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(Received November 9th, 1978)

Abstract. Direct photochemical excitation of the polycyclic azoalkane **1** yields a mixture of (CH)₆ isomers as major products at room temperature and the 1,2-diaza-cyclooctatetraene **2** as the major product at -78°C. The ratio of (CH)₆ isomers to **2** is strongly dependent on solvent. For example, at room temperature the ratio (CH)₆/**2** is 92/8 in pentane and 38/62 in dimethyl sulfoxide. Triplet photosensitized excitation of **1** yields **2** as the major product. The triplet reaction is insensitive to temperature and solvent. These results are consistent with reaction of S₁(**1**) to yield predominately (CH)₆ isomers via a thermally activated nitrogen extrusion, whereas T₁(**1**) yields predominantly **2** via a temperature and solvent independent rearrangement. Quantitative measurement of photochemical and photoluminescence parameters reveals that the solvent effect on the product distribution in the direct photolysis of **1** is due to a combination of the influence of solvent on the rate of reaction from S₁ and the rate of intersystem crossing from S₁.

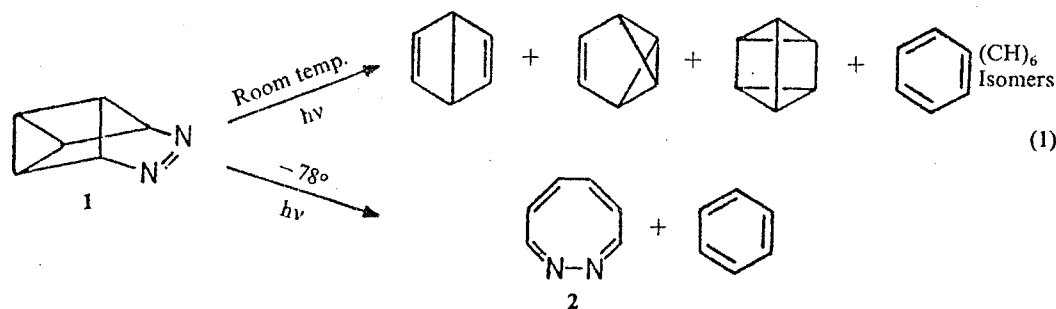
Introduction

The thermal¹, direct photochemical² and triplet sensitized³ decomposition of cyclic azoalkanes generally yield hydrocarbon products via diradical intermediates produced by nitrogen extrusion. The compound 7,8-diazatetracyclo-[3.3.0.0^{3,4}.0^{3,6}]oct-7-ene, (**1**) possesses an unusual photochemistry compared to other azoalkanes. Although nitrogen extrusion to yield (CH)₆ isomers is the major reaction pathway at room temperature, rearrangement to **2** is the predominant reaction at -78°C (eq. 1)^{4,5}. The ratio of (CH)₆ isomers to 1,2-diazacycloocta-2,4,6,8-tetraene (**2**) is very solvent dependent at room temperature. Triplet sensitized excitation of **1** yields **2** as the predominant product. We report here a study of the effect of temperature and solvent on the photochemistry of **1**. A quantitative evaluation of the photochemical and photophysical parameters of **1** as a function of solvent and determination of the triplet energy of **1** via phosphorescence quenching were also investigated.

Results

Products determination

The products produced in the photolysis of **1** have been characterized in previous reports^{4,5}. The NMR spectrum of a sample of **1** photolyzed in *c*-C₆D₁₂ (excitation wavelength 366 nm) is shown in Fig. 1. The spectrum demonstrates immediately the nature of the product mixture, which is stable for hours at room temperature. The ratio of the (CH)₆ isomers is invariant with the extent of photolysis. The ratio of individual (CH)₆ isomers is conveniently evaluated by analytical VPC analysis. Figure 2 shows a representative trace. The ratio of (CH)₆ isomers to **2** was established by integration of NMR spectra.



* Dedicated to Professor E. Havinga on the occasion of his 70th birthday.

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¹ C. H. Bamford and C. F. H. Tipper, eds., "Comprehensive Chemical Kinetics", vol. 6, Elsevier, New York, New York, 1972, p. 566.

² P. S. Engel and C. Steel, *Acc. Chem. Res.* **6**, 275 (1973).

³ H. Durr and B. Ruge, *Topics in Current Chemistry* **66**, 53 (1976).

⁴ B. M. Trost and R. M. Cory, *J. Am. Chem. Soc.* **93**, 5573 (1971);

T. Katz and N. Acton, *J. Am. Chem. Soc.* **95**, 2738 (1973).

⁵ N. J. Turro, C. A. Renner, W. H. Waddell and T. J. Katz, *J. Am. Chem. Soc.* **98**, 4320 (1976).

⁶ V. Ramamurthy, T. Katz and N. J. Turro, unpublished results.

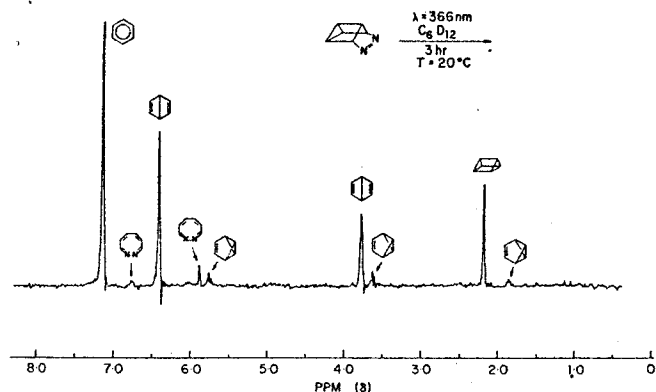


Fig. 1. Proton NMR spectrum of the product mixture produced by photolysis of **1** in C_6D_{12} .

Solvent effect on the product distribution in direct photolysis of 1

The results of an investigation of the solvent dependence of the product distribution from the direct photolysis of **1** are summarized in Table I. The ratio of total $(CH)_6$ isomers to **2** is strongly solvent dependent, the $(CH)_6$ isomers predominating in non-polar solvents such as cyclohexane and carbon tetrachloride and **2** predominating in polar solvents such as acetonitrile and dimethyl sulfoxide. NMR and VPC analysis provided no evidence for significant formation of products other than the $(CH)_6$ isomers and **2**. The product mixtures were also found to be stable during the periods required for analysis.

Table I Solvent effect on product distribution in the direct photolysis of **1**.

Solvent ^a					
$c-C_6H_{12}$	30	45	6	11	8
CCl_4	39	42	5	6	8
$CDCl_3$	23	27	—	—	50
CD_3CN	29	18	—	—	52
$(CD_3)_2CO$	34	20	—	—	41
$(CD_3)_2SO$	25	13	—	—	62

^a Reactions at room temperature. Solutions purged with nitrogen. Excitation wavelength >340 nm (450 watt Hg medium pressure lamp).

Table II Temperature effect on product distribution in the direct photolysis of **1**.

Temperature (°C)					
22	30	45	6	11	8
0	30	34	3	5	31
-35	20	5	—	—	75
-78	10	—	—	—	90
-194	10	—	—	—	90

^a Solvent hexane- d_{12} or 3-methylpentane. A Pyrex NMR tube as the reac-

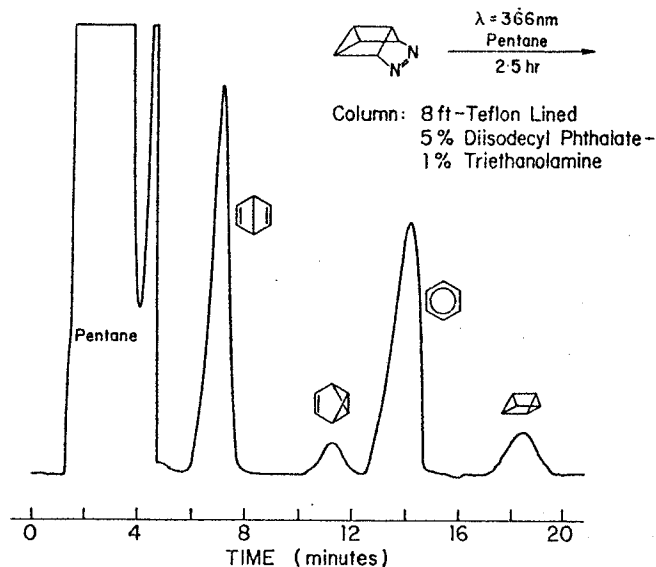


Fig. 2. Analytical VPC trace of the reaction mixture produced by photolysis of **1** in pentane. Only the $(CH)_6$ isomers are shown.

Temperature effect on the product distribution in direct photolysis of 1

The results of an investigation of the influence of temperature on the product distribution in the direct photolysis of **1** in hexane is summarized in Table II. The ratio $(CH)_6/2$ decreases sharply at temperatures below $22^\circ C$ to reach a constant value at some temperature below $-35^\circ C$. Control experiments demonstrated that the benzene produced at low temperatures is not the result of secondary photolysis of **2**.

Similar trends (i.e., strong favoring of **2** at low temperatures) were found when **1** was photolyzed in other solvents. For example, the ratio of $(CH)_6$ products to **2** from photolysis of **1** in ethanol fell from ~ 1.0 to 0.02 upon going from $22^\circ C$ to $-78^\circ C$.

Temperature effect on the product distribution in the benzophenone sensitized photolysis of 1

Triplet sensitized photolysis of **1** has been shown to yield benzene and **2** as products. No detectable (NMR) yield of valence isomers of benzene is produced under these conditions. The ratio of benzene to **2** produced via benzophenone triplet sensitized decomposition of **1** is insensitive to temperature in the range $+50^\circ C$ to $-60^\circ C$ (Table III). Since the triplet sensitized decomposition of **2** yields benzene as a product⁶, the ratio of benzene to **2** is probably larger than

Table III Temperature effect on product distribution in the benzophenone sensitized photolysis of **1**.

Temperature (°C)		
50	25	75
21	20	80
5	22	78
-60	20	80

the value for primary product formation. The values reported are for the lowest possible conversions consistent with requirements for accurate analyses. We do not feel that the difference between the limiting benzene **2** ratio achieved in direct photolysis of **1** at low temperatures ($\sim 10/90$) is sufficiently different from that achieved from benzophenone sensitized reaction ($\sim 20/80$) to be of mechanistic significance and that the "true" primary ratios should be considered identical within experimental error because of the complication of photosensitized conversion of **2** to benzene.

Table IV Phosphorescence quenching and reaction quantum yields. Correlation with triplet energy^a.

Phosphorescer	E_T (kcal/mole)	Φ_R^T	k_q^T (l.mol ⁻¹ .s ⁻¹)
Acetone	78	—	4×10^{10}
Acetophenone	74	—	3×10^9
Benzophenone	69	0.31	6×10^9
4,4'-Dibromobiphenyl	66	0.30	9×10^9
1,4-Dibromonaphthalene	60	0.31	2×10^9
Biacetyl	56	0.10	$<10^8$
Benzil	53	<0.05	$<10^8$

^a Acetonitrile solution at room temperature. Nitrogen purged. The Type II reaction of valerophenone in benzene ($\Phi = 0.33$) was employed as an actinometer. Sensitizer concentration ~ 0.1 mol/l [**1**] $\sim 10^{-2}$ mol/l. Excitation wavelength 313 nm.

Triplet quenching constants and triplet sensitized quantum yields. Evaluation of the triplet energy of **1**

The phosphorescence of a series of compounds of known triplet energy was quenched by **1**. Stern-Volmer analysis and direct measurement of phosphorescence lifetimes allowed derivation of k_q^T , the bimolecular rate constant for phosphorescence quenching by **1**. In addition, the quantum yields Φ_R^T for photosensitized reaction of **1** were measured. The data for k_q^T and Φ_R^T are summarized in Table IV. A sharp drop in both k_q^T and Φ_R^T is noted when the sensitizer energy (E_T) decreases from 60 kcal/mole to 56 kcal/mole. The quantum yield for benzophenone sensitized reaction of **1** is relatively insensitive to solvent. For example, $\Phi_R^T = 0.31$ in pentane and 0.28 in acetonitrile, respectively.

Quantitative photophysical and photochemical parameters of the singlet excited state of **1**

The photophysical parameters relevant to S_1 of **1** were measured in different solvents. The absorption maxima for

$S_0 \rightarrow S_1$ absorption, the emission maxima for $S_1 \rightarrow S_0$ fluorescence, the quantum yield for emission (Φ_F) and the singlet decay (τ_S) were evaluated. The resulting data are summarized in Table V. Although the $S_0 \rightarrow S_1$ absorption maxima are solvent independent, the $S_1 \rightarrow S_0$ fluorescence maxima, Φ_F and τ_S are all strikingly solvent dependent. The quantum yield for total reaction upon direct photolyses were also measured as a function of solvent. Based on the assumption that **2** is derived only from T_1 and that the triplet reaction quantum yields listed in Table IV represent state quantum yields (i.e., quantum yields based on excitation of T_1 only), the value of Φ_{ST} (intersystem crossing yield for $S_1 \rightarrow T_1$) may be evaluated. The results are listed in Table V. Finally, from knowledge of τ_S , Φ_F , Φ_R , and Φ_{ST} the rate constants k_F , k_R^S and k_{ST} (fluorescence from S_1 , reaction from S_1 and intersystem crossing from S_1 , respectively) are derived and summarized in Table V.

Discussion

The results of this investigation confirm the earlier conclusion^{5,8} that $S_1(\mathbf{1})$ yields $(\text{CH})_6 + \text{N}_2$ and that $T_1(\mathbf{1})$ yields benzene and **2**. The unusual solvent and temperature effects on the ratio of $(\text{CH})_6$ isomers to **2** may be understood in terms of the energy diagram shown in Figure 3, which

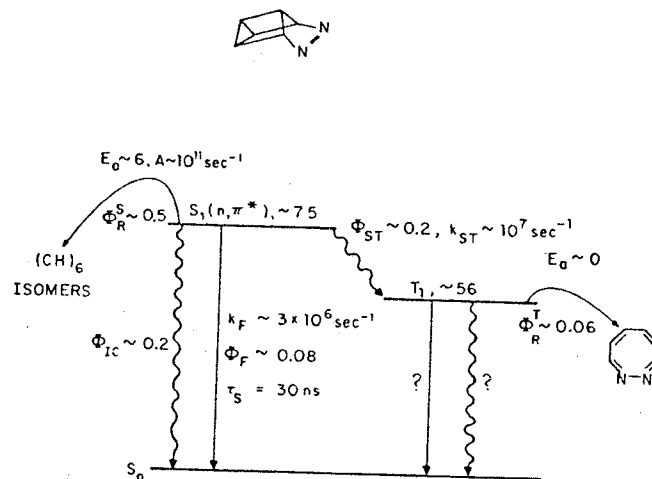


Fig. 3. Dynamic state energy diagram for **1** for direct photochemical excitation in pentane solvent at room temperature. Energies in kcal/mole, rate constants in s^{-1} .

⁷ M. F. Mirbach, M. J. Mirbach, K. C. Liu and N. J. Turro, J. Photochem. 8, 299 (1978).

⁸ N. J. Turro, W. R. Cherry, M. J. Mirbach, M. F. Mirbach and V. Ramamurthy, Mol. Photochem. 9, 111 (1978/79).

Table V Photochemical and photoluminescence parameters for **1** as a function of solvent.

Solvent	Absorption Maximum (nm)	Emission Maximum (nm)	Φ_F	τ_S (s)	Φ_R^S	Φ_R^T	Φ_{ST}^a	k_F (s^{-1})	k_R^S (s^{-1})	k_{ST} (s^{-1})	$(\text{CH})_6$ (%)	2 (%)
Pentane	370	395	0.056	20×10^{-9}	0.49	0.05	0.15	2.8×10^6	2.4×10^7	7×10^7	92	8
Cyclohexane	370	395	0.06	27×10^{-9}	0.48	0.06	0.18	2.2×10^6	1.8×10^7	6.7×10^6	92	8
CCl_4	370	405	0.106	39×10^{-9}	0.50	0.06	0.18	2.7×10^6	1.3×10^7	1.5×10^7	92	8
CDCl_3	370	423	0.033	14×10^{-9}	0.16	0.16	0.48	2.3×10^6	1.1×10^7	3×10^7	50	50
CD_3CN	370	425	0.076	30×10^{-9}	0.17	0.17	0.51	2.5×10^6	0.6×10^7	1.7×10^7	48	52
$\text{DMSO-}d_6$	370	425	0.092	38×10^{-9}	0.13	0.21	0.63	2.4×10^6	0.3×10^7	1.6×10^7	38	62

^a Φ_{ST} is calculated on the assumption of a triplet state quantum yield for reaction of 0.30 (see Table IV). Thus $\Phi_{ST} \sim \Phi_R^T / 0.3$.

