On the Question of 1,4-Diradical Intermediates in the Di-π-methane Rearrangement of Benzobicyclo[3.2.1]octadienes: Azoalkanes as Mechanistic Probes

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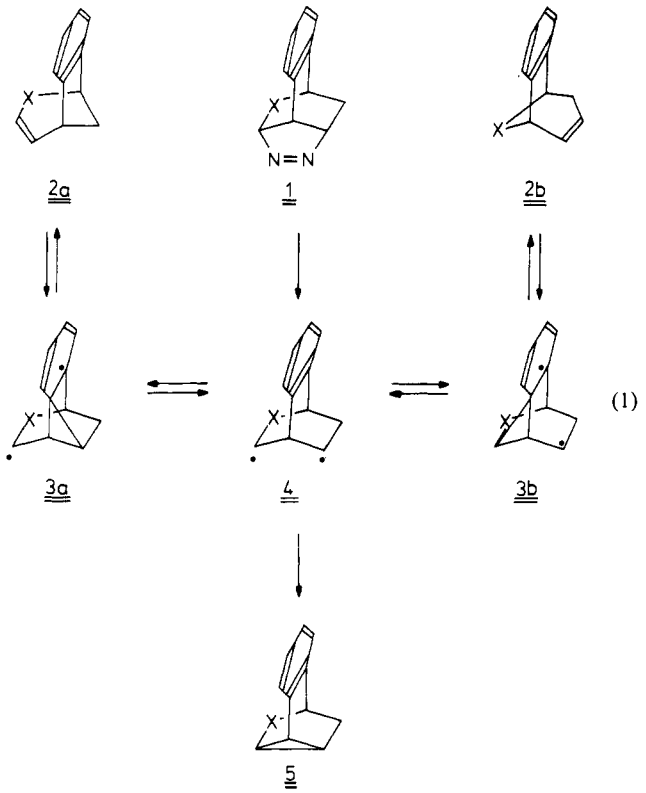
Abstract: Nitrogen extrusion of the azoalkane 8,9-benzo-4,5-diazatricyclo[4.3.1.$0^{3,7}$]deca-4,8-diene (**1**) and its deuterio and spirocyclopropane derivatives **D-1** and **S-1**, respectively, gave as major products 3,4-benzotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**5**) and its deuterio and spirocyclopropane derivatives **D-5** and **S-5**. As minor products 6,7-benzobicyclo[3.2.1]octa-2,6-diene (**2**) was formed from azoalkane **1**, but a 1:1 mixture of the two possible deuterio derivatives **D-2a,b** was obtained from azoalkane **D-1**. From spirocyclopropane derivative **S-1** the corresponding benzobicyclo[3.2.1]octadienes **S-2a,b** were formed, with the **S-2a** isomer predominating. On irradiation of bicycles **2**, **D-2a**, and **S-2a,b** only di-π-methane rearrangement products **5**, **D-5**, and **S-5**, respectively, were found. A composite mechanistic scheme is proposed for the formation of di-π-methane rearrangement products **5** from azoalkanes **1** and from bicycles **2**, in which the 1,3-diradicals **4** figure as a common reaction funnel for both processes **1** → **5** and **2** → **5**. If 1,4-diradicals **3** intervene in the transformations **2** → **5**, the interconverting sequence **2a** ⇌ **3a** ⇌ **4** ⇌ **3b** ⇌ **2b** cannot apply. The intermediate precursors to bicycles **2** from azoalkanes **1** are postulated to be diazenyl diradicals, leading to bicycles **2** via S_H2-type benzo migration directly during denitrogenation of the latter.

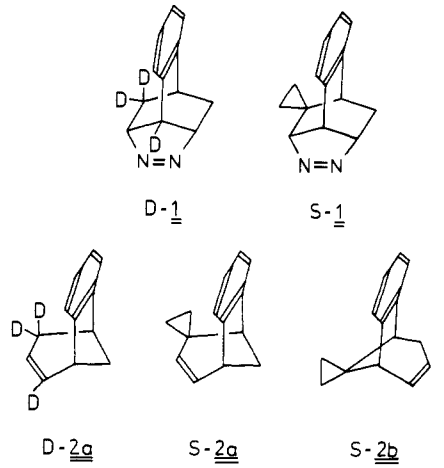
Photodenitrogenation of appropriate azoalkanes has been utilized as an independent entry into the diradical manifold postulated in the di-π-methane reaction.[2] In one of our early studies on this subject,[3] we showed that bicyclic azoalkane **1** (X = CH_2) afforded on denitrogenation (photolysis and thermolysis) bicyclooctadiene **2** and tricycloalkene **5** (eq 1). Since the latter



(1)

is the di-π-methane product of bicyclooctadiene **2**, the mechanistically expedient rationalization of these results was to postulate 1,3-diradical **4** as the initial intermediate, with the options of closing to di-π-methane product **5** or rearranging via 1,4-diradicals **3** to the bicyclooctadienes **2**. Consequently, the di-π-methane rearrangement of bicyclooctadienes **2** and the denitrogenation of azoalkane **1** were proposed to operate through the same diradical manifold. Although a detailed theoretical analysis[4] of the parent 1,4-pentadiene made the intervention of a cyclopropyldicarbinyl diradical intermediate plausible, it left open the possibility of a direct 1,2-aryl shift affording the 1,3-diradical without engaging such 1,4-diradicals. In fact, in a study employing deuterium-labeled benzonorbornadiene, the participation of 1,4-diradicals such as **3** was questioned.[5] It was argued that unless the proposed reversibility **2** ⇌ **3** ⇌ **4** in eq 1 indeed obtains, benzo bridging is only feasible in the form of transition-state structures.

To assess the validity of the reversible sequence **2** ⇌ **3** ⇌ **4** of eq 1, and therewith justifying the use of azoalkanes as a mechanistic probe for the di-π-methane rearrangement, we decided to utilize the unsymmetrically labeled azoalkanes **D-1** (**D** for



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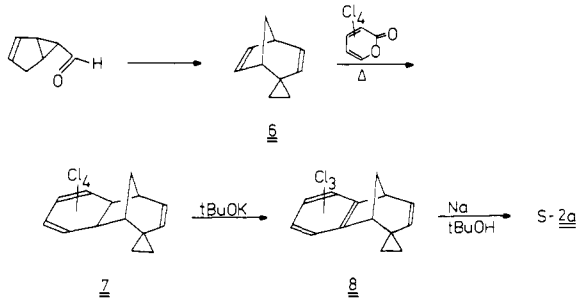
deuterium) and **S-1** (S for spirocyclopropane) and benzobicyclo[3.2.1]octadienes **D-2a** and **S-2a,b**. The deuterium label was chosen as a minimal perturbation, while the spirocyclopropyl moiety was expected to differentiate in the partitioning of the 1,3-diradical **S-4** into the 1,4-diradicals **S-3a** and **S-3b** via cyclopropylcarbinyl stabilization.[6] Presently we report that the mechanism in eq 1 involving bona fide cyclopropyldicarbinyl diradicals **3** is questionable. Rather, our results are in better concordance with benzo bridging via transition-state structures as the product-determining step, as proposed in the di-π-methane rearrangement of benzonorbornadienes.[5]

Results

Synthetic Work. Known compounds were prepared according to literature procedures and purified to match the reported physical constants and spectral data. Deuteriated bicyclooctadiene **D-2a** was obtained by base-catalyzed hydrogen–deuterium exchange of parent olefin **2** (X = CH_2) using *t*-BuOK in DMSO-d_6.[7] The extent of deuteriation was ca. 95%.

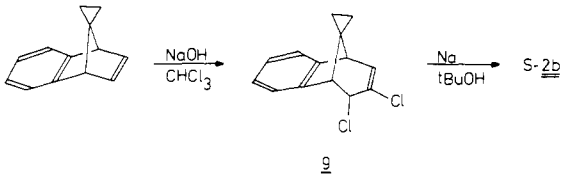
The synthesis of spirocyclopropane derivative **S-2a** is outlined in eq 2. The known aldehyde[8] was first converted in 95% yield



(2)

via a "one-pot" process to the new spiro diene **6** by Wittig reaction with in situ prepared spirocyclopropylidenetriphenylphosphorane.[9] The intermediary cyclopropylidene Wittig product underwent facile Cope rearrangement[10] to give the novel spiro diene **6**. Its Diels–Alder reaction with tetrachloro-α-pyrone[11] proceeded in 70% yield to give cycloadduct 7 under simultaneous decarboxylation. Dechlorination of **7** could be achieved only in poor yields via successive dehydrochlorination with potassium *tert*-butoxide[12] and reductive chlorine–hydrogen exchange[13] with sodium metal in *tert*-butyl alcohol. The intermediary trichlorobenzo derivative **8** was used without further purification in view of the low yield (ca. 10%) in the dehydrochlorination.

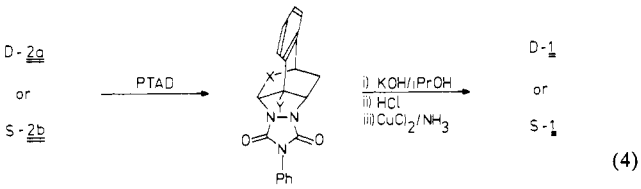
Spirocyclopropane isomer **S-2b** was prepared according to the sequence shown in eq 3. The known spiro diene[14] was converted



(3)

to the dichloro derivative **9** in 37% yield by cycloaddition of dichlorocarbene (generated from chloroform with sodium hydroxide) and subsequent in situ rearrangement.[15] Dechlorination with Na/*t*-BuOH afforded **S-2b**.

The synthesis of azoalkanes **D-1** and **S-1** followed the sequence reported[16] for the parent azoalkane **1** (X = CH_2) and is displayed in eq 4. The corresponding urazoles **D-10** and **S-10** were obtained



(4)

D-10 (X = CD_2 ; Y = D)

S-10 (X = C<CH2 CH2>; Y = H)

in moderate yields via cycloaddition of PTAD to the respective bicyclooctadienes **D-2a** and **S-2b** and converted to the respective azo compounds **D-1** and **S-1** employing the usual hydrolysis–oxidation method.[16]

Product Studies. Thermolyses. The thermal denitrogenations of azoalkanes **1**, **D-1**, and **S-1** were carried out under vacuum flash pyrolysis conditions by volatilizing the substrate at 15 Torr through a 35-cm hot tube kept at ca. 400 °C and condensing the pyrolysate into a cold trap at ca. −80 °C. The thermolysis product data are collected in Table I for the parent system **1** (entry 1), the deuteriated derivative **D-1** (entry 2), and the spirocyclopropyl derivative **S-1** (entry 3). Clearly, the main products were the tricycloalkenes **5**, **D-5**, and **S-5**, respectively. These di-π-methane products were characterized on the basis of their spectral and analytical data (cf. Experimental Section). Control experiments confirmed that these tricycloalkenes are stable under the pyrolysis conditions. Significant is the fact that appreciable amounts of the corresponding benzobicyclo[3.2.1]octadienes **2**, **D-2a,b**, and **S-2a,b** were obtained as well. Thus, for deuteriated derivative **D-1** equal amounts (ca. 5%) of the two possible octadienes **D-2a** and **D-2b** were formed (entry 2). However, appreciable differentiation is observed in spirocyclopropyl derivative **S-1**. First of all, the total yield of octadienes **S-2a,b** is significantly larger (entry 3) than for the parent (entry 1) and deuteriated (entry 2) azoalkanes; but more interestingly, **S-2a** predominates over **S-2b** by ca. fivefold, implying cyclopropylcarbinyl stabilization[6] of the radical site.

Direct Photolyses. The direct photolyses of azoalkanes **1**, **D-1**, and **S-1** were conducted in benzene, using either the 334-nm line of an argon ion laser or the 350-nm lamps in the Rayonet photoreactor. For benzobicyclooctadienes **2**, **D-2a**, and **S-2a** the irradiations were performed in the Rayonet photoreactor using 254-nm lamps. The results are summarized in Table I (entries 4–13).

In the direct photolyses of azoalkanes **1**, **D-1**, and **S-1** the main products were again tricycloalkenes **5**, **D-5**, and **S-5** (entries 4–9), with appreciable amounts of the respective benzobicyclo[3.2.1]-octadienes **2**, **D-2a,b**, and **S-2a,b**. Control experiments showed that the photoproducts **5**, **D-5**, and **S-5** as well as **2**, **D-2a,b**, and **S-2a,b** were stable under the direct photolysis conditions. Within experimental error the product compositions were the same in the laser and Rayonet irradiations (compare entries 4, 6, and 8 with entries 5, 7, and 9, respectively). Also, no significant differences in the product compositions were observed between the parent system **1** (entries 4 and 5) and deuteriated derivative **D-1** (entries 6 and 7), except that in the latter case both possible benzobicyclooctadienes **D-2a** and **D-2b** were formed in equal amounts (ca. 9%). Again, the deuterium labeling does not cause any discernible effects in the partitioning of **D-1** among **D-2a** and **D-2b** during the direct photolysis. However, such differentiation becomes clearly evident for spirocyclopropyl derivative **S-1** (entries 8 and 9). Thus, a 19-fold preference for **S-2a** over **S-2b** was

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Table I. Product Compositions[a] of the Thermolyses and Photolyses of the Azoalkanes **1**, **D-1**, and **S-1** and the Photolyses of the Benzobicyclo[3.2.1]octadienes **2**, **D-2a,b**, and **S-2a,b**

		conditions						rel yields,[b] %		
entry	substrate	mode[c]	λ, nm	T, °C	solvent[d]	sensitizer[e]	conv	**2a**	**2b**	**5**
1	**1**	VFP		400			100	11		89
2	**D-1**	VFP		400		100	100	5	5	90
3	**S-1**	VFP		400			100	21	4	75
4	**1**	LP	334	20	BE		100	19		81
5	**1**	RP	350	50	BE		100	22		78
6	**D-1**	LP	334	20	BE		100	9	9	82
7	**D-1**	RP	350	50	BE		100	10	10	80
8	**S-1**	LP	334	20	BE		100	19	1	66[f]
9	**S-1**	RP	350	50	BE		100	19	1	63[f]
10	**2**	RP	254	50	PE		100			100
11	**D-2a**	RP	254	50	PE		95		0	100
12	**S-2a**	RP	254	50	PE		40		0	100
13	**S-2b**	RP	254	50	PE		30	0		73[f]
14	**1**	RP	350	50	BE	BP	100	4		96
15	**D-1**	RP	350	50	BE	BP	100	2	2	96
16	**S-1**	RP	350	50	BE	BP	100	3	0	97
17	**2**	RP	300	50	AC	AC	100			100
18	**D-2a**	RP	300	50	AC	AC	95		0	100
19	**S-2a**	RP	300	50	AC	AC	80		0	100
20	**S-2b**	RP	300	50	AC	AC	90	0		85[f]

[a] For the parent systems, **2a** and **2b** are the same and correspond to **2**; for the deuterated derivatives, **2a,b** and **5** correspond to **D-2a,b** and **D-5**; for the spirocyclopropyl derivatives, **2a,b** and **5** correspond to **S-2a,b** and **S-5**. [b] Except for the deuterated derivatives **D-2a,b** and **D-5**, which were determined by quantitative ^{2}H 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. 1.0% of the stated values; for details cf. Experimental Section. Values were normalized to 100%; mass balance was for all cases within 85–95%. [c] VFP = vacuum flash pyrolysis, LP = laser photolysis, and RP = Rayonet Photolysis. [d] BE = benzene, AC = acetone, and PE = pentane. [e] BP = benzophenone and AC = acetone. [f] The remainder is made up of 3,4-benzo-1,3,5-cyclooctatriene. An authentic sample was synthesized according to reported procedures and found to be identical by spectral data, capillary GC retention times, and capillary GC–MS coupling. We have no mechanistic rationalization for this product.

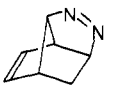
observed. Again, cyclopropylcarbinyl stabilization[6] presumably dictates also the photochemical partitioning of azoalkane **S-1** among the rearrangement products **S-2a,b**. Furthermore, this differentiation is much more pronounced for the direct photolysis of azoalkane **S-1** (entries 8 and 9) than for its pyrolysis (entry 3).

Remarkable results were obtained for the direct photolysis at 254 nm of benzobicyclo[3.2.1]octadienes **2**, **D-2a**, and **S-2a,b** (entries 10–13). In these photolyses only the corresponding di-π-methane products, namely, tricycloalkenes **5**, **D-5a**, and **S-5**, respectively, were observed. For deuteriated derivative **D-2a** (entry 11) small amounts of rearranged bicyclooctadiene **D-2b** may have gone undetected because the detection limit of quantitative ^{2}H NMR (ca. 3% under the conditions used) is lower compared to quantitative capillary GC (ca. 1 ppm). Furthermore, even for the latter more sensitive method, small amounts of rearranged bicyclooctadiene **S-2b** in the direct photolysis of **S-2a** (entry 12) may have gone undetected in view of the 19-fold preference of **S-2a** over **S-2b** in the direct photolysis of azoalkane **S-1** (entries 8 and 9). However, such argumentation becomes redundant in the direct photolysis of **S-2b** as substrate (entry 13), since now the 19-fold preference of isomer **S-2a** over **S-2b** observed for azoalkane **S-1** (entries 8 and 9) must manifest itself! We are obliged to conclude that in the direct photolyses of benzobicyclo[3.2.1]octadienes **2**, **D-2a**, and **S-2a,b** the corresponding rearranged octadienes are not formed in detectable amounts.

Triplet-Sensitized Photolyses. A similar product picture obtains in the triplet-sensitized photolyses of azoalkanes **1**, **D-1**, and **S-1** (entries 14–16) and octadienes **2**, **D-2a**, and **S-2a,b** (entries 17–20). In contrast to the direct photolyses, significantly smaller amounts (≤4%) of bicyclooctadienes were formed from the respective azoalkanes (entries 14–16). For deuteriated derivative **D-1** (entry 15), benzophenone sensitization gave isomeric dienes **D-2a** and **D-2b**, again in equal amounts (ca. 2%), the main product by far (ca. 96%) being tricycloalkene **D-5**. In the case of spirocyclopropyl derivative **S-1** (entry 16), only diene **S-2a** was detected; but in view of the large preference for **S-2a** (entries 8 and 9), the other isomer **S-2b** may have gone undetected. In the acetone sensitization of benzobicyclo[3.2.1]octadienes **2**, **D-2a**, and **S-2a,b** (entries 17–20) only the respective di-π-methane products **5**, **D-5**, and **S-5** were formed. Not even traces of the corresponding rearranged bicyclooctadienes were detected. Control experiments confirmed that the photoproducts were stable under the sensitized photolysis conditions of the respective azoalkanes.

Intermediacy of Diazoalkanes. Direct laser photolysis at elevated temperatures (ca. 60 °C) was previously established[17] to be optimal for the retrocleavage of azoalkanes into the corresponding diazoalkanes. These conditions were applied to azoalkanes **1** and **S-1**. With the full output of the argon ion laser at 334 nm, only for azoalkane **S-1** could trace quantities of a diazoalkane be detected by means of the characteristic IR (2060 cm^{-1}) and UV (ca. 450 nm) absorptions. Moreover, on prolonged photolysis no diazoalkane-derived products could be found for azoalkane **1**. Thus, photochemical retrocleavage for these azoalkanes is of subordinate importance in the product composition.

Kinetics of the Thermolyses. To test the influence of the deuterium and spirocyclopropane substitution on the thermal decomposition, the decomposition rate constants and activation parameters of azoalkanes **1**, **D-1**, and **S-1** were determined by means of isothermal kinetics in the temperature range 125–180 °C using decalin as solvent. For comparison, the activation parameters of the known azoalkanes **11** and **12**[18] were measured



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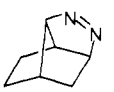

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(ethylene glycol as solvent) in order to probe the influence of the double bond on the thermal denitrogenation of azoalkanes **1**, **D-1**, and **S-1**. The first-order rate constants and Eyring activation parameters are given in Table II (cf. Experimental Section for details).

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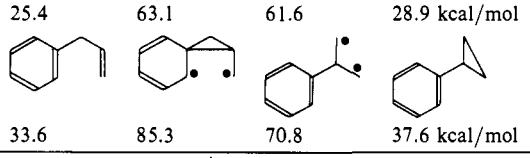
Table II. Thermal Decomposition Rate Constants and Eyring Activation Parameters of the Azoalkanes

azo-alkane	temp,[a] °C	$k \times 10^5$,[b] s^{-1}	$\Delta H^{\ddagger}$,[b] kcal/mol	$\Delta S^{\ddagger}$,[b] eu	$\Delta G^{\ddagger}$ at 150 °C,[b] kcal/mol
1[c]	157.7	1.72 ± 0.01	32.2 ± 0.7	−6.3 ± 1.1	34.8 ± 0.7
	161.6	2.06 ± 0.12			
	167.6	4.54 ± 0.07			
	176.9	8.48 ± 0.07			
D-1[c]	157.7	1.48 ± 0.02	32.2 ± 0.7	−6.1 ± 1.1	35.0 ± 0.7
	160.6	1.79 ± 0.06			
	167.6	3.95 ± 0.08			
	177.2	7.61 ± 0.08			
S-1[c]	125.2	1.47 ± 0.07	30.2 ± 0.7	−10.3 ± 1.3	32.6 ± 0.9
	130.5	2.24 ± 0.13			
	135.6	3.72 ± 0.19			
	146.2	12.2 ± 0.39			
	151.7	11.9 ± 0.90			
11[d]	137.4	2.46 ± 0.07	33.6 ± 0.5	1.2 ± 0.8	33.0 ± 0.5
	143.3	3.95 ± 0.11			
	148.8	6.62 ± 0.35			
	153.5	10.6 ± 0.59			
	158.4	16.9 ± 0.57			
12[d]	149.4	1.62 ± 0.12	33.5 ± 1.1	−1.8 ± 0.6	34.3 ± 1.1
	155.0	2.83 ± 0.13			
	160.3	4.51 ± 0.29			
	165.4	7.21 ± 0.40			
	170.3	11.4 ± 0.26			

[a] Isothermal conditions were achieved by means of a Lauda R42/2 thermoregulator; fluctuations were within ca. ±0.15 °C. [b] Error limits were determined by statistical treatment and represent standard deviations. [c] Decalin was used as solvent and benzophenone as internal standard in the capillary GC quantitation. [d] Ethylene glycol was used as solvent and quinoline as internal standard in the capillary GC quantitation.

Table III. Heats of Formation (ΔH_f, kcal/mol) of Substrates, Diradicals,[a] and Products of the Di-π-methane Rearrangement of 1,4-Pentadiene and Allylbenzene Computed by MNDO[b]



[a] Calculated as triplet states. [b] Reference 19.

The results in Table II reveal that no kinetic isotope effect can be discerned for parent azoalkane **1** versus deuteriated derivative **D-1**. Comparison of these with spirocyclopropyl system **S-1** shows that the latter is significantly more labile toward thermal decomposition (ca. 2 kcal/mol lower $\Delta G^{\ddagger}$ value). The spirocyclopropyl substitution seems to be responsible for this. Assistance by the double bond (benzo substituent) appears to be negligible since the unsaturated and saturated azoalkanes **11** and **12**, respectively, are equally stable within experimental error.

MNDO Calculations. To gain insight into the relative energies of the di-π-methane substrates, diradical intermediates, and products, MNDO calculations were performed.[19] In view of the computational capacity of the Olivetti M24 personal computer, instead of benzobicyclo[3.2.1]octadiene **2**, as model compounds allylbenzene, its 1,4- and 1,3-diradicals, and its di-π-methane product phenylcyclopropane were processed. The heats of formation (ΔH_f) are collected in Table III. The parent system, i.e., 1,4-pentadiene, its 1,4- and 1,3-diradicals, and its di-π-methane rearrangement product vinylcyclopropane (eq 1) were also computed (Table III). Our results of relative energies for the parent 1,4-pentadiene system match qualitatively those previously reported.[4]

The MNDO results in Table III suggest that the 1,4-diradical of the parent system (1,4-pentadiene) is only slightly higher in energy (ca. 1.5 kcal/mol) than the corresponding 1,3-diradical. On the other hand, for the benzo analogue (allylbenzene) the energy difference between the corresponding diradicals is appreciable (ca. 15 kcal/mol). Perturbation of the aromatic moiety must be responsible for the appreciably higher energy content of the 1,4-diradical derived from allylbenzene.

Mechanistic Discussion

Let us recapitulate those results which are essential for the mechanistic interpretations: (i) deuteriated azoalkane **D-1** gives on photolysis and thermolysis mainly tricyclooctane **D-5**, but appreciable amounts of bicyclooctenes **D-2a,b** are formed in equal proportion; (ii) however, deuteriated bicyclooctenes **D-2a,b** give on photolysis exclusively tricyclooctane **D-5** with no detectable amounts of **D-2b** from **D-2a** or vice versa; (iii) spirocyclopropanated azoalkane **S-1** gives on photolysis and thermolysis mainly tricyclooctane **S-5**, but appreciable amounts of bicyclooctenes **S-2a,b** are formed, with **S-2b** preferred over **S-2a** by ca. 19-fold; (iv) however, spirocyclopropanated bicyclooctenes **S-2a,b** give on photolysis exclusively tricyclooctane **S-5** with no detectable (by capillary GC) amounts of **S-2b** from **S-2a** and vice versa; (v) in the laser photolysis of spirocyclopropanated azoalkanes **S-1** small quantities of diazoalkanes **S-6a,b** are detected by infrared and visible absorption spectroscopy; (vi) the activation parameters, determined by isothermal kinetics, show that spirocyclopropanated azoalkane **S-1** denitrogenates more readily than parent azoalkane **1**, leading to **S-2a** as product in ca. 5-fold preference; (vii) MNDO calculations on model 1,3- and 1,4-diradicals suggest that 1,4-diradical **4** should lie at an energy considerably higher (ca. 15 kcal/mol) than 1,3-diradical **3**.

The reversible sequence **2a** ⇌ **3a** ⇌ **4** ⇌ **3b** ⇌ **2b** in eq 1 cannot account for our experimental observations. While in the photolysis of azoalkane **1**, bicycles **2a,b** are formed besides tricycle **5** (facts i and iii), in the photochemical transformation of bicycle **2a** only tricycle **5** and no isomeric bicycle **2b** are obtained (facts ii and iv), and vice versa. Indeed, the deuterium-labeling experiments[5] for the benzonorbornadiene substrates provided evidence against the invervention of 1,4-diradical intermediates such as **3a,b**, arguing in favor of benzo-bridged transition-state structures instead of the commonly postulated cyclopropyldicarbinyl diradicals. Thus, while 1,3-diradical **4** serves as a common reaction funnel to tricycle **5** both from azoalkane **1** and from bicycle **2**, the mechanistic details in the **1** → **4** and **2** → **4** steps must be distinct. Furthermore, once 1,3-diradical **4** is formed, rather than transforming into bicycles **2a,b** via a 1,2-shift, in view of the appreciable activation energy (ca. 5 kcal/mol),[20] the cyclization **4** → **5** is much preferred.[5d] Also our MNDO calculations (fact vii) suggest that 1,4-diradicals **3a,b** lie about 15 kcal/mol higher in energy than 1,3-diradical **4** since during benzo bridging aromaticity is sacrificed. Moreover, the STO-3G calculations[4] for the parent 1,4-pentadiene system attribute an appreciably higher energy (ca. 10 kcal/mol) to the cyclopropyldicarbinyl species.

We postulate that diazenyl diradicals are the immediate precursors to bicycles **2a,b** in the thermal and photochemical (direct and triplet sensitized) denitrogenation of azoalkanes **1**, formed by one-bond cleavage of the pyrazoline ring (eq 5). It is becoming to be accepted as general fact that in the thermolysis of cyclic azoalkanes diazenyl diradicals intervene.[21] Stimulated by theoretical predictions[22] that one-bond cleavage is the likely course

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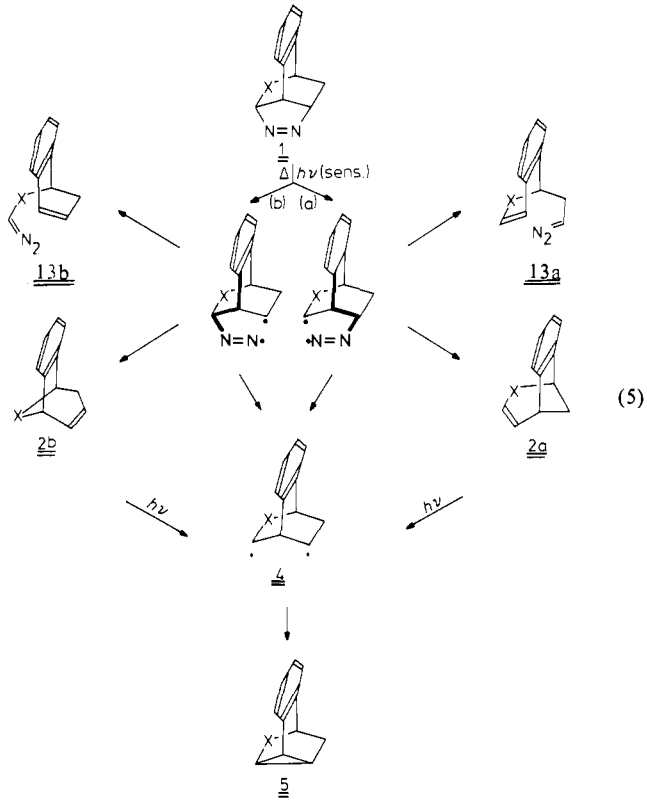


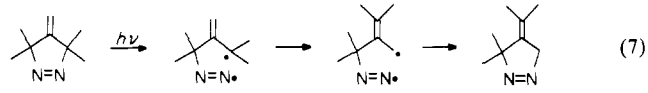
(5)

of action in the n,π^* excitation of cyclic azoalkanes, we recently proposed[17] that formation of diazoalkanes derives from retrocyclization of the intermediary diazenyl diradicals (eq 6). This

(6)

retrocleavage competes with the more usual loss of nitrogen, leading to 1,3-diradical cyclization products. Indeed, in the direct photolysis of spirocyclopropane-substituted azoalkane **S-1** small amounts of diazoalkane, presumably **S-13a,b** (eq 5), were detected (fact v).

Thus, the intermediary diazenyl diradicals have the options (eq 5) to denitrogenate into 1,3-diradical **4**, leading to tricycle **5** (major route), to retrocleave to diazoalkanes **13a,b** (minor route), to eliminate nitrogen with concomitant migration of the benzo moiety, affording bicycles **2a,b**, or to recyclize to the initial azoalkane **1**. For the recyclization process we have recently[23] provided precedence (eq 7).



(7)

The hypothesis that benzo migration accompanies nitrogen loss in the transformation of the diazenyl diradical to bicycles **2a,b** has precedents in the S_H2-type reactions that have been invoked in the nitrogen extrusion,[24] e.g., 2,3-diazobicyclo[2.2.1]hept-2-ene and 4-alkylidene-1-pyrazoline. In the present example (eq 5) the structural prerequisites (cf. molecular models) are optimal for such an S_H2 process. The benzo π-system is appropriately aligned for overlap with the incipient carbon radical site that is being generated on nitrogen loss, and the participating =N—CH—CH—C= fragment (marked boldface in the diazenyl diradical; cf. eq 5) is perfectly antiperiplanar for the 1,2-shift. Furthermore, in cationic rearrangements the [2.2.2] → [3.2.1] skeletal transformations are energetically favored in bicyclooctanes.[25] Although skeletal rearrangements of bicyclic radicals are rare,[26] in the present case the driving force is undoubtedly derived from the energy gain through nitrogen loss and formation of the double bond at the incipient radical site. Of course, nitrogen loss is only energetically feasible if $D_{\sigma,\sigma}$-type diazenyl diradicals are involved, since then ground-state nitrogen is formed.[17b] Thus, in the direct n,π^*-photolysis the initial $D_{\sigma,\pi}$-type diazenyl diradicals must first undergo surface crossing to the $D_{\sigma,\sigma}$-type diradicals. However, this requisite upholds also for the denitrogenation of the diazenyl diradical to 1,3-diradical **4** (eq 5).

An additional advantage of the mechanistic scheme proposed in eq 5 is that the 19-fold preference in the formation of bicycle **S-2a** over **S-2b** from spirocyclopropane-substituted azoalkane **S-1** (fact iii) can be straightforwardly rationalized. During one-bond cleavage of azoalkane **S-1**, route a in eq 5 should be preferred by at least by 2 kcal/mol[6] in view of cyclopropylcarbinyl stabilization. In fact, the spirocyclopropane moiety is aligned optimally in the bisected geometry with the incipient radical site. Also in the thermolysis of azoalkane **S-1** this anchimeric assistance by the spirocyclopropane moiety manifests itself in that the activation energy for denitrogenation is ca. 2 kcal/mol lower than that of azoalkane **1** (fact vi). In terms of a denitrogenated intermediate such as 1,3-diradical **S-4**, it would be difficult to account for the predominant formation of **S-2a** over **S-2b** in the photolysis and thermolysis of azoalkane **S-1**.

That the triplet-sensitized photolysis of azoalkanes **1** gives exclusively tricycles **5** (entries 14–16, Table I) is not surprising, as documented in the barrelene–semibullvalene transformation and its azoalkane photolysis, one of the earliest experimental confirmations that triplet 1,3-diradicals are discrete intermediates in the di-π-methane rearrangement.[2] Previous theoretical work[20] demonstrated that triplet trimethylene is less prone to rearrangement than the singlet species, affording exclusively cyclopropane instead of propene. We suggest that for the same reasons also triplet 1,3-diradical **4** is more selective than its singlet configuration.

The mechanistic scheme in eq 5 best explains the present results for the di-π-methane rearrangement of bicycles **2a,b** and the thermal and photochemical (direct and triplet sensitized) denitrogenation of azoalkanes **1** into the tricycles **5**. The common reaction funnel is 1,3-diradical **4** for both the **2a,b** → **5** and the **1** → **5** transformations. The interconversion along the sequence **2a** ⇌ **3a** ⇌ **4** ⇌ **3b** ⇌ **2b** (eq 1) has been ruled out on the basis of the present data, which is in accord with the previous observations for the benzonorbornadienes.[5] Entry from azoalkane **1** takes place via the diazenyl diradicals, which on denitrogenation afford 1,3-diradical **4**. In the direct photolysis (n,π^* excitation) the initial $D_{\sigma,\pi}$ diazenyl diradical must first transform into its $D_{\sigma,\sigma}$ configuration by means of surface crossing,[17b] before nitrogen loss becomes feasible. The $D_{\sigma,\sigma}$ diazenyl diradicals and not 1,3-diradical **4** are the immediate precursors to bicycles **2a,b**. Thus, partitioning of azoalkane **1** into photoproducts **5** and **2a,b** is dictated by the diazenyl diradicals.

Experimental Section

General Aspects. All melting points (uncorrected) were determined on a Kofler apparatus (Optische Werke C. Reichert (Austria)). ^1H NMR spectra were obtained on Hitachi Perkin-Elmer R-24B (60 MHz), Varian EM 390 (90 MHz), and Bruker WM-400 (400 MHz) spectrometers, ^2H NMR Spectra were measured on a Bruker WM-400 (61.4 MHz) instrument, and ^{13}C NMR spectra were obtained on WH-90 Bruker-Physik (22.6 MHz) and Bruker WM-400 (100.6 MHz) spectrometers. IR spectra were measured on a Beckman IR photometer Acculab 4 or a Perkin-Elmer 1420. Mass spectra were taken on a Varian MAT CH 7 or a Finnigan S200. Capillary gas chromatography was performed on a Carlo Erba Strumentazione 4100 and 4200 or a Fractovap 2900 Series. Electronic integration was accomplished with a Shimadzu C-R1B Chromatopac or Spectra-Physics System I. Elemental analyses were carried out in-house. Photolyses were accomplished by irradiating at 254, 300, and 350 nm in a Rayonet photochemical reactor

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(RPR-100 (75 W/250 V; Southern New England UV Co.), while a CR-18-SG Coherent-Laser Supergraphite argon ion laser was used for irradiations at 333.6, 351.1, and 363.8 nm. Vacuum flash pyrolyses were carried out at 200–450 °C in a 35-cm-long quartz pyrolysis tube, while at 400–800 °C a Heraeus Mikro U/D was employed. Solvents or commercially available (standard suppliers) reagents and compounds were purified to match reported physical and spectral data. Known substances were prepared according to reported procedures and purified accordingly.

6,7-Benzo-3,4-dichlorospiro[bicyclo[3.2.1]octa-2,6-diene-8,1′-cyclopropane] (9). Following the procedure for a similar compound,[13] from 19.7 g (117 mmol) of 5,6-benzospiro[bicyclo[2.2.1]hepta-2,5-diene-7,1′-cyclopropane], 93.7 mL (1.17 mol) of chloroform (d = 1.48 g/cm^3), 1.50 g (6.58 mmol) of benzyltriethylammonium chloride, and 300 mL of 50% aqueous NaOH was obtained after distillation 6.98 g (24%) of colorless oil, bp 100–110 °C/0.01 Torr, which crystallized on standing, colorless needles, mp 106–107 °C. IR (CCl_4): 3080, 3060, 3015, 3005, 2960, 1630, 1470, 1330, 1170, 1070, 1035, 970, 940, 850, 810 cm^{-1}. ^{1}H NMR ($CDCl_3$; 90 MHz): δ 0.5–1.0 (m, 2 H, cyclopropane H), 1.1–1.6 (m, 2 H, cyclopropane H), 2.67 (dd, $J_{1,2}$ = 6.6, J = 0.9 Hz, 1 H, 1-H), 3.01 (s, 1 H, 5-H), 4.40 (d, J = 1.8 Hz, 1 H, 4-H), 6.43 (d, $J_{1,2}$ = 6.6 Hz, 1 H, 2-H), 7.0–7.4 (m, 4 H, benzo H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 8.04 (t, cyclopropane C), 9.74 (t, cyclopropane C), 33.67 (s, C-8), 49.26 (d, C-1), 55.02 (d, C-5), 63.33 (d, C-4), 121.54 (d, benzo C), 124.93 (d, benzo C), 126.67 (d, benzo C), 127.11 (d, benzo C), 130.02 (s, C-3), 136.43 (d, C-2), 142.37 (s, C-6), 151.47 (s, C-7). MS (70 eV): m/e 254 (2%), 252 (14%), 250 (20%, M$^+$), 222 (35%), 215 (52%), 187 (78%), 179 (91%), 165 (38%), 162 (28%), 152 (100%), 141 (81%), 128 (28%), 115 (21%), 99 (25%). Anal. Calcd for $C_{14}H_{12}Cl_2$ (251.2): C, 66.95; H, 4.82. Found: C, 67.24; H, 4.71.

6,7-Benzospiro[bicyclo[3.2.1]octa-2,6-diene-8,1′-cyclopropane] (S-2b). Following the procedure for a similar compound,[13] from 11.2 g (486 mmol) of sodium, 5.85 g (78.9 mmol) of *tert*-butyl alcohol, 150 mL of ether, and 6.98 g (27.8 mmol) of **9** was obtained after distillation 4.53 g (90%) of colorless oil, bp 113–120 °C/20 Torr, which crystallized on standing, colorless needles, mp 52–53 °C. IR (CCl_4): 3060, 3010, 2990, 2920, 2880, 2820, 1635, 1470, 1465, 1430, 1015, 720, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.4–0.8 (m, 4 H, cyclopropane H), AB signal (δ_A 2.05, δ_B 2.61, J_{AB} = 17.4 Hz, 2 H, 4-H), 2.52 (s, 2 H, 1-H, 5-H), 5.2–5.4 (m, 1 H, 3-H), 6.11 (dd, J = 10.8, 8.7 Hz, 1 H, 2-H), 7.0–7.3 (m, 4 H, benzo H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 6.74 (t, cyclopropane C), 12.69 (t, cyclopropane C), 32.18 (t, C-4), 35.53 (s, C-8), 47.19 (d, C-5), 48.31 (d, C-1), 120.27 (d, C-3), 123.45 (d, benzo C), 124.66 (d, benzo C), 125.85 (d, benzo C), 125.95 (d, benzo C), 134.12 (d, C-2), 146.26 (s, C-6), 152.42 (s, C-7). MS (70 eV): m/e 183 (6%), 182 (43%, M$^+$), 167 (25%), 154 (100%), 153 (89%), 152 (42%), 141 (22%), 128 (30%), 115 (30%). Anal. Calcd for $C_{14}H_{14}$ (182.3): C, 92.26; H, 7.74. Found: C, 92.34; H, 7.56.

6,7-Benzo-2,4,4-trideuteriobicyclo[3.2.1]octa-2,6-diene (D-2a).[7] A 100-mL round-bottomed flask was charged with 5.75 g (51.3 mmol) of potassium *tert*-butoxide and flushed three times with nitrogen gas while heating. Under a nitrogen atmosphere and with magnetic stirring, 43.1 g (513 mmol) of DMSO-d_6 (d = 1.16 g/cm^3) was added by means of a syringe. After complete dissolution of the KO-*t*-Bu was added under nitrogen and by means of a syringe 8.00 g (51.3 mmol) of 6,7-benzobicyclo[3.2.1]octa-2,6-diene (**2**), resulting in a dark brown solution. The reaction mixture was stirred for 7 days at ca. 80 °C, 100 mL of H_2O was added, the mixture was extracted (5 × 50 mL) with petroleum ether (50–70 °C) and dried over Na_2SO_4, and the solvent was rotoevaporated (ca. 30 °C/20 Torr). The brown residue was distilled at water aspirator pressure (ca. 20 Torr), affording 6.88 g (84%; 95% deuteriation) of a pale yellow liquid, bp 102–110 °C/15 Torr. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.9–2.5 (m, 2 H, 8-H), 3.28 (mc, 2 H, 1-H, 5-H), 5.25 (s, 1 H, 3-H), 7.0–7.4 (m, 4 H, benzo H). ^{2}H NMR ($CFCl_3$, 61.4 MHz): δ 1.96 (s, 1 D, 4-D), 2.49 (s, 1 D, 4-D), 6.12 (s, 1 D, 2-**D**).

Spiro[bicyclo[3.2.1]octa-3,6-diene-2,1′-cyclopropane] (6). A 500-mL three-necked flask, provided with a reflux condenser and 250-mL dropping funnel, was charged with 69.6 g (150 mmol) of (3-bromopropyl)-triphenylphosphonium bromide. From the dropping funnel was added dropwise within 2 h a suspension of 33.6 g (299 mmol) of KO-*t*-Bu and 150 mL of ether, resulting in an intense yellow reaction mixture. While cooling with an ice bath, 15.3 g (142 mmol) of bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde[8] in 60 mL of ether was added dropwise. After 40 h of reflux, the reaction mixture was poured into 600 mL of H_2O, and the ether phase was separated and extracted with H_2O (3 × 100 mL). The combined ether phases were dried over $MgSO_4$, and the solvent was rotoevaporated (ca. 30 °C/20 Torr). Distillation of the residue gave 10.2 g (54%) of a colorless liquid, bp 69–72 °C/35 Torr. IR (film): 3050, 2995, 2950, 2860, 1620, 1335, 945, 910, 890, 740 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.40 (mc, 1 H, cyclopropane H), 0.53 (mc, 1 H, cyclopropane H), 0.60 (mc, 1 H, cyclopropane H), 0.74 (mc, 1 H, cyclopropane H), 1.91 (mc, 1 H, 1-H), 1.95–2.02 (m, 2 H, 8-H), 2.70 (mc, 1 H, 5-H), 4.65 (dd, J = 1.8, $J_{3,4}$ = 9.1 Hz, 1 H, 3-H), 5.70 (dd, $J_{6,7}$ = 5.5 Hz, J = 2.7 Hz, 1 H, 7-H), 6.02 (dd, J = 6.4, $J_{3,4}$ = 9.1 Hz, 1 H, 4-H), 6.26 (dd, $J_{6,7}$ = 5.5 Hz, J = 2.8 Hz, 1 H, 6-H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.81 (t, cyclopropane C), 13.61 (t, cyclopropane C), 21.04 (s, C-2), 38.74 (d, C-1), 41.20 (t, C-8), 47.87 (d, C-5), 129.07 (d, C-3), 131.18 (d, C-7), 132.21 (d, C-4), 139.12 (d, C-6). MS (70 eV): m/e 132 (42%, M$^+$), 117 (100%), 115 (31%), 91 (51%), 79 (32%), 78 (37%), 77 (28%), 51 (21%), 39 (30%). Anal. Calcd for $C_{10}H_{12}$ (132.2): C, 90.85; H, 9.15. Found: C, 90.98; H, 9.02.

3,4,5,6-Tetrachlorospiro[tricyclo[6.3.1.0^{2,7}]dodeca-3,5,10-triene-9,1′-cyclopropane] (7). Following the procedure for a similar compound,[11] a solution of 2.00 g (15.2 mmol) of olefin **7** and 3.55 g (15.2 mmol) of tetrachloro-α-pyrone in 20 mL of dry CCl_4 was heated in an autoclave for 26 h at ca. 120 °C. After rotoevaporation (ca. 30 °C/20 Torr) of the solvent, the residue was recrystallized from methanol, resulting in 2.98 g (61%) of light brown prisms, mp 170–171 °C. IR (KBr): 3020, 3000, 1600, 1435, 1328, 1196, 1073, 938, 790, 744 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.54–0.88 (m, 4 H, cyclopropane H), 1.78–1.86 (m, 2 H, 12-H), 1.96 (d, J = 10.0 Hz, 1 H, 8-H), 3.05 (mc, 1 H, 1-H), AB signal (δ_A = 3.16, δ_B = 3.26, J_{AB} = 12.3 Hz, 2H, 2-H, 7-H), 4.91 (dd, $J_{10,11}$ = 9.3, J = 1.1 Hz, 1 H, 10-H), 5.90 (dd, $J_{10,11}$ = 9.3, J = 6.8 Hz, 1 H, 11-H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 13.32 (t, cyclopropane C), 15.60 (t, cyclopropane C), 28.96 (s, C-9), 32.02 (t, C-12), 43.30 (d, C-8), 52.31 (d, C-1), 54.64 (d, C-2), 54.74 (d, C-7), 122.40 (s, C-6), 123.83 (s, C-3), 130.38 (d, C-10), 131.66 (s, C-5), 131.87 (s, C-4), 133.48 (d, C-11). MS (70 eV): m/e 322 (1%, M$^+$), 106 (16%), 91 (66%), 79 (12%), 78 (100%), 39 (6%), 28 (9%), 18 (17%). Anal. Calcd for $C_{14}H_{12}Cl_4$ (322.1): C, 52.21; H, 3.76. Found: C, 52.42; H, 3.83.

6,7-(Trichlorobenzo)spiro[bicyclo[3.2.1]octa-3,6-diene-2,1′-cyclopropane] (8). Following the procedure for a similar compound,[12] to a solution of 5.91 g (18.4 mmol) of the above tetrachloro derivative **7** in 60 mL of dry DMSO was added dropwise within 10 min at ca. 70 °C a solution of 5.15 g (46.0 mmol) of KO-*t*-Bu in 40 mL of DMSO while stirring magnetically. The reaction mixture turned black and was allowed to stir for 2 h at ca. 70 °C. After the mixture was cooled to ca. 20 °C by the addition of 50 g of ice, the resulting brown suspension was filtered to remove solids. The dark brown filtrate was extracted (4 × 50 mL) with petroleum ether (30–50 °C), the combined organic phases were washed with saturated aqueous NaCl solution (3 × 50 mL) and dried over Na_2SO_4, and the solvent was rotoevaporated (ca. 20 °C/20 Torr) until ca. 5-mL volume. The crude product was submitted to column chromatography on 50 g of silica gel (70–230 mesh) using CH_2Cl_2 as eluent. The yellow eluate gave on rotoevaporation (ca. 20 °C/20 Torr) 540 mg (10%) of a red brown viscous oil, which was used directly in the synthesis of **S-2a** without further purification. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.2–1.0 (m, 4 H, cyclopropane H), 2.30 (s, 2 H, 8-H), 2.76 (mc, 1 H, 1-H), 3.40 (dmc, 1 H, 5-H), 4.66 (d, $J_{3,4}$ = 10.0 Hz, 1 H, 3-H), 6.02 (dd, J = 18.1, $J_{3,4}$ = 10.0 Hz, 1 H, 4-H), 6.8–7.2 (m, 1 H, benzo H).

6,7-Benzospiro[bicyclo[3.2.1]octa-3,6-diene-2,1′-cyclopropane] (S-2a). Following the procedure for a similar compound,[13] 1.14 g (49.5 mol) of sodium (freshly cut in slices) was added to a solution of 597 mg (8.05 mmol) of freshly distilled *tert*-butyl alcohol in 25 mL of dry ether. While the solution was stirred, 540 mg (1.89 mmol) of **8** was added in one portion, and stirring and refluxing under sonication (Bandelin Sonorex RK 514H) were continued for 80 h. The dark brown suspension decolorized within 20 h. After completion of the reaction, excess sodium was destroyed by careful dropwise addition of ca. 20 mL of H_2O. The phases were separated and the aqueous phase was extracted with ether (3 × 20 mL). The combined ether phases were washed with H_2O (3 × 20 mL) and dried over Na_2SO_4. After removal of Na_2SO_4 by filtration and rotoevaporation (ca. 30 °C/20 Torr) of the solvent to ca. 1-mL volume, the product **S-2a** was collected by preparative gas chromatography on an SE 30 glass column (1.5 m long, 3-mm outer diameter), using column, injector, and detector temperatures of 150, 180, and 180 °C, respectively, and a nitrogen carrier gas pressure of 1.1 kg/cm^2, affording 110 mg (32%) of a colorless oil, which crystallized on standing, colorless needles, mp 30–35 °C. IR (film): 3040, 3000, 2980, 2950, 1620, 1460, 1420, 1300, 1030, 1010, 940, 920, 890, 740, 710, 610 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.44 (mc, 1 H, cyclopropane H), 0.64–0.88 (m, 3 H, cyclopropane H), 2.28 (mc, 1 H, 1-H), 2.39 (mc, 2 H, 8-H), 3.33 (dd, $J_{4,5}$ = 6.2 Hz, J = 3.6 Hz, 1 H, 5-H), 4.64 (dd, $J_{3,4}$ = 9.3 Hz, J = 1.2 Hz, 1 H, 3-H), 6.08 (dd, $J_{3,4}$ = 9.1 Hz, $J_{4,5}$ = 6.4 Hz, 1 H, 4-H), 7.00–7.29 (m, 4 H, benzo H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 12.67 (t, cyclopropane C), 15.31 (t, cyclopropane C), 24.13 (s, C-2), 40.80 (d, C-1), 41.75 (t, C-8), 49.67 (d, C-5), 120.59 (d, C-3), 123.75 (d, C-4), 125.98 (d, benzo C), 126.28 (d, benzo C), 131.17 (d, benzo C), 131.59 (d, benzo C), 144.57 (s, C-7), 150.86 (s, C-6). MS (70 eV): m/e 182 (60%, M$^+$), 168 (22%), 167 (100%), 166 (21%), 165

(30%), 153 (27%), 152 (32%), 128 (37%), 115 (25%). Anal. Calcd for $C_{14}H_{14}$ (182.3): C, 92.26; H, 7.74. Found: C, 92.04; H, 7.84.

8,9-Benzo-2,2,7-trideuterio-4,5-diazatricyclo[4.3.1.0^{3,7}]dec-8-ene-4,5-dicarboxylic Acid *N*-Phenylimide (D-10). Following the procedure for the protium compound,[16] from 5.00 g (31.4 mmol) of olefin **D-2a** and 11.0 g (63.0 mmol) of PTAD in 100 mL of CH_2Cl_2 was obtained after 40 h of reaction time 5.00 g (48%) of colorless needles, mp 201–202 °C from EtOH (lit.[16] mp 202–203 °C for protium derivative). IR (KBr): 2940, 1780, 1720, 1500, 1420, 1270, 1260, 1150, 1140, 1120, 760, 720, 690 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.7–2.3 (m, 2 H, 10-H), 3.22 (t, 1 H, 1-H), 4.40 (mc, 2 H, 3-H, 6-H), 7.1–7.7 (m, 9 H, benzo H).

8,9-Benzo-4,5-diazaspiro[tricyclo[4.3.1.0^{3,7}]dec-8-ene-2,1′-cyclopropane]-4,5-dicarboxylic Acid *N*-Phenylimide (S-10). Following the procedure for a similar compound,[16] from 3.00 g (16.5 mmol) of olefin **S-2b** and 4.32 g (24.7 mmol) of PTAD in 100 mL of CH_2Cl_2 was obtained after 72 h of reaction time 594 mg (10%) of colorless needles, mp 165–166 °C (ethanol). IR (CCl_4): 3070, 3040, 3020, 3000, 2940, 2850, 1765, 1710, 1500, 1410 cm^{-1}. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.3–1.2 (m, 4 H, 2′-H, 3′-H), 1.6–2.2 (m, 3 H, 1-H, 10-H), 3.51 (pseudo t, $J_{3,7}$ = 4.5 Hz, 1 H, 7-H), 3.79 (d, $J_{3,4}$ = 4.5 Hz, 1 H, 3-H), 4.42 (dd, J = 8.7 Hz, J = 5.4 Hz, 1 H, 6-H), 6.9–7.6 (m, 9 H, benzo H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 10.51 (t, cyclopropane C), 15.90 (t, cyclopropane C), 26.64 (s, C-2), 34.27 (t, C-10), 42.05 (d, C-1), 47.71 (d, C-7), 55.86 (d, C-3), 64.91 (d, C-6), 123.01 (d), 125.47 (d), 126.81 (d), 127.97 (d), 129.15 (d), 131.82 (s), 132.16 (s, C-8), 144.61 (s, C-9), 155.36 (s, carbonyl C), 155.64 (s, carbonyl C). MS (70 eV): *m/e* 358 (5%, M$^+$), 357 (20%), 180 (11%), 155 (100%), 128 (13%). Anal. Calcd for $C_{22}H_{19}N_3O_2$ (357.4): C, 73.99; H, 5.36; N, 11.76. Found: C, 73.99; H, 5.34; N, 11.59.

8,9-Benzo-4,5-diaza-2,2,7-trideuteriotricyclo[4.3.1.0^{3,7}]deca-4,8-diene (D-1). Following the procedure for the protium compound,[16] from 4.00 g (12.0 mmol) of urazole **D-10** and 6.73 g (120 mmol) of KOH in 100 mL of isopropyl alcohol was obtained after subliming (90–100 °C/20 Torr) 1.71 g (76%) of colorless, waxlike crystals, mp 123–124 °C (lit.[16] mp 124–125 °C for the protium derivative). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.0–1.9 (m, 2 H, 10-H), 3.16 (mc, 1 H, 1-H), 4.6–4.7 (m, 2 H, 3-H, 6-H), 7.1–7.4 (m, 4 H, benzo H). ^{2}H NMR ($CFCl_3$, 61.4 MHz): δ 1.05 (s, 1 D, 2-D_n), 1.54 (s, 1 D, 2-D_x), 3.45 (s, 1 **D**, 7-D).

8,9-Benzo-4,5-diazaspiro[tricyclo[4.3.1.0^{3,7}]deca-4,8-diene-2,1′-cyclopropane] (S-1). Following the procedure for a similar compound,[16] from 750 mg (2.10 mmol) of urazole **S-10** and 1.17 g (21.0 mmol) of KOH in 10 mL of isopropyl alcohol was obtained after sublimation (90–100 °C/20 Torr) 70.2 mg (16%) of colorless, waxlike crystals, mp 128–135 °C. IR (CCl_4): 3040, 3000, 2880, 2870, 2830, 1530, 1500, 1490, 1470, 1250, 1200, 1020, 910, 820 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.18–0.23 (m, 1 H, cyclopropane H), 0.26–0.31 (m, 1 H, cyclopropane H), 0.42–0.48 (m, 1 H, cyclopropane H), 1.07–1.11 (m, 1 H, cyclopropane H), 1.31 (ddd, $J_{10n,10x}$ = 14.4, $J_{6,10n}$ = 9.1, J = 1.9 Hz, 1 H, 10-H_n), 1.75 (br dd, $J_{10n,10x}$ = 14.4, J = 3.6 Hz, 1 H, 10-H_x), 2.13 (br s, 1 H, 1-H), 3.46 (pseudo t, $J_{3,7}$ = $J_{6,7}$ = 5.0 Hz, 1 H, 7-H), 4.08 (br d, $J_{3,7}$ = 5.0 Hz, 1 H, 3-H), 4.74 (dd, $J_{6,10n}$ = 9.1, $J_{6,7}$ = 5.0 Hz, 1 H, 6-H), 7.04–7.36 (m, 4 H, benzo H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 7.79 (t, cyclopropane C), 13.48 (t, cyclopropane C), 21.42 (s, C-2), 26.46 (t, C-10), 45.75 (d, C-1), 46.55 (d, C-7), 78.00 (d, C-3), 84.74 (d, C-6), 122.88 (d, benzo C), 126.55 (d, benzo C), 126.90 (d, benzo C), 127.54 (d, benzo C), 134.68 (s, C-9), 144.60 (s, C-8). MS (70 eV): *m/e* 182 (5%, M$^+$–N_2), 167 (26%), 153 (15%), 152 (11%), 141 (10%), 128 (13%), 93 (100%), 92 (11%), 66 (38%), 65 (21%). Anal. Calcd for $C_{14}H_{14}N_2$ (210.3): C, 79.96; H, 6.71; N, 13.32. Found: C, 79.78; H, 6.76; N, 13.41.

Photolyses of Benzobicyclo[3.2.1]octadienes 2, D-2a, and S-2a,b. In the direct photolyses ca. 5 mmol of the olefin was dissolved in 50 mL of *n*-pentane 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 Carbowax column, operated at column, injector, and detector temperatures of 120, 160, and 160 °C, respectively, and a nitrogen carrier gas pressure of 0.5 kg/cm^2. 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 those of authentic compounds. All products were tested for photostability under the photolysis conditions. The quantitative results are collected in Table I.

3,4-Benzo-2,6,6-trideuteriotricyclo[3.2.1.0^{2,7}]oct-3-ene (D-5) from the Photolysis of Olefin D-2a. Solutions of 750 mg (4.72 mmol) of olefin **D-2a** gave on direct (50 mL of benzene) and triplet-sensitized (50 mL of acetone) irradiation after 90% conversion tricycle **D-5** as the only product (Table I). After rotoevaporation (ca. 20 °C/20 Torr) of the solvent to ca. 5-mL volume, tricycle **D-5** was collected by preparative gas chromatography on a 10% Carbowax glass column (1.5 m long, 3-mm outer diameter), employing column, injector, and detector temperatures of 140, 170, and 170 °C, respectively, and a N_2 carrier gas pressure of 0.5 kg/cm^2. ^{2}H NMR ($CFCl_3$, 61.4 MHz): δ 0.92 (s, 1 D, 7-D), 1.82 (s, 1 D, 3-D_x), 2.10 (s, 1 D, 3-D_n).

3,4-Benzospiro[tricyclo[3.2.1.0^{2,7}]oct-3-ene-6,1′-cyclopropane] (S-5) from the Photolysis of Olefin S-2a. A solution of 22.3 mg (123 μmol) of olefin **S-2a** in 30 mL of pentane gave on irradiation at 254 nm in the Rayonet reactor until 40% conversion tricycle **S-5** as the only photoproduct (Table I). Tricycle **S-5** was collected by means of preparative gas chromatography on a 10% SE 30 glass column (1.5 m long, 3-mm outer diameter), employing column, injector, and detector temperatures of 120, 150, and 150 °C, respectively, and a N_2 carrier gas pressure of 0.5 kg/cm^2. IR (CCl_4): 3080, 3060, 3000, 2970, 1630, 1450, 1430, 1340, 1260, 905 cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.21–0.31 (m, 2 H, cyclopropane H), 0.48–0.53 (m, 1 H, cyclopropane H), 0.60–0.68 (m, 1 H, cyclopropane H), 1.08 (br d, $J_{8n,8x}$ = 11.5 Hz, 1 H, 6-H_n, 8-H_n), 1.16 (ddd, $J_{1,7}$ = 7.3, $J_{2,7}$ = 5.4, $J_{5,7}$ = 1.0 Hz, 1 H, 7-H), 1.81 (ddddd, J = 7.3, 5.4, 0.5, $J_{5,8x}$ = 3.0, $J_{5,7}$ = 1.0 Hz, 1 H, 5-H), 2.12 (ddd, $J_{8n,8x}$ = 11.5, J = 5.0, $J_{5,8x}$ = 3.0 Hz, 1 H, 6-H_x, 8-H_x), 2.19 (dt, $J_{2,7}$ = 5.0, J = 1.0 Hz, 1 H, 2-H), 2.20 (pseudo t, $J_{1,7}$ = 7.3 Hz, 1 H, 1-H), 6.90–7.30 (m, 4 H, benzo H). ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 4.65 (t, cyclopropane C), 9.47 (t, cyclopropane C), 17.70 (s, C-6), 20.10 (d, C-1), 24.31 (d, C-7), 25.40 (d, C-1), 28.53 (t, C-8), 44.98 (d, C-2), 123.29 (d, benzo C), 124.01 (d, benzo C), 125.12 (d, benzo C), 126.26 (d, benzo C), 124.68 (s, C-4), 125.83 (s, C-3). MS (70 eV): *m/e* 183 (13%, M$^+$ + 1), 182 (85%, M$^+$), 181 (21%), 168 (14%), 167 (100%), 166 (24%), 155 (12%), 154 (49%), 153 (59%), 152 (52%), 151 (12%), 142 (13%), 141 (91%), 129 (35%), 128 (78%), 127 (18%), 115 (35%), 89 (10%), 77 (13%), 76 (11%). Anal. Calcd for $C_{14}H_{14}$ (182.3): C, 92.26; H, 7.74. Found: C, 92.16; H, 7.65. The benzocyclooctatriene was identified by coinjection with authentic material on several capillary GC columns and by means of capillary GC–MS.

Photolysis of Olefin S-2b. A solution of ca. 2 mg (ca. 10 μmol) of olefin **S-2b** in ca. 3 mL of pentane was irradiated as above and gave tricycle **S-5** and 3,4-benzocycloocta-1,3,5-triene as the only photoproducts, as confirmed by coinjection of the authentic material on several capillary GC columns.

Photolyses of Azoalkanes 1, D-1, and S-1. In the direct photolysis, ca. 2 mmol of the azoalkanes dissolved in 10 mL of benzene was degassed by purging with nitrogen gas for 15 min and irradiated at 350 nm for 60 min in the Rayonet reactor at ca. 40 °C until complete conversion. The reaction progress was monitored by means of capillary GC on a 50-m Carbowax glass column, using column, injector, and detector temperatures of 120, 160, and 160 °C, respectively, and a N_2 carrier gas pressure of 0.5 kg/cm^2. The triplet-sensitized irradiations were carried out as above, except that a (5–10)-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 those of the authentic compounds. All products were tested for photostability under the photolysis conditions. The quantitative results are collected in Table I. The ^{2}H NMR ($CFCl_3$, 61.4 MHz) spectra are given below. 3,4-Benzo-2,6,6-trideuteriotricyclo[3.2.1.0^{2,7}]oct-3-ene (**D-5**): δ 0.92 (s, 1 D, 6-D), 1.82 (s, 1 D, 6-**D**), 2.10 (s, 1 D, 2-D). 6,7-Benzo-2,4,4-trideuteriobicyclo[3.2.1]octa-2,6-diene (**D-2a**): δ 1.96 (s, 1 D, 4-D), 2.49 (s, 1 D, 4-D), 6.12 (s, 1 D, 2-D). 6,7-Benzo-2,8,8-trideuteriobicyclo-[3.2.1]octa-2,6-diene (**D-2b**): δ 2.04 (s, 1 D, 8-D), 2.30 (s, 1 D, 8-**D**), 6.12 (s, 1 **D**, 2-D).

Detection of Diazoalkane in the Laser Photolysis of Azoalkane S-1. A solution of 55.7 mg (170 μmol) of azoalkane **S-1** (freshly sublimed) in 2 mL of dry tetrahydrofuran was degassed for 15 min with dry N_2 and irradiated for ca. 20 min at ca. 60 °C with the 334 nm (ca. 1 W) of the argon ion laser. After rotoevaporation (0 °C/20 Torr) of the solvent, the IR spectrum showed the characteristic absorption at 2060 cm^{-1} and the visible spectrum at 450 nm of the diazo group. On heating of the photolysate at ca. 80 °C for 30 min these absorption bands disappeared. Analysis by capillary GC revealed small quantities (<1%) of a new volatile product, presumably a carbene product of the diazoalkane, but this product could not be characterized because of insufficient material.

Thermolyses of Azoalkanes 1, D-1, and S-1. About 200 μmol of the freshly sublimed azoalkanes were placed into a 10-mL flask and volatilized slowly at ca. 80 °C/20 Torr directly into the Pyrex pyrolysis tube (35 cm long, 1-cm outer diameter), 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 gas chromatography. 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 to the pyrolysis conditions.

Kinetics. A ca. 5 μM stock solution of the azoalkane in ethylene glycol or decalin was prepared, containing quinoline or benzophenone as internal standard. The solution was degassed by purging for 15 min with N_2 gas and ca. 5-μL aliquots were transferred into melting point capillaries by means of a syringe, evacuated at water aspirator pressure (ca. 20 Torr) and sealed. Bundles of ca. 20 such tubes were placed into a constant (ca. ±0.15 °C) temperature bath (Fischer Spaltrohrsystem Model 0200/01) at 150–220 °C. After thermal equilibration (ca. 20 min), every 15 min a tube was removed, allowed to cool, and submitted to quantitative capillary gas chromatography, using a 40-m OV-101 column, operated at column, injector, and detector temperatures of 140, 250, and 250 °C, respectively, and a N_2 carrier gas pressure of 1.5 kg/cm^2. Electronic integration against the internal standard afforded the concentration–time data. The rate data were processed according to first-order kinetics to obtain the rate constants and from those the activation parameters according to the Eyring equation. The results are summarized in Table II.

Theoretical Calculations. The enthalpies of formation were calculated by means of the MNDO3 program.[19] All input parameters were optimized and processed without time limit, using an Olivetti M24 personal computer equipped with an arithmetic coprocessor (Intel 8087). The results are summarized in Table III.

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Conformational Properties of the THYME Polyethers. The Bis-THYME Cylinder: A Three-Dimensional Analogue of 18-Crown-6

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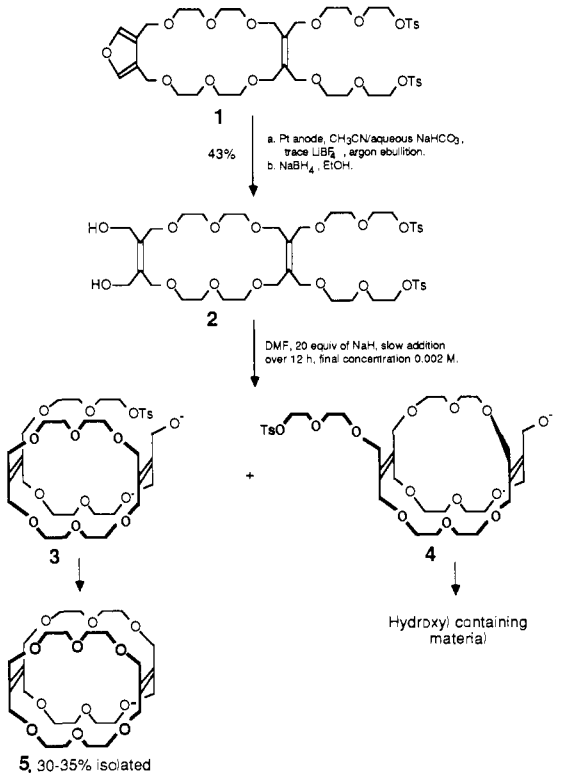
Abstract: The synthesis and crystal structure of the lowest homologue of the series of macropolycyclic tetrakis(hydroxymethyl)ethylene (THYME) fused-crown ethers, bis-THYME cylinder **5**, are described. Compound **5** was designed as a cylindrical host with a hydrophilic interior surface—a three-dimensional analogue of the "flat" host 18-crown-6. The characterization by X-ray crystallography of the novel trinuclear cascade complex $[K_2(OH_2)\cdot\mathbf{5}]^{2+}[PtCl_3(CH_3)_2SO]_2^-$ (**7**) serves to demonstrate that indeed, at least in the crystalline phase, host **5** does behave as a hydrophilic cylinder and is a remarkably faithful three-dimensional 18-crown-6 analogue. In addition, as the starting point for molecular mechanics study of the THYME polyethers, the free and bound forms of ligand **5** are characterized using MMII and compared with 18-crown-6.

We have recently reported on synthesis of several members of a novel class of molecules composed of crown ether rings fused by the tetrakis(hydroxymethyl)ethylene (THYME) unit.[2] The rationale motivating this project derives from the two separate, though somewhat related, research areas: host–guest chemistry[3] and topological stereochemistry.[4]

In both of these areas, knowledge of the *conformational properties* of the target THYME polyethers is crucially important. In this paper we report experimental details for synthesis of the simplest member of the series, bis-THYME cylinder **5**, details of the crystal structures of two crystalline forms of the material, and the crystal structure of a novel trinuclear cascade complex derived from this host. The results serve as a starting point for exploration of the applicability of the Allenger empirical force-field method[5] for modeling of the THYME polyethers.

Scheme I. Synthesis of the Bis-THYME Cylinder



Synthesis of the Bis-THYME Cylinder. From pioneering studies

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