mg) in dry THF (1.5 mL) was added 18-crown-6 (38.1 mg, 0.144 mmol) followed by potassium hydride (15.4 mg, 0.384 mmol). The reaction mixture was heated at 50 °C under an inert atmosphere, and conversion to product(s) was generally complete after 3-10 h. The contents were cooled to -78 °C and quenched by dropwise addition of methanol. In the case of **11a** and **11b**, the solution was warmed to 0 °C and stirred with excess sodium borohydride for 10 min. After dilution with ether (2 mL), the solution was washed with cold NH_4Cl solution (10 mL) and water (5 mL), dried, filtered, and analyzed by capillary GC. Rotary evaporation followed by MPLC on silica gel or preparative gas chromatography (column B at 180 °C) provided pure products.

For **42**: colorless oil; IR (neat, cm^{-1}) 3340, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 4.66-4.59 (m, 2 H), 3.66 (t, J = 6.4 Hz, 2 H), 2.29-2.10 (series of m, 2 H), 1.90-1.65 (series of m, 2 H), 1.60-1.03 (series of m, 9 H); 0.82 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.36, 107.88, 63.06, 50.18, 42.63, 32.56, 32.41, 32.16, 31.07, 27.77, 27.38, 21.56; MS m/z (M^+) calcd 210.1984, obsd 210.1990. Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: 79.97; H, 12.45.

For **43**: colorless oil; IR (neat, cm^{-1}) 3350, 1642; ^1H NMR (300 MHz, $CDCl_3$) δ 4.71-4.67 (m, 1 H)), 4.57-4.53 (m, 1 H), 3.67 (t, J = 6.4 Hz, 2 H), 2.00-1.90 (m, 1 H), 1.86-1.03 (series of m, 10 H), 1.00-0.83 (m, 2 H), 0.87 (s, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.59, 104.26, 63.43, 50.72, 42.57, 38.46, 34.41, 32.47, 30.57, 28.31, 27.49, 18.04; MS m/z (M^+) calcd 210.1984, obsd 210.1993. Anal. Calcd for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.75; H, 12.39.

For **48**: colorless liquid; IR (neat, cm^{-1}) 1721, 1650; ^1H NMR (300 MHz, $CDCl_3$) δ 9.79 (t, J = 1.8 Hz, 1 H), 4.87 (d, J = 1.2 Hz, 1 H), 4.63 (s, 1 H), 2.68 (s, 1 H), 2.50 (td, J = 8, 1.8 Hz, 2 H), 2.12 (s, 1 H), 1.95-1.82 (m, 1 H), 1.60-1.12 (series of m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.56, 159.83, 102.26, 47.87, 45.77, 42.85, 40.36, 35.76, 29.52, 28.69, 26.87; MS m/z (M^+) calcd 164.1201, obsd 164.1237. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.22; H, 9.80.

For **54**: colorless liquid; IR (neat, cm^{-1}) 1725, 1650; ^1H NMR (300 MHz, $CDCl_3$) δ 9.80 (t, J = 1.9 Hz, 1 H), 4.76-4.62 (m, 2 H), 2.58-2.45 (m, 1 H), 2.45-2.36 (m, 2 H), 2.12-1.97 (m, 1 H), 1.70-1.49 (m, 4 H), 1.45-1.08 (series of m, 2 H), 0.93 (s, 3 H), 0.89 (s, 3 H), 0.79 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.36, 163.22, 100.56, 52.25, 47.05, 46.84, 42.55, 42.33, 35.24, 23.40, 19.89, 19.13, 19.02, 12.71, MS m/z (M^+) calcd 206.1671, obsd 206.1707. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.71; H, 10.88.

For **55**: ^1H NMR (300 MHz, $CDCl_3$) δ 9.80 (t, J = 1.9 Hz, 1 H), 4.76-4.65 (m, 2 H), 2.58-2.45 (m, 2 H), 2.0-1.70 (m, 2 H), 1.70-1.49 (m, 4 H), 1.45-1.08 (series of m, 2 H), 0.92 (s, 3 H), 0.87 (s, 3 H), 0.82 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.65, 164.36, 100.42, 52.32, 49.00, 48.27, 45.93, 44.08, 34.00, 23.93, 21.37, 20.29, 19.25, 12.50.

Acknowledgment. Grateful acknowledgment is made to the National Science Foundation for support of this research and to Professor Robin D. Rogers for undertaking the X-ray crystallographic analyses of **26** and **29**.

Registry No. 9, 136087-45-1; **10**, 136087-46-2; **11a**, 141273-11-2; **11b**, 141273-10-1; **12a**, 141273-17-8; **12b**, 141273-18-9; **13a**, 141273-20-3; **13b**, 141273-21-4; **14**, 37027-64-8; **15**, 79705-01-4; (*E*)-**17**, 35998-93-7; (*Z*)-**17**, 35998-94-8; **18**, 89634-48-0; **19**, 81292-71-9; **20**, 141273-08-7; **21a**, 62222-99-5; **21b**, 141273-09-8; **22**, 141273-12-3; **23**, 141273-13-4; **24**, 141273-14-5; **25**, 141273-15-6; **26**, 141273-16-7; **28**, 694-90-6; **29**, 141273-19-0; **30**, 63883-67-0; **31**, 141273-22-5; (*R*)-**38**, 63215-85-0; (*S*)-**38**, 93904-58-6; **42**, 141273-23-6; **43**, 141273-24-7; **48**, 37814-44-1; **49**, 141273-25-8; **54**, 136034-34-9; **55**, 136087-47-3; 3-buten-2-ol, 598-32-3; allyl bromide, 106-95-6; 3-(phenylsulfonyl)-1-butene, 54897-36-8; 4-*tert*-butylcyclohexanone, 98-53-3.

Supplementary Material Available: Experimental crystallographic details for **26** and **29**, as well as tables of final positional and thermal parameters, bond lengths, and bond angles for these derivatives (12 pages). Ordering information is given on any current masthead page.

Comparative Study of the Pyrolysis, Photoinduced Electron Transfer (PET), and Laser-Jet and 185-nm Photochemistry of Alkyl-Substituted Bicyclic Azoalkanes

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Abstract: The gas-phase pyrolysis, photoinduced electron transfer (PET), and laser-jet and 185-nm photochemistry of 2,3-diazabicyclo[2.2.1]hept-2-ene (**1a**), *syn*-7-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (*syn*-**1b**), *anti*-7-methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (*anti*-**1b**), 1,4-dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**1c**), 7,7-dimethyl-2,3-diazabicyclo[2.2.1]-hept-2-ene (**1d**), and *syn*-7-(1-methylethyl)-2,3-diazabicyclo[2.2.1]hept-2-ene (*syn*-**1e**) were investigated and the results of their product studies compared with one another. Pyrolysis and conventional direct and benzophenone-sensitized 350-nm photolysis of the azoalkanes **1** yielded the bicyclo[2.1.0]pentanes **2** and negligible amounts of cyclopentenes **3**. PET and benzophenone-sensitized laser-jet and 185-nm photolysis of the azoalkanes **1** led to significant quantities of cyclopentene derivatives **3**, a behavior that is attributed to radical cation-type 1,3-cyclopentadiyl intermediates, which subsequently suffer hydrogen or alkyl migration. The polar character of the radical cation $D^{\cdot+}$ is clearly demonstrated by the Wagner-Meerwein rearrangement into 2,3-dimethylcyclopentene (**3'd**) in the PET and 185-nm photolysis of azoalkane **1d**. When the corresponding 1,3-cyclopentadiyl $D^{\bullet\bullet}$ was generated in the pyrolysis of 5,5-dimethylbicyclo[2.1.0]pentane (**2d**), the 3,3-dimethyl-1,4-pentadiene (**4d**) was obtained as the exclusive reaction product; instead of methyl migration, fragmentation into the 1,4-diene took place. The PET chemistry of the stereochemically labeled azoalkanes *syn*- and *anti*-**1b** revealed that the radical cations $D^{\cdot+}$ have a puckered geometry, because a stereochemical memory effect was observed for the cyclopentene products **3**. Specifically, the *pseudoaxial* substituent at the stereolabeled center migrates with preference, which speaks for a *coplanar* arrangement for the rearrangement in $D^{\bullet+}$. The common and distinct mechanistic features of the denitrogenation processes of the various thermal and photochemical activation modes will be discussed.

Unsubstituted or alkyl-substituted, saturated, cyclic azoalkanes have a weak absorption ($^1n,\pi^*$) at ca. 300-350 nm, which is separated from the $^1\pi,\pi^*$ transition by a spectral window between 250 and 300 nm.[1] Direct irradiation at 350 or 185 nm normally leads to significantly differing photoreactivity. This may be taken as evidence that Kasha's rule is being violated in these examples because of the large energy gap between S_1 and S_2. Kasha's rule[2]

† Undergraduate research participant, spring 1987.
‡ Undergraduate research participant, autumn 1990.

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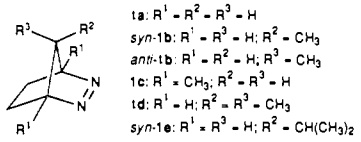
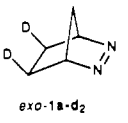
states that photochemical reactions take place out of the lowest singlet or triplet excited states of the substrates. The reason for this is fast, radiationless decay from the higher excited to the lowest excited S_1 or T_1 states, with which photochemical reactions (bond reorganization) cannot compete. For this reason, normally a pronounced wavelength dependence in photochemical reactions is not observed.

To explain the different wavelength-dependent products or product distributions on the basis of a Salem diagram, zwitterions have been postulated as intermediates of the 185-nm photolysis,[3] which are not accessible in the conventional 350-nm photolysis. Another possibility is the formation of radical cations, which analogous to the zwitterions represent high-energy intermediates compared to triplet or singlet diradicals.

In this paper we have undertaken a detailed mechanistic study of the transformations of alkyl-substituted cyclic azoalkanes **1a–e** induced by pyrolysis, photosensitized electron transfer (PET), and 185-nm, laser-jet, and 350-nm photolyses. Particularly the PET



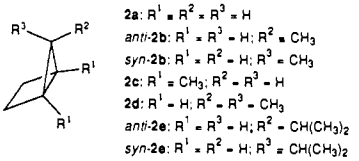


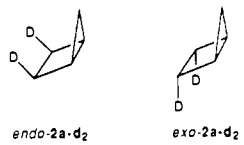
experiments constitute a suitable means for generating the radical cations of the 1,3-cyclopentadiyls derived from the azoalkanes **1a–e** by nitrogen extrusion. Parallel photochemical behavior is expected in the 185-nm photolysis, provided the same intermediates intervene. On the other hand, under the conditions of the high photon density available in the laser-jet technique,[4a–c] it is in principle feasible on triplet sensitization to generate with the first photon a 1,3-cyclopentadiyl in its triplet state (Ph_2CO^* as sensitizer) from the azoalkane and to excite the triplet diyl with a second photon (again Ph_2CO^* as sensitizer) to higher excited states. Under this premise, similar photoreactivity may be expected in the laser-jet and 185-nm photolyses modes. The conventional denitrogenation modes such as pyrolyses and 350-nm photolyses, which serve as sources for ground-state diradicals, have also been included to permit comparison of their reactivity with that of the high-energy intermediates. Such a mechanistic survey in the pyrolytic and photolytic denitrogenation of cyclic azoalkanes is lacking to date and we anticipated with this detailed study to provide better insight into the behavior of short-lived diyl-type species.

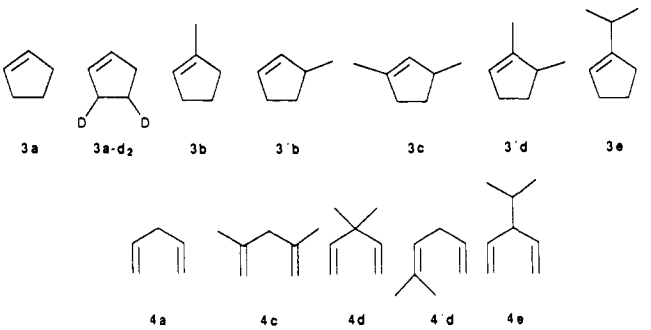
Results

Product Studies. In Table I are summarized the types of products and their composition for the pyrolyses and photolyses of the various azoalkanes **1**. As can be seen, the denitrogenation of the azoalkanes **1** leads to the bicyclopentanes **2** as cyclization products, the cyclopentenes **3** as rearrangement products, and the 1,4-pentadienes **4** as fragmentation products, together with various amounts of miscellaneous products such as dimers (laser-jet mode), cyclopentadienes (PET), and others. These products were identified by spectral and gas chromatographic comparison with the authentic materials.

Stereochemical Assignments. An X-ray analysis of the urazole precursor of *anti*-**1b** revealed that the stereochemistry of the azoalkanes *syn*- and *anti*-**1b** is opposite to that assigned in the literature.[6a,b] On the other hand, NOE experiments on the







housane *syn*-**2b** confirmed the previously reported structure assignment.[6c,d]

The stereochemistry of the azoalkane *syn*-**1e** was also assessed by NOE experiments. The interaction of 7-H with 5-H_x and 6-H_x clearly demonstrates the syn position of the isopropyl substituent. The decisive finding in support of the structure of the bicyclopentanes *syn*/*anti*-**2e** came from the fully coupled ^{13}C NMR spectra of mixtures that were obtained in the pyrolyses and photolyses of azoalkane *syn*-**1e**. The ^{13}C–^1H coupling constants are given in the section 185-nm photolysis of *syn*-**1e**. Thus the bicyclopentanes *syn*- and *anti*-**2e** exhibit three doublets in the ^{13}C NMR spectrum (C-1/C-4, C-5, and C-6), but only C-6 has the typical coupling constant of ca. 125 Hz for sp^3 carbons. The high-field shift of C-6 in *syn*-**2e** is proof that this carbon atom is positioned in a region of relatively high electron density, i.e., the concave side of the bicyclopentane.

Discussion

Transformation of the Azoalkanes 1. In Scheme I are displayed the mechanistic connections between the five denitrogenation modes of azoalkanes **1** under consideration. These different modes shall now be discussed by first addressing the conventional pyrolyses and 350-nm photolyses, followed by the special PET and 185-nm and laser-jet photolyses.

Pyrolyses. On thermal activation, the azoalkanes **1** produce by one-bond cleavage the corresponding diazenyl diradicals $^1D'_{\sigma,\sigma}$, which lose in a second step dinitrogen to give the bicyclopentanes **2**. The stepwise loss of dinitrogen has been established experimentally[7] and needs no further elaboration. The preferred ste-

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Table I. Product Studies of the Photolyses and Pyrolyses of the Azoalkanes **1a–e**

entry (ref)	substrate	conditions	conversion, %	mass balance or yield, %	product distribution,[a] % **2a**	**3a**	**4a**
1 (5a,b)	**1a**	TPT,[b] CH_2Cl_2, $\lambda > 400$ nm		80–90	20	80	0
2 (5c)	**1a**	185 nm, *n*-C_7H_{16}	42	34	52	38	8
3	**1a**	laser jet, *n*-C_7H_{16}, Ph_2CO[c]	55	67	45	10	0
4	**1a**	laser jet, *n*-C_7H_{16}	55	67	>99	<1	0

entry (ref)	substrate	conditions	conversion, %	mass balance or yield, %	product distribution,[a] % exo-**2a**-d_2	endo-**2a**-d_2	**3a**-d_2
5 (3)	exo-**1a**-d_2	180 °C/130 Torr	ca. 100	ca. 100	74	25	1
6 (5b,d)	exo-**1a**-d_2	333–364 nm, *n*-C_5H_{12}	ca. 100	ca. 100	75	25	trace
7 (5e)	exo-**1a**-d_2	350 nm, Ph_2CO, C_6H_6	ca. 100	ca. 100	50	50	trace
8 (3)	exo-**1a**-d_2	185 nm, *n*-C_7H_{16}			37	12	43
9	exo-**1a**-d_2	laser jet, C_6D_6, Ph_2CO[d]	ca. 35		30	30	7

entry (ref)	substrate	conditions	conversion, %	mass balance or yield, %	product distribution,[a] % syn-**2b**	anti-**2b**	**3b**	**3'b**
10	*syn*-**1b**	190 °C/100 Torr	90	45	80	15	5	0
11	*syn*-**1b**	230 °C/100 Torr	100	62	47	46	7	0
12	*syn*-**1b**	333–364 nm, CH_3CN, Ar	100	100	67	30	3	0
13	*syn*-**1b**	364 nm, CH_3CN, Ar, Ph_2CO	100	100	44	56	0	0
14	*syn*-**1b**	DCA,[e] CH_3CN, $\lambda > 400$ nm	25	70	9	13	78	0
15	*syn*-**1b**	185 nm, *n*-C_5H_{12}	85	90	43	29	18	2
16	*syn*-**1b**	laser jet, *n*-C_7H_{16}, Ph_2CO	ca. 35		43	46	2	2
17	*syn*-**1b**	laser jet, CH_3CN	ca. 35		57	40	3	0
18	*anti*-**1b**	190 °C/100 Torr	2		22	78	0	0
19	*anti*-**1b**	333–364 nm, CH_3CN, Ar	100	100	25	74	1	0
20	*anti*-**1b**	364 nm, CH_3CN, Ar, Ph_2CO	100	100	44	56	0	0
21	*anti*-**1b**	DCA, CH_3CN, $\lambda > 400$ nm	8	30	23	17	14	46
22	*anti*-**1b**	185 nm, *n*-C_5H_{12}	15	88	24	56	10	10
23	*anti*-**1b**	laser jet, *n*-C_5H_{12}, Ph_2CO	ca. 40		44	52	2	2

entry (ref)	substrate	conditions	conversion, %	mass balance or yield, %	product distribution,[a] % **2c**	**3c**	**4c**
24	**1c**	270 °C/760 Torr	100	55	>99	0	0
25	**1c**	350 nm, *n*-C_5H_{12}	100		100	0	0
26	**1c**	DCA, CH_3CN, $\lambda > 400$ nm	75	100	46	54	0
27	**1c**	185 nm, *n*-C_5H_{12}	100	43	43	32	10
28	**1c**	laser jet, *n*-C_5H_{12}, Ph_2CO	52	46	84	7	0
29	**1c**	laser jet, *n*-C_5H_{12}	52	46	100	0	0

entry (ref)	substrate	conditions	conversion, %	mass balance or yield, %	product distribution,[a] % **2d**	**3'd**	**4d**	**4'd**
30	**1d**	350 nm, *n*-C_5H_{12}	100	32	99	0	0	0
31a	**1d**	DCA, CH_3CN, $\lambda > 400$ nm[f]	12	57	19	70	0	0
31b	**2d**	540 °C/760 Torr	100	80	0	0	100	0
32	**1d**	185 nm, *n*-C_5H_{12}	100	18	65	17	3	10
33	**1d**	laser jet, CH_3CN, Ph_2CO	25		100	0	0	0

entry (ref)	substrate	conditions	conversion, %	mass balance or yield, %	product distribution,[a] % *syn*-**2e**	*anti*-**2e**	**3e**	**4e**
34a	*syn*-**1e**	270 °C/760 Torr	100	66	23	66	11	0
34b	*syn*-**2e**/*anti*-**2e**, 82:18	270 °C/760 Torr		94	23	64	13	0
35	*syn*-**1e**	350 nm, *n*-C_5H_{12}	100	68	80	17	3	0
36	*syn*-**1e**	350 nm, *n*-C_5H_{12}, Ph_2CO	100	62	77	23	0	0
37	*syn*-**1e**	185 nm, *n*-C_5H_{12}	100	16	65	16	14	5

[a] The difference to 100% consists of other volatile compounds. [b] TPT = triphenylpyryllium tetrafluoroborate. [c] 45% dimers were observed (cf. Experimental Section); variation of the Ph_2CO/**1a** ratios from 2:1, to 1:1, to 1:2 led to a decrease in the cyclopentene **3a** of 10, 6, and 4%. [d] 33% dimers were observed. [e] DCA = 9,10-dicyanoanthracene. [f] 11% dimethylcyclopentadiene was also detected.

reochemical course of this reaction for non-bridgehead-substituted azoalkanes is reflected in entry 5 of Table I, in which doubly inverted *exo*-**2a**-d_2 is obtained as major product. As second example may serve *syn*- and *anti*-**1b**, which also yield the doubly inverted bicyclopentanes (entries 10, 11, and 18 in Table I). In regard to azoalkane *syn*-**1e**, the situation is complicated by the fact that *syn*-**2e** (the product of the double inversion) isomerizes efficiently to *anti*-**2e** already below the temperature required for dinitrogen extrusion and thus obscures the stereochemical course (entries 34a,b in Table I).

350-nm Photolyses. In the case of the direct 350-nm photolyses, the azoalkanes **1** have several photochemical product channels. Some of these possibilities have been discussed by us a few years ago[3] and recently confirmed and extended by Weisman et al.[8] Thus, there seems to be a major and a minor pathway leading to the products (cf Scheme I):

The sequence **1** → $[^1n,\pi^*]$ → $^1D'_{\sigma,\pi}$ → $^1D'_{\sigma,\sigma}$ → **2** (inverted) is the major pathway. C–N bond cleavage of the $^1n,\pi^*$ excited azoalkanes **1** leads to the $^1D'_{\sigma,\pi}$ singlet diazenyl diradicals; col-

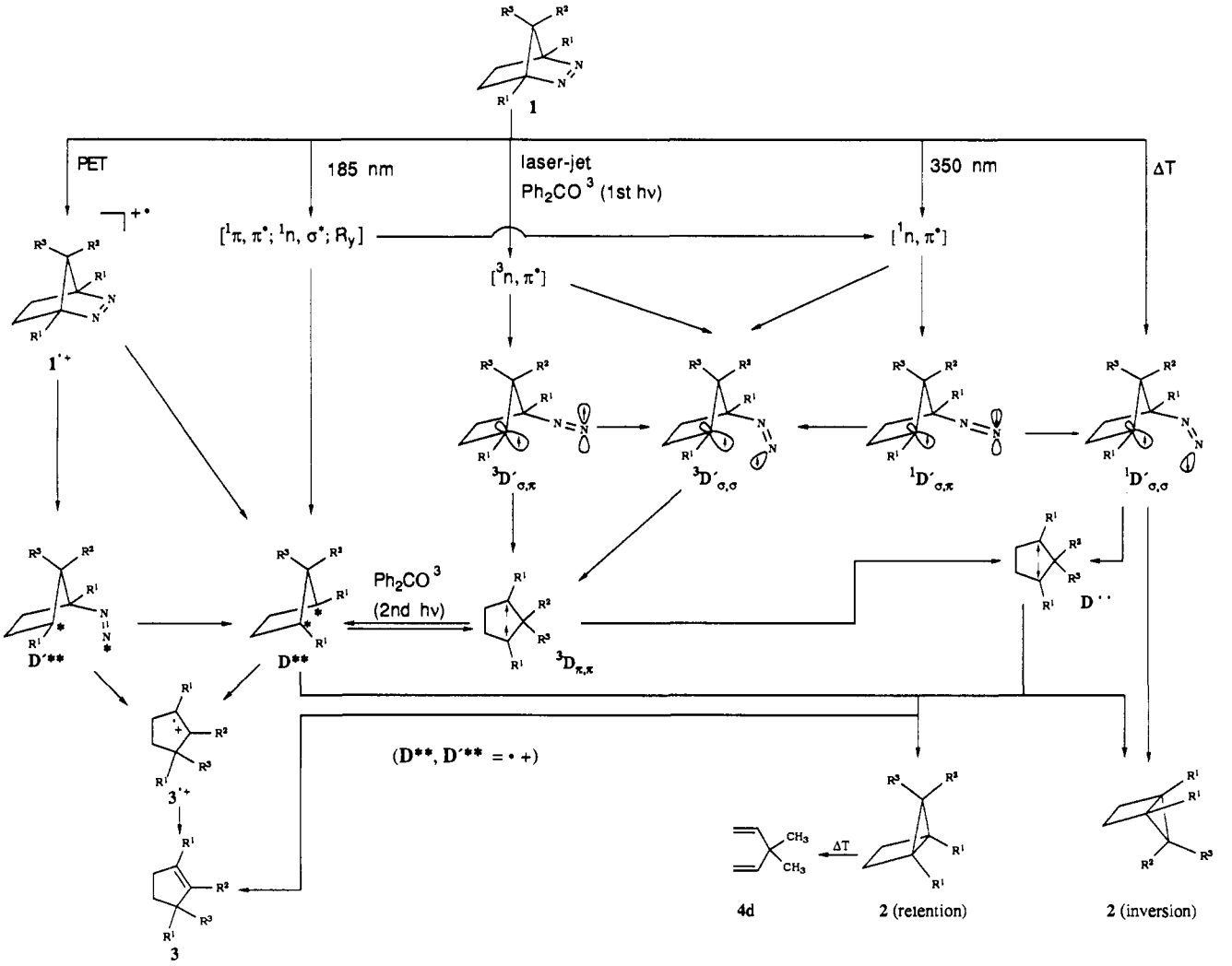
(8) Adams, J. S.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1990**, *112*, 9115.

(9) (a) Adam, W.; Bottle, S. *Tetrahedron Lett.* **1991**, *32*, 1405. (b) Adam, W.; Finzel, R., unpublished results. (c) Oppenländer, T. Dissertation, Universität Würzburg, 1984; p 117.

(10) Adam, W.; Chen, G.-F.; Walter, H.; Williams, F. *J. Am. Chem. Soc.*, in press.

(11) (a) Gerson, F.; Qin, X.-Z.; Ess, C.; Kloster-Jensen, E. *J. Am. Chem. Soc.* **1989**, *111*, 6456. (b) Williams, F.; Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F. *J. Chem. Soc., Chem. Commun.* **1989**, 1835.

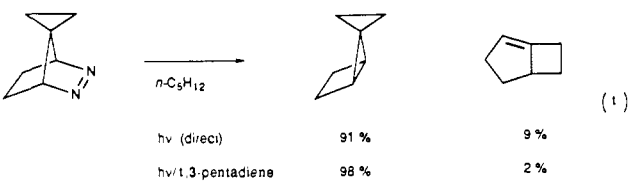
Scheme I. Mechanisms for the Photochemical and Thermal Denitrogenations of the Azoalkanes **1**



lision-induced internal conversion affords the $^1D'_{\sigma,\sigma}$ diazenyl diradicals, which readily eliminate ground-state dinitrogen by a S_H2 process[7j-n] to generate predominantly doubly inverted bicyclopentanes **2**.

The steps **1** → $[^1n,\pi^*]$ → $^1D'_{\sigma,\pi}$ → $^3D'_{\sigma,\sigma}$ → $^3D_{\pi,\pi}$ → **2** (inverted and retained) serve as the minor pathway. The $^1D'_{\sigma,\pi}$ diazenyl diradicals mentioned above give on internal conversion coupled with intersystem crossing the triplet $^3D'_{\sigma,\sigma}$ diazenyl diradicals, which then under loss of dinitrogen yield the planar triplet $^3D_{\pi,\pi}$ 1,3-cyclopentadiyls. Cyclization under spin inversion generates inverted and retained bicyclopentanes **2**. The key intermediate for the formation of inverted housane **2** in the 350-nm photolysis (also in the pyrolysis) is the diazenyl diradical $^1D'_{\sigma,\sigma}$ rather than the nitrogen-free diradical $^1D^{2\bullet}$.[7j-n] Taking the case of the deuterio-labeled azoalkane *exo*-**1a**-d_2 as example, the triplet diradical $^3D_{\pi,\pi}$ necessarily will give equal amounts of retained (endo) and inverted (exo) housanes **2a**-d_2 (cf. entries 7, 13, and 20 in Table I), because the $^1D_{\pi,\pi}$ is a planar species.[6b,12] However, the singlet diradical $^1D^{2\bullet}$ is, like the radical cation $D^{\bullet+}$,[10] expected to be puckered and should lead predominantly to the retained housane *endo*-**2a**-d_2; this is contrary to the observed facts (entries 5 and 6 in Table I). Thus, we propose that quite generally the diazenyl diradical $^1D'_{\sigma,\sigma}$ serves as a common intermediate in the 350-nm photolyses of the azoalkanes **1** (major pathway) and the pyrolyses (entries 5, 6, 10, 12, 18, and 19 in Table I). Competition between loss of N_2 with concomitant cyclization (S_H2 process[7j-n]) versus formation of the $^1D^{2\bullet}$ diradical explains not only why inverted housane **2** predominates but also why the ratios of inverted and retained bicyclopentanes **2** are often very similar.

Loss of diastereoselectivity in the denitrogenation, as already stated, is also attributed to the triplet pathway. Weisman's evidence for the generation of triplet 1,3-cyclopentadiyl in the gas-phase photolysis[8] (entries 10 and 12 in Table I) suggests that the loss of selectivity derives from a pronounced triplet channel in the 350-nm photolysis. Further experimental evidence for a triplet channel as a side route is the fact that in the direct photolysis of **1a** the corresponding triplet 1,3-cyclopentadiyl $^3D_{\pi,\pi}$ could be trapped in small quantities by nitroxide[9a] and triplet dioxygen.[9b] Additionally, it was observed that the 350-nm photolysis of spiro[cyclopropane-7,1'-[2,3]diazabicyclo[2.2.1]hept-2-ene] in the presence of 1,3-pentadiene yielded smaller amounts of the triplet rearrangement product bicyclo[3.2.0]hept-1-ene than without the triplet quencher (eq 1).[9c]



(1)

Photoinduced Electron Transfer (PET). The PET chemistry of the azoalkanes **1** shows the following common features:

Electron transfer from azoalkane **1** to an excited electron acceptor produces the radical cation $\mathbf{1}^{\bullet+}$ (Scheme I).

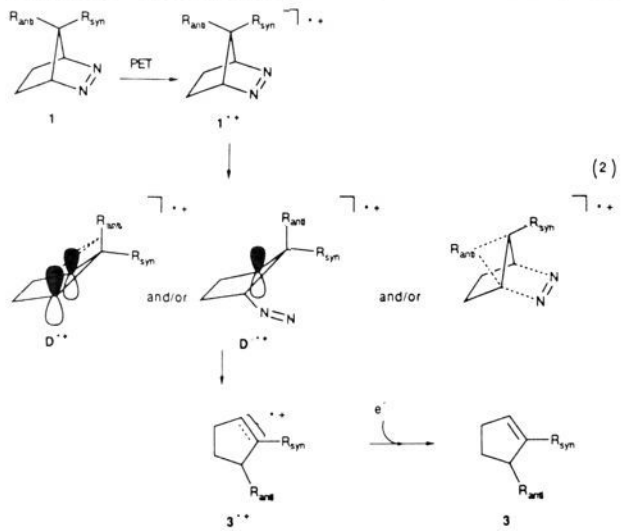
Concerted or stepwise dinitrogen loss gives the radical cations D** (** = $^{\bullet+}$ in Scheme I). These species exhibit a high tendency

(12) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165.

for hydrogen and even alkyl migration, which was first shown for azoalkane **1a** (entry 1 in Table I) and 2,3-diazatricyclo-[4.3.0.0^{4,9}]non-2-ene.[5a] These azoalkanes gave the respective Wagner–Meerwein rearrangement products cyclopentene **3a** (80%) and norbornene (94%). Further examples for such rearrangements are given in entries 14, 21, 26, and 31a of Table I. It should be mentioned that under the conditions at which the 1,3-cyclopentadiyl radical cations D$^{\bullet+}$ were observed in the γ-irradiation (matrix isolation) of the bicyclopentanes *syn*/*anti*-**2b**, only cyclopentene radical cations **3b**$^{\bullet+}$/**3′b**$^{\bullet+}$ were detected from the azoalkanes *syn*/*anti*-**1b**.[10] These facts imply the pathway **1**$^{\bullet+}$ → D′** → **3**$^{\bullet+}$ → **3** as an additional mechanistic possibility.

The best experimental evidence for radical cationic intermediates D′$^{\bullet+}$ or D$^{\bullet+}$ is given in entries 31a, b of Table I. When such species were generated from azoalkane **1d** under PET conditions (entry 31a), high amounts of methyl migration product **3′d** were obtained. On the other hand, pyrolysis of bicyclopentane **2d** (entry 31b) yielded exclusively 1,4-pentadiene **4d**, presumably from a vibrationally excited, nonpolar, singlet 1,3-cyclopentadiyl D$^{2\bullet}$. These results demonstrate the different chemical behavior of the diradical and radical cation intermediates.

Further information on the radical cations D$^{\bullet+}$ and/or D′$^{\bullet+}$ (Scheme I) was obtained by examining the PET chemistry of the azoalkanes *syn*/*anti*-**1b**. From entries 14 and 21 in Table I it is apparent that the substituent in the anti position to the azo group migrates preferentially to yield the corresponding cyclopentene products **3b** and **3′b**. This implies a puckered geometry for the nitrogen-free intermediates; because were they planar, the same product distribution from *syn*-**1b** as well as from *anti*-**1b** would be expected. Puckered 1,3-radical cations were inferred from ESR data in the γ-irradiation (matrix isolation) of bicyclo[1.1.0]butane,[11a] bicyclo[2.1.0]pentane,[11b] and *syn*-/*anti*-**2b**.[10] It was concluded that the radical cationic centers of the 1,3-cyclopentadiyl possess essentially p-character. Therefore, the original anti substituent at the intervening sp^3 center (eq 2) is in almost perfect coplanar alignment with the 2p orbital lobes, which facilitates its migration. As further mechanistic possibilities consider the



(2)

diazenyl radical cation D′$^{\bullet+}$, which denitrogenates with concomitant migration of the antiperiplanar substituent, or the one-step loss of dinitrogen from **1**$^{\bullet+}$ with concurrent migration of the substituent anti to the azo linkage.[10]

185-nm Photolyses. A striking feature in the 185-nm photolyses (entries 8, 15, 22, 27, 32, and 37 in Table I) is the fact that the cyclopentene products **3** are generated in much higher amounts than in the 350-nm photolyses (entries 6, 12, 19, 25, 30, and 35 in Table I) of the azoalkanes **1**. We interprete this to mean that 185-nm irradiation of azoalkanes **1** leads to higher excited states such as $^1\pi,\pi^*$, ^{1}n,σ^*, and Ry. Partial internal conversion to the ^{1}n,π^* states competes with the formation of excited 1,3-cyclopentadiyl intermediates D** (** = $^{\bullet+}$ and/or $^{+-}$ in Scheme I), whose reactivity is similar to that of the radical cations generated in the PET processes; therefore, the more pronounced cyclopentene formation is not surprising.

Of special mechanistic importance is the fact that the vibrationally excited 1,3-diradical D$^{2\bullet}$, generated from bicyclopentane **2d** (entry 31b in Table I) by pyrolysis at high temperatures, yields exclusively diene **4d** by fragmentation but no cyclopentene **3′d** by methyl migration. This is in support of polar intermediates in the rearrangement process that affords **3′d**, as observed in the 185-nm photolysis of **1d** (entry 32 in Table I). The diene products **4** are only generated in small amounts in the 185-nm photolyses of azoalkanes **1**. Control experiments confirmed that the dienes **4** are predominantly secondary photolysis products of the bicyclopentanes **2**.

Of mechanistic interest are the stereolabeled azoalkanes *syn*/*anti*-**1b** in regard to the stereochemistry of the rearrangement process to afford cyclopentenes **3b**/**3′b**. For example, entries 15 and 22 in Table I indicate the preferred migration of the substituent anti to the azo linkage, analogous to the PET process (entries 14 and 21 in Table I), as rationalized in eq 2. The equal amounts of cyclopentenes **3b** (10%) and **3′b** (10%) from azoalkane *anti*-**1b** (entry 22 in Table I), although the observed stereochemical memory effect[10] would demand a greater quantity of **3′b**, is presumably due to the fact that hydrogen migration to give **3b** is more facile than methyl migration to afford **3′b** under these conditions.

Laser-Jet Photolyses. As expected, direct photolyses under laser-jet conditions (entries 4, 17, and 29 in Table I) gave similar results as the conventional 350-nm photolyses in a Rayonet Photochemical Reactor. Thus, the lifetime of singlet diradicals is too short for the absorption of a photon and consequently no photochemistry of such short-lived transients is observed in the laser-jet photolyses.

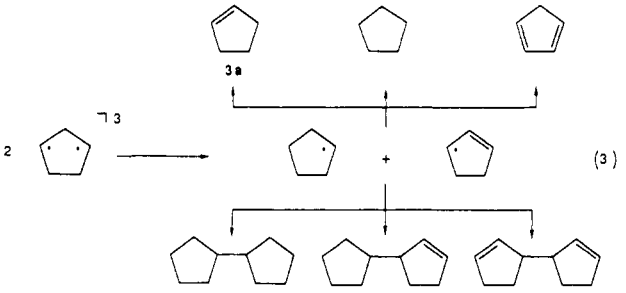
The situation is different for the much longer lived[12] triplet 1,3-cyclopentadiyls $^3D_{\pi,\pi}$ generated by benzophenone-sensitized photolysis. Compared to conventional triplet sensitization (entries 7, 20, and 36 in Table I), the cyclopentenes **3** (rearrangement) are found as new products in yields between 4 and 10% under laser-jet conditions (entries 3, 9, 16, 23, and 28 in Table I). The facts that the triplet diradical $^3D_{\pi,\pi}$ had no absorption above 300 nm[12] and the [Ph_2CO] is ca. 10^4 times greater than that of the transient triplet diradical ([$^3D_{\pi,\pi}$] is at the best micromolar) speak for triplet sensitization by Ph_2CO rather than direct absorption of $^3D_{\pi,\pi}$ to account for the novel rearrangement to cyclopentene (**3a**). That the lifetime of the triplet diradical is critical in observing photochemistry of these intermediates under laser-jet conditions is exhibited by entries 3, 28, and 33 in Table I. By using comparable substrate concentrations and laser power, the amount of cyclopentenes **3a** (10%), **3c** (7%), and **3d** (0%) decreases with the respective triplet lifetimes 96 ± 11,[12] 42 ± 7,[12] and < 0.1 ns.[12] Furthermore, the higher the benzophenone to azoalkane ratio (cf. footnote c in Table I), the more rearrangement products, i.e., the cyclopentenes **3**, are formed. This signifies that at higher triplet sensitizer concentration the probability of interaction with the transient triplet diradical is increased. Thus, novel photochemical transformations such as the rearrangement of triplet 1,3-cyclopentadiyls into cyclopentenes become observable.

Upper excited states of benzophenone do not appear to play an important role in these laser-jet experiments. It is known that upper excited Ph_2CO^{**} is efficiently quenched by benzene,[13] but also in this solvent the azoalkane **1a** gave the same amount of cyclopentene **3a** as in *n*-heptane on laser-jet photolysis. Furthermore, higher excited electronic configurations of the azoalkanes **1** appear not to be involved, because the photoreluctant 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) afforded no photoproducts even under laser-jet conditions. It is known that DBO efficiently loses dinitrogen (Φ = 0.5) in the 185-nm photolysis,[14] for which upper excited states are held responsible. In further control experiments the possibility that the bicyclopentanes **2** undergo photochemical transformations on benzophenone sensitization

(13) McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13.
(14) Adam, W.; Mazenod, F. *J. Am. Chem. Soc.* **1980**, *102*, 7131.

under laser-jet conditions was excluded. On the basis of these facts, we suggest that triplet-excited benzophenone sensitizes the azoalkanes **1** into their $^3n,\pi^*$ state by triplet energy transfer (Scheme I). One-bond cleavage of the latter leads to the diazenyl diradicals $^3D'_{\sigma,\pi}$ and $^3D'_{\sigma,\sigma}$, which denitrogenate into the 1,3-cyclopentadiyls $^3D_{\pi,\pi}$. These triplet diradicals yield after intersystem crossing the usual bicyclopentanes **2** or alternatively they collide with another triplet benzophenone to give the higher energy intermediates $D^{\bullet+}$. As for the PET process and the 185-nm photolyses, such polar forms suffer hydrogen or alkyl migration to produce cyclopentenes **3** as new products, which are normally not observed in the diyl photochemistry of azoalkanes. Thus, the sequence of events (cf. Scheme I) **1** + $^3Ph_2CO^* \rightarrow {}^3n,\pi^* \rightarrow {}^3D'_{\sigma,\pi}/{}^3D'_{\sigma,\sigma} \rightarrow {}^3D_{\pi,\pi}$ + $^3Ph_2CO^* \rightarrow D^{\bullet+} \rightarrow$ **3** may constitute a hitherto unprecedented *two-photon process*. The *first* photon (synthesis photon) acts through $^3Ph_2CO^*$ by triplet-sensitized denitrogenation to afford the triplet diyl $^3D_{\pi,\pi}$ and the *second* photon (reaction photon), again in the form of $^3Ph_2CO^*$, generates from the $^3D_{\pi,\pi}$ transient the activated polar species $D^{\bullet+}$ by electron transfer; finally, the cyclopentenes **3** result from the radical cation $D^{\bullet+}$.

As the yields of cyclopentenes **3b/3'b** were too low in the experiments with *syn/anti*-**1b**, it is not possible at the moment to make definitive conclusions about the stereochemical course of the last two steps in the above novel sequence. Furthermore, the question must be addressed for the parent system **1a** (entry 3 in Table I) as to whether some of the cyclopentene product arises from the disproportionation of a pair of $^3D_{\pi,\pi}$ diradicals, as outlined in eq 3, rather than exclusively from a 1,2-hydrogen shift. We



plan to generate mixtures of cyclopentyl and 3-cyclopentenyl radicals independently and look for cyclopentene as well as the expected cyclopentane and cyclopentadiene products.

In summary, the comparison of the experimental results on the denitrogenation of a number of azoalkanes **1** by a variety of activation modes (Scheme I), which include gas-phase pyrolysis (ΔT), n,π^* excitation (350 nm), photoinduced electron transfer (PET), and 185-nm and laser-jet photolyses, has enabled us to obtain more detailed mechanistic insights into the complex behavior of 1,3-cyclopentadiyl intermediates. In their ground state $D^{2\bullet}$ (pyrolysis, direct photolysis at 350 nm), these species almost exclusively cyclize into bicyclopentanes **2**. When vibrationally excited under gas-phase pyrolysis conditions (>500 °C), the predominating reaction channel is 1,2-hydrogen shift to give cyclopentenes **3**. If the 2-position is doubly alkylated, e.g., the 2,2-dimethyl-1,3-cyclopentadiyl derived from housane **2d**, the vibrationally excited $D^{2\bullet}$ is reluctant to suffer a 1,2-methyl shift and prefers fragmentation into the diene **4d**.

More complex and mechanistically less definitive is the behavior of the electronically excited 1,3-cyclopentadiyls D^{**}. When polar transients such as radical cations $D^{\bullet+}$ (PET and laser-jet chemistry) and radical cation-like species (185-nm photolysis) are produced, the characteristic transformations are 1,2-hydrogen as well as 1,2-alkyl shifts. In the latter case, the novel mechanistic feature is a stereochemical memory effect, in which the puckered radical cation $D^{\bullet+}$ preferentially undergoes migration of the *pseudoaxial* substituent (*coplanarity*).

Experimental Section

General Aspects. Photolyses. All photolyses were conducted by using degassed spectrograde solvents. *n*-Pentane was purified as reported.[15]

Table II. Spectral Energy Distribution of the Used Light Sources

capillary lamp No. 4, Gräntzel Co. λ, nm (%): 184.9 (7.9–9.7), 253.7 (66.0), 296.8 (1.0), 312/313 (2.7), 365/366 (2.4), 404.7/407.8 (4.5), 435.8 (7.3), 546.1 (6.5), 577/579 (1.8)
HNS 10W/U_{oz}, Osram. λ, nm (%): 184.9 (12), 253.7 (78.5), 296.8 (0.5), 302.3 (0.3), 312/313 (2.7), 365/366 (2.1), 404.7/407.8 (1.6), 435.8 (3.7), 546.1 (1.6), 577/579 (0.3)
TQ 150, Heraeus GmbH. λ, nm (watt): 405/408 (3.2), 436 (4.2), 546 (5.1), 577/579 (4.7)
INNOVA 100 argon ion laser, Coherent Co. λ, nm: 333.6, 335.5, 351.1, 351.4, 363.8

Photolysis Equipment. The 350-nm photolyses were performed in the Rayonet Photochemical Reactor of the Southern New England UV/Co. under nitrogen atmosphere.

The 185-nm photolyses on a 5-mL scale were carried out with the capillary lamp No. 4 (Gräntzel Company, Karlsruhe) under nitrogen atmosphere in a closed Suprasil quartz cuvette. With a Vycor M 235 cutoff filter, the capillary lamp could also be used for 254-nm photolyses on an analytical scale.

Preparative 185-nm photolyses were performed with a HNS 10W/U_{oz} lamp (Osram Co.) in an immersion well vessel. The photolysis solutions were externally cooled with ice water and irradiated under vigorous stirring in a gentle flow of nitrogen gas; for further cooling a reflux condenser was provided. Table II gives an overview of the spectral energy distribution of the lamps.

For the laser-jet photolyses a solution of the corresponding azoalkane and benzophenone was deoxygenated by four freeze–pump–thaw cycles. Then the solution was pumped with an HPLC pump (Model 2200, Bischoff Co.; analytical pump head with a pump rate of 0.01–4.99 mL/min and preparative pump head with a pump rate of 0.1–20 mL/min) through a capillary (diameter 100 or 75 μm)[4a] into the laser beam, which was focused exactly on the liquid beam by means of a quartz lens (f = 80 cm). The lens was fixed on an optical bench and could be adjusted with the motor mike control unit Model 18005 from the Oriel Corp. After passage through the irradiation zone, the photolysis solution was collected in a flask. All irradiations were carried out under argon gas and with all available UV lines (Table II) of the argon ion laser. The progress of the reaction was monitored by capillary GC. The identification of the products was achieved by coinjection with authentic material. The mass balances, conversions, and product distributions are collected in the Table I.

PET reactions on a 5-mL scale were carried out in a closed system provided with a gas inlet and a sampling outlet and allowing for internal cooling. The solutions were ca. 0.02 M in substrate, contained an appropriate GC standard (c-C_7H_{14} or n-C_9H_{20}), and were saturated with DCA. The solutions were deaerated by bubbling Ar for 20 min at −5 °C through them, while they were stirred magnetically, and irradiated at λ ≥ 400 nm (filtered light of a 150 W Heraeus TQ 150 high-pressure mercury arc) and −5 °C. The progress of the photolyses was monitored by capillary GC by making sure that adventitious proton catalysis did not falsify the initial product distribution. The identity of the products of the various photolyses was confirmed by GC–MS and GC coinjections of authentic materials.

Pyrolysis Equipment. For temperatures up to 350 °C a Pyrex tube of 35-cm length and 13-mm diameter with two standard joints connected to two 5-mL flasks was used. The tube was provided with a heating wire and was operated in the horizontal position. For temperatures higher than 350 °C a quartz tube of 50-cm length and 13-mm diameter was used, which was also operated in the horizontal position and heated with thermostated control. The substrate was placed in one of the flasks and cooled down to −78 °C under an argon gas atmosphere for the exclusion of moisture. The apparatus was evacuated to 15 Torr, and the substrate was allowed to warm up, thereby slowly distilling through the pyrolysis tube. The effluent was condensed into the receiving flask by cooling with liquid nitrogen.

Gas Chromatography. Preparative gas chromatographic separations were performed on a Carlo Erba, Model 4200, gas chromatograph (FID). Analytical separations and quantitative analyses were carried out with a Carlo Erba Strumentazione 4100 (FID), a Fractovap 2900 series capillary column GC or a HRGC 5160 Mega-Series. As integrators a Shimadzu C-R1B Chromatopac, a Carlo Erba Mega 2, or a Spectra-Physics System I Computing system were used. GC–MS analyses were performed either in the Institute of Pharmaceutical and Nutritional Chemistry by Dr. C. Kahre (Finnegan MAT 44 Quadrupole mass spectrometer, supplied with a SS 200 data evaluation system and coupled

(15) Adam, W.; Oppenländer, T. *Photochem. Photobiol.* **1984**, *39*, 719.

to a Varian Aerograph 1440) or in the Institute of Organic Chemistry by Dr. G. Lange (8200 Finnigan MAT mass spectrometer coupled with a Varian 3700 gas chromatograph).

Spectroscopy. Infrared spectra were recorded on a Perkin-Elmer infrared ratio recording spectrometer 1420. Capillary GC–FTIR analyses were performed by Dr. Kahre (Nicolet 20 SXB connected to a DANI 6500 gas chromatograph). ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AC 200 or WM 400 spectrometer by using Me_4Si or $CDCl_3$ as reference. UV spectra were recorded with a Hitachi U-3200 spectrometer.

Conversions, Yields, and Mass Balances. Error Limits. The conversion was determined by gas chromatography according to eq 4, where A_t = peak area after the reaction time t, A_0 = peak area before the reaction, S = substrate, and IS = internal standard (inert hydrocarbon or the solvent). Relative yields were determined by gas chromatography or

$$\% \text{ conversion} = [1 - [A_t(S)/A_t(IS)]/[A_0(S)/A_0(IS)]] \times 100 \quad (4)$$

NMR spectroscopy. As quantitative measure were used the peak areas in the gas chromatography or the peak area of characteristic NMR signals normalized to one proton (eq 5), where $A(P)$ = peak area of a product and $\sum A(P)$ = sum of the product peak areas. The mass bal-

$$\text{rel yield } (\%) = [A(P)/\textstyle\sum A(P)] \times 100 \quad (5)$$

ances were determined by gas chromatography according to eq 6. For

$$\% \text{ MB} = [\textstyle\sum A_t(P)/A_t(IS)]/[A_0(S)/A_0(IS) - A_t(S)/A_t(IS)] \times 100 \quad (6)$$

the PET reactions of the azoalkanes the mass balances were corrected for the response factors of the starting material relative to the products. Gas chromatographically determined yields are within an error of ca. 2%, while the yields determined by NMR spectroscopy have an error of ca. 5%.

Characterization of the Products. The identity of the products was confirmed either by spectral means after purification by preparative GC and/or by capillary GC coinjection with authentic materials.

Preparation of Starting Materials and Known Products. 2,3-Diazabicyclo[2.2.1]hept-2-ene (1a) and *exo*-5,6-dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene (*exo*-1a-d_2) were synthesized as reported.[3,16a-c]

***syn*- and *anti*-7-Methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (*syn*/*anti*-1b)** were obtained by modification of the original procedure.[6b] Substituting MTAD for PTAD in the cycloaddition reaction with 5-methylcyclopentadiene facilitated the separation of the diastereomers. The stereochemistry of *syn*/*anti*-**1b** was established X-ray analysis.[6a] After hydrogenation of the unsaturated urazoles, the azoalkanes were obtained by the usual hydrolysis–oxidation sequence.[17]

1,4-Dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1c) was prepared by following the literature procedure.[18a-c]

7,7-Dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1d) was obtained by a modification of the original procedure.[6b] Instead of 5,5-dimethylcyclopentadiene, the spiro[2.4]hepta-2,4-diene[19a] was used for the cycloaddition with diethyl azodicarboxylate. The resulting spiro[2,3-diaza-2,3-dicarbethoxybicyclo[2.2.1]hept-5-ene-7,1′-cyclopropane][19b] was hydrogenated over Pd–C as catalyst to yield spiro[2,3-diaza-2,3-dicarbethoxybicyclo[2.2.1]heptane-7,1′-cyclopropane]. A sample of 2.00 g (7.45 mmol) of this spiro compound was further hydrogenated in 15 mL of CH_3CO_2H with ca. 500 mg of PtO_2. After 4 days at 25 °C under 1 atm of H_2 pressure the catalyst was removed by filtration, and a saturated, aqueous solution of K_2CO_3 was added until cessation of CO_2 evolution. The solution was extracted with 6 × 50 mL of CH_2Cl_2 and the combined organic layers were dried over K_2CO_3. The solvent was removed by distillation, and the yellow oil [1.97 g (98%)] was further purified by radial chromatography on a Chromatotron (petroleum ether:diethyl ether = 8:2) to yield analytically pure diethyl 7,7-dimethyl-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate: IR (CCl_4) 2990, 2970, 1750, 1710, 1400, 1375, 1325, 1260, 1170, 1105, 1070 cm^{-1}; ^{1}H NMR (DMSO-d_6, 400 MHz, 80 °C) δ 1.07 (s, 3 H, 7-CH_3), 1.13 (s, 3 H, 7-CH_3), 1.28 (t, J = 7.0 Hz, 6 H, CH_2CH_3), 1.66 (m, 2 H, H_x or H_n), 2.02 (m, 2 H, H_x or H_n), 3.98 (br s, 2 H, bridgehead H), 4.19 (q, J = 7.0 Hz, 4 H, CH_2CH_3); ^{13}C NMR (DMSO-d_6, 100.6 MHz, 80 °C) δ 13.9 (q, CH_3), 17.9 (q, CH_3), 18.4 (q, CH_3), 26.4 (t, CH_2CH_2), 46.3 (s, C-7), 60.9 (t, CH_2CH_3), 66.7 (d, bridgehead C), 138.4 (s, COO); MS (70 eV), m/e 270 (16%, M^+), 198 (24), 197 (19), 130 (18), 125 (81), 97 (100), 95 (30), 81 (17), 69 (23), 56 (17), 41 (25), 29 (85). Anal. Calcd for $C_{13}H_{22}N_2O_4$: 270.1580. Found: 270.1575 (MS). The azo compound **1d** was obtained from this urazole by the usual hydrolysis–oxidation procedure.[6b,17]

***syn*-7-(1-Methylethyl)-2,3-diazabicyclo[2.2.1]hept-2-ene (*syn*-1e)** was obtained starting from diethyl 7-(1-methylethylidene)-2,3-diazabicyclo-[2.2.1]hept-5-ene-*N*,*N*′-dicarboxylate.[20] A sample of 39.6 g (0.141 mol) of this dicarboxylate in 300 mL of CH_3CO_2Et was hydrogenated at 21 °C and 1 atm of H_2 pressure for 14 h over ca. 20 mg of PtO_2 as catalyst. After the removal of the catalyst, the solvent was removed by distillation at 30 °C/20 Torr to yield 38.8 g (97%) of diethyl *syn*-7-(1-methylethyl)-2,3-diazabicyclo[2.2.1]heptane-*N*,*N*′-dicarboxylate, which was used without further purification: ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.9 (d, 6 H, 9-H), 1.2 (t, 6 H, CH_2CH_3), 1.7 (br s, 2 H, 1-H, 4-H), 0.8–2.2 (m, 6 H, 5-H, 6-H, 7-H, 8-H (superposed by the other signals)), 4.1 (q, 4 H, CH_2CH_3).

A sample of 38.8 g (0.136 mol) of the above hydrogenated dicarboxylate and 68.8 g (1.23 mol) of KOH in 600 mL of *i*-PrOH were refluxed for 15 h under a nitrogen atmosphere. To the reaction mixture were added ca. 2000 mL of H_2O and the solution was neutralized with 17 N HCl. Finally, azoalkane *syn*-**1e** was precipitated as the Cu complex by addition of a solution of saturated, aqueous $CuCl_2$. The precipitate was removed by filtration and taken up in 500 mL of 12.5% aqueous NH_3 solution, and *syn*-**1e** was extracted with 3 × 200 mL of CH_2Cl_2. The combined organic layers were washed with saturated, aqueous NH_4Cl solution and dried over $MgSO_4$, and CH_2Cl_2 was removed by distillation at 20 °C/20 Torr. After sublimation of the residue at 30 °C/17 Torr there were obtained 13.7 g (72%) of colorless needles, mp 54–55 °C: IR (CCl_4) 3010, 2960, 2870, 1495, 1468, 1369, 1275, 1204, 1195, 1103 cm^{-1}; UV (*n*-pentane) λ_{max} (log ϵ) 345 nm (2.140), 339 (2.015), 335 (1.980); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.70 (d, $J_{9,8}$ = 5.7 Hz, 6 H, 9-H), 0.80 (ps q, 2 H, 5-H_n, 6-H_n), 0.75–0.97 (m, 1 H, 8-H), 1.09 (d, $J_{7,8}$ = 9.8 Hz, 1 H, 7-H), 1.40–1.50 (m, 2 H, 5-H_x, 6-H_x), 5.00 (br s, 2 H, 1-H, 4-H) [the use of Eu(fod)$_3$ did not result in a better separation of 5-H_n, 6-H_n, and 8-H; by means of NOE the syn stereochemistry was established]; ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.9 (t, C-5, C-6), 21.7 (q, C-9), 23.2 (d, C-8), 62.4 (d, C-7), 78.4 (d, C-1, C-4); MS (70 eV), m/e 139 (0.14%, M^+ + 1), 110 (4), 95 (42), 67 (100). Anal. Calcd for $C_8H_{14}N_2$: C, 69.52; H, 10.21; N, 20.27. Found: C, 69.80; H, 10.07; N, 20.64.

***syn*- and *anti*-5-Methylbicyclo[2.1.0]pentane (*syn*/*anti*-2b).** A sample of 110 mg (0.999 mmol) of *syn*-**1b** was pyrolized at 230 °C/100 Torr by using glass beads within the pyrolysis tube. Preparative GC[6c] (3.0-m, 20% β,β'-oxydipropionitrile on Volaspher A2 column; N_2 flow of 0.65 kp/cm^2; oven, injector, and detector temperatures of 31, 130, and 130 °C) yielded ca. 25 mg (ca. 31%) of *syn*-5-methylbicyclo[2.1.0]pentane (*syn*-**2b**) and ca. 25 mg (ca. 31%) of *anti*-**2b**; R_t (*syn*-**2b**) = 17.0 min and R_t (*anti*-**2b**) = 11.5 min. An NOE of *syn*-**2b** confirmed the literature assignment of the stereochemistry.[6d] Examination of the crude reaction mixture by capillary GC (30-m, OV-1 column; N_2 flow of 0.7 kp/cm^2; oven temperature was kept at 20 °C for 10 min, raised at 35 °C/min to 80 °C, and held there for 15 min, injector and detector temperatures were 150 and 175 °C) gave a product distribution of *anti*-**2b**:*syn*-**2b**:**3b** = 46:47:7; R_t (*anti*-**2b**) = 6.1 min; R_t (**3b**) = 6.4 min; R_t (*syn*-**2b**) = 7.5 min.

1,4-Dimethylbicyclo[2.1.0]pentane (2c) was obtained in 90.0 mg (55%) yield by pyrolyzing 210 mg (1.69 mmol) of azoalkane **1c** at 270 °C/760 Torr through the Pyrex tube (cf. **General Aspects**). The spectral data were in accordance with literature.[6c]

5,5-Dimethylbicyclo[2.1.0]pentane (2d). A sample of 506 mg (4.07 mmol) of azoalkane **1d** in 100 mL of *n*-pentane was irradiated for 4 h at 21 °C in a Rayonet Photochemical Reactor at 350 nm. The workup procedure was the same as in the 185-nm photolysis of **1d** and yielded 100 mg (26%) bicyclopentane **2d**. The spectral data fitted with that of the literature.[6c]

***syn*/*anti*-5-(1-Methylethyl)bicyclo[2.1.0]pentane (*syn*/*anti*-2e).** Pyrolysis of a sample of 610 mg (4.41 mmol) of azoalkane *syn*-**1e** at 270 °C/760 Torr gave 320 mg (66%) of volatile products. Capillary GC (for conditions see 185-nm photolysis of *syn*-**1e**) showed that the volatile fraction consisted of *anti*-**2e** (66%), *syn*-**2e** (23%), and 11% 1-(1-methylethyl)cyclopentene (**3e**). *Syn*/*anti*-**2e** were isolated by preparative GC (for conditions, see 185-nm photolysis of *syn*-**1e**). Anal. Calcd for C_8H_{14} (110.1): C, 87.19; H, 12.80. Found: C, 86.97; H, 13.02. The spectral data are given in the section on 185-nm photolysis of *syn*-**1e**.

A ratio of *syn*-**2e**:*anti*-**2e** = 84:16 was obtained when 940 mg (6.80 mmol) of azoalkane *syn*-**1e** in 100 mL of *n*-pentane was irradiated at 350

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nm for 6.5 h at 21 °C in a Rayonet Photochemical Reactor up to total conversion. Following the workup procedure for the 185-nm photolysis of *syn*-**1e**, 510 mg (68%) of the *syn*/*anti*-**2e** mixture was isolated. When 191 mg (1.73 mmol) of a mixture of *anti*-**2e** (18%) and *syn*-**2e** (82%) was distilled at 270 °C/760 Torr through the Pyrex tube, one isolated 180 mg (94%) of a mixture of *anti*-**2e** (64%), *syn*-**2e** (23%), and cyclopentene **3e** (13%). A repeated pyrolysis under the same conditions yielded *anti*-**2e** (55%), *syn*-**2e** (20%), and **3e** (25%).

3,3-Dimethyl-1,4-pentadiene (4d) was obtained by pyrolizing a sample of 100 mg (1.04 mmol) of bicyclopentane **2d** at 540 °C/15 Torr through the quartz tube to yield 80.0 mg (80%) as colorless liquid.[21] **1-Methylcyclopentene (3b)** is a commercially available compound and **3-methylcyclopentene (3'b)** was synthesized as reported.[22a-c]

Transformations of 2,3-Diazabicyclo[2.2.1]hept-2-ene (1a). Laser-Jet Photolysis. A solution of the azoalkane **1a** (0.108 M) and benzophenone (0.229 M) in *n*-heptane was degassed and irradiated under laser-jet conditions (flow, 1.3 mL/min; laser power, 3.6 W; capillary diameter, 0.75 μm) as described above in the general procedure. After one pumping cycle, the progress of the reaction was monitored by capillary GC (50-m, OV 101 column; N_2 flow of 0.30 kp/cm^2; oven temperature of 25 °C kept for 15 min and raised at 30 °C/min to 140 °C, injector temperature of 150 °C, and detector temperature of 180 °C; R_t(**3a**) = 9.6 min, R_t(**2a**) = 10.0 min, R_t[bi(3-cyclopentenyl)] = 29.8 min, R_t(3-cyclopentylcyclopentene) = 30.3 min, R_t(bicyclopentyl) = 30.8 min). The identification of the products **2a** and **3a** was achieved by coinjection with authentic materials. The mass balance, conversion, and product distribution are described in Table I (entry 3). The dimers were identified by their ^{13}C NMR and GC–MS data.

3-Cyclopentylcyclopentene.[23a] GC–MS (70 ev), *m/e* 137 (3, M^+ + 1), 136 (21, M^+), 95 (26), 68 (49), 67 (100), 66 (43), 41 (28).

Bi(3-cyclopentenyl).[23a] GC–MS (70 eV), *m/e* 135 (2, M^+ + 1), 134 (12, M^+), 93 (14), 79 (8), 67 (100), 66 (87), 41 (20).

Bicyclopentyl.[23b] GC–MS (70 eV), *m/e* 139 (2, M^+ + 1), 138 (17, M^+), 109 (14), 96 (58), 95 (52), 82 (67), 81 (40), 69 (50), 68 (100), 67 (83), 55 (20), 54 (17), 53 (10), 41 (71).

Transformations of *exo*-5,6-Dideuterio-2,3-diazabicyclo[2.2.1]hept-2-ene (*exo*-1a-d_2). Laser-Jet Photolysis. A solution of the azoalkane *exo*-**1a**-d_2 (0.170 M) and benzophenone (0.348 M) in benzene-d_6 was degassed and irradiated under laser-jet conditions (flow, 2.0 mL/min; laser power, 3.6 W; capillary diameter, 0.75 μm) as described above in the general procedure. After one pumping cycle, the progress of the reaction was monitored by capillary GC and ^1H NMR. The identification of the products was achieved by coinjection of authentic materials. The mass balance, conversion, and product distribution are described in Table I (entry 9).

Transformations of *syn*-7-Methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (*syn*-1b). 185-nm Photolysis. A sample of 13.4 mg (0.122 mmol) of *syn*-**1b** in 5.00 mL of *n*-pentane was irradiated for 45 min with the capillary lamp. At a conversion of 85% and a mass balance of 90% the products in Table I (entry 15) were identified by coinjection with authentic materials (50-m, OV 101 column; N_2 flow of 0.3 kp/cm^2; oven temperature of 20 °C kept for 30 min and raised at 39 °C/min to 150 °C, injector temperature of 150 °C, and detector temperature of 180 °C; R_t(**3'b**) = 8.8 min, R_t(*anti*-**2b**) = 10.3 min, R_t(**3b**) = 10.9 min, R_t(*syn*-**2b**) = 12.1 min).

PET Reaction with 9,10-Dicyanoanthracene (DCA). A solution of 9.89 mg (8.95 × 10^{-2} mmol) of *syn*-**1b** and 5.0 μL of *c*-C_7H_{14} in 5.00 mL of CH_3CN was saturated with DCA. After irradiation at λ > 400 nm for 45 min the products denoted in Table I (entry 14) were obtained (25% conversion, 70% mass balance).

Laser-Jet Photolysis. A solution of the azoalkane *syn*-**1b** (0.119 M) and benzophenone (0.268 M) in *n*-heptane was degassed and irradiated under laser-jet conditions (flow, 2.0 mL/min; laser power, 3.6 W; capillary diameter, 100 μm) as described above in the general procedure. After one pumping cycle, the progress of the reaction was monitored by capillary GC. The identification of the products was achieved by coinjection with authentic materials. The conversion and product distribution are described in Table I (entry 16).

Transformations of *anti*-7-Methyl-2,3-diazabicyclo[2.2.1]hept-2-ene (*anti*-1b). 185-nm Photolysis. A sample of 13.9 mg (0.126 mmol) of *anti*-**1b** in 5.00 mL of *n*-pentane was irradiated for 10 min with the capillary lamp. At a conversion of 15% and a mass balance of 88% the products in Table I (entry 22) were obtained.

PET Reaction with DCA. A solution of 8.00 mg (7.27 × 10^{-2} mmol) of *anti*-**1b** and 5.0 μL of *c*-C_7H_{14} in 5.00 mL of CH_3CN was saturated with DCA. After irradiating at λ > 400 nm for 90 min, the products stated in Table I (entry 21) were obtained with a mass balance of 30% at a conversion of 8%.

Laser-Jet Photolysis. A solution of the azoalkane *anti*-**1b** (0.132 M) and benzophenone (0.322 M) in *n*-heptane was degassed and irradiated under laser-jet conditions (flow, 2.0 mL/min; laser power, 3.6 W; capillary diameter, 100 μm) as described above in the general procedure. After one pumping cycle, the progress of the reaction was monitored by capillary GC. The identification of the products was achieved by coinjection of authentic materials. The mass balance, conversion, and product distribution are described in Table I (entry 23).

Transformations of 1,4-Dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1c). 185-nm Photolysis. A sample of 361 mg (2.91 mmol) of **1c** in 280 mL of *n*-pentane was irradiated for 7 h at 21 °C in the preparative photolysis apparatus up to total conversion. Because of the high volatility of the photolysis products, the reflux condenser was cooled to −25 °C. After the irradiation, the volatile components were removed by distillation at 30 °C/15 Torr from the high-molecular-weight products. *n*-Pentane was removed by distillation on a 30-cm Vigreux column until about a final volume of ca. 2 mL and the residue was worked up by preparative GC (1.5-m, 10% UCON 50-HB-280-X on Volaspher A2 column; N_2 flow of 1.6 kp/cm^2; oven, injector, and detector temperatures of 70, 150, and 150 °C). The isolated yield was 120 mg (43%). The retention times in parentheses are capillary GC values (30-m, SE 30 column; N_2 flow of 0.35 kp/cm^2; oven, injector, and detector temperatures of 40, 175, and 175 °C): **1,4-dimethylbicyclo[2.1.0]pentane (2c)**,[6c] R_t = 8.0 (5.40) min, isolated yield of ca. 60 mg (ca. 0.62 mmol), relative yield of 43%; **2,4-dimethyl-1,4-pentadiene (4c)**,[24a,b] R_t = 10.0 (5.55) min, isolated yield of ca. 20 mg (ca. 0.21 mmol), relative yield of 10%; **1,3-dimethylcyclopentene (3c)**,[25] R_t = 13.5 (6.38) min, isolated yield of ca. 40 mg (ca. 0.42 mmol), relative yield of 32%.

Laser-Jet Photolysis. A solution of the azoalkane **1c** (0.142 M) and benzophenone (0.242 M) in *n*-pentane was degassed and irradiated under laser-jet conditions (flow, 2.0 mL/min; laser power, 3.6 W; capillary diameter, 0.75 μm) as described above in the general procedure. After one pumping cycle, the progress of the reaction was monitored by capillary GC. The identification of the products was achieved by coinjection with authentic materials (see above). The mass balance, conversion, and product distribution are described in Table I (entry 28).

PET Reaction with DCA. A solution of 11.7 mg (9.45 × 10^{-2} mmol) of **1c** and 5.69 mg (4.44 × 10^{-2} mmol) of *n*-nonane in 5.00 mL of CH_3CN was saturated with DCA. After 30 min of irradiation, the conversion amounted to 75% and the products (mass balance of 100%) are stated in Table I (entry 26).

Transformations of 7,7-Dimethyl-2,3-diazabicyclo[2.2.1]hept-2-ene (1d). 185-nm Photolysis. A sample of 404 mg (3.25 mmol) of **1d** in 280 mL of *n*-pentane was irradiated for 3.5 h at 21 °C in the preparative photolysis apparatus up to total conversion. The solvent and volatile products were removed by distillation at 21 °C/15 Torr from the residue. Finally, *n*-pentane was removed at 36 °C until a final volume of ca. 2 mL by distilling it on a 30-cm Vigreux column. The products were isolated by preparative GC in 16% yield (1.5-m, 10% SE 30 on Chromosorb WHP; N_2 flow of 1.6 kp/cm^2; oven, injector, and detector temperatures of 80, 160, and 160 °C). In an analytical experiment 11.3 mg (9.10 × 10^{-2} mmol) of **1d** in 5.00 mL of *n*-pentane was irradiated for 21 min at 20 °C with unfiltered light of the capillary lamp. At a conversion of 50% the relative yields given below were obtained. The retention times in brackets are capillary GC values (50-m, OV 101 column; N_2 flow of 0.40 kp/cm^2; oven, injector, and detector temperatures of 20 °C, kept for 30.0 min, raised at 36 °C/min to 150 °C, and kept there for 20.0 min, 150 °C, and 175 °C): **3,3-dimethyl-1,4-pentadiene (4d)**, R_t = — (12.8) min, relative yield of 3%, the product was identified by coinjection with the authentic material;[21] **5-methyl-1,4-hexadiene (4'd)**,[26] R_t = 6.0 (23.5) min, isolated yield of ca. 5 mg (ca. 0.052 mmol), relative yield of 10%; **2,3-dimethylcyclopentene (3'd)**,[27a,b] R_t = 7.5 (26.1) min, isolated yield of ca. 9 mg (ca. 0.094 mmol), relative yield of 17%; **5,5-dimethylbicyclo[2.1.0]pentane (2d)**,[6c] R_t = 7.5 (26.5) min, isolated yield of ca. 41 mg (ca. 0.43 mmol), relative yield of 65%.

Laser-Jet Photolysis. A solution of the azoalkane **1d** (0.137 M) and benzophenone (0.228 M) in CH_3CN was degassed and irradiated under laser-jet conditions (flow, 1.0 mL/min; laser power, 3.6 W; capillary

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diameter, 0.75 μm) as described above in the general procedure. After one pumping cycle, the progress of the reaction was monitored by capillary GC. The identification of the products was achieved by coinjection with authentic materials (see above). The conversion and product distribution are described in Table I (entry 33).

PET Reaction with DCA. A solution of 11.5 mg (9.24×10^{-2} mmol) of **1d** and 5.0 μL of c-C_7H_{14} in 5.00 mL of CH_3CN was saturated with DCA. After 2 h of irradiation at $\lambda > 400$ nm, 12% of the starting material had reacted and the products given in Table I (entry 31a) were observed in a mass balance of 57%.

Transformations of *syn*-7-(1-Methylethyl)-2,3-diazabicyclo[2.2.1]-hept-2-ene (*syn*-1e). 185-nm Photolysis. A sample of 501 mg (3.63 mmol) of *syn*-**1e** in 280 mL of *n*-pentane was irradiated for 24 h at 0 °C up to complete conversion in the preparative photolysis apparatus. High-molecular-weight products were removed by filtration over neutral Al_2O_3 (60–230 mesh, activity grade I). The solvent was removed by distillation at 36 °C on a 30-cm Vigreux column until above a final volume of 2 mL and the residue was worked up by means of preparative GC to yield 65.0 mg (16%) of hydrocarbons (1.5-m, 10% SE 30 on Chromosorb WHP; N_2 flow of 1.8 kp/cm^2; oven, injector, and detector temperatures of 80, 180, and 180 °C). The retention times in brackets are capillary GC values (50-m, OV 101 column; N_2 flow of 0.50 kp/cm^2; oven, injector, and detector temperatures of 60, 175, and 175 °C).

3-(1-Methylethyl)-1,4-pentadiene (4e):[26] R_t = 8.00 (8.58) min, isolated yield of ca. 5 mg (ca. 0.045 mmol), relative yield of 5%.

***anti*-5-(1-Methylethyl)bicyclo[2.1.0]pentane (*anti*-2e):** R_t = 14.0 (11.2) min, isolated yield of ca. 10 mg (ca. 0.091 mmol), relative yield of 16%; IR ($CDCl_3$, registered with a mixture of *syn*-**2e** and *anti*-**2e**) 3040, 2960, 2930, 2900, 2860, 1463, 1380, 1363, 1315, 1270, 1258, 1212, 820 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.68 (m_c, 2 H, 5-H, 6-H), 0.96 (d, $J_{7,6} = J_{7',6} = 6.3$ Hz, 6 H, 7-H, 7′-H), 1.28–1.37 (m, 4 H, 2-H_n, 3-H_n, 1-H, 4-H), 2.02 (m, 2 H, 2-H_x, 3-H_x); ^{13}C NMR ($CDCl_3$, 100.6 MHz, the C–H coupling constants were determined in a fully coupled ^{13}C NMR experiment) δ 20.5 (d, J_{CH} = 174 Hz, C-1, C-4), 22.6 (q, J_{CH} = 124 Hz, C-7, C-7′), 23.0 (t, J_{CH} = 134 Hz, C-2, C-3), 30.3 (d, J_{CH} = 125 Hz, C-6), 37.4 (d, J_{CH} = 159 Hz, C-5); GC–MS (70 eV), *m/e* 110 (1%, M^+), 95 (44), 93 (6), 81 (9), 79 (6), 77 (5), 69 (13), 68 (13), 67 (100), 66 (13), 65 (7), 55 (15), 53 (8), 44 (10), 43 (8), 41 (32), 39 (19), 29 (7), 27 (10).

***syn*-5-(1-Methylethyl)bicyclo[2.1.0]pentane (*syn*-2e):** R_t = 14.0 (11.5) min, isolated yield of ca. 40 mg (ca. 0.36 mmol), relative yield of 65%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.44 (dt, $J_{5,6} = 10.1$ Hz, $J_{5,1} = J_{5,4} = 5.9$ Hz, 1 H, 5-H), 1.01 (d, $J_{7,6} = J_{7',6} = 6.7$ Hz, 6 H, 7-H, 7′-H), 1.28–1.37 (m, 2 H, 2-H_n, 3-H_n), 1.55 (m_c, 2 H, 1-H, 4-H), 1.65 (m_c, 1 H, 6-H), 2.02 (m, 2 H, 2-H_x, 3-H_x); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.3 (d, J_{CH} = 175 Hz, C-1, C-4), 18.7 (t, J_{CH} = 136 Hz, C-2, C-3), 19.5 (d, J_{CH} = 126 Hz, C-6), 22.3 (q, J_{CH} = 124 Hz, C-7, C-7′), 30.7 (d, J_{CH} = 150 Hz, C-5); GC–MS (70 eV), *m/e* 110 (0.7%, M^+), 95 (5), 68 (9), 67 (100), 66 (16), 65 (7), 43 (5), 41 (19), 40 (5), 39 (11), 27 (7).

1-(1-Methylethyl)cyclopentene (3e):[28] R_t = 16.2 (12.7) min, isolated yield of ca. 10 mg (ca. 0.091 mmol), relative yield of 14%. The mass balance, conversion, and product distribution are described in Table I (entry 37).

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Registry No. 1a, 2721-32-6; *exo*-**1a**-d_2, 60400-43-3; *syn*-**1b**, 71805-59-9; *anti*-**1b**, 71805-62-4; **1c**, 71312-54-4; **1d**, 71805-61-3; *syn*-**1e**, 141119-43-9; **2a**, 185-94-4; *endo*-**2a**-d_2, 60426-74-6; *exo*-**2a**-d_2, 51794-28-6; *anti*-**2b**, 76898-65-2; *syn*-**2b**, 50338-79-9; **2c**, 17065-18-8; **2d**, 71805-64-6; *anti*-**2e**, 141196-87-4; *syn*-**2e**, 141119-44-0; **3a**, 142-29-0; **3a**-d_2, 93589-92-5; **3b**, 693-89-0; **3′b**, 1120-62-3; **3c**, 62184-82-1; **3′d**, 16491-15-9; **3e**, 1462-07-3; **4a**, 591-93-5; **4c**, 4161-65-3; **4d**, 1112-35-2; **4′d**, 763-88-2; **4e**, 41848-27-5; DCA, 1217-45-4; spiro[2,3-diaza-2,3-dicarbethoxybicyclo[2.2.1]heptane-7,1′-cyclopropane], 141119-45-1; 7,7-dimethyl-2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, diethyl ester, 141119-46-2; diethyl 7-(1-methylethylidene)-2,3-diazabicyclo-[2.2.1]hept-5-ene-*N*,*N*′-dicarboxylate, 16425-69-7; *syn*-7-(1-methylethyl)-2,3-diazabicyclo[2.2.1]heptane-*N*,*N*′-dicarboxylate, 141119-47-3; 3-cyclopentylcyclopentene, 2690-17-7; bi(3-cyclopentenyl), 141119-48-4; bi(cyclopentyl), 1636-39-1.

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New Extended π-Electron Donors. Tetrathiafulvalene Systems with Heterocyclic Spacer Groups

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Abstract: Nine new heterocyclic π-electron donors **10a–c**, **11a–c**, and **12a–c** based upon the well-known TTF (tetrathiafulvalene) system, but incorporating a pyrrole, thiophene, or furan ring between the 1,3-thiole rings, have been synthesized. The compounds show two single-electron reversible oxidation waves in cyclic voltammetry. Some TCNQ complexes and conductivity measurements are reported, indicating the new compounds to be good candidates for "organic metals". The influence of the central conjugated system on redox properties is discussed using MNDO-PM3 calculations.

Introduction

The unusual properties of TTF (**1**), to behave as a reversible electron donor and to form conducting charge-transfer complexes with various acceptor molecules, have stimulated much interest during the past 20 years in the synthesis of a wide variety of TTF analogs.[1] Many of these bear substituents at the 4,5-positions, while, in others, some or all of the sulfur atoms have been replaced by other chalcogens.[2] Among these, some partially oxidized salts of BEDT-TTF (**2**)[3] have been of particular interest, since they

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