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THE 185-NM PHOTOCHEMISTRY OF 2,3-DIAZABICYCLO[2.2.1]HEPTENE AND OF ITS DENITROGENATION PRODUCTS BICYCLO[2.1.0]PENTANE AND CYCLOPENTENE

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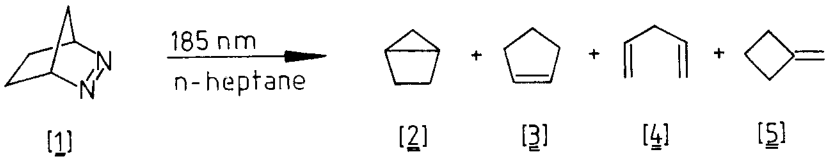
SUMMARY: The 185-nm denitrogenation of 2,3-diazabicyclo[2.2.1]heptene (1) afforded bicyclo[2.1.0]pentane (2) and cyclopentene (3) presumably via a "hot" cyclopentane-1,3-diyl diradical (8); 1,4-pentadiene (4) and methylenecyclobutane (5) were secondary products of the 185-nm photolysis of (2) and (3).

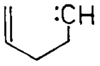
A recent communication[1] on the 185-nm photolysis of cyclopentene in solution obliges us to report our own results on 2,3-diazabicyclo[2.2.1]heptene (1), which we employed as actinometer in the dinitrogenation of reluctant azoalkanes.[2] Analogous to the photolysis of (1) at long wavelength (> 300 nm for n,π* excitation)[3], also at short wavelength (185 nm) denitrogenation in pentane took place with 100% efficiency.[2b] This was determined by comparison with the established[4] cis-cyclooctene actinometer for 185-nm photolysis. Since the long wavelength (> 300 nm) denitrogenations of (1) in solution produced bicyclo[2.1.0]pentane (2) as exclusive product[3] with only traces of cyclopentene (3), it was of interest to determine the products of the short wavelength (185 nm) denitrogenations. The fundamental photomechanistic point under scrutiny here was to compare the photochemistry of the azo chromophore as a function of excitation wavelength. To the best of our knowledge such data has not been reported in the solution photochemistry of azoalkanes.

The results of the 185-nm and 350-nm photolysis in heptane are given in Table 1. Clearly, the product composition of the 185-nm denitrogenation was considerably more complex than at 350 nm. For example, bicyclo[2.1.0]pentane (2) was still the major product, but large amounts of cyclopentene (3) were formed; however, more surprisingly appreciable quantities of 1,4-pentadiene (4) and methylenecyclobutene (5) were produced.

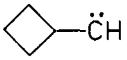


It was, therefore, important to establish whether these two additional products were directly formed in the denitrogenation of azoalkane (1), or whether these were secondary products derived from the prolonged photolysis of the denitrogenation products (2) and (3). Indeed, control experiments (Table 1) revealed that both the bicyclopentane (2) as well as cyclopentene (3) were photo-active at 185 nm irradiation. Thus, bicyclopentane (2) afforded cyclopentene (3), 1,4-pentadiene (4) and methylenecyclobutane (5), while cyclopentene (3)[9] led to bicyclopentane (2), methylenecyclobutane (5) and traces of 1,4-pentadiene (4). In fact, also 1,4-pentadiene (4) and methylenecyclobutane (5) were photo-active at 185 nm, but inefficiently, leading to complex product mixtures which contained bicyclo[2.1.0]pentane (2) and cyclopentene (3).

The pioneering work by Srinivasan and coworkers has shown similar transformations in the 185-nm solution photochemistry of cycloalkene[5] and cyclopropane[6] chromophores. Since in our study the bicyclo[2.1.0]pentane (2) and cyclopentene (3) were interconverted on 185-nm excitation, although at different efficiencies (Table 1), presumably the same set of intermediates are engaged in these interconversions. In analogy to Srinivasan's work on the higher homologs,



[6]



[7]

[8]

possible intermediates are the carbenes (6) and (7) and the 1,3-diradical (8). To sort out these mechanistic alternatives, deuterium labeling experiments are being conducted (Scheme I).

With respect to the denitrogenation of the azoalkane (1), presumably the 185-nm photolysis gave initially the 1,3-diradical (8), which then cyclized into bicyclo[2.1.0]pentane (2) or rearranged via hydrogen 1,2-shift into cyclopentene (3). Since the 350-nm solution photolysis yielded only (2), clearly a more energetic 1,3-diradical (8) must have intervened in the 185-nm denitrogenation. Indeed, in support of this suggestion we cite in Table 1 the results of the pyrolytic (150°C)[7] and gas phase photolytic (350 nm)[8] denitrogenations of (1), which in the latter case afforded appreciable amounts of cyclopentene. In the gas phase the 1,3-diradical (8) cannot efficiently dissipate its excess vibrational energy via collisions and consequently reacts via higher energy channels, e.g. cyclopentene formation, than in normal solution photolyses. However, since "hot" radical intermediates have been reported[9] in 185-nm solution photolyses, we postulate that the similarity in the 350-nm gas phase and 185-nm solution photochemistry of azoalkane (1) is due to the intervention of "hot" 1,3-diradical (8) intermediates.

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TABLE 1: Product Distributions in the Denitrogenation of 2,3-Diazabicyclo[2.2.1]heptene (1).

Substrate	Mode of N_2 Loss	Consumption (%)	Product Distribution (%)[a]				Product Balance (%)
			(2)	(3)	(4)[b]	(5)[b]	
(1)	185 nm[c,d,e] (n-heptane, 25°C)	41.7[f]	17.5	12.6	2.8	0.6	33.5
(1)	350 nm[g] (n-pentane, 30°C)	100[f]	> 99	traces	-	-	100
(1)	337 nm[h] (gas phase, 23°-28°C)		+	+	+	-	
(1)	160°C[i] (gas phase)	100	> 99.5	<0.3	-	-	100
(2)	185 nm[c,e,j] (n-heptane, 25°C)	23.9	-	12.0	16.0	1.6	29.6
(3)	185 nm[c,e,k] (n-heptane, 25°C)	8.6	1.5	-	<0.1	2.1	3.6

a) Determined by Capillary GC using a Carlo Erba Fractovap 2900, equipped with an 86-m polypropylene glycol coated capillary column, operated at column, injector and detector temperatures of 20°C, 125°C and 125°C, respectively and nitrogen carrier gas flow of 0.56 ml/min; calibration curves were constructed for the quantitative work; error limits within 10% - 15% of the given values. Identification of the products was carried out via GC-coinjection of authentic material and 400 MHz-NMR (Bruker Cryospec WM 400) of the reaction mixture after destillation and preparative GC collection of the C_5-fraction (1.5 m Apiezon L on Chromosorb W-HP; column, detector and injector temperatures,respectively 40°C, 150°C, and nitrogen flow of 25 ml/min).

b) These products were also photoactive at 185 nm, affording complex product mixtures which contain (2) and (3).

c) 185-nm photolysis were carried out as described in Ref. 10, using a low pressure mercury arc (10 W, Gräntzel) with an output of 10% 185 nm, 66% 254 nm and rest high wavelengths at a temperature of 25°C; it was essential to limit the duration of photolysis to 10 min, e.g. darkening, percipitation, etc. of the photolysate ensued.

d) [1] = 1.31 x 10^{-2}M in n-heptane; irradiated for 10 min.

e) Traces of cyclopentadiene (<< 1%) were formed.

f) Consumption of azoalkane (1) monitored UV-metrically at λ_{max} = 341 nm (ε = 420).

g) Photolysis carried out in a Rayonet Photoreactor using RPR-3500Å lamps; see also Ref. 3.

h) Ref. 8; gas phase photolysis of azoalkane (1) in the pressure range 10 - 1000 μ using high-pressure mercury arc, 23 - 28°C; product composition was pressure dependent and gave rise to cyclopentadiene and hydrogen; 1,4-pentadiene appeared to be formed in ca. 5% yield.

i) Ref. 7; above 200°C bicyclopentane (2) isomerized to cyclopentene (3).[3]

j) [2] = 7.5 x 10^{-3}M in n-heptane, irradiated for 10 min; consumption followed by Capillary GC.

k) [3] = 1.93 x 10^{-2}M in n-heptane, irradiated for 10 min; consumption followed by Capillary GC.

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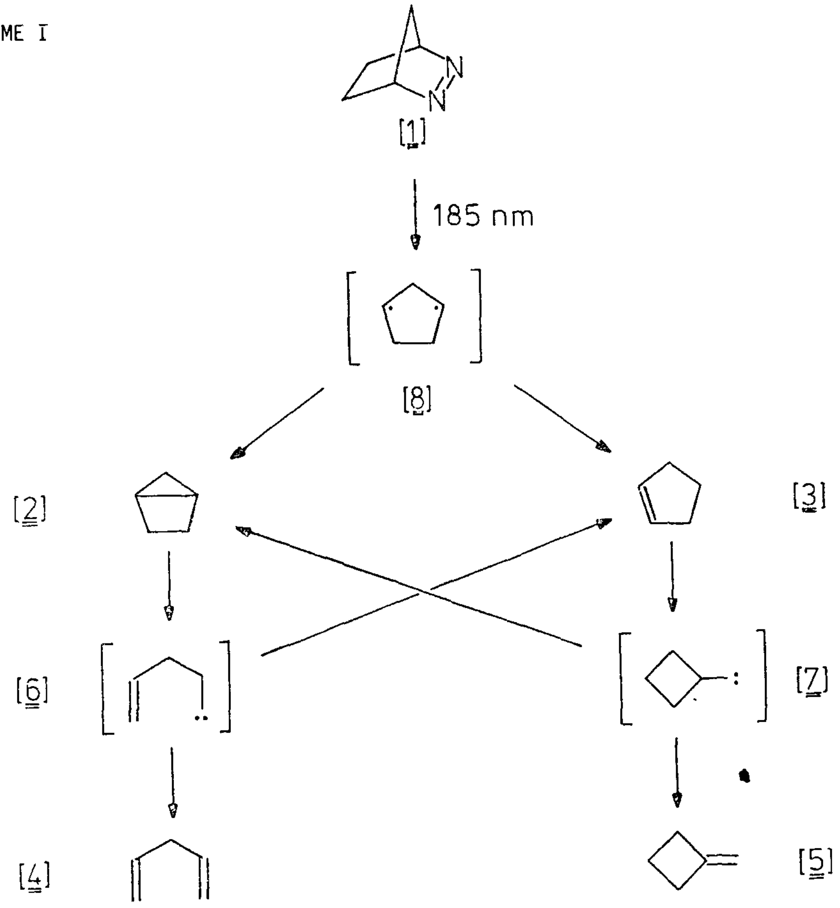
SCHEME I



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