphthobenzosemibullvalene was detected; 247 mg of benzo-2,3-naphthobarrelene; 17%; $\Phi_{dis} = 0.068$.

Run II-04: 106.0 mg (0.418 mmol); benzophenone, 966 mg (5.3 mmol); 740 ml of cyclohexane; filter B; 14.70 mEinsteins; 11.0 mg (0.043 mmol); 16.6 mg (0.065 mmol); 84.5%; $\Phi = 0.0030$; $\Phi_{dis} = 0.024$.

Fluorescence and Phosphorescence Studies. All studies were carried out on an Aminco-Kiers spectrophosphorimeter. Phosphorescence study of benzo-2,3-naphthobarrelene (6.5×10^{-5} *M*) in isopentane–methylcyclohexane (1:4) glass at 77°K gave the maximum energy peak (the 0–0 band) at 463 nm corresponding to triplet energy of 62 kcal/mol. Fluorescence spectra were measured in cyclohexane at room temperature and showed maximum at 330 nm. Intersection of emission and absorption spectra occurred at 325 nm, corresponding to singlet energy of 88 kcal/mol. The spectrum was essentially identical with that of naphthalene.

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