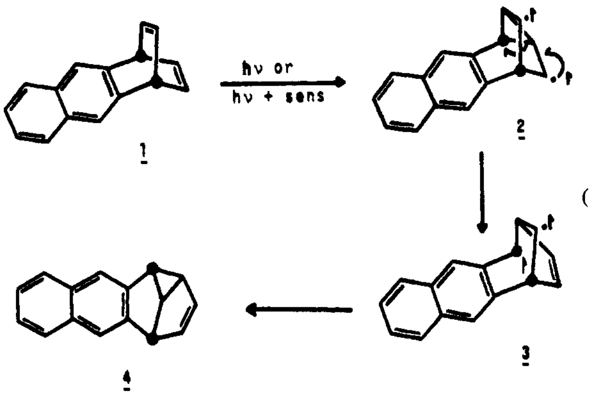
Photochemistry of Anthrabarrelene. Mechanistic and Exploratory Organic Photochemistry. LXXIX[1,2]

Howard E. Zimmerman* and David R. Amick

Contribution from the Chemistry Department of the University of Wisconsin, Madison, Wisconsin 53706. Received December 22, 1972

Abstract: 2,3-Anthrabarrelene (**8**) was synthesized for photochemical comparison with 2,3-naphthobarrelene, benzobarrelene, and barrelene itself. Irradiation of 2,3-anthrabarrelene afforded 2,3-anthrasemibullvalene (**9**) with a quantum efficiency of 0.25. The reaction course is analogous to the behavior of 2,3-naphthobarrelene but not 1,2-naphthobarrelene. Deuterium labeling studies revealed that the rearrangement proceeded *via* vinyl–vinyl bridging rather than anthraceno–vinyl bridging; this mechanism parallels the photochemistry of 2,3-naphthobarrelene but again contrasts with that of 1,2-naphthobarrelene. Triplet emission studies revealed T_1 at 43 kcal/mol, close to anthracene's 42 kcal/mol, and the vibrational structure was similar. Hence it was concluded that T_1 excitation is low in energy and heavily localized in the anthraceno moiety. Thus, T_1 excitation is localized at one end of the molecule but reaction must occur at the other end. In sensitization studies T_1 proved to be totally unreactive. This contrasts with the 2,3-naphthobarrelene situation. The difference is discussed in terms of sufficient energy being available to generate a partially rearranged excited species. The observed photochemistry is discussed in terms of T_2 as the reacting species.

The di-π-methane rearrangement[3] of barrelenes has proven to be an exceedingly general type of transformation. Thus, barrelene itself was shown in 1966 to rearrange to semibullvalene[4a] and the mechanism was elucidated.[4b] Benzobarrelene was subsequently found to give the same type of rearrangement,[5] and still later studies[6] revealed rearrangements of 1,2-naphthobarrelene and 2,3-naphthobarrelene to the corresponding semibullvalenes. The example of 2,3-naphthobarrelene (**1**) is given in eq 1 as illustrative.



(1)

Inspection of eq 1 shows that the mechanism proceeds by an initial vinyl–vinyl bridging despite the *a priori* possibility of an alternative mechanism beginning with vinyl–β-naphtho bonding; this preference for vinyl–vinyl bridging also occurs in the benzobarrelene case and has been interpreted in our earlier publications.[5–7] Also, the various barrelene to semibullvalene rearrangements have been shown to utilize triplet excited states.[4–6]

The present research began as an attempt to understand one intriguing aspect of the 2,3-naphthobarrelene rearrangement. Although the triplet excitation energy in the reactant was shown to be very heavily localized in the naphtho end of the molecule, it was the other end which was involved in the rearrangement (*i.e.*, with vinyl–vinyl bonding).[6] We were interested in using an attached aromatic moiety with still lower triplet excitation energy to see if this situation persisted. Additionally, an intriguing question was just how low in energy a triplet could be and still give this deep-seated rearrangement. The molecule selected for study was 2,3-anthrabarrelene.

Synthesis of 2,3-Anthrabarrelene. The synthesis selected was designed to generate anthracyne (**7**), which seemed likely to react with benzene to give 2,3-anthrabarrelene (**8**). We began with the known 2-amino-3-anthraquinonecarboxylic acid[8] (**5**). This was reduced with zinc under alkaline conditions to afford 2-amino-3-anthracenecarboxylic acid (**6**) which was then used as the anthracyne precursor. An *in situ* method[9] utilizing isoamyl nitrite in benzene at 55° proved most convenient and did indeed lead to anthrabarrelene (**8**), mp 269–271°, in yields ranging from 13 to 19%. Note Chart I and the Experimental Section for delineation of the synthetic method and details.

The structure assigned to 2,3-anthrabarrelene (**8**) rests on the mode of preparation, the great similarity of the vinyl and bridgehead hydrogen nmr pattern to that of the known benzobarrelene[5] and 2,3-naphthobarrelene,[6] and finally on the characteristic uv absorptions of the anthraceno moiety.

Deuteration of 2,3-Anthrabarrelene. Our earlier studies suggested the need for deuterium-labeled 2,3-anthrabarrelene. A convenient method had been de-

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(1) For paper LXXVIII of the series, note H. E. Zimmerman and W. Eberbach, *J. Amer. Chem. Soc.*, **95**, 3970 (1973).

(2) For a preliminary report of part of these studies see H. E. Zimmerman, D. R. Amick, and H. Hemetsberger, Abstracts of the 165th National Meeting of the American Chemical Society, Dallas, Texas, April 1973, ORGN-074

(3) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **91**, 1718 (1969).

(4) (a) H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **88**, 183 (1966); (b) H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, *ibid.*, **91**, 3316 (1969).

(5) H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, **90**, 4191, 6096 (1968).

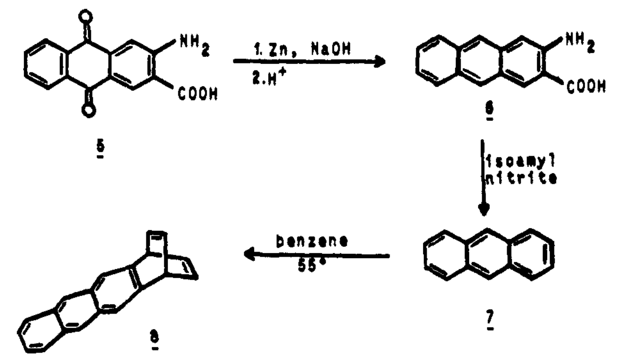
(6) H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **92**, 4366 (1970).

(7) H. E. Zimmerman and M.-L. Viriot-Villaume, *J. Amer. Chem. Soc.*, **95**, 1274 (1973).

(8) C. Willgerodt and F. Mafferzzoli, *J. Prakt. Chem.*, **82**, 205 (1910).

(9) L. Friedman and F. M. Logullo, *J. Org. Chem.*, **34**, 3089 (1969).

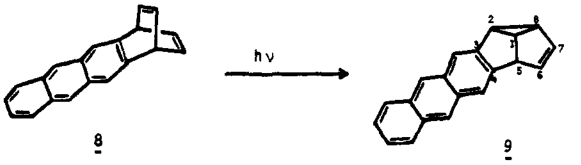
Chart I. Synthesis of 2,3-Anthrabarrelene



veloped in these laboratories. This utilized lithium *N*-deuteriocyclohexylamide in *N*,*N*-dideuteriocyclohexylamine, *i.e.*, a deuterated version of Streitwieser's base.[10]

This method led to exchange of all sp^2-hybridized hydrogens and thus to barrelenes having protium only at the bridgehead positions. Only two successive treatments with the deuterating base afforded a 90% yield of anthrabarrelene with 81% deuterium incorporated (*i.e.*, **8**-*d*) in the aromatic and vinyl positions with these two sites being equally labeled. The details of the assay of the deuterium are described in the Experimental Section. Finally, it should be noted that incomplete exchange presents no difficulties (*vide infra*).

Exploratory Photolyses and Irradiation of Labeled 2,3-Anthrabarrelene. The first runs were made on undeuterated material and using the Black Box apparatus[11] described by us earlier. Irradiation of 2,3-anthrabarrelene (**8**) to complete conversion gave 2,3-anthrasemibullvalene (**9**) in 89% yield as a 250–252° melting solid (eq 2). The *a priori* possible 2,3-anthracyclooctatetraene (**10**) was not formed.



(2)

Irradiation of the labeled 2,3-anthrabarrelene (**8**-*d*) gave labeled 2,3-anthrasemibullvalene (**9a**). Since incompletely labeled 2,3-anthrabarrelene was used, it was necessary to compare the product deuterium distribution with that expected from 81% deuterated reactant. This is done in Table II in the interpretative discussion and also is described in the Experimental Section. Presently the major point of interest is that the bridgehead label was found entirely at the benzylic positions of 2,3-anthrasemibullvalene (*i.e.*, at carbons 2 and 5).

Determination of Quantum Efficiencies and Energy Transfer Observation. Direct irradiations were carried out in our Black Box[11] apparatus and the semimicro optical bench described by us earlier[11] using cyclohexane solvent. Different filter solutions were used to allow irradiation of the S_1 band occurring at 300–380 nm in one set of runs and to permit excitation to S_2 and S_3 with a 255–305-nm filter solution. The quantum yields listed in Table I show no wavelength dependence.

Sensitized runs using fluorenone, acetophenone, and biacetyl are also described in Table I. It is seen that no conversion was obtained with these sensitizers. The small conversion obtained with acetophenone and biacetyl corresponds closely to the amount of direct light capture by the 2,3-anthrabarrelene reactant and thus does not arise from energy transfer.

That energy transfer was indeed occurring, although without rearrangement, was established by emission studies using biacetyl. It is known[12] that absorption of light by biacetyl leads to both fluorescence and phosphorescence. With 434-nm excitation and complete light capture by the biacetyl we observed two emission peaks to occur with a 1:7.9 peak height ratio using an Aminco-Bowman fluorometer. However, on addition of 0.00243 *M* 2,3-anthrabarrelene, the same concentration used in photolysis, the phosphorescence peak completely disappeared indicating complete energy transfer from biacetyl triplet (E_T = 55 kcal/mol) to the 2,3-anthrabarrelene (E_T = 43 kcal/mol, *vide infra*). These experiments are described in the Experimental Section.

Direct measurement of the triplet energy of 2,3-anthrabarrelene was carried out at 77°K in methylcyclohexane–isopentane (4:1) glass. A 0–0 triplet energy of 43 kcal/mol was obtained. Thus, triplet energy transfer should indeed occur with the three sensitizers used in photolyses.

With the idea that an upper triplet (*i.e.*, T_2) might be responsible for the 2,3-anthrabarrelene to 2,3-anthrasemibullvalene rearrangement, we attempted quenching using cyclohexadiene (E_T = 53 kcal/mol[13]). With increasing concentrations of cyclohexadiene it was observed that 2,3-anthrabarrelene fluorescence was increasingly quenched and at 0.2 *M* 36% had been quenched. However, in photolyses using 0.2 *M* cyclohexadiene the quantum yield of disappearance of 2,3-anthrabarrelene was diminished by only 36%. This demonstrates that only singlet quenching had occurred and that no triplets were being intercepted. These observations are summarized in the Experimental Section and the quantum yields with quencher added are included in Table I.

Table I. Quantum Yields for Anthrabarrelene Photolyses

Run	Anthra-barrelene concn	Sensitizer or quencher	Exciting wavelength, nm	Quantum yield
1	0.000158	None	305–380	0.25
2	0.000472	None	305–380	0.25
3	0.000130	None	255–305	0.23
4	0.002430	None	352–380	0.18
5	0.002430	Fluorenone[a]	390–420	0.00
6	0.002430	Acetophenone[b]	283–311	0.04
7	0.002430	Biacetyl[c]	390–420	0.01
8	0.002430	Cyclohexadiene[d]	352–380	0.11

[a] 0.002 *M*. [b] 0.25 *M*. [c] 0.0364 *M*. [d] 0.20 *M*.

Interpretative Discussion. Occurrence and Overall Mechanism of the Rearrangement. The first point to be noted is the striking result that the di-π-methane rearrangement still does occur with modest efficiency (*i.e.*, ϕ = 0.25) despite the low energies of the lowest

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

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

[12] (a) F. Wilkinson and J. T. Dubois, *J. Chem. Phys.*, 39, 377 (1963); (b) J. T. Dubois and R. L. Van Hemert, *ibid.*, 40, 923 (1964).

[13] A. J. Fry, R. S. H. Liu, and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 4781 (1966).

Table II. Observed and Theoretical Hydrogen Distributions in the Photolysis of Labeled 2,3-Anthrabarrelene to Give 2,3-Anthrasemibullvalene

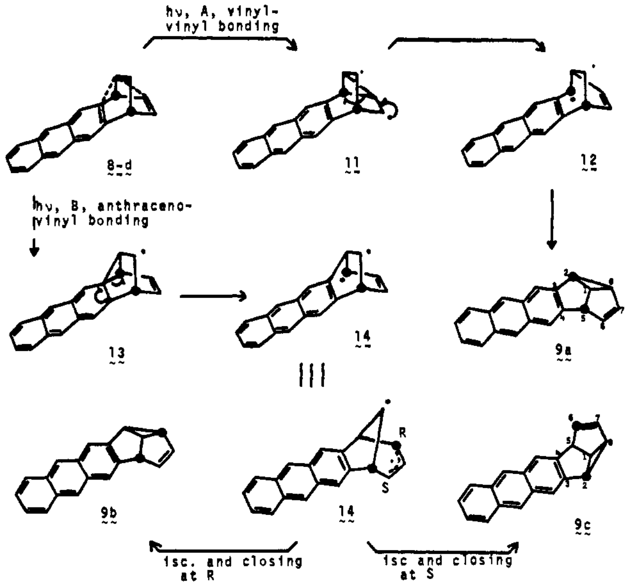
Case	Label distribution[a] H-1	H-2	H-5	H-6	H-7	H-8
Mech A, calcd	0.190 (± 0.010)	1.000	1.000	0.190 (± 0.010)	0.190 (± 0.010)	0.190 (± 0.010)
Mech B, calcd	0.190 (± 0.010)	0.595 (± 0.030)	0.595 (± 0.030)	0.595 (± 0.030)	0.190 (± 0.010)	0.595 (± 0.030)
Direct, exptl[b]	0.228 (± 0.046)	1.048 (± 0.105)	0.952 (± 0.095)	0.167 (± 0.040)	0.240 (± 0.048)	0.228 (± 0.046)

[a] Corrected for 19.0 ± 1.0% residual vinyl hydrogen in anthrabarrelene reactant. [b] Errors estimated from the scatter of nmr signal integrations.

excited states of 2,3-anthrabarrelene (*i.e.*, E_S = 76.3 kcal/mol and E_T = 43 kcal/mol). Thus, one of the first questions to be asked is whether or not the rearrangement is really the same as that of barrelene, benzobarrelene, and 2,3-naphthobarrelene.

Accordingly, it is of considerable interest to inspect the skeletal transformation during reaction. The available mechanisms are depicted in Chart II. Table II contains the distribution of hydrogen label expected for the vinyl–vinyl and anthraceno–vinyl bridging mechanisms leading to 2,3-anthrasemibullvalene. The hydrogen label distributions in Table II are corrected for residual vinyl hydrogen in the 2,3-anthrabarrelene (**8**-*d*) reactant. Additionally, as entry three in Table II, are the experimentally observed distributions of the hydrogen label.

Chart II. Vinyl–vinyl and Anthraceno–Vinyl Bonding Mechanisms for the Photochemical Rearrangement of 2,3-Anthrabarrelene



It is seen that the experimental distribution is in agreement with mechanism A which proceeds by vinyl–vinyl bridging but is in disagreement with mechanism B involving anthraceno–vinyl bonding. This is then the same structural course of the reaction as observed by us earlier for benzobarrelene[5] and 2,3-naphthobarrelene.[6]

Electronic Aspects of the Rearrangement. Interpretative Discussion. The first conclusion possible is that the reaction does not proceed *via* T_1, the first excited triplet. The evidence presented above strongly supports efficient transfer of triplet excitation from the triplet sensitizers used to 2,3-anthrabarrelene, and yet no 2,3-anthrasemibullvalene formation was observed. The sensitizers used, however, were capable of generating only the lowest triplet of reactant by exothermic energy transfer. Thus, even acetophenone with its 74 kcal/mol excitation energy is unlikely to be able to generate T_2, the second triplet of reactant, since T_2 for anthracene itself has been reported[14] as 74.4 kcal/mol.

Thus, with T_1 excluded as the reacting excited state, S_1 and T_2 remain as possibilities. One would expect[15] intersystem crossing of the 76.3-kcal/mol S_1 to the triplet manifold to proceed most efficiently with initial generation of the nearly isoenergetic T_2 and subsequent internal conversion in part to T_1. Hence, it is seen that T_2 is potentially available for rearrangement. Liu has put forth evidence that anthracene second triplets do have finite lifetimes.[16] In the present study, attempts to demonstrate selective quenching of T_2 in the presence of S_1 failed due to the facile quenching of the 2,3-anthrabarrelene singlets. However, this merely means that T_2 may rearrange and internally convert to T_1 faster than it can be intercepted by triplet quenchers.

Although rigorous evidence in favor of one of the two possible electronic states is not available, a preference for T_2 derives from analogy with the barrelene, benzobarrelene, and 2,3-naphthobarrelene cases where triplet multiplicity was preferred and also comes from consideration of the reasons for preferential triplet rearrangement.[3]

The failure of T_1 to rearrange is most striking and requires discussion. As a starting point it is to be noted that in our previous studies[5-7] evidence has accumulated that with the exception of the α-naphtho position, bridging to aromatic sites is unfavorable in the rearrangement of barrelenes and occurs only where enforced. Thus, benzobarrelene[5] and 2,3-naphthobarrelene[6] rearrange by vinyl–vinyl bridging rather than aromatic–vinyl bridging. In the case of benzo-2,3-naphthobarrelene,[7] where there is no option other than vinyl–aryl bridging, an abnormally low quantum efficiency was observed (*i.e.*, ϕ = 0.077 *vs.* 0.46 for 2,3-naphthobarrelene). Consideration of the sources of this effect reveals that breaking up an aromatic system effects almost as large a loss in total electronic energy in the excited state as in the ground state. This is equivalent to saying that a large fraction of the ground state delocalization energy remains after excitation.[17]

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(14) R. E. Kellogg, *J. Chem. Phys.*, **44**, 411 (1966).

(15) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **38**, 1187 (1963).

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

(17) This is intuitively reasonable if one considers that electronic excitation changes the configuration only slightly (*i.e.*, two MO's in a Hückel approximation) and hence the total energy will tend to reflect the electronic contributions from the undisturbed MO's. Configuration interaction calculations (unpublished results of T. W. Flechtner) on 2,3-naphthobarrelene, unperturbed and then partially bridged, show a parallel between loss of ground-state aromaticity and excited-state energy changes.

Hence, reluctance to bond β on an aromatic ring can be understood and seems to be a general phenomenon.

With anthraceno–vinyl bridging precluded, we note that insufficient energy is available for the 43-kcal/mol 2,3-anthrabarrelene triplet to vinyl–vinyl bond. In our previous publications[5,6] we noted that the triplet energy of the cisoid butadiene moiety engendered by vinyl–vinyl bridging in this system must be at about 57.5 kcal/mol. But 2,3-anthrabarrelene is endowed in its T_1 state with only 43 kcal/mol. Thus, vinyl–vinyl bridging of the lowest triplet (*i.e.*, T_1) would require some 57 kcal/mol supplied to the two vinyl bridges by the other end of the molecule (*i.e.*, the anthraceno moiety) which has only 43 kcal/mol available. Hence, it is not surprising that T_1 is unreactive. In contrast, T_2, with its 74-kcal/mol electronic excitation energy, is not subject to this limitation.

Thus, the photochemical rearrangement of the aromatic barrelenes has proven general in its preference of vinyl–vinyl bridging and utilization of the di-π-methane mechanism while revealing an energy requirement for rearrangement of the lowest triplet.

Experimental Section[18]

***o*-(1,2,3,4-Tetrahydro-6-naphthoyl)benzoic Acid.** A slight modification of the procedure of Sisido and Nozaki[19] was used. From 42 g (0.284 mol) of phthalic anhydride, 45 g (0.341 mol) of tetralin, 96 g (0.720 mol) of aluminum chloride, and 600 ml of carbon disulfide, there was obtained 55.44 g (70%) of *o*-(1,2,3,4-tetrahydro-6-naphthoyl)benzoic acid: mp 163–165°; ir (Nujol) 6.00, 7.00, 7.65, 7.75, 7.94, 10.50, 12.90, 13.49, 14.06 μ.

1,2,3,4-Tetrahydro-6,11-dioxonaphthacene. The following is an improvement of the procedure of Schroeter.[20] *o*-(1,2,3,4-Tetrahydro-6-naphthoyl)benzoic acid (60 g, 0.215 mol) was added to 200 ml of ice cooled 25% fuming sulfuric acid. The mixture was heated to 80°, allowed to react at that temperature for 5 min, and then poured over crushed ice. The solid collected was washed with water, 0.3 *M* potassium bicarbonate, and then water. The solid was recrystallized from 7 parts of benzene to give 21.7 g (38%) of the desired dione as pale yellow crystals: mp 214–216°; ir (Nujol) 6.00, 6.03, 6.31, 7.51, 7.77, 10.44, 14.08 μ; nmr ($CDCl_3$) τ 8.18 and 7.12 (two broad m, 8 H, CH_2), 1.68–2.81 (m, 6 H, arom).

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.53; H, 5.39.

Anthraquinone-2,3-dicarboxylic Acid. The procedure of Willgerodt[8] led to occasional explosions. A useful method was thus developed. A mixture of 142 g (0.542 mol) of 1,2,3,4-tetrahydrotetracene-6,11-quinone, 50 ml of nitrobenzene, and 2 l. of 20% nitric acid was stirred rapidly at 100° for 48 hr. The yellow solid was collected *via* filtration, thoroughly rinsed with benzene to remove nitrobenzene, and dried. The solid was extracted with warm chloroform to remove unreacted dione. The crude diacid (136.4 g, 85%) was used without further purification in the next step.

A portion of the crude diacid (5.86 g) was dissolved in 1 *N* potassium hydroxide and a red impurity was removed by filtration. Acidification of the filtrate with HCl afforded 4.42 g (67%) of a white solid which was crystallized twice from acetic acid to give mp 288–290°. The infrared spectrum showed bands at (Nujol) 3.0–4.5, 5.99, 6.30, 7.05, 7.54, 7.88, 12.60, and 14.14 μ. The mass spectrum (70 eV) showed the molecular ion at *m/e* 296.032 (calcd for $C_{16}H_8O_6$, 296.032).

Anthraquinone-2,3-dicarboxyanhydride. A mixture of 13 g of the impure 9,10-anthraquinone-2,3-dicarboxylic acid in 650 ml of acetic acid was stirred at reflux for 15 min, and then filtered while hot. To the filtrate at a temperature of 110° was added 130 ml of acetic anhydride and the solution was stirred at room temperature until the internal temperature reached 80° (about 15 min). The solution was cooled to room temperature and crystallized during 4 hr. The solid was collected and washed with ether to afford 6.11 g (50%) of 9,10-anthraquinon-2,3-anhydride. Two crystallizations from acetic acid afforded pure anhydride: mp 340–343°; ir (Nujol) 5.41, 5.62, 6.00, 6.31, 8.01, 11.15, 12.53, 13.28, 14.20 μ.

Anal. Calcd for $C_{16}H_6O_5$: C, 69.07; H, 2.17. Found: C, 68.87; H, 2.24.

2-Amido-3-anthraquinonecarboxylic Acid. A mixture of 3.0 g (0.011 mol) of 9,10-anthraquinon-2,3-anhydride and 600 ml of 50% ammonium hydroxide was heated, with stirring, at 40° for 15 min. A brown insoluble solid was removed by filtration and the filtrate was slowly acidified with hydrochloric acid to afford 2.88 g (91%) of 9,10-anthraquinon-2-amido-3-carboxylic acid. Two crystallizations from tetrahydrofuran gave pure material: mp 340–342°; ir (Nujol) 2.92, 3.13, 3.80, 5.83, 6.09, 6.30, 6.71, 7.10, 7.55, 7.73, 7.91, 8.08, 9.60, 10.47, 10.68, 10.91, 11.40, 12.56, 13.90, 14.10 μ.

Anal. Calcd for $C_{16}H_9O_5N$: C, 65.09; H, 3.07. Found: C, 65.12; H, 3.07.

2-Amino-3-anthraquinonecarboxylic Acid. A mixture of 5.0 g (16.9 mmol) of 9,10-anthraquinon-2-amido-3-carboxylic acid, 2.33 g of sodium hydroxide, and 93 ml of water was stirred at room temperature as 27.9 ml of a 0.645 *M* sodium hypochlorite solution[21] (18.0 mmol) was added during 10 min. The temperature was raised to 85° over 15 min. The reaction mixture was then cooled and a red solid collected. An orange solid was salted out of the filtrate with sodium chloride. The combined sodium salts were boiled in dilute hydrochloric acid and filtered to afford 3.87 g (86%) of 9,10-anthraquinon-2-amino-3-carboxylic acid. A portion of the sodium salt was crystallized twice from water and then acidified to the amino acid, which was recrystallized from tetrahydrofuran, giving mp >360°. The spectral properties were ir (Nujol) 2.88, 2.99, 6.01, 6.07, 6.21, 6.29, 6.38, 6.99, 7.49, 7.80, 7.92, 8.06, 13.99, 14.40, 14.84 μ. The mass spectrum (70 eV) showed the molecular ion at *m/e* 267.053 (calcd for $C_{15}H_9NO_4$, 267.053).

2-Amino-3-anthracenecarboxylic Acid. The general method of Fieser for reduction of anthrone to anthracene was used.[22] A suspension of 4.0 g of zinc dust in 30 ml of water was activated with 0.5 ml of Fehling's-I solution.[23] To the mixture was added 2.36 g (8.66 mmol) of 9,10-anthraquinon-2-amino-3-carboxylic acid, followed by 4.0 g of sodium hydroxide in 42 ml of water. The mixture was rapidly stirred at 100° for 3.5 hr. The zinc, coated with product, was filtered from the cooled solution and extracted with 1500 ml of 1 *N* potassium hydroxide at 80°. Acidification of the extract to pH 1 afforded 1.2 g (59%) of anthracen-2-amino-3-carboxylic acid. The infrared spectrum exhibited bands at (Nujol): 2.84, 2.93, 3.03–4.55, 6.04, 6.14, 6.30, 6.43, 7.62, 7.84, 8.12, 9.20, 10.49, 10.79, 11.00, 11.23, 11.41, 12.38, 12.60, 13.62, 14.34 μ.

An analytical sample was obtained by acidifying the hot potassium hydroxide extract to pH 10, cooling and isolating the potassium salt as yellow needles. The infrared spectrum of the salt showed bands at (Nujol): 2.91, 2.95–3.24, 6.14, 6.33, 6.62, 7.50, 7.80, 7.95, 8.22, 8.49, 9.10–9.70, 10.45, 10.54, 10.89, 11.24, 11.45, 12.22, 14.06 μ. The potassium salt was rinsed with water and then ether; it was dissolved in water and acidified to pH 1 with HCl, and the pure anthracen-2-amino-3-carboxylic acid was collected as a pink powder, dec 285°.

Anal. Calcd for $C_{15}H_{11}O_2N$: C, 75.93; H, 4.65; N, 5.90. Found: C, 75.76; H, 4.70; N, 5.83.

2,3-Anthrabarrelene. A mixture of 90 mg (0.38 mmol) of 2-aminoanthracene-3-carboxylic acid and 700 ml of benzene (distilled from calcium hydride) was stirred under nitrogen during 3 hr at 55°. Isoamyl nitrite (0.20 ml, 1.5 mmol) was added all at once and the reaction continued an additional 15 hr at 55°. The green mixtures from three such reactions were combined and concentrated; the resulting brown solid was extracted with 15% chloroform in hexane and concentrated. Using thick layer chromatography (silica gel, GF_{254}; 20 cm × 20 cm plates), two elutions with 15% chloroform in hexane gave two separated mobile bands. The slower band of each plate was ether extracted; the combined extracts afforded 56.2 mg (19.5%) of 2,3-anthrabarrelene. Two crystallizations from ethanol afforded pure material: mp 269–271°; ir (KBr) 3.26, 3.34, 5.59, 6.20, 6.38, 7.00, 7.52, 7.79, 8.17, 8.62, 9.00–9.50, 9.98, 10.53, 11.19, 12.98, 13.49, 14.43, 15.11, 15.62 μ; nmr ($CDCl_3$; XL-100) τ 1.84 (s, 2 H, arom), 2.04–2.18 (m, 2 H, arom), 2.44 (s, 2 H, arom), 2.58–2.71 (m, 2 H, arom), 3.18 (m, 4 H,

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

(19) K. Sisido and H. Nozaki, *J. Amer. Chem. Soc.*, **70**, 1609 (1948).

(20) G. Schroeter, *Ber.*, **54**, 2242 (1921).

(21) E. S. Wallis and J. F. Lane, *Org. React.*, **3**, 281 (1940).

(22) L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, **62**, 49 (1940).

(23) L. F. Fieser, "Organic Experiments," D. C. Heath, Boston, Mass., 1964, p 130.

vinyl), 5.10 (m, 2 H, bridgehead); uv max (cyclohexane) 238 nm sh (ε 17,900), 259 sh (81,200), 267 (144,700), 304 (1560), 317 (3180), 332 (5740), 349 (7700), 369 (6070); mass spectrum (70 eV) showed the molecular ion at *m/e* 254.109 (calcd for $C_{20}H_{14}$: 254.109).

Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.16; H, 5.77.

2,3-Anthrasemibullvalene from the Direct Photolysis of 2,3-Anthrabarrelene. A solution of 54 mg of anthrabarrelene (0.213 mmol) in 750 ml of cyclohexane was irradiated with 5.62 mEinsteins of light through filter A on the Black Box (*vide infra*). The photolysate was concentrated, dissolved in 50 ml of hexane, and chromatographed on a 5 cm × 5 cm silica gel column (60–200 mesh), eluting with hexane, to afford 46 mg (89%) of anthrasemibullvalene. Recrystallizaion from 10 ml of absolute ethanol gave 24 mg of pure anthrasemibullvalene: dec 250°; ir (KBr) 3.27, 3.38, 5.59, 6.17, 6.32, 7.00, 7.46, 7.78, 7.98, 8.22, 8.50, 8.62, 8.99, 9.12, 9.33, 9.99, 10.50, 11.14, 12.00, 12.44, 13.02, 13.20, 13.55, 13.93, 14.70, 15.09 μ; nmr ($CDCl_3$; XL-100) τ 1.70–2.82 (m, 8 H, arom), 4.42 (ABX q, J_{67} = 5.4 cps, J_{56} = 2.0 cps, 1 H, vinyl H-6), 4.67 (ABX q, J_{67} = 5.4 cps, J_{78} = 2.0 cps, 1 H, vinyl H-7), 5.83 (ABX q, J_{56} = 2.0 cps, J_{15} = 6.0 cps, 1 H, benzylic and allylic H-5), 6.62 (ABCD q, J_{15} = J_{12} = J_{18} = 7.0 cps, 1 H, interior cyclopropyl H-1), 6.94 (ABC t, J_{12} = J_{28} = 7.0 cps, 1 H, cyclopropyl and benzylic H-2), 7.36 (ABCX t of d, J_{78} = 2.0 cps, J_{18} = J_{28} = 7.0 cps, 1 H, cyclopropyl and allylic H-8); uv max (cyclohexane) 255 nm sh (ε 79,400), 263 (164,000), 315 sh (1430), 330 (2800), 344.5 (4900), 362 (6620), 382 (5110).

Anal. Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.17; H, 5.57.

***N,N*-Dideuteriocyclohexylamine.** To a solution of 130 ml (1.07 mol) of cyclohexylamine and 35 ml of deuterium oxide that had been stirred under nitrogen at 80° for 0.5 hr and then cooled was added 140 g of molecular sieve (Linde, Type 4A, activated at 400°). After the mixture had cooled to room temperature, the sieves were extracted with methylene chloride (3 × 200 ml). The extracts were combined and the methylene chloride was distilled from the solution, thus azeotroping off any remaining deuterium oxide. On repeating the deuteration three more times, there was obtained 30 ml of *N,N*-dideuteriocyclohexylamine, bp 130–132°.

Deuteration of 2,3-Anthrabarrelene. To a solution of 127 mg (0.5 mmol) of 2,3-anthrabarrelene in 15 ml (0.129 mmol) of *N,N*-dideuteriocyclohexylamine at 70° was added, under nitrogen, 2.60 ml (5.72 mmol) of 2.2 *M* butyllithium in hexane. The solution was stirred at 70° for 45 hr; an additional 2.00-ml (4.4 mmol) portion of 2.2 *M* butyllithium was added after the first 26 hr. The dark solution was cooled, quenched with 10.0 ml of deuterium oxide, and hexane extracted (2 × 400 ml); the extract was washed with 10% aqueous HCl (3 × 150 ml) and then water (2 × 250 ml). The extract was dried and concentrated *in vacuo* to give 143 mg of a pale yellow solid, 2,3-anthrabarrelene, 46 ± 4% deuterated in the aromatic positions and 78 ± 4% deuterated in the vinyl positions.

A second pass was made on the barrelene in another 15 ml (0.129 mmol) of *N,N*-dideuteriocyclohexylamine containing 3.0 ml of 2.2 *M* butyllithium for 43.5 hr at 68°; an additional 2.2-ml portion of butyllithium was added after the first 18.5 hr. This gave 174.3 mg of pale yellow 2,3-anthrabarrelene 80% ± 4% deuterated in the aromatic positions and 82 ± 4% deuterated in the vinyl positions. The deuterated material was purified in four portions by thick layer chromatography (silica gel, GF_{254}; 20 × 20 cm plates) using 15% chloroform in hexane to give a fluorescent mobile band which was extracted with ether. The ether extracts were combined to afford 114.3 mg of deuterated 2,3-anthrabarrelene in 90% yield.

Nmr Analysis of Deuterated 2,3-Anthrabarrelene. The nmr ($CDCl_3$; XL-100) of deuterated 2,3-anthrabarrelene consisted of peaks at τ 1.80 and 2.39 (s, arom), 2.06 and 2.60 (m, arom), 3.07–3.22 (m, vinyl), and 5.06 (s, bridgehead).

The per cent deuteration of vinyl positions is given by $\% D = 100(4 - B^*(V/B))/4$, where *V* and *B* are the vinyl and bridgehead areas, respectively; absence of bridgehead exchange is assumed and B^* is taken as 2.

The following results were obtained in the deuteration of 2,3-anthrabarrelene (*vide supra*): 1st pass, *V* (rel area 10.0 ± 0.5), and *B* (rel area 22.0 ± 1.0); 2nd pass, *V* (rel area 21.0 ± 1.0), and *B* (rel area 58.0 ± 2.0).

Direct Photolysis of Deuterated 2,3-Anthrabarrelene. A solution of 16.4 mg (0.0625 mmol) of deuterated 2,3-anthrabarrelene in 750 ml of cyclohexane was photolyzed to 70% conversion in the Black Box using filter A (*vide infra*). The solvent was removed *in vacuo* and the residue was analyzed by nmr.

The nmr ($CDCl_3$; XL-100) of the deuterated photolysate, ignoring aromatic peaks, consisted of: τ 3.14 br mult (vinyl H-6, rel area 3.3 ± 1.0), 4.64 s (vinyl H-7, rel area 5.0 ± 1.5), 5.06 s (barrelene bridgehead, rel area 17.0 ± 2.0), 5.82 s (H-5, rel area 20.0 ± 2.0), 6.56 mult (H-1, rel area 4.5 ± 1.5), 6.92 s (H-2, rel area 22.0 ± 2.0), 7.36 mult (H-8, rel area 4.0 ± 2.0).

Photolysis Equipment and Quantum Yield Determinations. Quantum yields employing direct irradiation were made with the Black Box apparatus[11] previously described,[24] 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. Sensitized runs were made on the semimicro optical bench described earlier;[11,24] this utilized a Bausch and Lomb high intensity monochrometer with an HBO 200-W high-pressure lamp and 40-ml, 10-cm cells. In both cases a beam splitter[24] and ferrioxalate actinometry[25] were used.

Two filter combinations were used in the Black Box apparatus having three 2.4-cm path length filter cells. Filter A: cell I, 50 g of nickel sulfate hexahydrate/l. of 10% sulfuric acid; cell II, 225 g of cobalt sulfate heptahydrate/l. of 10% sulfuric acid; cell III, 25 g of stannous chloride dihydrate/l. of 20% hydrochloric acid (by volume); transmission 305–380 nm, max at 335 nm (54%).

Filter B: cell I, 1 mol of nickel salt/l. of 10% sulfuric acid; cell II, 2 mol of cobalt salt/l. of 10% sulfuric acid; cell III, 10^{-4} mol of bismuth trichloride/l. of 20% hydrochloric acid (by volume); transmission 255–305 nm, max at 283 nm (46%).

For both direct and sensitized runs, vanadous-purified nitrogen[26] was bubbled through the solution for 45 min prior to photolysis and was continued during the irradiation.

Quantum yield determinations were obtained using nmr assay of the photolysate. Additionally, chromatographic assay was used. Using a standard size column (3.0 × 65 cm of silica gel) and hexane eluent it was determined that anthrabarrelene was eluted unchanged; however, between 45 and 55% of the semibullvalene was irreversibly adsorbed depending on the specific column utilized. For each run, a standard of anthrasemibullvalene was first run on the column to be used and the percentage eluting at fixed flow rate was determined. Assays assuming this loss were in agreement with the nmr assays within a 5% experimental error. Additionally, the semibullvalene assayed as formed, using this correction, proved in agreement with the amount of anthrabarrelene assayed as reacted.

Solvent. Cyclohexane was stirred with one-tenth of its volume of 10% fuming sulfuric acid for 8 hr, washed with 10% aqueous potassium hydroxide, dried (magnesium hydroxide), and distilled from calcium hydride.

Quantum Yield No. 1 for Direct Photolysis of 2,3-Anthrabarrelene ($S_0 - S_1$). A solution of 30 mg (0.118 mmol) of 2,3-anthrabarrelene in 750 ml of cyclohexane was irradiated with 0.146 mEinstein in the Black Box using filter A. Nmr analysis indicated 30% conversion to 2,3-anthrasemibullvalene. Chromatographic analysis (*vide supra*) with 40-ml fractions gave: fractions 27–38, 9.3 mg of 2,3-anthrasemibullvalene (corrected for 55% adsorption; upon passing 10.0 mg of the semibullvalene through the same column, 4.5 mg was collected while 5.5 mg was irreversibly adsorbed); fractions 39–55, 20.7 mg (69%) of 2,3-anthrabarrelene. ϕ(dis 2,3-anthrabarrelene) by chromatography was thus the same as that for the formation of 2,3-anthrasemibullvalene by both nmr and chromatography, *i.e.*, $\phi = 0.25$.

Quantum Yield No. 2 for Direct Photolysis of 2,3-Anthrabarrelene ($S_0 - S_1$). A solution of 90 mg (0.354 mmol) of 2,3-anthrabarrelene in 750 ml of cyclohexane was irradiated with 0.441 mEinstein in the Black Box using filter A. Nmr analysis indicated 30% conversion to 2,3-anthrasemibullvalene, $\phi_{\text{form}} = 0.25$. Column chromatography of one-third of the photolysate on silica gel (*vide supra*) indicated 9.3 mg of 2,3-anthrasemibullvalene after correction and 20.5 mg of recovered starting material. $\phi_{\text{dis}} = \phi_{\text{form}} = 0.25$.

Quantum Yield No. 3 for Direct Photolysis of 2,3-Anthrabarrelene ($S_0 - S_3$). A solution of 24.7 mg (0.098 mmol) of 2,3-anthrabarrelene in 750 ml of cyclohexane was irradiated with 0.091 mEinstein in the Black Box using filter B. Nmr analysis indicated 20.8% conversion to 2,3-anthrasemibullvalene, $\phi_{\text{form}} = 0.22$. Column separation (*vide supra*) indicated 5.1 mg of 2,3-anthrasemibullvalene after correction and 19.5 mg of recovered starting material; $\phi_{\text{dis}} = 0.23$, $\phi_{\text{form}} = 0.22$.

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Quantum Yield of Fluorenone Sensitized Photolysis of 2,3-Anthrabarrelene. A solution of 24.7 mg (0.098 mmol, 2.43 × 10^{-3} *M*) of 2,3-anthrabarrelene and 14.4 mg (0.08 mmol, 2.0 × 10^{-3} *M*) of 9-fluorenone ($E_T = 53.3$ kcal) in 40 ml of cyclohexane was irradiated at 390–420 nm with 0.122 mEinstein on the optical bench. The fluorenone absorbed >99% of the light under these conditions. Column separation (*vide supra*) gave 24.3 mg of recovered starting material and no 2,3-anthrasemibullvalene; 0.2 mg could have been detected. The sensitizer remained at the top of the column; $\phi_{dis} = \phi_{form} = 0$.

Quantum Yield of Acetophenone Sensitized Photolysis of 2,3-Anthrabarrelene. A solution of 24.7 mg (0.098 mmol, 2.43 × 10^{-3} *M*) of 2,3-anthrabarrelene and 1.20 g (0.01 mol, 0.25 *M*) of acetophenone ($E_T = 74$ kcal) in 40 ml of cyclohexane was irradiated at 283–311 nm with 0.149 mEinstein on the optical bench. The acetophenone absorbed 85 ± 5% of the light. Column separation gave 1.51 mg of 2,3-anthrasemibullvalene (corrected) and 23.1 mg of recovered starting material; $\phi_{dis} = \phi_{form} = 0.04$. The small amount of 2,3-anthrasemibullvalene that formed should be due to direct absorption by the 2,3-anthrabarrelene.

Quantum Yield of Biacetyl Sensitized Photolysis of 2,3-Anthrabarrelene. A solution of 24.7 mg (0.098 mmol, 2.43 × 10^{-3} *M*) of 2,3-anthrabarrelene and 125 mg (1.45 mmol, 3.64 × 10^{-2} *M*) of biacetyl ($E_T = 55$ kcal) in 40 ml of cyclohexane was irradiated at 390–420 nm with 1.34 mEinstein on the optical bench. The biacetyl absorbed ≥98% of the light under these conditions. Column separation (*vide supra*) gave 0.4 mg of 2,3-anthrasemibullvalene (corrected) and 24.1 mg of recovered 2,3-anthrabarrelene; $\phi_{dis} = \phi_{form} \leqq 0.01$.

Fluorescence–Phosphorescence Study of Biacetyl Triplet Energy Transfer to 2,3-Anthrabarrelene. This study was carried out on an Aminco-Kiers spectrophosphorimeter. The emission spectrum of a 3.65 × 10^{-2} *M* biacetyl solution (solution no. 1) was compared with that of a solution being 3.65 × 10^{-2} *M* in biacetyl and 2.43 × 10^{-3} *M* in 2,3-anthrabarrelene (solution no. 2); cyclohexane was the solvent for both solutions and each was degassed seven times. When 434 nm was the exciting wavelength, where biacetyl absorbs ≥98% of the light, the phosphorescence/fluorescence ratio for the biacetyl solution was 7.9:1.0, while that for solution no. 2 was 0.0 ± 0.3:1.0. Thus, triplet transfer from biacetyl ($E_T = 55$ kcal/mol) to 2,3-anthrabarrelene ($E_T = 43$ kcal/mol) is indicated.

Quantum Yield of Direct Photolysis of 2,3-Anthrabarrelene on the Optical Bench. A solution of 24.7 mg (0.098 mmol, 2.43 × 10^{-3} *M*) of 2,3-anthrabarrelene in 40 ml of cyclohexane was irradiated at 352–380 nm with 0.131 mEinstein on the optical bench. Column separation (*vide supra*) gave 6.1 mg of 2,3-anthrasemibullvalene (corrected value) and 18.6 mg of recovered starting material; $\phi_{dis} = \phi_{form} = 0.18$. The lower quantum yield on the optical bench (*vs.* that on the Black Box) seems to be due to concentration quenching since here 2,3-anthrabarrelene is 4.7 times more concentrated than in Black Box direct photolysis no. 2, and 14.1 times greater than that of direct photolysis no. 1.

Quantum Yield of 1,3-Cyclohexadiene Quenched Photolysis of 2,3-Anthrabarrelene. It was first demonstrated that 36.4% of the fluorescence of a 2.43 × 10^{-3} *M* solution of 2,3-anthrabarrelene was quenched when the solution was made 0.2 *M* in 1,3-cyclohexadiene. Next, a solution of 24.7 mg (0.098 mmol, 2.43 × 10^{-3} *M*) of 2,3-anthrabarrelene and 0.64 g (0.08 mol, 0.2 *M*) of 1,3-cyclohexadiene in 40 ml of cyclohexane was irradiated at 352–380 nm with 0.128 mEinstein on the optical bench; the 2,3-anthrabarrelene absorbed all of the light. Concentration of the photolysate *in vacuo* removed the quencher. Column separation (*vide supra*) gave 3.68 mg of 2,3-anthrasemibullvalene (corrected) and 16.6 mg of 2,3-anthrabarrelene. The extent of semibullvalene formation was thus the same as in the absence of quencher (reduced by 36%); $\phi_{form} = 0.11$. However, a 16% mass balance loss may be due to side reaction of 2,3-anthrabarrelene with quencher.[27]

Phosphorescence and Fluorescence Studies of 2,3-Anthrabarrelene. All studies were carried out on an Aminco-Kiers spectrophosphorimeter using a rotating shutter for phosphorescence and a Xenon lamp in general. Phosphorescence of a 3.9 × 10^{-4} *M* solution of 2,3-anthrabarrelene in an isopentane–methylcyclohexane (1:4) glass at 77°K (after 8 freeze–thaw–pump cycles) gave the 0–0 phosphorescence peak at 665 nm, corresponding to an energy of 43 kcal. The fluorescence spectrum was measured in cyclohexane at room temperature. Intersection of emission and absorption spectra of 2,3-anthrabarrelene occurred at 375 nm suggesting a singlet energy of 76.3 kcal/mol.

It was possible to measure the approximate fluorescence quantum yield of 2,3-anthrabarrelene by using anthracene ($\Phi_f = 0.30 \pm 0.05$)[28] as the standard, since the absorption and emission spectra of these two compounds were very similar in the 300–400-nm region. The concentration of a solution of anthracene in cyclohexane was adjusted so that the absorbance of the 0–3 band (323 nm) matched that of the 0–3 band of a 1.6 × 10^{-4} *M* cyclohexane solution of 2,3-anthrabarrelene (317 nm); each was irradiated at its respective 0–3 absorption maximum. $\Phi_{fl} = 0.24$.

Fluorescence Quantum Yield of 2,3-Anthrasemibullvalene. The concentration of a solution of anthracene in cyclohexane was adjusted so that the absorbance of the 0–3 band (323 nm) matched that of the 0–3 band of a 1.6 × 10^{-4} *M* cyclohexane solution of 2,3-anthrasemibullvalene (330 nm); each was irradiated at its respective 0–3 absorption maximum. $\Phi_{fl} = 0.0009$.

Acknowledgment. Support of this research by the National Science Foundation and by National Institutes of Health Grant GM07487 is gratefully acknowledged.

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