Nitrogen Extrusion from the Bis-Azoalkane [*anti*(*syn*)]-7,7'-Bi-2,3-diazabicyclo[2.2.1]hept-2-ene[1]

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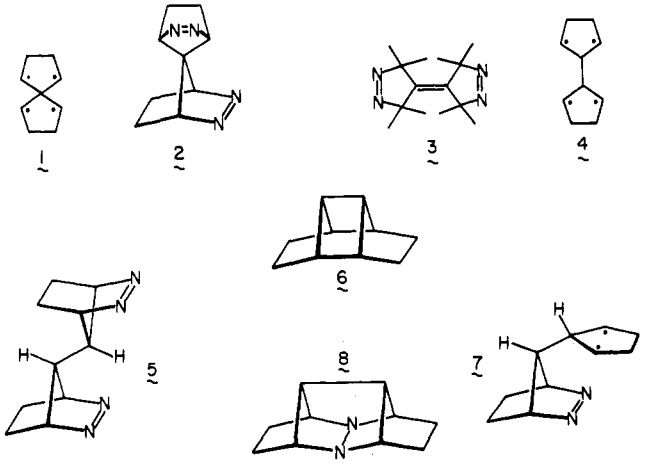
Abstract: The bis-azoalkane **5** has been synthesized and its loss of nitrogen studied under photochemical and thermal conditions. Even with intense argon laser irradiation, the photolysis of **5** proceeds through a stepwise loss of nitrogen to form the four isomeric azoalkanes **11a–d**. Prolonged irradiation leads to the further loss of nitrogen and the formation of the three isomeric bibicyclo[2.1.0]pentanes **12a–c**. Under the laser conditions applied in this work, no evidence was obtained for the formation of the tetrayl **4** through the simultaneous or near simultaneous loss of both nitrogen units. Thermolysis of **5** afforded similar results. At 450 °C, 1,1'-bicyclopentene (**13**) was the major product. This substance was shown to arise from the isomerization of the bibicyclo[2.1.0]pentanes **12**. The ratios of products derived from **5** and the isomers of **11** through the loss of nitrogen are dependent upon the reaction conditions, direct or sensitized photolysis and thermolysis. These product ratio studies provide some interesting insights into the possible mechanisms of these nitrogen extrusion reactions.

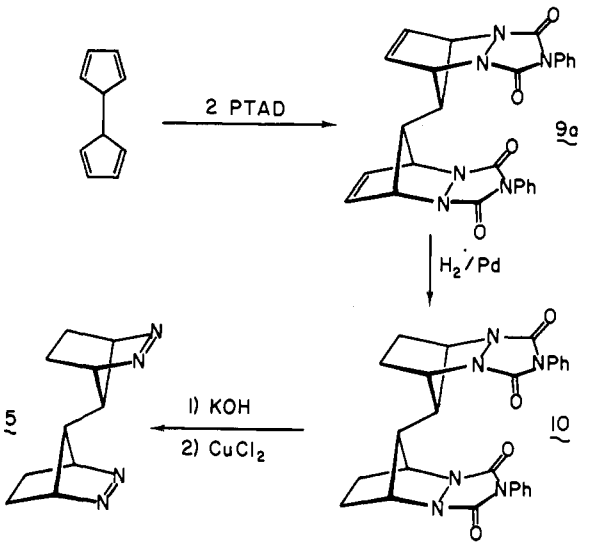
Recently, Dougherty and co-workers have discussed the formation of the tetrayl **1** derived from a double extrusion of nitrogen from the bis-azoalkane **2**.[3] Other bis-azoalkanes are known from which tetrayl formation might be feasible.[4] However, in the case of **3**, for example, no tetrayl formation has been observed.[5] In this account we wish to report our initial efforts to observe the formation of the tetrayl **4** through the nitrogen extrusion from the bis-azoalkane **5**. This system is particularly appealing since the tetrayl **4** might be expected to collapse to the known hydrocarbon **6**.[6] Consequently, the observation of **6** among the nitrogen extrusion products of **5** might be taken as evidence for the formation of tetrayl **4**. The additional intriguing possibility exists that a single nitrogen extrusion from the *anti*-diazabicycloheptene moiety of **5** would give rise to the diyl **7**, which in turn might undergo intramolecular trapping[7] with the remaining azo linkage to form the hydrazine **8**.



Synthesis of the Bis-Azoalkane 5. The bis-azoalkane **5** is readily available from the known biurazole **9**, which is formed in the double Diels–Alder addition of *N*-phenyltriazolinedione (PTAD) to 9,10-dihydrofulvalene (Scheme I).[8] Catalytic hydrogenation of **9** to the saturated biurazole **10** followed by hydrolysis and oxidation affords the bis-azoalkane **5** in high yield.

The stereochemistry of the double PTAD adduct with 9,10-dihydrofulvalene was not established previously.[8] In this work a single-crystal X-ray structure determination for the bis-azoalkane **5** derived from Paquette's PTAD adduct **9** demonstrates that the series of compounds shown in Scheme I has the unsymmetrical

Scheme I



anti–syn stereochemistry (see Figure 1 and the Experimental Section for the crystallographic parameters).[9]

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(1) For a preliminary communication of this work, see: Adam, W.; Hannemann, K.; Peters, E.-M.; Peters, K.; Schnering, H. G.; Wilson, R. M. *Angew. Chem.* **1985**, *97*, 417 (*Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 421).
(2) This work constitutes part of the Ph.D. Thesis of K. Hannemann, Würzburg, 1984.
(3) (a) McElwee-White, L.; Goddard, W. A., III; Dougherty, D. A. *J. Am. Chem. Soc.* **1984**, *106*, 3461. (b) McElwee-White, L.; Dougherty, D. A. *Ibid.* **1984**, *106*, 3466.
(4) Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.
(5) Bushby, R. J.; Mann, S.; Jesudason, M. V. *Tetrahedron Lett.* **1983**, *24*, 4743.
(6) Paquette, L. A.; Davis, R. F.; James, D. R. *Tetrahedron Lett.* **1974**, 1615. We thank Professor Paquette for providing us with an ^1H NMR spectrum of the hydrocarbon **6**.
(7) For other examples of intramolecular diyl trapping reactions, see: Little, R. D.; Muller, G. W. *J. Am. Chem. Soc.* **1979**, *101*, 7129. Little, R. D.; Stone, K. J. *Ibid.* **1983**, *105*, 6976.
(8) Paquette, L. A.; Wyvratt, M. J.; Berk, H. C.; Moerck, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 5845.
(9) The stereochemical descriptors, anti–syn and endo–exo, used in this paper for compounds **5**, **11a–d**, and **12a–c** are applied in accord with section 203(B) and -(C) of Appendix IV to the 1985 *Chemical Abstracts Index Guide*. Thus, for **5** and **11a–d** the anti and syn descriptors reference the configuration of the one-carbon bridge of the 2,3-diazabicyclo[2.2.1]hept-2-ene moieties to the azo bridge. For **11a–d** and **12a–c**, the endo and exo descriptors reference the configuration of the one-carbon bridge of the bicyclo[2.1.0]-pentane moieties to the two-carbon bridge. We thank K. L. Loening for his suggestions regarding the nomenclature of these molecules.

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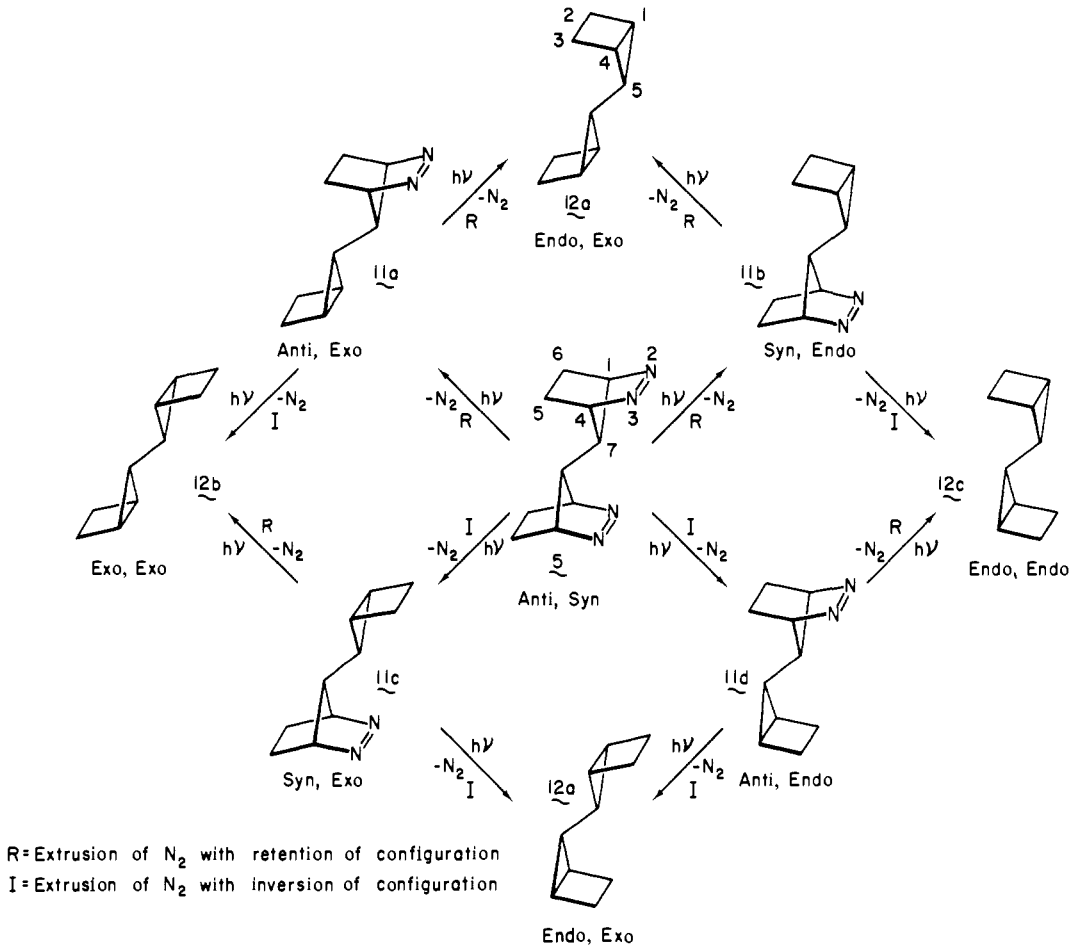
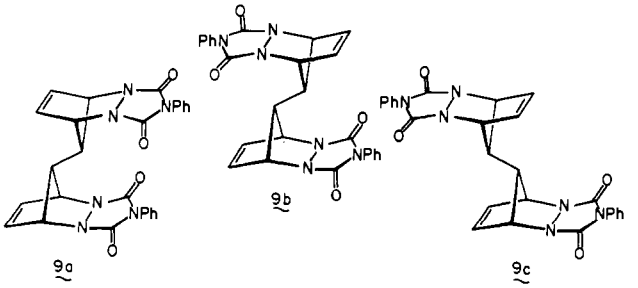
Scheme II



No particular mechanistic significance is attached to the formation of **9a** as the major isolable adduct in the PTAD addition to 9,10-dihydrofulvalene. This may be simply an artifact of the isolation procedure, since substantial quantities of insoluble material are formed in this reaction. From this insoluble residue, a small quantity of a sparingly soluble substance could be obtained which had MS and IR properties which were very similar to those of **9a** but which exhibited a 400-MHz ^{1}H NMR spectrum that indicated it had a symmetrical structure. These data are consistent with either the symmetrical syn,syn- or more probably the anti,anti bis-adduct, **9b** or **9c**, respectively.[10] Nevertheless, due to the extreme insolubility of this material, its further characterization and conversion to the bis-azoalkane were not pursued. The more readily manipulated unsymmetrical adduct **9a** was the sole source of bis-azoalkane starting material used in the studies described below.



Low-Intensity Irradiation of the Bis-Azoalkane 5. The direct irradiation of the bis-azoalkane **5** at 350 nm in a Rayonet photochemical reactor gave rise to seven products. The progress of the reaction was monitored by means of capillary GLC. In the early stages of the photolysis, four products with comparable retention times could be detected (see Table I and Scheme II). As the photolysis proceeded, three additional photoproducts with much shorter GLC retention times appeared. Prolonged irradiation leads to the disappearance of the four initially formed products until only the three short retention time products remained. Benzophenone-sensitized photolysis of **5** leads to the formation of the same products with a similar time profile but with somewhat different product ratios (see Table I and Scheme II).

By use of a combination of column chromatography on silica gel and preparative GLC, compounds **11a,b,d**, and **12a,b** could be isolated as pure substances, but **11c** was obtained contaminated with **11a** and **12c** with **12a**.

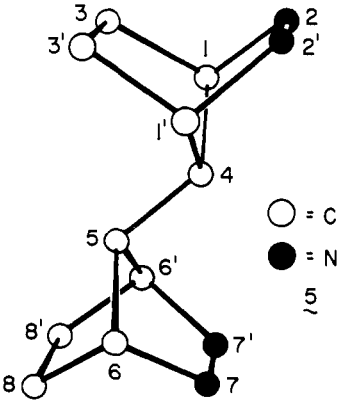


Figure 1. Drawing of the anti-syn bis-azoalkane **5** derived from X-ray crystallographic data. See Tables VI and VII for the structural parameters of **5**.

(10) The PTAD addition to 5-methylcyclopentadiene gave the anti isomer as the major product. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688. See also ref 14b.

Table I. Photochemical and Thermal Extrusion of Nitrogen from the Bis-Azoalkane 5

		monoazoalkanes 11a–c[a]					bibicyclopentanes 12[a]				
			isomer ratios 11a:11b:11c:11d					isomer ratios 12a:12b:12c			
	conversion of 5 (%)	yield 11a–c (%)	11a	11b	11c	11d	yield 12a–c (%)	12a	12b	12c	yield 13 (%)
					Direct Photolysis[b]						
irradiation time (min)											
1	4	4	32	8	16	44	traces				
6	61	43	31	8	17	44	18	55	28	17	
35	100	traces					100	55	27	18	
					Sensitized Photolysis[c]						
irradiation time (min)											
1	33	29	19	33	20	28	4	57	20	23	
4	78	44	18	34	20	28	34	55	20	25	
12	100	traces					100	56	19	25	
					Pyrolysis						
temp (°C)											
240	37	34	26	5	5	64	3	37	27	42	traces
290	93	65	33	2	3	61	21	46	34	20	2
350	100	5	64			36	84	38	51	11	4
410	100	0					66	37	52	11	21
450	100	0					40	37	51	12	41

[a] Determined by capillary GLC:error ±1%. [b] 1×10^{-2} M 5 in benzene irradiated at 350 nm. [c] 1×10^{-2} M 5 and 8×10^{-2} M benzophenone in benzene irradiated at 350 nm.

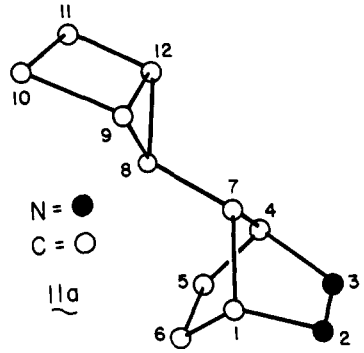


Figure 2. Drawing of the anti-exo monoazoalkane 11a derived from X-ray crystallographic data. See Tables VIII and IX for the structural parameters of 11a.

The ^{1}H NMR spectra of the four initially formed products, 11a–d,[9] each exhibited only a single signal for the bridgehead protons in the δ 4.7–5.2 region as well as signals for cyclopropyl protons in the δ 1–0 region. In addition they all exhibited UV absorption between 330 and 350 nm, and an elemental analysis of the isomer mixture was in accord with an elemental composition of $C_{10}H_{14}N_2$. The ^{1}H NMR spectra of the three terminal photoproducts, 12a–c,[9] exhibited signals only in the aliphatic region (δ <2.5) and had an elemental analysis that indicated these products were nitrogen free. These data indicate that the bisazoalkane 5 extrudes nitrogen in a stepwise fashion and that each azo linkage undergoes nitrogen extrusion to form a bicyclo[2.1.0]pentane moiety in a fashion analogous to the parent 2,3-diazabicyclo[2.2.1]hept-2-ene.[11,12]

The stereoisomers that might be formed through nitrogen extrusion from the bisazoalkane 5 are outlined in Scheme II. The loss of a single nitrogen molecule from 5 would lead to the four monoazobicyclopentane isomers, 11a–d. Whereas, the loss of the second nitrogen unit would be expected to form only the three bibicyclopentane isomers, 12a–c.

The assignment of stereochemistry to these products has been greatly facilitated through a single-crystal X-ray study of the monoazoalkane 11a (Figure 2). This isomer has an anti-substituted diazabicyclo[2.2.1]heptene moiety and an exo-substituted bicyclo[2.1.0]pentane moiety.[9] The stereochemistries of all of the other isomers of 11 and 12 could be related to the firmly established stereochemistry of 11a as follows. Irradiation of each of the monoazoalkane isomers 11a–d yielded only two of the three possible bibicyclo[2.1.0]pentane isomers 12a–c (see Scheme II and Table II). In all cases, the unsymmetrical *endo,exo*-bibicyclopentane 12a is one of the two isomers formed. For example, irradiation of 11a yields this common isomer, which must have structure 12a, and another more symmetrical isomer, which could only have the exo,exo stereochemistry, 12b. The remaining bibicyclo[2.1.0]pentane isomer must then be assigned the endo,endo stereochemistry of 12c. Furthermore, the *exo,exo*-bibicyclopentane 12b was formed from both 11a and 11c. Since 11c must have the exo configuration at the bicyclopentane moiety (the same configuration as 11a), it must have the syn configuration at the diazabicycloheptane moiety (the opposite configuration as 11a). The remaining two monoazoalkane isomers, 11b and 11d, must contain a *endo*-bicyclopentane moiety. However, the relative configurations of the diazabicycloheptene moieties in 11b and 11d could not be assigned on the basis of these photochemical correlations alone. Fortunately, it was noted that 11a was formed during the thermolysis of 11d at 370 °C. This could only occur through the well-known thermal isomerization of the bicyclo[2.1.0]pentane system,[13,14] and thus, 11a and 11d should have the

Table II. Direct and Sensitized Photolyses of the Monoazoalkanes 11

monoazoalkanes 11a–d	relative isomer distribution direct photolysis,[a,b] % 12a	12b	12c	relative isomer distribution sensitized photolysis,[a,c] % 12a	12b	12c
11a	39	61		52	48	
11b	52		48	56		44
11c[d]	50	50		57	43	
11d	72		28	63		37

[a] Relative isomeric distribution determined by capillary GLC (±1%). [b] Ca. 1×10^{-2} M azoalkane in benzene, irradiated at 350 nm. [c] Ca. 1×10^{-2} M azoalkane and 5×10^{-2} M benzophenone in benzene, irradiated at 350 nm. [d] 85% pure, contains 15% 11b.

(11) (a) Thomas, T. F.; Steel, C. *J. Am. Chem. Soc.* **1965**, *87*, 5290. (b) Solomon, B. S.; Thomas, T. F.; Steel, C. *Ibid.* **1968**, *90*, 2249.
(12) (a) Roth, W. R.; Martin, M. *Liebigs Ann. Chem.* **1967**, *702*, 1. (b) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695.
(13) Roth, W. R.; Enderer, K. *Liebigs Ann. Chem.* **1970**, *733*, 44.

Table III. ^{13}C NMR Data for the Monoazoalkanes **11** and the Bibicyclopentanes **12**[a]

	bicyclo[2.1.0]pentane units						diazabicyclo[2.1.0]heptene units					
	C(1,4)[b]		C(5)[b]		C(2,3)[c]		C(1,4)[b]		C(7)[b]		C(5,6)[c]	
	5-exo	5-endo	5-exo	5-endo	5-exo	5-endo	7-anti	7-syn	7-anti	7-syn	7-anti	7-syn
12a	22.08	17.29	22.63[e]	21.69[e]	23.36	19.11						
12b	20.32		28.48		22.95							
12c		16.76		14.09		19.06						
11a	20.68		24.26		22.73		78.94		54.50		18.62	
11b		17.21		16.79		18.28		80.79		47.59		21.25
11c	20.61		24.04		22.52			80.51		54.47		20.89
11d		17.0		17.00		18.50	78.73		45.24		18.50	
5							77.95[e]	79.53[e]	46.87[e]	51.19[e]	17.96	20.89
2,3-diazabicyclo[2.2.1]hept-2-ene[f]							76.0		40.5[c]		20.3	
bicyclo[2.1.0]pentane[d]	13.8		15.9		23.5							

[a] In $CDCl_3$, in ppm downfield from Me_4Si. [b] Displays a doublet in off-resonance spectrum. [c] Displays a triplet in off-resonance spectrum. [d] Reference 15. [e] Assignment uncertain. [f] Reference 16.

Table IV. Flash Vacuum Pyrolyses of the Monoazoalkanes **11a** and **11d** and the Bibicyclopentane **12a**[a]

			bibicyclopentanes **12**					
				isomer ratios **12a**:**12b**:**12c**				
compd	temp (°C)	conversion (%)	yield **12a–c** (%)[b]	**12a**	**12b**	**12c**	yield **13** (%)[b]	yield other (%)[b]
11a	290	5	100	50	33	17	0	traces
	350	92	94	37	53	10	2	4
	410	100	61	37	51	12	23	16
11d	320	54	83	42	43	14	1	16[c]
	410	100	45	36	51	13	37	18
12a	290	46	99	54	35	8	traces	1
	350	63	82	42	49	9	3	15
	410	98	12	23	64	13	43	45

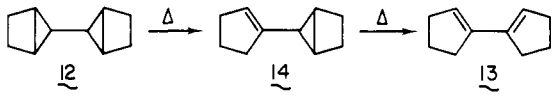
[a] Product analysis by means of capillary GLC (±1%). [b] Percentage of the isolated product mixture. [c] Contains 14% of the azoalkane **11a**.

same stereochemistry in the diazabicycloheptene moiety. Consequently, **11d** must be anti with respect to the diazabicycloheptene moiety and endo with respect to the bicyclopentane moiety. This leaves **11b**, which must have the syn,endo configuration.

These structural assignments are strongly supported by the NMR data for these compounds. The ^{13}C NMR spectra for the bibicyclopentanes **12b** and **12c** exhibit only three signals, in accord with their assignments to the more symmetrical structures. In contrast, the spectrum of **12a** displays six signals (Table III). The exo,exo and endo,endo configurations can be assigned to the more symmetrical isomers **12b** and **12c**, respectively, on the basis of their ^1H NMR spectra. The signal for the proton on C(5) in **12b** (see Scheme II for position assignments), δ 0.78, is a singlet; the signal for the analogous proton in **12c**, δ 0.45, is a triplet. In other bicyclo[2.1.0]pentanes, the C(5) proton exhibits no coupling with the bridgehead protons if they bear a trans relationship to each other.[14b] Thus, the lack of coupling in this signal for **12b** is consistent with its assignment as the exo,exo isomer, and the 5-Hz coupling constant observed for **12c** is consistent with its assignment as the endo,endo isomer. In a similar fashion, the observation of this type of coupling in **11b** and **11d** confirms the endo geometry for these bicyclopentane moieties, and the lack of this coupling in **11a** and **11c** is in accord with an exo geometry for these bicyclopentane units.

In addition, the chemical shifts of the signals in the ^{13}C NMR spectra of these compounds are quite sensitive to the configuration of the substituents (Table III). In general, the ^{13}C signals of the 5-endo-substituted bicyclopentane moieties (**11b**, **11d**, and **12c**) occur at higher field than those of the exo-substituted moieties. In contrast, the bridgehead and bridge carbons, C(1,4) and C(5,6), respectively, of the diazabicycloheptene moieties appear at lower field in the 7-syn-substituted units.[17] The chemical shifts of C(7) carbon signals of the diazabicycloheptene system seem to be determined by the endo or exo configuration of the attached bicyclopentane unit rather than by the configuration of the diazabicycloheptene system itself.

Scheme III



Laser Photolysis of the Bis-Azoalkane 5. In an effort to excite both azo chromophores in the bis-azoalkane **5** and form the tetrayl **4**, a benzene solution of **5** was irradiated with a focused argon ion laser beam (all UV lines, total output 3 W). Experiments of this type were conducted both with and without benzophenone as a sensitizer. In all cases, only the usual photoproducts, **11a–d** and **12a–c**, were observed. Analysis by capillary GLC displayed no peaks that might be ascribed to either **6** or **8**, and time-resolved analysis indicated that nitrogen extrusion occurs in a stepwise fashion just as in the low-intensity experiments.

Pyrolysis of the Bis-Azoalkane 5. Flash vacuum pyrolysis of the bis-azoalkane **5** at temperatures above about 240 °C gave rise to the same products, **11a–d** and **12a–c**, observed in the photochemical studies (Table I). The ratios of the bibicyclopentane isomers, **12a–c**, were found to vary with the pyrolysis temperature below about 350 °C but became constant above this temperature. Essentially the same bibicyclopentane isomer ratios were observed when the monoazoalkanes **11a** and **11d** were subjected to flash vacuum pyrolysis at higher temperatures (Table IV). In these pyrolyses, each monoazoalkane **11a–d** gave rise to all three of the bibicyclopentane isomers **12a–c**. This is easily rationalized as being due to the known thermal isomerization of bicyclopentane systems.[13,14] In a control experiment the pure bibicyclopentane isomer **12a** was thermally converted to the other two isomers, **12b** and **12c** (Table IV). In addition, partial thermolysis of the monoazoalkane **11d** led to the formation of the isomerized monoazoalkane **11a** in 14% yield.

Pyrolysis of the bis-azoalkane **5** at temperatures higher than 300 °C led to the formation of a new product in addition to the normal products. Above 450 °C, this new substance became the major product and could be isolated by preparative GLC. It was shown to have the bicyclopentene structure **13** by comparison with

(14) (a) Tufariello, J. J.; Bayer, A. C.; Spadaro, J. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 3309. (b) Tufariello, J. J.; Chang, J. H.; Bayer, A. C. *Ibid.* **1979**, *101*, 3315.

(15) Christl, M. *Chem. Ber.* **1975**, *108*, 2781.

(16) Snyder, J. P., University of Copenhagen, personal communication to M. Christl, University of Würzburg.

(17) Similar observations have been made with related compounds: Adam, W.; Hannemann, K.; Wilson, R. M., unpublished results.

Table V. Ratios of Inversion to Retention in the Nitrogen Extrusion from the Bis-Azoalkane 5[a] and the Monoazoalkanes 11a–d[b]

compd	stereochem of azo from which N_2 extrusion occurred	inversion:retention product	inversion:retention		
			thermolysis at 240 °C	direct irradiation	sensitized irradiation
5	syn	**11d:11a**	2.5:1	1.4:1[c]	1.5:1[c]
	anti	**11c:11b**	1:1	2.0:1[c]	1:1.7[c]
11a	anti	**12b:12a**		1.6:1	1:1.1
11b	syn	**12c:12a**		1:1.1	1:1.3
11c	syn	**12a:12b**		1:1	1.3:1
11d	anti	**12a:12c**		2.6:1	1.7:1

[a] Values calculated from data in Table I and rounded to ±0.1. [b] Values calculated from data in Table II and rounded to ±0.1. [c] After 1 min of irradiation.

authentic material.[18] This same material was also formed from the pyrolysis of the monoazoalkanes **11a** and **11d** and bibicyclopentane **12a** (Table IV). Consequently, **13** is clearly a secondary product arising from the bicyclopentane–cyclopentene isomerization shown in Scheme III.[11,12] These complex pyrolyses mixtures contained other minor products that could not be isolated and identified, but presumably these minor products included the intermediate cyclopentenylbicyclopenatane isomers **14**.

Discussion

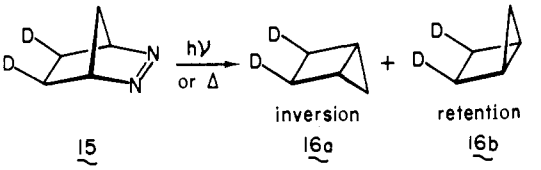
In this initial study, evidence in support of the formation of the tetrayl **4** from the bis-azoalkane **5** was not obtained. Instead, nitrogen extrusion from this azoalkane occurs in a sequential fashion under all conditions employed in this work: direct or sensitized photolysis and flash vacuum pyrolysis. Even high-intensity UV light delivered by means of a focused argon ion laser beam (ca. 10^{22} photons/(cm^2-s)) was ineffective in forming the tetrayl **4**. Apparently, formation of the tetrayl **4** from the bis-azoalkane **5** will require more specialized conditions such as irradiation in low-temperature matrices or with more powerful pulsed laser sources.

Because of the unsymmetrical nature of the *anti,syn*-bis-azoalkane **5**, the first nitrogen extrusion can lead to different products depending on whether the nitrogen is lost from the anti or syn azo moiety. An extrusion of nitrogen from the anti moiety would give rise to the monoazoalkanes **11b** or **11c** (Scheme II). Whereas, extrusion from the syn moiety would give rise to the monoazoalkanes **11a** or **11d**. The data outlined in Table I indicate that there is a distinct preference for the loss of nitrogen from the syn moiety in **5** upon direct photolysis or thermolysis. Thus, the ratios (**11a** + **11d**):(**11b** + **11c**) for direct photolysis is 3.2:1 and for pyrolysis is ca. 9:1. In contrast, the loss of nitrogen in the sensitized photolysis does not display a similar preference; (**11a** + **11d**):(**11b** + **11c**) is 1:1.1. Furthermore, the syn-substituted monoazoalkanes **11b** and **11c** seem to be less stable than their anti-substituted counterparts, **11a** and **11d**. This correlation is most conspicuous in the pyrolysis of **5** at 350 °C, where none of the isomers of **11** containing the *syn*-azoalkane units, **11b** and **11e**, could be detected among the reaction products.

In the thermal decompositions, it would seem reasonable to attribute the lower stability of the *syn*-azoalkane units to the more sterically congested environment of the departing nitrogen molecule. Thus, the extrusion of nitrogen from the *syn*-azoalkane units might be assisted to a greater extent by relief of this steric strain.

The interpretation of the photochemical results is less straightforward. It is unlikely that differences in the absorption coefficients of the anti and syn azo chromophores play a significant role in the direct photolyses. Known 7-*anti*- and 7-*syn*-azoalkane isomers display only small differences in their extinction coefficients.[10,14b] Therefore, both azo chromophores in **5** probably undergo excitation with more or less equal efficiencies. The fact that the relative labilities of the singlet excited azo moieties parallels their relative thermal labilities, the syn configuration more labile than the anti configuration, indicates that at least to some extent the singlet excitation is exchanged between the azo units via intramolecular Förster singlet–singlet energy transfer.[19] If

Scheme IV



the same relative ease of nitrogen extrusion is followed in the triplet azo states, and there seems to be no obvious reason why it should not be, then the approximately statistical (1:1) loss of nitrogen from the anti and syn azo units would suggest that intramolecular triplet–triplet energy transfer between the azo moieties is appreciably slower than carbon–nitrogen bond cleavage. Of course it must be stressed that any quantitative assessment of the relative ease of nitrogen extrusion from the anti and syn units of **5** is complicated by the further loss of nitrogen from the products, **11a–d**. Thus, before any meaningful conclusions can be drawn from these qualitative observations a thorough quantum yield study would have to be conducted and these results compared with data from simple 7-anti- and 7-syn-substituted diazabicyclo[2.2.1]-heptenes.

Yet another very interesting aspect of the nitrogen extrusions from 2,3-diazabicyclo[2.2.1]heptenes is the stereochemistry of the resulting bicyclo[2.1.0]pentanes. Roth and Martin found that both pyrolysis and direct irradiation of the exo-deuteriated azoalkane **15** afforded the inversion product **16a** as the major isomer (Scheme IV).[12a] A similar preference for the inversion products has been observed for the 7-spirocyclpropyl-[13,20] and the 5-methoxy-2,3-diazabicyclo[2.2.1]hept-2-enes.[21] However, direct irradiation of other 7-substituted azoalkanes leads to retention as the major decomposition pathway.

In this work the stereochemical consequences of the nitrogen extrusions from the bis-azoalkane **5** and the monoazoalkanes **11a–d** are summarized in Table V. Thermal decomposition of **5** leads to an excess of the inversion product **11d** when the nitrogen is lost from the syn azo unit and about equal amounts of the inversion and retention products when the nitrogen is lost from the anti azo unit. Direct irradiation of **5** also leads to net inversion. However, in this case inversion predominates whether the nitrogen is lost from the syn or the anti azo unit. Inversion is also the favored mode of decomposition upon the direct irradiation of the monoazoalkanes **11a** and **11d**. In contrast, the direct irradiation of the monoazoalkanes **11b** and **11c** leads to about equal amounts of inversion and retention.

The inversion–retention ratios for the thermolysis and photolysis of **5** (Table V) may not provide an accurate quantitative measure of the kinetic behavior of the singlet biradicals derived from **5**. These ratios could be altered through the subsequent thermal isomerization of the bicyclopentane units[12,14] or through the loss of a second nitrogen molecule from the azoalkane units of the products **11a–d**. Nevertheless, the ratios recorded for both the thermolysis and direct photolysis of **5** would seem to indicate a

(18) Greidinger, D. S.; Ginsburg, D. *J. Org. Chem.* **1957**, *22*, 1406.

(19) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978.

(20) Adam, W.; Oppenländer, T.; Zang, G. *J. Org. Chem.* **1985**, *50*, 3303.

(21) Allred, E. L.; Smith, R. L. *J. Am. Chem. Soc.* **1969**, *91*, 6766.

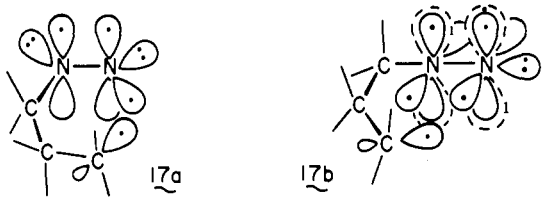
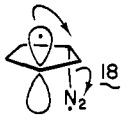


Figure 3. Electronic configurations of a σ,σ-diazenyl biradical (**17a**) and of a σ,π-diazenyl biradical (**17b**).

distinct tendency for these biradicals to collapse with net inversion.

Both the thermal and unsensitized photochemical decomposition processes would be expected to proceed through singlet biradical species. Various mechanisms involving either symmetrical or unsymmetrical carbon–nitrogen bond cleavage and in which the nitrogen may play a crucial role in biasing the incipient biradical in favor of inversion have been proposed. For example, if the loss of nitrogen occurs in a stepwise process, the intermediate diazenyl biradical might be generated in different singlet states depending upon whether it is formed in a thermal or photochemical process. Theoretical calculations for diimines[22] which can be easily extrapolated to azoalkanes indicate that thermolysis might proceed through the σ,σ-diazenyl biradical **17a** shown in Figure 3. Whereas, direct irradiation might produce the σ,π-diazenyl biradical **17b**. According to this model, thermolysis and photolysis could produce nitrogen-free 1,3-biradicals on different regions of their hypersurface, and this could lead to different inversion–retention ratios. Alternatively, a diazenyl biradical such as **18** might collapse via backside attack of the carbon-centered radical on the diazenyl carbon with displacement of nitrogen.[12b] A

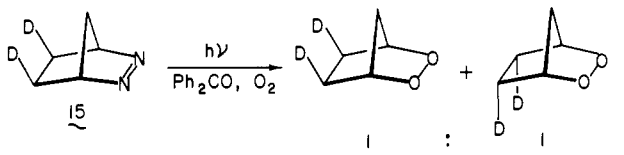


contribution from this type of stepwise process might well account for the inversion excess. On the other hand, it has been argued that a biradical in which both carbon–nitrogen bonds have broken, but where the nitrogen molecule is still in close proximity to the biradical, may be involved in the inversion process.[23] In this model the nitrogen is used to perturb the biradical orbitals in favor of collapse with inversion. In support of all of these models in which the nitrogen plays an active role in the determination of the product stereochemistry is the observation that at low pressure in the gas phase, where nitrogen is lost more readily and where vibrationally hot biradicals can result, a more or less statistical inversion–retention ratio results.[12b] This observation would also seem to exclude a "recoil" mechanism for singlet biradical inversion in solution[21], since such a mechanism would seem to require a nitrogen-free and presumably hot biradical.

On the basis of these considerations, it is interesting to note that for the direct irradiation of **5** and **11a–d** the smaller inversion–retention ratios seem to arise when nitrogen is extruded from the more congested syn azo units (Scheme II and Table V). This is particularly pronounced in the cases of **11b** and **11c** where statistical ratios of inversion to retention are observed. Perhaps the steric influence of the syn substituent leads to a more facile loss of nitrogen to form a nitrogen-free 1,3-biradical from which closure with inversion or retention can occur statistically. Alternatively, inversion simply may be inhibited in these syn azo systems, since it would lead to the more sterically hindered endo-substituted bicyclo[2.1.0]pentanes.

In contrast to direct irradiation, sensitized decomposition of the bis-azoalkane **5** and the monoazoalkanes **11a–d** is significantly more complex. As shown in Table V and Scheme II, net inversion is favored in only about half of the cases, and there seems to be a tendency to form the more hindered *endo*-bicyclo[2.1.0]pentane

Scheme V



moiety over the less hindered exo geometry. Thus, sensitized photodecomposition of the bis-azoalkane **5** affords an excess of the *endo*-bicyclo[2.1.0]pentanes (**11d > 11a** and **11b > 11c**), and the monoazoalkanes **11a** and **11c** also give rise to an excess of the more hindered *bis*-bicyclo[2.1.0]pentane (**12a > 12b**). Only in the extreme cases where the most hindered *endo,endo*-bibicyclo[2.1.0]pentane (**12c**) might be formed from **11b** and **11d** is the less hindered isomer **12a** favored (see Figure 4).

While the singlet biradicals arising from direct irradition would probably not survive long enough to achieve thermal equilibrium, the corresponding triplet biradicals would be expected to survive long enough to reach thermal equilibrium and the time-averaged planar geometries **19a** and **19b** shown in Figure 4. That this is the case for the parent triplet 1,3-cyclopentadiyl biradical derived from **15** has been demonstrated by means of oxygen trapping (Scheme V).[24a] In this system oxygen trapping occurs quantitatively and with equal probability from either face of the biradical. Furthermore, quantitative oxygen trapping studies indicate that 1,3-cyclopentadiyl has a lifetime of about 140 ns,[24b] which would seem to be more than enough time to establish thermal equilibrium. Consequently, there seems to be good reason to believe that a thermally equilibrated triplet biradical is involved in the sensitized reaction of the parent 1,3-cyclopentadiyl. If this is indeed the case, then the collapse of these triplet 1,3-cyclopentadiyl analogues to bicyclopentanes must be influenced to a significant extent by factors other than simple thermodynamics. For example, in Figure 4 the singlet and triplet hypersurfaces for the biradicals **19a** and **19b** are approximated. While these hypersurfaces have not been calculated for these specific species, similar hypersurfaces have been determined for the parent 1,3-cyclopentadiyl,[25] and the surfaces in Figure 4 have been patterned after these calculated surfaces. The model outlined in Figure 4 has been modified in two significant respects. First, the ground-state energies of the bis-bicyclopentane product isomers are increased upon going from the exo to the endo geometry of each bicyclopentane unit. Second, the slope of the triplet surface is thought to be steeper on the more hindered side with the *endo*-geomery. While this latter modification is somewhat crude and will require a rigorous quantitative treatment in order to be absolutely certain of its validity, the qualitative model shown in Figure 4 does seem quite reasonable. In addition this model has two significant features. In the hypersurfaces of biradical **19a** the triplet-to-singlet crossing at point A (of Figure 4) should occur at somewhat lower energy than that at point B, and a similar relationship should exist for the crossings of biradical **19b** with crossing at point C occurring at lower energy than that at point D. If this model does accurately reflect the relationships between the hypersurfaces of biradicals **19a** and **19b**, then one would predict that the conformationally equilibrated triplet biradical **19a** would tend to undergo intersystem crossing (ISC) more frequently at point A than point B. This in turn would lead to the formation of **12b** in excess of **12a**. A similar argument when applied to triplet biradical **19b** would indicate the major ISC route to be through point C, leading to the formation of **12a** in excess of **12c**. The data presented in Table V clearly show that this model adequately describes the behavior of **19b** but not that of **19a** where ISC through the higher energy crossing at point B

(22) Bigot, B.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 2639.
(23) Collins, F. S.; George, J. K.; Trindle, C. *J. Am. Chem. Soc.* **1972**, *94*, 3732.

(24) (a) Adam, W.; Hannemann, K.; Wilson, R. M. *J. Am. Chem. Soc.* **1986**, *108*, 929. (b) The triplet lifetime of 1,3-cyclopentadiyl originally quoted in ref 24a (720 ns) should be revised downward (ca. 140 ns) on the basis of new oxygen quenching rate constant data: Adam, W.; Grabowski, S.; Wilson, R. M.; Hannemann, K.; Wirz, J. *J. Am. Chem. Soc.*, submitted for publication.
(25) Conrad, M. P.; Pitzer, R. M.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 2245.

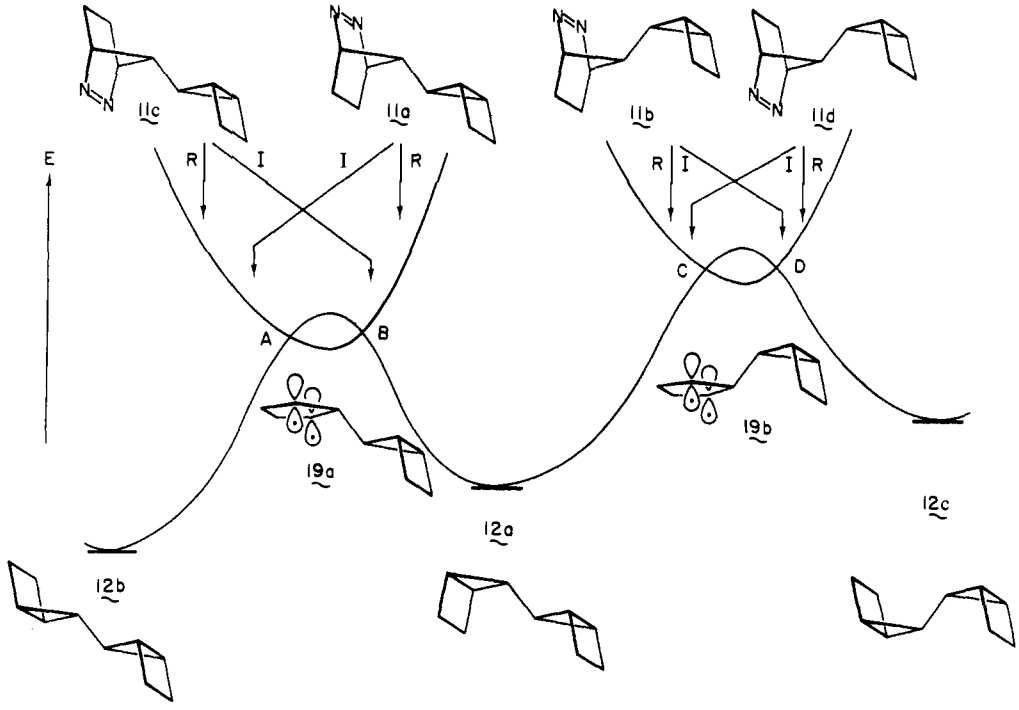


Figure 4. Qualitative energy diagram for the formation of the bibicyclopentanes **12a–c** from the excited triplet states of azoalkanes **11a–d**.

is favored and an excess of **12a** over **12b** results.

It is most informative to apply this same line of reasoning to the sensitized photodecomposition of **15** (Scheme IV). Here the corresponding biradical crossing points leading to **16a** and **16b** would certainly occur at the same energy relative to the energy minimum of the triplet biradical hypersurface. On this basis alone one would predict an equal probability for the formation of **16a** and **16b**. Indeed the sensitized decomposition of **15** leads to a small but significant excess of **16a** over **16b** (**16a**:**16b** = 1.15:1).[20] This observation along with the results presented in this work demonstrates that ISC from the triplet 1,3-cyclopentadiyl biradicals is not governed exclusively by the relative energies of the singlet–triplet crossing points. Apparently, some other factor or factors play an important role in determining the favored crossing point geometry, and as shown by these results, this favored crossing point can be at higher energy than other apparently more accessible crossing points.

One other most curious observation made in these systems must be noted. Returning to Figure 4, one can readily see that if conformationally equilibrated triplet biradicals are involved in the processes outlined here, then the same ratio of bis-bicyclo[2.1.0]pentane isomers might be expected to result regardless of whether the triplet biradical is formed on the "eastern" or "western" slope of the triplet hypersurface. Thus, for example, the ratio **12a**:**12b** might be expected to be the same whether one starts from **11a** or **11c**, and the same might be expected for the ratio **12a**:**12c**. The ratios of the isomers of **12** shown in Table V clearly show that this is not the case. Therefore, it would appear that in these substituted systems the bicyclopentane isomers are not derived exclusively from thermally equilibrated triplet biradicals. Furthermore, there seems to be a slight tendency for the loss of nitrogen to occur with inversion even in these triplet biradical systems where the stepwise loss of nitrogen is a distinct possibility.

Before any suggestions might be offered as to the possible origins of these effects, it must be stressed that no quantitative data is available for the relative energies of the singlet and triplet hypersurfaces of 2-substituted 1,3-cyclopentadiyls. Indeed, if one attempts to use the detailed hypersurface calculated by Doubleday, McIver, and Page[26] for trimethylene with planar spin-bearing carbons as models for these 1,3-cyclopentadiyls, one encounters no singlet–triplet crossings within the range of unstrained geometries accessible to 1,3-cyclopentadiyl. Thus, the distinct possibility exists that there are no singlet–triplet crossings for 1,3-cyclopentadiyl on the hypersurface slice for planar spin-bearing carbons (in which case the simple model based upon the planar biradicals **19a** and **19b** shown in Figure 4 might be inadequate and pyramidalization of the spin-bearing carbons might be necessary in order to produce the requisite singlet–triplet crossings).

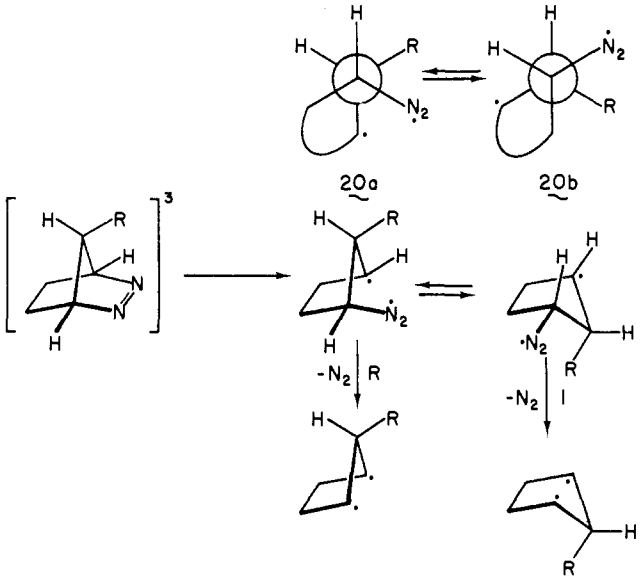
In spite of the many uncertainties that exist regarding the shapes and relationships of these biradical hypersurfaces, two suggestions do seem justified based upon the observations made in this work. On the one hand, the expectation that the same ratio of bicyclo[2.1.0]pentane isomers should result from both eastern and western triplet hypersurface approaches is based on the premise that the difference in the slopes of the triplet and singlet hypersurfaces is great in the singlet–triplet crossing regions (points A and B in Figure 4, for example).[27] In this situation the newly formed triplet biradical would be born upslope from the crossing and could pass through the crossing regions quickly without appreciable crossing to the singlet hypersurface. The biradicals would then become thermally equilibrated, and the same or very nearly the same ratios of bicyclopentane isomers should result from both the eastern and western approaches. If, on the other hand, the difference in the slopes of the triplet and singlet hypersurfaces is small in the singlet–triplet crossing regions, which would be the case if these hypersurfaces were relatively flat, then the newly formed biradical would "meander" toward the triplet hypersurface minimum, spend much more time in the singlet–triplet crossing regions, and undergo much more efficient crossing to the singlet hypersurface in the first crossing that it encounters on its way to thermal equilibrium. This latter scenario might account for the data generated in this work, if one assumes that nitrogen is lost with net inversion of stereochemistry (the entries to the triplet hypersurfaces labeled I in Figure 4).

It is instructive to compare this mechanism with the "recoil" mechanism previously proposed.[21] In that mechanism a vibrationally hot biradical is injected onto the triplet hypersurface with retention (pathways R in Figure 4). It then moves along the triplet hypersurface through the minimum and enters into the crossing

(26) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533.

(27) Kauzman, W. *Quantum Chemistry*; Academic: New York, 1957, p 539.

Scheme VI

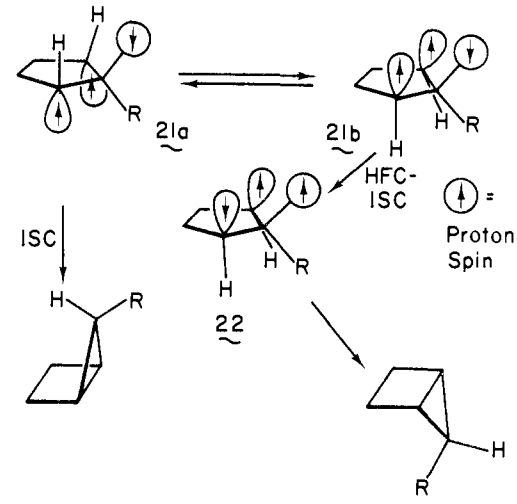


region on the opposite slope where it resides long enough for a significant number of crossing events to occur and the product distribution to become biased toward net inversion. Convincing arguments against this mechanism have been presented[23] and will not be recounted here. In the "first crossing encountered" mechanism proposed here, the favored pathway for 1,3-biradical formation would not be through the "vertical" loss of nitrogen (pathways labeled R in Figure 4) but through the "diagonal" loss of nitrogen (pathways labeled I). This diagonal route would seem to require the existence of an intermediate diazenyl biradical which would be not at all surprising in these triplet processes.[20] Both the vertical and diagonal pathways to the triplet biradical hypersurface are detailed in Scheme VI. As can be seen here, the only requirement for a diagonal pathway to the triplet hypersurface is that the intermediate diazenyl biradical **20** have a long enough lifetime to insure that it can become conformationally equilibrated. For the unsubstituted biradical (**20a** and **20b**, R = H in Scheme VI), **20b** should be the favored conformation, and entry to the triplet hypersurface with inversion should be favored. The introduction of the alkyl substituent to the systems studied here makes a decision less straightforward as to which diazenyl biradical conformation, **20a** or **20b**, is the more stable. Thus a diagonal approach to the triplet hypersurface is probably relatively more important in the parent, unsubstituted system shown in Scheme IV than in the substituted analogues under consideration here. Nevertheless, there seems to be no problem rationalizing a diagonal approach to the triplet biradical hypersurface via a diazenyl biradical. Finally, it should be stressed that the product distributions of triplet reactions can be affected significantly by the first crossing encountered and that this concept may be of general utility in understanding many triplet reactions.

Triplet biradical conformational equilibrium would become established after the biradical passes through the first crossing point. From this stage on the relative amounts of the two bicyclo[2.1.0]pentane isomers formed would depend upon the relative energies of the two crossing points on the eastern and western slopes and on the relative efficiencies of ISC at these two crossing points. However, as mentioned earlier, of the four cases studied here (the formation of **11a,d**, **11b,c**, **12a,b**, and **12a,c**), only in the last case does crossing through the lower energy point seem to be favored to form the less hindered bicyclopentane isomer (see Table V and Figure 4). Thus, it would seem that there must be some factor(s) which favors ISC through higher energy points in these systems. The extremely intriguing possibility exists that this factor is hyperfine coupling (HFC).

A HFC mechanism for ISC might be expected to play a relatively more important role in intrinsically long-lived biradicals such as the 1,3-cyclopentadiyls under consideration here. The

Scheme VII



mechanism by which this might occur is outlined in Scheme VII. In this model the spin-bearing carbon atoms would probably have to be pyramidalized. Goldberg and Dougherty have discussed the crucial role played by substituent bonds in the 2-position in the through-bond interaction of the spin-bearing orbitals.[28] With the pyramidalized geometries **21a** and **21b** shown in Scheme VII, it can be seen that in geometry **21a** this through-bond interaction would be most effectively mediated by the bond to the 2-alkyl substituent and in **21b** by the bond to the 2-hydrogen substituent, which is represented in Scheme VII by the circle with the nuclear spin enclosed. Furthermore, Turro has noted that the rate constant for ISC via HFC is directly proportional to some power of the hyperfine coupling constant.[29] The overlap considerations outlined above play a central role in determining the magnitude of the β-hyperfine coupling constant ($\alpha_\beta^H = B_0 + B_2 \cos^2 \theta$, where θ is the dihedral angle between the axis of the spin-bearing orbital and the adjacent σ-bonds).[30] Thus, in geometry **21a** interaction between the biradical electrons and the β-carbon atom of the 2-alkyl substituent would be maximized, but interaction with the 2-hydrogen would be ineffective. Exactly the opposite would be true for the geometry **21b**. Since the carbon-12 nucleus has no magnetic moment, but the hydrogen nucleus does, the contribution of HFC to ISC from the triplet to singlet 1,3-cyclopentadiyl should be maximized by geometry **21b** and minimized by geometry **21a**. As can be seen in Scheme VII, the geometric bias provided by this β-HFC mechanism would be expected to favor ISC from **21b** to **22**, which in turn should lead to a preference for formation of the more hindered *endo*-bicyclo[2.1.0]pentane isomer.

Finally, it must be noted that this model is based on the assumption that the spin-bearing carbons are pyramidalized. If these same carbons are planar, then the stereochemical interpretation of the affect of HFC on the course of the reaction is much less straightforward. Nevertheless, this model does provide an excellent basis for the rational design of future experiments to more thoroughly test the extent of involvement of HFC in triplet biradical chemistry.

Conclusions

The bis-azoalkane **5** has yet to yield evidence for the formation of the tetraradical **4** under conventional and laser photochemical conditions. Nevertheless, the thermal and photochemical decompositions of **5** as well as the monoazoalkanes **11a–d** have provided a number of interesting observations which seem to bear directly on the mechanism of nitrogen extrusion from azoalkanes and collapse of triplet 1,3-cyclopentadiyls to bicyclo[2.1.0]pentanes.

(28) Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284.
(29) Turro, N. J.; Kraeutler, B. *Diradicals*; Borden, W. T., Ed.; Wiley-Interscience: New York, 1982; p 259 and references therein.
(30) Gordy, W. *Theory and Applications of Electron Spin Resonance*; West, W., Ed.; Wiley: New York, 1980; pp 497, 524.

These results indicate that further, more quantitative insights might be obtained through a systematic study of simpler 2-alkyl-1,3-cyclopentadiyls.

Experimental Section

All melting points are uncorrected. The infrared spectra were recorded with a Perkin-Elmer 157G Spectrometer, UV spectra with a Varian Cary 17 spectrophotometer, mass spectra with a Varian MAT CH 7 mass spectrometer, and NMR spectra with a Bruker WH 400 spectrometer. GLC analyses were conducted with a Carlo Erba Fractovap 2900 gas chromatograph equipped with a 40-m Carbowax 20 M glass capillary column (i.d. = 0.3 mm). Preparative GLC separations were conducted with a Carlo Erba Fractovap 4200 gas chromatograph equipped with a 20% Carbowax 20 M on Volaspher A2 (0.15–0.18 mm, Merck), 3-m (5-mm-i.d.) column. Flash column chromatography[31] (silica gel, 40–63 μm) was used for preparative column separations. Photochemical reactions were carried out in a Rayonet photochemical reactor equipped with 350-nm lamps. A Coherent Supergraphite CR 18 argon ion laser equipped with a selected UV tube was used for laser photolyses.

Preparation of [*anti* (*syn*)]-10,10′-Bi-5,8-dihydro-2-phenyl-5,8-methano-(1*H*)-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (9a). The azoalkane precursor **9a** was prepared according to the literature procedure,[8] using sodium (7 g, 0.3 mol), freshly distilled cyclopentadiene (10.1 g, 0.153 mol), iodine (20 g, 0.079 mol), and *N*-phenyltriazolinedione (16.7 g, 0.095 mol). Column chromatography (silica gel, gradient elution, CH_2Cl_2:CH_2Cl_2/ethyl acetate 4:1) yielded the previously described products. The double adduct **9a** (3.14 g, 14%) was obtained as colorless needles following recrystallization from ethyl acetate: mp 205–212 °C dec; IR (KBr) 1775, 1725, 1500, 1395, 1235, 1015, 910, 780, 740, 685, 630 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.02 (br d, J = 8 Hz, 1 H), 3.03 (br d, J = 8 Hz, 1 H), 4.83 (m, 2 H), 5.13 (m, 2 H), 6.44 (m, 2 H), 6.45 (m, 2 H), 7.3–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 57.15 (d), 57.27 (d), 66.56 (d), 66.79 (d), 125.42 (d), 125.51 (d), 128.47 (d), 128.60 (d), 129.09 (d), 129.18 (d), 129.48 (d), 131.27 (s), 132.18 (d), 158.13 (s), 158.43 (s); mass spectrum (70 eV), *m/e* (relative intensity) 480 (0.3, M^+), 305 (63, M^+ – PTAD), 144 (22), 130 (26), 129 (94), 128 (71), 119 (100), 115 (52), 91 (71).

In addition to this previously described adduct **9a**, 304 mg (1%) of a white solid, mp 250 °C dec, was isolated and was only slightly soluble in the common solvents: IR (KBr) 1780, 1720, 1500, 1410, 1245, 1140, 1015, 785, 745, 690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 2.58 (s, 2 H), 5.02 (m, 4 H), 6.53 (m, 4 H), 7.35–7.53 (m, 10 H); mass spectrum (70 eV), *m/e* (relative intensity) 480 (0.05), 305 (50), 177 (43), 144 (33), 129 (62), 128 (69), 119 (100), 91 (50).

Preparation of [*anti* (*syn*)]-10, 10′-Bi-5,6,7,8-tetrahydro-2-phenyl-5,8-methano-(1*H*)-[1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (10). The bis adduct **9a** (1.79 g, 3.37 mmol) and 20 mg of 5% Pd/C in 800 mL of ethyl acetate were vigorously stirred at 20–25 °C for 24 h under a hydrogen atmosphere. Removal of the catalyst by filtration and the solvent under reduced pressure yielded 1.73 g (96%) of **10**, which after recrystallization from ethyl acetate was obtained as colorless needles: mp 282–285 °C; IR (KBr) 3060, 3010, 1775, 1715, 1505, 1410, 1130, 1080, 770, 760, 750, 690, 625 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 1.90–2.15 (m, 9 H), 2.49 (br d, J = 10 Hz, 1 H), 4.44 (m, 2 H), 4.58 (m, 2 H), 7.3–7.5 (m, 10 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 26.07 (t), 27.79 (t), 46.41 (d), 48.99 (d), 61.98 (two overlapping doublets), 125.27 (d), 128.24 (d), 128.37 (d), 129.09 (d), 129.15 (d), 131.53 (s), 155.43 (s), 156.37 (s); mass spectrum (70 eV), *m/e* (relative intensity) 484 (100, M^+), 307 (20), 163 (82), 119 (78), 91 (56), 79 (39), 67 (41). Anal. Calcd for $C_{26}H_{24}N_6O_4$: C, 64.45; H, 4.99; N, 17.35. Found: C, 64.44; H, 4.86; N, 16.98.

Preparation of [*anti* (*syn*)]-7,7′-Bi-2,3-diazabicyclo[2.2.1]hept-2-ene (5). Potassium hydroxide (2.80 g, 50 mmol) was dissolved in 60 mL of 2-propanol with heating. The urazole **10** (1.63 g, 3.36 mmol) was added and the mixture refluxed under nitrogen for 12 h. Then the mixture was cooled in an ice bath, and concentrated HCl was added until a pH of 2 was reached. The pH was adjusted to 5–6 with concentrated NH_4OH, and 10 mL of a 3 M $CuCl_2$ solution was added dropwise. A reddish brown complex precipitated. The complex was isolated by suction filtration and dissolved in 50 mL of concentrated NH_4OH. After 15 min, the NH_3 solution was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed twice with 50 mL of brine and dried over $MgSO_4$. Evaporation of the solvent gave 605 mg (95%) of the crude product, which was further purified by flash column chromatography (silica, CH_2Cl_2:EtOAc 85:15) and recrystallized from ethanol to yield **5** (517 mg, 81%) as colorless needles: mp 190 °C dec; IR (KBr) 3010, 2980, 2950, 2870, 1495, 1285, 1275, 1255, 1230, 1170, 855, 845, 830 cm^{-1}; UV (CH_2Cl_2) λ_{max} (ε) 313 (40), 334 (170), 342 nm (210); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.87 (br d, J = 11 Hz, 1 H), 0.90–1.03 (m, 4 H), 1.19 (d, J = 11 Hz, 1 H), 1.47–1.63 (m, 4 H), 4.82 (br s, 2 H), 5.03 (br s, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.96 (t), 20.89 (t), 46.87 (d), 51.19 (d), 77.95 (d), 79.53 (d); mass spectrum (70 eV), *m/e* (relative intensity) 191 (0.7, M^+ + 1), 93 (26), 91 (91), 79 (27), 77 (34), 67 (100), 66 (27), 41 (75), 39 (49). Anal. Calcd for $C_{10}H_{14}N_4$: C, 63.13; H, 7.42; N, 29.45. Found: C, 63.00; H, 7.20; N, 29.04.

Direct Photolysis of the Bis-Azoalkane 5. A 1.16×10^{-2} M solution of **5** in benzene (1 mL) was irradiated under nitrogen at 350 nm. At various time intervals 50-μL samples were taken, mixed with 50 μL of standard solution (3.52×10^{-3} M dodecane in benzene), and analyzed by capillary GLC (temperature programmed: 80 °C (10 min) and then 30 °C/min up to 160 °C), retention times (min): dodecane 5.5, **12b**: 7.5, **12a**: 7.8, **12c**: 9.2, **11b**: 23.1, **11a**: 23.5, **11c**: 23.8, **11d**: 25.5. The bis-azoalkane **5** was analyzed by using a 50-m OV 101 glass capillary column (temperature programmed: 110 °C (13 min) and then 30 °C/min up to 160 °C), retention times (min): dodecane 12.9, **5**: 37.2. The results are summarized in Table I.

Sensitized Photolysis of the Bis-Azoalkane 5. A benzene solution (1 mL) which was 1.16×10^{-2} M in **5** and 7.8×10^{-2} M in benzophenone was irradiated under nitrogen at 350 nm. At various time intervals 50-μL samples were analyzed as described above. The results are reported in Table I.

Preparative Photolysis of the Bis-Azoalkane 5. The bis-azoalkane **5** (312 mg, 1.64 mmol) was dissolved in 40 mL of benzene and irradiated under nitrogen at 350 nm. The progress of the reaction was monitored by capillary GLC as described above, and the reaction was stopped at ca. 60% conversion after 50 min of irradiation. Evaporation of the solvent and subsequent flash chromatography (silica gel, CH_2Cl_2:ethyl acetate 95:5) yielded the following fractions: 28 mg (13%, colorless oil) of the isomeric mixture of **12a–c**, 94 mg (35%) of a mixture of **11a** and **11d**, 12 mg (5%) of a mixture of the monoazoisomers **11b–d**, and 14 mg (5%) of a mixture of **11b** and **11c**. In addition, 122 mg (39%) of unreacted starting material, **5**, could be recovered.

Bibicyclo[2.1.0]pentanes 12a–c. An analytical sample of the isomeric mixture was obtained by Kugelrohr distillation (120 °C, 14 mm): IR (film) 3035, 2970, 2930, 2900, 2865, 1460, 1440, 1275, 1260, 1210, 935, 910, 780 cm^{-1}; mass spectrum (70 eV), *m/e* (relative intensity) 134 (1, M^+), 91 (59), 79 (28), 77 (31), 67 (100), 66 (26), 65 (20), 41 (41), 39 (30). Anal. Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.34; H, 10.65. The bibicyclopentanes **12a–c** could be separated by means of preparative GLC (3-m Carbowax 20 M, 80 °C). The isomers **12a** and **12c** were obtained pure, and **12b** was obtained as a mixture with small amounts of **12a**.

5-*endo*,5′-*exo*-Bibicyclo[2.1.0]pentane (12a): ^1H NMR ($CDCl_3$, 400 MHz) δ 0.13 (br dt, J = 8, 5.8 Hz, 1 H), 1.03 (br d, J = 8 Hz, 1 H), 1.45–1.49 (m, 2 H), 1.51–1.58 (m, 4 H), 1.60–1.66 (m, 2 H), 2.07–2.21 (m, 4 H); ^{13}C NMR (see Table III).

5-*exo*,5′-*exo*-Bibicyclo[2.1.0]pentane (12b): ^1H NMR ($CDCl_3$, 400 MHz) δ 0.78 (s, 2 H), 1.30–1.37 (m, 8 H), 2.00–2.07 (m, 4 H); ^{13}C NMR (see Table III).

5-*endo*,5′-*endo*-Bibicyclo[2.1.0]pentane (12c): ^1H NMR ($CDCl_3$, 400 MHz) δ 0.92–0.98 (br t, J = 5 Hz, 2 H), 1.56–1.62 (m, 4 H), 1.62–1.70 (m, 4 H), 2.06–2.16 (m, 4 H); ^{13}C NMR (see Table III).

Azoalkanes 11a–d. Analysis of the fraction containing **11a–d** yielded the following. Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.26. Found: C, 74.35; H, 8.97; N, 17.04. The azoalkanes **11a**, **11b**, and **11d** could be separarted by preparative GLC (3-m Carbowax 20 M; 150 °C). Following recrystallization, these isomers were obtained in pure form. However, these same procedures produced isomers **11c** as a mixture containing about 15% of **11b**.

7-*anti*-[(*exo*)-Bicyclo[2.1.0]pent-5-yl]-2,3-diazabicyclo[2.2.1]hept-2-ene (11a): mp 123–124 °C (EtOH, colorless needles); IR (KBr) 3030, 2960, 2920, 2850, 1485, 1280, 1260, 1250, 900 cm^{-1}; UV (Pentane) λ_{max} (ε) 344 nm (194); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.55 (br s, 2 H), 1.00–1.06 (m, 2 H), 1.32–1.38 (m, 4 H), 1.83–1.89 (m, 2 H), 2.04–2.11 (m, 2 H), 4.88 (br s, 2 H); ^{13}C NMR (see Table III); mass spectrum (70 eV), *m/e* (relative intensity) 163 (1, M^+ + 1), 93 (28), 91 (79), 79 (35), 77 (34), 67 (100), 41 (57), 39 (41). Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.26. Found: C, 73.95; H, 8.70; N, 17.22.

7-*syn*-[(*endo*)-Bicyclo[2.1.0]pent-5-yl]-2,3-diazabicyclo[2.2.1]hept-2-ene (11b): mp 105–107 °C (EtOH, colorless needles); UV (pentane) λ_{max} (ε) 342 nm (112); ^1H NMR ($CDCl_3$, 400 MHz) δ 0.24 (dt, J = 10.1, 5.9 Hz, 1 H), 0.95–1.01 (m, 2 H), 1.22–1.27 (m, 2 H), 1.47–1.52 (m, 2 H), 1.62–1.68 (m, 3 H), 2.04–2.12 (m, 2 H), 5.17 (br s, 2 H); ^{13}C NMR (see Table III).

7-*syn*-[(*exo*)-Bicyclo[2.1.0]pent-5-yl]-2,3-diazabicyclo[2.2.1]hept-2-ene (11c): ^1H NMR ($CDCl_3$, 400 MHz) δ 0.45 (d, J = 9.3 Hz, 1 H), 0.77

(31) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Table VI. Positional and Thermal Parameters (Å^2) for the Bis-Azoalkane **5**[a-c]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.4181 (4)	0.3592 (7)	0.045 (1)	0.039 (3)	0.042 (3)	0.056 (4)	0.008 (3)	0.003 (3)	−0.004 (3)
N(2)	0.4964 (3)	0.3143 (6)	−0.044 (1)	0.042 (3)	0.079 (4)	0.071 (4)	0.006 (4)	0.013 (3)	−0.004 (3)
C(3)	0.4198 (4)	0.3285 (7)	0.311 (1)	0.062 (4)	0.041 (4)	0.035 (3)	−0.005 (3)	−0.011 (3)	−0.008 (4)
C(4)	0.3654 (5)	0.25	−0.057 (1)	0.041 (5)	0.052 (5)	0.021 (4)	0	0.010 (4)	0
C(5)	0.2791 (5)	0.25	0.015 (1)	0.035 (4)	0.055 (5)	0.023 (4)	0	−0.001 (4)	0
C(6)	0.2283 (4)	0.1398 (6)	−0.095 (1)	0.043 (3)	0.034 (3)	0.046 (4)	0.004 (3)	−0.008 (3)	0.003 (3)
N(7)	0.2232 (3)	0.1863 (5)	−0.3474 (9)	0.048 (3)	0.054 (3)	0.032 (3)	−0.006 (3)	0.000 (3)	−0.001 (3)
C(8)	0.1469 (3)	0.1713 (7)	0.009 (1)	0.032 (3)	0.047 (4)	0.063 (4)	0.009 (4)	0.008 (3)	−0.007 (3)

[a] U_{ij} is defined for exp $[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^*)]$. [b] The standard deviations are given in parentheses. [c] Since atoms C(4) and C(5) lie on the mirror plane of the unit cell, no standard deviations are given for the y coordinate, and the U_{23} and U_{12} parameters are set to 0.

Table VII. Bond Lengths (pm) and Angles (deg) for the Bis-Azoalkane **5**[a]

C(1)–N(2)	149.5 (9)	C(3)–C(3′)	154.9 (13)	C(5)–C(6) }	153.2 (9)	C(6)–C(8)	153.7 (9)
C(1)–C(3)	152.9 (9)	C(4)–C(1) }	151.7 (9)	C(5)–C(6′) }		M(7)–N(7′)	125.7 (11)
N(2)–N(2′)	126.8 (12)	C(4)–C(1′) }		C(6)–N(7)	149.8 (8)	C(8)–C(8′)	155.3 (13)
		C(4)–C(5)	153.4 (12)				

N(2)–C(1)–C(3)	104.6 (5)	C(1)–C(4)–C(1′)	90.5 (7)	C(5)–C(6)–N(7)	102.2 (5)
N(2)–C(1)–C(4)	101.1 (5)	C(1)–C(4)–C(5) } 117.5 (5)		C(5)–C(6)–C(8)	102.0 (5)
C(3)–C(1)–C(4)	104.1 (5)	C(1′)–C(4)–C(5) }		N(7)–C(6)–C(8)	104.2 (5)
C(1)–N(2)–H(2′)	107.2 (3)	C(4)–C(5)–C(6) } 115.2 (5)		C(6)–N(7)–N(7′)	107.9 (3)
C(1)–C(3)–C(3′)	101.4 (3)	C(4)–C(5)–C(6′) }		C(6)–C(8)–C(8′)	101.7 (3)
		C(6)–C(5)–C(6′)	90.5 (6)		

[a] The standard deviations are given in parentheses.

Table VIII. Positional and Thermal Parameters (Å^2) for the Monoazoalkane **11a**[a,b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	9499 (11)	1987	2180 (15)	46 (4)	66 (6)	54 (5)	−14 (5)	−10 (3)	16 (4)
N(2)	8806 (12)	2426 (15)	9932 (14)	102 (6)	103 (8)	39 (4)	−11 (6)	9 (4)	24 (6)
N(3)	8796 (10)	3719 (15)	9949 (14)	54 (4)	99 (8)	52 (5)	13 (6)	−4 (3)	1 (5)
C(4)	9537 (15)	4216 (6)	2281 (16)	105 (6)	63 (6)	46 (5)	6 (5)	−5 (5)	−8 (6)
C(5)	8060 (5)	3917 (5)	3675 (8)	49 (2)	57 (3)	59 (3)	−1 (2)	3 (2)	23 (2)
C(6)	8088 (14)	2354 (15)	3701 (15)	78 (6)	100 (8)	42 (5)	13 (5)	0 (4)	−4 (5)
C(7)	864 (4)	3177 (18)	2828 (6)	47 (2)	85 (3)	42 (2)	−12 (6)	12 (1)	−2 (6)
C(8)	1793 (4)	3166 (19)	5179 (6)	43 (2)	74 (3)	47 (2)	4 (7)	5 (1)	−4 (6)
C(9)	3442 (12)	2317 (12)	5447 (17)	73 (6)	58 (5)	54 (6)	3 (5)	2 (5)	−6 (4)
C(10)	4189 (14)	2308 (15)	8031 (18)	101 (6)	79 (7)	49 (5)	−5 (5)	−5 (4)	15 (6)
C(11)	4173 (11)	3900 (13)	7821 (18)	46 (4)	74 (6)	79 (6)	−11 (5)	−9 (4)	−3 (5)
C(12)	3462 (10)	3866 (15)	5503 (17)	41 (4)	79 (7)	67 (6)	10 (6)	3 (4)	−21 (5)

[a] U_{ij} is defined as $[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^*)]$. [b] The standard deviations are given in parentheses.

Table IX. Bond Lengths (pm) and Angles (deg) for the Monoazoalkane **11a**[a]

C(1)–N(2)	146.5 (12)	N(2)–M(3)	125.4 (20)	C(5)–C(6)	151.5 (16)	C(9)–C(10)	160.1 (14)
C(1)–C(6)	153.5 (14)	N(3)–C(4)	153.7 (13)	C(7)–C(8)	151.9 (5)	C(9)–C(12)	150.1 (18)
C(1)–C(7)	158.6 (14)	C(4)–C(5)	151.3 (12)	C(8)–C(9)	151.4 (14)	C(10)–C(11)	154.8 (19)
		C(4)–C(7)	145.3 (15)	C(8)–C(12)	145.6 (13)	C(11)–C(12)	144.5 (14)

N(2)–C(1)–C(6)	105.3 (7)	C(4)–C(5)–C(6)	100.7 (5)	C(8)–C(9)–C(10)	109.0 (8)
N(2)–C(1)–C(7)	100.9 (7)	C(1)–C(6)–C(5)	103.7 (7)	C(8)–C(9)–C(12)	57.7 (8)
C(8)–C(1)–C(7)	100.5 (6)	C(1)–C(7)–C(4)	90.5 (4)	C(10)–C(9)–C(12)	89.0 (8)
C(1)–N(2)–N(3)	106.5 (8)	C(1)–C(7)–C(8)	117.7 (9)	C(9)–C(10)–C(11)	85.2 (8)
N(2)–N(3)–C(4)	108.6 (8)	C(4)–C(7)–C(8)	118.3 (9)	C(10)–C(11)–C(12)	93.2 (9)
N(3)–C(4)–C(5)	102.1 (7)	C(7)–C(8)–C(9)	114.7 (8)	C(8)–C(12)–C(9)	61.6 (9)
N(3)–C(4)–C(7)	100.4 (7)	C(7)–C(8)–C(12)	116.9 (8)	C(8)–C(12)–C(11)	112.8 (8)
C(5)–C(4)–C(7)	107.4 (6)	C(9)–C(8)–C(12)	60.7 (7)	C(9)–C(12)–C(11)	92.7 (9)

[a] The standard deviations are given in parentheses.

(d, J = 9.3 Hz, 1 H), 0.86–0.92 (m, 2 H), 1.24–1.28 (m, 2 H), 1.48–1.53 (m, 4 H), 1.96–2.03 (m, 2 H), 5.09 (br s, 2 H); ^{13}C NMR (see Table III).

***7-anti*-[(*endo*)-Bicyclo[2.1.0]pent-5-yl]-2,3-diazabicyclo[2.2.1]hept-2-ene (11d)**: mp 87–88 °C (EtOH, colorless plates); UV (pentane) λ_{max} (ϵ) 344 nm (163); ^{1}H NMR (C_6D_6, 400 MHz) δ −0.07 (dt, J = 9.7, 5.9 Hz, 1 H), 0.87–0.93 (m, 2 H), 1.02–1.09 (m, 2 H), 1.27–1.32 (m, 2 H), 1.33–1.38 (m, 2 H), 1.51 (br d, J = 9.7 Hz, 1 H), 1.82–1.88 (m, 2 H), 4.80 (q, J = 1.7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) (see Table III); ^{13}C NMR (C_6D_6) δ 17.01 (d), 17.23 (d), 18.68 (t), 18.92 (t), 44.87 (d), 78.73 (d).

Direct Photolysis of the Monoazoalkanes 11a–d. About 1 mg of each azoalkane **11a–d** was dissolved in 0.5 mL of benzene and irradiated under nitrogen at 350 nm for 5 min. The reactions were monitored by capillary GLC as described above. The results are summarized in Table II.

Sensitized Photolysis of the Monoazoalkanes 11a–d. About 1 mg of each azoalkane **11a–d** and 5 mg of benzophenone were dissolved in 0.5 mL of benzene and irradiated under nitrogen at 350 nm for 5 min. The reactions were monitored by capillary GLC, and the results are summarized in Table II.

Laser Photolysis of Bis-Azoalkane 5. Benzene solutions of the bis-azoalkane **5** (1.16×10^{-2} M) both with and without benzophenone (0.1 M) were irradiated under nitrogen with a focused beam of an argon ion laser (total UV output of 3 W using the 333-, 351-, and 364-nm lines). The progress of the reaction was monitored by capillary GLC. Only the usual photoproducts **11a–d** and **12a–c** were obtained.

Flash Vacuum Thermolysis of Bis-Azoalkane 5. The bis-azoalkane **5** (2 mg) was sublimed (160 °C/0.1 mm) through a thermolysis tube at various temperatures. The thermolysate was collected in a liquid nitrogen cooled trap, dissolved in benzene, and analyzed by capillary GLC (for GLC conditions see above). The results are summarized in Table I. In a preparative run, 90 mg (0.47 mmol) of **5** was thermolized at 450 °C to obtain 61 mg of a crude product mixture. Preparative GLC (3-m Carbowax 20 M, 80 °C) afforded 15 mg (24%) of a colorless liquid which was identified as 1,1′-bicyclopentene (**13**) by GLC and NMR

comparison with an authentic sample:[18] ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.92 (q, J = 7.5 Hz, 4 H), 2.43 (m, 4 H), 2.49 (m, 4 H), 5.59 (m, 2 H).

Flash Vacuum Thermolysis of Monoazoalkanes 11a and 11d. The azoalkanes **11a** and **11d** (2 mg of each) were thermolized as described above. The results are shown in Table IV.

Flash Vacuum Thermolysis of Bibicyclopentane 12a. The bibicyclopentane **12a** was thermolized as described above. The results are summarized in Table III.

X-ray Structure Analysis of the Bis-Azoalkane 5. A clear colorless crystal of **5** with dimensions 0.12 × 0.28 × 0.08 mm was optically centered on a Syntex P3 four-circle diffractometer. The orientation matrix and cell parameters were determined on the basis of 15 reflections. The intensities of 1313 *hkl* reflections were measured according to the ω method (Mo Kα, graphite monochromator) using a scan range of 1° and a scan speed between 0.5 and 24.0°/min as a function of the intensity of the reflections. In the range $3.0° \leq 2\theta \leq 55.0°$, 656 reflections were obtained that were utilized in the structure determination. For the evaluation, SHELXTL on an Eclipse S/250 at the Max-Planck-Institut für Festkörperforschung was employed. The structure was solved by direct-phase determination. The phases of 297 strong relflections were determined, and on the resulting E map approximate positions of all C, N, and O atoms could be easily determined. Positional and thermal parameters could be refined by anisotropic least-squares cycles to R = 0.113.

The bis-azoalkane **5** crystallizes orthorhombically in the space group P_{nma} (No. 62) with a = 1705.9 (4) pm, b = 986.9 (2) pm, and c = 562.9 (1) pm. The unit cell contains z = 4 formula units, and the density was calculated to be 1.333 mg cm^{-3}. The labeling of the atoms is shown in Figure 1. All atomic parameters are given in Table VI and the bond distances and bond angles in Table VII.

X-ray Structure Analysis of the Monoazoalkane 11a. A clear colorless crystal of the monoazoalkane **11a** with dimensions 0.19 × 3.69 × 0.07 mm was analyzed by the same procedure described above. The intensities of 951 *hkl* reflections were determined, and 951 of these used in the structure determination. The phases of 232 strong reflections were determined. Positional and thermal parameters could be refined by anisotropic least-squares cycles to R = 0.060.

The monoazoalkane **11a** crystallizes monoclinically in the space group $P2_1$ (No. 4) with a = 774.8 (3) pm, b = 969.1 (5) pm, c = 600.7 (2) pm, and β = 95.78 (2)°. The unit cell contains Z = 2 formula units, and the density was calculated to be 1.201 mg cm^{-3}. The labeling of the atoms is shown in Figure 2. All atomic parameters are given in Table VIII and the bond distances and bond angles in Table IX.

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Registry No. 5, 96412-10-1; **9a**, 108943-58-4; **10**, 108868-13-9; **11a**, 96479-38-8; **11b**, 96412-11-2; **11c**, 96479-37-7; **11d**, 96479-39-9; **12a**, 96479-40-2; **12b**, 96412-12-3; **12c**, 96479-41-3; **13**, 934-02-1.

Light-Induced Self-Nitrosation of Polycyclic Phenols with Nitrosamine. Excited State Proton Transfer

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Abstract: Photoexcitation of polycyclic phenols in the presence of *N*-nitrosodimethylamine caused the self-nitrosation of the phenols to give 1,2- or 1,4-quinone monooximes. With use of naphthols as models, the key step of the photonitrosation was shown to be a dual sensitization process from the lowest singlet excited state of naphthols by proton transfer followed by energy migration within an exciplex to cause the known homolysis of the nitrosamine; it is assumed that the resulting radical species undergo nitrosation of naphtholates. The crucial requirement of the excited state proton transfer (ESPT) reaction is established by quenching of the photonitrosation by general bases, such as water and TEA, with quenching rate constants close to those of naphthol fluorescence by these bases.

Förster[1] pioneered the theoretical work on excited state acidity as a thermodynamic property. On the basis of both steady-state and time-resolved measurements, Weller[2] has demonstrated the validity of acid dissociation constants in excited states (pK_a*). This stimulates much interest on the mechanism of the most basic acid–base equilibria. Particularly, the advent of fast kinetic spectrometry enables the precise measurements of the various parameters of excited state proton transfer (ESPT) reactions in water and protic solvents. While literally hundreds of examples of ESPT reactions[3,4] have been described, most of the mechanistic investigations utilize naphthols as model compounds.[5-14] Most of these reactions are concerned about acid–base equilibria in the singlet excited state manifold in aqueous or protic solution rather than dealing with substantive chemical transformations that may be promoted by enhanced excited state acidity (EESA).[15-17] Such EESA-promoted reactions are severely limited by the short lifetimes of singlet excited states, typically in the order of 10 ns or shorter.[16] That is, a substantive chemical transformation must occur within the lifetime of singlet excited states so that the

(1) (a) Förster, Th. *Naturwissenschaften* **1949**, *36*, 186. (b) Förster, Th. *Z. Electrochem.* **1950**, *54*, 531.
(2) (a) Weller, A. *Z. Electrochem.* **1952**, *56*, 662. (b) Weller, A. *Prog. React. Kinet.* **1961**, *1*, 187.
(3) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*, 131.
(4) Martynov, I. Yu.; Demyashkevich, A. B.; Uzhinov, B. M.; Kuzmin, M. G. *Usp. Khim. (Engl. Trans.)* **1977**, *46*, 3.
(5) Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 891.
(6) Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 1366.
(7) Rosenberg, J. L.; Brinn, I. *J. Phys. Chem.* **1972**, *76*, 3558.
(8) Tsutsumi, K.; Shizuka, H. *Z. Phys. Chem. (Wiesbaden)* **1983**, *122*, 129.
(9) Tabita, S.; Shizuka, H. *Chem. Phys. Lett.* **1980**, *75*, 140.
(10) Shizuka, H.; Tobita, S. *J. Am. Chem. Soc.* **1982**, *104*, 6919.
(11) Webb, S. P.; Philips, L. A.; Yeh, S. W.; Tolbert, L. M.; Clark, J. H. *J. Phys. Chem.* **1986**, *90*, 5154.
(12) Lee, J.; Robinson, G. W.; Webb, S. P.; Philips, L. A.; Clark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 6538.
(13) Webb, S. P.; Yeh, S. W.; Philips, L. A.; Tolbert, M. A.; Clark, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 7286.
(14) Lee, J.; Griffin, R. D.; Robinson, G. W. *J. Chem. Phys.* **1985**, *82*, 4920.
(15) Saeva, F. D.; Olin, G. R. *J. Am. Chem. Soc.* **1975**, *97*, 5631. The proposal of an excited state acidity catalyzed reaction described in this paper remains unconfirmed upon a different opinion expressed in ref 16.
(16) Chandross, E. A. *J. Am. Chem. Soc.* **1976**, *98*, 1053.
(17) Kalanderopoulos, P.; Yates, K. *J. Am. Chem. Soc.* **1986**, *108*, 6290.

0002-7863/87/1509-5260$01.50/0