Independent Generation of Cyclopropyldicarbinyl Diradical Species of the Di-π-methane Rearrangement. Excited Singlet, Triplet, and Ground-State Hypersurfaces of Barrelene Photochemistry. Mechanistic and Exploratory Organic Photochemistry[1,2]

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Abstract: Three azo compounds were synthesized which are formal homo Diels–Alder adducts of nitrogen to barrelene, benzobarrelene, and 2,3-naphthobarrelene (2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene, its 8,9-benzo derivative, and its 8,9-naphtho relative). These were used as convenient precursors to the cyclopropyldicarbinyl diradicals proposed as involved in the di-π-methane rearrangement of barrelenes to semibullvalenes. It was observed that the ground-state diradical species, generated by thermolysis of the azo compounds, led to Grob fragmentation and cycloreversion to the corresponding barrelenes. The triplets instead led preferentially to the semibullvalenes. The excited singlets showed a greater preference for barrelene formation.

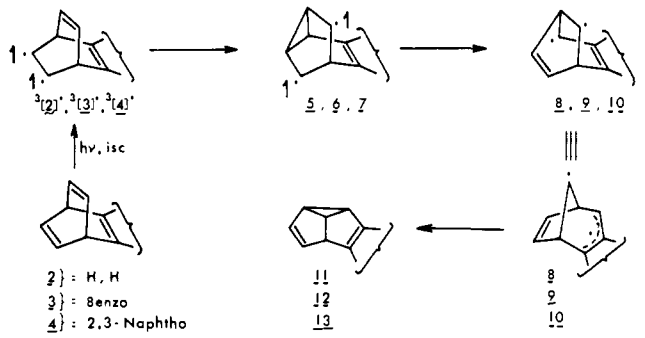
Introduction

The di-π-methane rearrangement[3] has proven to be one of the most general of photochemical transformations and has been the subject of particularly intensive investigation.[4] We have proposed the cyclopropyldicarbinyl diradical species **1** as occurring on the hypersurface leading from excited state of di-π-methane reactant to ground state of product.[3,5] In the

1

di-π-methane rearrangements of barrelene (**2**),[3a,5] benzobarrelene (**3**),[6] and 2,3-naphthobarrelene (**4**)[7] the qualitative resonance mechanism utilizes the triplet cyclopropyldicarbinyl diradicals **5, 6,** and **7**; note Chart I.

Chart I. Mechanism of the Di-π-methane Rearrangement



One puzzling aspect of this mechanism derives from the realization that diradical species such as **1** have invariably been described in the ground[8a-d] and excited[8e,f] state literature as undergoing the Grob fragmentation[9] and give no indication of di-π-methane type reactivity; note Chart II.

The present research was designed to generate such cyclopropyldicarbinyl diradicals independently in order to determine their behavior. To this end, the diradicals postulated in the barrelene, benzobarrelene, and 2,3-naphthobarrelene rearrangements were selected for study.

As precursors for the desired diradicals the azo compounds **17, 18,** and **19** were chosen; note Chart III. Our choice of the

Chart II. Alternative Modes of Cyclopropyldicarbinyl Diradical Reactivity

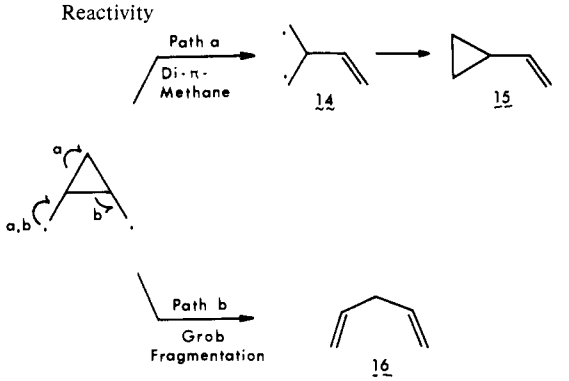
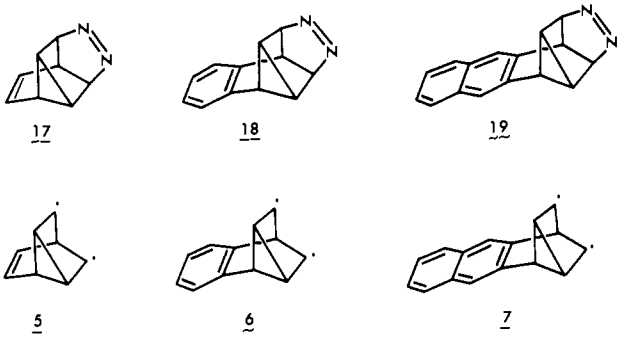


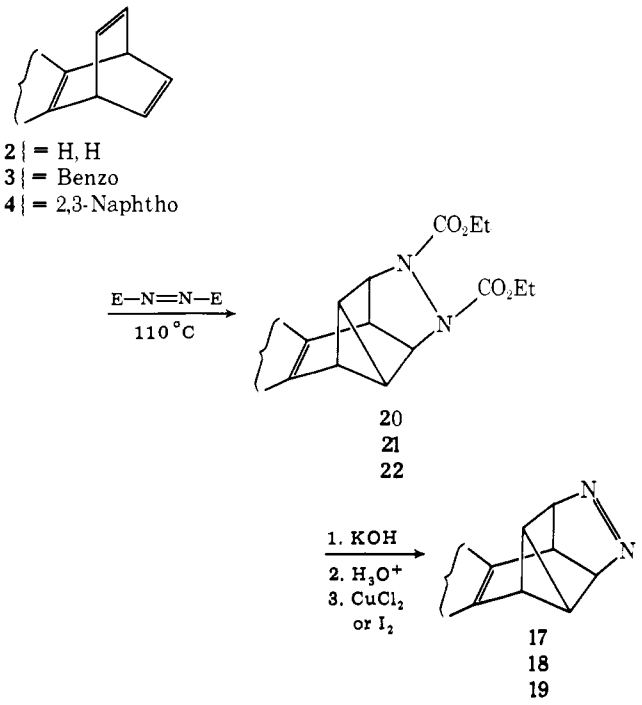
Chart III. Azo Precursors and Derived Diradicals



azo compounds as sources of the desired diradicals is reasonable, since the species obtained in each case can be considered to be the diradical, perturbed at most by a nitrogen molecule in juxtaposition (note discussion below).

Synthesis of Azo Compounds. The synthesis of the desired azo compounds was suggested by the knowledge[10] that dienophiles react with barrelene to give 2,6-homo Diels–Alder adducts. Thus, as outlined in Chart IV, diethyl azodicarboxylate was reacted at 110 °C with barrelene, benzobarrelene, and 2,3-naphthobarrelene to give the corresponding 2,6-adducts **20, 21,** and **22.** Saponification and decarboxylation gave the corresponding hydrazo compounds which were oxidized directly. Cupric chloride was used for the barrelene and ben-

Chart IV. Synthesis of Azo Compounds



zobarrelene derivatives while iodine was used in the 2,3-naphthobarrelene case.

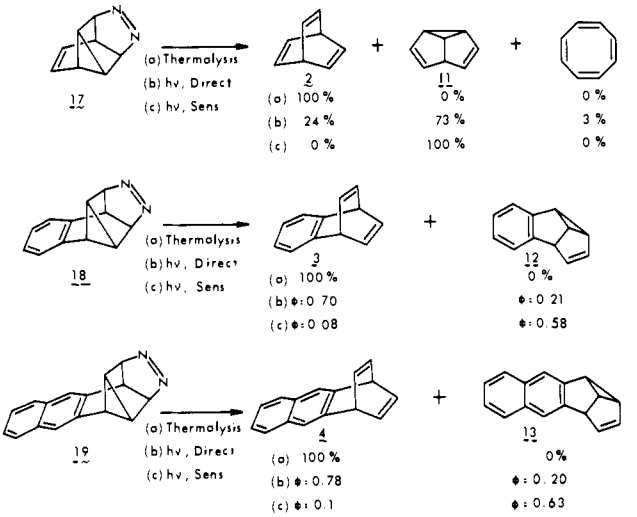
Thermal and Photochemical Nitrogen Expulsion. Results. The azo compounds were found to lose nitrogen with facility at 50–80 °C. In each case the reaction proceeded essentially quantitatively to afford exclusively the corresponding barrelene. No semibullvalene or cyclooctatetraene could be discerned. These thermolysis results are included in Chart V.

In contrast, the photochemical reactions of the three azo compounds led to both the corresponding barrelenes **2, 3,** and **4,** and also the corresponding semibullvalenes **11, 12,** and **13.** The ratio of barrelenes to semibullvalenes depended on whether the photolysis was direct or sensitized.

In the sensitized irradiations benzophenone was used as sensitizer for the barrelene azo compound **17** and also the benzobarrelene azo compound **18.** *m*-Methoxyacetophenone was used with the naphthobarrelene azo compound **19.** All three sensitized irradiations led primarily to the corresponding semibullvalene. These results are summarized in Chart V along with the other types of decompositions of the azo compounds. The 0.1 quantum yield of 2,3-naphthobarrelene formed in the naphtho series may be due to experimental difficulties. Thus, this minor reaction course seemed not to arise from direct light absorption by the naphthobarrelene azo compound, since increasing the concentration of the sensitizer and decreasing concentration of the azo compound did not change the quantum yield. However, it is possible that some thermal decomposition occurred during the run and workup. Similarly, the very minor amount of cyclooctatetraene formed in direct irradiation of the barrelene azo compound **17** may arise from light capture by semibullvalene or barrelene.

One might concern himself that the semibullvalenes being formed in the sensitized irradiations derive from sensitizer delivering energy to an initially formed barrelene which then undergoes the known[3a,5-7] sensitized conversion of barrelenes to semibullvalenes. This was found not to be the case. Thus benzophenone (E_T = 69 kcal/mol), the sensitizer used with benzobarrelene azo compound **18,** was almost totally incapable (Φ = 0.031) of sensitizing the conversion of benzobarrelene to benzosemibullvalene. The still higher energy sensitizer acetophenone (E_T = 74 kcal/mol) gave a quantum yield of 0.52. That this rearrangement can be effected even with this higher

Chart V. Summary of Thermal and Photochemical Nitrogen Loss



energy sensitizer is unusual in that the vertical triplet energy of benzobarrelene is 79.3 kcal/mol[11] and the rearrangement is thus remarkably efficient for a nonvertical process. However, the point is clear that benzophenone sensitizer cannot be effecting the two-photon process by rearranging initially formed benzobarrelene as considered above. This is particularly clear in view of the relatively low (ca. 11%) conversions in sensitized reactions of the azo compounds.

The same argument applies in the case of sensitized photolysis of the naphthobarrelene azo compound **19.** We note (see Experimental Section) that the conversions of the naphthobarrelene azo compound **19** averaged 10%. Of this product ca. one-seventh was naphthobarrelene. During the run the amount of total product averaged 5%, and the average amount of naphthobarrelene present was thus ($1/20$) × ($1/7$) or 0.71% of the reaction mixture. This compares with there being an average of 95% of residual azo compound present during the run. Assuming that azo compound **19** and naphthobarrelene are equally capable of accepting energy from the triplet sensitizer, and with the ratio of these two acceptors being ca. 1:100 favoring azo compound **19** over naphthobarrelene, we see that there is not much likelihood of transfer to naphthobarrelene. Further, with any naphthosemibullvalene deriving from this route requiring two photons, the quantum yield of naphthosemibullvalene formed by this route could at most be ($1/2$) × ($1/100$) = 0.005. Hence the complication is not a real one.

Finally, turning to the direct irradiation results, we find that these gave more of the barrelene product (note Chart V again) than in the corresponding sensitized runs. Only from the barrelene azo compound **17** was there more semibullvalene formed than barrelene in direct irradiation.

Interpretative Discussion. A Diversion to Consider Validity of the Azo Model. The first point needing discussion is a diversion to consider the relationship and relevance of the azo compound model reactions to the matter of cyclopropyldicarbinyl photochemistry.[12a] Three approaches to the question are possible: (1) a theoretical one, (2) a consideration of the literature situation and precedent, and (3) a pragmatic comparison of the observed azo compound chemistry with that found in nitrogen-free di-π-methane photochemistry of barrelenes. We will consider all three.

From a theoretical standpoint we can depict the situation as in Figures 1, 2, and 3.[13] Here we include three cross sections of the energy hypersurfaces of interest in the form of a prism. There are three energy ordinates (prism edges). One is for the MO's of the azo compound reactant (**23**) under consideration, one is for the cyclopropyldicarbinyl diradical with molecular nitrogen removed from the system to infinity (i.e., **24**), and the

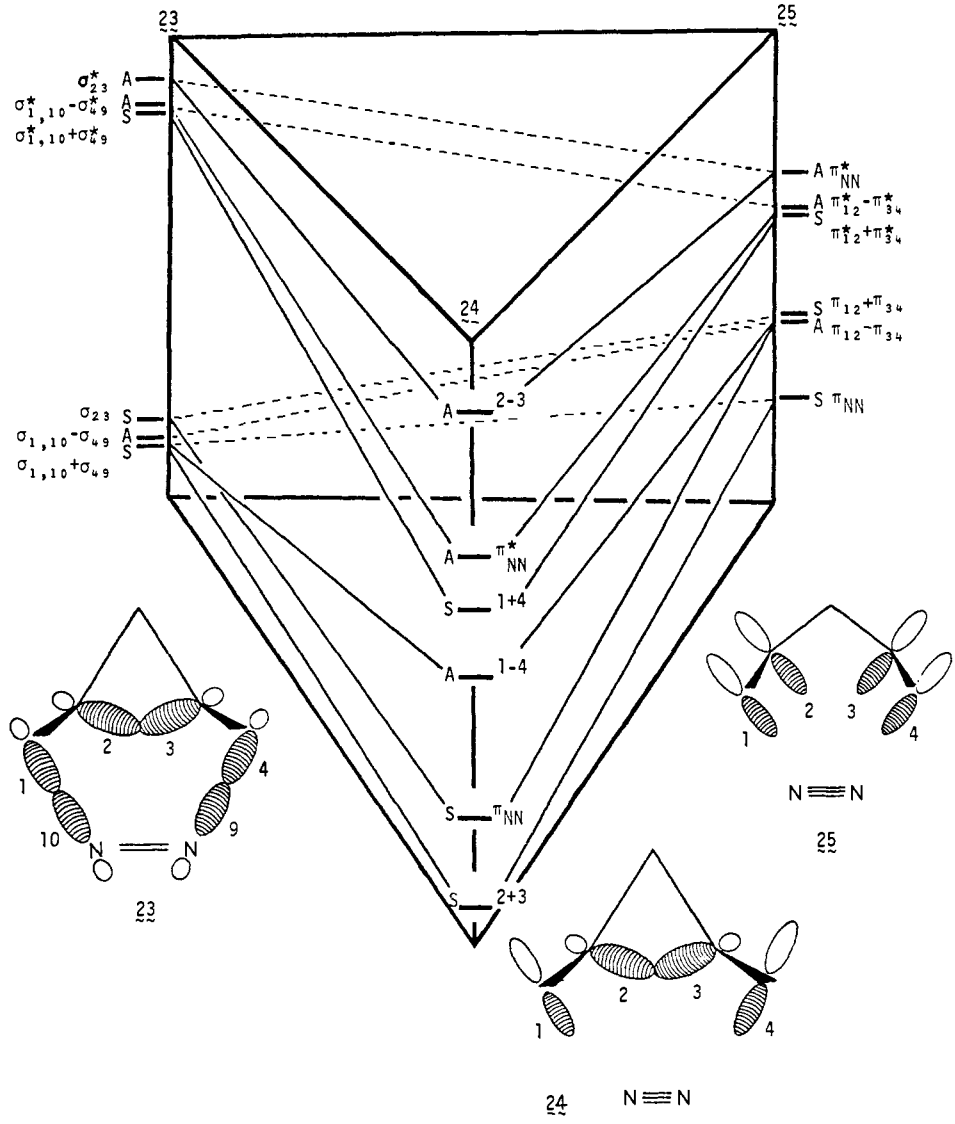


Figure 1.

last ordinate gives the MO's of the barrelene plus nitrogen products (i.e., **25**). On each face of the prism a correlation diagram can be drawn relating MO's of interest as found on two prism edges. We can also consider MO surfaces lying within the prism.

If we were to neglect the nonbonding electrons of the azo group and the σ orbitals of the three-ring except for the bond broken, the correlation would be that of a concerted ${}_{\sigma}2_{s} + {}_{\sigma}2_{s} + {}_{\sigma}2_{s}$ cycloreversion.[14] Such a designation[14] is exactly tantamount to terming the reaction Hückel[15] with six electrons and hence aromatic and allowed; note Figure 1. The inclusion of the nitrogen nonbonding electrons and the full set of Walsh orbitals of the three-ring presents a picture (note Figure 2) which appears more complex. Nevertheless, the basic features of the correlations remain analogous. Thus, for the concerted, ground-state cycloreversion (**23** → **25**), the highest occupied MO's of reactant and product remain bonding throughout in both schemes. However, in the more extended basis set diagram (Figure 2) admixture of MO's of similar symmetry alters the character of the simplistic MO's of the simpler picture (Figure 1).

We see that with inclusion of extra basis orbitals the MO's correlating are admixtures of several MO's of the same symmetry, but this does not alter basic conclusions drawn.

The same comments can be made for the excited-state transformation along the concerted reaction coordinate (i.e., the back face of the prisms; **23*** → **25***), except here one really needs to use Figure 2 in order to allow depiction of an azo n-π^* excited-state reactant.

Again in the case of the diradical route, leading from azo reactant **23** to diradical **24** to products **25**, the basic correlation is the same. Here both the simpler version (Figure 1) and the more complex picture (Figure 2) proceed without crossing of bonding and antibonding MO's; in each case the highest occupied and lowest vacant MO's are minus and plus combinations of the terminal p-orbitals 1 and 4, respectively, of the diradical **24**.

Finally, from the theoretical viewpoint, we conclude that the process **23** → **24** → **25** is just an extreme limiting version of a continuum of mechanisms leading from **23** to **25**; in this extreme the nitrogen is removed to infinity. One can envisage all gradations of mechanisms (note Figure 3), each differing from the last by decreasing nitrogen separation until the totally concerted mechanism (**23** → **25**) is reached.

It is seen that the totally concerted transition state (**24n**) is then a juxtaposition of the diradical (**24** minus nitrogen) and a nitrogen molecule brought in from infinity. This is a truism. We thus argue that the fully separated diradical plus nitrogen pair (i.e., **24**) will differ from the concerted, cyclic transition-state **24n** primarily in degree rather than in fundamentally

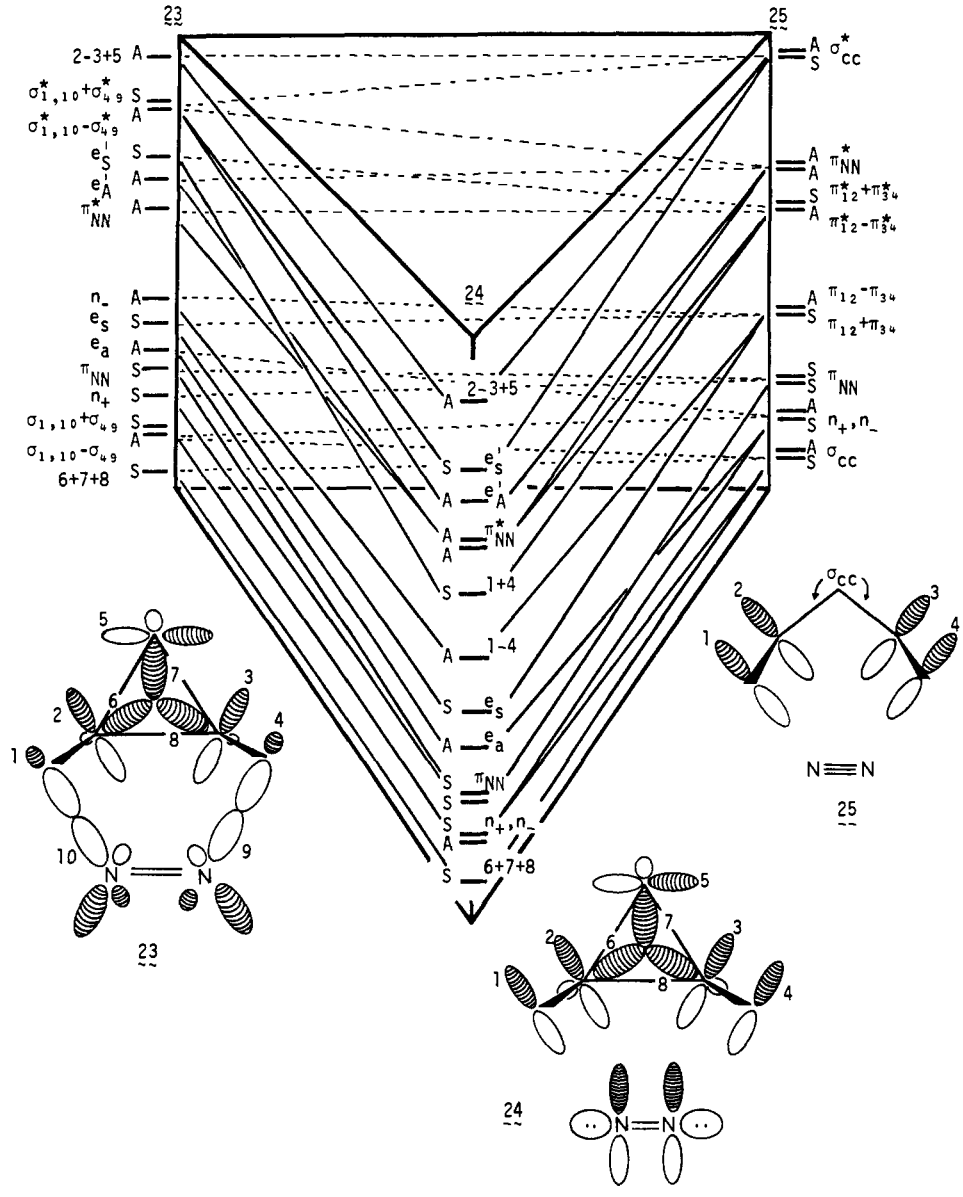
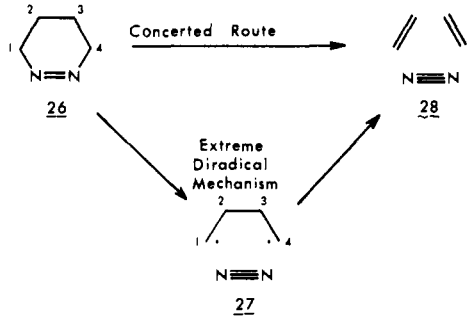


Figure 2.

different behavior, with intermediate stages of geometries (i.e., **24a, 24b, 24c,** etc.) being just gradations.[16] This means that whichever gradation is involved in the present azo chemistry will provide an approximation for the diradical utilized in the di-π-methane rearrangement. Refer to Chart VI.

Chart VI. Mechanisms of Central Bond Fission in Azo Compounds



A look at the literature reveals evidence in favor of all of these gradations. Thus in systems such as **26,** evidence has been presented by Berson[8f] that the ground-state process is concerted if the central bond 2-3 is part of a strained, three- or four-ring. With less strained central bonds the mechanism appears diradical. Allred[8c,d,g,h] has arrived at parallel conclusions except that in his systems with the central bond being in a four-ring the mechanism is borderline. Porter and Bartlett[8i] suggest a diradical pathway for a case where the central bond is unstrained.[8j]

For photochemical azo central bond fission, in cases with central three-ring bonds being broken, stereospecificity is observed[8e] but concertedness is not felt to be necessarily involved. In another photochemical study Tanida[17] suggests that three-ring bond fission is not concerted with loss of nitrogen, although a diradical mechanism was not advanced explicitly.

Hence the literature of azo chemistry provides evidence for the various gradations of mechanism in the thermal process in which Grob fragmentation occurs with structural factors controlling the gradation. Photochemically less information is relevant.

The most important point to be noted for the interim is that a continuum of mechanisms is potentially available. Each gradation differs in the location of the departing nitrogen at half-reaction. Hence it would be unusual if the behavior of a

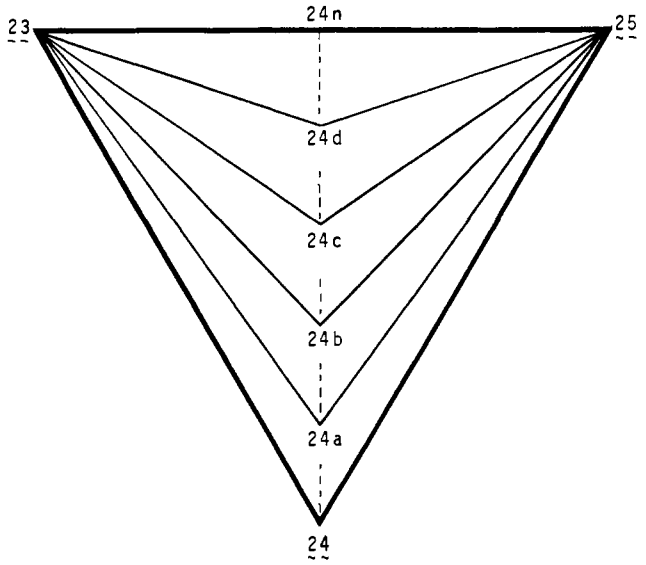


Figure 3.

species at one point along the continuum were grossly different from that at another point.

In concluding our discussion of relevance of the azo chemistry presently of compounds **17, 18,** and **19** to diradicals **5, 6,** and **7,** we note that we must rely on the similarity of the reaction course observed presently to that of di-π-methane photochemistry as considered in connection with the following section dealing with interpretation of the experimental results. Our own observations are unique in that, for the first time, we have found systems giving di-π-methane behavior in addition to Grob fragmentation photochemically.

Interpretative Discussion of Results. The first observation to be considered is the formation of the corresponding barrelenes in the thermal decomposition of the three azo compounds **17, 18,** and **19.** As noted above, it is recognized that this is the expected reaction of a cyclic cyclopropyldicarbinyl azo compound, as judged from literature precedent.[8] With the reasoning of the previous section in mind, we take the $_{\sigma}2_s + _{\sigma}2_s + _{\sigma}2_s$ cycloreversion transition state as an excellent model for the ground-state cyclopropyldicarbinyl diradical of interest, since it is indeed composed of this diradical forced into close geometric proximity to a nitrogen molecule. That the ground-state diradical plus a nitrogen molecule brought in from infinity affords the concerted transition state is a truism, as noted earlier. It should be recognized, however, that all biradicals will not necessarily correspond to energy minima. In any event, the behavior of this transition state provides the best presently available model for the behavior of the bare diradical.

We now turn to the photochemical results. Our first observation is that the direct and sensitized runs give different product distributions with the sensitized runs giving more of the semibullvalenes relative to the direct runs which tended to give more of the barrelenes. This difference signifies that intersystem crossing of the azo compounds is inefficient. This is expected from literature precedent.[18] Thus it is concluded that, in general, it is the triplet which shows a preference for semibullvalene formation while the singlet S_1 shows a preference for formation of the barrelene.

Most importantly, the sensitized results are reminiscent (note Table I) of the triplet photochemistry of the corresponding barrelenes **2, 3,** and **4.** Consequently the results are indeed consistent with the triplet diradicals **5, 6,** and **7** (note Chart I) as intermediates in the rearrangements of the barrelenes to the corresponding semibullvalenes as has been previously postulated.[3a,5-7]

Table I. Summary of the Photochemistry of the Barrelenes

Reactant	Direct irradiation product	Sensitized irradiation product	Ref
Barrelene	Cycloocta-tetraene	Semibullvalene major product (94%) Cyclooctatetraene minor product (6%)	5
Benzo-barrelene	Benzocyclo-octatetraene	Benzosemibullvalene major product (91%) Benzocyclooctatetraene minor product (9%)	6
2,3-Naphtho-barrelene	2,3-Naphtho-semibullvalene (Φ = 0.46)[a]	2,3-Naphthosemibullval-ene (Φ = 0.46)	7

[a] The formation of naphthosemibullvalene from both direct and sensitized runs in the same quantum yields was attributed[7] to facile intersystem crossing in this case.

Parenthetically, it is of interest to consider a mechanism in which triplet azo compound affords triplet barrelene which then rearranges to give the corresponding semibullvalene. However, Chart V shows the high ratios of semibullvalene to barrelene product found in all three cases. The known quantum yield of triplet-sensitized formation of benzosemibullvalene (Φ = 0.52) from benzobarrelene means that a product distribution of ca. 1:1 would result from such a mechanism. The Φ = 0.46 quantum yield[7] for the 2,3-naphthobarrelene to naphthosemibullvalene conversion via the triplet again requires the same nonobserved result.

The above finding of a high ratio of semibullvalenes to barrelenes in these sensitized irradiations of the azo compounds **17, 18,** and **19** is of further importance. From this we can conclude that any inefficiency in the photolysis of barrelenes to give semibullvalenes must be in formation of the cyclopropyldicarbinyl diradicals and not due either to subsequent steps or to diradical reversion to the barrelene. Thus, the triplet cyclopropyldicarbinyl diradical proceeds onward with considerable efficiency to give the allylic diradical (i.e., **8, 9,** and **10** in Chart I).

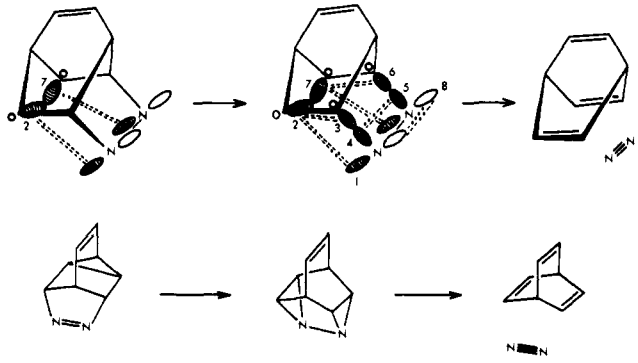
We now turn to the reasons for the preference for semibullvalene formation from T_1 and the greater tendency of S_1 to give barrelenes. Our one-electron three-dimensional (i.e., extended Hückel[19]) calculations[5] roughly define the nature of the potential energy hypersurfaces. These give excited-state minima approximately corresponding to the cyclopropyldicarbinyl diradical **5** and the allylic diradical **8.** The first minimum is directly above a ground-state surface leading back to barrelene (note Figure 4). The second excited-state minimum is poised over a ground-state minimum which has a barrier leading onward to semibullvalene. This barrier is lower than the barrier leading backwards to barrelene. Hence, in the chemistry of the triplet diradicals of interest there seems to be an accumulation of the allylic diradicals (**8, 9,** and **10**) and decay to product semibullvalenes. However, in the chemistry of S_1 there is formation of the cyclopropyldicarbinyl diradicals (**5, 6,** and **7**) which then decay to barrelenes. This situation is depicted in Figure 4.

We note that the allylic diradical has greater electron-electron separation and contrasts with the cyclopropyldicarbinyl diradical which is more compressed. This accounts for the difference in T_1 and S_1 behavior, since S_1 excited states tend to have wave functions composed of ionic, two-electron terms and thus favor tight geometries.[20] This differs from the T_1 situation where the wave function is covalent, leading to a preference for extended geometries.[20]

Remaining for discussion is the fact that S_1 leads heavily to

barrelenes despite the reaction being formally orbitally forbidden with its six electrons and Hückel electronics. This may mean that a diradical mechanism is utilized. However, a concerted pathway cannot be ruled out. In this connection we have previously discussed "minimization of forbiddenness" [21] and application of the concept to the present situation is relevant. We find that the reaction forbiddenness is diminished by overlap of the π system of the azo moiety with the three-ring bond 2-7 (note Chart VII). One way to picture this minimization of forbiddenness is to envisage the reaction as proceeding in two steps, one involving ${}_{\sigma}2_s + {}_{\pi}2_s$, excited-state allowed cycloaddition.[22] The second step is then nitrogen loss. This is also excited state allowed being Hückel with eight electrons, or equivalently a ${}_{\sigma}2_s + {}_{\pi}2_s + {}_{\sigma}2_s + {}_{\pi}2_s$ disengagement.[23] In Chart VII the orbital overlap is followed by the resonance picture showing the two processes as discrete steps, although the separation into two steps represents a mechanistic extreme and may not actually be realized. The intriguing present point is that a process composed of two allowed steps may be forbidden in one.

Chart VII



In conclusion, we remark that the concept of generating species on photochemical hypersurfaces, by methods independent of the original photochemistry of interest, has proven again of utility in determining photochemical intricacies.[24] Presently, the diradical postulated in our research 8 years ago[5] has been given substance.

Experimental Section[25]

Bicyclo[2.2.2]-2,5,7-octatriene. (Barrelene). Barrelene was synthesized by the method of Zimmerman et al.[26]

Benzenediazonium-2-carboxylate.[27] A solution of 12.0 g (0.088 mol) of anthranilic acid in 125 ml of anhydrous tetrahydrofuran was placed in a 250-ml Erlenmeyer flask specially fitted with a fritted disk at the bottom to allow filtration. Then 0.03 ml of trifluoroacetic acid was added, followed by the dropwise addition of 20 ml (0.14 mol) of isoamyl nitrite. An orange precipitate formed immediately, and after stirring at room temperature for 15 min the mixture was cooled in an ice bath for 15 min to complete precipitation. The mixture was then filtered through the frit, washed several times with tetrahydrofuran and finally with benzene to leave a tan solid. This benzenediazonium-2-carboxylate was kept wet with benzene and used immediately.

Benzobarrelene. The method of Friedman[27] was scaled up and modified to remove benzobarrelene from the reaction mixture while maintaining a very high dilution of the benzenediazonium-2-carboxylate in benzene to avoid secondary reaction.

Benzenediazonium-2-carboxylate from the previous experiment was slowly thermally decomposed in benzene suspension at 45–50 °C in a 20-l. round-bottom flask containing ca. 12 l. of benzene. Solution was periodically withdrawn through a filter stick and new solvent added in order to remove the product and maintain high dilution. Four batches of the salt (vide supra) were decomposed sequentially. The concentrated product solution was diluted with 4 l. of hexane, filtered, and the filtrate washed with 3 l. of 5% aqueous potassium hydroxide, 1 l. of 5% hydrochloric acid, 500 ml of saturated sodium bicarbonate, and finally with 2 l. of water. Solvent removal in vacuo and sublimation

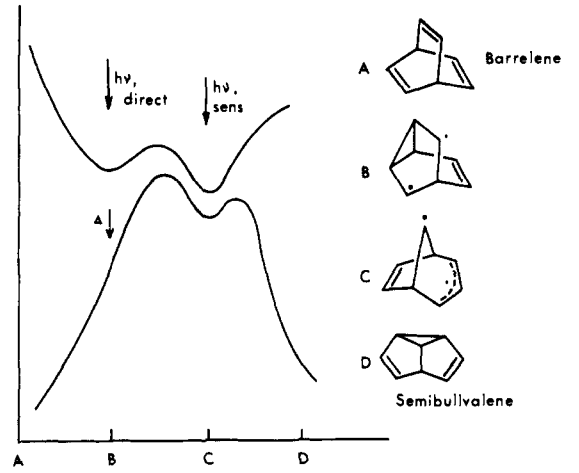


Figure 4. Potential energy surfaces for the barrelene to semibullvalene rearrangement.

of the resulting crystals yielded 5.53 g of benzobarrelene. The remaining crude material was chromatographed on a 4.5 × 75 cm column of Silicar CC-7 (Mallinckrodt, 100–200 mesh), slurry packed and eluted with hexane. The first 1400 ml contained nothing, and the next 2200 ml, after concentration and sublimation, gave 2.05 g of benzobarrelene. The total yield was thus 7.58 g (14%) of benzobarrelene, mp 65.5–66 °C.

Reaction of Barrelene with Diethyl Azodicarboxylate.[28] Barrelene (99 mg, 0.95 mmol) was mixed with 180 mg (1.03 mmol) of diethyl azodicarboxylate and a trace amount (0.8 mg) of hydroquinone and heated in a sealed heavy-walled Pyrex ampule at 100 °C for 10.5 h. After cooling, the ampule was opened carefully and the contents chromatographed on a 2 × 120 cm column of Silicar CC-7 (Mallinckrodt, 100–200 mesh), slurry packed and eluted with 15% ether–hexane. The eluate was scanned at 240 nm, and 40-ml fractions were taken. Fractions 5–8 contained barrelene and benzene, fractions 9–13 contained unreacted diethyl azodicarboxylate, and fractions 71–98 yielded 66 mg (15%) of an oily 1:1 adduct which, on the basis of its NMR spectrum and analogy with a similar adduct of benzobarrelene and diethyl azodicarboxylate, is characterized as 3,4-diaza-6-oxatricyclo[6.2.2.$0^{2,7}$]-3-carbethoxy-5-ethoxydodeca-4,9,11-triene. After many attempts, this material finally crystallized from ether, mp 68–70 °C.

The spectral data were: NMR ($CDCl_3$) τ 3.59 (m, 4 H, vinyl), 5.37 (m, 1 H, methine), 5.81 (complex, 7 H, CH, bridgeheads, and CH_3CH_2O–), 8.69 (t of d, 6 H, CH_3CH_2O–); uv $\lambda_{sh}^{cyclohexane}$ 250 (740).

Fractions 106–124 yielded 191 mg (43%) of a second 1:1 adduct, characterized on the basis of its spectral data and chemical reactivity as 2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-2,3-dicarbethoxydeca-8-ene. Material from several runs was recrystallized from ether to constant mp 75.5–76 °C.

The spectral data were: NMR ($CDCl_3$) τ 3.76 (d of d, 1 H, J = 4.5, 8 Hz, vinyl next to cyclopropyl), 4.33 (t of d, 1 H, J = 8, 1.5 Hz, vinyl), 5.75 (q, 4 H, CH_3CH_2O–), 5.88 (s, 2 H, –CHNR), 8.28 (s, 3 H, cyclopropyl), 7.41 (d, 1 H, bridgehead), 8.69 (t, 6 H, CH_3CH_2O–), ir (KBr) 5.85 μ; uv λ^{EtOH} no maximum, 240 (ϵ 434).

Anal. Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.27; H, 6.47; N, 10.18.

Reaction of Benzobarrelene with Diethyl Azodicarboxylate. Benzobarrelene (863 mg, 5.62 mmol) and 2.60 g (14.9 mmol) of diethyl azodicarboxylate were mixed, sealed into two heavy-walled Pyrex ampules and heated at 100 °C for 122 h. After cooling, the tubes were opened and the contents chromatographed on a quartz 4.5 × 70 cm Silicar CC-7 (Mallinckrodt, 100–200 mesh) column containing ca. 0.5% of a lead and manganese doped calcium silicate phosphor, slurry packed with 40% ether in hexane. Elution was with ether in hexane, starting with 10% and increasing to 70% at a rate of 5% per liter, and the separation was monitored with a uv hand lamp. The results were: 0–1500 ml, 172 mg (20%) of benzobarrelene; 1500–2350 ml, 361 mg (14%) of diethyl azodicarboxylate; 2350–5300 ml, 339 mg (18%) of a 1:1 adduct, mp 125–126 °C. This material was characterized as 9,10-benzo-3,4-diaza-6-oxatricyclo[6.2.2.$0^{2,7}$]-3-carbethoxy-5-ethoxydodeca-4,9,11-triene, on the basis of its spectral data.

The spectral data were: NMR ($CDCl_3$) τ 2.78 (complex, 4 H, arom), 3.42 (t, 2 H, J = 3 Hz, vinyl), 5.27 (d of d, 1 H, J = 8.5, 4 Hz, methine), 5.44–6.10 (complex, 7 H, methine, bridgeheads, and CH_3CH_2O–), 8.67 (overlapping triplets, 6 H, CH_3CH_2O–); ir (KBr) 3.36, 6.56, 7.00, 7.12, 7.25, 7.51, 7.80, 8.18, 9.15, 9.82, 10.17, 12.42, 13.22, 13.95 μ; mass spectrum (70 eV) *m/e* (rel intensity) 328 (2) parent (calcd for $C_{18}H_{20}N_2O_4$, 328.142; found, 328.147), 256 (4), 200 (59) (calcd for $C_8H_{12}N_2O_0$, 200.080; found, 200.081), 128 (96) (calcd for $C_5H_8N_2O_4$, 128.059; found, 128.058), 100 (100) (calcd for $C_3H_4N_2O_4$, 100.027; found: 100.027).

A second 1:1 adduct (800 mg, 44%) eluted after 6550 ml and was recrystallized along with material from other similar runs to mp 88–92 °C. This major product was characterized as the homo Diels–Alder adduct 8,9-benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-2,3-dicarbethoxydeca-2,8-diene on the basis of its spectral data and chemical reactivity.

The spectral data were: NMR ($CDCl_3$) τ 2.90 (complex, 4 H, arom), 5.80 (complex, 6 H, CH_3CH_2O– and –CHNR–), 7.10 (br, 1 H, bridgehead), 7.80 (t, 1 H, J = 7 Hz, cyclopropyl bridgehead), 8.16 (br d, 2 H, J = 7 Hz, cyclopropyl), 8.72 (t, 6 H, J = 7 Hz, CH_3CH_2O–); ir (KBr) 3.39, 3.36, 5.29, 5.40, 7.30, 7.50, 7.72, 8.21, 8.65, 9.00, 9.59, 12.00, 13.45 μ; mass spectrum (70 eV) *m/e* (rel intensity) 328 (28) parent, 256 (21), 239 (44), 211 (25), 183 (66), 167 (100), 153 (51), 128 (46), 115 (40).

Anal. Calcd for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.81; H, 6.04; N, 8.57.

2,3-Diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene.[29] A mixture of 200 mg (0.72 mmol) of 2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-2,3-carbethoxydeca-8-ene and 198 mg (3.54 mmol) of powdered potassium hydroxide was dissolved in 2.0 ml of oxygen-free ethylene glycol and heated for 1 h at 125 °C under nitrogen. Upon cooling, 1.4 g of ice was added, 1.3 ml (5.5 mmol) of concentrated HCl was added slowly (gas evolved), and the mixture was warmed to 40 °C for 5 min. After careful neutralization with 5 N ammonium hydroxide, 2 N cupric chloride was added dropwise, with periodic neutralization with ammonium hydroxide to keep the pH in the range 5–6. Addition was ceased when no more brick-red precipitate was formed, and the mixture was filtered, washed with 20% ammonium chloride (1 ml), twice with 95% ethanol (1 ml), and finally with 1 ml of water. A suspension of this precipitate in 2 ml of water was cooled in ice and treated with ca. 1 ml of 99% hydrazine hydrate. Ether extraction at low temperature and concentration in vacuo afforded 76 mg (80%) of colorless, crystalline 2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-deca-2,8-diene; mp 36–38 °C.

The spectral data were: NMR ($CDCl_3$) τ 3.68 (t, 1 H, J = 6 Hz, 1 H, vinyl), 4.25 (d of t, 1 H, J = 8 Hz, J = 2 Hz, vinyl), 5.48 (br, 2 H, –CHN=), 7.53 (q of d, 1 H, J = 6 Hz, J = 2 Hz, cyclopropyl bridgehead), 7.87 (d, 1 H, J = 7 Hz, bridgehead), 8.45 (d, 2 H, J = 6 Hz, cyclopropyl); uv λ_{max}^{EtOH} 257 (ϵ 732), 323$_{sh}$ (ϵ 106), 335 (ϵ 132).

8,9-Benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene.[29] Oxygen-free ethylene glycol (1 ml) was heated with stirring to 110 °C and 187 mg (3.34 mmol) of potassium hydroxide was added, followed by a solution of 200 mg (0.61 mmol) of 8,9-benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-2,3-dicarboethoxydeca-8-ene in ca. 1 ml of hot ethylene glycol. After stirring for 1 h the mixture was allowed to cool and 1–2 g of ice added, followed by 1 ml of 6 N HCl (gas evolved). After warming to 40 ° for 5 min, the solution was neutralized with 5 N ammonium hydroxide, and 2 N cupric chloride was added dropwise, with occasional neutralization with ammonium hydroxide to keep the pH in the range 5–6.

When no more brick-red precipitate formed, the mixture was filtered, washed with 1 ml of 20% ammonium chloride, 2 ml of 95% ethanol, and 1 ml of water. The still moist precipitate was slurried in 2 ml of water, cooled in ice, and treated with ca. 1 ml of 99% hydrazine hydrate. Ether extraction and concentration in vacuo afforded 86 mg (77%) of colorless, crystalline 8,9-benzo-2,3-diazatetracyclo-[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene, mp 85–89 °C dec.

The spectral data were: NMR ($CDCl_3$) τ 2.75 (m, 4 H, arom), 5.17 (br, 2 H, –CHN=), 7.10 (t, 1 H, J = 6 Hz, cyclopropyl bridgehead), 7.36 (m, 1 H, bridgehead), 8.20 (d, 2 H, J = 6 Hz, cyclopropyl); uv (95% EtOH) 244 (4150), 264 (1480), 279 (1740), 328 (164), 333 (153), 343 (131).

Anal. Calcd for $C_{12}H_{10}N_2$: C, 79.08; H, 5.54. Found: C, 78.94, 78.80; H, 5.57, 5.66.

Thermolysis of 2,3-Diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene. In a typical run 38 mg of the azo compound in 0.2 ml of perdeuteriotoluene plus 10% Me_4Si was decomposed at a constant temperature in the NMR probe, and reaction progress was periodically monitored by integration. After virtually complete consumption of starting material, the only detectable product by NMR and VPC (Column A: 15% Carbowax 20 M on Chromosorb W, 60–80 mesh, 1/4 in. × 22 ft, 96 °C) was barrelene.

Thermolysis of 8,9-Benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-deca-2,3-diene. The thermal decomposition of this azo compound was monitored by NMR and showed very slow decomposition at room temperature, whereas heating a sample of 86 mg to 60 °C for 2 h converted the azo compound essentially quantitatively to benzobarrelene, the only product observable by NMR.

Direct Irradiation of 2,3-Diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene. A solution of 58 mg (0.44 mmol) of 2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene in 1.5 ml of perdeuteriotoluene was deoxygenated with nitrogen and placed in an NMR tube strapped to the outside of a 450-W, water-cooled irradiation apparatus, fitted with a Pyrex filter, cooling jacket, and vacuum insulation jacket.[30] During irradiation the sample was cooled externally with a dry ice–methanol bath (−72 °C), and progress of the reaction was monitored by periodic low-temperature (−74 °C) NMR spectroscopy. The products appeared smoothly with time, and after 77.4% conversion, the product mixture consisted of barrelene (23.3%), semibullvalene (73.3%), and cyclooctatraene (3.4%) as determined by NMR (yields based on reacted material). The product identity was confirmed by GLC (Column A above).

Sensitized Irradiation of 2,3-Diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-deca-2,8-diene. A solution of 50 mg (0.38 mmol) of 2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene and 690 mg (3.79 mmol) of benzophenone in 0.75 ml of perdeuteriotoluene plus 0.10 ml of cyclopentane was placed in an NMR tube and strapped to the immersion well of a 450-W Hanovia medium-pressure lamp. The light was filtered through a solution of 4.2 g of potassium dichromate and 42.0 g of potassium carbonate in 2 l. of water, which was circulated through the lamp cooling system. This filter transmitted light from 300–330 nm, with 20% transmittance at the maximum. Irradiation was carried on for 5.25 h with external ice cooling and analysis by NMR (0 °C) showed 29% conversion to semibullvalene as the only product (at least 3% of barrelene could have been detected).

Direct Irradiation of 8,9-Benzo-2,3-diazatetracyclo[4.4.0.-$0^{4,10}$.$0^{5,7}$]deca-2,8-diene. The Blackbox apparatus[31] was used and the band-pass was controlled by the following filter solutions (Filter Solution A): 0.19 M $NiSO_4 \cdot 6H_2O$ in 5% H_2SO_4, 1.07 M $CoSO_4 \cdot 7H_2O$ in 5% H_2SO_4, and 4.43×10^{-2} M $SnCl_2 \cdot 2H_2O$ in 15% HCl; transmission was from 315–365 nm with a maximum of 20% at 340 nm. A solution of 206 mg (1.13 mmol) of 8,9-benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene in 750 ml of purified isopentane was irradiated for 1 h. Concentration in vacuo was followed by chromatography on a 2 × 30 cm silicic acid column (Silicar, Mallinckrodt CC-7, 200–325 mesh). Elution was with hexane, and 100-ml fractions were collected. The results were: fractions 3–5, 78 mg of a mixture of benzosemibullvalene and benzobarrelene; fractions 7–8, 65 mg of recovered starting material. The total mass balance was 82%. NMR analysis of the hydrocarbon fraction showed that it consisted of 17.5 mg (0.114 mmol) of benzosemibullvalene and 60.5 mg (0.393 mmol) of benzobarrelene.

Quantum Yield for the Direct Photolysis of 8,9-Benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene. The quantum yield was determined using our optical bench apparatus[31] employing a 200-W high-pressure mercury lamp as light source and a Bausch and Lomb monochromator at a wavelength of 335 nm. A solution of 22.6 mg (0.124 mmol) of 8,9-benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]-deca-2,8-diene in 40 ml of purified isopentane was degassed 40 min with deoxygenated nitrogen. The photolysis was conducted at 5–10 °C and the azo compound absorbed 0.0187 mEinstein of light. Workup consisted of concentration in vacuo below room temperature followed by column chromatography on a jacketed 1 × 26 cm silica gel column cooled at −35 to −30 °C by circulating cold 95% ethanol. Elution with hexane taking 25-ml fractions gave the hydrocarbon products in fractions 1–23. Elution with 10% ether in hexane gave the azo compound in fractions 29–43. The hydrocarbon fractions were combined and assayed by VPC using a 6 ft × 1/4 in. column of 15% UCON on 60–80 mesh Chromosorb P (Column B) at 145 °C with a 39 ml/min flow of nitrogen carrier gas. Biphenyl was added to the hydrocarbon fractions to serve as internal standard. The retention

times were as follows: benzobarrelene, 28.3 min; benzosemibullvalene, 36.0 min; and biphenyl, 45 min. Peak areas were measured by planimetry, and the flame ionization detector of the VPC was calibrated for the relative responses of the components using a known mixture. The analysis gave 0.0130 mmol of benzobarrelene, $\Phi = 0.696$, and 0.00389 mmol of benzosemibullvalene, $\Phi = 0.208$. The total conversion was 10.8%.

Sensitized Photolysis of 8,9-Benzo-2,3-diazatetracyclo[4.4.0.-$0^{4,10}$.$0^{5,7}$]deca-2,8-diene. The Blackbox apparatus[31] and Filter Solution A were used as with the direct run. A solution of 106 mg (0.585 mmol) of the azo compound and 1.02 g (5.62 mmol) of benzophenone in 750 ml of purified isopentane (degassed with deoxygenated nitrogen) was irradiated 1 h. The photolysate was concentrated in vacuo and chromatographed on a 2 × 100 cm silicic acid (Mallinckrodt CC-7, 200–325 mesh) column. Elution with hexane in 100-ml fractions gave 43.2 mg (0.280 mmol) of benzosemibullvalene in fraction 4; no benzobarrelene was detected by NMR.

Quantum Yields for the Sensitized Irradiation of 8,9-Benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene. Quantum yield determinations were made using our optical bench apparatus[31] employing a 200-W high-pressure mercury lamp as light source and a Bausch and Lomb monochromator at a wavelength of 340 nm. For all irradiations, 40-ml cells were used, benzophenone was the sensitizer, and purified isopentane (degassed with deoxygenated nitrogen) was the solvent. Photolyses were conducted at 0–5 °C in all cases. The workup consisted of concentration in vacuo below room temperature, followed by column chromatography on a jacketed 1 × 26 cm silica gel column cooled to −26 °C by circulating cold 95% ethanol. Elution with hexane taking 25-ml fractions gave the hydrocarbon products in fractions 1–14. These were combined, and either biphenyl or naphthalene (retention time 17.5 min) was added as an internal standard; assay was then performed by VPC on Column B as with the direct run (vide supra).

The data are listed as follows: starting 8,9-benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene (mmol), benzophenone (mmol), light absorbed, benzobarrelene (mmol), quantum yield, benzosemibullvalene (mmol), quantum yield, and percent conversion.

Run 1. Starting azo compound (5.99×10^{-2} mmol), benzophenone (1.62 mmol), 1.03×10^{-2} mEinstein, benzobarrelene (9.23×10^{-4} mmol), $\Phi = 0.0896$, benzosemibullvalene (5.80×10^{-3} mmol), $\Phi = 0.563$, 11.2% conversion.

Run 2. Starting azo compound (5.38×10^{-2} mmol), benzophenone (0.698 mmol), 9.99×10^{-3} mEinstein, benzobarrelene not analyzed, benzosemibullvalene (5.84×10^{-3} mmol), $\Phi = 0.586$, ca. 11% conversion.

Run 3. Starting azo compound (6.15×10^{-2} mmol), benzophenone (0.766 mmol), 1.13×10^{-2} mEinstein, benzobarrelene (9.22×10^{-4} mmol), $\Phi = 0.0817$, benzosemibullvalene (5.40×10^{-3} mmol), $\Phi = 0.478$, 10.3% conversion.

Preparative Sensitized Irradiation of Benzobarrelene. The Blackbox apparatus[31] was used, and the band-pass was controlled by the following filter solutions (Filter Solution B): 2.0 M $NiSO_4 \cdot 6H_2O$ in 5% H_2SO_4, 0.8 M $CoSO_4 \cdot 7H_2O$ in 5% H_2SO_4, and 0.02 M $SnCl_2 \cdot 2H_2O$ in 15% HCl; transmission was from 306–353 nm with a maximum of 20% at 323 nm. A solution of 116 mg (0.753 mmol) of benzobarrelene and 4.98 g (41.7 mmol) of acetophenone in 750 ml of isopentane was degassed for 1.5 h with deoxygenated nitrogen and then irradiated for 6 h until ca. 4.4 mEinsteins of light was absorbed. The photolysate was concentrated in vacuo and chromatographed on a 3 × 72 cm silica gel column taking 100-ml fractions to obtain the following chromatogram: fractions 1–5 (hexane), nil; fractions 6–8 (0.5% ether in hexane), nil; fractions 9–10 (1% ether in hexane), nil; fractions 11–21 (2% ether in hexane), 112 mg of benzosemibullvalene[6] containing ca. 5% benzobarrelene (by NMR) and no detectable benzocyclooctatetraene (by NMR); fractions 22–30 (2% ether in hexane), acetophenone. Molecular distillation at 36–40 °C (0.75 mm) afforded 85.0 mg of benzosemibullvalene[6] as a colorless oil and contained 5.38% benzobarrelene by assay on Column B (above).

Quantum Yields for the Sensitized Irradiation of Benzobarrelene. Irradiations were conducted on the microbench irradiation apparatus[31] (vide supra) using a 40-ml cell and purified isopentane as solvent (degassed with deoxygenated nitrogen). The wavelength used was 340 nm when benzophenone was used as sensitizer and 325 nm for acetophenone as sensitizer. Workup of photolysates in each case consisted of concentration in vacuo, addition of naphthalene as internal standard, and assay by VPC as described for sensitized irradiations of 8,9-benzo-2,3-diazatetracyclo[4.4.0.$0^{4,10}$.$0^{5,7}$]deca-2,8-diene on Column B.

The data are listed as follows: starting benzobarrelene (mmol), sensitizer (mmol), light absorbed, benzosemibullvalene (mmol), quantum yield, and percent conversion. The acetophenone absorbed at least 97% of the light and benzophenone 99.9%.

Run 1A. Starting benzobarrelene (7.21×10^{-2} mmol), benzophenone (0.720 mmol), 2.37×10^{-2} mEinstein, benzosemibullvalene (7.46×10^{-4} mmol), $\Phi = 0.0314$, 1.04% conversion.

Run 2B. Starting benzobarrelene (7.01×10^{-2} mmol), acetophenone (3.48 mmol), 4.54×10^{-3} mEinstein, benzosemibullvalene (2.56×10^{-3} mmol), $\Phi = 0.563$, 3.65% conversion.

Run 3B. Starting benzobarrelene (6.56×10^{-2} mmol), acetophenone (3.97 mmol), 7.08×10^{-3} mEinstein, benzosemibullvalene (3.42×10^{-3} mmol), $\Phi = 0.484$, 5.21% conversion.

2-Amino-3-naphthoic Acid. The procedure of Allen and Bell[32] was followed using 334 g (1.78 mol) of 2-hydroxy-3-naphthoic acid (Pfaltz and Bauer technical grade) to afford, after acid–base purification as described,[32] 220 g (66%) of the crude 2-amino-3-naphthoic acid.

Purification of 2-Amino-3-naphthoic Acid. Two procedures, described below, gave amino acid suitable for use in the preparation of 2,3-naphthobarrelene. Material which was not purified in this way gave large quantities of naphthalene at the expense of 2,3-naphthobarrelene, which suggests the presence of some impurity which serves as an efficient hydrogen donor to the naphthyne which is generated.

Procedure A. To a suspension of 9.22 g of 2-amino-3-naphthoic acid in 100 ml of water was added 100 ml of 20% sodium hydroxide, followed by sufficient hot water to effect dissolution of most of the material. The warm solution was washed twice with chloroform acidified with hydrochloric acid to Congo Red, and the *warm* solution was washed twice more with chloroform, neutralized with 10% sodium hydroxide, and cooled, and the resulting precipitate of the 2-amino-3-naphthoic acid was filtered, washed with water, sucked as dry as possible, and then dried at 60 °C for 12 h to yield 3.0 g of the bright-yellow amino acid. Recovery of material using this procedure is usually quite low (30–40%), due largely to the tendency of the hydrochloride salt of the amino acid to precipitate from aqueous solution if the solution does not stay warm enough. Procedure B takes advantage of this tendency and is generally preferable.

Procedure B. To a suspension of 20 g of 2-amino-3-naphthoic acid in 300 ml of water was added 100 ml of 20% sodium hydroxide and 200 ml of hot water. The resulting solution was washed twice with chloroform, acidified to Congo Red with hydrochloric acid, and cooled, and the hydrochloride salt of the amino acid was filtered, sucked as dry as possible, then washed well with chloroform, again sucked as dry as possible, and slurried in water, and 20% sodium hydroxide was added to dissolve the material. The warm solution was acidified to Congo Red with hydrochloric acid and finally neutralized with 10% sodium hydroxide to a Congo Red end point. After cooling, the resultant precipitate of 2-amino-3-naphthoic acid was filtered, washed with water, sucked as dry as possible, and finally dried at 60 °C to afford 13 g (65%) of the bright-yellow amino acid.

2,3-Naphthobarrelene.[7] The original Bender procedure[7] was modified to provide a more convenient in situ preparation. A 1-l. three-neck flask equipped with Trubore stirrer, 125-ml addition funnel, and a reflux condensor with nitrogen inlet was charged with 500 ml of dry benzene (freshly distilled from calcium hydride), and the benzene was brought to reflux. In the meantime, a solution of 1.50 g (8.0 mmol) of finely ground 2-amino-3-naphthoic acid in 200 ml of benzene was brought to near reflux by warming on the steam bath. All of the material would not dissolve in the benzene. To the refluxing benzene in the reaction vessel was added 3.1 ml of isoamyl nitrite in one portion, and this was followed immediately by the *rapid* addition of the 2-amino-3-naphthoic acid in hot benzene.

After addition was complete, the resulting solution was refluxed under nitrogen for 3.5 h, then cooled, concentrated in vacuo to ca. 200 ml, diluted with 800 ml of hexane, filtered, and concentrated in vacuo. The residue was dissolved in a minimal amount of benzene and applied to a 2 × 38 cm silica gel column, slurry packed, and eluted with 30% benzene in hexane. The first 500 ml of eluent was concentrated in vacuo to afford 0.359 g of crystallizing orange oil. The orange oils obtained from two such identical runs were combined and rechromatographed on a 1.8 × 70 cm silica gel column, slurry packed, and eluted with hexane. Concentration in vacuo of the 250–600-ml fraction

afforded 0.425 g (13%) of 2,3-naphthobarrelene as colorless solid, mp 128–130 °C, pure by NMR and TLC analysis. The spectral data were as previously obtained.[7]

8,9-Naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}] -2,3- dicarbethoxydeca-8-ene. Into each of two heavy-walled Pyrex ampules was placed 1.00 g (4.90 mmol) of 2,3-naphthobarrelene and 8.50 g (47.8 mmol) of diethyl azodicarboxylate (Aldrich). The ampules were chilled in dry ice, sealed, heated at 110 °C for 7 days, again chilled in dry ice, and opened cautiously using a torch. The contents were removed using ca. 50 ml of ether, and the ether solution was then diluted to 100 ml with hexane, heated to reflux on the steam bath, and chilled to −28 °C. The crystals which formed were filtered and washed with hexane to afford 1.38 g (37%) of the desired adduct, mp 176–177 °C, pure by NMR analysis. Recrystallization from ether–pentane gave fine needles, mp 180–180.5 °C.

The spectral data were: ir ($CHCl_3$) 3.27, 3.33, 3.35, 3.36, 3.41, 3.43, 5.75, 5.88, 6.64, 6.78, 6.84, 6.91, 7.14, 7.29, 7.52, 7.61, 7.72, 7.87, 7.97, 8.03, 8.20, 8.55, 8.61, 8.97, 9.39, 9.53, 9.91, 10.00, 10.28, 10.50, 10.60, 11.06, 11.35, 11.61, 12.02, and 12.29 μ; NMR ($CDCl_3$) τ 2.10–2.75 (m, 6 H, arom), 5.52 (br s, 2 H, C*H*NR), 5.70 (q, 4 H, J = 8 Hz, $-CO_2CH_2CH_3$), 6.82 (br s, 1 H, bridgehead), 8.60 (t, 1 H, J = 8 Hz, cyclopropyl bridgehead), 8.00 (br d, 2 H, J = 8 Hz, cyclopropyl), 8.68 (t, 6 H, J = 8 Hz, $-CO_2CH_2CH_3$); uv (95% EtOH) 324 (790), 317 (400), 310 (710), 303 (sh, 450), 290 (3740), 279 (6220), 268 (6180), 260 (5190), 233 (21 990).

Anal. Calcd for $C_{22}H_{22}O_4N_2$: C, 69.82; H, 5.86. Found: C, 69.63; H, 5.78.

8,9-Naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene. Into a heavy-walled Pyrex tube (fitted with a 19/38 standard taper joint to allow for attachment to a high vacuum line) were placed 0.300 g (0.794 mmol) of 8,9-naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]-2,3-dicarbethoxydeca-8-ene, 1.79 g (31.75 mmol) of finely ground potassium hydroxide, and 3.5 ml of ethylene glycol. The tube was then degassed by four freeze–pump–thaw cycles on a high vacuum line, sealed under vacuum, and heated at 160 °C for 1.5 h. After cooling to room temperature, the tube was cracked open, and the contents were removed by dissolution in water. The solution was diluted to ca. 70 ml with water, acidified to Congo Red with 1 N hydrochloric acid, and heated at 50 °C under nitrogen for 5 min. Gas evolution was observed during this time. The resulting solution was cooled to 0 °C, made basic with ammonium hydroxide, and extracted with 2 × 50 ml portions of CH_2Cl_2, then with 2 × 50 ml portions of ether. The combined organic phases were dried over potassium carbonate, filtered, and concentrated in vacuo to afford a white solid, which exhibited R_f 0.0 on TLC analysis (GF-254 silica gel) with either 50% ether–hexane or 100% ether. The solid was dissolved in 75 ml of methylene chloride and cooled to 0 °C, iodine was added until the iodine color persisted, and the mixture was then stored at −28 °C for 10 h. The resulting solution was washed with 10 ml of saturated sodium thiosulfate solution to remove iodine and made basic with ammonium hydroxide. The aqueous phase was diluted with water and extracted with methylene chloride, and the combined organic phases were dried over potassium carbonate and concentrated in vacuo to afford 164 mg (88.5%) of the desired azo compound as a nearly white solid, pure by NMR analysis. This material was dissolved in 110 ml of methylene chloride, decolorized with Norite, and concentrated in vacuo to afford 156 mg (84%) of the azo compound (pure by NMR and TLC analysis) as a colorless solid, R_f 0.33 in 50% ether–hexane, mp ($-N_2$ from solid ca. 80 °C, s 110 °C, hardens ca. 112 °C, remelts 131–133 °C).

The spectral data were: ir ($CHCl_3$) 3.33, 3.38, 3.41, 3.48, 3.50, 6.06, 6.70, 6.82, 6.86, 7.12, 7.24, 7.39, 7.47, 7.73, 8.47, 8.98, 9.99, 10.50, 11.11, 11.30, 11.51, and 11.93 μ; NMR ($CDCl_3$) 2.60–3.15 (m, 6 H, arom), 5.40 (br s, 2 H, CHN=), 7.25 (t, 1 H, J = 7 Hz, cyclopropyl bridgehead), 7.47 (br s, 1 H, bridgehead), 8.31 (br d, 2 H, J = 7 Hz, cyclopropyl); uv ($CHCl_3$) 323 (1140), 316 (710), 309 (1070), 294 (5480), 282 (6660), 271 (5590).

Anal. Calcd for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21. Found: C, 81.55; H, 5.12.

Sensitized Photolysis of 8,9-Naphtho-2,3-diazatetracyclo-[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene. A solution of 110 mg (0.474 mmol) of 8,9-naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene and 1.22 g (8.14 mmol) of *m*-methoxyacetophenone in 200 ml of methylene chloride was purged with nitrogen for 45 min and swept with nitrogen while irradiated with a 450-W Hanovia lamp through a Pyrex filter for 3 min. The photolysate was concentrated in vacuo and chromatographed on a 2 × 120 cm silica gel column, slurry packed in hexane; 40-ml fractions were collected with uv scanning at 275 nm. Elution with hexane gave 48.8 mg (49.6%) of 2,3-naphthosemibullvalene, spectroscopically identical with authentic material, in fractions 32–49, and 5.8 mg (5.9%) of 2,3-naphthobarrelene in fractions 49–59.

Thermolysis of 8,9-Naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]-deca-2,8-diene. A solution of 11.6 mg of 8,9-naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene in 50 ml of cyclohexane was warmed to reflux on the steam bath. All of the material dissolved before reflux commenced, and gas evolution was observed. TLC monitoring of consumption of the azo compound (50% ether–hexane) revealed that loss of starting material was completed within 5 min at reflux. The solution was concentrated in vacuo to afford 10.2 mg (98%) of colorless solid, mp 130–132 °C. NMR, VPC (10% SE-54 at 180 °C), and TLC (three elutions with hexane) analyses all showed 2,3-naphthobarrelene as the sole product of the thermolysis; no trace of 2,3-naphthosemibullvalene could be detected.

Quantum Yield Determinations for 8,9-Naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene. Direct Irradiations. Quantum yields were measured using our optical bench[31] apparatus, with a 22-nm band-pass at half-height from the Bausch and Lomb monochromator. A 200-W high-pressure mercury lamp was the light source. A wavelength of 324 nm was used for all irradiations. Ferrioxalate actinometry was employed. Photolyses were conducted at either 25 or 0 °C. Workup in each case consisted of concentration in vacuo followed by column chromatography at either room temperature or 0 °C. The hydrocarbon band obtained was then analyzed quantitatively by VPC, using a 6 ft × $\frac{1}{8}$ in. column of 10% SE-54 operated at 180 °C with 26 ml/min flow of nitrogen carrier gas. Anthracene was added to the hydrocarbon band to serve as internal standard. The retention times which were obtained were: anthracene, 12.0 min; 2,3-naphthobarrelene, 17.2 min; and 2,3-naphthosemibullvalene, 21.2 min. Peak areas were measured by planimetry. The flame ionization detector of the VPC was calibrated for the relative responses of the components using a known mixture. Methylene chloride was used as solvent for all photolyses due to the extreme insolubility of the azo compound in solvents commonly used for photochemical work.

Summary of the Quantum Yield Results for the Direct Irradiation of 8,9-Naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene. For each of the direct runs, the microbench apparatus with 40-ml cells was used. The data are listed as follows: starting 8,9-naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene (mmol), light absorbed, 2,3-naphthobarrelene (mmol), quantum yield; 2,3-naphthosemibullvalene (mmol), quantum yield, and percent conversion.

Run 1. Starting azo compound (8.75×10^{-2} mmol), 9.70×10^{-3} mEinsteins, 2,3-naphthobarrelene not determined; 2,3-naphthosemibullvalene (1.96×10^{-3} mmol), $\Phi = 0.202$, ca. 8% conversion.

Run 2. Starting azo compound (17.28×10^{-2} mmol), 1.16×10^{-2} mEinsteins, 2,3-naphthobarrelene (1.022×10^{-2} mmol), $\Phi = 0.89$; 2,3-naphthosemibullvalene (2.433×10^{-3} mmol), $\Phi = 0.209$, 8.0% conversion.

Run 3. Starting azo compound (8.75×10^{-2} mmol), 10.88×10^{-3} mEinsteins, 2,3-naphthobarrelene (7.87×10^{-3} mmol), $\Phi = 0.72$; 2,3-naphthosemibullvalene (2.227×10^{-3} mmol), $\Phi = 0.205$, 11.5% conversion.

Run 4. Starting azo compound (8.32×10^{-2} mmol), 7.42×10^{-3} mEinsteins, 2,3-naphthobarrelene (5.417×10^{-3} mmol), $\Phi = 0.73$; 2,3-naphthosemibullvalene (1.336×10^{-3} mmol), $\Phi = 0.183$, 8.2% conversion.

Run 5. Starting azo compound (8.75×10^{-2} mmol), 8.03×10^{-3} mEinsteins, 2,3-naphthobarrelene (8.092×10^{-3} mmol), $\Phi = 1.01$; 2,3-naphthosemibullvalene (1.576×10^{-3} mmol), $\Phi = 0.198$, 11% conversion.

Quantum Yield Determinations for 8,9-Naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene. Sensitized Irradiations. Quantum yield determinations were made using our optical bench apparatus as described for the direct irradiations. Methylene chloride was used as solvent for all runs; *m*-methoxyacetophenone was used as sensitizer for all runs. Concentrations of substrate and sensitizer were adjusted such that the sensitizer was expected to absorb >99% of the incident irradiation. Since 2,3-naphthobarrelene was found to be the major product in the direct runs and was observed as a minor product in the runs described below, in one run (note run 5 below) the concentration of substrate was cut in half and the sensitizer concentration doubled to insure that the barrelene product observed did not, in fact, result from direct absorption of light by the azo compound. The quantum

yield for 2,3-naphthobarrelene in this run was unchanged within experimental error.

Workup of photolysates in each case involved concentration in vacuo below room temperature and isolation of hydrocarbons by chromatography at room temperature on a 1.2 × 15 cm column of silica gel slurry packed in hexane, eluted with hexane. The hydrocarbon products were then analyzed by VPC as described for the direct irradiations.

Summary of the Quantum Yield Results for the Sensitized Irradiation of 8,9-Naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene. The data are listed as follows: starting 8,9-naphtho-2,3-diazatetracyclo[4.4.0.0^{4,10}.0^{5,7}]deca-2,8-diene (mmol), *m*-methoxyacetophenone sensitizer (mmol), mEinsteins of light absorbed by sensitizer, 2,3-naphthobarrelene (mmol), quantum yield; 2,3-naphthosemibullvalene (mmol), quantum yield, percent conversion.

Run 1. Starting azo compound (8.62×10^{-2} mmol), *m*-methoxyacetophenone (1.43 mmol), 1.608×10^{-2} mEinstein, 2,3-naphthobarrelene (1.37×10^{-3} mmol), $\Phi = 0.085$; 2,3-naphthosemibullvalene, (1.013×10^{-2} mmol), $\Phi = 0.63$, 13% conversion.

Run 2. Starting azo compound (8.62×10^{-2} mmol), *m*-methoxyacetophenone (1.43 mmol), 1.339×10^{-2} mEinstein, 2,3-naphthobarrelene (1.346×10^{-3} mmol), $\Phi = 0.10$; 2,3-naphthosemibullvalene (7.918×10^{-3} mmol), $\Phi = 0.59$, 10.5% conversion.

Run 3. Starting azo compound (8.49×10^{-2} mmol), *m*-methoxyacetophenone (1.48 mmol), 1.081×10^{-2} mEinstein, 2,3-naphthobarrelene (1.477×10^{-3} mmol), $\Phi = 0.137$; 2,3-naphthosemibullvalene (6.776×10^{-3} mmol), $\Phi = 0.627$, 9.3% conversion.

Run 4. Starting azo compound (9.31×10^{-2} mmol), *m*-methoxyacetophenone (1.48 mmol), 1.089×10^{-2} mEinstein, 2,3-naphthobarrelene (1.562×10^{-3} mmol), $\Phi = 0.143$; 2,3-naphthosemibullvalene (6.737×10^{-3} mmol), $\Phi = 0.619$, 9.5% conversion.

Run 5. Starting azo compound (4.31×10^{-2} mmol), *m*-methoxyacetophenone (2.80 mmol), 6.276×10^{-3} mEinstein, 2,3-naphthobarrelene (0.61×10^{-3} mmol), $\Phi = 0.097$; 2,3-naphthosemibullvalene (3.564×10^{-3} mmol), $\Phi = 0.568$, 9.5% conversion.

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References and Notes

(1) (a) This is paper 102 of our photochemical series. (b) For the previous paper of the series (paper 101) note H. E. Zimmerman, G. E. Keck, and J. L. Pflederer, *J. Am. Chem. Soc.*, **98**, 5574 (1976). (c) For paper 100 of the series see H. E. Zimmerman, *Science*, 523 (1976). (d) For paper 99, see D. Döpp and H. E. Zimmerman, "Methoden der Organischen Chemie", (Houben–Weyl), Photochemie I, Georg Thieme Verlag, Stuttgart, 1975, p 413.

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(3) (a) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Am. Chem. Soc.*, **89**, 3932 (1967); (b) H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969); (c) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

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(12) (a) This point has been questioned by a number of the referees. The present section is designed to clarify matters. (b) Rather than consider formation of both barrelene and semibullvalene, we will restrict attention to the portion of the surface interconnecting diradical with azo compound and with barrelene. For simplicity we exclude the di-π-methane process, the third course of reaction from the diradical. This seems sufficient exploration of the hypersurface.

(13) (a) The correlation diagram is drawn using photoelectron spectroscopic levels reported[13b,c] for structurally related cyclopropyldicarbinylazo compounds for species **23**.[13d] For diradical species **24** a first-order SCF calculation, truncated to the eight orbitals involved and using appropriate valence state ionization potentials and resonance integrals calculated with appropriate hybridization and geometry, was employed; (b) H. Schmidt, A. Schweig, B. M. Trost, H. B. Neubold, and P. H. Scudder, *J. Am. Chem. Soc.*, **98**, 622 (1974); (c) R. J. Boyd, J. G. Bünzli, and J. P. Snyder, *ibid.*, **98**, 2398 (1976). (d) Note also the related correlation diagram by D. M. Lemal and S. D. McGregor, *ibid.*, **88**, 1335 (1966).

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(16) Of course, a diradical such as **24** would be potentially susceptible to such special processes as loss of stereochemistry. Also, the tendency to break particular bonds (e.g., the central one) should be common to all gradations. That the di-π-methane rearrangement is stereospecific strongly suggests but does not demand some concertedness.

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(21) H. E. Zimmerman, *Acc. Chem. Res.*, **5**, 393 (1972).

(22) (a) Interestingly, this $2\pi + 2\sigma$ photochemical addition has exact parallel in examples with a [2.2.1]bicyclo system with nitrogen replaced by carbon;[22b] note P. v. R. Schleyer and E. Wiskott, *Angew. Chem., Int. Ed. Engl.*, **6**, 694 (1967). Presently, however, as the bisaziridine is approached, the second allowed reaction of nitrogen loss becomes available. (b) C. F. Huebner, E. Donoghue, L. Dorfman, E. Wenkert, W. E. Streth, and S. W. Donely, *Chem. Commun.*, 419 (1966); (c) H. Prinzbach and D. Hunkler, *Chem. Ber.*, **108**, 1804 (1973).

(23) (a) As noted earlier by us[15b] and most recently by Day,[23b] the Hückel–Möbius and generalized Woodward–Hoffmann treatments[14] are perfectly analogous, since the number of sign inversions in a pericyclic transition state is simply equal to the number of antara components in the generalized Woodward–Hoffmann rule. (b) A. C. Day, *J. Am. Chem. Soc.*, **97**, 2431 (1975).

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(30) For a more complete description of the apparatus, see H. E. Zimmerman and H. Iwamura, *J. Am. Chem. Soc.*, **90**, 4763 (1968).

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