The Di-π-methane Rearrangement of the Naphthobarrelenes. Mechanistic and Exploratory Organic Photochemistry. L[1]

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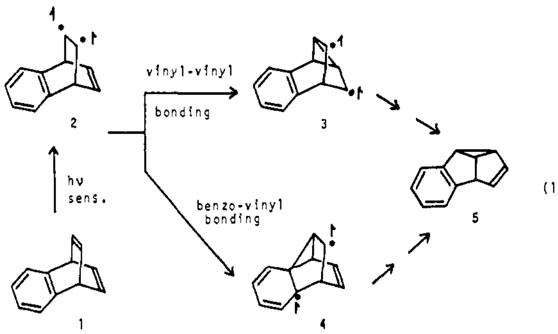
Abstract: 1,2-Naphthobarrelene (**8**) and 2,3-naphthobarrelene (**11**) were synthesized. Direct irradiation of 1,2-naphthobarrelene (**8**) in cyclohexane afforded 1,2-naphthocyclooctatetraene (**14**) as the major product (74%) along with equal amounts of the *syn* and *anti* isomers (**12** and **13**) of naphtho[1,2-*c*]tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (1,2-naphthosemibullvalene) as the minor products (26%), the latter arising from di-π-methane rearrangements. In contrast, the benzophenone sensitized reaction afforded solely the *syn*- and *anti*-1,2-naphthosemibullvalenes (**12** and **13**). The direct irradiation was shown by deuterium-labeling studies to proceed by naphtho–vinyl bonding of the excited state in the case of the naphthocyclooctatetraene formation. Similarly, the naphthosemibullvalene formation was demonstrated to result primarily from naphtho–vinyl bridging with vinyl–vinyl bridging as a lesser route. In the case of the sensitized reaction, only naphtho–vinyl bonding was encountered. The quantum yield for disappearance of 1,2-naphthobarrelene (**8**) was 0.49 for both the direct and sensitized reactions. Similar studies on 2,3-naphthobarrelene (**11**) were carried out. Here direct and sensitized runs led to the same results in terms of products, deuterium distribution, and (within experimental error) the quantum yields. Irradiation of 2,3-naphthobarrelene (**11**) afforded naphtho[2,3-*c*]tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (2,3-naphthosemibullvalene, **15**) by a vinyl–vinyl bonding route and with a quantum efficiency of 0.46. It is concluded that in general the least preferred process for the excited states studied is β-naphtho–vinyl bridging with vinyl–vinyl bridging intermediate and α-naphtho–vinyl bridging most preferred. The evidence supports a single excited triplet as responsible for the photochemistry in the 2,3-series while the lowest energy triplet is one of two reacting excited states in the 1,2-series.

In our previous study of the di-π-methane photochemical rearrangement of benzobarrelene[2] (**1**) to form benzosemibullvalene (**5**) the reaction mechanism involved initial vinyl–vinyl bonding of the excited triplet despite the *a priori* possibility of either this or benzo–vinyl bonding. One argument advanced to rationalize remarkable selectivity involved the distribution of electronic excitation between the vinyl and benzo moieties and the way in which this was affected by the two alternative bridging processes. It was concluded that vinyl–vinyl bridging led to a lower energy species.

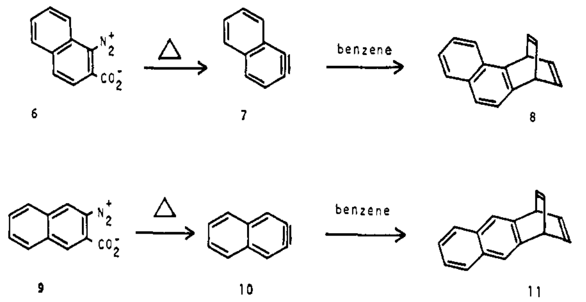


(1)

The intriguing possibility presented itself of utilizing fused aromatic barrelenes in which the aromatic portion would have lower triplet energies than ethylene. Concentration of the excitation at one end of the molecule seemed a possible way of forcing aromatic–vinyl bridging. 1,2-Naphthobarrelene (**8**) and 2,3-naphthobarrelene (**11**) were selected for study, since here an additional question was posed, namely, the relative reactivity of the α and β positions of the electronically excited naphthalene moiety.

Synthetic Aspects. The syntheses of 1,2-naphthobarrelene (**8**) and 2,3-naphthobarrelene (**11**) were conveniently achieved by the addition of 1,2-naphthyne (**7**) and 2,3-naphthyne (**10**), respectively, to benzene.[3] 1,2-Naphthyne (**7**) and 2,3-naphthyne (**10**) were generated thermally in refluxing benzene from the corresponding diazonium carboxylates (**6** and **9**) and gave the barrelenes, **8** and **11**, in low yield (6–7%). This synthetic sequence is presented in Chart I.

Chart I. Synthesis of the Naphthobarrelenes



The structures assigned to the naphthobarrelenes rest on the mode of preparation, the great similarity of the bridgehead hydrogen nmr pattern to that of the known[2] benzobarrelene (**1**), and finally, on the lithium cyclohexylamide[4] catalyzed reverse Diels–Alder reaction to afford phenanthrene from 1,2-naphthobarrelene (**8**) and anthracene from 2,3-naphthobarrelene (**11**). The reaction with lithium cyclohexylamide is an interesting one, occurring under mild conditions (80°), which obtains its driving force not only from

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(1) For paper XVIII of this series, note H. E. Zimmerman, E. F. McBride, and S. S. Hixson, *J. Amer. Chem. Soc.*, **92**, 2000 (1970). For paper IL and our preliminary communication note H. E. Zimmerman and C. O. Bender, *ibid.*, **91**, 7516 (1969).

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

(3) R. Huisgen and L. Zirngibl [*Chem. Ber.*, **91**, 1437 (1958)] have reported the generation of these species from strong base treatment of halonaphthylenes, and L. F. Fieser and M. J. Haddadin [*Can. J. Chem.*, **43**, 1599 (1965)] have described a procedure using 2,3-naphthalenediazoniumcarboxylate generated *in situ*.

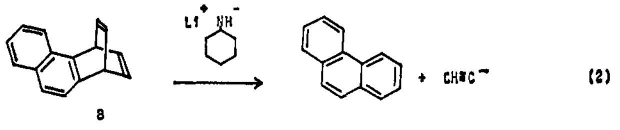
(4) A. Streitwieser, Jr., and W. C. Langworthy, *J. Amer. Chem. Soc.*, **85**, 1757 (1963).

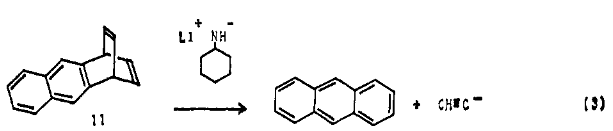
Table I. Nmr Spectra of the Semibullvalenes[a,b]

Description and assignment[d]	Signal position, τ			
	Benzo-SB[c]	2,3-Naphtho-SB[c]	*syn*-1,2-Naphtho-SB[c]	*anti*-1,2-Naphtho-SB[c]
Multiplet, aromatic	2.67–3.20	2.36–2.93	2.04–2.90	2.18–2.74
ABX quartet, H-6	4.43–4.62	4.49–4.63	4.42–4.50	4.45–4.53
ABX quartet, H-7	4.83–5.00	4.83–4.96	4.93–5.00	4.92–4.99
ABX quartet, H-5	6.10–6.28	6.00–6.13	6.05–6.14	5.63–5.72
ABCD quartet, H-1	6.74–6.98	6.63–6.94	6.62–6.80	6.62–6.81
ABC triplet, H-2	7.02–7.25	6.98–7.22	6.49–6.62	6.83–6.95
ABCDX doublet of triplets, H-8	7.25–7.55	7.39–7.62	7.07–7.22	7.19–7.35

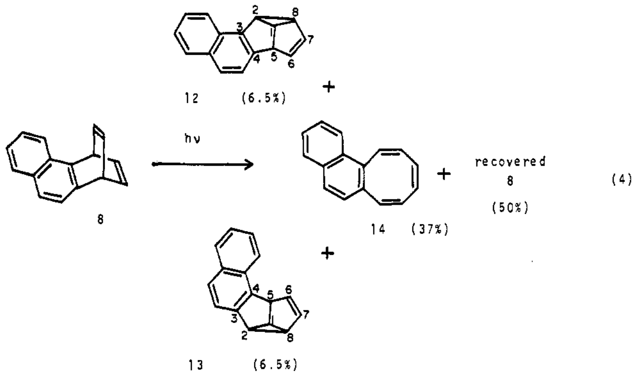
[a] Run on 100-MHz nmr in CCl_4 with TMS as internal standard. [b] Corresponding coupling constants were within 0.5 Hz, typically $J_{12} = J_{15} = J_{18} = J_{28} = 6.5$ Hz, $J_{56} = J_{78} = 2.0$ Hz, $J_{67} = 5.0$ Hz. [c] Semibullvalene (SB). [d] Structures in eq 4 give skeletal numbering.

aromatization but also heavily from conversion of a relatively unstable and highly basic anion (*i.e.*, lithium cyclohexylamide, $pK_a \cong 40$) to a more stable one, namely, acetylide anion ($pK_a \cong 25$). The reactions are depicted in eq 2 and 3.[5]

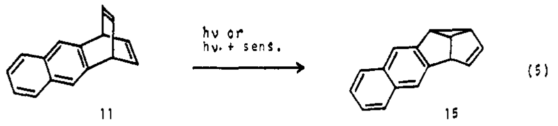




Exploratory Photochemical Efforts. Initial efforts revealed that both naphthobarrelene isomers were highly photochemically reactive. Thus, direct irradiation of 1,2-naphthobarrelene (**8**) was observed to afford 1,2-naphthocyclooctatetraene (**14**) as the major product along with lesser amounts of the *syn*- and *anti*-naphtho-[1,2-*c*]tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (**12** and **13**; or more simply *syn*- and *anti*-1,2-naphthosemibullvalene, respectively).[6] The reaction proved especially clean with a perfect mass balance (note eq 4). In contrast to this product distribution, the benzophenone-sensitized reaction led exclusively to the *syn*- and *anti*-1,2-naphthosemibullvalenes (**12** and **13**).



The reaction course taken by 2,3-naphthobarrelene was less complex in that both direct and sensitized reactions afforded the single product, naphtho[2,3-*c*]-tricyclo[3.3.0.0^{2,8}]octa-3,6-diene (*i.e.*, 2,3-naphthosemibullvalene, **15**) (see eq 5). Again the mass balance was excellent.



The structures of the semibullvalene photoproducts derived from the nmr spectra, which in all three cases proved to be remarkably similar to one another and to that of the known[2] benzosemibullvalene (**5**). Spin decoupling clearly defined the relative locations of all hydrogens and thus the molecular skeleton (see Experimental Section; note eq 4 for numbering of carbon framework). Finally, the assignment of *syn vs. anti* structures derived from the downfield shift found for the three-ring benzylic hydrogen at C-2 in the *syn* isomer relative to the *anti*, and the upfield shift of the benzylic hydrogen at C-5 in the *syn* isomer compared to the *anti* one. Implicit in the reasoning is the assumption that hydrogens external and close to the second naphthalene ring will be deshielded by ring current effects (*cf.* the τ 0.19 downfield shift of α- *vs.* β-methylnaphthalene). The nmr data are summarized in Table I.

To determine whether naphthocyclooctatetraenes might be derived from secondary photolysis of the naphthosemibullvalenes, the photochemistry of these compounds was inspected. It was found that although the 1,2-naphthosemibullvalene isomers (**12** and **13**) did give appreciable (42%, based on unrecovered reactant) amounts of the cyclooctatetraene (**14**), 2,3-naphthosemibullvalene (**15**) reacted only slowly, and the cyclooctatetraene seemed to be absent, and identifiable product was not obtained. In the case of 1,2-naphthocyclooctatetraene, labeling studies (*vide infra*) were required to establish that this compound did not arise from secondary photolysis of the 1,2-naphthosemibullvalene isomers.

Deuteration of the Naphthobarrelenes. For a study of the molecular details of the reaction mechanisms involved in the photolyses, naphthobarrelenes specifically labeled at the bridgehead positions were required. A convenient method had been developed in these laboratories, involving the use of lithium N-deuteriocyclohexylamide in N,N-dideuteriocyclohexylamine. In the present studies it was found that after two to four such treatments (see Experimental Section) deuterium was smoothly incorporated at the vinyl and aryl positions with 88.5 ± 1.0% vinyl deuterium incorporation in the case of 1,2-naphthobarrelene (**8**) and 92.4 ± 0.5% for 2,3-naphthobarrelene

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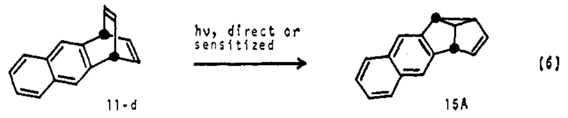
(5) The reaction has analogy in the reaction of norbornadiene with amylsodium which undergoes a similar reverse Diels–Alder as described by F. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

(6) *syn* and *anti* designations prove convenient in this paper to indicate the proximity of the three-ring to the second aromatic ring. Similar nomenclature is useful in describing the two types of vinyl, benzylic, etc., positions in the 1,2-naphtho series.

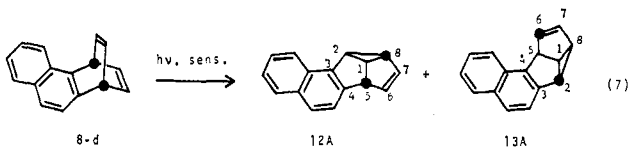
(11). This extent of deuteration proved quite satisfactory for following the residual bridgehead label although it was necessary to correct for unexchanged vinyl hydrogens. Two further points are important. First, implicit in the analysis of these results is the assumption of absence of bridgehead hydrogen exchange; the absence of such bridgehead exchange has been firmly established by mass spectral studies in the case of barrelene and benzobarrelene[2] (1). Second, incomplete exchange presents no difficulty in following the residual hydrogen label as long as all the vinyl positions are equally exchanged. For 2,3-naphthobarrelene (**11**) this was assured by molecular symmetry and for 1,2-naphthobarrelene (**8**) this was established by inspection of the nmr spectrum of the naphthocyclooctatetraene (**14-d**) formed from direct irradiation of labeled 1,2-naphthobarrelene (**8-d**). The *syn*- and *anti*-situated benzylic hydrogen[6] nmr peaks of this product were equally intense, showing that the deuterated 1,2-naphthobarrelene (**8-d**) precursor had its *syn* and *anti* vinyl hydrogens also equally exchanged. Nmr analysis of the deuterated 1,2-naphthobarrelene (**8-d**) itself supported this conclusion but was less definitive.

Photolysis of Labeled Reactants. Results. With the bridgehead labeled naphthobarrelenes in hand, our next objective became the determination of the disposition of the label in the photolysis products. Interestingly, the direct and sensitized irradiation of bridgehead labeled perdeuterated 2,3-naphthobarrelene (**11-d**) afforded product with the same distribution of label, this distribution being determined by nmr. The label was found exclusively in the benzylic positions as shown in eq 6; see Table III below and Experimental Section.

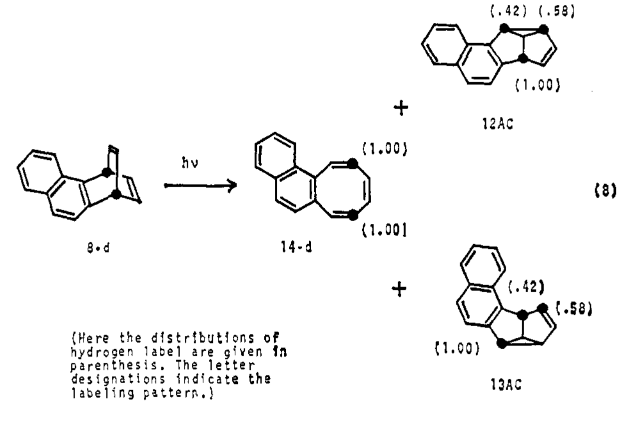


Here ● represents hydrogen label.

Similar studies were carried out with labeled 1,2-naphthobarrelene (**8-d**). However, here the direct and sensitized runs gave different results. Benzophenone sensitized irradiation of **8-d** gave an equal mixture of the perdeuterated *syn*- and *anti*-1,2-naphthosemibullvalenes (**12A** and **13A**) as was anticipated from the runs on unlabeled reactant. It was found (note Table IV and Experimental Section) that the *syn* product **12A** was labeled exclusively at C-5 and C-8 while the *anti* **13A** had the label totally at C-2 and C-6. Note eq 7.



In the case of the direct photolysis of perdeuterated 1,2-naphthobarrelene (**8-d**), the distribution of the hydrogen label was inspected for the two isomeric 1,2-naphthosemibullvalenes as well as for the 1,2-naphthocyclooctatetraene. The results, corrected for residual vinyl hydrogen, are illustrated in eq 8 (note also Table IV and the Experimental Section). The distribution of label in the 4 and 7 positions of the 1,2-naphthocyclooctatetraene contrasted with the finding of label in *three* locations in the 1,2-naphthosemibullvalenes (note eq 8) reveals that the naphthocyclooctatetraene does not arise from secondary photolysis of the semibullvalenes.



(Here the distributions of hydrogen label are given in parenthesis. The letter designations indicate the labeling pattern.)

Quantum Efficiencies. Quantum yields were determined using the parabolic reflector–parallel beam AH6 apparatus described by us earlier,[7] together with solution filters and ferrioxalate actinometry.[8] Precautions were taken to make certain that neither products nor absorbing impurities were appreciably capturing light. In sensitized runs, concentrations were adjusted so that benzophenone absorbed over 95% of the light and the acceptor concentration was selected to allow triplet transfer but to preclude transfer by the shorter lived benzophenone singlet. The quantum yields for both direct and benzophenone sensitized runs are listed in Table II.

Table II. Quantum Yields for Naphthobarrelene Photolyses

Run	Reactant	Sensitizer	Quantum yields Semibullvalenes	Quantum yields Cyclooctatetraene
1	1,2-NB[a]	None	0.13[b]	0.36
2	1,2-NB	Benzophenone[c]	0.50[b]	None
3	2,3-NB	None	0.45	None
4	2,3-NB	Benzophenone[d]	0.47	None

[a] Naphthobarrelene (NB). [b] Equally divided between *syn* and *anti* isomers. [c] 0.014 *M*. [d] 0.017 *M*.

Emission from the Excited Singlet. Results. It seemed important to determine the fluorescence quantum yield relative to that of naphthalene. However, only in the case of 2,3-naphthobarrelene (**11**) did this prove practical. It was found that 2,3-naphthobarrelene (**11**) was only 0.34 as efficient an emitter as naphthalene. Since the latter has been reported[9] to have a fluorescence quantum yield of 0.23, a reasonable but approximate value for 2,3-naphthobarrelene (**11**) is 0.08.

Interpretative Discussion of Mechanism. Molecular Details. 2,3-Naphthobarrelene. As noted earlier, a major goal in the present study was to ascertain the effect of the added fused ring on the direction of bridg-

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(7) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

(8) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

(9) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965, p 104.

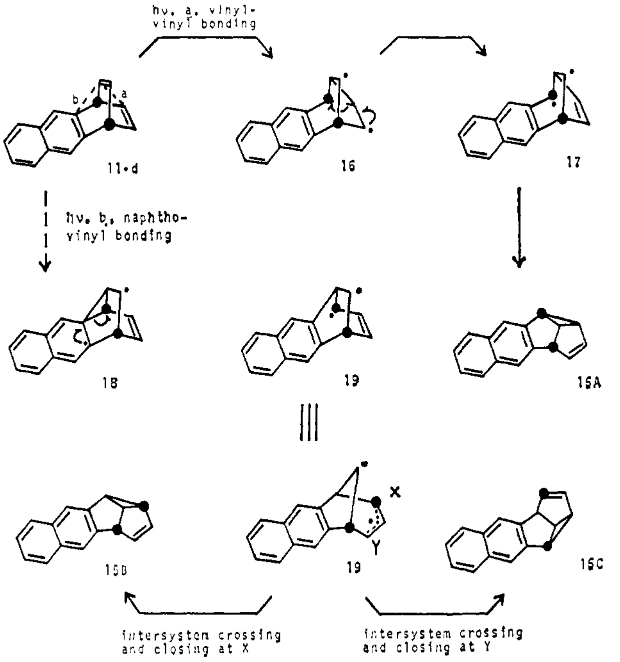
Table III. Observed and Theoretical Hydrogen Distributions in the Photolysis of Labeled 2,3-Naphthobarrelene to give **15A**

Case	Label distribution[a]					
	H-1	H-2	H-5	H-6	H-7	H-8
Mech *a*, calcd	0.076 (±0.005)	1.000	1.000	0.076 (±0.005)	0.076 (±0.005)	0.076 (±0.005)
Mech *b*, calcd	0.076 (±0.005)	0.538 (±0.003)	0.538 (±0.003)	0.538 (±0.003)	0.076 (±0.005)	0.538 (±0.003)
Sensit, exptl[b]	0.112 (±0.014)	0.948 (±0.056)	0.976 (±0.056)	0.084 (±0.014)	0.084 (±0.014)	0.098 (±0.028)
Direct, exptl[b]	0.081 (±0.004)	0.943 (±0.058)	1.035 (±0.092)	0.104 (±0.004)	0.081 (±0.004)	0.058 (±0.012)

[a] Corrected for 7.6 ± 0.5% residual vinyl hydrogen in naphthobarrelene reactant. [b] Errors estimated from the scatter of nmr signal integrations.

ing. The observation, outlined in eq 6, that the bridgehead atoms of 2,3-naphthobarrelene (**11**) become the benzylic positions in 2,3-naphthosemibullvalene (**15**) on either direct or sensitized photolysis clearly can be seen to be in accord with a di-π-methane mechanism[22] in which vinyl-vinyl bridging occurs and is inconsistent with the alternative naphtho-vinyl bridging process (Chart II). Thus vinyl-vinyl bonding (*i.e.*, process *a*, Chart II) does lead to **15A**, the observed product with the hydrogen label at the benzylic positions, while the alternative pathway beginning with naphtho-vinyl bonding (process *b*, Chart II) leads to the symmetrical allylic biradical **19** which should have an equal probability of ring closing at positions X and Y and thus should afford an equal distribution of product labeled as in **15B** and **15C**. This alternative distribution is not observed. Table III outlines the observed and expected label distributions with inclusion of the correction for incompletely labeled reactant.

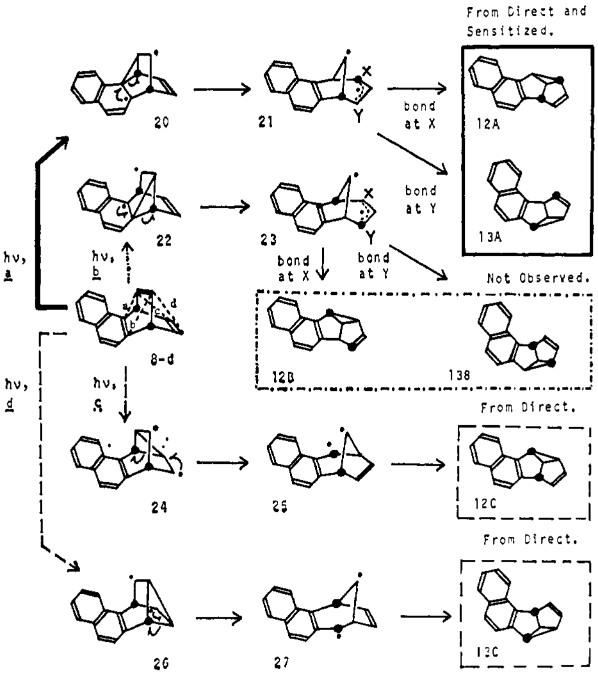
Chart II. Vinyl-Vinyl and Naphtho-Vinyl Bonding Mechanisms for 2,3-Naphthobarrelene



Hence both sensitized and direct photolyses of 2,3-naphthobarrelene (**11**) proceed with preferential vinyl-vinyl bridging in complete analogy with the benzobarrelene (**1**) example studied earlier.

Interpretative Discussion of Mechanism. Molecular Details. 1,2-Naphthobarrelene. In proceeding to consider the structural details of the sensitized and direct irradiations of 1,2-naphthobarrelene, we find Chart III useful. This outlines the possible types of bridging and the label distributions in each case. It can be seen that the situation here is more complex due to the possibility of two types of vinyl-vinyl bonding and two types of naphtho-vinyl bonding of the excited species. These are labeled *a*, *b*, *c*, and *d* in Chart III. Additionally, following each type of initial naphtho-vinyl bonding (*a* and *b*) there are two ways in which the penultimate allylic biradical (**21** and **23**) may close: by bonding at carbon X or at carbon Y. This leads to the two possible products **12** and **13**, each having two potential labeling patterns. The labeling patterns are designated A and B. The third labeling pattern, C, derives from vinyl-vinyl bonding processes (*c* and *d*, Chart III).

Chart III. Mechanisms Potentially Available. Two Pathways Each for Vinyl-Vinyl and Naphtho-Vinyl Bonding in 1,2-Naphthobarrelene Photolysis[a]



[a] Pathway *a* involves initial excited state α-naphtho-vinyl bonding, *b* involves β-naphtho-vinyl bonding, *c* involves α-vinyl-vinyl bonding, and *d* involves β-vinyl-vinyl bonding. Patterned lines surround products from any one mechanism: ———→, mechanism *a*, observed exclusively in sensitized photolysis and as a heavy contributor in direct irradiation; - - - →, mechanisms *c* and *d*, found in direct irradiation as a contributor; —·—·→, mechanism *b*, not observed.

The experimentally observed label distributions in the two products, **12** and **13**, are given in Tables IV and V along with the calculated distributions expected for the various types of initial excited state bonding and final biradical closure. Inspection of this table shows that the observed distribution of label for sensitized photolysis accords nicely with complete utiliza-

Table IV. Observed and Theoretical Hydrogen Distributions in the Photolyses of 1,2-Naphthobarrelene to give **12** and **13**

Case	Label distribution^a H-1	H-2	H-5	H-6	H-7	H-8
	A. Distributions calculated and found for **12**					
Mech *a*, calcd	0.115 (±0.010)	0.115 (±0.010)	1.000	0.115 (±0.010)	0.115 (±0.010)	1.000
Mech *b*, calcd	0.115 (±0.010)	1.000	0.115 (±0.010)	1.000	0.115 (±0.010)	0.115 (±0.010)
Mech *c*, calcd	0.115 (±0.010)	1.000	1.000	0.115 (±0.010)	0.115 (±0.010)	0.115 (±0.010)
Mech *d*, calcd	Does not lead to product **12**					
58% mech *a* + 42% mech *c*, calcd	0.115 (±0.010)	0.487 (±0.007)	1.000	0.115 (±0.010)	0.115 (±0.010)	0.626 (±0.004)
Direct, exptl^b	0.126 (±0.036)	0.530 (±0.045)	0.943 (±0.054)	0.117 (±0.009)	0.117 (±0.009)	0.629 (±0.054)
Sensit, exptl^b	0.128 (±0.051)	0.141 (±0.038)	0.999 (±0.077)	0.115 (±0.026)	0.128 (±0.051)	0.948 (±0.977)
	B. Distributions calculated and found for **13**					
Mech *a*, calcd	0.115 (±0.010)	1.000	0.115 (±0.010)	1.000	0.115 (±0.010)	0.115 (±0.010)
Mech *b*, calcd	0.115 (±0.010)	0.115 (±0.010)	1.000	0.115 (±0.010)	0.115 (±0.010)	1.000
Mech *c*, calcd	Does not lead to product **13**					
Mech *d*, calcd	0.115 (±0.010)	1.000	1.000	0.115 (±0.010)	0.115 (±0.010)	0.115 (±0.010)
58% mech *a* + 42% mech *d*, calcd	0.115 (±0.010)	1.000	0.487 (±0.007)	0.626 (±0.004)	0.115 (±0.010)	0.115 (±0.010)
Direct, exptl^b	0.12 (±0.037)	0.967 (±0.075)	0.436 (±0.051)	0.668 (±0.056)	0.131 (±0.019)	0.131 (±0.019)
Sensit, exptl^b	0.151 (±0.025)	1.004 (±0.050)	0.126 (±0.025)	0.929 (±0.076)	0.126 (±0.025)	0.126 (±0.025)

^{a} Corrected for 11.5 ± 1.0 residual vinyl hydrogen in naphthobarrelene reactant. ^{b} Errors estimated from the scatter of nmr signal integrations.

Table V. Distribution of *syn* and *anti* Isomers (**12** and **13**)

	Distribution **12**	**13**
Calcd^a	1.000	1.000
Direct, exptl	1.000 ± 0.006	1.000 ± 0.004
Sensit, exptl	1.068 ± 0.006	1.000 ± 0.010

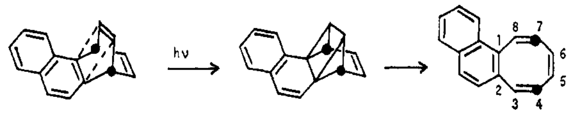
^{a} Calculated assuming equal closure at allylic centers X and Y in mechanisms *a* and *b* (Chart III) and equal participation of mechanisms *c* and *d* (Chart III).

tion of mechanism *a*, that is, α-naphtho–vinyl bonding for both formation of the *syn* product **12** and for the *anti* product **13**.

Strikingly, in the direct photolysis, α-naphtho–vinyl bonding (*i.e.*, mechanism *a*) is not the only process occurring. Table IV shows that labeled *syn*- and *anti*-1,2-naphthosemibullvalene (**12** and **13**) are formed 58 ± 6% by the α-naphtho–vinyl bonding mechanism (*i.e.*, *a*) and 42 ± 6% by α- and β-vinyl–vinyl bridging (*i.e.*, *c* and *d*). The errors, although small, are sufficient that any deviation from equal participation of bonding at X and Y in mechanism *a* would not be detected. This corresponds to the symmetric allylic biradical observed earlier in barrelene photochemistry where closure at the two allylic centers occurred with equal probability. Finally, the two types of vinyl–vinyl bonding presently possible, α or β (*i.e.*, mechanisms *c* and *d*), are seen to be occurring with essentially equal facility within experimental error.

In summary, the photochemical formation of *syn*- and *anti*-1,2-naphthosemibullvalene (**12** and **13**) from 1,2-naphthobarrelene (**8**) is by α-naphtho–vinyl bonding for the sensitized reaction, while a change in mechanism occurs on direct irradiation with the result that 42% of the reaction pathway is diverted through mechanisms *c* and *d* involving vinyl–vinyl bonding.

Finally, the distribution of the hydrogen label at C-4 and C-7 noted in the 1,2-naphthocyclooctatetraene (**14d**) product obtained from the direct photolysis of labeled material is in accord with a four center cycloaddition mechanism proceeding through the tetracyclic intermediate **28**. This has close analogy in the photochemistry of benzobarrelene[2] where direct photolysis gave a similar result.



8-d 28 14-d (9)

Multiplicity and Reaction Efficiency. Interpretative Discussion. Beginning with the reaction of 2,3-naphthobarrelene (**11**), we find that the same quantum yield of 2,3-naphthosemibullvalene (**15**), that is, $\Phi = 0.46 \pm 0.02$ (note Table II, runs 3 and 4), is observed in the sensitized and direct irradiations. In the sensitized case it is quite certain that the lowest triplet T_1 (62 kcal/mol; see Experimental Section) is formed. This conclusion derives from analogy with the well-known quenching of benzophenone (69 kcal/mol) with naphthalene (61 kcal/mol) itself[10] and the expectation that T_2 of naphthalene should be too high in energy to be accessible from benzophenone sensitization. Thus it has been noted[11] that T_2–T_1 separations are in the range of 25 kcal/mol for hydrocarbons and this would place T_2 of 2,3-naphthobarrelene (**11**) at about 87 kcal/mol or too high to be formed.[12]

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(10) A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

(11) H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **91**, 5307 (1969).

(12) The average T_2–T_1 separation of 25 kcal/mol is derived from both observed and calculated energies. Liu[13] has observed the separation in anthracene to be 32 kcal, while calculations by Pariser[14] gave a value of 27 kcal/mol. For 1,3-butadiene, Evans[15] has observed the separation to be 23 kcal/mol and this value agrees exactly with that calculated by Sidman.[16] The calculations of Pariser[14] for benzene and naphthalene give T_2–T_1 separations of 13 and 29 kcal/mol, respectively.

(13) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **91**, 1492 (1969).

(14) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

(15) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(16) J. W. Sidman, *J. Chem. Phys.*, **27**, 429 (1957).

Table VI. Summary of and Deductions from the Photochemistry

Reactant and conditions	Bonding[a]
1,2-NB,[b] sensitized	α-Naphtho–vinyl
1,2-NB, direct	α-Naphtho–vinyl (17%), vinyl–vinyl (13%), Naphtho–vinyl cycloaddition (70%)
2,3-NB, sensitized	Vinyl–vinyl
2,3-NB, direct	Vinyl–vinyl
Order of preference of processes	
For the triplet	α-Naphtho–vinyl bridging > vinyl–vinyl bridging > β-naphtho–vinyl bridging
For the singlet	α-Naphtho–vinyl bridging ≅ vinyl–vinyl bridging > β-naphtho–vinyl bridging

[a] All are two-center bridging processes except for the four-center cycloaddition indicated. [b] Naphthobarrelene (NB).

One difficulty present in this interpretation is the requirement that intersystem crossing for 2,3-naphthobarrelene (**11**) be essentially unity so that no efficiency be lost in this step; naphthalene[17] itself has an intersystem crossing efficiency of only 0.39. However, it was observed experimentally that the fluorescence quantum efficiency of 2,3-naphthobarrelene (**11**) was only 34% of that of naphthalene[9] and only 20% of the efficiency of 2,3-dimethylnaphthalene[18] which is perhaps a better model.[19] The considerably diminished fluorescence of 2,3-naphthobarrelene (**11**) may indeed derive from a much more efficient intersystem crossing which would then be consistent with the above view.

Supporting this view that the same species T_1 is involved in the direct irradiations as established (*vide supra*) for the sensitized runs is the observation of precisely the same label distribution in the two types of experiments (note Table III, entries 3 and 4).

Turning now to the photochemistry of 1,2-naphthobarrelene (**8**), we find the situation less straightforward. However, several conclusions can be made without difficulty. First, we can infer that the 1,2-naphthocyclooctatetraene (**14**) formed in the direct irradiations does not arise from the T_1 of 1,2-naphthobarrelene (**8**), since generation of T_1 by benzophenone sensitization affords no 1,2-naphthocyclooctatetraene (**14**).

Furthermore, in these sensitized runs, the *syn*- and *anti*-1,2-naphthosemibullvalene (**12** and **13**) formed can be taken as arising from the lowest energy triplet T_1 (63 kcal/mol from phosphorescence emission; see Experimental Section). For the same reasons given above in connection with transfer to 2,3-naphthobarrelene (**11**), benzophenone seems unlikely to have sufficient energy to generate T_2 and the concentrations were adjusted to preclude any transfer from the excited singlet of benzophenone.

The matter of the excited state(s) responsible for formation of the 1,2-naphthosemibullvalenes (**12** and **13**) in the direct irradiation of 1,2-naphthobarrelene is less unambiguous. Thus we can exclude T_1 as the major excited state responsible, since the labeling pattern obtained for these semibullvalenes is different in the direct runs than in the sensitized ones where T_1 is purposely generated. This, however, leaves both S_1 and T_2 as candidates for the reacting excited state. The *ca.* 25 kcal/mol T_2–T_1 separation coupled together with the measured T_1 energy of 63 kcal/mol for 1,2-naphthobarrelene (**8**) suggests that T_2 should be near 88 kcal/mol. The 1,2-naphthobarrelene (**8**) singlet excited state generated was found to be *ca.* 85 kcal/mol (note Experimental Section for fluorescence emission and uv absorption data) above ground state and therefore to have just barely sufficient energy to lead to T_2. Hence S_1 seems a more likely possibility but T_2 cannot be excluded with rigor. The same situation holds true for the 1,2-naphthocyclooctatetraene (**14**) product formed on direct irradiation; that is, this product most likely arises from S_1 but T_2 again cannot be totally ruled out.[20] This emphasizes the general difficulty in differentiating between involvement of S_1 and T_2 in photochemical reactions as a result of their similarities in lifetime and energy.

Interpretation of Factors Controlling the Rearrangements. The structural details of the molecular transformations observed for 1,2-naphthobarrelene (**8**) and 2,3-naphthobarrelene (**11**) under the direct and sensitized conditions have been given in Charts II and III and eq 9. The bridging preferences may succinctly be summarized in Table VI.

The striking aspects are (1) the remarkable preference for the electronically excited naphthalene moiety to bridge α and its disinclination to bond at the β position, (2) the preference for α-naphtho–vinyl over vinyl–vinyl bridging processes for the triplet and the contrasting near equivalence found in the minor singlet process, (3) the heavy incursion of the cycloaddition reaction to afford naphthocyclooctatetraene product from the singlet excited state except where bridging at two β positions is required, and finally (4) the occurrence of a bicyclic di-π-methane rearrangement not only *via* the triplet but also to some extent by way of a singlet, seemingly violating the tentative generalization proposed by Zimmerman and Mariano.[22]

With respect to the first point, it should be noted that the preferential bonding to the α position of the naphtho ring could not have been predicted at first glance, since excited state reactivity need not parallel that of the ground state. However the results do suggest that the excited naphthalene moiety tends

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[17] A. A. Lamola, Ph.D. Thesis, Pasadena, California Institute of Technology, 1965.

[18] Reference 9, p 110.

[19] Alkyl substitution on naphthalene in general increases the fluorescence quantum yield.[18]

[20] A similar uncertainty exists for the direct irradiation of benzobarrelenes[21] where the singlet excited state has been suggested to be responsible for the formation of benzocyclooctatetraene products on direct irradiation, contrasting with benzosemibullvalene formation on sensitized photolysis. Similar reasoning using the 85 kcal/mol T_1 energy for benzene together with the singlet energy available shows that T_2 cannot be rigorously excluded in this case either with the present evidence.

[21] (a) Reference 2; (b) J. P. N. Brewer and H. Heaney, *Chem. Commun.*, 811 (1967); (c) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *J. Amer. Chem. Soc.*, 90, 4465 (1968).

[22] H. E. Zimmerman and P. S. Mariano, *ibid.*, 91, 1718 (1969).

to be more reactive α than β. One rationale which is in accord with observation is obtained by considering the excited state energetics of bringing a vinyl group endwise to overlap with the α-naphthalene position with the energetics of such overlap with the β position. Hückel considerations show the simplest π–π* excited configuration to be lower in energy with α-naphtho–vinyl bonding than with β-naphtho–vinyl overlap.[23] While this reasoning is very approximate, it does correspond with observation.

Actually the second point—that is, the preference for α-naphtho–vinyl over vinyl–vinyl bridging for the triplet—is closely related to the matter just considered, and evidence on this second result also bears on the first. Thus, another approach to estimating the relative energies of molecules following different triplet excited state routes is to find experimental triplet energies for molecules having similar delocalized systems. In lieu of experimental values for the triplets of α-vinylnaphthalene and β-vinylnaphthalene, α-naphthaldehyde and β-naphthaldehyde serve as approximate models; these are[24] 56.3 and 59.5 kcal/mol, respectively. The acetonaphthones have similar and parallel triplet energies. Thus bridging of a two orbital moiety to the α position of triplet naphthalene in preference to β bridging is understood in terms of energy minimization.

Simple Hückel considerations are not useful for inclusion of a butadienoid species, resulting from endwise vinyl–vinyl overlap, in the comparison. Here configuration interaction should play a role widely different than in the two vinylnaphthalenes, and Hückel theory here is inadequate for comparing two types of systems. However, we do know that butadienoid triplets are in the range of 53–61 kcal/mol depending on substitution and conformation. It is perfectly reasonable then that the triplet species resulting during vinyl–vinyl bridging of the triplet will lie between the 56 kcal/mol estimate for α-naphtho–vinyl bonding and 60 kcal/mol for β-naphtho–vinyl bridging.

The near equivalence of α-naphtho–vinyl and vinyl–vinyl bonding found in the minor process deriving from the singlet excited state seems to derive from totally different considerations than the triplet process just discussed, since a butadienoid singlet should be of much higher energy than a vinylnaphthalene-like one. Here processes subsequent to initial bridging may become controlling. However, β bridging is still unobserved. One possibility is that the rate of loss of excitation energy with internal conversion to ground state is controlling.

The third experimental finding, namely cycloaddition becoming the major reaction of the singlet except where bridging at two β positions is required, is consistent with (i) the usual preference for cycloaddition of singlets and specifically reminiscent of the preferred benzo–vinyl bonding found in the singlet photochemistry of benzobarrelene[2] (**1**), and (ii) the reluctance for β-bonding in the excited state as already discussed. However here β bonding is especially unfavorable. We note that excited state energy is a combination of the initial ground state contribution plus an excitation energy. Therefore, the loss of aromaticity in *both* rings due to bonding at *two* β positions leads to especially high excited state energy.

The argument used[2] in the benzobarrelene study to rationalize the preference of benzo–vinyl over vinyl–vinyl bonding invoked the lower energy of the excited benzo moiety relative to the ethylenic bridges and suggested that the energy was heavily concentrated in the benzo ring in the singlet state and in pathways leading toward cycloaddition product. This argument holds in the present case and even more strongly due to the lower excitation energy of the naphtho group.

Finally, with respect to point four, it may be that the occurrence of the 1,2-naphthosemibullvalenes (**12** and **13**) in the direct irradiation of 1,2-naphthobarrelene (**8**) does provide an example of a bicyclic di-π-methane rearrangement arising from a singlet excited state. The generalization[22] presented by us earlier is now known to rely on modes of energy dissipation available to acyclic di-π-methane triplets[25a] which preclude triplet but not singlet pathways. However, for the constrained (*e.g.*, bicyclic) di-π-methane excited states, it appears that the preference for the triplet route arises from other type reactions (*e.g.*, cycloaddition) commonly but not invariably being faster for the singlet.

Nevertheless, as noted above, the present evidence does not unambiguously differentiate between T_2 and S_1 being responsible in the direct irradiation, and in any case, the tendency[22] for the bicyclic reactants to utilize the triplet pathway does seem to extend to the presently studies systems.[25b,26]

Experimental Section[28]

Photolysis Apparatus and Equipment. Photolyses were carried out in either of the two following instruments. **Apparatus A.** A quartz Hanovia 450-W water-cooled, medium-pressure immersion lamp was used along with glass filters. The irradiation flask was

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[23] This is equivalent to comparing the simple excitation energy of α-vinylnaphthalene with that of β-vinylnaphthalene (0.996β *vs.* 1.092β) and corrections for a 0.020β ground-state difference favoring the α position. The implicit assumption is that excitation corresponds to the simplest excited configuration possible.

[24] For references and a summary of data note J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 298.

[25] (a) In independent studies by H. E. Zimmerman and A. C. Pratt and H. E. Z. with G. Epling [*J. Amer. Chem. Soc.*, **92**, 1411 (1970)], evidence has been advanced that acyclic di-π-methane triplets dissipate energy by a free rotor effect which cannot operate in the present, constrained bicyclic systems. (b) Recently R. C. Hahn and L. J. Rothman [*ibid.*, **91**, 2409 (1969)] have presented the example of a bicyclic reactant, benzo[6,7]bicyclo[3.1.0]octa-2,6-diene which gave the di-π-methane rearrangement on direct photolysis and noted that the singlet state was possibly involved.

[26] One point which is nonphotochemical, and therefore not relevant to the main theme, is important enough to merit comment. This regards the question of electron delocalization in barrelene, benzobarrelene, and the naphthobarrelenes. It has been noted[27] that barrelene is a molecule with electron delocalization but with zero delocalization energy. This is predicted on the differing form and energy of the MO's relative to isolated ethylenic moieties. Because of the zero transannular bond orders, this may seem intellectually bothersome. However, the present cases along with that of benzobarrelene clarify matters. Thus these barrelene derivatives are found to have nonzero transannular bond orders in the Hückel approximation (*e.g.*, 0.0002 for vinyl–vinyl overlap in benzobarrelene and 0.0009 for vinyl–vinyl overlap in 2,3-naphthobarrelene). Analogously, the delocalization energy for benzobarrelene is 0.017β. Hence the zero delocalization energy and zero bond order in barrelene are due to symmetry and not germane to the matter of electron delocalization. Furthermore, Hückel calculations predict a low electron density in the barrelene moiety of the aromatic barrelenes and a high electron density in the aromatic rings. This (small but finite) effect derives from these molecules being nonalternant when transannular overlap is included.

[27] (a) H. E. Zimmerman and R. M. Paufler, *J. Amer. Chem. Soc.*, **82**, 1514 (1960); (b) H. E. Zimmerman, G. L. Grunewald, R. M. Paufler, and M. A. Sherwin, *ibid.*, **91**, 2330 (1969).

[28] All melting points were taken on a hot-stage apparatus and are corrected.

fitted with a nitrogen inlet, a stirring bar, and a capillary outlet. **Apparatus B.** The light source was a GE AH6 high-pressure mercury arc located at the focal point of a parabolic aluminum reflector 13.8 cm long and 14.0 cm in diameter. The light was filtered by a cell of three water-cooled compartments, separated by gasketed quartz disks, 2.4 cm thick and 12 cm in diameter. The photolysis cell consisted of two 12.0 cm diameter × 5.0 cm path length compartments in series. The faces and partition of the cell were quartz disks. The cell was equipped with a Trubore stirrer, nitrogen inlet and capillary gas outlet, a heat-exchanger coil, and a thermistor probe. An RCA 935 phototube mounted between the filter and irradiation cells was used to monitor the light output. All irradiations were carried out at 25.0 ± 0.2°.

Two combination filter solutions were used. For the preparation of the filter solutions, nickel sulfate hexahydrate, cobalt sulfate heptahydrate, and copper sulfate pentahydrate were used in 10% sulfuric acid. Stannous chloride dihydrate was used in 20% hydrochloric acid.

The properties of filter 1 were: cell 1, 10 g of copper salt/l.; cell 2, 225 g of cobalt salt/l.; cell 3, 250 g of nickel salt plus 500 ml of concentrated (15 *M*) ammonium hydroxide/l.; transmittance was 275–330 nm, with a maximum at 304 nm (19%).

The properties of filter 2 were: cell 1, 50 g of nickel salt/l.; cell 2, 225 g of cobalt salt/l.; cell 3, 375 g of tin salt/l.; transmittance was 340–380 nm, with a maximum at 358 nm (8%).

Before irradiations in either apparatus A or B, vanadous-purified nitrogen[29] was bubbled through the solution for 30 min; a positive pressure of nitrogen was maintained over the solution during the irradiation.

Actinometry. A potassium ferrioxalate actinometer[8] was employed, and a value of 1.23[3] was used for the quantum efficiency. Each determination required three runs: (1) irradiation with both compartments containing actinometer, (2) irradiation with the first compartment containing photolysis solution and the second compartment containing actinometer, (3) irradiation with both compartments containing actinometer.

Solvent and Sensitizer. Cyclohexane was stirred with 30% fuming sulfuric acid for 8 hr, washed with 10% aqueous sodium hydroxide, dried ($MgSO_4$), and distilled from calcium hydride. Benzophenone was crystallized twice from 95% ethanol, mp 47–49°.

α-Naphthoxindole.[30] A mixture of 104 g (0.39 mol) of glyoxal, di(sodium bisulfite), and 56 g (0.39 mol) of α-naphthylamine in 1.2 l. of 50% aqueous ethanol was refluxed for 24 hr and then filtered hot. Concentration *in vacuo* of the filtrate to 400 ml gave a yellow solid which was refluxed with 1 l. of water, cooled, and filtered. The filtrate was treated with 150 ml of concentrated HCl and stirred at 90° for 30 min. The solid which formed was washed with water, decolorized with Norit, and recrystallized from absolute ethanol to give 23.3 g (29%) of α-naphthoxindole as a colorless solid, mp 245–248° (lit.[31] mp 245°).

1-Amino-2-naphthoic Acid. A mixture of 5.055 g (0.028 mol) of finely ground α-naphthoxindole and 40 ml of 30% aqueous H_2O_2 in 500 ml of 10% aqueous NaOH was stirred at 40° until a clear solution resulted (~30 hr). Acidification with HCl precipitated 4.446 g (86%) of the amino acid, mp 200–202° (lit.[31] mp 205°).

1,2-Naphthobarrelene. To an ice-cooled, stirred solution of 3.005 g (0.016 mol) of 1-amino-2-naphthoic acid in 200 ml of absolute ethanol acidified with 10 ml of concentrated H_2SO_4, 5.0 ml of isoamyl nitrite was added dropwise over 2 min. The cooling was removed and the stirring was continued for 90 min. Dilution of the mixture with 600 ml of ether afforded the yellow diazonium acid sulfate which was washed with ether: infrared spectrum (Nujol) 4.10 br (COOH), 4.43 ($N{\equiv}N^+$) and 5.83 μ ($C{=}O$).

An ice-cooled solution of 1.205 g (0.021 mol) of KOH in 12 ml of water was added dropwise over 5 min to an ice-cooled, stirred solution of the diazonium acid sulfate in 24 ml of water. After stirring for 30 min at 0°, the reaction mixture was poured into 240 ml of absolute ethanol and 1.8 l. of ether. The yellow 1-diazonium-2-naphthalenecarboxylate precipitate was filtered, washed with ether and tetrahydrofuran, and then with benzene: infrared spectrum (Nujol) 4.5 ($N{\equiv}N^+$) and 6.25 μ ($C{=}O$).

The 1-diazoniumnaphthalene-2-carboxylate was decomposed in 750 ml of dry benzene by refluxing for 10 hr under nitrogen. The mixture was then concentrated to 50 ml and chromatographed, with benzene as solvent, on a 4 × 10 cm silicic acid column. The first 500 ml of eluent was collected, concentrated, and rechromatographed on a 2 × 63 cm silicic acid column. Elution was with hexane; 250-ml fractions were collected. Fractions 7–9 contained 202.7 mg (6%) of 1,2-naphthobarrelene, mp 80–82°. Recrystallization from ethanol gave colorless crystals: mp 83–85°; ir (Nujol) strong 7.56, 12.14, 13.20, 13.45, 14.75, 15.08; medium 6.36, 6.64, 7.43, 8.03, 8.22, 8.32, 8.70, 9.52, 9.81, 11.66, 13.85, 14.03, and 15.75 μ; uv max (cyclohexane) 232 (37,400), 244 sh (17,500), 295 (2720), 298 (2890), 305 (3060), 309 (2720), 317 (2340), 322 sh (1700), and 332 nm (2000); nmr (CCl_4) τ 1.89–2.83 (m, 6 H, arom), 3.04–3.17 (m, 4 H, vinyl), 4.23–4.46 (m, 1 H, *syn* bridgehead), and 4.86–5.10 (m, 1 H, *anti* bridgehead).

Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.17; H, 5.90.

***syn*- and *anti*-1,2-Naphthosemibullvalene from the Benzophenone Sensitized Irradiation of 1,2-Naphthobarrelene.** A solution of 298.9 mg (1.47 mmol) of 1,2-naphthobarrelene and 2.9803 g (16.5 mmol) of benzophenone in 730 ml of cyclohexane was photolyzed for 2 hr in apparatus B using filter combination 2. The solvent was evaporated under a stream of nitrogen and the residue was chromatographed on a 2.5 × 75 cm silicic acid column. Elution was with 2 l. of hexane and 1 l. of 10% ether in hexane; 100-ml fractions were collected. Fractions 9–11 gave 169.6 mg (57%) of *syn*- and *anti*-1,2-naphthosemibullvalene (1:1 mixture by nmr) as a colorless oil; 13–16, 101.6 mg (34%) of 1,2-naphthobarrelene, mp 73–76°; 24–28, 2.7267 g (91%) of benzophenone, mp 45–47°.

Separation of *syn*- and *anti*-1,2-Naphthosemibullvalenes. A 1:1 mixture of 183.7 mg of *syn*- and *anti*-1,2-naphthosemibullvalene was subjected to liquid–liquid partition chromatography on a 3 × 210 cm column of polystyrene beads (Dow, X2, 2% cross-linked, 100–200 mesh) impregnated with the upper phase of 1:1 methanol–cyclohexane and slurry packed in the lower phase. Elution was with the lower phase of 1:1 methanol–cyclohexane; 20-ml fractions were collected and the eluent absorbance was scanned at 300 nm.

One broad peak was observed in the scan: fractions 123–137 contained 80.2 mg of 86% enriched *syn* isomer; 138–154 contained 72.7 mg of 70% enriched *anti* isomer.

Recycling the fractions enriched in the *syn* isomer gave a broad peak: sublimation (60°, 0.1 mm) of fractions 110–135 gave 18.9 mg (10%) of pure *syn*-1,2-naphthosemibullvalene, mp 44–46°; fractions 136–160 gave 42.2 mg (23%) of an oily mixture of *syn* and *anti* isomers.

Recycling the fractions enriched in the *anti* isomer gave a broad peak: fractions 120–142 contained 38.6 mg (21%) of an oily mixture of *syn* and *anti* isomers; sublimation (65°, 0.1 mm) of fractions 143–167 gave 23.7 mg (13%) of pure *anti*-1,2-naphthosemibullvalene, mp 81–83°.

The spectral data of the *syn* isomer were ir (KBr) strong 12.20, 12.50, 13.05, 13.60, 13.85; medium 6.40, 6.65, 7.45, 7.70, 8.05, 8.60, 10.60, 10.65, 10.75, and 11.25 μ; uv max (cyclohexane) 232 (32,900), 239 (32,400), 291 (4800), 297 (4900), 302 (4800), 306 sh (3750), 316 (2650), 323 (1550), and 331 nm (2050); nmr (CCl_4) τ 2.04–2.90 (m, 6 H, arom), 4.42–4.50 (ABX q, 1 H, vinyl H-6, J_{87} = 5.0 Hz, J_{58} = 2.0 Hz), 4.93–5.00 (ABX q, 1 H, vinyl H-7, J_{67} = 5.0 Hz, J_{78} = 2.0 Hz), 6.05–6.14 (ABX q, 1 H, benzylic and allylic H-5, J_{58} = 2.0, J_{15} = 6.5 Hz), 6.49–6.62 (ABC t, 1 H, cyclopropyl and benzylic H-2, $J_{12} = J_{28}$ = 6.5 Hz), 6.62–6.80 (ABCD q, 1 H, interior cyclopropyl H-1, $J_{15} = J_{12} = J_{18}$ = 6.5 Hz), and 7.07–7.22 (ABCX d of t, 1 H, cyclopropyl and allylic H-8, J_{78} = 2.0 Hz, $J_{18} = J_{28}$ = 6.5 Hz). Double resonance was performed on the 100-MHz nmr. Protons that were not affected or were in the oscillating side band are not included in the following: irradiation of H-6 (556 Hz, 410 mV) collapsed H-7 to a doublet (J_{78} = 2.0 Hz) and H-5 to a doublet (J_{15} = 6.5 Hz); H-7 irradiated (507 Hz, 425 mV) H-6 to a doublet (J_{56} = 2.0 Hz) and H-8 to a triplet ($J_{28} = J_{18}$ = 6.5 Hz); H-5 irradiated (395 Hz, 425 mV) H-6 to a doublet (J_{67} = 5.0 Hz) and H-1 to a triplet ($J_{12} = J_{18}$ = 6.5 Hz); H-1 irradiated (330 Hz, 400 mV) H-5 to a doublet (J_{58} = 2.0 Hz), and H-8 irradiated (288 Hz, 400 mV) H-7 to a doublet (J_{67} = 2.0 Hz).

Mass spectrum (70 eV, direct inlet) showed molecular ion at *m/e* 204.096 (100%). Calcd for $C_{16}H_{12}$: 204.096.

The spectral data of the *anti* isomer were ir (KBr) strong 7.70, 10.90, 12.25 br, 12.54, 13.48, 13.60, 13.95 br, 14.35, 15.86; medium 6.25, 6.70, 7.50, 8.06, 8.72, 9.14, 9.50, 9.92, 10.12, 10.74, 11.17, 11.40, 11.55, 11.68, 12.75, and 13.10 μ; uv max (cyclohexane) 240 (27,000) 245 sh (25,000), 265 sh (5700), 278 (3900), 283 (4000), 288 (4400), 292 sh (4000), 301 (3400), 318 (1100), 326 (700), 333 nm (1100); nmr (CCl_4) τ 2.18–2.74 (m, 6 H, arom), 4.45–4.53 (ABX

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(29) L. Meites, *Anal. Chem.*, 20, 984 (1948).

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q, 1 H, vinyl H-6, J_{67} = 5.0 Hz, J_{58} = 2.0 Hz), 4.92–4.99 (ABX q, 1 H, vinyl H-7, J_{67} = 5.0 Hz, J_{78} = 2.0 Hz), 5.63–5.72 (ABX q, 1 H, benzylic and allylic H-5, J_{58} = 2.0 Hz, J_{15} = 6.5 Hz), 6.62–6.81 (ABCD q, 1 H, interior cyclopropyl H-1, J_{15} = J_{12} = J_{18} = 6.5 Hz), 6.83–6.95 (ABC t, 1 H, cyclopropyl and benzylic H-2, J_{12} = J_{28} = 6.5 Hz), and 7.19–7.35 (ABCX d of t, 1 H, cyclopropyl and allylic H-8, J_{78} = 2.0 Hz, J_{18} = J_{28} = 6.5 Hz). Double resonance was performed on the 100-MHz nmr. Irradiation of H-6 (553 Hz, 350 mV) collapsed H-7 to a doublet (J_{28} = 2.0 Hz) and H-5 to a doublet (J_{15} = 6.5 Hz); H-7 irradiated (510 Hz, 350 mV) H-6 to a doublet (J_{56} = 2.0 Hz) and H-8 to a triplet (J_{28} = J_{18} = 6.5 Hz); H-5 irradiated (437 Hz, 350 mV) H-6 to a doublet (J_{67} = 5.0 Hz) and H-1 to a triplet (J_{12} = J_{18} = 6.5 Hz); H-1 irradiated (337 Hz, 350 mV) H-5 to a doublet (J_{58} = 2.0 Hz), and H-8 irradiated (275 Hz, 450 mV) H-7 to a doublet (J_{67} = 5.0 Hz).

Mass spectrum (70 eV, direct inlet) showed molecular ion at *m*/*e* 204.093 (100%).

1,2-Naphthocyclooctatetraene from the Direct Irradiation of 1,2-Naphthobarrelene. A solution of 200.4 mg (0.98 mmol) of 1,2-naphthobarrelene in 730 ml of cyclohexane was photolyzed for 15 min in apparatus B using filter combination 1. The solvent was concentrated under nitrogen below room temperature and the residue was chromatographed on a 2 × 80 cm silicic acid column. Elution was with hexane; 100-ml fractions were collected. Fractions 12–15 gave 73.7 mg (37%) of 1,2-naphthocyclooctatetraene as a yellow solid, mp 51–53°; 17–20, 26.1 mg (13%) of *syn*- and *anti*-1,2-naphthosemibullvalene (1:1 mixture by nmr); 23–27, 98.3 mg (50%) of 1,2-naphthobarrelene, mp 83–85°.

Sublimation (90°, 0.1 mm) of 1,2-naphthocyclooctatetraene from fractions 12–15 raised the melting point to 52–54°. Spectral data were ir (KBr) strong 11.56, 12.17, 12.64, 13.04, 13.20, 13.68 br, 14.14, 14.43, 14.90 br, 15.80; medium 6.30, 6.68, 7.07, 7.26, 7.65, 8.56, 8.80, 9.79, 10.38, 10.53, 11.36, and 11.85 μ; uv max (cyclohexane) 230 (40,000), 241 (35,300), 258 sh (11,000), 294 nm sh (2900); nmr (CCl_4) τ 2.19–2.77 (m, 5 H, arom), 3.07 (d, 1 H, arom, J = 8.5 Hz), 3.21 (d, 1 H, *syn*-vinyl H-8, J_{78} = 11.5 Hz), 3.42 (d, 1 H, *anti*-vinyl H-3, J_{34} = 11.5 Hz), and 3.77–4.32 (m, 4 H, vinyl, H-4, H-5, H-6, and H-7). Double resonance was performed on the 100-MHz nmr. Irradiation of the aromatic region (754 Hz, 350 mV) collapsed τ 3.07 doublet to a singlet; and irradiation of the vinyl region (619 Hz, 250 mV; and 597 Hz, 250 mV) collapsed H-8 to a singlet and H-3 to a singlet, respectively.

2,3-Naphthobarrelene. To a stirred, ice-cooled mixture of 12.0 g (0.064 mol) of 3-amino-2-naphthoic acid in 800 ml of absolute ethanol acidified with 40 ml of concentrated H_2SO_4, 20 ml of isoamyl nitrite was added over 5 min. The cooling was stopped and the stirring continued for a further 3 hr. Dilution with 1 l. of ether precipitated 3-diazonium-2-naphthoic acid sulfate, which was washed with ether and used in the next stage without further purification: infrared spectrum (Nujol) 4.10 br (COOH), 4.38 ($N{\equiv}N^+$), 5.90 μ ($C{=}O$).

An ice-cooled solution of 5.00 g (0.090 mol) of KOH in 40 ml of water was added during 10 min to an ice-cooled solution of the 3-diazonium-2-naphthoic acid sulfate in 60 ml of water. After stirring for a further 60 min, the dark-red mixture was filtered and the filtrate was added to 800 ml of ethanol and 2.5 l. of ether. The resulting yellow 3-diazoniumnaphthalene-2-carboxylate was filtered off and washed with ether and tetrahydrofuran, and then with benzene. The solid was not purified further: infrared spectrum (Nujol) 4.42 ($N{\equiv}N^+$), 6.16 μ ($C{=}O$).

The diazonium carboxylate was decomposed in 2.5 l. of dry benzene by refluxing for 10 hr in a nitrogen atmosphere. Concentration *in vacuo* was followed by chromatography of the residue on a 4 × 8 cm column of silicic acid with benzene as eluting solvent. The first 500 ml of eluent was concentrated and chromatographed on a 3 × 80 cm silicic acid column. Elution was with hexane; 500-ml fractions were collected. Sublimation (100°, 0.1 mm) of the contents of fractions 7–10 gave 921.5 mg (7%) of 2,3-naphthobarrelene, mp 125–127°. Crystallization from 75% of aqueous ethanol raised the melting point to 130–132°. Spectral data were ir (Nujol) strong 7.47, 11.37, 12.44, 13.09, 13.30, 14.40, 15.00; medium 3.27, 6.23, 6.37, 6.70, 7.55, 7.92, 8.13, 8.40, 9.44, 9.81, 10.50, 11.11, 11.59, and 15.63 μ; uv max (cyclohexane) 234 (49,000), 254 (8400), 263 (9300), 272 (8500), 283 (4800), 296 (390), 302 (300), 305 (310), 309 (600), 318 (280), and 323 nm (620); nmr (CCl_4) τ 2.42–2.89 (m, 6 H, arom), 3.29–3.36 (m, 4 H, vinyl), and 5.10–5.34 (m, 2 H, bridgehead).

Anal. Found: C, 93.98; H, 5.92.

2,3-Naphthosemibullvalene from the Direct Photolysis of 2,3-Naphthobarrelene. A solution of 227.3 mg (1.1 mmol) of 2,3-naphthobarrelene in 200 ml of cyclohexane was photolyzed for 30 min in apparatus A using a Pyrex filter. The solvent was removed *in vacuo* and the residue was chromatographed on a 3 × 80 cm silicic acid column with hexane as eluting solvent; 500-ml fractions were collected. Sublimation (100°, 0.1 mm) of the contents of fractions 9–13 gave 101.4 mg (45%) of 2,3-naphthosemilbullvalene, mp 139–141°. Sublimation (100°, 0.1 mm) of the contents of fractions 15–22 gave 120.4 mg (53%) of 2,3-naphthobarrelene, mp 129–131°.

The spectral data of 2,3-naphthosemibullvalene were ir (Nujol) strong 3.29, 11.42, 12.25, 13.40, 13.82, 14.28; medium 7.46, 10.55, 11.12, 12.76, and 15.15 μ; uv max (cyclohexane) 237 (79,000), 276 (6100), 283 (6500), 291 sh (5100), 312 (1110), 319 (630), and 327 nm (1260); nmr (CCl_4) τ 2.36–2.93 (m, 6 H, arom), 4.49–4.63 (ABX q, 1 H, vinyl H-6, J_{67} = 5.0 Hz, J_{56} = 2.0 Hz), 4.83–4.96 (ABX q, 1 H, vinyl H-7, J_{67} = 5.0 Hz, J_{78} = 2.0 Hz), 6.00–6.13 (ABX q, 1 H, benzylic and allylic H-5, J_{56} = 2.0 Hz, J_{15} = 6.0 Hz), 6.63–6.94 (ABCD q, 1 H, interior cyclopropyl H-1, J_{15} = J_{12} = J_{18} = 6.5 Hz), 6.98–7.22 (ABC t, 1 H, cyclopropyl and benzylic H-2, J_{12} = J_{28} = 6.5 Hz), and 7.39–7.62 (ABCX d of t, 1 H, cyclopropyl and allylic H-8, J_{78} = 2.0 Hz, J_{18} = J_{28} = 6.5 Hz). Double resonance was performed on the 100-MHz nmr. Irradiation of H-6 (547 Hz, 300 mV) collapsed H-7 to a doublet (J_{28} = 2.0 Hz) and H-5 to a doublet (J_{15} = 6.0 Hz); H-7 irradiated (515 Hz, 300 mV) H-8 to a triplet (J_{28} = J_{18} = 6.5 Hz); H-5 irradiated (401 Hz, 300 mV) H-6 to a doublet (J_{67} = 5.0 Hz) and H-1 to a triplet (J_{12} = J_{18} = 6.5 Hz); H-1 irradiated (329 Hz, 300 mV) H-5 to a doublet (J_{56} = 2.0 Hz); and H-8 irradiated (258 Hz, 250 mV) H-7 to a doublet (J_{67} = 5.0 Hz).

Anal. Found: C, 93.88; H, 5.98.

Action of Lithium Cyclohexylamide on 1,2-Naphthobarrelene. A solution of 387.4 mg (1.91 mmol) of 1,2-naphthobarrelene, 50 ml of cyclohexylamine, and 4 ml (8.8 mmol) of 2.2 *M* butyllithium in hexane was stirred at 80° for 42 hr in a nitrogen atmosphere. After quenching with 10 ml of water, the organic phase was diluted with 400 ml of hexane and thoroughly extracted with 10% HCl and then with water. The hexane was removed *in vacuo* and the residue was chromatographed on a 4 × 40 cm silicic acid column with hexane as eluting solvent; 500-ml fractions were collected. Sublimation (90°, 0.1 mm) of fractions 4 and 5 gave 81.9 mg (24%) of a white solid, mp 97–99°, identical (ir, tlc, mixture melting point) with phenanthrene; sublimation (100°, 0.1 mm) of fractions 9–12 gave 258.7 mg (67%) of 1,2-naphthobarrelene, mp 76–78°.

Action of Lithium Cyclohexylamide on 2,3-Naphthobarrelene. A solution of 443.5 mg (2.19 mmol) of 2,3-naphthobarrelene, 50 ml of cyclohexylamine, and 4 ml (8.8 mmol) of 2.2 *M* butyllithium in hexane was stirred at 80° for 21 hr in a nitrogen atmosphere. The work-up procedure was the same as that used for 1,2-naphthobarrelene (*vide supra*), except that a 5 × 35 cm silicic acid column and solvent hexane were used for chromatography. Fractions 5 and 6 gave 71.3 mg (18%) of a colorless solid, mp 200–203°, and raised to 216–218° by crystallization from ethanol, identical (ir, tlc, mixture melting point) with anthracene; 9–12, 309.3 mg (70%) of 2,3-naphthobarrelene, mp 129–131°.

N,N-Dideuteriocyclohexylamine. A solution of 300 ml (0.248 mol) of cyclohexylamine and 40 ml of deuterium oxide was refluxed for 15 min in a dry, carbon dioxide free, nitrogen atmosphere. Dilution with 700 ml of CH_2Cl_2 gave a two-phase system, the lower phase of which was fractionally distilled to give partially deuterated cyclohexylamine, bp 130–132°. On repeating the deuteration five times, there was obtained 52 g of N,N-dideuteriocyclohexylanine, bp 130–132°.

Deuteration of 2,3-Naphthobarrelene. A solution of 44.7 g of N,N-dideuteriocyclohexylamine, 1.988 g (9.75 mmol) of 2,3-naphthobarrelene, and 4.0 ml (8.8 mmol) of 2.2 *M* butyllithium in hexane was stirred under nitrogen at 70° for 50 hr. An additional 4.0-ml portion of 2.2 *M* butyllithium was added after 8 hr. The dark blue mixture was quenched with 10 ml of deuterium oxide, diluted with 400 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 1.992 g of orange material which contained 2,3-naphthobarrelene that was 65.3 ± 1.0% deuterated in the aromatic and vinyl positions and 76.3 ± 1.8% deuterated in the vinyl positions.

A second pass on the barrelene in 27.8 g of N,N-dideuteriocyclohexylamine containing 4.0 ml of 2.2 *M* butyllithium for 24 hr at 65° (an additional 4.0-ml portion of butyllithium was added after 12 hr) gave 1.988 g of orange material containing 2,3-naphthobarrelene which was 74.4 ± 4.9% deuterated in the aromatic and vinyl positions, and 84.9 ± 3.2% deuterated in the vinyl positions.

A third pass on the barrelene in 65.0 g of N,N-dideuteriocyclohexylamine containing 4.0 ml of 2.2 *M* butyllithium for 100 hr at 70° (additional 4.0-ml portions of butyllithium were added after 24, 50, and 74 hr) was carried out. The orange product was dissolved in 120 ml of hexane and chromatographed in 30-ml portions on a 2 × 60 cm silicic acid column. Elution was with hexane; 500-ml fractions were collected. Fractions 3 and 4 contained 848 mg of 2,3-naphthobarrelene, mp 130–132°, that was 84.0 ± 2.1% deuterated in the aromatic and vinyl positions and 83.7 ± 1.3% deuterated in the vinyl positions.

A fourth pass on the barrelene in 52 g of N,N-dideuteriocyclohexylamine containing 4.0 ml of 2.2 *M* butyllithium for 24 hr at 65° afforded, after chromatography, 754 mg of 2,3-naphthobarrelene, mp 130–132°, which was 87.7 ± 0.4% deuterated in the aromatic and vinyl positions, and 92.4 ± 0.5% deuterated in the vinyl positions.

Deuteration of 1,2-Naphthobarrelene. The procedure was the same as that used with 2,3-naphthobarrelene (*vide supra*). The reaction was carried out on 2.1312 g (10.5 mmol) of 1,2-naphthobarrelene in 55.0 g of N,N-dideuteriocyclohexylamine containing 4 ml of 2.2 *M* butyllithium for 24 hr at 65°, and afforded 2.1923 g of solid which was 49.5 ± 0.4% deuterated in the aromatic and vinyl positions, and 78.5 ± 0.4% deuterated in the vinyl positions.

A second pass on the barrelene in 65 g of N,N-dideuteriocyclohexylamine containing 5.0 ml of 2.2 *M* butyllithium for 62 hr at 70° (additional 5.0-ml portions of butyllithium were added after 24 and 48 hr) was carried out. The product was dissolved in 50 ml of hexane and chromatographed in 25-ml portions on a 2 × 70 cm silicic acid column. Elution was with hexane; 500-ml fractions were collected. Fraction 3 contained 165.2 mg of deuterated phenanthrene, mp 92–95°; fractions 6–8 contained 1.8671 g of 1,2-naphthobarrelene, mp 83–85°, which was 60.8 ± 2.8% deuterated in the aromatic and vinyl positions and 88.5 ± 1.0% deuterated in the vinyl positions.

Nmr Analysis of Deuterated 2,3-Naphthobarrelene. The nmr (CCl_4) of deuterated 2,3-naphthobarrelene consisted of τ 2.50, 2.72, and 2.79 (br s, arom), 3.32 (br d, vinyl, J = 6.5 Hz), and 5.29 (br s, bridgehead).

The per cent deuteration of aromatic plus vinyl hydrogens is given by $\% D = 100(10 - B^*(A + V)/B)/10 = 20(5 - (A + V)/B)$, where A, V, and B are the aromatic, vinyl, and bridgehead areas, respectively; absence of bridgehead exchange is assumed and B^* is taken as 2. The per cent deuteration of vinyl hydrogens is given by $\% D' = 100(4 - B^*(V/B))/4 = 50(2 - V/B)$.

The following results were obtained in the deuteration of 2,3-naphthobarrelene (*vide supra*): first pass, A (relative area 83.3 ± 0.7), V (relative area 22.8 ± 1.2), and B (relative area 48.0 ± 1.0); second pass, A (relative area 60.6 ± 4.4), V (relative area 14.3 ± 1.3), and B (relative area 47.3 ± 5.7); third pass, A (relative area 54.0 ± 5.0), V (relative area 22.0 ± 1.0), and B (relative area 67.5 ± 2.5); fourth pass, A (relative area 55.6 ± 0.9), V (relative area 13.9 ± 0.6), and B (relative area 90.5 ± 1.5).

Nmr Analysis of Deuterated 1,2-Naphthobarrelene. The nmr (CCl_4) of deuterated 1,2-naphthobarrelene consisted of τ 1.97–2.13, 2.30–2.44, and 2.65–2.89 (m, arom), 3.12–3.29 (m, vinyl), 6.48 (br s, *syn* bridgehead), and 5.12 (br s, *anti* bridgehead). The following results were obtained in the deuteration of 1,2-naphthobarrelene (*vide supra*): first pass, A (relative area 148.5 ± 0.5), V (relative area 25.3 ± 0.3), and B (relative area 58.8 ± 0.3); second pass, A (relative area 138.7 ± 4.7), V (relative area 16.3 ± 0.8), and B (relative area 70.7 ± 2.7).

Direct Photolysis of Deuterated 2,3-Naphthobarrelene. A solution of 195.2 mg (0.917 mmol) of deuterated 2,3-naphthobarrelene in 730 ml of cyclohexane was photolyzed in apparatus B using filter combination 1 for 10 min. The solvent was removed *in vacuo* and the residue was chromatographed on a 4.5 × 150 cm water-jacketed (28°) column, dry packed with 700 g of Celite (Eagle Picher Co., Celatom FW-80) impregnated with a solution of 300 g of silver nitrate in 160 g of water. The column was eluted with water-saturated ether and the eluent absorbance was scanned at 280 nm; 40-ml fractions were collected. Two peaks were observed in the scan: sublimation (100°, 0.1 mm) of fractions 40–50 gave 54.1 mg (28%) of deuterated 2,3-naphthosemibullvalene, mp 136–138°; sublimation (100°, 0.1 mm) of fractions 65–82 gave 136.0 mg (70%) of recovered starting material, mp 129–131°, that was 88.4 ± 0.5% deuterated in the aromatic and vinyl positions, and 92.9 ± 0.3% deuterated in the vinyl positions.

The nmr (CCl_4) of the deuterated 2,3-naphthosemibullvalene consisted of τ 2.39 and 2.77 singlet (arom, relative area 43.0 ± 2.0), 4.56 br singlet (vinyl H-6, relative area 4.5 ± 1.5), 4.88 singlet (vinyl H-7, relative area 3.5 ± 1.5), 6.03 singlet (H-5, relative area 45.0 ± 4.0), 6.70–6.82 triplet (H-1, relative area 3.5 ± 1.0), 7.08 singlet (H-2, relative area 41.0 ± 2.5), and 7.37–7.43 doublet (H-8, relative area 2.5 ± 0.5).

Benzophenone Sensitized Photolysis of Deuterated 2,3-Naphthobarrelene. A solution of 200.8 mg (0.950 mmol) of deuterated 2,3-naphthobarrelene and 504.0 mg (2.78 mmol) of benzophenone in 730 ml of cyclohexane was photolyzed in apparatus B using filter combination 2 for 60 min. The solvent was removed *in vacuo* and the residue was chromatographed on a 4.5 × 150 cm silver nitrate, liquid–liquid partition column (*vide supra*); 50-ml fractions were collected. Two peaks were observed on the scan. Sublimation (100°, 0.1 mm) of fractions 48–58 gave 168 mg (84%) of recovered starting material, mp 120–122°, that was 87.7 ± 0.5% deuterated in the aromatic and vinyl positions and 92.4 ± 0.5% deuterated in the vinyl positions. Fractions 27–40 contained a mixture of benzophenone and deuterated 2,3-naphthosemibullvalene, which was separated by chromatography on a 2 × 30 cm alumina column (Fisher 80–200 mesh). Elution was with 1.5 l. of hexane and 2.0 l. of benzene; 250-ml fractions were collected. Fractions 5 and 6 gave 20.6 mg (10%) of the deuterated semibullvalene, mp 134–136°; sublimation (100°, 0.1 mm) of fractions 10–14 gave 470 mg (93%) of benzophenone, mp 46–48°.

The nmr (CCl_4) of the deuterated 2,3-naphthosemibullvalene consisted of τ 2.39 and 2.77 (s, arom, relative area 33.0 ± 2.5), 4.56 (br s, vinyl H-6, relative area 3.0 ± 0.5), 4.88 (s, vinyl H-7, relative area 3.0 ± 0.5), 6.03 (s, H-5, relative area 35.0 ± 2.0), 6.70–6.82 (t, H-1, relative area 4.0 ± 0.5), 7.08 (s, H-2, relative area 33.0 ± 1.0), and 7.37–7.43 (d, H-8, relative area 3.5 ± 1.0).

Direct Photolysis of Deuterated 1,2-Naphthobarrelene. A solution of 517 mg (2.55 mmol) of deuterated 1,2-naphthobarrelene in 730 ml of cyclohexane was photolyzed for 50 min in apparatus B using filter combination 1. The solvent was removed *in vacuo* and the residue was chromatographed on a 3 × 75 cm silicic acid column. Elution was with hexane; 250-ml fractions were collected. Sublimation (100°, 0.1 mm) of fractions 11–17 gave 72.0 mg (14%) of deuterated 1,2-naphthocyclooctatetraene, mp 46–48°; fractions 18–26 gave 38.2 mg (7%) of deuterated *syn*- and *anti*-1,2-naphthosemibullvalene as a colorless oil; sublimation (100°, 0.1 mm) of fractions 27–51 gave 401.0 mg (78%) of recovered starting material, mp 81–83°, that was 62.9 ± 1.5% deuterated in the aromatic and vinyl positions and 88.8 ± 1.0% deuterated in the vinyl positions.

A second run on 523.5 mg (2.58 mmol) of deuterated 1,2-naphthobarrelene in 730 ml of cyclohexane, photolyzed for 3 hr, gave 197.0 mg (38%) of deuterated 1,2-naphthocyclooctatetraene, mp 51–53°; 71.8 mg (14%) of deuterated *syn*- and *anti*-1,2-naphthosemibullvalene as an oil; and 255.8 mg (49%) of recovered starting material, mp 77–79°.

A third run on 465.8 mg (2.30 mmol) of deuterated 1,2-naphthobarrelene in 730 ml of cyclohexane photolyzed for 1.5 hr gave 128.5 mg (28%) of deuterated 1,2-naphthocyclooctatetraene, mp 51–53°; 38.9 mg (8%, mechanical losses) of deuterated *syn*- and *anti*-1,2-naphthosemibullvalene as an oil; and 249.7 mg (54%) of recovered starting material, mp 81–83°.

The deuterated *syn*- and *anti*-1,2-naphthosemibullvalenes from runs 1–3 were combined and separated by liquid–liquid partition chromatography on a 3 × 210 cm column of polystyrene beads (*vide supra*); 20-ml fractions were collected.

One broad peak was observed on the scan: fractions 130–140 contained 51.7 mg of an oil; 141–150, 63.4 mg of an oil.

Recycling fractions 130–140 gave a single broad scan: fractions 129–145 gave 11.2 mg of pure deuterated *syn*-1,2-naphthosemibullvalene, mp 41–43°; 146–165, 15.9 mg of an oily mixture of deuterated *syn*- and *anti*-1,2-naphthosemibullvalene.

Recycling fractions 141–150 gave a single broad scan: fractions 133–152 gave 32.8 mg of an oily mixture of deuterated *syn* and *anti* isomers; 153–163, 15.2 mg of pure deuterated *anti*-1,2-naphthosemibullvalene, mp 75–77°.

The nmr (CCl_4) of deuterated *syn*-1,2-naphthosemibullvalene consisted of τ 2.00–3.10 (m, arom, relative area 246.0 ± 6.0), 4.45 (br, vinyl H-6, relative area 6.5 ± 0.5), 4.95 (br, vinyl H-7, relative area 6.5 ± 0.5), 6.09 (s, H-5, relative area 52.5 ± 3.0), 6.56 (br, H-2, relative area 29.5 ± 2.5), 6.66 (m, H-1, relative area 7.0 ± 2.0), and 7.13 (s, H-8, relative area 35.0 ± 3.0).

The nmr (CCl_4) of deuterated *anti*-1,2-naphthosemibullvalene consisted of τ 2.15–3.10 (m, arom, relative area 210.0 ± 11.0), 4.49 (s, vinyl H-6, relative area 35.7 ± 3.0), 4.90–5.00 (m, vinyl H-7, relative area 7.0 ± 1.0), 5.67 (s, H-5, relative area 23.3 ± 2.7), 6.62–6.76 (t, H-1, relative area 6.7 ± 2.0), 6.89 (s, H-2, relative area 51.7 ± 4.0), and 7.24–7.31 (d, H-8, relative area 7.0 ± 1.0).

The nmr (CCl_4) of deuterated 1,2-naphthocyclooctatetraene consisted of τ 2.21–2.72 (m, arom, relative area 109.7 ± 1.1), 3.06–3.14 (t, arom, relative area 13.5 ± 0.5), 3.17–3.28 (d, H-8, relative area 4.3 ± 0.3), 3.38–3.49 (d, H-3, relative area 5.2 ± 0.3), 3.88 (s, H-4, relative area 36.3 ± 0.8), 4.06 (s, H-7, relative area 34.2 ± 1.2), 4.10–4.35 (m, H-5 and H-6, relative area 7.0 ± 0.5).

Benzophenone Sensitized Photolysis of Deuterated 1,2-Naphthobarrelene. A solution of 524.1 mg (2.58 mmol) of deuterated 1,2-naphthobarrelene and 5.1580 g (0.026 mol) of benzophenone in 730 ml of cyclohexane was photolyzed for 3 hr in apparatus B using filter combination 2. The solvent was removed and the residue was chromatographed on a 3 × 65 cm silicic acid column. Elution was with 8 l. of hexane and 2 l. of 20% ether in hexane; 500-ml fractions were collected. Fractions 5–11 contained 228.3 mg (44%) of an oily mixture of deuterated *syn*- and *anti*-1,2-naphthosemibullvalene; sublimation (100°, 0.1 mm) of fractions 12–16 gave 269.2 mg (51%) of recovered starting material, mp 78–80°, that was 62.4 ± 3.2% deuterated in the aromatic and vinyl positions and 87.2 ± 0.4% deuterated in the vinyl positions; sublimation (100°, 0.1 mm) of fractions 17–20 gave 5.0521 g (98%) of benzophenone, mp 46–48°.

The mixture of deuterated *syn*- and *anti*-1,2-naphthosemibullvalene was separated by liquid-liquid partition chromatography on a 3 × 210 cm column of polystyrene beads (*vide supra*); 20-ml fractions were collected.

One broad peak was observed in the scan: fractions 125–145 contained 92.1 mg of an oil; 146–165, 124.2 mg of an oil.

Recycling fractions 125–145 gave a single broad scan: fractions 125–137 contained 27.9 mg of pure deuterated *syn*-1,2-naphthosemibullvalene, mp 40–42°; 138–162, 56.7 mg of an oily mixture of deuterated *syn*- and *anti*-1,2-naphthosemibullvalene.

Recycling fractions 146–165 gave a single broad scan: fractions 126–150 contained 87.3 mg of an oily mixture of *syn* and *anti* isomers; 151–175, 29.0 mg of pure deuterated *anti*-1,2-naphthosemibullvalene, mp 81–83°.

The nmr (CCl_4) of deuterated *syn*-1,2-naphthosemibullvalene consisted of τ 2.02–3.07 (m, arom, relative area 353.0 ± 15.0), 4.48 (br, vinyl H-6, relative area 9.0 ± 2.0), 4.95 (br, vinyl H-7, relative area 10.0 ± 4.0), 6.10 (s, H-5, relative area 78.0 ± 6.0), 6.48–6.62 (m, H-2, relative area 11.0 ± 3.0), 6.63–6.76 (m, H-1, relative area 10.0 ± 4.0), and 7.13 (s, H-8, relative area 74.0 ± 6.0).

The nmr (CCl_4) of deuterated *anti*-1,2-naphthosemibullvalene consisted of τ 2.16–3.02 (m, arom, relative area 268.0 ± 13.0), 4.48 (s, vinyl H-6, relative area 37.0 ± 3.0), 4.90–4.96 (d, vinyl H-7, relative area 5.0 ± 1.0), 5.67 (br s, H-5, relative area 5.0 ± 1.0), 6.62–6.78 (m, H-1, relative area 6.0 ± 1.0), 6.87 (s, H-2, relative area 40.0 ± 2.0), and 7.21–7.29 (d, H-8, relative area 5.0 ± 2.0).

Direct Photolysis of *syn*- and *anti*-1,2-Naphthosemibullvalene. A solution of 126.9 mg (0.62 mmol) of a 1:1 mixture of *syn*- and *anti*-1,2-naphthosemibullvalene in 200 ml of cyclohexane was photolyzed for 50 min in apparatus A using a Pyrex filter. Concentration *in vacuo* was followed by chromatography on a 3 × 50 cm silicic acid column. Elution was with hexane; 500-ml fractions were collected. Fraction 5 contained 43.7 mg (35%) of 1,2-naphthocyclooctatetraene, mp 50–52°; fractions 7 and 8 contained 21.7 mg (17%) of the recovered oily mixture of *syn* and *anti* isomers (1:1 by nmr).

Quantum Yield of Direct Photolysis of 2,3-Naphthobarrelene. A solution of 209.6 mg (1.03 mmol) of 2,3-naphthobarrelene in 730 ml of cyclohexane was irradiated with 0.272 mEinstein in apparatus B using filter combination 1. Column chromatography of the concentrated photolysate on silicic acid (*vide supra*) gave 24.7 mg (12%) of 2,3-naphthosemibullvalene and 176.4 mg of recovered starting material. Quantum yield for the appearance of 2,3-naphthosemibullvalene is 0.45.

Quantum Yield of Sensitized Photolysis of 2,3-Naphthobarrelene. A solution of 211.7 mg (1.04 mmol) of 2,3-naphthobarrelene and 2.229 g (0.0127 mol) of benzophenone in 730 ml of cyclohexane was irradiated with 0.415 mEinstein in apparatus B using filter combination 2. Column chromatography of the concentrated photolysate on silicic acid (*vide supra*) gave 40.0 mg (19%) of 2,3-naphthosemibullvalene, 167.2 mg (79%) of recovered 2,3-naphthobarrelene, and 2.2162 g (97%) of recovered benzophenone. Quantum yield for the appearance of 2,3-naphthosemibullvalene is 0.47.

Quantum Yield of Direct Photolysis of 1,2-Naphthobarrelene. A solution of 199.3 mg (0.98 mmol) of 1,2-naphthobarrelene in 730 ml of cyclohexane was irradiated with 0.404 mEinstein in apparatus B using filter combination 1. Column chromatography of the concentrated photolysate on silicic acid (*vide supra*) gave 29.3 mg (15%) of 1,2-naphthocyclooctatetraene, 10.6 mg (5%) of 1,2-naphthosemibullvalene, and 155.6 mg (78%) of recovered starting material. Quantum yield for the appearance of 1,2-naphthocyclooctatetraene is 0.36, and the quantum yield for the appearance of 1,2-naphthosemibullvalene is 0.13.

Quantum Yield of Sensitized Photolysis of 1,2-Naphthobarrelene. A solution of 202.4 mg (0.99 mmol) of 1,2-naphthobarrelene and 1.9934 g (0.010 mol) of benzophenone in 730 ml of cyclohexane was irradiated with 0.424 mEinstein in apparatus B using filter combination 2. Column chromatography of the concentrated photolysate on silicic acid (*vide supra*) gave 43.5 mg (21%) of 1,2-naphthosemibullvalene, 151.2 mg (75%) of recovered 1,2-naphthobarrelene, and 1.9660 g (99%) of recovered benzophenone. Quantum yield for appearance of 1,2-naphthosemibullvalene is 0.50.

Fluorescence and Phosphorescence Studies. All studies were carried out on an Aminco-Kiers spectrophosphorimeter. Sample solutions (*ca.* 3×10^{-5} *M*) were purged with nitrogen. Phosphorescence studies of 1,2- and 2,3-naphthobarrelene in isopentane–methylcyclohexane (1:4) glass at 77°K gave the maximum energy peak (the 0–0 band) at 455 and 461 nm, respectively, corresponding to energies of 63 and 62 kcal/mol. Fluorescence spectra of 1,2- and 2,3-naphthobarrelene were measured in cyclohexane at room temperature and showed maxima at 368 and 354 nm, respectively. Intersection of emission and absorption spectra of 1,2- and 2,3-naphthobarrelene occurred at 338 and 335 nm, respectively, corresponding to singlet energies of 85 kcal/mol in each case.

In the case of 2,3-naphthobarrelene it was possible to measure the approximate fluorescence quantum yield by using naphthalene as the standard since the absorption and emission spectra of these two compounds were very similar in the 270–320- and 300–350-nm range, respectively. The concentration of a solution of naphthalene in cyclohexane was adjusted so that the absorbance matched that of a 2.76×10^{-5} cyclohexane solution of 2,3-naphthobarrelene over the 270–320-nm wavelength range. Fluorescence intensities of the naphthalene and 2,3-naphthobarrelene solutions at 335 nm were in the ratio of 1.00:0.34.

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