

Figure 16. Absorption (—) and circular dichroism (---) spectra of (top) met azide mollusc hemocyanin (*Busycon*); (middle) met azide arthropod hemocyanin (*Limulus*); (bottom) met azide tyrosinase (*Neurospora*).

showing analogous charge-transfer bands at 370 nm ($\epsilon = 2200 \text{ M}^{-1} \text{ cm}^{-1}$) in absorbance and 420 nm ($\Delta\epsilon = -2 \text{ M}^{-1} \text{ cm}^{-1}$) in the CD. However, the absorbance spectrum also exhibits an additional charge-transfer band at 500 nm ($\epsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$) which

corresponds to the peak in the *Busycon* resonance Raman profile. The CD absorbance selection rules observed in *Busycon* appear to hold for the *Limulus* site, indicating that the *Limulus* site can also be treated by considering two equivalent copper azide transition moments in a *cis* μ -1,3 structure. However, the 500-nm band is more intense in *Limulus* met azide which reflects a greater mixing of the Π^{nb}_o and Π^{nb}_v orbitals and, thus, an increased distortion of the coordinated azide.

While the charge-transfer spectra of met azide tyrosinase (Figure 16C) show similar features in the absorbance spectrum (360 nm, $\epsilon = 2100 \text{ M}^{-1} \text{ cm}^{-1}$ and 420 nm, $\epsilon = 1400 \text{ M}^{-1} \text{ cm}^{-1}$), the CD spectrum is quite different from that of the met azide hemocyanins. The intense 360-nm band has the dominant CD intensity ($\Delta\epsilon = -8.7 \text{ M}^{-1} \text{ cm}^{-1}$), whereas the CD of the lower energy band is much weaker ($\Delta\epsilon = -2.1 \text{ M}^{-1} \text{ cm}^{-1}$). Assuming one azide is binding, the presence of the two Π^{nb}_o absorption bands at energies and intensities similar to the hemocyanins indicates that the azide also bridges the two copper(II)s. However, in contrast to the hemocyanins, the tyrosinase charge-transfer spectrum is more appropriately treated as resulting from two inequivalent copper azide transition moments because of the lack of the C_{2v} dimer absorbance-CD selection rules in Table IV. Thus, variations in the azide-to-copper charge-transfer spectra of the binuclear copper centers in the met arthropod and mollusc hemocyanins and tyrosinase appear to reflect quantitative structural differences in these coupled binuclear copper active sites and in particular inequivalent copper centers in the case of tyrosinase.

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On the Mechanism of the Di- π -methane Rearrangement of Bicyclo[3.2.1]octa-2,6-diene: Deuterium Labeling and Generation of Diradical Intermediates via Photolysis and Thermolysis of Appropriate Azoalkanes

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Abstract: The direct (254 nm) and acetone-sensitized (300 nm) photolyses of 2,4,4-trideuteriobicyclo[3.2.1]octa-2,6-diene (D-1) gave exclusively 3,5,5-trideuteriotricyclo[4.2.0.0^{2,8}]oct-3-ene (D-7) and 2,6,6-trideuteriotricyclo[3.2.1.0^{2,7}]oct-3-ene (D-8) but no rearranged diene, namely, 2,8,8-trideuteriobicyclo[3.2.1]octa-2,6-diene (D-1'). Pyrolysis (400 °C) and direct (334 nm) and benzophenone-sensitized (364 nm) photolyses of the azoalkane 3,5,5-trideuterio-9,10-diazatricyclo[4.4.0.0^{2,8}]deca-3,9-diene (D-9) afforded a mixture of tricyclooctenes D-7 (major product) and D-8 and bicyclooctadiene D-1, but no rearranged diene D-1'. These three modes of denitrogenation of the azoalkane 2,2,7-trideuterio-4,5-diazatricyclo[4.3.1.0^{3,7}]deca-4,8-diene (D-10) led only to the tricyclooctene D-8 (major product) and equal amounts of the bicyclooctadienes D-1 and D-1'. Distinct temperature profiles were observed in the product fingerprints of the direct photolysis (334 nm) of the azoalkanes 9 and 10. For both azoalkanes 9 and 10 the quantum yields of denitrogenation increased with rising temperature. In none of these transformations could bicyclo[3.3.0]octa-2,7-diene (2) be detected. These results imply that the di- π -methane rearrangement of the bicyclooctadienes 1 (D-1) and the denitrogenations of the azoalkanes 9 (D-9) and 10 (D-10) are disjoint chemical events. The intervention of diazenyl diradicals (one-bond cleavage of the azoalkanes) is postulated to be responsible for this disparity. The intervention of cyclopropyldicarbonyl diradical 3 as bona fide reaction intermediate in the di- π -methane rearrangement of bicyclooctadiene 1 is questioned.

In a recent publication² we demonstrated that the mechanism of the di- π -methane rearrangement of benzobicyclo[3.2.1]octa-

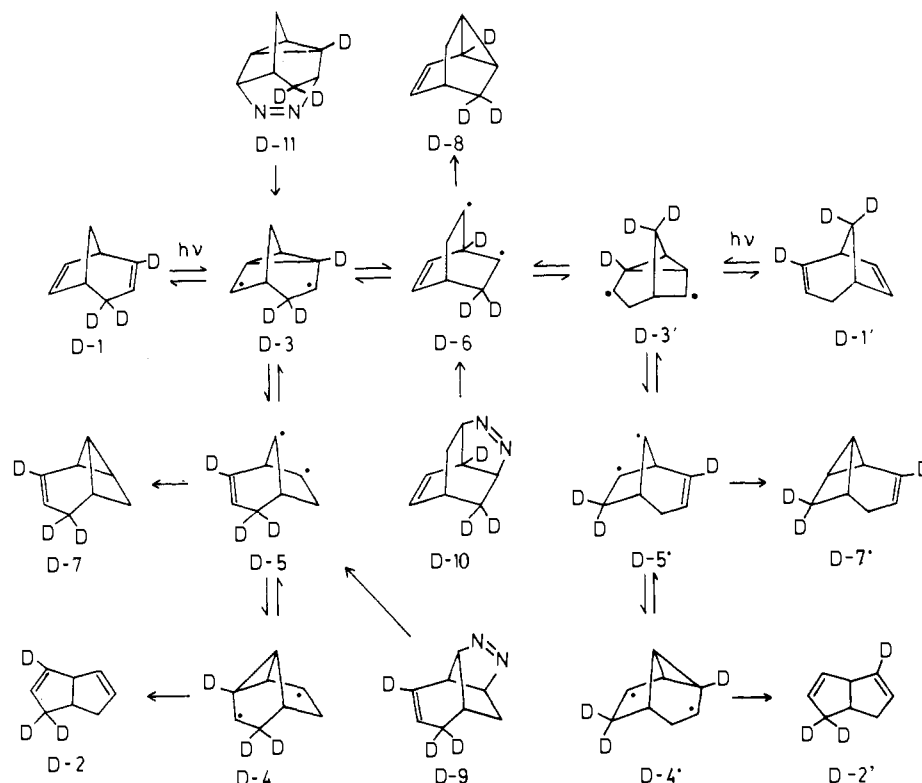
diene is more complex than initially proposed.³ As suggested on the basis of deuterium labeling experiments for the related ben-

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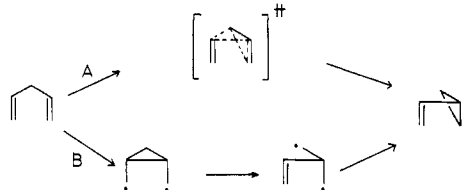
[†] University of Sassari.

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Scheme I



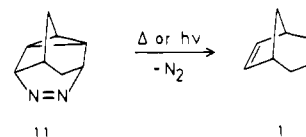
zonorbordienes,⁴ neither the fully concerted route (path A in eq 1) nor the more general stepwise route via the 1,4-diradical



(path B in eq 1) accounted all the experimental facts. The results suggested a concerted vinyl 1,2-shift leading directly to the 1,3-diradical, which serves as immediate precursor to the vinylcyclopropane, thereby bypassing the 1,4-diradical.

Since in these benzo-annelated derivatives the formation of a 1,4-diradical requires benzo-vinyl bridging, such substrates might constitute exceptions to the accepted mechanistic picture³ displayed in eq 1. For this reason we decided to investigate the alicyclic parent case, namely bicyclo[3.2.1]octa-2,6-diene (**1**) and its deuterium-labeled derivative D-1. Assuming reversible interconversion⁵ between the 1,4- and 1,3-diradicals that were postulated in the di- π -methane rearrangement of **16** extension to its deuterated derivative D-1 leads to the generalized mechanism shown in Scheme I. To probe the validity of this complex diradical manifold, in addition to the deuterium labeling of the bicyclo-octadiene, it was of interest to generate the postulated diradicals via authentic pathways, e.g. via photolysis (direct and triplet-sensitized) and thermolysis of appropriate azoalkanes.⁷ Con-

venient entry points into the postulated diradical manifold of Scheme I are the 1,3-diradicals **5** and **6** by denitrogenation of the known⁸ azoalkanes **9** and **10**. Azoalkane **11** constitutes the precursor to the 1,4-diradical **3**, but previous work² showed that on thermolysis and photolysis diene **1** exclusively resulted (eq. 2).



Results

Synthetic Work. The synthesis of D-9 and D-10 followed the sequence reported⁸ for the parent azoalkanes, involving 4-phenyl-4*H*-1,2,4-triazole-3,5-dione (PTAD) cycloaddition to the known¹⁶ D-1 and oxidative hydrolysis of the resulting urazoles.

Thermolyses. The thermal denitrogenations of **9** (D-9) and **10** (D-10) were carried out under vacuum flash pyrolysis conditions at ca. 400 °C. The product data of the thermolyses are given in Table I (entries 1-4). The main products were **7** (D-7) and **8** (D-8). In both cases significant amounts of **1** (D-1) were produced. On thermolysis of **9** (D-9) small amounts (entries 1 and 2 in Table I) of **8** (D-8) were obtained as well, while the pyrolysis of **10** (D-10) gave no **7** (D-7) (entries 3 and 4 in Table I). The thermolysis of D-9 (entry 2 in Table I) gave no D-1', while in the thermolysis of D-10 (entry 4 in Table I) D-1 and D-1' were produced in equal amounts. Dienes **2** (D-2) could not be detected in the pyrolyses of **9** (D-9) or **10** (D-10). Control experiments confirmed that **1**, **7**, and **8** were stable under the pyrolysis conditions.

Direct Photolyses. The direct irradiations of **9** (D-9) and **10** (D-10) were conducted in acetonitrile, using the 334-nm line of the argon ion laser. The main products were again **7** (D-7) and **8** (D-8) (entries 5-8, Table I); however, **9** (D-9) gave appreciably more **8** (D-8) in the direct photolysis (entries 5 and 6, Table I) compared to their thermolyses (entries 1 and 2, Table I). Like

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Table I. Product Data^a of the Thermolyses and Photolyses of the Azoalkanes **9** (D-**9**) and **10** (D-**10**) and the Photolyses of the Bicyclo[3.2.1]octadienes **1** (D-**1**)

entry	substrate	mode ^b	conditions				% conv	rel % yields ^a		
			λ , nm	T , °C	solvent ^c	sensitizer ^d		1 (1') ^e	7	8
1	9	VFP		400			100	14	84	2
2	D- 9	VFP		400			100	14(0)	84	2
3	10	VFP		400			100	18	0	82
4	D- 10	VFP		400			100	9(9)	0	82
5	9	LP	334	35	AN		100	1	89	10
6	D- 9	LP	334	35	AN		100	1(0)	89	10
7	10	LP	334	35	AN		100	28	0	72
8	D- 10	LP	334	35	AN		100	14(14)	0	72
9	1	RP	254	50	AN		20		95	5
10	D- 1	RP	254	50	AN		95	(0)	95	5
11	9	LP	364	20	AN	BP	100	8	70	22
12	D- 9	LP	364	20	AN	BP	100	8(0)	70	22
13	10	LP	364	20	AN	BP	100	17	0	83
14	D- 10	LP	364	20	AN	BP	100	9(9)	0	82
15	1	RP	300	50	AC	AC	95		21	79
16	D- 1	RP	300	50	AC	AC	95	(0)	19	81

^a Except for the deuterated derivatives D-**1** (D-**1'**), which were determined by quantitative ²H NMR (error ca. 3% of the stated values), the remaining quantitative product studies were acquired by capillary GC using electronic integration against an internal standard (error ca. 2% of the stated values), for details cf. the Experimental Section; values were normalized to 100%; the mass balance was for all cases within 85–100%. Previously it was reported⁵ that azoalkane **11** gave exclusively diene **1** on thermolysis and photolysis (cf. eq 2). ^b VFP = vacuum flash pyrolysis; LP = laser photolysis; RP = Rayonet photolysis. ^c AN = acetonitrile and AC = acetone. ^d BP = benzophenone and AC = acetone. ^e The deuterated systems **1**, **1'**, **7** and **8** correspond to D-**1**, D-**1'**, D-**7** and D-**8**, respectively.

Table II. Product Fingerprints in the Temperature-Dependent Photolyses^a of the Azoalkanes **9** and **10**

azoalkane	T , °C	quantum yield (Φ) ^b	relative % yields ^c		
			1	7	8
9	-18	0.36	1	70	30
	1	0.53	1	79	21
	34	0.57	1	90	10
	64	0.60	1	91	9
10	-18	0.42	19	0	81
	5	0.56	21	0	79
	32	0.66	28	0	72
	63	0.75	31	0	69

^a The irradiations were carried out at 334 nm (laser) with solutions 0.02 M in acetonitrile; conversion was 100% in all cases and the mass balance was between 90% and 95%. ^b See the Experimental Section for details. ^c The quantitative product studies were performed on a capillary GC, using electronic integration against an internal standard; the values are normalized to 100%; the error is ca. 2% of the stated values.

in the thermolyses (entries 3 and 4, Table I), no **7** (D-**7**) were observed in the direct photolyses (entries 7 and 8, Table I) of **10** (D-**10**). While **10** (D-**10**) formed considerable amounts (entries 7 and 8, Table I) of **1** (D-**1**), only small quantities (entries 5 and 6, Table I) of these dienes were detected in the direct photolyses of **9** (D-**9**). Moreover, the direct photolysis of D-**9** (entry 6, Table I) led exclusively to D-**1** but not to D-**1'**, while D-**10** (entry 8, Table I) gave D-**1** and D-**1'** in equal amounts. In all the laser photolyses of **9** (D-**9**) and **10** (D-**10**) no diazoalkanes were detected by means of IR (2060 cm⁻¹) and UV-vis spectroscopy (450 nm). Control experiments confirmed that the bicyclooctadienes and tricyclooctenes were stable under the photolysis conditions. No **2** (D-**2**) could be detected.

The direct photolyses of **1** (D-**1**) were conducted in acetonitrile at 254 nm. Tricycles **7** (D-**7**) and **8** (D-**8**) were formed exclusively in a ratio of 95:5 (entries 9 and 10, Table I). Control experiments confirmed that **7** (D-**7**) and **8** (D-**8**) were stable under 254-nm irradiation. No **2** (D-**2**) and D-**1'** were detected.

In the temperature-dependent photolyses of **9** and **10** the quantum yields of denitrogenation almost doubled with increasing temperature (Table II). Moreover, while for **9** the major product **7** increased with increasing temperature at the expense of the minor product **8**, **1** remained constant at ca. 1%. A contrary trend was observed for **10**, in that the minor product **1** increased with increasing temperature at the expense of **8**, the major product, and **7** was not formed at all.

Triplet-Sensitized Photolyses. For **9** (D-**9**) and **10** (D-**10**) these photolyses were performed in acetonitrile and benzophenone as

Table III. Calculated^a Heats of Formation and Strain Energies of Hydrocarbons, Diradicals, and Radicals

molecule	ΔH_f	SE,	molecule	ΔH_f	SE,
	kcal/mol	kcal/mol		kcal/mol	kcal/mol
1	30	14	7	54	60
3	104	52	8	34	39
5	88	17	15a	43	14
6	86	16	15b	46	17

^a Calculated by means of MMPMI method (ref 9).

triplet sensitizer, irradiating with the 364-nm line of the argon ion laser. **9** (D-**9**) again gave **7** (D-**7**) as major products (entries 11 and 12, Table I); but besides **8** (D-**8**), significantly more of **1** (D-**1**) was produced than in the direct photolyses (entries 5 and 6, Table I). Only D-**1** but no D-**1'** was produced in the triplet-sensitized photolysis of D-**9**.

For **10** (D-**10**) the triplet-sensitized photolyses (entries 13 and 14, Table I) were not substantially distinct from their direct irradiations (entries 7 and 8, Table I). For D-**10** (entry 14, Table I) D-**1** and D-**1'** were produced in equal amounts. The photolysis products were stable toward the conditions of triplet sensitization. No **2** (D-**2**) were detected.

The triplet-sensitized photolyses of **1** (D-**1**), using acetone as solvent and triplet sensitizer, were conducted at 300 nm up to 95% conversion. The major products (entries 15 and 16, Table I) were **8** (D-**8**) and the minor ones **7** (D-**7**). No **2** (D-**2**) were detected, no did D-**1** afford D-**1'**.

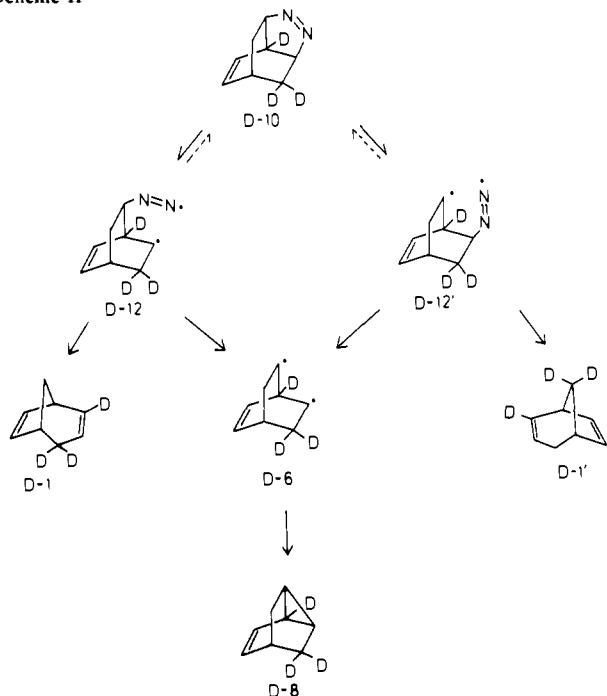
Molecular Mechanics Calculations (MMPMI). The heats of formation (ΔH_f) and strain energies (SE) of the bicyclooctadiene **1**, the tricyclooctenes **7** and **8**, and the postulated di- π -methane 1,4-diradical **3** and 1,3-diradicals **5** and **6** were computed by means of the MMPMI molecular mechanics program.⁹ The results are summarized in Table III. Unfortunately, the force-field parameters for the diazenyl diradicals D-**13a,b** were not available to us, so that the simple bicyclic radicals **15a,b** were computed as model compounds (Table III).

Mechanistic Discussion

Even only a cursory inspection of these compiled facts reveals that the photochemical behavior of the bicyclooctadienes **1** (D-**1**) and azoalkanes **9** (D-**9**) and **10** (D-**10**) match in most part at least qualitatively that of the corresponding benzo derivatives.² Thus, like for the benzo substrates, for the parent system the reversible

(9) Serena Software, Bloomington, IN. We thank K. E. Gilbert and J. J. Gajewski for making this program available to us.

Scheme II



interconversions between the various diradicals in Scheme I presumably do not operate, because (a) the photolysis of D-1 gives no D-1' (ca. 4:1 ratio of D-8 to D-7), (b) the photolysis of D-9 gives no D-1' and only little (1%) D-1 (ca. 9:1 ratio of D-7 to D-8), (c) the photolysis of D-10 gives D-1' and D-1 in a 1:1 ratio as well as D-8 (ca. 3:1 ratio of D-8 to D-1 and D-1'), (d) photolysis of 11 gives only 1, and (e) the temperature profiles of the product distribution in the photolysis of 9 and 10 are quite distinct.

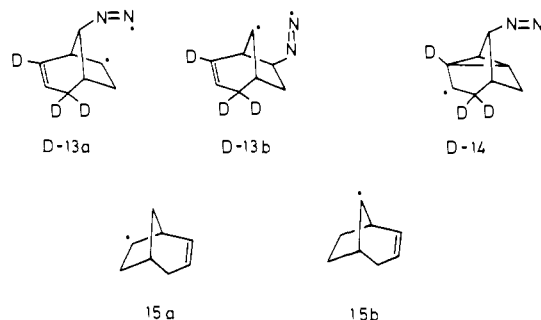
If the 1,3-diradical D-3 is an intermediate in the photolysis reactions $D-9 \rightarrow D-1 + D-7 + D-8$ and $D-10 \rightarrow D-1 + D-1' + D-8$, then the photolysis of D-1 also should have formed D-1'. Thus, the 1,3-diradicals 5 (D-5) and 6 (D-6) apparently serve as the immediate precursors to 7 (D-7) and 8 (D-8). Any overlap in the photolysis products of 1 (D-1) and 9 (D-9) and 10 (D-10) must have a chemical origin distinct from the reversible sequence $D-5 \rightleftharpoons D-3 \rightleftharpoons D-6$! We conclude, therefore, that the *di- π -methane rearrangement of 1 and the photo-denitrogenations of 9–11 are disconnected chemical events.*

The legitimate question arises, what then is the chemical origin of the D-1 and D-1' in the denitrogenations of D-10? Analogous to the benzo derivative,² we postulate that the diazenyl diradicals D-12 and D-12' intervene in the photolysis and the thermolysis of the parent azoalkane D-10 (Scheme II). In view of the symmetrical nature of azoalkane D-10 (except for deuterium labeling), one-bond cleavage^{2,10} affords D-12 and D-12' in equal amounts. Denitrogenation with simultaneous S_H2 -type^{11,12} vinyl 1,2-shift generates D-1 from D-12 and D-1' from D-12'. The structural prerequisites (molecular models) are optimal for such a S_H2 displacement.

Alternatively, both diazenyl diradicals may denitrogenate to the 1,3-diradical D-6, the immediate precursor to the main product D-8. At elevated temperature the rearrangement product 1 increases at the expense of the cyclization product 8, indicating that the differences in the activation energies are small. Also, the diazenyl diradicals D-12 and D-12' may reclose to D-10, this step

serving as energy dissipation.^{10e} Indeed, the quantum yield of denitrogenation increased with increasing temperature, suggesting a small but notable activation energy for denitrogenation of the diazenyl diradical.

The situation is not quite as clear-cut for 9 (D-9), because their product fingerprints overlap with those of 10 (D-10) and 1 (D-1). Were it not for the crossover to 8 (D-8), a mechanism analogous to that of 10 (D-10) (Scheme II) would obtain. We postulate that the diazenyl diradicals 13a,b (D-13a,b) serve as precursors to 7 (D-7) and 1 (D-1).



Uncertain is the origin of 8 (D-8) in the denitrogenations of 9 (D-9). We postulate that the diazenyl diradical D-13a transforms into D-14 via cyclopropylcarbiny rearrangement¹³ and denitrogenation affords mainly D-8 and a little (1%) D-1 via the 1,3-diradical D-6. Molecular mechanics calculations on the model radicals 15a,b suggest that D-13a should be a few kilocalories/mole lower in energy than D-13b. This also suggests a plausible explanation for the unusual temperature profile in the product distribution for the direct photolysis of 9 (D-9). At elevated temperatures a greater proportion of D-13b is produced and channeled into D-7.

This leaves us to comment on the *genuine* di- π -methane process of 1 (D-1) leading to 7 (D-7) and 8 (D-8). If the 1,4-diradicals 3 (D-3) are bona fide intermediates in the di- π -methane rearrangement of 1 (D-1), their formation and transformation to the 1,3-diradicals must be irreversible.⁴ Although theoretical work on 1,4-pentadiene¹⁴ made plausible the intermediacy of a 1,4-diradical, it left open the possibility of the direct formation of the desired 1,3-diradicals via vinyl 1,2-shifts. Since the labile azoalkane 11 denitrogenated exclusively to 1 (eq 2), we question the intervention of the 1,4-diradicals 3 (D-3) in this di- π -methane rearrangement. Furthermore, molecular mechanics calculations place the 1,4-diradical 3 ca. 15 kcal/mol higher in energy content than the 1,3-diradicals 5 and 6. Consequently, application of Ockham's razor¹⁵ suggests that the 1,3-diradicals 5 (D-5) and 6 (D-6) are formed directly in the di- π -methane rearrangement of 1 (D-1), the respective 1,4-diradicals 3 (D-3) not being necessary. This is in agreement with other mechanistic work on the di- π -methane rearrangement of benzonorbornadienes,⁴ however, our present results cannot exclude the completely concerted rearrangement of the electronically excited 1 (D-1) directly into 7 (D-7) and 8 (D-8) via path A in eq 1.

In conclusion, we advise *caution* in employing azoalkanes as mechanistic probes to elucidate the intricacies of the diradical manifold postulated for the di- π -methane rearrangement, and possibly for photochemical transformations in general. Diazenyl diradicals that are formed on one-bond cleavage of the azoalkanes¹⁰ may obscure the mechanistic details. The fact that the same

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photoproducts are obtained may be mere coincidence and should be carefully scrutinized by investigating the mechanistic details.

Experimental Section

General Aspects. ^1H NMR spectra: Hitachi Perkin-Elmer R-24B (60 MHz), Bruker WM-400 (400 MHz). ^2H NMR spectra: Bruker WM-400 (61.4 MHz). ^{13}C NMR spectra: WH-90-Bruker-Physik (22.6 MHz), Bruker WM-400 (100.6 MHz). IR spectra: Beckman IR Photometer Acculab 4 or Perkin-Elmer 1420. Capillary gas chromatography: Carlo Erba Strumentazione 4100 or Fractovap 2900 Series. Electronic integration: Shimadzu C-R1B Chromatopac or Spectraphysic System I. Elementary analyses were carried out in-house. Photolyses: irradiations at 254, 300, and 350 nm were carried out in a Rayonet Photochemical Reactor, RPR-100 75 W/250 V, Southern New England UV Co., while a CR-18-SG Coherent Supergraphite argon ion laser was used for irradiations at 334 and 364 nm.

Vacuum flash pyrolyses: At ca. 400 °C a 35-cm-long Pyrex pyrolysis tube was used, while at 400–800 °C an Heraeus Mikro U/D apparatus was employed.

Solvents or commercially (standard suppliers) available reagents and compounds were purified to match reported physical and spectral data. Known substances were prepared according to reported procedures and purified accordingly.

Photolyses of Bicyclo[3.2.1]octa-2,6-dienes 1 (D-1). In the direct photolyses ca. 5 mmol of the dienes were dissolved in 50 mL of acetonitrile and degassed by purging with N_2 for ca. 15 min. The solution was irradiated at 254 nm in the Rayonet reactor at 40–60 °C. The reaction progress was monitored by means of capillary GC, using a 50-m OV-101 column, operated at column, injector, and detector temperatures of 70, 150, and 150 °C, respectively and a nitrogen carrier gas pressure of 0.4 kg/cm². In the triplet-sensitized photolyses, acetone was used as sensitizer and solvent, irradiating in the Rayonet reactor at 300 nm. The products were identified by retention times (coinjection with authentic materials) on several capillary GC columns and when necessary by comparison of their spectral properties (MS, NMR, IR) with authentic compounds. All products were tested for photostability under the photolysis conditions. The quantitative results are collected in Table I.

Tricyclo[4.2.0.0^{2,8}]oct-3-ene (7) and Tricyclo[3.2.1.0^{2,7}]oct-3-ene (8) from the Photolysis of Bicyclooctadiene 1. Solutions of 1.00 g (9.43 mmole of diene 1 gave on direct (in 100 mL of acetonitrile) and triplet-sensitized (in 100 mL of acetone) irradiation the tricyclooctenes 7 and 8 as only products (Table I). After rotoevaporation (ca. 20 °C at 20 Torr) of the solvent to ca. a 5-mL volume, the tricyclooctenes 7 and 8 were collected by preparative gas chromatography on a 10% Apiezon L glass column (1.5-m long, 8-mm o.d.), employing column, injector, and detector temperatures of 80, 150, and 150 °C.

Tricyclo[4.2.0.0^{2,8}]oct-3-ene (7). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.23 (ddd, J = 1.7, 1.8, $J_{2,1}$ = 5.6 Hz; 1 H, 2-H), 1.44 (d, $J_{7n,7x}$ = 10.5 Hz; 1 H, 7-H_n), 1.47 (m; 1 H, 5-H), 1.68 (dd, $J_{1,8}$ = 4.5, $J_{1,2}$ = 5.4 Hz; 1 H, 1-H), 1.79 (dd, $J_{8,1}$ = 4.5, $J_{8,7x}$ = 9.5 Hz; 1 H, 8-H), 2.07 (dd, J = 2.5, 5.5 Hz; 1 H, 5-H), 2.41 (ddd, J = 4.0, $J_{7x,8}$ = 9.5, $J_{7x,7n}$ = 10.5 Hz; 1 H, 7-H_x), 2.57 (mc; 1 H, 6-H), 5.68 (m; 1 H, 4-H), 5.87 (m; 1 H, 3-H).

Tricyclo[3.2.1.0^{2,7}]oct-3-ene (8). ^1H NMR (CDCl_3 , 400 MHz): δ = 0.71 (d, $J_{8n,8x}$ = $J_{6n,6x}$ = 11.2 Hz; 2 H, 8-H_n, 6-H_n), 1.40 (d, J = 7.1 Hz; 2 H, 1-H, 7-H), 1.53 (dd, $J_{6x,5}$ = $J_{8x,5}$ = 4.5, $J_{6x,6n}$ = $J_{8x,8n}$ = 11.0 Hz; 2 H, 6-H_x, 8-H_x), 1.59 (m; 1 H, 2-H), 2.50 (d, $J_{5,6x}$ = $J_{5,8x}$ = 4.5; 1 H, 5-H), 5.87 (m; 2 H, 3-H, 4-H).

3,5,5-Trideuteriotricyclo[4.2.0.0^{2,8}]oct-3-ene (D-7) and 2,6,6-Trideuteriotricyclo[3.2.1.0^{2,7}]oct-3-ene (D-8) from the Photolysis of Bicyclooctadiene D-1. Solutions of 1.50 g (13.8 mmol) of diene D-1 gave on direct (100 mL of acetonitrile) and triplet-sensitized (100 mL of

acetone) irradiation after 95% conversion the tricyclooctenes D-7 and D-8 as the only products (Table I). The workup followed that for the undeuterated diene 1.

3,5,5-Trideuteriotricyclo[4.2.0.0^{2,8}]oct-3-ene (D-7). ^1H NMR (CDCl_3 , 400 MHz): δ = 1.22 (dd, J = 5.5, $J_{2,1}$ = 5.6 Hz; 1 H, 2-H), 1.43 (d, $J_{7n,7x}$ = 10.5 Hz; 1 H, 7-H_n), 1.68 (d, $J_{1,8}$ = 4.5, $J_{1,2}$ = 5.4 Hz; 1 H, 1-H), 1.79 (dd, $J_{7x,8}$ = 9.5, $J_{1,8}$ = 4.5 Hz; 1 H, 8-H), 2.41 (dd, $J_{7x,8}$ = 9.5, $J_{7x,7n}$ = 10.5 Hz; 1 H, 7-H_x), 2.56 (mc; 1 H, 6-H), 5.66 (s; 1 H, 4-H). ^2H NMR (CFCl_3 , 61.4 MHz): δ = 1.47 (s; 1 D, 5-D), 2.07 (s; 1 D, 5-D), 5.89 (s; 1 D, 3-D).

2,6,6-Trideuteriotricyclo[3.2.1.0^{2,7}]oct-3-ene (D-8). ^1H NMR (CDCl_3 , 400 MHz): δ = 0.71 (d, $J_{7n,8x}$ = 11.2 Hz; 1 H, 8-H_n), 1.40 (s; 2 H, 1-H, 7-H), 1.52 (dd, $J_{8x,5}$ = 4.5, $J_{8x,8n}$ = 11.0 Hz; 1 H, 8-H_x), 2.48 (m; 1 H, 5-H), 5.87 (d, J = 6.4 Hz; 2 H, 3-H, 4-H). ^2H NMR (CFCl_3 , 61.4 MHz): δ = 0.71 (s; 1 D, 6-D_n), 1.53 (s; 1 D, 6-D_x), 1.59 (s; 1 D, 2-D).

Photolyses of Azoalkanes 9 (D-9) and 10 (D-10). In the direct photolysis ca. 1 mmol of the azoalkanes, dissolved in 5 mL of acetonitrile, was degassed by purging with nitrogen gas for 15 min and irradiated at 334 nm (argon ion laser) until complete conversion. The reaction progress was monitored by means of capillary GC on a 50-m OV-101 glass column, using column, injector, and detector temperatures of 70, 150, and 150 °C, and a N_2 carrier gas pressure of 0.4 kg/cm². The triplet-sensitized irradiations were carried out as above at 364 nm, except that a 5- to 10-fold molar excess of benzophenone was used. The products were identified by retention times (coinjection with authentic materials) on several capillary GC columns and when necessary by comparison of their spectral properties (MS, NMR, IR) with the authentic compounds. All products were tested for photostability under the photolysis conditions. The quantitative results are collected in Table I.

^2H NMR (CFCl_3 , 61.4 MHz) of D-1: δ = 1.74 (s; 1 D, 8-D), 1.95 (s; 1 D, 8-D), 6.03 (s; 1 D, 2-D).

Thermolyses of the Azoalkanes 9 (D-9) and 10 (D-10). About 200 μmol of freshly sublimed azoalkane was placed into a 10-mL flask and volatilized slowly at ca. 80 °C and 20 Torr directly into the Pyrex pyrolysis tube (35-cm long, 1-cm o.d.), held at 350–400 °C, collecting the effluent on a cold finger at –78 °C. The pyrolysate was dissolved in benzene and analyzed by capillary GC. The products were identified as described in the photolysis procedure and the quantitative results are summarized in Table I. Control experiments showed that the products were stable under the pyrolysis conditions.

Determination of the Quantum Yields in the Temperature-Dependent Photolyses of the Azoalkanes 9 and 10. A 2-mL sample of a 0.02 M solution of the corresponding azoalkane in acetonitrile was placed into a 1-cm UV cell and degassed by purging with nitrogen gas for 15 min. The solution was irradiated with the 334-nm line of the argon ion laser, once a constant output power of 60 mW was reached. More than 99% of the incident light was absorbed by the azoalkane solution. The time-dependent decrease of the azoalkanes was monitored by means of UV spectroscopy (350 nm) at 30-min intervals, diluting the sample appropriately. The quantum yield (Φ) of the azoalkane decomposition was calculated according to

$$\Phi = hcNm(1 - E_t/E_v)/\lambda MPt$$

where h = 6.62×10^{-34} J s, c = 3×10^8 m/s, N = 6.023×10^{23} mol⁻¹, m = mass (g) of azoalkane, E_t and E_v are the absorbances after and before irradiation, λ = wavelength (nm) of irradiation, M = molar mass (g) of azoalkane, P = laser power (W), and t = irradiation time (s).

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