2/1

Nicholas J., Turro and V. Ramamurthy

Department of Chemistry, Columbia University New York, New York 10027 (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 $S_1(1)$ to yield predominately $(CH)_6$ isomers via a thermally activated nitrogen extrusion, whereas $T_1(1)$ 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-tatraene (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 I 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- C_6D_{12} (excitation wavelength 366 nm) is shown in Fig. 1. The spectrum demonstration strates 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

Present address: Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India.

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

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

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

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.

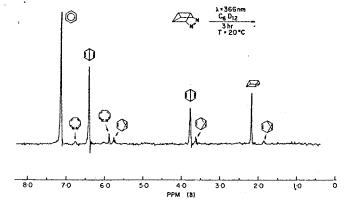


Fig. 1. Proton NMR spectrum of the product mixture produced by photolysis of 1 in C_6D_{12} .

Solvent effect on the product distribution in direct photolysis of $\mathbf{1}$

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					N-N
c-C ₆ H ₁₂	30	45	6	11	8
CCl ₄	39	42	5	6	8
CDCl ₃	23	27	-		50
CD ₃ CN	29	18			52
(CD ₃) ₂ CO	34	20		-	41
(CD ₃) ₂ SO	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^a.

Tempera- ture (°C)					N-N
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-

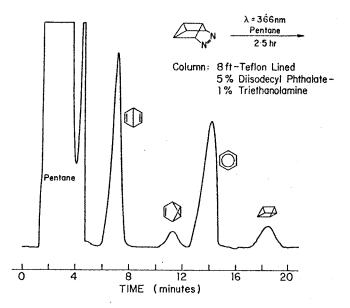


Fig. 2. Analytical VPC trace of the reaction mixture produced by photolysis of 1 in pentane. Only the (CH)₆ isomers are shown.

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°C to reach a constant value at some temperature below -35°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°C to -78°C.

Temperature effect on the product distribution in the benzophenone sensitized photolysis of ${\bf 1}$

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° 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)		N-N		
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 energy².

Phosphorescer	E _T (kcal/mole)	Φ_{R}^{T}	$k_{\mathbf{q}}^{T}(\mathrm{l.mol}^{-1}.\mathrm{s}^{-1})$
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°
1,4-Dibromonaphthalene	60	0.31	2×10^{9}
Biacetyl	56	0.10	< 108
Benzil	53	< 0.05	< 108

^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 quanching 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 $k_{\rm q}^{\rm T}$, the bimolecular rate constant for phosphorescence quenching by 1. In addition, the quantum yields $\Phi_{\rm R}^{\rm T}$ for photosensitized reaction of 1 were measured. The data for $k_{\rm q}^{\rm T}$ and $\Phi_{\rm R}^{\rm T}$ are summarized in Table IV. A sharp drop in both $k_{\rm q}^{\rm T}$ and $\Phi_{\rm R}^{\rm T}$ is noted when the sensitizer energy ($E_{\rm T}$) 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, $\Phi_{\rm R}^{\rm T}=0.31$ 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

 $S_0 \to S_1$ absorption, the emission maxima for $S_1 \to S_0$ 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 $S_0 \to S_1$ absorption maxima are solvent independent, the $S_1 \to S_0$ 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 $S_1(1)$ yields $(CH)_6 + N_2$ and that $T_1(1)$ yields benzene and 2. The unusual solvent and temperature effects on the ratio of $(CH)_6$ isomers to 2 may be understood in terms of the energy diagram shown in Figure 3, which

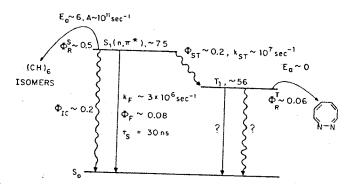


Fig. 3. Dynamic state energy diagram for 1 for direct photochemical excitation in pentane solvent at room temperature. Energies in kcal/mole, rate constants in s^{-1} .

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

J. Photochem. 8, 299 (1978).

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)	$\Phi_{\mathbf{F}}$	τ _s (s)	ΦS	Φ_{R}^{T}	Φ _{ST} ^a	$k_{\rm F}$ (s ⁻¹)	$k_{\rm R}^{\rm S}$ (s ⁻¹)	k _{ST} (s ⁻¹)	(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}	7 107		
Cyclohexane	370	395	0.06	27×10 ⁻⁹				Į.		7×10^7	92	8
CCl₄	370	-			0.48	0.06	0.18	2.2×10^6	1.8×10^{7}	6.7×10^{6}	92	8
		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		-
CD ₃ CN	370	425	0.076	30×10^{-9}	0.17		-				50	50
DMSO-d ₆	220	-			0.17	0.17	0.51	2.5×10^{6}	0.6×10^7	1.7×10^7	48	52
21130-46	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

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

perature in a non-polar solvent.

A key to the interpretation of the photochemistry of 1 is the different dependence of the decay processes from S_1 on reaction conditions (environment and temperature). The temperature dependence of the singlet decay of 1 demonstrates that an activation energy of ~ 6 kcal/mol exists7 for α -cleavage of S_1 . On the other hand, the inherent fluorescence rate constant k_F is temperature independent. Likewise, $k_{\rm F}$ is solvent insensitive but the rates of radiationless processes (k_R^S, k_{ST}) are sensitive to solvent. For example, at room temperature k_R^S varies from $\sim 2 \times 10^7 \, \mathrm{s}^{-1}$ in pentane to $\sim 0.3 \times 10^7 \, \mathrm{s}^{-1}$ in dimethyl sulfoxide, a variation of a factor of ~ 7 . The variation in rate of intersystem crossing is a factor of \sim 4. It is the interplay of temperature and environmental influences on k_R^S and k_{ST} that causes the striking variation in the ratio of (CH)₆ isomers to 2.

For example, at room temperature in pentane k_R^S is maximal and $k_{\rm ST}$ is minimal for the solvents studied. Thus, $\Phi_{\rm ST}$ is small (~ 0.15) and the (CH)₆ isomers dominate in the product mixture. At the other extreme, at room temperature in dimethyl sulfoxide k_R^S is minimal and k_{ST} is close to

maximal. Thus, Φ_{ST} is large (~ 0.6).

Similarly, $k_{\rm R}^{\rm S}$ is strongly temperature dependent ($E_{\rm a}\sim 6$ kcal/ mol) in the temperature region $\sim 0^{\circ}-50^{\circ}\mathrm{C}$, whereas k_{ST} is relatively temperature insensitive. Thus, for $T>0^{\circ}\mathrm{C}$ $k_{\mathrm{R}}^{\mathrm{S}}>$ $k_{\rm ST}$ so that $\Phi_{\rm ST}$ is small and $\Phi_{\rm S}^{\rm S}$ is relatively large. At low temperatures ($T<-30^{\circ}$) $k_{\rm ST}\gg k_{\rm R}^{\rm S}$ so that $\Phi_{\rm ST}\sim 1.0$ and reaction from S_1 is very inefficient. The sum $\Phi_{\rm F}+\Phi_{\rm ST}+\Phi_{\rm R}^{\rm S}$ is less than unity. For example in pentage, the sum of these quantum violations and $T_{\rm ST}\sim 1.0$

in pentane, the sum of these quantum yields is ~ 0.7 . The difference between 1.0 and the sum of these quantum yields

equated to Φ_{IC} , the quantum yield for internal conversion from $S_1(1)$ to $S_0(1)$. It is interesting to note that Φ_{IC} is not very sensitive to solvent ($\Phi_{IC}\sim0.3$ in pentane and $\Phi_{\rm IC} \sim 0.2$ in acetonitrile). Furthermore, the quantum yield for reaction from $T_1(1)$ is much less than Φ_{ST} . This means that the major radiationless deactivation pathway of $T_1(1)$ regenerates $S_0(1)$.

Conclusion

The results of this investigation support the occurrence of $S_1(1)$ as the excited state precursor of the benzene valence isomers and $T_1(1)$ as the excited state precursor of 2 in the direct photolysis of 1. Small yields of benzene are produced from both $S_1(1)$ and $T_1(1)$. The solvent and temperature dependence of the products produced from direct irradiation of 1 is mainly due to the variation of k_R^s with solvent polarity and temperature, although k_{ST} is also somewhat solvent dependent. However, these studies do not reveal why $k_{\rm R}^{\rm S}$ is solvent sensitive or why nitrogen extrusion possesses an activation barrier in $S_1(1)$ but no barrier for rearrangement exists for $T_1(1)$. Future research will be required before the basis of the solvent and temperature sensitivity of k_R^S is well understood.

Acknowledgement

The authors wish to thank the National Science Foundation for generous support of this research.

Photochemical cycloaddition of an aromatic ketone to a 1-alkynyl ether. Kinetics and mechanism*1†

H. Polman**, J. P. B. Baaij and H. J. T. Bos

Laboratory of Organic Chemistry of the University, Croesestraat 79, 3522 AD Utrecht, The Netherlands (Received February 10th, 1978)

Abstract. In this paper kinetics and mechanism of the photoaddition of 10,11-dihydro-5H-dibenzo-[a,d]cyclohepten-5-one (dibenzosuberone, 4) to 1-methoxy-1-propyne (5) with the formation of the unsaturated ester 8, are studied. In benzene at 25.0°C a limiting quantum yield $\Phi = 0.04$ was found. The rate constant k_2 of the addition of triplet ketone 4 to ground state 5 amounted to $1.9 \cdot 10^7$ l.mol⁻¹.s⁻¹. The unexpected regiospecificity is not caused by attack of triplet alkyne on ground state ketone. The low quantum yield is mainly caused by the high revertibility of the addition reaction. The intermediacy of a triplet exciplex is discussed.

Introduction

Photoadditions of aromatic ketones $Ar_2C=0$ to 1-alkynyl ethers (1, R = alkyl, R' = H, alkyl)² give rise to α,β -unsaturated esters 3 via the unstable oxete 2; cf. 3-5 (Scheme 1).

$$Ar_2C=0 + RO-C\equiv C-R' \xrightarrow{h\nu} \begin{bmatrix} RO & R' \\ O-C & O-C \\ O-C & O-C \end{bmatrix} \longrightarrow RO-C-C-R' \xrightarrow{H'} \begin{bmatrix} RO & R' \\ O-C & O-C \\ O-C & O-C \\ O-C & O-C \end{bmatrix}$$
(1)
(2)
(3)

Scheme 1

* Part of the dissertation of H. Polman, University of Utrecht,

Present address: Unilever Research Laboratories, Duiven. Dedicated to Prof. Dr. E. Havinya on the occasion of his 70th birthday.

Photochemical reactions of Acetylenes VIII; previous publica-

tions ref. 4,5. Chemistry of Acetylenic Ethers 114. H. J. T. Bos, H. T. van der Bend, J. S. M. Boleij, C. J. A. Everaars and H. Polman, Recl. Trav. Chim. Pays-Bas 91, 65 (1972).

³ D. R. Arnold, Adv. Photochem. 6, 301 (1968).

⁴ A. Mosterd, H. J. Matser and H. J. T. Bos, Tetrahedron Lett.

A. Mosterd, L. J. de Noten and H. J. T. Bos, Recl. Trav. Chim. Pays-Bas 96, 16 (1977).