

PHOTOELIMINATION OF NITROGEN FROM CYCLIC AZO ALKANES. AN EXCEPTIONALLY LABILE
AND AN EXCEPTIONALLY RELUCTANT DIAZABICYCLO[2.2.2]OCTENE

Nicholas J. Turro* and Jong-Min Liu

Chemistry Department, Columbia University, New York, NY 10027, U.S.A.

and

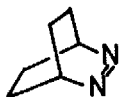
Hans-Dieter Martin* and Michael Kunze

Institut für Organische Chemie der Universität am Hubland, D-8700 Würzburg, West Germany

The photochemistry of an unusually reactive diazabicyclo[2.2.2]octene has been found to be extremely solvent and temperature dependent; an exceptionally stable diazabicyclo[2.2.2]octene has been found to undergo a novel fragmentation as a result of vapor phase photoexcitation.

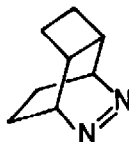
Introduction

Since diazabicyclo[2.2.2]octene structure (1) is generally characterized (in degassed, hydrocarbon solvents at room temperature) by a very low quantum yield for photodecomposition,¹ a large quantum yield for fluorescence², and a long singlet lifetime,² this class of azoalkanes is considered to be "reluctant" to eliminate N₂, an obvious and palpably straightforward photo-reaction. We report here the



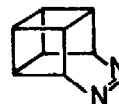
1

$$\phi_F = 0.20$$
$$\phi_{N_2} = 0.022$$



2

$$\phi_F = 0.11$$
$$\phi_{N_2} = 0.20$$



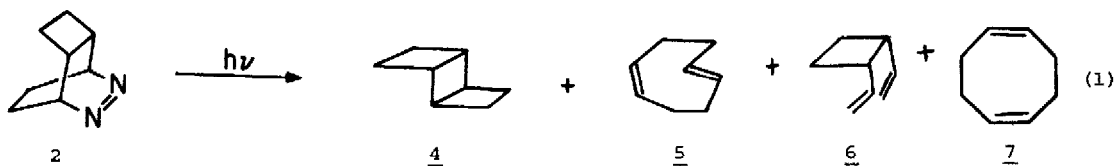
3

$$\phi_F \approx 0.2$$
$$\phi_{N_2} < 0.02$$

results of our investigations on the photochemistry of 2 and of 3. The former represents an interesting example of an exceptionally photolabile [2.2.2] system whereas the latter represents one of the most reluctant [2.2.2] systems.

Results. Photochemistry of 2.

An early report indicated that 2 underwent facile nitrogen extrusion (even at low temperatures).³ It was later shown⁴ that the major products (eq. 1) of photolysis of 2 were the tricyclooctane (4) and cis,trans-1,5-cyclooctadiene (5), in addition to minor products:



cis-1,2-divinyl cyclobutane (6) and cis,cis-1,5-cyclooctadiene (7). We find that the photolysis of 2 yields 4-7 as the only significant products in a variety of solvents, at various temperatures, and in the presence and absence of oxygen. However, the relative yields of these products change substantially as environmental conditions are varied. Table 1 summarizes some typical results. Since the sum of the yields of 4 and 5 is generally ~70-80% under all the conditions investigated, we shall consider the mechanism of formation of only these two products.

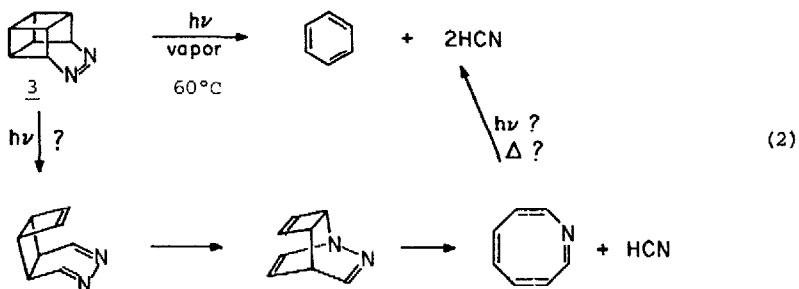
The formation of 5 is enhanced by (a) decreasing temperature (e.g., Runs 7-10); (b) triplet photoexcitation (Runs 8 and 11); (c) high concentrations of O₂ (Runs 5 and 6). The yield of 5 varies with solvent (Runs 1-5) but a straightforward correlation of yield with the usual solvent parameters was not apparent.

The quantum yields for direct photolysis of 2 ($\phi = 0.20$ in hexane, $\phi = 0.32$ in acetonitrile) are much higher than that reported for 1 ($\phi = 0.02$ in hexane).⁵ Furthermore, the quantum yield for benzophenone sensitized decomposition of 2 at room temperature ($\phi = 0.25$) is more than an order of magnitude greater than that for 1 ($\phi \sim 0.02$).⁵ For a given photosensitizer, the ratio of products was not found to be very solvent (Runs 14, 16 and 17) or temperature dependent (Runs 14 and 15).

Although the ratio of products produced by a series of sensitizers is different, the sum of the yields of 5 + 7 is nearly constant. We interpret this result to mean that 5 is, in part, isomerized to 7 under conditions of photosensitization. Our results are summarized in Fig. 1.

Photochemistry of 3.

The azoalkane 3 has been a source of puzzlement and of disappointment because of its remarkable reluctance to eliminate N₂. We have found that the S₁ state of 3 is strongly fluorescent ($\phi_F = 0.2$) and is extremely long lived ($\tau_F = 310$ ns) in hexane solution. Although 3 is prone to undergo thermal reactions which lead to strongly colored products(s), very little photodecomposition occurs when 3 is photoexcited in conventional organic solvents even at temperature ~70°C. However, 3 undergoes photolysis (eq. 2) in the vapor phase at 60° to produce benzene (50%) and HCN (25%) as the only products detected by vpc analysis.



Discussion

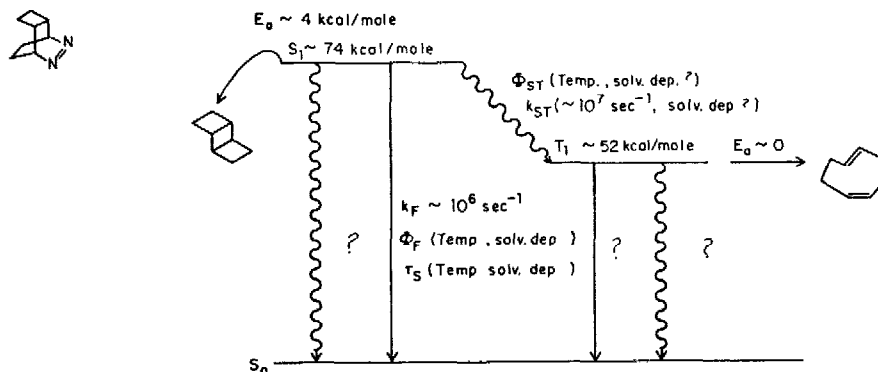
The data in Table 1 are consistent with the postulate that S_1 and T_1 of 2 yield different ratios of 4 and 5. The observation that 5 is the dominant product under triplet photosensitized excitation ($5/4 = 70/10$), suggests that 5 is the major product from T_1 whereas 4 is mainly from S_1 state upon direct excitation. This postulate is readily reconciled with the observation that the yield of 5 is enhanced by low temperatures (reaction from S_1 is activated)⁶ and by the presence of a high concentration of oxygen (intersystem crossing from S_1 is oxygen catalyzed).^{6,7}

Contrasting photochemistry from S_1 and T_1 has been observed in other cyclic azoalkanes^{6,7} and may be a rule rather than an exception. It is not known whether the differing chemistries of S_1 and T_1 result from different behavior of spin isomeric hydrocarbon diradicals and/or isomeric diazenyl diradicals. Further work is needed in order to tie together the S_0 , S_1 and T_1 hypersurfaces of the various species involved in the photochemistry of 2.

The photochemistry of 3 is exceptional. Unimolecular fragmentation processes other than loss of N_2 are practically unknown in the photochemistry of rigid cyclic azoalkanes. A plausible mechanistic scheme is given in eq. 2. The processes shown have analogy in the thermolysis⁸ of 3. Trapping of the several reactive intermediates to form "heavy" products would explain the lack of a good mass balance.

Acknowledgements. The authors at Columbia thank the National Science Foundation for its generous support of this work. The authors at Würzburg thank the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie for financial support.

Fig. 1.



References

1. For a discussion and references see N.J. Turro, K.C. Liu, W. Cherry, J.M. Liu and B. Jacobson, Tetrahedron Letters, 555 (1978); P.S. Engel and C. Steel, Acc. Chem. Res., **6**, 275 (1973).
2. M.J. Mirbach, K.C. Liu, M.F. Mirbach, W.R. Cherry, N.J. Turro and P.S. Engel, J. Am. Chem. Soc., **100**, 5122 (1978).
3. H. Tanida, S. Teratake, Y. Hata and M. Watanabe, Tetrahedron Letters, 5341 (1969).
4. H.D. Martin, B. Heiser and M. Kunze, Angew. Chem., **90**, 7351 (1978) intern. ed. Eng., **17**, 696 (1978).
5. W.D.K. Clark and C. Steel, J. Am. Chem. Soc., **93**, 6347 (1971).
6. This result is diagnostic of a temperature dependent reaction from S₁ that competes with a temperature independent intersystem crossing to T₁. See N.J. Turro, W.R. Cherry, M.J. Mirbach and V. Ramamurthy, Molec. Photochem., **9**, 111 (1978/79).
7. N.J. Turro, W.R. Cherry, M.F. Mirbach and M.J. Mirbach, J. Am. Chem. Soc., **99**, 7388 (1977).
8. D.W. McNeil, M.E. Kent, E. Hedaya, P.E. D'Angelo and P.O. Schissel, J. Am. Chem. Soc., **93**, 3817 (1971).

Table 1. Variation of Photoproducts from Photolysis of 4 as a Function of Environmental Conditions.

Run	Solvent	Sensitizer	T(C°)	Products (%)			
				4	5	6	7
1	water	-	25°	18	58	11	13
2	t-butanol	-	25°	41	34	12	13
3	acetone	-	25°	24	59	10	7
4	CH ₃ CN	-	25°	25	56	12	7
5	hexanes	-	25°	38	38	14	8
6	hexanes ^a	-	25°	19	63	8	10
7	isooctane	-	95°	36	44	11	10
8	isooctane	-	25°	31	48	12	8
9	isooctane	-	-40°	14	60	11	15
10	3-M pentane	-	-78°	11	67	11	11
11	isooctane	Φ ₂ CO	25°	9	61	8	22
12	methanol	Φ ₂ CO	25°	10	44	9	37
13	methanol	1,4-dibromo-naphthalene	25°	17	38	11	34
14	methanol	CH ₃ COCOCH ₃	25°	8	71	9	12
15	methanol	CH ₃ COCOCH ₃	-13°	8	70	9	13
16	acetonitrile	CH ₃ COCOCH ₃	25°	9	68	9	14
17	3-M pentane	CH ₃ COCOCH ₃	25°	9	70	9	12

(a) Oxygen purged solution. All other entries correspond to nitrogen purged solutions.

(Received in USA 10 January 1980)